

## **Dielectrics and Ferroelectric Materials**

**Updated on :-01/03/2021**

**Semiconductor Fundamentals:** Band structure, indirect and direct band gap, optical properties, carrier statistics

**Semiconductor Growth:** semiconductor material purification and crystal growth, epitaxy, CVD and MBE,

**Processing:** Specific material requirements, Doping by implantation and diffusion, dielectric and insulators, ohmic and barrier contacts, band edge behaviour, empirical rule, alloy design, PN Junction, Schottky and MaS device structures.,

**Dielectric & Ferroelectrics Materials:** Dielectric constant and polarization, polarization mechanism, linear and nonline dielectric, pyro-piezo, and ferroelectric properties, application

**Magnetism:** diamagnetism paramagnelism, polypararnagnetism, ferro, antiferro, and ferrimagnatism. Soft and hard magnet materials, permanent magnet and transformers.

**Books and References:**

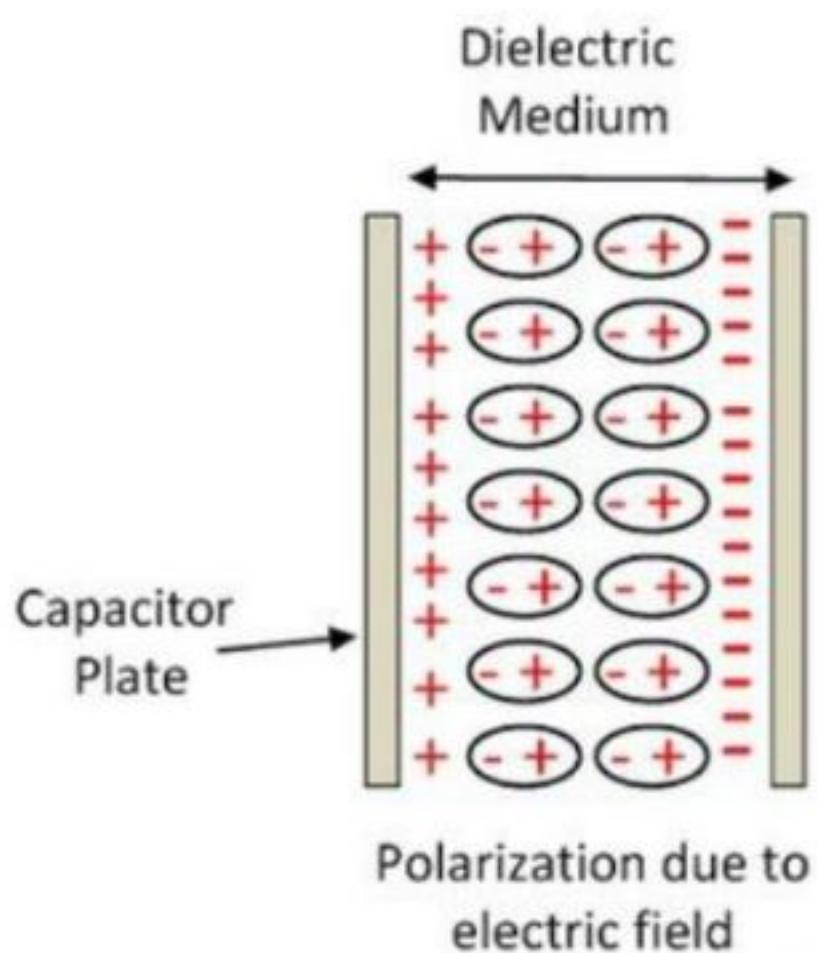
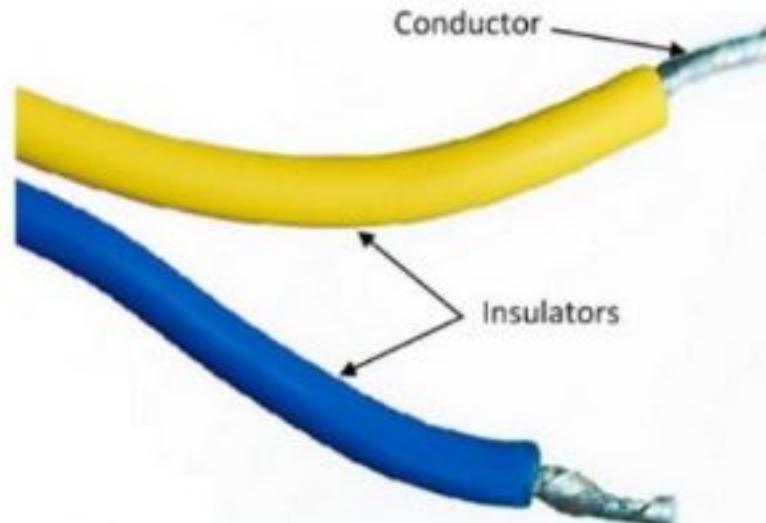
1. Elements of Materials Science and Engineering, L. H. Van Vlack (Addison-Wesley)
2. Materials Science and Engineering: An Introduction, W. D. Callister, (WILEY)
3. The Science and Engineering of Materials, Donald R. Askeland (Chapman & Hall)
4. Solid State electronic Devices, B. G. Streetman (PHI)

# Dielectric Material

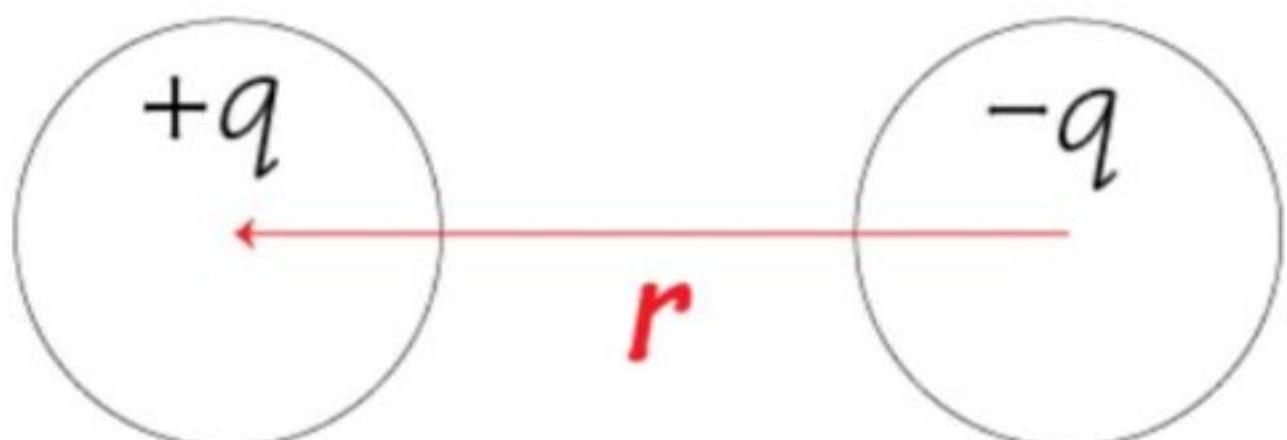
A **dielectric** material is one that is electrically insulating (nonmetallic) and exhibits or may be made to exhibit an **electric dipole** structure (molecular or atomic level).

In principle all insulators are dielectric, although the capacity to support charge varies greatly between different insulators

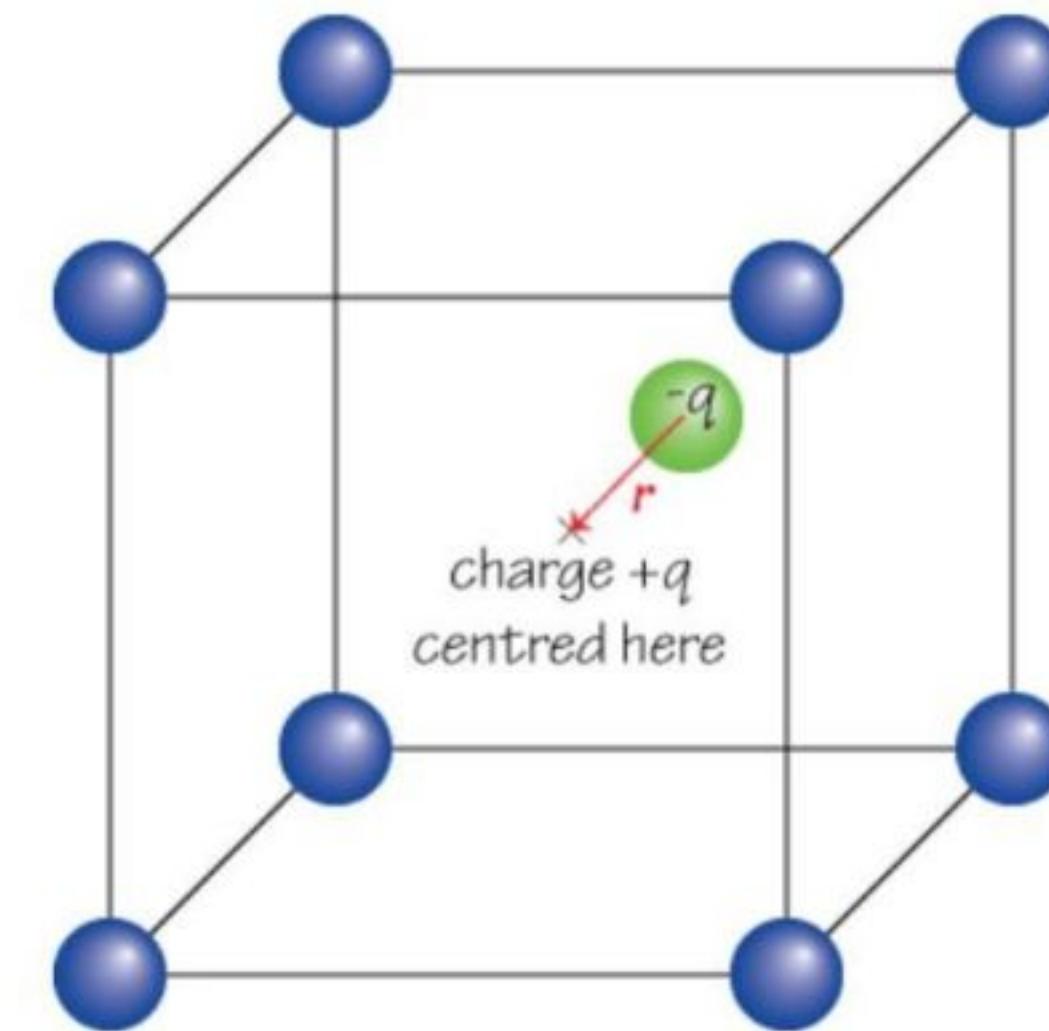
Dielectric materials are used in many applications, from simple electrical insulation to sensors and circuit components.



# Electric Dipole



$$\mu = qr$$



Key

- Blue sphere = cation
- Green sphere = anion

# Dielectric Constant

**Dielectric Constant:** Also known as relative permittivity

$$\epsilon_r = \frac{\epsilon}{\epsilon_0}$$

$\epsilon$  = Permittivity of medium

$\epsilon_0$  Permittivity of vacuum ( $8.854 \times 10^{-12} F/m$ )

Material	Dielectric Constant		Dielectric Strength (V/mil) <sup>a</sup>
	60 Hz	1 MHz	
<i>Ceramics</i>			
Titanate ceramics	—	15–10,000	50–300
Mica	—	5.4–8.7	1000–2000
Steatite (MgO–SiO <sub>2</sub> )	—	5.5–7.5	200–350
Soda-lime glass	6.9	6.9	250
Porcelain	6.0	6.0	40–400
Fused silica	4.0	3.8	250
<i>Polymers</i>			
Phenol-formaldehyde	5.3	4.8	300–400
Nylon 6,6	4.0	3.6	400
Polystyrene	2.6	2.6	500–700
Polyethylene	2.3	2.3	450–500
Polytetrafluoroethylene	2.1	2.1	400–500

<sup>a</sup> One mil = 0.001 in. These values of dielectric strength are average ones, the magnitude being dependent on specimen thickness and geometry, as well as the rate of application and duration of the applied electric field.

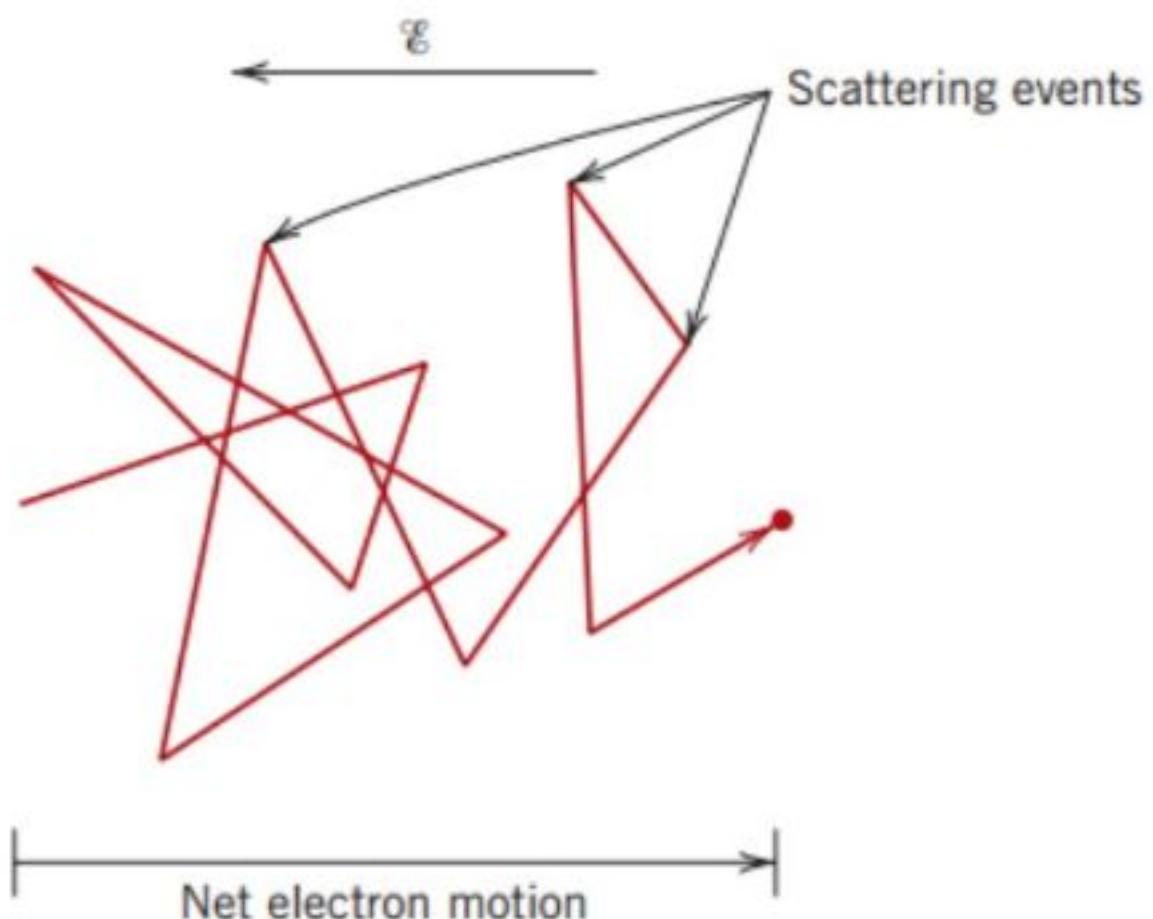
# Electron Mobility

These frictional forces result from the scattering of electrons by imperfections in the crystal lattice, including impurity atoms, vacancies, interstitial atoms, dislocations, and even the thermal vibrations of the atoms themselves.

To describe the extent of this scattering; these include the *drift velocity* and the **mobility** of an electron. The drift velocity represents the average electron velocity in the direction of the force imposed by the applied field.

$$v_e = \mu_e E$$

$$\sigma = n|e|\mu_e$$



## THE HALL EFFECT

To determine the material's majority charge carrier type, concentration, and mobility.

MAGNETIC FIELD applied perpendicular to the direction of motion of a Charged particle exerts a FORCE ON THE PARTICLE PERPENDICULAR to both the magnetic field and the particle motion directions.

$$V_H = \frac{R_H I_x B_z}{d}$$

$V_H$  = Hall Voltage

$d$  = Specimen thickness

In this expression  $R_H$  is termed the *Hall coefficient*, which is a constant for a given material. For metals, wherein conduction is by electrons,  $R_H$  is negative and equal to

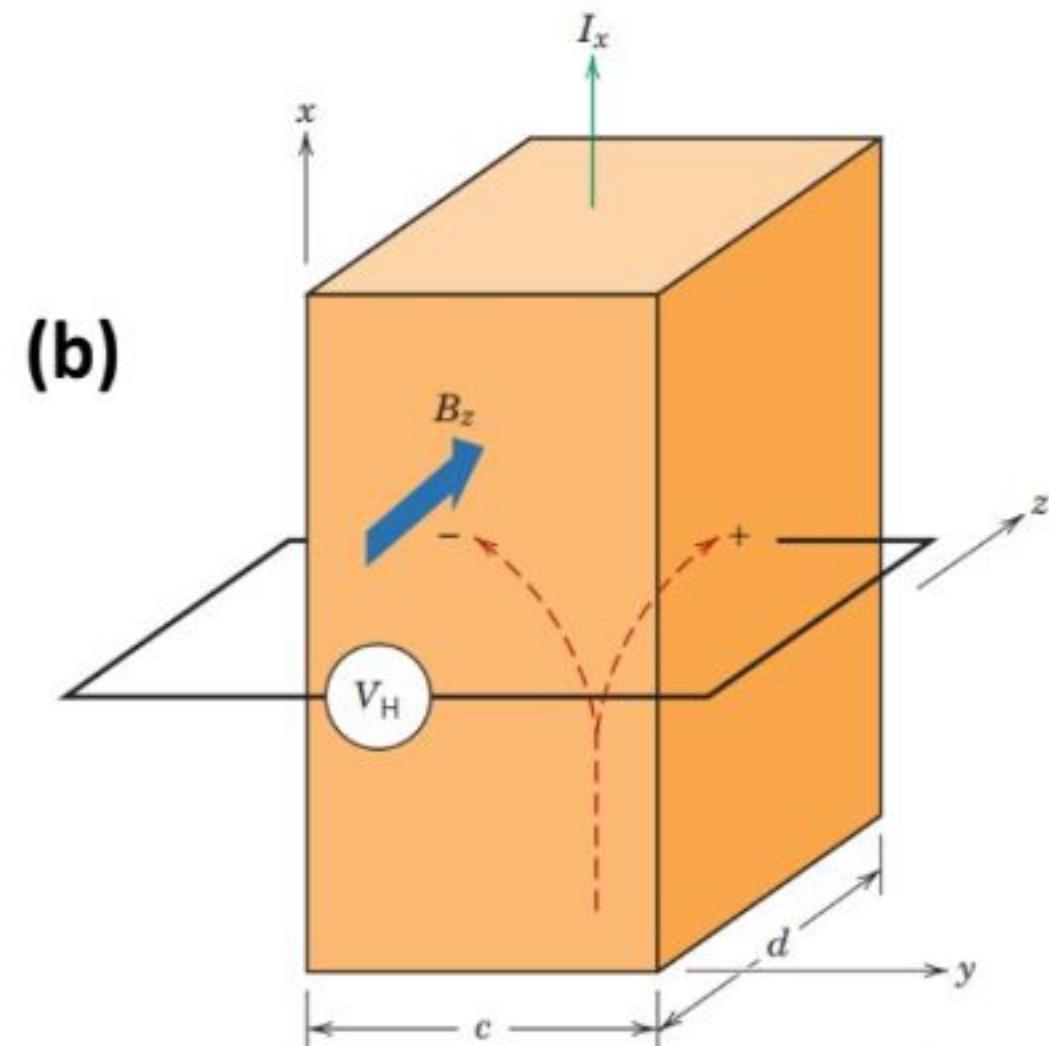
$$R_H = \frac{1}{n|e|}$$

electron mobility  $\mu_e$

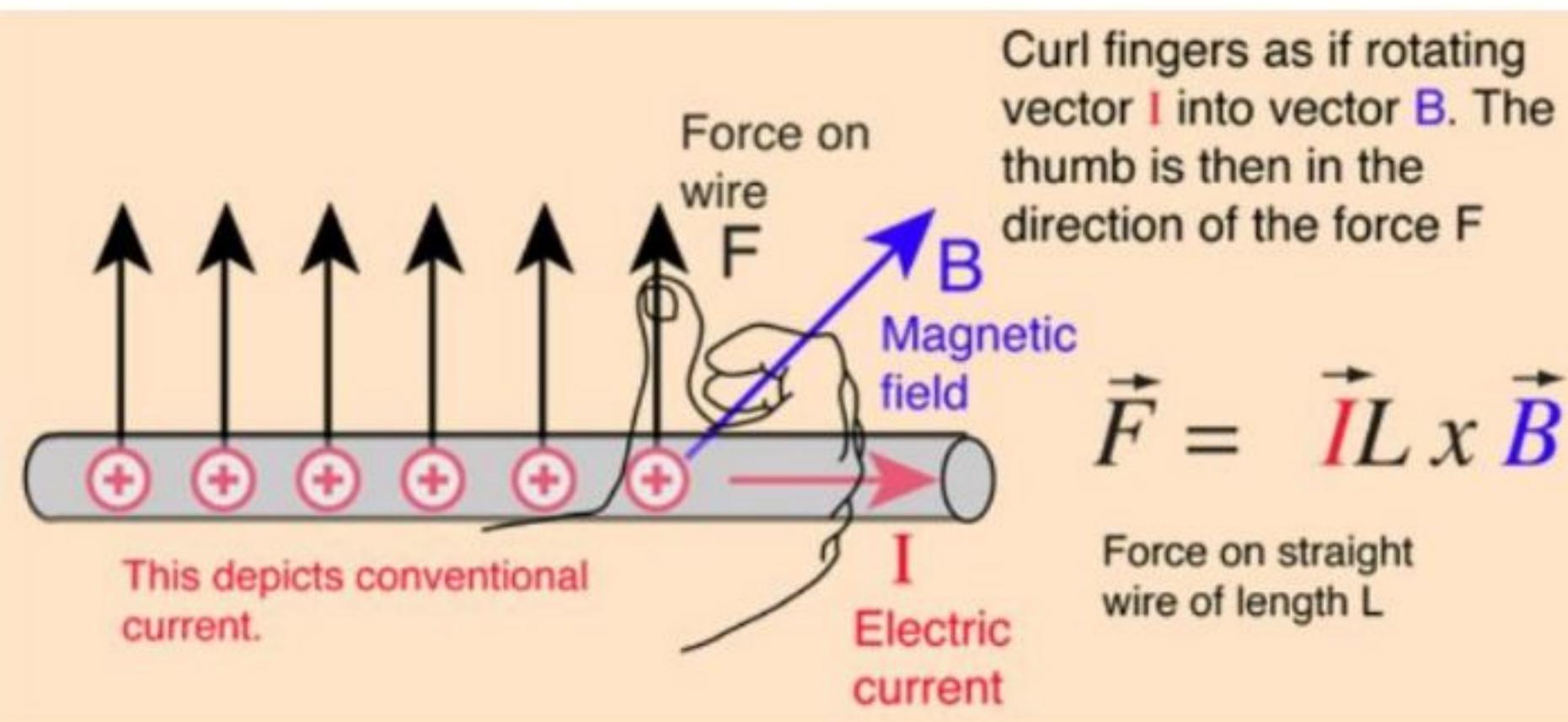
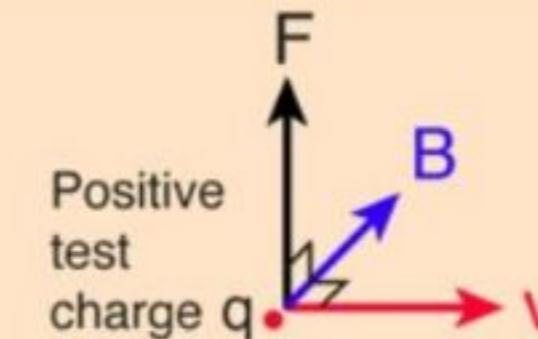
conductivity  $\sigma$

$$\mu_e = \frac{\sigma}{n|e|}$$

$$\mu_e = |R_H|\sigma$$



$$\vec{F} = q\vec{v} \times \vec{B}$$

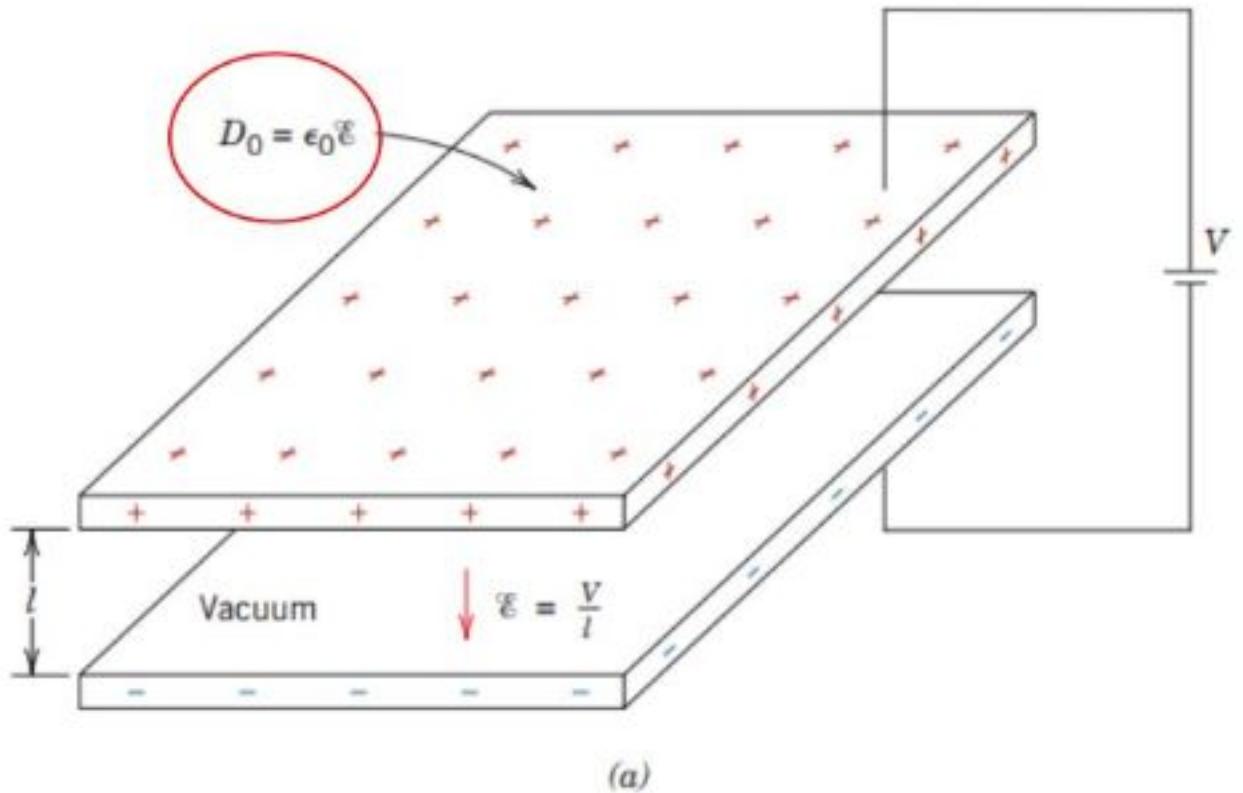


# Dielectric Strength

The **dielectric strength**, sometimes called the breakdown strength, represents the magnitude of an electric field necessary to produce breakdown.

Sometimes localized melting, burning, or vaporization produces irreversible degradation and perhaps even failure of the material

## Electric Displacement



(a)

Charge per unit area that would be displaced across a layer of conductor placed across an electric field.

Also known as **electric flux density** or **Surface charge density**.

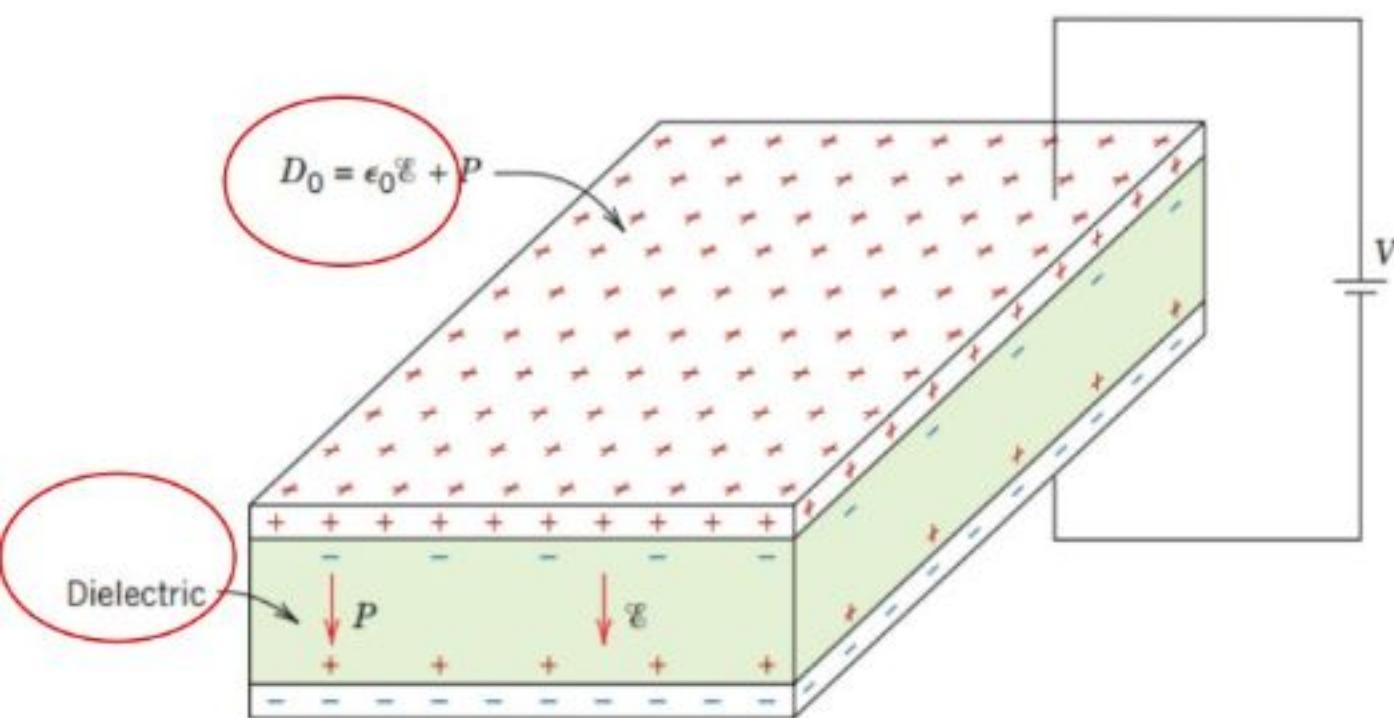
Electric displacement is used in the dielectric material to find the response of the materials on the application of an electric field  $\mathbf{E}$ .

The **SI unit Coulomb per meter square ( $C\ m^{-2}$ )**.

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$$

- $\epsilon_0$ : Vacuum permittivity
- $\mathbf{P}$ : Polarization density
- $\mathbf{E}$ : Electric field
- $\mathbf{D}$ : Electric displacement field

The surface charge density  $D$ , or quantity of charge per unit area of capacitor plate ( $C/m^2$ ), is proportional to the electric field



The **electric displacement field  $\mathbf{D}$**  represents how an electric field  $\mathbf{E}$  influences the organization of electric charges in a given medium, including charge migration and electric **dipole** reorientation.

## Electric flux Density (D):

Electric flux density is defined as charge per unit area and it has same units of dielectric polarization.

Electric flux density D at a point in a free space or air in terms of Electric field strength is

$$D_0 = \epsilon_0 E \quad \text{--> (1)}$$

At the same point in a medium is given by

$$D = \epsilon E \quad \text{--> (2)}$$

As the polarization measures the additional flux density arising from the presence of material as compared to free space

$$\text{i.e., } D = \epsilon_0 E + P \quad \text{--> (3)}$$

Using equations 2 & 3 we get

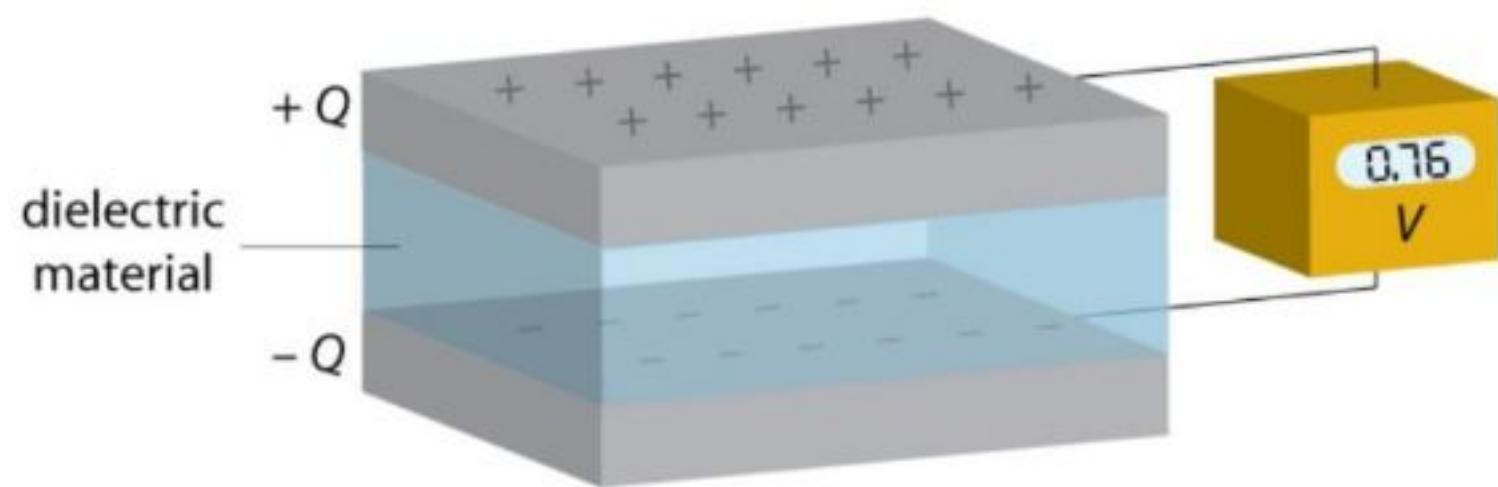
$$\epsilon E = \epsilon_0 E + P$$

$$(\epsilon - \epsilon_0) E = P$$

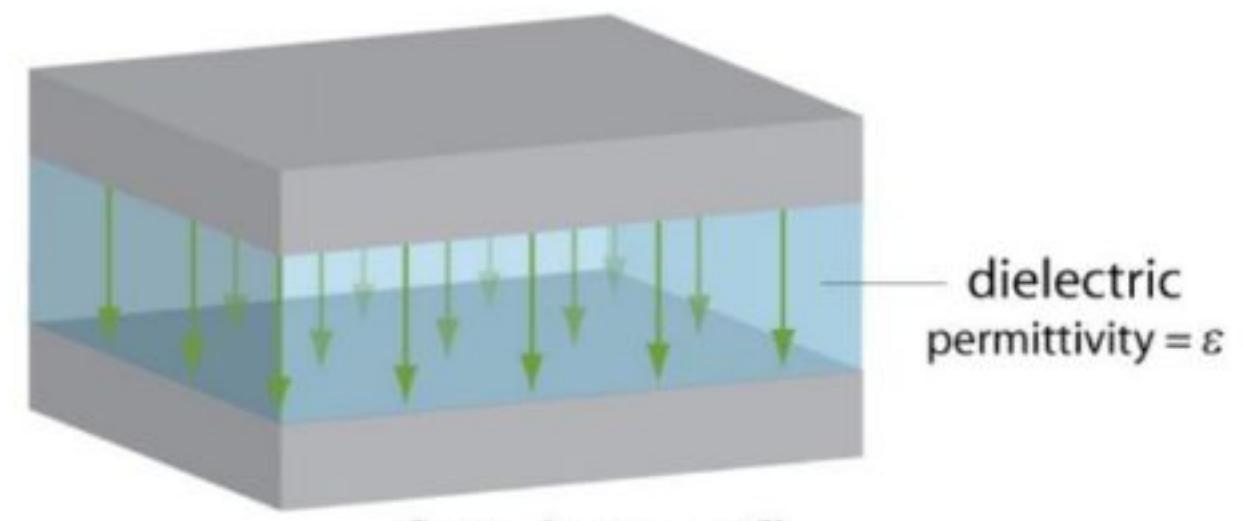
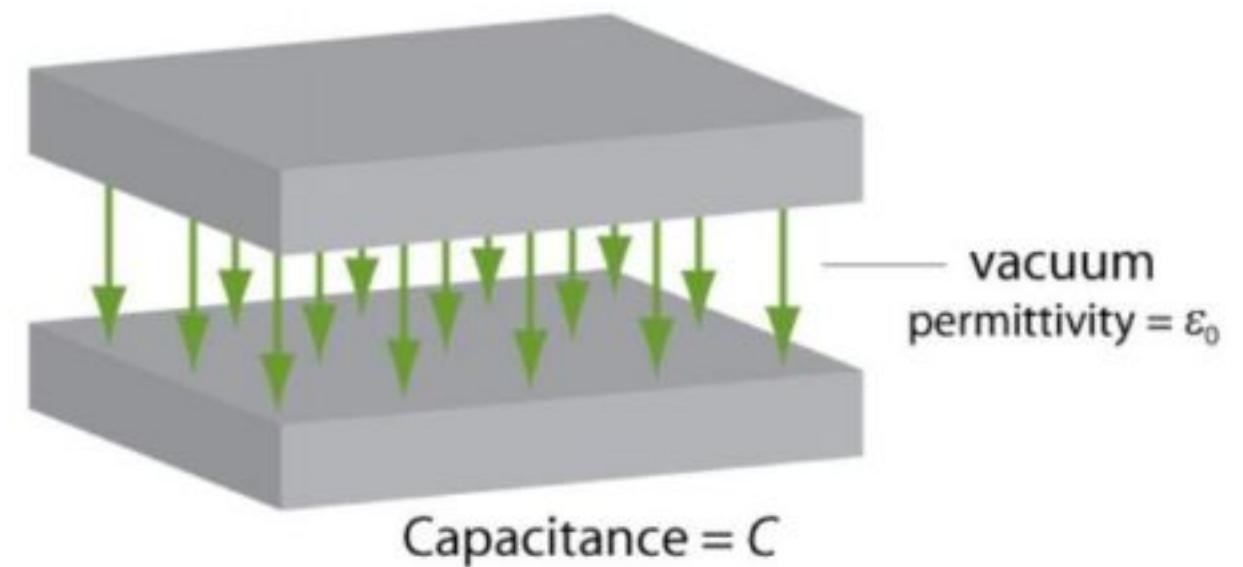
$$(\text{or}) \quad (\epsilon_r \cdot \epsilon_0 - \epsilon_0) E = P$$

$$(\epsilon_r - 1) \epsilon_0 \cdot E = P$$

# Capacitor



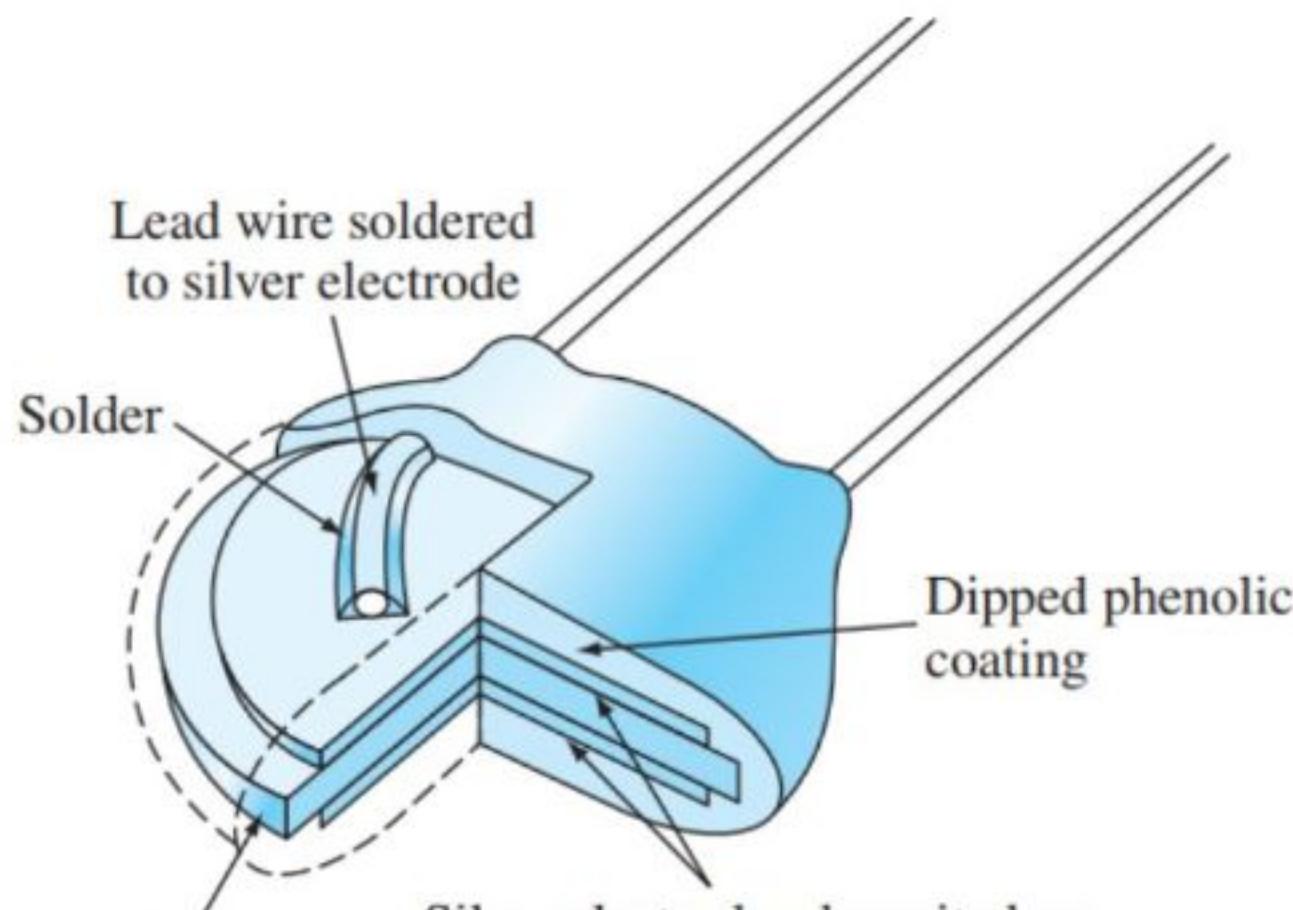
$$Q = CV$$



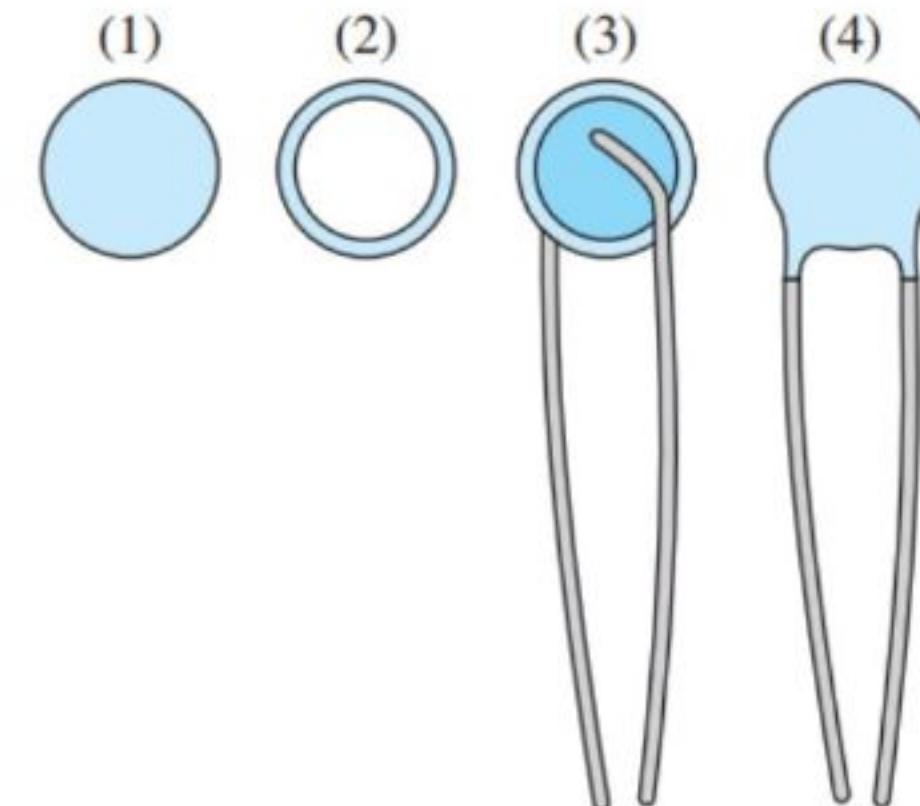
$$\kappa = C'/C$$

$$\kappa = \epsilon/\epsilon_0$$

# Capacitor



(a)



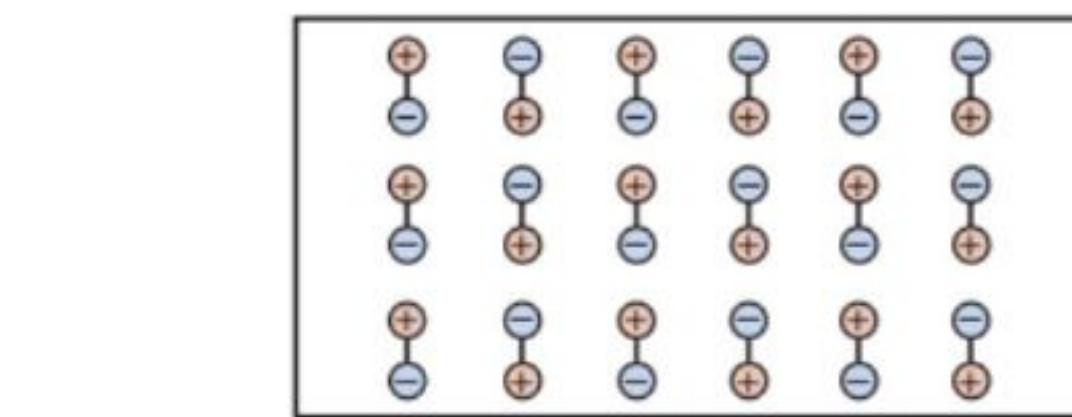
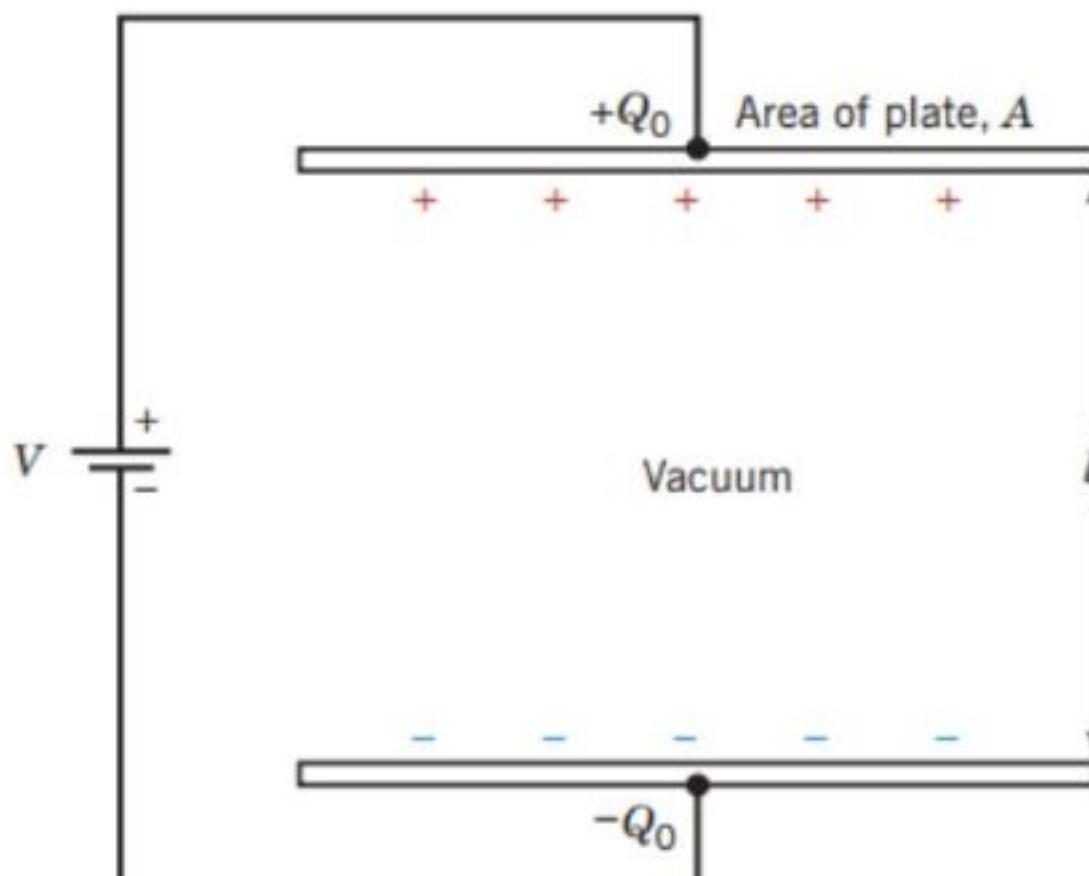
(b)

Ceramic capacitors. (a) Section showing construction. (b) Steps in manufacture: (1) after firing ceramic disk; (2) after applying silver electrodes; (3) after soldering leads; (4) after applying dipped phenolic coating.

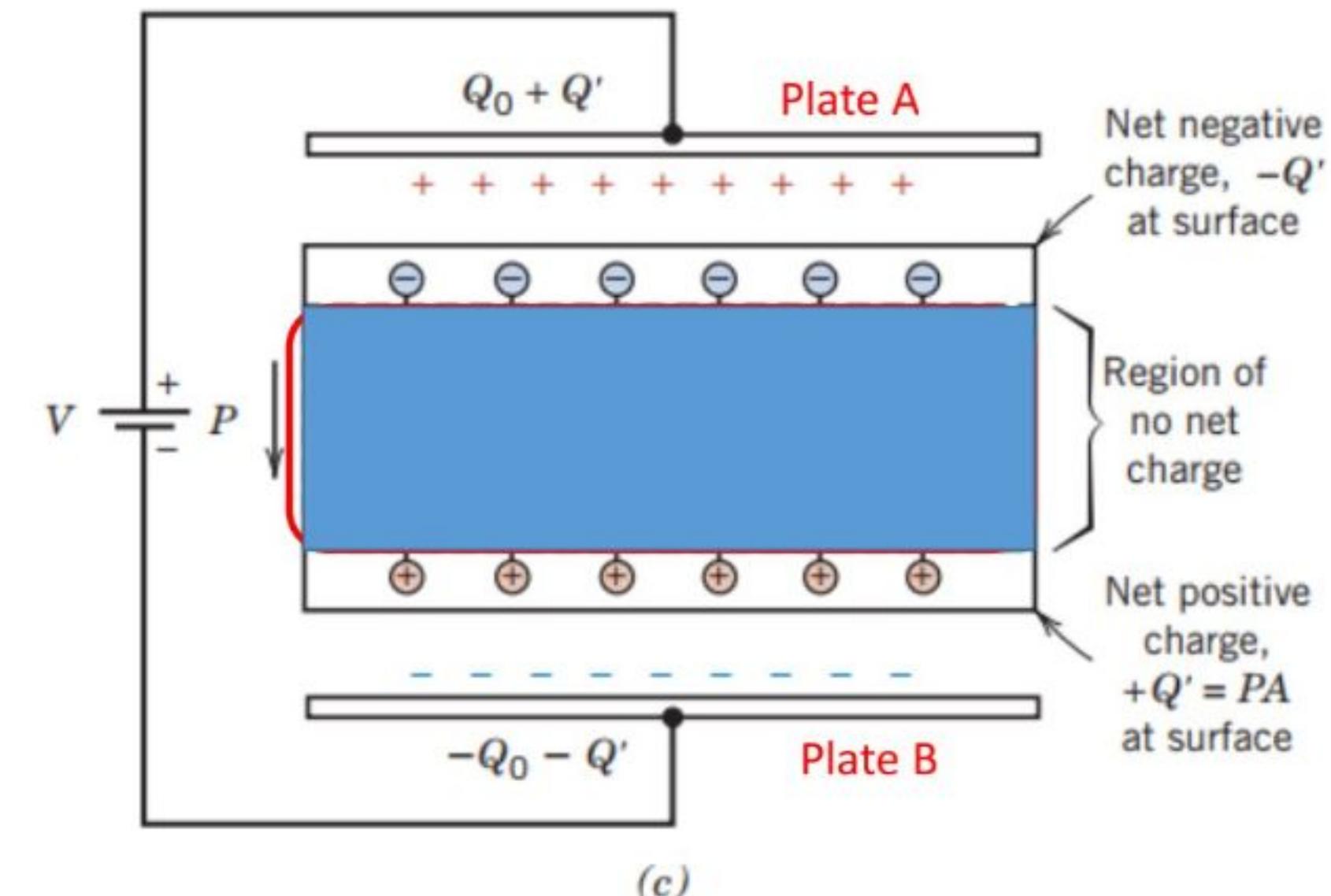
Representative formulations for some ceramic dielectric materials for capacitors

Dielectric Constant $\kappa$	Formulation
325	$\text{BaTiO}_3 + \text{CaTiO}_3 + \text{low \% Bi}_2\text{Sn}_3\text{O}_9$
2100	$\text{BaTiO}_3 + \text{low \% CaZrO}_3$ and $\text{Nb}_2\text{O}_5$
6500	$\text{BaTiO}_3 + \text{low \% CaZrO}_3$ or $\text{CaTiO}_3 + \text{BaZrO}_3$

# Parallel Plate Capacitor in the presence of dielectric

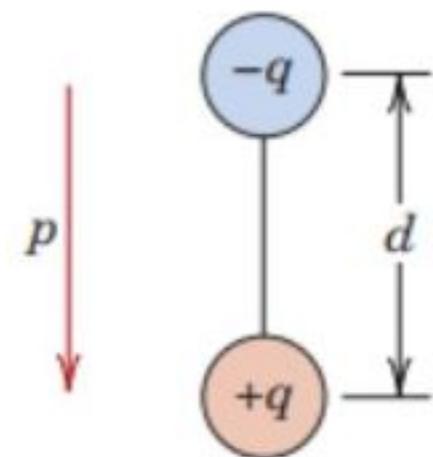


(a)



$$\mathbf{D} = \mathbf{E}\epsilon_0 + \mathbf{P}$$

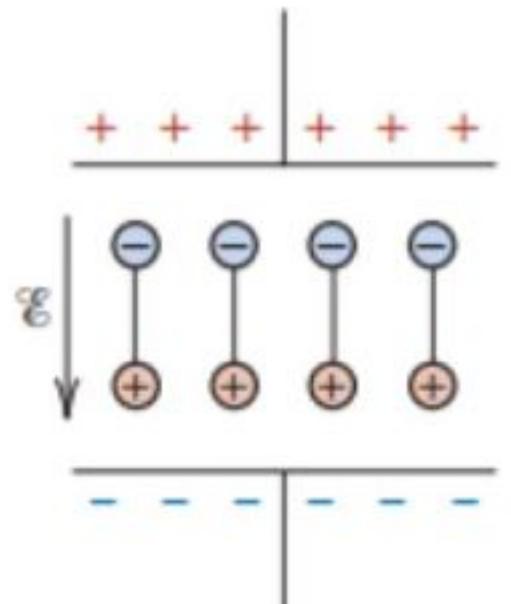
## Dipole orientations for change in orientation of electric field.



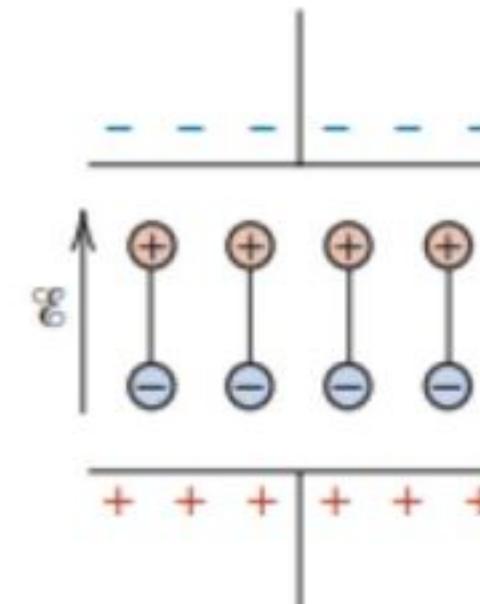
In reality, a dipole moment is a vector that is directed from the negative to the positive charge

In the presence of an electric field  $E$ , which is also a vector quantity, a force (or torque) will come to bear on an electric dipole to orient it with the applied field.

The process of dipole alignment is termed **polarization**.



(a)



(b)

<i>Quantity</i>	<i>Symbol</i>	<i>Derived</i>	<i>SI Units</i>	<i>Primary</i>
Electric potential	$V$	volt		$\text{kg}\cdot\text{m}^2/\text{s}^2\cdot\text{C}$
Electric current	$I$	ampere		$\text{C}/\text{s}$
Electric field strength	$\mathcal{E}$	volt/meter		$\text{kg}\cdot\text{m}/\text{s}^2\cdot\text{C}$
Resistance	$R$	ohm		$\text{kg}\cdot\text{m}^2/\text{s}\cdot\text{C}^2$
Resistivity	$\rho$	ohm-meter		$\text{kg}\cdot\text{m}^3/\text{s}\cdot\text{C}^2$
Conductivity	$\sigma$	$(\text{ohm-meter})^{-1}$		$\text{s}\cdot\text{C}^2/\text{kg}\cdot\text{m}^3$
Electric charge	$Q$	coulomb		$\text{C}$
Capacitance	$C$	farad		$\text{s}^2\cdot\text{C}^2/\text{kg}\cdot\text{m}^2$
Permittivity	$\epsilon$	farad/meter		$\text{s}^2\cdot\text{C}^2/\text{kg}\cdot\text{m}^3$
Dielectric constant	$\epsilon_r$	dimensionless		dimensionless
Dielectric displacement	$D$	farad-volt/ $\text{m}^2$		$\text{C}/\text{m}^2$
Electric polarization	$P$	farad-volt/ $\text{m}^2$		$\text{C}/\text{m}^2$

# Polarization

Polarization direction -ve to +ve

Polarization is dipole moment per unit volume

Polarization is the alignment of permanent or induced atomic or molecular dipole moments with an externally applied electric field.

## Electronic polarization

Results from a displacement of the center of the negatively charged electron cloud relative to the positive nucleus of an atom by the electric field

This polarization type is found in all dielectric materials and, of course, exists only while an electric field is present.

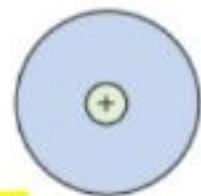
## Ionic Polarization

**Ionic polarization** occurs only in materials that are ionic. An applied field acts to displace **cations in one direction and anions in the opposite direction**, which gives rise to a net dipole moment.

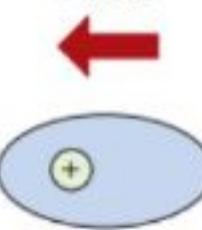
## Orientation or dipolar Polarization

It is found only in substances that possess permanent dipole moments. Polarization results from a rotation of the permanent moments into the direction of the applied field, This alignment tendency is counteracted by the thermal vibrations of the atoms, such that polarization decreases with increasing temperature.

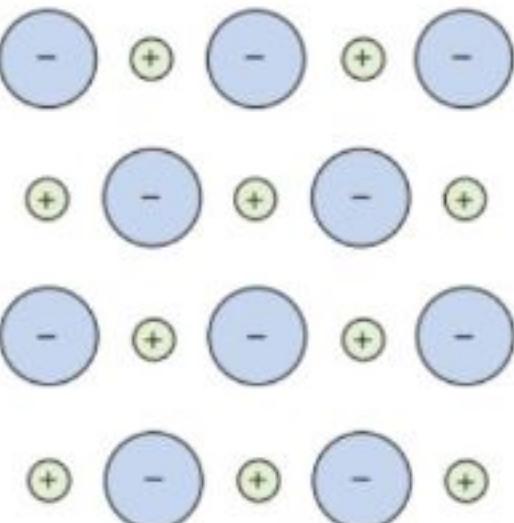
No field



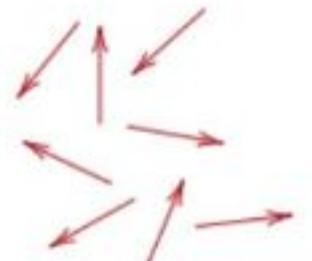
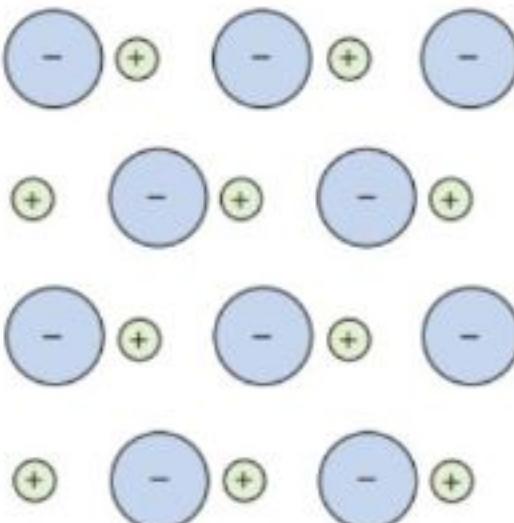
Applied  
E field



(a)



(b)



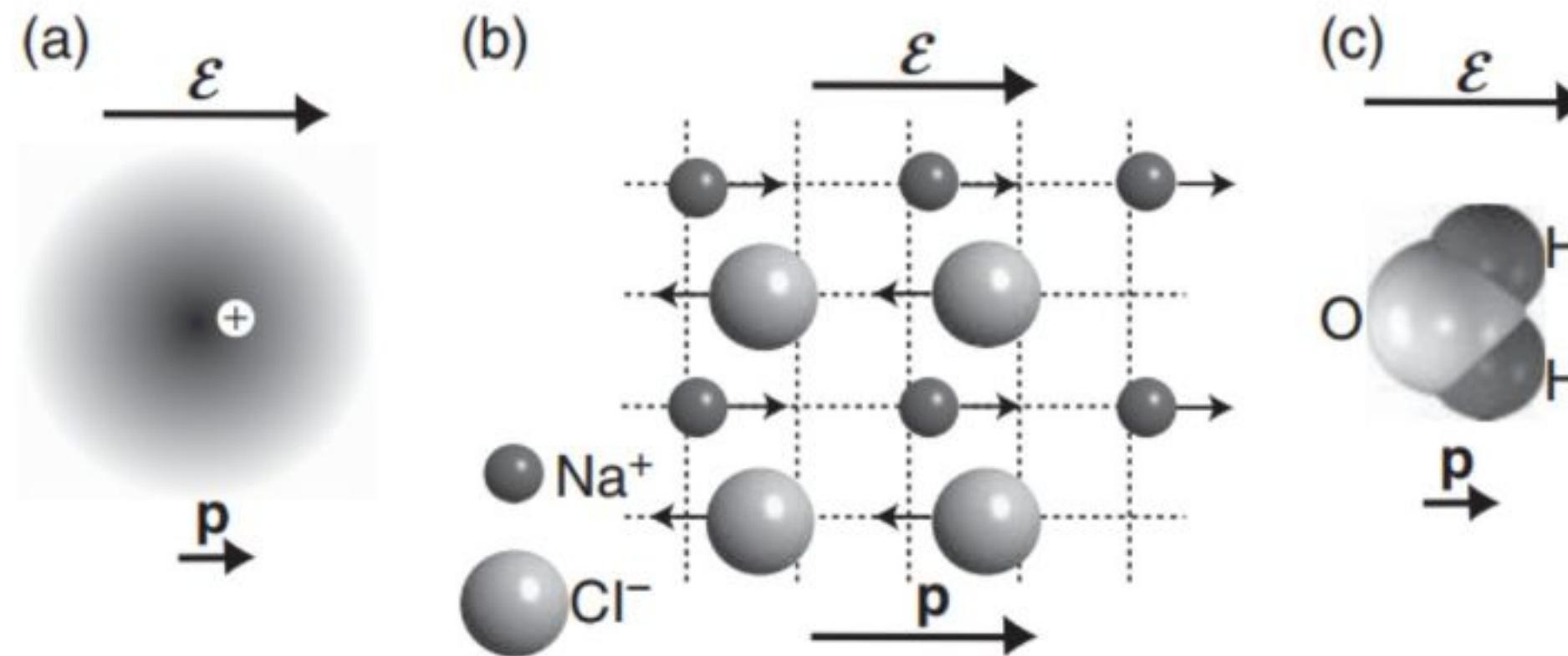
(c)

## Schematic Illustrations

$$\mathbf{P} = \chi_e \epsilon_0 \mathcal{E}$$

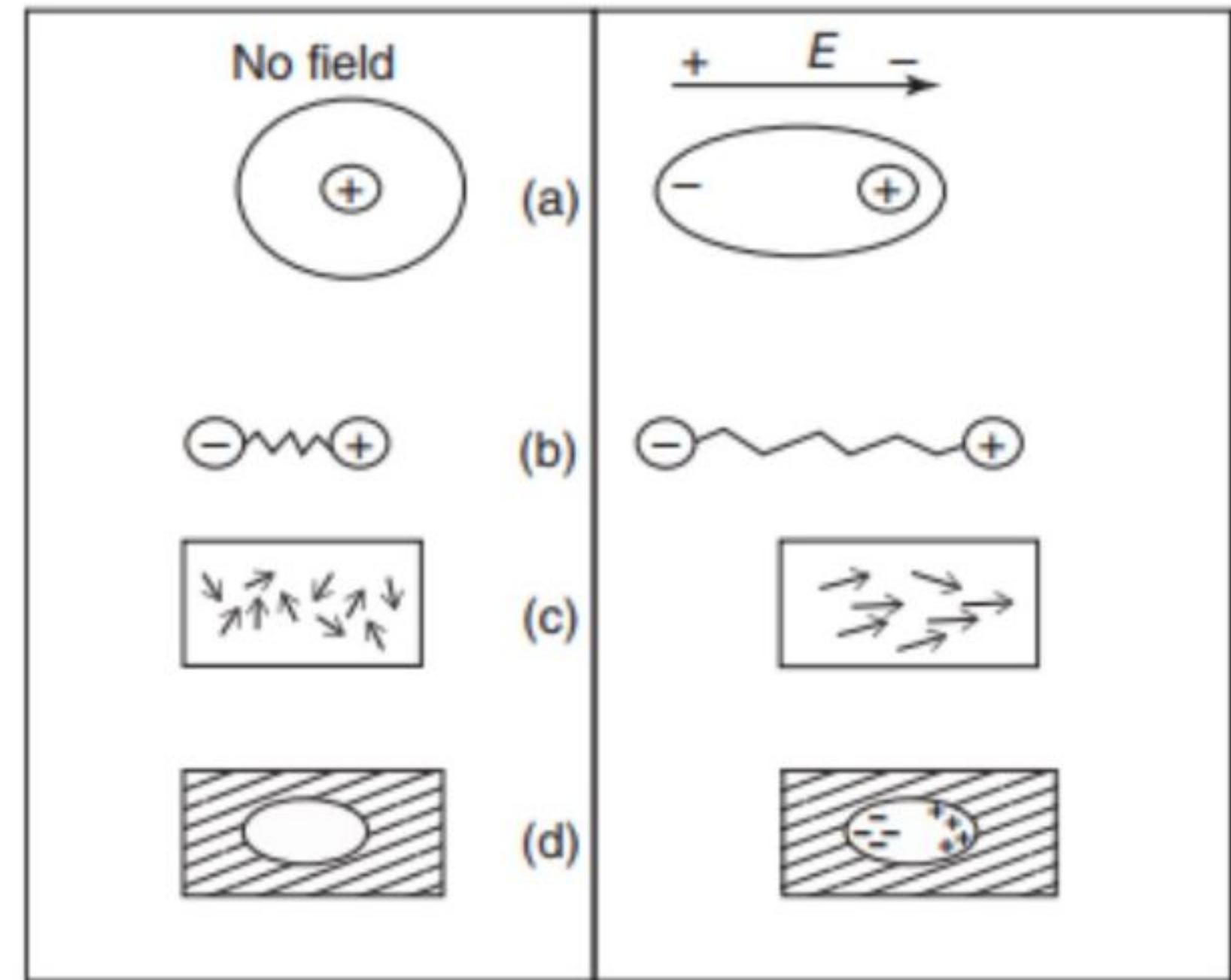
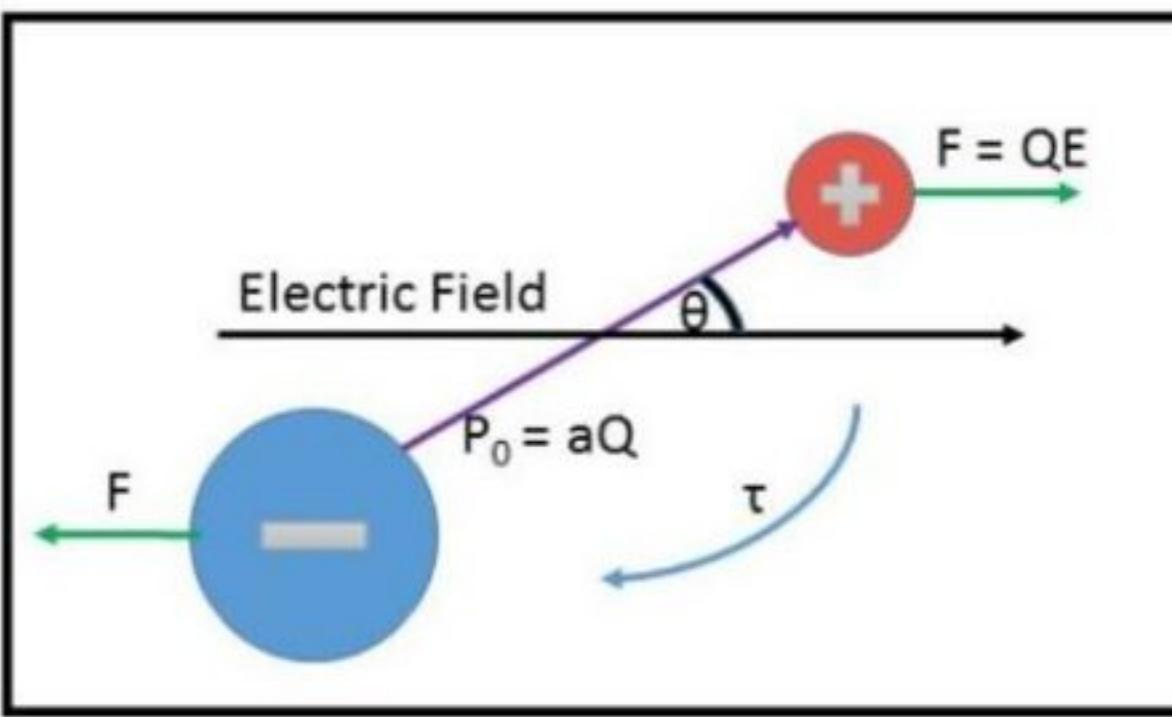
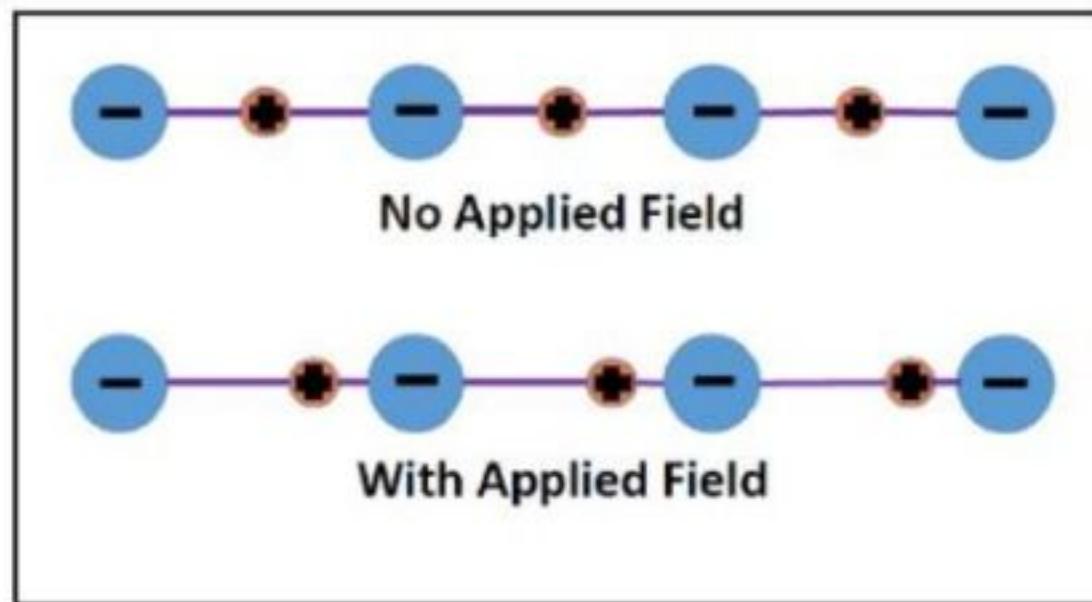
Electric field

$\chi_e$  is the **electric susceptibility** and  $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$



**Figure 9.2** Mechanisms leading to microscopic electric polarization. (a) The electric field polarizes all the atoms in the solid. (b) In ionic solids, like NaCl, the lattice can be polarized, giving rise to local electric dipoles. The dashed grid gives the position of the

ions without an applied field. (c) If there are permanent dipoles in the solid and these are free to rotate, they orient themselves parallel to the field. A molecule with a permanent dipole is, for example, water.

