16

Dielectrics and Ferroelectrics

NOTATION:

(CGS) $\epsilon_0 = 10^7/4\pi c^2$;

$D = E + 4\pi P = \epsilon E = (1 + 4\pi\chi)E$; $\alpha = p/E_{\text{local}}$;

(SI) $D = \epsilon_0 E + P = \epsilon\epsilon_0 E = (1 + \chi)\epsilon_0 E$; $\alpha = p/E_{\text{local}}$;

$\epsilon_{\text{CGS}} = \epsilon_{\text{SI}}$; $4\pi\chi_{\text{CGS}} = \chi_{\text{SI}}$; $\alpha_{\text{SI}} = 4\pi\epsilon_0\alpha_{\text{CGS}}$.

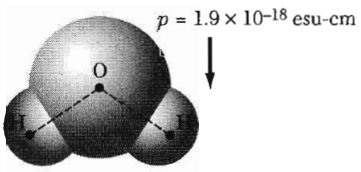

Figure 1 The permanent dipole moment of a molecule of water has the magnitude 1.9×10^{-18} esu-cm and is directed from the O^{2-} ion toward the midpoint of the line connecting the H^+ ions. (To convert to SI units, multiply p by $\frac{1}{3} \times 10^{11}$.)

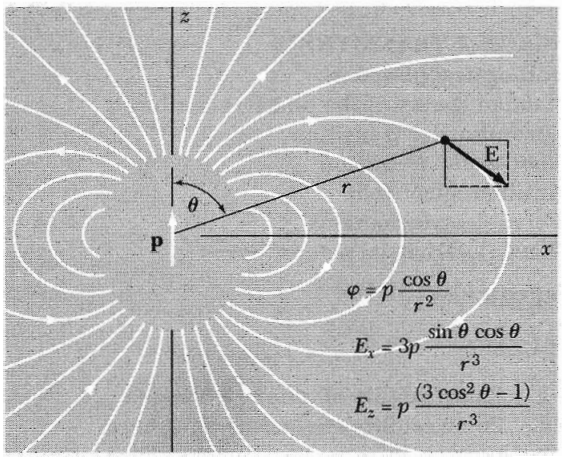

Figure 2 Electrostatic potential and field components in CGS at position r, θ for a dipole **p** directed along the z axis. For $\theta = 0$, we have $E_x = E_y = 0$ and $E_z = 2p/r^3$; for $\theta = \pi/2$ we have $E_x = E_y = 0$ and $E_z = -p/r^3$. To convert to SI, replace p by $p/4\pi\epsilon_0$. (After E. M. Purcell.)

First we relate the applied electric field to the internal electric field in a dielectric crystal. The study of the electric field within dielectric matter arises when we ask:

- What is the relation in the material between the dielectric polarization **P** and the macroscopic electric field **E** in the Maxwell equations?
- What is the relation between the dielectric polarization and the local electric field which acts at the site of an atom in the lattice? The local field determines the dipole moment of the atom.

Maxwell Equations

(CGS)	(SI)
$\text{curl}\,\mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial}{\partial t}(\mathbf{E} + 4\pi\mathbf{P})$;	$\text{curl}\,\mathbf{H} = \mathbf{j} + \frac{\partial}{\partial t}(\epsilon_0\mathbf{E} + \mathbf{P})$;
$\text{curl}\,\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t}$;	$\text{curl}\,\mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$;
$\text{div}\,\mathbf{E} = 4\pi\rho$;	$\text{div}\,\epsilon_0\mathbf{E} = \rho$;
$\text{div}\,\mathbf{B} = 0$;	$\text{div}\,\mathbf{B} = 0$.

Polarization

The **polarization P** is defined as the **dipole moment per unit volume**, averaged over the volume of a cell. The total dipole moment is defined as

$$\mathbf{p} = \Sigma q_n \mathbf{r}_n \ , \tag{1}$$

where $\mathbf{r}_n$ is the position vector of the charge q_n. The value of the sum will be independent of the origin chosen for the position vectors, provided that the system is neutral: Let $\mathbf{r}_n' = \mathbf{r}_n + \mathbf{R}$; then $\mathbf{p} = \Sigma q_n \mathbf{r}_n' = \mathbf{R}\Sigma q_n + \Sigma q_n \mathbf{r}_n = \Sigma q_n \mathbf{r}_n$. The dipole moment of a water molecule is shown in Fig. 1.

The electric field at a point **r** from a dipole moment **p** is given by a standard result of elementary electrostatics:

$$\text{(CGS)}\quad \mathbf{E}(\mathbf{r}) = \frac{3(\mathbf{p}\cdot\mathbf{r})\mathbf{r} - r^2\mathbf{p}}{r^5} \ ; \qquad \text{(SI)}\quad \mathbf{E}(\mathbf{r}) = \frac{3(\mathbf{p}\cdot\mathbf{r})\mathbf{r} - r^2\mathbf{p}}{4\pi\epsilon_0 r^5} \ . \tag{2}$$

The lines of force of a dipole pointing along the z axis are shown in Fig. 2.

MACROSCOPIC ELECTRIC FIELD

One contribution to the electric field inside a body is that of the applied electric field, defined as

$$\boxed{\mathbf{E}_0 \equiv \text{field produced by fixed charges external to the body .}} \tag{3}$$

The other contribution to the electric field is the sum of the fields of all charges that constitute the body. If the body is neutral, the contribution to the average field may be expressed in terms of the sum of the fields of atomic dipoles.

We define the average electric field $\mathbf{E}(\mathbf{r}_0)$ as the **average field over the volume of the crystal cell** that contains the lattice point $\mathbf{r}_0$:

$$\mathbf{E}(\mathbf{r}_0) = \frac{1}{V_c}\int dV\, \mathbf{e}(\mathbf{r}) \ , \tag{4}$$

where $\mathbf{e}(\mathbf{r})$ is the microscopic electric field at the point $\mathbf{r}$. The field $\mathbf{E}$ is a much smoother quantity than the microscopic field $\mathbf{e}$. We could well have written the dipole field (2) as $\mathbf{e}(\mathbf{r})$ because it is a microscopic unsmoothed field.

We call $\mathbf{E}$ the **macroscopic electric field**. It is adequate for all problems in the electrodynamics of crystals provided that we know the connection between $\mathbf{E}$, the polarization $\mathbf{P}$, and the current density $\mathbf{j}$, and provided that the wavelengths of interest are long in comparison with the lattice spacing.[1]

To find the contribution of the polarization to the macroscopic field, we can simplify the sum over all the dipoles in the specimen. By a famous theorem of electrostatics[2] the macroscopic electric field caused by a uniform polarization is equal to the electric field in vacuum of a fictitious surface charge

[1]A detailed derivation of the Maxwell equations for the macroscopic fields $\mathbf{E}$ and $\mathbf{B}$, starting from the Maxwell equations in terms of the microscopic fields $\mathbf{e}$ and $\mathbf{h}$, is given by E. M. Purcell, *Electricity and magnetism*, 2nd ed., McGraw-Hill, 1985.

[2]The electrostatic potential in CGS units of a dipole $\mathbf{p}$ is $\varphi(\mathbf{r}) = \mathbf{p} \cdot \text{grad}(1/r)$. For a volume distribution of polarization $\mathbf{P}$ we have

$$\varphi(\mathbf{r}) = \int dV \left(\mathbf{P} \cdot \text{grad}\,\frac{1}{r}\right) ,$$

which by a vector identity becomes

$$\varphi(\mathbf{r}) = \int dV \left(-\frac{1}{r}\,\text{div}\,\mathbf{P} + \text{div}\,\frac{\mathbf{P}}{r}\right) .$$

If $\mathbf{P}$ is constant, then div $\mathbf{P} = 0$ and by the Gauss theorem we have

$$\varphi(\mathbf{r}) = \int dS\,\frac{P_n}{r} = \int dS\,\frac{\sigma}{r} \ ,$$

where σdS is an element of charge on the surface of the body. This completes the proof.

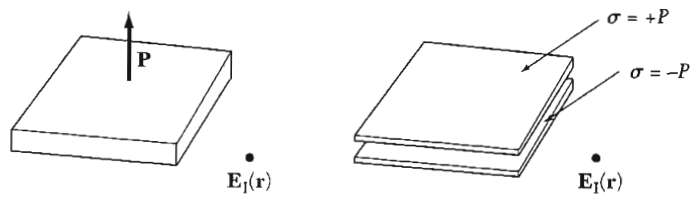

Figure 3 (a) A uniformly polarized dielectric slab, with the polarization vector **P** normal to the plane of the slab. (b) A pair of uniformly charged parallel plates which give rise to the identical electric field $\mathbf{E}_1$ as in (a). The upper plate has the surface charge density $\sigma = +P$, and the lower plate has $\sigma = -P$.

density $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P}$ on the surface of the body. Here $\hat{\mathbf{n}}$ is the unit normal to the surface, drawn outward from the polarized matter.

We apply the result to a thin dielectric slab (Fig. 3a) with a uniform volume polarization **P**. The electric field $\mathbf{E}_1(\mathbf{r})$ produced by the polarization is equal to the field produced by the fictitious surface charge density $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P}$ on the surface of the slab. On the upper boundary the unit vector $\hat{\mathbf{n}}$ is directed upward and on the lower boundary $\hat{\mathbf{n}}$ is directed downward. The upper boundary bears the fictitious charge $\sigma = \hat{\mathbf{n}} \cdot \mathbf{P} = P$ per unit area, and the lower boundary bears $-P$ per unit area.

The electric field $\mathbf{E}_1$ due to these charges has a simple form at any point between the plates, but comfortably removed from their edges. By Gauss's law

$$\text{(CGS)} \quad E_1 = -4\pi|\sigma| = -4\pi P \ ; \qquad \text{(SI)} \quad E_1 = -\frac{|\sigma|}{\epsilon_0} = \frac{P}{\epsilon_0} \ . \tag{4a}$$

We add $\mathbf{E}_1$ to the applied field $\mathbf{E}_0$ to obtain the total macroscopic field inside the slab, with $\hat{\mathbf{z}}$ the unit vector normal to the plane of the slab:

$$\text{(CGS)} \qquad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - 4\pi P\hat{\mathbf{z}} \ ; \tag{5}$$

$$\text{(SI)} \qquad \mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - \frac{P}{\epsilon_0}\hat{\mathbf{z}} \ .$$

We define

$$\boxed{\mathbf{E}_1 \equiv \text{field of the surface charge denisty } \hat{\mathbf{n}} \cdot \mathbf{P} \text{ on the boundary} \ .} \tag{6}$$

This field is smoothly varying in space inside and outside the body and satisfies the Maxwell equations as written for the macroscopic field **E**. The reason $\mathbf{E}_1$ is a smooth function when viewed on an atomic scale is that we have replaced the discrete lattice of dipoles $\mathbf{p}_j$ with the smoothed polarization **P**.

Depolarization Field, $\mathbf{E}_1$

If the polarization is uniform within the body, the only contributions to the macroscopic field are from $\mathbf{E}_0$ and $\mathbf{E}_1$:

$$\boxed{\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 \ .} \tag{7}$$

Here $\mathbf{E}_0$ is the applied field and $\mathbf{E}_1$ is the field due to the uniform polarization.

