Insulating Materials

Dr. G. Naga Raju

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About the author:

Dr G. NagaRaju has 18 years experience in Education and Research. He is presently working as Associate Professor in the Department of Physics at Acharya Nagarjuna University, AndhraPradesh. He has obtained his Master degree in Physics with Solid State Physics as specialization and secured **Gold Medal** from Acharya Nagarjuna University. He obtained M.Phil and Ph.D. degree in Physics from the same University in the area of Glass Science. He has 53 research publications in refereed International Journals in the area of Glass Science, Material Science and Nano-Technology. His research interest includes Glass Ceramics, Nonlinear Optical Studies and Luminescence. He has presented more than 80 research papers in National & International Conferences/Seminars. He has guided and awarded Four (04) M.Phil and Three (03) Ph.D degrees. Presently he is guiding research scholars for their M.Phil. and Ph.D. degree in the Department of Physics, Acharya Nagarjuna University in the area of Glass Science. **He also published a chapter titled "**Dielectric dispersion in $ZnO-ZnF_2-B_2O_3$ glasses doped with WO_3"**Focus on Condensed Matter Physics** Chapter 5(2005) 147-181 (**Nova Science Publishers, U.S.A**). and **published a Book titled "Influence of some transition metal oxides into zinc oxy fluoro borate glasses".** (**ISBN: 978-93-84502-75-1, Agri-Biovet Press, New Delhi**).

Dr. G. Naga Raju
Associate Professor
Department of Physics
Acharya Nagarjuna University
Guntur-522 510
Email: gnaga9@gmail.com

DIELECTRIC PROPERTIES OF MATERIALS

1. Introduction

Dielectrics are insulators i.e., non-conductors of electricity. The function of any insulator is to prevent the flow of electricity through it when a potential difference is applied across its ends. These materials prevent the leakage of electrical charges in electrical devices. Substances like bakelite, PVC used in electrical wiring and pipes, polymer materials etc., come under this category. Dielectrics possess high resistivity values in the range 10^6 Ω-m to $10^{16}\Omega$-m. Under high voltage bias, they allow very little current (10^{-6} A to 10^{-14} A). They withstand very high voltages. The conduction phenomenon in dielectrics is mostly associated with ionic motion through defects or hopping of charges. They have no free charges. They consist of positively and negatively charged particles bound together. The fundamental action of the electrical field is to separate positive and negative charges of the entire volume of the dielectric, causing what is known as the polarization of the dielectric. Fig.1. shows the effect of polarization in a dielectric when external field E_0 is applied on a dielectric. We see that the net polarization charges produced at the faces of the dielectric, a positive charge on the right and a negative on the left; inside the medium there is no excess charge in any given volume element. The medium as a whole remains neutral, and the positive charge on the right is equal in magnitude to the negative charge on the left. These induced charges create their own electric field E_p called polarization field that is directed to the left, and thus oppose the external field E_0. When we add this polarization field E_p to the external
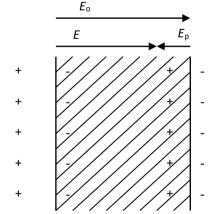

Fig.1. Effect of polarization in a dielectric.

field E_0, so as to obtain the effective field E, we find that $E<E_0$. Therefore, effect of introducing insulating substance (i.e., dielectric) results in reduction in applied field or reduction in surface charge density. Thus, the polarization of the medium reduces the electric field in its interior. During the polarization the

charges in the dielectric are displaced from their equilibrium positions by distances that are considerably less than atomic diameter. There is no transfer of charge over macroscopic distances such as occur when a current is set up in a conductor.

Dielectrics: Dielectrics are the insulating materials having electric dipoles permanently or temporarily by inducement during the application of electric field.

Electric Field Strength or Intensity (E): The space around the charged body, up to where its influence felt is called Electric Field. Suppose an additional infinitesimal test charge q_0 is brought into the electric field and at a certain point in it, it experiences an electrostatic force **F**. The electric field strength or intensity **E** at the point is a vector and defined by

$$\mathbf{E} = \frac{F}{q_0} \qquad \text{volt/metre}$$

Electric Field Induction (or) Flux density (or) Displacement Vector (D): Consider a charge q at the centre of a sphere of radius r. The charge q will send q lines of force and this will be received by surface area $4\pi\, r^2$. The number of electric lines of force received by a unit area is called flux density or electric displacement **D**.

$$\text{i.e., } D = \frac{q}{4\pi\, r^2} = \frac{q}{A} \text{ ; where } A \text{ is the surface area of the sphere,}$$

The unit of electric flux density is coulomb/metre^2.

Electric dipoles: The system of two equal and opposite charges separated by certain distance is called electric dipole is shown in Fig. 2.
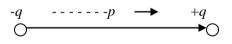

Fig.2 An electric dipole

Electric Dipole moment: The product of any one of two charges of dipole and the separation between them is called electric dipole moment.

Let the two charges are +q and –q separated by a distance r. The moment of this dipole is defined as

$$p = qr$$

The dipole moment is therefore equal to the magnitude of the one of the charges times the distance between them. The unit of electric dipole moment is esu-cm   (10^{-18} esu-cm = 3.3 x 10^{-30} C-m = 1 debye)

Polarization (P): The process of producing electric dipoles out of neutral atoms and molecules is known as polarization. Polarization **P** in a solid is defined as the total dipole moment per unit volume:

$$\mathrm{P} = \sum_n p_i \quad = \quad \frac{\sum_n q_i r_i}{V}$$

Here P is the total dipole moment (including the induced and permanent) and n is the number of dipoles per unit volume. Polarization P has the same units as the surface charge density (C-m^{-2}). This equivalence is substantiated by the fact that electric field induces charges on the surface of the dielectric and the density of charges is a measure of the extent of polarization.

Dielectric Constant: Dielectric constant or relative permittivity is defined as the ratio of permittivity of the substance to the permittivity of the free space,

Consider a parallel plate capacitor consisting of two plane parallel plates of area A and separation d, charged with a surface charge density σ. If the space between the plates is vacuum and if d is small compared with the dimensions of the plates.

Suppose now that the space between the plates is filled with an insulating substance the charge on the plates being kept constant. The new potential difference V is lower than V_{vac} and the capacitance is increased.

The **static dielectric constant**ε is then defined by

$$\varepsilon = \frac{V_{vac}}{V} \quad = \frac{C}{C_{vac}}$$

Thus, the field strength is reduced from the value E_{vac} to the value E, where

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

in other words, the effective surface charge density on the plates is now changed from $\sigma = \dfrac{E_{vac}}{4\pi}$

to $\sigma^1 = \dfrac{E}{4\pi}$.

The effect of introducing the insulating substance is thus to reduce the surface charge density by an amount

$$\sigma - \sigma^1 \quad = \quad \frac{E_{vac}}{4\pi} - \frac{E}{4\pi} \quad = (\varepsilon - 1) \frac{E}{4\pi}$$

Since the charge on the plates is being kept constant, the positive plate thus acquires a negative induced surface charge density $(\sigma - \sigma^1)$ and vice versa; whole of the dielectric becomes a single dipole of moment $(\sigma - \sigma^1)Ad$. Under this condition, and using equation we see that $(\sigma - \sigma^1) = P$. Thus, the quantity on the left hand side of the of equation is the *polarization* of the dielectric and we can write

$$P = (\varepsilon - 1) \frac{E}{4\pi}$$

The above explanation of the induction of charges at the surface of the dielectric is in accordance with that considered earlier.

$$D = E + 4\pi P = \varepsilon E$$

Dielectric constant expresses the properties of the medium: all dielectric and optical properties of the medium are contained in this constant.

Susceptibility (χ): It is defined as polarization per unit electric field.

$$\chi \quad = \frac{P}{E} \,;$$

It measures the amount of polarization a given field produces. In empty space P=0, $\chi = 0$, $\varepsilon = 1$.

Polarizability(α): The strength of the induced dipole moment an atom acquires is directly proportional to the strength of the external applied field

$$\text{i.e., } p \propto E$$

$$p = \alpha E$$

 where α is known as dielectric polarizability. We can relate polarizability α, which is an atomic property to the macroscopic property polarization P. It has the dimensions of volume.

1.1 polarizability:

Polarization occurs due to several microscopic mechanisms. Polarization is a consequence of the fact that when an electric field acts on a molecule/atom, its positive charges (nuclei) are displaced along the field while the negative charges (electrons) in a direction opposite to that of the filed. The opposite charges are thus pulled apart and the molecule is polarized. The displacements of electrical charges result

the formation of dipoles. Particularly in d.c. electric fields, the macroscopic polarization vector P is created by three types of mechanisms and hence polarization can be broadly classified into three types:

1. Electronic Polarization
2. Ionic Polarization
3. Orientational Polarization

1.1. (a) Electronicpolarization: Electronic polarization is due to displacement of charge centres of electron cloud (negative charge centre) and nucleus (positive charge centre) of an atom in the presence of an applied electric field.

Although we are interested in the dielectric properties of solids, it will be useful to consider first the much simpler problem of the behaviour of free atoms and molecules in an external field.

Consider an atom of a dielectric material such that its atomic number is equal to 'Z' and atomic radius 'r'. The centres of gravities of charges of electron cloud and positive nucleus are at the same point and hence there is no displacement. Suppose if the atom is placed in a d.c. electric field of strength 'E', the nucleus and the electron cloud experiences Lorentz forces of magnitude "ZeE" in opposite directions. i.e., nucleus and electron cloud are pulled apart, therefore an attractive coulomb force develop between them. When the Lorentz force and coulomb attractive forces are equal and opposite, there is a new equilibrium between the nucleus and the electron cloud of the atom and hence dipole is formed. Let the distance of separation between the centres of the displaced nucleus and electron cloud is 'd'.

In Fig. 3 atom without any field and atom with field.

Fig. 3. Atom without any field and atom with field.