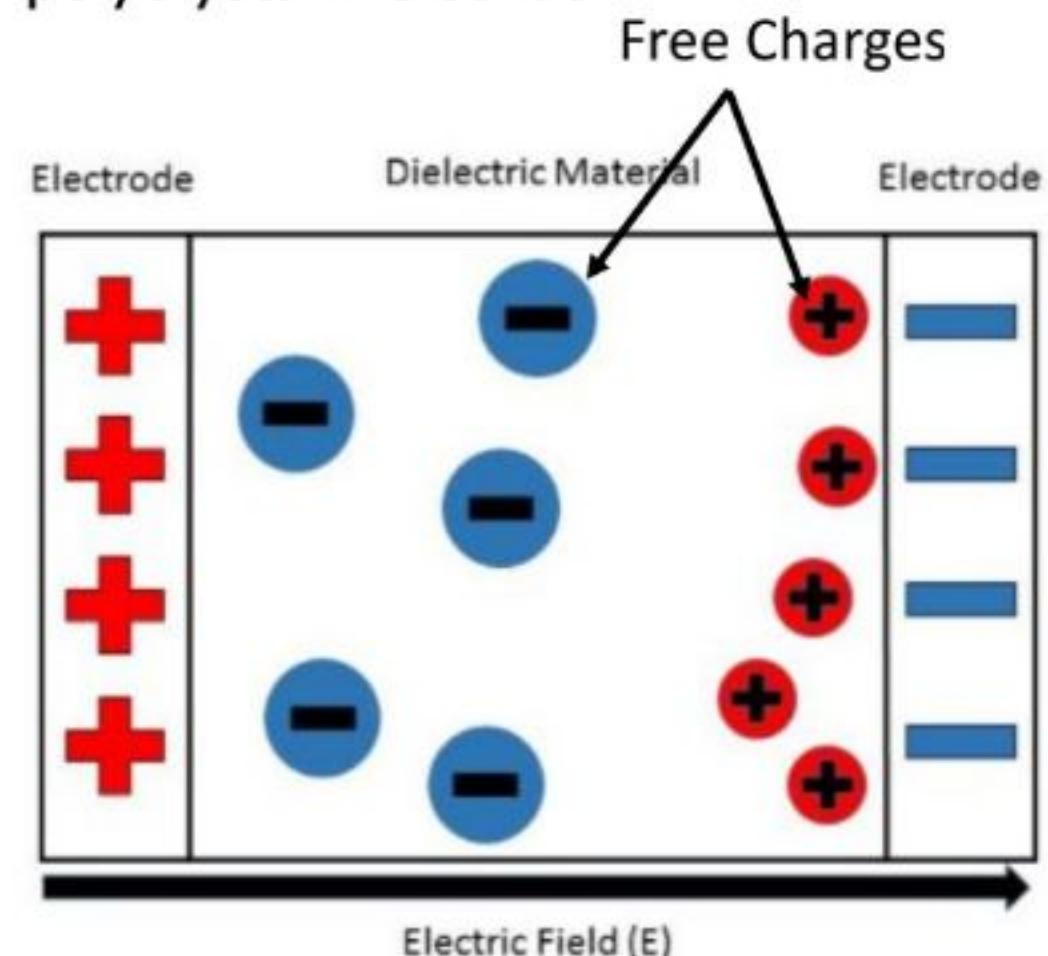


**Figure 1.8** Polarization processes:  
 (a) electronic polarization, (b) ionic polarization,  
 (c) orientational polarization, and (d) space charge polarization.

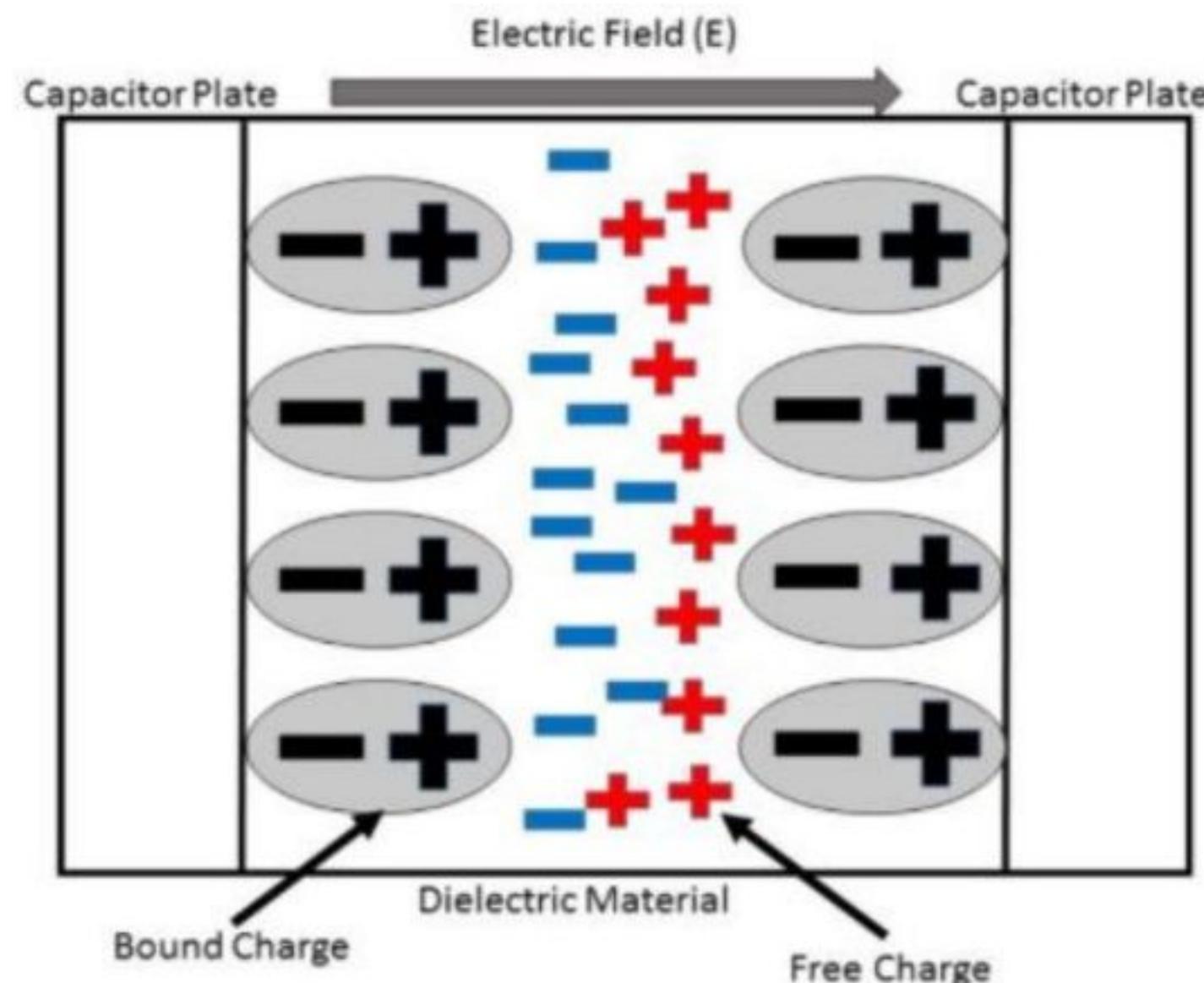
## Interfacial Polarization or Space Charge Polarization

- It occurs when there is an accumulation of charge at an interface between two materials or between two regions within a material because of an external field. This can occur when there is a compound dielectric, or when there are two electrodes connected to a dielectric material.
- This type of electric polarization is different from orientational and ionic polarization because instead of affecting bound positive and negative charges i.e. ionic and covalent bonded structures, interfacial polarization also affects free charges as well.
- As a result interfacial polarization is usually observed in amorphous or polycrystalline solids.

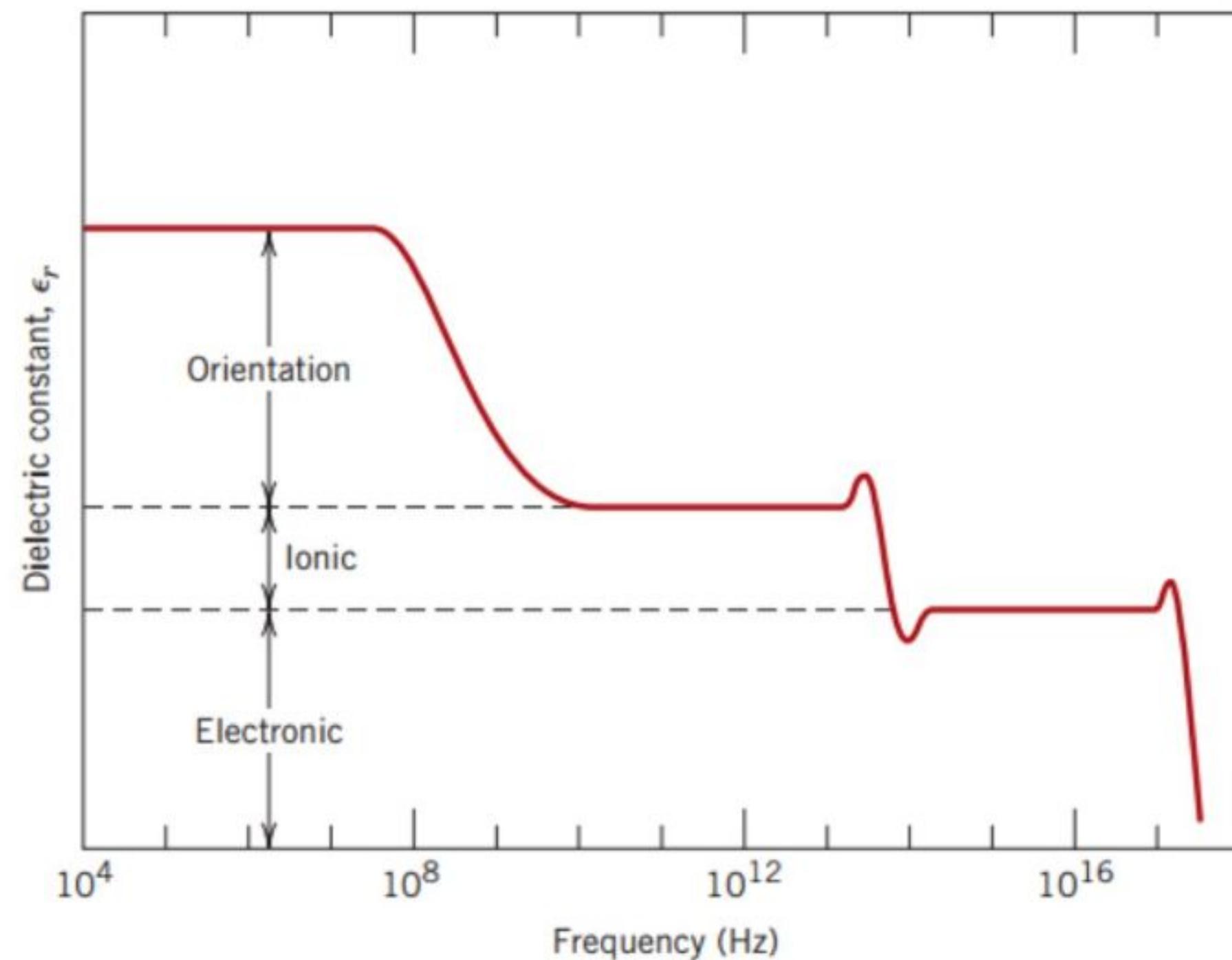
- The electric field will cause a charge imbalance because of the dielectric material's insulating properties.
- However, the mobile charges in the dielectric will migrate over maintain charge neutrality. This then causes interfacial polarization



## Dielectric Polarization



# Dielectric Constant



### Dielectric constant of some well known substances

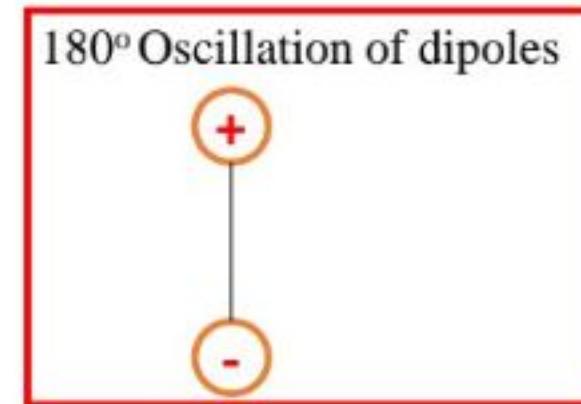
Material	$\epsilon_r$
Air (1 atm)	1.00054
Water (20°C)	80.4
C <sub>2</sub> H <sub>5</sub> OH	25
Diamond	6.6
Glass	19
Paper	3.5
Polystyrene	6.2

- A dielectric becomes polarised in an electric field. Now imagine switching the direction of the field. The direction of the polarisation will also switch in order to align with the new field. This cannot occur instantaneously: some time is needed for the movement of charges or rotation of dipoles.
- If the field is switched, there is a characteristic time that the orientational polarisation (or average dipole orientation) takes to adjust, called the relaxation time.
- Typical relaxation times are  $\sim 10^{-11}$  s.
- Therefore, if the electric field switches direction at a frequency higher than  $\sim 10^{11}$  Hz, the dipole orientation cannot ‘keep up’ with the alternating field, the polarisation direction is unable to remain aligned with the field, and this polarisation mechanism ceases to contribute to the polarisation of the dielectric.

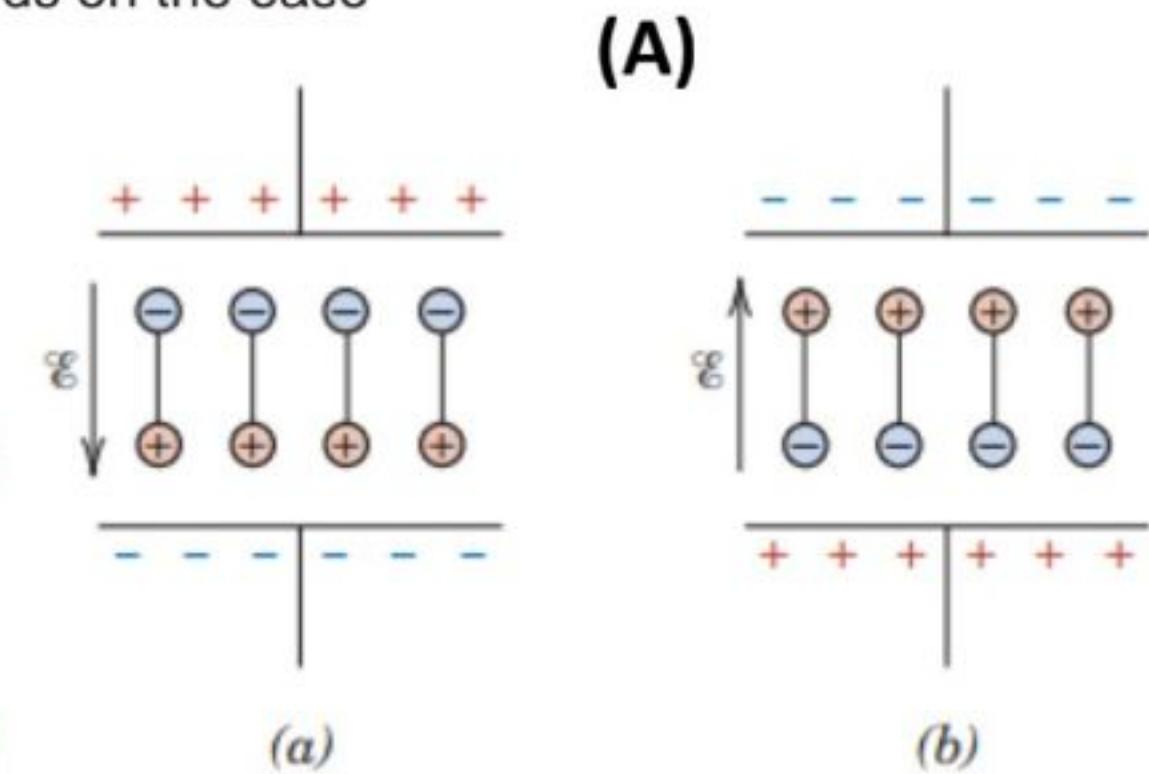
## Dielectrics Losses

- For each polarization type, some **minimum reorientation time exists**, which depends on the ease with which the particular dipoles are capable of realignment.
- A **relaxation frequency** is taken as the reciprocal of this minimum reorientation time
- A dipole cannot keep shifting orientation direction when the frequency of the applied electric field exceeds its relaxation frequency and, therefore, will not make a contribution to the dielectric constant.
- The absorption of electrical energy by a dielectric material that is subjected to an alternating electric field is termed **dielectric loss**.
- A low dielectric loss is desired at the frequency of utilization.

(B)



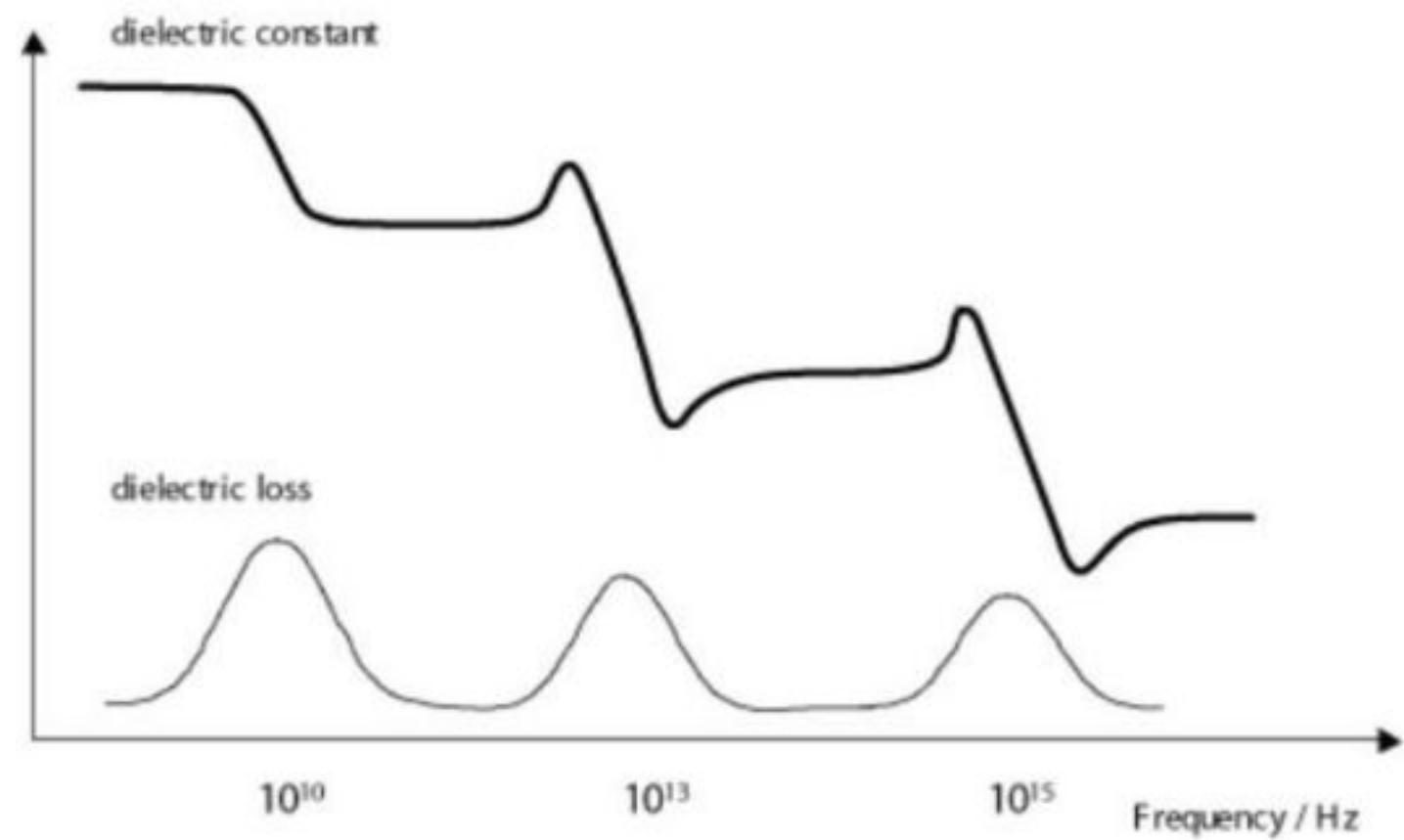
Animation



# Dielectric Loss

- Dielectric loss is the dissipation of energy through the movement of charges in an alternating electromagnetic field as polarisation switches direction.
- Dielectric loss is especially high around the relaxation or resonance frequencies of the polarisation mechanisms as the polarisation lags behind the applied field, causing an interaction between the field and the dielectric's polarisation that results in heating.
- Dielectric loss tends to be higher in materials with higher dielectric constants. This is the downside of using these materials in practical applications.
- Dielectric loss is utilized to heat food in a microwave oven

the frequency of the microwaves used is close to the relaxation frequency of the orientational polarisation mechanism in water, meaning that any water present absorbs a lot of energy that is then dissipated as heat. The exact frequency used is slightly away from the frequency at which maximum dielectric loss occurs in water to ensure that the microwaves are not all absorbed by the first layer of water they encounter, therefore allowing more even heating of the food.



## Dielectric Loss Factor

- If the voltage used to maintain the charge on a capacitor is sinusoidal, as is generated by an alternating current, **the current leads the voltage by 90 degrees when a loss-free dielectric is between the plates of a capacitor.**
- However, when a real dielectric is used in the capacitor, the current leads the voltage by  $(90^\circ - \delta)$ , where the angle  $\delta$  is called the **dielectric loss angle**.
- The product of dielectric constant( $\kappa$ )  $\tan \delta$  is designated the **loss factor** and is a **measure of the electric energy lost (as heat energy)** by a capacitor in an ac circuit.

In circuits with primarily capacitive loads, current leads the voltage. This is true because current must first flow to the two plates of the capacitor, where charge is stored. Only after charge accumulates at the plates of a capacitor is a voltage difference established.

## Dielectric Breakdown

If the electric field across an insulator is too high, the insulator will start to conduct a current. This phenomenon is known as dielectric breakdown.

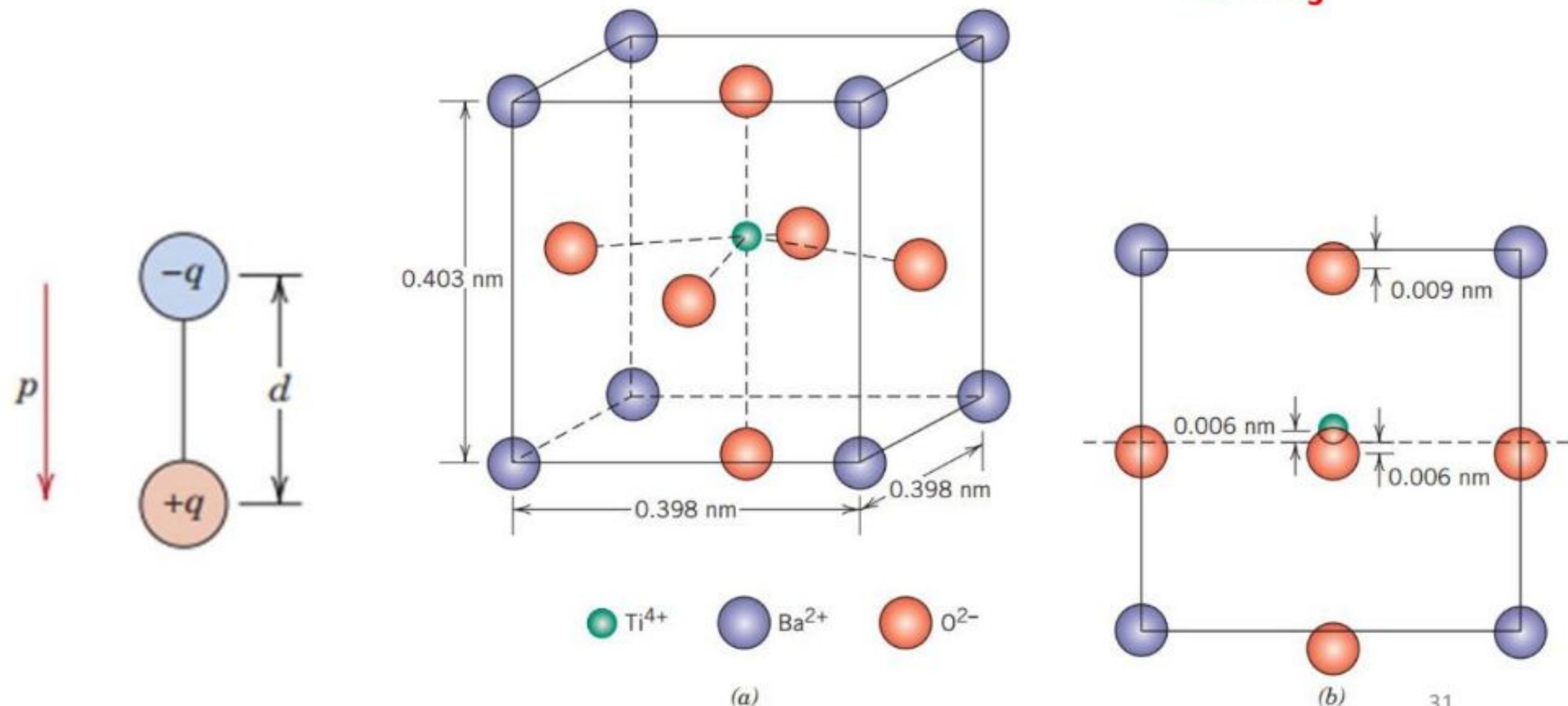
The mechanism for the breakdown is that some free carriers (e.g., caused by impurities) are accelerated in the field, so much that they can ionize other atoms and generate more free carriers. Then, the breakdown proceeds like an avalanche.

The breakdown can be facilitated by operating the material close to a resonance frequency where much energy is dissipated, the material is heated, and the probability of having free carriers is increased.

# Ferroelectric Materials

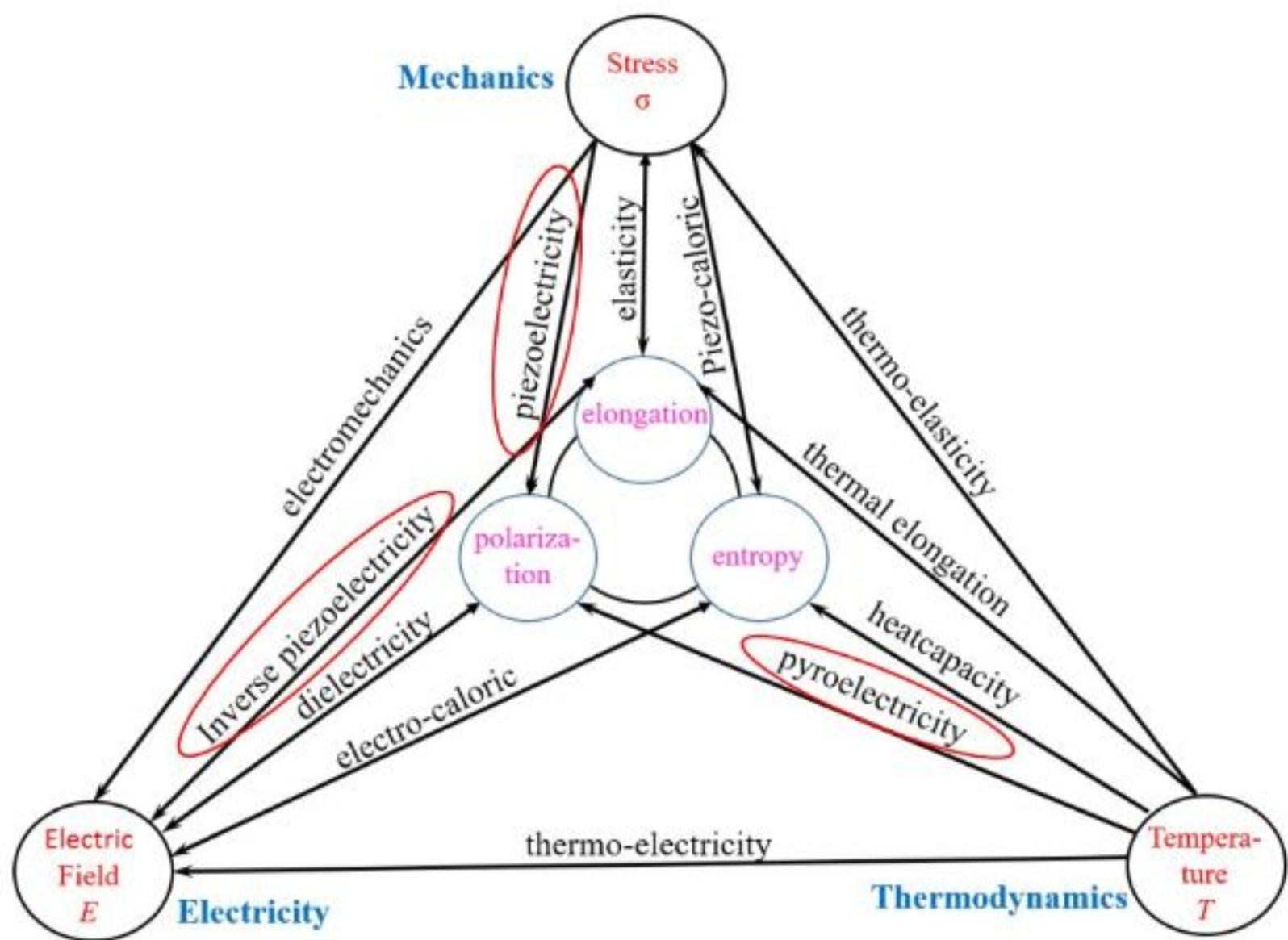
# FERROELECTRICITY

The group of dielectric materials called **ferroelectrics** exhibit spontaneous polarization—that is, polarization in the absence of an electric field. They are the dielectric analogue of ferromagnetic materials, which may display permanent magnetic behavior.



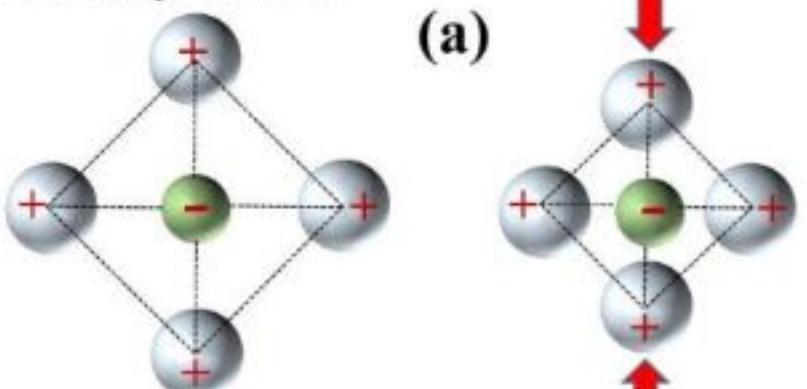
# Ferroelectric materials:

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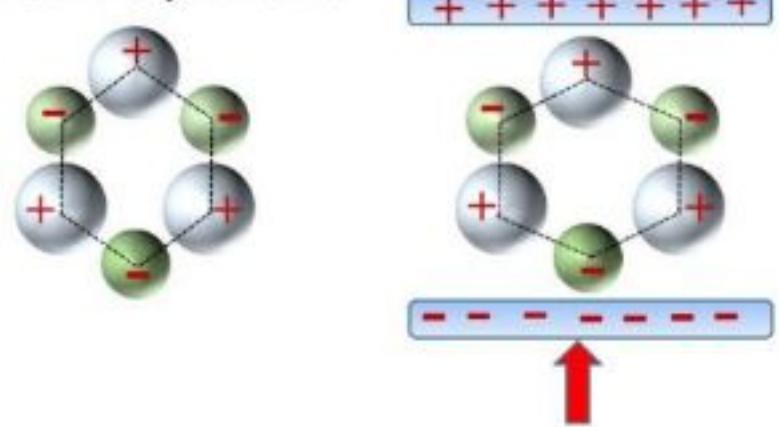


Conversion of energy in ferroelectric materials (Heckmann diagram).

Centrosymmetric



Non-Centrosymmetric

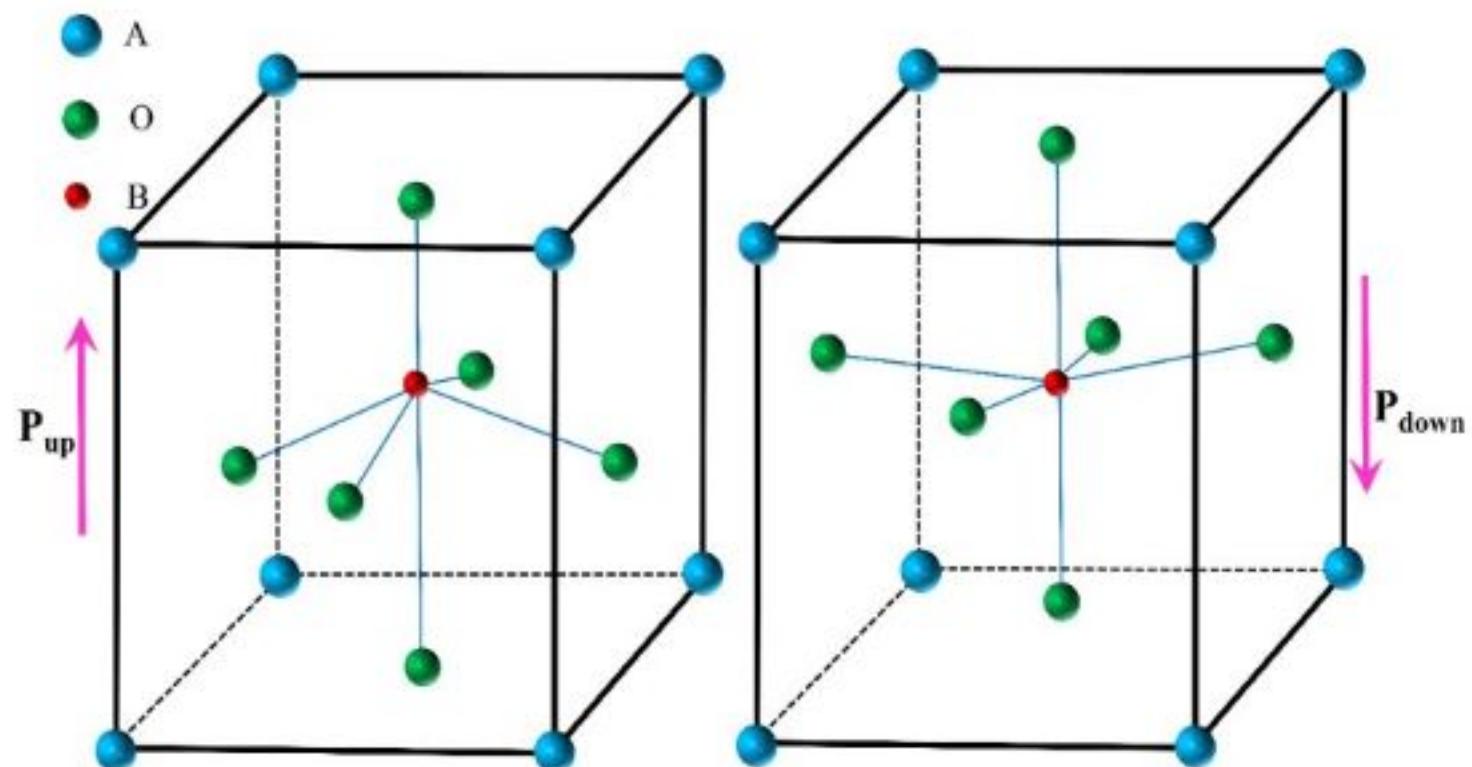


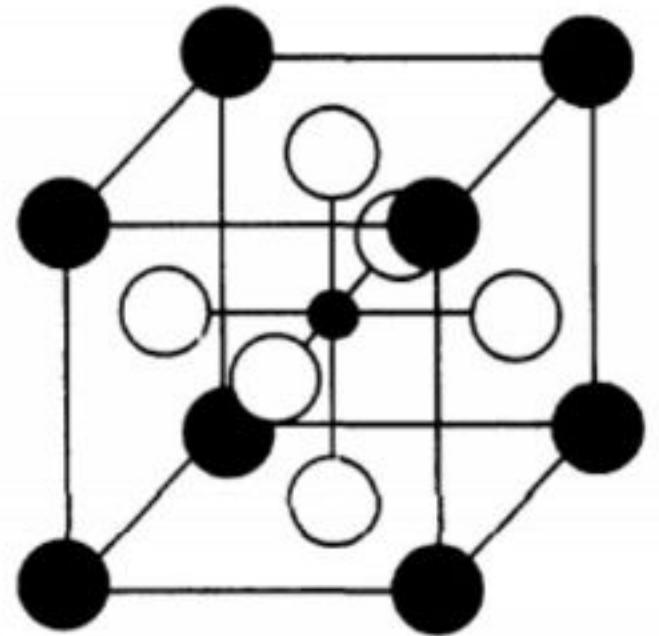
Perovskite structure of oxides  $\text{ABO}_3$

ferroelectric

phase with upward and downward polarization.

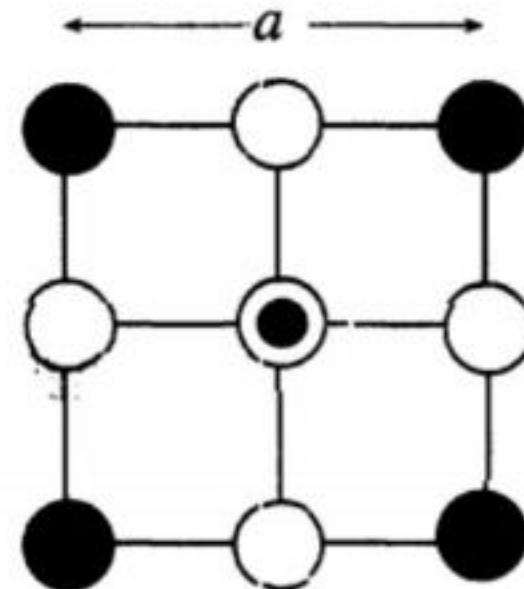
Non-centrosymmetric structure and origin of piezoelectricity (a) centrosymmetric structure and (b) non-centrosymmetric structure



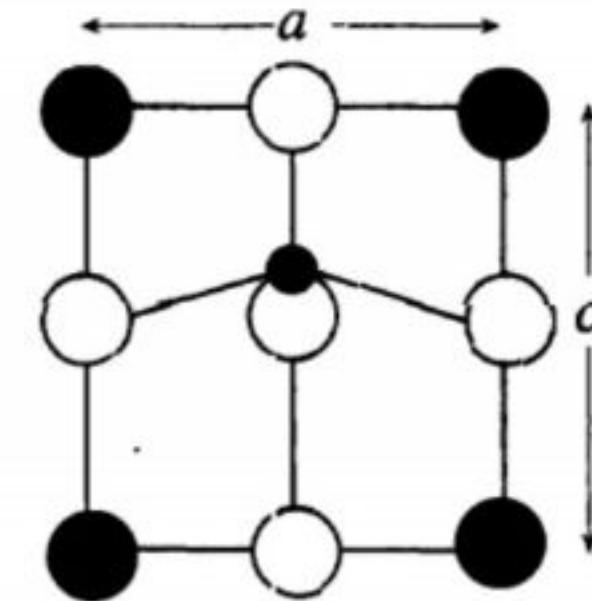


(a)  $\text{BaTiO}_3$  cubic crystal structure  
above  $130\text{ }^\circ\text{C}$

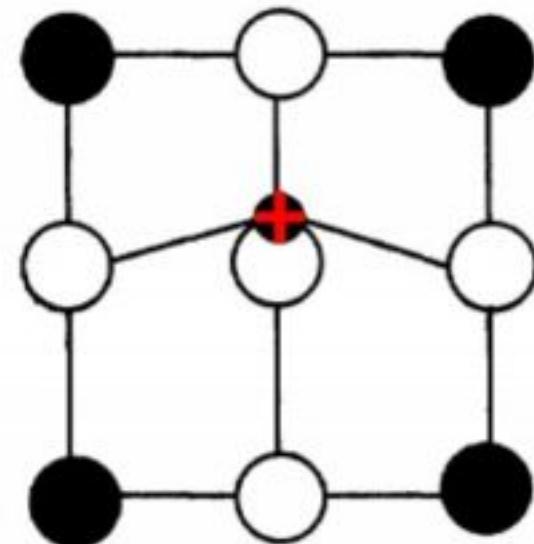
●  $\text{Ba}^{2+}$   
○  $\text{O}^{2-}$   
●  $\text{Ti}^{4+}$



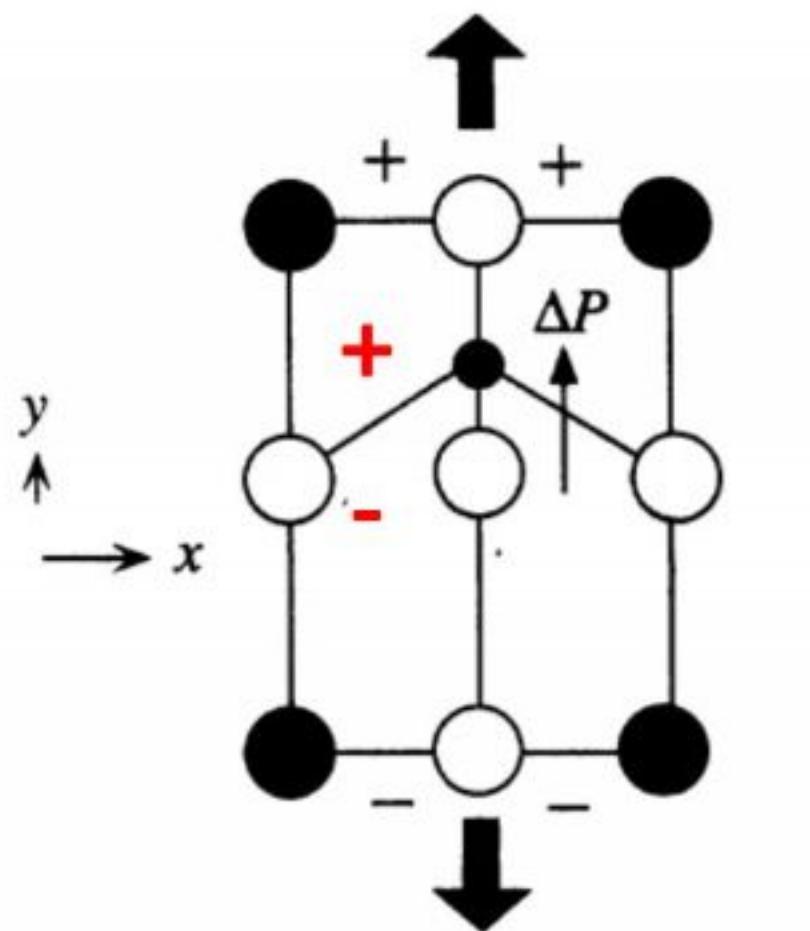
(b)  $\text{BaTiO}_3$  cubic structure  
above  $130\text{ }^\circ\text{C}$



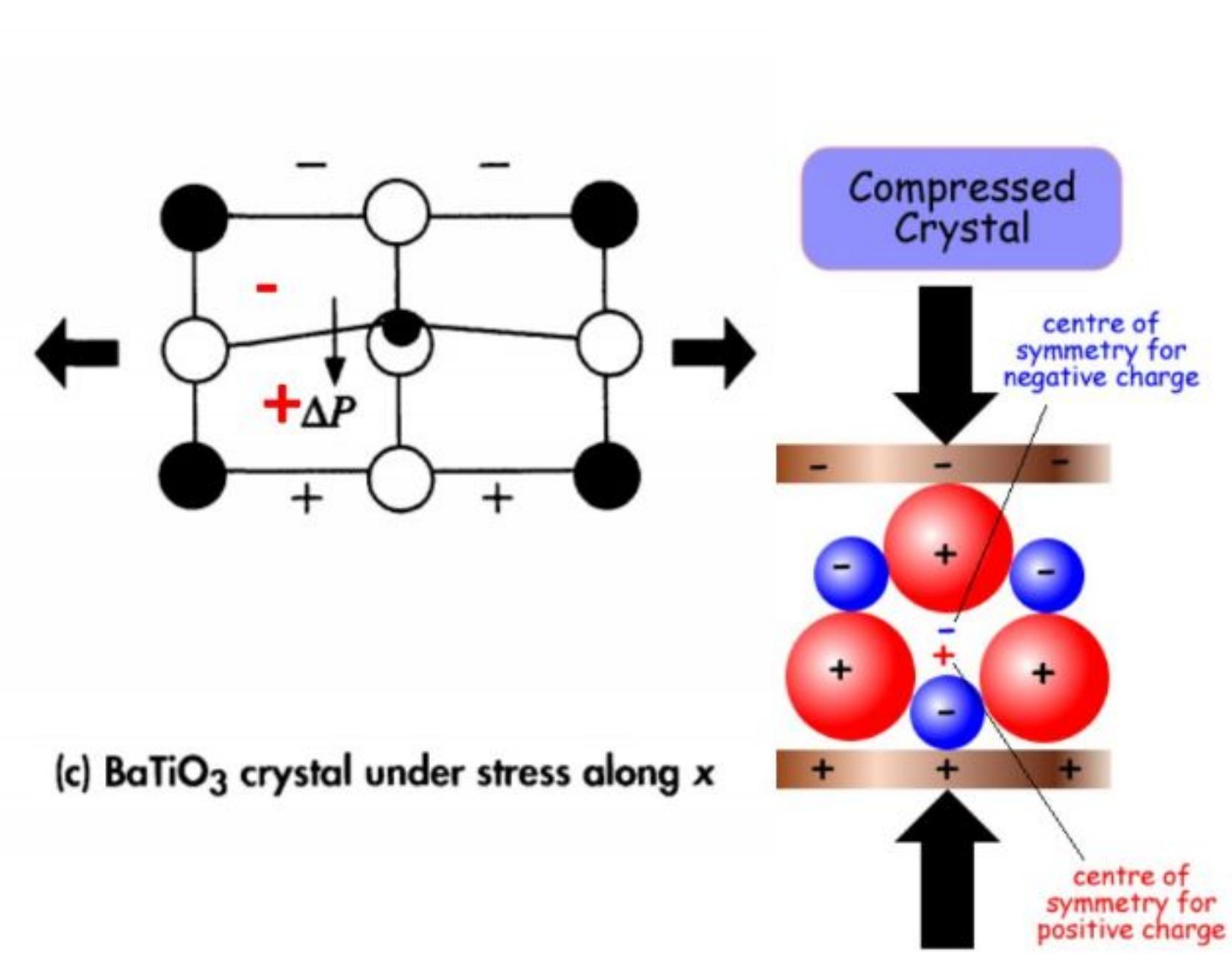
(c)  $\text{BaTiO}_3$  tetragonal structure  
below  $130\text{ }^\circ\text{C}$



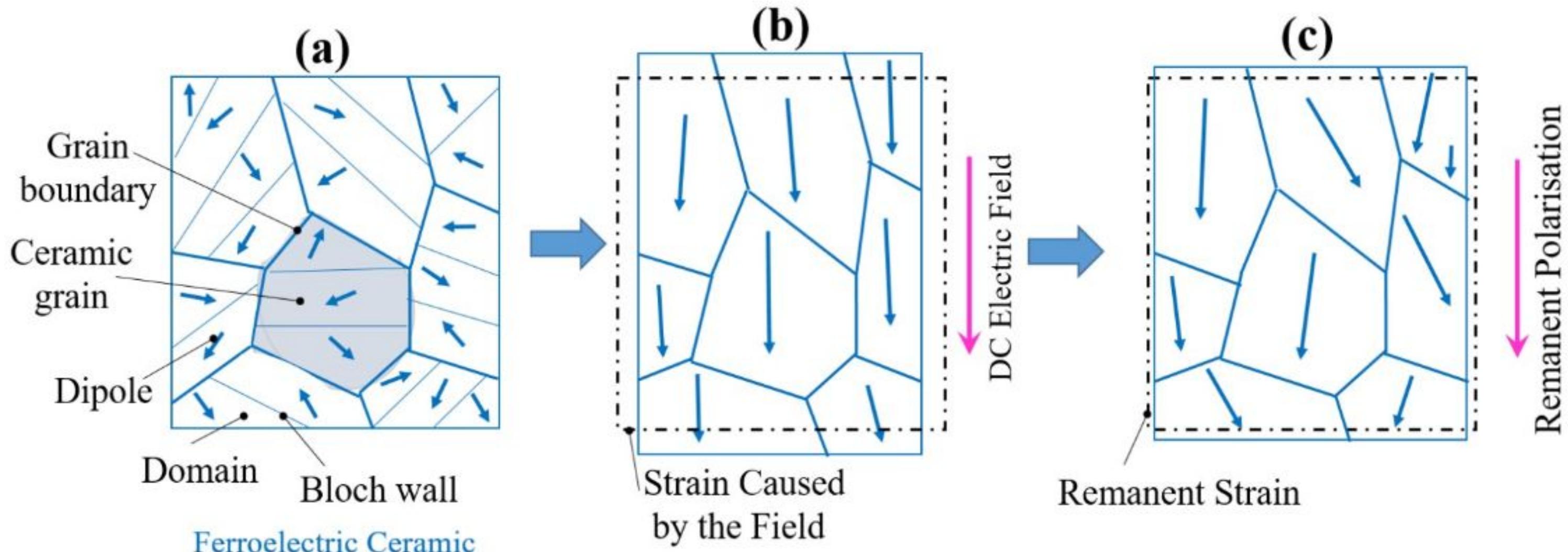
(a)  $\text{BaTiO}_3$  tetragonal structure below 130 °C



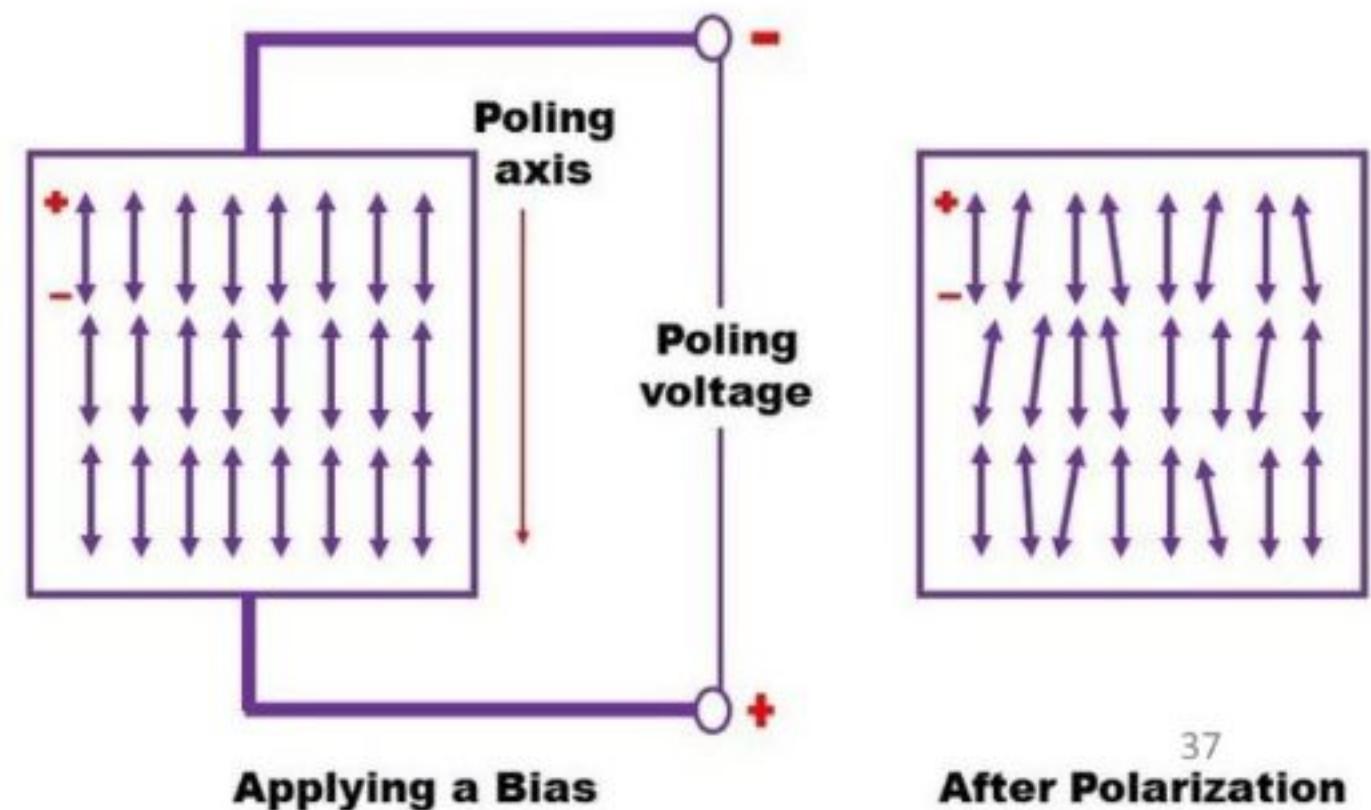
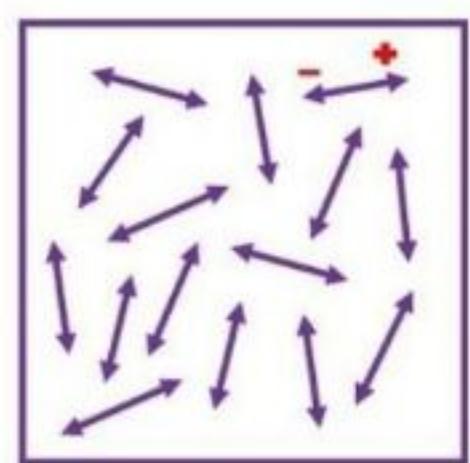
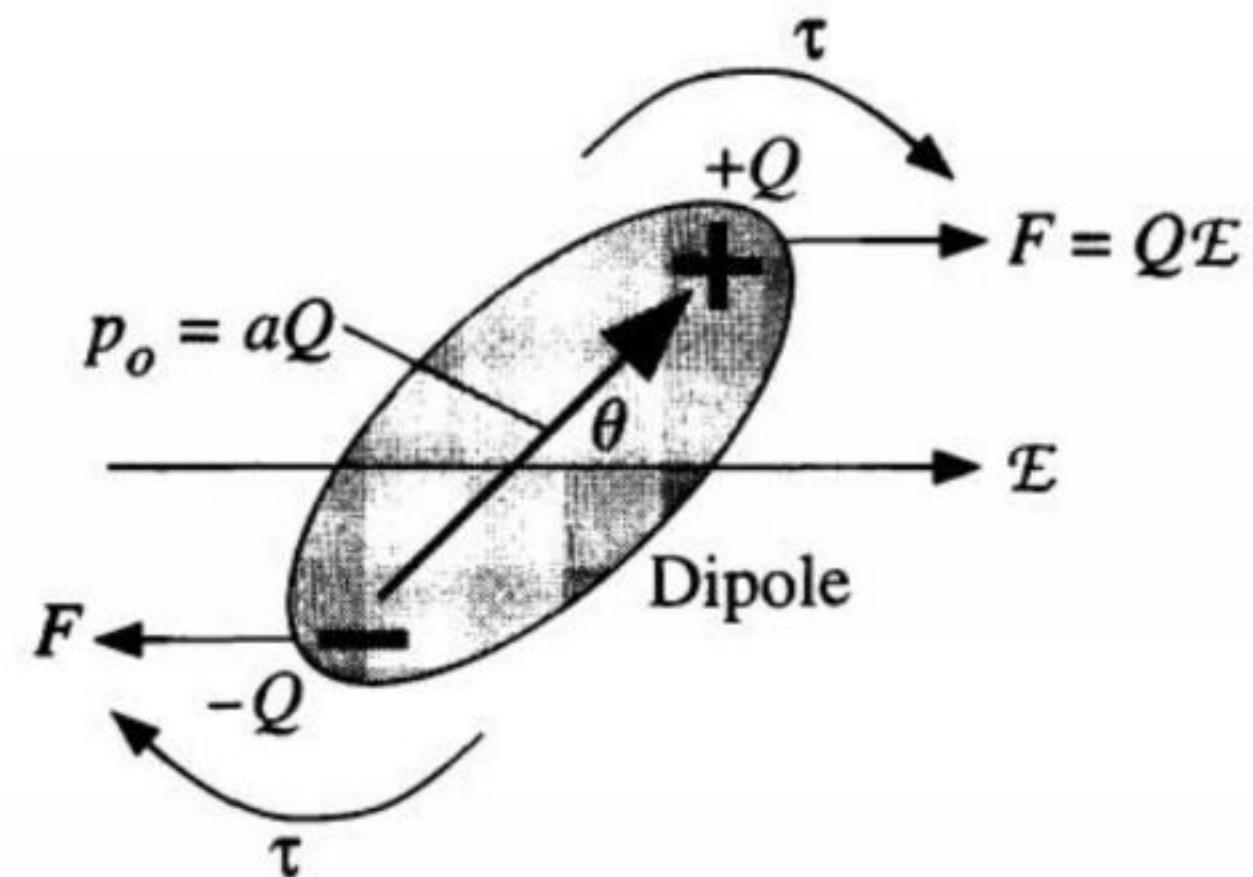
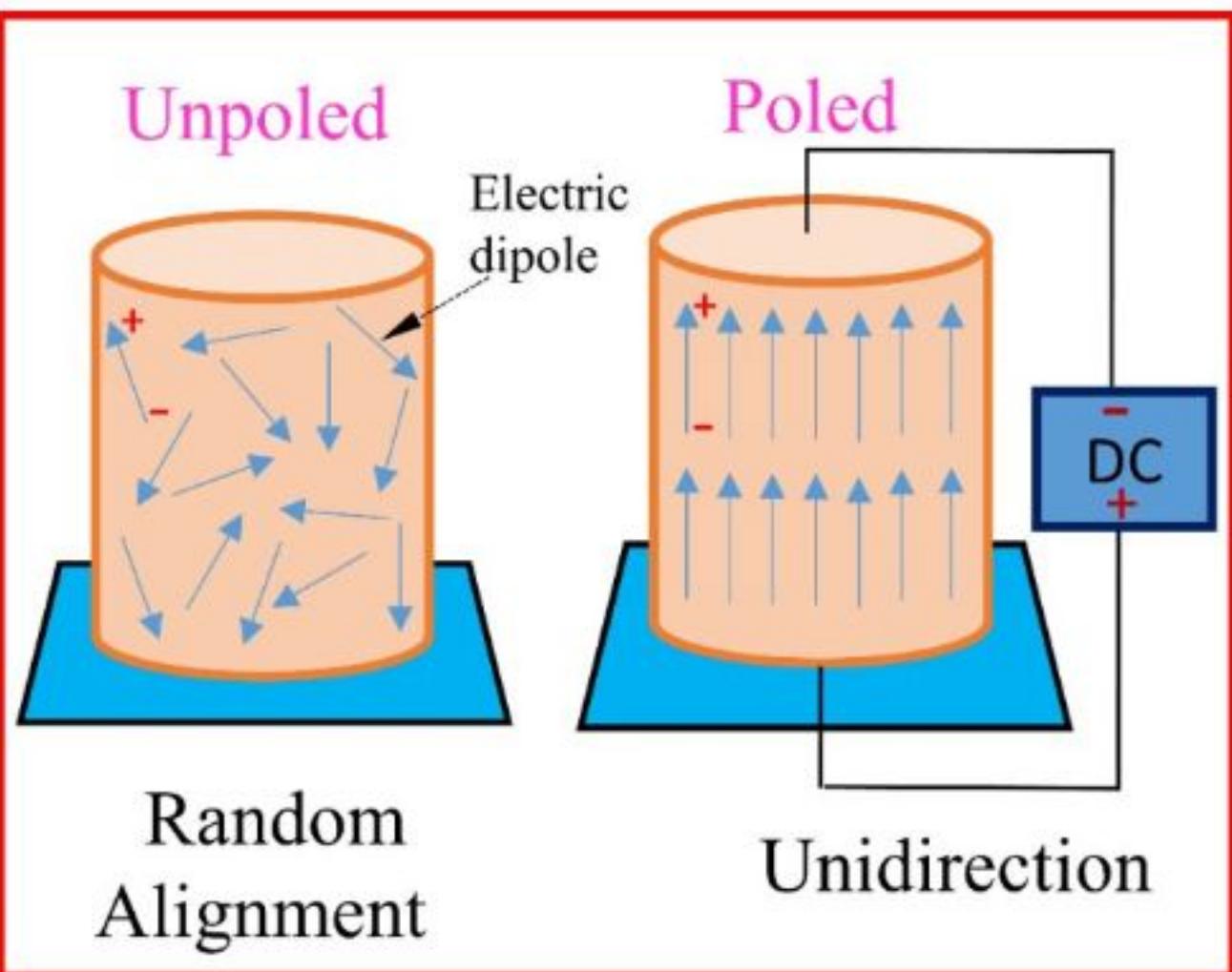
(b)  $\text{BaTiO}_3$  crystal under stress along  $y$

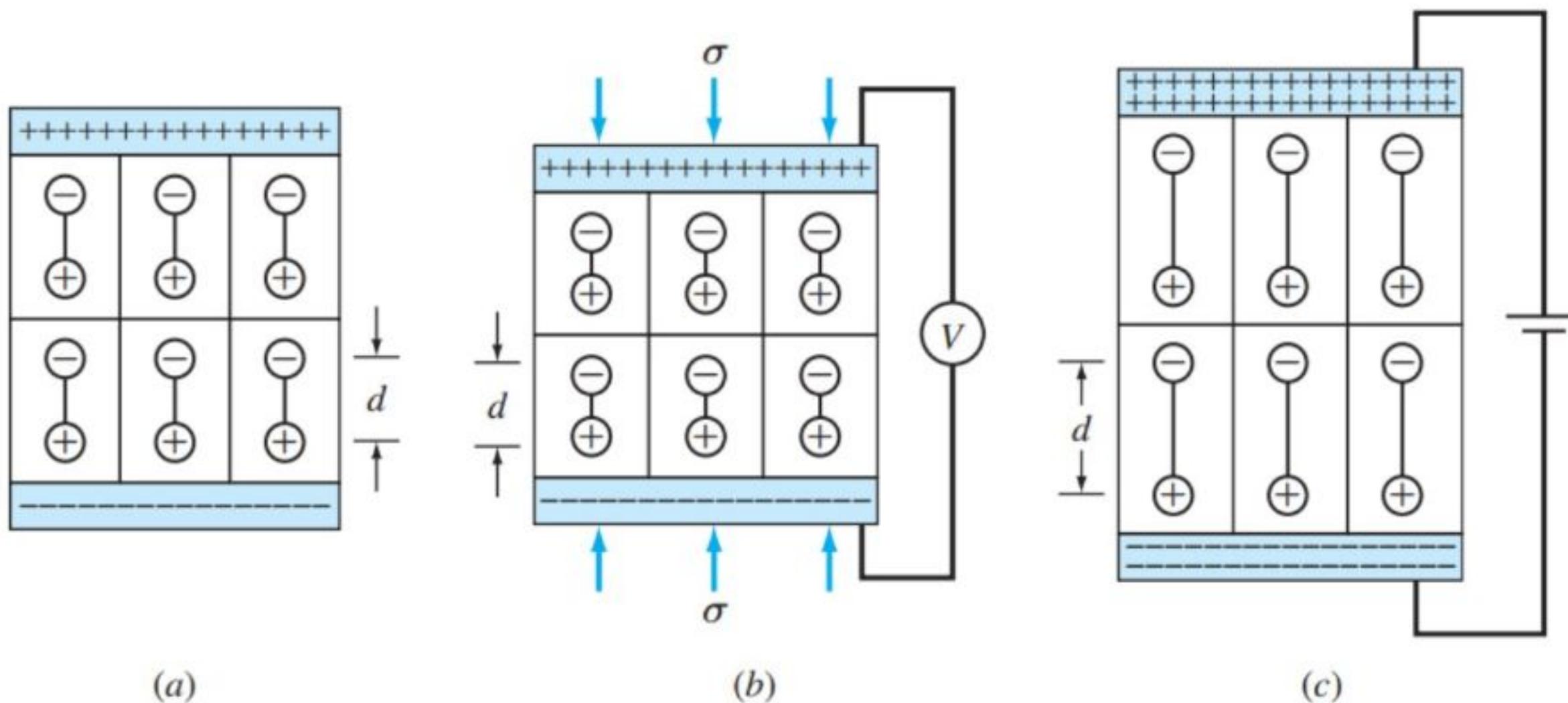


(c)  $\text{BaTiO}_3$  crystal under stress along  $x$



**Fig. 5** Dipole configuration in ferroelectric mateirals.

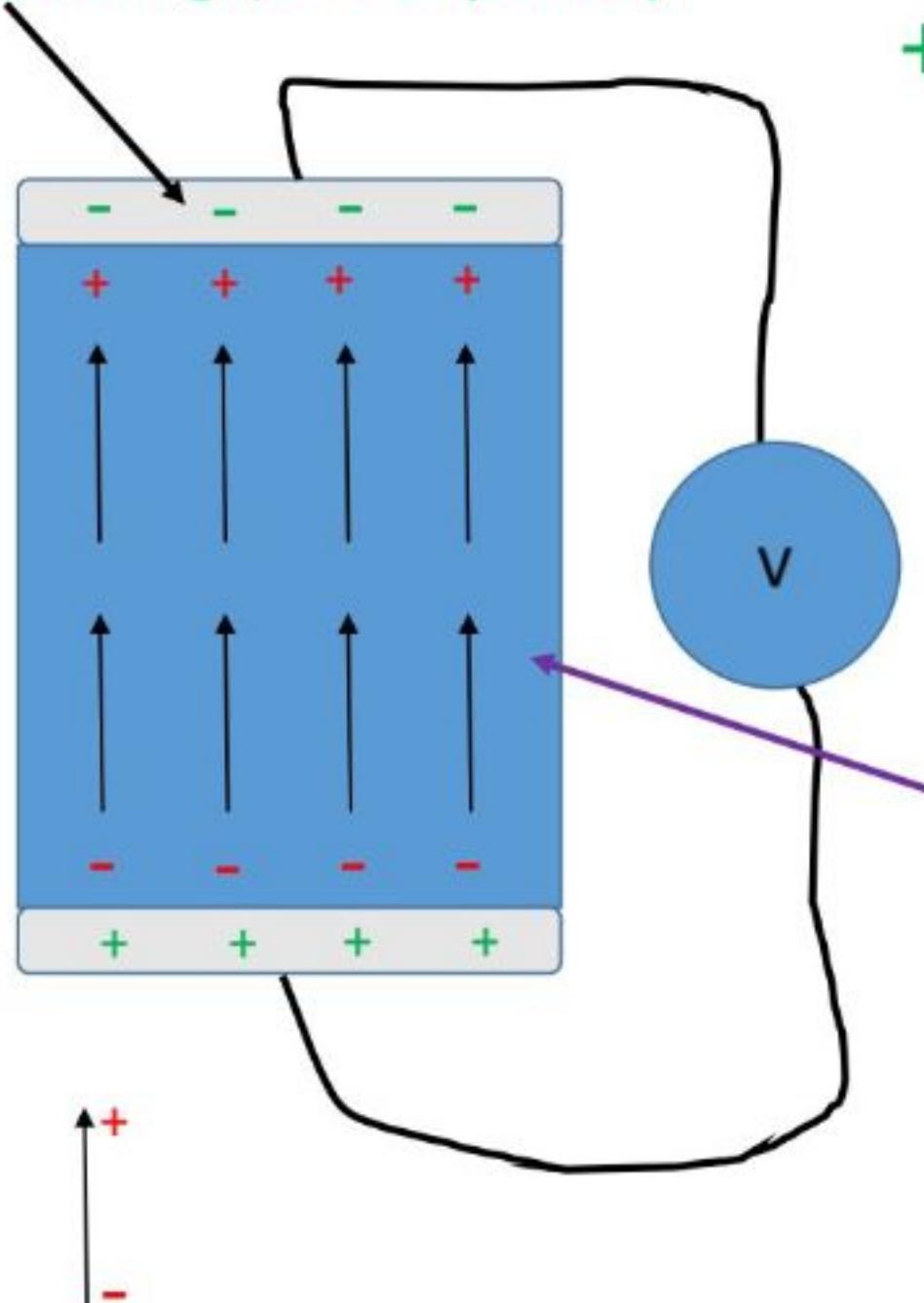




- (a) Schematic illustration of electric dipoles within a piezoelectric material.
- (b) Compressive stresses on material cause a voltage difference to develop due to change in electric dipoles.
- (c) Applied voltage across ends of a sample causes a dimensional change and changes the electric dipole moment.

# Review of Voltage or Charge Measurement in Piezo and Pyroelectrics

Electroding (Silver paste)



+ - = Bounded Charge

+ - = Free Charge

Bounded Charge density changes due to the change in the Polarisation state of the sample which is further dependent on the external stimulus such as mechanical force or change in temperature

# Depolarisation

## 1. Thermal depoling

If the material is exposed to excessive heat, such that its temperature approaches its Curie temperature, the dipole moments regain their unaligned state. At the Curie temperature, a ferroelectric becomes entirely unaligned. In order to prevent this occurring, it is sensible to use piezoelectrics well below their Curie temperature.

## 2. Electrical depoling

A strong electric field, when applied in the reverse direction to the already poled material, will lead to depoling. If an alternating field is used to produce ultrasound waves (see later) the field will depolarise the piezoelectric during the periods in which it is opposing the polarisation.

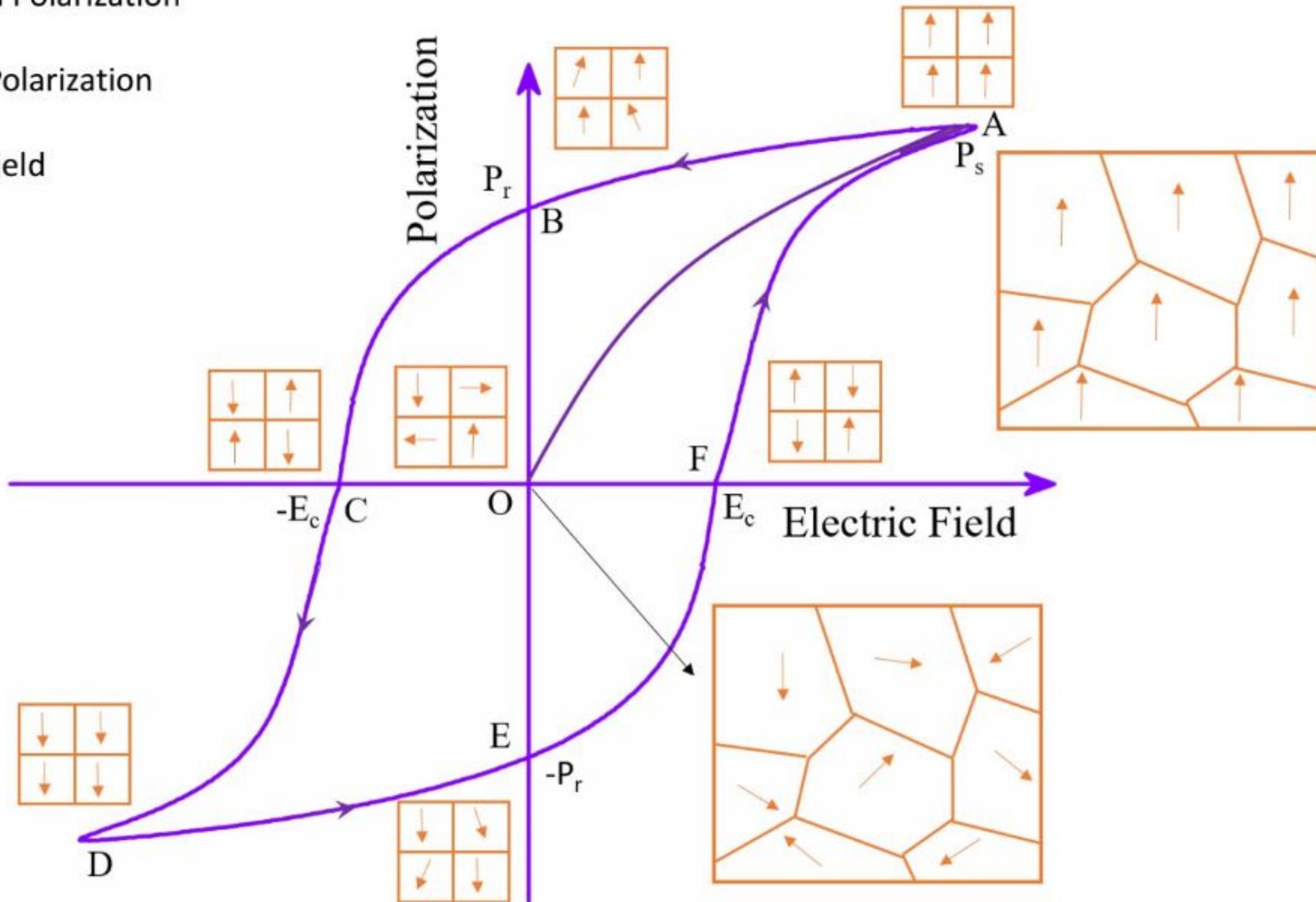
## 3. Mechanical depoling

If the stress placed on a piezoelectric is too high, it is possible to immediately depolarise the piezoelectric as the atom positions are altered. This completely ruins its properties.

