

## 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.<sup>30</sup> Such crystals (examples are given in Table 27.4) are called ferroelectrics.<sup>31</sup> The transition from the unpolarized to the pyroelectric state is called first order if it is discontinuous (i.e., if  $\mathbf{P}$  acquires a nonzero value immediately below  $T_c$ ) and second or higher order, if it is continuous (i.e., if  $\mathbf{P}$  grows continuously from zero as  $T$  drops below  $T_c$ ).<sup>32</sup>

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  $\mathbf{P}$ . 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.

<sup>30</sup> 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.

<sup>31</sup> 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.

<sup>32</sup> Sometimes the term "ferroelectric" is reserved for crystals in which the transition is second order.

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is the perovskite  
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Figure 27.10

The perovskite  
titanate ( $\text{BaTiO}_3$ )  
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Table 27.4  
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Barium  
Lead titanate  
Cadmium  
Potassium

Rochelle

Deuterium

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## PROBLEMS

1. Elect  
Far from t

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 ( $\text{BaTiO}_3$ ) class of ferroelectrics in the unpolarized phase. The crystal is cubic, with  $\text{Ba}^{++}$  ions at the cube corners,  $\text{O}^{--}$  ions at the centers of the cube faces, and  $\text{Ti}^{4+}$  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  $\text{Ba}^{++}$  and  $\text{Ti}^{4+}$  are, but the  $\text{O}^{--}$  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.

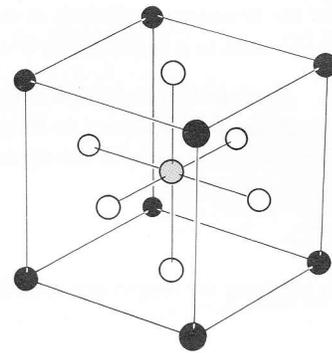


Table 27.4

SELECTED FERROELECTRIC CRYSTALS

NAME	FORMULA	$T_c$ (K)	$P$ ( $\mu\text{C}/\text{cm}^2$ )	at $T$ (K)
Potassium dihydrogen phosphate	$\text{KH}_2\text{PO}_4$	123	4.75	96
Potassium dideuterium phosphate	$\text{KD}_2\text{PO}_4$	213	4.83	180
Rubidium dihydrogen phosphate	$\text{RbH}_2\text{PO}_4$	147	5.6	90
Rubidium dideuterium phosphate	$\text{RbD}_2\text{PO}_4$	218	—	—
Barium titanate	$\text{BaTiO}_3$	393	26.0	300
Lead titanate	$\text{PbTiO}_3$	763	> 50	300
Cadmium titanate	$\text{CdTiO}_3$	55	—	—
Potassium niobate	$\text{KNbO}_3$	708	30.0	523
Rochelle salt	$\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{D}_2\text{O}$	$\left\{ \begin{matrix} 297 \\ 255 \end{matrix} \right\}^a$	0.25	278
Deuterated Rochelle salt	$\text{NaKC}_4\text{H}_2\text{D}_2\text{O}_6 \cdot 4\text{D}_2\text{O}$	$\left\{ \begin{matrix} 308 \\ 251 \end{matrix} \right\}^a$	0.35	279

<sup>a</sup> 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  $\phi$  will be that of a point dipole of moment  $p = 4\pi P a^3/3$ :

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

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

$$\frac{A \cos\theta}{r^2} + Br \cos\theta, \quad (27.81)$$

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  $\mathbf{r}$  due to the dipole at  $\mathbf{r}'$  is

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

By applying the restrictions of cubic symmetry to the tensor

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

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

## 3. Polarizability of a Single Hydrogen Atom

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

$$\psi_0 \propto e^{-r/a_0}. \quad (27.84)$$

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

$$\psi \propto \psi_0(1 + \gamma x) = \psi_0 + \delta\psi, \quad (27.85)$$

and determine  $\gamma$  by minimizing the total energy.

(b) Calculate the polarization

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

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  $\text{OH}^-$  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  $\theta$  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

$$Np\langle \cos\theta \rangle = NpL\left(\frac{pE}{k_B T}\right), \quad (27.87)$$

where  $L(x)$ , the "Langevin

(b) Typical dipole field of order  $10^4$  volt

5. Generalized L. Suppose that the dielectric (27.57) but has the

Show directly from

where the  $\omega_i^0$  are degree polynomials polynomial at  $\omega$

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

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

(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

$$\alpha = \frac{p^2}{3k_B T}. \quad (27.89)$$

### 5. Generalized Lyddane-Sachs-Teller Relation

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

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

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

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

where the  $\omega_i^0$  are the frequencies at which  $\epsilon$  vanishes. (*Hint*: Write the condition  $\epsilon = 0$  as an  $n$ th-degree polynomial in  $\omega^2$ , 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  $\omega_i$  and  $\omega_i^0$ ?