The negative charge enclosed in the sphere of radius 'r' is equal to $\frac{4}{3}\pi d^3 \rho$

Where 'ρ' is the charge density of electron cloud, and is equal to $\left[\dfrac{-Ze}{\dfrac{4}{3}\pi r^3} \right]$

Therefore charge enclosed in the sphere of radius, d is,

$$= \frac{4}{3}\pi d^3 \left[\frac{-Ze}{\frac{4}{3}\pi r^3} \right] \qquad = \left[\frac{-Zed^3}{r^3} \right]$$

Therefore, Coulomb force of attraction, F_c

$$= \frac{Ze.[\text{charge enclosed in the sphere of radius d}].}{d^2}$$

$$F_c = \frac{-Ze.Zed^3}{d^2 r^3} = \frac{-Z^2 e^2 d}{r^3}$$

Lorentz force of repulsion experienced by the electron due to applied field 'E' is

$$F_L = -ZeE$$

In equilibrium condition,

$$\frac{-Z^2 e^2 d}{r^3} = -ZeE$$

$$E = \frac{Zed}{r^3}$$

$$d = \frac{r^3}{Ze}E$$

$$\Rightarrow d \propto E$$

i.e., the separation between the two charge centres is proportional to the applied field 'E'.

The induced electric dipole moment,
$$p = Zed = r^3 E,$$

and the induced polarizability

$$\alpha_e = \frac{p}{E} = r^3$$

Hence, α_e has the dimensions of a volume. It is also evident that in general atoms with many electrons tend to have a larger polarizability than those with few electrons.   Electrons in the outer electronic shells

will contribute more to α_e than do electrons in the inner shells, because the former are not so strongly bound to the nucleus as the latter. Positive ions therefore will

have relatively small polarizabilities compared with the corresponding neutral atoms: for negative ions the reverse is true.

1.1. (b) Ionic polarization

Ionic polarization is due to the displacement of positive ion and negative ion of a molecule in the presence of an applied electric field and occurs in ionic crystals. One might suppose that an ionic crystal would possess polarization even in the absence of an electric field, since each ion pair constitutes an electric dipole. But this is not so, because the lattice symmetry ensures that these dipoles cancel each other every where. So, the polarization in ionic crystals arises due to the fact that the ions are displaced from their equilibrium positions by the force of the applied electric field.

Consider an ionic compound composed of positive and negative ions separated by inter atomic distance, r_0, then the dipole moment is 'er_0' in the absence of applied field. When the field E_0 is applied to the molecule, the positive ion is displaced in the direction of field and negative ion is displaced in opposite direction until ionic bonding forces stop the process.

Due to the ionic displacement the resultant dipole moment increases and is given by

$$p = e\,(x_1 + x_2)$$

where x_1 is the shift of positive ion and x_2 is the shift of negative ion with respect to their equilibrium position.

Due to the application of static electric field $\mathbf{E_0}$, the force produced may be taken as $\mathbf{F}$ newtons and the restoring force on positive ion is $\beta_1 x_1$ and the restoring force on negative ion is $\beta_2 x_2$. Here β_1 and β_2 are restoring force constants which depend upon the mass of ion and angular frequency of the molecule in which ions are present.

Therefore, under equilibrium

$$F = \beta_1 x_1 = \beta_2 x_2$$

$$x_1 = \frac{F}{\beta_1} = \frac{eE_0}{m\omega_0^2}$$

where m is the mass of the positive ion and

$$F = eE_0 \text{ and } \beta_1 = m\omega_0^2$$

Similarly, for negative ion

$$x_2 = \frac{eE_0}{M\omega_0^2}$$

where M is the mass of negative ion.

Therefore, $(x_1+x_2) = \dfrac{eE_0}{\omega_0^2}\left(\dfrac{1}{m}+\dfrac{1}{M}\right)$

dipole moment

$$p = e(x_1+x_2) = \frac{e^2 E_0}{\omega_0^2}\left(\frac{1}{m}+\frac{1}{M}\right)$$

Ionic polarizability

$$\alpha_i = \frac{p}{E_0} = \frac{e^2}{\omega_0^2}\left(\frac{1}{m}+\frac{1}{M}\right)$$

Thus ionic polarizability α_i is inversely proportional to the square of the natural frequency of the ionic molecule and to its reduced mass where reduced mass

$$\left(\frac{1}{m}+\frac{1}{M}\right)^{-1}$$

1.1.(c) OrientationalPolarization

 Orientation polarization is due to the alignment of dipoles of polar molecules in the presence of applied electric field. Polar molecules have permanent dipole moments even in the absence of an electric field. These polar molecular dipoles are randomly distributed in space in the absence of an electric field and hence the net dipole moment of the dielectric is zero. But when dielectric is kept under electric field, the field produces a torque in individual dipoles and there is a tendency for the field to align dipole with the field and a net dipole moment per unit volume is originated in the dielectric. If the field is strong enough, the dipoles may completely be aligned along the field direction. The polarization due to the orientation, i.e, orientational polarizability 'α_o'. Fig. 4.Represents the orientational polarization of dipoles.

E=0 $\vec{E}$

(a)   (b)

dipoles in the   dipoles in the

absence of 'E'   presence of 'E'
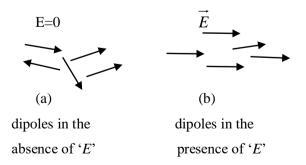
Fig. 4. Orientational polarization.

Consider for example, a gas containing a large number of identical molecules, each with a permanent dipole moment p. Without an external field, the dipoles will be oriented at random and the gas as a whole will have no resulting dipole moment. An external field E will exert a torque on each dipole and will tend to orient the dipoles in the direction of the field. In Fig. 5torque applied by a field on a dipole.
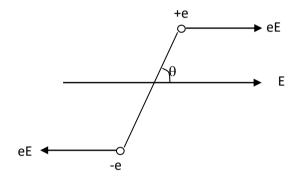

Fig. 5 Torque applied by a field on a dipole.

On the other hand, the thermal motion of the dipoles will counteract this ordering influence of the external field. Therefore, an equilibrium state will reach in which different dipoles will make zero to π radian angles with the field direction, producing a net polarization in the direction of the field. It is this polarization that we are going to calculate.

Let us define the potential energy of a dipole making a 90^0 angle with the external field as zero. The potential energy corresponding to an angle θ between p and E is equal to

$$-p\,E\,\cos\theta = p.E$$

According to statistical mechanics, the probability for a dipole to make an angle between θ and $\theta+d\theta$ with the electric field is then proportional to

$$2\pi \sin\theta \, d\theta \, \exp[(pE\cos\theta)/kT]$$

where $2\pi \sin\theta \, d\theta$ is the solid angle between θ and $\theta+d\theta$. The number of dipoles having their orientation between θ and $\theta+d\theta$ is also proportional to this probability. Now a dipole of moment p making an angle θ with the field direction contributes to the polarization a component $p\cos\theta$. Hence the contribution made by the above number of dipoles is

$$p\cos\theta.\ 2\pi \sin\theta \, d\theta \, \exp[(pE\cos\theta)/kT]$$

and the average contribution per dipole $\bar{p}$ is given by

$$\bar{p} = \frac{\int\limits_0^\pi p\cos\theta\, 2\pi\sin\theta\, d\theta\, \exp\!\left[(pE\cos\theta)/kT]\right]}{\int\limits_0^\pi 2\pi\sin\theta\, d\theta\, \exp[(pE\cos\theta)/kT]}$$

($\theta = 0$ corresponds to parallel alignment and $\theta = \pi$ corresponds to anti parallel alignment of dipoles).

Dividing numerator and denominator by 2π and letting

$$a = \frac{pE}{kT}\ , \qquad\qquad x = a\cos\theta\ , \qquad\qquad dx = -a\sin\theta\, d\theta,$$

$$\bar{p} = \frac{p\int\limits_a^{-a} x e^x\, dx}{a\int\limits_a^{-a} e^x\, dx}$$

$$\frac{\bar{p}}{p} = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} = \coth a - \frac{1}{a} = L(a)$$

The function L(a) is called the Langevin function, since this first derived by Langevin in connection with the theory of paramagnetism.   As a increases, the function continues to increase, approaching the saturation value unity as $a \to \infty$. This situation corresponds to complete alignment of the dipoles in the field direction.
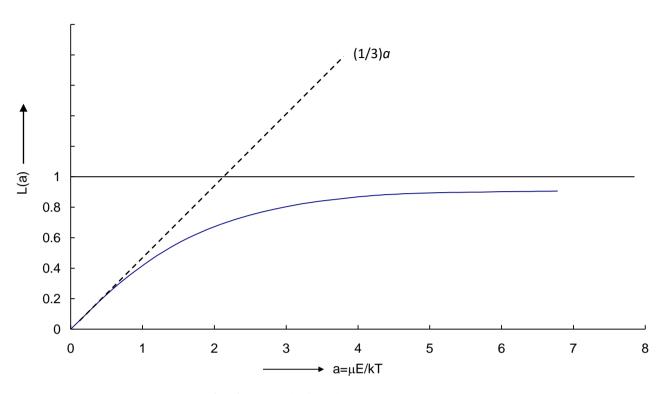
Fig. 6. Langevin function L(a) verses a

The above Fig. 6 presents the as long as the field strength is not too high and the temperature is not too low, the situation may be strongly simplified by making the approximation a<<1 or $\frac{pE}{kT}$ <<kT. Under these circumstances the Langevin function L(a) = a/3,

$$\frac{\overline{p}}{p} = L(a) = \frac{a}{3} = \frac{pE}{3kT}$$

$$\overline{p} = \frac{p^2}{3kT} E$$

Hence, orientational or dipolar polarizability

$$\alpha_o = \frac{\overline{p}}{E} = \frac{p^2}{3kT}$$

Hence, orientational polarizability α_o decreases with temperature. Since higher is the temperature, greater is the thermal agitation and lower is 'α_o'

A large number of molecules have polarizability, yet not all the molecules. The deciding factor for its existence is simply whether or not the molecules have a permanent moment. The existence of a permanent moment is purely a matter of molecular geometry. For example, CO_2 has no permanent moment at all, because its atoms are in line. On the other hand different geometry of H_2O molecule gives p=1.87 Debye units to it.

Actually applicable to liquids and gases, because only in these substances the molecular dipole moment may rotate as continuously and freely as has been assumed in its derivation. In solids, a dipole may hop back and forth between certain discrete orientations in a manner which depends on the temperature and the electric field.