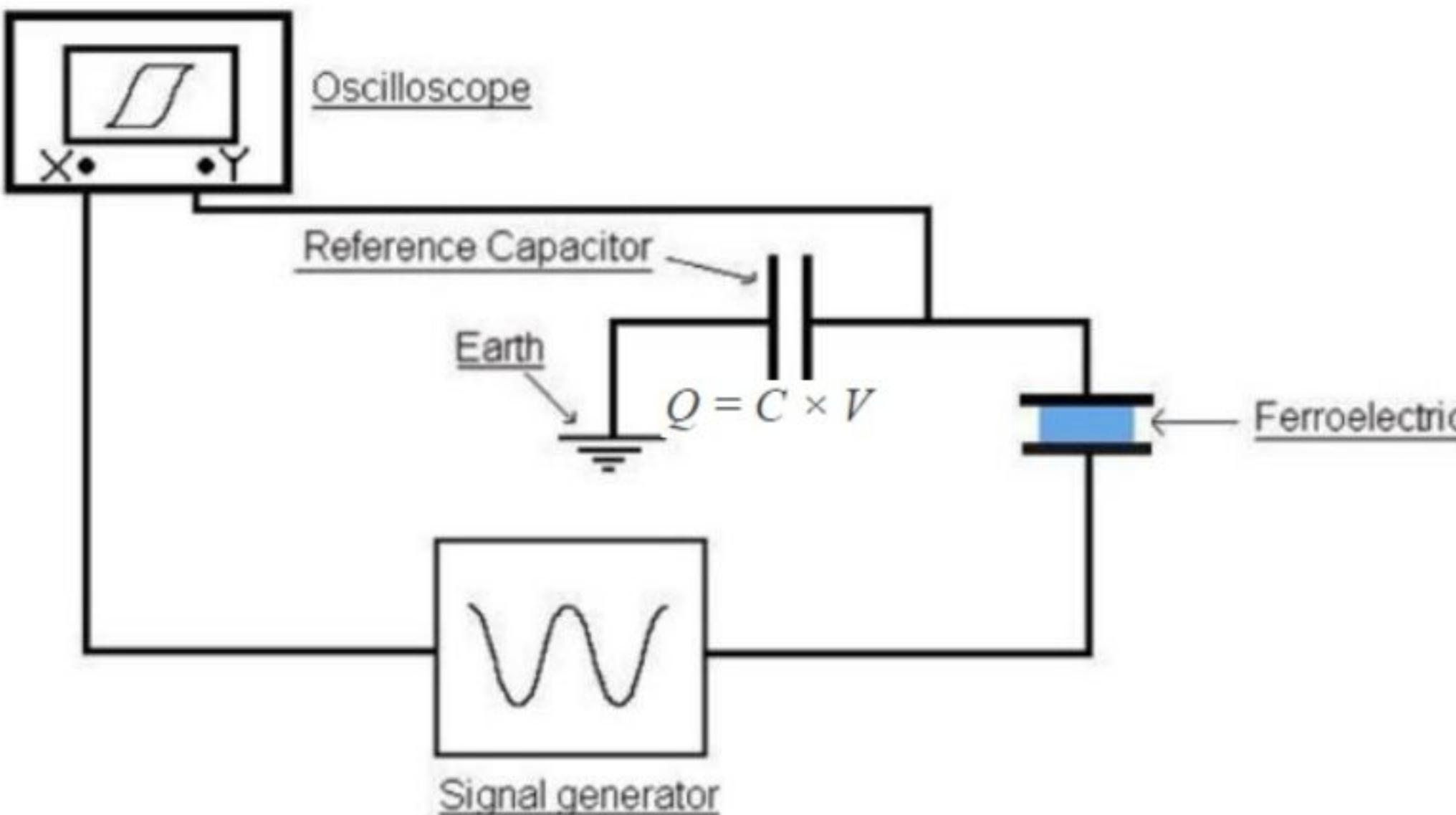
A = Saturation Polarization

B= Remnant Polarization

C= Coercive Field



# Sawyer Tower Circuit for P-E loop measurement



Polarization = Dipole moment / Volume

= C.m /m<sup>3</sup>

= C/m<sup>2</sup>

= Charge/ Area

## Explanation:

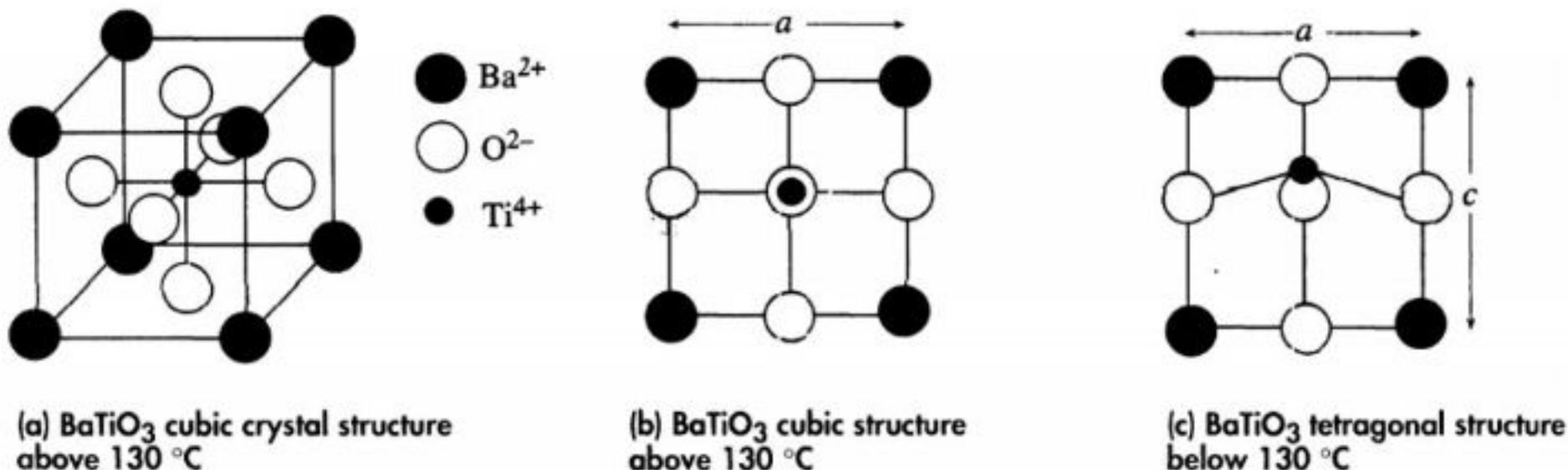
- In this experiment, the voltage is cycled by the signal generator. Its direction is reversed at high frequency, and the voltage across the reference capacitor is measured.
- The charge on the capacitor must be the same as the charge over the ferroelectric capacitor, as they are in series. This means the charge on the ferroelectric can be found by:

$$Q = C \times V$$

where  $C$  is the capacitance of the reference capacitor, and  $V$  is the voltage measured over this capacitor.

- We can therefore represent the polarisation of a material in an oscillating electric field, by plotting the voltage applied to the material on the x-axis of the oscilloscope, and the surface charge on the y-axis.
- This can be done because the capacitance of the reference capacitor is much higher than the capacitance of the ferroelectric, so most of the voltage lies over the ferroelectric. It is only possible to measure  $P$  by cycling the polarisation through cycling the voltage across the ferroelectric. We cannot measure absolute values instantaneously , but can deduce absolute values from the changes measured when cycling the polarisation.

**Curie Temperature:** The temperature at which the Ferroelectric properties or the capability to get spontaneous polarization is lost.

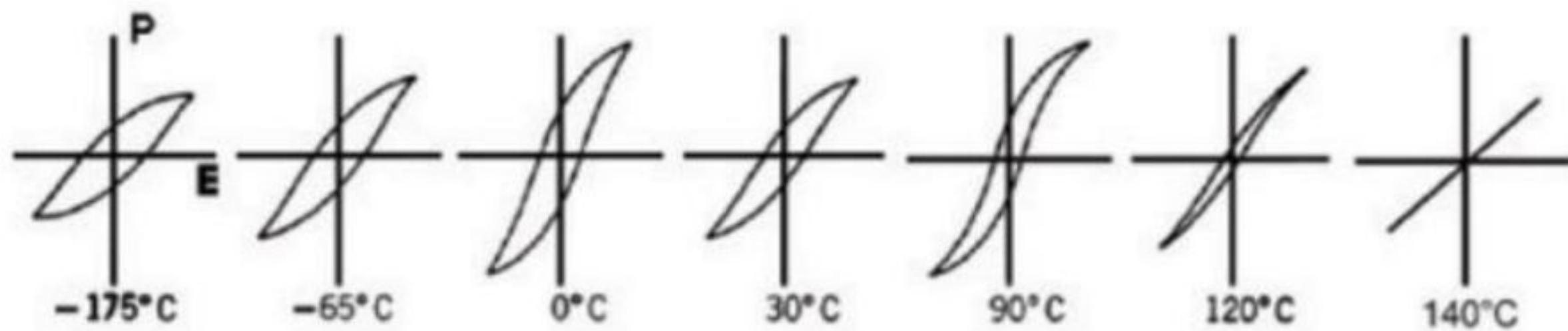


Material	$T_c$ /°C
Barium titanate, $\text{BaTiO}_3$	120
Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	Between -18 and +24
Potassium niobate, $\text{KNbO}_3$	434
Potassium dihydrogenphosphate, KDP, $\text{KH}_2\text{PO}_4$	-150
Lead titanate, $\text{PbTiO}_3$	490
Lithium niobate, $\text{LiNbO}_3$	1210
Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	675
Gadolinium molybdate, GMO, $\text{Gd}_2(\text{MoO}_4)_3$	159
Lead zirconate titanate, PZT, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$	Depends on $x$

## Temperature dependence of the Hysteresis loop

We have only observed it at one particular temperature, one at which the material is ferroelectric. What happens if the temperature is raised?

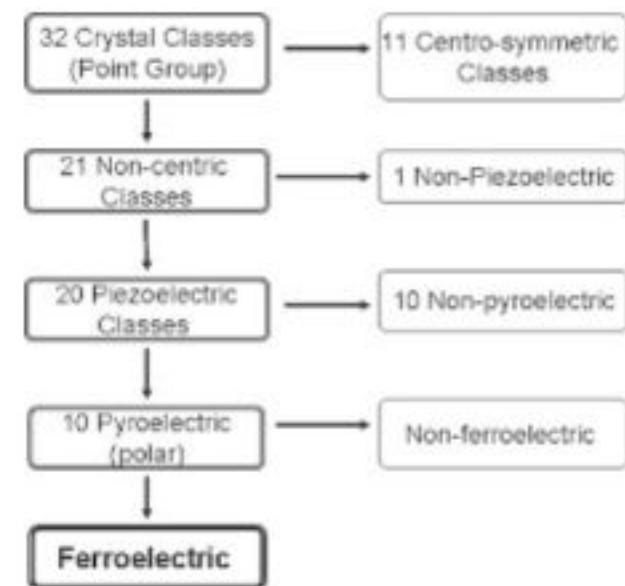
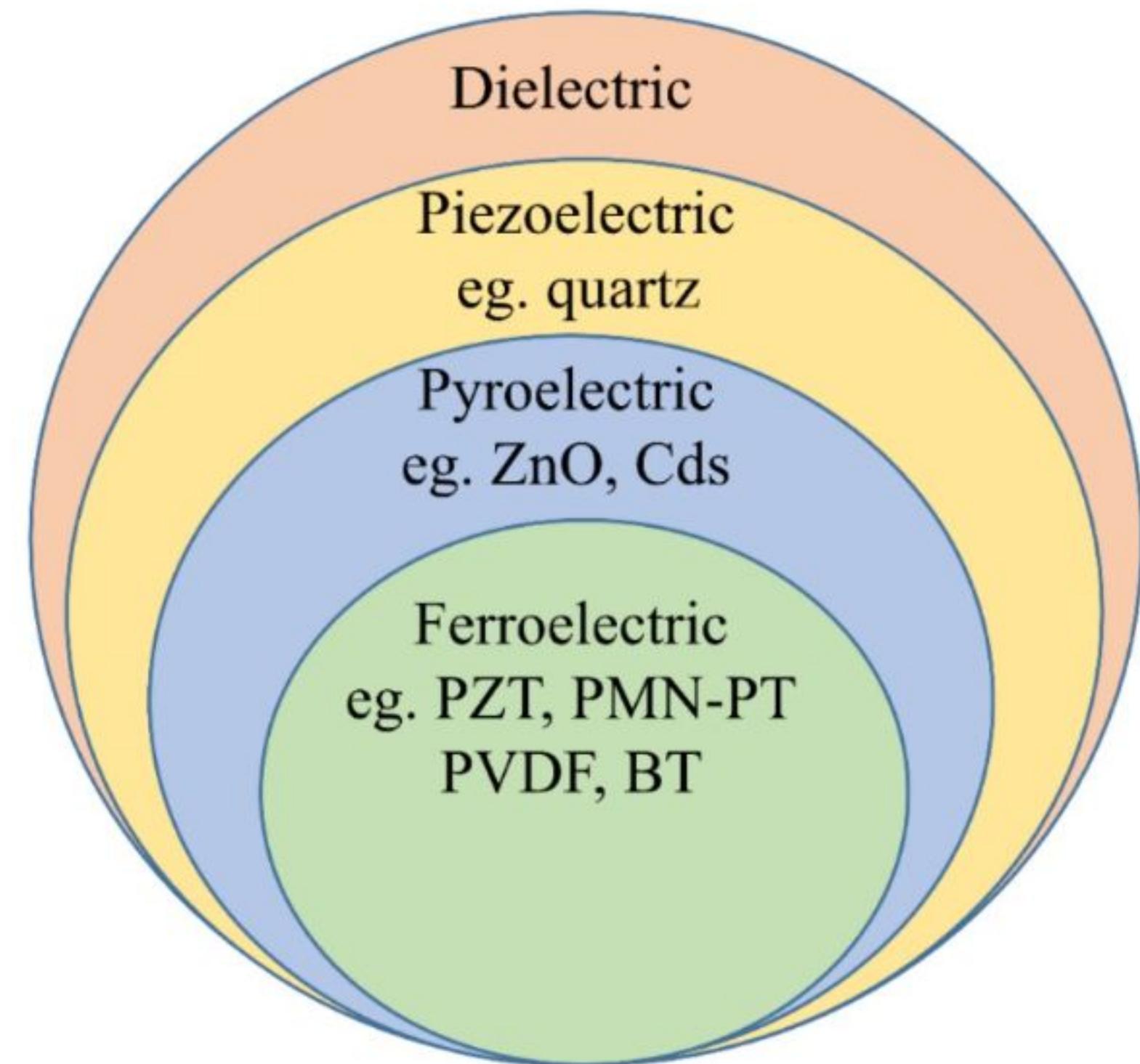
The hysteresis loop changes with temperature, becoming sharper and thinner, and eventually disappearing



As you can see, the polarisation increases at  $90^{\circ}\text{C}$ , as a result of a phase transition. Between this temperature and room temperature, the polarisation increases steadily, as a direct relation with temperature, such that:

$$\Delta P = p \Delta T$$

where  $p$  = pyroelectric coefficient ( $\text{C m}^{-2} \text{T}^{-1}$ ).



## Brief History of Pyroelectricity

Pyroelectricity as a phenomenon has been known for 24 centuries—the Greek philosopher **Theophrastus** probably wrote the earliest known account. He described a stone, called *lyngourion* in Greek or *lyncurium* in Latin, that had the **property of attracting straws and bits of wood.**

Those attractions were no doubt the effects of electrostatic charges produced by temperature changes most probably in the mineral tourmaline.

Theophrastus and other writers of the two millennia that followed were far more interested in the origin of the stone and its physical explanations. Theophrastus proposed that lyngourion was formed from the urine of a wild animal .

## Introduction

- Pyroelectrics are the bridge between ferroelectrics and piezoelectrics.
- They possess a spontaneous polarisation which is not necessarily switchable by an electric field.
- If their polarisation is switchable, i.e. they are ferroelectric, then they are mainly used in situations in which ferroelectric properties are required.
- However, if they are not ferroelectric, then their properties as pyroelectrics are more useful.
- Whether a given sample possesses a net dipole moment depends on domain configurations, which in turn depend on sample history. This polarisation will change when a stress is applied to the material, as pyroelectrics are a sub-set of piezoelectrics.
- But it will not reverse under the application of an electric field because it will breakdown first, i.e. the coercive field exceeds the breakdown field.
- This is only true for a pyroelectric material which is not ferroelectric, whereas if it is ferroelectric, the coercive field is smaller than the breakdown field. In other words, ferroelectrics are a subset of pyroelectrics.

# Pyroelectricity

Pyro =fire," "heat," "high temperature

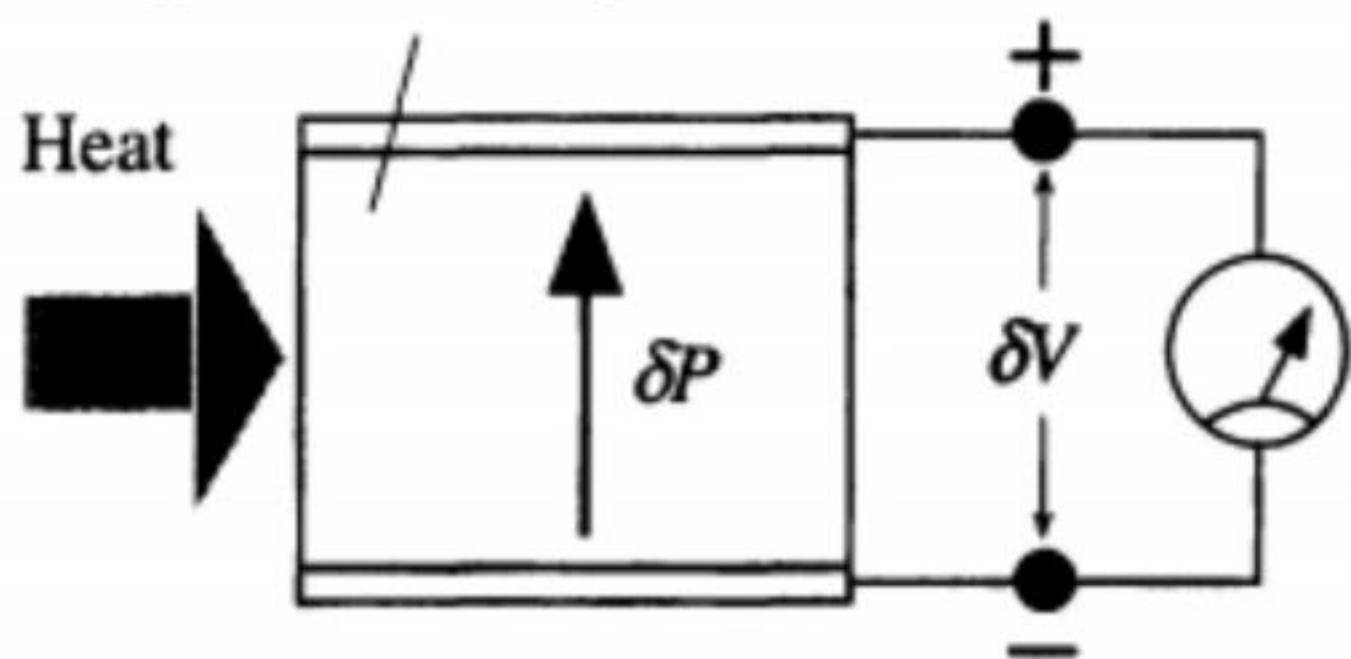
Pyroelectricity is the property presented by certain materials that exhibit an electric polarization  $\Delta P$  when a temperature variation  $\Delta T$  is applied uniformly: **Temperature change =  $\delta T$**

$$\Delta P = \gamma \cdot \Delta T$$

where  $\gamma$  is the pyroelectric coefficient at constant stress.

Pyroelectric crystals actually have a spontaneous polarization,

but the pyroelectric effect can only be observed during a temperature change ( $\Delta T$ ).



- If a spontaneous polarization is already present, a change of temperature alters it.
- The change in temperature modifies the positions of the atoms slightly within the crystal structure, such that the polarization of the material changes.
- This polarization change gives rise to an electric polarization across the crystal.
- If the temperature stays constant at its new value, the pyroelectric polarization gradually disappears due to leakage current (the leakage can be due to electrons moving through the crystal, ions moving through the air, current leaking through a voltmeter attached across the crystal, and so on)

- To observe pyroelectricity, we can heat a crystal uniformly and observe the change in polarization.
- This experiment can be performed in **two different ways**:
- Either the shape and size of the crystal can be held fixed during the heating or,

OR

- The crystal may be released so that thermal expansion can occur quite freely. The magnitude of the effect observed in the two experiments would be different.
- In the first case, with the crystal clamped, the effect observed is called ***primary pyroelectricity***.
- In the second case, with free expansion, which is much easier to achieve experimentally, there is an additional effect called ***secondary pyroelectricity***; what is observed in this case is the primary effect plus the ***secondary*** effect.

## CASE I

If a pyroelectric crystal with an intrinsic dipole moment (top) is fashioned into a circuit with electrodes attached on each surface (FIG. 1), an increase in temperature  $T$  prompts the spontaneous polarization  $P_S$  to decrease as the dipole moments, on average, diminish in magnitude. The horizontal tilting of the dipoles, (pictured at bottom of FIG. 1), signifies the effect. A current flows to compensate for the change in bound charge that accumulates on the crystal edges.

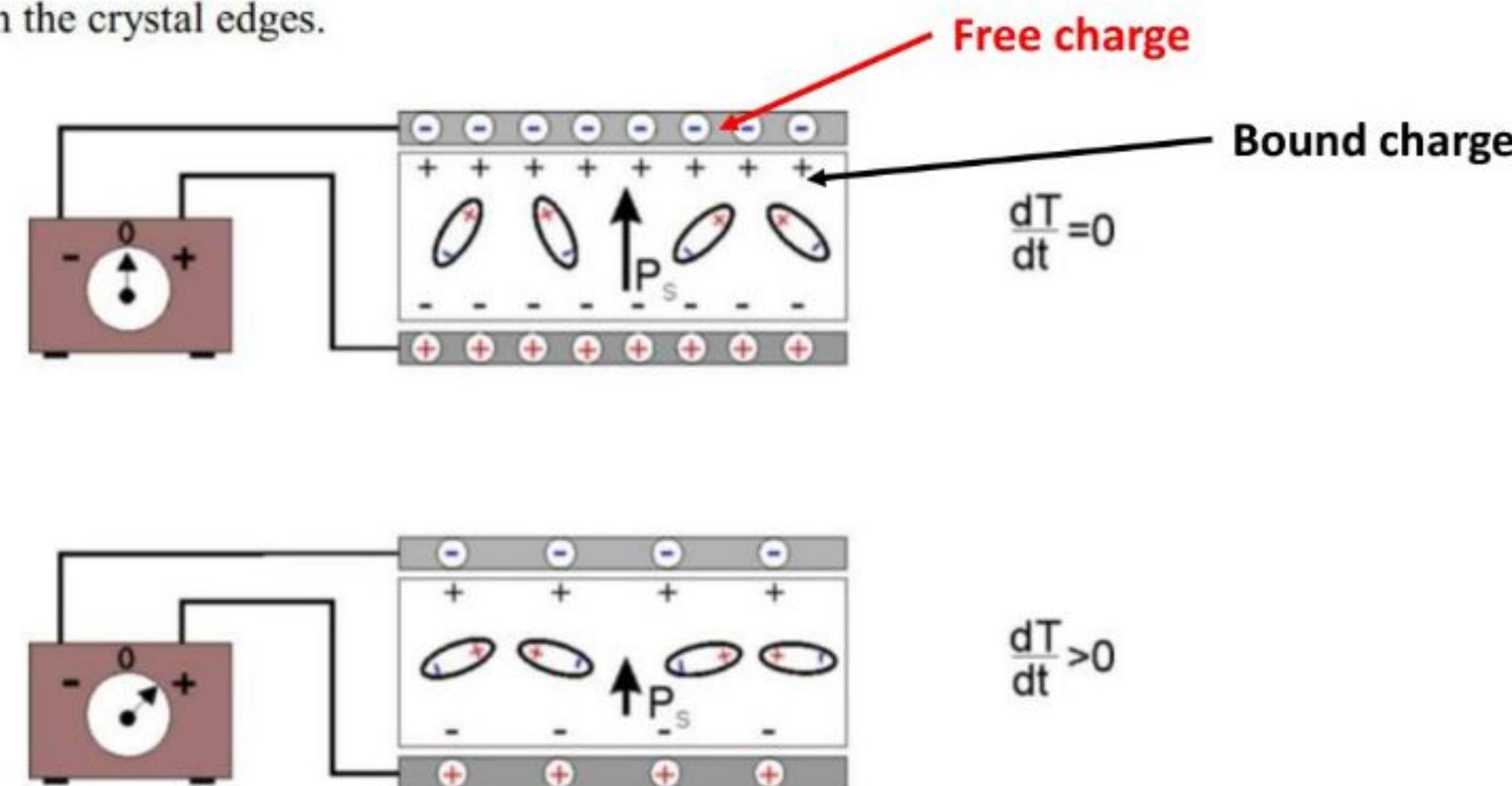


FIG. 1 Schematic drawing showing the origin of the pyroelectric current.

## CASE II

Another definition of pyroelectricity is ability to generation of induced charges on the crystal surface when they are heated or cooled. It is explained as a migration of positive and negative charges (and therefore establishment of electric polarization) to opposite ends of a crystal's polar axis as a result of change in temperature. This can be expressed as follows:

$$\Delta Q = \gamma \cdot S \Delta T \quad (3)$$

where:

$\Delta Q$  – charges generated on the crystal surface,

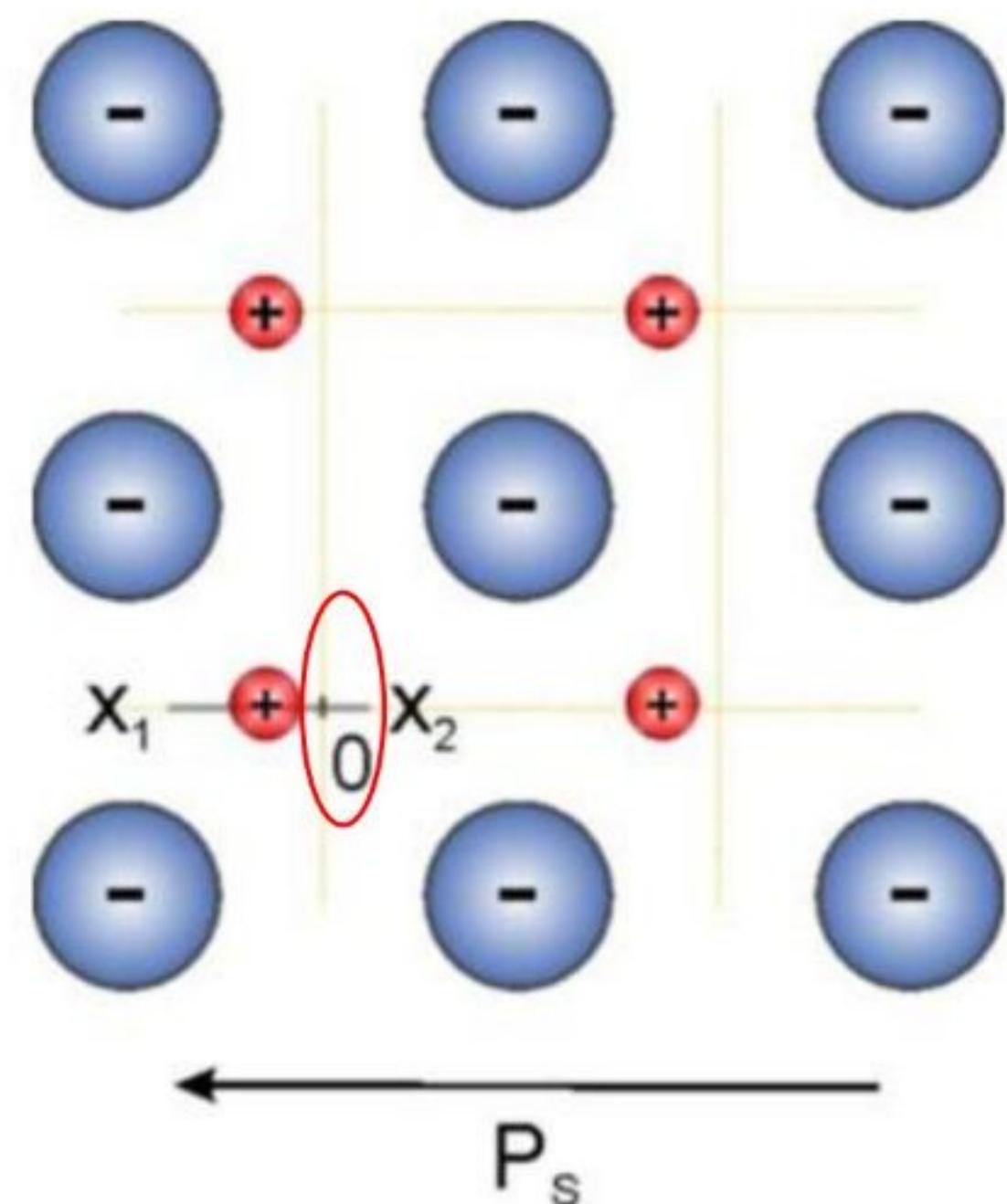
$S$  – surface of the crystal.

The relation between generated charges and polarization is:

$$Q = \Delta P \cdot S \quad (4)$$

The unit of the polarization is  $\left[ \frac{C}{m^2} \right]$ .

## Simple model of the pyroelectric effect



# Types of Ferroelectric Materials and Their Applications

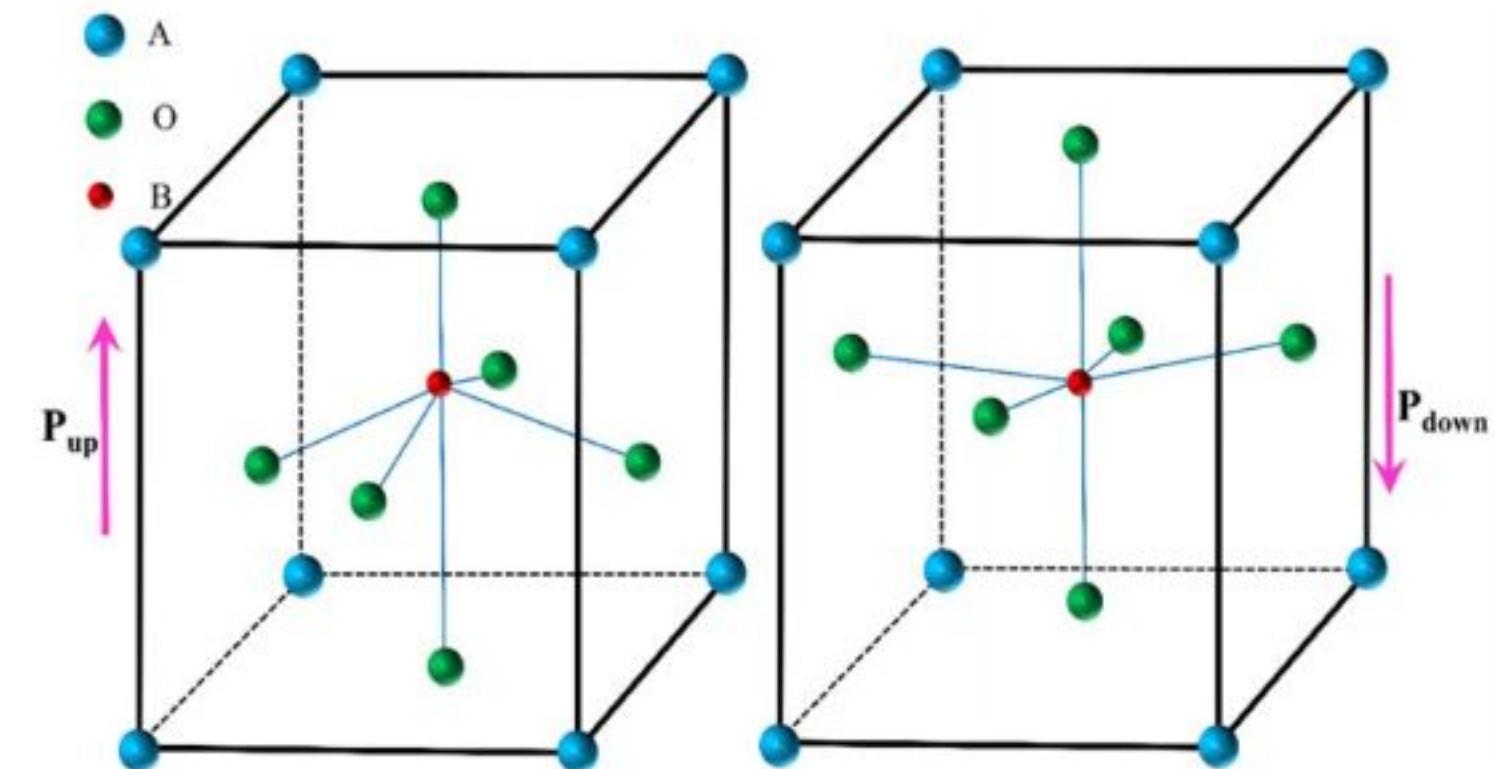
# Types of Ferroelectric Materials

## Perovskite-Type Structures

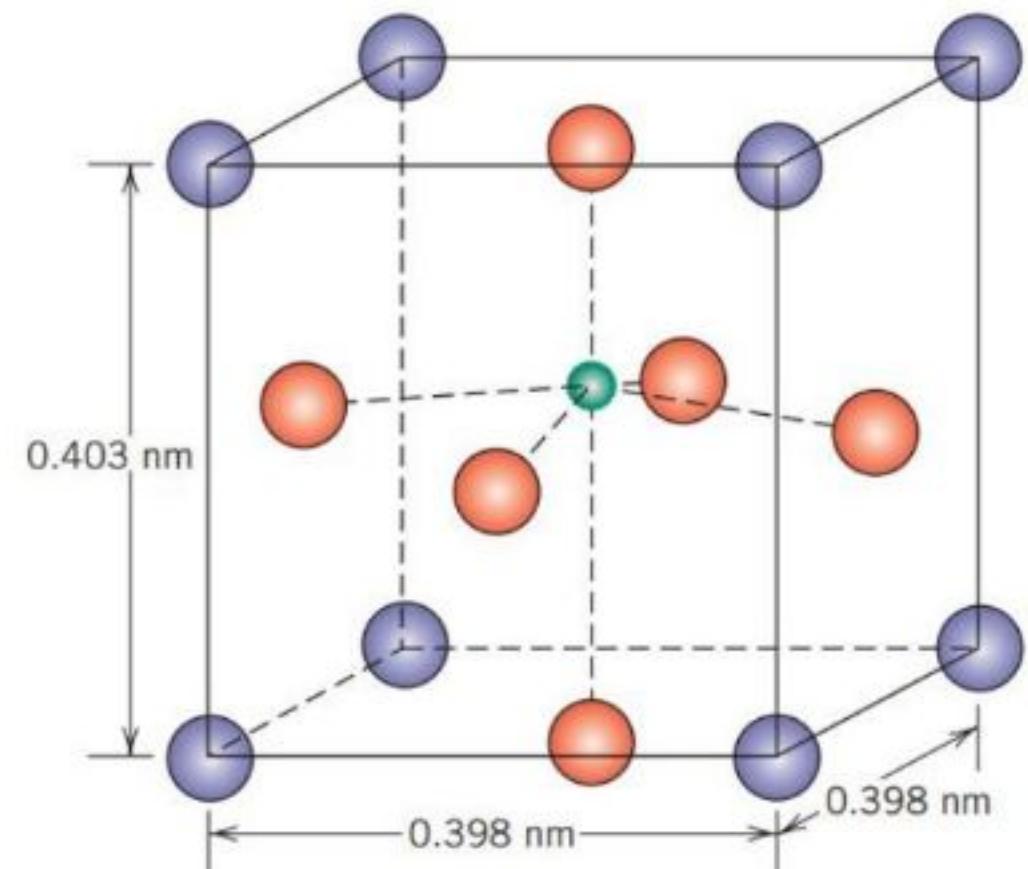
Perovskite is a family name of a group of materials having the mineral name of calcium titanate ( $\text{CaTiO}_3$ ) exhibiting a structure of the type  $\text{ABO}_3$ . Many piezoelectrics including FE ceramics such as

- Barium titanate ( $\text{BaTiO}_3$ )
- Strontium titanate (STO) ( $\text{SrTiO}_3$ )
- Barium strontium titanate (BST)
- Lead titanate ( $\text{PbTiO}_3$ ), *Lead Zirconate Titanate (PZT)*
- Lead Lanthanum Zirconate Titanate (PLZT)
- *Lead Magnesium Niobate (PMN)*
- Potassium niobate (KN) ( $\text{KNbO}_3$ ),
- Potassium sodium niobate ( $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ ),
- and Potassium tantalate niobate ( $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ )

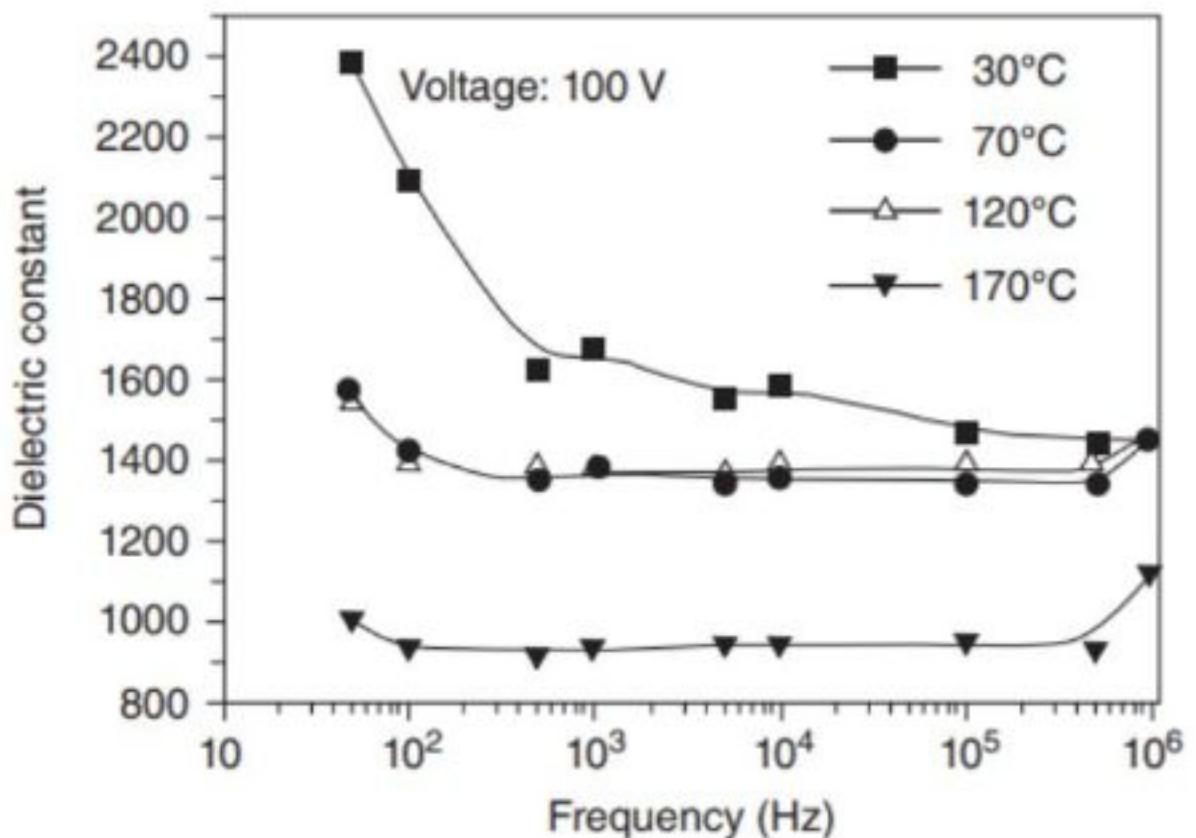
have a perovskite-type structure.



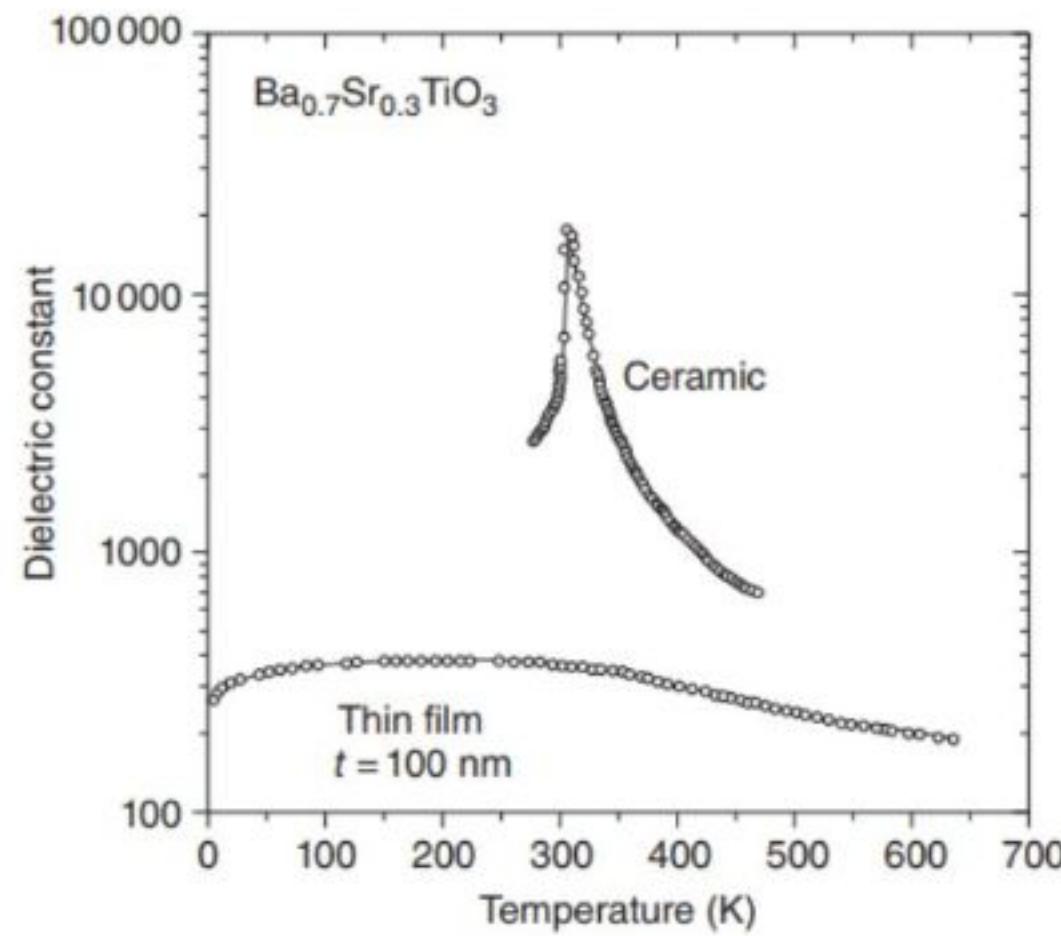
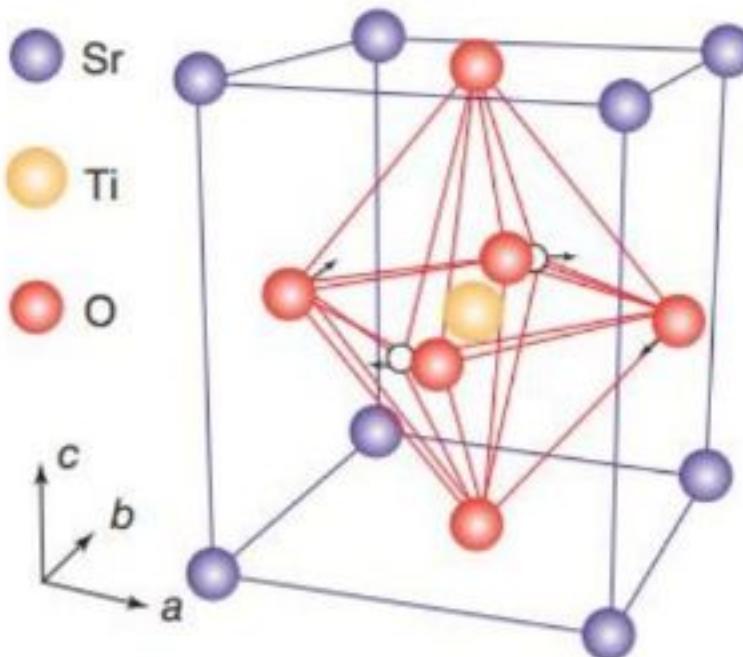
# Barium titanate ( $\text{BaTiO}_3$ )



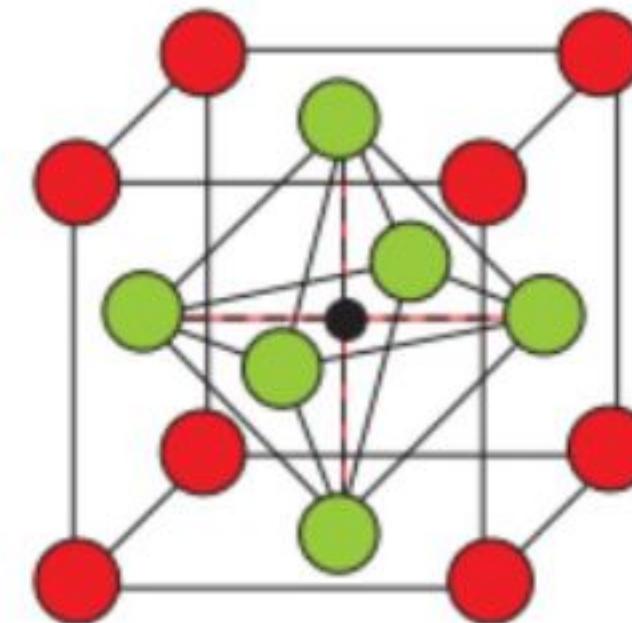
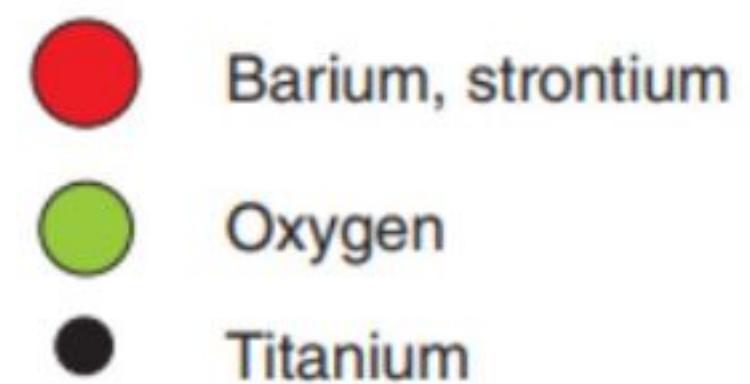
(a)



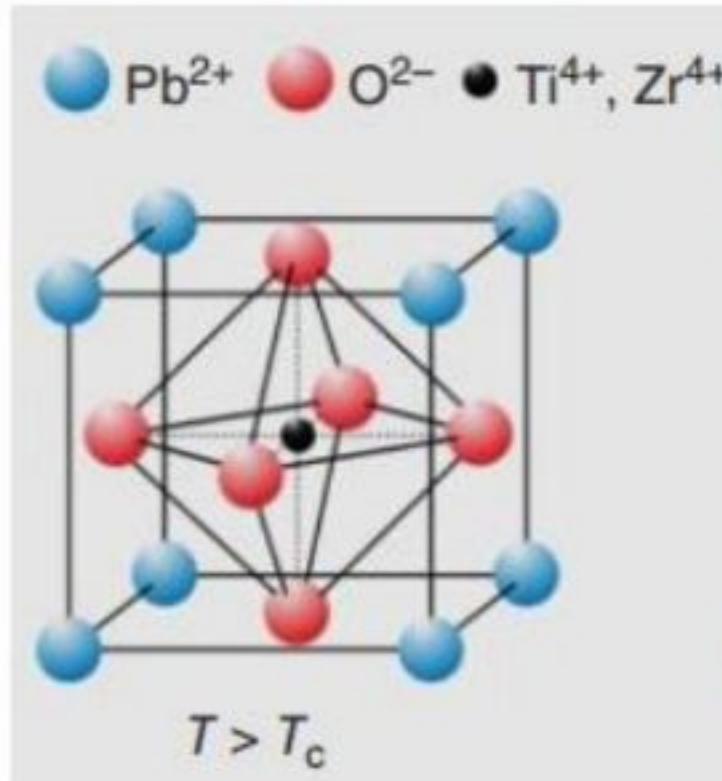
## **Strontium Titanate ( $SrTiO_3$ )**



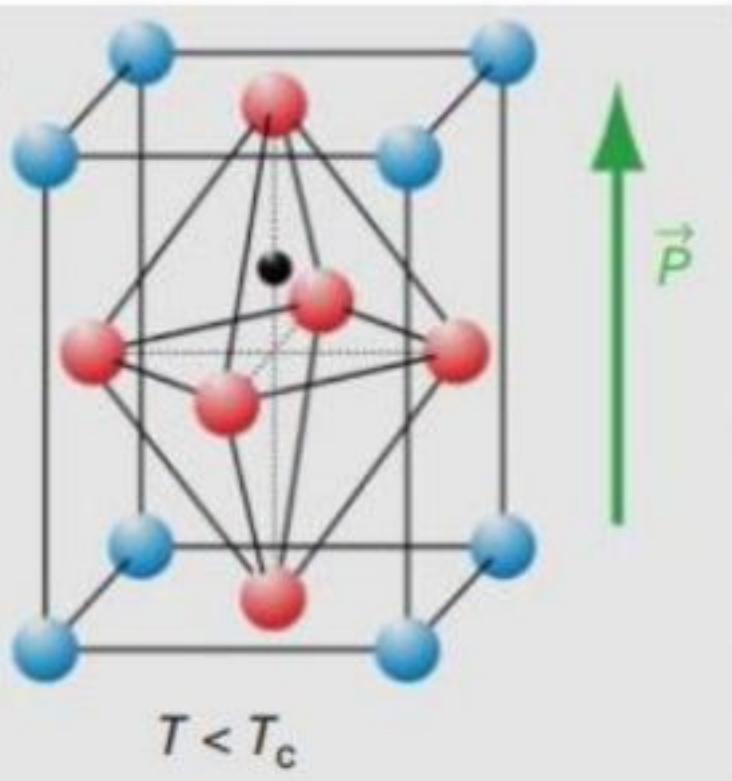
## **Barium Strontium Titanate (BST)**



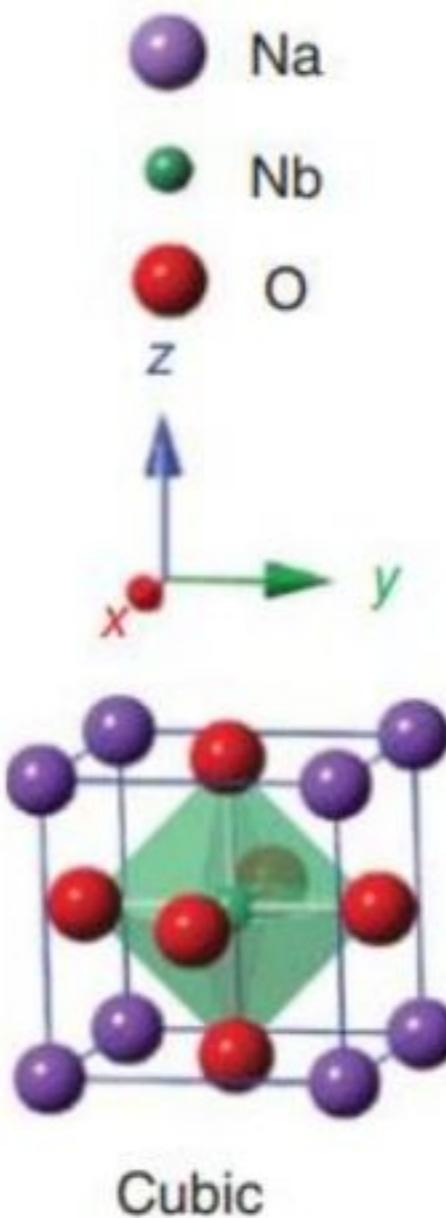
**Lead Titanate ( $PbTiO_3$ )**



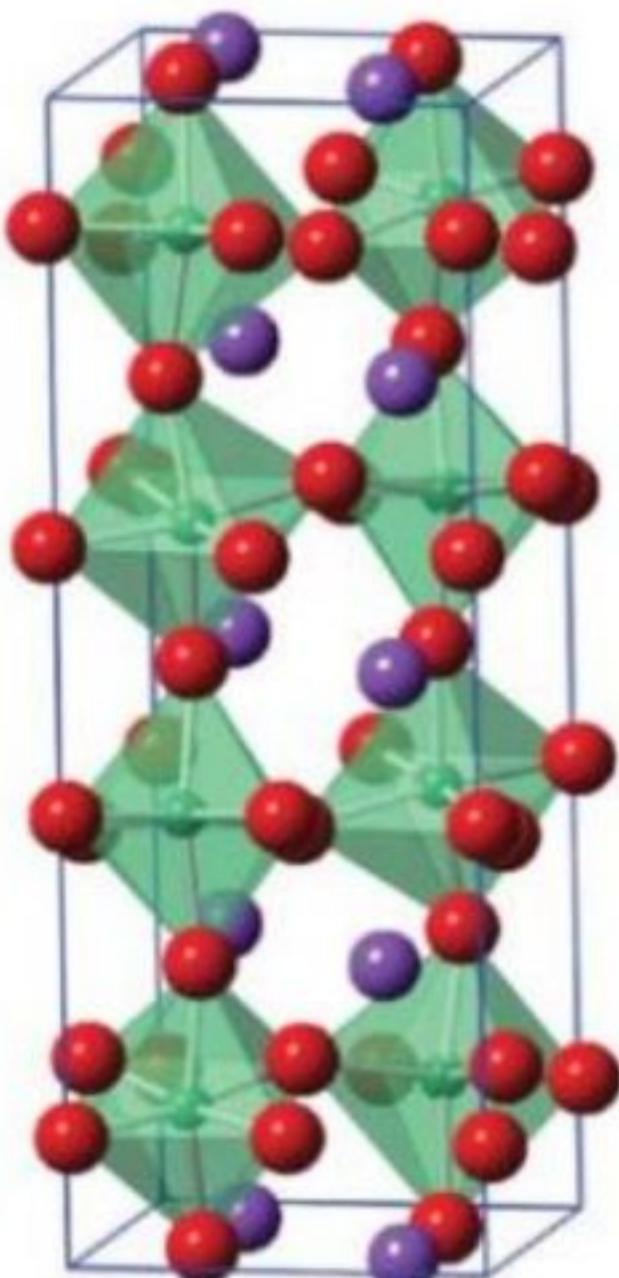
**Lead Zirconate Titanate (PZT)**



**Sodium Niobate ( $NaNbO_3$ )**



Cubic



Orthorhombic 59

# Polymers based Piezoelectrics

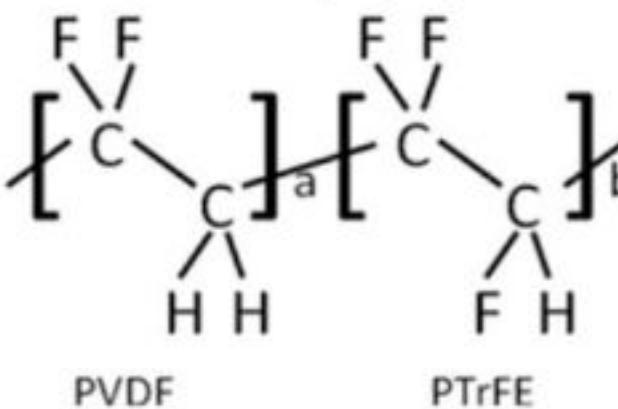
## Organic Polymers

Molecular structure of ferroelectric polymer

(a) Polyvinylidene fluoride or Polyvinylidene difluoride (PVDF) and

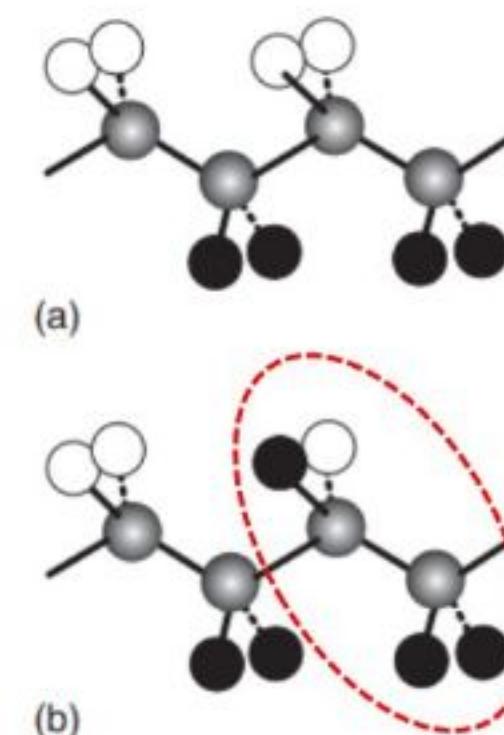
(b) Polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE)

P(VDF-TrFE) copolymer



(a)

(b)



## Ceramic Polymer Composites

- Ceramic polymer materials are **inorganic–organic composites consisting of ceramic fillers and a matrix of organic polymers**. The formation of ceramic polymer is based on thermal curing of functionalized resins being able to form ceramic-like structures as a result of heat treatment above 200 deg.C.
- Processed by a broad variety of plastic-forming techniques such as high-pressure injection molding or extrusion.
- Ceramic Polymer composites are characterized by **high thermal stability** (possible service temperatures above 600 deg. C), **low shrinkage**, **high stability of shape**, and **high dimensional accuracy**.
- Relevant usage properties (e.g., electrical conductivity, thermal conductivity) and processing parameters can be adjusted by the choice of appropriate functional fillers, binder systems, and plasticizing additives.
- The application of ceramic polymer materials could pay off if a cost-efficient, easy processing of the material including plastic-forming techniques in order to realize complex shaped parts is required and the thermal stability of standard materials such as plastics does not suffice.

## Electrets

- An electret can be considered a piece of dielectric material with the presence of **quasi-permanent real charges** on the surface or in the bulk of the material, or frozen-in aligned dipoles in the bulk. An electret behaves like a battery or acts as an electrical counterpart of a permanent magnet. A piece of poled ferroelectric material can also be an electret.
- The term ***quasi-permanent*** implies that the amount of charges stored in the material does not remain the same permanently, but decays very slowly depending on the situation, and the decay time is normally much longer than the time period over which the electret is in use.
- Historically, electrets were made by first melting a suitable dielectric material such as a polymer or wax that contains polar molecules and then allowing it to resolidify in a powerful electrostatic field.
- The polar molecules of the dielectric align themselves to the direction of the electrostatic field, producing a dipole electret with a permanent electrostatic “bias.”

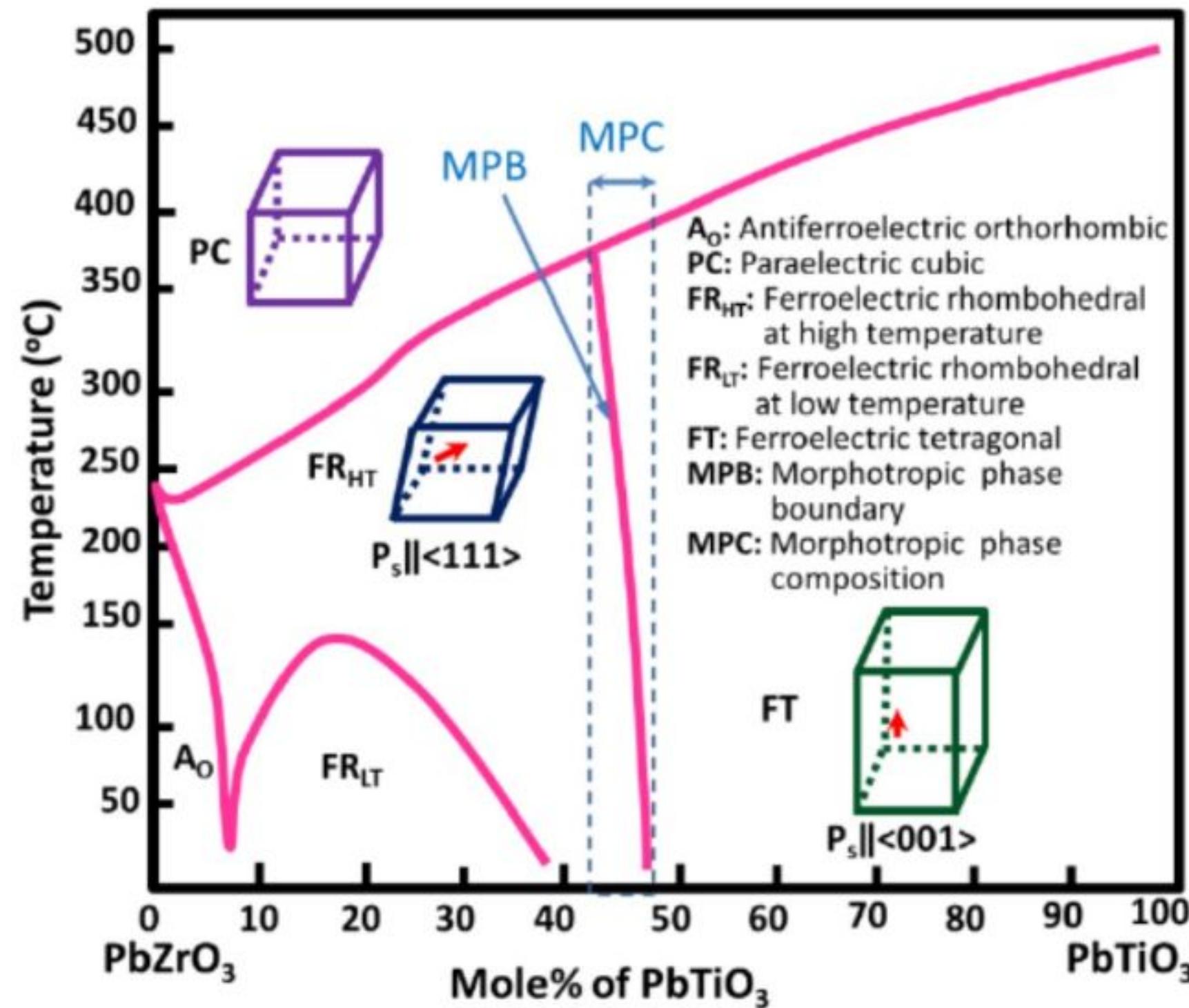
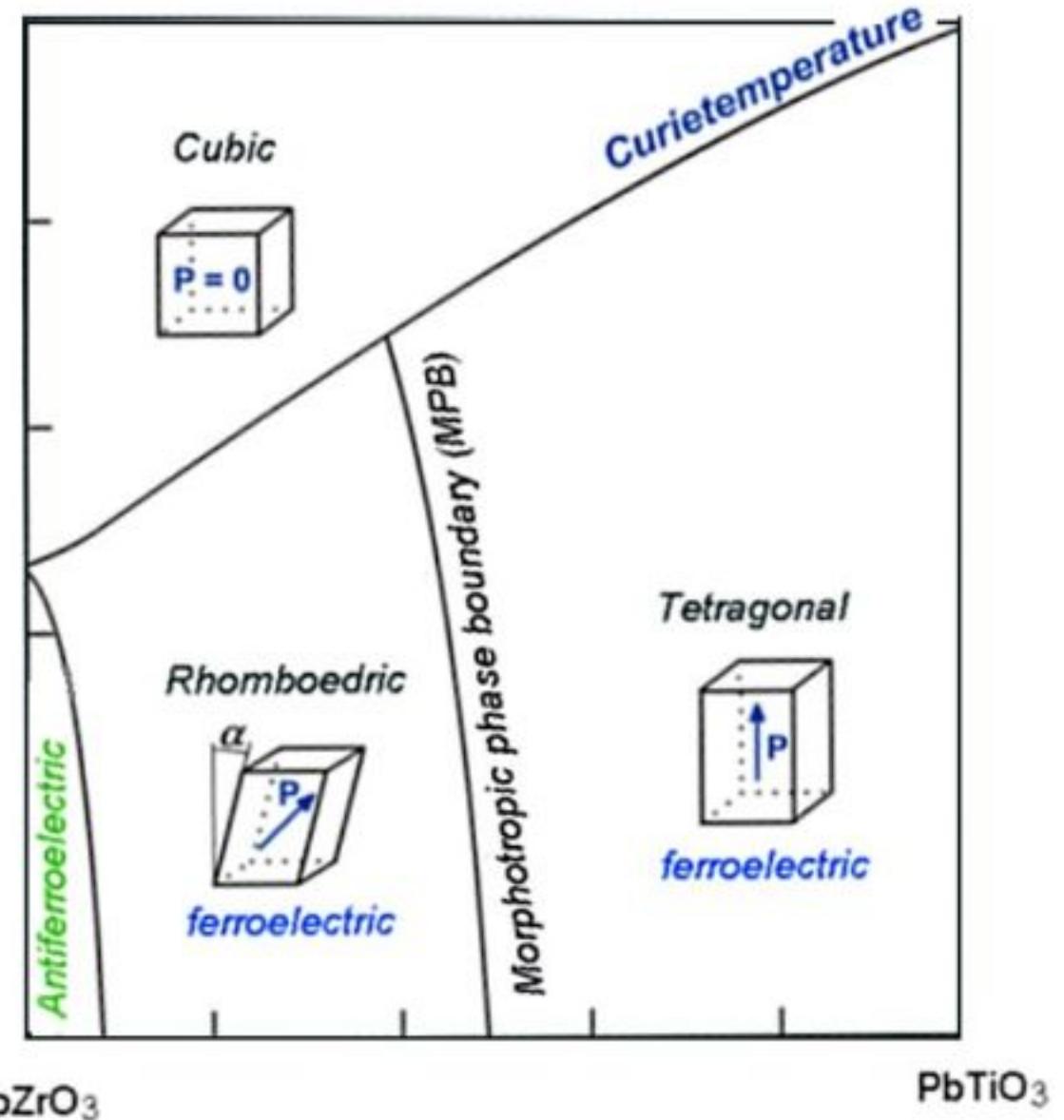
## **Applications:**

- Electret materials were proposed as **condenser microphone elements** several times, but they were considered impractical until the foil electret type was invented at Bell Laboratories in 1962 by Gerhard Sessler and Jim West using a thin metallized Teflon foil.
- This became the most common type used in many applications from **high-quality recording to built-in microphones in small sound recording devices and telephones.**
- Electret materials have found commercial and technical interest. For example, they are used in electret microphones and in copy machines.
- They are also used in some types of **air filters, for electrostatic collection of dust particles**, in electret ion chambers for measuring ionizing radiation or radon, and in vibration energy harvesting.

# Phase Diagram

**MPB:** Coexistence of Rhombohedral and Tetragonal Phases

Good Piezoelectric properties due to the coexistence of two phases.



