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Dielectric Properties of Insulators

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Because charge cannot flow freely in insulators, applied electric fields of substantial amplitude can penetrate into their interiors. There are at least three broad contexts in which it is important to know how the internal structure of an insulator, both electronic and ionic, readjusts when an additional electric field is superimposed on the electric field associated with the periodic lattice potential:

1. We may place a sample of the insulator in a static electric field such as that existing between the plates of a capacitor. Many important consequences of the resulting internal distortion can be deduced if one knows the static dielectric constant ϵ_0 of the crystal, whose calculation is therefore an important aim of any microscopic theory of insulators.
2. We may be interested in the optical properties of the insulator—i.e., in its response to the AC electric field associated with electromagnetic radiation. In this case the important quantity to calculate is the frequency-dependent dielectric constant $\epsilon(\omega)$, or, equivalently, the index of refraction, $n = \sqrt{\epsilon}$.
3. In an ionic crystal, even in the absence of externally applied fields, there may be long-range electrostatic forces between the ions in addition to the periodic lattice potential, when the lattice is deformed from its equilibrium configuration (as, for example, in the course of executing a normal mode). Such forces are often best dealt with by considering the additional electric field giving rise to them, whose sources are intrinsic to the crystal.

In dealing with any of these phenomena the theory of the macroscopic Maxwell equations in a medium is a most valuable tool. We begin with a review of the electrostatic aspects of this theory.

MACROSCOPIC MAXWELL EQUATIONS OF ELECTROSTATICS

When viewed on the atomic scale, the charge density $\rho^{\text{micro}}(\mathbf{r})$ of any insulator is a very rapidly varying function of position, reflecting the microscopic atomic structure of the insulator. On the same atomic scale the electrostatic potential $\phi^{\text{micro}}(\mathbf{r})$ and the electric field $\mathbf{E}^{\text{micro}}(\mathbf{r}) = -\nabla\phi^{\text{micro}}(\mathbf{r})$ also have strong and rapid variations since they are related to $\rho^{\text{micro}}(\mathbf{r})$ by

$$\nabla \cdot \mathbf{E}^{\text{micro}}(\mathbf{r}) = 4\pi\rho^{\text{micro}}(\mathbf{r}). \tag{27.1}$$

On the other hand, in the conventional *macroscopic* electromagnetic theory of an insulator the charge density $\rho(\mathbf{r})$, potential $\phi(\mathbf{r})$, and electric field $\mathbf{E}(\mathbf{r})$ show no such rapid variation.[1] Specifically, in the case of an insulator bearing no excess charge beyond that of its component ions (or atoms or molecules), the macroscopic electrostatic field is determined by the macroscopic Maxwell equation:[2]

$$\nabla \cdot \mathbf{D}(\mathbf{r}) = 0, \tag{27.2}$$

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[1] Indeed, in an insulating medium in the absence of any externally applied fields, $\phi(\mathbf{r})$ is zero (or constant).

[2] More generally, one writes $\nabla \cdot \mathbf{D} = 4\pi\rho$, where ρ is the so-called free charge—i.e., that part of the macroscopic charge density due to excess charges not intrinsic to the medium. Throughout the following discussion we assume that there is no free charge, so that our macroscopic charge density is always the so-called bound charge of macroscopic electrostatics. The inclusion of free charge is straightforward, but not relevant to any of the applications we wish to make here.

in conjunction with the equation giving the macroscopic electric field $\mathbf{E}$ in terms of the electric displacement $\mathbf{D}$ and polarization density $\mathbf{P}$,

$$\mathbf{D}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r}). \tag{27.3}$$

These imply (in the absence of free charge) that the macroscopic electric field satisfies

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = -4\pi\nabla \cdot \mathbf{P}(\mathbf{r}), \tag{27.4}$$

where $\mathbf{P}$ (to be defined in detail below) is generally a very slowly varying function of position inside an insulator.

Although it is very convenient to work with the macroscopic Maxwell equations, it is also essential to deal with the microscopic field acting on individual ions.[3] One must therefore keep the relation between macroscopic and microscopic quantities clearly in mind. The connection, first derived by Lorentz, can be made as follows:[4]

Suppose we have an insulator (not necessarily in its equilibrium configuration) that is described (at an instant) by a microscopic charge density $\rho^{\text{micro}}(\mathbf{r})$, which reflects the detailed atomic arrangement of electrons and nuclei and which gives rise to the rapidly varying microscopic field, $\mathbf{E}^{\text{micro}}(\mathbf{r})$. The macroscopic field $\mathbf{E}(\mathbf{r})$ is defined to be an average of $\mathbf{E}^{\text{micro}}$ over a region about $\mathbf{r}$ that is small on the macroscopic scale, but large compared with characteristic atomic dimensions a (Figure 27.1). We make the averaging procedure explicit by using a positive normalized weight function f, satisfying:

$$f(\mathbf{r}) \geqslant 0; \quad f(\mathbf{r}) = 0, \quad r > r_0; \quad \int d\mathbf{r}\, f(\mathbf{r}) = 1; \quad f(-\mathbf{r}) = f(\mathbf{r}). \tag{27.5}$$

The distance r_0 beyond which f vanishes is large compared with atomic dimensions

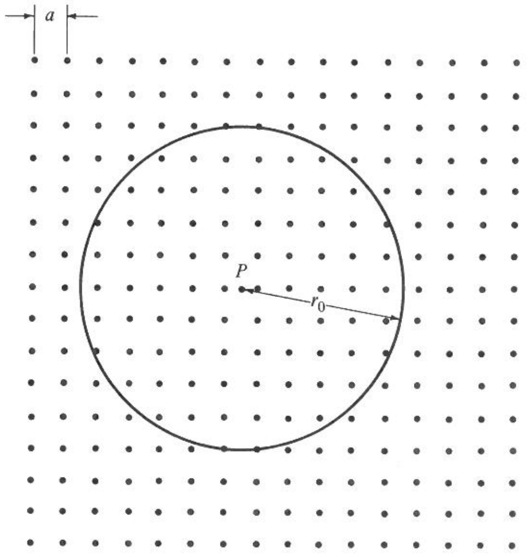

Figure 27.1
The value of a macroscopic quantity at a point P is an average of the microscopic quantity over a region of dimensions r_0 in the neighborhood of P, where r_0 is large compared to the interparticle spacing a.

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[3] We continue with our convention of using the single term "ion" to refer to the ions in ionic crystals, but also the atoms or molecules making up molecular crystals.

[4] The following discussion is very similar to a derivation of all the macroscopic Maxwell equations by G. Russakoff, *Am. J. Phys.* **10**, 1188 (1970).

a, but small on the scale over which macroscopically defined quantities vary.[5] We also require that f vary slowly; i.e., $|\nabla f|/f$ should not be appreciably greater than the minimum value, of order $1/r_0$, required by Eqs. (27.5). Beyond these assumptions, the form of the macroscopic theory is independent of the properties of the weight function f.

We can now give a precise definition of the macroscopic electric field $\mathbf{E}(\mathbf{r})$ at the point $\mathbf{r}$: it is the average of the microscopic field in a region of radius r_0 about $\mathbf{r}$, with points displaced by $-\mathbf{r}'$ from $\mathbf{r}$ receiving a weight proportional to $f(\mathbf{r}')$; i.e.,

$$\mathbf{E}(\mathbf{r}) = \int d\mathbf{r}'\, \mathbf{E}^{\text{micro}}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}'). \tag{27.6}$$

Loosely speaking, the operation specified by (27.6) washes out those features of the microscopic field that vary rapidly on the scale of r_0, and preserves those features that vary slowly on the scale of r_0 (Figure 27.2). Note, for example, that if $\mathbf{E}^{\text{micro}}$ should happen to vary slowly on the scale of r_0 (as would be the case if the point $\mathbf{r}$ were in empty space, far from the insulator), then $\mathbf{E}(\mathbf{r})$ would equal $\mathbf{E}^{\text{micro}}(\mathbf{r})$.

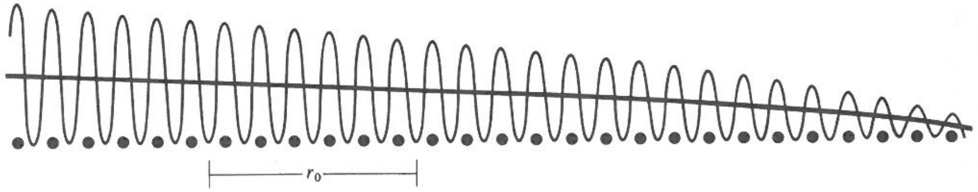

Figure 27.2
The lighter rapidly oscillatory curve illustrates the characteristic spatial variation of a microscopic quantity. The heavier curve is the corresponding macroscopic quantity. Only spatial variations that occur on a scale comparable to or larger than r_0 are preserved in the macroscopic quantity.

Equations (27.6) and (27.1) immediately imply that

$$\begin{aligned}\nabla \cdot \mathbf{E}(\mathbf{r}) &= \int d\mathbf{r}'\, \nabla \cdot \mathbf{E}^{\text{micro}}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}') \\ &= 4\pi \int d\mathbf{r}'\, \rho^{\text{micro}}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}').\end{aligned} \tag{27.7}$$

Therefore, to establish (27.4) we must show that

$$\int d\mathbf{r}'\, \rho^{\text{micro}}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}')\, d\mathbf{r}' = -\nabla \cdot \mathbf{P}(\mathbf{r}), \tag{27.8}$$

where $\mathbf{P}(\mathbf{r})$ is a slowly varying function that can be interpreted as a dipole moment density.

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[5] More precisely, the macroscopic Maxwell equations are valid only when the variation in the macroscopic fields is sufficiently slow that their minimum characteristic wavelength allows a choice of r_0 satisfying $\lambda \gg r_0 \gg a$. This condition can be satisfied by the field associated with visible light ($\lambda \sim 10^4 a$), but not by the field associated with X rays ($\lambda \sim a$).

We shall discuss only the case in which the microscopic charge density can be resolved into a sum of contributions from ions (or atoms or molecules) located at positions $\mathbf{r}_j$ characterized by individual charge distributions $\rho_j(\mathbf{r} - \mathbf{r}_j)$:

$$\rho^{\text{micro}}(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j). \tag{27.9}$$

Such a resolution is quite natural in ionic or molecular solids, but is rather more difficult to achieve in covalent crystals, where important parts of the electronic charge distribution are not readily associated with a particular site in the crystal. Our discussion is therefore primarily applicable to the former two insulating categories. Quite a different approach is required to calculate the dielectric properties of covalent crystals. We shall return to this point below.

