Figure 1.1(b) Schematics of arrangement of points in space

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1.2 A Brief Review of Bonding in Materials

Bonding in materials is a very important criterion and determines many of the physical properties of the materials. For basics of bonding, you can refer to any elementary materials science book (see bibliography) to get familiar with the fundamental aspects of bonding between atoms i.e. how to determine the equilibrium distance, bond energy and fundamental properties like young's modulus. Bonding in materials can be divided in two categories:

- Primary bonding
- Secondary bonding

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1.2.1 Primary Bonding

There are three types of primary bonding mechanisms: metallic, covalent and ionic bonding.

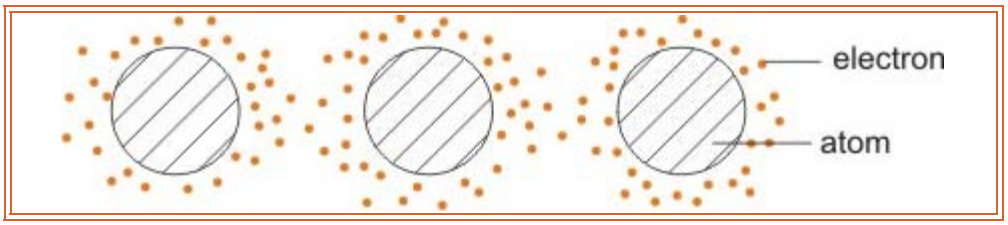


Figure 1.9 Metallic Bonding

1.2.1.1 Metallic bonding :

- This kind of bonding is characterized by presence of a sea of electrons around atoms in metal giving rise to flexible bonds, good malleability, high electrical and thermal conductivity. Most metals such as Ni, Fe, Cu, Au, Ag etc exhibit this kind of bonding.

1.2.1.2 Covalent Bonding:

- In this bonding, atoms share their outer shell unpaired electrons leading to a stronger and directional bonding.

- Examples of materials showing this bonding are mainly group IV elements and compounds such as Si, C, Ge, and SiC and gases like methane.

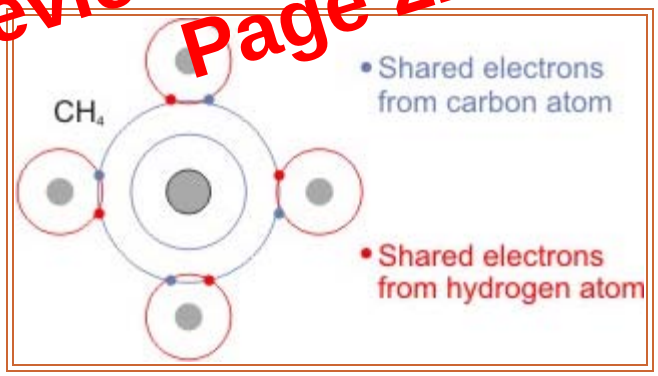
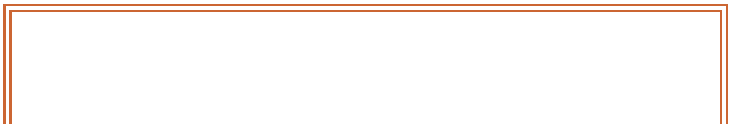


Figure 1.10 Schematic of covalent bonding

1.2.1.3 Ionic Bonding :

- This bonding occurs due to large differences in the electronegativities of two elements, for example in NaCl, MgO etc.

- This type of bonding typically leads to high bond energies, high bond strength, high modulus, brittle nature, generally low thermal and electrical conductivities making them excellent insulators.



- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(AB)O_4$.
- Most ferrite follow this structure such as Fe_3O_4 (or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.
- In this structure, ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+} ions occupy the octahedral sites (now you can hopefully make sense of the formula in the previous line).

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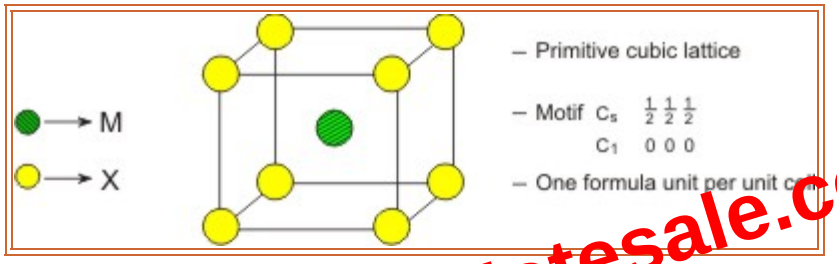
1.8.3 CsCl Structure

- MX type compounds, parent compound being CsCl.
- Examples: Halides such as CSCl, AgI, AgBr etc.
- Radius ratio governs cubic co-ordination of both cations and anions.
- Lattice type: Primitive cubic lattice.
- Motif: Anions (X): 0 0 0, Cations (M): ½ ½ ½
- One formula unit per unit cell.



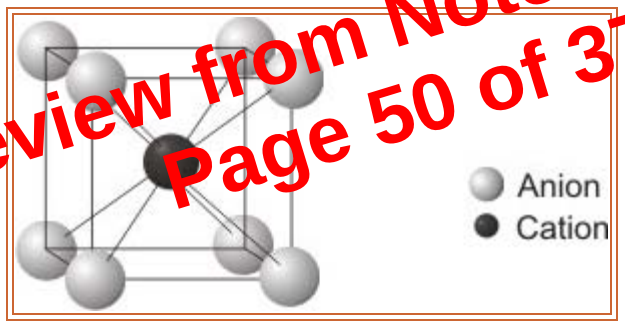


Figure 1.34 (a) CsCl structure (b) Ball-stick model

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1.10.1 Wurtzite (MX) structured compounds

- Compounds with $M^{2+}X^{2-}$ stoichiometry
- Examples are the polymorphs of Sphalerite structured compounds such as ZnS ZnO, SiC.
- Co-ordination of both anions and cations is 4, as in Sphalerite structured compounds.
- Anions form an HCP lattice with ½ of the tetrahedral sites occupied by cations.
    - The only difference to Sphalerite structure is that here anions pack in the form of ABCABC… stacking.

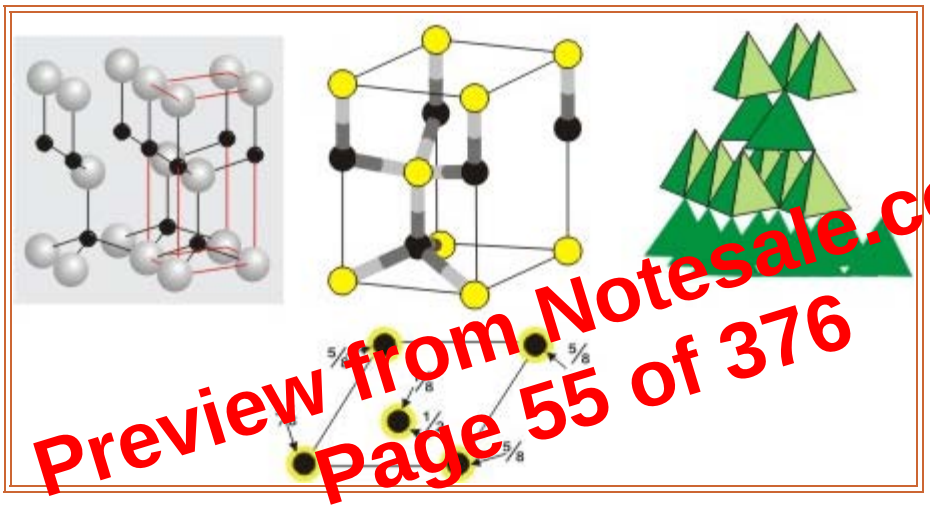

Figure 1.38 Wurtzite structure and polyhedral model

- As you can notice, all the tetrahedrons point in one direction i.e. along the c-axis of the unit-cell and they share the corners.
- Lattice type: Primitive, HCP
- Motif: M: 0 0 0 and ; X: and
- The filling of structure can be seen below.

Figure 1.39 Layer by layer filling in Wurtzite

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Module 2: Defect Chemistry

Defect Structures in Non-Stoichiometric Oxides

2.5.1 Oxygen Deficient Oxides

- Formation of oxygen vacancies or metal interstitials or both are possible.
- Formation occurs only at the surface.

2.5.1.1 If oxygen vacancies are the dominating defects

- Depicted by MO_{2-x} (x is the extent of non-stoichiometry) and overall reaction as

$$MO_2 \rightleftharpoons MO_{2-x} + {}^{x}/_{2}\, O_2\uparrow$$

- Due to loss of oxygen, possible defect reactions would be
  - Electronic compensation leading to creation oxygen vacancies and of electrons

$$O_0 \rightleftharpoons V_O^{\bullet\bullet} + \tfrac{1}{2}\, O_2 + 2e'$$

  - Ionic compensation leads to formation of oxygen vacancies and reduction of metal ions on their sites.

$$O_0 \rightleftharpoons V_O^{\bullet\bullet} + \tfrac{1}{2}\, O_2 + 2M_M$$

2.5.1.2 If metal interstitials are the dominating defects then,

- Depicted as $(M_{1+y}O_2$ is the extent of non-stoichiometry)
- Possible defect reactions are
  - Ionic compensation leading to the formation of metal interstitials and reduction of metal ions on their sites

$$M_M \rightleftharpoons M_i^{\bullet\bullet\bullet\bullet} + 4\, M'_M \qquad \text{OR}$$

  - Electronic compensation leading to the formation of metal interstitials and free electrons

$$M \rightleftharpoons M_i^{\bullet\bullet\bullet\bullet} + 4e'$$

- Creation of quasi-free electrons (extra charge is represented as M')
- Conduction occurs due to transport of electrons
- Typically n-type conductors.
- Example: TiO_2, ZrO_2, CeO_2, Nb_2O_5

2.5.2 Metal Deficient Oxides

- Formation of either metal vacancies or oxygen interstitials (excess oxygen)
- Formation occurs typically at the surface.

The following cases are possible:

2.5.2.1 If metal deficiency is dominating defect then

- Depicted as metal deficient oxide $M_{1-y}O$ (*y* is the extent of non-stoichiometry)
- Possible defect reaction is that of electronic compensation.

$$\frac{1}{2}O_2 \rightleftharpoons O_O + V_M'' + 2\dot{h}$$

- Creation of holes
- Conduction due to holes i.e. a p- type conductor
- Examples of oxides showing this characteristics are MnO, NiO, CoO, FeO etc.

2.5.2.2 If metal deficiency is dominating defect then

- Oxides denoted as MO_{2+x}
- Oxygen interstitials can form due to following reaction

$$\frac{1}{2}O_2 \rightleftharpoons O_i'' + 2\dot{h}$$

- P-type conductor
- Example can be an oxide like UO_2.

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$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{2kT}\right).\exp\left(\frac{\Delta S_v}{2kT}\right)$$

Assuming that exp ($\Delta S_v/2kT$) ~1 as vibrational entropy change is very small, and hence

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{2kT}\right) \qquad (2.14)$$

Similarly, for Schottky defects, you can work out that

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_s}{2kT}\right) \qquad (2.15)$$

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$$K_F[M_M] = [M_i^{\bullet\bullet}][V_M'']$$

At reasonably low defect concentrations when

=

$[M_i^{\bullet\bullet}]$ and $[V_M'']$ << M_M and M_M~1

Thus

$$[M_i^{\bullet\bullet}][V_M'']=K_F \qquad (2.26)$$

If Frenkel defects dominate, then

$$[M_i^{\bullet\bullet}]=[V_M'']$$

i.e.

$$[M_i^{\bullet\bullet}]=[V_M'']=K_F^{1/2} \qquad (2.27)$$

In a similar manner what we did above for Schottky defects, one can now write

$$[M_i^{\bullet\bullet}]=[V_M'']= K_O^{1/2} \exp\left(-\frac{\Delta H_F}{2RT}\right) \qquad (2.28)$$

Again we can see that the defect is independent of pO_2.