The field $\mathbf{E}_1$ is called the **depolarization field**, for within the body it tends to oppose the applied field $\mathbf{E}_0$ as in Fig. 4. Specimens in the shape of ellipsoids, a class that includes spheres, cylinders, and discs as limiting forms, have an advantageous property: a uniform polarization produces a uniform depolarization field inside the body. This is a famous mathematical result demonstrated in classic texts on electricity and magnetism.[3]

If P_x, P_y, P_z are the components of the polarization $\mathbf{P}$ referred to the principal axes of an ellipsoid, then the components of the depolarization field are written

$$\text{(CGS)} \qquad E_{1x} = -N_x P_x \ ; \qquad E_{1y} = -N_y P_y \ ; \qquad E_{1z} = -N_z P_z \ ; \tag{8}$$

$$\text{(SI)} \qquad E_{1x} = -\frac{N_x P_x}{\epsilon_0} \ ; \qquad E_{1y} = -\frac{N_y P_y}{\epsilon_0} \ ; \qquad E_{1z} = -\frac{N_z P_z}{\epsilon_0} \ .$$

Here N_x, N_y, N_z are the **depolarization factors**; their values depend on the ratios of the principal axes of the ellipsoid. The N's are positive and satisfy the sum rule $N_x + N_y + N_z = 4\pi$ in CGS, and $N_x + N_y + N_z = 1$ in SI.

Values of N parallel to the figure axis of ellipsoids of revolution are plotted in Fig. 5. Additional cases have been calculated by Osborn[4] and by Stoner. In limiting cases N has the values:

Shape	Axis	N (CGS)	N (SI)
Sphere	any	$4\pi/3$	1/3
Thin slab	normal	4π	1
Thin slab	in plane	0	0
Long circular cylinder	longitudinal	0	0
Long circular cylinder	transverse	2π	1/2

We can reduce the depolarization field to zero in two ways, either by working parallel to the axis of a long fine specimen or by making an electrical connection between electrodes deposited on the opposite surfaces of a thin slab.

[3]R. Becker, *Electromagnetic fields and interactions*, Blaisdell, 1964, pp. 102–107.

[4]J. A. Osborn, Phys. Rev. **67**, 351 (1945); E. C. Stoner, Philosophical Magazine **36**, 803 (1945).

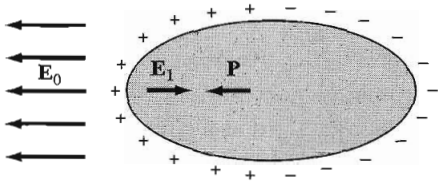

Figure 4 The depolarization field $\mathbf{E}_1$ is opposite to **P**. The fictitious surface charges are indicated: the field of these charges is $\mathbf{E}_1$ within the ellipsoid.

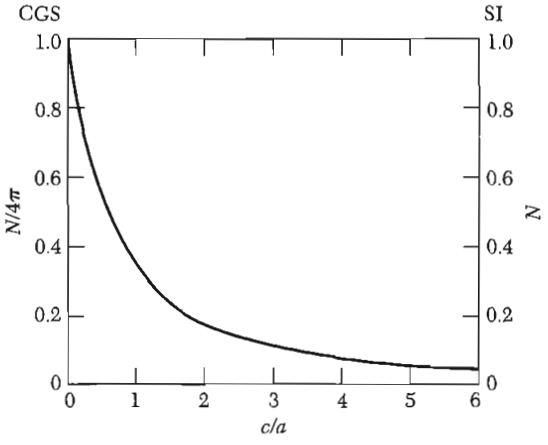

Figure 5 Depolarization factor N parallel to the figure axis of ellipsoids of revolution, as a function of the axial ratio c/a.

A uniform applied field $\mathbf{E}_0$ will induce uniform polarization in an ellipsoid. We introduce the **dielectric susceptibility** χ such that the relations

$$\text{(CGS)} \quad \mathbf{P} = \chi \mathbf{E} \ ; \qquad \text{(SI)} \quad \mathbf{P} = \epsilon_0 \chi \mathbf{E} \ , \tag{9}$$

connect the macroscopic field **E** inside the ellipsoid with the polarization **P**. Here $\chi_{\text{SI}} = 4\pi\chi_{\text{CGS}}$.

If $\mathbf{E}_0$ is uniform and parallel to a principal axis of the ellipsoid, then

$$\text{(CGS)} \quad E = E_0 + E_1 = E_0 - NP \ ; \qquad \text{(SI)} \quad E = E_0 - \frac{NP}{\epsilon_0} \ , \tag{10}$$

by (8), whence

$$\text{(CGS)} \quad P = \chi(E_0 - NP) \ ; \qquad P = \frac{\chi}{1 + N\chi} E_0 \ ; \tag{11}$$

$$\text{(SI)} \quad P = \chi(\epsilon_0 E_0 - NP) \ ; \qquad P = \frac{\chi \epsilon_0}{1 + N\chi} E_0 \ .$$

The value of the polarization depends on the depolarization factor N.

LOCAL ELECTRIC FIELD AT AN ATOM

The value of the local electric field that acts at the site of an atom is significantly different from the value of the macroscopic electric field. We can convince ourselves of this by consideration of the local field at a site with a cubic arrangement of neighbors[5] in a crystal of spherical shape. The macroscopic electric field in a sphere is

(CGS) $$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - \frac{4\pi}{3}\mathbf{P} \; ; \tag{12}$$

(SI) $$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_1 = \mathbf{E}_0 - \frac{1}{3\epsilon_0}\mathbf{P} \; ,$$

by (10).

But consider the field that acts on the atom at the center of the sphere (this atom is not unrepresentative). If all dipoles are parallel to the z axis and have magnitude p, the z component of the field at the center due to all other dipoles is, from (2),

(CGS) $$E_{\text{dipole}} = p \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} = p \sum_i \frac{2z_i^2 - x_i^2 - y_i^2}{r_i^5} \; . \tag{13}$$

In SI we replace p by $p/4\pi\epsilon_0$. The x, y, z directions are equivalent because of the symmetry of the lattice and of the sphere; thus

$$\sum_i \frac{z_i^2}{r_i^5} = \sum_i \frac{x_i^2}{r_i^5} = \sum_i \frac{y_i^2}{r_i^5} \; ,$$

whence $E_{\text{dipole}} = 0$.

The correct local field is just equal to the applied field, $\mathbf{E}_{\text{local}} = \mathbf{E}_0$, for an atom site with a cubic environment in a spherical specimen. Thus the local field is not the same as the macroscopic average field $\mathbf{E}$.

We now develop an expression for the local field at a general lattice site, not necessarily of cubic symmetry. The local field at an atom is the sum of the electric field $\mathbf{E}_0$ from external sources and of the field from the dipoles within the specimen. It is convenient to decompose the dipole field so that part of the summation over dipoles may be replaced by integration.

We write

$$\boxed{\mathbf{E}_{\text{local}} = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 \; .} \tag{14}$$

[5]Atom sites in a cubic crystal do not necessarily have cubic symmetry: thus the O^{2-} sites in the barium titanate structure of Fig. 10 do not have a cubic environment. However, the Na^+ and Cl^- sites in the NaCl structure and the Cs^+ and Cl^- sites in the CsCl structure have cubic symmetry.

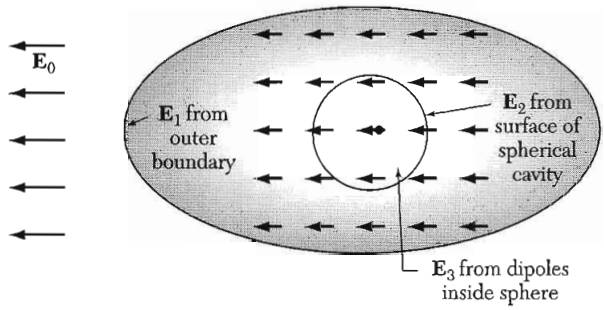

Figure 6 The internal electric field on an atom in a crystal is the sum of the external applied field $\mathbf{E}_0$ and of the field due to the other atoms in the crystal. The standard method of summing the dipole fields of the other atoms is first to sum individually over a moderate number of neighboring atoms inside an imaginary sphere concentric with the reference atom: this defines the field $\mathbf{E}_3$, which vanishes at a reference site with cubic symmetry. The atoms outside the sphere can be treated as a uniformly polarized dielectric. Their contribution to the field at the reference point is $\mathbf{E}_1 + \mathbf{E}_2$, where $\mathbf{E}_1$ is the depolarization field associated with the outer boundary and $\mathbf{E}_2$ is the field associated with the surface of the spherical cavity.

Here

$\mathbf{E}_0$ = field produced by fixed charges external to the body;

$\mathbf{E}_1$ = depolarization field, from a surface charge density $\hat{\mathbf{n}} \cdot \mathbf{P}$ on the outer surface of the specimen;

$\mathbf{E}_2$ = Lorentz cavity field: field from polarization charges on inside of a spherical cavity cut (as a mathematical fiction) out of the specimen with the reference atom as center, as in Fig. 6; $\mathbf{E}_1 + \mathbf{E}_2$ is the field due to uniform polarization of the body in which a hole has been created;

$\mathbf{E}_3$ = field of atoms inside cavity.

The contribution $\mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$ to the local field is the total field at one atom caused by the dipole moments of all the other atoms in the specimen:

$$\text{(CGS)} \qquad \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 = \sum_i \frac{3(\mathbf{p}_i \cdot \mathbf{r}_i)\mathbf{r}_i - r_i^2 \mathbf{p}_i}{r_i^5} , \qquad (15)$$

and in SI we replace $\mathbf{p}_i$ by $\mathbf{p}_i/4\pi\epsilon_0$.

Dipoles at distances greater than perhaps ten lattice constants from the reference site make a smoothly varying contribution to this sum, a contribution which may be replaced by two surface integrals. One surface integral is taken over the outer surface of the ellipsoidal specimen and defines $\mathbf{E}_1$, as in Eq. (6). The second surface integral defines $\mathbf{E}_2$ and may be taken over any interior surface that is a suitable distance (say 50 Å) from the reference site. We count in $\mathbf{E}_3$ any dipoles not included in the volume bounded by the inner and outer surfaces. It is convenient to let the interior surface be spherical.

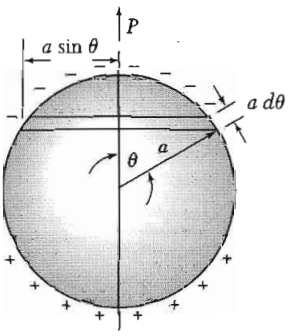

Figure 7 Calculation of the field in a spherical cavity in a uniformly polarized medium.