We are interested in nonequilibrium configurations of the insulator in which the ions are displaced from their equilibrium positions $\mathbf{r}_j^0$ and are deformed from their equilibrium shapes,[6] which are described by charge densities ρ_j^0. Thus $\rho^{\text{micro}}(\mathbf{r})$ will not, in general, be equal to the equilibrium microscopic charge density,

$$\rho_0^{\text{micro}}(\mathbf{r}) = \sum_j \rho_j^0(\mathbf{r} - \mathbf{r}_j^0). \tag{27.10}$$

Using (27.9) we can write (27.7) as:

$$\begin{aligned}\nabla \cdot \mathbf{E}(\mathbf{r}) &= 4\pi \sum_j \int d\mathbf{r}'\, \rho_j(\mathbf{r} - \mathbf{r}_j - \mathbf{r}') f(\mathbf{r}') \\ &= 4\pi \sum_j \int d\bar{\mathbf{r}}\, \rho_j(\bar{\mathbf{r}}) f(\mathbf{r} - \mathbf{r}_j^0 - (\bar{\mathbf{r}} + \boldsymbol{\Delta}_j)),\end{aligned} \tag{27.11}$$

where $\boldsymbol{\Delta}_j = \mathbf{r}_j - \mathbf{r}_j^0$. The displacement $\boldsymbol{\Delta}_j$ of the jth ion from its equilibrium position is a microscopic distance of order a or less. Furthermore the charge density $\rho_j(\bar{\mathbf{r}})$ vanishes when $\bar{r}$ exceeds a microscopic distance of order a. Since the variation in the weight function f is very small over distances of order a, we can expand (27.11) in what is effectively a series in powers of a/r_0 by using the Taylor expansion:

$$f(\mathbf{r} - \mathbf{r}_j^0 - (\bar{\mathbf{r}} + \boldsymbol{\Delta}_j)) = \sum_{n=0}^{\infty} \frac{1}{n!} \left[-(\bar{\mathbf{r}} + \boldsymbol{\Delta}_j) \cdot \nabla \right]^n f(\mathbf{r} - \mathbf{r}_j^0). \tag{27.12}$$

If we substitute the first two terms[7] from (27.12) into (27.11) we find that

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = 4\pi \left[\sum_j e_j f(\mathbf{r} - \mathbf{r}_j^0) - \sum_j (\mathbf{p}_j + e_j \boldsymbol{\Delta}_j) \cdot \nabla f(\mathbf{r} - \mathbf{r}_j^0) \right], \tag{27.13}$$

where

$$e_j = \int d\bar{\mathbf{r}}\, \rho_j(\bar{\mathbf{r}}), \quad \mathbf{p}_j = \int d\bar{\mathbf{r}}\, \rho_j(\bar{\mathbf{r}}) \bar{\mathbf{r}}. \tag{27.14}$$

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[6] We have in mind applications (a) to monatomic Bravais lattices (in which the $\mathbf{r}_j^0$ are just the Bravais lattice vectors $\mathbf{R}$ and all of the functions ρ_j^0 are identical, and (b) to lattices with a basis, in which the $\mathbf{r}_j^0$ run through all vectors $\mathbf{R}$, $\mathbf{R} + \mathbf{d}$, etc., and there are as many distinct functional forms for the ρ_j^0 as there are distinct types of ions in the basis.

[7] We shall find that the first ($n = 0$) term makes no contribution to (27.11), and we must therefore retain the next ($n = 1$) term to get the leading contribution.

The quantities e_j and $\mathbf{p}_j$ are simply the total charge and dipole moment of the jth ion.

In the case of a monatomic Bravais lattice the charge of each "ion" must be zero (since the crystal is neutral and all "ions" are identical). In addition the equilibrium positions $\mathbf{r}_j^0$ are the Bravais lattice sites $\mathbf{R}$, so (27.13) reduces to

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = -4\pi\nabla \cdot \sum_{\mathbf{R}} f(\mathbf{r} - \mathbf{R})\mathbf{p}(\mathbf{R}), \tag{27.15}$$

where $\mathbf{p}(\mathbf{R})$ is the dipole moment of the atom at site $\mathbf{R}$.

With a straightforward generalization of the definition of $\mathbf{p}(\mathbf{R})$, this result remains valid (to leading order in a/r_0) even when we allow for ionic charge and a polyatomic basis. To see this, suppose that the $\mathbf{r}_j^0$ now run through the sites $\mathbf{R} + \mathbf{d}$ of a lattice with a basis. We can then label p_j and e_j by the Bravais lattice vector $\mathbf{R}$ and basis vector $\mathbf{d}$ specifying the equilibrium position of the jth ion:[8]

$$\mathbf{p}_j \to \mathbf{p}(\mathbf{R}, \mathbf{d}), \quad e_j \to e(\mathbf{d}), \quad \mathbf{r}_j^0 \to \mathbf{R} + \mathbf{d}, \quad \Delta_j \to \mathbf{u}(\mathbf{R}, \mathbf{d}). \tag{27.16}$$

Since d is a microscopic length of order a, we can perform the further expansion:

$$f(\mathbf{r} - \mathbf{R} - \mathbf{d}) \approx f(\mathbf{r} - \mathbf{R}) - \mathbf{d} \cdot \nabla f(\mathbf{r} - \mathbf{R}). \tag{27.17}$$

Substituting this into (27.13) and dropping terms of higher than linear order in a/r_0, we again recover (27.15), where $\mathbf{p}(\mathbf{R})$ is now the dipole moment of the entire primitive cell[9] associated with $\mathbf{R}$:

$$\mathbf{p}(\mathbf{R}) = \sum_{\mathbf{d}} [e(\mathbf{d})\mathbf{u}(\mathbf{R}, \mathbf{d}) + \mathbf{p}(\mathbf{R}, \mathbf{d})]. \tag{27.18}$$

Comparing (27.15) with the macroscopic Maxwell equation (27.4), we find that the two are consistent if the polarization density is defined by

$$\mathbf{P}(\mathbf{r}) = \sum_{\mathbf{R}} f(\mathbf{r} - \mathbf{R})\mathbf{p}(\mathbf{R}). \tag{27.19}$$

If we are dealing with distortions from equilibrium whose form does not vary much from cell to cell on the microscopic scale, then $\mathbf{p}(\mathbf{R})$ will vary only slowly from cell to cell, and we can evaluate (27.19) as an integral:

$$\mathbf{P}(\mathbf{r}) = \frac{1}{v}\sum_{\mathbf{R}} v f(\mathbf{r} - \mathbf{R})\mathbf{p}(\mathbf{R}) \approx \frac{1}{v}\int d\bar{\mathbf{r}}\, f(\mathbf{r} - \bar{\mathbf{r}})\mathbf{p}(\bar{\mathbf{r}}), \tag{27.20}$$

where $\mathbf{p}(\bar{\mathbf{r}})$ is a smooth, slowly varying continuous function equal to the polarization of the cells in the immediate vicinity of $\bar{\mathbf{r}}$, and v is the volume of the equilibrium primitive cell.

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[8] Ions separated by Bravais lattice vectors have the same total charge, so e_j depends only on $\mathbf{d}$, and not on $\mathbf{R}$.

[9] In deriving (27.18) we have used the fact that the total charge of the primitive cell, $\Sigma e(\mathbf{d})$, vanishes. We have also neglected an additional term, $\Sigma\, \mathbf{d}e(\mathbf{d})$, which is the dipole moment of the primitive cell in the undistorted equilibrium crystal. In most crystals this term vanishes for the most natural choices of primitive cell. If it did not vanish, the crystal would have a polarization density in equilibrium in the absence of distorting forces or external electric fields. Such crystals do exist, and are known as pyroelectrics. We shall discuss them later in this chapter, where we shall also make clearer what is meant by "most natural choices of primitive cell" (see page 554).

We shall restrict our use of the macroscopic Maxwell equations to situations in which the variation in cellular polarization is appreciable only over distances large compared with the dimensions r_0 of the averaging region; this is certainly the case for fields whose wavelengths are in the visible part of the spectrum or longer. Since the integrand in (27.20) vanishes when $\bar{\mathbf{r}}$ is more than r_0 from $\mathbf{r}$, then if $\mathbf{p}(\bar{\mathbf{r}})$ varies negligibly over a distance r_0 from $\bar{\mathbf{r}}$, we can replace $\mathbf{p}(\bar{\mathbf{r}})$ by $\mathbf{p}(\mathbf{r})$, and bring it outside the integral to obtain:

$$\mathbf{P}(\mathbf{r}) = \frac{\mathbf{p}(\mathbf{r})}{v}\int d\bar{\mathbf{r}}\, f(\mathbf{r} - \bar{\mathbf{r}}). \tag{27.21}$$

Since $\int d\mathbf{r}'\, f(\mathbf{r}') = 1$, we finally have

$$\mathbf{P}(\mathbf{r}) = \frac{1}{v}\mathbf{p}(\mathbf{r}); \tag{27.22}$$

i.e., provided the dipole moment of each cell varies appreciably only on the macroscopic scale, then the macroscopic Maxwell equation (27.4) holds with the polarization density $\mathbf{P}(\mathbf{r})$ defined to be the dipole moment of a primitive cell in the neighborhood of $\mathbf{r}$, divided by its equilibrium volume.[10]

THEORY OF THE LOCAL FIELD

To exploit macroscopic electrostatics, a theory is required relating the polarization density $\mathbf{P}$ back to the macroscopic electric field $\mathbf{E}$. Since each ion has microscopic dimensions, its displacement and distortion will be determined by the force due to the *microscopic* field at the position of the ion, diminished by the contribution to the microscopic field from the ion itself. This field is frequently called the local (or effective) field, $\mathbf{E}^{\text{loc}}(\mathbf{r})$.