# Phase Changes in PZT

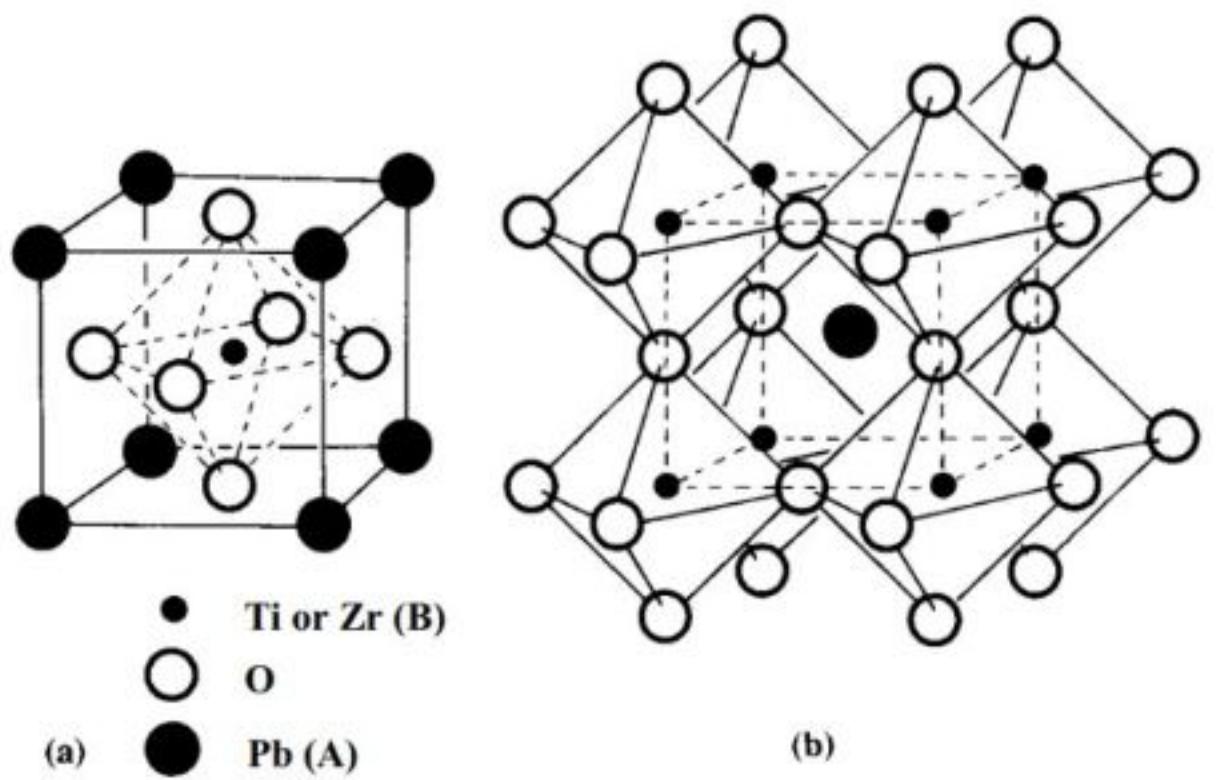
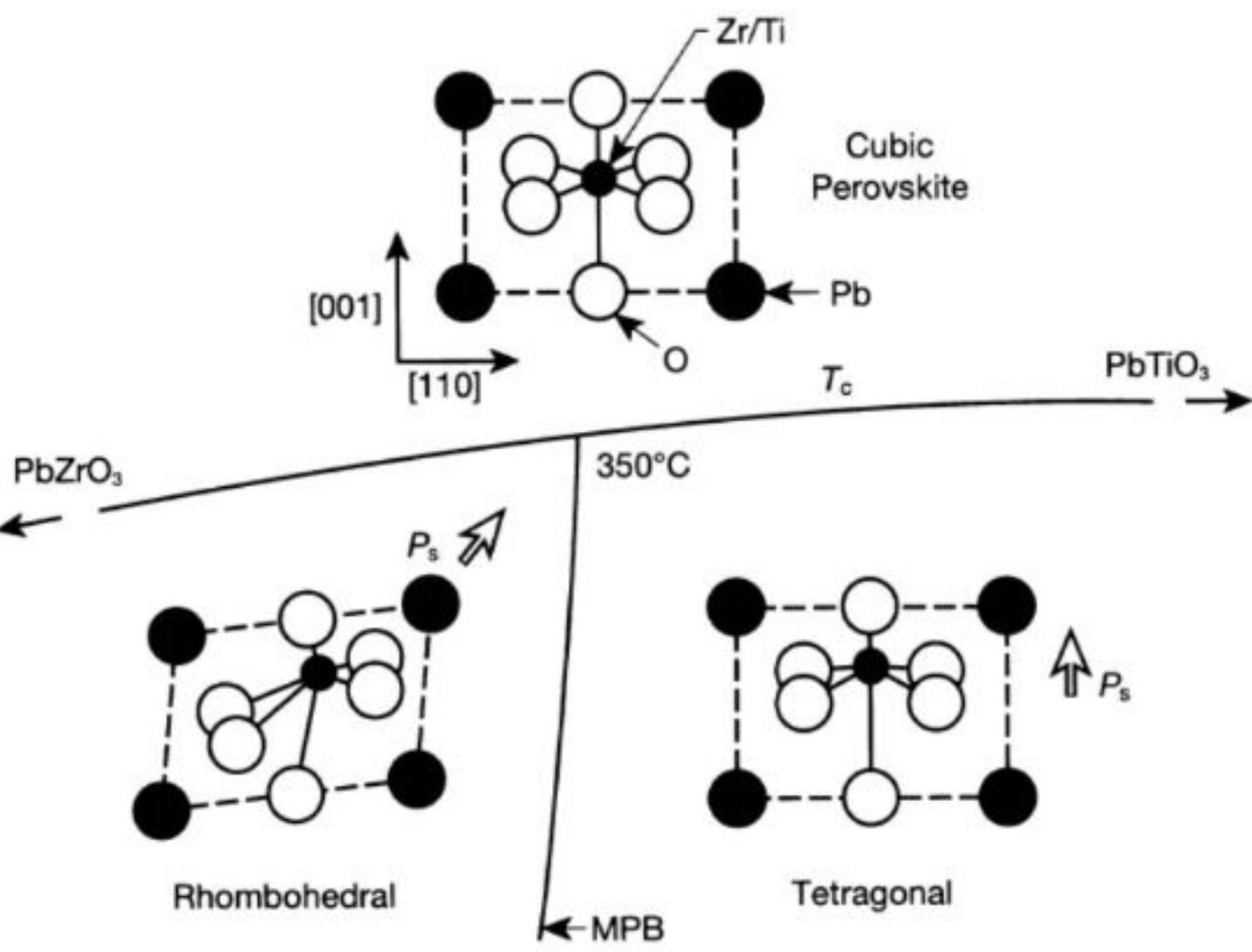
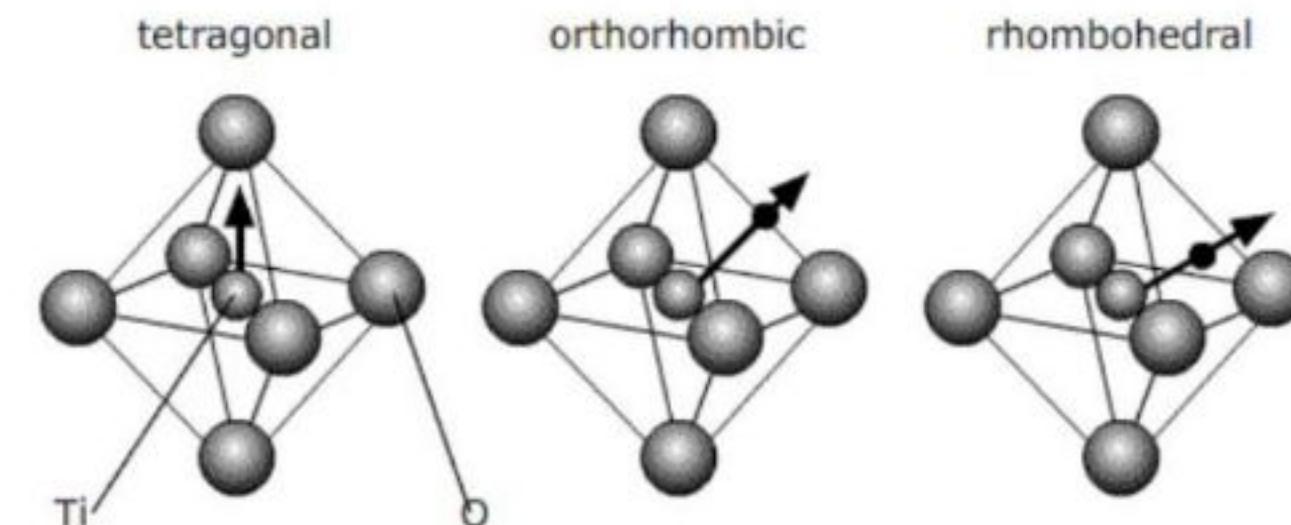
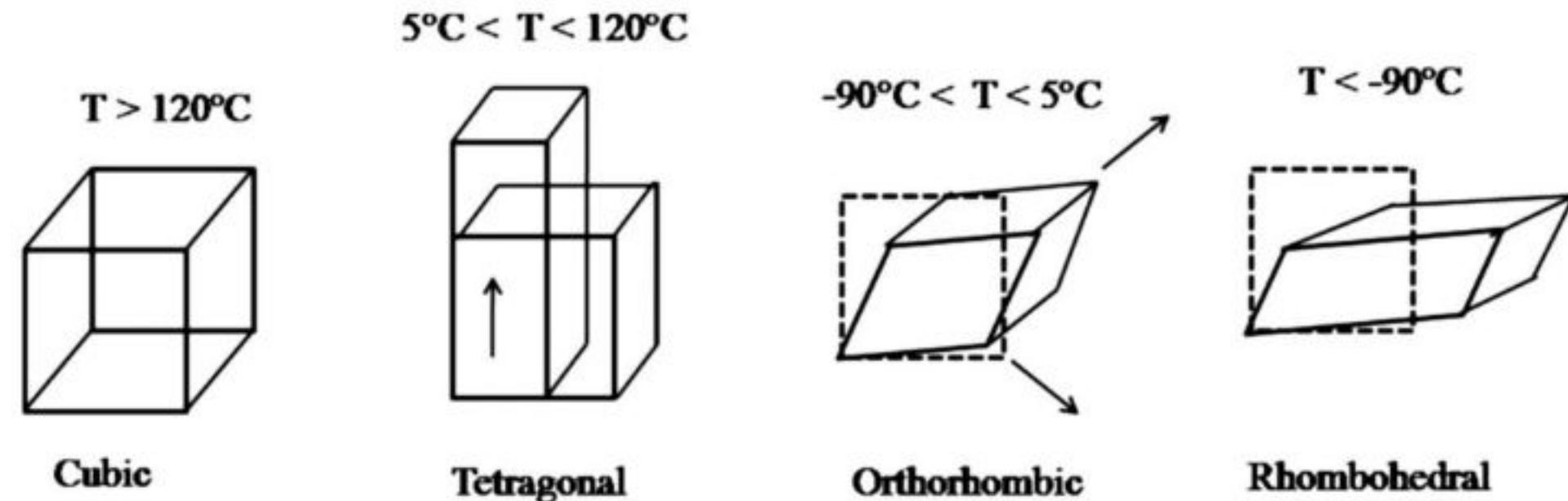
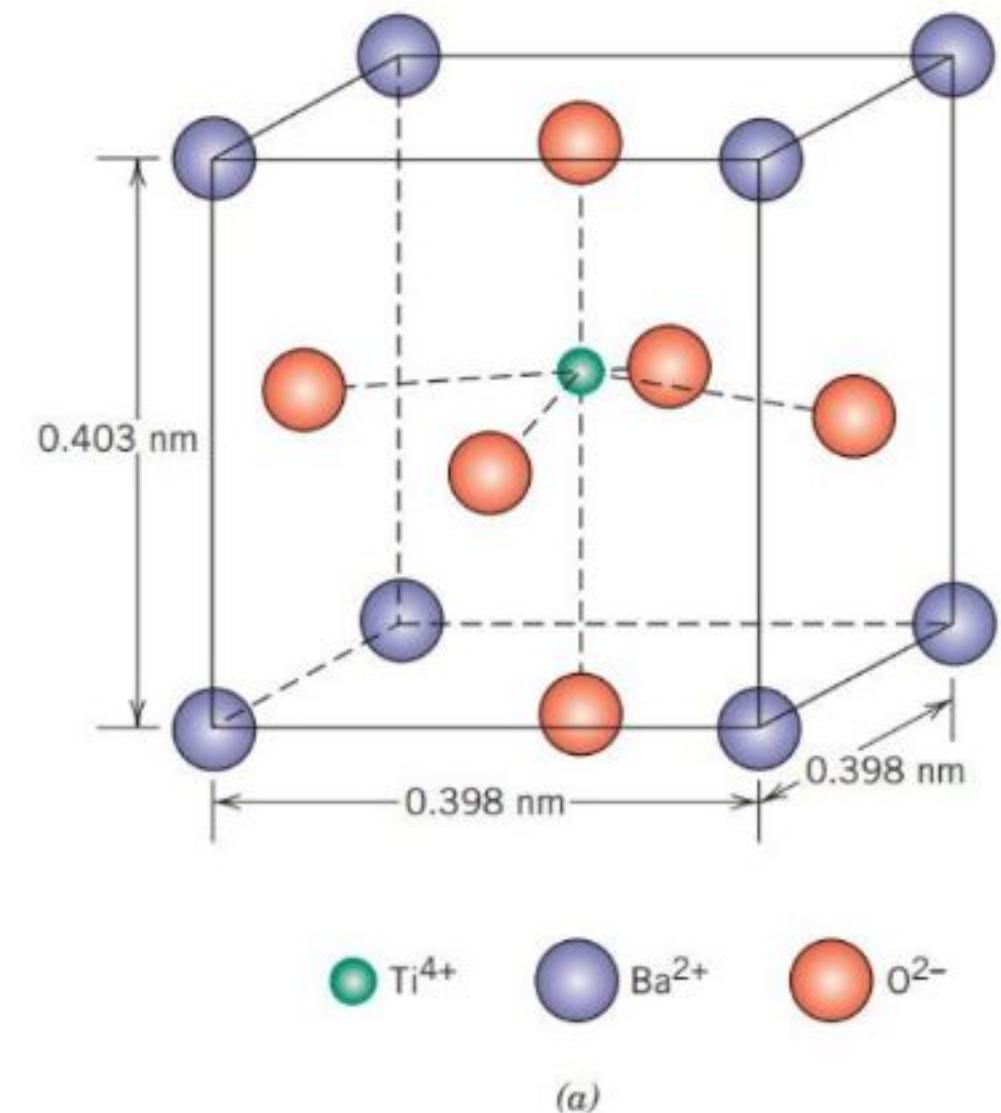


Fig. 2.4. Basic structural unit of perovskite PZT. The basic structural unit is a cube (a). Titanium or zirconium atoms (B) lie at the centre; eight lead atoms (A) occupy the corners and six oxygen atoms (O) are at the surface centres.



# Phase Changes in BaTiO<sub>3</sub>



No. of Favorable  
Polarization  
directions = 6

No. of Favorable  
Polarization  
directions = 8

# Doping

Ceramic ferroelectrics properties can be modified by adjusting the composition and the ceramic microstructure.

Additions and the substitution of alternative cations can have the following effects:

- 1. Shift the Curie point and other transition temperatures;**

Changing the Curie point enables the peak permittivity to be put in a temperature range in which it can be exploited. The substitution of  $\text{Sr}^{2+}$  form  $\text{Ba}^{2+}$  in  $\text{BaTiO}_3$  lowers  $T_c$  whilst the substitution of  $\text{Pb}^{2+}$  increases it.

- 2. Restrict domain wall motion;**

number of transition ions ( $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ) that can occupy  $\text{Ti}^{4+}$  sites reduce that part of the dissipation factor due to domain wall motion

#### **4. Control crystallite size;**

Cations that have a higher valency than those they replace, when present at levels exceeding about 0.5 cation percent, e.g.  $\text{La}^{3+}$  in place of  $\text{Ba}^{2+}$  or  $\text{Nb}^{5+}$  in place of  $\text{Ti}^{4+}$ , generally inhibit crystal growth.

Crystal size is also controlled by sintering conditions. It has important effects on the electro-optical behaviour.

#### **5. Control the oxygen content and the valency of the Ti ion.**

Higher-valency substituents at low concentrations in  $\text{BaTiO}_3$  lead to low resistivity.

However, lower-valency substituents, such as  $\text{Mn}^{3+}$  on  $\text{Ti}^{4+}$  sites, act as acceptors and enable high-resistivity dielectrics to be sintered in atmospheres with low oxygen contents

# Type of Dopants

## Donor Dopants

- Donor dopants, i.e. higher charge than that of the ions they replace, are compensated by cation vacancies
- Acceptors, i.e. dopants of lower charge than that of the replaced ions, are compensated by oxygen vacancies
- Significant difference between oxygen vacancies and cation vacancies in perovskite-type structures is the higher mobility of the former
- Cations and cation vacancies tend to be separated by oxygen ions so that there is a considerable energy barrier to be overcome before the ion and its vacancy can be interchanged.
- Oxygen ions, however, form a continuous lattice structure so that oxygen vacancies have oxygen ion neighbors with which they can easily exchange.

## Acceptor Dopants

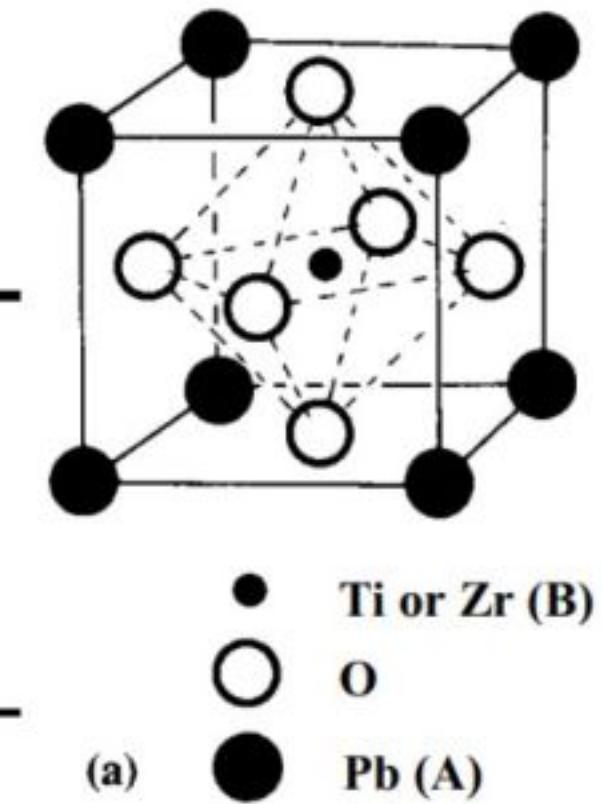
- Donor–cation vacancy combinations can be assumed to have a stable orientation so that their initially random state is unaffected by spontaneous polarization or applied fields.
- Acceptor–oxygen vacancy combinations are likely to be less stable and thermally activated reorientation may take place in the presence of local or applied fields.
- The dipoles, once oriented in a common direction, will provide a field stabilizing the domain structure.

**Inhibition of wall movement** : A reduction in permittivity, dielectric and mechanical loss and an increase in the coercive field.

---

A-site donors	$\text{La}^{3+}$ , $\text{Bi}^{3+}$ , $\text{Nd}^{3+}$
B-site donors	$\text{Nb}^{5+}$ , $\text{Ta}^{5+}$ , $\text{Sb}^{5+}$
A-site acceptors	$\text{K}^+$ , $\text{Rb}^+$
B-site acceptors	$\text{Co}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Sc}^{3+}$ , $\text{Ga}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Mn}^{3+}$ , $\text{Mn}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Cu}^{2+}$

---



## Dopants which gives rise to soft and hard PZT properties

Additives	Major Effects
<u>Isovalent additives</u> Ba <sup>2+</sup> (0.134) or Sr <sup>2+</sup> (0.112) for Pb <sup>2+</sup> (0.132) Sn <sup>4+</sup> (0.071) for Zr <sup>4+</sup> (0.068) or Ti <sup>4+</sup> (0.079)	Lower Curie point Higher permittivity
<u>Soft dopants</u> La <sup>3+</sup> (0.122), Nd <sup>3+</sup> (0.115), Sb <sup>3+</sup> (0.090), Bi <sup>3+</sup> (0.114) or Th <sup>4+</sup> (0.110) for Pb <sup>2+</sup> (0.132) Nb <sup>5+</sup> (0.069), Ta <sup>5+</sup> (0.068), Sb <sup>5+</sup> (0.063) or W <sup>6+</sup> (0.065) for Ti <sup>4+</sup> (0.068) or Zr <sup>4+</sup> (0.079)	Higher permittivity Higher K <sub>p</sub> Much lower Q <sub>m</sub> Resistivity about 10 <sup>3</sup> higher
<u>Hard dopants</u> K <sup>+</sup> (0.133) or Na <sup>+</sup> (0.094) for Pb <sup>2+</sup> (0.132) Fe <sup>3+</sup> (0.067), Al <sup>3+</sup> (0.057), Sc <sup>3+</sup> (0.083), In <sup>3+</sup> (0.092) or Cr <sup>3+</sup> (0.064) for Ti <sup>4+</sup> (0.068) or Zr <sup>4+</sup> (0.079)	Lower permittivity Lower dielectric loss Lower K <sub>p</sub> Much higher Q <sub>m</sub>

# Doping in PZT

Donor doping in PZT would be expected to reduce the concentration of oxygen vacancies, leading to a reduction in the concentration of domain-stabilizing defect pairs and so to lower ageing rates.

The resulting increase in wall mobility causes the observed increases in permittivity, dielectric losses, elastic

compliance and coupling coefficients, and reductions in mechanical Q and coercivity.

**e.g. Soft and Hard PZT**

Characteristic	Soft Ceramic	Hard Ceramic
Piezoelectric Constants	larger	smaller
Permittivity	higher	lower
Dielectric Constants	larger	smaller
Dielectric Losses	higher	lower
Electromechanical Coupling Factors	larger	smaller
Electrical Resistance	very high	lower
Mechanical Quality Factors	low	high
Coercive Field	low	higher
Linearity	poor	better
Polarization / Depolarization	easier	more difficult

# **Piezoelectric Constants one needs to know**

## ◆ Piezoelectric constants

- $d$  [C/N] = (charge developed)/(applied stress)
- $g$  [V-m/N] = (Electric field developed)/(applied stress)

Charge Constant

Voltage Constant

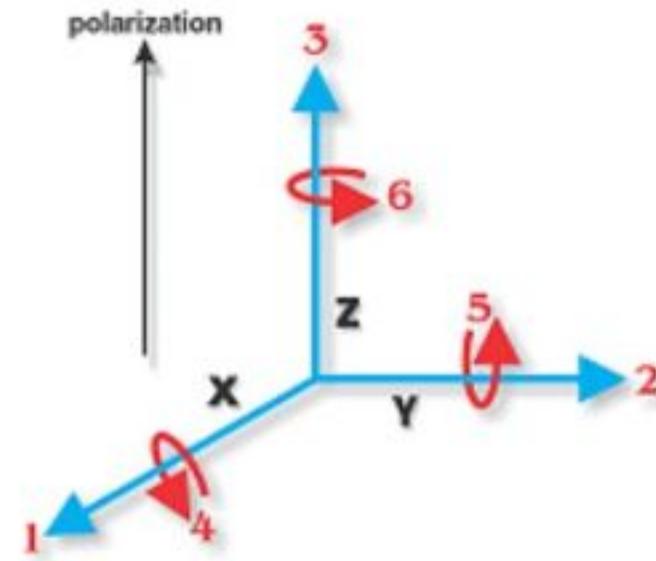
## ◆ Electromechanical coupling coefficient ( $k$ )

- Parameter used to compare different piezoelectric materials
- A measure of the interchange of electrical & mechanical energy

## Piezoelectric Charge Constant

- $d_{33}$  induced polarization in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 3  
or  
induced strain in direction 3 per unit electric field applied in direction 3
- $d_{31}$  induced polarization in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 1 (perpendicular to direction in which ceramic element is polarized)  
or  
induced strain in direction 1 per unit electric field applied in direction 3
- $d_{15}$  induced polarization in direction 1 (perpendicular to direction in which ceramic element is polarized) per unit shear stress applied about direction 2 (direction 2 perpendicular to direction in which ceramic element is polarized)  
or  
induced shear strain about direction 2 per unit electric field applied in direction 1

**Figure 1.6** Directions of forces affecting a piezoelectric element



$$d = \frac{\text{Polarization}}{\text{Mechanical Stress}}$$

## Piezoelectric Voltage Constant

- §33      induced electric field in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 3  
**or**  
induced strain in direction 3 per unit electric displacement applied in direction 3
- §31      induced electric field in direction 3 (parallel to direction in which ceramic element is polarized) per unit stress applied in direction 1 (perpendicular to direction in which ceramic element is polarized)  
**or**  
induced strain in direction 1 per unit electric displacement applied in direction 3
- §15      induced electric field in direction 1 (perpendicular to direction in which ceramic element is polarized) per unit shear stress applied about direction 2 (direction 2 perpendicular to direction in which ceramic element is polarized)  
**or**  
induced shear strain about direction 2 per unit electric displacement applied in direction 1

$$d = \frac{\text{Electric Field}}{\text{Mechanical Stress}}$$

## Permittivity Constant

The *permittivity*, or *dielectric constant*,  $\epsilon$ , for a piezoelectric ceramic material is the dielectric displacement per unit electric field.  $\epsilon^T$  is the permittivity at constant stress,  $\epsilon^S$  is the permittivity at constant strain. The first subscript to  $\epsilon$  indicates the direction of the dielectric displacement; the second is the direction of the electric field.

The relative dielectric constant, K, is the ratio of , the amount of charge that an element constructed from the ceramic material can store, relative to the absolute dielectric constant, 0 , the charge that can be stored by the same electrodes when separated by a vacuum, at equal voltage ( $0 = 8.85 \times 10^{-12}$  farad / meter).

$\epsilon_{11}^T$       permittivity for dielectric displacement and electric field in direction 1 (perpendicular to direction in which ceramic element is polarized), under constant stress

$\epsilon_{33}^S$       permittivity for dielectric displacement and electric field in direction 3 (parallel to direction in which ceramic element is polarized), under constant strain

$$\epsilon = \frac{\text{Dielectric Displacement}}{\text{Electric Field}}$$

## Elastic and Compliance

Inverse of Modulus of Elasticity

*Elastic compliance*,  $s$ , is the strain produced in a piezoelectric material per unit of stress applied and, for the 11 and 33 directions, is the reciprocal of the modulus of elasticity (Young's modulus,  $Y$ ).  $s^D$  is the compliance under a constant electric displacement;  $s^E$  is the compliance under a constant electric field. The first subscript indicates the direction of strain, the second is the direction of stress.

$$S = \frac{\text{Mechanical Strain}}{\text{Mechanical Stress}}$$

$s^E_{11}$  elastic compliance for stress in direction 1 (perpendicular to direction in which ceramic element is polarized) and accompanying strain in direction 1, under constant electric field (short circuit)

$s^D_{33}$  elastic compliance for stress in direction 3 (parallel to direction in which ceramic element is polarized) and accompanying strain in direction 3, under constant electric displacement (open circuit)

## Young's Modulus

*Young's modulus*,  $Y$ , is an indicator of the stiffness (elasticity) of a ceramic material.  $Y$  is determined from the value for the stress applied to the material divided by the value for the resulting strain in the same direction.

## Electromechanical Coupling Factor

The *electromechanical coupling factor*,  $k$ , is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy, or converts mechanical energy into electrical energy. The first subscript to  $k$  denotes the direction along which the electrodes are applied; the second denotes the direction along which the mechanical energy is applied, or developed.

- $k_{33}$  factor for electric field in direction 3 (parallel to direction in which ceramic element is polarized) and longitudinal vibrations in direction 3  
(ceramic rod, length >10x diameter)
- $k_t$  factor for electric field in direction 3 and vibrations in direction 3  
(thin disc, surface dimensions large relative to thickness;  $k_t < k_{33}$ )
- $k_{31}$  factor for electric field in direction 3 (parallel to direction in which ceramic element is polarized) and longitudinal vibrations in direction 1 (perpendicular to direction in which ceramic element is polarized)  
(ceramic rod)
- $k_p$  factor for electric field in direction 3 (parallel to direction in which ceramic element is polarized) and radial vibrations in direction 1 and direction 2 (both perpendicular to direction in which ceramic element is polarized)  
(thin disc)

$$k = \frac{\text{Electrical Energy}}{\text{Mechanical Energy}} \quad \text{OR} \quad \frac{\text{Mechanical Energy}}{\text{Mechanical Energy}}$$

## Constitutive Equation of Piezoelectricity

- For mechanical problems, a constitutive equation describes how a material strains when it is stressed, or vice-versa.
- Constitutive equations exist also for electrical problems; they describe how charge moves in a (dielectric) material when it is subjected to a voltage, or vice-versa.
- Engineers are already familiar with the most common mechanical constitutive equation that applies for everyday metals and plastics. This equation is known as Hooke's Law and is written as:

$$\mathbf{S} = \mathbf{s} \cdot \mathbf{T}$$

In words, this equation states: **Strain = Compliance × Stress**.

- However, since piezoelectric materials are concerned with electrical properties too, we must also consider the constitutive equation for common dielectrics:

$$\mathbf{D} = \boldsymbol{\epsilon} \cdot \mathbf{E}$$

In words, this equation states: **Charge Density = Permittivity × ElectricField**.

## Constitutive Equation of Piezoelectricity

$$\begin{aligned} S &= s T + d^t E \\ D &= d T + \epsilon E \end{aligned}$$

Diagram illustrating the Constitutive Equations of Piezoelectricity:

- Strain ( $S$ ):** Indicated by a blue arrow pointing to the left term in the first equation.
- Stress ( $T$ ):** Indicated by a blue arrow pointing to the right term in the first equation.
- Electric field ( $E$ ):** Indicated by a blue arrow pointing to the right term in the second equation.
- Permittivity ( $\epsilon$ ):** Indicated by a blue arrow pointing to the right term in the second equation.
- matrix for the direct piezoelectric effect ( $d$ ):** Indicated by a blue arrow pointing to the left term in the second equation.
- Electric charge density displacement ( $D$ ):** Indicated by a blue arrow pointing to the left term in the second equation.

## Effect of Grain Size

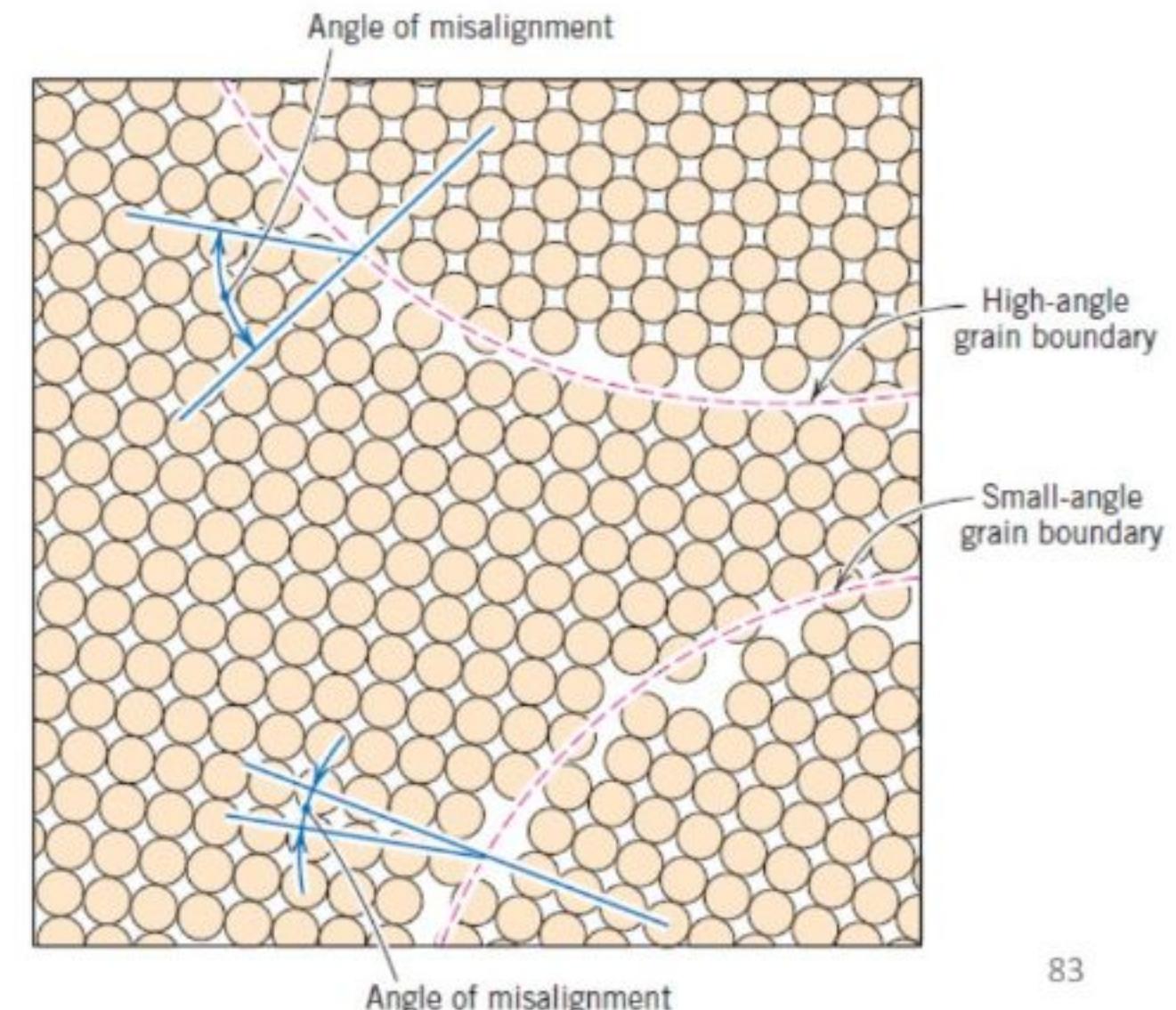
- The grain size of PZT ceramics depends on the compositions and sintering conditions.
- In general, the grain size of PZT ceramics increases with the increasing sintering temperatures and sintering time, from submicron to about  $10\text{ }\mu\text{m}$ .
- Metal oxide dopants will affect the grain growth during sintering process. Some metal oxide may restrain the grain growth in the ceramics.
- The deterioration of the piezoelectric properties with decreasing grain size is probably related to fewer domains and less mobile domain walls [Martirena & Burfoot, 1974].
- Below a critical size, the formation of ferroelectric domains is not energetically favourable [Mishra and Pandey, 1995] .

- It has been confirmed that the undoped PZT ceramics possess p-type conductivity (hole-type semiconductor) due to the lead oxide evaporation from the PZT sample during the sintering process, which creates Pb vacancies in the sintered PZT ceramic [Gerson, 1960].
- Therefore, in a PZT ceramic with hard doping ions, space charge, i.e. both centres of negative charges and hole-carriers, increase dramatically; which cause an internal field  $E_s$  inside the grains of PZT, and this field  $E_s$  may inhibit domain motion.
- The inhibition of domain motion reduces the dielectric loss (including the energy loss in domain vibration hysteresis).

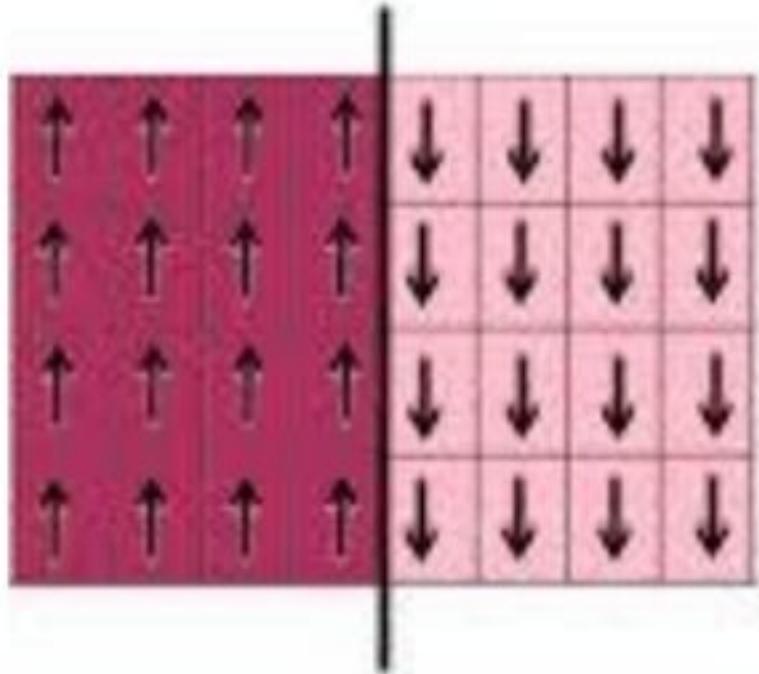
# High Angle and Low Angle grain boundaries

Generally, it is assumed that **low-angle grain boundaries** (LAGBs) are those with a misorientation less than about 5 degrees.

In contrast, the misorientation of **high-angle grain boundaries** (HAGBs) is greater than about 5 degrees.

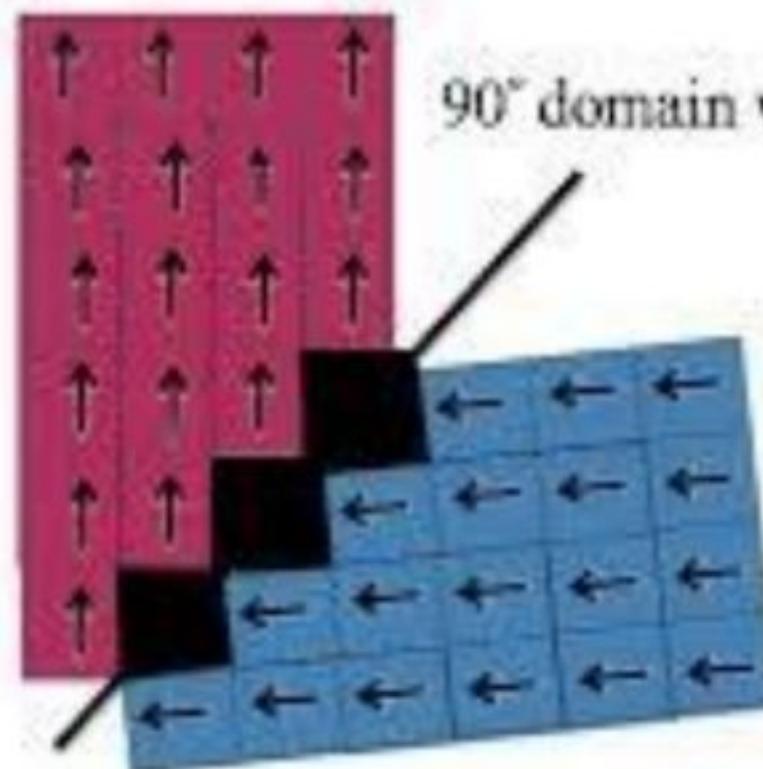


180° domain wall



(a)

90° domain wall



(b)

# Applications of Ferroelectric Materials

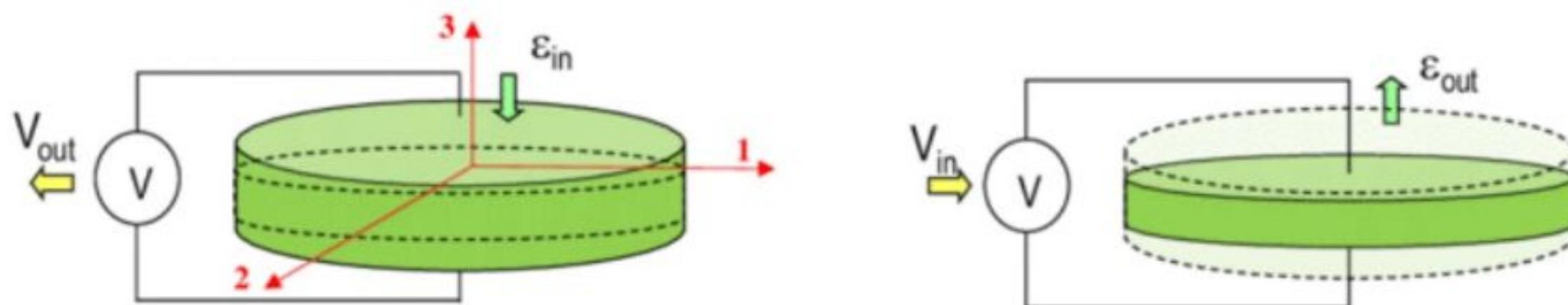
## Use in Camera Flash

Ferroelectrics are very useful for devices and are used in many different ways today. If a ferroelectric is used in its linear region, above  $T_C$  it makes a very good capacitor, as its dielectric constant can be very high indeed. These are often used in cameras as a way of powering a flash.

A battery slowly stores a charge on a capacitor, which when connected to a bulb, releases a burst of high current, creating the flash.

First, the battery charges the ferroelectric capacitor and then, once fully charged, the ferroelectric is connected to the bulb and causes it to flash.

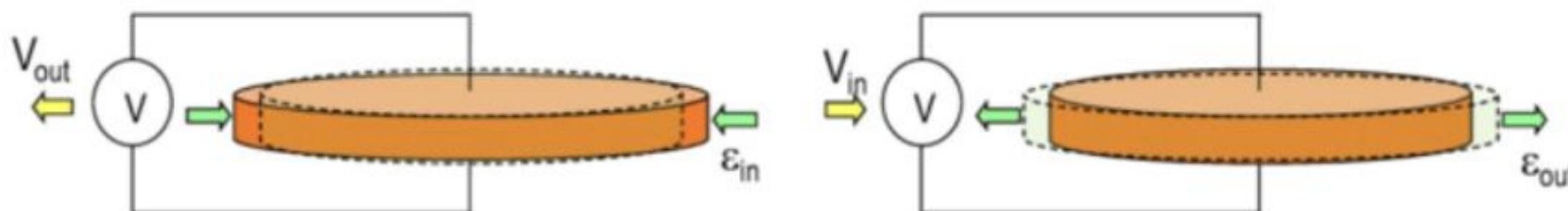
# Sensors and Actuators



**Direct Effect - Sensor**

Deformation  $\rightarrow$  Charge and Voltage

(a) Longitudinal ( $d_{33}$ ) sensor and actuator



**Direct Effect - Sensor**

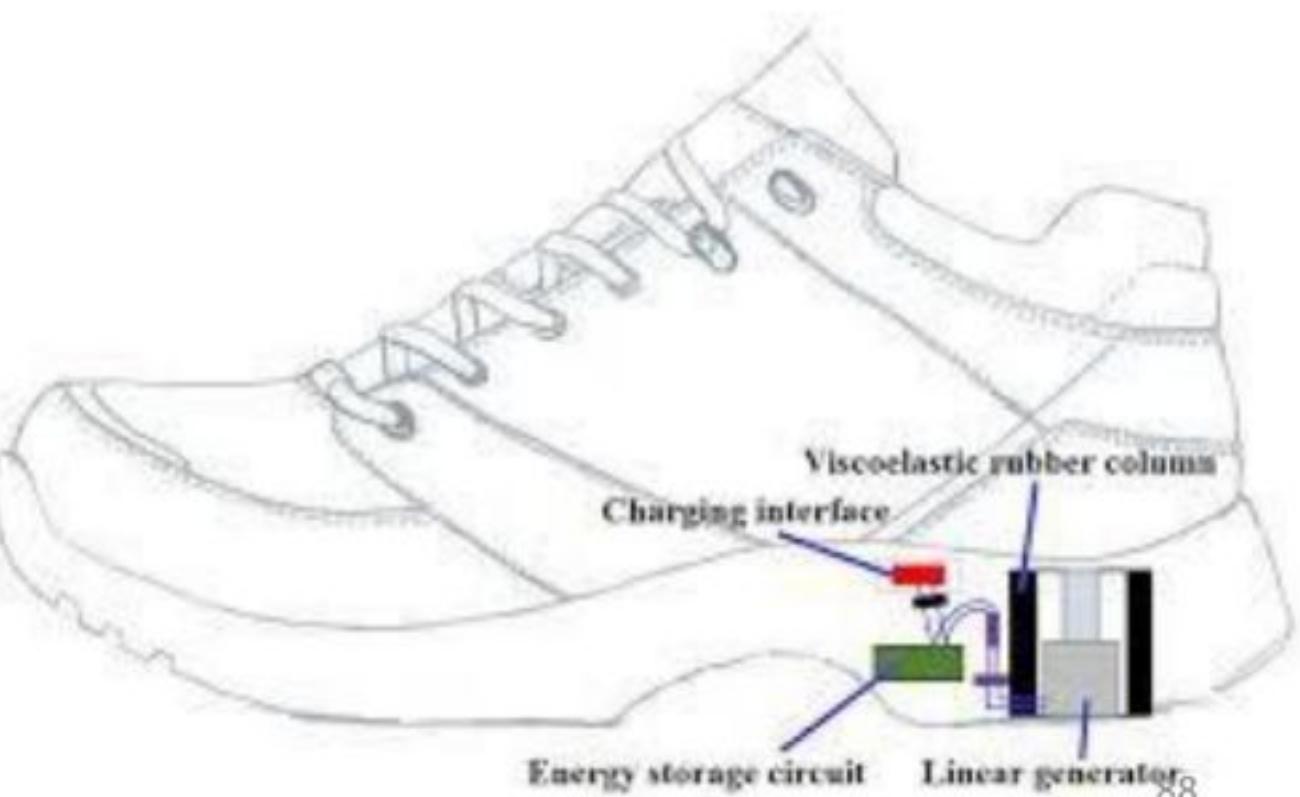
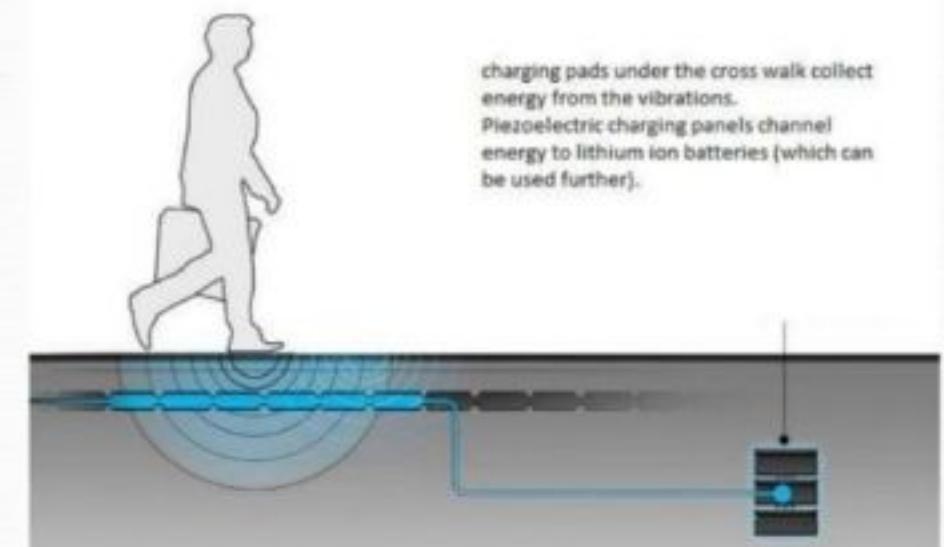
Deformation  $\rightarrow$  Charge and Voltage

(b) Transverse ( $d_{31}$ ) sensor and actuator

# Energy Harvesting

- Sidewalks
- Shoes
- Gyms and Work Places
- Piezoelectric Tiles, Floor mats and Carpets
- Mobile Keypads and Keyboards

## POWER GENERATING SIDEWALK



# Other Applications

## 1. As sensing elements

Detection of pressure variations in the form of sound is the most common sensor application, e.g. piezoelectric microphones. Sound waves bend the piezoelectric material, creating a changing voltage.

## 2. Ultrasound imaging

Piezoelectric sensors are used with high frequency sound in ultrasonic transducers for medical imaging . For many sensing techniques, the sensor can act as both a sensor and an actuator. Ultrasonic transducers, for example, can inject ultrasound waves into the body, receive the returned wave, and convert it to an electrical signal (a voltage).

## 3. Sonar sensors

Piezoelectric elements are also used in the detection and generation of sonar waves. Applications include power monitoring in high power applications such as medical treatment, sonochemistry and industrial processing etc.

## 4. As chemical and biological sensors

Piezoelectric microbalances are used as very sensitive chemical and biological sensors. Piezo are also used as strain gauges.

## **5. In Music instruments**

Piezoelectric transducers are used in electronic drum pads to detect the impact of the drummer's sticks.

## **6. Automotive application**

Automotive engine management systems use a piezoelectric transducer to detect detonation by sampling the vibrations of the engine block. Ultrasonic piezosensors are used in the detection of acoustic emissions in acoustic emission testing.

## **7. Piezoresistive silicon devices**

The Piezoresistive effect of semiconductors has been used for sensor devices employing all kinds of semiconductor materials such as germanium, polycrystalline silicon, amorphous silicon, and single crystal silicon. Since silicon is today the material of choice for integrated digital and analog circuits the use of Piezoresistive silicon devices has been of great interest. It enables the easy integration of stress sensors with Bipolar and CMOS circuits.

## **8. Piezoresistors**

Piezoresistors are resistors made from a Piezoresistive material and are usually used for measurement of mechanical stress. They are the simplest form of Piezoresistive device.

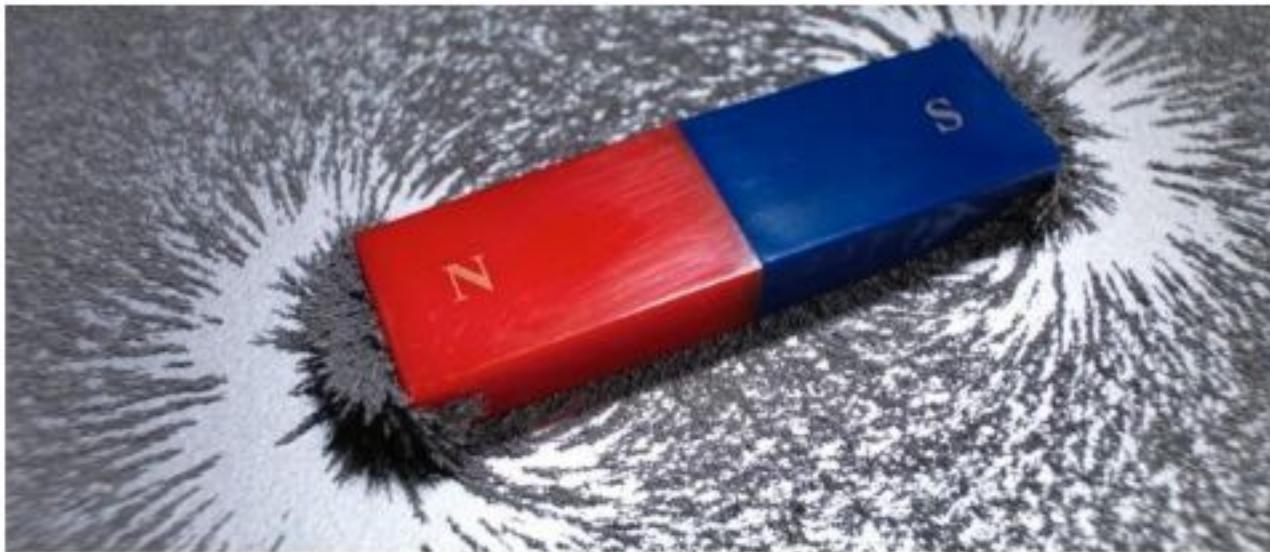
## Application of a Pyroelectric-Infrared detection

**Refer to the link :** <https://www.doitpoms.ac.uk/tplib/pyroelectricity/infrared.php>

## Pollutant Control

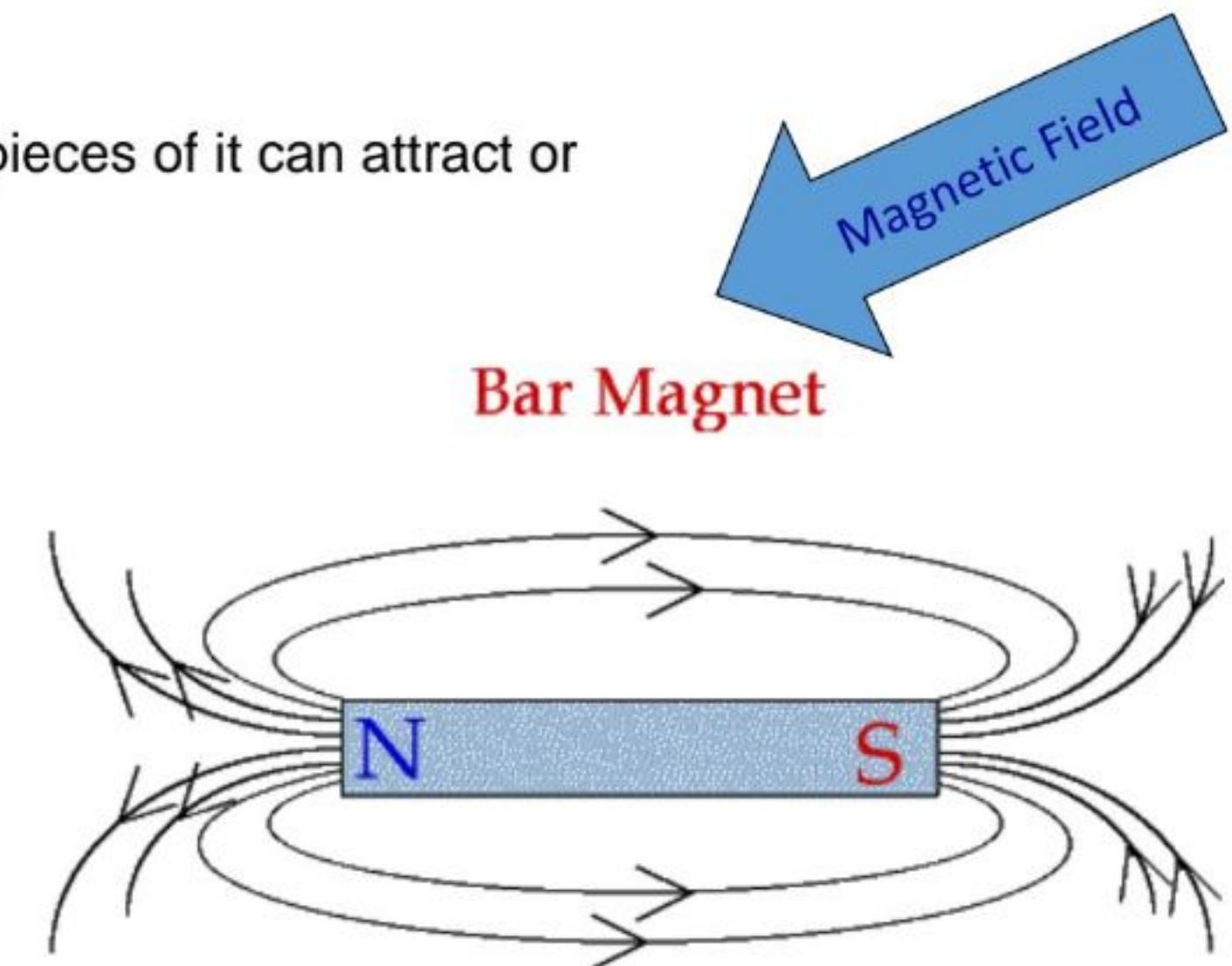
**Refer to the link:** <https://www.doitpoms.ac.uk/tplib/pyroelectricity/pollution.php>

# Magnetism



- The earliest experiences with magnetism involved **magnetite**, the only material that occurs naturally in a magnetic state.
- This mineral was also known as **lodestone**, after its property of aligning itself in certain directions if allowed to rotate freely, thus being able to indicate the positions of north and south, and to some extent also latitude. "course stone" or "leading stone"
- The other well-known property of lodestone is that two pieces of it can attract or even repel each other

### Magnetic Dipoles



Cutting a bar magnet in half produces TWO bar magnets, each with N and S poles.

## Day to day applications

Many of our modern technological devices rely on magnetism and magnetic materials; these include **electrical power generators and transformers, electric motors, radio, television, telephones, computers, and components of sound and video reproduction systems**



Loud Speaker



Printer



Medical Equipment



Magnetic Levitation



Motor



Sensor



Mobile Cover



Gift Box Packing



Magnetic Toy



Car holder



Wind Turbine



VCM

## Origin of Magnetism

Macroscopic  
(*Charge currents*)

Microscopic  
(*Atomic scale*)

- ❑ If a loop of area A is carrying a current I, the **intrinsic intensity of the magnetic field** is given by the magnetic moment vector (**m** or  **$\mu$** ) directed from the north pole to the south pole; such that the magnitude of **m** is given by:  $m = IA$  (units: [ $\text{Am}^2$ ]).
- ❑ The magnetic moment is the **measure of the strength of the magnet** and is the ability to *produce (and be affected by)* a magnetic field.

### Important quantities in magnetism

- **Magnetic Moment Vector (m or  $\mu$ ).**  $|\mathbf{m}| = IA$ , Units: [ $\text{Am}^2$ ] or equivalently [Joule/Tesla].

Measure of the strength of the magnet.

- **Magnetic field strength/Magnetizing force (**H**).** Units: [ $\text{A/m}$ ]

Measure of the strength of the externally applied field.

**Magnetic induction**, or **Magnetic flux density**, denoted by  $B$ , represents the magnitude of the internal field strength within a substance that is subjected to an  $H$  field.

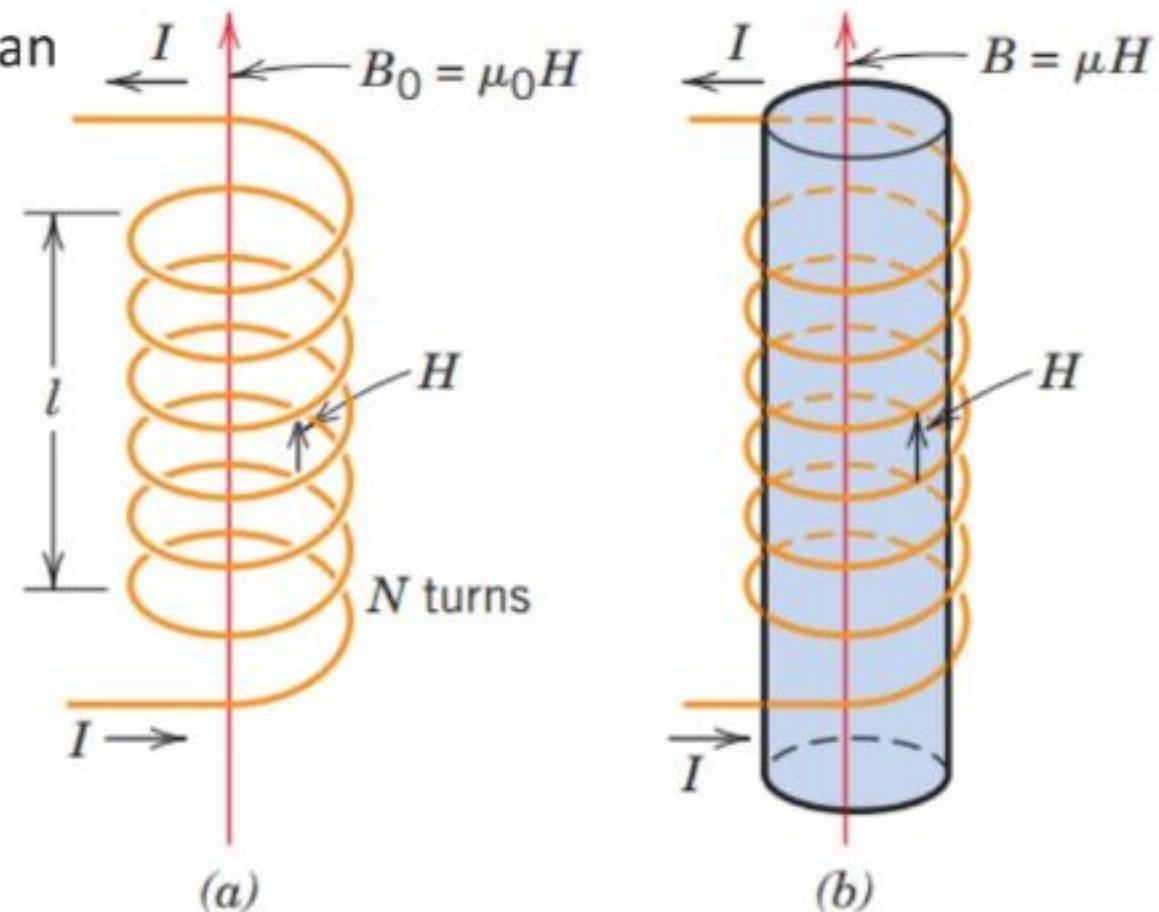
$$B = \mu H$$

$M$ , called the **magnetization** of the solid

$$B = \mu_0 H + \mu_0 M$$

In the presence of an  $H$  field, the magnetic moments within a material tend to become aligned with the field and to reinforce it by virtue of their magnetic fields; is given by the term  $\mu_0 M$

**B** and **H** are analogous to **D** and **E** discussed in Ferroelectrics



Quantity	Symbol
Magnetic induction (flux density)	$B$
Magnetic field strength	$H$
Magnetization	$M$ (SI) $I$ (cgs-emu)
Permeability of a vacuum	$\mu_0$
Relative permeability	$\mu_r$ (SI) $\mu'$ (cgs-emu)
Susceptibility	$\chi_m$ (SI) $\chi'_m$ (cgs-emu)

- Magnetization (**M**) = magnetic moment (**m**) per unit volume (**V**). Units: [A/m]

$$M = \frac{m}{V}$$

**M** measures the materials response to the applied field **H** (of course we know from our experience with permanent magnets that **M** can exist even if **H** is removed). **M** is the magnetization induced by the applied external field **H**.

- **$\sigma$**  = magnetic moment per unit mass = m/mass. Units: [Am<sup>2</sup>/kg]
- Magnetic induction/Magnetic flux density (**B**) = Magnetic flux per unit area. Units: [Tesla = Weber/m<sup>2</sup> = Vs/m<sup>2</sup> = Kg/s<sup>2</sup>/A]

**B** is the magnetic flux density inside the material.

➤ **B** =  $\mu_0 (\mathbf{H} + \mathbf{M})$  ( $\mu_0$  is the magnetic permeability of vacuum  
= H/m = Wb/A/m = mKg/s<sup>2</sup>A<sup>2</sup>)

- **Permeability ( $\mu$ )**. Units: [dimensionless]

$$\mu = \frac{\mathbf{B}}{\mathbf{H}}$$

- **Magnetic susceptibility ( $\chi$ )**. (volume susceptibility) Units: [dimensionless]

$\chi = \frac{\mathbf{M}}{\mathbf{H}}$  (the symbol  $\chi_v$  is also used to emphasize that the quantity is per unit volume).

- **Magnetic anisotropy**

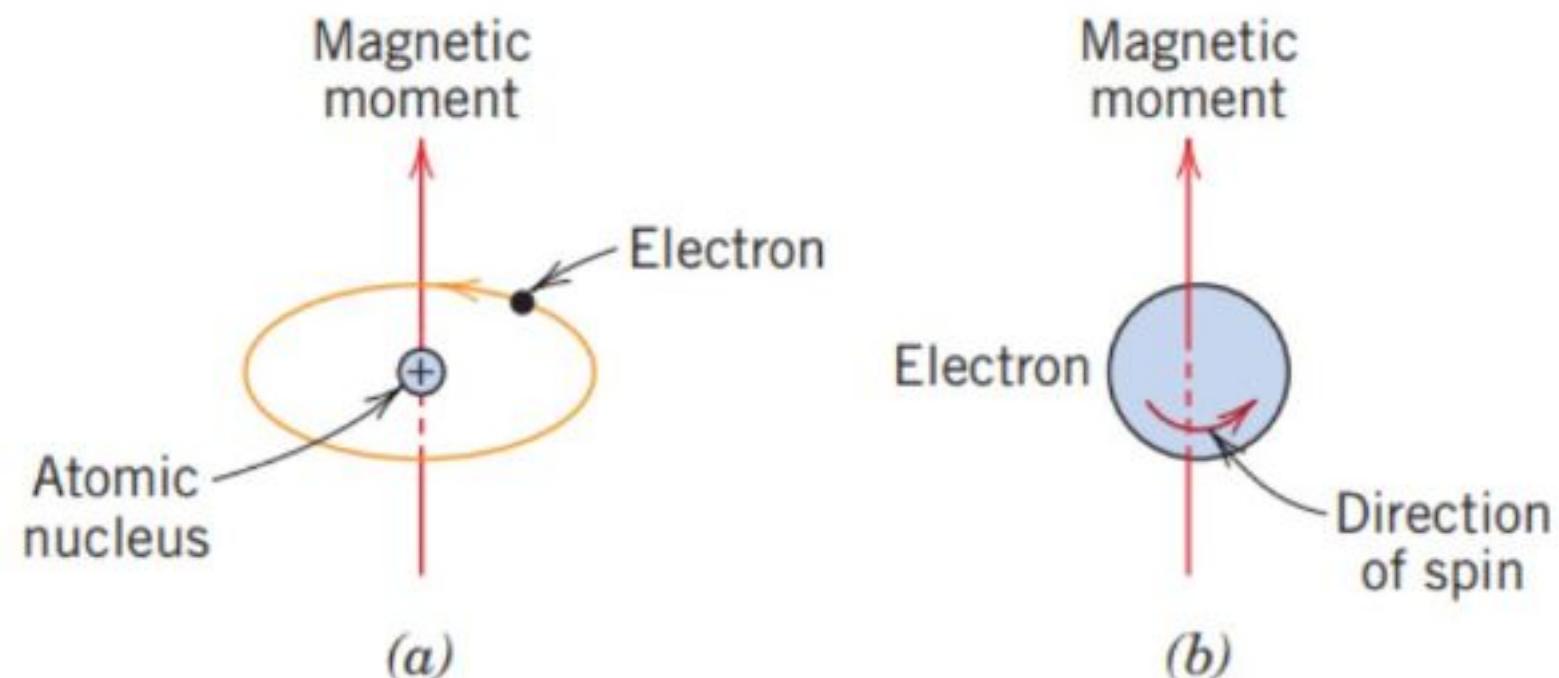
Anisotropy means that various directions in the crystals are non-equivalent with respect magnetization ( $\mathbf{M}$ ) and this implies that  $\mathbf{M}$  may not be in the same direction of the applied field. There are many contributions to this anisotropy as we shall see later, crystalline (magneto-crystalline) anisotropy being the prominent one.

# Origin of Magnetic Moments

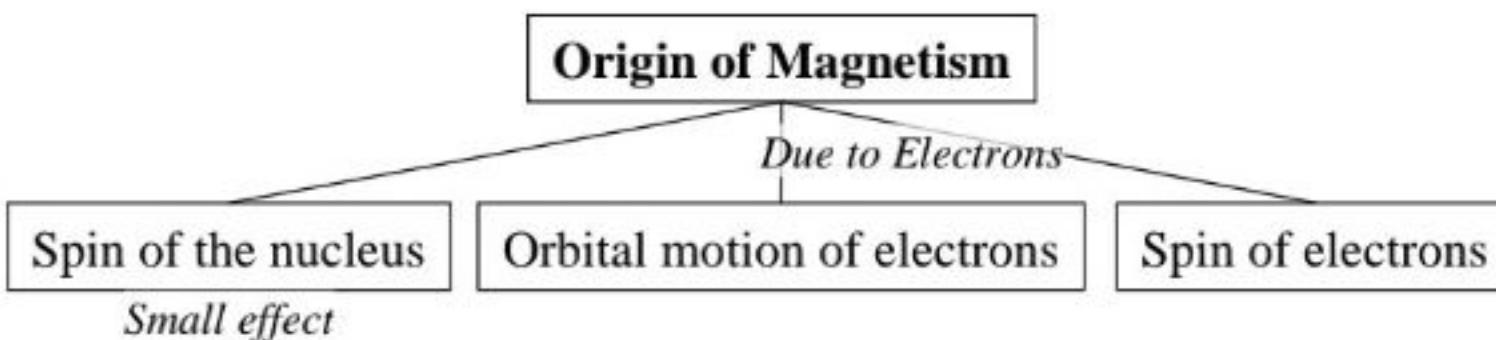
- In each individual atom, orbital moments of some electron pairs cancel each other; this also holds for the spin moments.
- For an atom having completely filled electron shells or subshells, when all electrons are considered, there is total cancellation of both orbital and spin moments.
- Thus materials composed of atoms having completely filled electron shells are not capable of being permanently magnetized. This category includes the inert gases (He, Ne, Ar, etc.) as well as some ionic materials.

Most free atoms possess net angular momentum and therefore have magnetic moments, but when atoms combine to form molecules or solids, the electrons interact so that the resultant angular momentum is nearly always zero.

Exceptions are atoms of the elements of the three transition series which, because of their incomplete inner electron shells, have a resultant magnetic moment.



## Atomic origin of magnetic moments



This is classical way of looking at a quantum effect !

- i) Nuclear spin (which is slow and has a small contribution to the overall magnetic effect)

*Note: at very low temperatures magnetism due to nuclear spin may become important*

- ii) Spin of electrons
- iii) Orbital motion of electrons around the nucleus

The magnetic moment due to spin is equal to the magnetic moment due to orbital motion (in the first Bohr orbit) and is approximately expressed in terms of the **Bohr magneton** ( $\mu_B$ ):

$$m_B = \mu_B = \frac{e\hbar}{4\pi m} = 9.27 \times 10^{-24} \text{ Am}^2$$

## Magnetic Moment of a Single Unpaired Atomic Electron

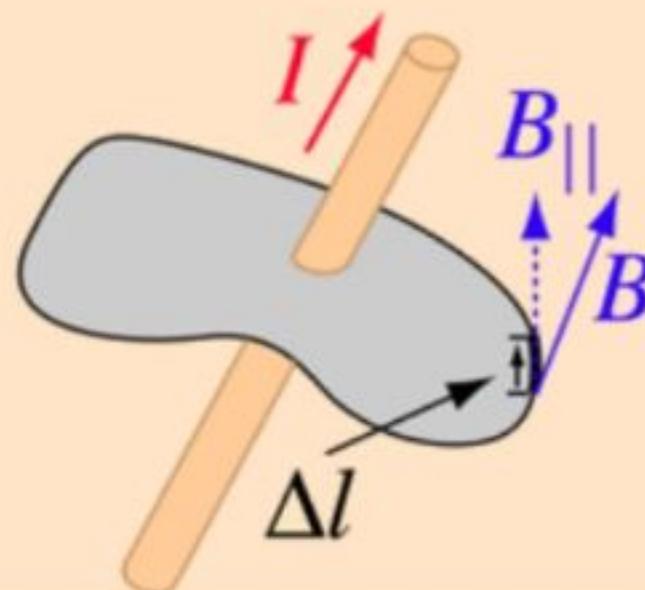
Each electron spinning on its own axis behaves as a magnetic dipole and has a dipole moment called the **Bohr magneton**  $\mu_B$ . This dipole moment has a value of

$$\mu_B = \frac{e\hbar}{4\pi m}$$

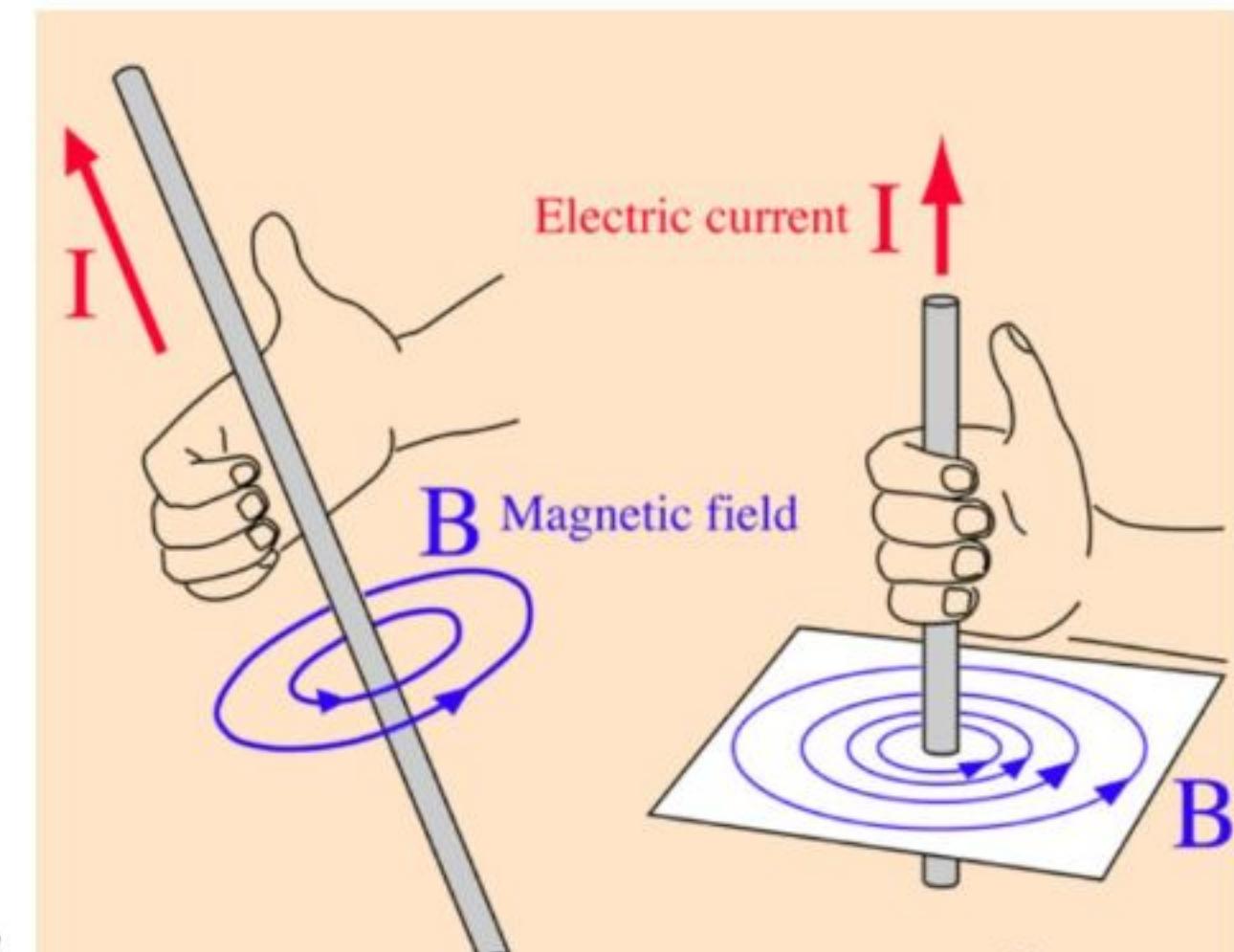
where  $e$  = electronic charge,  $h$  = Planck's constant, and  $m$  = electron mass. In SI units,  $\mu_B = 9.27 \times 10^{-24} \text{ A} \cdot \text{m}^2$ . In most cases, electrons in atoms are paired, and so the positive and negative magnetic moments cancel. However, unpaired electrons in inner electron shells can have small positive dipole moments, as is the case for the  $3d$  electrons of Fe, Co, and Ni.

