# INSULATORS, STRUCTURE OF

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### INTRODUCTION

Most of the substances around us, whether natural or synthetic, are electrical insulators. The distinction between insulators and metals has been recognized for centuries, and even children can tell the difference: metals are typically soft and malleable and can be polished to a high luster, while common insulators are hard, brittle, and often rather dull. Most electrical insulators are also thermal insulators. Hot beverages are served in electrical insulators, not metals, to retain the heat better and to prevent injury to the hand while drinking. These are among the more common properties, but insulators exhibit a broad range of characteristics that are perhaps less obvious, but just as important.

Insulators are needed whenever electrical current flow must be controlled, whether as a nerve impulse in a living organism, a bit of information in a digital computer, or the

industrial transmission of electrical power. Certain insulators greatly enhance the performance of capacitors by increasing the amount of charge that can be maintained using a particular applied voltage. Other insulators respond to mechanical, thermal, magnetic, electrical, or optical stress in ways that make possible a wide variety of applications such as transducers, filters, motors, detectors, resonators, oscillators, imagers, memory devices, video displays, and many more. The tremendous variation of the properties of insulators plays a major role in the modern technological world, and it is important, therefore, to have some understanding of the relationship between their structure and their properties.

An insulator may be defined as any material that does not allow net movement of electric charge from one region of the material to any other region. The distinction between insulator and conductor, however, is relative and concerns both the conductivity of

the surrounding medium and the duration of the observation. Every material conducts electricity to some extent, so that given enough time even the best electrical insulators will allow some charge motion. Among the best electrical insulators are diamonds, with electrical conductivities of  $10^{-13}$  S m<sup>-1</sup> or less. But the best metals, like silver, have conductivities of around  $10^8$  S m<sup>-1</sup>, more than 20 orders of magnitude larger. As a rough guideline, anything with a conductivity less than  $10^{-3}$  S m<sup>-1</sup> may be considered an insulator.

All materials are composed of atomic nuclei and enough electrons to maintain charge neutrality. An electron in such a material may be tightly bound, always remaining near a particular atomic nucleus (or group of nuclei), or it may be free to migrate from one region in the material to another. A material with a large number of free electrons is either a semiconductor or a metal. In an insulator, there is a negligible number of free carriers and a substantial activation energy for the creation of free carriers from the bound electrons.

Electrical insulation can result from a number of distinct mechanisms. In gases, the thermal activation energy is a result of the high ionization energy of isolated atoms. In liquids, glasses, and amorphous solids the thermal activation energy is a result of the atomic disorder that makes migration of carriers a relatively tortuous process. Crystalline solids sometimes have exactly enough electrons to fill entire bands of electronic states completely, leaving the next state available for free electrons at a significantly higher energy, called the band-gap energy. In plastic, polymeric, and liquid-crystal materials various combinations of ionization energies, disorder, and band filling may contribute to a substantial activation energy.

This binding of electrons in an insulator implies that the electrical conductivity, which is proportional to the number of free carriers, will be thermally activated:

$$\sigma = \sigma_o e^{-E_g/2kT},\tag{1}$$

where  $E_g$  is the band-gap energy (or possibly some other, related activation energy). The division is somewhat arbitrary, but typically the term "electrical insulator" is reserved for a material with a band gap of at least 3 eV. The following sections are most appropriate for

the properties and structure of homogeneous, crystalline insulators, but some other insulators will be briefly mentioned, and the concepts involved are of general utility. For more detailed information on amorphous materials, electronic structure of solids, polymers, liquid crystals, ceramics, and composite materials see the related articles in this encyclopedia. An overview of the important properties of insulators follows, including a brief discussion of the "soft mode" concept. The section on materials discusses the occurrence of insulating solids among the elements, binary compounds, and certain classes of more complex materials.

#### 1. PROPERTIES OF INSULATORS

#### 1.1 Dielectric Properties

The term "dielectric" emphasizes the response of an insulator to an applied field. The principal properties of interest in this regard are the permittivity ( $\epsilon$ ) and the loss tangent ( $\tan\delta$ ), which characterize both the degree of polarization in an applied field and the losses that result from application of an alternating frequency field. A brief outline of dielectric properties is provided below, but for a more complete discussion see DIELECTRIC PROPERTIES OF INSULATORS.

1.1.1 The Complex Permittivity. When an electric field E is applied to a dielectric material, the charges within the material experience forces that tend to redistribute the charges. This redistribution is characterized by the polarization P, which represents the electric dipole moment induced in the material by the applied electric field. It is also convenient to define a third quantity, called the displacement field D, which represents the effects of the actual charges in the material and is given by

$$D = \epsilon_{v} E + P, \tag{2}$$

where  $\epsilon_{\rm v}$  is the permittivity of the vacuum.

In an ordinary dielectric, the polarization, the electric field, and the displacement field will all be proportional to each other. We define

$$D = \epsilon E = \epsilon_{v} \epsilon_{r} E, \tag{3}$$

where  $\epsilon_r$  is the relative permittivity, a unitless quantity sometimes called the dielectric constant, although this term is more properly reserved for situations in which  $\epsilon_r$  is actually independent of frequency. The polarization is now given by

$$P = \epsilon_{v}(\epsilon_{r} - 1)E. \tag{4}$$

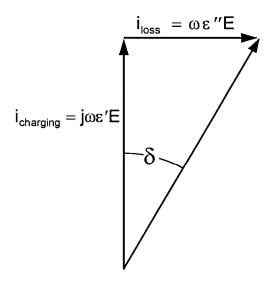
The vacuum clearly has no polarization and  $\epsilon_r^{\text{vacuum}} = 1$ .

As an example, consider a capacitor in a simple charging circuit. The effect of inserting a dielectric material between the plates of the capacitor is to increase the capacitance (the charge the capacitor can hold) by the factor  $\epsilon_r$ . If the applied voltage is held constant, eventually only a small leakage current will flow because of parasitic conduction through the dielectric material. If the applied voltage is sinusoidal in time, there will be a leakage current in phase with the applied voltage as well as a charging current that precedes the applied voltage by a 90° phase angle.

Thus, the total current through the capacitor (Fig. 1) is given by

$$i = j\omega\epsilon' E + \omega\epsilon'' E = \epsilon \frac{dE}{dt}$$
, (5)

where the first term represents the charging current and the second term represents the loss current. The permittivity is now consid-



**FIG. 1.** Charging and loss currents, where  $\tan\delta$  is the loss tangent.

ered to be a complex quantity with both a real and an imaginary component:

$$\epsilon = \epsilon' - j\epsilon'',$$
 (6)

where the imaginary component is connected to the frequency-dependent electrical conductivity as

$$\sigma = \omega \epsilon''$$
. (7)

A useful quantity for characterizing an insulator is the so-called loss tangent (also called the dissipation factor), defined as the ratio of the loss current to the charging current:

$$tan \delta = \frac{i_{loss}}{i_{charging}} = \frac{\epsilon''}{\epsilon'}.$$
(8)

The loss tangent is a material property related to the complex permittivity, which characterizes the electrical losses in an insulator.