We can exploit macroscopic electrostatics to simplify the evaluation of $\mathbf{E}^{\text{loc}}(\mathbf{r})$ by dividing space into regions near to and far from $\mathbf{r}$. The far region is to contain all external sources of field, all points outside the crystal, and only points inside the crystal that are far from $\mathbf{r}$ compared with the dimensions r_0 of the averaging region used in (Eq. (27.6)). All other points are said to be in the near region (Figure 27.3). The reason for this division is that the contribution to $\mathbf{E}^{\text{loc}}(\mathbf{r})$ of all charge in the far region will vary negligibly over a distance r_0 about $\mathbf{r}$, and would be unaffected if we were to apply the averaging procedure specified in (27.6). Therefore the contribution to $\mathbf{E}^{\text{loc}}(\mathbf{r})$ of all charge in the far region is just the macroscopic field, $\mathbf{E}_{\text{far}}^{\text{macro}}(\mathbf{r})$, that would exist at $\mathbf{r}$ if only the charge in the far region were present:

$$\mathbf{E}^{\text{loc}}(\mathbf{r}) = \overset{\equiv\text{micro}}{\mathbf{E}_{\text{near}}^{\text{loc}}}(\mathbf{r}) + \mathbf{E}_{\text{far}}^{\text{micro}}(\mathbf{r}) = \overset{\equiv\text{micro}}{\mathbf{E}_{\text{near}}^{\text{loc}}}(\mathbf{r}) + \mathbf{E}_{\text{far}}^{\text{macro}}(\mathbf{r}). \tag{27.23}$$

Now $\mathbf{E}(\mathbf{r})$, the full macroscopic field at $\mathbf{r}$, is constructed by averaging the microscopic field within r_0 of $\mathbf{r}$ due to all charges, in both the near and the far regions; i.e.,

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_{\text{far}}^{\text{macro}}(\mathbf{r}) + \mathbf{E}_{\text{near}}^{\text{macro}}(\mathbf{r}), \tag{27.24}$$

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[10] The derivation of this intuitive result permits us to estimate corrections when required.

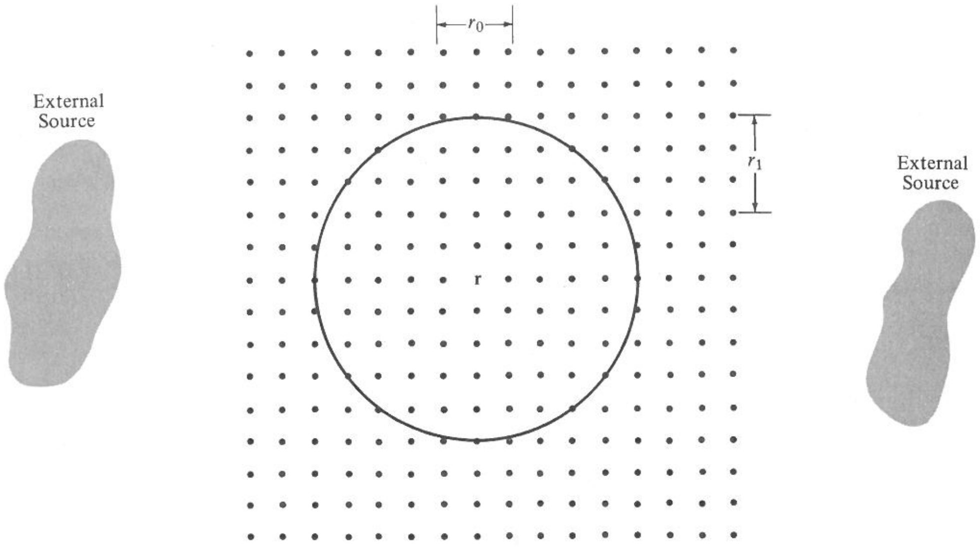

Figure 27.3
In calculating the local field at a point r it is convenient to consider separately contributions from the *far region* (i.e., all the crystal outside the sphere of radius r_1 about **r** and all external sources of field) and from the *near region* (i.e., all points within the sphere about **r**). The far region is taken to be far from **r** on the scale of the averaging length r_0, to insure that the microscopic field due to charges in the far region is equal to its macroscopic average.

where $\mathbf{E}^{\text{macro}}_{\text{near}}(\mathbf{r})$ is the macroscopic field that would exist at **r** if only the charges in the near region[11] were present. We can therefore rewrite Eq. (27.23) as:

$$\boxed{\mathbf{E}^{\text{loc}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \mathbf{E}^{\text{loc}}_{\text{near}}(\mathbf{r}) - \mathbf{E}^{\text{macro}}_{\text{near}}(\mathbf{r}).} \tag{27.25}$$

Thus we have related the unknown local field at **r** to the macroscopic electric field[12] at **r** and additional terms that depend only on the configuration of charges in the near region.

We shall apply (27.25) only to nonequilibrium configurations of the crystal with negligible spatial variation from cell to cell over distances of order r_1, the size of the near region.[13] In such cases $E^{\text{macro}}_{\text{near}}(\mathbf{r})$ will be the macroscopic field due to a *uniformly* polarized medium, whose shape is that of the near region. If we choose the near region to be a sphere, then this field is given by the following elementary result of electrostatics (see Problem 1): The macroscopic field anywhere inside a uniformly polarized sphere is just $\mathbf{E} = -4\pi\mathbf{P}/3$, where **P** is the polarization density. Therefore if the near region is a sphere over which **P** has negligible spatial variation, then Eq. (27.25) becomes

$$\mathbf{E}^{\text{loc}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \mathbf{E}^{\text{loc}}_{\text{near}}(\mathbf{r}) + \frac{4\pi\mathbf{P}(\mathbf{r})}{3}. \tag{27.26}$$

We are thus left with the problem of calculating the microscopic local field $\mathbf{E}^{\text{loc}}_{\text{near}}(\mathbf{r})$ appropriate to a spherical region whose center is taken to be the ion on which the field acts. Inside this region the charge density is the same in every cell (except for the removal of the ion at the center on which we are calculating the force). In most applications this calculation is done under the following simplifying assumptions:

1. The spatial dimensions and the displacement from equilibrium of each ion are considered to be so small that the polarizing field acting on it can be taken to be uniform over the whole ion and equal to the value of $\mathbf{E}^{\text{loc}}$ at the equilibrium position of the ion.
2. The spatial dimensions and the displacement from equilibrium of each ion are considered to be so small that the contribution to the local field at the equilibrium position of the given ion, from the ion whose equilibrium position is $\mathbf{R} + \mathbf{d}$, is accurately given by the field of a dipole of moment $e(\mathbf{d})\mathbf{u}(\mathbf{R} + \mathbf{d}) + \mathbf{p}(\mathbf{R} + \mathbf{d})$.

Since the dipole moments of ions at equivalent sites (displaced from each other by Bravais lattice vectors **R**) are identical within the near region over which **P** has negligible variation, the calculation of $\mathbf{E}^{\text{loc}}_{\text{near}}$ at an equilibrium site reduces to the type of lattice sum we described in Chapter 20. Furthermore, in the special case in which every equilibrium site in the equilibrium crystal is a center of cubic symmetry, it is easily shown (Problem 2) that this lattice sum must vanish; i.e., $\mathbf{E}^{\text{loc}}_{\text{near}}(\mathbf{r}) = 0$ at every equilibrium site. Since this case includes both the solid noble gases and the alkali halides, it is the only one we consider. For these crystals we may assume that the field polarizing each ion in the neighborhood of **r** is[14]

$$\boxed{\mathbf{E}^{\text{loc}}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{4\pi\mathbf{P}(\mathbf{r})}{3}.} \tag{27.27}$$

This result, sometimes known as the Lorentz relation, is widely used in theories of dielectrics. It is very important to remember the assumptions underlying it, particularly that of cubic symmetry about every equilibrium site.

Sometimes (27.27) is written in terms of the dielectric constant ϵ of the medium, using the constitutive relation[15]

$$\mathbf{D}(\mathbf{r}) = \epsilon\mathbf{E}(\mathbf{r}), \tag{27.28}$$

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[11] Including, of course, the ion on which we are calculating the force.

[12] A further complication of a purely macroscopic nature is peripheral to the argument here, in which **E(r)** is assumed to be given. If the internal field and polarization are produced by placing the sample in a specified field $\mathbf{E}^{\text{ext}}$, then an additional problem in macroscopic electrostatics must be solved to determine the macroscopic field **E** in the interior of the sample, since the discontinuity in the polarization density **P** at the surface of the sample acts as a bound surface charge, and contributes an additional term to the macroscopic field in the interior. For certain simply shaped samples in uniform external fields the induced polarization **P** and the macroscopic field **E** in the interior will both be constant and parallel to $\mathbf{E}^{\text{ext}}$, and one can write: $\mathbf{E} = \mathbf{E}^{\text{ext}} - N\mathbf{P}$, where N, the "depolarization factor," depends on the geometry of the sample. The most important elementary case is the sphere, for which $N = 4\pi/3$. For a general ellipsoid (in which **P** need not be parallel to **E**) see E. C. Stoner, *Phil. Mag.* **36**, 803 (1945).

[13] Note that we are now very macroscopic indeed, requiring that $\lambda \gg r_1 \gg r_0 \gg a$.

[14] Note that implicit in this relation is the fact that the local field acting on an ion depends only on the general location of the ion but not (in a lattice with a basis) on the type of ion (i.e., it depends on **R** but not on **d**). This convenient simplification is a consequence of our assumption that every ion occupies a position of cubic symmetry.