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2.12.1.2 Case II: If interstitial metal or metal excess is present

Here, the defect reaction will be

$$M_M + O_O \rightleftharpoons M_i^{\bullet\bullet} + \frac{1}{2}O_2 \uparrow + 2\acute{e}$$

The equilibrium constant can be written as

$$K_S = \frac{\left[M_i^{\bullet\bullet}\right] pO_2^{1/2} . n_e^2}{[M_M]\,[O_O]} \qquad (2.34)$$

Both $[M_M]$ and $[O_O]$ can be assumed to be ~1 if $[M_i^{\bullet\bullet}] << [M_M]$ and $[O_O]$.

According to the electrical neutrality condition

$$n_e = 2[M_i^{\bullet\bullet}] \qquad (2.35)$$

Thus

$$\frac{1}{2}K = n_e^{\,3}\; pO_2^{\,1/2} \quad \text{OR}$$

$$n_e = \left(\frac{1}{2}K\right)^{1/3} pO_2^{-1/6} \qquad (2.36)$$

The plot will be similar to that of the above case.

2.12.2 Metal Deficient Oxides

Now we turn towards the case of MO type oxides with deficient of metal which can be reflected either by metal vacancies or oxygen interstitials or presence of both. Here we do analysis only for metal vacancies while other two cases can be done in a similar fashion as shown in previous paragraph.

For MO oxide, assuming complete ionization of vacancies, we can write

$$\frac{1}{2}O_2 \rightleftharpoons O_O + V_M'' + 2\dot{h}$$

whose equilibrium constant will be

$$K = \frac{[O_O][V_M''].n_h^{\,2}}{(pO_2)^{1/2}} \qquad (2.45)$$

If $[O_O] = 1$ and $[V_M^{\cdot\cdot}] << [O_O]$ then

$$K = [V_M''] \, n_h^{\,2}.pO_2^{\,-1/2} \qquad (2.46)$$

According to the electrical neutrality condition

$$n_h = 2[V_M''] \qquad (2.47)$$

Again, the concentration of defects is proportional to $pO_2^{1/6}$.

One can do similar exercise for the cases when oxygen interstitial is the main defect and also when there is mixed presence of metal vacancies and oxygen interstitials. This is left to the readers to perform themselves.

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and corresponding reaction constant is

$$K_i = n_e . n_h \qquad (2.52)$$

- Similarly formation of oxygen Frenkel defects (Anti-) leads to

$$O_O \rightleftharpoons O_i'' + V_O^{\bullet\bullet}$$

with reaction constant as

$$K_F = [O_i''] . [V_O^{\bullet\bullet}] \qquad (2.53)$$

- From the above four relations, we can write

$$K_F . K_i^{\,2} = K_{V_O^{\bullet\bullet}} K_{O_i''} \qquad (2.54)$$

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2.13.1 Limiting Conditions

Now we need to determine the limiting condition for determining the boundaries of pO_2 across which various defect concentrations can be plotted as a function of oxygen partial pressure. These three regions are regions of

- Low pO_2,
- Intermediate pO_2, and
- High pO_2

These regions depict oxygen deficit (or metal excess), stoichiometric composition and oxygen excess (or metal deficiency) respectively. Following sections eluciate the process for determining these boundaries for a metal oxide with either of oxygen deficit, stoichiometric composition and oxygen excess for an oxide considering anti-Frenkel defects.

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2.19.3 Electronic vs Ionic Compensation of Solutes

Here we will discuss which of the electronic or ionic compensation of solute incorporation in oxides is favoured and what are the conditions determining this.

In oxide semiconductors, the effectiveness of a donor or an acceptor is not only governed by their ionization energies, it is also governed by the extent of oxidation and reduction, even in case of shallow dopants with smaller ionization energies. This is due to the fact that an aliovalent impurity in an ionic compound can be charge compensated by ionic defects (ionically compensated) or by electrons or holes (electronically compensated) or by a combination of the two. Variables governing the extent of these are pO_2, dopant concentration and temperature.

We will take the example of Nb_2O_5 doping in TiO_2.

The defect reactions are written as

Ionic compensation $$2Nb_2O_5 \rightleftharpoons 4Nb_{Ti}^{\cdot} + 10\,O_O^x + V_{Ti}^{''''} \quad (1)$$

Electronic compensation $$2Nb_2O_5 \rightleftharpoons 4Nb_{Ti}^{\cdot} + 8\,O_O^x + O_2\uparrow + 4e' \quad (2)$$

Combination of the two reactions i.e. ((1) – (2)) leads to

$$O_2 + 4e' \rightleftharpoons 2O_O^x + V_{Ti}^{''''} \quad (3)$$

Equation (3) shows that as pO_2 increases, oxidation is favored and hence formation of titanium vacancies is more likely. Similarly, as the temperature reduces, oxidation is again favored.

Thus Nb doping of TiO_2 tends to be compensated by V_{Ti}'''' if Nb_2O_5 concentration is large, pO_2 is high and the temperature is low ,whereas the inverse conditions favour the electronic compensation.

In any case, the electrical neutrality condition requires that

$$[Nb_{Ti}^{\cdot}] \rightleftharpoons 4[V_{Ti}^{''''}] + 4n_e \quad (4)$$

Similar effects are observed in care of titanates such as $BaTiO_3$.

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Module 3: Defects, Diffusion and Conduction in Ceramics

Introduction

In this module, we will discuss about migration of the defects which happens via an atomistic process called as diffusion. Diffusivity of species in the materials is also related to their physical properties such as electrical conductivity and mobility via Nernst-Einestein relation which we shall derive. As we shall also see, the conductivity in ceramics is a sum of ionic and electronic conductivity and the ratio of two determines the applicability of ceramic materials for applications. Subsequently framework will be established for understanding the temperature dependence of conductivity via a simple atomistic model leading to the same conclusions as predicted by the diffusivity model. Subsequently we will look into the conduction in glasses and look at some examples of fast ion conductors, material of importance for a variety of applications. Presence of charged defects in ceramics also means the existence of electrical potential gradients, in addition to the chemical gradient, which results in a unified equation for electrochemical potential. Finally, we will look at a few important applications for conducting ceramic materials.

The Module contains:

Suggested Reading:

$$c_1 = \frac{n_1}{\lambda} \quad \text{and} \quad c_2 = \frac{n_2}{\lambda} \qquad (3.6)$$

if area is considered as unit area (=1) and λ is the distance between two atomic planes.

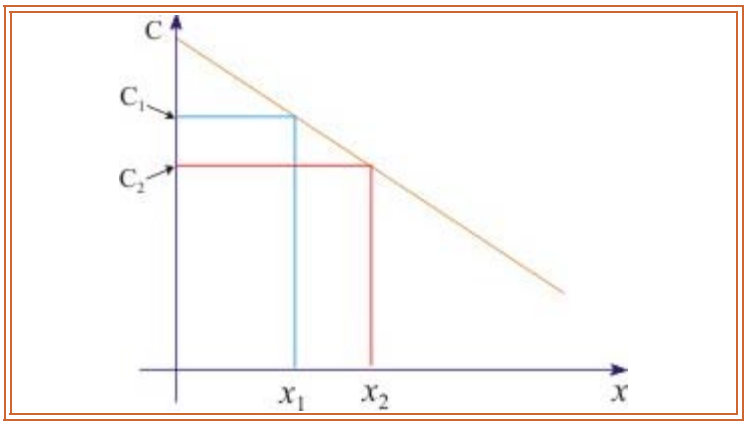

Figure 3. 2 Schematic diagram showing concentration gradient between two planes of atoms

Concentration gradient can be written as (note the minus sign)

$$-\frac{dc}{dx} = \frac{c_1}{\lambda} - \frac{c_2}{\lambda} = \frac{c_1 - c_2}{\lambda} = \frac{n_1 - n_2}{\lambda^2} \qquad (3.7)$$

Hence, flux can now be expressed as

$$J = \frac{1}{2}\left(-\lambda^2 \frac{dc}{dx}\right)\Gamma = -\left(\frac{1}{2}\lambda^2\Gamma\right).\frac{dc}{dx}$$

$$= -\,D\,.\,\frac{dc}{dx} \qquad (3.8)$$

where D = ½ λ^2 t with unit cm^2/s in 1-D and can easily show to become D = 1/6 λ^2 t in a 3-D cubic co-ordination scenario.

In general, diffusivity can be expressed as

$$D = \gamma\,\lambda^2\,\Gamma \qquad (3.9)$$

where γ is governed by the possible number of jumps at an instant and λ is the jump distance and is governed by the atomic configuration and crystal structure.

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Naturally when for a predominantly electronic conductor,

$$t = t_{electronic} \approx 1$$

and for a predominantly ionic conductor

$$t = t_{ionic} \approx 1$$

and for mixed conduction

$$t_{elec} \approx t_{ionic}$$

As shown below, Table 3.2 lists the transference numbers for some conducting oxide ceramics.

Compound	T(°C)	t_i^+	t_i^-	$t_{e,h}$
ZrO_2+7%CaO	>700	0	1.0	10^{-4}
$Na_2O.11Al_2O_3$	<800	1 (Na^+)	--	$<10^{-6}$
FeO	800	SiO_2	--	1.0
ZrO_2+18%CeO_2	1500	--	0.52	0.48
ZrO_2+50%CeO_2	1500	--	0.15	0.85
$Na_2O.CaO.SiO_2$ Glass		1 (Na^+)	-	-
15%($FeO.Fe_2O_3$)$CaO.SiO_2$-Al_2O_3-Glass	1500	0.1 (Ca^{2+})	-	0.9

- Typically ionic conductors exhibit a temperature dependence of mobility, i.e. mobility is thermally activated. Typically conductivities of ionic conductors are in the range of 10^{-5} to 100 S/m, depending on the temperature and are about 3 - 5 orders of magnitude lower than the metallic conductors but about 10 - 15 orders of magnitude higher than the ceramic insulators.
- Easily reducible oxides such as TiO_2 , SnO_2 , ZnO, $BaTiO_3$ and $SrTiO_3$ show an n-type semiconducting behaviour due to creation of oxygen vacancies and compensating electrons, whilst easily oxidizable oxides are CoO, FeO types which have cation deficiency and exhibit p–type behaviour.

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[4] Principles of Electronic Ceramics, L.L. Hench and J.K. West, Wiley, Table 4.2

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3.13.3 Ionic conduction in cubic ZrO_2

Zirconia, ZrO_2, is made stable in cubic form by doping with small amounts, ~8-10%, of aliovalent CaO or type of impurities. Cubic ZrO_2 is considered as a very good and fast ion conductor. Oxygen vacancies, the prevailing defects in Cubic ZrO_2 are created according to

$$CaO \xrightarrow{ZrO_2} Ca''_{Zr} + O_O^x + V_O^{\cdot\cdot}$$

Small energy of migration $(Z_i)e$ of oxygen vacancies results in an unusually high diffusion of oxygen vacancies in ZrO_2.

Example: Take the case of $Ca_{0.14}$,$Zr_{0.86,}$ $O_{1.86}$. Bandgap of ZrO_2 is ~5.2 eV.

