Part II Electrical Properties of Materials

Chap. 7 Electrical Conduction in Metals and Alloys

Chap. 8 Semiconductors

Chap. 9 Electrical Properties of Polymers, Ceramics, Dielectrics, and Amorphous Materials

9.1 Conducting Polymers and Organic Metals

Polymers consist of (macro)molecules which are long and chainlike. Several atoms combine and form a specific building block, called a **monomer**, and thousands of monomer combine to a polymer. (see Fig. 9.1)

(a) (b)

Figure 9.1. (a) Polyethylene. (b) Polyvinylchloride. (The dashed enclosures mark the repeat unit. Polyethylene is frequently depicted as two CH_2 repeat units for historical reasons.

The binding force between individual atoms within a chain: usually covalent and sometimes ionic in nature

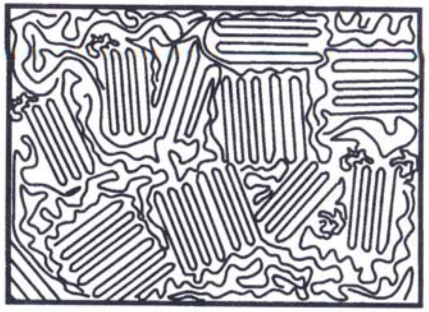


Figure 9.2. Simplified representation of a semicrystalline polymer (folded-chain model).

The binding force between macromolecules: a weak Van der Walls type

Degree of order or degree of periodicity of the atoms in polymers: dependent on the length of the molecules and on the regularity of molecular structure. Certain heat treatment affects some structural parameters; e.g. slow cooling yield, for certain polymer, a crystalline structure (Fig. 9.2)

9.1 Conducting Polymers and Organic Metals

A high degree of crystallinity and a relatively high conductivity have been found in polyacetylene, a simplest conjugated organic polymer; the prototype of a conducting polymer

A conjugated polymer has alternating single and double bonds between the carbons (see Fig. 9.3)

Two principle isomers: *trans, cis*

trans : the hydrogen atoms are alternately bound to opposite sides of the carbon

cis : the hydrogen atoms are situated on the same side of the double-bond carbons

Trans-polyacetylene is obtained as silvery flexible film that has a conductivity comparable to that of silicon (Fig. 9.4)

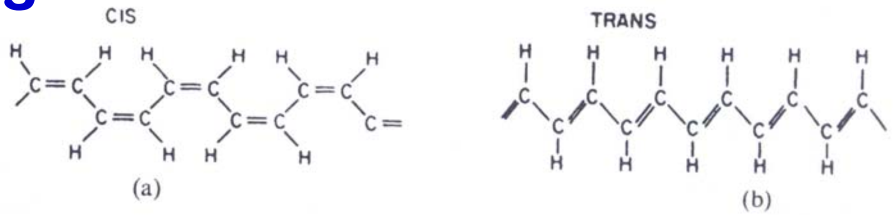


Figure 9.3. Theoretical isomers of polyacetylene (a) *cis*-transoidal isomer, (b) *trans*-transoidal isomer. Polyacetylene is synthesized as *cis*-$(CH)_x$ and is then isomerized into the *trans*-configuration by heating it at 150°C for a few minutes.

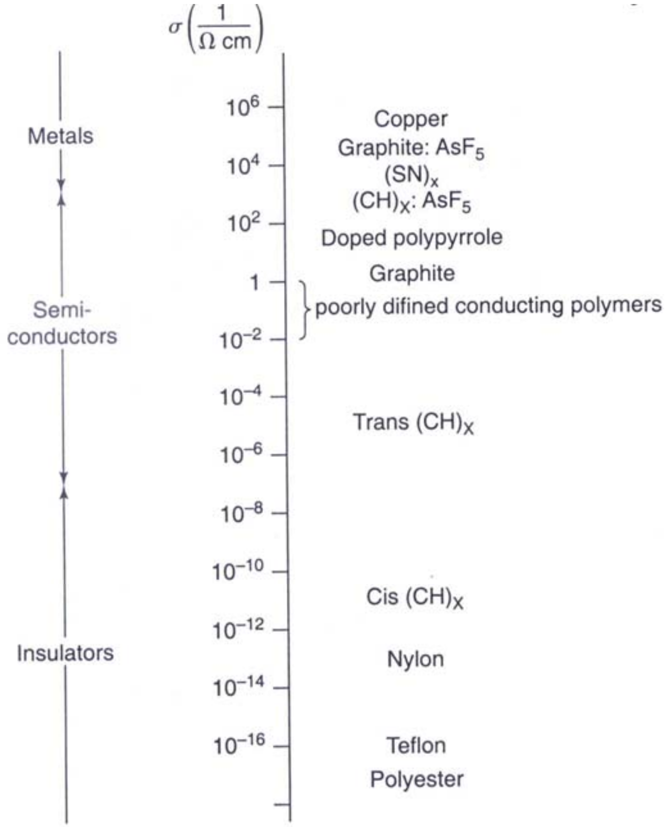


Figure 9.4. Conductivities of polymers in $\Omega^{-1}\ \mathrm{cm}^{-1}$. (Compare with Fig. 7.1.)

9.1 Conducting Polymers and Organic Metals

Calculated band structure for *trans*-(CH)x

assuming different distances between the carbon atoms

- Fig 9.5(a) all carbon length are equal, the resulting band in the highest is partially filled : metal behavior ; the electrons in the double bond of a conjugated polymer (called π-electron) are loosely bound to the neighboring carbon atoms, thus one of these electron is easily dissociated from carbon atom by a small energy → contribute to electrical conduction