[15] In noncubic crystals **P**, and therefore **D**, need not be parallel to **E**, so ϵ is a tensor.

together with the relation (27.3) between **D**, **E**, and **P**, to express **P**(**r**) in terms of **E**(**r**):

$$\mathbf{P}(\mathbf{r}) = \frac{\epsilon - 1}{4\pi}\,\mathbf{E}(\mathbf{r}). \tag{27.29}$$

Using this to eliminate **P**(**r**) from (27.27), one finds that

$$\boxed{\mathbf{E}^{\mathrm{loc}}(\mathbf{r}) = \frac{\epsilon + 2}{3}\,\mathbf{E}(\mathbf{r}).} \tag{27.30}$$

Yet another way of expressing the same result is in terms of the *polarizability*, α, of the medium. The polarizability $\alpha(\mathbf{d})$ of the type of ion at position **d** in the basis is defined to be the ratio of its induced dipole moment to the field actually acting on it. Thus

$$\mathbf{p}(\mathbf{R} + \mathbf{d}) + e\mathbf{u}(\mathbf{R} + \mathbf{d}) = \alpha(\mathbf{d})\,\mathbf{E}^{\mathrm{loc}}(\mathbf{r})\big|_{\mathbf{r}\approx\mathbf{R}}. \tag{27.31}$$

The polarizability α of the medium is defined as the sum of the polarizabilities of the ions in a primitive cell:

$$\alpha = \sum_{\mathbf{d}} \alpha(\mathbf{d}). \tag{27.32}$$

Since (cf. (27.18) and (27.22)).

$$\mathbf{P}(\mathbf{r}) = \frac{1}{v}\sum_{\mathbf{d}}\Big[\mathbf{p}(\mathbf{R}, \mathbf{d}) + e(\mathbf{d})\mathbf{u}(\mathbf{R}, \mathbf{d})\Big]_{\mathbf{R}\approx\mathbf{r}}, \tag{27.33}$$

it follows that

$$\mathbf{P}(\mathbf{r}) = \frac{\alpha}{v}\,\mathbf{E}^{\mathrm{loc}}(\mathbf{r}). \tag{27.34}$$

Using (27.29) and (27.30) to express both **P** and $\mathbf{E}^{\mathrm{loc}}$ in terms of **E**, we find that (27.34) implies that

$$\boxed{\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\alpha}{3v}.} \tag{27.35}$$

This equation, known as the Clausius-Mossotti relation,[16] provides a valuable link between macroscopic and microscopic theories. A microscopic theory is required to calculate α, which gives the response of the ions to the actual field $\mathbf{E}^{\mathrm{loc}}$ acting on them. The resulting ϵ can then be used, in conjunction with the macroscopic Maxwell equations, to predict the optical properties of the insulator.

THEORY OF THE POLARIZABILITY

Two terms contribute to the polarizability α. The contribution from **p** (see Eq. (27.31)), the "atomic polarizability," arises from the distortion of the ionic charge distribution.

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[16] When written in terms of the index of refraction, $n = \sqrt{\epsilon}$, the Clausius-Mossotti relation is known as the Lorentz-Lorenz relation. (In the recent physics and chemistry literature of England and the United States it has become the widespread practice to misspell the last name of O. F. Mossotti with a single "s," and/or to interchange his initials.)

The contribution from $e\mathbf{u}$, the "displacement polarizability," arises from ionic displacements. There is no displacement polarizability in molecular crystals where the "ions" are uncharged, but in ionic crystals it is comparable to the atomic polarizability.

Atomic Polarizability

We allow the local field acting on the ion in question to be frequency-dependent, writing

$$\mathbf{E}^{\mathrm{loc}} = \mathrm{Re}\,(\mathbf{E}_0 e^{-i\omega t}), \tag{27.36}$$

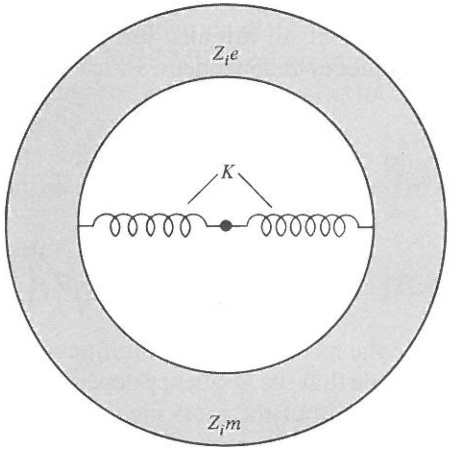

Figure 27.4
Crude classical model of atomic polarizability. The ion is represented as a charged shell of charge Z_ie and mass Z_im tied to an immobile nucleus by a spring of force constant $K = Z_im\omega_0^2$.

where $\mathbf{E}_0$ is independent of position (assumption 1, page 541). The simplest classical theory of atomic polarizability treats the ion as an electronic shell of charge Z_ie and mass Z_im tied to a heavy, immobile, undeformable ion core, by a harmonic spring, of spring constant $K = Z_im\omega_0^2$ (Figure 27.4). If the displacement of the shell from its equilibrium position is given by

$$\mathbf{r} = \mathrm{Re}\,(\mathbf{r}_0 e^{-i\omega t}), \tag{27.37}$$

then the equation of motion of the shell,

$$Z_im\ddot{\mathbf{r}} = -K\mathbf{r} - Z_ie\mathbf{E}^{\mathrm{loc}}, \tag{27.38}$$

implies that

$$\mathbf{r}_0 = -\frac{e\mathbf{E}_0}{m(\omega_0^2 - \omega^2)}. \tag{27.39}$$

Since the induced dipole moment is $\mathbf{p} = -Z_ie\mathbf{r}$, we have

$$\mathbf{p} = \mathrm{Re}\,(\mathbf{p}_0 e^{-i\omega t}), \tag{27.40}$$

with

$$\mathbf{p}_0 = \frac{Z_ie^2}{m(\omega_0^2 - \omega^2)}\,\mathbf{E}_0. \tag{27.41}$$

Defining the frequency-dependent atomic polarizability by

$$\mathbf{p}_0 = \alpha^{\mathrm{at}}(\omega)\mathbf{E}_0, \tag{27.42}$$

we have

$$\alpha^{\mathrm{at}}(\omega) = \frac{Z_i e^2}{m({\omega_0}^2 - \omega^2)}. \tag{27.43}$$

The model leading to (27.43) is, of course, very crude. However, for our purposes the most important feature of the result is that if ω is small compared with ω_0, the polarizability will be independent of frequency and equal to its static value:

$$\alpha^{\mathrm{at}} = \frac{Z_i e^2}{m{\omega_0}^2}. \tag{27.44}$$

We would expect ω_0, the frequency of vibration of the electronic shell, to be of the order of an atomic excitation energy divided by $\hbar$. This suggests that, unless $\hbar\omega$ is of the order of several electron volts, we can take the atomic polarizability to be independent of frequency. This is confirmed by more accurate quantum-mechanical calculations of α.

Note that we can also use (27.44) to estimate the frequency below which α^{at} will be frequency-independent, in terms of the observed static polarizabilities:

$$\begin{aligned}\hbar\omega_0 &= \sqrt{\frac{\hbar^2 Z_i e^2}{m\alpha^{\mathrm{at}}}} \\ &= \sqrt{\frac{4{a_0}^3 Z_i}{\alpha^{\mathrm{at}}}\frac{e^2}{2a_0}}, \qquad a_0 = \frac{\hbar^2}{me^2}, \\ &= \sqrt{Z_i\left(\frac{10^{-24}\ \mathrm{cm}^3}{\alpha^{\mathrm{at}}}\right)} \times 10.5\ \mathrm{eV}.\end{aligned} \tag{27.45}$$

Since the measured polarizabilities (see Table 27.1) are of the order of $10^{-24}\ \mathrm{cm}^3$, we conclude that the frequency dependence of the atomic polarizability will not come into play (in all but the most highly polarizable of ions) until frequencies corresponding to ultraviolet radiation.

Table 27.1

ATOMIC POLARIZABILITIES OF THE HALOGEN IONS, NOBLE GAS ATOMS, AND ALKALI METAL IONS[a]

HALOGENS		NOBLE GASES		ALKALI METALS	
		He	0.2	Li^+	0.03
F^-	1.2	Ne	0.4	Na^+	0.2
Cl^-	3	Ar	1.6	K^+	0.9
Br^-	4.5	Kr	2.5	Rb^+	1.7
I^-	7	Xe	4.0	Cs^+	2.5

[a] In units of $10^{-24}\ \mathrm{cm}^3$. Note that entries in the same row have the same electronic shell structure, but increasing nuclear charge.

Source: A. Dalgarno, *Advances Phys.* **11**, 281 (1962).

Displacement Polarizability

In ionic crystals we must consider the dipole moment due to the displacement of the charged ions by the electric field, in addition to the atomic polarization resulting

from the deformation of their electronic shells by the field. We begin by ignoring the atomic polarization (*rigid-ion approximation*). To simplify the discussion we also consider only crystals with two ions per primitive cell, of charges e and $-e$. If the ions are undeformable, then the dipole moment of the primitive cell is just

$$\mathbf{p} = e\mathbf{w}, \qquad \mathbf{w} = \mathbf{u}^+ - \mathbf{u}^-, \tag{27.46}$$

where $\mathbf{u}^{\pm}$ is the displacement of the positive or negative ion from its equilibrium position.

To determine $\mathbf{w}(\mathbf{r})$ we note that the long-range electrostatic forces between ions are already contained in the field $\mathbf{E}^{\mathrm{loc}}$. The remaining short-range interionic forces (e.g., higher-order electrostatic multipole moments and core-core repulsion) will fall off rapidly with distance, and we may assume that they produce a restoring force for an ion at $\mathbf{r}$ that depends only on the displacement of the ions in its vicinity. Since we are considering disturbances that vary slowly on the atomic scale, in the vicinity of $\mathbf{r}$ all ions of the same charge move as a whole with the same displacement, $\mathbf{u}^+(\mathbf{r})$ or $\mathbf{u}^-(\mathbf{r})$. Thus the short-range part of the restoring force acting on an ion at $\mathbf{r}$ will simply be proportional to[17] the relative displacement $\mathbf{w}(\mathbf{r}) = \mathbf{u}^+(\mathbf{r}) - \mathbf{u}^-(\mathbf{r})$ of the two oppositely charged sublattices in the neighborhood of $\mathbf{r}$.

Consequently in a distortion of the crystal with slow spatial variation on the microscopic scale, the displacements of the positive and negative ions satisfy equations of the form:

$$\begin{aligned}M_+\ddot{\mathbf{u}}^+ &= -k(\mathbf{u}^+ - \mathbf{u}^-) + e\mathbf{E}^{\mathrm{loc}}, \\ M_-\ddot{\mathbf{u}}^- &= -k(\mathbf{u}^- - \mathbf{u}^+) - e\mathbf{E}^{\mathrm{loc}},\end{aligned} \tag{27.47}$$

which can be written

$$\ddot{\mathbf{w}} = \frac{e}{M}\mathbf{E}^{\mathrm{loc}} - \frac{k}{M}\mathbf{w}, \tag{27.48}$$

where M is the ionic reduced mass, $M^{-1} = (M_+)^{-1} + (M_-)^{-1}$. Letting $\mathbf{E}^{\mathrm{loc}}$ be an AC field of the form (27.36), we find that

$$\mathbf{w} = \mathrm{Re}(\mathbf{w}_0 e^{-i\omega t}), \quad \mathbf{w}_0 = \frac{e\mathbf{E}_0/M}{\bar{\omega}^2 - \omega^2}, \tag{27.49}$$

where

$$\bar{\omega}^2 = \frac{k}{M}. \tag{27.50}$$

Accordingly,

$$\alpha^{\mathrm{dis}} = \frac{p_0}{E_0} = \frac{ew_0}{E_0} = \frac{e^2}{M(\bar{\omega}^2 - \omega^2)}. \tag{27.51}$$

Note that the displacement polarizability (27.51) has the same form as the atomic polarizability (27.43). However the resonant frequency $\bar{\omega}$ is characteristic of lattice vibrational frequencies, and therefore $\hbar\bar{\omega} \approx \hbar\omega_D \approx 10^{-1}$ to 10^{-2} eV. This can be 10^2 to 10^3 times smaller than the atomic frequency ω_0, and therefore, in contrast to the atomic polarizability, the displacement polarizability has a significant frequency dependence in the infrared and optical range.