ALTERNATING FIELDS OF DIELECTRIC MATERIALS

2.1 Introduction

We now take up the study of the behaviour of dielectrics in alternating electric fields. Here again we make use of the same basic atomic models used earlier and study the behaviour of this model in alternating electric field. This study reveals that the dielectric constant under these conditions is a complex quantity. The imaginary part of this complex dielectric constant determines the dielectric losses of the material.

In the macroscopic theory of isotropic dielectrics under static fields, the electric flux density D is proportional to the electric filed intensity E, so the D = ε E, where ε is a constant defined as the electric permittivity and is a property of the dielectric.

When a dielectric material is subjected to an alternating field the orientation of the dipoles, and hence the polarization, will tend to reverse every time the polarity of the field changes. As long as the frequency remains low (<10^6 c/s) the polarization follows the alternations of the field without any significant lag and the permittivity is independent of the frequency and has the same magnitude as in static field. When the frequency is increased the dipoles will no longer be able to rotate sufficiently rapidly so that their oscillations will begin to lag behind those of the field. As the frequency is further raised the permanent dipoles, if present in the medium, will be completely unable to follow the field and the contribution to the static permittivity from this molecular process, the orientation polarization ceases; this usually occurs in the radio frequency range (10^6-10^{11} Hz) of the electromagnetic spectrum. At still higher frequencies, usually in the infra-red (10^{11}-10^{14} Hz) the relatively heavy positive and negative ions cannot follow the field variations so that the contribution to the permittivity from the atomic or ionic polarization ceases and only the electronic polarization remains.

The above effects lead to fall in the permittivity of a dielectric material with increasing frequency, a phenomenon which is usually referred to as **anomalous dielectric dispersion**.

Dispersion arising during the transition from full atomic polarization at radio frequencies to negligible atomic polarization at optical frequency is usually referred to as **resonance absorption.**

Dispersion arising during the transition from full orientational polarization at zero or low frequencies to negligible orientational polarization at high radio frequencies is referred to as **dielectric relaxation.**

It should be possible to explain the frequency dependence of the dielectric constant directly in terms of the electronic structure. It is known that the refractive index varies with the wavelength of light in the optical region the phenomenon being known as dispersion. Dispersion can be explained on the basis of classical theory which assumes that atom contains electrons vibrating at certain natural frequencies characteristic of the atom and that the application of an alternating field sets such electrons into forced vibration. Since the molecules in a dielectric are represented as dipoles on bound charges, there must be equal number of positive charges and negative charges because the dielectric is a neutral medium. When an electromagnetic wave impinges on this bound charge, it is caused to oscillate and therefore to radiate. If the frequency of the wave is not equal to the natural frequency of the bound charge the forced oscillation will have small amplitude and the radiation is very weak. This corresponds to molecular scattering. If the frequency of the wave is equal to the natural frequency of the bound charge, there is resonance and a much larger energy form the wave goes into the charge. In solid, liquid or gas at high pressure there is strong intermolecular action and friction type forces cause heavy damping with the result that the dipole energy is quickly dissipated. This corresponds to true absorption. In a gas at low pressure there is no damping and the dipole radiate strongly. This is resonance radiation. The absorption of an electromagnetic wave by a conducting medium is easily explained because the conduction has a large number of free electrons. When the wave arrives its energy makes the charge move. The moving charge constitutes current and the usual dissipation of energy by the current explains the absorption of energy.

At optical frequencies the permittivity is almost entirely due to the electronic polarization. To determine the dependence of the electronic polarizability on the frequency of the applied field we shall use the classical model of an electron elastically bound to the atom.

2.2 The complex dielectric constant and Dielectric Losses

When a dielectric is kept between a capacitor plates is subjected to an alternating field the polarization P also varies periodically with time and so does the displacement D. In general however P and D may lag behind in phase relative to E so that for example if

$$E = E_o \cos\omega t$$

we have

$$D = D_0 \cos(\omega t - \delta)$$

$$=D_0 \cos \delta \cos \omega t + D_0 \sin \delta \sin \omega t$$

$$= D_1 \cos \omega t + D_2 \sin \omega t$$

where δ is the phase angle,

$$D_1 = D_0 \cos \delta \text{ and } \qquad D_2 = D_0 \sin \delta.$$

For most dielectric D_o is proportional to E_o but the ratio (D_o/E_o) is generally frequency dependent. To describe this situation one may thus introduce two frequency dependent dielectric constants,

$$\varepsilon^1 = \frac{D_1}{E_o} = \frac{D_o}{E_o} \cos \delta$$

$$\varepsilon^{11} = \frac{D_2}{E_0} = \frac{D_0}{E_0} \sin \delta$$

It is frequently convenient to sum these two constants into a single complex dielectric constant,

$$\varepsilon^* = \varepsilon^1 - i\varepsilon^{11}$$

Thus $$D = \varepsilon^* E_0 e^{i\omega t} = \varepsilon^* E_0 (\cos \omega t + i \sin \omega t)$$

Also we see that

$$\tan \delta = \frac{\varepsilon^{''}}{\varepsilon^{'}}$$

Because both ε^1 and ε^{11} are frequency dependent the phase angle δ is also frequency dependent. We shall now show that the energy dissipated in the dielectric in form of heat is proportional to ε^{11}.

The current density in the capacitor is equal to $\dfrac{d(D)}{dt}$.

Thus $$J = \frac{d}{dt}(\sigma) \quad = \quad \frac{1}{4\pi} \frac{dD}{dt}$$

$$= \frac{\omega}{4\pi} \left(-D_1 \sin \omega t + D_2 \cos \omega t \right)$$

The energy dissipated or absorbed per second in the dielectric is given by

$$W = \left(\frac{\omega}{4\pi} \right) \int_0^{2\pi/\omega} JE \, dt$$

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$$W = \frac{\omega}{4\pi} \left[\int_{0}^{2\pi/\omega} \omega \left(-D_1 \sin \omega t + D_2 \cos \omega t \right) E_o \cos \omega t \, dt \right]$$

$$W = \frac{\omega}{4\pi} \left[-\omega \int_{0}^{2\pi/\omega} E_0 D_1 \sin \omega t \cos \omega t \, dt \quad + \omega \int_{0}^{2\pi/\omega} E_o D_2 \cos^2 \omega t \, dt \right]$$

The value of integral containing D_1 is equal to zero and we are left with

$$W = \left(\frac{\omega}{8\pi}\right) D_2 E_o = \frac{\omega}{8\pi} E_0^2 \varepsilon^{11}$$

the amount of energy absorbed is proportional to $\sin\delta$ since $\varepsilon^{11} = (D_0/E_0) \sin \delta$. The energy so dissipated in the dielectric medium is referred to as the dielectric loss. For this reason $\sin\delta$ is called the loss factor and δ is the loss angle (but it is customary) to call $\tan\delta$ as the loss factor; this is correct only for small values of δ because $\tan\delta \approx \sin\delta \approx\delta$. The dielectric loss at low frequencies is mainly due to d.c. resistivity. But at high frequencies the dielectric loss is mostly due to dipole rotations or to ionic transitions from the lower energy states to higher energy states. Because of the upward transition the energy is absorbed from the applied field. The losses associated with ions, the frequency of which fall in the infrared region, are usually referred to as optical infrared absorption. Similarly, the losses in the optical region, associated with the electrons, are referred to as optical absorption.

2.3 Dielectric Losses and Relaxation time

Let us consider a dielectric, for which the total polarization P_s in a static field is determined by three contributions,

$P_s = P_e + P_i + P_o$

In general, when such a substance is suddenly exposed to an external static field, a certain length of time is required for P to be built up to its final value. In the present section it will be assumed that the values of P_e and P_i are attained instantaneously, i.e., we shall be concerned with frequencies appreciably smaller than infrared frequencies. The time required for orientational polarization, P_o to reach its static value may vary between days and 10^{-12} second, depending on temperature, chemical constitution of the material, and its physical state is called relaxation time.

To begin with we shall give a phenomenological description of the transient effects based on the assumption that a relaxation time can be defined; we can then proceed to consider the case of an

alternating field. Let P_{os} denote the saturation value of P_o as function of the time after the field has been switched on is given by

$$P_o(t) = P_{os}(1- e^{-t/\tau})$$

where τ is the relaxation time.

$$dP_o/dt = (1/\tau) [P_{os} - P_o (t)]$$

For the decay occurring after the field has been switched off, this leads to a well–known proportionality with $e^{-t/\tau}$. In the case of an alternating field $E = E_0 e^{i\omega t}$, equation may employed if we make the following change: P_{os} must be replaced by a function of time $P_{os}(t)$ representing the saturation value which would be obtained in static field equal to the instantaneous value $E(t)$. Hence for alternating fields we shall employ the differential equation

$$dP_o/dt =(1/\tau) [[P_{os}(t) - P_o (t)]$$

Now, our final goal is to express the real and imaginary parts of the dielectric constant in terms of the frequency ω and the relaxation time τ. For this purpose we shall define the "instantaneous" dielectric constant ε_{ei} by

$$P_e + P_i = (\varepsilon_{ei} - 1)/4\pi \quad E$$

We may then write

$$P_{os} = P_s - (P_e + P_i) = (\varepsilon_s - \varepsilon_{ei})/4\pi \quad E$$

Where ε_s is the static dielectric constant and εei is the dielectric constant arising due to electronic and ionic polarization.   Substitution of P_{os}

$$dP_o/dt = (1/\tau)[(\varepsilon_s - \varepsilon_{ei})/4\pi \quad E_0 e^{i\omega t}- P_o]$$

Solving this equation, we obtain

$$P_o(t) = Ce^{-t/\tau} + 1/4\pi \ (\varepsilon_s - \varepsilon_{ei})/(1+i\omega\tau) E_0 e^{i\omega t}$$

The first term represents a transient. The total polarization is now also a function of time and is given by $P(t) = P_e + P_i + P_o(t)$. Hence, for the displacement one obtains

$$D(t)= \varepsilon^* E(t) = E(t) + 4\pi P(t)$$

where ε^* is the complex dielectric constant. From the last two equations and from the definition $\varepsilon^* = \varepsilon^1 - i \varepsilon^{11}$ the following expressions result:

$$\varepsilon^1(\omega) = \varepsilon_{ei} + (\varepsilon_s - \varepsilon_{ei})/(1+i\omega^2\tau^2)$$

$$\varepsilon^{11}(\omega) = (\varepsilon_s - \varepsilon_{ei}) \ \omega\tau/(1+i\omega^2\tau^2)$$

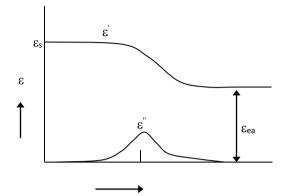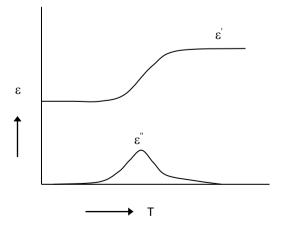These equations are frequently referred to as the **Debye's equations is shown in Fig. 1..**

Fig. 1 Debye curves for ε' and ε'' as function of frequency for a dielectric with a single relaxation time

loss, which is proportional to ε^{11}, exhibits a maximum for $\omega\tau = 1$, i.e., for an angular frequency equal to $1/\tau$. Also, for frequencies appreciably less than $1/\tau$, the real part of the dielectric constant ε^1 become equal to the static dielectric constant. In this frequency range, therefore, the losses vanish and the dipoles contribute their full share to the polarization. On the other hand, for frequencies larger than $1/\tau$, the dipoles are no longer able to follow the field variations and the dielectric constant ε^1 approaches ε_{ei}.