**1.1.2 Polarization Mechanisms.** To understand the origin of polarization effects in materials it is best to begin with the smallest structural units involved, either the individual atoms or small groups of atoms. The electric dipole moment of a single atom (or small group) is taken to be proportional to the local electric field as

$$p_i = \alpha_i E_{\text{local}}$$
, (9)

where  $\alpha_i$  is the polarization factor. The polarization factor is a microscopic quantity and is convenient because it can be calculated from theory. However, the  $\alpha_i$ 's are connected to the local electric field, not to macroscopic quantities that may be measured in the laboratory: E, P, and D. In the simplest approximation, the local field is given by

$$E_{\text{local}} = E + P/3\epsilon_{\text{v}}$$
 (10)

Combining Eqs. (4), (9), and (10) leads to the Clausius-Mossotti equation, completing the required relationship between the microscopic polarization factors and the macroscopic relative permittivity:

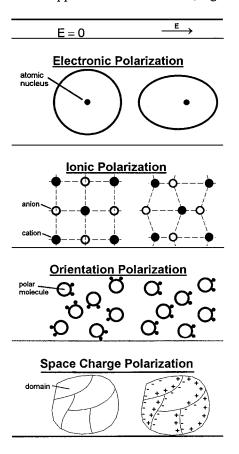
$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_v} \sum_i N_i \alpha_i \,, \tag{11}$$

where  $N_i$  is the number density of dipoles with polarization factor  $\alpha_i$ .

The polarization has its origins in the structure of the insulator and may have a number

of contributing factors. Figure 2 summarizes the most important mechanisms for polarization in a solid. All materials are subject to electronic polarization (also called atomic or optical polarization) because in an applied electric field the atomic nucleus is displaced with respect to the surrounding electrons, inducing a dipole moment. In the absence of an applied field, the charges within an atom will tend to restore the symmetry of the atom and remove the dipole moment. An atom, therefore, may be thought of as a simple harmonic oscillator with a rather high natural frequency, typically in the ultraviolet range due to the small mass of the electrons. Using this description, and including a damping term to represent losses in the oscillator, the electronic polarization can be shown to have the form given in Fig. 3.

Ionic polarization results from the displacement of cations (positive ions) in the direction of the applied field and anions (negative



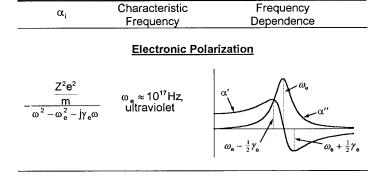
**FIG. 2.** Major polarization mechanisms. The displacement of the charges has been strongly exaggerated.

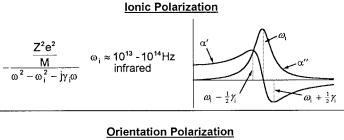
ions) in the opposite direction, as indicated schematically in Fig. 2. These processes also may be thought of as resulting from simple harmonic oscillators, in this case involving the relative motion of cations and anions in the crystal. Ionic polarization, then, has the same functional form as electronic polarization, but since the motion here involves entire atoms, the natural frequencies of the oscillators are much lower and correspond to lattice vibration frequencies, typically in the infrared or visible region.

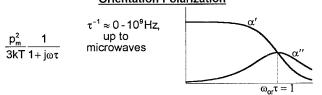
Orientation (or dipole) polarization occurs when a structural repeat unit or a polar domain with a permanent dipole moment  $(p_m)$  experiences a torque, tending to orient the dipole in the direction of the applied field. Thermal motion tends to randomize the orientation of dipoles. In the absence of an applied field a system of oriented dipoles will "relax" toward a random distribution of orientations with a characteristic time  $\tau$ , called the relaxation time. Using this relaxation model, the orientation polarization can be shown to have the form shown in Fig. 3, with characteristic frequencies  $(\tau^{-1})$  ranging into the microwave region.

Space charge (or interfacial) polarization represents the contribution from charge carriers that normally are free to move through the solid, but become impeded by grain boundaries, electrodes, and the like as suggested in Fig. 2. In this case, a space charge eventually builds up, generating a field to counter the applied field until current ceases to flow.

**1.1.3 Typical Permittivity Behavior.** For the electronic, ionic, and orientational mechanisms three distinct frequency regimes may be identified: first, a low-frequency regime, where the applied field varies slowly enough for the polarization to track the applied field closely and the polarization factor is essentially a real constant; second, a high-frequency regime where the applied fields vary so rapidly that the polarization can not track the applied field at all and the polarization factor tends to zero; and finally, an intermediate regime near the characteristic frequency of the oscillators or relaxation mechanism, where both the real and imaginary components of the polarization factor vary relatively rapidly with frequency. It is only in this intermediate-frequency regime that  $\alpha''$  becomes of significant magnitude.







**FIG. 3.** Frequency dependence of the major polarization mechanisms.

Ordinarily the four polarization mechanisms may be considered as acting independently, in which case the total polarization factor is given by a sum of the four contributions:

$$\alpha_i = \alpha_{i,e} + \alpha_{i,i} + \alpha_{i,o} + \alpha_{i,s} , \qquad (12)$$

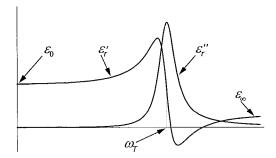
where the second subscript indicates the contributions from the different mechanisms. Often, since the characteristic frequencies are so different for the different mechanisms, only one of the contributions will have a strong frequency dependence in any particular range of frequencies and the other mechanisms can be considered to provide a frequency-independent background.

The relative permittivity of a material can now be calculated using the sum of the individual contributions to the polarization factor and the Clausius-Mossotti relation. The relative permittivity typically has a frequency dependence similar to the frequency dependence of the contributing polarization factors, represented in Fig. 3. The real component of the relative permittivity is larger at low frequencies (usually called the static dielectric constant,  $\epsilon_0$ ) than at high frequencies (usually called the optical dielectric constant,  $\epsilon_\infty$ ) and will vary rapidly only over a relatively narrow range around the characteristic frequency. At frequencies well beyond the ultraviolet, the relative permittivity would drop even further as even electronic polarization processes cannot track the applied field at these frequencies.

At frequencies below the ultraviolet, many materials exhibit a frequency-independent contribution to the polarization from electronic polarization processes and a frequency-dependent contribution to the polarization from ionic polarization processes. The relative permittivity in this case is given by

$$\epsilon_r(\omega) = \epsilon_{\infty} + \frac{\epsilon_{\infty} - \epsilon_0}{\omega^2 / \omega_T^2 - 1},$$
 (13)

where



**FIG. 4.** Real and imaginary components of the relative permittivity typical of an ionic contribution to the polarization.

$$\omega_T^2 = (\omega_i^2 + j\gamma_i\omega) \left(\frac{\epsilon_{\infty} + 2}{\epsilon_0 + 2}\right). \tag{14}$$

The real and imaginary components are shown in Fig. 4, where the change in sign of the real component just above  $\omega_T$  is typical of an ionic contribution to the polarization.