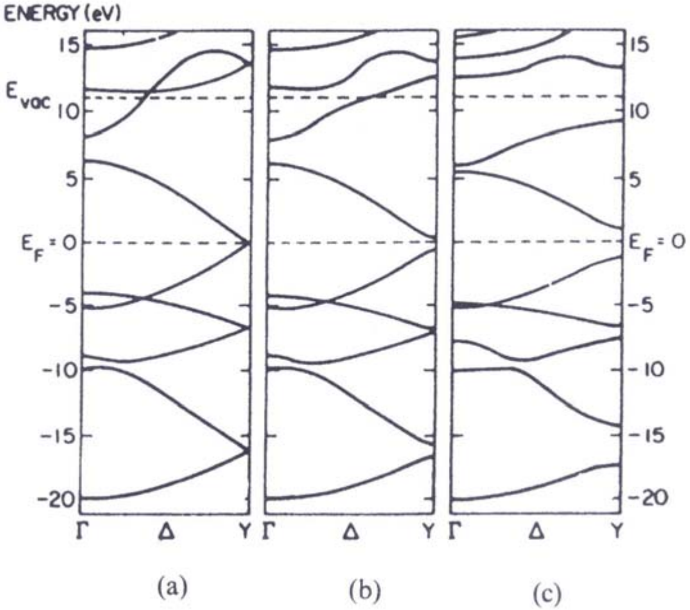


Figure 9.5. Calculated band structure of *trans*-$(CH)_x$ for different carbon–carbon bond lengths: (a) uniform (1.39 Å); (b) weakly alternating (C═C, 1.36 Å; C—C, 1.43 Å); and (c) strongly alternating (C═C, 1.34 Å; C—C, 1.54 Å). Note the band gaps at *Y* as bond alternation occurs. Reprinted with permission from P.M. Grant and I.P. Batra, *Solid State Comm.* **29**, 225 (1979).

- Fig 9.5(b),(c) : Real case; the distance between the carbon atoms alternate because of single and double bonds. The width of band gap near the Fermi level depends mainly on the extent of alternating bond lengths : semiconductor or insulator. In order to improve the conductivity of $(CH)_x$: decrease the disparity in the carbon-carbon bond lengths, thus approaching uniform bond length.

9.1 Conducting Polymers and Organic Metals

Conductivity increase by doping in polymer-based semiconductor : Fig 9.4 and Fig 9.6

- The dopant molecules diffuse between the $(CH)_x$ chains and provide a charge transfer between the polymer and the dopant

- Doping level in polymer “20 ~ 40 %”

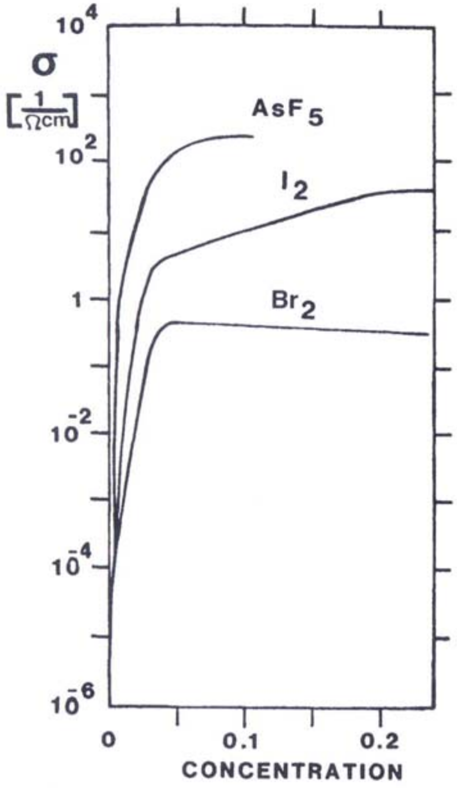


Figure 9.6. Conductivity change of polyacetylene as a result of doping.

Conduction mechanism in polyacetylene :

“**soliton**” is a structural distortion in a conjugated polymer and is generated when a single bond meets another single bond as shown in Fig 9.7.

At the distortion point a localized nonbonding electron state is generated in the center of forbidden band.

Near the center of a soliton, the bond lengths are equal : uniform bond length constitute a metal.

When many solitons have been formed and their sphere of influence overlap, a metal-like conductor would result.

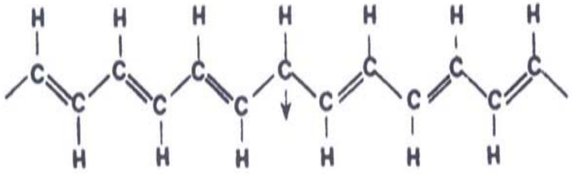


Figure 9.7. A broken symmetry in polyacetylene creates a *soliton*. (An *antisoliton* is the mirror image of a soliton.)

9.1 Conducting Polymers and Organic Metals

Other conductive polymers: polyanilines, polypyrroles, polythiophenes, polyphenylenes, polypphenylene vinylene, and their derivatives

Charge-transfer complexes : the conduction is increased by producing a mixture of easily ionized electron donors and electron acceptors, The charge is shared between the donors and acceptors: graphite, AsF_5-doped graphite (higher conductivity)

Charge-transfer salts :a donor molecule, such as tetrathiafulvalene (TTF), transfer electrons to an acceptor molecule, like tetracyanoquinodimethane (TCNQ) : the planar molecules stack on top of each other in sheets, thus allowing an overlap of wave functions and a formation of conduction bands that are partially filled with electron due to the charge transfer ; doped complexes of C60 (so called Buckyball) which exhibits superconductivity at low temperature.

9.2 Ionic Conduction

The ionic conduction is caused by the movement of some charged ions which hop from lattice site to lattice site under the influence of electric field.

This ionic conductivity,

$$\sigma_{\text{ion}} = N_{\text{ion}} e \mu_{\text{ion}}$$

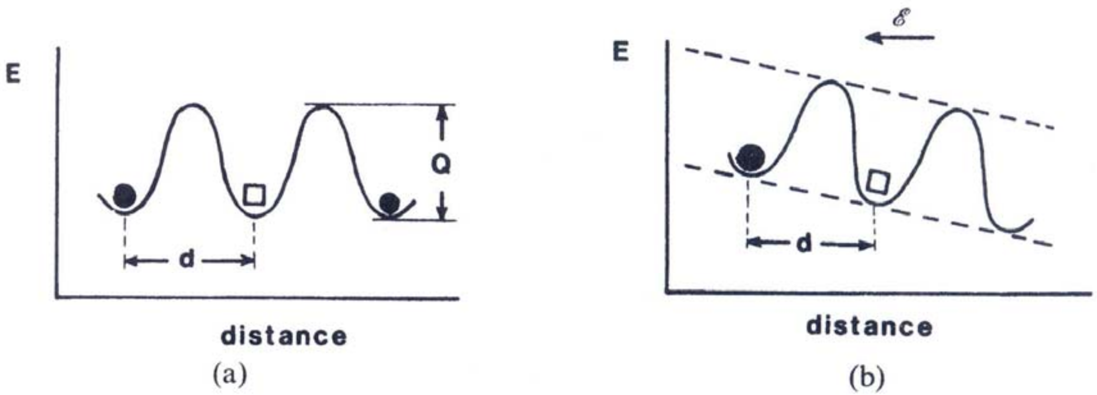


Figure 9.8. Schematic representation of a potential barrier, which an ion (●) has to overcome to exchange its site with a vacancy (□). (a) Without an external electric field; (b) with an external electric field. d = distance between two adjacent, equivalent lattice sites; Q = activation energy.