Note that for this type of mechanism the relaxation time decreases with increasing temperature as so does the saturation polarization. It is of interest to observe that if the quantities ε^1 and ε^{11} are measured at a constant frequency but at different temperatures, the curves as indicated in Fig. 2 may be expected to result.

Fig.2 The dielectric constant as a function of temperature at a given frequency, as predicted from the model discussed in the text

2.4 The classical theory of electronic polarization and optical absorption

The concept of the static polarizability due to elastic displacements of electrons and ions was introduced. In the present section the classical theory of this phenomenon in alternating fields will be discussed. We have seen that restoring force determining the displacement is in first approximation proportional to the displacement itself. The discussion is therefore based on the model of a displacement itself. The discussions is therefore based on the model of an elastically bound particle of charge e and mass m in an alternating field $E_0 e^{i\omega t}$ may be written

$$m\frac{d^2x}{dt^2} + m\gamma\frac{dx}{xt} + m\omega_0^2 x = e\ E_0 e^{i\omega t}$$

where ω_0 is the natural angular frequency of the particle; $\omega_0 = (f/m)^{1/2}$ where f is the restoring force constant ; the second term on the left – hand side is a damping term, which results from the fact that the particle emits radiation as a consequence of its acceleration and γ is the damping factor. The solution for this forced damped vibration is

$$x(t) = \frac{e}{m} \cdot \frac{E_0 e^{i\omega t}}{\omega_0^2 - \omega^2 + i\gamma\omega}$$

We first of all note that in a static field, for $\omega = 0$, this reduces simply to

$$x = eE_0/m\omega_0^2 \text{ or } \alpha_s = ex/E_0 = e^2/m\omega_0^2 \text{ for } \omega = 0$$

Where α_s is static polarizability associated with the elastically bound particle. If we take for e and m the electronic charge and mass, this expression would correspond to the contribution of a particular electron to the electron polarizability. The electronic polarizabilities are of the order of 10^{-24} cm^3; this gives a natural frequency $\nu_0 = \omega_0/2\pi \cong 10^{15}$ per second. Thus, even for frequencies corresponding to the visible spectrum, the electronic polarizability may be considered constant. If e and m refer to an ion, the natural frequencies are of the order of 10^{13} per second, corresponding to the infrared part of the spectrum.

The electronic polarizability is therefore

$$\alpha_e = \frac{ex}{E} = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega}$$

The complex dielectric constant is then given by

$$\varepsilon(\omega) = 1 + \frac{4\pi Ne^2}{m} \cdot \frac{1}{\omega_0^2 - \omega^2 + i\gamma\omega}$$

where N is the number of electrons per unit volume. This follows by using P = Nex and $\varepsilon = 1 + 4\pi P/E$.

Now, from the definition of the complex dielectric constant $\varepsilon(\omega) = \varepsilon^1(\omega) - i\varepsilon^{11}(\omega)$

One finds

$$\varepsilon^1(\omega) = 1 + \frac{4\pi Ne^2}{m} \frac{\omega_{0-}^2\omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}$$

$$\varepsilon^{11}(\omega) = \frac{4\pi Ne^2}{m} \frac{\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}$$

It may be noted that $\varepsilon^1(\omega)$ gives us the value of the dielectric constant and from $\varepsilon^{11}(\omega)$ we get the power dissipated and hence the damping loss. The variation of $(\varepsilon^1 - 1)$ and ε^{11} these with frequency is shown in Fig .3.
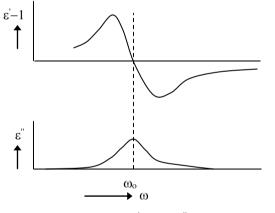

Fig.3 Behaviour of $\varepsilon_o{}'$ and $\varepsilon_o{}''$ as function of frequency in the vicinity of the resonance frequency ω_o

maximum at $\omega = \omega_0$. The meaning of this maximum is that the material absorbs energy at the natural frequency; this type of absorption is called resonance absorption. In the absorption region, the dielectric constant ε^1 depends on frequency and one speaks in this connection of **dispersion**. The region for which ε^1 decreasing with frequency is referred to as the region of **anomalous dispersion**.

2.5.Total Polarizability

Let us now discuss the total polarizability $\alpha = \alpha_o + \alpha_i + \alpha_e$. It has been found that the total polarizability of a dielectric substance shows marked difference in behavior when studied as a function of frequency. To summarize the frequency-dependence of the polarizability we have represented, in Fig.4, $\alpha(\omega)$ for a dipolar substance. It is clear that as we go from the static to the optical region, the polarizability α decreases by a substantial amount. Speaking in terms of dielectric constant, the dielectric constant of water, for example is 81 at zero frequency while it is only 1.8 at optical frequencies. Moreover, the decrease in polarizability α is not uniform –remarkable decrease occurs only in the microwave, infrared and ultra-violet regions.
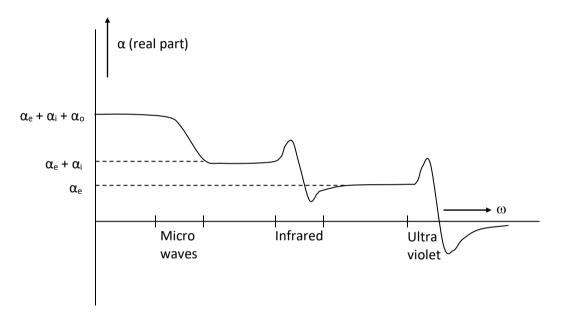

Fig. .4 Variation of total polarizability as a function of frequency.

The behaviour of polarizability can be understood from the various possesses and from the concept of the relaxation time for each process. When the frequency of the applied field is much greater than the inverse of the relaxation time for a particular polarization process, that particular polarization process fails and so it does not contribute to polarizability. Thus, the decrease of total polarizability with increase in frequency is due to the disappearance of α_o, α_i and α_e successively.

2.6 Measurement of Dielectric constant

Dielectric constant of a given substance is usually measured by comparing the capacity C_d of a condenser filled with the substance and the capacity C_0 of a the empty condenser . The ratio $\dfrac{C_d}{C_0}$ = ε, is the dielectric constant. The capacities C_d and C_0 may be measured by resonance method as shown in the Fig .5.
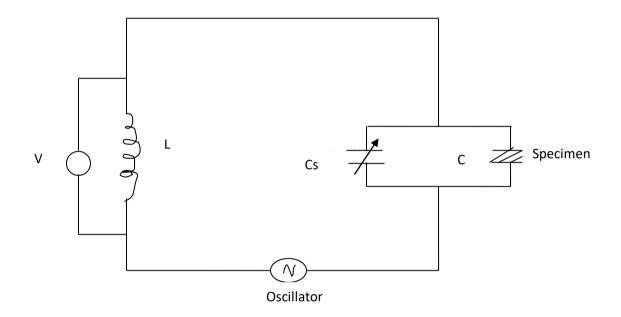

Fig. 5 Principle of the resonance method for measuring C_o and C_d.

In the figure, Cs is a calibrated variable condenser and C is the condenser in which the given substance which is taken in the form of a thin disc may be placed. By varying Cs so keep the resonance frequency

$$\omega o = \frac{1}{\sqrt{[L(C_s + C)]}}$$

constant when C is empdty and then filled, we may determine C0 and Cd, and hence ε. The voltmeter V measures the response of the resonant circuit.

This method is generally used to measure the dielectric constant up to frequencies 100 Mhz. At the microwave region ($\sim 10^3$ to $\sim 10^5$ Mhz) the frequencies are so high that the dimensions of the apparatus are comparable with or greater than the wavelength, and the specimen hen can no longer be treated as if it were in quasi-static fields. Rather, it has to be treated as a medium for the propagation of electromagnetic waves. Here we may measure the dielectric constant of the specimen by measusring the wavelength of the microwave radiation in the specimen and using the relation

$$\frac{\lambda_{vvacuum}}{\lambda_{specimen}} = (\varepsilon\mu)^{1/2}$$

where μ is the permeability; for non-magnetic materials,$\mu \approx 1$. For optical and infrared frequencies, ε can be measured by measuring the refractive index, n as

$$n^2 = \varepsilon\mu \approx\varepsilon$$

2.7 Outline of the lesson

When a dielectric material is subjected to an alternating field the orientation of the dipoles alter in accordance with the field changes. At higher frequencies dipoles will no longer be able to rotate sufficiently rapidly and unable to follow the field and the permittivity of the material decreases. The average time taken by the dipoles to orient in the field direction is known as relaxation time.

When a dielectric is subjected to an alternating field, the polarization and displacement vector also vary periodically with time and this gives rise to complex dielectric constant. Dielectric constant depends on the frequency of the applied electric field.When a dielectric is subjected to alternating field, the electrical energy is absorbed by the material and dissipated in the form of heat. This dissipation of energy is called dielectric loss. Debye's equations relating dielectric loss and relaxation time are

$$\varepsilon^1(\omega) = \varepsilon_{ei} + (\varepsilon_s - \varepsilon_{ei})/(1+i\omega^2\tau^2)$$

$$\varepsilon^{11}(\omega) = (\varepsilon_s - \varepsilon_{ei})\ \omega\tau/(1+i\omega^2\tau^2)$$

The losses associated with ions, the frequency of which fall in the infrared region, are called as **opticalinfrared absorption**and the losses in the optical region, associated with the electrons, are referred   to   as   **optical   absorption**.