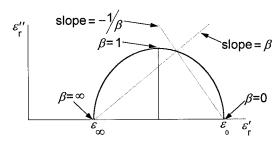
Qualitatively different behavior characterizes the dipole orientation polarization mechanism, where the relative permittivity is given by

$$\epsilon_r(\omega) = \epsilon_{\infty} + (\epsilon_0 - \epsilon_{\infty})/(1 + j\beta)$$
 (15)

with

$$\beta = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)]\omega\tau. \tag{16}$$

Here  $\epsilon'_r(\omega)$  decreases monotonically from  $\epsilon_0$ at low frequencies to  $\epsilon_{\infty}$  at high frequencies, mimicking the frequency dependence of the orientation polarization factor shown in Fig. 3. In this case, a plot of  $\epsilon_r''(\omega)$  as a function of  $\epsilon_r'(\omega)$  has the particularly simple form of a circle, as indicated in Fig. 5. This type of graphical representation, called a Cole-Cole diagram, can be used to determine the relaxation time,  $\tau$ . The procedure involves connecting a point  $(\epsilon'_r(\omega), \epsilon''_r(\omega))$  at any particular frequency with either the high-frequency limit  $(\epsilon_{\infty},0)$  or the low-frequency limit  $(\epsilon_{0},0)$ , as indicated by the straight dotted lines in Fig. 5.  $\beta$  may be estimated from the slope of either line and the relaxation time is then given by Eq. (16). Cole-Cole diagrams are useful in identifying relaxation-type polarization behavior, such as is typical of dipole orientation polarization, since other mechanisms appear more complex and qualitatively distinct when represented in this manner, as suggested in Fig. 6.



**FIG. 5.** Cole-Cole diagram for an ideal relaxation-time mechanism.

1.1.4 Piezoelectricity. Piezoelectric materials exhibit two characteristic effects: polarization in response to applied mechanical stress, and mechanical deformation in response to an applied electric field. Both effects are linear and change sign when the applied stress (mechanical or electrical) changes sign. A crystal with a center of symmetry cannot be piezoelectric, since mechanical stress alone will not disturb the balance among the dipole moments within a unit cell. Crystals with a center of symmetry will mechanically deform in an applied electric field, but the deformation will be proportional to the square of the applied electric field. This effect, also called electrostriction, is independent of the sign of the applied field and is usually quite small in magnitude.

Piezoelectricity is possible in any noncentrosymmetric crystal (which includes all the pyroelectric materials discussed below), as illustrated in Fig. 7. The Curie brothers (1880) discovered piezoelectricity in quartz, tourmaline {Na(Mg,Fe,Mn,Li,Al)<sub>3</sub>Al<sub>6</sub>[Si<sub>6</sub>O<sub>18</sub>]-(BO<sub>3</sub>)<sub>3</sub>(OH,F)<sub>4</sub>}, and Rochelle salt. More recently (see PIEZOELECTRIC DEVICES) there has been great interest in organic materials such as polyvinylidene fluoride (PVDF).

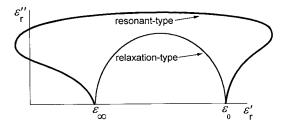
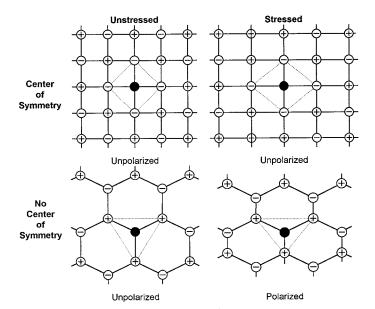


FIG. 6. Cole-Cole diagram illustrating qualitatively distinct behavior for different polarization mechanisms.



**FIG. 7.** Crystals with a center of symmetry are not polarized, even under stress. Piezoelectrics, without a center of symmetry, polarize under stress.

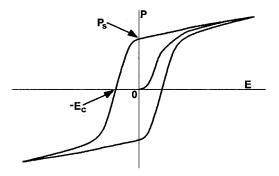
1.1.5 Pyroelectricity. Certain materials are called pyroelectric because they appear to generate a spontaneous polarization when heated (or cooled). In fact, polarization is always present internally in these materials, but is ordinarily masked by neutralizing charges collecting on the exposed surfaces. A net polarization is temporarily observed with temperature changes until the surface charges can reequilibrate with the temperature-dependent internal polarization. The observation of an internal polarization implies severe constraints on the symmetry of the crystal: there can be no mirror planes perpendicular to the axis of polarization and no rotational symmetry except along an axis parallel to the polarization axis.

**1.1.6 Ferroelectricity.** A material that is nonpyroelectric above a certain temperature  $T_{\rm C}$  (the Curie temperature) and pyroelectric below  $T_{\rm C}$  is called a ferroelectric. Just below  $T_{\rm C}$  the spontaneous polarization is usually small and may be readily reversed in direction by an applied field opposing the original polarization, as shown by the characteristic hysteresis loop in Fig. 8. This hysteretic behavior in the polarization and the ability to reverse the polarization by an applied field is sometimes taken as the defining property of a ferroelectric. The term ferroelectric is in analogy to similar behavior observed in the magnetization of ferromagnetic materials.

The origin of ferroelectricity lies in the interaction between the local polarization and the macroscopic electric field. Solving Eqs. (9) and (10) for the total polarization yields

$$P = \frac{\sum_{i} N_{i} \alpha_{i}}{1 - (1/3\epsilon_{0}) \sum_{i} N_{i} \alpha_{i}} E.$$
 (17)

The orientational contribution to the polarization,  $\alpha_{i,o}$ , typically increases as 1/T as the temperature decreases, leading eventually to a zero in the denominator of Eq. (17) at some temperature, implying spontaneous polarization. Here, the local field produced by a dipole has a sufficiently strong effect on neighboring dipoles that all of the dipoles prefer to orient in the same direction, even in the absence of



**FIG. 8.** The ferroelectric hysteresis loop indicating the spontaneous polarization  $(P_s)$  and coercive force  $(-E_c)$  required to reduce  $P_s$  to zero.

an applied field. This critical temperature is the Curie temperature  $T_{\rm C}$ , and the dielectric susceptibility takes the form

$$\chi \equiv \epsilon_r - 1 = C/(T - T_C), \tag{18}$$

where C is a constant, again in close analogy to the magnetic susceptibility of a ferromag-

The dipole moments that can be induced by applied fields or stress above  $T_{\rm C}$  become permanent below  $T_{\rm C}$ . The mechanisms responsible for ferroelectricity vary from material to material and will be discussed in the materials section below. Generally, however, ferroelectricity results from a lowering of the symmetry of the crystal lattice, similar to that suggested in Fig. 7 except that an applied stress is no longer required to maintain the polarized state. Blinc and Žekš (1974) list over 300 known inorganic ferroelectric compounds (not counting solid solutions), and Fousek (1991) estimates that over 50 families of liquidcrystal ferroelectrics are now known. A few representative materials exhibiting a variety of properties are listed in Table 1.