# Ampere's Law

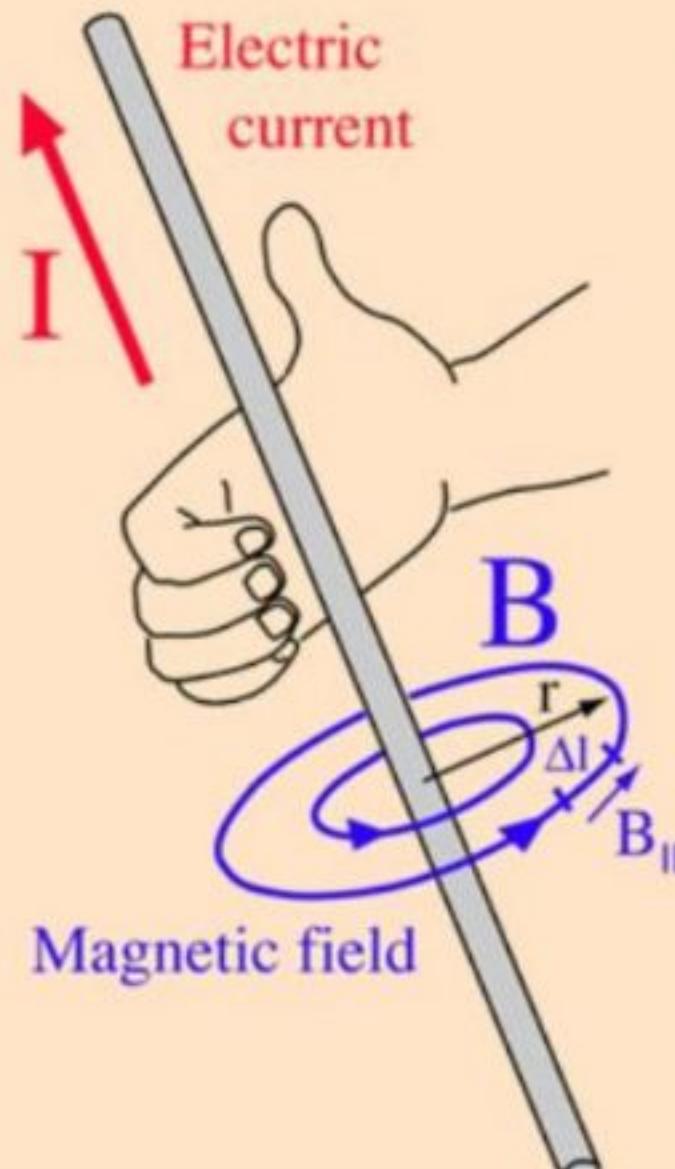
The magnetic field in space around an electric current is proportional to the electric current which serves as its source, just as the electric field in space is proportional to the charge which serves as its source. Ampere's Law states that for any closed loop path, the sum of the length elements times the magnetic field in the direction of the length element is equal to the permeability times the electric current enclosed in the loop.



$$\sum B_{||} \Delta l = \mu_0 I$$



# Magnetic Field of Current



The magnetic field of an infinitely long straight wire can be obtained by applying Ampere's law. Ampere's law takes the form

$$\sum B_{||} \Delta l = \mu_0 I$$

and for a circular path centered on the wire, the magnetic field is everywhere parallel to the path. The summation then becomes just

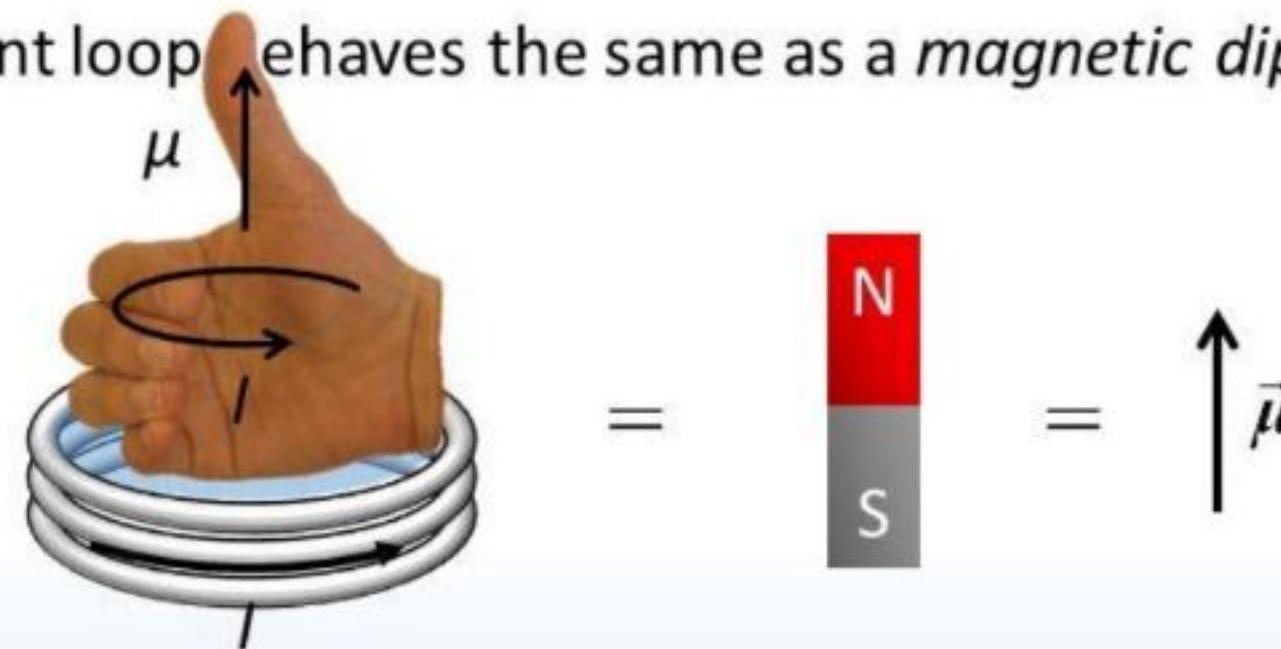
$$\sum B_{||} \Delta l = B 2\pi r$$

$$B = \frac{\mu_0 I}{2\pi r}$$

The constant  $\mu_0$  is the permeability of free space.

# Magnetic dipole & current loop

A current loop behaves the same as a *magnetic dipole*



Equivalent magnetic dipole moment:

Magnitude

$$\mu = NIA$$

True for flat loop of *any shape*

Direction

For a loop with  $N$  turns of wire

Another “right hand rule”: Curl fingers along  $I$   
 $\vec{\mu}$  along thumb

## Magnetic permeability ( $\mu$ )

is the ability of a magnetic material **to support magnetic field development**. In other words, magnetic permeability is the constant in the proportionality between magnetic induction and magnetic field intensity.

The **greater the magnetic permeability of the material, the greater the conductivity for magnetic lines of force**, and vice versa.

The magnetic permeability of a material indicates the ease with which an external magnetic field can create a higher magnetic force of attraction in the material.

$$B = \mu H$$

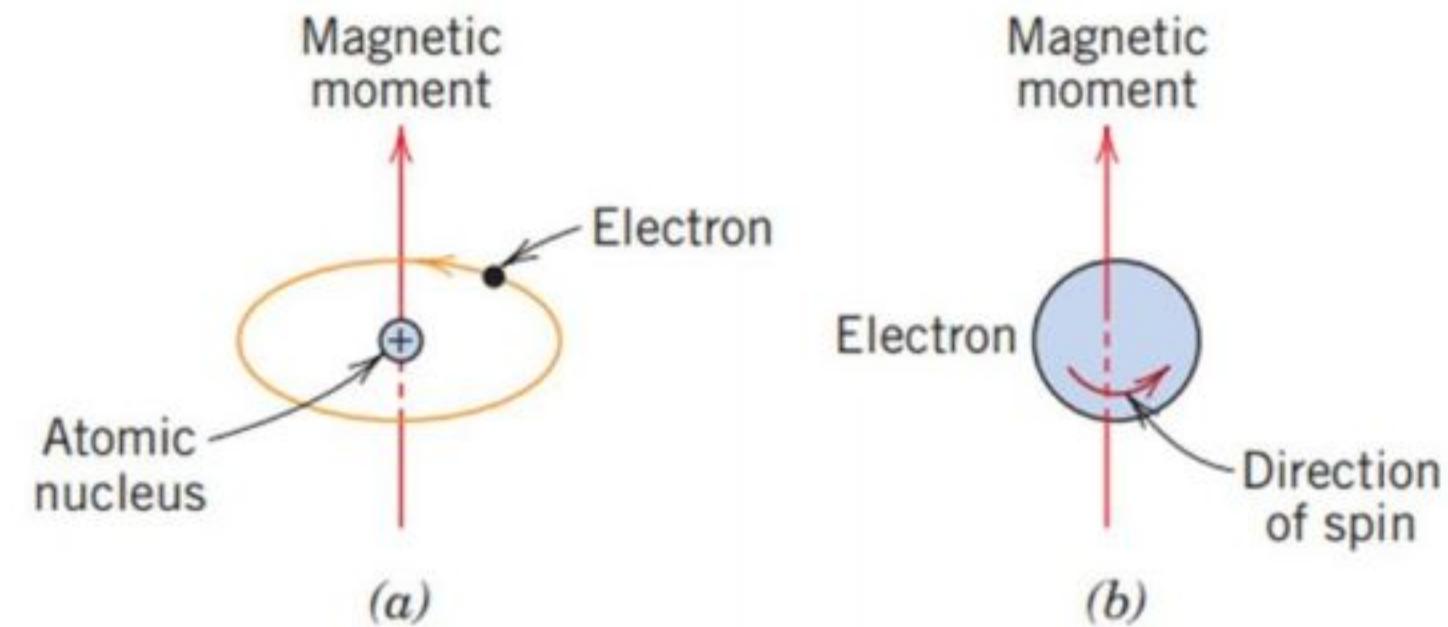
## Magnetic susceptibility ( $\chi$ )

is a measure of **how much a material will become magnetized in an applied magnetic field**. It is the ratio of magnetization  $M$  (magnetic moment per unit volume) to the applied magnetizing field intensity  $H$ .

$$\chi_m = \frac{M}{H}$$

## The Bohr magneton $\mu_B$

is a physical constant and the natural unit for expressing the magnetic moment of an electron caused by either its orbital or spin angular momentum.



## Value of Bohr Magneton

$$\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-21}$$

## Diamagnetism

- An external magnetic field acting on the atoms of a material slightly unbalances their orbiting electrons and creates small magnetic dipoles within the atoms that oppose the applied field.
- This action produces a negative magnetic effect known as **diamagnetism**.
- The diamagnetic effect produces a very small negative magnetic susceptibility on the order of  $\chi_m \approx -10^{-6}$ .
- Diamagnetism occurs in all materials, but in many its negative magnetic effect is canceled by positive magnetic effects.
- Diamagnetic behavior has no significant engineering importance.

## Paramagnetism

- Materials that exhibit a small positive magnetic susceptibility in the presence of a magnetic field.
- The paramagnetic effect in materials disappears when the applied magnetic field is removed.
- Paramagnetism is produced by the alignment of individual magnetic dipole moments of atoms or molecules in an applied magnetic field.
- Since thermal agitation randomizes the directions of the magnetic dipoles, an increase in temperature decreases the paramagnetic effect.
- The atoms of some transition and rare earth elements possess incompletely filled inner shells with unpaired electrons.
- These unpaired inner electrons in atoms, since they are not counterbalanced by other bonding electrons in solids, cause strong paramagnetic effects and in some cases produce very much stronger ferromagnetic and ferrimagnetic effects

## DIAMAGNETISM AND PARAMAGNETISM

### Non-Magnetic

Diamagnetism very weak, nonpermanent and persists only while an external field is being applied.

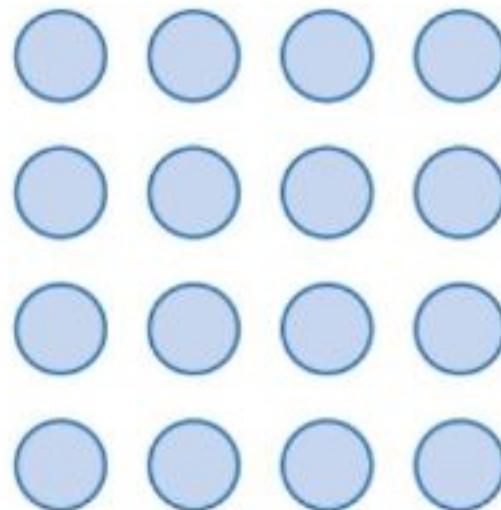
induced by a change in the orbital motion of electrons due to an applied magnetic field.

For some solid materials, each atom possesses a permanent dipole moment by virtue of incomplete cancellation of electron spin and/or orbital magnetic moments.

In the absence of an external magnetic field, the orientations of these atomic magnetic moments are random, such that a piece of material possesses no net macroscopic magnetization.

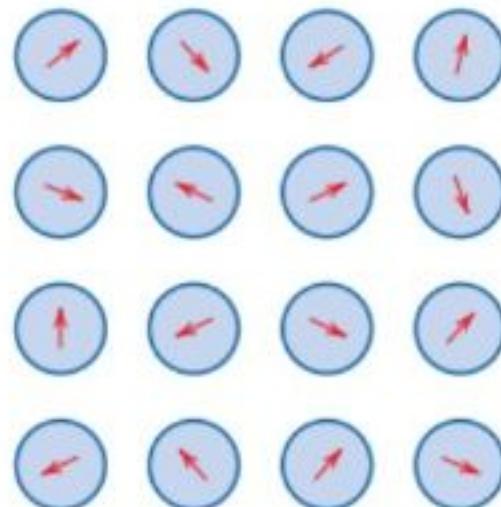
These atomic dipoles are free to rotate, and paramagnetism results when they preferentially align, by rotation, with an external field

$$H = 0$$



(a)  
**Paramagnetism**

$$H = 0$$

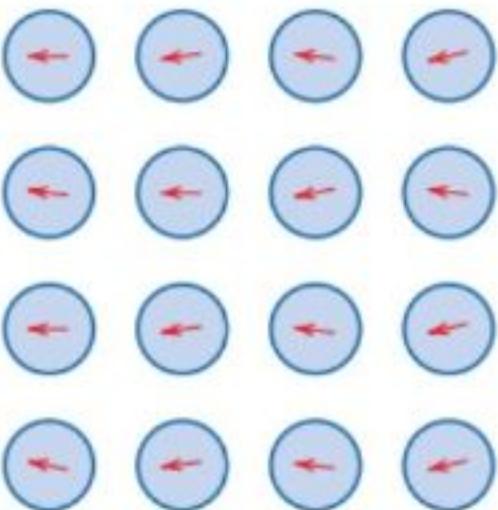


(b)

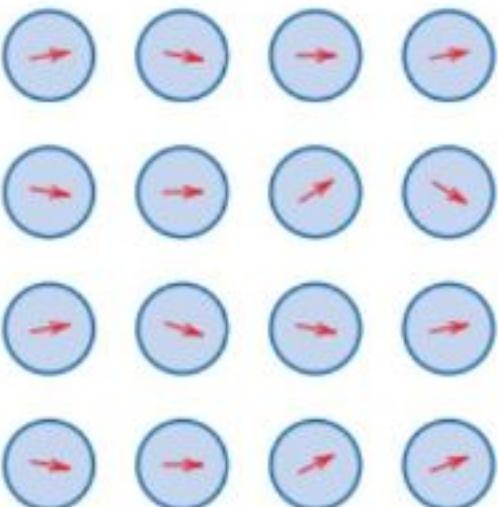
electron spin and/or orbital magnetic moments

### Diamagnetism

$$H$$

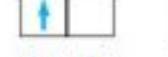
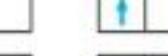
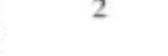


$$H$$

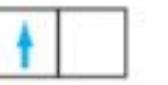
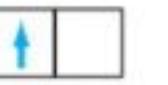
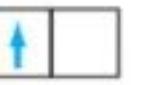
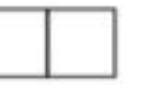
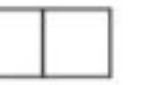
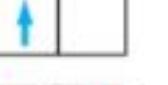
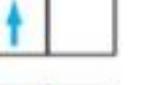
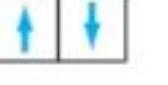
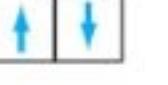
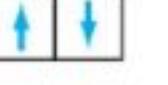
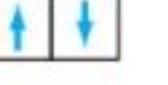
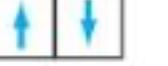


## Ferromagnetism

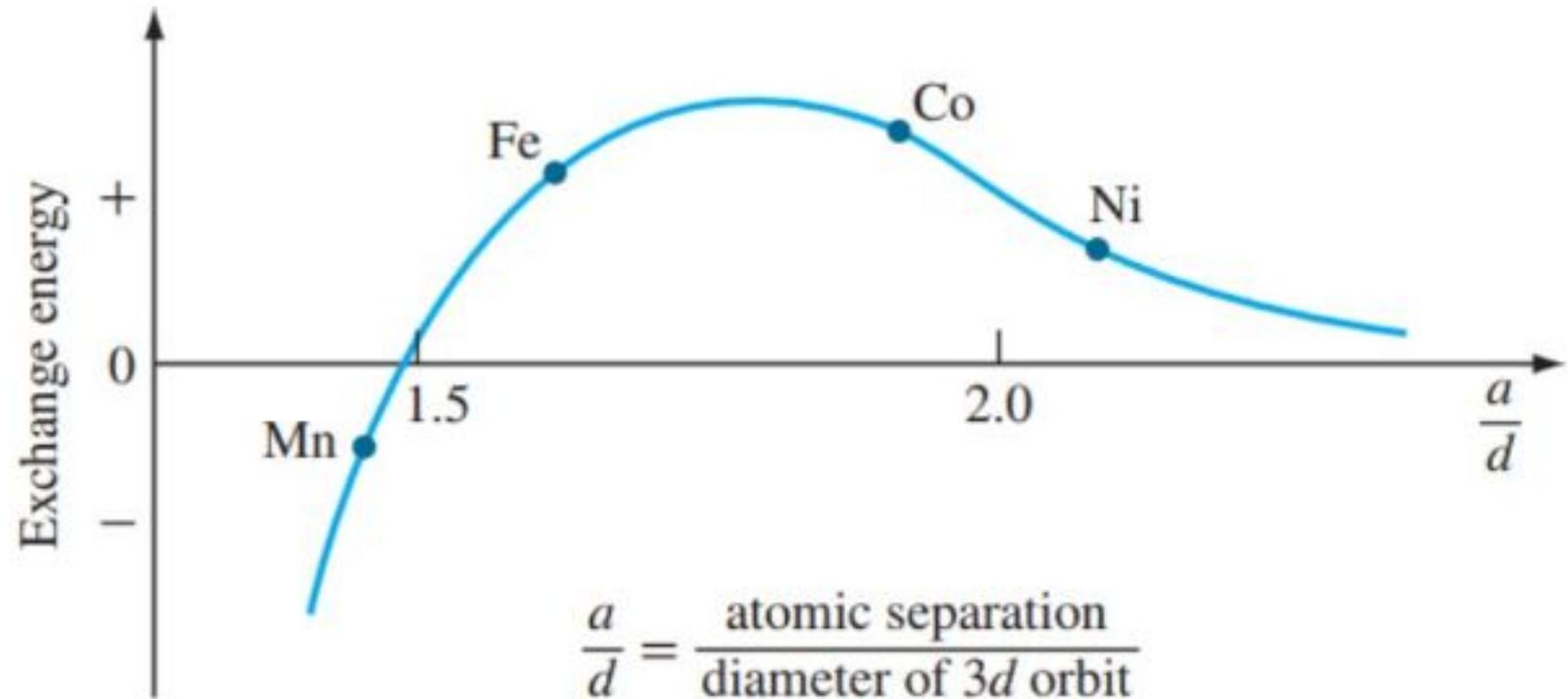
- **Ferromagnetism**, is of great engineering importance.
- Large magnetic fields that can be retained or eliminated as desired can be produced in ferromagnetic materials.
- The most important ferromagnetic elements from an industrial standpoint are iron (Fe), cobalt (Co), and nickel (Ni)
- Gadolinium (Gd), a rare earth element, is also ferromagnetic below 16°C but has little industrial application
- The ferromagnetic properties are due to the way the spins of the inner unpaired electrons are aligned in their crystal lattices.
- The inner shells of individual atoms are filled with pairs of electrons with opposed spins, and so they do not contribute to the resultant magnetic dipole moments.
- In solids, the outer valence electrons of atoms are combined with each other to form chemical bonds, and so there is no significant magnetic moment due to these electrons.

Unpaired 3d electrons	Atom	Number of electrons	Electronic configuration 3d orbitals					4s electrons
3	V	23						2
5	Cr	24						1
5	Mn	25						2
4	Fe	26						2
3	Co	27						2
2	Ni	28						2
0	Cu	29						1

In Fe, Co, and Ni, the unpaired inner 3d electrons are responsible for the ferromagnetism that these elements exhibit

Unpaired 3d electrons	Atom	Number of electrons	Electronic configuration 3d orbitals					4s electrons
3	V	23						2
5	Cr	24						1
5	Mn	25						2
4	Fe	26						2
3	Co	27						2
2	Ni	28						2
0	Cu	29						1

- In a solid sample of Fe, Co, or Ni at room temperature, the spins of the 3d electrons of adjacent atoms align in a parallel direction by a phenomenon called *spontaneous magnetization*. This parallel alignment of atomic magnetic dipoles occurs only in microscopic regions called **magnetic domains**.
- The parallel alignment of the magnetic dipoles of atoms of Fe, Co, and Ni is due to the creation of a positive exchange energy between them.
- For this parallel alignment to occur, the ratio of the atomic spacing to the diameter of the 3d orbit must be in the range from about 1.4 to 2.7. Thus Fe, Co, and Ni are ferromagnetic, but manganese (Mn) and chromium (Cr) are not.



Magnetic exchange interaction energy as a function of the ratio of atomic spacing to the diameter of the  $3d$  orbit for some  $3d$  transition elements. Those elements that have positive exchange energies are ferromagnetic; those with negative exchange energies are antiferromagnetic.

# FERROMAGNETISM

Certain metallic materials possess a permanent magnetic moment in the absence of an external field, and manifest very large and permanent magnetizations.

These are the characteristics of **ferromagnetism**, and they are displayed by the transition metals iron (as BCC -ferrite), cobalt, nickel, and some of the rare earth metals such as gadolinium (Gd).

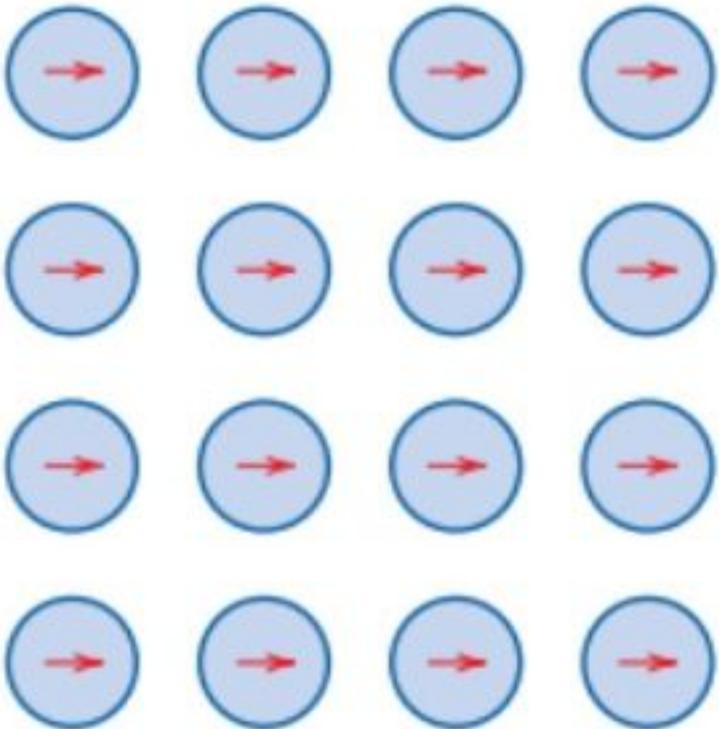
Due to uncancelled electron spins

Orbital magnetic moment contribution that is small in comparison to the spin moment

Coupling interactions cause net spin magnetic moments of adjacent atoms to align with one another, even in the absence of an external field

Mutual spin alignment exists over relatively large-volume regions of the crystal called **domains**

$$H = 0$$



Spin Coupling

## ANTIFERROMAGNETISM

This phenomenon of magnetic moment coupling between adjacent atoms or ions occurs in materials other than those that are ferromagnetic.

In one such group, this coupling results in an antiparallel alignment; the alignment of the spin moments of neighboring atoms or ions in exactly opposite directions is termed **antiferromagnetism**.

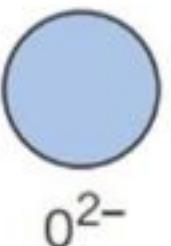
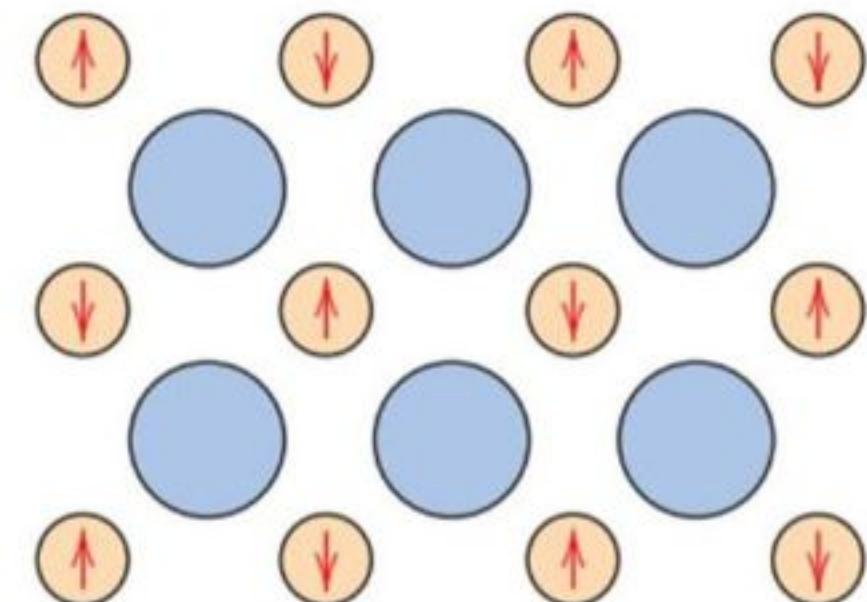
No net magnetic moment is associated with the  $O^{2-}$  ions, because there is a total cancellation of both spin and orbital moments.

Manganese oxide ( $MnO$ ) is one material that displays this behavior.

Manganese oxide is a ceramic material that is ionic in character, having both  $Mn^{2+}$  and  $O^{2-}$  ions.

No net magnetic moment is associated with the  $O^{2-}$  ions, because there is a total cancellation of both spin and orbital moments. However, the  $Mn^{2+}$  ions possess a net magnetic moment that is predominantly of spin origin.

These  $Mn^{2+}$  ions are arrayed in the crystal structure such that the moments of adjacent ions are antiparallel



**Antiferromagnetic  
manganese oxide**

## FERRIMAGNETISM

Some ceramics also exhibit a permanent magnetization, termed **ferrimagnetism**.

The macroscopic magnetic characteristics of ferromagnets and ferrimagnets are similar; the distinction lies in the source of the net magnetic moments.

However, the net ferromagnetic moment arises from the incomplete cancellation of spin moments

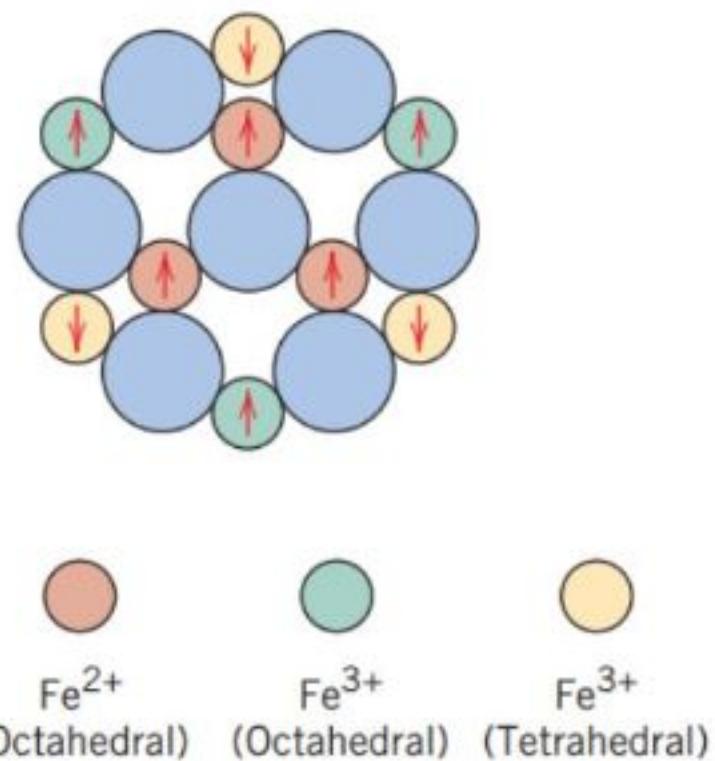
There are antiparallel **spin-coupling interactions** between the Fe ions, similar in character to antiferromagnetism.

The formula for  $\text{Fe}_3\text{O}_4$  may be written as  $\text{Fe}^{2+}\text{O}^{2-}-(\text{Fe}^{3+})_2(\text{O}^{2-})_3$ , in which the Fe ions exist in both +2 and +3 valence states in the ratio of 1:2. A net spin magnetic moment exists for each  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ion, which corresponds to 4 and 5 Bohr magnetons, respectively, for the two ion types.

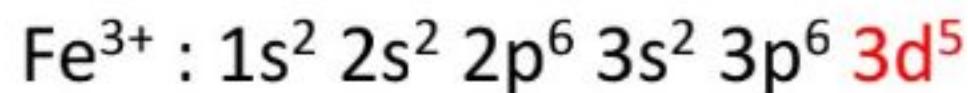
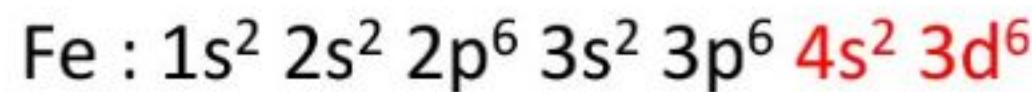
The spin moments of all the  $\text{Fe}^{3+}$  ions in the octahedral positions are aligned parallel to one another; however, they are directed oppositely to the  $\text{Fe}^{3+}$  ions disposed in the tetrahedral positions, which are also aligned.

This results from the antiparallel coupling of adjacent iron ions. Thus, the spin moments of all  $\text{Fe}^{3+}$  ions cancel one another and make no net contribution to the magnetization of the solid.

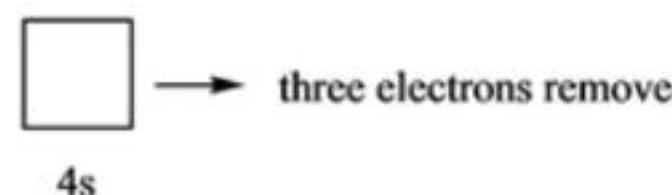
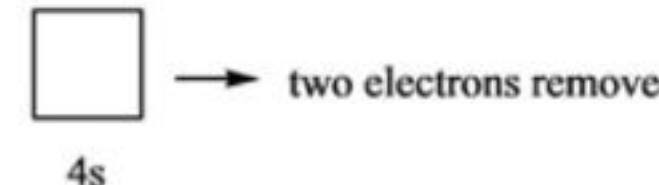
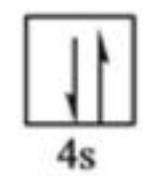
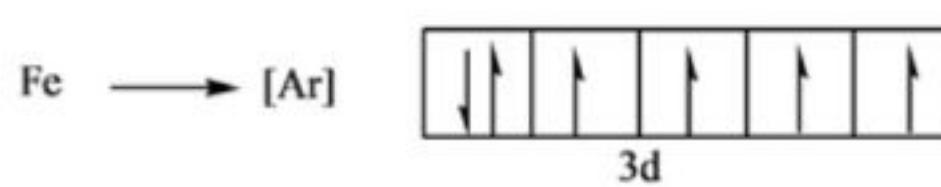
All the  $\text{Fe}^{2+}$  ions have their moments aligned in the same direction; this total moment is responsible for the net magnetization



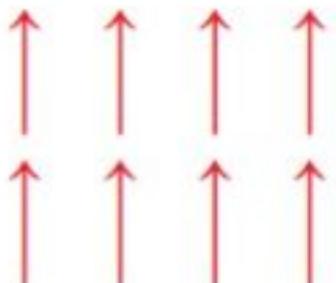
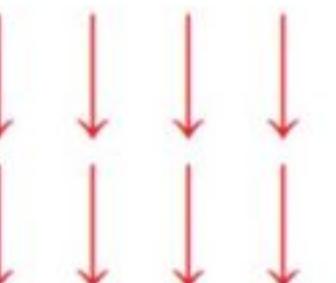
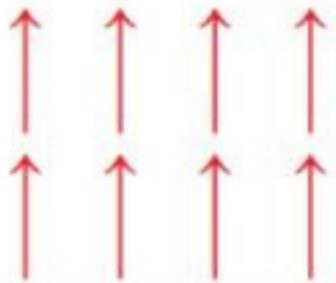
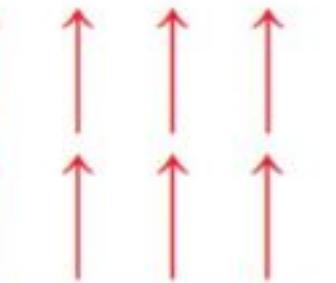
the net ferrimagnetic moment arises from the incomplete cancellation of spin moments.



This leaves 5 electrons that cannot all be paired off. It turns out that the magnetic moments arising from the orbital motion of these electrons do cancel out, but that the spin moments of all the electrons are parallel to one another. The ion therefore has a net magnetic moment.



Order of Subshell filling							
1s	2	1s2	2s2	2p6	3s2	3p6	4s2
2s	2	2s	2p	6	3s2	3p6	4s2
3s	2	3s	3p	6	3d	10	3d10
4s	2	4s	4p	6	4d	10	4d10
5s	2	5s	5p	6	5d	10	5f14
6s	2	6s	6p	6	6d	10	6g
7s	2	7s	7p	6	7d	10	7?
8s	2	8s	8p	6	8d	10	8?
					8f	14	8g
							8?
							8?

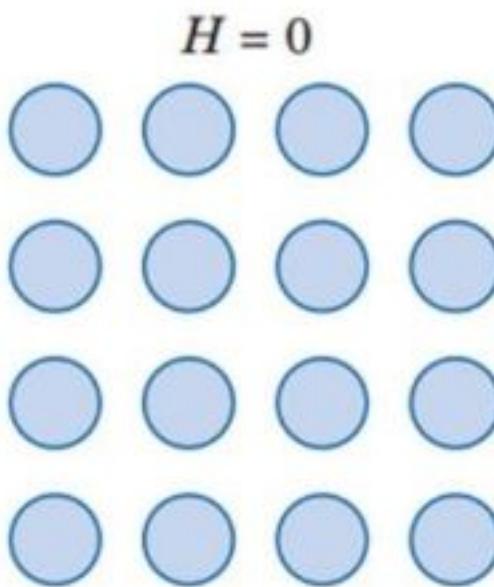
<i>Cation</i>	<i>Octahedral Lattice Site</i>	<i>Tetrahedral Lattice Site</i>	<i>Net Magnetic Moment</i>
$\text{Fe}^{3+}$			Complete cancellation
$\text{Fe}^{2+}$		—	

<sup>a</sup> Each arrow represents the magnetic moment orientation for one of the

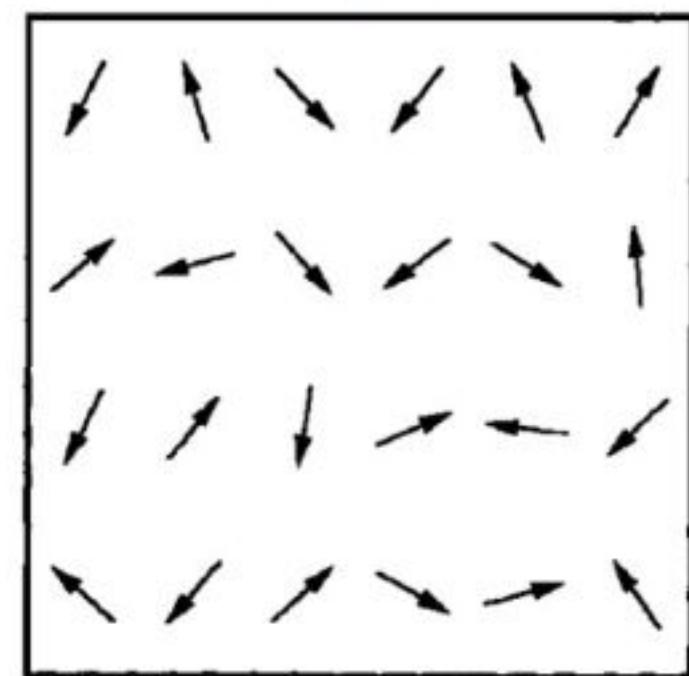
<i>Cation</i>	<i>Net Spin Magnetic Moment (Bohr magnetons)</i>
$\text{Fe}^{3+}$	5
$\text{Fe}^{2+}$	4
$\text{Mn}^{2+}$	5
$\text{Co}^{2+}$	3
$\text{Ni}^{2+}$	2
$\text{Cu}^{2+}$	1

# Recap

## Diamagnetic

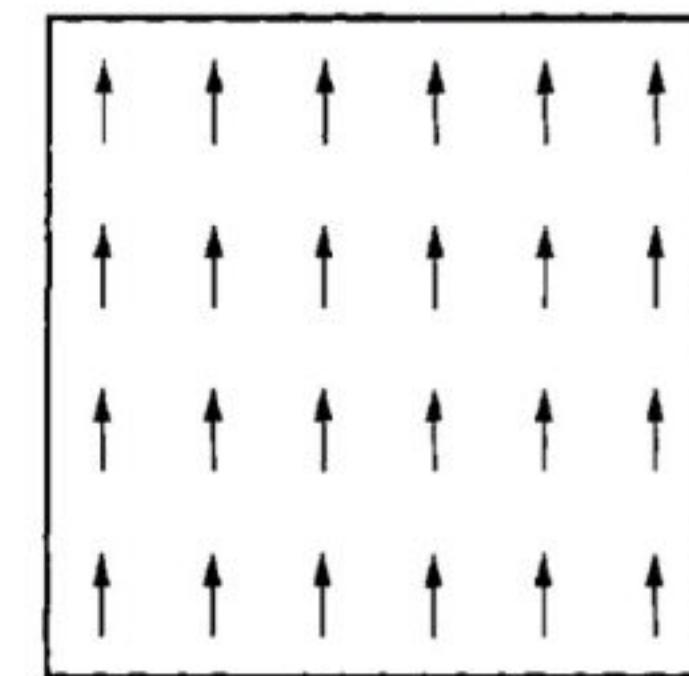


## Paramagnetic



$H = 0$

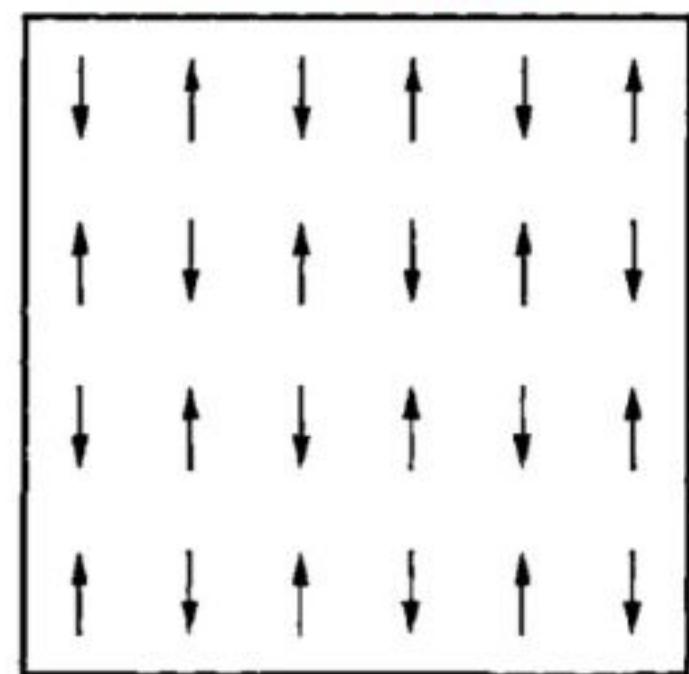
## Ferromagnetic



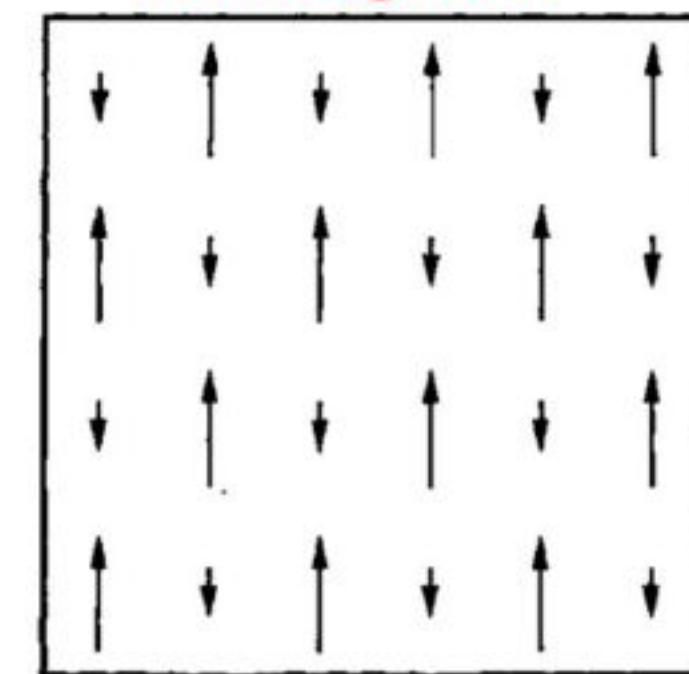
(a)

(b)

## Antiferromagnetic



## Ferrimagnetic



(No. or size in  
one  
direction  
Is greater than  
the other)

# Domains in Magnetic Materials

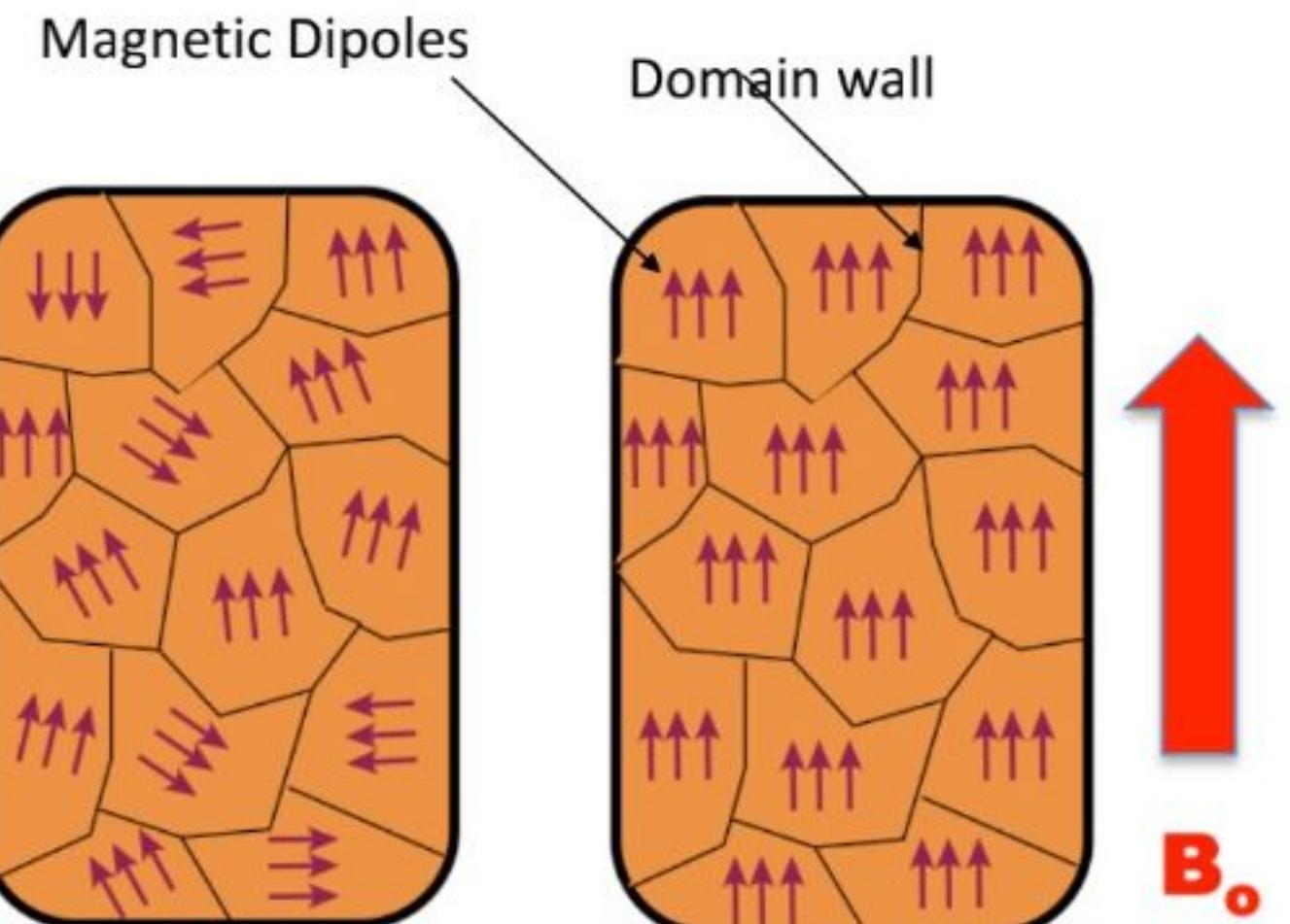
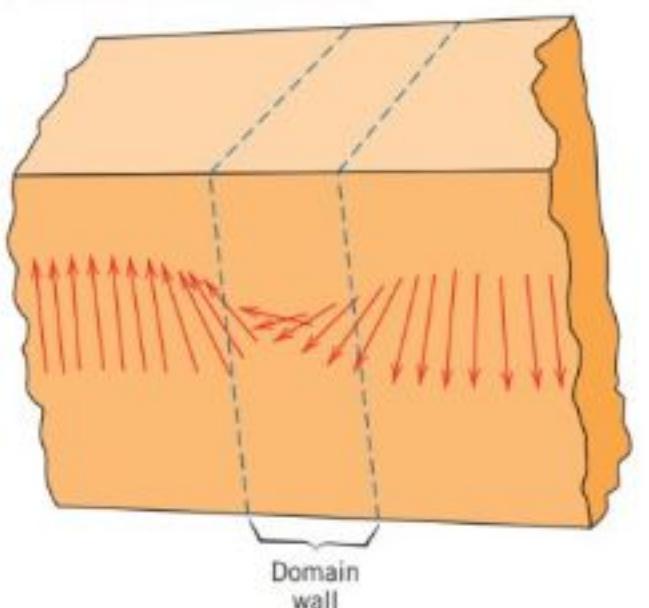
Region where magnetic dipoles are aligned in one particular direction

domains are microscopic in size,

Single Crystal: One domain

polycrystalline specimen : large no. of grains and each grain may consist of more than a single domain.

Thus, in a macroscopic piece of material, large number of domains, and all may have different magnetization orientations.



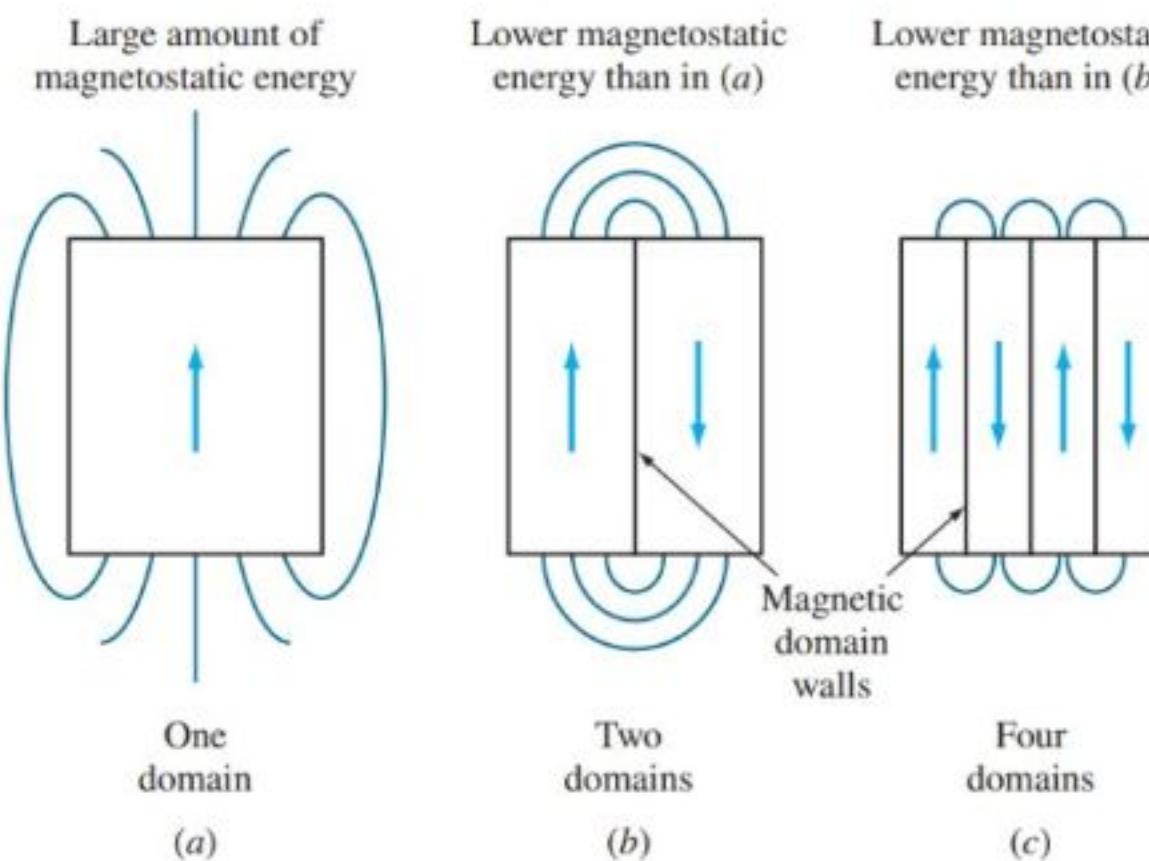
Domains randomly aligned

Domains aligned with external field

# TYPES OF ENERGIES THAT DETERMINE THE STRUCTURE OF FERROMAGNETIC DOMAINS

## Exchange Energy

- The potential energy *within* a domain of a ferromagnetic solid is minimized when all its atomic dipoles are aligned in one direction (**exchange energy**).
- This alignment is associated with a positive exchange energy.
- Even though the potential energy within a domain is minimized, its external potential energy is increased by the formation of an external magnetic field.



Schematic illustration showing how reducing the domain size in a magnetic material decreases the magnetostatic energy by reducing the external magnetic field.

(a) One domain, (b) two domains, and (c) four domains.

## Magnetostatic Energy

**Magnetostatic energy** is the **potential magnetic energy** of a ferromagnetic material produced by its external field. This potential energy can be minimized in a ferromagnetic material by domain formation.

For a unit volume of a ferromagnetic material, a single-domain structure has the highest potential energy, as indicated.

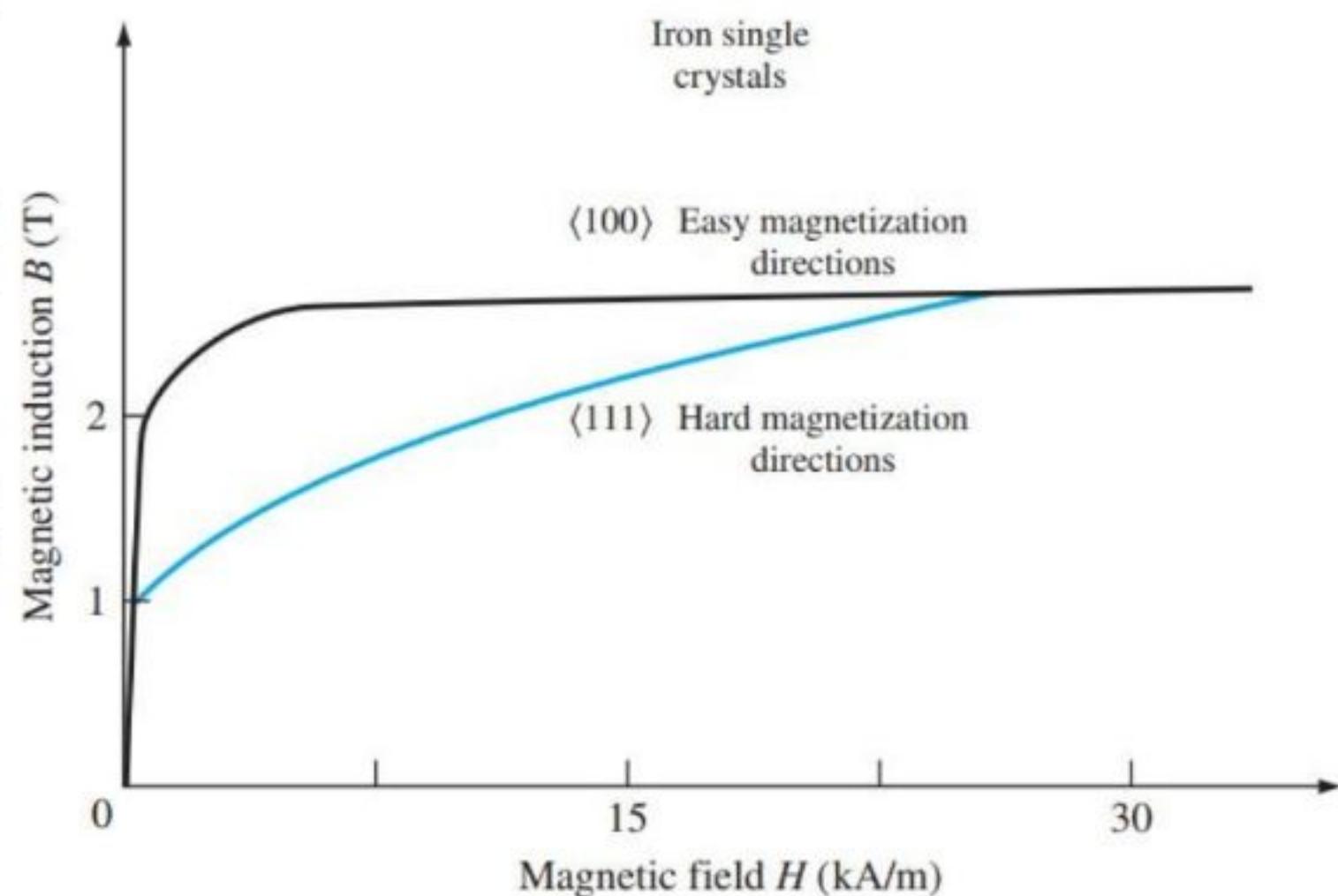
By dividing the single domain of into two domains, the intensity and extent of the external magnetic field are reduced. By further subdividing the single domain into four domains, the external magnetic field is reduced still more.

Since the **intensity of the external magnetic field** of a ferromagnetic material is **directly related** to its **magnetostatic energy**, the formation of multiple domains reduces the magnetostatic energy of a unit volume of material.

- Domain, Alignment of domains= Potential energy of a domain
- External magnetic field due to domain
- Potential magnetic energy due to the External Manetic Field = Magnetostatic Energy

## Magnetocrystalline Anisotropy Energy

- Grains whose orientations are in the easy direction of magnetization will saturate at low applied fields.
- Grains oriented in the hard directions must rotate their resultant moment in the direction of the applied field and thus will reach saturation under much higher fields.
- The work done to rotate all the domains because of this anisotropy is called the **magnetocrystalline anisotropy energy**.



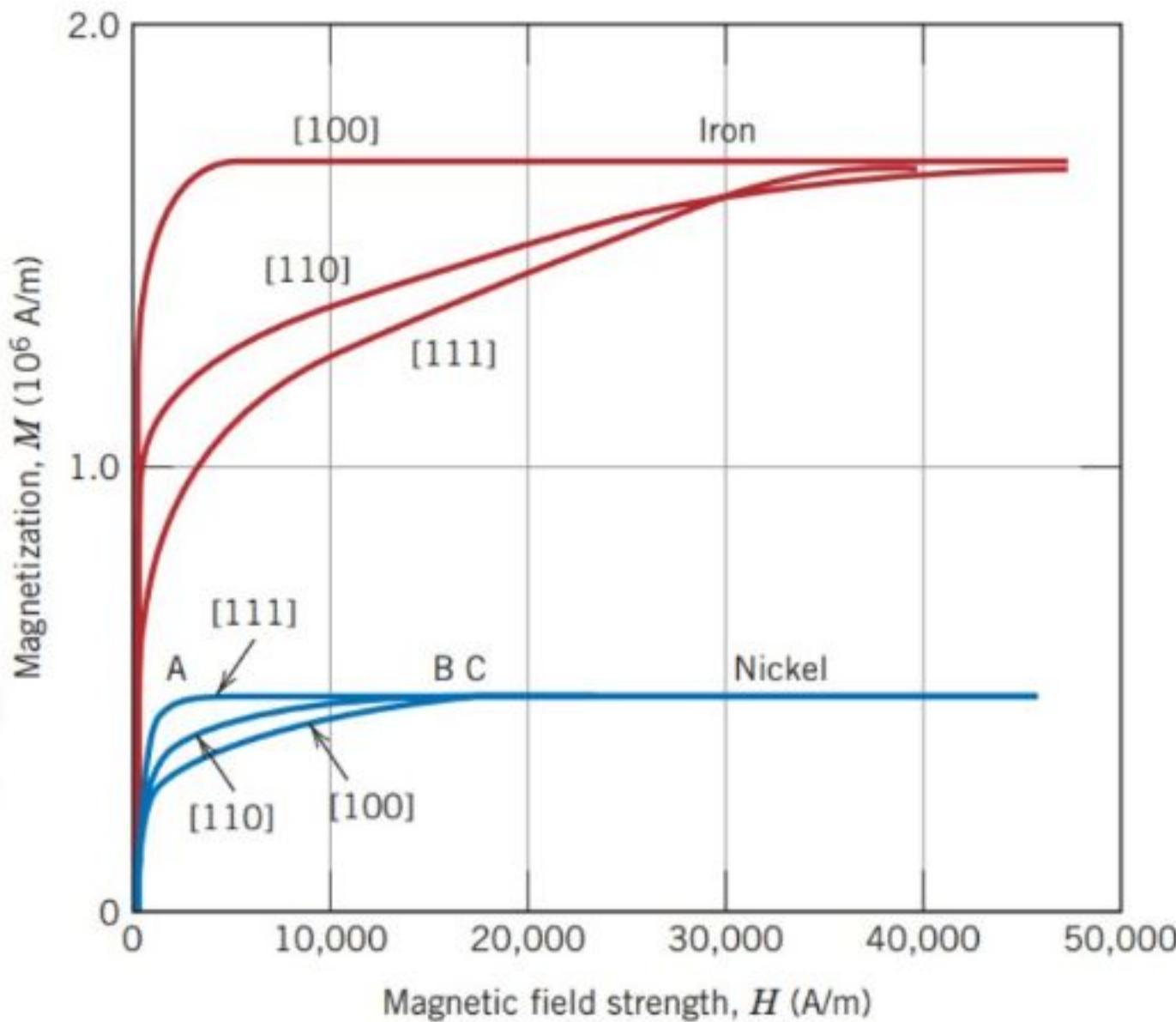
# Magnetic Anisotropy

Magnetic Hysteresis depends on

- (1) Whether the specimen is a **single crystal** or **polycrystalline**;
- (2) If polycrystalline, **any preferred orientation of the grains**;
- (3) The presence of **pores or second-phase particles**; and
- (4) Other factors such as **temperature** and, if a mechanical stress is applied, the **stress state**

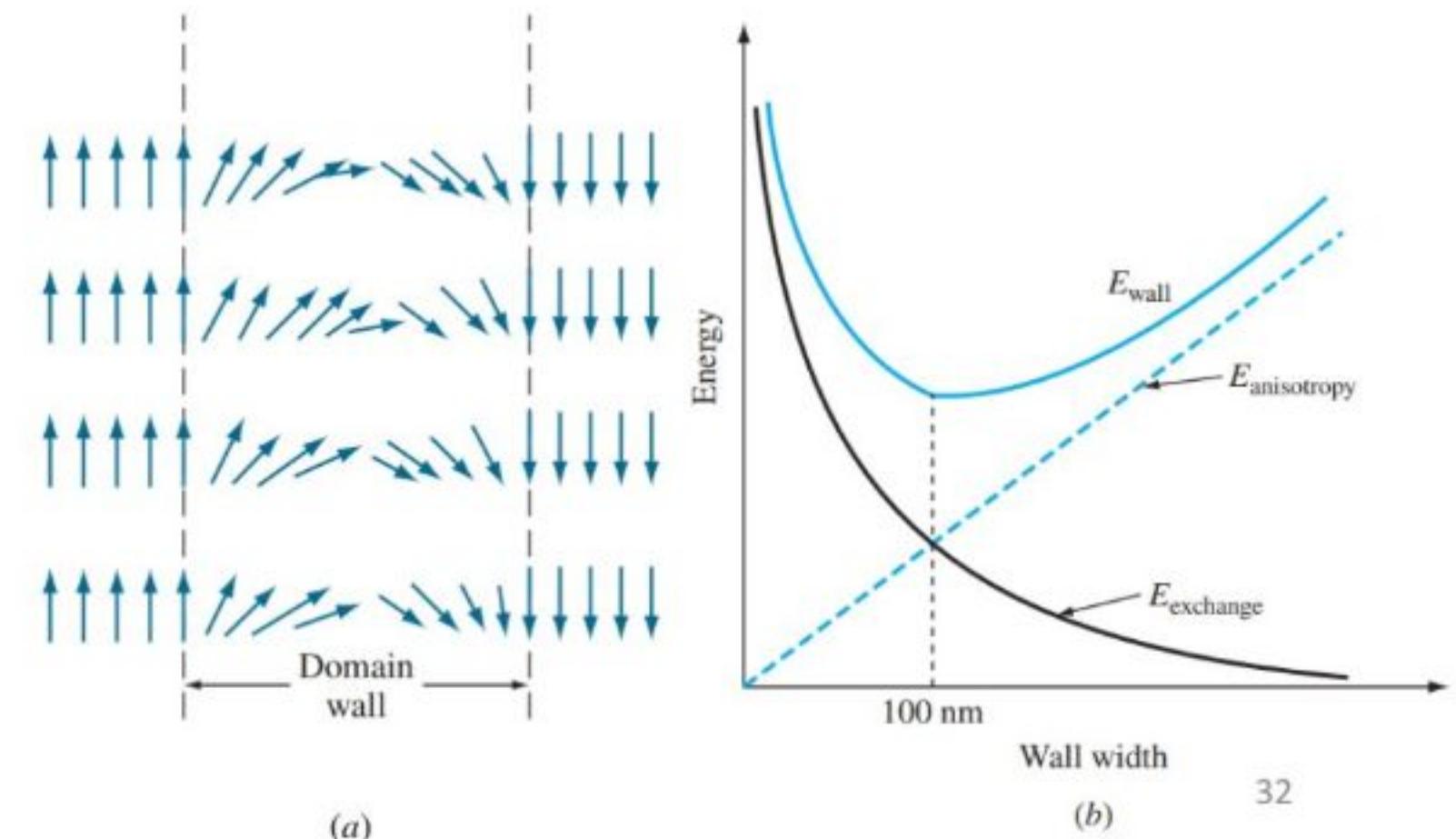
Dependence of magnetic behavior on crystallographic orientation is termed **magnetic anisotropy** (or sometimes **magnetocrystalline**).

For each of these materials there is one crystallographic direction in which magnetization is easiest—that is, saturation (of  $M$ ) is achieved at the lowest  $H$  field; this is termed a direction of **easy magnetization**



## Domain Wall Energy

- In contrast to a **grain boundary**, at which grains change orientation abruptly and which is **about three atoms wide**, a domain changes orientation gradually with a **domain boundary** being about 300 atoms wide.
- The large width of a domain wall is due to a balance between two forces: **exchange energy** and **magnetocrystalline anisotropy**.
- When there is only a **small difference** in orientation between the dipoles, the **exchange forces between the dipoles are minimized** and the exchange energy is reduced.
- Thus, the exchange forces will tend to widen the domain wall.



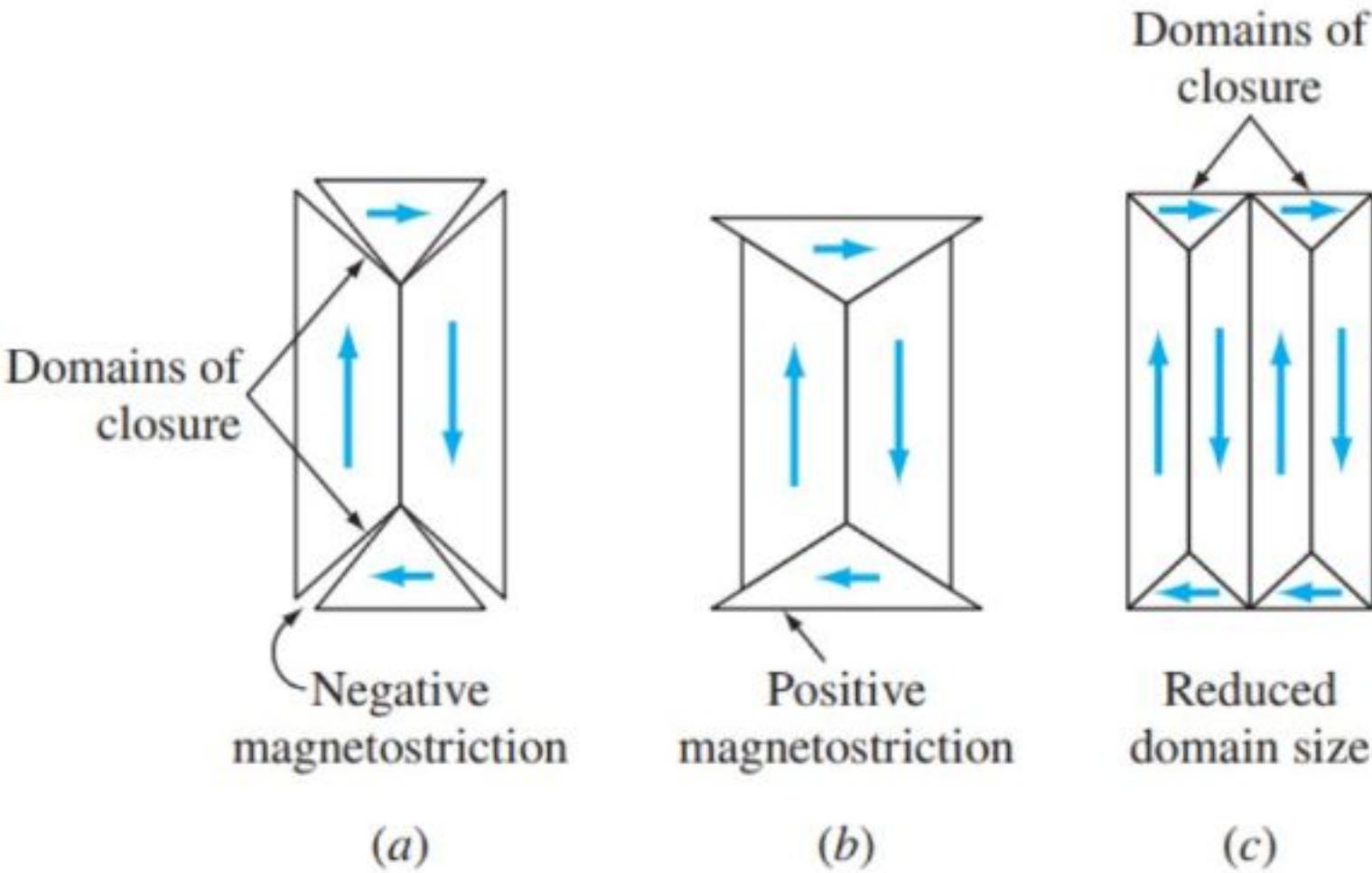
(a)

(b)

## Magnetostrictive Energy

- When a ferromagnetic material is magnetized, its **dimensions change slightly**, and the sample being magnetized either expands or contracts in the direction of magnetization.
- This magnetically induced reversible elastic strain ( $\Delta l/l$ ) is called **magnetostriction** and is of the order of  $10^{-6}$ .
- The energy due to the mechanical stresses created by magnetostriction is called **magnetostrictive energy**.
- The **cause of magnetostriction** is attributed to the change in the bond length between the atoms in a ferromagnetic metal when their electron-spin dipole moments are rotated into alignment during magnetization.
- The fields of the dipoles may attract or repel each other, leading to the contraction or expansion of the metal during magnetization.

- Because of the cubic symmetry of the crystals, the formation of triangular-shaped domains, called *domains of closure*, at the ends of the crystal eliminates the magnetostatic energy associated with an external magnetic field and hence lowers the energy of the material.
- It might appear that very large domains would be the lowest energy and most stable configuration since there is minimum wall energy.
- However it is not the case since **magnetostrictive stresses introduced during magnetization tend to be larger for larger domains.**
- Smaller magnetic domains, reduce magnetostrictive stresses but increase domain wall area and energy.
- The equilibrium domain configuration is reached when the sum of the magnetostrictive and **domain wall energies** is a minimum.



Magnetostriction in cubic magnetic materials. Schematic exaggeration of (a) negative and (b) positive magnetostriction pulling apart the domain boundaries of a magnetic material. (c) Lowering of magnetostrictive stresses by the creation of a smaller-domain-size structure.

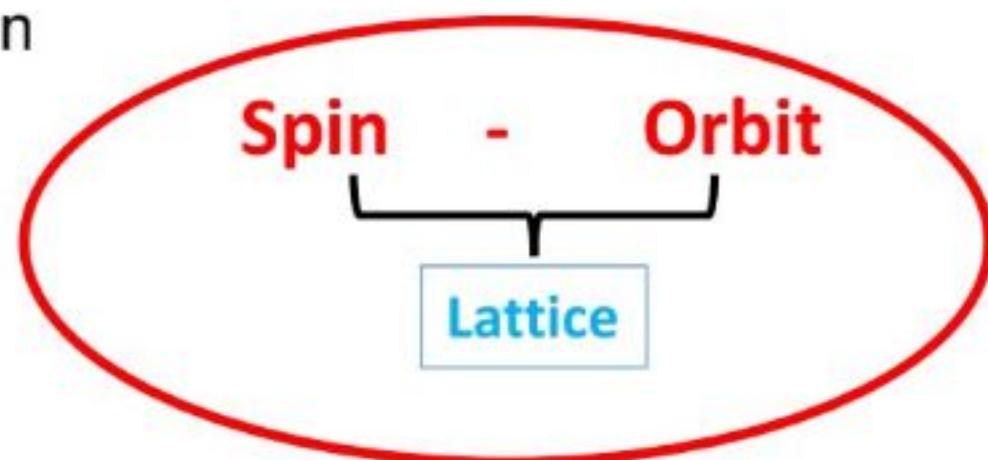
# Magnetostriction

# Spin - Orbit - Lattice

A restraint leading to finite permeabilities in magnetic materials is caused by a coupling *between the spins and the crystal lattice through the agency of the orbital motion of the electron.*

This **spin-orbit lattice coupling results in orientation of the spins relative to the crystal lattice in a minimum energy direction**, the so-called 'easy direction' of magnetization

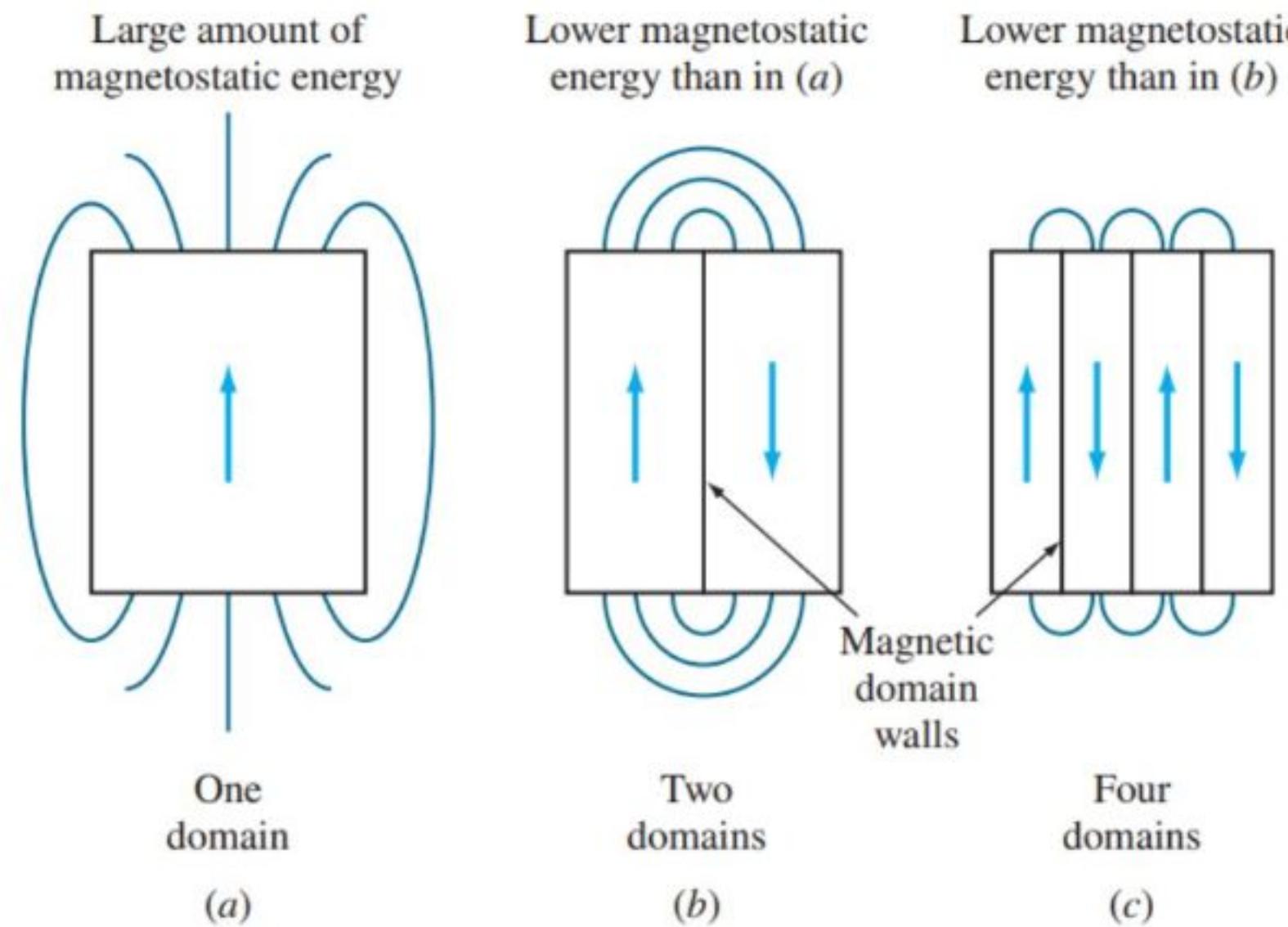
Change in the dimension of material with applied Magnetic Field



Because of the spin-orbit lattice coupling, changes in the spin directions result in changes in the orientation of the orbits which, because they are restrained by the lattice, have the effect of slightly altering the lattice dimensions.