Charge on ring = $2\pi a \sin\theta \cdot a\, d\theta \cdot P \cos\theta$

Lorentz Field, $\mathbf{E}_2$

The field $\mathbf{E}_2$ due to the polarization charges on the surface of the fictitious cavity was calculated by Lorentz. If θ is the polar angle (Fig. 7) referred to the polarization direction, the surface charge density on the surface of the cavity is $-P \cos\theta$. The electric field at the center of the spherical cavity of radius a is

$$\text{(CGS)} \qquad \mathbf{E}_2 = \int_0^{\pi} (a^{-2})(2\pi a \sin\theta)(a\, d\theta)(\mathbf{P}\cos\theta)(\cos\theta) = \frac{4\pi}{3}\mathbf{P}\ ; \tag{16}$$

$$\text{(SI)} \qquad \mathbf{E}_2 = \frac{1}{3\epsilon_0}\mathbf{P}\ .$$

This is the negative of the depolarization field $\mathbf{E}_1$ in a polarized sphere, so that $\mathbf{E}_1 + \mathbf{E}_2 = 0$ for a sphere.

Field of Dipoles Inside Cavity, $\mathbf{E}_3$

The field $\mathbf{E}_3$ due to the dipoles within the spherical cavity is the only term that depends on the crystal structure. We showed for a reference site with cubic surroundings in a sphere that $\mathbf{E}_3 = 0$ if all the atoms may be replaced by point dipoles parallel to each other. The total local field at a cubic site is, from (14) and (16),

$$\text{(CGS)} \qquad \mathbf{E}_{\text{local}} = \mathbf{E}_0 + \mathbf{E}_1 + \frac{4\pi}{3}\mathbf{P} = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}\ ; \tag{17}$$

$$\text{(SI)} \qquad \mathbf{E}_{\text{local}} = \mathbf{E} + \frac{1}{3\epsilon_0}\mathbf{P}\ .$$

This is the **Lorentz relation**: the field acting at an atom in a cubic site is the macroscopic field $\mathbf{E}$ of Eq. (7) plus $4\pi\mathbf{P}/3$ or $\mathbf{P}/3\epsilon_0$ from the polarization of the other atoms in the specimen. Experimental data for cubic ionic crystals support the Lorentz relation.

DIELECTRIC CONSTANT AND POLARIZABILITY

The **dielectric constant** ϵ of an isotropic or cubic medium relative to vacuum is defined in terms of the macroscopic field E:

(CGS) $$\epsilon = \frac{E + 4\pi P}{E} = 1 + 4\pi\chi \ ; \tag{18}$$

(SI) $$\epsilon = \frac{\epsilon_0 E + P}{\epsilon_0 E} = 1 + \chi \ .$$

Remember that $\chi_{SI} = 4\pi\chi_{CGS}$, by definition, but $\epsilon_{SI} = \epsilon_{CGS}$.

The susceptibility (9) is related to the dielectric constant by

(CGS) $$\chi = \frac{P}{E} = \frac{\epsilon - 1}{4\pi} \ ; \qquad \text{(SI)} \ \chi = \frac{P}{\epsilon_0 E} = \epsilon - 1 \ . \tag{19}$$

In a noncubic crystal the dielectric response is described by the components of the susceptibility tensor or of the dielectric constant tensor:

(CGS) $$P_\mu = \chi_{\mu\nu} E_\nu \ ; \quad \epsilon_{\mu\nu} = \delta_{\mu\nu} + 4\pi\chi_{\mu\nu} \ . \tag{20}$$

(SI) $$P_\mu = \chi_{\mu\nu}\epsilon_0 E_\nu \ ; \quad \epsilon_{\mu\nu} = \delta_{\mu\nu} + \chi_{\mu\nu} \ .$$

The **polarizability** α of an atom is defined in terms of the local electric field at the atom:

$$p = \alpha E_{\text{local}} \ , \tag{21}$$

where p is the dipole moment. This definition applies in CGS and in SI, but $\alpha_{SI} = 4\pi\epsilon_0\alpha_{CGS}$. The polarizability is an atomic property, but the dielectric constant will depend on the manner in which the atoms are assembled to form a crystal. For a nonspherical atom α will be a tensor.

The polarization of a crystal may be expressed approximately as the product of the polarizabilities of the atoms times the local electric field:

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{\text{loc}}(j) \ , \tag{22}$$

where N_j is the concentration and α_j the polarizability of atoms j, and $E_{\text{loc}}(j)$ is the local field at atom sites j.

We want to relate the dielectric constant to the polarizabilities; the result will depend on the relation that holds between the macroscopic electric field and the local electric field. We give the derivation in CGS units and state the result in both systems of units.

If the local field is given by the Lorentz relation (17), then

$$\text{(CGS)} \qquad P = (\Sigma N_j \alpha_j)\left(E + \frac{4\pi}{3}P\right) ;$$

and we solve for P to find the susceptibility

$$\text{(CGS)} \qquad \chi = \frac{P}{E} = \frac{\Sigma N_j \alpha_j}{1 - \frac{4\pi}{3}\Sigma N_j \alpha_j} . \tag{23}$$

By definition $\epsilon = 1 + 4\pi\chi$ in CGS; we may rearrange (23) to obtain

$$\text{(CGS)} \quad \frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}\Sigma N_j \alpha_j ; \qquad \text{(SI)} \quad \frac{\epsilon - 1}{\epsilon + 2} = \frac{1}{3\epsilon_0}\Sigma N_j \alpha_j , \tag{24}$$

the **Clausius-Mossotti relation**. This relates the dielectric constant to the electronic polarizability, but only for crystal structures for which the Lorentz local field (17) obtains.

Electronic Polarizability

The total polarizability may usually be separated into three parts: electronic, ionic, and dipolar, as in Fig. 8. The electronic contribution arises from the displacement of the electron shell relative to a nucleus. The ionic contribution comes from the displacement of a charged ion with respect to other ions. The dipolar polarizability arises from molecules with a permanent electric dipole moment that can change orientation in an applied electric field.

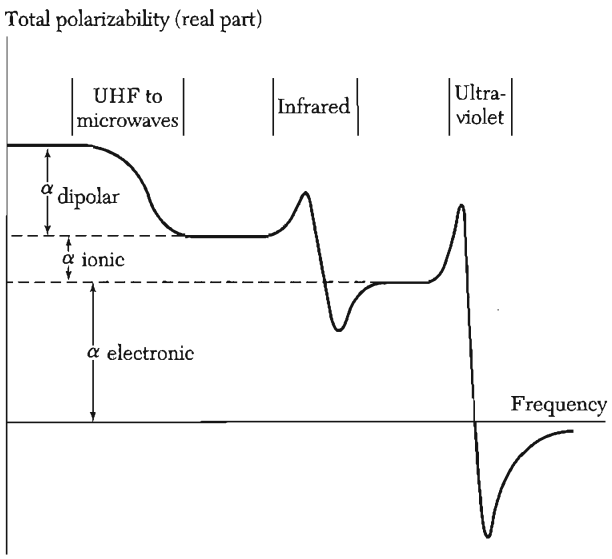

Figure 8 Frequency dependence of the several contributions to the polarizability.

In heterogeneous materials there is usually also an interfacial polarization arising from the accumulation of charge at structural interfaces. This is of little fundamental interest, but it is of considerable practical interest because commercial insulating materials are usually heterogeneous.[6]

The dielectric constant at optical frequencies arises almost entirely from the electronic polarizability. The dipolar and ionic contributions are small at high frequencies because of the inertia of the molecules and ions. In the optical range (24) reduces to

$$\text{(CGS)} \qquad \frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\Sigma N_j\alpha_j(\text{electronic}) \ ; \qquad (25)$$

here we have used the relation $n^2 = \epsilon$, where n is the refractive index.

By applying (25) to large numbers of crystals we determine in Table 1 empirical values of the electronic polarizabilities that are reasonably consistent with the observed values of the refractive index. The scheme is not entirely self-consistent, because the electronic polarizability of an ion depends somewhat on the environment in which it is placed. The negative ions are highly polarizable because they are large.

Table 1 Electronic polarizabilities of atoms and ions, in 10^{-24} cm^3

			Hc	Li^+	Be^{2+}	B^{3+}	C^{4+}
Pauling			0.201	0.029	0.008	0.003	0.0013
JS				0.029			
	O^{2-}	F^-	Ne	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}
Pauling	3.88	1.04	0.390	0.179	0.094	0.052	0.0165
JS-(TKS)	(2.4)	0.858		0.290			
	S^{2-}	Cl^-	Ar	K^+	Ca^{2+}	Se^{3+}	Ti^{4+}
Pauling	10.2	3.66	1.62	0.83	0.47	0.286	0.185
JS-(TKS)	(5.5)	2.947		1.133	(1.1)		(0.19)
	Se^{2-}	Br^-	Kr	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}
Pauling	10.5	4.77	2.46	1.40	0.86	0.55	0.37
JS-(TKS)	(7.)	4.091		1.679	(1.6)		
	Te^{2-}	I^-	Xe	Cs^+	Ba^{2+}	La^{3+}	Ce^{4+}
Pauling	14.0	7.10	3.99	2.42	1.55	1.04	0.73
JS-(TKS)	(9.)	6.116		2.743	(2.5)		

Values from L. Pauling, Proc. R. Soc. London **A114**, 181 (1927); S. S. Jaswal and T. P. Sharma, J. Phys. Chem. Solids **34**, 509 (1973); and J. Tessman, A. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953). The TKS polarizabilities are at the frequency of the D lines of sodium. The values are in CGS; to convert to SI, multiply by 9×10^{-15}.

[6]For references see D. E. Aspnes, Am. J. Phys. **50**, 704 (1982).

Classical Theory of Electronic Polarizability. An electron bound harmonically to an atom will show resonance absorption at a frequency $\omega_0 = (\beta/m)^{1/2}$, where β is the force constant. The displacement x of the electron occasioned by the application of a field E_{loc} is given by

$$-eE_{loc} = \beta x = m\omega_0^2 x \ , \tag{26}$$

so that the static electronic polarizability is

$$\alpha(\text{electronic}) = p/E_{loc} = -ex/E_{loc} = e^2/m\omega_0^2 \ . \tag{27}$$

The electronic polarizability will depend on frequency, and it is shown in the following example that for frequency ω

$$\text{(CGS)} \qquad \alpha(\text{electronic}) = \frac{e^2/m}{\omega_0^2 - \omega^2} \ ; \tag{28}$$

but in the visible region the frequency dependence (dispersion) is not usually very important in most transparent materials.

EXAMPLE: *Frequency dependence.* Find the frequency dependence of the electronic polarizability of an electron having the resonance frequency ω_0, treating the system as a simple harmonic oscillator.

The equation of motion in the local electric field $E_{loc} \sin \omega t$ is

$$m\frac{d^2x}{dt^2} + m\omega_0^2 x = -eE_{loc} \sin \omega t \ ,$$

so that, for $x = x_0 \sin \omega t$,

$$m(-\omega^2 + \omega_0^2)x_0 = -eE_{loc} \ .$$

The dipole moment has the amplitude

$$p_0 = -ex_0 = \frac{e^2 E_{loc}}{m(\omega_0^2 - \omega^2)} \ ,$$

from which (28) follows.