#### 1.1.7 Lattice Dynamics and Soft Modes.

The permanent polarization in the low-temperature form of a ferroelectric represents a modification of the lattice compared to the more symmetric, high-temperature form of the material. The lattice modification can be examined with experiments such as x-ray or neutron diffraction that are sensitive to the atomic positions. Cochran (1959) and Anderson (1959) introduced the concept that ferroelectricity results from an instability of one of the normal lattice vibrational modes. The characteristic frequency of the so-called soft

mode, referring to the unstable lattice vibration, decreases on approach to the Curie temperature,  $T_{\rm C}$ , and the restoring force tending to return the displaced atoms to their normal positions approaches zero. The soft mode then freezes in and the atoms become permanently displaced, resulting in the ferroelectric state.

While a detailed discussion of soft modes is well beyond the scope of this article, it is important to emphasize the close connection between the stability of the lattice with respect to distortion and the occurrence of ferroelectricity. Much of the study of ferroelectrics has been directed toward a detailed understanding of the occurrence, symmetry characteristics, and energetics of soft modes. Blinc and Zěkš (1974) provide a review of theoretical and experimental techniques in the study of soft modes. Articles in this encyclopedia on phonons and lattice vibrations may also be of interest in this regard.

#### 1.1.8 Antiferroelectric and More Complex

While individual dipoles orient in the same direction in a ferroelectric (at least within a single domain), this is by no means the only possible arrangement of dipoles. The first soft-phonon mode to freeze into a static displacement may have a periodicity identical to the original lattice unit cell or a simple multiple of the unit cell, or may even be incommensurate with the original lattice. In an antiferroelectric material, for example, there are two sets of dipole moments, each in a regular arrangement and alternating in direction. In this case there is no net polarization as one set of dipoles precisely cancels the other. PbZrO3, the first known antiferroelec-

Table 1. Typi	cal ferro	electric (F)	) and ant	iferroelectr	ic (A)	materials.
---------------	-----------	--------------	-----------	--------------	--------	------------

<sub>3</sub> ·H <sub>2</sub> SO <sub>4</sub> F	322		
· • ·	322	0.03	293
$\mathbf{F}$	123	0.05	96
4 A	148	_	
Α	627	_	
F	763	> 0.50	300
$_6 \cdot 4D_2O$ F	297 <sup>a</sup> 255 <sup>b</sup>	0.003	278
F	≈370	0.1	300
	A A F F F F F F F F F F F F F F F F F F	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

<sup>&</sup>lt;sup>b</sup>Lower  $T_{\rm C}$ .

tric, was identified by Kittel (1951), who also coined the term.

Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> has been found to be a ferroelectric, but the transition to the ferroelectric state is not associated with any observable dielectric anomaly and the substance is called an "improper" ferroelectric since the spontaneous polarization does not alter the symmetry of the crystal. Other and increasingly subtle types of dipole ordering are now recognized, in both homogeneous and inhomogeneous materials, and have been reviewed by Fousek (1991).

### 1.2 Magnetism

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) may have been used as a compass by the Chinese as early as 2500 B.C., and magnetic materials continue to play an important role today as inductor cores, magnetic recording media, and permanent magnets for use in motors, generators, loudspeakers, and much more. Insulating magnetic materials are preferred to electrically conducting magnetic materials for high-frequency applications because the absence of induced eddy currents, which reduces power losses, makes them especially important for the manufacture of inductors.

The magnetic behavior of materials is no less varied than the electrical behavior described in the preceding sections. A more complete discussion is provided in the articles on magnetism and magnetic devices, but in broad terms the magnetic field H, the magnetic induction B, magnetic permeability  $\mu$ , and magnetic susceptibility  $\chi_m$  parallel the roles of the electric field E, the displacement field D, the permittivity  $\epsilon$ , and the electric susceptibility  $\gamma$  already described. Caution must be exercised in pressing the analogies too far, however, because the physical origin of local magnetic-dipole moments is quite distinct from the origin of local electric-dipole moments, as will be described in the following sections.

1.2.1 Diamagnetism. Insulators composed of ions with all electronic shells filled are typically diamagnetic, and the total diamagnetic susceptibility may be reliably estimated from the contributions of the individual ions. The effect of an applied magnetic field, in this case, has been described as inducing a microscopic current in the orbital

electrons about each atom. According to Lenz's law, the induced currents produce a weak magnetic field tending to cancel the applied magnetic field. A complete description of this behavior requires a quantum-mechanical treatment, but the effect is called diamagnetism. Under certain conditions superconducting materials exhibit "perfect diamagnetism," where the induced currents completely cancel the applied field and prevent the penetration of magnetic field to the interior of the superconductor. Diamagnetism arising from the orbital motion of electrons within an atom is about a million times weaker than perfect diamagnetism and is temperature independent. Although typical of most insulators, this weak diamagnetism is of little technological interest.

1.2.2 Paramagnetism. Paramagnetism refers to an induced magnetic field in the same direction as the applied field, which is to say, a positive magnetic susceptibility. Paramagnetism occurs in insulators composed of ions with partially filled 3d (Ni, Fe, Mn, etc.) or 4f(Sm, Gd, Dy, etc.) shells, representing first-row transition-metal ions and the lanthanides, respectively. The electrons occupying an incompletely filled shell experience electron-electron Coulomb interactions as well as an interaction between the electron spin and the orbital motion. These two interactions tend to keep the electron spins aligned, with the result that the ion has a permanent magnetic-dipole moment. The magnetic response of a solid composed of such ions will depend on temperature following Curie's law, analogous to Eq. (18), where the decrease in the susceptibility at high temperatures reflects the inability of an applied field to overcome the increased thermal agitation of the local moments.

1.2.3 Ferromagnetism. When in close proximity, the magnetic field produced by one localized magnetic moment may directly influence the orientation of the magnetic moment of a neighboring ion. In this case, the localized moments no longer behave entirely independently, and large numbers of moments may spontaneously orient in the same direction. This behavior is called ferromagnetism [Fig. 9(a)], and the temperature at which ferromagnetic order sets in will depend on the strength of the interaction between

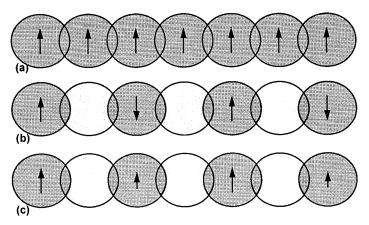


FIG. 9. (a) Direct exchange, local moments directly overlap leading to ferromagnetic order; (b) superexchange, local moments interact via an intermediate nonmagnetic ion leading to antiferromagnetic order; and (c) superexchange leading to ferrimagnetic order.

local moments. Above the ordering temperature, such materials exhibit paramagnetic behavior.