This effect is known as **magnetostriction**.

The magnetostriction constant  $\lambda_m$  is defined as the strain induced by a saturating field; it is given a positive sign if the field causes an increase in dimensions in the field direction. For single crystals  $\lambda_m$  varies with the crystallographic direction, and so for the ceramic form it is an average of the single-crystal values



Schematic illustration showing how reducing the domain size in a magnetic material decreases the magnetostatic energy by reducing the external magnetic field. (a) One domain, (b) two domains, and (c) four domains.

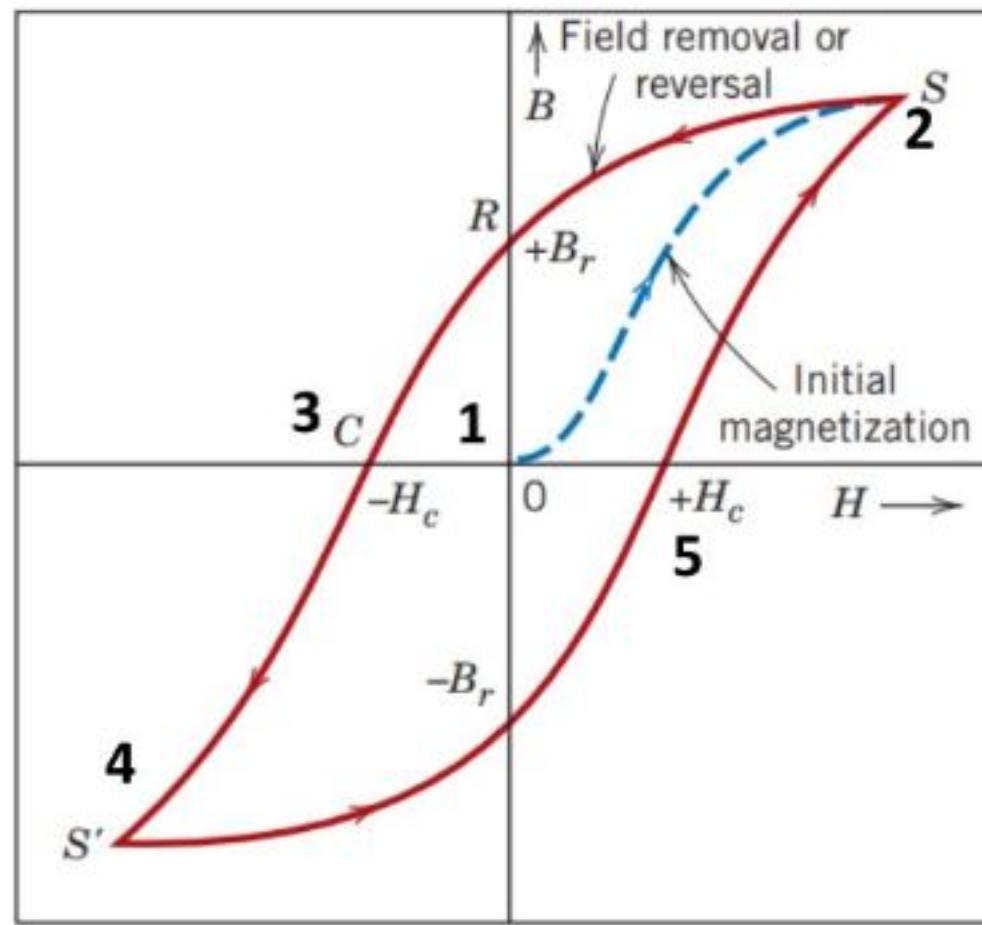
# DOMAINS AND HYSTERESIS

S : Saturation Magnetization

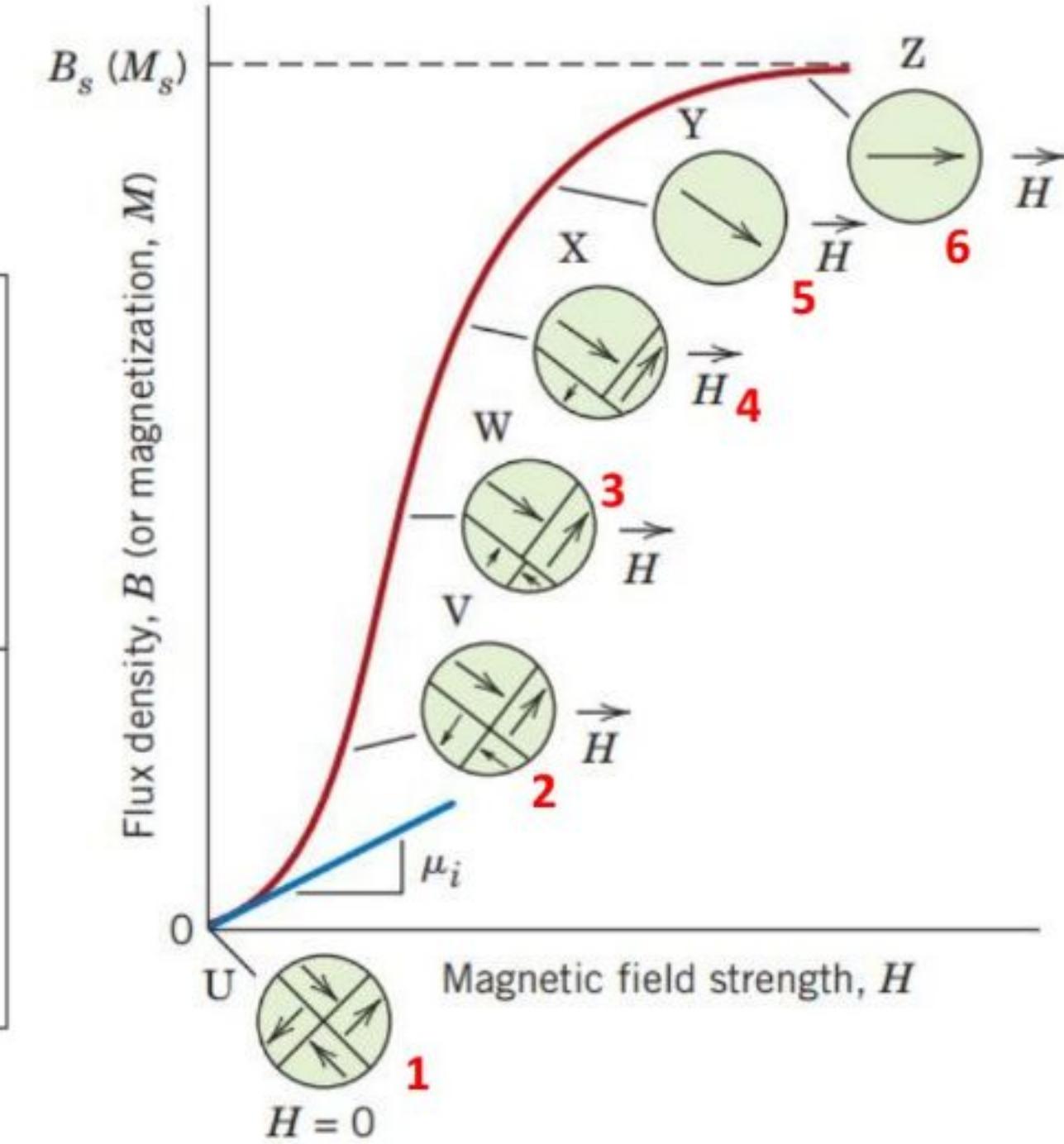
R: Remanent magnetization

C: Corecive Magnetic Field

At C magnetization (**B**) is zero



**Corecive Magnetic Field:** Magnetic field required to demagnetize the specimen by applying  $H$  in a direction which is opposite to the initially applied  $H$

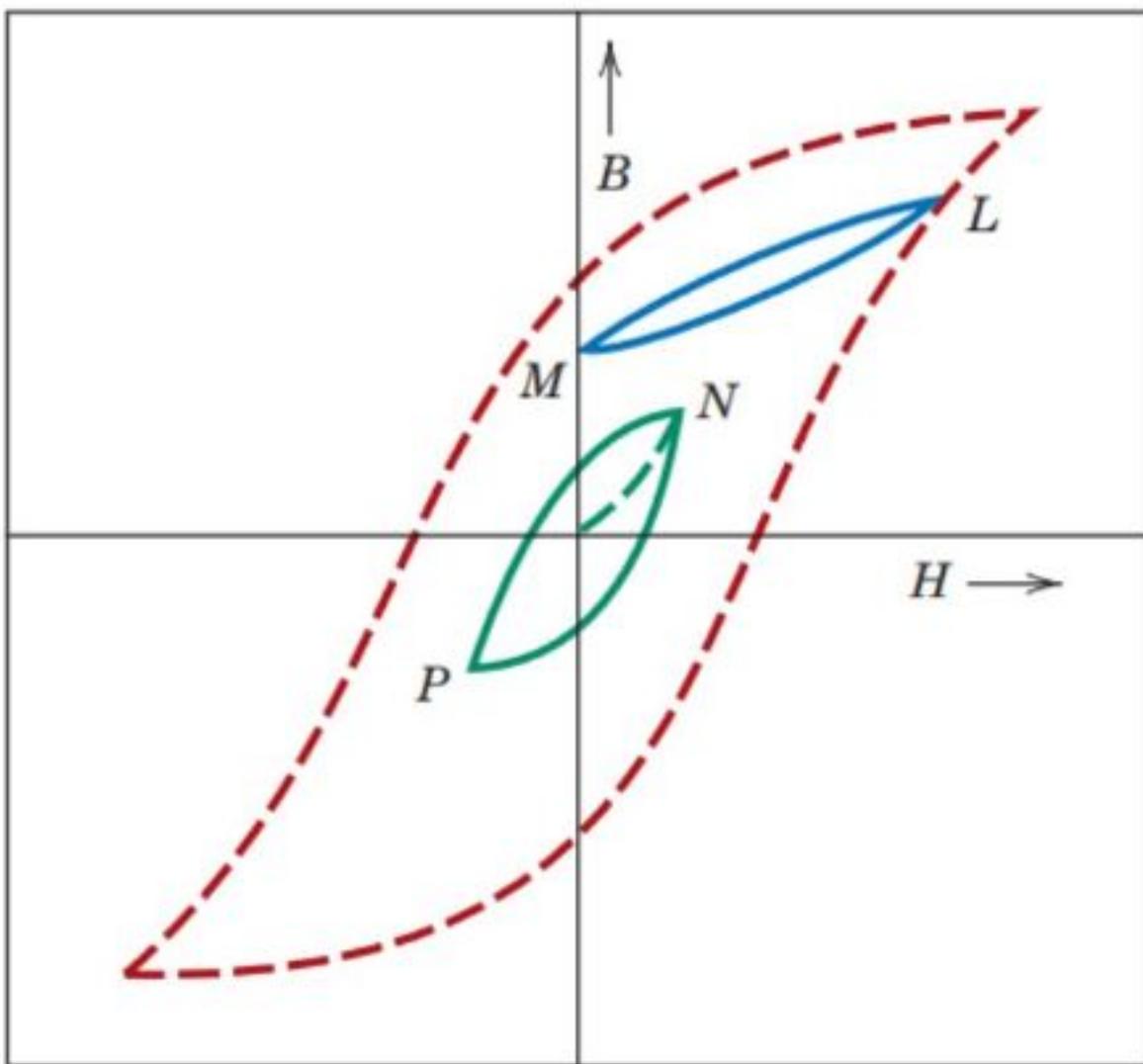


*Domains whose directions of easy magnetization are most closely aligned with the  $H$  field grow, at the expense of the other domains that shrink*

it is not necessary to increase the  $H$  field to saturation before reversing the field direction

L-M When  $H$  is reversed before Saturation  $B$

N-P Hysteresis loop with low saturation point

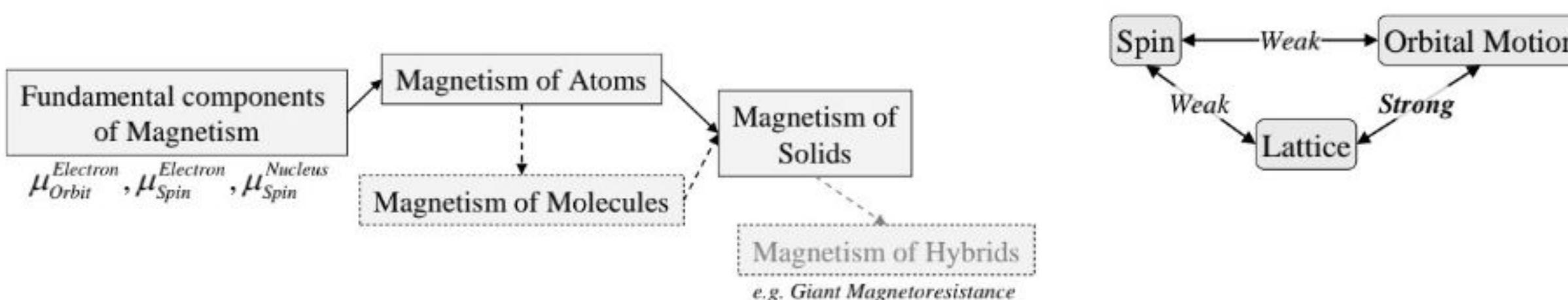


One method of demagnetizing a ferromagnet or ferrimagnet is to repeatedly cycle it in an  $H$  field that alternates direction and decreases in magnitude

**Understanding magnetism** (and formulating theories) to understand the effects observed:

- **Direct coupling** → Moments (spin, orbital motion, nuclear) localized to an atom and their direct interaction with moments in neighbouring atoms
- **Mediated interaction** → Moments (magnetism) arising from itinerant electrons in the bands of metals (with the possibility of mediation of interaction via free electrons).
- **Superexchange** → Local magnetic moments interacting with other local moments via the mediation of non-magnetic elements (super-exchange) → e.g. antiferromagnetism in MnO.

From magnetism of the fundamental components to magnetism of devices



## Diamagnetic and paramagnetic

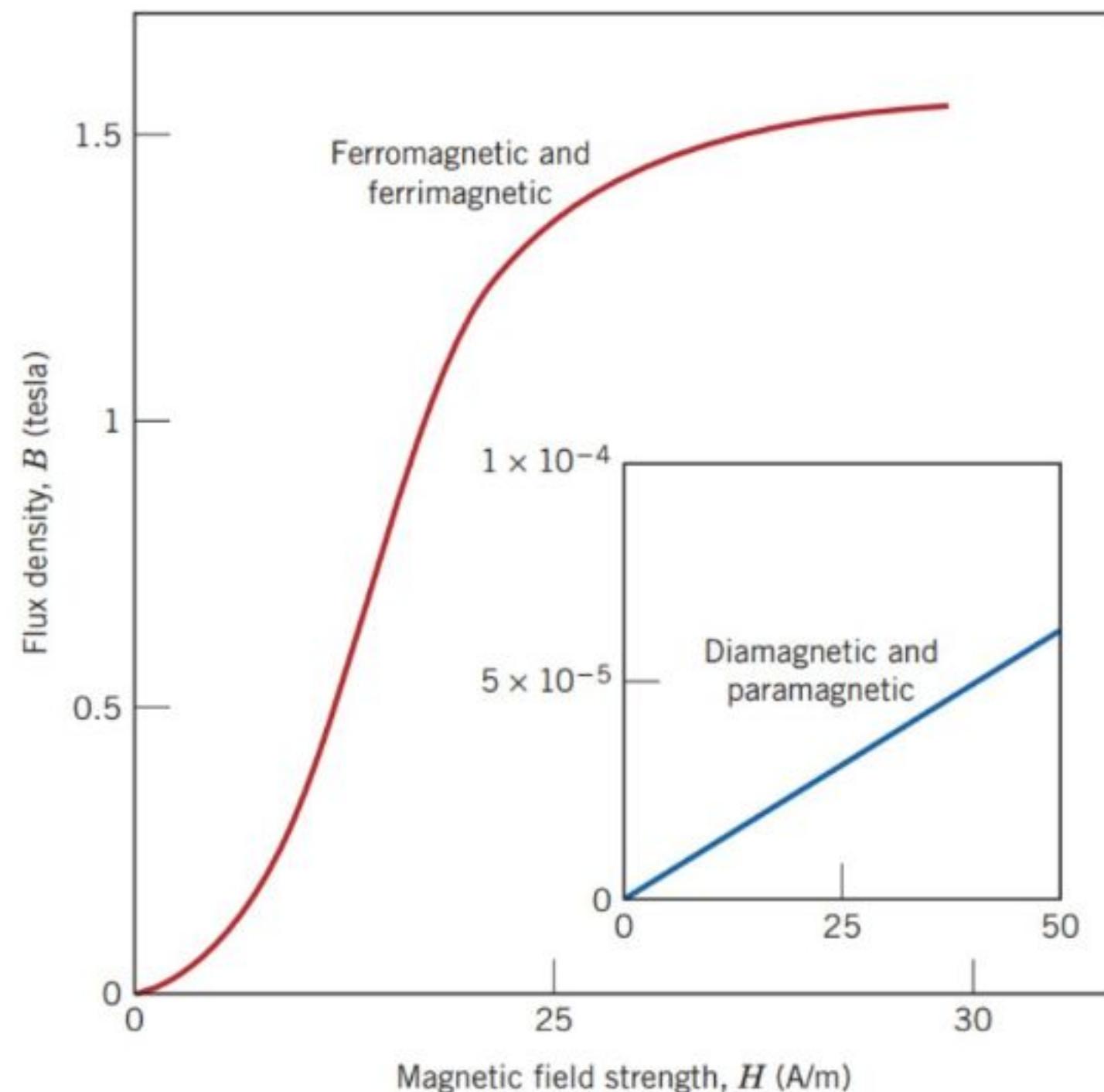
- Linear B and H Plot
- Value of B is very very less

At  $H = 50 \text{ A/m}$   
 $B = 0.00005 \text{ tesla}$

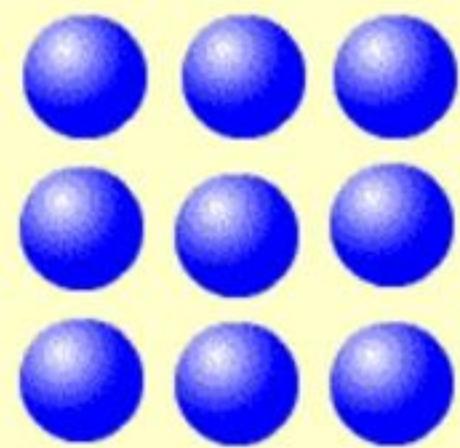
## Ferromagnetic and Ferrimagnetic

- Non Linear B and H Plot
- Value of B is comparatively high

At  $H = 50 \text{ A/m}$   
 $B = 1.5 \text{ tesla}$

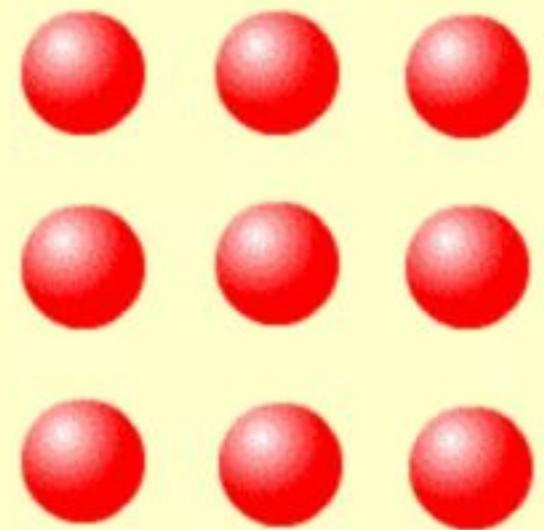


# High Temperature Vibrations



All particles in a solid  
vibrate - even when  
cold.

A Cyberphysics graphic 2010



At higher temperatures they  
vibrate faster and take up more  
room - expand - but the  
particles themselves are still the  
same size.

**Animation**

# THE INFLUENCE OF TEMPERATURE ON MAGNETIC BEHAVIOR

The atomic magnetic moments are free to rotate;

Randomize the orbital and spin moments

The increased thermal motion of the atoms tends to randomize the directions of any moments that may be aligned.

For ferromagnetic, antiferromagnetic, and ferrimagnetic materials, the atomic thermal motions counteract the coupling forces between the adjacent atomic dipole moments, causing some dipole misalignment, regardless of whether an external field is present.

This results in a decrease in the saturation magnetization for both ferro and ferrimagnets.

At 0 K thermal vibrations are the least

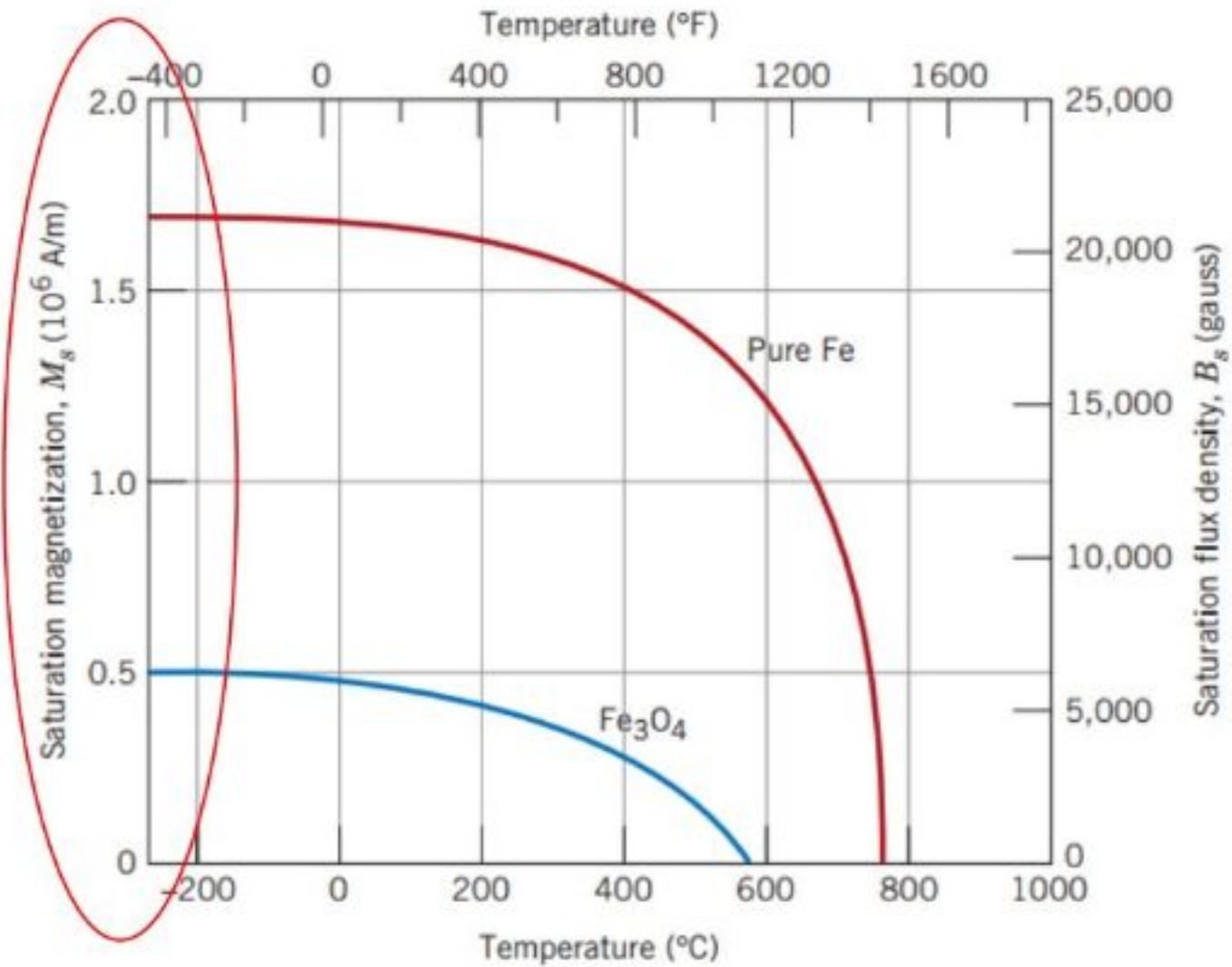
The saturation magnetization is a maximum at 0 K, at which the thermal vibrations are a minimum. With increasing temperature, the saturation magnetization diminishes gradually and then abruptly drops to zero at what is called the **Curie temperature**  $T_c$ .

Antiferromagnetism is also affected by temperature; this behavior vanishes at what is called the *Néel temperature*. At temperatures above this point, antiferromagnetic materials also become paramagnetic.

At  $T_c$  the mutual spin-coupling forces are completely destroyed, such that for temperatures above  $T_c$  both ferromagnetic and ferrimagnetic materials are paramagnetic.

The magnitude of the Curie temperature varies from material to material; for example, for iron, cobalt, nickel, and  $\text{Fe}_3\text{O}_4$ , the respective values are 768, 1120, 335, and 585 deg. C.

Antiferromagnetism is also affected by temperature; this behavior vanishes at what is called the *Néel temperature*. At temperatures above this point, antiferromagnetic materials also become paramagnetic.



# SOFT and HARD MAGNETIC MATERIALS

The area within a loop represents a magnetic energy loss per unit volume of material per magnetization–demagnetization cycle; this energy loss is manifested as heat and is capable of raising its temperature.

**Soft magnetic materials** are used in devices that are subjected to alternating magnetic fields and in which energy losses must be low

high initial permeability and a low coercivity

saturation field or magnetization depends on composition

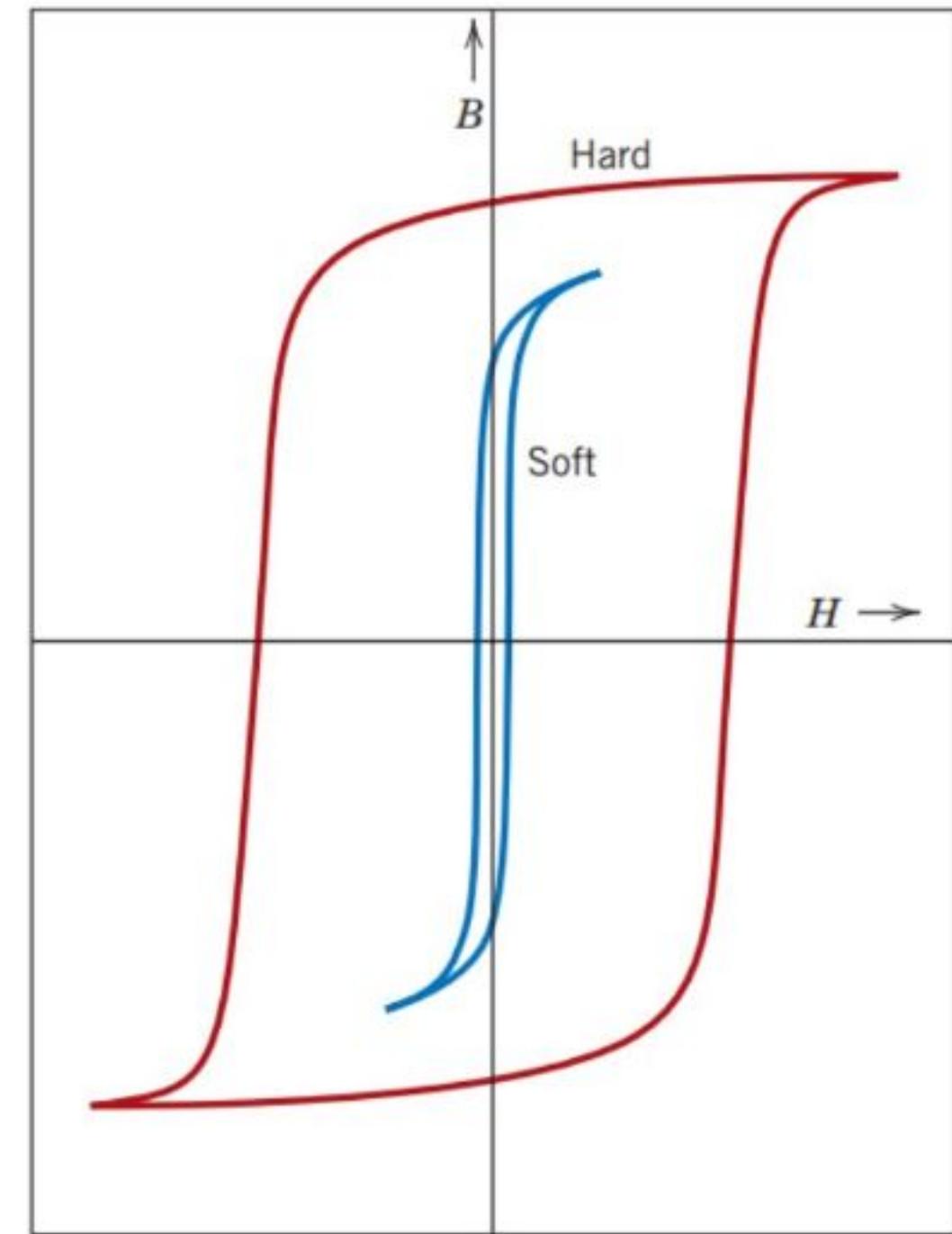
susceptibility and coercivity ( $H_c$ ), which also influence the shape of the hysteresis curve, are sensitive to structural variables

Structural defects such as particles of a nonmagnetic phase or voids in the magnetic material tend to restrict the motion of domain walls, and thus increase the coercivity.

soft magnetic material must be free of such structural defects

High electrical resistivity to reduce eddy currents

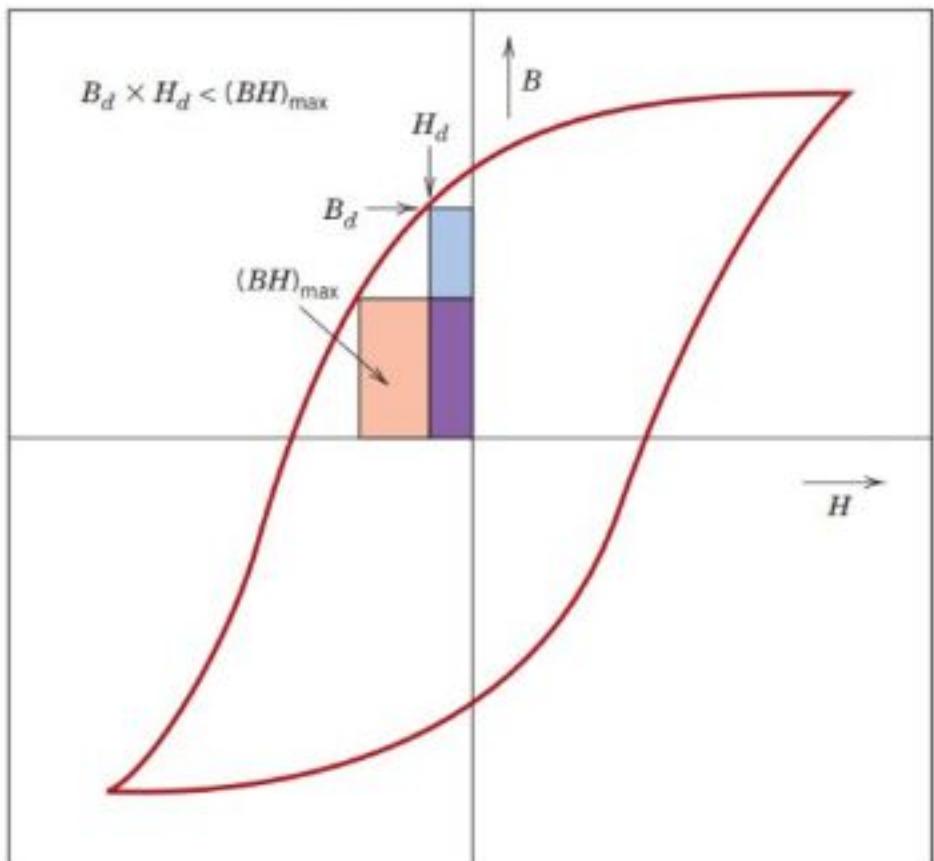
soft magnetic materials are used in generators, motors, dynamos, and switching circuits.



in cubic ferrites, substitution of a divalent metal ion such as  $\text{Ni}^{2+}$  for  $\text{Fe}^{2+}$  in  $\text{FeO}-\text{Fe}_2\text{O}_3$  will change the saturation magnetization

# HARD MAGNETIC MATERIALS

- high remanence,
- High coercivity, and
- High saturation flux density,
- low initial permeability and
- high hysteresis energy losses



by impeding domain wall motion, the coercivity and susceptibility are enhanced, such that a large external field is required for demagnetization.

Furthermore, these characteristics are interrelated to the microstructure of the material.

Main factors which decide their hard properties :

The **coercivity** and the **energy product**, designated as **( $BH$ )<sub>max</sub>**

$(BH)_{\max}$  corresponds to the area of the largest  $B$ - $H$  rectangle that can be constructed within the second quadrant of the hysteresis curve

## Conventional Hard Magnetic Materials

- The conventional materials have  $(BH)_{\max}$  values that range between about 2 and 80 kJ/m<sup>3</sup> (0.25 and 10 MGOe).
- These include ferromagnetic materials—magnet steels, cunife (Cu–Ni–Fe) alloys, alnico (Al–Ni–Co) alloys—as well as the hexagonal ferrites ( $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ )
- Hard magnet steels are normally alloyed with tungsten and/or chromium.
- Under the proper heat-treating conditions these two elements readily combine with carbon in the steel to form tungsten and chromium carbide precipitate particles, which are especially effective in obstructing domain wall motion.
- For other metal alloys, an appropriate heat treatment forms extremely small single-domain and strongly magnetic iron–cobalt particles within a nonmagnetic matrix phase.

## Soft Magnetic Materials

<i>Material</i>	<i>Composition (wt %)</i>	<i>Initial Relative Permeability <math>\mu_i</math></i>	<i>Saturation Flux Density <math>B_s</math> [tesla (gauss)]</i>	<i>Hysteresis Loss/Cycle [J/m<sup>3</sup> (erg/cm<sup>3</sup>)]</i>	<i>Resistivity <math>\rho</math> (<math>\Omega \cdot m</math>)</i>
Commercial iron ingot	99.95Fe	150	2.14 (21,400)	270 (2700)	$1.0 \times 10^{-7}$
Silicon–iron (oriented)	97Fe, 3Si	1400	2.01 (20,100)	40 (400)	$4.7 \times 10^{-7}$
45 Permalloy	55Fe, 45Ni	2500	1.60 (16,000)	120 (1200)	$4.5 \times 10^{-7}$
Supermalloy	79Ni, 15Fe, 5Mo, 0.5Mn	75,000	0.80 (8000)	—	$6.0 \times 10^{-7}$
Ferroxcube A	48MnFe <sub>2</sub> O <sub>4</sub> , 52ZnFe <sub>2</sub> O <sub>4</sub>	1400	0.33 (3300)	~40 (~400)	2000
Ferroxcube B	36NiFe <sub>2</sub> O <sub>4</sub> , 64ZnFe <sub>2</sub> O <sub>4</sub>	650	0.36 (3600)	~35 (~350)	$10^7$

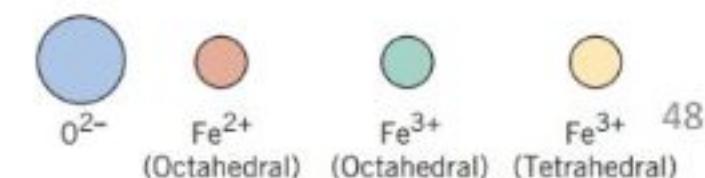
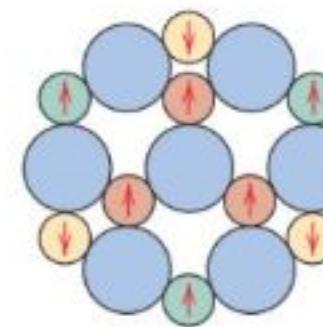
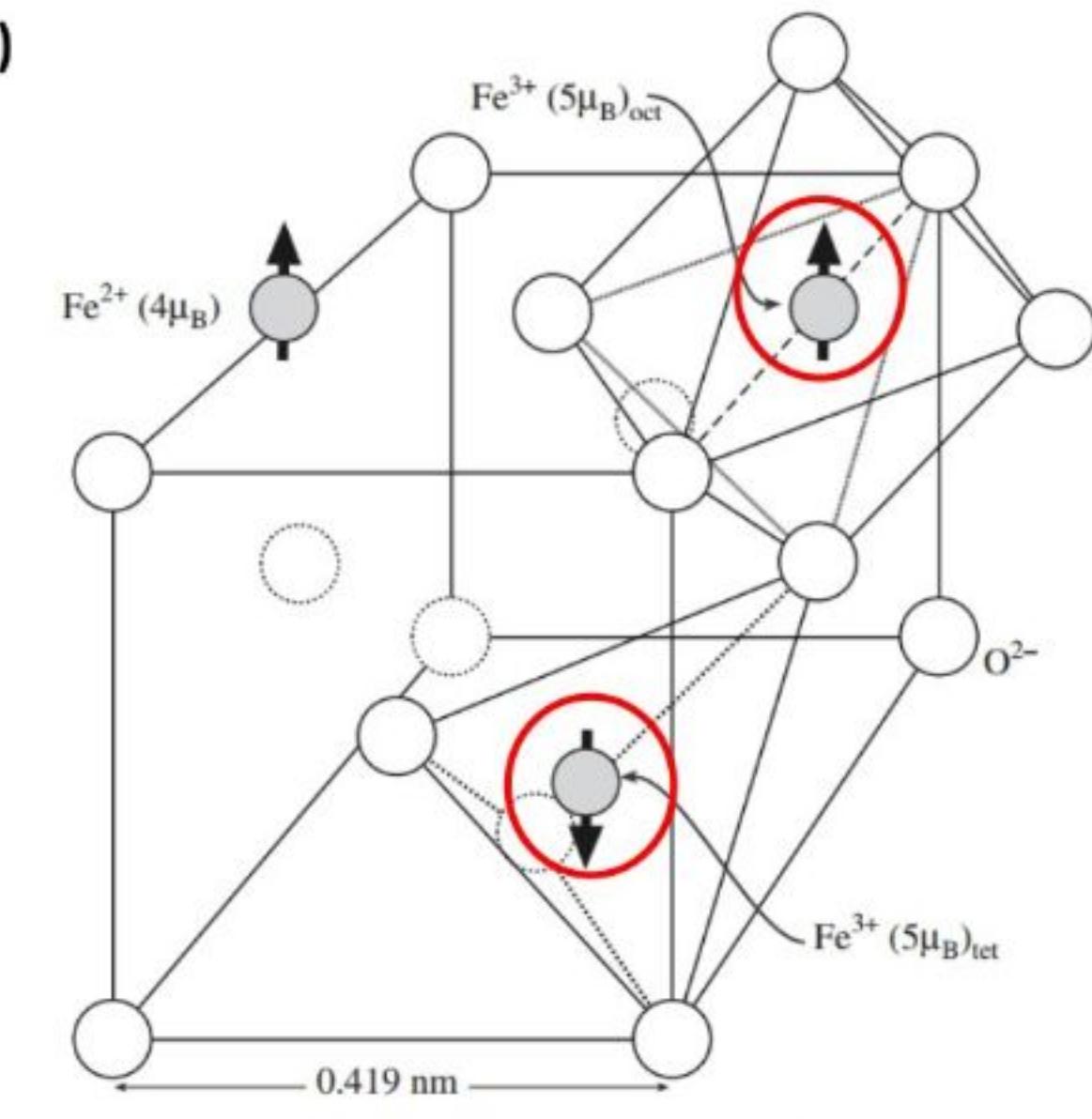
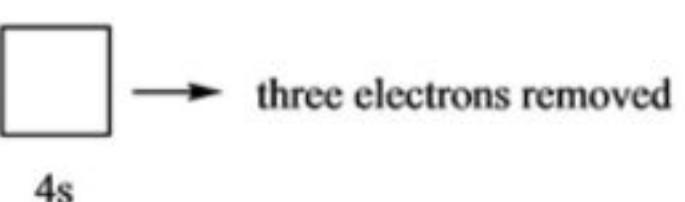
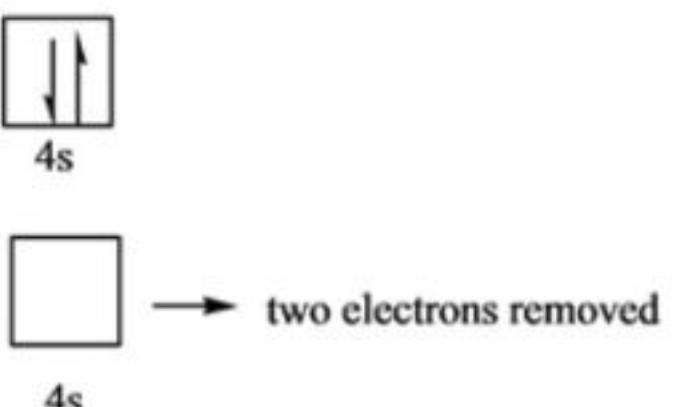
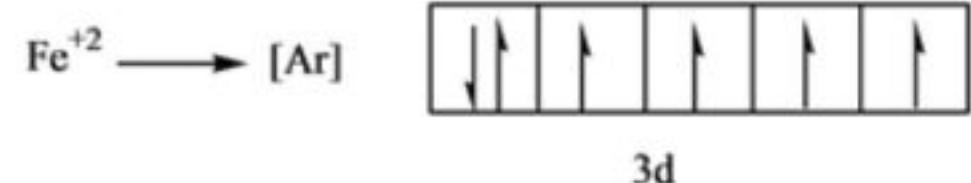
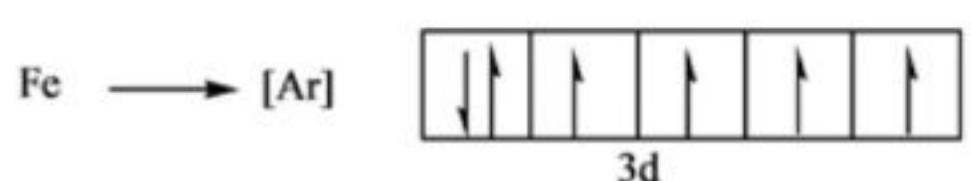
## Hard Magnetic Materials

<i>Material</i>	<i>Composition (wt%)</i>	<i>Remanence <math>B_r</math> [tesla (gauss)]</i>	<i>Coercivity <math>H_c</math> [amp-turn/m (Oe)]</i>	<i>(BH)<sub>max</sub> [kJ/m<sup>3</sup> (MGoe)]</i>	<i>Curie Temperature <math>T_c</math> [°C (°F)]</i>	<i>Resistivity <math>\rho</math> (<math>\Omega \cdot m</math>)</i>
Tungsten steel	92.8 Fe, 6 W, 0.5 Cr, 0.7 C	0.95 (9500)	5900 (74)	2.6 (0.33)	760 (1400)	$3.0 \times 10^{-7}$
Cunife	20 Fe, 20 Ni, 60 Cu	0.54 (5400)	44,000 (550)	12 (1.5)	410 (770)	$1.8 \times 10^{-7}$
Sintered alnico 8	34 Fe, 7 Al, 15 Ni, 35 Co, 4 Cu, 5 Ti	0.76 (7600)	125,000 (1550)	36 (4.5)	860 (1580)	—
Sintered ferrite 3	BaO–6Fe <sub>2</sub> O <sub>3</sub>	0.32 (3200)	240,000 (3000)	20 (2.5)	450 (840)	$\sim 10^4$
Cobalt rare earth 1	SmCo <sub>5</sub>	0.92 (9200)	720,000 (9,000)	170 (21)	725 (1340)	$5.0 \times 10^{-7}$
Sintered neodymium–iron–boron	Nd <sub>2</sub> Fe <sub>14</sub> B	1.16 (11,600)	848,000 (10,600)	255 (32)	310 (590)	$1.6 \times 10^{-6}$

# Spinel Ferrite ( $\text{Fe}_3\text{O}_4$ )

$\text{Fe} : 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 4s^2 \ 3d^6$

$\text{Fe}^{3+} : 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^5$



- Ceramic materials other than the cubic ferrites are also ferrimagnetic; these include the **HEXAGONAL FERRITES** and garnets. Hexagonal ferrites have a crystal structure similar to the inverse spinel, with **hexagonal symmetry rather than cubic**.

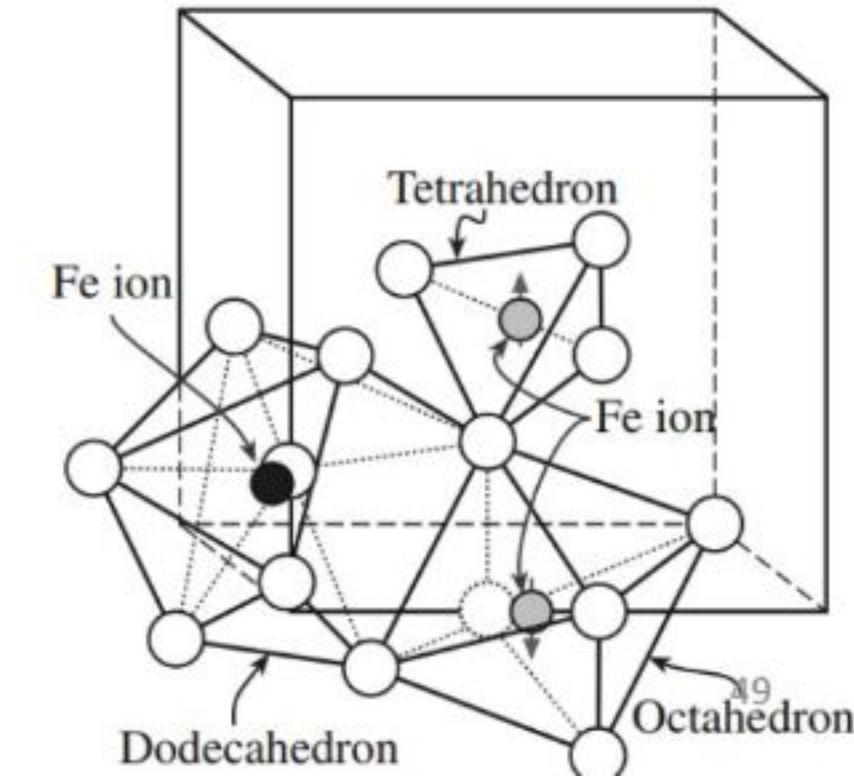
- The chemical formula for these materials may be represented by  $AB_{12}O_{19}$ , in which A is a divalent metal such as barium, lead, or strontium, and B is a trivalent metal such as aluminum, gallium, chromium, or iron. The two most common examples of the hexagonal ferrites are  $PbFe_{12}O_{19}$  and  $BaFe_{12}O_{19}$ .

- 

The **GARNETS** have a very complicated crystal structure, which may be represented by the general formula  $M_3Fe_5O_{12}$ ; here, M represents a rare earth ion such as samarium, europium, gadolinium, or yttrium. Yttrium iron garnet ( $Y_3Fe_5O_{12}$ ), sometimes denoted YIG, is the most common material of this type.

**Detailed Reference:** Electroceramics A.J Moulson

Material	$\theta_c$ (K)	$B_{sat}$ (T) at RT
<b>Spinel ferrites [AO·B<sub>2</sub>O<sub>3</sub>]</b>		
Fe <sup>3+</sup> [Cu <sup>2+</sup> Fe <sup>3+</sup> ]O <sub>4</sub>	728	0.20
Fe <sup>3+</sup> [Ni <sup>2+</sup> Fe <sup>3+</sup> ]O <sub>4</sub>	858	0.34
Fe <sup>3+</sup> [Co <sup>2+</sup> Fe <sup>3+</sup> ]O <sub>4</sub>	1020	0.50
Fe <sup>3+</sup> [Fe <sup>2+</sup> Fe <sup>3+</sup> ]O <sub>4</sub>	858	0.60
Fe <sup>3+</sup> [Mn <sup>2+</sup> Fe <sup>3+</sup> ]O <sub>4</sub>	573	0.51
Fe <sup>3+</sup> [Li <sub>0.5</sub> Fe <sub>1.5</sub> ]O <sub>4</sub>	943	
Mg <sub>0.1</sub> Fe <sub>0.9</sub> [Mg <sub>0.9</sub> Fe <sub>1.1</sub> ]O <sub>4</sub>	713	0.14
<b>Hexagonal ferrites</b>		
BaO:6Fe <sub>2</sub> O <sub>3</sub>	723	0.48
SrO:6Fe <sub>2</sub> O <sub>3</sub>	723	0.48
Y <sub>2</sub> O <sub>3</sub> :5Fe <sub>2</sub> O <sub>3</sub>	560	0.16
BaO:9Fe <sub>2</sub> O <sub>3</sub>	718	0.65
<b>Garnets</b>		
YIG[Y <sub>3</sub> ][Fe <sub>2</sub> ]Fe <sub>3</sub> O <sub>12</sub>	560	0.16
(Gd <sub>3</sub> )[Fe <sub>2</sub> ]Fe <sub>3</sub> O <sub>12</sub>	560	
<b>Binary oxides</b>		
EuO	69	
CrO <sub>2</sub>	386	0.49



## High-Energy Hard Magnetic Materials

- Permanent magnetic materials having **energy products in excess of about  $80 \text{ kJ/m}^3$**  are considered to be of the high-energy type.
- These are recently developed intermetallic compounds that have a variety of compositions

### **Samarium–Cobalt Magnets**

- $\text{SmCO}_5$  is a member of a group of alloys that are combinations of cobalt or iron and a light rare earth element; a number of these alloys exhibit high-energy, hard magnetic behavior, but  $\text{SmCo}_5$  is the only one of commercial significance.
- The energy product of these  $\text{SmCo}_5$  materials [between  $120$  and  $240 \text{ kJ/m}^3$ ] are considerably higher than the conventional hard magnetic materials large coercivities.
- Powder metallurgical techniques are used to fabricate  $\text{SmCO}_5$  magnets.
  - *The appropriately alloyed material is first ground into a fine powder; the powder particles are aligned using an external magnetic field and then pressed into the desired shape. The piece is then sintered at an elevated temperature, followed by another heat treatment that improves the magnetic properties.*

## **Neodymium–Iron–Boron Magnets** $\text{Nd}_2\text{Fe}_{14}\text{B}$

- Samarium is a rare and relatively expensive material; furthermore, the price of cobalt is variable and its sources are unreliable.
- The magnetization–demagnetization behavior of these materials is a function of domain wall mobility, which, in turn, is controlled by the final microstructure—that is, the size, shape, and orientation of the crystallites or grains, as well as the nature and distribution of any second-phase particles that are present.
- One common application is in motors.
- Permanent magnets are far superior to electromagnets in that their magnetic fields are continuously maintained and without the necessity of expending electrical power; furthermore, no heat is generated during operation.

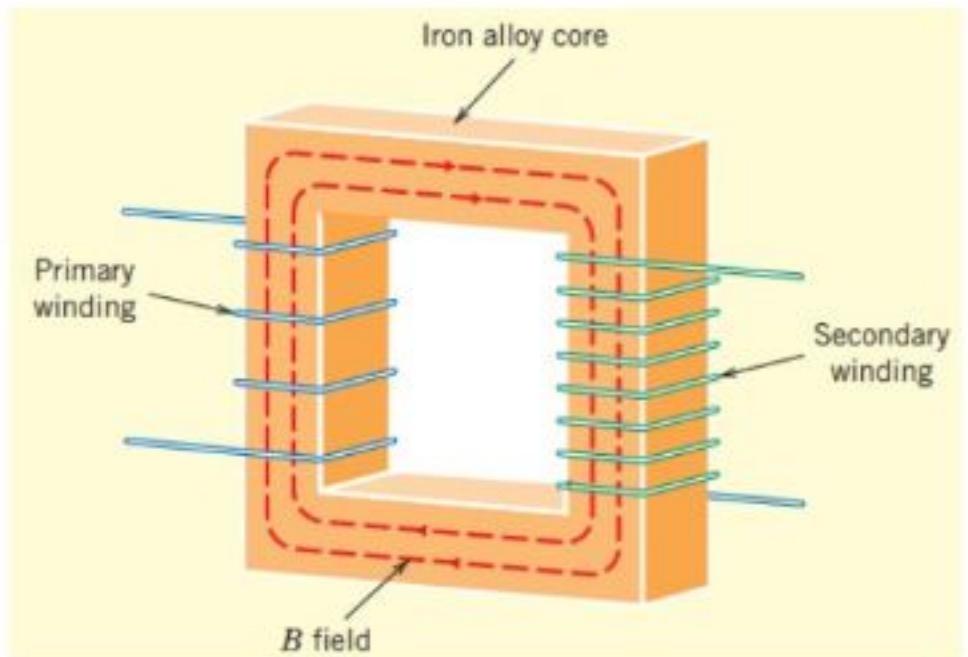
**powder metallurgy (sintering) and  
rapid solidification (melt spinning).**

# Applications

## Transformer Cores

### Fe – Si Alloy

Transformer cores require the use of soft magnetic materials, which are easily magnetized and demagnetized (and also have relatively high electrical resistivities).



Magnetic materials are important in the area of information storage; in fact, magnetic recording has become virtually the universal technology for the storage of electronic information.

## Magnetic Storage

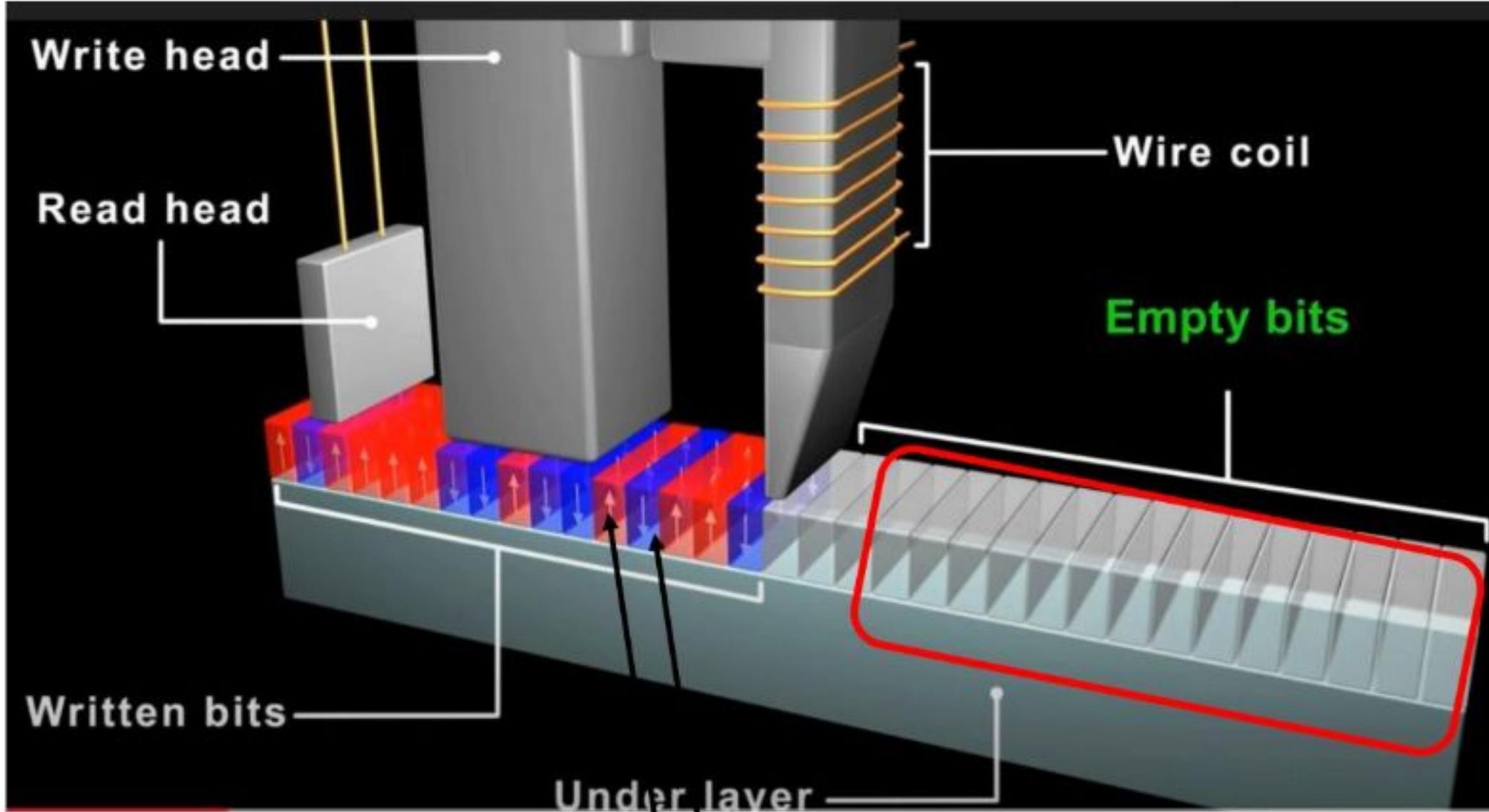
- Magnetic Tape
- Hard Disk

In computers, semiconductor elements serve as primary memory, magnetic hard disks are normally used for secondary memory because they are capable of storing larger quantities of information and at a lower cost; however, their transfer rates are slower

- Magnetic Tape

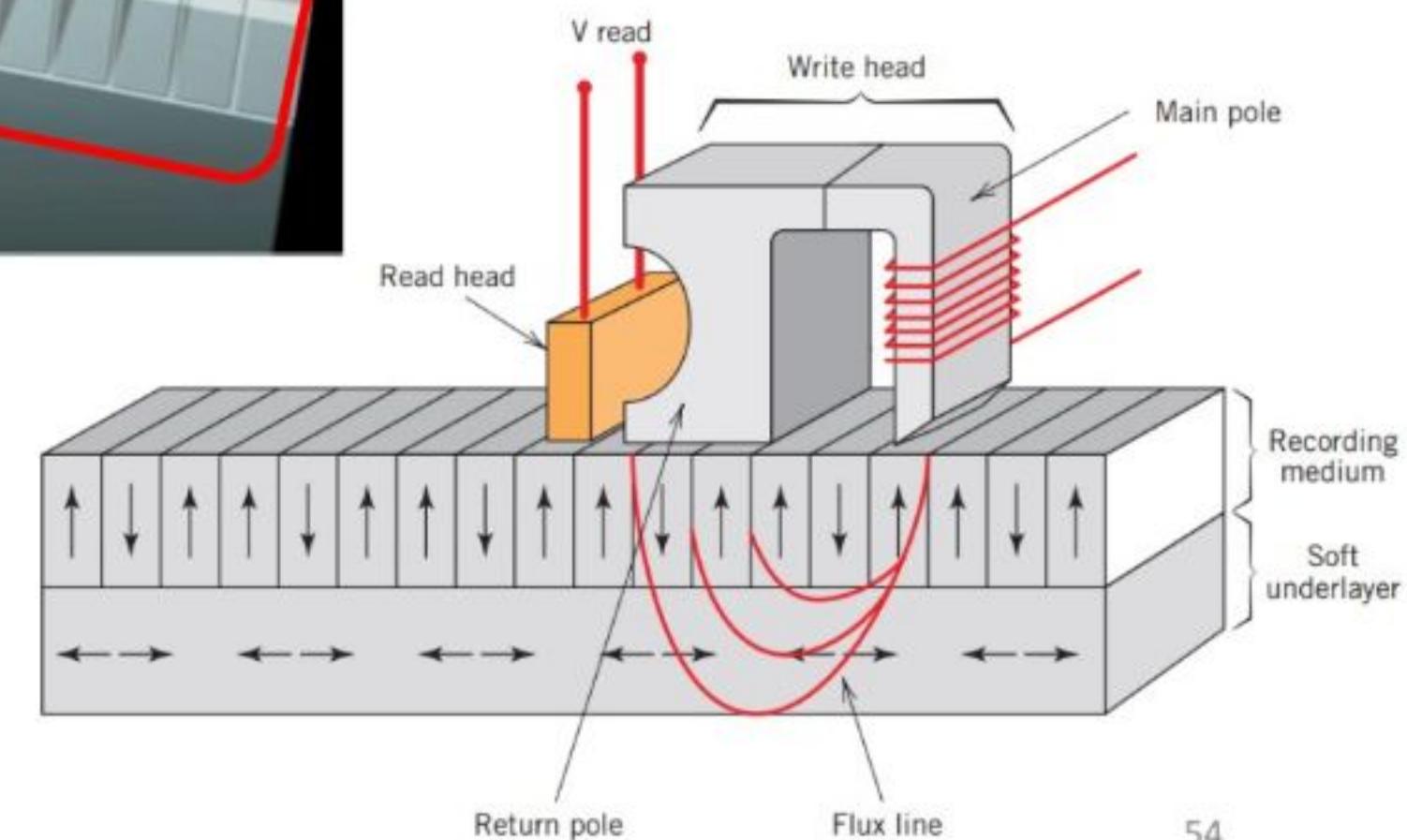


- In essence, computer bytes, sound, or visual images in the form of electrical signals are recorded magnetically on very small segments of the magnetic storage medium—a tape or disk.
- For the current HDD technology, “magnetic bits” point up or down perpendicular to the plane of the disk surface; this scheme is appropriately called *perpendicular magnetic recording* (abbreviated PMR)
- Data retrieval from the storage medium is accomplished using a **magneto resistive read head**. During read-back, magnetic fields from the written magnetic patterns are sensed by this head; these fields produce changes in electrical resistance.



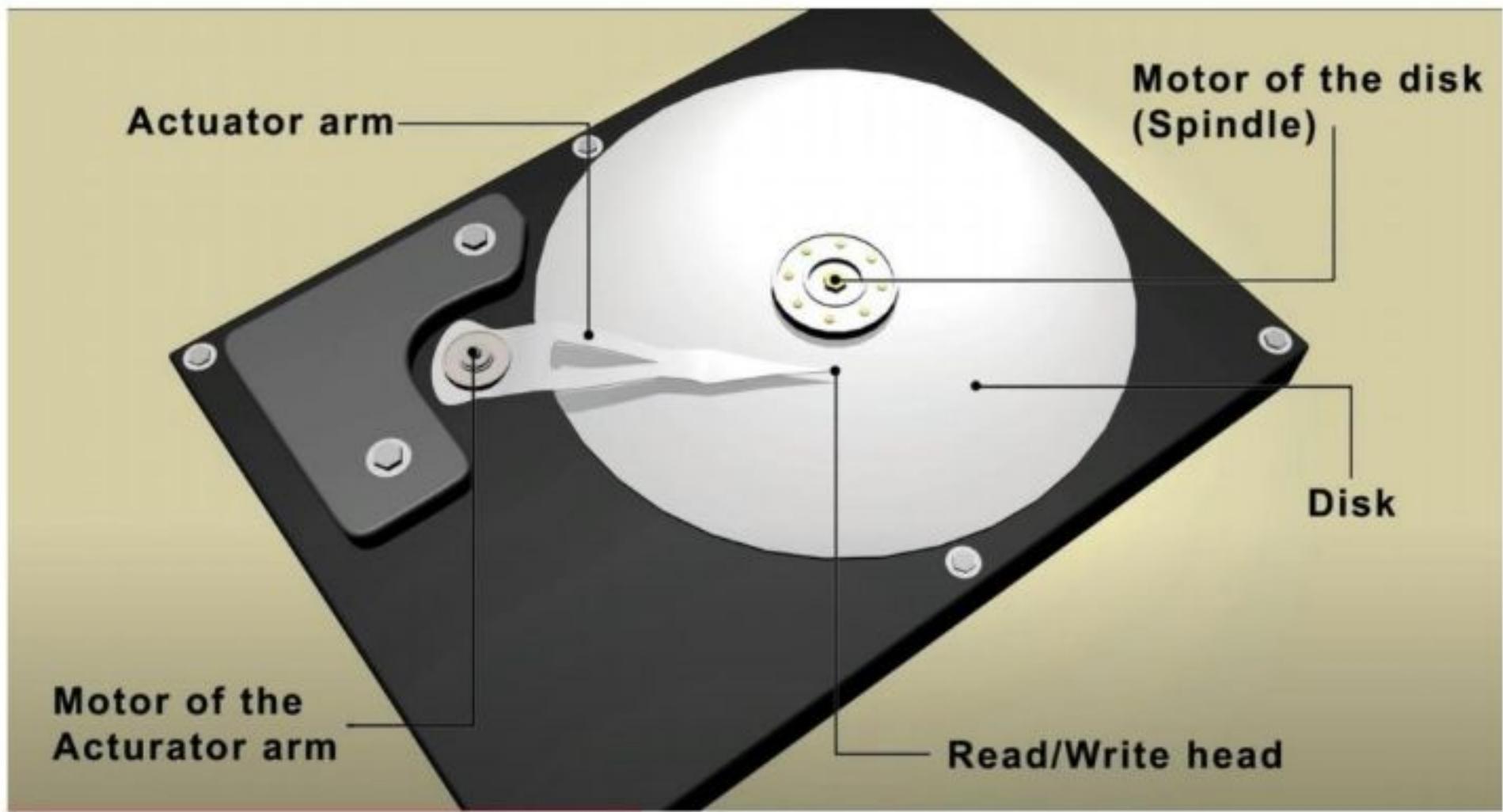
**Change Electric Field direction  
In wire coil changes direction of  
Magnetic Field**

0 1



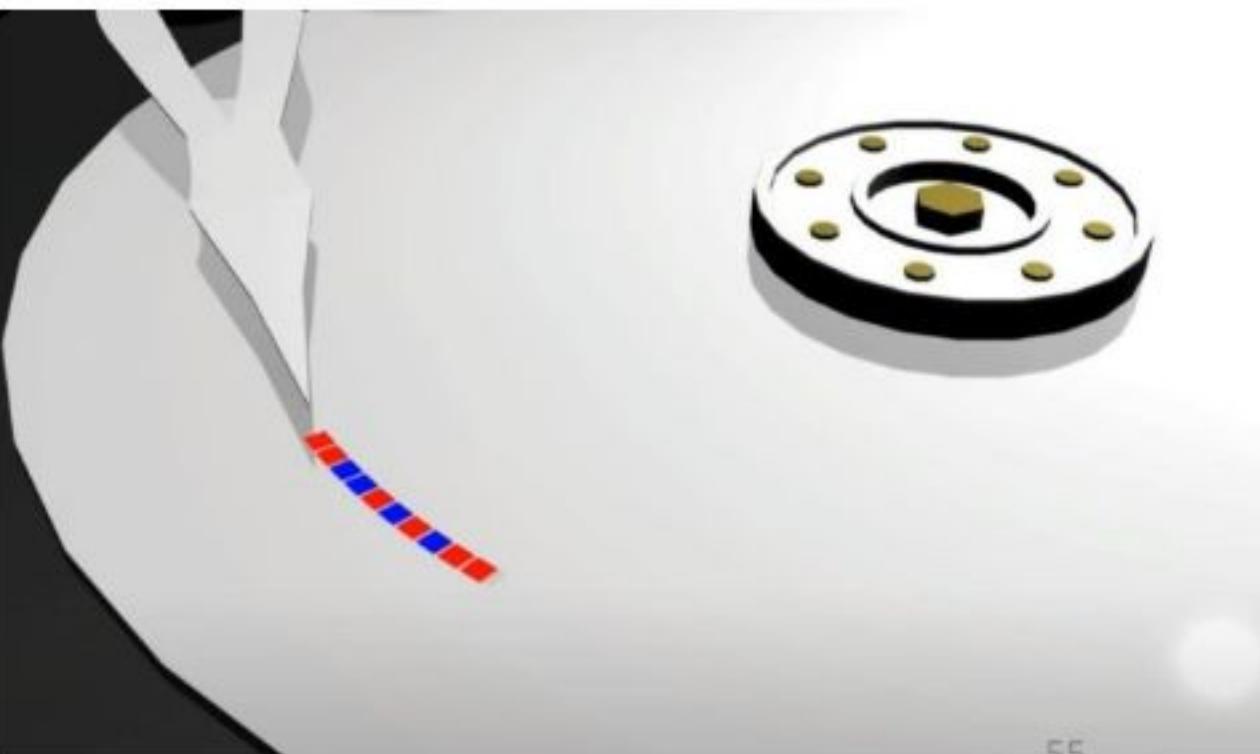
**Byte**

A = 01000001  
a = 01100001  
B = 01000010  
b = 01100010  
C = 01000011  
c = 01100011



**Hard Disk Drive**

**Areal density** is a measure of the quantity of information bits that can be **stored** on a given length of track, **area of surface**, or in a given volume of a computer **storage** medium.



## Magnetic Tapes

- The development of magnetic tape storage preceded that for the hard disk drives.
- Today, tape storage is less expensive than HDD; however, areal storage densities are lower for tape (by a factor of on the order of 100).
- Tapes [of standard 0.5-in. (12.7- mm) width] are wound onto reels and enclosed within cartridges, for protection and to facilitate handling.
- During operation, a tape drive, using precision-synchronized motors, winds the tape from one reel onto another past a read/write head system in order to access a point of interest.
- Typical tape speeds are 4.8 m/s; some systems, however, run as high as 10 m/s.

# Fundamentals of Semiconductors

## Electronic Properties of Metals: Classical Approach

- One could argue that metals are good conductors of heat and electricity, whereas semiconductors and insulators are not.
- In the case of heat conduction, we know that diamond, which is an insulator, conducts even better than most metals.
- Electrical conductivity is not of much help either: *Some semiconductors such as silicon conduct electricity reasonably well.*
- Yet another possibility is to define metals by the fact that they look “shiny” or “metallic.”
- But this applies to some semiconductors, too, and again silicon can be taken as an example.
- It turns out that a proper definition has to wait until we treat electronic states in a quantum mechanical model.

# Drude's Model

## Drude's Assumptions

1. Matter consists of *light negatively charged electrons* which are mobile, & *heavy, static, positively charged ions*.
2. The only interactions are electron-ion collisions, which take place in a very short time **t**.

German Physicist Paul Drude

- The electrons in a solid behave like a classical ideal gas. They do not interact with each other at all. There is no Coulomb interaction and, as opposed to a classical gas model, they do not collide with each other either.

Neglecting the electron-electron interactions is

*The Independent Electron Approximation.*

- The positive charge is located on immobile ion cores. The electrons can collide with the ion cores. These collisions instantaneously change their velocity. However, in between collisions, the electrons do not interact with the ions either. This is known as the **free electron approximation**.

Neglecting the electron-ion interactions is

*The Free Electron Approximation.*

## Drude's Assumptions (Contd.)

3. Electron-ion collisions are assumed to dominate. These will abruptly alter the electron velocity & maintain thermal equilibrium. At room temperature, this results in an average speed of  $vt \approx 10^5 \text{ ms}^{-1}$

4. The probability of an electron suffering a collision in a short time  **$dt$  is  $\equiv dt/\tau$** ,

where  **$1/\tau \equiv \text{Electron Scattering Rate}$** .