STATIC ELECTRIC FIELDS OF DIELECTRIC MATERIALS

3.1 Introduction

In this chapter how the internal field influences the dielectric constant is described in detail. The Classius –Mossotti relation that connects dielectric constant with the polarizabilities is also derived

3.2 Static Dielectric Constant of Gases

We are now in a position to give an atomic interpretation of static dielectric constant of a gas. It will be assumed that the number of molecules per unit volume is small enough so that the interaction between them may be neglected. In that case, the field acting at the location of a particular molecule is to a good approximation equal to the applied field E. Suppose the gas contains N molecules per unit volume; the properties of the molecules will be characterized by an electronic polarizability α_e, an ionic polarizability α_i, and a permanent dipole moment p. From the discussion in the preceding two sections it follows that, as a result of the external field E, there will exist a resulting dipole moment per unit volume:

$$P = N(\alpha_e + \alpha_i + p^2/3kT)E$$

Note that only the permanent dipole moment gives a temperature dependent contribution, because α_e and α_i are essentially independent of T. If the gas fills the space between two capacitor plates of area A and separation d, the total dipole moment between the plates will be equal to

$$M = PAd$$

This simple relation shows immediately that the same total dipole moment would be obtained by assuming that the dielectric acquires an induced surface charge density P at the boundaries facing the capacitor plates, as discussed in section 1.1.1. Hence the quantity P introduced in moment per unit volume is identical with the quantity P introduced in section 1.1.1, where it represented the induced surface charge density at the dielectric-plate interface. The **Debye formula** for the static dielectric constant of gas.
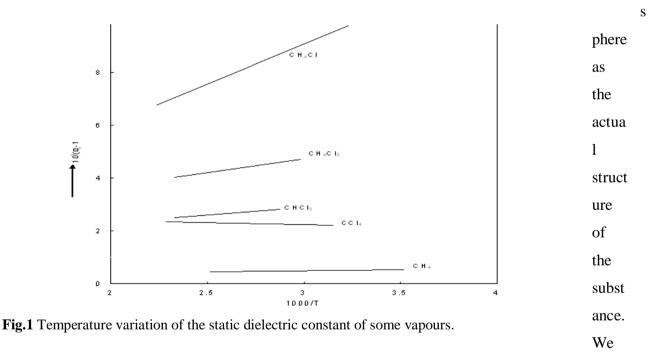
$$P = (\varepsilon - 1)\ \frac{E}{4\pi}\ \ \ \ = N(\alpha_e + \alpha_i + p^2/3kT)E$$

$$(\varepsilon-1) = 4\pi P/E = 4\pi N(\alpha_e + \alpha_i + p^2/3kT)$$

As an example of an application of this formula, the temperature dependence of some organic substances in the gaseous state. The values of $(\varepsilon - 1)$ versus the reciprocal of absolute temperature have been plotted, leading to straight lines. From the slope of the lines and   knowledge of the number of molecules per unit volume, the dipole moment p may be obtained. Also, form the extrapolated intercept of the lines with the ordinate, one can calculate $(\alpha_e + \alpha_i)$. The determination of dipole moments has contributed a great deal to

our knowledge of molecular structure. For example, CCl_4 and CH_4, do not possess permanent dipole moments (indicated by zero slope), in agreement with the symmetric structure of these molecules. Similarly, the fact that H_2O has dipole moment of 1.84 Debye units, whereas CO_2 has no dipole moment, indicates that CO_2 molecule has a linear structure, whereas in H_2O the two OH bonds must make an angle different from 180^0 with each other.

3.3 Internal Field or Local Field

In solids a molecule or atom experiences not only the external field, but the fields produced by the dipoles as well. As a result of the long range of Coulomb forces, the later contribution cannot be neglected. This resultant field is called the *local field*, and is responsible for polarizing individual molecules or atoms of solids.

To calculate the local field, we follow the method suggested by Lorentz. According to this method, we select a small spherical region from the dielectric with the atom for which the local field must be calculated at the centre. The radius of the sphere is chosen large enough to consider the region outside the sphere as a continuum whiles the region inside the sphere as the actual structure of the substance. We suppose that, placing it in a uniform electric field between two oppositely charged parallel plates has uniformly polarized the given dielectric.

Fig.1 Temperature variation of the static dielectric constant of some vapours.
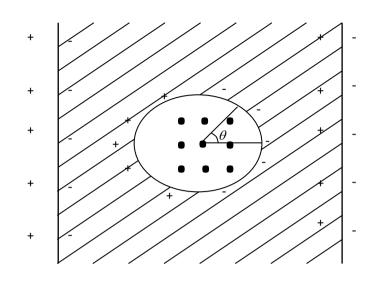
Fig. 2 Illustrating the calculation of the internal field as described in the text

Now, since the part of the dielectric external to the sphere may be replaced by a system of charges induced at the spherical surface as shown in Fig.2, the electric field at the center of the sphere may be written as

$$E_{loc} = E_0 + E_p + E_s + E_m$$

Here E_0 is the primary electric field due to the charge on the plates, E_p is the field due to the polarization charges at the plate-dielectric interface, E_s is the field due to the charges induced at the spherical surface and E_m due to all the dipoles of the atoms inside the spherical region.

Now we know that $E_0 + E_p = E$, the macroscopic electric field inside dielectric. Hence,

$$E_{loc} = E + E_s + E_m$$

Further, if we are considering crystals of high symmetry (such as cubic crystals) $E_m = 0$. This is because E_m is due to all the dipoles inside the spherical surface, and in such crystals these are randomly distributed in position.

We may then write

$$E_{loc} = E + E_s$$

As the assumption $E_m = 0$ is not rue for them. To determine the E_s we proceed as follows:
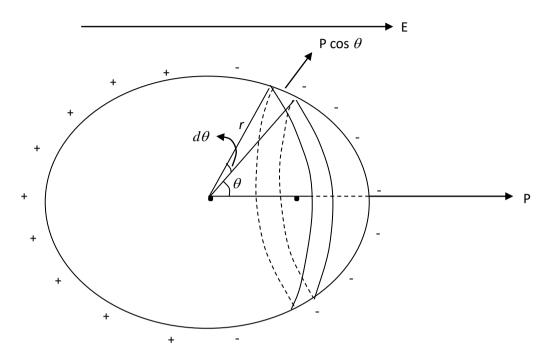
Fig. 3 Enlarged view of the sphere.

Fig.3represents enlarged view of the sphere shown in Fig.3. The charge element on a surface element dS of the sphere is equal to the normal component of the polarization times the surface element, that is, -P cosθ dS. According to Coulomb's law, this charge element produces a force, given by

$$dF = q_1 q_2 / r^2 = -\frac{qP\cos\theta\, dS}{r^2}$$

acting on a test charge q assumed at the centre of the sphere in this direction of r. Hence, the field dE, at the centre due to this charge element is

$$dE_s = dF/q = -\frac{P\cos\theta\, dS}{r^2}$$

Now resolving dE_s into components parallel and perpendicular to the direction of P, we can see a perpendicular component will be cancelled due to an equal contribution from another symmetrically situated surface element. Thus only the component of dE_s along the direction of P will contribute the entire surface.

Thus, $E_s = \int \dfrac{P \cos^2 \theta \, dS}{r^2}$

Now the appropriate surface element dS in this case is the ring shown in Fig.3 so that $dS = 2\pi \, r \, \sin\theta \, r \, d\theta = 2\pi \, r^2 \sin\theta \, d\theta$, and the limits of integration with respect to θ are from 0 to π. Thus,

$$E_s = \int_0^\pi \dfrac{P \cos^2 \theta}{r^2} 2\pi \, r^2 \sin\theta \, d\theta,$$

$$= 2\pi \, P \int_0^\pi \cos^2\theta \, \sin\theta \, d\theta,$$

This integral can be evaluated directly by making the substitution

$z = \cos\theta$ and $dz = -\sin\theta \, d\theta$,

so that

$$E_s = -2\pi \, P \int_1^{-1} z^2 \, dz = -2\pi \, P \left[\dfrac{z^3}{3} \right]_1^{-1}$$

$$= \dfrac{4\pi \, P}{3}$$

$$E_{loc} = E + \dfrac{4\pi \, P}{3}$$

This equation is called Lorenz relation. This shows that E_{loc} is indeed different from E, as it is expected. The former field is larger than latter, so the molecules are more effectively polarized.

Substituting value of P

$$E_{loc} = \dfrac{\varepsilon + 2}{3}.$$

This field is referred as Lorentz field.

The assumption Em = 0 is valid for simple cubic lattice. It is also valid for f.c.c. and b.c.c. lattices and for crystals such as NaCl. It does not hold for all cubic crystals. For example, in barium titanate, which has cubic symmetry E_m does not vanish.

Each type of atom in a given crystal has its own internal field because the environment of the different atoms is generally different. Thus the internal field at the location of atoms of type 1, 2, etc. may be written in the form

$$E_{loc1} = E + \gamma_1 P; \quad E_{loc2} = E + \gamma_2 P, \text{ etc}$$

where the γ's are the internal field constants. Only if Em = 0 do we have $\gamma = 4\pi/3$.