1.2.4 Antiferromagnetism and More Complex Order. In many crystal structures, local magnetic moments are separated by nonmagnetic ions, as illustrated in Fig. 9(b). Since the direct interaction between local moments decreases rapidly with increasing distance, the nonmagnetic ion can mediate a magnetic interaction that is stronger than the direct interaction. This type of interaction is called superexchange and is typically negative in sign, leading to the alternating spin-up, spin-down arrangement known as antiferromagnetism, as suggested in Fig. 9(b). An antiferromagnet exhibits no net magnetization, and the magnetic susceptibility, which peaks in a cusp at the antiferromagnetic ordering temperature, need not reach extremely large values. Complex crystal structures with more than one type of magnetic ion may exhibit a wide variety of magnetic ordering behavior with the magnetic moment varying in magnitude, as suggested by Fig. 9(c), or direction from one crystallographic site to another.

#### 1.3 Thermal Properties

The heat capacity of insulators is remarkably well behaved, and even relatively simple models based on the statistical mechanics of phonons provides a quite accurate description. At high temperatures, each possible vibrational mode of an insulator is equally excited and the heat capacity approaches the temperature-independent Dulong-Petit value of 3k for each atom in the crystal. At low

temperatures, the lattice vibrations decrease rapidly and the heat capacity varies as  $T^3$  with relatively minor and well-understood deviations, except for materials with special considerations such as phase transitions.

Metals are typically good thermal conductors because of the ability of free electrons to conduct heat as well as electricity. The thermal conductivity of insulators is somewhat more complex, as discussed in more detail in THERMAL CONDUCTION IN SOLIDS, and can be either large or small depending on the material. Essentially, the heat carried by phonons in an insulator can be estimated from a knowledge of how fast and how far a phonon moves between scattering events. The thermal conductivity may be expressed as

$$\lambda = \frac{1}{3}Cyl, \qquad (19)$$

where C is the heat capacity per unit volume,  $v_s$  is the speed of sound, and l is the phonon mean free path. The speed of sound typically reflects the bond strength, and high-meltingpoint materials tend to have a high sound velocity and, therefore, high thermal conductivity. If there is only one atom per unit cell, all the phonon modes are acoustic modes with relatively high propagation velocities. As the crystal structure becomes more complex, the unit cell grows, and more phonon modes become optical in character with very low propagation velocity. Thus, the more complex the crystal structure, the lower the thermal conductivity is expected to be. Amorphous materials, such as fused silica, may be considered the limiting case in regard to structural complexity, and indeed these materials have among the lowest thermal conductivity values known.

In materials relatively free of defects, phonons may propagate a long distance before scattering, and in this case the long mean free path leads to a high thermal conductivity. Classic examples are diamond and aluminum nitride, which have thermal conductivity values greater than metals. Even if no other defects are present, the phonons themselves may be thought of as deviations from the ideal crystal structure and phonon-phonon scattering is often the limiting factor. At high temperatures, phonon-phonon scattering leads to a 1/T temperature dependence. At low temperatures, as phonon-phonon scattering decreases, the phonon mean free path becomes larger until the walls of the specimen prevent further propagation. Eventually, the thermal conductivity decreases as  $T^3$  with decreasing temperature, reflecting the temperature dependence of the heat capacity discussed above.

#### 2. INSULATING MATERIALS

Electrically insulating materials are far too common to enumerate in any complete way, but some appreciation of the trends and patterns may be achieved by a brief survey. Some of the more important materials will be discussed, as well as the connection between the structure of the materials and their properties.

#### 2.1 Elemental Insulators

The rare gases, hydrogen, nitrogen, oxygen, and fluorine and chlorine are insulating gases under standard conditions and remain insulators even when they condense to liquids and finally solids at sufficiently low temperatures. Bromine is an insulating liquid and iodine and astatine are insulating solids under standard conditions. The common, stable form of selenium has infinite helical chains and is, like tellurium, semiconducting, but Se<sub>8</sub> polymorphs are red insulators similar to solid S<sub>8</sub>, which is a very poor electrical conductor. Arsenic is a semimetal, and the electrical conductivity of phosphorus varies greatly among the four known allotropes, but the volatility and reactivity of these elements severely limit their use as solid insulators. Boron, the only refractory nonmetallic element other than carbon, occurs in two distinct crystal structures (the  $\alpha$  and  $\beta$  forms), both of

which are semiconductors with band gaps around 1.5 to 2.0 eV.

Carbon, in the diamond crystal structure shown in Fig. 10, is expected to become increasingly important since the development of diamondlike thin films. The diamond crystal structure may be described as two identical, interpenetrating face-centered-cubic (fcc) lattices. The second fcc lattice is displaced from the first by a translation along a diagonal of the cube by a distance of  $\frac{1}{4}$  of the length of the diagonal. With its tightly bound electrons and strong covalent bonds, diamond is uniquely suited for many applications. The electrical properties of diamond are dominated by the very large band gap of 5.4 eV, which leads to electrical conductivity values as low as  $10^{-13}$  S m<sup>-1</sup>, although doping can increase this value to  $10^0$  S m<sup>-1</sup> or more. The strong bonds and small mass of carbon lead to sound velocity and thermal conductivity values among the highest known. For more information the reader is referred to DIAMOND AND DIAMONDLIKE CARBON.

Other forms of carbon are not electrical insulators. Graphite, for example, consists of two-dimensional sheets of hexagonally bonded carbon with only weak bonding between the sheets. Graphite is typically a fairly good electrical conductor, with conductivity values on the order of  $10^5$  S m<sup>-1</sup>. Thus, by changing the crystal structure from the diamond arrangement to the graphite arrangement the

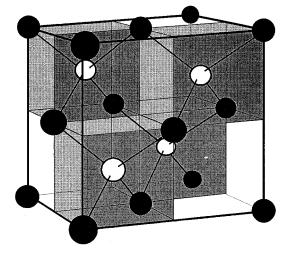


FIG. 10. The sphalerite (or zinc-blende) crystal structure. Also, the diamond crystal structure when the solid and open circles represent the same atom.

Table 2. Selected covalent insulators.

Structure type	Compound
Diamond	С
Sphalerite	BAs, BP, BeTe, ZnSe, BeSe, ZnS, CuBr, BN, BeS, ZnO, MgO
Wurtzite	BP, AgI, SiC, ZnS, BN, GaN, AlN, ZnO, BeO
Hexagonal	$\alpha$ -Si $_3$ N $_4$ , $\beta$ -Si $_3$ N $_4$ , SiO $_2$

conductivity can increase by 18 orders of magnitude, which emphasizes the role of structure in determining the electrical properties

All of the remaining elements are semiconductors, semimetals, or true metals. Thus, among the elements, solid electrical insulators are relatively rare.

#### 2.2 Binary Compound Insulators

2.2.1 Covalent Insulators. Many covalently bonded compounds are semiconductors, but some important insulators found in this group are listed in Table 2. The first group includes those compounds that share the same basic structure as diamond, except that the two interpenetrating sublattices shown in Fig. 10 are occupied by different atoms. This is the sphalerite (or zinc-blende) structure type, and Table 2 lists a number of common insulators with this structure. The sphalerite structure is symmetric about each atom in the unit cell and therefore is neither pyroelectric nor piezoelectric.