N_{ion} : number of ions per unit volume that can change their position under the influence of an electric filed

μ_{ion} : the mobility of ions

The conditions for ions to move in a crystalline solid

1. They must have sufficient energy to pass over an *energy barrier.* (Fig. 9.8)

2. The lattice site next to a conducting ion must be empty. → N_{ion} depends on the vacancy concentration in the crystal (i.e., on the number of *Schotty defects*)

9.2 Ionic Conduction

Diffusion theory links the mobility of ions with the diffusion coefficient, *D* through Einstein relation

$$\mu_{\text{ion}} = \frac{De}{k_B T} \quad , \qquad D = D_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right]$$

Arrhenius equation

***Q* is the activation energy, *D_0* is a pre-exponential factor that depends on the vibrational frequency of atoms and some structural parameter.**

Combining with $\sigma_{\text{ion}} = N_{\text{ion}} e \mu_{\text{ion}}$ **yields**

$$\sigma_{\text{ion}} = \frac{N_{\text{ion}} e^2 D_0}{k_B T} \exp\left[-\left(\frac{Q}{k_B T}\right)\right] \qquad \sigma_{\text{ion}} = \sigma_0 \exp\left[-\left(\frac{Q}{k_B T}\right)\right]$$

$$\ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B}\right)\frac{1}{T}$$

9.2 Ionic Conduction

$$\ln \sigma_{\text{ion}} = \ln \sigma_0 - \left(\frac{Q}{k_B}\right)\frac{1}{T}$$

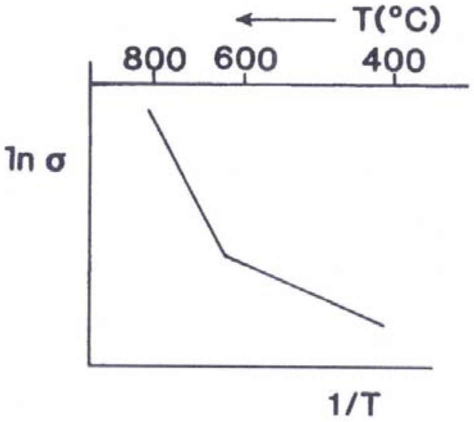


Figure 9.9. Schematic representation of $\ln \sigma$ versus $1/T$ for Na^+ ions in sodium chloride. (Arrhenius plot.)

- From the slopes of the straight lines in Arrhenius plots, the activation energy *Q* is calculated.

- In Fig. 9.9, two different activation barriers.

- *Extrinsic region at low temperature*:

Activation energy is small.
The thermal energy is just sufficient to allow the hopping of ions already existing vacancy

- Intrinsic region at higher temperature:

The thermal energy is large enough to create additional vacancies. The related activation energy is thus the sum of the activation energies for vacancy creation and ion movement.

9.2 Ionic Conduction

Whenever vacant lattice site is created, an overall charge neutrality needs to be maintained.

- Both a cation and anion are removed from a lattice (**Schottky defect**)

- Formation of vacancy- interstitial pair (**Frenkel defect**)

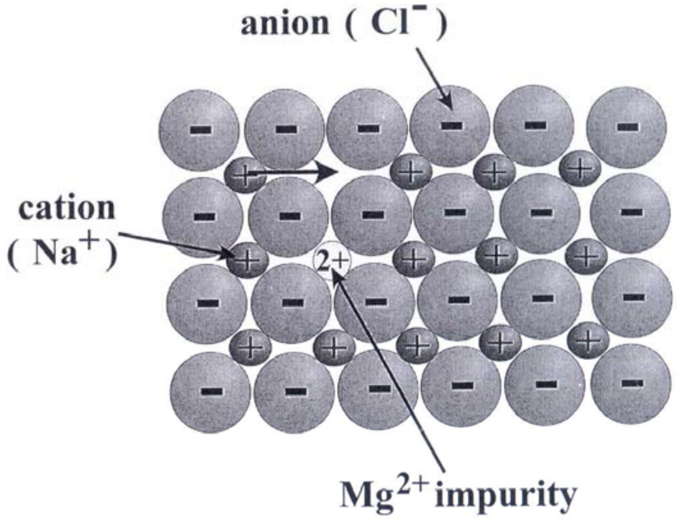


Figure 9.10. Schematic representation of a {100} plane of an ionic crystal having the NaCl structure. The diffusion of a cation into a cation vacancy is shown. Also depicted is the creation of a cation vacancy when replacing a Na^+ ion with a Mg^{2+} ion.

- Vacancies creation by differently charged impurities : By replacing a monovalent metal atom with a divalent atom a positively charged vacancy needs to be introduced.

(Examples)

1. Mg^{2+} ion substitutitution for a monovalent Na^+ ion: extra Na^+ ion has to be removed to restore charge neutrality (Fig.9.10).
2. Calcia(CaO)-stabilized Zirconia(ZrO_2): Ca^{2+} ions substitute for Zr^{4+} ions, and then an anion vacancy needs to be created to maintain charge neutrality.

9.3 Conduction in Metal Oxides

Metal oxide can be insulating, have metallic conduction properties, or be semiconducting : For understanding the mechanisms involved in metal oxides, their electronic configuration in the orbital (or band structure) should be considered. (Appendix 3. p.409)

1. TiO_2 (O : $1s^2\ 2s^2 2p^4$, Ti: $3d^2 4s^2$)

- Noble gas configuration, insulator

- Oxygen have four 2*p*-electrons in its outermost shell. Two more electrons will bring O^{2-} into the closed-shell configuration and four electrons are obviously needed to accomplish the same for two oxygen ions: 4 electrons are provided from Ti 3*d*- and 4*s*-shells.

- Since ionic bonds are involved, any attempted removal of electrons would require a considerable amount of thermal energy : insulator with wide band gap.