In quantum theory the expression corresponding to (28) is

$$\text{(CGS)} \qquad \alpha(\text{electronic}) = \frac{e^2}{m} \sum_j \frac{f_{ij}}{\omega_{ij}^2 - \omega^2} \ , \tag{29}$$

where f_{ij} is called the **oscillator strength** of the electric dipole transition between the atomic states i and j. Near a transition the polarizability changes sign (Fig. 8).

STRUCTURAL PHASE TRANSITIONS

It is not uncommon for crystals to transform from one crystal structure to another as the temperature or pressure is varied. The stable structure A at absolute zero generally has the lowest accessible internal energy of all the possible structures. Even this selection of a structure A can be varied with application of pressure, because a low atomic volume will favor closest-packed or even metallic structures. Hydrogen and xenon, for example, become metallic under extreme pressure.

Some other structure B may have a softer or lower frequency phonon spectrum than A. As the temperature is increased the phonons in B will be more highly excited (higher thermal average occupancies) than the phonons in A. Because the entropy increases with the occupancy, the entropy of B will become higher than the entropy of A as the temperature is increased.

It is thereby possible for the stable structure to transform from A to B as the temperature is increased. The stable structure at a temperature T is determined by the minimum of the free energy $F = U - TS$. There will be a transition from A to B if a temperature T_c exists (below the melting point) such that $F_A(T_c) = F_B(T_c)$.

Often several structures have nearly the same internal energy at absolute zero. The phonon dispersion relations for the structures may, however, be rather different. The phonon energies are sensitive to the number and arrangement of nearby atoms; these are the quantities that change as the structure is changed.

Some structural phase transitions have only small effects on the macroscopic physical properties of the material. However, if the transition is influenced by an applied stress, the crystal may yield mechanically quite easily near the transition temperature because the relative proportions in the two phases will change under stress. Some other structural phase transitions may have spectacular effects on the macroscopic electrical properties.

Ferroelectric transitions are a subgroup of structural phase transitions, a subgroup marked by the appearance of a spontaneous dielectric polarization in the crystal. Ferroelectrics are of theoretical and technical interest because they often have unusually high and unusually temperature-dependent values of the dielectric constant, the piezoelectric effect, the pyroelectric effect, and electro-optical effects, including optical frequency doubling.

FERROELECTRIC CRYSTALS

A ferroelectric crystal exhibits an electric dipole moment even in the absence of an external electric field. In the ferroelectric state the center of positive charge of the crystal does not coincide with the center of negative charge.

The plot of polarization versus electric field for the ferroelectric state shows a hysteresis loop. A crystal in a normal dielectric state usually does not

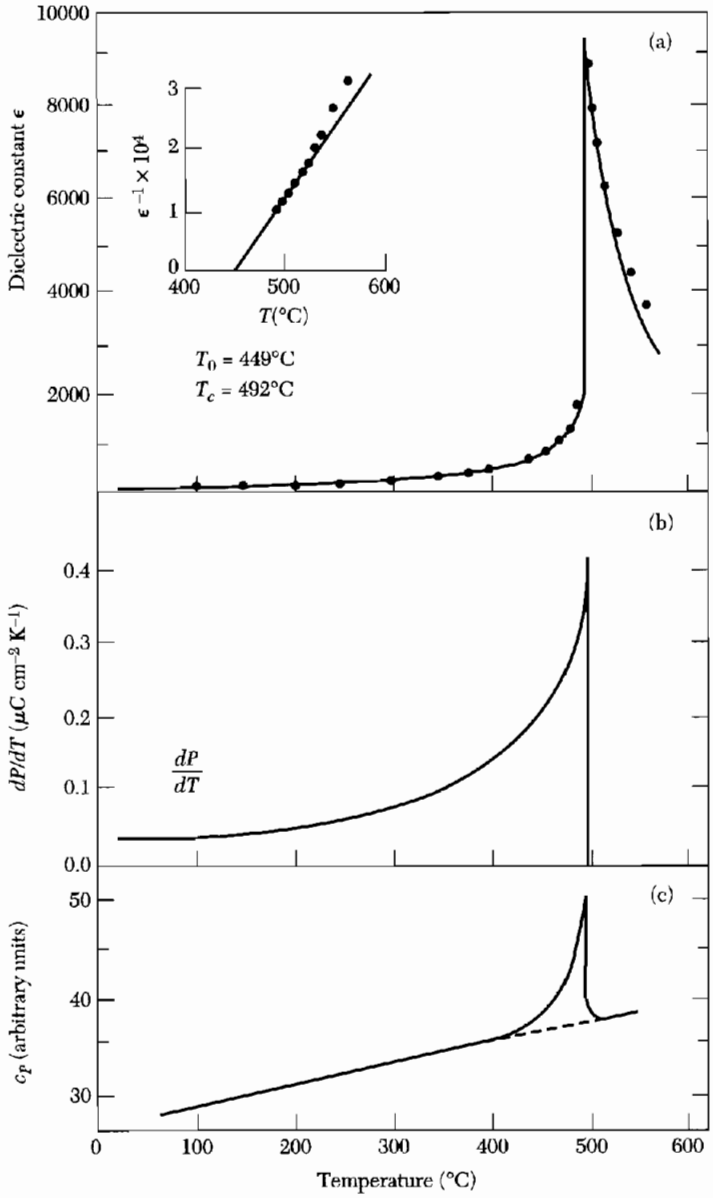

Figure 9 The temperature variation of (a) the dielectric constant ϵ, (b) the pyroelectric coefficient dP/dT, and (c) the specific heat c_p, of $PbTiO_3$. (After Remeika and Class.)

show significant hysteresis when the electric field is increased and then reversed, both slowly.

Ferroelectricity usually disappears above a certain temperature called the transition temperature. Above the transition the crystal is said to be in a **paraelectric** state. The term paraelectric suggests an analogy with paramagnetism:

there is usually a rapid drop in the dielectric constant as the temperature increases.

In some crystals the ferroelectric dipole moment is not changed by an electric field of the maximum intensity which it is possible to apply before causing electrical breakdown. In these crystals we are often able to observe a change in the spontaneous moment when the temperature is changed (Fig. 9). Such crystals are called **pyroelectric**. Lithium niobate, $LiNbO_3$, is pyroelectric at room temperature. It has a high transition temperature (T_c = 1480 K) and a high saturation polarization (50 $\mu C/cm^2$). It can be "poled," which means given a remanent polarization, by an electric field applied over 1400 K.

Classification of Ferroelectric Crystals

We list in Table 2 some of the crystals commonly considered to be ferroelectric, along with the transition temperature or Curie point T_c at which the crystal changes from the low-temperature polarized state to the high-temperature unpolarized state. Thermal motion tends to destroy the ferroelectric order. Some ferroelectric crystals have no Curie point because they melt before leaving the ferroelectric phase. The table also includes values of the spontaneous polarization P_s. Ferroelectric crystals may be classified into two main groups, order-disorder or displacive.

One may define the character of the transition in terms of the dynamics of the lowest frequency ("soft") optical phonon modes. If a soft mode can propagate in the crystal at the transition, then the transition is displacive. If the soft mode is only diffusive (non-propagating) there is really not a phonon at all,

Table 2 Ferroelectric crystals

To obtain the spontaneous polarization P_s in the CGS unit of esu cm^{-2}, multiply the value given in $\mu C\ cm^{-2}$ by 3×10^3.

		T_c, in K	P_s, in $\mu C\ cm^{-2}$, at T K	
KDP type	KH_2PO_4	123	4.75	[96]
	KD_2PO_4	213	4.83	[180]
	RbH_2PO_4	147	5.6	[90]
	KH_2AsO_4	97	5.0	[78]
	GeTe	670	—	—
TGS type	Tri-glycine sulfate	322	2.8	[29]
	Tri-glycine selenate	295	3.2	[283]
Perovskites	$BaTiO_3$	408	26.0	[296]
	$KNbO_3$	708	30.0	[523]
	$PbTiO_3$	765	>50	[296]
	$LiTaO_3$	938	50	
	$LiNbO_3$	1480	71	[296]

but is only a large amplitude hopping motion between the wells of the order-disorder system. Many ferroelectrics have soft modes that fall between these two extremes.

The order-disorder class of ferroelectrics includes crystals with hydrogen bonds in which the motion of the protons is related to the ferroelectric properties, as in potassium dihydrogen phosphate (KH_2PO_4) and isomorphous salts. The substitution of deuterons for protons nearly doubles T_c, although the fractional change in the molecular weight of the compound is less than 2 percent:

	KH_2PO_4	KD_2PO_4	KH_2AsO_4	KD_2AsO_4
Curie temperature	123 K	213 K	97 K	162 K

This extraordinarily large isotope shift is believed to be a quantum effect involving the mass-dependence of the de Broglie wavelength. Neutron diffraction data show that above the Curie temperature the proton distribution along the hydrogen bond is symmetrically elongated. Below the Curie temperature the distribution is more concentrated and asymmetric with respect to neighboring ions, so that one end of the hydrogen bond is preferred by the proton over the other end, giving a polarization.

The displacive class of ferroelectrics includes ionic crystal structures closely related to the perovskite and ilmenite structures. The simplest ferroelectric crystal is GeTe with the sodium chloride structure. We shall devote ourselves primarily to crystals with the perovskite structure, Fig. 10.

Consider the order of magnitude of the ferroelectric effects in barium titanate: the observed saturation polarization P_s at room temperature (Fig. 11)

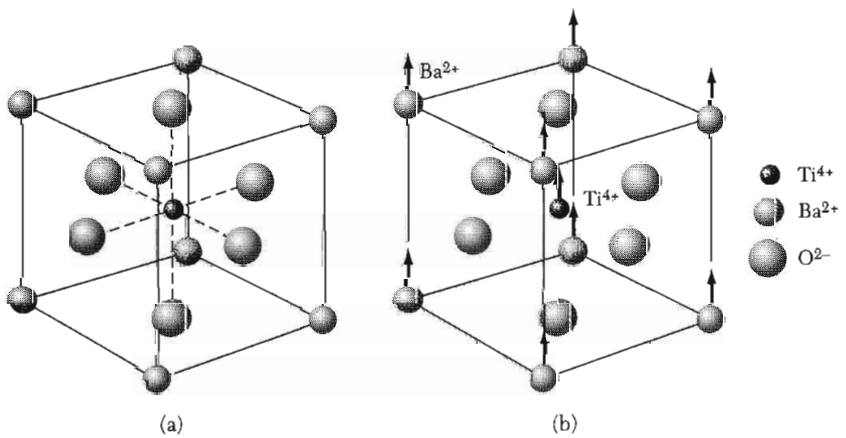

Figure 10 (a) The crystal structure of barium titanate. The prototype crystal is calcium titanate (perovskite). The structure is cubic, with Ba^{2+} ions at the cube corners, O^{2-} ions at the face centers, and a Ti^{4+} ion at the body center. (b) Below the Curie temperature the structure is slightly deformed, with Ba^{2+} and Ti^{4+} ions displaced relative to the O^{2-} ions, thereby developing a dipole moment. The upper and lower oxygen ions may move downward slightly.