Other covalent insulators form in the wurtzite structure, which can be considered as two interpenetrating close-packed hexagonal lattices. As in the sphalerite structures, each atom is tetrahedrally coordinated with four atoms of the opposite type. BN can be found in the zinc-blende or wurtzite forms, as well as in a graphitelike hexagonal structure, all of which are good insulators. SiC forms in a large number of closely related structures composed of sphalerite and wurtzite layers, and although it has interesting semiconducting properties, all SiC polytypes may be considered insulators if sufficiently pure. The ease with which the covalent bond is polarized generally increases with atomic number, which can lead to somewhat larger static dielectric constants than expected for a nonpolarizable bond, but qualitatively the permittivity behaves very much as expected on the basis of the ionic polarization mechanism described in Figs. 2, 3, and 4.

2.2.2 Ionic Insulators. The ionic crystal structures for sodium chloride (NaCl) and cesium chloride (CsCl) are shown in Fig. 11. Under ordinary conditions, all of the alkali halides form in the NaCl-type structure, except CsCl, CsBr, and CsI, which form in the CsCl-type structure. Both are high-symmetry structures, exhibit no piezoelectric or pyroelectric effects, and have dielectric behavior in good accord with the ionic polarization mechanism described above. In Table 3 note the distinctly greater polarizability of the CsCltype compounds compared to the trends among the NaCl-type as indicated by the relatively larger static dielectric constants  $\epsilon_0$  of the former compounds. This indicates that even closely related crystal structures with similar bonding can exhibit distinct proper-

2.2.3 Binary Oxides and Other Binary Although both insulators and Insulators. conductors can be found in almost any family of materials, many binary chalcogenides (especially oxides and sulfides) and pnictides

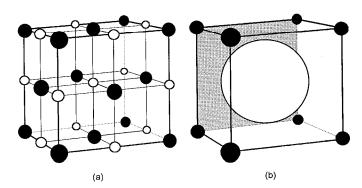


FIG. 11. (a) Sodium chloride and (b) CsCl crystal structure types.

(including nitrides and phosphides) and practically all halides are typically good electrical insulators. These compounds are neither purely covalent nor purely ionic, and while many are insulators, they tend to have relatively high symmetry crystal structures and fairly ordinary dielectric properties.

Most of the binary oxides are insulators, and materials such as alumina ( $Al_2O_3$ ), magnesia (MgO), and beryllia (BeO) see widespread use for their dielectric properties. 3d transition-metal oxides such as  $Fe_3O_4$  and  $CrO_2$  are typically magnetic and exhibit the characteristic phenomena of saturation and hysteresis so important for magnetic recording applications. Many other 3d oxides such as MnO, FeO, and CrO are antiferromagnets, and in most cases the superexchange mechanism is responsible for the magnetic order.

Practically all the binary carbides and most of the borides not listed above, however, have at most relatively small band-gap energies and are semiconductors, and many, in fact, are metallic compounds. Only a handful of binary compounds (such as FeS, Bi<sub>2</sub>S<sub>3</sub>, WO<sub>3</sub> and

**Table 3.** Alkali halide ionic insulators in the NaCl structure type, except where indicated (after Knox and Teegarden, 1968).

			$\hbar\omega_T/k$
Compound	$\epsilon_0$	$\epsilon_{\scriptscriptstyle \infty}$	(K)
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
CsCla	7.2	2.42	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 <sup>a</sup>	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	118
$CsI^a$	6.59	2.62	95
<sup>a</sup> CsCl struct			

possibly a few others) are ferroelectrics. Indeed, the scarcity of ferroelectric behavior among binary compounds left the impression for many years that ferroelectricity was rather rare, an impression later dispelled by studies of more complex materials. Finally, SiO<sub>2</sub> in its various forms deserves special attention and is discussed in dedicated articles on GLASSES and OUARTZ.

## 2.3 Multinary Compound Insulators

As increasingly complex materials have come under investigation, new types of behavior have been observed and characterized. Often, these new behaviors have no precedent among the binary compounds or among the elements. As far as ordinary dielectric properties are concerned, polystyrene, polyethylene, Mylar, Teflon, and similar materials are not qualitatively superior to or even especially distinct from the classic binary compounds discussed above. Still, modern plastics and polymers are often vastly preferred in dielectric applications for cost, packaging, or other practical considerations.

Many of the more complex materials exhibit effects completely unobserved in the binary compounds. Table 4, for example, provides an overview of the ferroelectric materials now known to exist. Typically, as each class of materials has been developed, new theoretical concepts have been required as well

**2.3.1 Rochelle Salts and Other Order/ Disorder Systems.** The earliest known ferroelectrics were the Rochelle salts (also called Seignette salts), such as NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 4H<sub>2</sub>O (Valasek, 1920, 1921). The orientation polarization mechanism is vividly demonstrated in these materials in that the hydrogen bonding is sufficiently weak to allow a type of hindered rotation of the water molecules. The orientation of one water molecule influences the preferred orientation of others nearby, and as the temperature is lowered through the Curie temperature, the water molecules tend to order with respect to each other, establishing a net polarization.

An interesting feature of the Rochelle salts is the presence of two critical temperatures, as indicated in Table 1. Above the upper transition temperature and below the lower temperature, two different sublattices of water mol-

Table 4. Overview of ferroelectric materials (modified from Fousek, 1991).

## I. Inorganic compounds

Perovskites, BaTiO<sub>3</sub> LiNbO<sub>3</sub> type, LiTaO<sub>3</sub> Manganites, YMnO<sub>3</sub> Tungsten bronze type, PbNb<sub>2</sub>O<sub>6</sub> Pyrochlore type, Cd<sub>2</sub>Nb Layer structure oxides, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> Molybdates, Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>32</sub>O<sub>7</sub> Vanadates, Ca<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> Other double oxides, SbNbO<sub>4</sub> Nonhydrated

K<sub>2</sub>SO<sub>4</sub> type, K<sub>2</sub>SeO<sub>4</sub>
Langbeinites, (NH<sub>4</sub>)<sub>2</sub>Cd<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>
Sulfates, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>
Selenites, LiH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>
Nitrites, NaNO<sub>2</sub>
Nitrates, KNO<sub>3</sub>
Thiophosphates, Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>
Potassium dihydrogen
phosphate (KDP) type, KH<sub>2</sub>PO<sub>4</sub>

Barium fluoride type,BaMnF<sub>4</sub> Halides, HCl Antimony sulfide iodine, SbSBr Oxyfluorides,Rb<sub>3</sub>MoO<sub>3</sub>F<sub>3</sub> Boracites, Mg<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Cl Iodates, NH<sub>4</sub>IO<sub>3</sub> Oxyiodates, Sb<sub>5</sub>O<sub>7</sub>I