At high temperatures, the diffusion coefficient is given as

$$D_{V_O^{\cdot\cdot}} = 1 * 10^3 \exp\ [-0.84\,ev/kT]\ cm^2/s$$

From the defect reaction

$$[Ca''_{Zr}] = [V_O^{\cdot\cdot}]$$

You can show that 14% molar concentration of CaO in ZrO_2 gives rise to an oxygen vacancy concentration of ~ $3.9*10^{21}$ cm^{-3}.

Now, ionic conductivity can be written as

$$\sigma_{ionic} = \sigma_{V_O} = C_{V_O}\ Z_{V_O}\ e\ \mu_{V_O^{\cdot\cdot}}$$

Mobility can be derived by using Nernst-Einstein equation as the following

$$\mu_{V_O^{\cdot\cdot}} = \frac{2\,e\,D_{V_O}}{kT} = \frac{2 \times 1.6 * 10^{-19} C}{1.38 * 10^{-23} J/K \times 1873 K} \times 1 * 10^3 \frac{cm^2}{V.s} \times \exp\left(\frac{0.84 eV \times 1.6 * 10^{-19} C}{1.38 * 10^{-23} J/K \times 1873 K}\right) = 68.3\ cm^2/V.s$$

Hence, ionic conductivity is

$$\sigma_{ionic} = 3.9 * 10^{21} cm^{-3} \times 2 \times 1.6 * 10^{-19} C \times 68.3 (\Omega\,cm)^{-1} = 8.5 * 10^4 (\Omega\,cm)^{-1}$$

Electronic conductivity is calculated as

$$\sigma_{el} = n_e\ e\ \mu_e$$

At 1823 K, electron concentration, n_e , using band model, is estimated to be $1.32*10^{13}$ cm^{-3} and electron mobility, μ_e , is 24 $cm^2/V.s$

Hence, the electronic conductivity is

$$\sigma_e = 1.32 * 10^{13}\ cm^{-3} \times 1.6 * 10^{-19} C \times 24\ \frac{cm^2}{V.s} = 5.1 * 10^{-5} (\Omega\,cm)^{-1}$$

3.16 Examples of Ionic Conductors in Engineering Applications

- Conducting ceramics are used in a variety of applications such as
  - SiC and $MoSi_2$ as heating elements and electrodes
  - ZnO and SiC as varistors for circuit protection
  - YSZ, ß -Alumina as electrolytes in fuel cells and batteries
  - Materials like YSZ in gas sensing applications
- While heating elements and varistors utilize the electronic conduction properties of the ceramics, fuel cells and sensors typically utilize ionic conductivity characteristics.
- Since details of each and every application is beyond the scope of this course, you are referred to the contents of the book titled ***Electroceramics, written by A.J. Moulson and J.M. Herbert and published by Wiley.***
- In the following sections, we will briefly discuss the major applications of conducting ceramics *viz* . three applications: varistors, solid oxide fuel cells and exhaust sensors in automobiles.

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Summary

Migration of defects plays a very crucial role in determining conduction in ceramic materials. Migration of ionic defects such as vacancies or interstitials is basically a diffusive process and is governed by the law of diffusion. The diffusivity of species is a strongly temperature dependent parameter with an exponential dependence on the temperature. The diffusivity related to electrical conductivity is shown by Nernst-Einstein relationship. As a result, conductivity in the ionic systems also follows a temperature dependent Arhenious type behavior. In ionic systems, to utilize the ionic conduction of materials, it is essential that ionic conductivity is a dominant contribution towards the total conductivity which typically happens at either higher temperatures or at reasonably high doping levels unless the electron concentration is extremely low. The examples of ceramic materials with high ionic conductivity are materials like fast ion conductors and a few ceramic glasses. The presence of composition gradients of charged defects also leads to electrical potential gradients and this when combined with the chemical potential gradients, gives rise to an expression for electro chemical-potential, called Nernst equation. This equation is often employed in designing the sensors for use in automotives where differential pO_2 gives rise to a voltage which can be used as a feedback to regulate the fuel/air supply in the engines. Ceramic conductors are used in a variety of applications, for example, ZnO as varistors, doped ZrO_2 as solid electrolytes in fuel cells and as oxygen sensors in the automobile exhaust.

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Module 4: Dielectric Ceramics: Basic Principles

Introduction

Dielectrics are insulating or non-conducting ceramic materials and are used in many applications such as capacitors, memories, sensors and actuators. For the sake of simplicity, we can assume that there is no long range moment of charges. First we will look the simple properties of dielectric materials such as dipole moment, polarization, susceptibility, polarizability and polarization mechanisms. Then we will do analytical treatment of polarizabilities for each of the polarization mechanisms to understand the meaning of these polarizabilities. Subsequently, we will do detailed analysis of dielectric properties for each of the polarization mechanisms under the influence of alternating field, important from the point of understanding the behaviour of these materials in real conditions. Finally, we will look at the breakdown mechanisms which lead to failure of dielectric materials.

The Module contains

Suggested Reading:

- Principles of Electronic Ceramics, by L. L. Hench and J. K. West, Wiley
- Dielectrics and Waves, by Arthur R. von Hippel, John Wiley and Sons Inc.

4.1 Basic Properties: Dielectrics in DC Electric Field

Upon application of a dc or static electric field, there is a long range migration of charges. However, there is a limited movement of charges leading to the formation of charge dipoles and the material, in this state, is considered as polarized. These dipoles are aligned in the direction of the applied field.
The applied field can also align the dipoles that were already present in the material i.e. material containing dipoles without application of the field.

Of course, both these effects may be present in a single material i.e. dipoles can be aligned as well as be induced by the applied field.

The net effect is called Polarization of the material.

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Summary

Summary

So far, we have learnt that the effect of an applied field on a dielectric material is to polarize it which is quantified by parameters such as dielectric constant, e_r ; polarization, P; and dielectric susceptibility, χ. Next we will learn about the polarization mechanisms and local field inside a dielectric.

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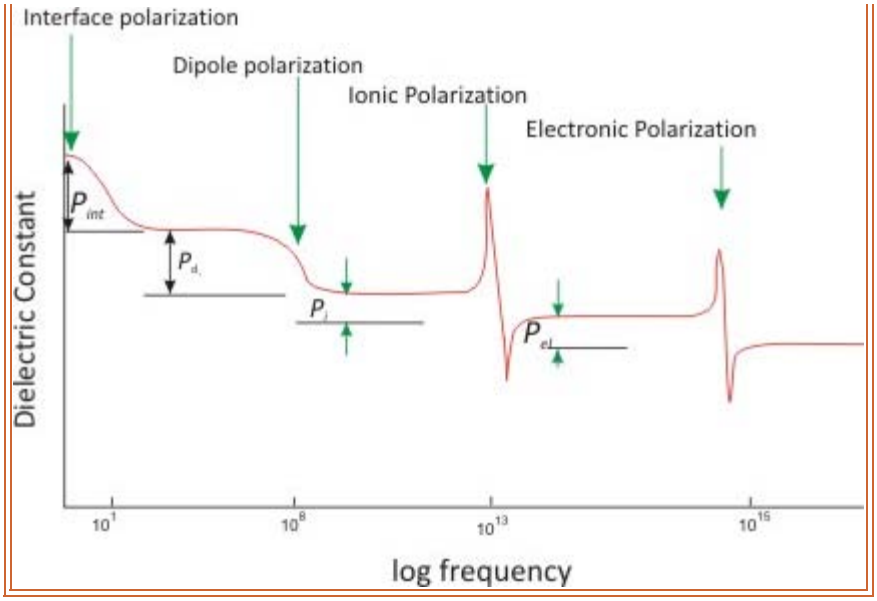

Figure 4.7 Schematic figures between dielectric constant ***vs*** frequency showing various mechanisms

The following table shows the values of e_r and n^2 for a variety of materials and the dominant polarization processes in them:

Material	e_r	n^2	Dominant mechanisms
C (Diamond)	~5.7	5.83	Electronic
Ge	~16	16.73	Electronic
NaCl	~5.9	2.37	Electronic and Ionic
Water (H_2O)	~80	1.77	Electronic, Ionic and Dipolar

So, you can see that while carbon and germanium being single elemental materials show electronic polarization only and as a result their dielectric constants match well with the values of n^2. However, the same is not the case with NaCl or water which have strong contributions of ionic and ionic and dipolar polarization respectively. We will discuss more about these processes in the latter sections.

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4.5 Analytical Treatment of Polarizability

Here we discuss the simple analytical solutions for determining the polarizability and polarization for each of the above polarization mechanisms. The analysis will shed some light on the dependence of polarizability on the material parameters as well as any external parameters.

4.5.1 Electronic Polarization

To achieve this, let us first imagine an atom as a perfect sphere, having +Ze charge at the center of the nucleus and an equivalent –Ze charge of electrons around it. Here R is the radius of the atom.

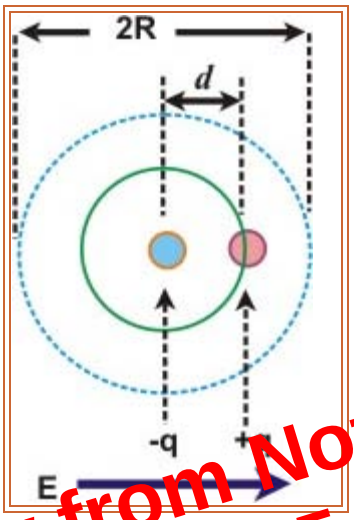

Figure 4.1 Schematic of electronic polarization

Under the application of a electric field, E, the force F_1, on the charges is given as

$$F = Ze.E \qquad (4.29)$$

As a result, positive and negatives charges experience forces in different direction and their center move away from each other by a distance, d.

However, d has to be finite values because this force is balanced by Coulomb force of attraction between opposite charges which can be calculated by simple electrostatistics and is given as

$$F_2 = \left(\frac{q(\text{nucleus})^{*}\, q(\text{electrons inside the distance d})}{4\,\pi\varepsilon_0.d^2}\right)$$

$$= \left(\frac{Ze^{*}\, Ze\left(\frac{(4/3)\pi d^3}{(4/3)\pi R^3}\right)}{4\pi\varepsilon_0.d^2}\right) = \left(\frac{Z^2e^2d}{4\pi\varepsilon_0.R^3}\right) \qquad (4.30)$$

Equating the two forces, gives the equilibrium separation distance d_o, i.e.

$$d_o = \frac{4\pi\varepsilon_0.R^3E}{Ze} \qquad (4.31)$$

4.5.2 Ionic Polarization

The figure below shows that in an ionic solid, in the absence of an external electric field, all the dipoles (formed by each Na^+ and Cl^- pair with an equilibrium separation distance as d_o cancel each other due to crystal symmetry and hence net dipole moment is equal to zero. Remember, in these solids, no dipole rotation is allowed.

However, when a finite field, E, is applied, the force experienced by the ions leads them to move away from their equilibrium positions , as shown in the figure, giving rise to unequal dipole moments in different directions and as a result, the material will have net dipole moment.