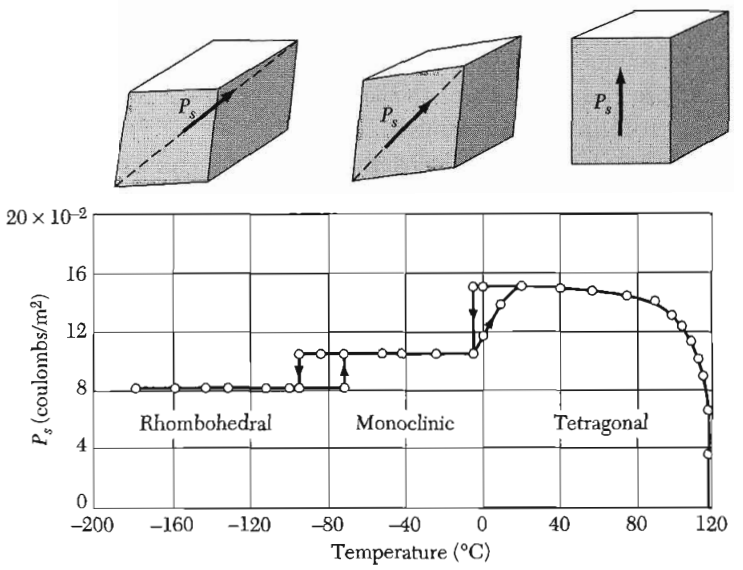

Figure 11 Spontaneous polarization projected on cube edge of barium titanate, as a function of temperature. (After W. J. Merz.)

is 8×10^4 esu cm^{-2}. The volume of a cell is $(4 \times 10^{-8})^3 = 64 \times 10^{-24}$ cm^3, so that the dipole moment of a cell is

(CGS) $p \cong (8 \times 10^4 \text{ esu cm}^{-2})(64 \times 10^{-24} \text{ cm}^{-3}) \cong 5 \times 10^{-18}$ esu cm ;

(SI) $p \cong (3 \times 10^{-1} \text{ C m}^{-2})(64 \times 10^{-30} \text{ m}^3) \cong 2 \times 10^{-29}$ C m .

If the positive ions Ba^{2+} and Ti^{4+} were moved by $\delta = 0.1$ Å with respect to the negative O^{2-} ions, the dipole moment of a cell would be $6e\delta \cong 3 \times 10^{-18}$ esu cm. In $LiNbO_3$ the displacements are considerably larger, being 0.9 Å and 0.5 Å for the lithium and niobum ions respectively, giving the larger P_s.

DISPLACIVE TRANSITIONS

Two viewpoints contribute to an understanding of a ferroelectric displacive transition and by extension to displacive transitions in general. We may speak of a polarization catastrophe in which for some critical condition the polarization or some Fourier component of the polarization becomes very large. Equally, we may speak of the condensation of a transverse optical phonon. Here the word condensation is to be understood in the Bose-Einstein sense (*TP*, p. 199) of a time-independent displacement of finite amplitude. This can occur when the corresponding TO phonon frequency vanishes at some point in the Brillouin zone. LO phonons always have higher frequencies than the TO phonons of the same wavevector, so we are not concerned with LO phonon condensation.

In a polarization catastrophe the local electric field caused by the ionic displacement is larger than the elastic restoring force, thereby giving an asymmetrical shift in the positions of the ions. Higher order restoring forces will limit the shift to a finite displacement.

The occurrence of ferroelectricity (and antiferroelectricity) in many perovskite-structure crystals suggests that this structure is favorably disposed to a displacive transition. Local field calculations make clear the reason for the favored position of this structure: the O^{2-} ions do not have cubic surroundings, and the local field factors turn out to be unusually large.

We give first the simple form of the catastrophe theory, supposing that the local field at all atoms is equal to $\mathbf{E} + 4\pi\mathbf{P}/3$ in CGS or $\mathbf{E} + \mathbf{P}/3\epsilon_0$ in SI. The theory given now leads to a second-order transition; the physical ideas can be carried over to a first-order transition. In a second-order transition there is no latent heat; the order parameter (in this instance, the polarization) is not discontinuous at the transition temperature. In a first-order transition there is a latent heat; the order parameter changes discontinuously at the transition temperature.

We rewrite (24) for the dielectric constant in the form

$$\text{(CGS)} \qquad \epsilon = \frac{1 + \frac{8\pi}{3}\Sigma N_i\alpha_i}{1 - \frac{4\pi}{3}\Sigma N_i\alpha_i} , \tag{30}$$

where α_i is the electronic plus ionic polarizability of an ion of type i and N_i is the number of ions i per unit volume. The dielectric constant becomes infinite and permits a finite polarization in zero applied field when

$$\text{(CGS)} \qquad \Sigma N_i\alpha_i = 3/4\pi . \tag{31}$$

This is the condition for a polarization catastrophe.

The value of ϵ in (30) is sensitive to small departures of $\Sigma N_i\alpha_i$ from the critical value $3/4\pi$. If we write

$$\text{(CGS)} \qquad (4\pi/3)\Sigma N_i\alpha_i = 1 - 3s , \tag{32}$$

where $s \ll 1$, the dielectric constant in (30) becomes

$$\epsilon \simeq 1/s . \tag{33}$$

Suppose near the critical temperature s varies linearly with temperature:

$$s \simeq (T - T_c)/\xi , \tag{34}$$

where ξ is a constant. Such a variation of s or $\Sigma N_i\alpha_i$ might come from normal thermal expansion of the lattice. The dielectric constant has the form

$$\epsilon \simeq \frac{\xi}{T - T_c} , \tag{35}$$

close to the observed temperature variation in the paraelectric state, Fig. 12.

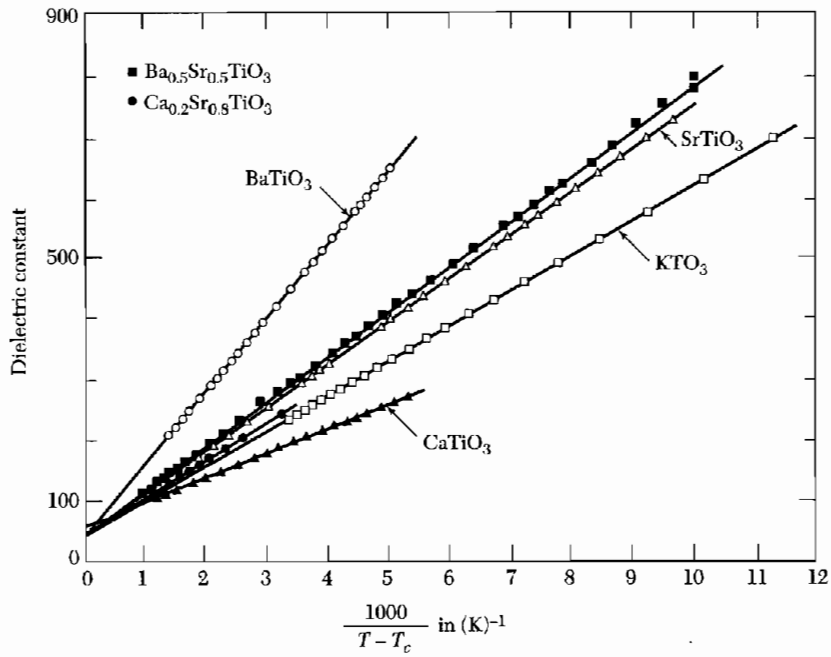

Figure 12 Dielectric constant versus $1/(T - T_c)$ in the paraelectric state ($T > T_c$) of perovskites, after G. Rupprecht and R. O. Bell.

Soft Optical Phonons

The Lyddane-Sachs-Teller relation (Chapter 14) is

$$\omega_T^2/\omega_L^2 = \epsilon(\infty)/\epsilon(0) \quad . \tag{36}$$

The static dielectric constant increases when the transverse optical phonon frequency decreases. When the static dielectric constant $\epsilon(0)$ has a high value, such as 100 to 10,000, we find that ω_T has a low value.

When $\omega_T = 0$ the crystal is unstable and $\epsilon(0)$ is infinite because there is no effective restoring force. The ferroelectric $BaTiO_3$ at 24°C has a TO mode at 12 cm^{-1}, a low frequency for an optical mode.

If the transition to a ferroelectric state is first order, we do not find $\omega_T = 0$ or $\epsilon(0) = \infty$ at the transition. The LST relation suggests only that $\epsilon(0)$ extrapolates to a singularity at a temperature T_0 below T_c.

The association of a high static dielectric constant with a low-frequency optical mode is supported by experiments on strontium titanate, $SrTiO_3$. According to the LST relation, if the reciprocal of the static dielectric constant has a temperature dependence $1/\epsilon(0) \propto (T - T_0)$, then the square of the optical mode frequency will have a similar temperature dependence: $\omega_T^2 \propto (T - T_0)$, if ω_L is independent of temperature. The result for ω_T^2 is very well confirmed by Fig. 13. Measurements of ω_T versus T for another ferroelectric crystal, SbSI, are shown in Fig. 14.

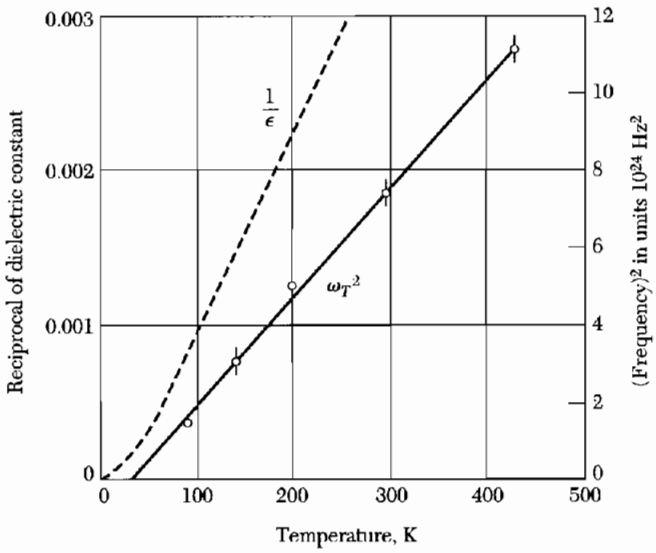

Figure 13 Plot of the square of the frequency of the zero wavevector transverse optical mode against temperature, for $SrTiO_3$, as observed in neutron diffraction experiments by Cowley. The broken line is the reciprocal of the dielectric constant from the measurements of Mitsui and Westphal.

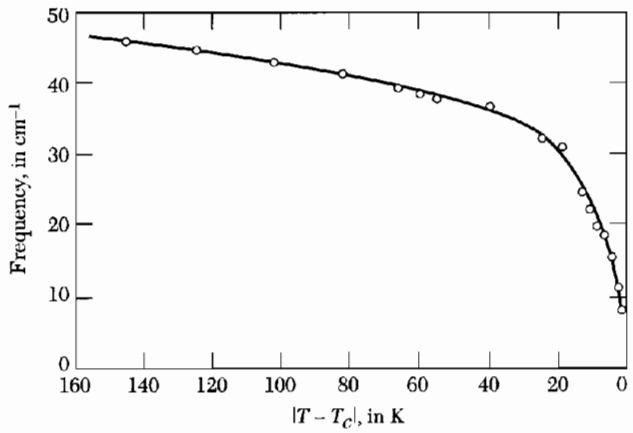

Figure 14 Decrease of a transverse phonon frequency as the Curie temperature is approached from below, in the ferroelectric crystal antimony sulphoiodide, SbSI. (After Raman scattering experiments by C. H. Perry and D. K. Agrawal.)