Colemanite, Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub> · 5H<sub>2</sub>O Sulfates, NaNH<sub>4</sub>SO<sub>4</sub> · 2H<sub>2</sub>O  $\begin{array}{c} \textit{Hydrated} \\ \text{Potassium cyanides,} \\ K_4 Mn (CN)_6 \cdot 3H_2O \\ \text{Uranospinite,} \\ H_2 (VO_2)_2 (AsO_4)_2 \cdot 8H_2O \end{array}$ 

Alums, NH<sub>4</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 12H<sub>2</sub>O

#### II. Organic-inorganic compounds

#### Nonhydrated

Triglycine sulfate (TGS), (CH $_2$ NH $_2$ COOH) $_3 \cdot$ H $_2$ SO $_4$ Betaines, (CH $_3$ ) $_3$ NCH $_2$ COO  $\cdot$ H $_3$ AsO $_4$ Chloracetates, (CH $_2$ ClCOO) $_2$ HNH $_4$ Alkyl ammonium halogenantimonates, (CH $_3$ NH $_3$ ) $_3$ Sb $_2$ Br $_9$ 

Sarcosine salt,  $(CH_3NHCH_2COOH)_3CaCl_2$ Tetramethyl ammonium salt,  $N(CH_3)_4 \cdot HgCl_3$ Propionate,  $(CH_3CH_2COO)_6Ca_2Sr$ 

#### Hydrated

Rochelle salts (tartrates), NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>4H<sub>2</sub>O Triglycine sulfate (TGS),(CH<sub>2</sub>NH<sub>2</sub>COOH)<sub>2</sub>  $\cdot$  MnCl<sub>2</sub>  $\cdot$  2H<sub>2</sub>O Betaines, (CH<sub>3</sub>)<sub>3</sub>NCH<sub>2</sub>COO  $\cdot$  CaCl<sub>2</sub>  $\cdot$  2H<sub>2</sub>O

Formates, Cu(HCOO) $_2 \cdot 4H_2O$ Alums, CH $_3$ NH $_3$ Al(SO $_4$ ) $_2 \cdot 12H_2O$ Guanidinium salts, C(NH $_2$ ) $_3$ Al(SO $_4$ ) $_2 \cdot 6H_2O$ 

# III. Organics

Thioruea,  $SC(NH_2)_2$  Tanane,  $C_9H_{18}NO$  Benzil,  $C_{14}H_{10}O_2$  Phenanthrene,  $C_{14}H_{10}$  PVDF type,  $(CH_2CF_2)_n$  and copolymers with  $CHF=CF_2$ ,  $CF_2=CF_2$  Liquid crystals,  $\approx 50$  distinct homologues known Langmuir-Blodgett films:  $\omega$ -tricosenoic acid  $(CH_2=CHC_{21}H_{42}COOH)$ +docosylamine  $(C_{22}H_{45}NH_2)$ 

ecules are equally polarized, but in opposite directions resulting in no net polarization. Between the two transition temperatures the two sublattices are still polarized in opposite directions, but the polarizations do not exactly cancel. Fairly detailed models, which may be described as a competition between two distinct relaxation times rather than the single relaxation time assumed in Fig. 3, have been developed to describe the Rochelle salts and their heavy-water analogs (Blinc and Žekš, 1974).

Materials systems with related order-disorder transitions generally involve hydrogen bonding. Examples include the heavily studied potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub> or KDP) type system, sulfates, selenites, ni-

trites, triglycine sulfate (TGS), formates, colemanite, alums, and more. These systems have been rather extensively studied and are reasonably well described by relaxation-time, order/disorder models.

### 2.3.2 Perovskites and Displacive Transi-

tions. Figure 12 shows the typical perovskite crystal structure in the high-temperature, cubic phase. The oxygen atoms in the centers of the cube faces have two titanium nearest neighbors (atoms) along an axis perpendicular to the cube face, but there are no titanium atoms in the cube faces at all. Although the overall lattice is cubic, the oxygen atoms do not experience full cubic symmetry

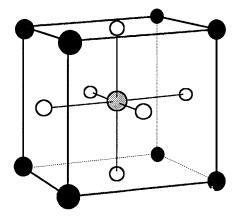


FIG. 12. The perovskite crystal structure for BaTiO<sub>3</sub>. Ba atoms are at the cube corners, a Ti atom is at the cube center, and O atoms are at the centers of the cube faces. Note that each oxygen atom has only two titanium nearest neighbors, which is the origin of the ferroelectric behavior instability.

and can displace within the plane much more easily than in a direction perpendicular to the plane.

It is this asymmetric movement of the oxygen atoms that leads to an instability in the lattice, a rather clear example of a soft-mode instability. And indeed, upon cooling the unit cell distorts to a tetragonal structure and a net polarization develops along the direction of a

cube edge, as shown in Fig. 13. On further cooling, the unit cell distorts again, this time along a diagonal in the face of the cube, and finally at still lower temperatures a rhombohedral distortion sets in, with a net polarization along a full cube diagonal.

The perovskites are called displacive ferroelectrics, since the mechanism involves a permanent displacement of atoms. Above the Curie temperature the resonant frequency (from Fig. 3) goes to zero as

$$\omega_i^2 \propto T - T_{\rm C}$$
, (20)

a typical soft-mode signature.

**2.3.3** Bronzes, Pyrochlores, and Nonmagnetic Oxides. The metal oxides (niobates, manganites, tungsten bronzes, pyrochlores, molybdates, vanadates, and some others) listed in Table 4 undergo displacive transitions upon cooling and exhibit resonant behavior in the dielectric properties characteristic of an ionic soft mode, as with the perovskites. The theory of these ferroelectric materials can be said to be reasonably mature. Important for some time as commercial ceramics (see Table 5), many of these oxides continue to be the subject of research in the form of thin films, composites, and layered structures (see Material Properties of Ceramics).

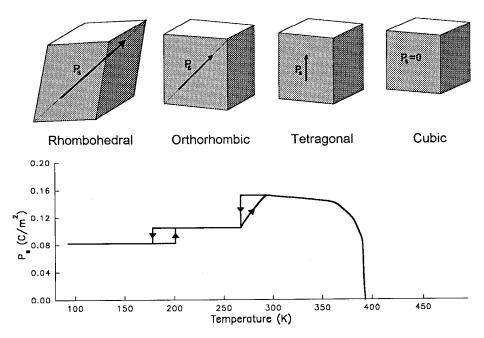


FIG. 13. Projection of the spontaneous polarization of BaTiO<sub>3</sub> onto one edge of the unit cell (modified from Merz, 1949).