---

[17] The proportionality constant in general will be a tensor, but it reduces to a constant in a crystal of cubic symmetry, the only case we consider here.

Note also that because the ionic mass M is about 10^4 times the electronic mass m, the static ($\omega = 0$) ionic and displacement polarizabilities may well be of the same size. This means that the rigid-ion model we have used is unjustifiable, and (27.51) must be corrected to take into account the atomic polarizability of the ions as well. The most naive way to do this is simply to add the two types of contribution to the polarizability:

$$\alpha = (\alpha^+ + \alpha^-) + \frac{e^2}{M(\bar{\omega}^2 - \omega^2)}, \tag{27.52}$$

where α^+ and α^- are the atomic polarizabilities of the positive and negative ions. There is no real justification for this, since the first term in (27.52) was calculated on the assumption that the ions were immobile but polarizable, while the second was calculated for ions that could be moved, but not deformed. Evidently a more reasonable approach would combine the models that lead on the one hand to (27.43) and, on the other, to (27.51), calculating in one step the response to the local field of ions that can be both displaced and deformed. Such theories are known as *shell model* theories. They generally lead to results that differ considerably in numerical detail from those predicted by the more naive (27.52), but have many of the same basic structural features. We therefore explore the consequences of (27.52) further, indicating later how it should be modified in a more reasonable model.

In conjunction with the Clausius-Mossotti relation (27.35), the approximation expressed by (27.52) leads to a dielectric constant $\epsilon(\omega)$ for an ionic crystal, given by

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi}{3v}\left(\alpha^+ + \alpha^- + \frac{e^2}{M(\bar{\omega}^2 - \omega^2)}\right). \tag{27.53}$$

In particular, the static dielectric constant is given by

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi}{3v}\left(\alpha^+ + \alpha^- + \frac{e^2}{M\bar{\omega}^2}\right), \qquad (\omega \ll \bar{\omega}), \tag{27.54}$$

while the high-frequency[18] dielectric constant satisfies

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi}{3v}(\alpha^+ + \alpha^-), \qquad (\bar{\omega} \ll \omega \ll \omega_0). \tag{27.55}$$

It is convenient to write $\epsilon(\omega)$ in terms of ϵ_0 and ϵ_∞, since the two limiting forms are readily measured: ϵ_0 is the static dielectric constant of the crystal, while ϵ_∞ is the dielectric constant at optical frequencies, and is therefore related to the index of refraction, n, by $n^2 = \epsilon_\infty$. We have

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{1}{1 - (\omega^2/\bar{\omega}^2)}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right), \tag{27.56}$$

---

[18] In this context, by "high frequencies" we shall always mean frequencies high compared with lattice vibrational frequencies, but low compared with atomic excitation frequencies. The frequency of visible light generally satisfies this condition.

which can be solved for $\epsilon(\omega)$:

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_\infty - \epsilon_0}{(\omega^2/\omega_T^2) - 1}, \tag{27.57}$$

where

$$\omega_T^2 = \bar{\omega}^2\left(\frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\right) = \bar{\omega}^2\left(1 - \frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 + 2}\right). \tag{27.58}$$

Application to Long-Wavelength Optical Modes of Ionic Crystals

To calculate the normal mode dispersion relations in an ionic crystal we could proceed by the general techniques described in Chapter 22. However, we would encounter severe computational difficulties because of the very long range of the interionic electrostatic interactions. Techniques have been developed for dealing with this problem, similar to those exploited in calculating the cohesive energy of an ionic crystal (Chapter 20). However, for long-wavelength optical modes one can avoid such calculations by stating the problem as one in macroscopic electrostatics:

In a long-wavelength ($\mathbf{k} \approx \mathbf{0}$) optical mode the oppositely charged ions in each primitive cell undergo oppositely directed displacements, giving rise to a nonvanishing polarization density $\mathbf{P}$. Associated with this polarization density there will in general be a macroscopic electric field $\mathbf{E}$ and an electric displacement $\mathbf{D}$, related by

$$\mathbf{D} = \epsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P}. \tag{27.59}$$

In the absence of free charge, we have

$$\nabla \cdot \mathbf{D} = 0. \tag{27.60}$$

Furthermore, $\mathbf{E}^{\text{micro}}$ is the gradient of a potential.[19] It follows from (27.6) that $\mathbf{E}$ is also, so that

$$\nabla \times \mathbf{E} = \nabla \times (-\nabla\phi) = 0. \tag{27.61}$$

In a cubic crystal $\mathbf{D}$ is parallel to $\mathbf{E}$ (i.e., ϵ is not a tensor) and therefore, from (27.59), both are parallel to $\mathbf{P}$. If all three have the spatial dependence,

$$\begin{Bmatrix}\mathbf{D}\\ \mathbf{E}\\ \mathbf{P}\end{Bmatrix} = \operatorname{Re}\begin{Bmatrix}\mathbf{D}_0\\ \mathbf{E}_0\\ \mathbf{P}_0\end{Bmatrix} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{27.62}$$

then (27.60) reduces to $\mathbf{k} \cdot \mathbf{D}_0 = 0$, which requires that

$$\mathbf{D} = 0 \quad \text{or} \quad \mathbf{D}, \mathbf{E}, \text{and } \mathbf{P} \perp \mathbf{k}, \tag{27.63}$$

while (27.61) reduces to $\mathbf{k} \times \mathbf{E}_0 = 0$, which requires that

$$\mathbf{E} = 0 \quad \text{or} \quad \mathbf{E}, \mathbf{D}, \text{and } \mathbf{P} \parallel \mathbf{k}. \tag{27.64}$$

In a longitudinal optical mode the (nonzero) polarization density $\mathbf{P}$ is parallel to $\mathbf{k}$,

---

[19] At optical frequencies one might worry about keeping only electrostatic fields, since the right side of the full Maxwell equation, $\nabla \times \mathbf{E} = -(1/c)\,\partial\mathbf{B}/\partial t$ need not be negligible. We shall see shortly, however, that a full electrodynamic treatment leads to very much the same conclusions.

and Eq. (27.63) therefore requires that **D** must vanish. This is consistent with (27.59) only if

$$\mathbf{E} = -4\pi\mathbf{P}, \quad \epsilon = 0 \qquad \text{(longitudinal mode).} \tag{27.65}$$

On the other hand, in a transverse optical mode the (nonzero) polarization density **P** is perpendicular to **k**, which is consistent with (27.64) only if **E** vanishes. This, however, is consistent with (27.59) only if

$$\mathbf{E} = 0, \quad \epsilon = \infty \qquad \text{(transverse mode).} \tag{27.66}$$

According to (27.57), $\epsilon = \infty$ when $\omega^2 = \omega_T{}^2$, and therefore the result (27.66) identifies ω_T as the frequency of the long-wavelength ($\mathbf{k} \to 0$) transverse optical mode. The frequency ω_L of the longitudinal optical mode is determined by the condition $\epsilon = 0$ (Eq. (27.65)), and (27.57) therefore gives

$$\boxed{\omega_L{}^2 = \frac{\epsilon_0}{\epsilon_\infty}\,\omega_T{}^2.} \tag{27.67}$$

This equation, relating the longitudinal and transverse optical-mode frequencies to the static dielectric constant and index of refraction, is known as the *Lyddane-Sachs-Teller relation.* Note that it follows entirely from the interpretation that (27.65) and (27.66) lend to the zeros and poles of $\epsilon(\omega)$, together with the functional form of (27.57)—i.e., the fact that in the frequency range of interest ϵ as a function of ω^2 is a constant plus a simple pole. As a result, the relation has a validity going well beyond the crude approximation (27.52) of additive polarizabilities, and also applies to the far more sophisticated shell model theories of diatomic ionic crystals.

Since the crystal is more polarizable at low frequencies[20] than at high, ω_L exceeds ω_T. It may seem surprising that ω_L should differ at all from ω_T in the limit of long wavelengths, since in this limit the ionic displacements in any region of finite extent are indistinguishable. However, because of the long range of electrostatic forces, their influence can always persist over distances comparable to the wavelength, no matter how long that wavelength may be; thus longitudinal and transverse optical modes will always experience different electrostatic restoring forces.[21] Indeed, if we use the Lorentz relation (27.27) we find from (27.65) that the electrostatic restoring force in a long-wavelength longitudinal optical mode is given by the local field

$$(\mathbf{E}^{\text{loc}})_L = \mathbf{E} + \frac{4\pi\mathbf{P}}{3} = -\frac{8\pi\mathbf{P}}{3} \qquad \text{(longitudinal),} \tag{27.68}$$

while (from (27.66)) it is given in a long-wavelength transverse optical mode by

$$(\mathbf{E}^{\text{loc}})_T = \frac{4\pi\mathbf{P}}{3} \qquad \text{(transverse).} \tag{27.69}$$

---

[20] At frequencies well above the natural vibrational frequencies of the ions, they fail to respond to an oscillatory force, and one has only atomic polarizability. At low frequencies both mechanisms can contribute.

[21] This argument, based on instantaneous action at a distance, must be reexamined when the electrostatic approximation (27.61) is dropped (see footnotes 19 and 25).

Thus in a longitudinal mode the local field acts to reduce the polarization (i.e., it adds to the short-range restoring force proportional to $k = M\bar{\omega}^2$) while in a transverse mode it acts to support the polarization (i.e., it reduces the short-range restoring force). This is consistent with (27.58), which predicts that ω_T is less than $\bar{\omega}$ (since $\epsilon_0 - \epsilon_\infty$ is positive). It is also consistent with (27.67), which, with the aid of (27.58), can be written:

$$\omega_L{}^2 = \bar{\omega}^2\left(1 + 2\,\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 + 2}\,\frac{1}{\epsilon_\infty}\right), \tag{27.70}$$

which indicates that ω_L exceeds $\bar{\omega}$.