9.3 Conduction in Metal Oxides

2. TiO (O : $1s^2\ 2s^2 2p^4$, Ti: $3d^2 4s^2$)

- Metallic

- Only two titanium valence electrons are needed to fill the 2*p*-shell of one oxygen ion, two more titanium electrons are free to serve as conduction electron

3. ZnO (O : $1s^2\ 2s^2 2p^4$, Zn: $3p^{10} 4s^2$)

- Insulator for stoichiometric : a filled *2p*-band and an empty zinc 4*s*-band employing a gap energy of 3.3 eV

- *n*-type semiconductor for non-stoichiometric : if interstitial Zn atoms (or oxygen vacancy) are introduced into the lattice, then the valence electrons of these Zn interstitials are loosely bound to their nuclei ; first ionization energy is 0.05 eV (act as a donor)

9.3 Conduction in Metal Oxides

4. SnO_2 (some times doped with In_2O_3)

- Transparent in the visible region and a reasonable conductor in the 1 $\Omega^{-1}cm^{-1}$ range

- Optoelectronics to provide electrical contacts without blocking the light from reaching a device: **indium-tin-oxide (ITO)**

5. NiO (O : $1s^2\ 2s^2 2p^4$,Ni: $3p^8 4s^2$)

- Insulator for stoichiometric : a filled oxygen 2*p*-band and empty nickel 4*s*-band ; deep-lying localized electron states in the forbidden band close to the upper edge of the valence band are observed

- *p*-type semiconductor for nonstoichiometric; obtained by removing some nickel atoms, thus creating vacancies.

9.4 Amorphous Materials (Metallic Glasses)

Structural features of amorphous materials

- Random arrangement of atoms
- Short range order
- Diffraction patterns consist of diffuse rings
- Positional disorder (in case of pure materials), compositional disorder (more than one element): the individual species are randomly distributed

Many elements and compounds that are generally known to be crystalline under equilibrium conditions can also be obtained in the nonequilibrium amorphous state by applying rapid solidification techniques: fast quenching, melt spinning, vapor deposition, sputtering, radiation damage, filamentary casting in continuous operation, spark-processing, etc.

The degree of amorphousness (or, the degree of short range order) can be varied by the severity of quench

ex) **metallic glasses or *glassy metals*, amorphous semiconductor**

9.4 Amorphous Materials (Metallic Glasses)

Atomic structure of amorphous metals and alloy

- Dense random packing of hard spheres model (Fig. 9.11) (**Bernal model**) : ideal

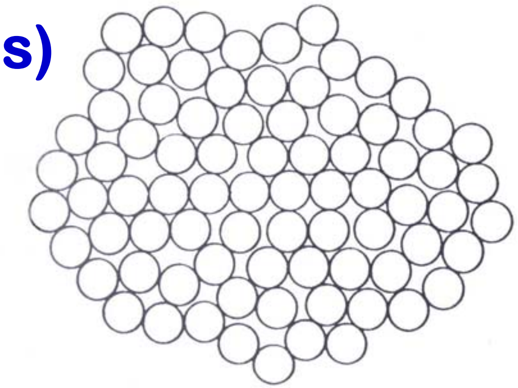
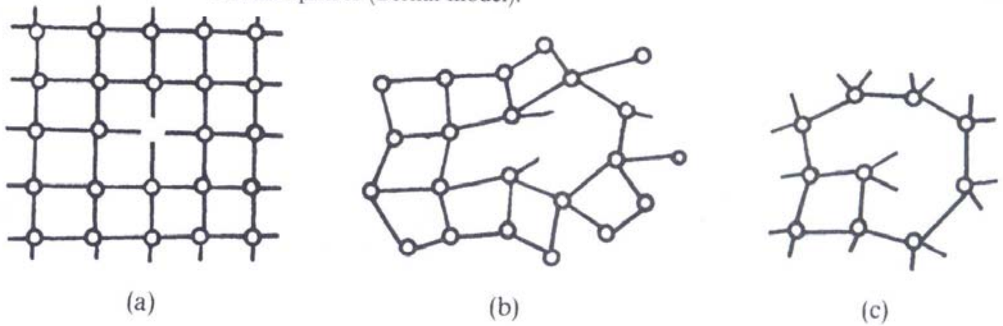


Figure 9.11. Two-dimensional schematic representation of a dense random packing of hard spheres (Bernal model).

- In transition metal-metalloid compounds (such as Ni-P) it is thought that the small metalloid atoms occupy the holes which occur as a consequence of this packing (Bern-Polk model)

The atoms in amorphous semiconductors : no close packing



(a) (b) (c)

Figure 9.12. Defects in crystalline and amorphous silicon. (a) Monovacancy in a crystalline semiconductor; (b) one and (c) two dangling bonds in a continuous random network of an amorphous semiconductor. (Note the deviations in the interatomic distances and bond angles.)

- Atoms of group IV elements (covalent bond): Often arranged in a continuous random network with ordering up to the third or fourth nearest neighbors (Fig 9.12b,c) - Amorphous pure silicon contains numerous dangling bonds similar to those found in the crystalline silicon in the presence of vacancies (Fig 9.12a)

9.4 Amorphous Materials (Metallic Glasses)

The calculation of electronic structure for amorphous metals and alloys: **cluster model approach**

e.g.) Fig 9.13 : the electronic structure of amorphous Zr-Cu

- A series of clusters were assumed which exhibit the symmetry of closed-packed lattice fcc (as Cu) and hcp (as for Zr)

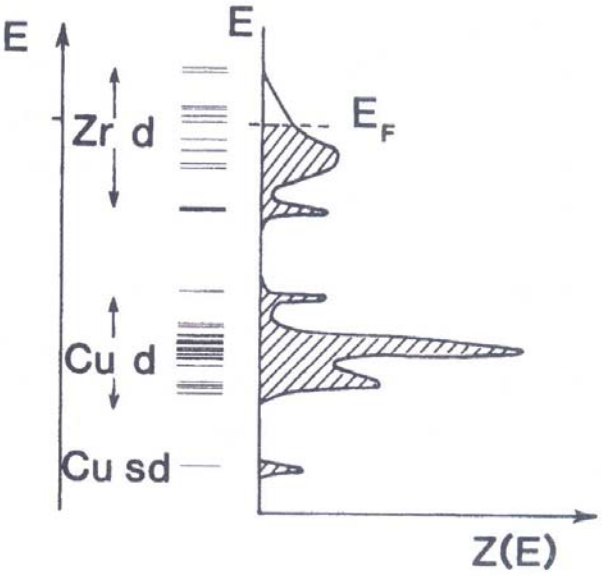


Figure 9.13. Schematic representation of the molecular orbital energy level diagram and the density of states curves for Zr–Cu clusters. The calculated density of states curves agree reasonably well with photoemission experiments.