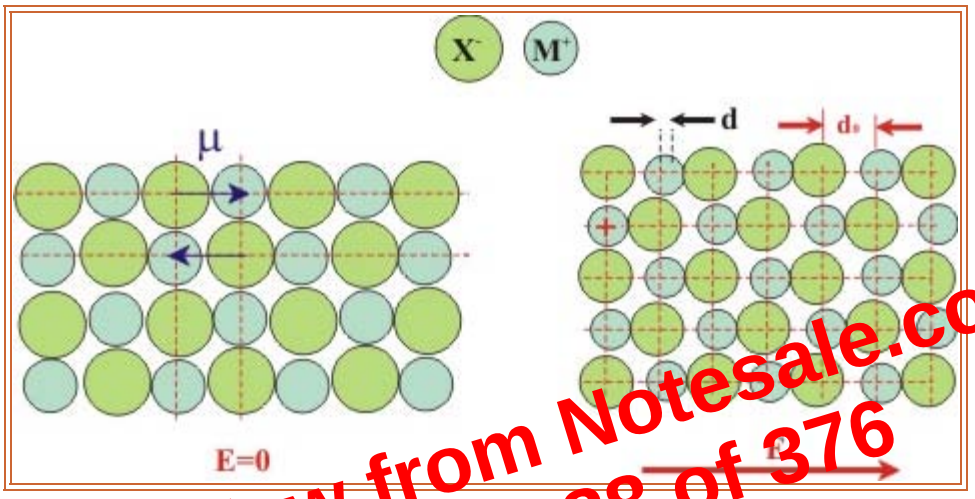

Figure 4.11 Schematic of the ionic polarization

As you can now see, the distance between the ions decreases by ‘d’ in one direction and increases by ‘d’ in the opposite direction.

Now we calculate the magnitude of ‘d’.

The force, F_1, which increases the distance between the ions of charge, q, can be expressed as

$$F_1 = q.E \qquad (4.35)$$

However, there is a force, F_2, in the other direction trying to restore the equilibrium between the ions which is expressed as

$$F_2 = k_i.E \qquad (4.36)$$

Where k_i can be considered as spring constant of the bond between ions assuming ionic dipoles behave like springs.

The spring constant can be expressed in terms of elastic modulus, Y, and can be expressed as

$$k_i = Y.d_o \qquad (4.37)$$

At equilibrium, $F_1 = F_2$ and by combining equations (4.35-4.37), we get an estimate of *d* i.e.

$$d = \frac{q.E}{Y.d_o} \qquad (4.38)$$

Hence, induced 'extra' dipole moment, μ, will be

$$\mu = q.d = \frac{q^2.E}{Y.d_o} = \alpha_i E \qquad (4.39)$$

where a_i is ionic polarizability. Thus the polarization, P, can be written as

$$P = N.\mu = \frac{N.q^2.E}{Y.d_o} \qquad (4.40)$$

where N is the dipole density per unit volume.

Note: Here we considered the electric field, E, parallel to the main crystallographic axis. If this is not the case, one needs to take the component of dipole moment in the direction of the field before adding them together.

This is a very a rough guide to the calculation of the ionic polarization and can be more complex in the case of many ionic solids, especially when ions do not have similar charges. For example, in calcium fluoride, CaF_2, a material used for making lenses for lithography machine, the dielectric constant is approximately equal to n^2. This enables the lenses to be made of dimensions of about 0.1 mm.

The above expressions also tell us that stronger bonds lead to smaller polarization which seems obvious because then you wouldn't be able to stretch the atoms too far!

The following are the values of the dielectric constant of some materials where ionic polarization contributes (in addition to electronic polarization of course) (source : "Solid State Physics" by N.W. Ashcroft and N.D. Mermin):

ZnO	4.6
ZnS	5.1
ZnSe	5.8
CdSe	7.0
MgO	3.0
CdS	5.2
BeO	3.0

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4.6 Effect of Alternating Field on the Behavior of a Dielectric Material

Here we will examine the behavior of real and ideal dielectric materials under the influence of an alternating electric field, giving an account of the real situations to which dielectric materials are subjected.

4.6.1 Behavior of an Ideal Dielectric

While most of the above discussion has been for d.c. or static fields, in most practical applications, dielectrics are used under alternating fields. Hence, it is imperative to work out their characteristics in alternating fields.

Let us apply a sinusoidal field

$$V = V_o . \exp(i\omega t) \qquad (4.54)$$

This leads to the development of a charging current, I_c, due to a change in the charge with time which is

$$I_c = \frac{dQ}{dt} = C.\frac{dV}{dt} = i\omega CV \qquad (4.55)$$

$$= \omega C.V_o . \exp(i\omega t) . \exp(i\pi/2)$$

$$= \omega C.V_o . \exp[i(\omega t + \pi/2)] \qquad (4.56)$$

The term + p/2 implies that the current leads the voltage by 90° in a perfect dielectric. This current voltage relationship can also be understood from a phasor diagram as shown below.

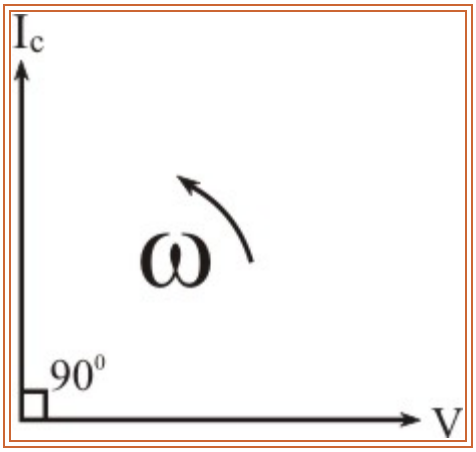

Figure 4.18 Phasor diagram for a perfect dielectric

Summary

Summary

We have investigated the behavior of dielectric materials in alternating electric fields. We see that for ideal dielectrics, the current leads the voltage by 90° and power dissipation is equal to zero. On the other hand, in real dielectrics, the current leads voltage by an angle 90° - d where d is the loss angle. This results in real and imaginary parts of the dielectric constant and the ratio of imaginary to real part is loss tangent, depicting the power loss in a real dielectric.

Next we will look into the frequency dependence of the dielectric properties.

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$$= \frac{q_i^2 E_o \exp(i\omega t)}{m_i\left[(\omega_{o,i}^2 - \omega^2) + i\gamma_i\omega\right]} \quad (4.81)$$

$$= \alpha_i . E_o \exp(iwt) \quad (4.82)$$

where $a_i$is the electronic or ionic polarizability as be the case. If the friction term is neglected, then frequency dependent polarizability is

$$\alpha_i = \frac{q_i^2}{m(\omega_{o,i}^2 - \omega^2)} \quad (4.83)$$

Here mass, m_i, is either the mass of electrons in atoms or ions in crystals.

In case of ionic polarization, one takes the reduced mass which is given as $\{M^+ M^- / (M^+ + M^-)\}$ where M^+ and M^- are cation and anion masses respectively. Similarly q_i will be charge on the particle as appropriate and $\omega_{0,i}$ will be natural frequency of electronic or ionic polarization mechanisms.

The polarization can then be written as

$$P_i^* = N.\mu_i \quad (4.84)$$

Hence using equations (4.15) and (4.16) we get the expressions for the susceptibility and dielectric constant as

$$\chi_{i,\infty}^* = \frac{N.q_i^2}{m_i\varepsilon_o}\left\{\frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma\omega}\right\} \quad (4.85)$$

and

$$\varepsilon_{r,\infty}^* = 1 + \frac{N.q_i^2}{m_i\varepsilon_o}\left\{\frac{1}{(\omega_{o,i}^2 - \omega^2) + i\gamma\omega}\right\} \quad (4.86)$$

Here * implies that these are complex quantities which was also mentioned earlier when we discussed power dissipation characteristics in real dielectrics.

The subscript 8 signifies the susceptibility and dielectric constants at frequencies below the resonance frequencies. Resonance for electronic polarization occurs at about 10^{15} s^{-1} and for ionic polarization occurs at about 10^{13} s^{-1}.

Now, we can separate out the real and imaginary parts of the dielectric constants as following

$$\varepsilon_{r,\infty}' = 1 + \frac{N.q_i^2}{m_i\varepsilon_o}\left\{\frac{\omega_{o,i}^2 - \omega^2}{(\omega_{o,i}^2 - \omega^2)^2 + \gamma^2\omega^2}\right\} \quad (4.87)$$

and

Now ignoring the transient time dependent term of (4.95) and substituting (4.96) into (4.94), we get

$$\varepsilon_r^* = \varepsilon'_{r\infty} + \frac{\varepsilon'_{rs} - \varepsilon'_{r\infty}}{1 + i\omega t} \qquad (4.104)$$

We also know that $e_r^* = e_r' - ie_r''$, hence, now we can separate the real and imaginary parts as

$$\varepsilon'_r - i\varepsilon''_r = \varepsilon'_{r\infty} + \frac{\varepsilon'_{rs} - \varepsilon''_{r\infty}}{1 + i\omega t} \qquad \text{OR}$$

$$\varepsilon'_r = \varepsilon'_{r\infty} + \frac{\varepsilon'_{rs} - \varepsilon'_{r\infty}}{1 + \omega^2\tau^2} \qquad (4.105a)$$

$$\varepsilon''_r = \frac{\omega\tau}{1 + \omega^2\tau^2}(\varepsilon'_{rs} - \varepsilon'_{r\infty}) \qquad (4.105b)$$

and the loss tangent is

$$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r} = \frac{(\varepsilon'_{rs} - \varepsilon'_{r\infty})\omega\tau}{\varepsilon'_{rs} + \varepsilon'_{r\infty}\omega^2\tau^2} \qquad (4.106)$$

The above equations are called Debye equations.

The graphical representation of these is shown below:

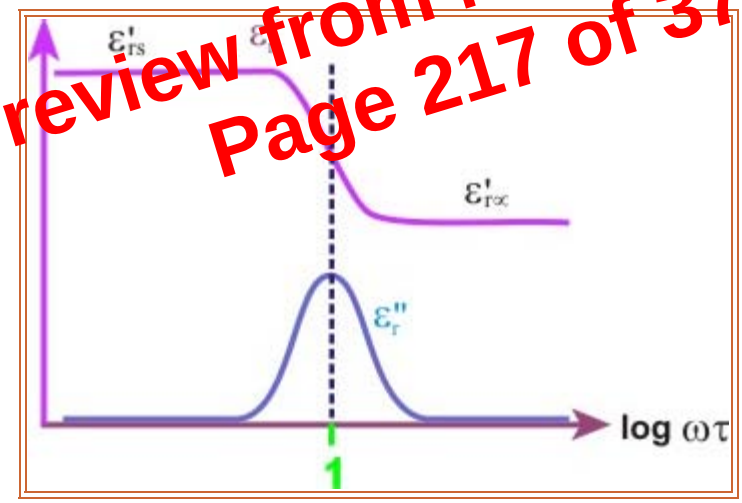


Figure 4.24 Graphical representation of Debye equations

Here, the relaxation frequency ω_r is defined as inverse of the relaxation time *i.e.* 1/t.

The equation (4.98) and the above figure suggest that e_r' is independent of frequency at values corresponding to the sum of three polarizations i.e. $P_d+P_i+P_e$. As the applied field frequency approaches value ω = 1/t, e_r' passes an inflection and then drops off to e_{r8}' which is dependent only on (P_i+P_e).

At ω = 1/t, the oscillating charges are coupled with the applied field and absorb maximum energy

as depicted by the peak in e_r" magnitude of e_r" peak being (e_{rs}" - e_{r8}')/2 depending upon the number of oscillating charges and distance of motion.

It is also seen that tand is also goes than a maximum, but at higher frequencies with $\omega = (e_{rs}'/e_{r8}')^{1/2}/t$.

Now since, we have understood that polarization develops by temperature dependent diffusional processes which also give rise to the *d.c.* conductivity, temperature dependence of the relaxation time, t can be expressed as

$$\tau = \tau_0 . \exp\left(Q_a/kT\right) \qquad (4.107)$$

where Q_a is the activation energy for dipole relaxation and t_0 is the intrinsic relaxation time.