3.4The Clausius-Mossotti Relation

Now we are in a position to relate the microscopicand macroscopic quantities defined above. The dipole moment p of a single atom is proportional to the local field, that is,

$$p = \alpha \, E_{loc}$$

Where α is the electrical polarizability of the atom. If there are different types of atoms, the polarizabilities are additive and the total polarization of an insulator containing N types is

$$P = \sum_{i=1}^{N} n_i \, \alpha_i \, E_{loc} = E_{loc} \sum_{i=1}^{N} n_i \, \alpha_i$$

Where n_i is the number of i atoms per unit volume having polarizabilities α_i and acted on by local field E_{loc} .

$$P = (E + \frac{4\pi P}{3}) \sum_{i=1}^{N} n_i \, \alpha_i$$

or, after rearranging terms

$$\frac{P}{E} = \frac{\sum_{i}^{N} n_i \alpha_i}{1 - \left(\frac{4\pi}{3}\right) \sum_{i}^{N} n_i \alpha_i}$$

$$\frac{P}{E} = \frac{\varepsilon - 1}{4\pi}$$

$$\frac{\varepsilon - 1}{4\pi} = \frac{\sum_{i}^{N} n_i \alpha_i}{1 - \left(\frac{4\pi}{3}\right) \sum_{i}^{N} n_i \alpha_i}$$

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \sum_{i} n_i \alpha_i$$

If all the atoms i are the same, then $\sum_{i} n_i \alpha_i = n\alpha$ and $n = \frac{\rho N_a}{M}$, where ρ =density, N_a is Avogadro number, and M is molecular weight. So, equation (12.14) can be written in this case as

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{\rho N_a}{M} \alpha$$

or $$\frac{M}{\rho} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N_a \alpha$$

The Clausius-Mossotti equation. It can be used to determine the polarizabilities of the atoms if the dielectric constant is known. Further, the dielectric constants of new materials can be predicted from

knowledge of the polarizabilities. This equation thus provides the necessary relation between the microscopic and macroscopic quantities.

3.5 The static dielectric constant of solids

From the discussions in the preceding sections it is evident that in general the dielectric polarization P may be considered the sum of three contributions,

$$P = P_e + P_i + P_o$$

where the subscripts e, i and o refer, respectively, to electric, ionic and orientation polarization. This provides a basis for the classification of dielectrics into three classes:

(i) Substances for which $P_i = P_o = 0$ so that $P = P_e$

(ii) Substances for which $P_o = 0$ and $P = P_e + P_i$

(iii) Substances for which all three contributions are different from zero.

Although the calculation of internal field is usually complicated by the fact that the Lorentz expression does not apply, some remarks may be made about each of these classes in so far as they apply to solids.

(i)   Substances for which the static polarization is entirely due to electronic displacements are necessarily elements, such as diamond. one obtains from the relation

$$P_e = N\alpha_e E_{loc} = (\varepsilon - 1)E/4\pi$$

The following expression for the dielectric constant:

$$\varepsilon - 1 = 4\pi N \alpha_e/(1 - N\gamma\alpha_e)$$

Where N represents the number of atoms per unit volume. In the particular case for which the Lorentz expression for the internal field $\gamma = 4\pi/3$. The resulting expression is then usually written in the form of Clausius-Mossotti formula.

$$(\varepsilon - 1)/(\varepsilon + 2) = (4\pi/3)N\alpha_e$$

It has therefore been applied mainly to gases. For solid elements one would have to vary the temperature in order to vary N and the possible range of N values is of course very limited.

It may be noted that for this class of substances under consideration, the dielectric constant is equal to the square of the index of refraction, $\varepsilon = n^2$. The reason is, that α_e is constant even for frequencies in the visible spectrum. This relationship has been confirmed experimentally for diamond and the dielectric constant of diamond is 5.68±0.03.

(ii)   In general, solids containing more than one type of atom, but no permanent dipoles, exhibit electronic as well as atomic or ionic polarization. Of particular interest in this respect are the crystals, such as the alkali halides. Consider, for example, a NaCl crystal in an external static field E. Apart from the electronic displacements in the ions relative to the nuclei, the positive ion lattice will tend to move as a whole relative to the negative ion lattice. Consequently, a considerable contribution to the total

polarization may be expected to arise from the ionic displacements (P_i). That this is indeed the case, becomes apparent from a comparison of the values of the static dielectric constant defined by

$$P_e + P_a = (\varepsilon - 1) \, E/4\pi$$

and the "high-frequency dielectric constant" ε_0 defined by

$$P_e = (\varepsilon_0 - 1) \, E/4\pi$$

Hence P_i is about two or three times P_e in these compounds. In non-ionic compounds, on the other hand, P_i is usually a relatively small fraction of P_e.

The observed difference between the static and high- frequency dielectric constants is because of the difficulties involved in calculating quantitatively the internal field.

It may be noted that the force constant and the masses of the positive and negative ions determine the infrared frequency associated with the lattice vibrations. It is therefore possible to express the difference (ε_s - ε_0) in terms of infrared absorption frequency of the lattice.

(iii)   In substances composed of molecules which bear permanent electric dipole moments, the total polarization is made up of three contributions,

$$P = P_e + P_i + P_o$$

Were P_o corresponds to the dipolar contribution. There exists no general quantitative theory for dipolar solids because first of all the same difficulties arises in evaluating the internal fields as in class (ii), and further more, the dipoles in such solids may not able to rotate at all or only to some extent. The discussion must therefore be limited to some qualitative remarks. As an example of a dipolar solid which behaves in a relatively manner, the dielectric constant measured as function of temperature for $C_6H_5NO_2$(nitrobenzene). It is observed that at the melting point there is large increase in dielectric constant. This is interpreted as an indication that in the solid the dipoles cannot rotate freely and P_o is essentially zero; in the liquid, alignment of the dipoles in the field direction is possible, so that the increase in ε is determined by the now freely rotating dipoles. The subsequent slow decrease in ε is a consequence of the thermal motion of particles. In other cases, the behaviour may be more complicated, in which ε versus T has been plotted for H_2s. the melting point of H_2S is 187.7_0K. in this case, the dipoles are apparently "frozen in" at temperature below 103.5^0K;at this temperature the structure changes in such a manner that the dipolar groups become mobile; as the temperature is further increased, the dielectric constant decreases as a result of increased thermal motion. The other changes evidently affect essentially the   density   of   the   material,   i.e.,   N   is   reduced   at   these   transition   points.

FERROELECTRIC   MATERIALS

4.1 Introduction

When the centre of a positive charge does not coincide with the centre of negative charge in a primitive cell, the primitive cell possesses an electric dipole moment even in the absence of applied electric field. Thus the crystal as a whole has a polarization implying that it is spontaneously polarized The shifting of positive charge from the centre of negative charge is exhibited in the lack of centre of symmetry in the crystal. Out of 32 crystal point groups, 21 point groups do not have a centre of symmetry. Except one point group, which is highly symmetric, the rest 20 point groups represent an extremely useful class of materials, known as piezoelectrics.

Piezoelectrics: Piezoelectric crystals show electric polarization on being externally strained and conversely, show deformation when placed under the influence of an applied electric field.   If the crystal belongs to any one of the above 20 point groups, it can be predicted that the crystal would be piezoelectric.   Ammonium phosphate, quartz, PZT (Lead Zirconate Titanate) are some examples of piezoelectric crystals.

Pyroelectrics: Among the class of 20 crystal point groups which lack centre of symmetry, 10 crystal point groups are spontaneously polarized. These spontaneously polarized dielectric crystals are called pyroelectric crystals. The polarization in pyroelectric crystals is usually masked by surface charges that accumulate on the surface from the atmosphere and subsequently neutralize the layers of ions. But, when

the temperature of the crystal is altered, the masking is no longer complete as the polarization changes because of thermal expansion or contraction of the crystal. Owing to the thermal effect on polarization, these crystals are named pyroelectric (pyro means fire). The thermal effect accompanying deformation thus supports the piezoelectric property of the crystals. This only confirms that all pyroelectric crystals are piezoelectric, though converse is not true.

While maintaining the crystalline properties, the symmetry operations of a pyroelectric crystal must preserve the direction of polarization P. This imposes severe restrictions on the point group symmetries as a result of which only 10 point groups are found to meet the conditions of pyroelectric crystals. The rotation is allowed about only one axis that is parallel to P and there cannot exist mirror planes perpendicular to this axis. The structural scrutiny of crystal groups reveals that only the following point groups meet the restrictions of pyroelectric crystals:

C_n, C_{nv} (n =2,3,4,6), C_1 and C_{1h}

Thus the pyroelectric property too, like piezoelectricity, is solely determined by the symmetry properties of crystals.

Ferroelectrics: Ferroelectric crystals have additional property that the polarization in them can be changed and even reversed by an external electric field. On the other hand, this is not possible in pyroelectrics even with the maximum electric field that may be applied without causing electrical breakdown. The additional feature of ferroelectrics that distinguishes them as a special class of pyroelectrics does not follow

from the characteristics of crystal structure. It is established only on the basis of dielectric measurement.

Furthermore, the additional feature of ferroelectrics mentioned above converts the usual linear relationship between polarization and applied electric field into a hysteresis loop. Since the dielectric behaviour of these materials is in many respects analogous to the magnetic behaviour of ferromagnetic materials, they are called ferroelectric solids, or ferroelectrics. The ferroelectric behaviour is observed only below a certain temperature, called the Curie point, T_c. A ferroelectric is spontaneously polarized, i.e., it is polarized in the absence of external field; the direction of the spontaneous polarization may be altered under influence of an applied electric field. In general, the direction of spontaneous polarization is not the same throughout a macroscopic crystal. Rather, the crystal consists of a number of domains; within each domain the polarization has a specific direction, but this direction varies from one domain to another.

4.2. Representative crystal types of ferroelectrics

In general the ferroelectric crystals may be broadly classified into four representative groups such as i) Ilmenites and Perovskites, ii) KDP type iii) TGS type and iv) Rochelle salt. The table gives the Curie point T_c and the spontaneous polarization P_s for a number of common ferroelectric crystals. The electric susceptibility χ in the Para electric phase

is related to temperature by the Curie- Weiss law: $\chi = \dfrac{C}{T - T_c}$

where C is the Curie constant.

The ferroelectric crystals are also distinguished on the basis of oscillatory nature of the atomic displacements that destroy the ferroelectric dipole order above the Curie temperature. In the ferroelectric phase of some crystals, the atomic displacements can be viewed as oscillations about a **polar site**. In the paraelectric phase these oscillations take place about a **non-polar site**. The phase transition that brings about this transformation in the nature of oscillations is called a **Displacive phase transition**. These crystals are accordingly identified as **Displacive type**. The well-known examples of this class are ionic crystals with ilmenite and perovskite structures. The GeTe is the simplest ferroelectric crystal having the ilmenite structure (i.e., NaCl structure) and $BaTiO_3$ is the representative crystal of perovskites.