- Partially filled electron states: *metal-like* conduction, $Z(E)$ near E_F is small, which suggest relatively small values for conductivity. (σ for Cu-Zr = $5 \times 10^3 / \Omega\, cm$)

- The electrical resistivity of many metallic glasses (such as $Pd_{80}Si_{20}$ or $Fe_{32}Ni_{36}Cr_{14}P_{12}B_{16}$) stays constant over a wide temperature range : resistance standards

9.4 Amorphous Materials (Metallic Glasses)

The energy level diagram and density of states curves for amorphous semiconductors

- stronger binding forces between the atoms in covalently bound materials, the valence electrons are tightly bound, or localized → the density of state for localized state extends into the "band gap" (Fig 9.14)

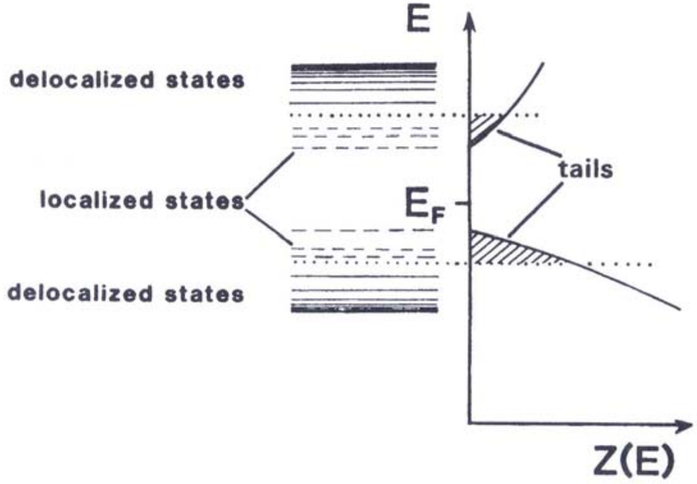


Figure 9.14. Localized and delocalized states and density of states $Z(E)$ for amorphous semiconductors. Note the band tails, which are caused by the localized states.

Electrical conductivity for amorphous semiconductors

$$\sigma_A = N_A e \mu_A$$

Density of carriers (N_A) in amorphous semiconductor is extremely small ; electrons are localized, mobility of charge carriers is small – incoherent scattering (absence of periodic lattice)

$$\sigma_{\mathrm{A}} = \sigma_0 \exp\left[-\left(\frac{Q_A(T)}{k_B T}\right)\right]$$

Temperature-dependent activation process; activation energy Q_A

9.4. Amorphous Materials (Amorphous Semiconductor)

9.4.1. Xerography or electrophotography

- An important application of amorphous semiconductor : selenium, silicon

- When deposited on a cylindrically shaped metallic substrate, constitutes the photoreceptor drum (Fig. 9.15)

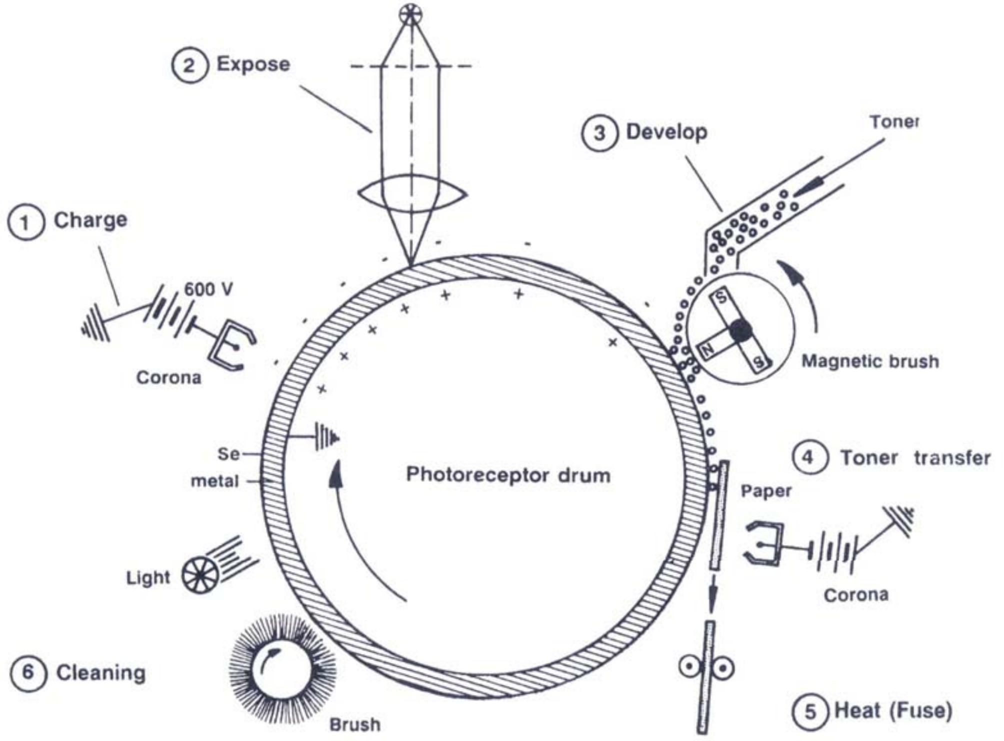


Figure 9.15. Schematic representation of the electrophotography process. The individual steps are explained in the text.