Combining Debye equations with (4.99) we can obtain the frequencies (= ωt) at which maxima for e_r" as well as tand occur and you will that these frequencies for the maxima change with temperature because t is temperature dependent. The plots below show this trend for $Li_2O.2SiO_2$ glass ceramic.

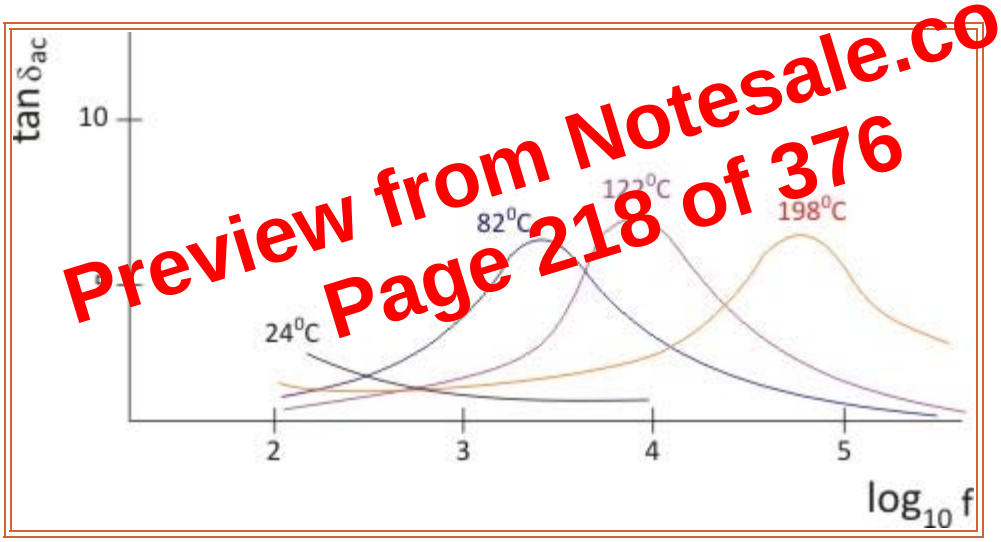
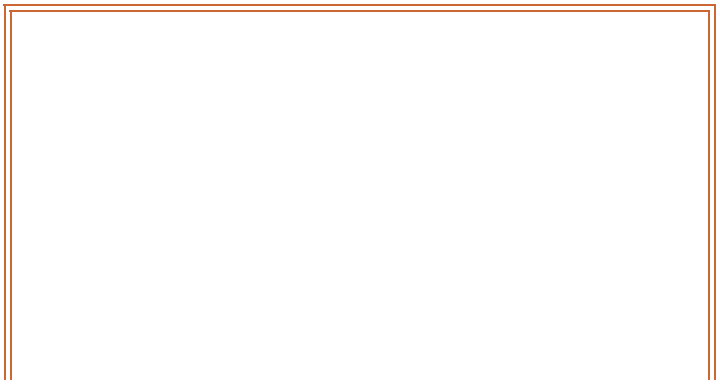


Figure 4.25 Shift of tand peak in $Li_2O.2SiO_2$ glass due to increasing temperature (Reproduced from Principle of Electronic Ceramics, L.L. Hench & J.K. West, P206)



4.8.3 Complete Picture of Frequency Dependence of the Dielectric Constant

So, now we can plot the contributions to the dielectric constant from all the mechanisms.

In case of an ideal dielectric material exhibiting all four basic mechanisms, we would expect the following curve.

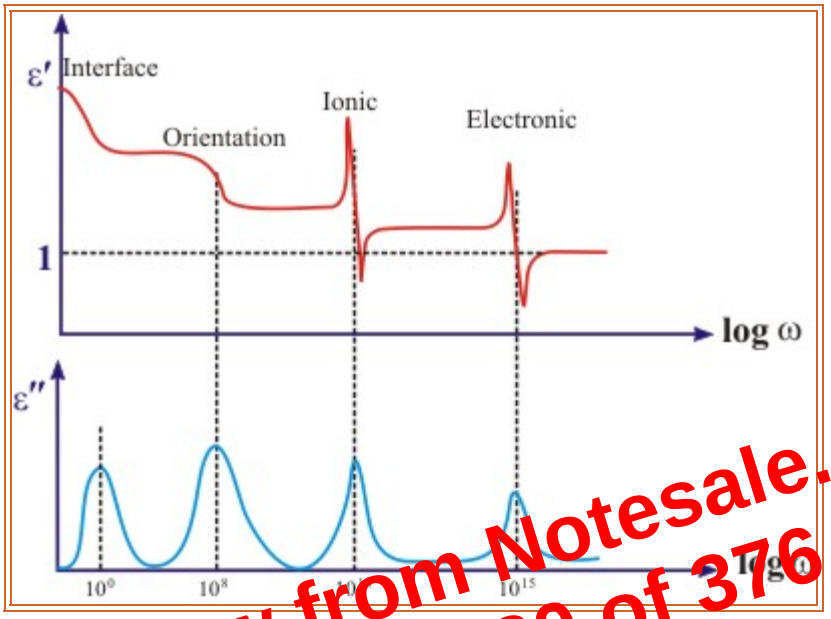


Figure 4.27 Complete plot of frequency dependence of dielectric constant and loss (note that frequency is not to scale)

Although the above plot represents an ideal material, yet the plot gives an idea of what you might expect when you measure dielectric constant of a material as a function of frequency.

Although the real plots may look quite different (look for dielectric constant data for electronic ceramics in journal publications), you can expect a correlation between the real and imaginary part of the curve i.e. we can still clearly see the absorption peak.

As, mentioned earlier, for a non-magnetic dielectric solid, Maxwell's electromagnetic equations predicts that e_r be equal to n^2.

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4.9 Circuit Representation of a Dielectric and Impedance Analysis

Data analysis after dielectric characterization often requires modeling of dielectrics which is helped by their representation as equivalent electrical circuits. Incidentally, a perfect dielectric material can be modeled by an equivalent RC parallel circuit as shown below.

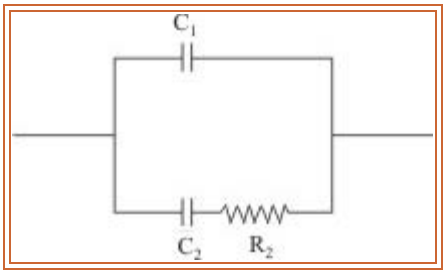

Figure 4.28 Equivalent circuit model of a dielectric

Let us consider the admittance (Y) of the material representing the above circuit which is inverse of the impedance (Z), and is expressed as

$$Y = \frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2} \qquad (4.108)$$

where $Z_1 = \frac{1}{i\omega C_1}$ and $Z_2 = \frac{1}{i\omega C_2} + R_2$ (4.109)

Hence admittance now is

$$Y = i\omega C_1 + \frac{1}{R_2 + \frac{1}{i\omega C_2}} \qquad (4.110)$$

Now if we consider time constant for the segment R_2C_2 as $t_2 = R_2C_2$, then admittance can be written as

$$Y = i\omega C_1 + \frac{C_2}{\tau_2 + \frac{1}{i\omega}}$$

$$= \frac{\omega^2 \tau_2 C_2}{1 + \omega^2 \tau_2^2} + i\omega \left(C_1 + \frac{C_2}{1 + \omega^2 \tau_2^2} \right) \qquad (4.111)$$

Now, since admittance can be related to the dielectric constant as

(4.112)

4.10 Impedance Spectroscopy

The frequency response of the impedance of above circuit would also yields a semi-circle in the complex plot between real and imaginary parts of the dielectric constant and such a response represent a capacitor with losses. Such technique of characterizing dielectrics is called Impedance Spectroscopy.

The intercepts of the semi-circle on the *x*-axis represent high and low frequency dielectric constants or e_{r8}' and e_{rs}' respectively.

The maxima of the semi-circle occurs at

$$\omega\tau = 1 \text{ or } \omega R_2 C_2 \qquad (4.115)$$

The semicircle equation turns out to be

$$(\varepsilon_r'(\omega) - \frac{1}{2}(\varepsilon_{rs}' + \varepsilon_{r\infty}')) + \varepsilon_r''(\omega)^2 = \frac{1}{4}(\varepsilon_{rs}' - \varepsilon_{r\infty}')^2$$

which can be obtained by removing ωt from the equations (4.105a) and (4.105b).

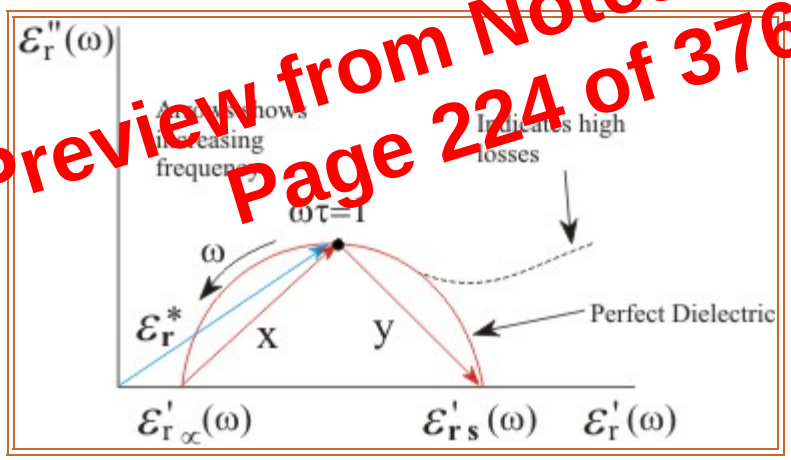

Figure 4.29 Cole-Cole Plot

Alternatively in a semi-circle one can draw two vectors, X and Y which are always perpendicular to each other and are related as y = -iωt.xThis relation can easily be obtained just by using the Debye's equation (4.98) and simple vector additions and subtractions.

Basically any point on the surface of the semi-circle of diameter (e_{rs}' - e_{r8}') in this complex plane can be defined by these vectors.

In the figure above, a perfect semicircle represents a narrow distribution of relaxation times indicating only one primary mechanism of polarization.

However, if there is the presence of a tail on the low frequency side, as shown by dashed line i.e.

Module 5: Nonlinear Dielectrics

Introduction

So far, we have discussed linear dielectrics whose dielectric constant increases linearly with the applied field accompanied by an increase in the polarization depending upon the presence of polarization mechanisms in the materials.

In addition, there are a few special classes of dielectric materials which show large dielectric constants, non-zero polarization in the absence of electric field and nonlinearity in the dielectric constant.
These also show extraordinary special effects such as

- Coupling of strain and electric field (piezoelectric ceramics),
- Temperature dependence of the polarization (pyroelectric ceramics) and
- Presence of large polarization in absence of electric field *i.e.* spontaneous polarization (ferroelectric ceramics).

Most of these materials happen to be oxides and as you can very well understand now, these properties will be greatly affected by the defect chemistry and process variables.

The presence of these features makes these materials extremely useful for a variety of applications such as sensors, actuators, transducers, temperature detectors, imaging, permanent data storage etc. In this module, we will discuss origin of these properties with a crystallographic and thermodynamic framework and associated mathematical representations along with a few examples of materials and devices.