There is another very interesting class of crystals in whose non-ferroelectric state the potential energy function around certain atomic sites is double-well or multiple-well shaped. On the transition to the ferroelectric state the atomic displacements about those sites are executed as oscillations in an ordered subset of the referred potential wells. It involves an order-disorder type of phase transition. Common examples of these crystals, classified as order-disorder type, are some

hydrogen bonded solids, namely KDP type crystals. The replacement of hydrogen by deuterium in KDP type crystals raises the Curie point in an amazing proportion. Though the increase in the molecular weight is less than 2 percent, the T_c rises from 123K to 213K in the deuterated KDP and from 96K to 162K in KD_2AsO_4.

For specific description, Rochelle salt and $BaTiO_3$ are chosen as the two representative compounds of ferroelectrics whose properties are uniquely different.

1). Rochelle Salt

The first solid which was recognized to exhibit ferroelectric properties is Rochelle salt, the sodium-potassium salt of tartaric acid; it has the chemical formula $NaKC_4H_4O_6.4H_2O$. It was first prepared in 1672 by a pharmacist Seignette who lived in Rochelle. It represents the tartaric group of salts whose other well known member are lithium ammonium tartrate and lithium tantalum tartrate. The most noteworthy characteristic of Rochelle salt is that it is ferroelectric between two temperatures (255K and 296K). On account of its two transition temperatures, Rochelle salt becomes a special and peculiar example of ferroelectrics.

The crystal structure of Rochelle salt is somewhat complex. Above 296K and bellow 255K the structure is orthorhombic (three mutually perpendicular axes a,b,c). It has a monoclinic symmetry in the ferroelectric phase such that the angle β(between the c- and a- axes) differs from 90^0 and the spontaneous polarization is along the original orthorhombic a-axis. Thus Rochelle salt has only one polar axis and two possible polarization directions (+ and – along the a- axis).

Halblutzel has measured the dielectric constant of Rochelle salt along the three crystal axes over the whole useful range of temperatures. The Curie-Weiss law applies above 296 K and below

255 K. With the help of the experimental data it is easy to confirm that the two regions have different values of Curie constants. The dielectric constant measured along the polar axis ε_a peaks at both transition temperatures, assuming a value as high as 4000.

2). $BaTiO_3$

The $BaTiO_3$ is the most important and most completely investigated representative of the perovskites type ferroelectrics. In the non-ferroelectric state (i.e. above 393 K). The Ba^{2+} ions are positioned at the corners, O^{2-} ions at the centre of the faces and the Ti^{4+} ion is located at the centre of the cube. It has an arrangement of highly polarizable oxygen ions in the form of an octahedron with a small titanium ion at the centre

The curves clearly indicate that there are three ferroelectric phases of crystal

Temperature range	Direction of P_s	Crystalline symmetry
278-393 K	[001]	Tetragonal
193-278 K	[011]	Orthorhombic
< 193 K	[111]	Rhombohedral

The dipole moment p can alternatively be estimated by multiplying P_s by the unit cell volume. Treating the unit cell as a simple cube of edge 4 A^0 even in the ferroelectric state, we get p = $0.3(4 \times 10^{-10})^3$ = 1.92×10^{-29} C m. Thus we find this value agrees very

well with that obtained on the basis of the observed deformation of the unit cell. The

order of magnitude gives a measure of the ferroelectric effect in $BaTiO_3$.The effect,

however, is fairly large in some other perovskites (e.g. $LiNbO_3$).

The P_s along the [001] direction, warrants our further attention. This

implies that we must multiply by $\sqrt{2}$ and $\sqrt{3}$ to obtain the actual values in the regions

193 K < T < 278 K and T<193K, respectively, because the direction of P_s in these regions

is along the [011] and [111] directions, respectively. It is then quite interesting to note

that spontaneous polarization (same as the saturation polarization) remains almost

constant below 300K.

4.3. Theory of the ferroelectric displacive transitions

The theory that gives a good account of transitions in perovskites type crystals merits a

separate treatment on account of having stood the test of vast experimental data.

These crystals generally undergo a displacive transition at the Curie point. We can

follow two approaches for finding interpretation to a displacive transition. One

approach is the **polarization catastrophe** and the other one is the **soft mode approach**.

The polarization catastrophe refers to an unusual situation in which the

polarization becomes infinitely large. In this condition the force exerted by the local

electric field is greater than the elastic restoring force. This produces an asymmetric

shift in the positions of positive and negative ions. The shift is, however, limited to a

finite displacement by the anharmonic restoring forces.

In the soft mode approach a transverse optical (TO) mode is frozen, i.e. its frequency vanishes at some point in the Brillouin zone below the Curie temperature. This TO mode is known as a soft mode. When $\omega_T = 0$, the crystal becomes unstable because of the absence of an effective restoring force.

Polarization Catastrophe

The Clausius-Mossotti relation can be rearranged in the form

$$\varepsilon = 1 + \frac{3(N_i\alpha_i + N_e\alpha_e)}{3\varepsilon_0 - (N_i\alpha_i + N_e\alpha_e)}$$

where

N_i and N_e are the density of polarizable ion pairs and electrons, respectively and

α_i and α_e are the ionic and electronic polarizabilities, respectively.

the dielectric constant becomes infinite , giving the state of polarization catastrophe. Further,

$$P = (N_i\alpha_i + N_e\alpha_e)\, E_{loc}$$

$$= (N_i\alpha_i + N_e\alpha_e)\left[E + \frac{P}{3\varepsilon_0}\right]$$

for a cubic crystal (using Lorentz expression for E_{loc}).

If E = 0,

$$P\left(\frac{N_i\alpha_i + N_e\alpha_e}{3\varepsilon_0} - 1\right) = 0$$

But, when the polarization catastrophe occurs, the quantity within the brackets equals

zero

This requires that

$$P \neq 0$$

The order to understand the above situation, let us consider a highly polarizable ionic

crystal of cubic symmetry. Let α be the total polarizability and p the dipole moment of

an ion pair. Let us assume that some transient stray field starts polarizing the ion pairs.

The ion pairs will keep on polarizing until some resistance develops to stop the process.

The resistance that finally stops the process of polarization exists in the form of

anharmonic restoring forces. The dipole moment of a single ion pair with ion separation

x is

$$P = q.x = \alpha \ E_{loc} = \left(\frac{\alpha F}{q} \right)$$

where F is the restoring force that tends to bring the positive and negative ions together

and q is the charge on each ion.

The work required to create N such dipoles in the unit volume of the crystal is

$$E_1 = N \int F.dx = \frac{Nq^2}{\alpha} \int x.dx = \frac{Np^2}{2\alpha}$$

$$= \frac{P^2}{N2\alpha}$$

On the other hand, the energy density associated with the electrical displacement due

to E_{loc} is

$E_2 = \int$ Eloc. dP

$$= \int \left(E + \frac{P}{3\varepsilon_0} \right). \, dP$$

$$= \frac{P^2}{6\varepsilon_0} + \int E.dP$$

since E_1 is set against E_2, the net energy density of a polarized dielectric is

$$E_2 - E_1 = \frac{P^2}{2N\alpha} \left(\frac{N\alpha}{3\varepsilon_0} - 1 \right) + \int E.dP$$

This shows that even when E = 0, E2>E1, provided that

$$N\alpha \geq 3\varepsilon_0$$

The above condition in a general case is written in the form

$$\sum_j N_j \alpha_j \geq 3\varepsilon_0$$

where Nj stands for the density of the j th type of particles (ions/electrons) in the crystal

and α_j denotes the polarizability of a single particle of this type.

$$\sum_j N_j \alpha_j \equiv N_i \, A_i + N_e \, \alpha_e$$

the energy of the crystal becomes smaller in the presence of induced dipoles. The

minimum value of $\sum_j N_j \alpha_j$ for which the ferroelectricity would occur is $3\varepsilon_0$. In any real

ferroelectric crystal the situation that exactly corresponds to the polarization

catastrophe is not found. However, a small deviation in the value of $\sum_{j} N_{j}\alpha_{j}$ from $3\varepsilon_0$

changes the value of ε by a large amount.

If we express $\sum_{j} N_{j}\alpha_{j}$ = $3\varepsilon_0$-3β

with β<<1 we get

$$\varepsilon \propto \frac{1}{\beta}$$

If we assume that β is a linear function of temperature near the Curie point and given by

$$\beta = \frac{T - T_c}{\eta}$$

η being a constant, then

$$\varepsilon \propto \frac{1}{T - T_c}$$

The temperature dependence of ε as a given by this relation is in excellent agreement with the observed behaviour in several perovskite crystals.

Ferroelectricity in perovskite crystal is understood in view of the following remarks made in respect of barium titanate:

1. **The titanium ion motion**. The barium ions situated at the cube corners leave a big void at the centre position. Since titanium ion is smaller than barium ion, it is unable to fill the void and is free to rattle around in the void. Because the ionic polarizability is a measure of the ease of displacement, its value increased.

2. **The non-cubic symmetry around oxygen ions**.   Unlike the barium and titanium ions, the oxygen ions are in the non-cubic environment. An oxygen ion has only two nearest neighbours in the form of titanium ions. Because of this reason, E_{loc} is greater than the value given by Lorentz expression.

A larger value of α predicted under point 1 leads to a smaller value of deformation energy E_1 or the work required to create induced dipoles. Similarly, a large value of E_{loc} as expected under point 2 implies that the dipolar attraction will be larger. Thus, larger values of both α and E_{loc} are favourable to the onset of ferroelectricity.

Soft mode approach

As mentioned earlier, a ferroelectric state can be regarded as a **frozen in** TO phonon.

According to Lyddane-Sachs-Teller relation (popularly known as LST relation)

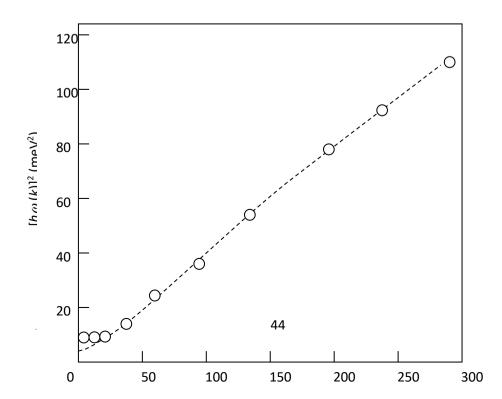$$\frac{\omega_{TO}^2}{\omega_{LO}^2} = \frac{\varepsilon_\infty}{\varepsilon_s}$$

where ε_s is the static dielectric constant , ε_∞ is the dielectric constant   at optical frequencies, ω_{TO} and ω_{LO} are the transverse and longitudinal optical mode frequencies.