Before copying, the photoreceptor is charged by corona wire to which a high voltage is applied. 2. Light which have been reflected from the document to be copied fall on the photoreceptor, electron hall pair formed causing photoreceptor to become conducting. This step discharge the affected parts on the drum, creating a latent image on the photoreceptor. 3. Toner develop ; 4. Toner transfer to papers ; 5. Heat (toner is fused)

9.5 Dielectric Properties

Capacitance, *C*: the ability to store an electric charge, *q* per unit applied voltage, *V*.

$$C = \frac{q}{V} \quad \text{and} \quad C = \varepsilon\, \varepsilon_0 \frac{A}{L}$$

where $$\varepsilon = \frac{C}{C_{\text{vac}}}$$

Area, *A* of the plate, the distance, *L* between electrodes

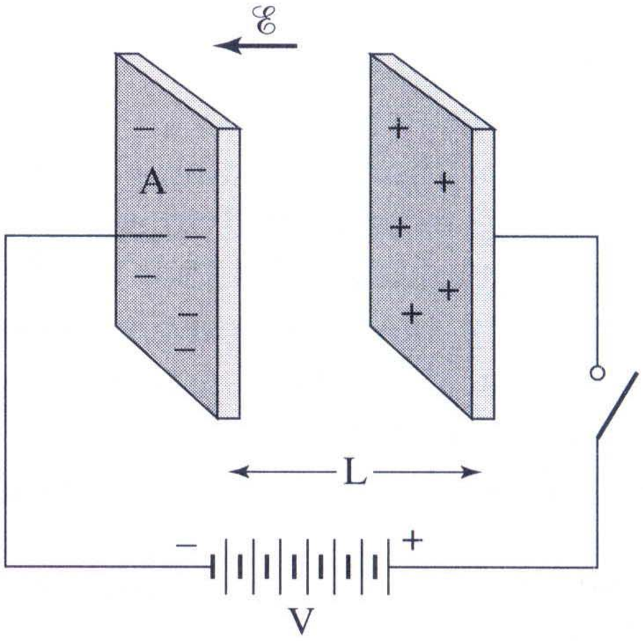


Figure 9.16. Two metal plates, separated by a distance, L, can store electric energy after having been charged momentarily by a battery.

Determine the magnitude of the added storage capability;

ε : dielectric constant (unitless), or *relative permittivity,* ε_r

ε_0 : permittivity of empty space , 8.85×10^{-12} F/m

9.5 Dielectric Properties

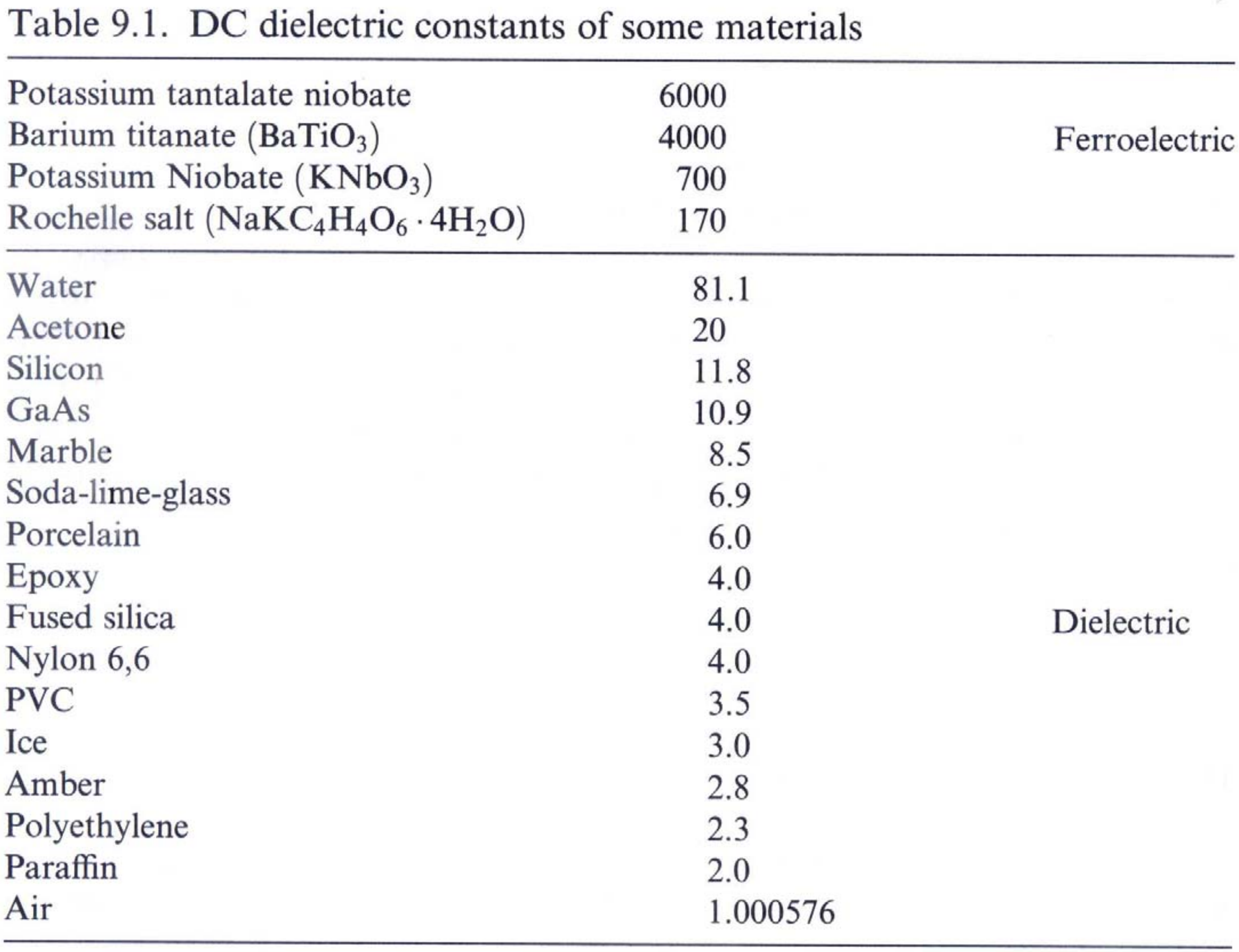


Table 9.1. DC dielectric constants of some materials

Potassium tantalate niobate	6000	Ferroelectric
Barium titanate ($BaTiO_3$)	4000	
Potassium Niobate ($KNbO_3$)	700	
Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$)	170	
Water	81.1	Dielectric
Acetone	20	
Silicon	11.8	
GaAs	10.9	
Marble	8.5	
Soda-lime-glass	6.9	
Porcelain	6.0	
Epoxy	4.0	
Fused silica	4.0	
Nylon 6,6	4.0	
PVC	3.5	
Ice	3.0	
Amber	2.8	
Polyethylene	2.3	
Paraffin	2.0	
Air	1.000576	