The Module contains:

Suggested Reading:

- Principles of Electronic Ceramics, by L. L. Hench and J. K. West, Wiley
- Principles and applications of ferroelectrics and related materials, M. E. Lines and A. M. Glass, Oxford University Press
- Electroceramics: Materials, Properties, Applications, by A. J. Moulson and J. M. Herbert, Wiley

5.3.6 Case – II: First Order Transition

Another situation to consider is that when a < 0, b < 0 but c > 0. What this means is that free energy vs polarization plot has three equal minima, one for P = 0 and the other two for P ≠ 0 at the same temperature i.e. at the same value of 'a' at a temperature T = T_0, Curie temperature, which is now more than T_0. This gives rise to the following free energy vs polarization plot.

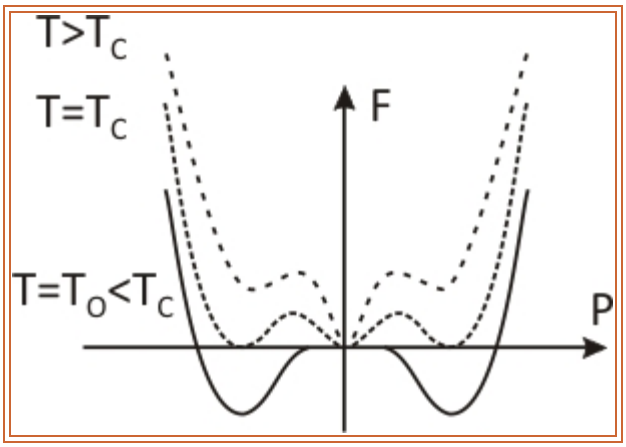

Figure 5.9 Free energy vs polarization schematic plot for a first order phase transition

The most important feature of this phase transition is that polarization i.e. the order parameter drops from P ≠ 0 to zero discontinuously at T = T_c and is called as first order phase transition. This is also very clearly demonstrated by a discontinuity in the reciprocal of dielectric susceptibility as seen below. For example, solid-liquid phase transition is a first order phase transition while among various ferroelectrics, barium titanate is a fine example of first order transition among ferroelectrics.

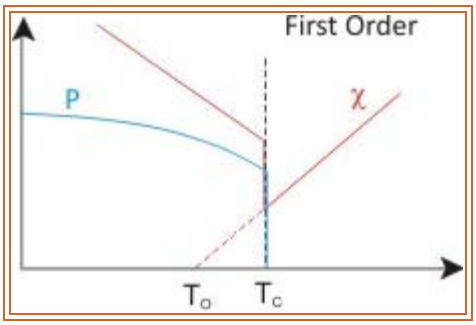

Figure 5.10 Polarization and reciprocal susceptibility plot for a first order phase transition

In order to compute the non-zero polarization (P_0) and susceptibility at the transition, the value of free energy (5.13) for P = 0 and P = P_0 must be equal at T = T_c i.e.

$$G(0) = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 = 0 \qquad (5.25)$$

On the other hand, field E must also be zero for the polarization to be spontaneous i.e.

$$\frac{dG}{dP} = E = aP + bP^3 + cP^5 \qquad (5.26)$$

The polarization and susceptibility at T_c are obtained by solving two equations and are given as

$$P_o^2(T_c) = \frac{3}{4}\left(-\frac{b}{c}\right) \qquad (5.27)$$

and

$$(\chi(T_c))^{-1} = a = \frac{3}{16}\left(\frac{b}{c}\right)^2 \qquad (5.28)$$

The fact that there are three minima at $T=T_c$ is reflected in whether the T_c is approached while heating or cooling. More specifically, the material will be in other of the two non-zero polarization states if is heated from an initial temperature that is lower than T_c whereas, if it is cooled from a temperature higher than T_c, the sample will be in paraelectric state. This results in thermal hysteresis when these materials are thermally cycled across T_c.

If you are interested in further reading about the phase transitions in ferroelectrics, refer to the following texts:

- Principles and Applications of Ferroelectrics and Related Materials, M. Lines and A. Glass, Clarendon Press, Oxford
- Solid State Physics, A.J. Dekker, Macmillan Publishing
- Ferroelectric Crystals, F. Jona and G. Shirane, Dover Publishing

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of all domains in the direction of field (path FG) and the loop can be completed by following the path GHD.
This relation between P and E is called a ferroelectric hysteresis loop which is an important characteristic of a ferroelectric crystal. The principle feature of a ferroelectric crystal is not only the presence of spontaneous polarization but also the fact that this polarization can be reversed by application of an electric field.

Domain switching in a previously polarized ferroelectric sample can also be viewed in the following animation.

Figure 5. 14 Domain switching animation in a ferroelectric material (Reproduced from DOITPOMS Library, University of Cambridge, UK)

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5.4.7.4 Actuators

In the precision engineering applications, precise linear or rotational movements are required for achieving technological perfection. In piezoelectrics, application of high electric fields (without using oscillations) correspond to only tiny changes in the crystal dimension and these changes can be very precise, achieving better than a micrometer precision. This ability makes these materials useful as precise actuators for achieving very precise motions.

In these applications, typically multilayer ceramics consisting of layers thinner than 100 microns, are used. One can achieve very high field in the multilayered materials using voltages lower than 150-200 V, not very high voltages.

You can have it in two forms:

- Direct Piezo Actuators with strokes lower than 100 microns or so and
- Amplified Piezoelectric Actuators which can yield millimeter long strokes.

Some of the examples of applications are

- Piezoelectric motors consisting of piezoelectric elements which apply a directional force to an axle, causing it to rotate. As the distances travelled are extremely small, it is a very high-precision replacement for the conventional stepper motor.
- Scanning force microscopes use inverse piezoelectric effect to keep the sensing needle close to the probe.
- Laser mirror alignment in the laser electronics helping maintain accurate optical conditions inside the laser cavity to optimize the beam output.
- Loudspeakers: Voltage is converted to mechanical movement of a piezoelectric polymer film.
- In inkjet printers where piezoelectrics are used to control ink flow from the print head to the paper.
- As fuel injectors in diesel engines in place of commonly used solenoid valve devices.

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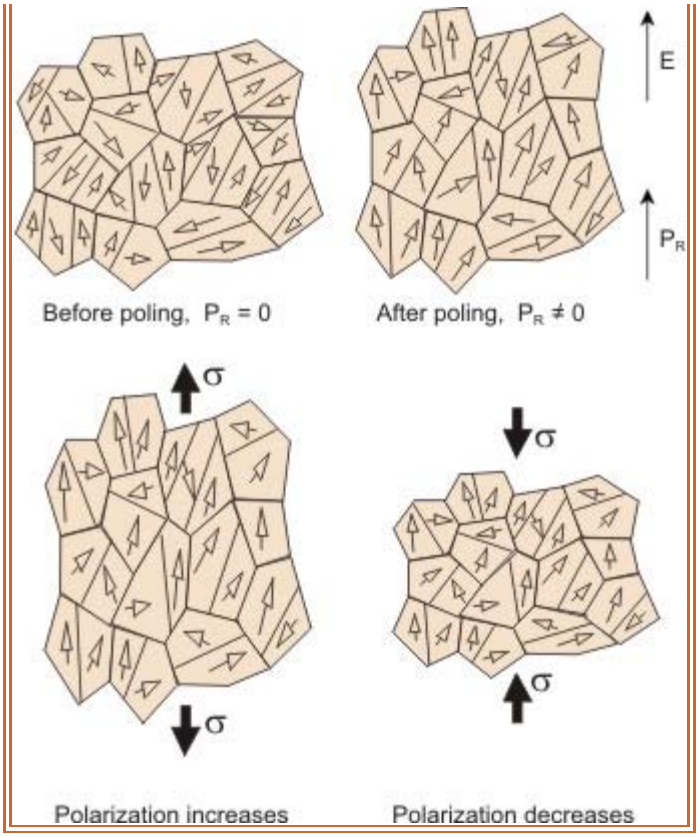

Figure 5.21 Poling of ferroelectrics and application of stress on poled material

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5.5.1 Difference between Pyroelectric and Ferroelectric Material

Although both ferroelectric and pyroelectric materials must be non-centrosymmetric and polar, the essential difference between them lies when an electric field is applied. While a change in temperature below Curie temperature leads to the creation of dipole along the polar axis by slight movement of atoms from their neutral positions (A), a reverse electric field can reverse the direction of polarization in a ferroelectric but not in a pyroelectric material (B). However, when the material is heated above Curie temperature, the atoms come back to their equilibrium positions (C).

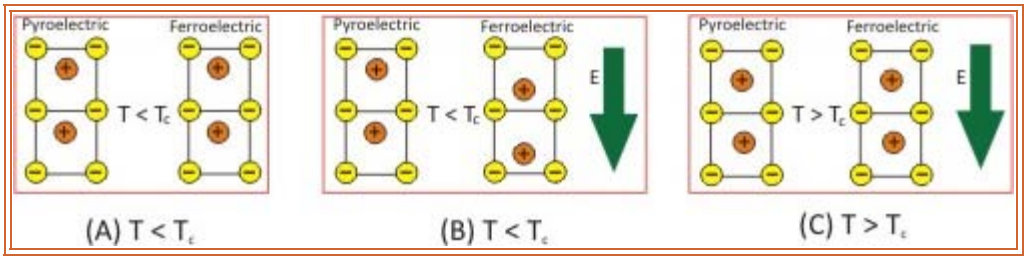

Figure 5.29 Difference between a ferroelectric and pyroelectric material

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6.1 Magnetic Moments

Magnetism in materials is crudely explained as mutual attraction between two pieces of a material, say iron or iron ore. There are various microscopic mechanisms of magnetism in materials which are shown later. The strength of magnetism is quantitatively judged by a quantity called as 'magnetic moment'. This magnetic moment should not be confused with dipole moment as we learnt in Module 4.

The major contributors of magnetic moment in a material are

- Motion of electrons in an orbit of an atom. Orbital moment can be related to the current flowing in a loop of a wire of zero (negligible) resistance.
- Spinning of electron around it own spin axis gives rise to a moment.
- Nuclear magnetic moment due to nuclei.

The first two contributions are quite significant and contribute to most of the magnetic character of a material while the third component, nuclear magnetic moment, is rather insignificant in the context of most magnetic materials of practical interest and can be neglected.

6.1.1 Orbital Moment

According to Ampere's law, when a current flows through a coil, it gives rise to a magnetic field in a direction perpendicular to the plane of the loop. The field is related to the current by

$$H = NI \qquad (6.1)$$

where N is the number of loops per unit length of the coil, I is the current in Amperes and H is the induced magnetic field in Ampere per m i.e. $A.m^{-1}$.

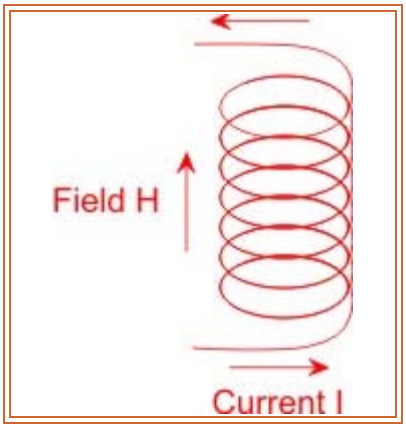

Figure 6.1 A current carrying coil

Now based on classical physics, the current, *I*, is nothing but charge per unit time and is expressed as

$$B = \mu_o H (1 + \chi_m)$$

or

$$B = \mu_o \mu_r H \qquad (6.13)$$

Here, χ_m, similar to dielectric materials, can be thought of as a parameter which expresses magnetic response of electron in a material to the applied magnetic field and is a dimensionless quantity. Here, $\mu_r = (1+ \chi_m)$ is the, in a similar manner to relative dielectric permittivity, e_r.