In between collisions, the electrons move freely. The mean length of this free movement is called the **mean free path**

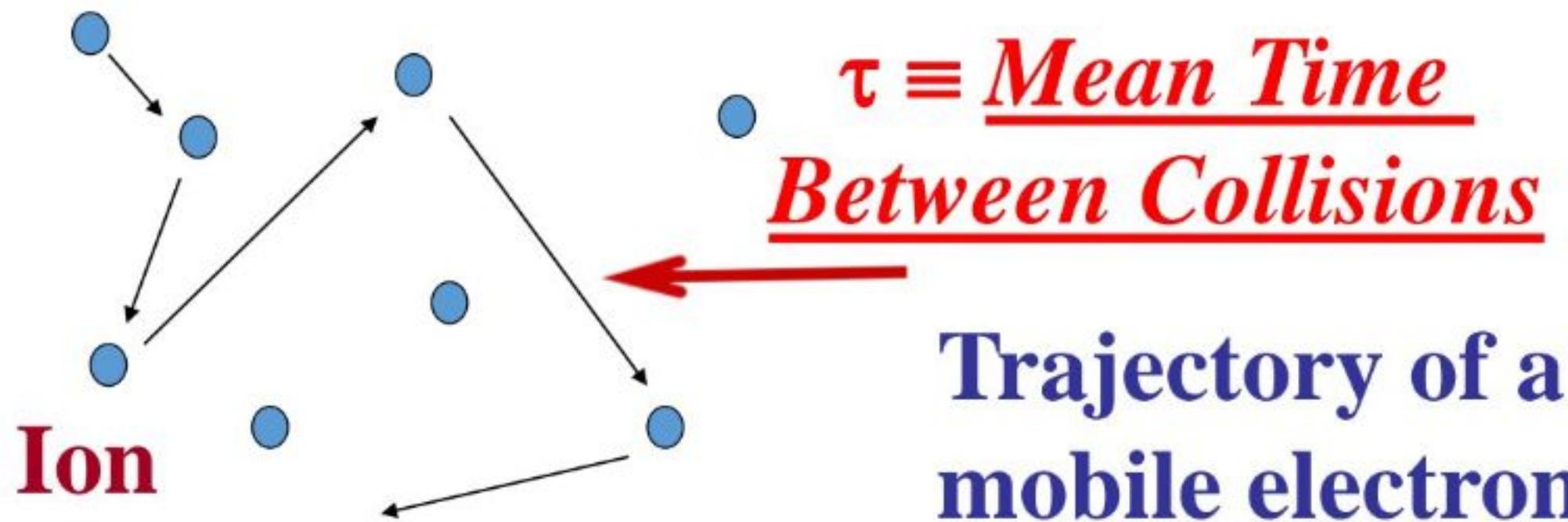
In between collisions, the electrons move freely. The mean length of this free movement is called the **mean free path**  $\lambda$ . Knowing the typical packing density of the ions, we can estimate that  $\lambda \approx 1$  nm. Given the average speed  $v_t$ , the mean free path also corresponds to a mean time between collisions given by  $\tau = \lambda/v_t$ .  $\tau$  is called the **relaxation time** and plays a fundamental role in the theory. With  $\lambda = 1$  nm and  $v_t$  at room temperature, we estimate that  $\tau \approx 1 \times 10^{-14}$  s.

- The probability of an electron suffering a collision in a short time  $dt$  is  $\equiv dt/\tau$ , where

$1/\tau \equiv \underline{\text{The Electron Scattering Rate.}}$

- Electrons emerge from each collision with both the direction & magnitude of their velocity changed.

$1/\tau$  is often an adjustable parameter. See figure.



For the description of almost all properties within the Drude model, it is essential to know the density of the gas formed by the free electrons.

This is known as the **conduction electron density**  $n$ , that is, the number of conduction electrons per volume .

## Drude Conductivity: Ohm's "Law" $V = IR$

- The Resistance  $R$  is a property of a conductor (e.g. a wire) which depends on its dimensions,  $V$  is a voltage drop &  $I$  is a current.
- In microscopic physics, it is more common to express **Ohm's "Law"** in terms of a dimension-independent conductivity (or resistivity) which is intrinsic to the *material* the wire is made from.
- In this notation, Ohm's "Law" is written

$$E \equiv rj \text{ or } j \equiv sE \quad (1)$$

$E$  = Electric Field,  $j$  = Current Density,  
 $r$  = Resistivity,  $s$  = Conductivity

### Macroscopic Form of Ohm's Law

$$i = \frac{V}{R}$$

where  $i$  = current, A

$V$  = voltage, V

$R$  = resistance,  $\Omega$

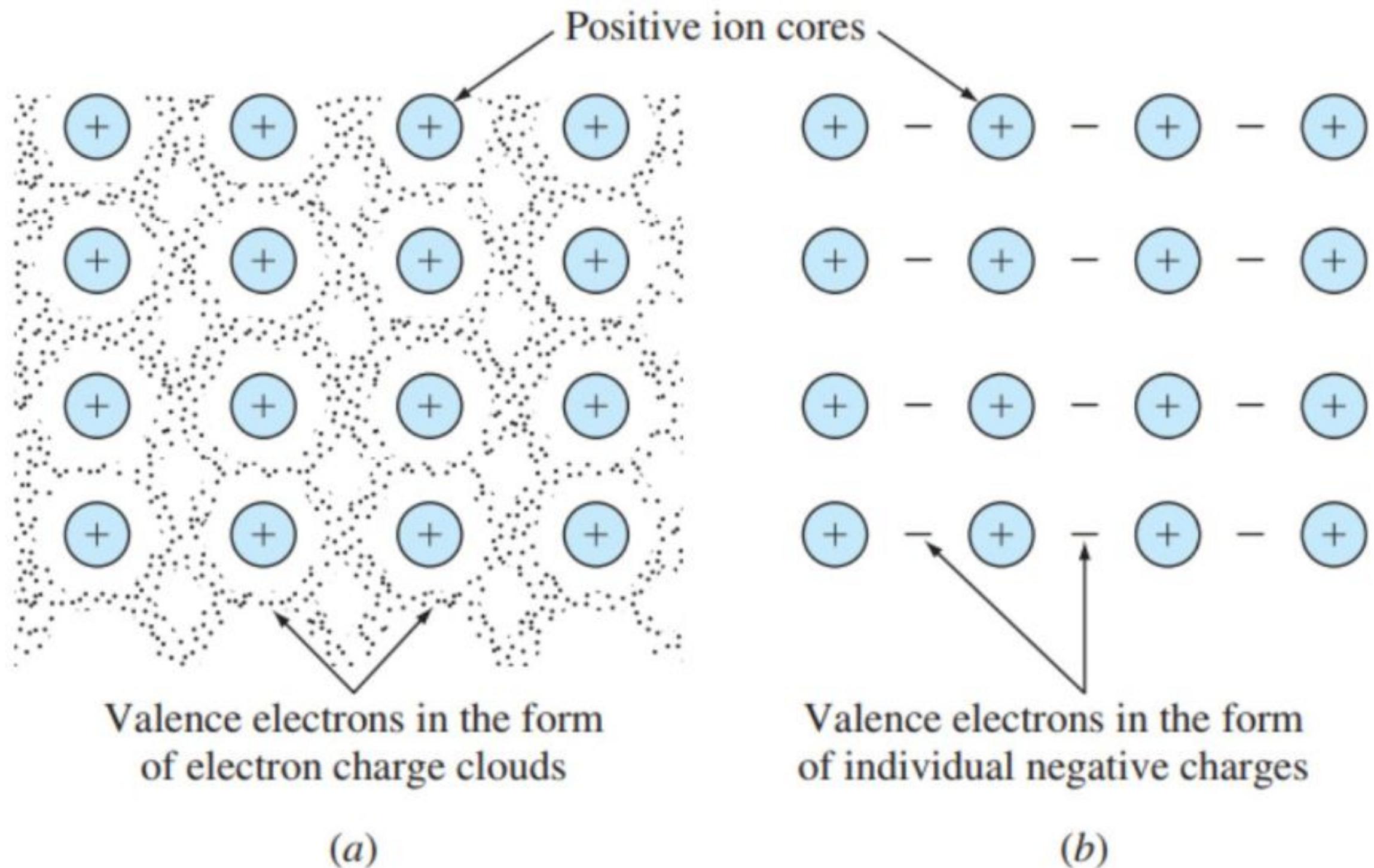
### Microscopic Form of Ohm's Law

$$\mathbf{J} = \frac{\mathbf{E}}{\rho}$$

where  $\mathbf{J}$  = current density,  $\text{A}/\text{m}^2$

$\mathbf{E}$  = electric field,  $\text{V}/\text{m}$

$\rho$  = electrical resistivity,  $\Omega \cdot \text{m}$



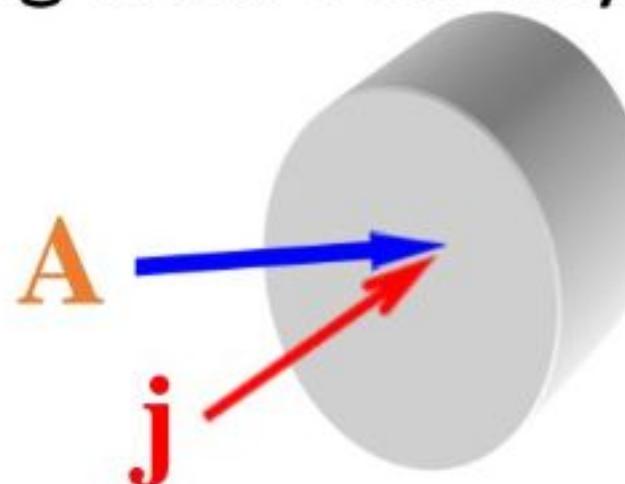
(a)

(b)

# Drude Conductivity

- Ohm's "Law":  $E \equiv \rho j$  or  $j \equiv \sigma E$  (1)  
**E = Electric Field, j = Current Density,**  
 **$\rho \equiv Resistivity, \sigma \equiv Conductivity$**

- Consider a wire of cross sectional area **A**, with current flowing in it. Current consists of **n** electrons per unit volume, all moving with velocity **v**:



- The number of electrons crossing area **A** in time **dt** is **nAvdt**

- The charge crossing **A** in **dt** is **-nevAdt**, so

$$j = -nev. \quad (2)$$

*j = current density*

- In the real material, we expect the electrons to be moving randomly even in zero electric field due to thermal energy. However, they will have an average, or **drift velocity** along the field direction.

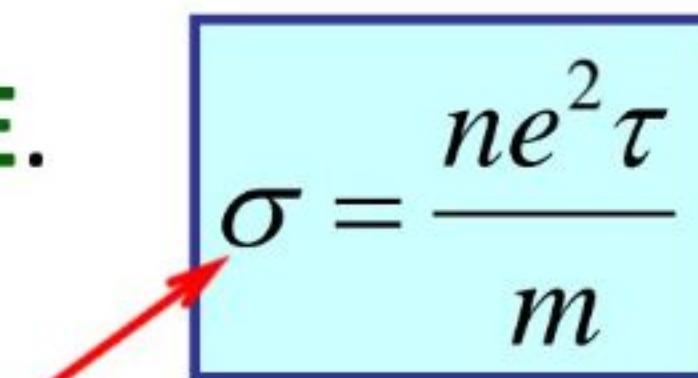
$$v_{\text{drift}} = -(e\tau/m)E \quad (3)$$

- This comes from integrating Newton's 2<sup>nd</sup> Law over the time  **$\tau$** . This is the velocity that must be related to **j**. Combining **(2) & (3)** gives

$$j = (ne^2\tau / m)E.$$

- Comparison of this with  **$j = \sigma E$**  gives

## The Drude Conductivity:

$$\sigma = \frac{ne^2\tau}{m}$$


- As is often true for physics models, this result for  $\sigma$  has been obtained using some ***very simple assumptions***, which surely cannot be correct in reality! How can this result be **tested**?

- **First ask:**

***Does the Drude assumption of scattering from ions seem reasonable?***

- Check it **experimentally** by measuring  $\sigma$  for a series of known metals &, using sensible estimates for ***n, e*** and ***m, estimate  $\tau$ .***
- Results show that, at least for “simple metals”

**$\tau \approx 10^{-14}$  s at room temperature.**

- Often, instead of a scattering time  $t$ , it's useful to formulate a theory of conductivity in terms of

*An average distance between collisions.*

- This distance is called *The mean free path* between collisions.
- To do this, we have to consider the average electron velocity. This should not be  $v_{\text{drift}}$ , which is the electron velocity due to the electric field.
- Instead, it should be  $v_{\text{random}}$ , the velocity associated with the intrinsic thermal energy of the electrons.

- Estimate  $v_{\text{random}}$  by treating the electrons as a classical ideal gas & using the result from classical statistical physics:

**The Equipartition Theorem:**

$$\left(\frac{1}{2}\right)m(v_{\text{random}})^2 = \left(\frac{3}{2}\right)(k_B)T$$

(For a simple derivation, see any Physics I textbook!)

- Results: The mean free path is

$$l = v_{\text{random}}t \approx 1-10 \text{ \AA}$$

- This is of the order of interatomic distances, *so it is reasonable!*

# Equipartition of Energy

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is

$$\frac{1}{2}kT \text{ per molecule}$$

$$\frac{1}{2}RT \text{ per mole}$$

$k$  = Boltzmann's constant

$R$  = gas constant

$$\frac{3}{2}kT$$

$$\frac{3}{2}RT$$

For three translational degrees of freedom, such as in an ideal monoatomic gas.

The equipartition result

$$KE_{avg} = \frac{3}{2}kT$$

$$KE_{avg} = \left[ \frac{1}{2}mv^2 \right] = \frac{3}{2}kT$$

## Success of classical free electron theory:

- (1). It verifies Ohm's law.
- (2). It explains the electrical and thermal conductivities of metals.
- (3). It derives Wiedemann – Franz law. (i.e., the relation between electrical conductivity and thermal conductivity)
- (4). It explains optical properties of metalsl.

## Electrical Resistivity of Metals

$$\rho_{\text{total}} = \rho_T + \rho_r$$

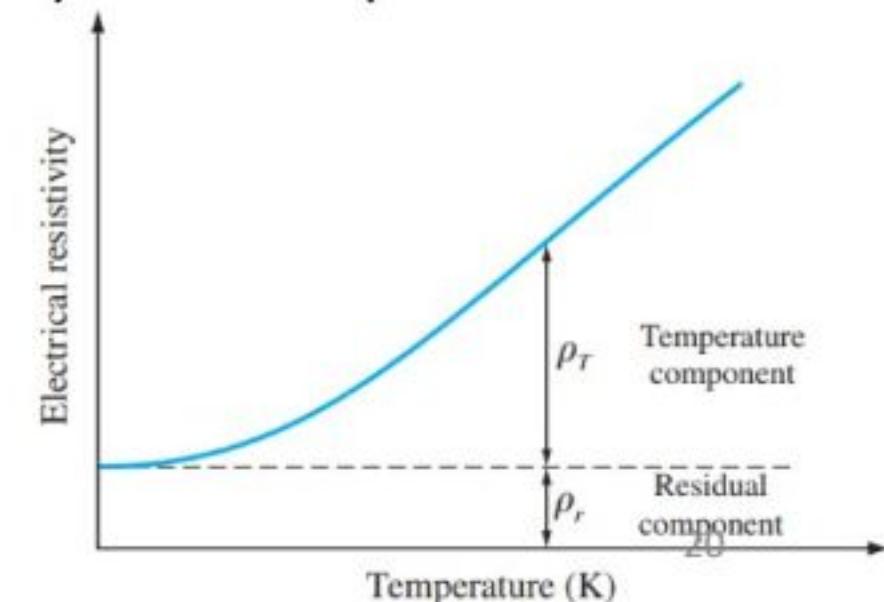
The **thermal component** arises from the vibrations of the positive-ion cores about their equilibrium positions in the metallic crystal lattice.

As the temperature is increased, the ion cores vibrate more and more, and a large number of thermally excited elastic waves (called *phonons*) scatter conduction electrons and decrease the mean free paths and relaxation times between collisions.

Thus as the temperature is increased, the electrical resistivities of pure metals increase.

The **residual component** of the electrical resistivity of pure metals is small and is caused by structural imperfections such as dislocations, grain boundaries, and impurity atoms that scatter electrons.

The residual component is almost independent of temperature and becomes significant only at low temperatures

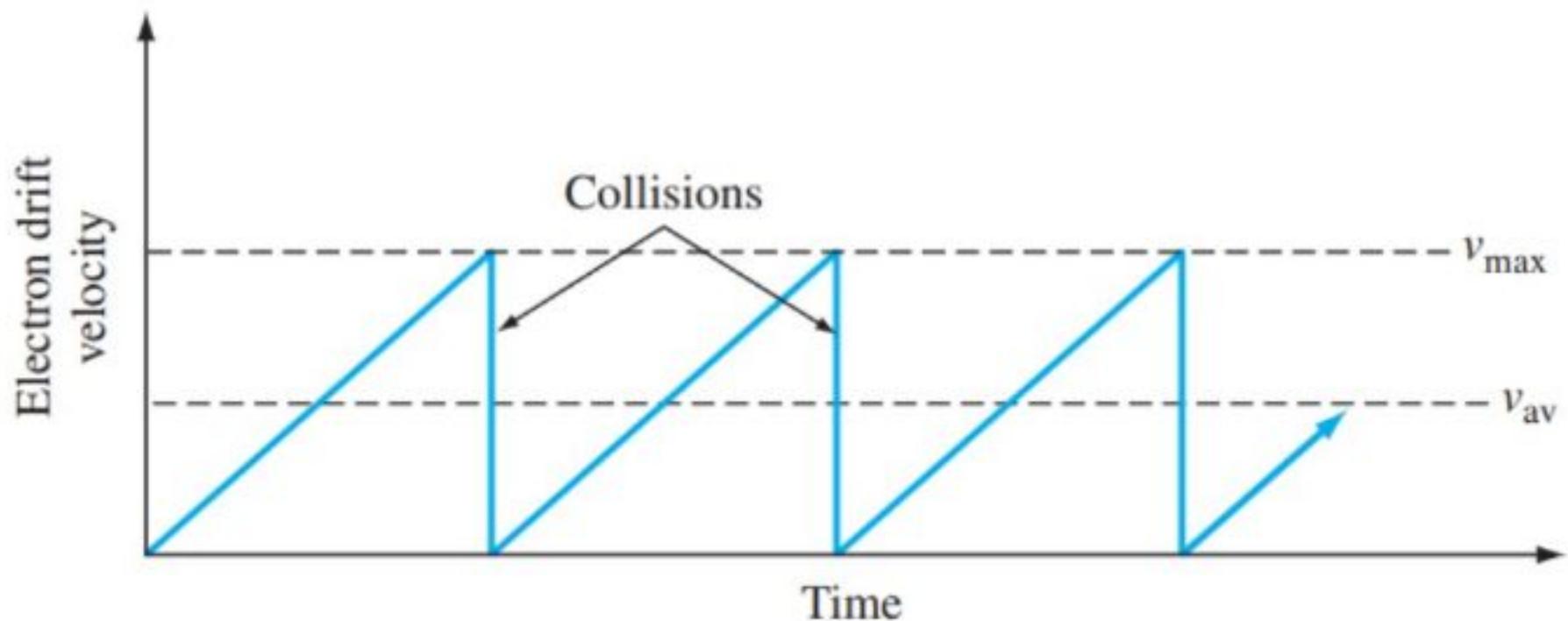


## Drift Velocity of Electrons in a Conducting Metal

$$v_e = \mu_e E$$

The rate of charge flow per unit area

$$\sigma = n|e|\mu_e$$



Electron drift velocity versus time for classical model for electrical conductivity of a free electron in a metal

## A Very Important Experimental Result for Metals: “The Wiedemann-Franz Law”

- Since 1853, it has been known that a universal property of metals is an experimentally well verified relationship between the thermal & electrical conductivities. As just discussed, *in the presence of an external electric field E*, the current density  $\mathbf{j}$  is given by

$$\text{Ohm's "Law": } \mathbf{j} = \sigma \mathbf{E}$$

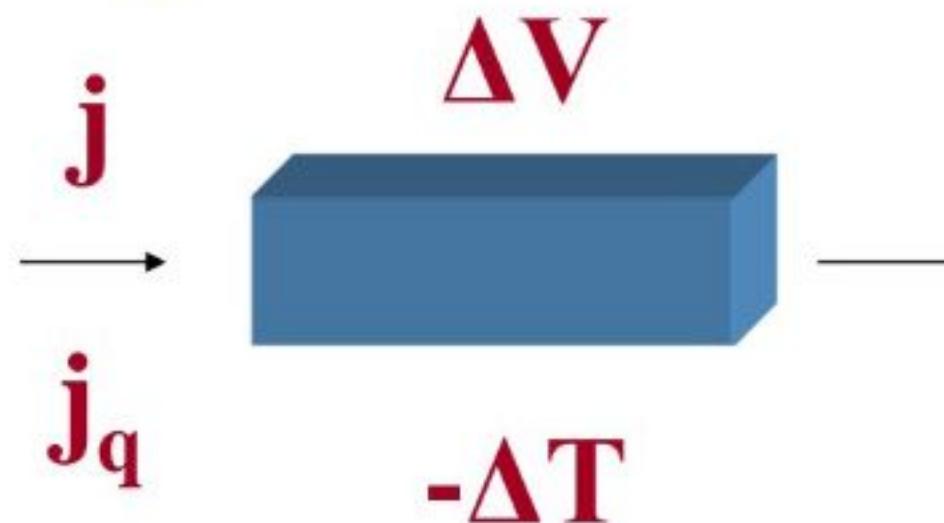
- In a simple one dimensional geometry as in the figure,

$$\mathbf{j} = \sigma \mathbf{E} = \sigma dV/dx$$

- The thermal analogue of this is

$$\mathbf{j}_q = -\kappa dT/dx.$$

$\kappa \equiv$  Thermal Conductivity.



- Drude's assumption was that  $\kappa$  in metals is dominated by the electronic contribution. A result from elementary kinetic theory of classical ideal gasses is:

$$\kappa = \left(\frac{1}{3}\right) v_{\text{random}} \ell c_{\text{el}} \quad (4)$$

where  $c_{\text{el}}$  is the *electronic specific heat per unit volume*.

- Each electron has an energy  $(\frac{3}{2})k_B T$  so, for  $n$  electrons per unit volume:

$$E_{\text{tot}} = \left(\frac{3}{2}\right) n k_B T, \quad c_{\text{el}} = (dE_{\text{tot}}/dT) = \left(\frac{3}{2}\right) n k_B T$$

- Recall that  $\ell = v_{\text{random}} \tau$ , & divide  $\kappa$  by  $\sigma = (ne^2 \tau / m)$  giving:

$$\frac{\kappa}{\sigma} = \frac{1}{2} m v_{\text{random}}^2 \quad \frac{k_B}{e^2} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 T$$

$$KE_{\text{avg}} = \left[ \frac{1}{2} m v^2 \right] = \frac{3}{2} kT$$

**Wiedemann-Franz law** is the law which relates the thermal conductivity ( $\kappa$ ) and the electrical conductivity ( $\sigma$ ) of a material which consists of somewhat freely moving electrons in it.

- **Thermal Conductivity ( $\kappa$ ):** It is the degree (measure) of capacity of a material to conduct heat.
- **Electrical Conductivity ( $\sigma$ ):** It is the degree (measure) of capacity of a material to conduct electricity.  $\left(\frac{1}{\rho}\right)$

- Dividing by  $\mathbf{T}$  gives the simple result that

$$\frac{\kappa}{\sigma T} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2$$

- This is a very nice result!! All the parameters that might be regarded in some way as poorly known have dropped out, **leaving what looks like it might be a universal quantity.**

**Experimentally, this is indeed the case.**

- The measured value is a factor of 2 different from this result, but in Drude's original work, a numerical error made the agreement appear to be exact!

- So, **Drude's Model** appeared to be reasonably accurate in identifying electron-ion collisions as the main scattering mechanism, & had a triumph regarding the most universal known property of metals.
- This was enough to set it up as the main theory of metals for two decades.

## However, fundamental problems with Drude's Theory began to emerge:

1. It could not explain the observation of positive Hall coefficients in many metals.
2. As more became known about metals at low temperatures, it was obvious that since the conductivity increased sharply,  $\ell$  was far too long to be explained by simple electron-ion scattering.
3. A vital part of the thermal conductivity analysis is the use of the kinetic theory value of  $\frac{3}{2}nk_B$  for the electronic specific heat. Measurements gave no evidence for a contribution of this size.

- The solution to these issues and the other unpleasant difficulties like the existence of insulators would not have come if we had been restricted to classical physics.

*“The physics of solids is deeply quantum mechanical; indeed condensed matter is arguably the best ‘laboratory’ for studying subtle quantum mechanical effects in the 21st century.”*

### Successes of the Drude theory:

- Many transport properties are correctly predicted (also finite-frequency conductivity, which we do not treat here)
- Hall coefficient measurements seem good for many materials
- Still useful today as a simple model of conductivity, and accurate for some materials, especially those with low densities of electrons, particularly semiconductors.

### Shortcomings of the Drude theory:

- The Hall coefficient is found to have the wrong sign for some metals
- We still cannot explain heat capacities at low temperatures for metals – kinetic theory would suggest that we have

$$C_V = \frac{3}{2} NkT$$

just like for gases

## Models of electrons in solids



- **Drude Theory (1900):** Attempts to understand conduction of electrons in metals using a model analogous to kinetic theory in gases. This deals with free electrons in a metal like molecules of a gas in a box.
- **Sommerfeld Theory (1920s):** Combines our understanding of Fermi-Dirac statistics with Drude theory in order to understand properties of metals that were previously not explained by Drude theory. Deals with free electrons in a box, but now treats them as fermions, not classical particles
- **Beyond the free electron model:** As we go further in the course, we will see improvements on these models. By considering the crystal structure of solids, we can produce a band theory, which explains which materials are conductors, insulators and semi-conductors, as well as the properties of each type of material. Beyond that, we will investigate interactions between electrons, which give rise, e.g., to superconductivity and other complex properties of materials.

# Fermi-Dirac Details

The probability that  
a particle will have  
energy E

$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

At absolute zero, fermions will fill up all available energy states below a level  $E_F$  called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

For low temperatures, those energy states below the Fermi energy  $E_F$  have a probability of essentially 1, and those above the Fermi energy essentially zero.

The quantum difference which arises from the fact that the particles are indistinguishable.

# Fermions

- Fermions are particles which have half-integer [spin](#) and therefore are constrained by the [Pauli exclusion principle](#).
- Particles with integer spin are called [bosons](#). Fermions include [electrons](#), [protons](#), [neutrons](#).
- The fact that electrons are fermions is foundational to the buildup of the periodic table of the elements since there can be only one electron for each state in an atom (only one electron for each possible set of quantum numbers).
- The fermion nature of electrons also governs the behavior of [electrons in a metal](#) where at low temperatures all the low energy states are filled up to a level called the [Fermi energy](#). This filling of states is described by [Fermi-Dirac statistics](#).

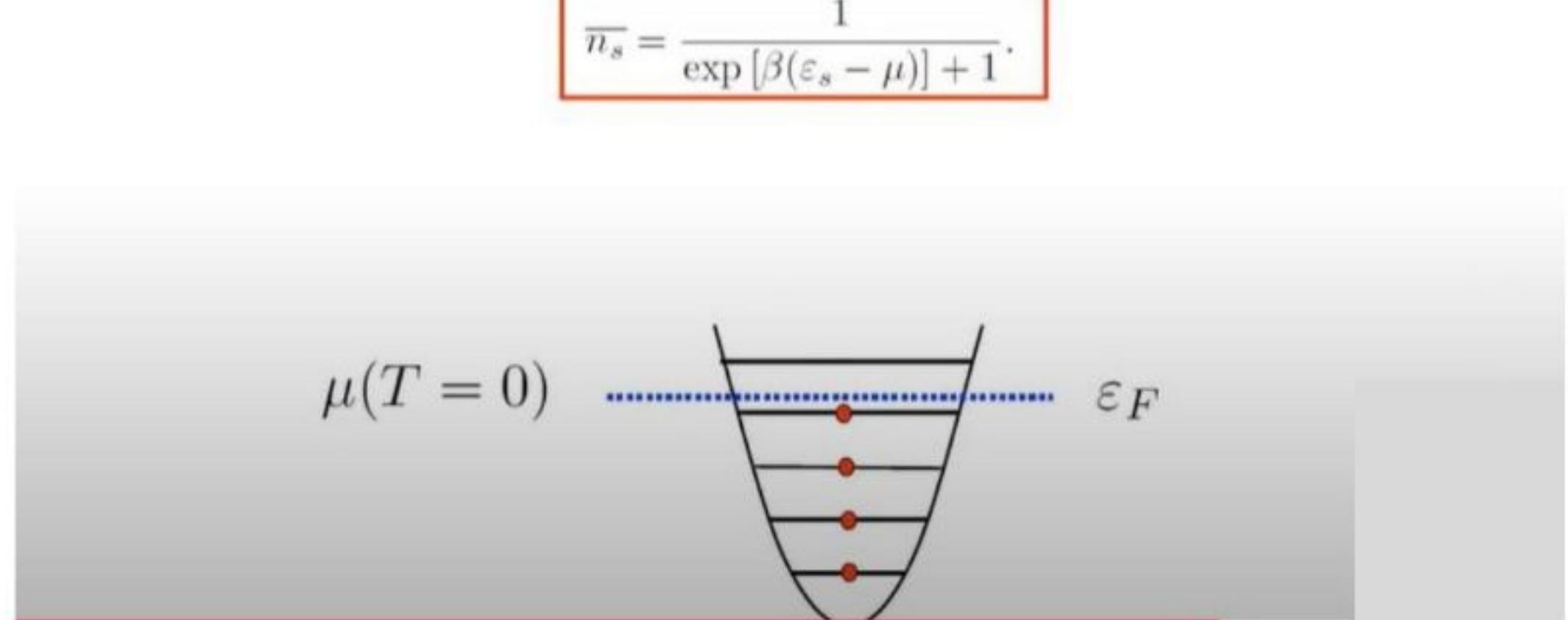
## Sommerfeld Theory

- Electrons inside a solid are free electrons.
- Electrons are not interacting with each other.
- Electrons are not interacting with ions.
- Electrons are not interacting with impurities and defects in solids.

## Sommerfeld Theory

- In the mid 1920s, Sommerfeld modified Drude's theory to account for Fermi-Dirac statistics, making a free electron theory that properly accounted for the fact that electrons are fermions
- As before, at finite temperature, the mean occupation number of momentum states is given by the Fermi-Dirac distribution,

$$\overline{n}_s = \frac{1}{\exp [\beta(\varepsilon_s - \mu)] + 1}.$$



Sommerfeld's model of  
an  $e^-$  in a solid.

### Fermi - Dirac Statistics

$$f_D(\varepsilon - \mu) = \frac{1}{1 + e^{(\varepsilon - \mu)/k_B T}}$$

Probability distribution of  $e^-$ 's  
as a function of energy  $\varepsilon$ .

## Fermi-Dirac Statistics Distribution function:

\* Fermi distribution function ' $F(E)$ ' is used to calculate the probability of an electron occupying a certain energy level.

\* The distribution of electrons among the different energy levels as a function of temperature is known as Fermi-Dirac distribution function.

$$F(E) = \frac{1}{1 + \exp[(E - E_f)/kT]}$$

Where,

$E_f$  → Fermi energy

$k$  → Boltzmann Constant

$T$  → Temperature in K.

The probability value  $F(E)$  lies between 0 and 1

→ If  $F(E) = 1$ , the energy level is occupied by an electron

→ If  $F(E) = 0$ , the energy level is vacant

→ If  $F(E) = 0.5$  or  $\frac{1}{2}$ , then there is a 50% chance for finding the electron in the energy level.

## Effect of Temperature on Fermi function:

(i) At  $T=0\text{K}$

At  $0\text{K}$ , the electrons are filled upto a maximum energy level called Fermi Energy Level  $E_F$ . All the energy levels above the Fermi Energy level are empty.

Case (ii): At  $T=0\text{K}$  and  $E < E_F$

$$F(E) = \frac{1}{1+e^{\infty}} = \frac{1}{1} = 1$$

∴ The probability of electrons to occupy the energy level between Fermi energy level is 100%.

Electrons with Fermi energy move with Fermi velocity and the same is related to the Fermi temperature by the relation,

$$\gamma m v_F^2 = kT$$

Case (iii): At  $T=0\text{K}$  and  $E > E_F$

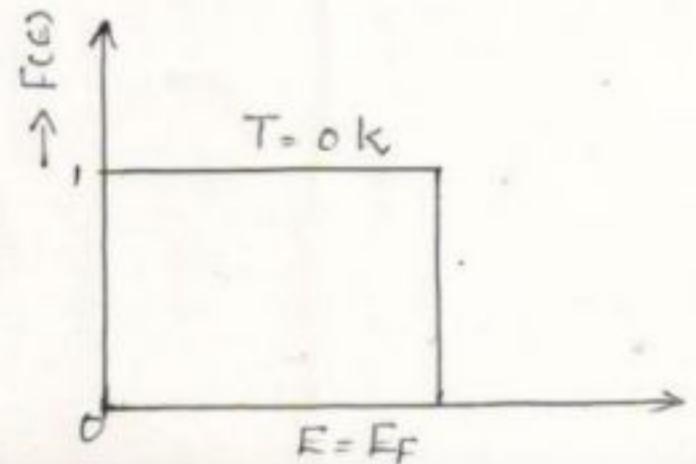
$$F(E) = \frac{1}{1+e^{\infty}} = \frac{1}{1+\infty} = 0$$

This means that at  $0\text{K}$ , electrons are completely occupied below ' $E_F$ ' and above ' $E_F$ ' electrons are unoccupied.

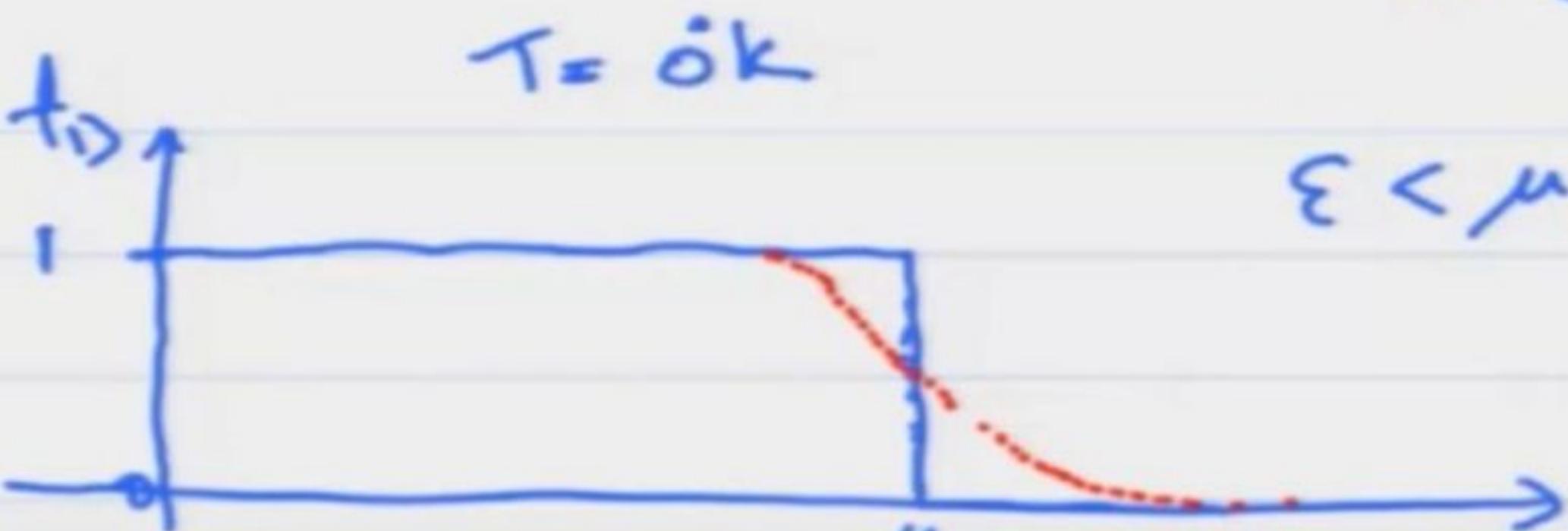
Case (iv): At  $T>0\text{K}$  and  $E=E_F$

$$F(E) = \frac{1}{1+1} = \frac{1}{2} = 0.5$$

The Fermi-function at  $0\text{K}$  can also be graphically represented as,



$$f_D(\varepsilon - \mu) = \frac{1}{1 + e^{\frac{\varepsilon - \mu}{kT}}}$$



$\mu$ : Called chemical potential of the system.

$$T = 0\text{K}$$

$$t_D(\varepsilon - \mu) = 1 \quad (\varepsilon < \mu)$$

$$\varepsilon = 0 \quad \varepsilon > \mu$$

Particle which confined in a box of length  $L$ .



- \* Free particle
- \* Schrodinger eqn
- \* 1-Dimension

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

→

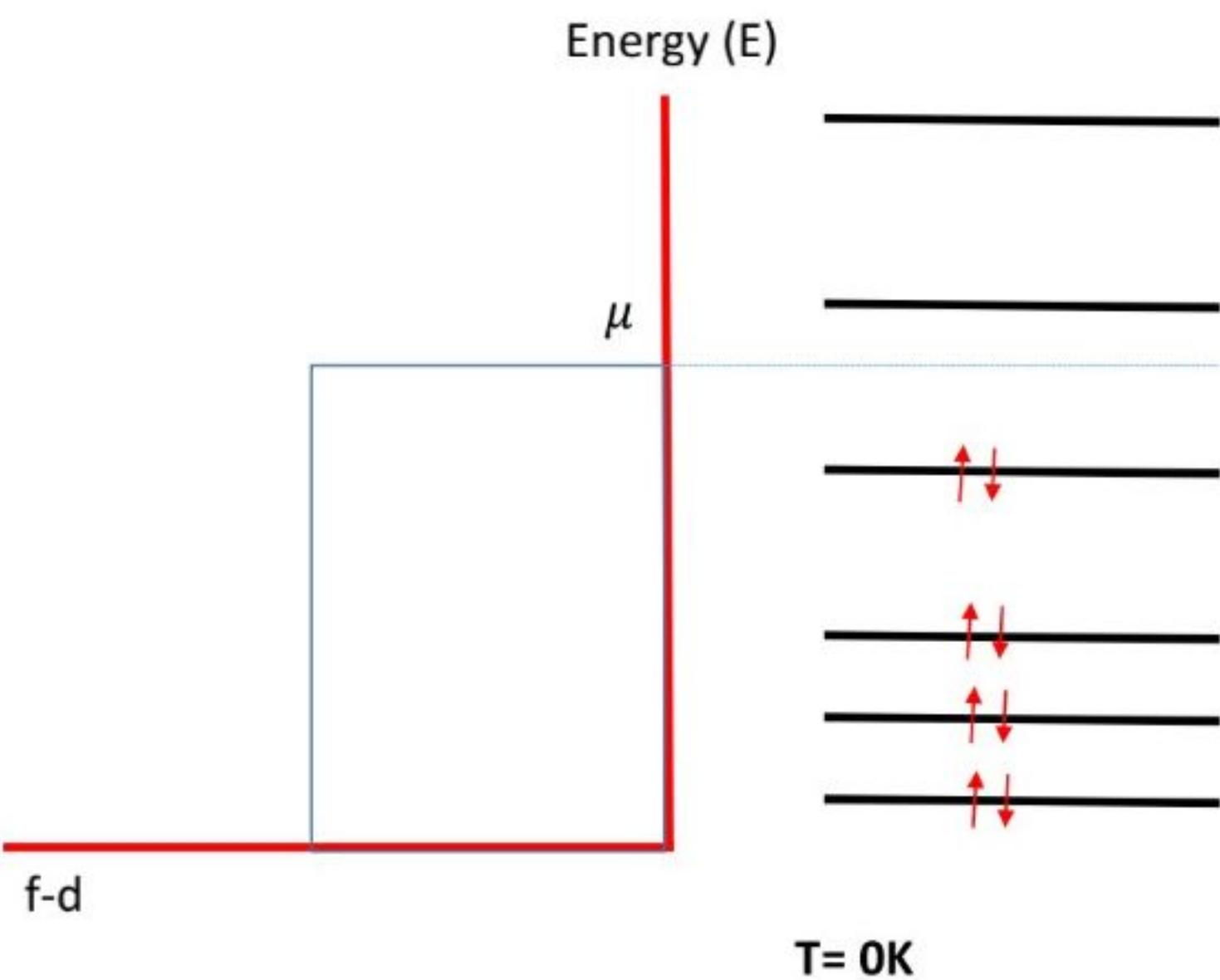
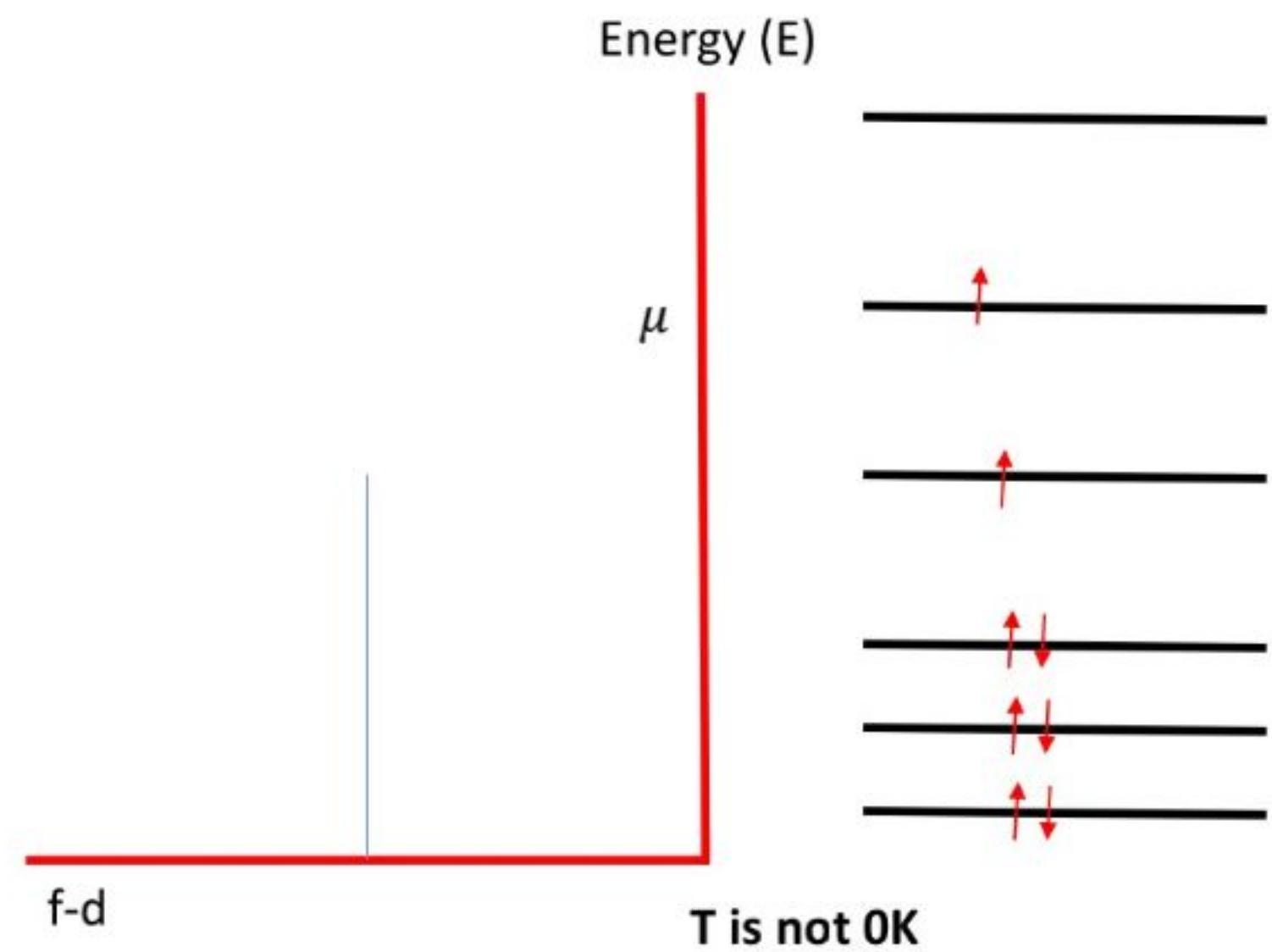
$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad \begin{matrix} \nearrow 0 \text{ at } x=L \\ \partial x = 0 \end{matrix}$$



Energy States that are available in the system

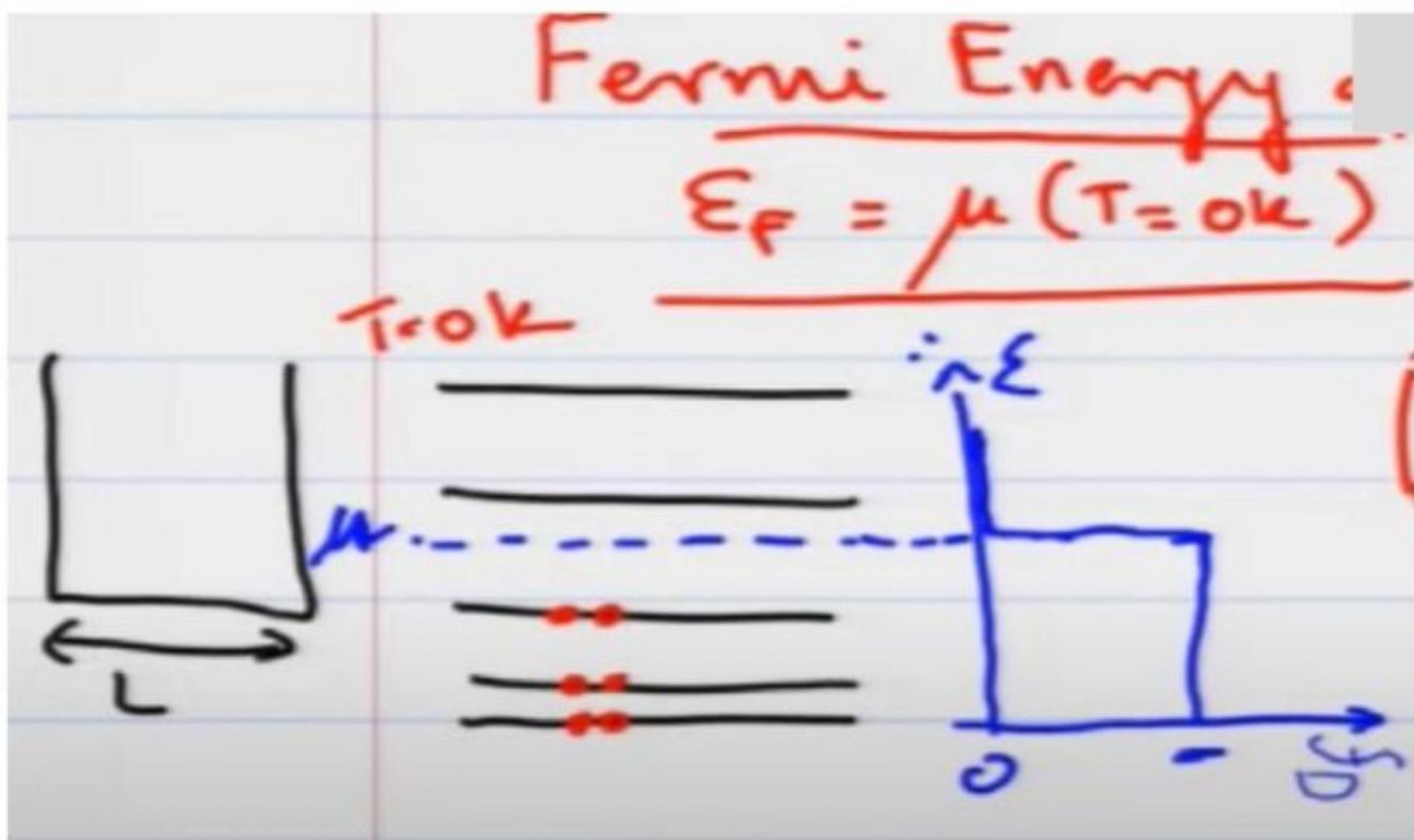
$$\mathcal{E}_n = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2$$



Filling of states follows Pauli's Exclusion Principle

Maxwells distribution which is followed by Drude's model depends on temp.

$$KE_{avg} = \left[ \frac{1}{2}mv^2 \right] = \frac{3}{2}kT$$



## **Importance of Fermi Energy:**

- Fermi energy is used to separate the vacant and filled states at 0 K.
- It is used to know the status of the electrons.
- Electrons are completely filled below fermi energy level and completely empty above the fermi level at 0K
- Above 0 K some electrons absorb thermal energy and they jumps to the higher energy levels.

## **Work Function:**

The minimum energy given to an electron in a metal to liberate it from the surface of that metal at absolute zero is called work function. It depends upon.

1. The nature of the metal.
2. The surface conditions.

There are **four different ways** of supplying energy to the electrons of a metal.

- When the energy is supplied to the electrons **thermally by heating the metal**, then the work function is called **thermionic work function**.
- When the energy is supplied to the electrons optically **by exposing it with the incident light**, then the work function is called **photoelectric work function**.
- When the **energy is received from electrons or ions that strike the metal surface from outside**, then the work function is called **secondary emission work function**.
- When the energy is received **from the applied electric field**, then the work function is called **field emission work function**.

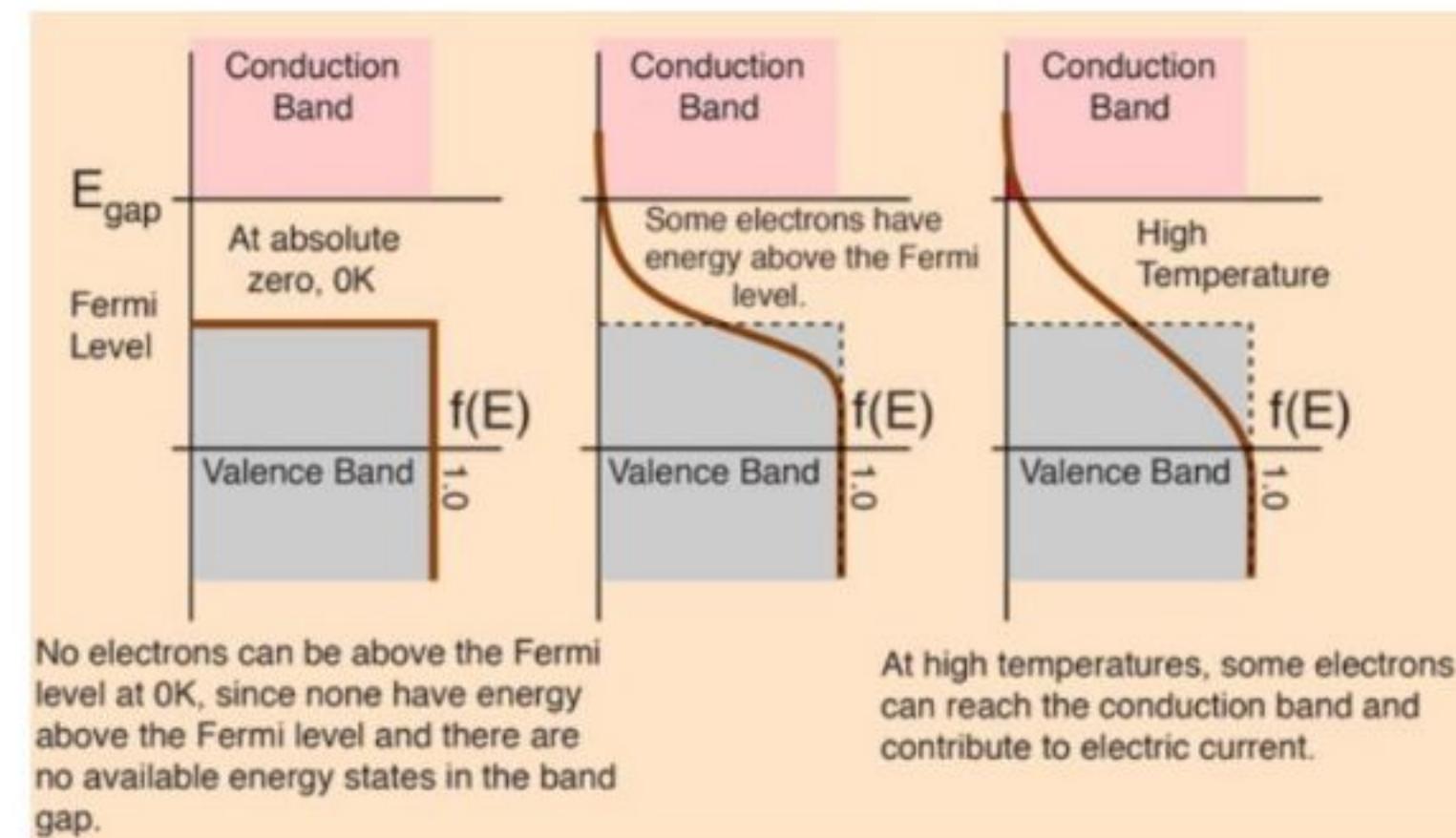
- At higher temperatures a certain fraction, characterized by the [Fermi function](#), will exist above the Fermi level. The Fermi level plays an important role in the [band theory of solids](#). In doped semiconductors, [p-type](#) and [n-type](#), the Fermi level is shifted by the impurities, illustrated by their [band gaps](#). The Fermi level is referred to as the electron chemical potential in other contexts.
- In metals, the Fermi energy gives us information about the velocities of the electrons which participate in ordinary electrical conduction.

- The amount of energy which can be given to an electron in such conduction processes is on the order of micro-electron volts, so only those electrons very close to the Fermi energy can participate.

- The [Fermi velocity](#) of these conduction electrons can be calculated from the Fermi energy.

$$v_F = \sqrt{\frac{2E_F}{m}}$$

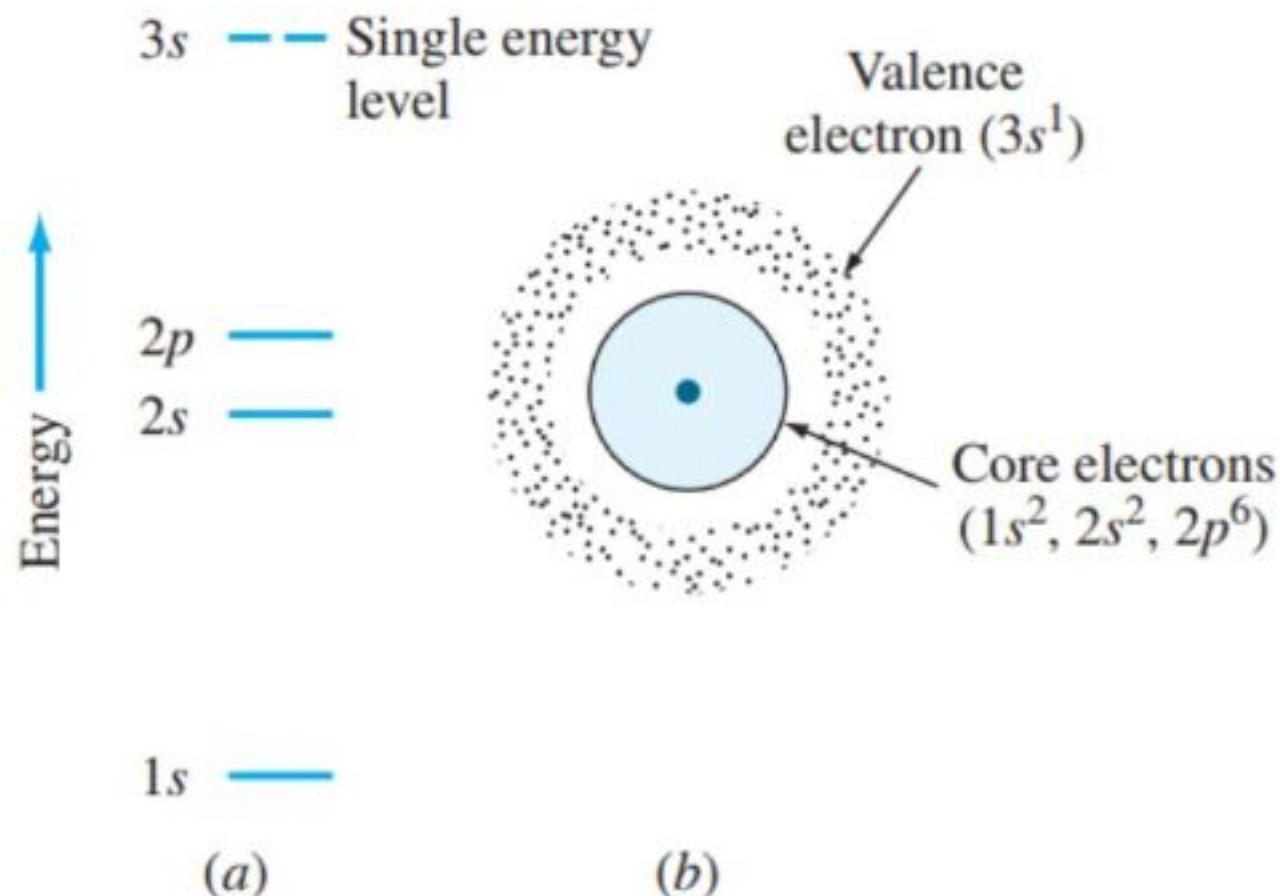
- This speed is a part of the [microscopic Ohm's Law](#) for electrical conduction. For a metal, the [density of conduction electrons](#) can be implied from the Fermi energy.



# Band Theory of Solids

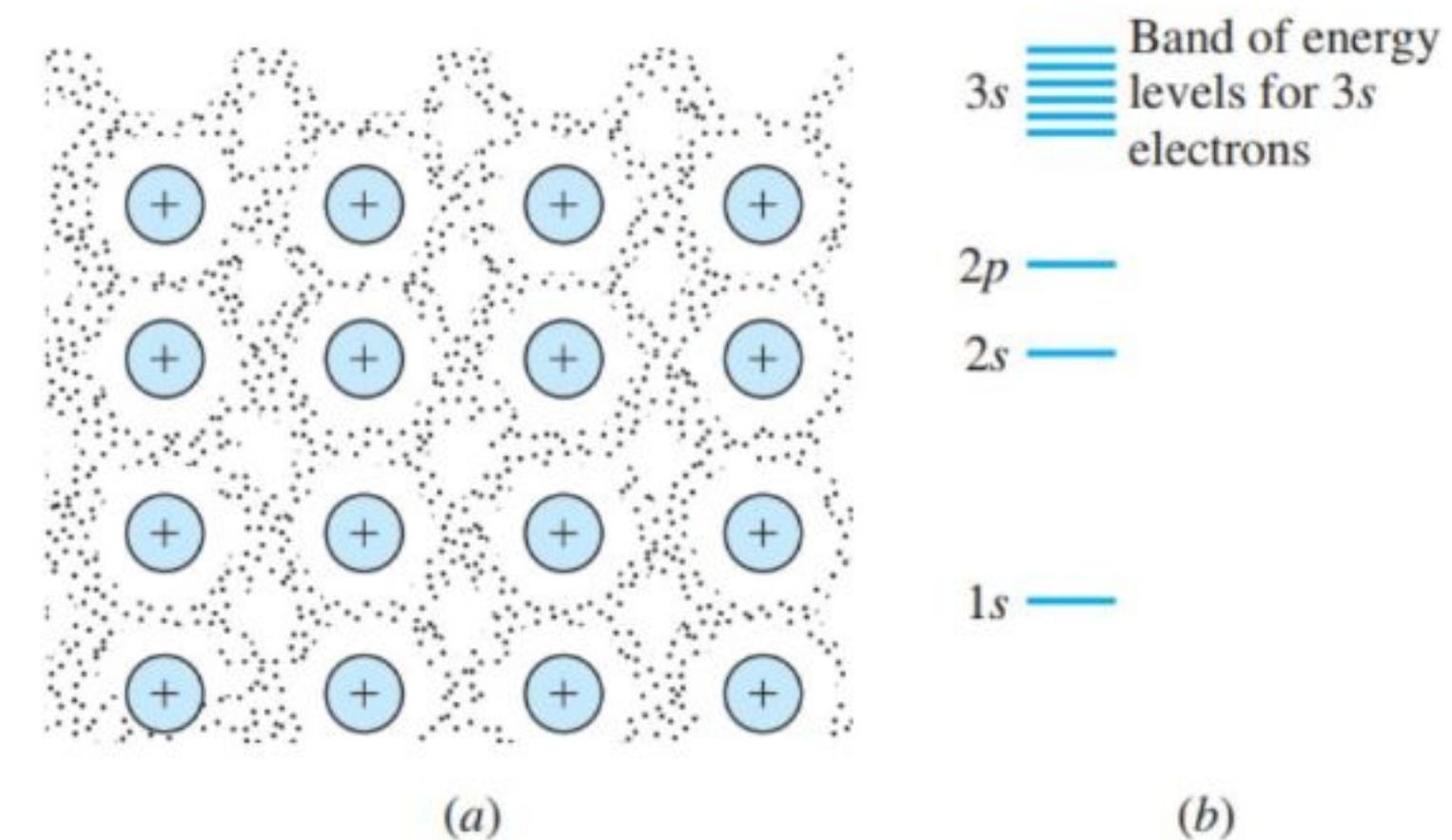
- A useful way to visualize the difference between [conductors](#), [insulators](#) and [semiconductors](#) is to plot the available energies for electrons in the materials. Instead of having [discrete energies](#) as in the case of free atoms, the available energy states form [bands](#).
- Crucial to the conduction process is whether or not there are electrons in the conduction band.
- In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap.
- With such a small gap, the [presence of a small percentage of a doping material can increase conductivity](#) dramatically.
- An important parameter in the band theory is the [Fermi level](#), the top of the available electron energy levels at low temperatures.
- The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.

## ENERGY-BAND MODEL FOR ELECTRICAL CONDUCTION



- (a) Energy levels in a single sodium atom.  
(b) Arrangement of electrons in a sodium atom.

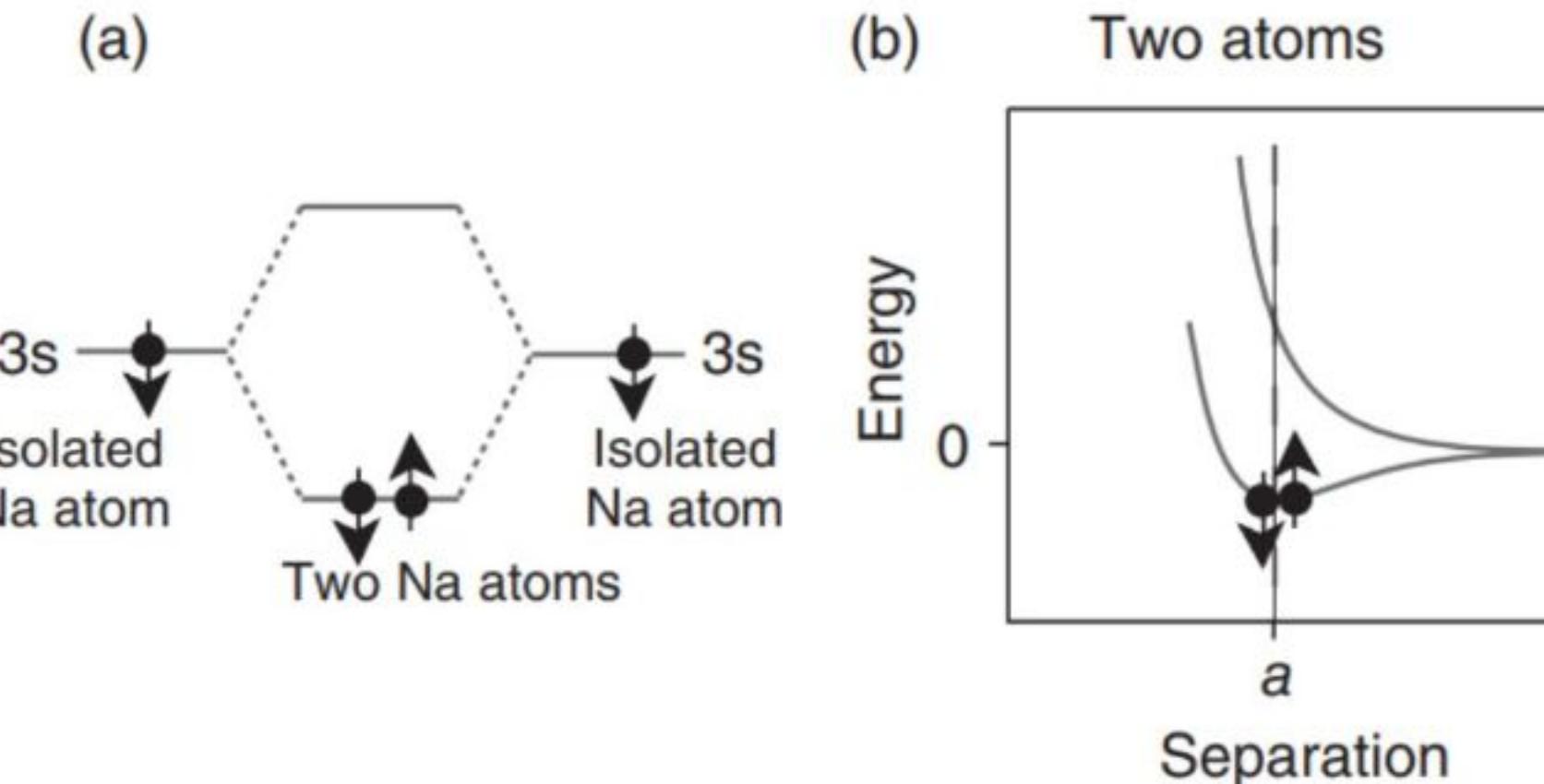
The outer  $3s^1$  valence electron is loosely bound and is free to be involved in metallic bonding.



- (a) Delocalized valence electrons in a block of sodium metal.  
(b) Energy levels in a block of sodium metal; note the expansion of the  $3s$  level into an energy band and that the  $3s$  band is shown closer to the  $2p$  level since bonding has caused a lowering of the  $3s$  levels of the isolated sodium atoms.

## The formation of energy bands in solids.

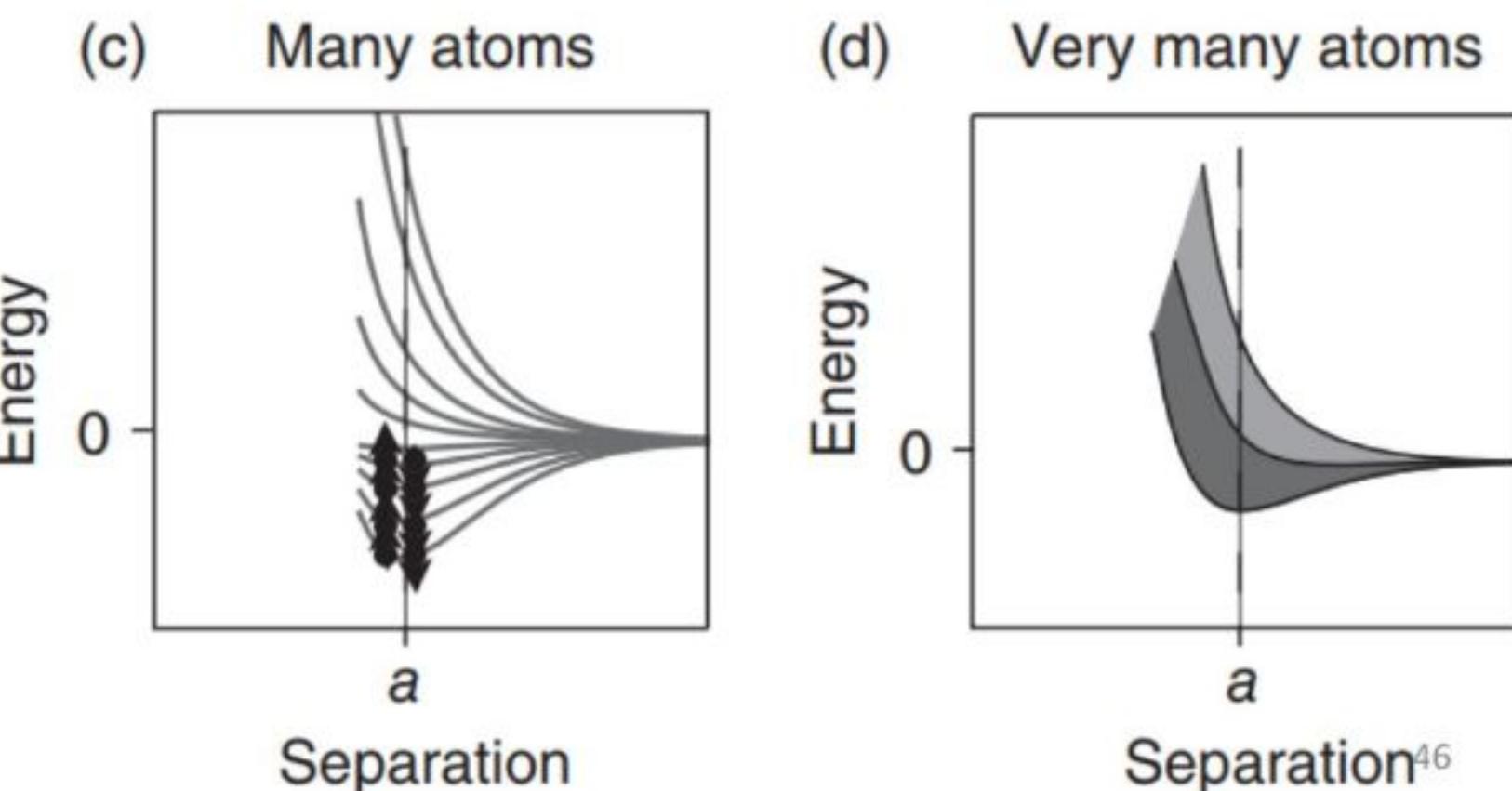
(a) Bonding and antibonding energy levels and their occupation for a molecule constructed from two Na atoms. The black dots and arrows symbolize the electrons with their spin.

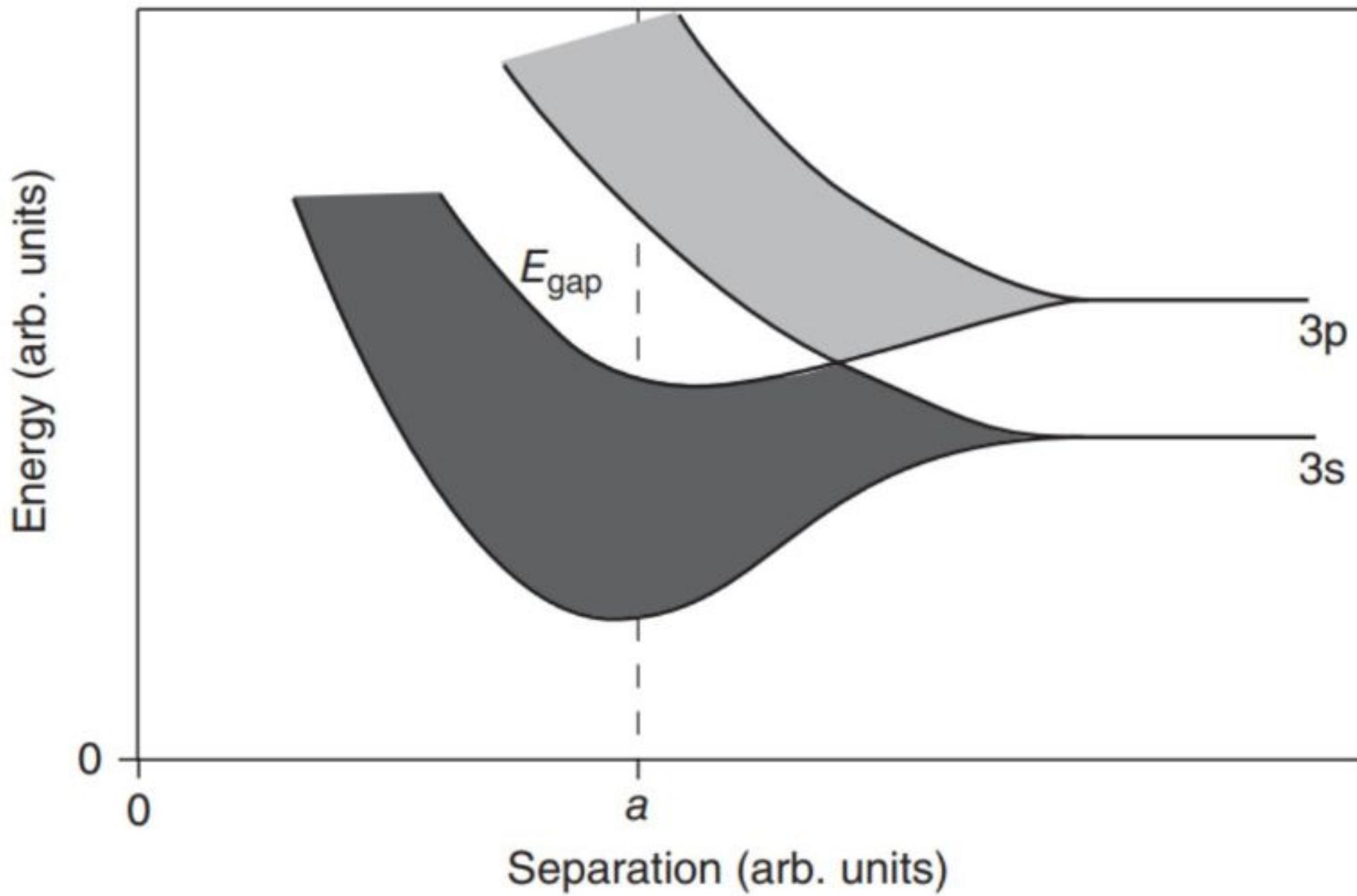


(b) The molecule's energy levels as a function of interatomic separation.