9.5 Dielectric Properties

Electric dipole moment

$$p = q \cdot x$$

x **is the separation between the positive and negative charge (Fig 9.17c)**

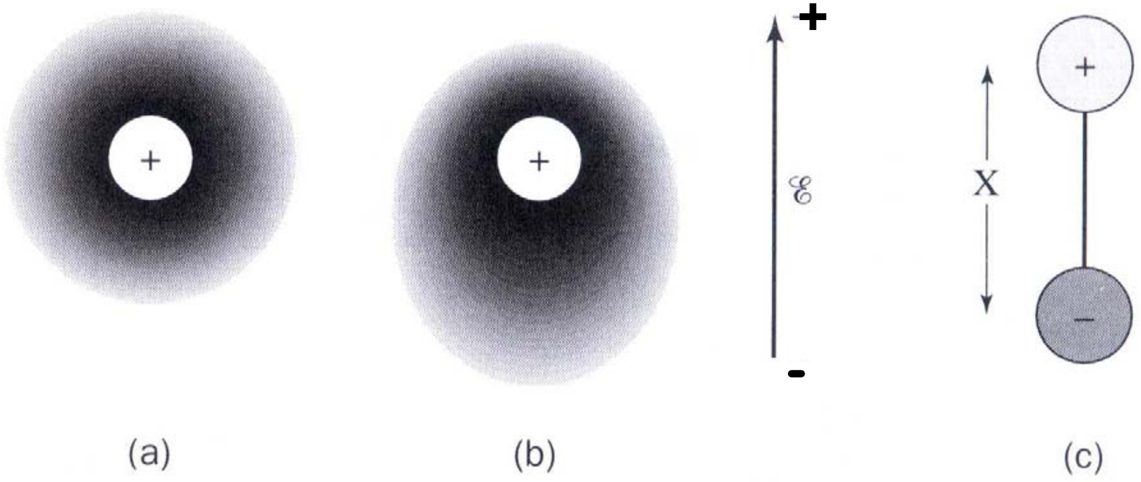


Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).

- The dipole moment is a vector pointing from the negative to charge.

Polarization : the process of dipole formation (or alignment of already existing dipoles) under the influence of an external electric field that has an electric field strength, *E*

9.5 Dielectric Properties

- Dipole formation of all involved atoms within a dielectric material cause a charge redistribution so that the surface nearest to the positive capacitor plate is negatively charge (and vice versa): Fig. 9.18a

- Electric field lines within a dielectric material are weakened due to polarization: Fig 9.18b

$$E = \frac{E_{\text{vac}}}{\varepsilon}$$

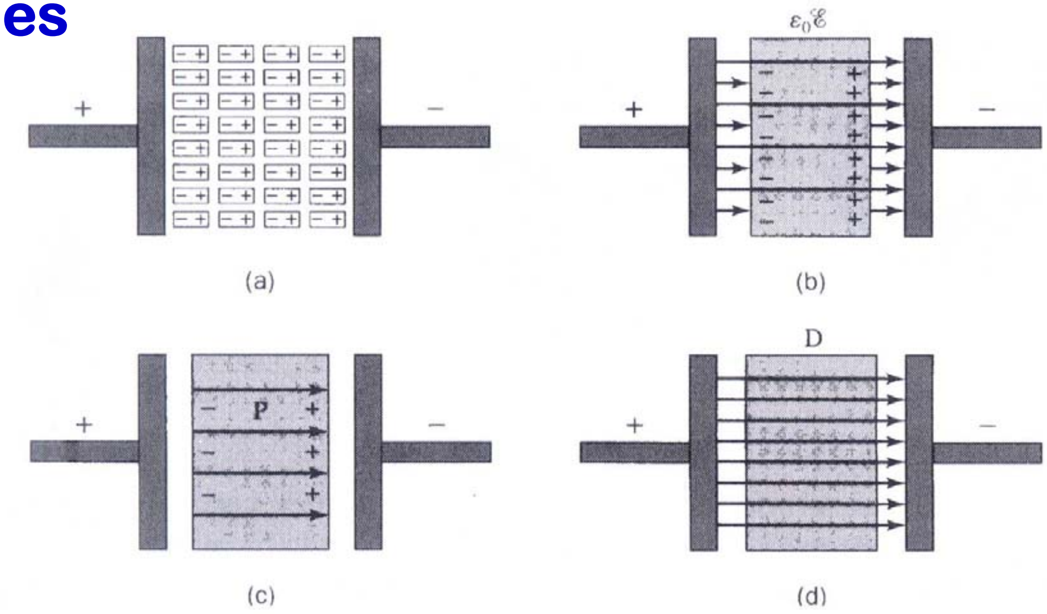


Figure 9.18. Schematic representation of two capacitor plates between which a dielectric material is inserted. (a) Induction of electric dipoles of opposite charge. (b) Weakening of the electric field *within* the dielectric material [Eq. (9.13)]. (c) The direction of the polarization vector is from the negative induced charge to the positive induced charge see Fig. 9.17(b). (d) The dielectric displacement, *D*, within the dielectric material is the sum of $\varepsilon_0\mathscr{E}$ and *P* [Eq. (9.15)].

$$D = \varepsilon\varepsilon_0 E = \frac{q}{A}$$

Dielectric displacement, *D* or surface charge density

Dielectric polarization *P*, the induced electric dipole moment per unit volume (Fig 9.18 c and d)

$$D = \varepsilon_0 E + P$$

Units for *D* and *P* are C m^{-2}

9.5 Dielectric Properties

The mechanism of polarization

- **Electric polarization** (Fig 9.17)
- **Ionic polarization**: cations and anions are somewhat displaced from the equilibrium positions under the influence of an external field and thus give rise to a net dipole moment