Landau Theory of the Phase Transition

A ferroelectric with a first-order phase transition between the ferroelectric and the paraelectric state is distinguished by a discontinuous change of the saturation polarization at the transition temperature. The transition between the normal and superconducting states is a second-order transition, as is the

transition between the ferromagnetic and paramagnetic states. In these transitions the degree of order goes to zero without a discontinuous change as the temperature is increased.

We can obtain a consistent formal thermodynamic theory of the behavior of a ferroelectric crystal by considering the form of the expansion of the energy as a function of the polarization P. We assume that the Landau[7] free energy density $\hat{F}$ in one dimension may be expanded formally as

$$\hat{F}(P;T,E) = -EP + g_0 + \tfrac{1}{2}g_2P^2 + \tfrac{1}{4}g_4P^4 + \tfrac{1}{6}g_6P^6 + \cdots , \tag{37}$$

where the coefficients g_n depend on the temperature.

The series does not contain terms in odd powers of P if the unpolarized crystal has a center of inversion symmetry, but crystals are known in which odd powers are important. Power series expansions of the free energy do not always exist, for nonanalytic terms are known to occur, especially when very near a transition. For example, the transition in KH_2PO_4 appears to have a logarithmic singularity in the heat capacity at the transition, which is not classifiable as either first or second order.

The value of P in thermal equilibrium is given by the minimum of $\hat{F}$ as a function of P; the value of $\hat{F}$ at this minimum defines the Helmholtz free energy $F(T,E)$. The equilibrium polarization in an applied electric field E satisfies the extremum condition

$$\frac{\partial \hat{F}}{\partial P} = 0 = -E + g_2P + g_4P^3 + g_6P^5 + \cdots . \tag{38}$$

In this section we assume that the specimen is a long rod with the external applied field E parallel to the long axis.

To obtain a ferroelectric state we must suppose that the coefficient of the term in P^2 in (37) passes through zero at some temperature T_0:

$$g_2 = \gamma(T - T_0) , \tag{39}$$

where γ is taken as a positive constant and T_0 may be equal to or lower than the transition temperature. A small positive value of g_2 means that the lattice is "soft" and is close to instability. A negative value of g_2 means that the unpolarized lattice is unstable. The variation of g_2 with temperature is accounted for by thermal expansion and other effects of anharmonic lattice interactions.

Second-Order Transition

If g_4 in (37) is positive, nothing new is added by the term in g_6, and this may then be neglected. The polarization for zero applied electric field is found from (38):

$$\gamma(T - T_0)P_s + g_4P_s^3 = 0 , \tag{40}$$

[7]In *TP*, see pp. 69 and 298 for a discussion of the Landau function.

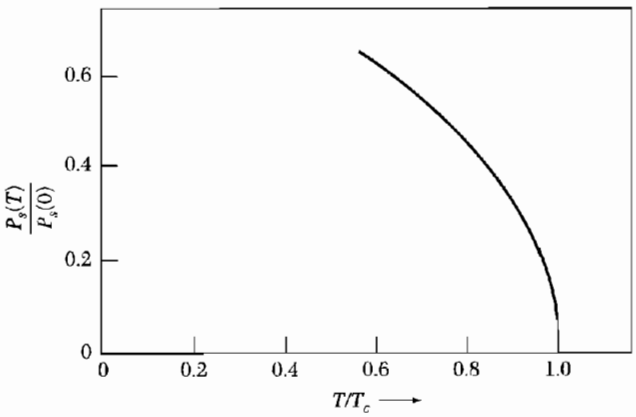

Figure 15 Spontaneous polarization versus temperature, for a second-order phase transition.

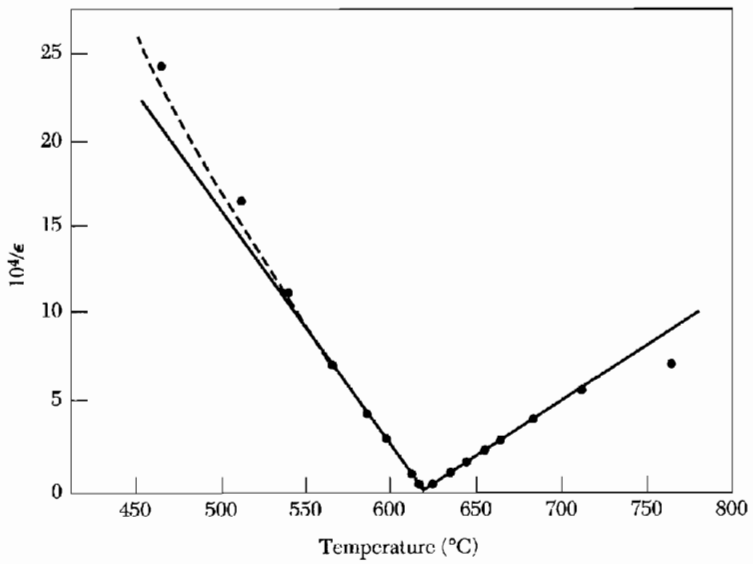

Figure 16 Temperature variation of the polar-axis static dielectric constant of $LiTaO_3$. (After Glass.)

so that either $P_s = 0$ or $P_s^2 = (\gamma/g_4)(T_0 - T)$. For $T \geq T_0$ the only real root of (40) is at $P_s = 0$, because γ and g_4 are positive. Thus T_0 is the Curie temperature. For $T < T_0$ the minimum of the Landau free energy in zero applied field is at

$$|P_s| = (\gamma/g_4)^{1/2}(T_0 - T)^{1/2} , \tag{41}$$

as plotted in Fig. 15. The phase transition is a second-order transition because the polarization goes continuously to zero at the transition temperature. The transition in $LiTaO_3$ is an example (Fig. 16) of a second-order transition.

First-Order Transition

The transition is first order if g_4 in (37) is negative. We must now retain g_6 and take it positive in order to restrain $\hat{F}$ from going to minus infinity (Fig. 17). The equilibrium condition for $E = 0$ is given by (38):

$$\gamma(T - T_0)P_s - |g_4|P_s^3 + g_6 P_s^5 = 0 \ , \tag{42}$$

so that either $P_s = 0$ or

$$\gamma(T - T_0) - |g_4|P_s^2 + g_6 P_s^4 = 0 \ . \tag{43}$$

At the transition temperature T_c the free energies of the paraelectric and ferroelectric phases will be equal. That is, the value of $\hat{F}$ for $P_s = 0$ will be equal to the value of $\hat{F}$ at the minimum given by (43). In Fig. 18 we show the characteristic variation with temperature of P_s for a first-order phase transition;

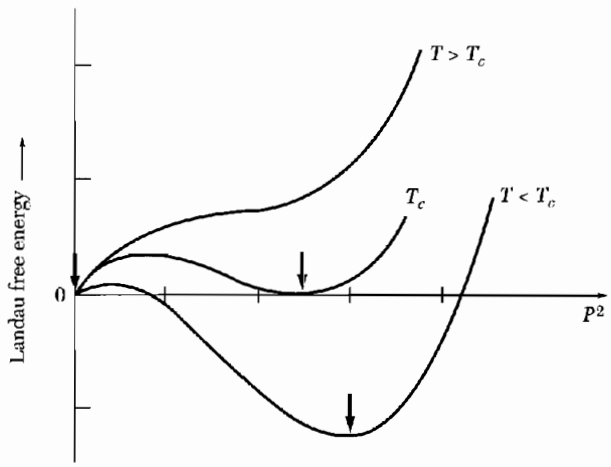

Figure 17 Landau free energy function versus (polarization)^2 in a first-order transition, at representative temperatures. At T_c the Landau function has equal minima at $P = 0$ and at a finite P as shown. For T below T_c the absolute minimum is at larger values of P; as T passes through T_c there is a discontinuous change in the position of the absolute minimum. The arrows mark the minima.

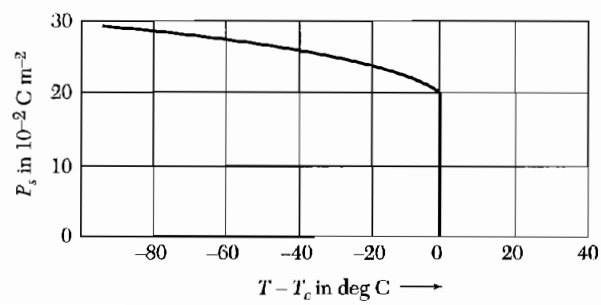

Figure 18 Calculated values of the spontaneous polarization as a function of temperature, with parameters as for barium titanate. (After W. Cochran.)

contrast this with the variation shown in Fig. 15 for a second-order phase transition. The transition in $BaTiO_3$ is first order.

The dielectric constant is calculated from the equilibrium polarization in an applied electric field E and is found from (38). In equilibrium at temperatures over the transition, the terms in P^4 and P^6 may be neglected; thus $E = \gamma(T - T_0)P$, or

$$\text{(CGS)} \qquad \epsilon(T > T_c) = 1 + 4\pi P/E = 1 + 4\pi/\gamma(T - T_0) \ , \qquad (44)$$

of the form of (36). The result applies whether the transition is of the first or second order, but if second order we have $T_0 = T_c$; if first order, then $T_0 < T_c$. Equation (39) defines T_0, but T_c is the transition temperature.