The Lyddane-Sachs-Teller relation (27.67) has been confirmed by comparing measurements of ω_L and ω_T from neutron scattering, with measured values of the dielectric constant and index of refraction. In two alkali halides (NaI and KBr), ω_L/ω_T and $(\epsilon_0/\epsilon_\infty)^{1/2}$ were found to agree to within the experimental uncertainty of the measurements (a few percent).[22]

However, because it is merely a consequence of the analytic form of $\epsilon(\omega)$, the validity of the Lyddane-Sachs-Teller relation does not provide a very stringent test of a theory. A more specific prediction can be constructed from Eqs. (27.54), (27.55), and (27.58), which combine together to give

$$\frac{9}{4\pi}\frac{(\epsilon_0 - \epsilon_\infty)}{(\epsilon_\infty + 2)^2}\,\omega_T{}^2 = \frac{e^2}{Mv}. \tag{27.71}$$

Since e^2/Mv is determined entirely by the ionic charge, the ionic reduced mass, and the lattice constant, the right side of (27.71) is known. However, measured values of ϵ_0, ϵ_∞, and ω_T in the alkali halides lead to a value for the left side of (27.71) that can be expressed in the form $(e^*)^2/Mv$, where e^* (known as the *Szigeti charge*) ranges between about $0.7e$ and $0.9e$. This should *not* be taken as evidence that the ions are not fully charged, but as a telling sign of the failure of the crude assumption (27.52) that atomic and displacement polarizabilities simply add to give the total polarizability.

To remedy this defect, one must turn to a shell model theory in which atomic and displacement polarizations are calculated together, by allowing the electronic shell to move relative to the ion core (as done above in calculating the atomic polarizability) at the same time as the ion cores are themselves displaced.[23] The general structural form (27.57) of $\epsilon(\omega)$ is preserved in such a theory, but the specific forms for the constants ϵ_0, ϵ_∞, and ω_T can be quite different.

Application to the Optical Properties of Ionic Crystals

The above discussion of the transverse optical mode is not completely accurate, based as it is on the electrostatic approximation (27.61) to the Maxwell equation:[24]

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}. \tag{27.72}$$

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[22] A. D. B. Woods et al., *Phys. Rev.* **131**, 1025 (1963).

[23] An early and particularly simple model is given by S. Roberts, *Phys. Rev.* **77**, 258 (1950).

[24] Our discussion of the longitudinal optical mode is founded entirely on the Maxwell equation $\nabla \cdot \mathbf{D} = 0$ and remains valid in a fully electrodynamic analysis.

When (27.61) is replaced by the more general (27.72), the conclusion (27.66) that the transverse optical mode frequency is determined by the condition $\epsilon(\omega) = \infty$ must be replaced by the more general result (Eq. (1.34)) that transverse fields with angular frequency ω and wave vector $\mathbf{k}$ can propagate only if

$$\epsilon(\omega) = \frac{k^2c^2}{\omega^2}. \tag{27.73}$$

Thus for optical modes with wave vectors satisfying $kc \gg \omega$, the approximation $\epsilon = \infty$ is reasonable. The frequencies of optical phonons are of order $\omega_D = k_D s$, where s is the speed of sound in the crystal, so this requires that

$$\frac{k}{k_D} \gg \frac{s}{c}. \tag{27.74}$$

Since k_D is comparable to the dimensions of the Brillouin zone, while s/c is of order 10^{-4} to 10^{-5}, the electrostatic approximation is fully justified except for optical modes whose wave vectors are only a small fraction of a percent of the dimensions of the zone from $\mathbf{k} = 0$.

We can describe the structure of the transverse modes all the way down to $\mathbf{k} = 0$, by plotting ϵ vs. ω (Eq. (27.57)) (Figure 27.5). Note that ϵ is negative between ω_T and ω_L, so Eq. (27.73) requires kc to be imaginary. Thus no radiation can propagate in the crystal between the transverse and longitudinal optical frequencies. Outside this forbidden range ω is plotted vs. k in Figure 27.6. The dispersion relation has two branches, lying entirely below ω_T and entirely above ω_L. The lower branch has the form $\omega \equiv \omega_T$ except when k is so small as to be comparable to ω_T/c. It describes the electric field accompanying a transverse optical mode in the constant-frequency region. However, when k is of order ω_T/c the frequency falls below ω_T, vanishing as $kc/\sqrt{\epsilon_0}$, a relation characteristic of ordinary electromagnetic radiation in a medium with dielectric constant ϵ_0.

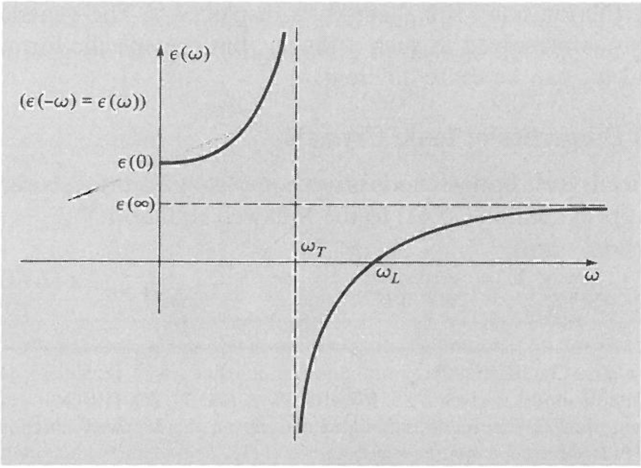

Figure 27.5
Frequency-dependent dielectric constant for a diatomic ionic crystal.

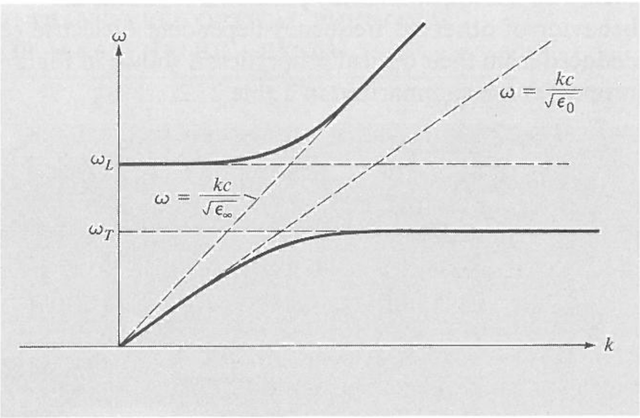

Figure 27.6
Solutions to the dispersion relation $\omega = kc/\sqrt{\mathcal{E}(\omega)}$ for *transverse* electromagnetic modes propagating in a diatomic ionic crystal. (The relation to Figure 27.5 is most readily seen by rotating the figure through 90° and considering it to be a plot of $k = \omega\sqrt{\mathcal{E}(\omega)}/c$, vs. ω.) In the linear regions one mode is clearly photonlike and one clearly optical phononlike. In the curved regions both modes have a mixed nature, and are sometimes referred to as "polaritons."

The upper branch, on the other hand, assumes the linear form $\omega = kc/\sqrt{\epsilon_\infty}$, characteristic of electromagnetic radiation in a medium with dielectric constant ϵ_∞, when k is large compared with ω_T/c, but as k approaches zero, the frequency does not vanish linearly, but levels off to ω_L.[25]

Finally, note that if the dielectric constant is a real number, then the reflectivity of the crystal is given by (see Eq. (K.6) in Appendix K)

$$r = \left(\frac{\sqrt{\epsilon} - 1}{\sqrt{\epsilon} + 1}\right)^2. \tag{27.75}$$

As $\epsilon \to \infty$, the reflectivity approaches unity. Thus all incident radiation should be perfectly reflected at the frequency of the transverse optical mode. This effect can be amplified by repeated reflections of a ray from crystal faces. Since n reflections will diminish the intensity by r^n, after very many reflections only the component of radiation with frequencies very close to ω_T will survive. This surviving radiation is known as the *reststrahl* (residual ray). Such repeated reflections provide a very precise way of measuring ω_T, as well as a method for producing very monochromatic radiation in the infrared.

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[25] Thus as $k \to 0$ a transverse mode *does* occur at the same frequency as the longitudinal mode (see page 548). The reason this behavior emerges in an electrodynamic, but not an electrostatic, analysis is basically the finite velocity of signal propagation in an electrodynamic theory. Electromagnetic signals can only propagate with the speed of light, and therefore no matter how long their spatial range, they can be effective in distinguishing longitudinal from transverse modes only if they can travel a distance comparable to a wavelength in a time small compared with a period (i.e., $kc \gg \omega$). The argument on page 548, which explains why ω_L and ω_T differ, implicitly assumes that Coulomb forces act instantaneously at a distance, and becomes invalid when this assumption fails.

To the extent that the lattice vibrations are anharmonic (and therefore damped) ϵ will also have an imaginary part. This broadens the reststrahl resonance. The typical behavior of observed frequency-dependent dielectric constants in ionic crystals, as deduced from their optical properties, is shown in Figure 27.7. Alkali halide dielectric properties are summarized in Table 27.2.