In general, both susceptibility and permeability are tensors and assuming that vectors are collinear wherever there is vector notation is not used.

Naturally for vacuum, $\chi_m = 0$.. However, unlike dielectric materials, χ_m can acquire both positive and negative values.

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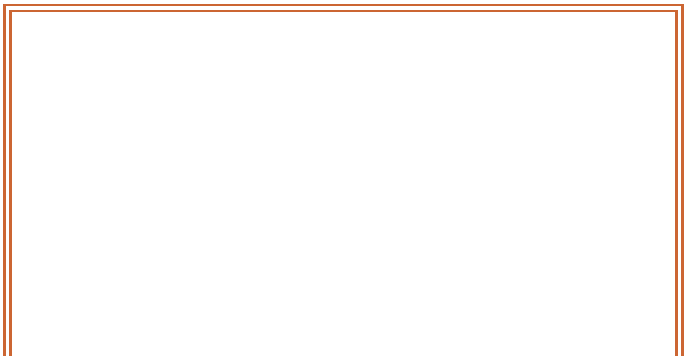
Si	-4.1×10^{-6}	-0.32×10^{-6}	0.99999	
Water	-9.14×10^{-6}	-0.73×10^{-6}	0.99999	
Superconductors (only in superconducting state)	-1.0	$\sim -8 \times 10^{-2}$	0	
ß-Sn	$+2.4 \times 10^{-6}$	$+0.19 \times 10^{-6}$	1	Paramagnetic
W	$+77.7 \times 10^{-6}$	$+6.18 \times 10^{-6}$	1.00008	
Al	$+20.7 \times 10^{-6}$	$+1.65 \times 10^{-6}$	1.00002	
Pt	$+264.4 \times 10^{-6}$	$+21.04 \times 10^{-6}$	1.000026	
Low carbon steel	$\approx 5 \times 10^{3}$	3.98×10^{2}	5×10^{3}	Ferromagnetic
Fe-3%Si (Grain Oriented)	4×10^{3}	3.18×10^{3}	4×10^{4}	
Ni-Fe-Mo superalloy	10^{6}	7.96×10^{4}	10^{6}	

It should be noted, also as we will see, that except for diamagnetic materials, magnetic susceptibilities are temperature dependent. Sign of susceptibility can also be related (qualitatively) to the penetration of magnetic flux inside the material.

This says that for diamagnetic materials, when an external field is applied, the magnetic moment that is induced is in opposite direction to the field direction i.e. opposite magnetization as shown below. This is an inherent effect present in all materials. It is just that some materials like silver, gold, silicon are only diamagnetic i.e. they don't have any other effect present in them.

In many other materials, on top of the diamagnetic effect which is inherent to all materials, other effects are present which contribute significantly to the magnetization and all of these tend to have induced magnetization that is in the direction of the applied i.e. positive susceptibility. This means that magnetic flux penetrates into the material as shown below. We will discuss these effects one by one.



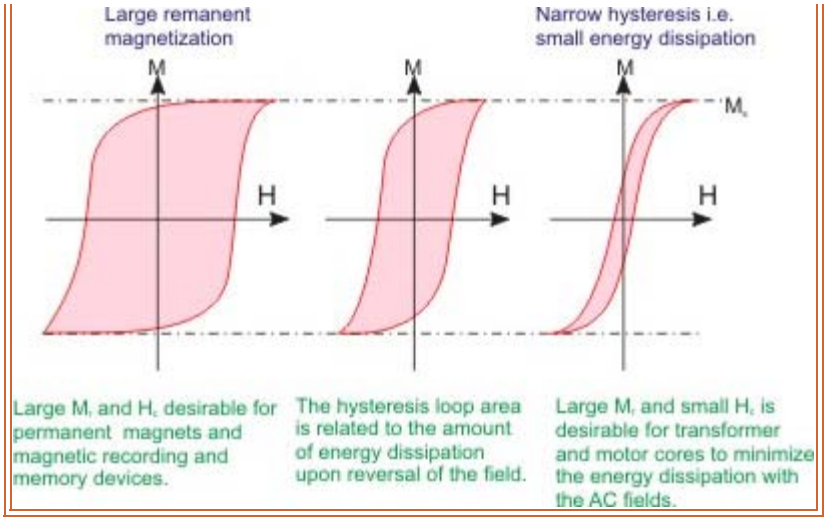


Figure 6.12 Representation of hard and soft magnets

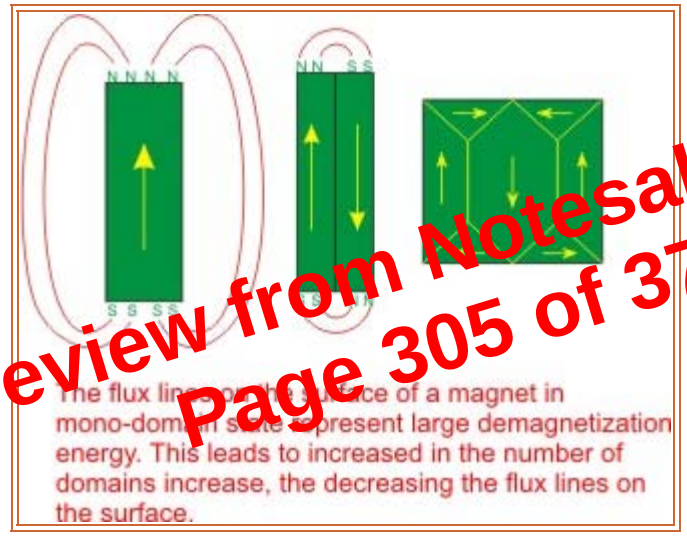


Figure 6.13 Formation of domains in a ferromagnetic material

Again, the formation of domains and their size in these materials is basically due to balance between various kinds of energies associated:

- Exchange energy (we will see its origin later) which makes the magnetic moments align in one direction without violating Pauli's exclusion principle;
- Magnetostatic energy in response to the flux lines at the surface of the material in the mono-domain state which increases as alignment increases or in other words high surface magnetic charges;
- Magnetocrystalline or anisotropy energy which, due to coupling between the spins and crystal lattice or spin-orbit coupling, is dependent on the crystal structure governing the direction of magnetic moment orientation as there are some crystallographic directions along which the sample is easy to magnetize than others such as for most cubic materials [111] is the easy axis except for those containing cobalt which have [100] as easy axis. As a consequence, hard and easy directions have different coercivities; and

6.6.4 Molecular Field Theory

Now the question arises: What leads to this ordering and what is the effect of the ordering of magnetic moment? This ordering or shall we say a neighbour effect gives rise to a modified internal field experience by these magnetic moments (often denoted as magnetic dipoles) in a sort of a similar manner as we witnessed in the derivation of Claussis Mossotti relation in dielectrics.

In 1907, Weiss postulated that mutual interaction between the magnetic moments keeps them parallel and aligned together (wrongly!) subscribing this to an internal field (not wrong!). This extra field or called as Weiss molecular field, H_w plays a crucial role in keeping the moments aligned in one direction.

H_w is expressed as a product of magnetization with a molecular field constant γ a characteristic of the material. Hence, this internal field can be expressed as

$$H_i = H + H_w = H + \gamma M \tag{6.32}$$

Now, for a ferromagnetic material, we need to replace H with H_i in equation (6.23 and 6.24) which leads to

$$\frac{M}{H + \gamma M} = \frac{C}{T} \tag{6.33}$$

OR

$$M = \frac{CH}{T - \gamma C} \tag{6.34}$$

OR

$$\frac{M}{H} = \frac{C}{T - T_c} \tag{6.35}$$

where $T_C = \gamma C$ and it has a unit of temperature and is called as Curie temperature. This is Curie-Weiss Law!

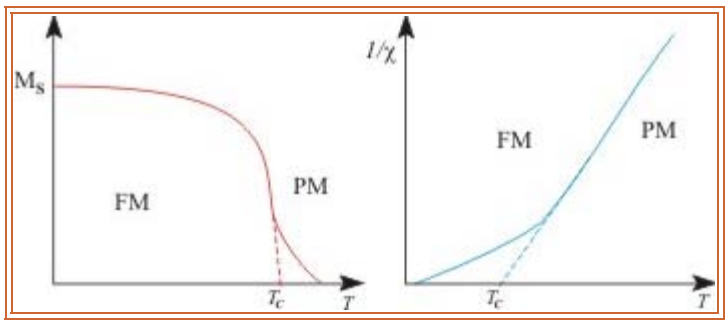


Figure 6.15 Schematic plot of susceptibility and magnetization vs

6.8 Ferrimagnetic Materials

These are materials which again, like antiferromagnetic materials, show antiparallel alignment of moments at particular atomic sites i.e. magnetic moment of one crystal sub-lattice is anti-parallel to the other. But since most of these materials consist of cations of two or more types, sub-lattices contain two different types of ions with different magnetic moment for two types of atoms and as a result, net magnetization is not equal to zero. The examples of such materials are various kinds of cubic spinel ferrites such as $NiFe_2O_4$, $CoFe_2O_4$, Fe_3O_4 (or $FeO.Fe_2O_3$), $CuFe_2O_4$ etc. Other examples are hexagonal ferrites likes $BaFe_{12}O_{19}$, garnets such as $Y_3Fe_5O_{12}$, represented by a general formula $R_3Fe_5O_{12}$ where R, in addition to yttrium can be one of lanthanide atoms such as lanthanum, cerium, samarium etc.

A schematic representation of this inequality in the neighbouring magnetic moment can be like this:

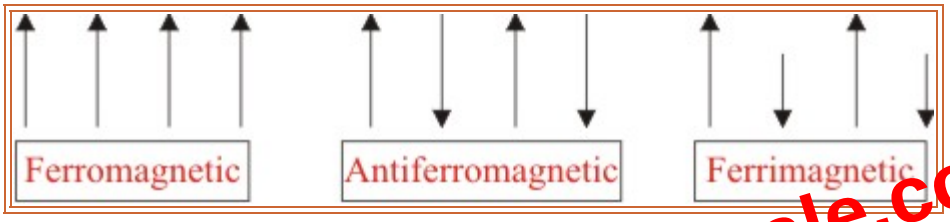


Figure 6.18 Magnetic moment arrangements in magnetically ordered materials

These materials also follow a temperature dependence of magnetization and susceptibility near Curie transition (actually Néel transition) in a similar manner as shown by the ferromagnetic materials. These materials, like ferromagnetic materials, show significantly large magnetization below the magnetic transition temperature and hence, often the temperature dependent behavior is clubbed with that of ferromagnetic materials.

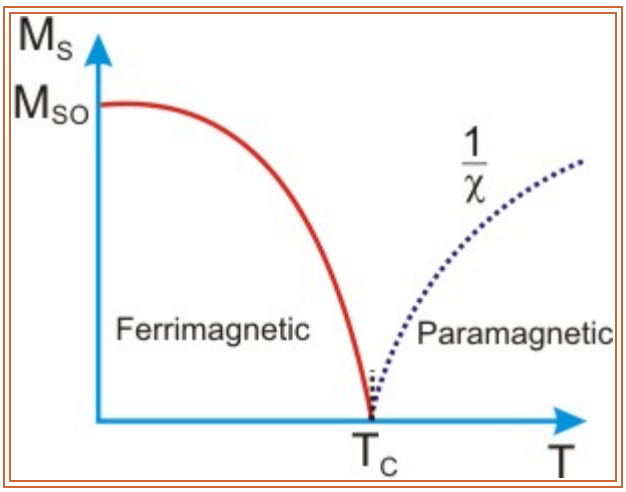


Figure 6.19 Temperature dependence of magnetization and susceptibility in a ferrimagnetic material

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6.11.5 Applications of Magnetic Ceramics

- **In electronic inductors, transformers and electromagnets**

  Soft ferrites like Mn-Zn and Ni-Zn ferrites are used as core materials in these applications in the frequencies ranging from a 100 kHz to 100 MHz. Typically these ferrites have high electrical resistance which results in very low eddy current losses. Most common radio magnets, including those used in loudspeakers, are ferrite magnets. Ferrite magnets have largely displaced Alnico magnets in these applications.