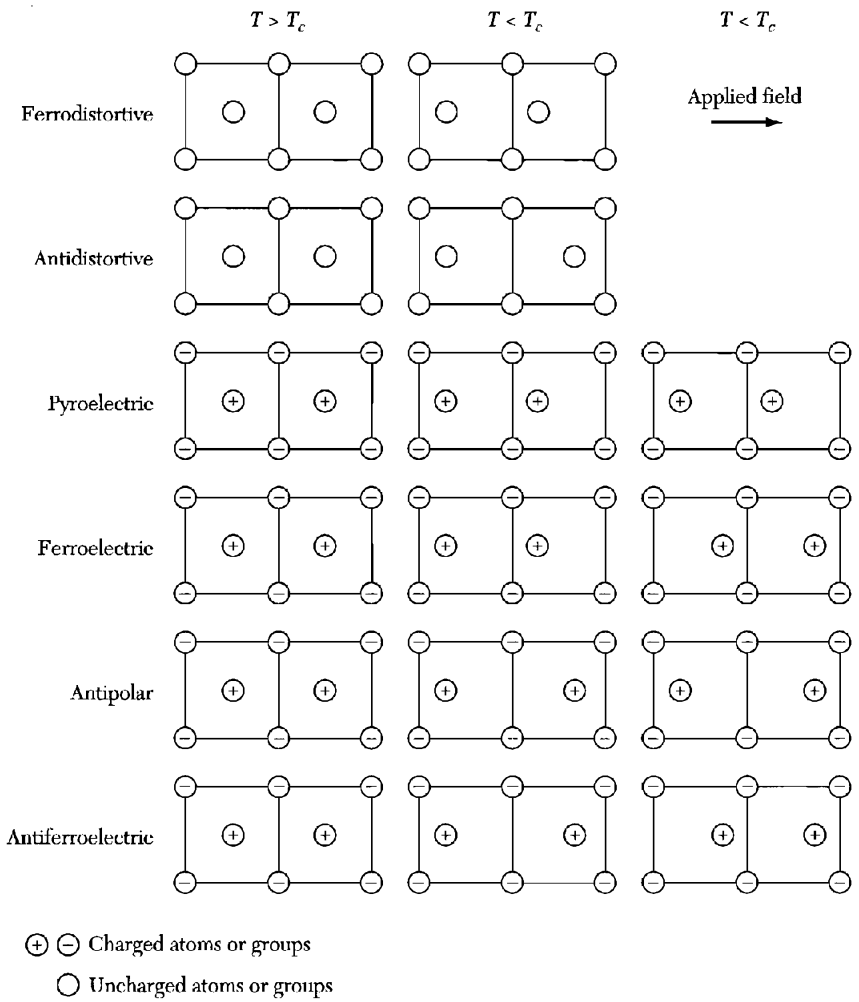

Figure 19 Schematic representation of fundamental types of structural phase transitions from a centrosymmetric prototype. (After Lines and Glass.)

Antiferroelectricity

A ferroelectric displacement is not the only type of instability that may develop in a dielectric crystal. Other deformations occur, as in Fig. 19. These deformations, even if they do not give a spontaneous polarization, may be accompanied by changes in the dielectric constant. One type of deformation is called **antiferroelectric** and has neighboring lines of ions displaced in opposite senses. The perovskite structure appears to be susceptible to many types of deformation, often with little difference in energy between them. The phase diagrams of mixed perovskite systems, such as the $PbZrO_3$–$PbTiO_3$ system, show transitions between para-, ferro-, and antiferroelectric states (Fig. 20). Several crystals believed to have an ordered nonpolar state are listed in Table 3.

Ferroelectric Domains

Consider a ferroelectric crystal (such as barium titanate in the tetragonal phase) in which the spontaneous polarization may be either up or down the c axis of the crystal. A ferroelectric crystal generally consists of regions called **domains** within each of which the polarization is in the same direction, but in adjacent domains the polarization is in different directions. In Fig. 21 the polarization is in opposite directions. The net polarization depends on the difference in the volumes of the upward- and downward-directed domains. The

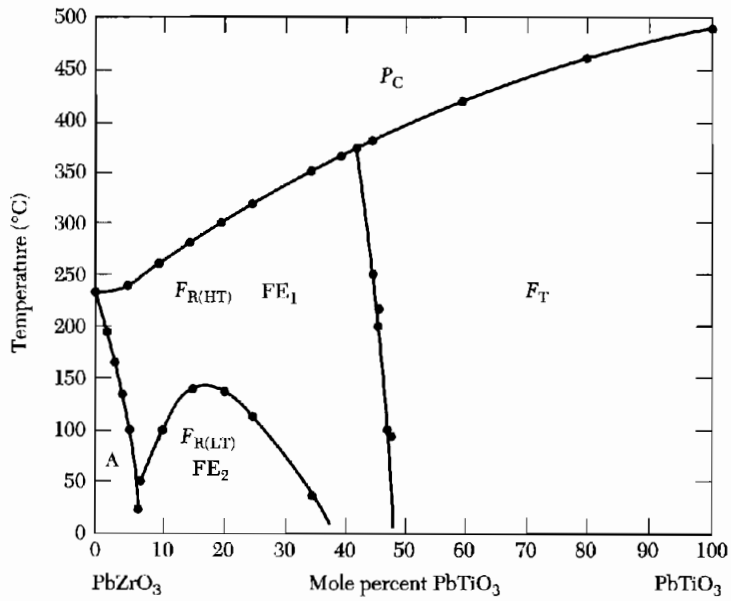

Figure 20 Ferroelectric F, antiferroelectric A, and paraelectric P phases of the lead zirconate–lead titanate solid solution system. The subscript T denotes a tetragonal phase; C a cubic phase; R a rhombohedral phase, of which there are high-temperature (HT) and low-temperature (LT) forms. Near the rhombohedral–tetragonal phase boundaries one finds very high piezoelectric coupling coefficients. (After Jaffe.)

Table 3 Antiferroelectric crystals

Crystal	Transition temperature to antiferroelectric state, in K
WO_3	1010
$NaNbO_3$	793, 911
$PbZrO_3$	506
$PbHfO_3$	488
$NH_4H_2PO_4$	148
$ND_4D_2PO_4$	242
$NH_4H_2AsO_4$	216
$ND_4D_2AsO_4$	304
$(NH_4)_2H_3IO_6$	254

From a compilation by Walter J. Merz.

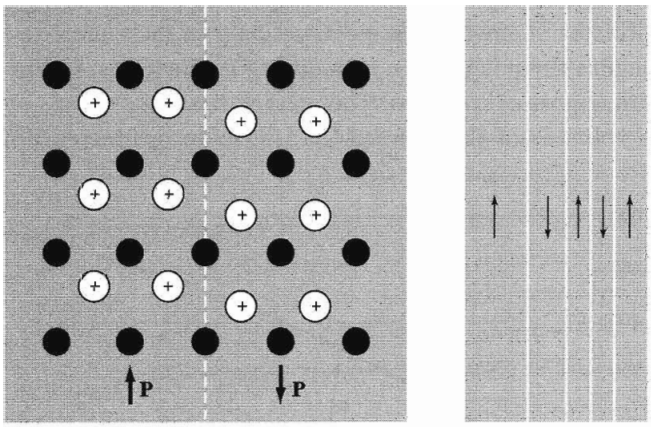

Figure 21 (a) Schematic drawing of atomic displacements on either side of a boundary between domains polarized in opposite directions in a ferroelectric crystal; (b) view of a domain structure, showing 180° boundaries between domains polarized in opposite directions.

crystal as a whole will appear to be unpolarized, as measured by the charge on electrodes covering the ends, when the volumes of domains in opposite senses are equal. The total dipole moment of the crystal may be changed by the movement of the walls between domains or by the nucleation of new domains.

Figure 22 is a series of photomicrographs of a single crystal of barium titanate in an electric field normal to the plane of the photographs and parallel to the tetragonal axis. The closed curves are boundaries between domains polarized into and out of the plane of the photographs. The domain boundaries change size and shape when the intensity of the electric field is altered.

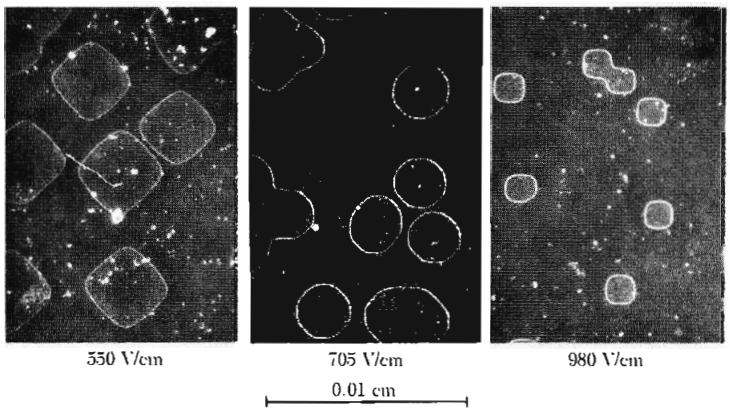

Figure 22 Ferroelectric domains on the face of a single crystal of barium titanate. The face is normal to the tetragonal or c axis. The net polarization of the crystal as judged by domain volumes is increased markedly as the electric field intensity parallel to the axis is increased from 550 volts/cm to 980 V/cm. The domain boundaries are made visible by etching the crystal in a weak acid solution. (R. C. Miller.)

Piezoelectricity

All crystals in a ferroelectric state are also piezoelectric: a stress Z applied to the crystal will change the electric polarization (Fig. 23). Similarly, an electric field E applied to the crystal will cause the crystal to become strained. In schematic one-dimensional notation, the piezoelectric equations are

$$\text{(CGS)} \qquad P = Zd + E\chi; \quad e = Zs + Ed \ , \tag{45}$$

where P is the polarization, Z the stress, d the **piezoelectric strain constant**, E the electric field, χ the dielectric susceptibility, e the elastic strain, and s the elastic compliance constant. To obtain (45) in SI, replace χ by $\epsilon_0\chi$. These relations exhibit the development of polarization by an applied stress and the development of elastic strain by an applied electric field.

A crystal may be piezoelectric without being ferroelectric: a schematic example of such a structure is given in Fig. 24. Quartz is piezoelectric, but not ferroelectric; barium titanate is both. For order of magnitude, in quartz $d \approx 10^{-7}$ cm/statvolt and in barium titanate $d \approx 10^{-5}$ cm/statvolt. The general definition of the piezoelectric strain constants is

$$d_{ik} = (\partial e_k/\partial E_i)_Z \ , \tag{46}$$

where $i \equiv x, y, z$ and $k \equiv xx, yy, zz, yz, zx, xy$. To convert to cm/stat-V from values of d_{ik} given in m/V, multiply by 3×10^4.

The lead zirconate–lead titanate system (called the PZT system), Fig. 20, is widely used in polycrystalline (ceramic) form with compositions of very high piezoelectric coupling. The synthetic polymer polyvinylidenfluoride (PVF_2) is

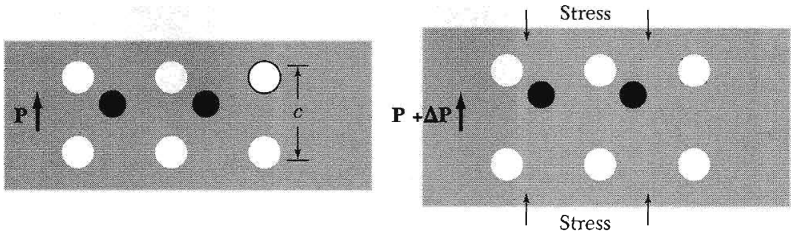

Figure 23 (a) Unstressed ferroelectric crystal and (b) stressed ferroelectric crystal. The stress changes the polarization by **ΔP**, the induced piezoelectric polarization.