2.3.4 Ferrites: Spinels and Garnets. The term ferrite is typically used to refer to ferrimagnetic oxides. These materials are hard, brittle, and poor electrical conductors widely used in inductors, particularly at high frequencies. An important family of ferrites are the spinels with the chemical formula MFe<sub>2</sub>O<sub>4</sub>, where the iron is trivalent and M denotes one of the divalent ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , or  $Cd^{2+}$ . Spinels have a cubic crystal structure containing 8 chemical formula units with 32 oxygen sites per unit cell. The metal ions occupy one of two types of sites within the unit cell, designated A and B, and are coordinated by either four or six nearest-neighbor oxygen ions, respectively. Thus, there are two types of magnetic moments, corresponding to the Fe<sup>3+</sup> ions or the divalent metal ions, and ferrimagnetic behavior due to the superexchange mechanism dominates the magnetic properties. There are two structural variants, called normal and inverse spinels, depending on whether the divalent ions occupy A sites or B sites, respectively, and real materials are typically mixtures of both structural variants.

The garnets, with chemical formula  $3M_2O_3 \cdot 2Fe_2O_3 \cdot 3Fe_2O_3$ , have 160 atoms per unit cell and three distinct types of crystallographic sites occupied by magnetic ions. In these materials M represents one of the trivalent rare-earth elements; perhaps the best

**Table 5.** Oxides often used in insulating ceramics (modified from von Hippel, 1954).

Kaolinite	Al <sub>2</sub> (OH) <sub>4</sub> Si <sub>2</sub> O <sub>5</sub>
Quartz	$SiO_2$
Feldspar	$K_xNa_{1-x}[Al \cdot Si_3]O_8$
Mullite	$Al_6Si_2O_{13}$
Cordierite	$Mg_2Al_2Si_5O_{15}$
Alumina (corundum)	$Al_2O_3$
Steatite (talc)	$Mg_3 \cdot (OH)_2 \cdot Si_4O_{10}$
Clinoenstatite	$MgSiO_3$
Forsterite	$Mg_2SiO_4$
Zircon	ZrSiO <sub>4</sub>
Spodumene	$\text{Li}_2\text{Al}_2\text{Si}_4\text{O}_{12}$
Wollastonite	CaSiO <sub>3</sub>
Rutile	$TiO_2$
Barium titanate	BaTiO <sub>3</sub>
Sodium tantalate	NaTaO <sub>3</sub>
Sodium niobate	NaNbO <sub>3</sub>
Cadmium niobate	$Cd_2Nb_2O_7$
Magnetite	$Fe_3O_4$
Spinel	$MgAl_2O_4$
Ferrite spinel	$Ni_xZn_{1-x}Al_2O_4$

known example is yttrium iron garnet, abbreviated YIG, which is notable for particularly low magnetic losses at high frequencies.

**2.3.5 Organics.** Plastics, polymers, and organic materials of many types have become increasingly important for a variety of applications, from packaging to textiles (see POLYMERS, MATERIAL PROPERTIES OF ). Organic chemistry techniques applied to ferroelectric materials have led to the development of novel structures with unique properties. A few examples follow.

Polyvinylidene fluoride (PVDF) is an organic polymer that can be prepared from solvents in the form of thin films. As prepared, PVDF crystallizes in a nonpolar  $\alpha$  phase, which upon stretching transforms to a ferroelectric  $\beta$  phase. Mixtures of PVDF and trifluoroethylene (and other copolymers) will crystallize directly in the ferroelectric phase without further mechanical treatment, and the Curie temperature can be adjusted in the range of 330 K to 400 K. PVDF and related materials may be inexpensively prepared in thin layers ( $<10 \mu m$ ) and have therefore received considerable attention for various piezoelectric and pyroelectric applications, particularly those requiring rapid response times (Gerhard-Multhaupt et al., 1987).

Liquid crystals represent a second family of organic insulators with particularly interesting ferroelectric properties. Liquid-crystal ferroelectrics typically consist of relatively long, rodlike molecules which "crystallize" in regular layers, as suggested in Fig. 14. These layered phases, called smectic phases, come in a variety of types enumerated alphabetically, as in SmA for the smectic A-type arrangement and so on. The arrangement depicted in Fig. 14 is the SmC arrangement, indicating that the long axes of the molecules are not quite in the direction normal to the planes, but are tilted somewhat. Within the layers, however, the molecules have no long-range order and behave essentially as a liquid, but the molecules remain essentially parallel and from plane to plane behave much like a crystal.

If the molecules in a smectic-C type phase are also chiral, meaning that the molecule has distinct right-handed and left-handed versions, then the liquid crystal will exhibit ferroelectric properties. Liquid-crystal ferroelectrics have become increasingly important for their potential in low-cost flat-panel displays,

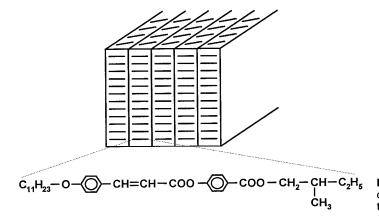


FIG. 14. Typical ferroelectric liquid crystal molecule, shown in the smectic-C arrangement.

and most of the new ferroelectric materials identified recently are liquid crystals (Fousek, 1991). For a more detailed discussion of liquid crystals, see LIQUID CRYSTALS, STRUCTURE

Finally, the Langmuir-Blodgett technique is another powerful method for preparing organic thin-film structures with well-defined symmetry (Roberts, 1985). Typically, molecules with a hydrophilic head and a hydrophobic tail are dissolved in an organic solvent and spread on a water surface, and the solvent is evaporated. Monomolecular layers of the film-forming material can then be collected on a solid substrate by repeated passes through the water surface. A pyroelectric material can be produced by depositing alternating layers of fatty acids and amines, as shown in Fig. 15.

## 3. SUMMARY

The list of insulating materials has not been exhausted here. Rubbers, elastomers, plastics, polyvinyl chloride (PVC), gases, liquids, most minerals, glasses, and more have been nearly excluded. But the basic polarization mechanisms described (electronic, ionic, orientational, and space charges) provide a sound foundation for understanding the major insulating properties of a wide variety of materials. The principles of crystal structure and symmetry in allowing or forbidding various kinds of electric dipole ordering will also play a key role, regardless of the material or application in question.

The theoretical understanding of the classical insulating materials is quite mature and provides a firm foundation for further developments. The advent of liquid-crystal ferroelectrics and the ability to design and manufacture new structures nearly at will is sure to have an impact on future sensor, imaging, memory, and video technologies.

#### GLOSSARY

Critical Temperature: Typically a cusp or other sharp feature in the temperature dependence of an observable property, representing an abrupt change in the order among physical objects such as ions, electric dipoles, or magnetic dipoles.

Dielectric: A material that internally redistributes charges in response to an applied electric field.

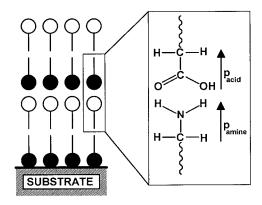


FIG. 15. Langmuir-Blodgett film of alternate acid/ amine layers to produce a pyroelectric (redrawn from Roberts, 1985).

**Phonon:** A single lattice vibration mode representing physical displacement of atoms or ions about their equilibrium positions.

**Polarization:** The electric-dipole moment induced in a dielectric by an applied electric field.

**Soft Mode:** An unstable lattice vibration requiring little or no energy to displace atoms or ions from their equilibrium positions.

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