  Ferrites are also used for power transformers which are used to transmit either over a single frequency or within a range such as in ultrasonic generators. For high frequency applications, upto about 5 MHz, Ni-Zn ferrites are useful while for frequencies upto 100 kHz, Mn-Zn ferrites are preferred due to their higher permeabilities.

- **Equipment shielding**

  Here, due to their high impedance to high frequency currents, ferrite components of Ni-Zn and Mn-Zn ferrites are able to prevent high frequency electrical noise due to electromagnetic interference from exiting or entering the equipment.

- **Data storage (e.g. magnetic recording tapes and hard disks)**

  In the magnetic tapes, elongated 0.2-.5 μm long hard magnetic oxide particles of γ - Fe_2O_4 are embedded in nonmagnetic binder. The particles have single domains magnetized along their major axes which are aligned in the plane of the tape. The coercive fields are typically between 50-100 $kA.m^{-1}$. In magnetic hard-disks, core element is produced by forming several layers of materials (nonmagnetic underlayer, magnetic layer, overcoat, plus layer of lubricants on a nonmagnetic disk substrate). Here, the read/write head is not in direct contact with the hard disk (in contrast to floppy disk) due to an air bearing (˜ 50 nm); air flow is caused by the relative velocity between disk and head. These memories have high storage density of about 10 $GB.in^{-2}$ and short access time.

  Early computer memories stored data in the residual magnetic fields of hard ferrite cores, which were assembled into arrays of core memory. Ferrite powders are used in the coatings of magnetic recording tapes. One such type of material is iron (III) oxide.

- **Absorbing materials**

  In stealth aircrafts, ferrite particles are used as a component of radar-absorbing materials or coatings and in the absorption tile lining in the rooms used for electromagnetic compatibility measurements.

- **Microwave applications in the frequency ranges of 1-300 GHz**

  Materials like Mg-ferrites, Li-doped Ferrites and garnets are used for such applications such as phase shifters, circulators and isolators.

Summary

In this module, we have learnt the basics of magnetism where we saw that while diamagnetism is inherently present in all materials, the contribution is masked by paramagnetism or ferromagnetism in some materials. Diamagnetism in most materials is characterized by small but negative magnetic susceptibility while paramagnetic materials exhibit small and positive susceptibilities. In contrast ferro- and ferrimagnetic materials show large and positive susceptibilities representing a strong magnetic response of the materials. While most ferromagnetic materials happen to be metals or alloys, many spinel structured oxide ceramics, especially those containing iron and other magnetic elements, e.g. Fe_3O_4 tend to be ferrimagentic. However, there are other oxide ceramics such as hexagonal ferrites and garnet structured oxides which also show reasonably large magnetic moments. These ferrites are useful for a variety of applications including electromagnets, shields, data storage devices and microwave applications.

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7.2 Meissner Effect

Meissner effect essentially describes the response of a superconducting material when placed in a magnetic field. It was discovered by W. Meissner and R. Ochsenfeld in Germany in 1933.

When a superconductor is placed in an external magnetic field H ($H < H_c$) and cooled belowT_C, the magnetic field does not penetrate into the material completely. The field penetrates up to a very small depth decaying exponentially and is of the order of 100 nm or so, and is called as London penetration depth, *l*.

The Meissner effect is often confused with the diamagnetism as predicted by Lenz's law which states that application of a changing magnetic field to a conductor induced a magnetic moment which opposes the applied field magnetic field. In a perfect conductor, an arbitrarily large current can be induced, and the resulting magnetization exactly cancels the applied field giving rise to $\chi = -1$.

In contrast, Meissner effect implies spontaneous expulsion of magnetic flux lines which occurs during transition to superconductivity. So when the material is in normal state at $T > T_C$, the flux lines would penetrate but when it reaches superconducting state at $T < T_C$, the magnetic flux lines would be abruptly expelled which is NOT Lenz's law. It is not a diamagnetic effect which, in a normal material, is caused by opposite moment developed due to orbiting electrons.

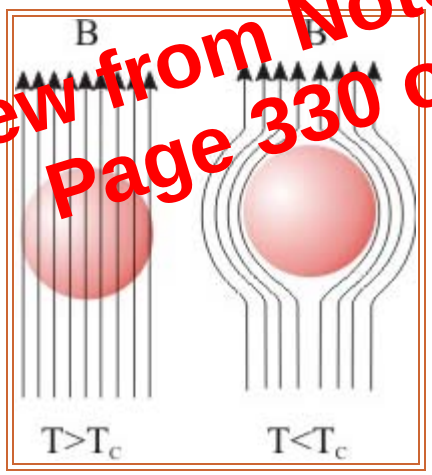

Figure 7.2 Meissner Effect

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Zero resistance is potentially a fantastic property to have for conductors but since transition temperatures are below RT, the commercial applications are not financially viable. At the same time, wires of only YBCO would be very brittle given that it is a ceramic material. However, a few firms in US are trying to make taped wires where YBCO is grown on top of a nickel tape which provides it the strength without compromising on the T_C and current carrying capacity. However, any commercial products are yet to be witnessed.

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Summary

Summary

Superconductors are the materials which show a sudden drop of electrical resistance at a certain temperature when cooled below room temperature. While most superconductors of early generation were low T_C materials, next generation superconductors, layered oxides based on perovskite structure, were called as high T_C as materials showing T_C in the excess of liquid N_2 temperature. These have been successfully fabricated in various forms and examined at various places across the world. While the BCS theory explains the origin the superconductivity in the low T_C superconductors quite well, a well agreed theory for the high T_C ceramic oxides is yet to evolve. These have found applications in magnetically levitated trains and magnetic resonance imaging for medical applications.

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8.3 Requirements of a Magnetoelectric and Multiferroic Material

There are many material requirements which need to be fulfilled for a material to be called as multiferroic. For instance, for ferroelectricity, a material must be non-centrosymmetric to possess spontaneous electrical polarization and there are only a limited number of point groups (out of 32) which allow an unique polar direction. Similarly, spontaneous magnetic moment is permitted by 31 point groups. Out of these, 13 point groups allow occurrence of both the properties simultaneously. Since this is not a small number; it is probably unlikely that symmetry plays an important role in determining a multiferroic.

Electrically, while a ferroelectric material must be an insulator, it is not a constraint for a ferromagnetic material. For most ferromagnets, electronically speaking, the conductivity is due to high density of states at the Fermi level while the same is not true for ferroelectrics and insulators. However, there are a few magnetic oxides, such as half metallic magnets and ferrimagnetic oxides which show reasonable spontaneous magnetism while simultaneously being semiconducting or insulating.

As far as the chemistry of the material is concerned, most ferroelectrics require ions whose shells are filled and in case of perovskites the B-atom at the centre of BO_6 octahedra must have d^0 type electron configuration. In contrast, magnetic systems require d-orbitals to be partially occupied for magnetic ordering to develop. Latter also puts constraints to maintaining the center of symmetry in these systems.

Among type I multiferroics, multiple mechanisms of ferroelectricity have been proposed[5]. For example, in mixed perovskites, it has been suggested that d^0 ions being ferroelectrically active shift from the center of O_6 octaehdra while magnetic order is maintained by dn ions. In contrast, in materials like $BiFeO_3$, ferroelectricity is believed to arise due to the ordering of lone pairs of Bi in one direction such as [111]. Another proposed mechanism for ferroelectricity is charge ordering i.e. if after charge ordering has occurred, the sites have different charges and bonds turn out to be of unequal lengths. This is seen in materials like $TbMn_2O_5$. Finally, materials like $YMnO_3$ exhibit geometric ordering due to tilting of rigid MnO_5 polyhedra, resulting in Y and O atoms coming closer to each other forming dipoles.

Another factor that could be analyzed is the size of small cation, especially in the perspective of perovskites. However, upon comparison, one finds that this is not a valid argument as sizes vary considerably for different kinds of compounds.

Another contrast between ferroelectric and ferromagnetically ordered systems is that the way structure is distorted. While ferroelectrics undergo a phase transition as temperature changes, low temperature phase being non-centrosymmetric, ferromagnetic materials show significant Jahn-Teller distortion arising from partially filled d-shells. The latter is almost absent in most ferroelectrics as it has been postulated that Jahn-Teller distorted structure may have less driving force for off-center displacement of B-ions in the octahedra.

Another condition which ferroelectric materials show is that they possess a time reversal symmetry but do not exhibit a space inversion symmetry (i.e. polarization reverses in space). On the other

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the MnO_5 biprism is very small and cannot be considered to contribute toward ferroelectricity. Apparently it turns out that R ions (Y, here) contributes most toward ferroelectricity by having large R-O dipole moments. However, in reality, ferroelectricity in these materials has different origin and can be considered as accidental by-product. Similar to BO_6 octahedra in perovskite oxides (ABO_3), MnO_5 trigonal biprism in $RMnO_3$, tilts and rotates in order to ensure closest packed structure. Such tilting of MnO_5 trigonal biprism results in loss of inversion symmetry in the structure and brings about ferroelectricity.[22] Since the mechanisms of ferroelectric and magnetic ordering in the above materials are quite different in nature, giant effect of magnetoelectric coupling is understandably not present.[22]

Table 8.1 Lattice parameters, Neel temperature (T_N) and ferroelectric Curie (T_C) temperature, effective paramagnetic moment (μ_{eff}) and spontaneous polarization (P_S) of some common hexagonal manganites.[23,24,25]

Compound	a(Å)	c(Å)	T_N(K)	T_C(K)	μ_{eff} (in μ_B)	P_S ($\mu C.cm^{-2}$)
$ScMnO_3$	5.833	11.17	129	-	-	-
$YMnO_3$	6.139	11.39	80	920	89	5.5
$HoMnO_3$	6.142	11.42	76	873	11.1	5.6
$ErMnO_3$	6.112	11.40	80	833	10.5	-
$TmMnO_3$	6.092	11.37	86	>573	8.6	0.1
$YbMnO_3$	6.062	11.36	87	990	6.4	5.5
$LuMnO_3$	6.042	11.32	96	>750	5.2	7.5

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9.2.6 Liquid Phase Epitaxy (LPE)

In this process liquids are used to grow the films on a single crystal substrate in near-equilibrium processing conditions. It involves the precipitation of a crystalline phase as the film from a supersaturated melt onto a substrate which acts as both the template for epitaxy and a physical support for the film. Above liquidus temperature all the constituents dissolve into the liquid. However, for film growth as the liquid cools down, some of the constituents precipitate out of the solution and grow epitaxially on a suitable substrate. The typical growth rates for this process vary between 1 to 10 mm/min. LPE offers several advantages over other epitaxial deposition processes such as low-cost operation, good control of composition and thickness, and faster deposition rates. However disadvantages can be poor surface finish, complications in chemistry for the case of complex ternary or higher order systems and presence of volatile elements. LPE could be an attractive process for making coated conductors based on YBCO films and is being extensively studied.[29]

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