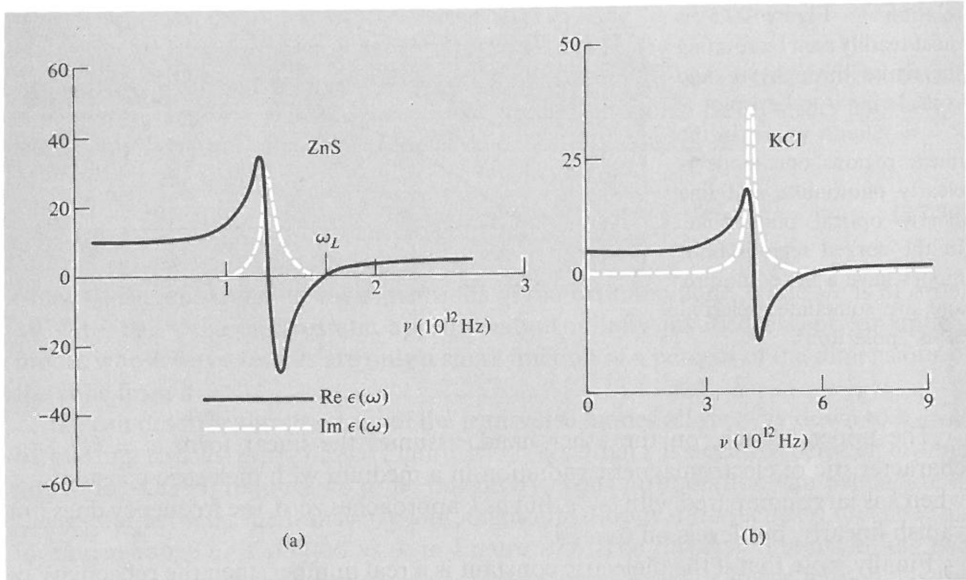

Figure 27.7
(a) Real (solid line) and imaginary (dashed line) parts of the dielectric constant of zinc sulfide. (After F. Abeles and J. P. Mathieu, *Annales de Physique* 3, 5 (1958); quoted by E. Burstein, *Phonons and Phonon Interactions*, T. A. Bak, ed., W. A. Benjamin, Menlo Park, California, 1964.) (b) Real (solid line) and imaginary (dashed line) parts of the dielectric constant of potassium chloride. (After G. R. Wilkinson and C. Smart; quoted by D. H. Martin, *Advances Phys.* **14**, 39 (1965).)

COVALENT INSULATORS

The above analysis of ionic and molecular crystals has relied on the possibility of resolving the charge distribution of the crystal into contributions from identifiable ions (atoms, molecules) as in (27.9). In covalent crystals, however, appreciable electronic charge density resides between ions (forming the so-called covalent bonds). This part of the total charge distribution is uniquely a property of the condensed state of matter, bearing no resemblance to the charge distribution of single isolated ions (atoms, molecules). Furthermore, since it comes from the most loosely bound atomic electrons, it makes a very important contribution to the polarizability of the crystal. Therefore, in calculating dielectric properties of covalent crystals one must deal with the polarizability of the crystal as a whole, either invoking band theory from the start or developing a phenomenology of "bond polarizabilities."

We shall not pursue this subject here, except to point out that covalent crystals can have quite large dielectric constants, reflecting the relatively delocalized structure of their electronic charge distributions. Static dielectric constants for selected covalent crystals are listed in Table 27.3. As we shall see (Chapter 28), the fact that the dielectric

Table 27.2
STATIC DIELECTRIC CONSTANT, OPTICAL DIELECTRIC CONSTANT, AND TRANSVERSE OPTICAL PHONON FREQUENCY FOR ALKALI HALIDE CRYSTALS

COMPOUND	ϵ_0	ϵ_∞	$\hbar\omega_T/k_B$[a]
LiF	9.01	1.96	442
NaF	5.05	1.74	354
KF	5.46	1.85	274
RbF	6.48	1.96	224
CsF	—	2.16	125
LiCl	11.95	2.78	276
NaCl	5.90	2.34	245
KCl	4.84	2.19	215
RbCl	4.92	2.19	183
CsCl	7.20	2.62	151
LiBr	13.25	3.17	229
NaBr	6.28	2.59	195
KBr	4.90	2.34	166
RbBr	4.86	2.34	139
CsBr	6.67	2.42	114
LiI	16.85	3.80	—
NaI	7.28	2.93	167
KI	5.10	2.62	156
RbI	4.91	2.59	117.5
CsI	6.59	2.62	94.6

[a] From the reststrahl peak; in degrees Kelvin.
Source: R. S. Knox and K. J. Teegarden, *Physics of Color Centers*, W. B. Fowler, ed., Academic Press, New York, 1968, page 625.

Table 27.3
STATIC DIELECTRIC CONSTANTS FOR SELECTED COVALENT AND COVALENT-IONIC CRYSTALS OF THE DIAMOND, ZINCBLENDE, AND WURTZITE STRUCTURES[a]

CRYSTAL	STRUCTURE	ϵ_0	CRYSTAL	STRUCTURE	ϵ_0
C	*d*	5.7	ZnO	*w*	4.6
Si	*d*	12.0	ZnS	*w*	5.1
Ge	*d*	16.0	ZnSe	*z*	5.8
Sn	*d*	23.8	ZnTe	*z*	8.3
SiC	*z*	6.7	CdS	*w*	5.2
GaP	*z*	8.4	CdSe	*w*	7.0
GaAs	*z*	10.9	CdTe	*z*	7.1
GaSb	*z*	14.4	BeO	*w*	3.0
InP	*z*	9.6	MgO	*z*	3.0
InAs	*z*	12.2			
InSb	*z*	15.7			

[a] Quoted by J. C. Phillips, *Phys. Rev. Lett.* **20**, 550 (1968).

constants can be quite substantial is a point of considerable importance in the theory of impurity levels in semiconductors.

PYROELECTRICITY

In deriving the macroscopic equation

$$\nabla \cdot \mathbf{E} = -4\pi \nabla \cdot \mathbf{P} \tag{27.76}$$

for ionic crystals, we assumed (see footnote 9) that the equilibrium dipole moment of the primitive cell,

$$\mathbf{p}_0 = \sum_{\mathbf{d}} \mathbf{d}e(\mathbf{d}), \tag{27.77}$$

vanished, and therefore ignored a term

$$\Delta \mathbf{P} = \frac{\mathbf{p}_0}{v} \tag{27.78}$$

in the polarization density **P**. As Figure 27.8 demonstrates, the value of the dipole moment $\mathbf{p}_0$ is not independent of the choice of primitive cell. However, since only the divergence of **P** has physical significance, an additive constant vector $\Delta\mathbf{P}$ does not affect the physics implied by the macroscopic Maxwell equations.

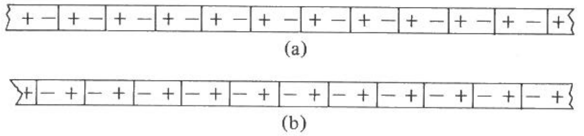
(a)
(b)

Figure 27.8
The dipole moment of the primitive cell depends on the choice of primitive cell. This is illustrated for a one-dimensional ionic crystal.

There would be nothing more to say if all crystals were infinite in extent. However, real crystals have surfaces, at which the macroscopic polarization density **P** drops discontinuously to zero, thereby contributing a singular term on the right side of (27.76). This term is conventionally interpreted as a bound surface charge per unit area, whose magnitude is the normal component of **P** at the surface, P_n. Thus an additive constant in **P** is far from inconsequential in a finite crystal.

In a finite crystal, however, we must reexamine our assumption that each primitive cell has zero total charge:

$$\sum_{\mathbf{d}} e(\mathbf{d}) = 0. \tag{27.79}$$

In an infinite crystal of identical cells this is merely the statement that the crystal as a whole is neutral, but in a crystal with surfaces, only the interior cells are identically occupied, and charge neutrality is perfectly consistent with partially filled, and therefore charged, surface cells (Figure 27.9). Should one's choice of cell lead to surface cells containing net charge, an additional term would have to be added to (27.76) to represent this bound surface charge, ρ_s. When the choice of cell is changed, both P_n and ρ_s will change, in such a way that the total net macroscopic surface charge density, $P_n + \rho_s$, is unchanged.

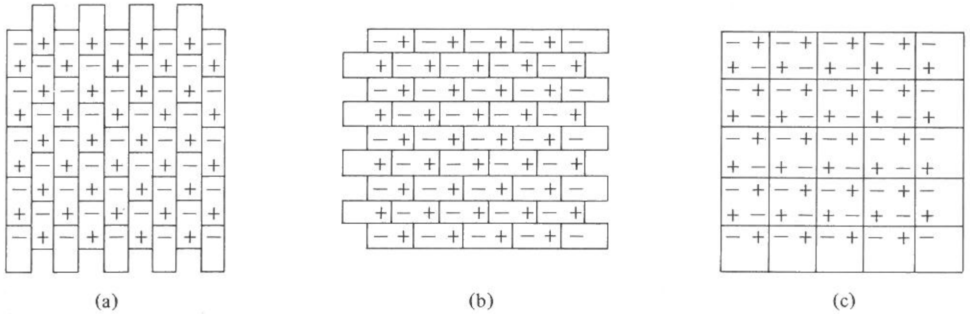
(a) (b) (c)

Figure 27.9
The "natural" choice of primitive cell is one that leads to uncharged cells at the surface. The cells chosen in (a) and (b) violate this criterion, and their contribution to the polarization density is cancelled by the contribution from the charged surface cells. The cell in (c) (which is nonprimitive) leads to uncharged surface cells and has no dipole moment.

Thus the "natural" choice of cell for which (27.76) is valid without an additional term representing the unbalanced charge in surface cells, is a cell whose neutrality is maintained even at the surfaces of actual physical specimens.[26]

Crystals whose natural primitive cells have a nonvanishing dipole moment $\mathbf{p}_0$ are called *pyroelectric*.[27] In equilibrium a perfect specimen of a pyroelectric crystal has a total dipole moment of $\mathbf{p}_0$ times the number of cells in the crystal,[28] and thus a polarization density $\mathbf{P} = \mathbf{p}_0/v$ throughout the crystal, even in the absence of an external field. This immediately implies some severe restrictions on the point-group symmetries of a pyroelectric crystal, for a symmetry operation must preserve all crystalline properties and, in particular, the direction of **P**. Thus the only possible rotation axis is one parallel to **P**, and furthermore there cannot be mirror planes perpendicular to that axis. This excludes all point groups except (Table 7.3) C_n and C_{nv} ($n = 2, 3, 4, 6$) and C_1 and C_{1h}. A glance at Table 7.3 reveals that these are the only point groups compatible with the location of a directed object (an arrow, for example) at each site.[29]

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[26] This often requires a cell that is not primitive (see Figure 27.9), but it is easily verified that the earlier analysis in this chapter is in no way affected by using a larger microscopic cell.

[27] The name (pyro = fire) reflects the fact that under ordinary conditions the moment of a pyroelectric crystal will be masked by neutralizing layers of ions from the atmosphere that collect on the faces of the crystal. If, however, the crystal is heated, then the masking will no longer be complete, since the polarization will change due to thermal expansion of the crystal, neutralizing ions will be evaporated, etc. Thus the effect was first thought to be the production of an electric moment by heat. (Sometimes the term "polar crystal" is used instead of "pyroelectric crystal." However, "polar crystal" is also widely used as a synonym for "ionic crystal" (whether pyroelectric or not), and the term is therefore best avoided.) The net polarization can also be masked by a domain structure, as in ferromagnets (see Chapter 33).