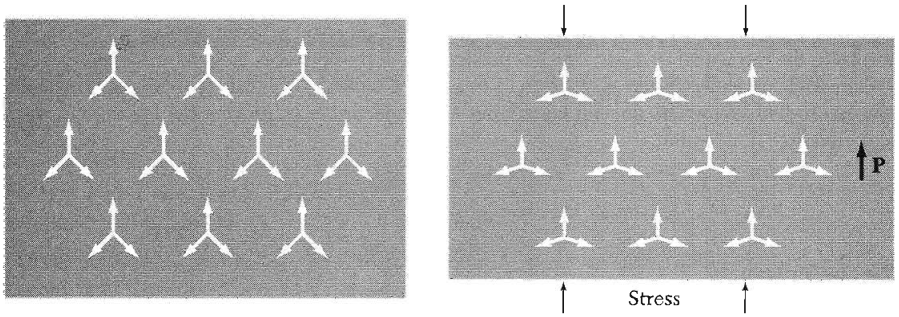

Figure 24 (a) The unstressed crystal has a threefold symmetry axis. The arrows represent dipole moments; each set of three arrows represents a planar group of ions denoted by $A_3^+B^{3-}$, with a B^{3-} ion at each vertex. The sum of the three dipole moments at each vertex is zero. (b) The crystal when stressed develops a polarization in the direction indicated. The sum of the dipole moments about each vertex is no longer zero.

five times more strongly piezoelectric than crystalline quartz. Thin stretched films of PVF_2 are flexible and as ultrasonic transducers are applied in medicine to monitor blood pressure and respiration.

SUMMARY

(In CGS Units)

- The electric field averaged over the volume of the specimen defines the macroscopic electric field **E** of the Maxwell equations.
- The electric field that acts at the site $\mathbf{r}_j$ of an atom j is the local electric field, $\mathbf{E}_{\text{loc}}$. It is a sum over all charges, grouped in terms as $\mathbf{E}_{\text{loc}}(\mathbf{r}_j) = \mathbf{E}_0 + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3(\mathbf{r}_j)$, where only $\mathbf{E}_3$ varies rapidly within a cell. Here:
  $\mathbf{E}_0$ = external electric field;
  $\mathbf{E}_1$ = depolarization field associated with the boundary of the specimen;
  $\mathbf{E}_2$ = field from polarization outside a sphere centered about $\mathbf{r}_j$;
  $\mathbf{E}_3(\mathbf{r}_j)$ = field at $\mathbf{r}_j$ due to all atoms inside the sphere.

- The macroscopic field $\mathbf{E}$ of the Maxwell equations is equal to $\mathbf{E}_0 + \mathbf{E}_1$, which, in general, is not equal to $\mathbf{E}_{\text{loc}}(\mathbf{r}_j)$.
- The depolarization field in an ellipsoid is $E_{1\mu} = -N_{\mu\nu}P_\nu$, where $N_{\mu\nu}$ is the depolarization tensor; the polarization $\mathbf{P}$ is the dipole moment per unit volume. In a sphere $N = 4\pi/3$.
- The Lorentz field is $\mathbf{E}_2 = 4\pi\mathbf{P}/3$.
- The polarizability α of an atom is defined in terms of the local electric field as $\mathbf{p} = \alpha\mathbf{E}_{\text{loc}}$.
- The dielectric susceptibility χ and dielectric constant ϵ are defined in terms of the macroscopic electric field $\mathbf{E}$ as $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = \epsilon\mathbf{E} = (1 + 4\pi\chi)\mathbf{E}$, or $\chi = P/E$. In SI, we have $\chi = P/\epsilon_0 E$.
- An atom at a site with cubic symmetry has $\mathbf{E}_{\text{loc}} = \mathbf{E} + (4\pi/3)\mathbf{P}$ and satisfies the Clausius-Mossotti relation (24).

Problems

1. ***Polarizability of atomic hydrogen.*** Consider a semiclassical model of the ground state of the hydrogen atom in an electric field normal to the plane of the orbit (Fig. 25), and show that for this model $\alpha = a_H^3$, where a_H is the radius of the unperturbed orbit. *Note:* If the applied field is in the x direction, then the x component of the field of the nucleus at the displaced position of the electron orbit must be equal to the applied field. The correct quantum-mechanical result is larger than this by the factor $\frac{9}{2}$. (We are speaking of α_0 in the expansion $\alpha = \alpha_0 + \alpha_1 E + \cdots$.) We assume $x \ll a_H$. One can also calculate α_1 on this model.

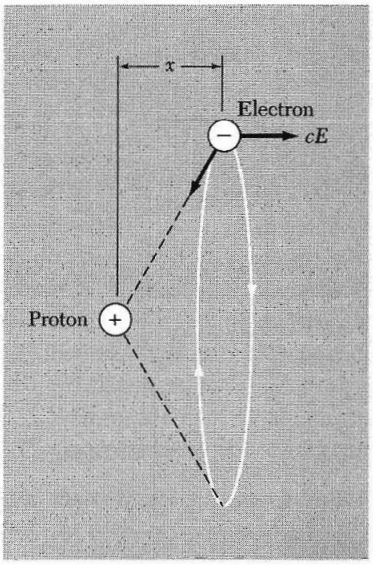

Figure 25 An electron in a circular orbit of radius a_H is displaced a distance x on application of an electric field E in the $-x$ direction. The force on the electron due to the nucleus is e^2/a_H^2 in CGS or $e^2/4\pi\epsilon_0 a_H^2$ in SI. The problem assumes $x \ll a_H$.

2. ***Polarizability of conducting sphere.*** Show that the polarizability of a conducting metallic sphere of radius a is $\alpha = a^3$. This result is most easily obtained by noting that $E = 0$ inside the sphere and then using the depolarization factor $4\pi/3$ for a sphere (Fig. 26). The result gives values of α of the order of magnitude of the observed polarizabilities of atoms. A lattice of N conducting spheres per unit volume has dielectric constant $\epsilon = 1 + 4\pi N a^3$, for $Na^3 \ll 1$. The suggested proportionality of α to the cube of the ionic radius is satisfied quite well for alkali and halogen ions. To do the problem in SI, use $\frac{1}{3}$ as the depolarization factor.

3. ***Effect of air gap.*** Discuss the effect of an air gap (Fig. 27) between capacitor plates and dielectric on the measurement of high dielectric constants. What is the highest apparent dielectric constant possible if the air gap thickness is 10^{-3} of the total thickness? The presence of air gaps can seriously distort the measurement of high dielectric constants.

4. ***Interfacial polarization.*** Show that a parallel-plate capacitor made up of two parallel layers of material—one layer with dielectric constant ϵ, zero conductivity, and thickness d, and the other layer with $\epsilon = 0$ for convenience, finite conductivity σ,

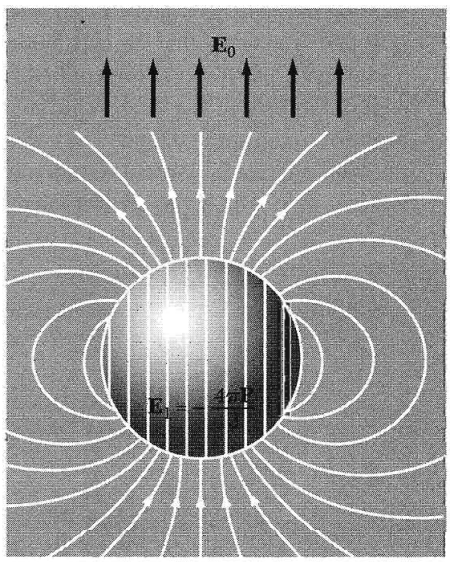

Figure 26 The total field inside a conducting sphere is zero. If a field $\mathbf{E}_0$ is applied externally, then the field $\mathbf{E}_1$ due to surface charges on the sphere must just cancel $\mathbf{E}_0$, so that $\mathbf{E}_0 + \mathbf{E}_1 = 0$ within the sphere. But $\mathbf{E}_1$ can be simulated by the depolarization field $-4\pi\mathbf{P}/3$ of a uniformly polarized sphere of polarization $\mathbf{P}$. Relate $\mathbf{P}$ to $\mathbf{E}_0$ and calculate the dipole moment $\mathbf{p}$ of the sphere. In SI the depolarization field is $-\mathbf{P}/3\epsilon_0$.

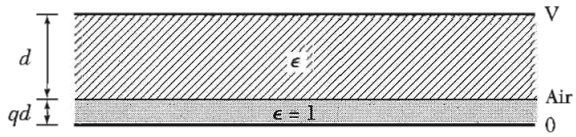

Figure 27 An air gap of thickness qd is in series in a capacitor with a dielectric slab of thickness d.

and thickness qd—behaves as if the space between the condenser plates were filled with a homogeneous dielectric with dielectric constant

$$\epsilon_{\text{eff}} = \frac{\epsilon(1+q)}{1-(i\epsilon\omega q/4\pi\sigma)} ,$$

where ω is the angular frequency. Values of ϵ_{eff} as high as 10^4 or 10^5 caused largely by this Maxwell-Wagner mechanism are sometimes found, but the high values are always accompanied by large ac losses.

5. ***Polarization of sphere.*** A sphere of dielectric constant ϵ is placed in a uniform external electric field E_0. (a) What is the volume average electric field E in the sphere? (b) Show that the polarization in the sphere is $P = \chi E_0/[1 + (4\pi\chi/3)]$, where $\chi = (\epsilon - 1)/4\pi$. Hint: You do not need to calculate E_{loc} in this problem; in fact it is confusing to do so, because ϵ and χ are defined so that $P = \chi E$. We require E_0 to be unchanged by insertion of the sphere. We can produce a fixed E_0 by placing positive charges on one thin plate of an insulator and negative charges on an opposite plate. If the plates are always far from the sphere, the field of the plates will remain unchanged when the sphere is inserted between them. The results above are in CGS.

6. ***Ferroelectric criterion for atoms.*** Consider a system of two neutral atoms separated by a fixed distance a, each atom having a polarizability α. Find the relation between a and α for such a system to be ferroelectric. Hint: The dipolar field is strongest along the axis of the dipole.

7. ***Saturation polarization at Curie point.*** In a first-order transition the equilibrium condition (43) with T set equal to T_c gives one equation for the polarization $P_s(T_c)$. A further condition at the Curie point is that $\hat{F}(P_s, T_c) = \hat{F}(0, T_c)$. (a) Combining these two conditions, show that $P_s^2(T_c) = 3|g_4|/4g_6$. (b) Using this result, show that $T_c = T_0 + 3g_4^2/16\gamma g_6$.

8. ***Dielectric constant below transition temperature.*** In terms of the parameters in the Landau free energy expansion, show that for a second-order phase transition the dielectric constant below the transition temperature is

$$\epsilon = 1 + 4\pi\Delta P/E = 1 + 2\pi/\gamma(T_c - T) .$$

This result may be compared with (44) above the transition.

9. ***Soft modes and lattice transformations.*** Sketch a monatomic linear lattice of lattice constant a. (a) Add to each of six atoms a vector to indicate the direction of the displacement at a given time caused by a longitudinal phonon with wavevector at the zone boundary. (b) Sketch the crystal structure that results if this zone boundary phonon becomes unstable ($\omega \to 0$) as the crystal is cooled through T_c. (c) Sketch on one graph the essential aspects of the longitudinal phonon dispersion relation for the monatomic lattice at T well above T_c and at $T = T_c$. Add to the graph the same information for phonons in the new structure at T well below T_c.

10. ***Ferroelectric linear array.*** Consider a line of atoms of polarizability α and separation a. Show that the array can polarize spontaneously if $\alpha \geq a^3/4\Sigma n^{-3}$, where the sum is over all positive integers and is given in tables as 1.202. . . .