(c) The energy levels for a cluster of many Na atoms as a function of their separation.

(d) For very many atoms, there is a quasi continuum between the lowest and highest energy levels. This energy band is half-filled with electrons (dark area) and halfempty (bright area).





Band formation in Si. The lower band corresponds to the  $\text{sp}^3$  states and is completely filled.

# Energy Bands Comments

## Energy of electrons

Conduction Band

Fermi level in gap.

Valence Band

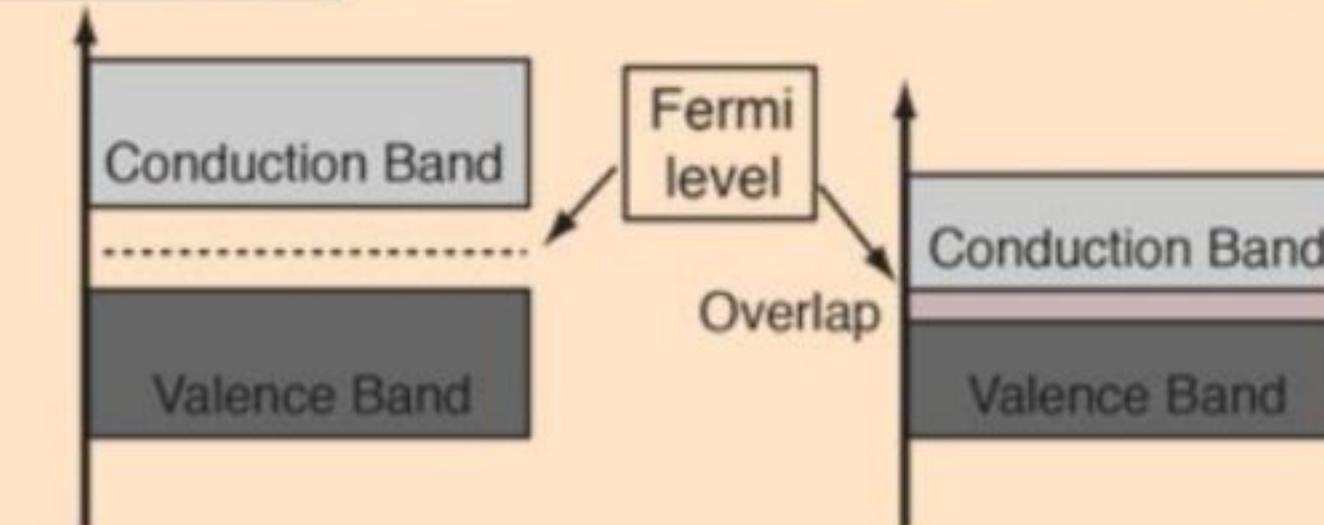
The large energy gap between the valence and conduction bands in an insulator says that at ordinary temperatures, no electrons can reach the conduction band.

In semiconductors, the band gap is small enough that thermal energy can bridge the gap for a small fraction of the electrons. In conductors, there is no band gap since the valence band overlaps the conduction band.

a. Insulator

b. Semiconductor

c. Conductor



**Electron volt** is defined as the amount of energy one electron gains by moving through a [potential difference](#) of one volt. Hence, one electron volt is equal to elementary charge ( $1.60217657 \times 10^{-19}$  coulombs (C)) multiplied by one volt.

It can be written as

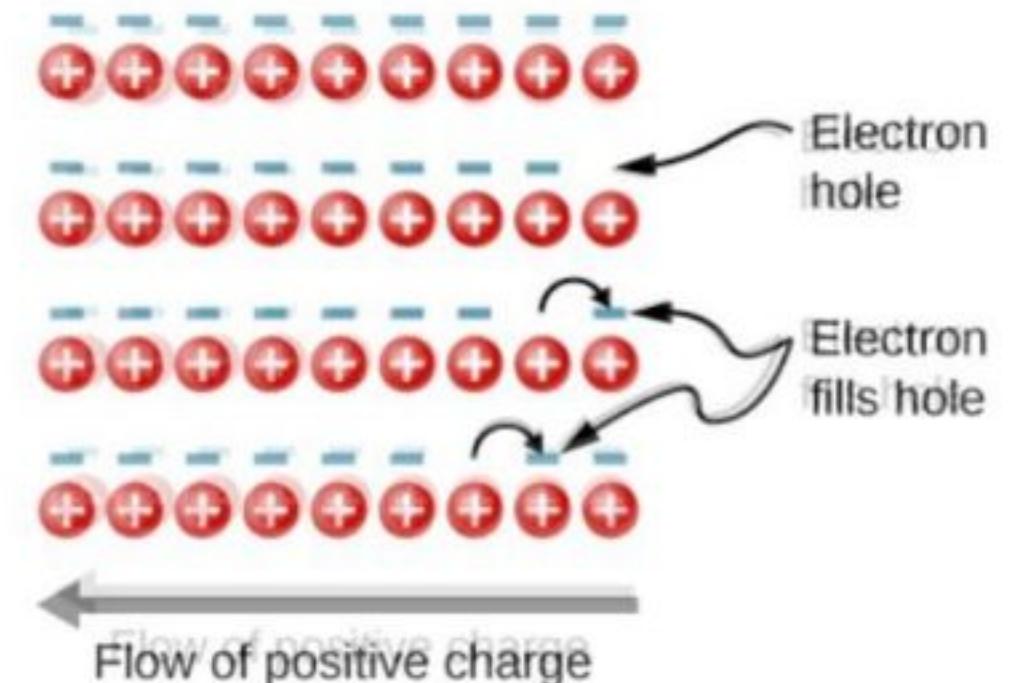
$$eV = (1.60217657 \times 10^{-19} \text{ C}) (1\text{V})$$

Therefore,  $1eV = 1.60217657 \times 10^{-19} \text{ J}$ .

## Electron-hole movement

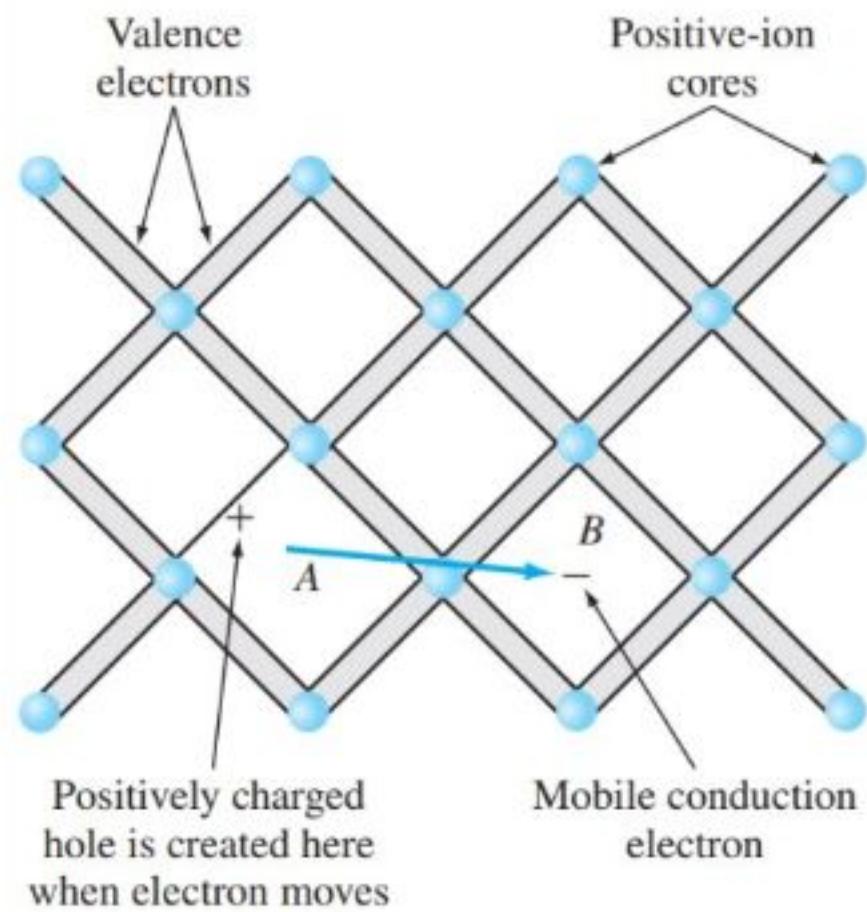
- Till now we have considered only the contribution to the electric current due to electrons occupying states in the conduction band.
- However, moving an electron from the valence band to the conduction band leaves an unoccupied state or **hole** in the energy structure of the valence band, which a nearby electron can move into.
- As these holes are filled by other electrons, new holes are created.
- The electric current associated with this filling can be viewed as the collective motion of many negatively charged electrons or the motion of the positively charged electron holes.

- Assume that each lattice atom contributes one valence electron to the current. As the hole on the right is filled, this hole moves to the left. The current can be interpreted as the flow of positive charge to the left.
- The density of holes, or the number of holes per unit volume, is represented by **p**.
- Each electron that transitions into the conduction band leaves behind a hole. If the conduction band is originally empty, the conduction electron density **p** is equal to the hole density,  $n=p$

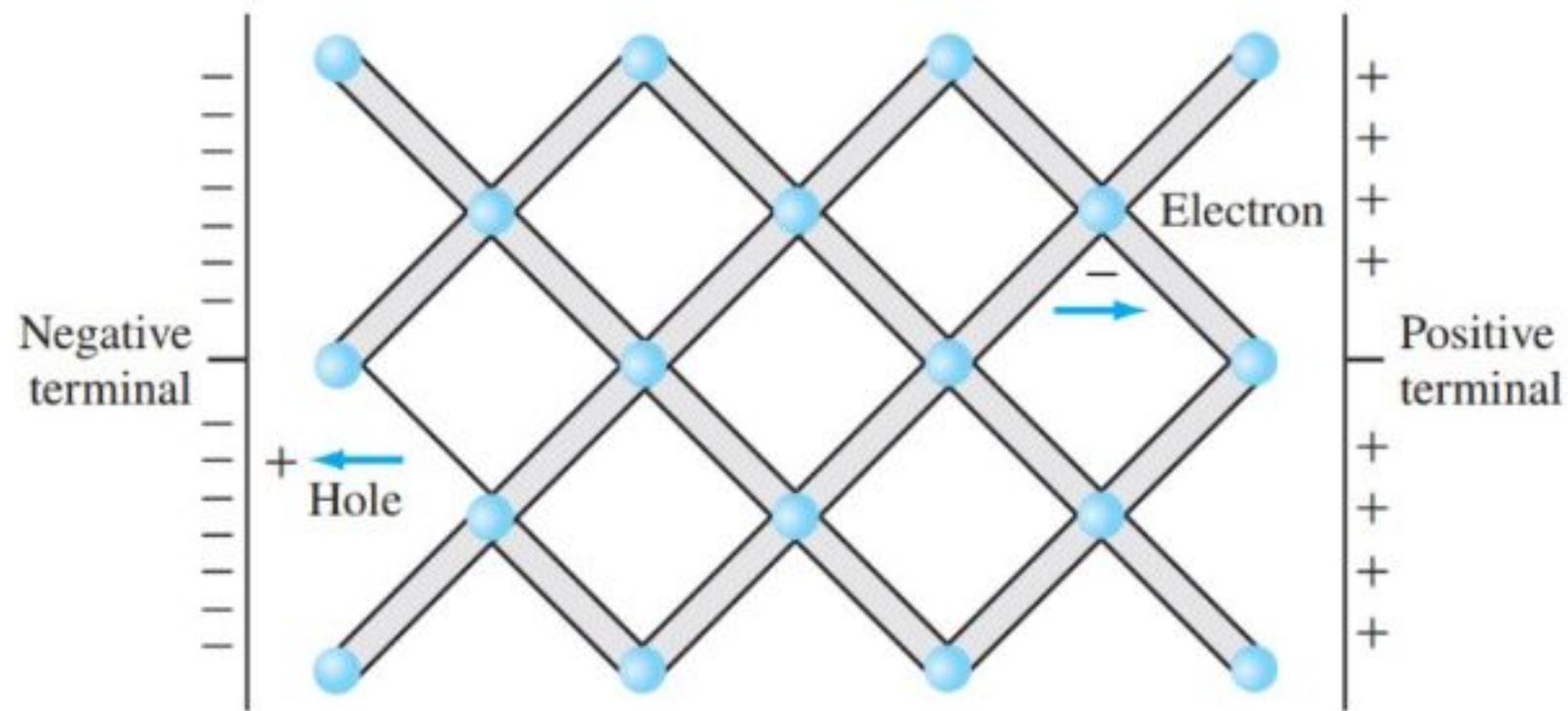


The motion of holes in a crystal lattice. As electrons shift to the right, an electron hole moves to the left. 50

## The Mechanism of Electrical Conduction in Intrinsic Semiconductors



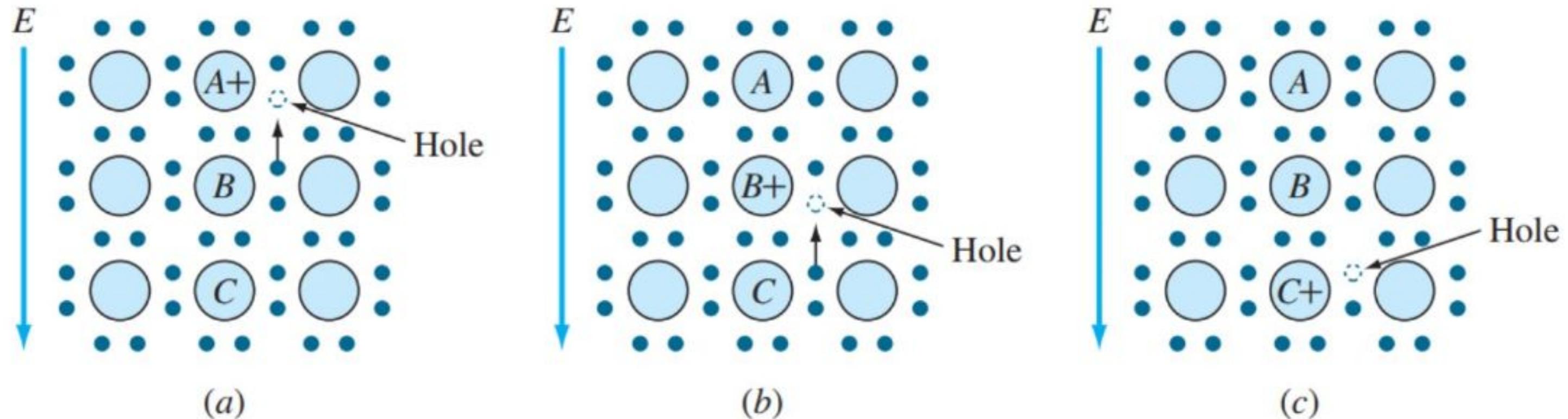
Two-dimensional representation of the diamond cubic lattice of silicon or germanium showing positive-ion cores and valence electrons.  
Electron has been excited from a bond at A and has moved to point B



Electrical conduction in a semiconductor such as silicon showing the migration of electrons and holes in an applied electric field

When a critical amount of energy is supplied to a valence electron to excite it away from its bonding position, it becomes a free conduction electron and leaves behind a positively charged “hole” in the crystal lattice

## Electrical Charge Transport in the Crystal Lattice of Pure Silicon



Schematic illustration of the movement of holes and electrons in a pure silicon semiconductor during electrical conduction caused by the action of an applied electric field.

## Quantitative Relationships for Electrical Conduction in Elemental Intrinsic Semiconductors

During electrical conduction in intrinsic semiconductors, the current density  $\mathbf{J}$  is equal to the sum of the conduction due to *both* electrons and holes. Using Eq. 14.6,

$$\mathbf{J} = nq \mathbf{v}_n^* + pq \mathbf{v}_p^* \quad (14.9)$$

where  $n$  = number of conduction electrons per unit volume

$p$  = number of conduction holes per unit volume

$q$  = absolute value of electron or hole charge,  $1.60 \times 10^{-19} \text{ C}$

$\mathbf{v}_n, \mathbf{v}_p$  = drift velocities of electrons and holes, respectively.

Dividing both sides of Eq. 14.9 by the electric field  $\mathbf{E}$  and using Eq. 14.4,  $\mathbf{J} = \sigma \mathbf{E}$ ,

$$\sigma = \frac{\mathbf{J}}{\mathbf{E}} = \frac{nq \mathbf{v}_n}{\mathbf{E}} + \frac{pq \mathbf{v}_p}{\mathbf{E}} \quad (14.10)$$

The quantities  $\mathbf{v}_n/\mathbf{E}$  and  $\mathbf{v}_p/\mathbf{E}$  are called the *electron* and *hole mobilities*, respectively, since they measure how fast the electrons and holes in semiconductors drift in an applied electric field. The symbols  $\mu_n$  and  $\mu_p$  are used for the mobilities of electrons

and holes, respectively. Substituting electron and hole mobilities for  $\nu_n/E$  and  $\nu_p/E$  in Eq. 14.10 enables the electrical conductivity of a semiconductor to be expressed as

$$\sigma = nq\mu_n + pq\mu_p \quad (14.11)$$

The units for mobility  $\mu$  are

$$\frac{\nu}{E} = \frac{\text{m/s}}{\text{V/m}} = \frac{\text{m}^2}{\text{V} \cdot \text{s}}$$

In intrinsic elemental semiconductors, electrons and holes are created in pairs; thus, the number of conduction electrons equals the number of holes produced, so that

$$n = p = n_i \quad (14.12)$$

where  $n$  = intrinsic carrier concentration, carriers/unit volume.

Equation 14.11 now becomes

$$\sigma = n_i q (\mu_n + \mu_p) \quad (14.13)$$

Table 14.4 lists some of the important properties of intrinsic silicon and germanium at 300 K.

The mobilities of electrons are always greater than those of holes. For intrinsic silicon the electron mobility of  $0.135 \text{ m}^2/(\text{V} \cdot \text{s})$  is 2.81 times greater than the hole mobility of  $0.048 \text{ m}^2/(\text{V} \cdot \text{s})$  at 300 K (Table 14.4). The ratio of electron-to-hole mobility for intrinsic germanium is 2.05 at 300 K.

**Table 14.4** Some physical properties of silicon and germanium at 300 K

	<b>Silicon</b>	<b>Germanium</b>
Energy gap, eV	1.1	0.67
Electron mobility $\mu_n$ , $\text{m}^2/(\text{V} \cdot \text{s})$	0.135	0.39
Hole mobility $\mu_p$ , $\text{m}^2/(\text{V} \cdot \text{s})$	0.048	0.19
Intrinsic carrier density $n_i$ , carriers/ $\text{m}^3$	$1.5 \times 10^{16}$	$2.4 \times 10^{19}$
Intrinsic resistivity $\rho$ , $\Omega \cdot \text{m}$	2300	0.46
Density, $\text{g}/\text{m}^3$	$2.33 \times 10^6$	$5.32 \times 10^6$

## Effect of Temperature on Intrinsic Semiconductivity

In contrast to metals, whose conductivities decrease with increasing temperatures, the conductivities of semiconductors *increase* with increasing temperatures for the temperature range over which this process predominates

$$n_i \propto e^{-(E_g - E_{av})/kT} \quad (14.14)$$

where  $E_g$  = band energy gap

$E_{av}$  = average energy across band gap

$k$  = Boltzmann's constant

$T$  = temperature, K

For intrinsic semiconductors such as pure silicon and germanium,  $E_{av}$  is halfway across the gap, or  $E_g/2$ . Thus Eq. 14.14 becomes

$$n_i \propto e^{-(E_g - E_g/2)/kT} \quad (14.15a)$$

or

$$n_i \propto e^{-E_g/2kT} \quad (14.15b)$$

Since the electrical conductivity  $\sigma$  of an intrinsic semiconductor is proportional to the concentration of electrical charge carriers,  $n_i$ , Eq. 14.15b can be expressed as

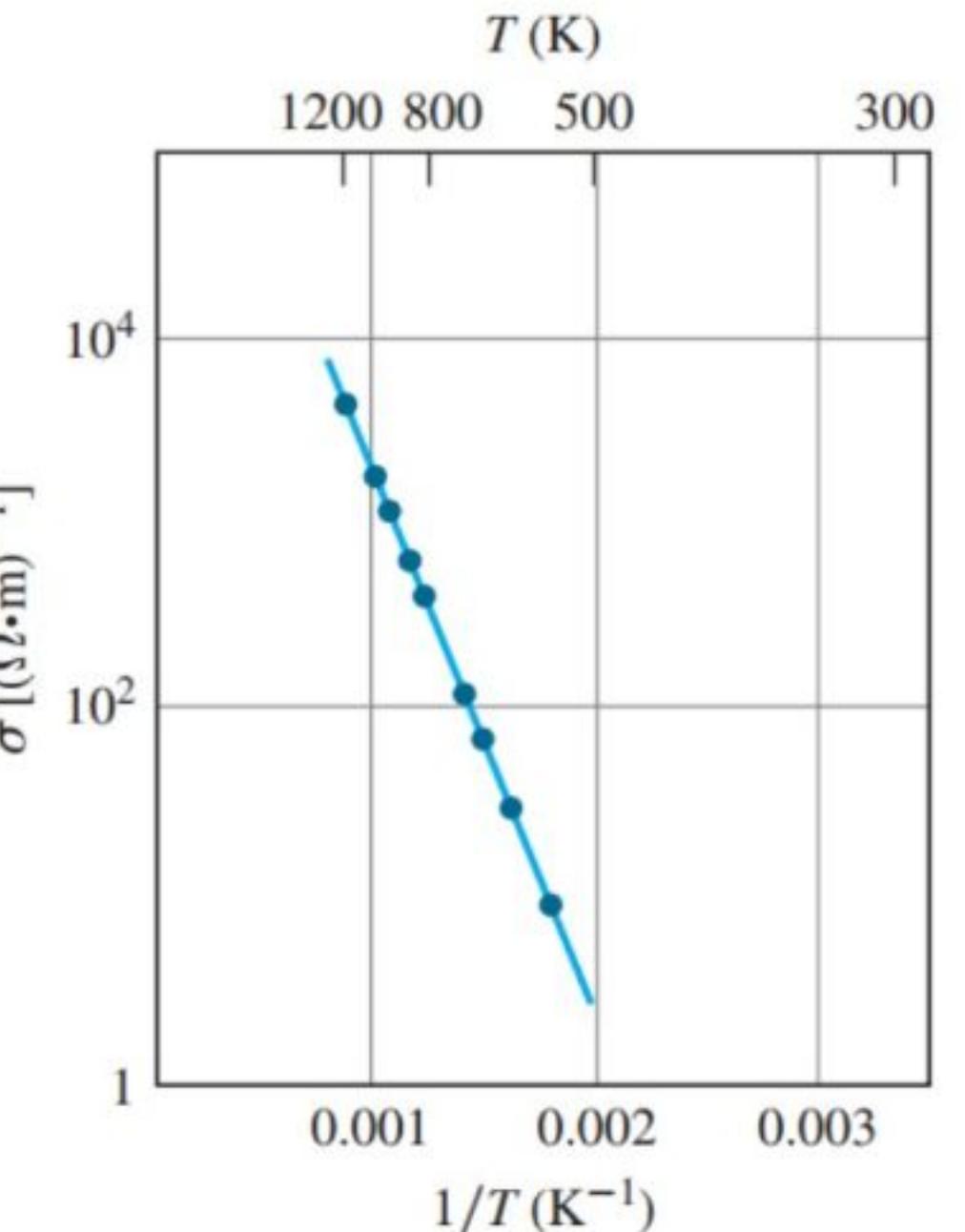
$$\sigma = \sigma_0 e^{-E_g/2kT} \quad (14.16a)$$

or in natural logarithmic form,

$$\ln \sigma = \ln \sigma_0 - \frac{E_g}{2kT} \quad (14.16b)$$

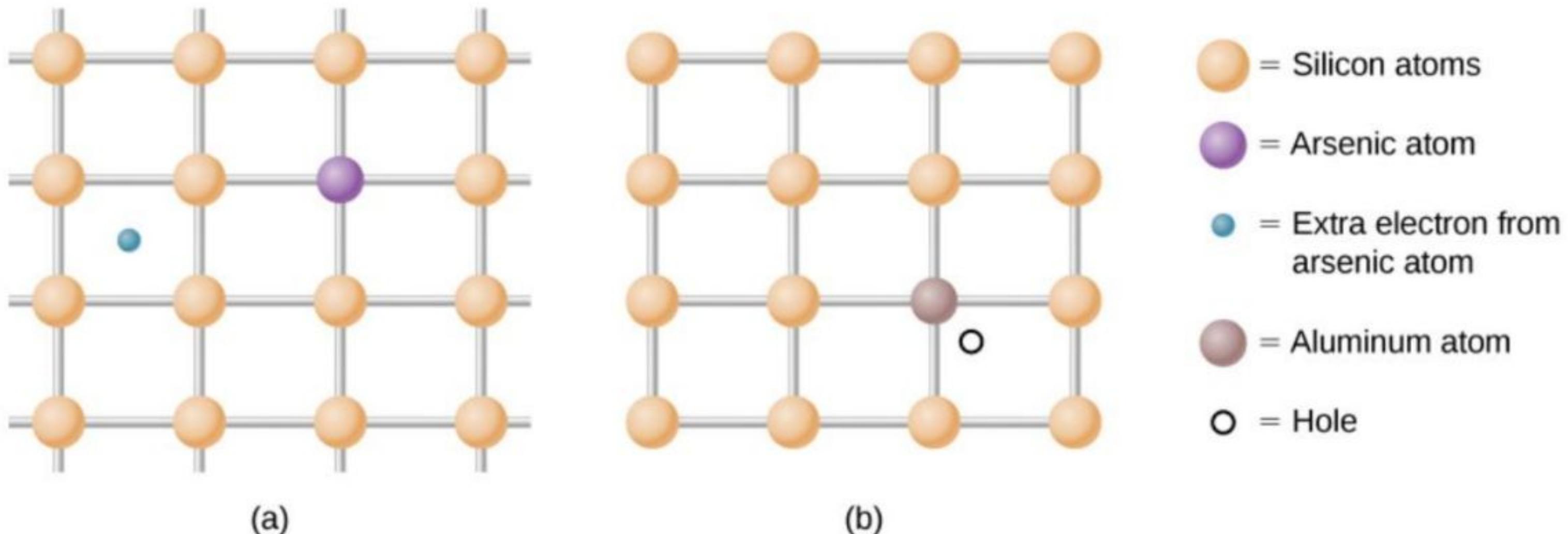
where  $\sigma_0$  is an overall constant that depends mainly on the mobilities of electrons and holes. The slight temperature dependence of  $\sigma_0$  on temperature will be neglected in this text.

Since Eq. 14.16b is the equation of a straight line, the value of  $E_g/2k$  and hence  $E_g$  can be determined from the slope of the plot of  $\ln \sigma$  versus  $1/T$ ,  $K^{-1}$ . Figure 14.20 shows an experimental plot of  $\ln \sigma$  versus  $1/T$ ,  $K^{-1}$  for intrinsic silicon.



Electrical conductivity as a function  
of reciprocal absolute temperature  
for intrinsic silicon.

Arsenic has **five** valence electrons.  
Silicon has **four** valence electron.



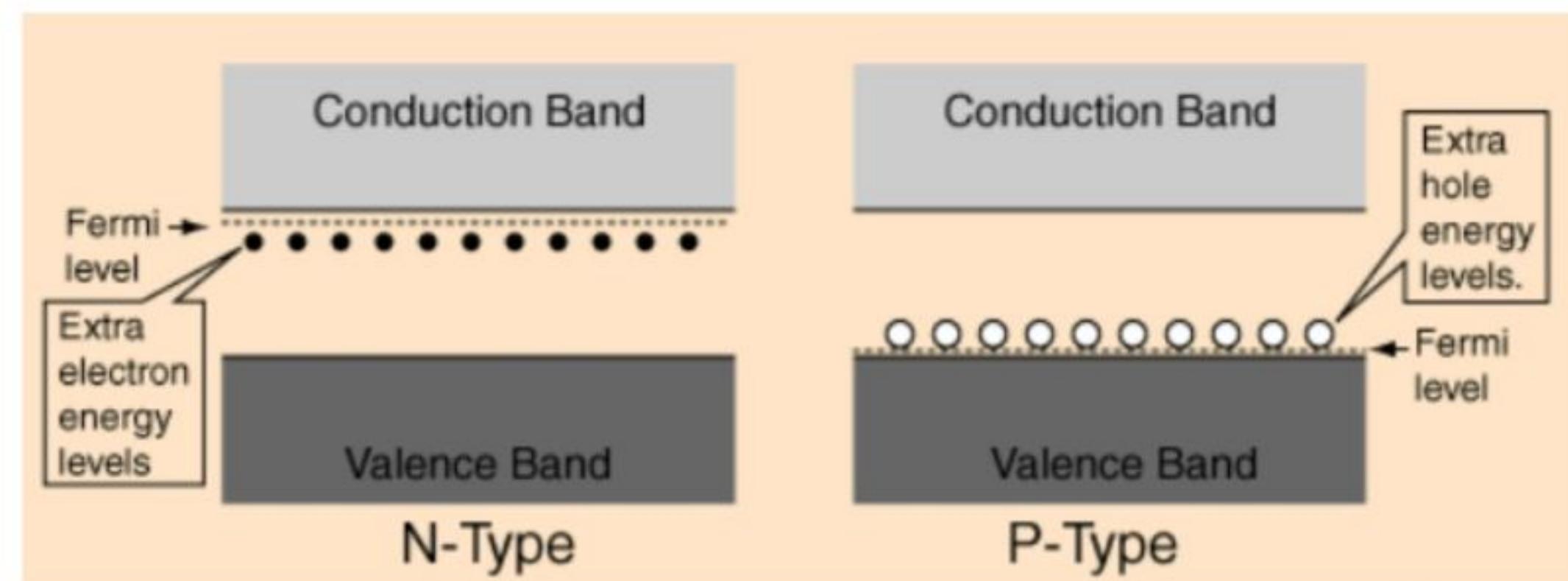
**Fig. (a)** A donor impurity and **(b)** an acceptor impurity.

The introduction to impurities and acceptors into a semiconductor significantly changes the electronic properties of this material.

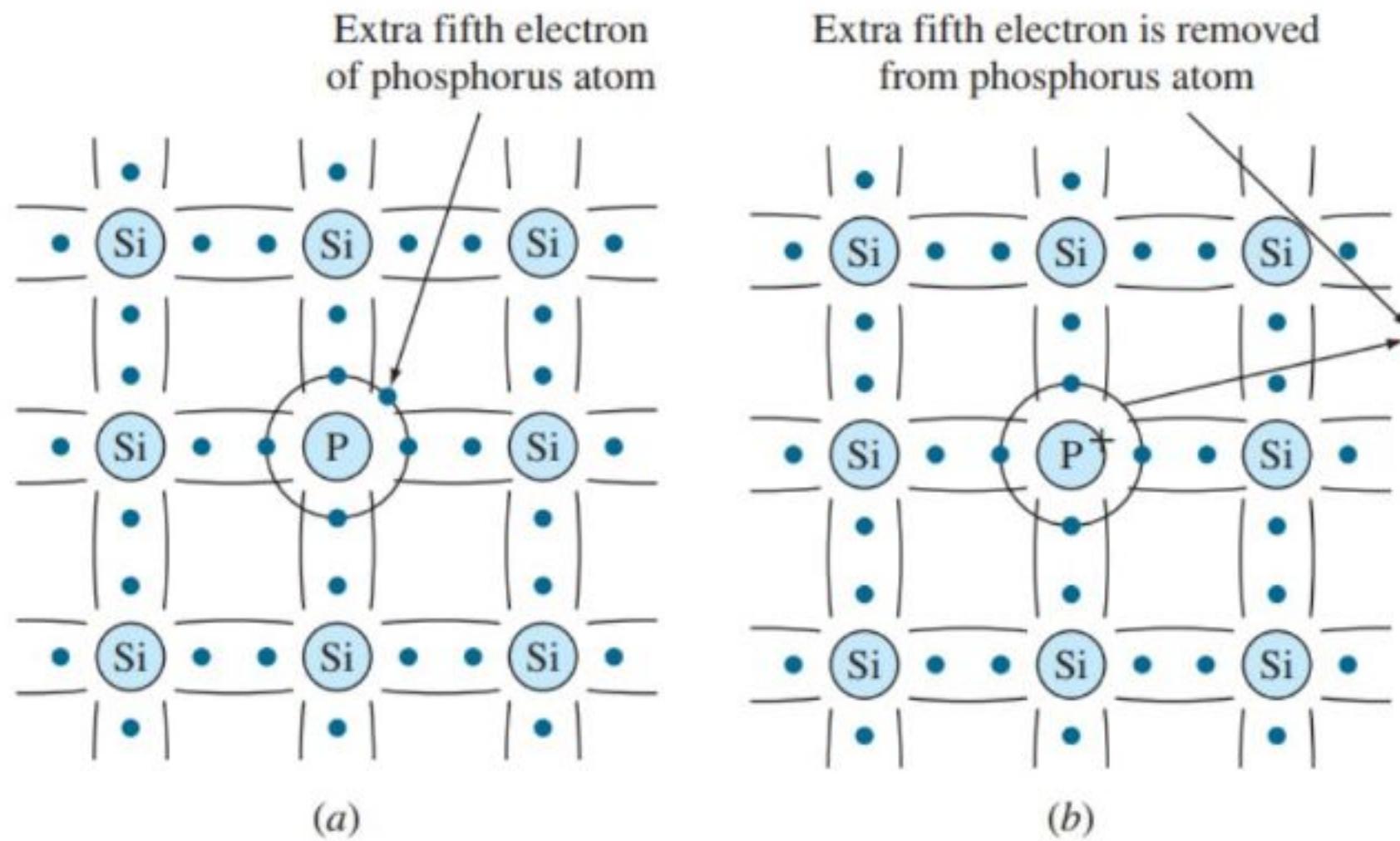
## EXTRINSIC SEMICONDUCTORS

### Bands for Doped Semiconductors

- The application of band theory to n-type and p-type semiconductors shows that **extra levels have been added by the impurities**.
- In **n-type material** there are **electron energy levels near the top of the band gap** so that they can be easily excited into the conduction band.
- In p-type material, **extra holes in the band gap** allow excitation of valence band electrons, leaving mobile holes in the valence band.



## n-Type (Negative-Type) Extrinsic Semiconductors



- (a) The addition of a pentavalent phosphorus impurity atom to the tetravalent silicon lattice provides a fifth electron that is weakly attached to the parent phosphorus atom. Only a small amount of energy (0.044 eV) makes this electron mobile and conductive.
- (b) Under an applied electric field the excess electron becomes conductive and is attracted to the positive terminal of the electrical circuit. With the loss of the extra electron, the phosphorus atom is ionized and acquires a + 1 charge.

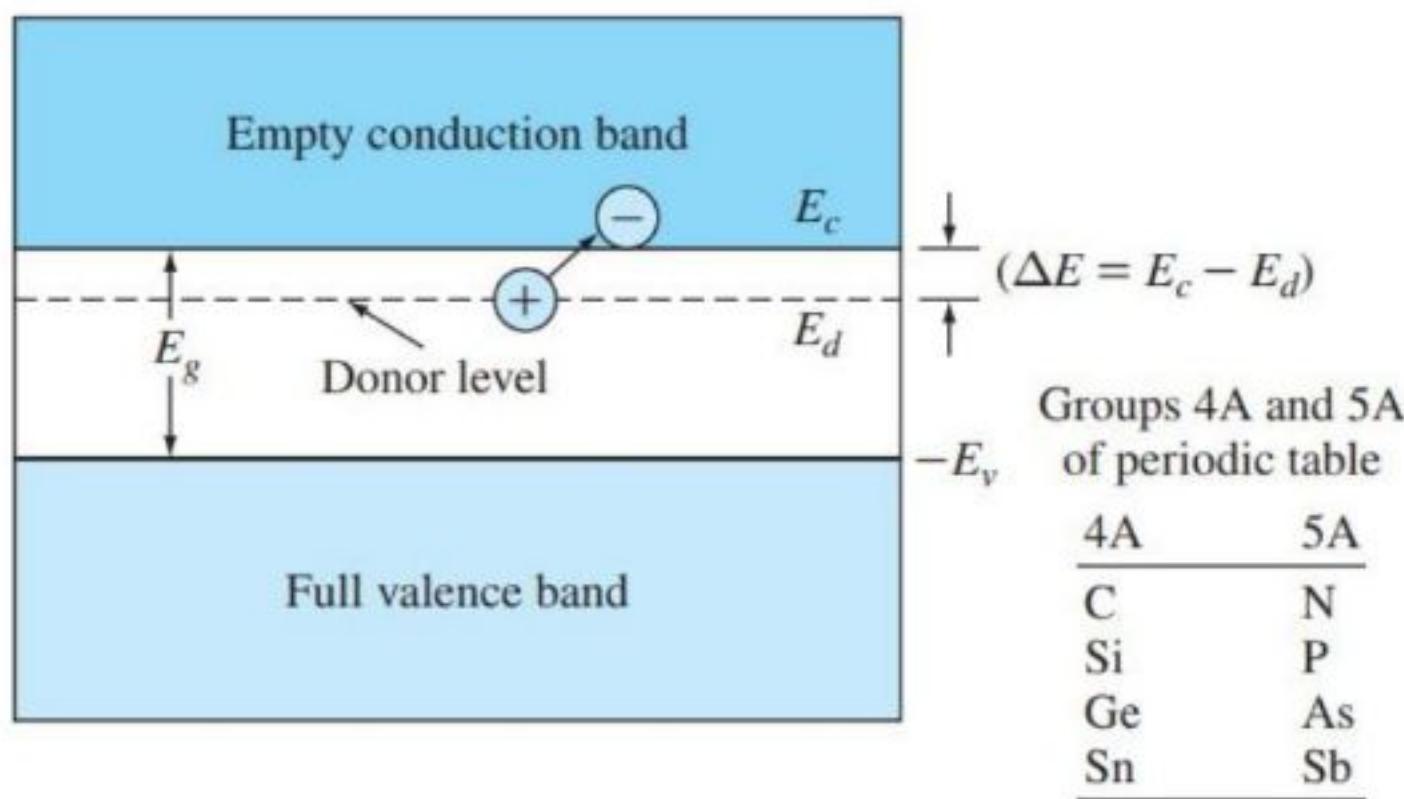
# Periodic Table of the Elements

The figure is a detailed periodic table of elements. At the top center, element 1 (Hydrogen) is highlighted with a green background, showing its atomic number (1), symbol (H), name (Hydrogen), atomic weight (1.008), state of matter (gas), and subcategory (alkaline metal). A legend below it defines the color coding for other elements: red for Alkaline metals, blue for Lanthanides, light blue for Transition metals, orange for Alkaline earth metals, teal for Actinides, yellow for Metalloids, green for Polyatomic nonmetals, purple for Diatomic nonmetals, pink for Noble gases, and grey for Unknown chemical properties. The main body of the table lists elements from Hydrogen to Oganesson, arranged by group and period, with each element's atomic number, symbol, name, atomic weight, state of matter, and subcategory listed.

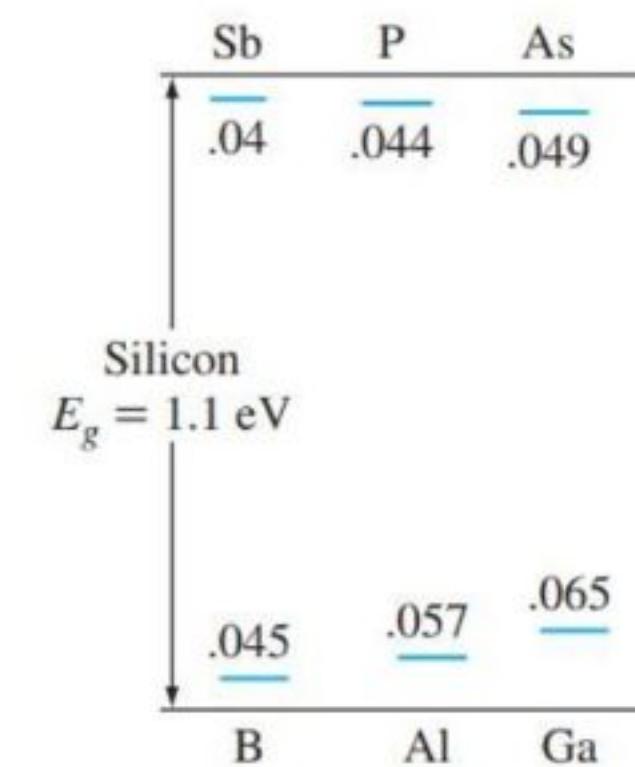
<b>57</b> <b>La</b> Lanthanum 108.90447	<b>58</b> <b>Ce</b> Cerium 140.119	<b>59</b> <b>Pr</b> Praseodymium 140.90765	<b>60</b> <b>Nd</b> Neodymium 144.242	<b>61</b> <b>Pm</b> Promethium (145)	<b>62</b> <b>Sm</b> Samarium 150.90384	<b>63</b> <b>Eu</b> Europium 151.90644	<b>64</b> <b>Gd</b> Gadolinium 157.90518	<b>65</b> <b>Tb</b> Terbium 158.90518	<b>66</b> <b>Dy</b> Dysprosium 161.90518	<b>67</b> <b>Ho</b> Holmium 164.90525	<b>68</b> <b>Er</b> Erbium 167.90525	<b>69</b> <b>Tm</b> Thulium 168.90542	<b>70</b> <b>Yb</b> Ytterbium 175.90542	<b>71</b> <b>Lu</b> Lutetium 174.90590
<b>89</b> <b>Ac</b> Actinium 227	<b>90</b> <b>Th</b> Thorium 232.0377	<b>91</b> <b>Pa</b> Protactinium 231.03698	<b>92</b> <b>U</b> Uranium 238.02891	<b>93</b> <b>Np</b> Neptunium (237)	<b>94</b> <b>Pu</b> Plutonium (239)	<b>95</b> <b>Am</b> Americium (240)	<b>96</b> <b>Cm</b> Curium (240)	<b>97</b> <b>Bk</b> Berkelium (241)	<b>98</b> <b>Cf</b> Californium (249)	<b>99</b> <b>Es</b> Einsteinium (252)	<b>100</b> <b>Fm</b> Fermium (257)	<b>101</b> <b>Md</b> Mendelevium (258)	<b>102</b> <b>No</b> Neptunium (259)	<b>103</b> <b>Lr</b> Lawrencium (260)

Group VA impurity atoms such as P, As, and Sb when added to silicon or germanium provide easily ionized electrons for electrical conduction.

Since these group VA impurity atoms donate conduction electrons when present in silicon or germanium crystals, they are called *donor impurity atoms*. Silicon or germanium semiconductors containing group V impurity atoms are called **n-type (negative-type) extrinsic semiconductors** since the majority charge carriers are elect



Electrons at the donor energy level require only a small amount of energy ( $\Delta E = E_c - E_d$ ) to be excited into the conduction band. When the extra electron at the donor level jumps to the conduction band, a positive immobile ion is left behind.

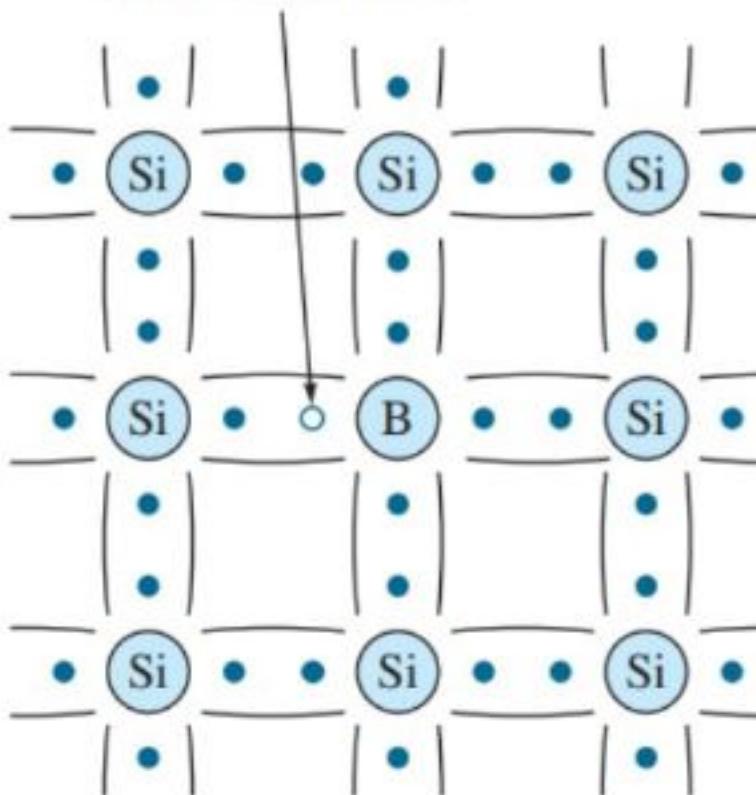


Ionization energies (in electron volts) for various impurities in silicon.

## p-Type (Positive-Type) Extrinsic Semiconductors

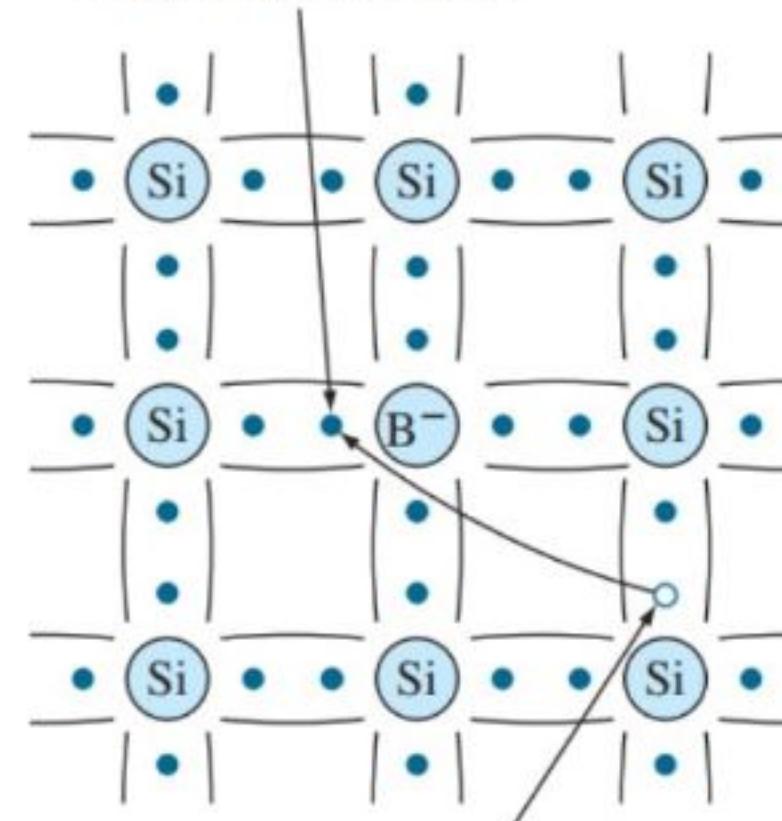
When a trivalent group IIIA element such as boron (B) is substitutionally introduced in the silicon tetrahedrally bonded lattice, one of the bonding orbitals is missing, and a hole exists in the bonding structure of the silicon

Fourth bonding electron of  
boron atom is missing  
and creates a hole

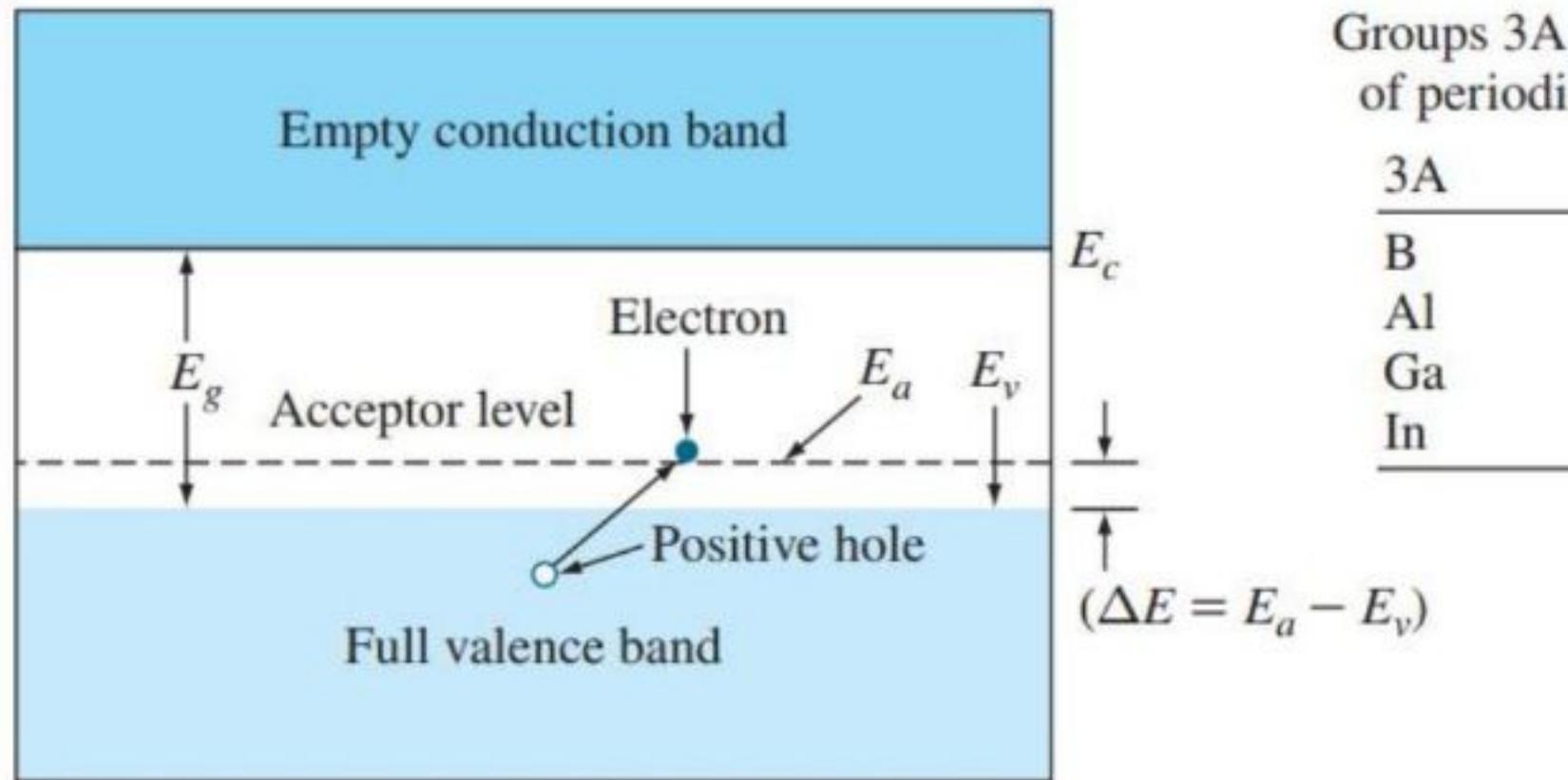


(a)

Electron is attracted from  
a silicon atom to fill hole  
in boron-silicon bond



(b)



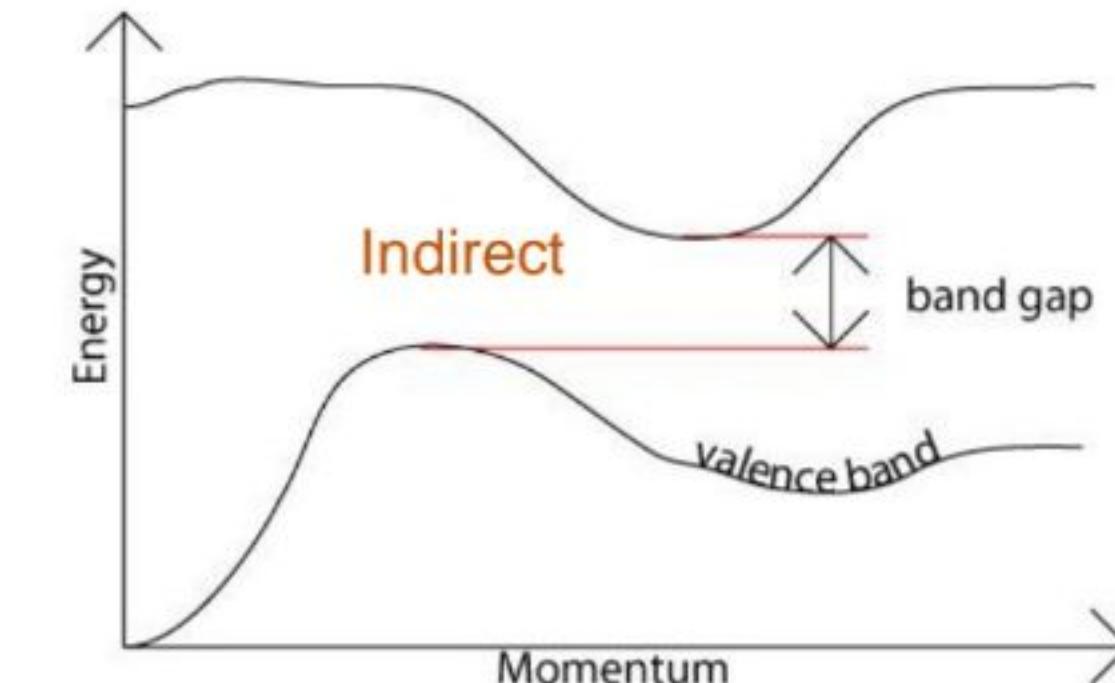
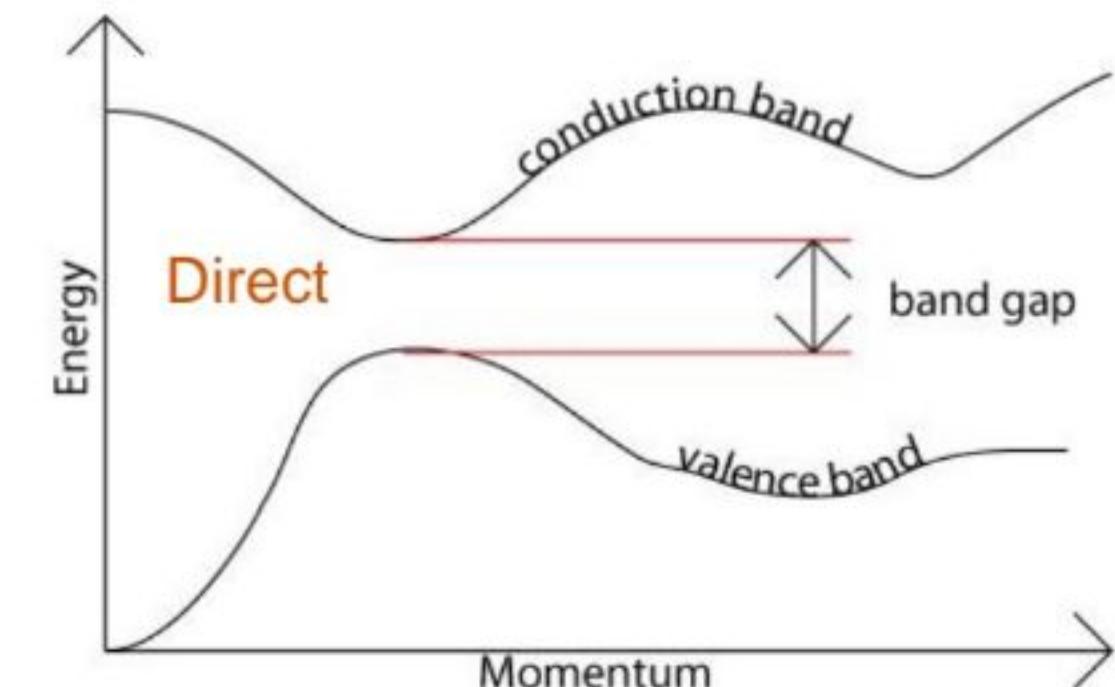
Groups 3A and 4A  
of periodic table

3A	4A
B	C
Al	Si
Ga	Ge
In	Sn

Only a small amount of energy ( $\Delta E = E_a - E_v$ ) is necessary to excite an electron from the valence band to the acceptor level, thereby creating an electron hole (charge carrier) in the valence band.

## Direct and Indirect Band Gap Semiconductors

- A photon of energy  $E_g$ , where  $E_g$  is the band gap energy, can produce an electron-hole pair in a direct band gap semiconductor quite easily, because the electron does not need to be given very much momentum.
- However, an electron must also undergo a significant change in its momentum for a photon of energy  $E_g$  to produce an electron-hole pair in an indirect band gap semiconductor.
- This is possible, but it requires such an electron to interact not only with the photon to gain energy, but also with a lattice vibration called a phonon in order to either gain or lose momentum.
- The indirect process proceeds at a much slower rate, as it requires three entities to intersect in order to proceed: an electron, a photon and a phonon.
- Analogy to chemical reactions, where, in a particular reaction step, a reaction between two molecules will proceed at a much greater rate than a process which involves three molecules.



## Doping of Extrinsic Silicon Semiconductor Material

- The most commonly used method of doping silicon semiconductors is the *planar process*.
- In this process, dopant atoms are introduced into selected areas of the silicon from one surface in order to form regions of p- or n-type material.
- The wafers are usually about 4 in. (10 cm) in diameter and about a few hundred micrometers thick.
- In the diffusion process for doping silicon wafers, the dopant atoms are typically deposited on or near the surface of the wafer by a gaseous deposition step, followed by a drive-in diffusion that moves the dopant atoms farther into the wafer.
- A high temperature of about 1100°C is required for this diffusion process.

## Effect of Doping on Carrier Concentrations in Extrinsic Semiconductors

### The Mass Action Law

- In semiconductors such as silicon and germanium, mobile electrons and holes are constantly being generated and recombined. At constant temperature under equilibrium conditions the product of the negative free electron and positive hole concentrations is a constant.

The general relation is

$$np = (n_i)^2$$

where  $n$  is the intrinsic concentration of carriers in a semiconductor and is a constant at a given temperature.

This relation is valid for both intrinsic and extrinsic semiconductors.

- In an extrinsic semiconductor the increase in one type of carrier (n or p) reduces the concentration of the other through recombination so that the product of the two (n and p) is a constant at any given temperature.
- The carriers whose concentration in extrinsic semiconductors is the larger are designated the **majority carriers**, and those whose concentration is the smaller are called the **minority carriers**.
- The concentration of electrons in an n-type semiconductor is denoted by  $n_n$  and that of holes in n-type material by  $p_n$ .
- Similarly, the concentration of holes in a p-type semiconductor is given by  $p_p$  and that of electrons in p-type material by  $n_p$ .

Semiconductor	Majority-Carrier Concentrations	Minority-Carrier Concentrations
n-type	$n_n$ (concentration of electrons in n-type material)	$P_n$ (concentration of holes in n-type material)
p-type	$P_p$ (concentration of holes in p-type material)	$n_p$ (concentration of electrons in p-type material)

## Charge Densities in Extrinsic Semiconductors

- A second fundamental relationship for extrinsic semiconductors is obtained from the fact that the total crystal must be electrically neutral. This means that the charge density in each volume element must
- The concentration of the positive donor ions is denoted by  $N_d$  and that of the negative acceptor ions by  $N_a$ .
- The mobile charge carriers originate mainly from the ionization of the impurity atoms in the Si or Ge, and their concentrations are designated by  $n$  for the negatively charged electrons and  $p$  for the positively charged holes.

Since the semiconductor must be electrically neutral, the magnitude of the total negative charge density must equal the total positive charge density. The total negative charge density is equal to the sum of the negative acceptor ions  $N_a$  and the electrons, or  $N_a + n$ . The total positive charge density is equal to the sum of the positive donor ions  $N_d$  and the holes, or  $N_d + p$ . Thus,

$$N_a + n = N_d + p \quad (14.18)$$

In an n-type semiconductor created by adding donor impurity atoms to intrinsic silicon,  $N_a = 0$ . Since the number of electrons is much greater than the number of holes in an n-type semiconductor (that is,  $n \gg p$ ), then Eq. 14.18 reduces to

$$n_n \approx N_d \quad (14.19)$$

Thus, in an n-type semiconductor the free-electron concentration is approximately equal to the concentration of donor atoms. The concentration of holes in an n-type semiconductor is obtained from Eq. 14.17. Thus,

$$p_n = \frac{n_i^2}{n_n} \approx \frac{n_i^2}{N_d} \quad (14.20)$$

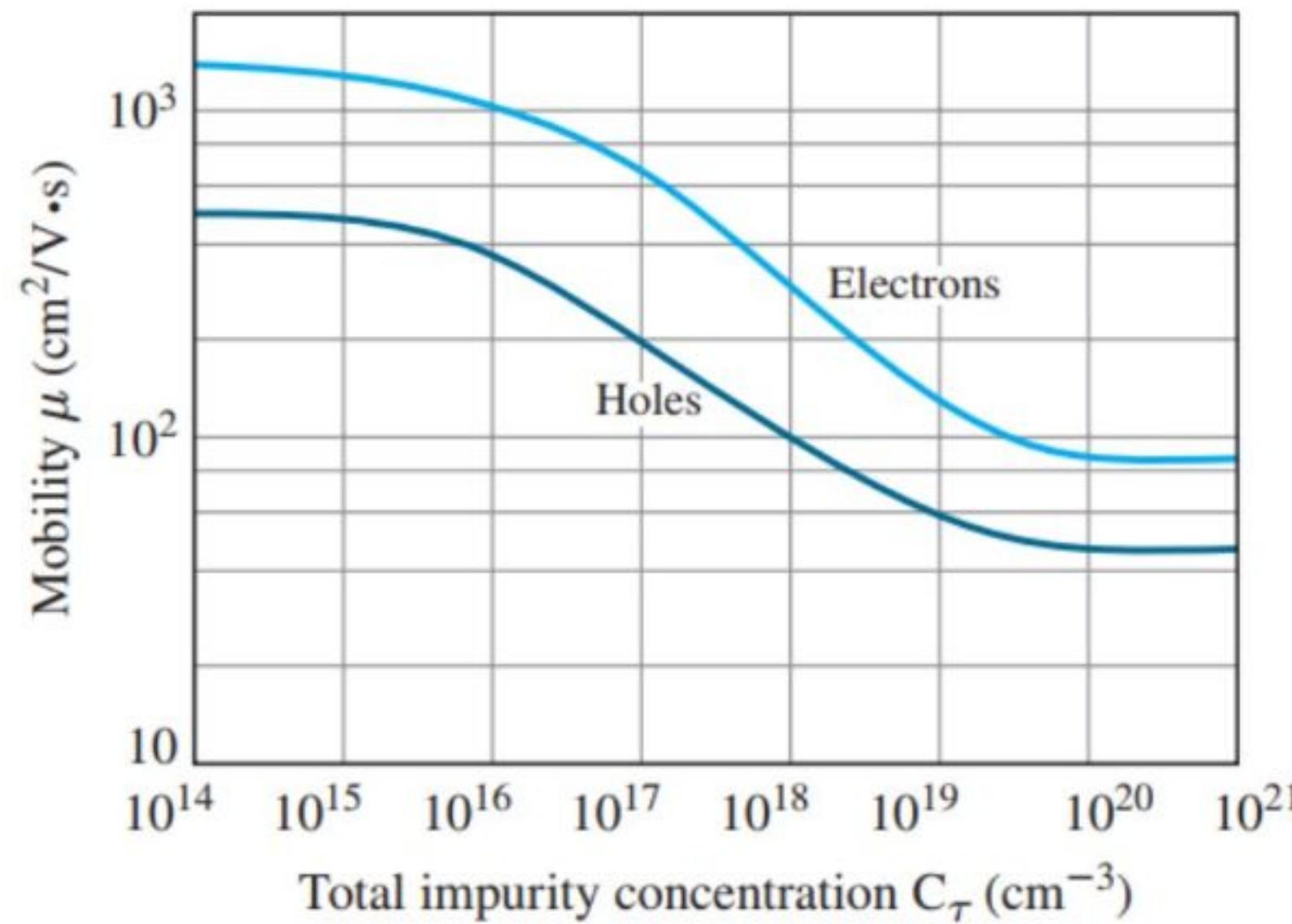
The corresponding equations for p-type semiconductors of silicon and germanium are

$$p_p \approx N_a \quad (14.21)$$

and

$$n_p = \frac{n_i^2}{p_p} \approx \frac{n_i^2}{N_a} \quad (14.22)$$

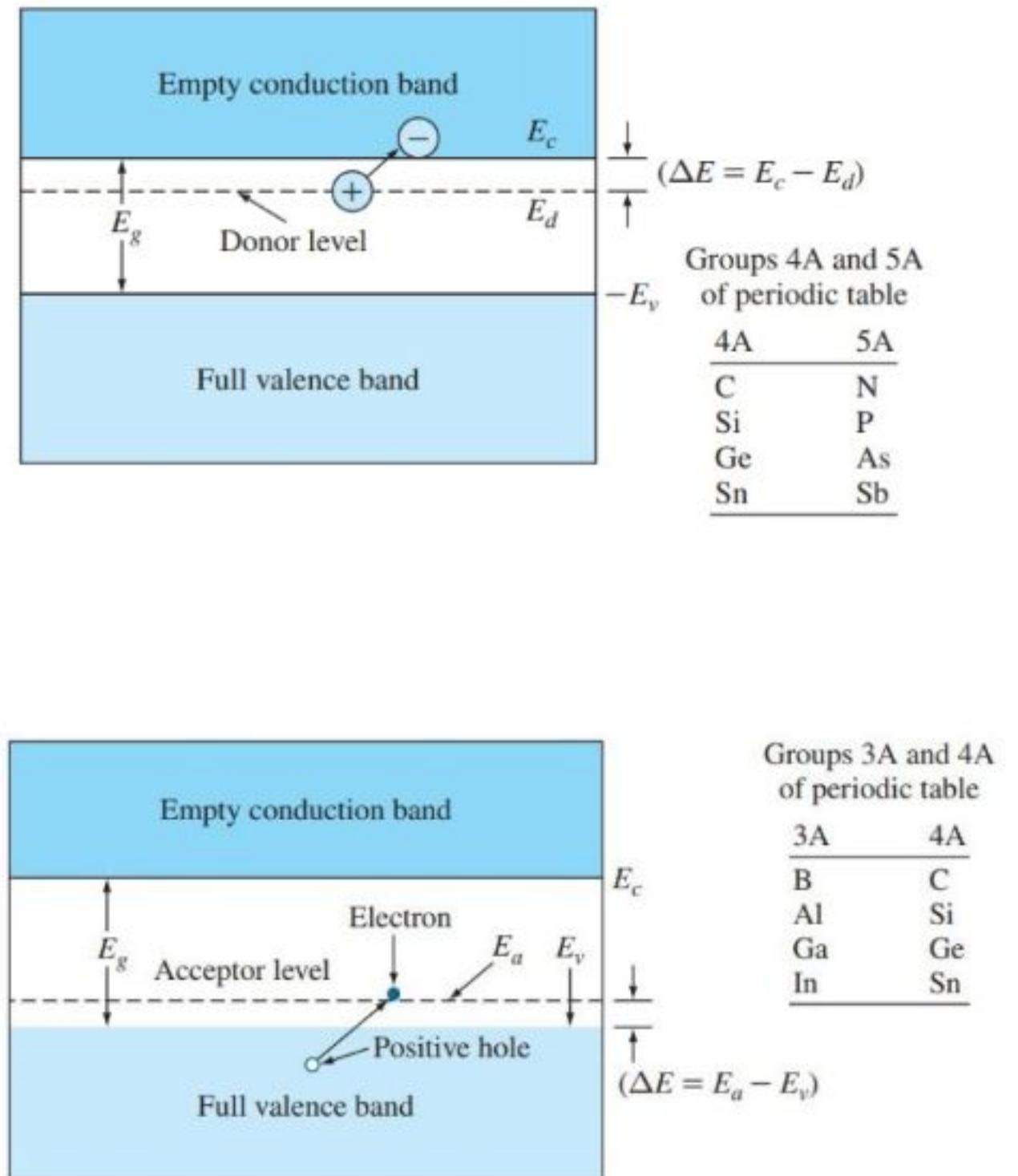
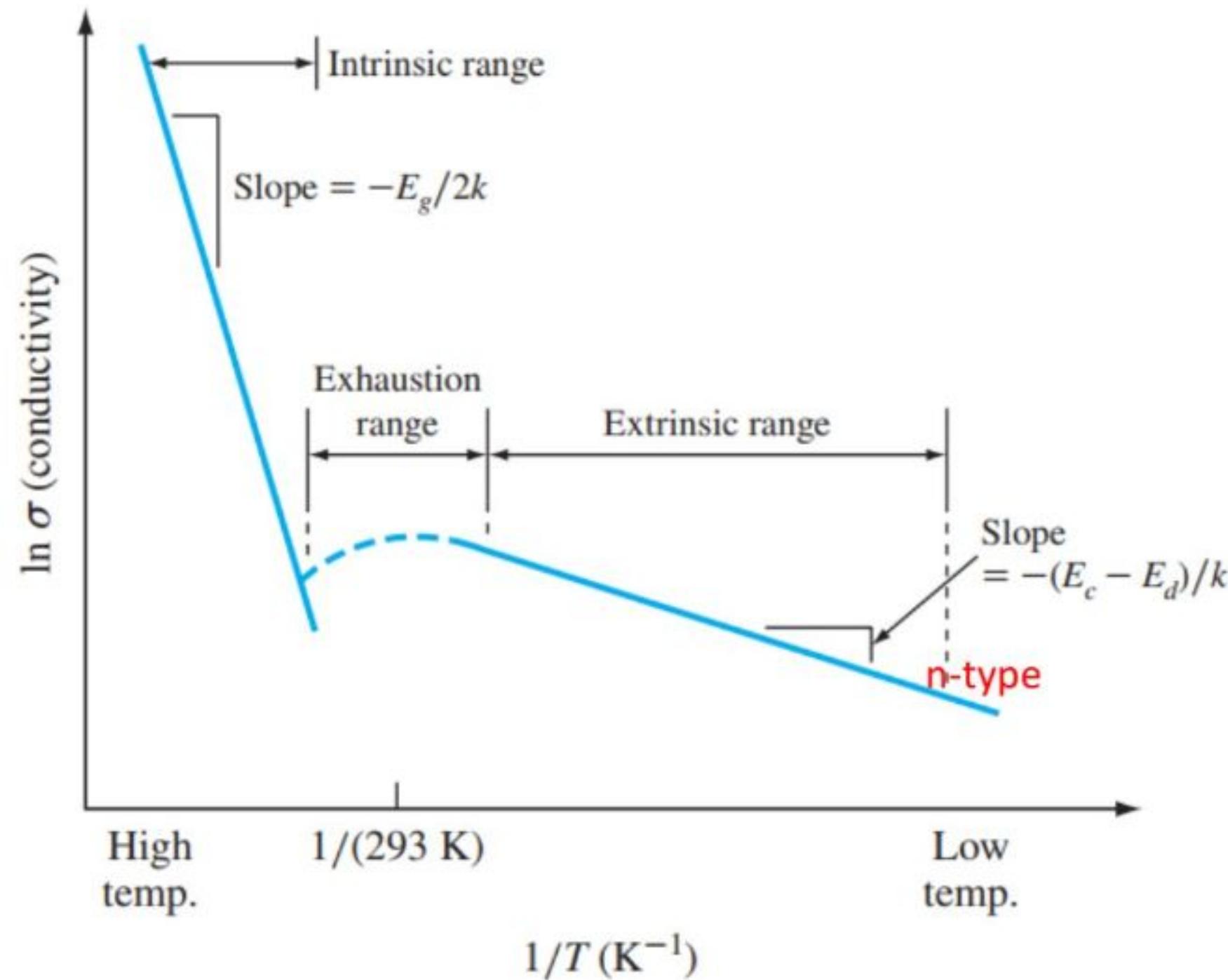
## Effect of Total Ionized Impurity Concentration on the Mobility of Charge Carriers in Silicon at Room Temperature



The effect of total ionized impurity concentration on the mobility of charge carriers in silicon at room temperature.

## Effect of Temperature on the Electrical Conductivity of Extrinsic Semiconductors

- At lower temperatures, the number of impurity atoms per unit volume activated (ionized) determines the electrical conductivity of the silicon.
- As the temperature is increased, more and more impurity atoms are ionized, and thus the electrical conductivity of extrinsic silicon increases with increasing temperature in the extrinsic range.
- For a certain temperature range above that required for complete ionization, an increase in temperature does not substantially change the electrical conductivity of an extrinsic semiconductor. For an n-type semiconductor, this temperature range is referred to as the *exhaustion range* since donor atoms become completely ionized after the loss of their donor electrons .
- For p-type semiconductors, this range is referred to as the *saturation range* since acceptor atoms become completely ionized with acceptor electrons. To provide an exhaustion range at about room temperature (300 K), silicon doped with arsenic requires about  $10^{21}$  carriers/m<sup>3</sup>



Schematic plot of  $\ln \sigma$  (conductivity) versus  $1/T (K_1)$  for an n-type extrinsic semiconductor.