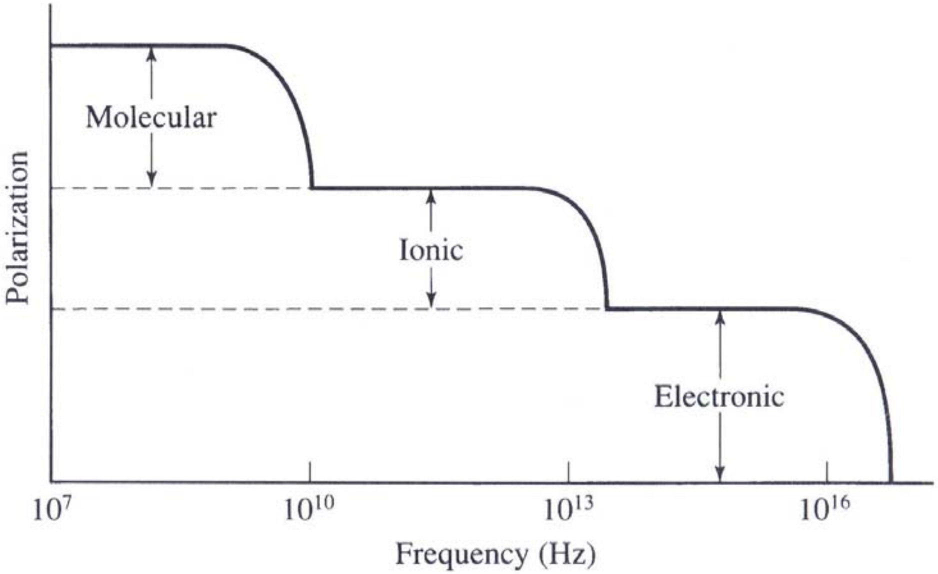


Figure 9.19. Schematic representation of the polarization as a function of excitation frequency for different polarization mechanisms.

- **Orientation polarization**: permanent dipole align to the external electric filed; *molecular polarization*

How quickly do the dipoles to reorient or to align under a rapidly changing electric filed (in alternating circuit)

Polarization mechanisms which can respond equally quick to an alternating electric field (Fig. 9.19)

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

Ferroelectric materials

- A spontaneous polarization without the presence of an external electric field : suitable for the manufacturing of small sized, highly efficient capacitors

- Hysteresis loop (Fig. 9.20)

P_S: saturation polarization
P_r : remanent polarization
E_C : coercive filed

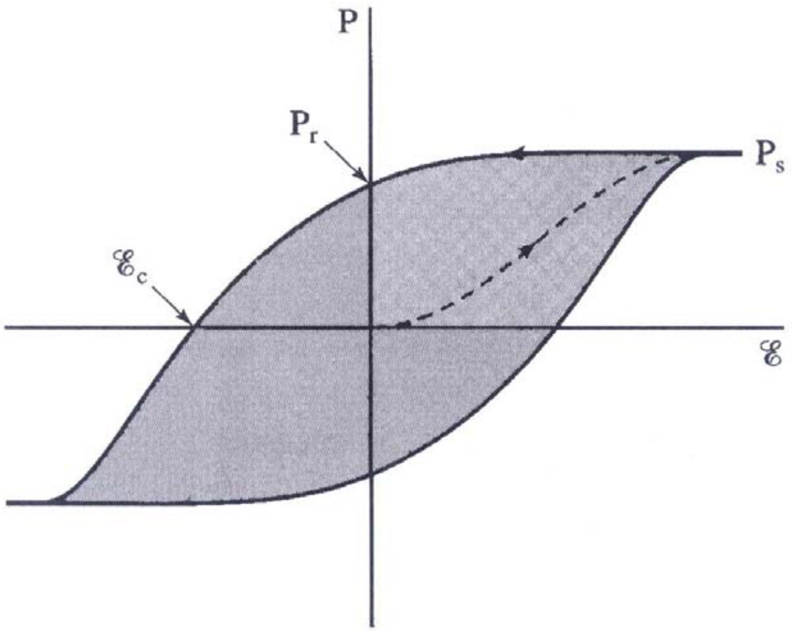


Figure 9.20. Schematic representation of a hysteresis loop for a *ferroelectric* material in an electric field. Compare to Figure 15.6.

- A critical temperature (called, Curie temperature) exists, above which the ferroelectric effect are destroyed and the material becomes paraelectric (a kind of dielectric)

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

Why do certain material possess spontaneous polarization?

- **Tetragonal $BaTiO_3$: the negatively charged oxygen ions and the positively charged Ti^{4+} ion are slightly displaced from their symmetrical position (Fig 9.21)**
- **A large number of such dipole moment line up in a clusters (also called *domains*)**
- **In virgin state, the polarization directions of the individual domains are randomly oriented: no net polarization**
- **An external field orients the dipoles of favorably oriented domains parallel to *E*: those domains in which the dipoles are already nearly parallel to *E* at the expense of unfavorably oriented domains**

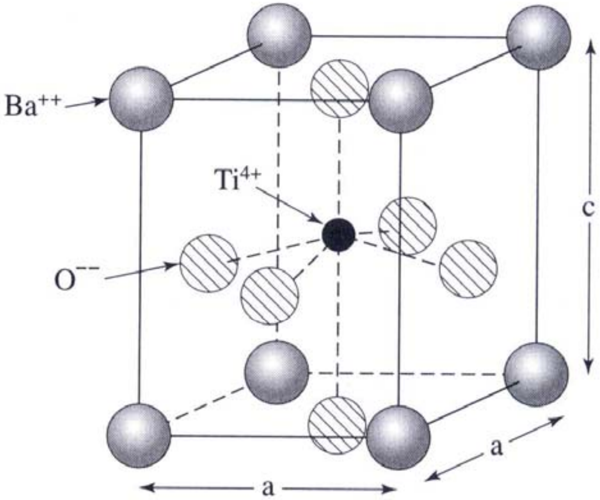


Figure 9.21. Tetragonal crystal structure of barium titanate at room temperature. Note the upward displacement of the Ti^{4+} ion in the center compared to the downward displacement of all surrounding O^{2-} ions. $a = 0.398$ nm; $c = 0.403$ nm.

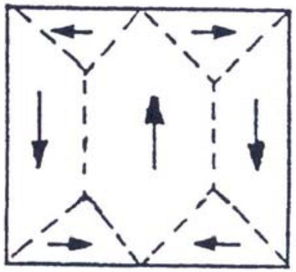


Figure 9.22. Schematic representation of spontaneous alignments of electric dipoles within a domain and random alignment of the dipole moments of several domains in a ferroelectric material such as $BaTiO_3$. Compare to Figure 15.9.

9.5 Ferroelectricity, Piezoelectricity, and Electrostriction

- **Piezoelectricity** : If pressure is applied to a ferroelectric material, such as $BaTiO_3$, a change in the polarization occur, which results in a small voltage across the sample

Transducers : convert mechanical strain onto electricity ; strain gages, microphones, sonar detectors, and phonograph pickups

- **Electrostriction** : inverse mechanism of piezoelectricity; an electric field produce a change on dimensions in a ferroelectric material

An earphone, quartz crystal resonator (which is used in electronic devices as a *frequency selective element*)