[28] The dipole moment of the surface cells need not be $\mathbf{p}_0$, but in the limit of a large crystal this will have a negligible effect on the total dipole moment, since the overwhelming majority of cells will be in the interior.

[29] Some crystals, though nonpyroelectric in the absence of external stresses can develop a spontaneous dipole moment when mechanically strained; i.e., by suitable squeezing, their crystal structures can be distorted to ones that can sustain a dipole moment. Such crystals are called *piezoelectric*. The point group of a piezoelectric crystal (when unstrained) cannot contain the inversion.

FERROELECTRICITY

The most stable structure of some crystals is nonpyroelectric above a certain temperature T_c (known as the *Curie temperature*) and pyroelectric below it.[30] Such crystals (examples are given in Table 27.4) are called ferroelectrics.[31] The transition from the unpolarized to the pyroelectric state is called first order if it is discontinuous (i.e., if **P** acquires a nonzero value immediately below T_c) and second or higher order, if it is continuous (i.e., if **P** grows continuously from zero as T drops below T_c).[32]

Just below the Curie temperature (for a continuous ferroelectric transition) the distortion of the primitive cell from the unpolarized configuration will be very small, and it is therefore possible, by applying an electric field opposite to this small polarization, to diminish and even reverse it. As T drops farther below T_c, the distortion of the cell increases, and very much stronger fields are required to reverse the direction of **P**. This is sometimes taken as the essential attribute of ferroelectrics, which are then defined as pyroelectric crystals whose polarization can be reversed by applying a strong electric field. This is done to include those crystals one feels would satisfy the first definition (existence of a Curie temperature), except that they melt before the conjectured Curie temperature can be reached. Well below the Curie temperature, however, the reversal of polarization may require so drastic a restructuring of the crystal as to be impossible even in the strongest attainable fields.

Immediately below the Curie temperature of a continuous ferroelectric transition, the crystal spontaneously and continuously distorts to a polarized state. One would therefore expect the dielectric constant to be anomalously large in the neighborhood of T_c, reflecting the fact that it requires very little applied field to alter substantially the displacement polarization of the crystal. Dielectric constants as large as 10^5 have been observed near ferroelectric transition points. In an ideal experiment the dielectric constant should actually become infinite precisely at T_c. For a continuous transition this simply expresses the fact that as T_c is approached from above, the net restoring force opposing a lattice distortion from the unpolarized to the polarized phase vanishes.

If the restoring force opposing a particular lattice distortion vanishes, there should be a zero-frequency normal mode whose polarization vectors describe precisely this distortion. Since the distortion leads to a net dipole moment and therefore involves a relative displacement between ions of opposite charge, the mode will be an optical mode. In the vicinity of the transition, relative displacements will be large, anharmonic terms will be substantial, and this "soft" mode should be rather strongly damped.

These two observations (infinite static dielectric constant and a zero-frequency optical mode) are not independent. One implies the other by the Lyddane-Sachs-Teller relation (27.67), which requires the transverse optical-mode frequency to vanish whenever the static dielectric constant is infinite.

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[30] Transitions back and forth are also known: e.g., there can be a range of temperatures for the pyroelectric phase, above and below which the crystal is unpolarized.

[31] The name stresses the analogy with ferromagnetic materials, which have a net *magnetic* moment. It is not meant to suggest that iron has any special relation to the phenomenon.

[32] Sometimes the term "ferroelectric" is reserved for crystals in which the transition is second order.

Perhaps the simplest type of ferroelectric crystal (and the one most widely studied) is the perovskite structure, shown in Figure 27.10. Other ferroelectrics tend to be substantially more complex. Some characteristic examples are given in Table 27.4.

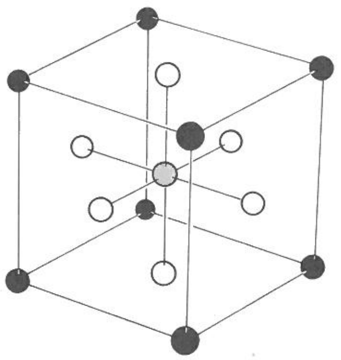

Figure 27.10
The perovskite structure, characteristic of the barium titanate ($BaTiO_3$) class of ferroelectrics in the unpolarized phase. The crystal is cubic, with Ba^{++} ions at the cube corners, O^{--} ions at the centers of the cube faces, and Ti^{4+} ions at the cube centers. The first transition is to a tetragonal structure, the positive ions being displaced relative to the negative ones, along a [100] direction. The perovskite structure is an example of a cubic crystal in which every ion is *not* at a point of full cubic symmetry. (The Ba^{++} and Ti^{4+} are, but the O^{--} ions are not.) Therefore the local field acting on the oxygen ions is more complicated than that given by the simple Lorentz formula. This is important in understanding the mechanism for the ferroelectricity.

Table 27.4
SELECTED FERROELECTRIC CRYSTALS

NAME	FORMULA	T_c (K)	P ($\mu C/cm^2$) at	T (K)
Potassium dihydrogen phosphate	KH_2PO_4	123	4.75	96
Potassium dideuterium phosphate	KD_2PO_4	213	4.83	180
Rubidium dihydrogen phosphate	RbH_2PO_4	147	5.6	90
Rubidium dideuterium phosphate	RbD_2PO_4	218	—	—
Barium titanate	$BaTiO_3$	393	26.0	300
Lead titanate	$PbTiO_3$	763	>50	300
Cadmium titanate	$CdTiO_3$	55	—	—
Potassium niobate	$KNbO_3$	708	30.0	523
Rochelle salt	$NaKC_4H_4O_6 \cdot 4D_2O$	$\left\{\begin{matrix}297\\255\end{matrix}\right\}^a$	0.25	278
Deuterated Rochelle salt	$NaKC_4H_2D_2O_6 \cdot 4D_2O$	$\left\{\begin{matrix}308\\251\end{matrix}\right\}^a$	0.35	279

[a] Has upper and lower T_c.
Source: F. Jona and G. Shirane, *Ferroelectric Crystals*, Pergamon, New York, 1962, p. 389.

PROBLEMS

1. *Electric Field of a Neutral Uniformly Polarized Sphere of Radius* a

Far from the sphere, the potential ϕ will be that of a point dipole of moment $p = 4\pi Pa^3/3$:

$$\phi = \frac{P \cos \theta}{r^2}, \tag{27.80}$$

(where the polar axis is along **P**). Using the fact that the general solution to $\nabla^2\phi = 0$ proportional to $\cos\theta$ is

$$\frac{A\cos\theta}{r^2} + Br\cos\theta, \tag{27.81}$$

use the boundary conditions at the surface of the sphere to show that the potential inside the sphere leads to a uniform field $\mathbf{E} = -4\pi\mathbf{P}/3$.

2. *Electric Field of an Array of Identical Dipoles with Identical Orientations, at a Point with Respect to Which the Array Has Cubic Symmetry*

The potential at **r** due to the dipole at **r**′ is

$$\phi = -\mathbf{p}\cdot\nabla\frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{27.82}$$

By applying the restrictions of cubic symmetry to the tensor

$$\sum_{\mathbf{r}'}\nabla_\mu\nabla_\nu\frac{1}{|\mathbf{r}-\mathbf{r}'|}, \tag{27.83}$$

and noting that $\nabla^2(1/r) = 0$, $\mathbf{r}\neq 0$, show that $\mathbf{E}(\mathbf{r})$ must vanish, when the positions **r**′ of the dipoles have cubic symmetry about **r**.

3. *Polarizability of a Single Hydrogen Atom*

Suppose an electric field **E** is applied (along the x-axis) to a hydrogen atom in its ground state with wave function

$$\psi_0 \propto e^{-r/a_0}. \tag{27.84}$$

(a) Assume a trial function for the atom in the field of the form

$$\psi \propto \psi_0(1+\gamma x) = \psi_0 + \delta\psi, \tag{27.85}$$

and determine γ by minimizing the total energy.

(b) Calculate the polarization

$$p = \int d\mathbf{r}\,(-e)\,x\,(\psi_0\,\delta\psi^* + \psi_0^*\,\delta\psi), \tag{27.86}$$

using the best trial function, and show that this leads to a polarizability $\alpha = 4a_0{}^3$. (The exact answer is $4.5a_0{}^3$.)

4. *Orientational Polarization*

The following situation sometimes arises in pure solids and liquids whose molecules have permanent dipole moments (such as water or ammonia) and also in solids such as ionic crystals with some ions replaced by others with permanent moments (such as OH⁻ in KCl).

(a) An electric field tends to align such molecules; thermal disorder favors misalignment. Using equilibrium statistical mechanics, write down the probability that the dipole makes an angle in the range from θ to $\theta + d\theta$ with the applied field. If there are N such dipoles of moment p, show that their total dipole moment in thermal equilibrium is

$$Np\langle\cos\theta\rangle = NpL\left(\frac{pE}{k_BT}\right), \tag{27.87}$$

where $L(x)$, the "Langevin function," is given by

$$L(x) = \coth x - \left(\frac{1}{x}\right). \tag{27.88}$$

(b) Typical dipole moments are of order 1 Debye unit (10^{-18} in esu). Show that for an electric field of order 10^4 volts/cm the polarizability at room temperature can be written as

$$\alpha = \frac{p^2}{3k_BT}. \tag{27.89}$$

5. *Generalized Lyddane-Sachs-Teller Relation*

Suppose that the dielectric constant $\epsilon(\omega)$ does not have a single pole as a function of ω^2 (as in (27.57)) but has the more general structure:

$$\epsilon(\omega) = A + \sum_{i=1}^{n}\frac{B_i}{\omega^2-\omega_i{}^2}. \tag{27.90}$$

Show directly from (27.90) that the Lyddane-Sachs-Teller relation (27.67) is generalized to

$$\frac{\epsilon_0}{\epsilon_\infty} = \prod\left(\frac{\omega_i^0}{\omega_i}\right)^2, \tag{27.91}$$

where the ω_i^0 are the frequencies at which ϵ vanishes. (*Hint:* Write the condition $\epsilon = 0$ as an nth-degree polynomial in ω^2, and note that the product of the roots is simply related to the value of the polynomial at $\omega = 0$.) What is the significance of the frequencies ω_i and ω_i^0?