Above expression shows that as ε_s increases, ω_{TO} decreases; thus, in the case of an infinitely large ε_s, which happens at the Curie point (T_c), ω_{TO} may even be zero. In practice , ε_s remains finite on approaching T_c. The TO modes in question are called soft modes. Such TO modes have surprisingly low frequencies. For example, $BaTiO_3$ has a soft mode of frequency 12 cm^{-1} at 297 K which is low for a TO mode.

We are not concerned here with LO phonons whose frequency is higher for the same value of the wave vector. At the transition point T_c when ω_{TO} approaches the zero value, the crystal becomes unstable and anharmonic elastic forces come into play. In the presence of anharmonic forces, ω_{TO} may show a temperature dependence of the form

$$\omega_{TO}^2 \propto (T - Tc)$$

On assuming that ω_{TO} are temperature dependent, the LST relation

$$\frac{1}{\varepsilon_s} \propto (T - Tc)$$

Experimental results on several perovskite ferroelectrics strongly support that a large static dielectric constant (ε_s) is associated with a low TO phonon (the soft mode). The temperature dependence of the energy of a low frequency TO phonon can be directly compared with that of the inverse dielectric constant, for a KTaO3 crystal. To have a clear idea, a schematic representation of the temperature dependence of $\varepsilon_s^{-1}, \omega_{TO}^2$ and the saturation polarization Ps is shown in Fig. 1

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4.4. Thermodynamic theory of the ferroelectric transition

It is of interest to investigate the behaviour of a ferroelectric in the vicinity of its transition temperature T_c on the basis of thermodynamic arguments. A thermodynamic theory has the advantage of being independents of any particular atomic model and thus leads to quite general conclusions. Although such a theory does not provide the physical mechanism responsible for the ferroelectric properties of a given material, it does point to certain features one should look for in atomic models.

Consider a crystal which is ferroelectric for temperature T < Tc. Let x denote the relative displacement of the centres of the positive and negative ions in the crystal during a particular mode of vibration. If F_0 be the free energy of the unpolarized crystal, the free energy of the polarized crystal F is a function of the even powers of x. That is,

$$F\text{-}F_o = \phi_2\, x^2 + \phi_4\, x^4 + \phi_6\, x^6 + \ldots$$

The constants ϕ are functions of all other displacements and given by their thermal average values. They are thus functions of temperature. Since the electric polarization P is proportional to the displacement x, we have

$$F - F_o = \frac{1}{2}\lambda_2 P^2 + \frac{1}{4}\lambda_4 P^4 + \frac{1}{6}\lambda_6 P^6 + \ldots$$

The constants λ are the functions of temperature. The numerical factors are introduced to facilitate calculations.

Consider first the paraelectric phase of the crystal, i.e., for T>Tc. If a small electric field E is applied in the absence of any external pressure, the following thermodynamic relation holds good :

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dF = - SdT + E dP

where S represents the entropy of the crystal.

For smaller E, P will also be smaller, and hence we retain only the first term in

$$E = \left(\frac{\partial F}{\partial P}\right)_T = \lambda_2 P$$

The electric susceptibility χ_P in the paraelectric phase is given by

$$\frac{1}{\chi_P} = \frac{\varepsilon_0}{P}\left(\frac{dE}{dP}\right) = \varepsilon_0\lambda_2$$

using the Curie-Weiss law, we have

$$\varepsilon_0\lambda_2 = \frac{T - Tc}{C}$$

or $\lambda_2 = C_1(T\text{-}T_c)$

where C1 is another constant.

shows that λ_2 increases linearly with increase in temperature.   As a result of this temperature dependence, λ_2 varies from positive values to negative values as the temperature is lowered from above T_c to below T_c.

In the state of thermal equilibrium, the free energy is minimum which requires that

$$\left(\frac{\partial F}{\partial P}\right)_T = 0$$

$\lambda_2 P + \lambda_4 P^3 + \lambda_6 P^5 + \ldots \ldots = 0$

The spontaneous polarization is bound to satisfy and

$$P_s(\lambda_2 + \lambda_4 P s^2 + \lambda_6 P s^4 + ...) = 0$$

We find that P_s = 0 is always a root of For this solution the free energy has a

minimum provided λ_2 is positive $\left(\dfrac{\partial^2 F}{\partial P^2} = \lambda_2 \right)$. However, if λ_2, λ_4 and λ_6 are all positive

and higher order terms are neglected, the condition is satisfied only for P_s = 0. Thus, P_s

=0 corresponds to the only minimum of the free energy and the paraelectric phase

exists for the positive sign of λ_2, λ_4 and λ_6.

When the temperature is lowered through the transition point, λ_2 goes from

positive do negative values while passing through λ_2 = 0 at the transition point. There

are two interesting situations that are identified in terms of the signs of λ_2, λ_4 and λ_6.

These characterize two cases of particular interest namely **second-order** and **first-order**

transitions.

Second-order Transitions: If the coefficients λ_4, λ_6, ... are all positive and the value of

λ_2 varies from positive to negative as the temperature is lowered, the free energy

changes as shown in Fig. 2.   Neglecting the terms beyond the second term in are

negligible, we get

$$P_s^2 = -\frac{\lambda_2}{\lambda_4} = \frac{C_1(T_c - T)}{\lambda_4}$$

Hence Ps is a continuous function of temperature and falls continuously to zero at T = Tc

It is useful to examine the spontaneously polarized state in terms of the frequency of normal modes.

$$\phi_2 \text{ or } \lambda_2 = \omega_i^2(k)$$

$$\omega_i^2(k) \propto (T - T_c)$$

where $\omega_i(k)$ is the frequency of the normal mode i (a TO mode). The transition takes place when $\omega_i(k) \to 0$. This decrease in the mode frequency is called ***softening***. This indicates that the harmonic restoring forces are becoming very weak, permitting a large displacement which is limited solely by anharmonic forces. When $\omega i^2(k)$ or λ_2 is small and positive then the crystal lattice becomes soft and close to instability. Below T_c, λ_2 is negative and hence also $\omega_i^2(k)$; which implies that the unpolarized lattice is unstable and the crystal is in the spontaneously polarized ferroelectric state.

The heat capacity is given by

$$C_v = C_1^2 T/\lambda_4$$

The heat capacity falls discontinuously to zero at T =Tc (see Fig. 2). But there is no latent heat at the transition. Such a transition is called a second-order transition.
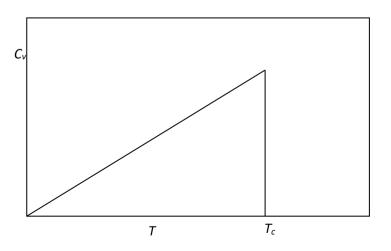

Fig. 2 Temperature dependence of specific heat showing anomaly at
a second-order phase transition

The transitions in Rochelle salt, KH_3PO_4 and $LiTaO_3$ are some examples of the second-order transition. The transition to the superconducting state is the most popular example of this type of transition.

First-order Transitions

We have seen that when λ_2 is negative and λ_4 is positive, the transition is of the second-order type. We now consider a situation where λ_4 is negative and λ_6 is positive. Positive values of λ_6 are considered to restrain the free energy from going to minus infinity. λ_2 varies from positive to negative as the crystal is cooled through the Curie point.

The thermal equilibrium condition, $\dfrac{\partial F}{\partial P}$ = 0, in the absence of the applied electric field gives

$$\lambda_2 P_s + \lambda_4 P_s^3 + \lambda_6 P_s^5 = 0$$

which implies that either P_s = 0, or

$$\lambda_2 + \lambda_4 P_s^2 + \lambda_6 P_s^4 = 0$$

At $T = T_c$, the free energy in the paraelectric state is equal to that in the ferroelectric state, i.e.,

$$F_0(T_c) = F(T_c)$$

$$0 = \frac{1}{2}\lambda_2 P_s^2\,(T_c) + \frac{1}{4}\lambda_4 Ps^4\,(T_c) + \frac{1}{6}\lambda_6 Ps^6(T_c) + ..$$

$$\lambda_2 + \lambda_4 P_s^2\ (T_c) + \lambda_6 P_s^4\ (T_c) = 0$$

$$P_s^2(T_c) = -\frac{3}{4}\left(\frac{\lambda_4}{\lambda 6}\right) = \frac{3}{4}\frac{|\lambda_4|}{\lambda_6}$$

And with

$$\lambda_2 = \frac{3}{16}\left(\frac{\lambda_4^2}{\lambda_6}\right)$$

$$P_s^4(T_c) = \frac{3\lambda_2}{\lambda_6}$$

At the transition point there are two minima of free energy with equal value; one at

$P_s(T_c) = 0$ in the paraelectric phase and the other for the value of $P_s(T_c)$. Thus there is a

jump in the value of P_s at T_c, meaning thereby that the spontaneous polarization (the

order parameter) drops discontinuously to zero at $T = T_c$ when a ferroelectric crystal is

heated slowly. Such transitions are called the first-order transitions. The other

important property of these transitions is that there is a latent heat at the transition. A

well known example of this type of transition is the upper transition in a $BaTiO_3$ crystal.

 Free energy as a function of polarisation as the temperature is varied near a first order

phase transition. (b) Fall of the spontaneous polarisation below the transition point T_c in

a first order phase transition.

4.5 Ferroelectric Domains

When a ferroelectric is cooled from the paraelectric phase through the Curie

temperature, the polarized phase may be nucleated at several points in the crystal.

These nuclei generally differ in the direction of polarization since there may be several equivalent crystallographic directions in which the spontaneous polarization can occur. In the case of $BaTiO_3$, the spontaneous polarization may occur along any one of the three edges, giving six possible directions for the spontaneous polarization. Thus, as the nuclei grow through the crystal in the ferroelectric crystal in the ferroelectric phase, they form several regions or domains differing in their direction of polarization. The vector sum of these polarizations may not be always big enough to show up macroscopically.

Polarization is accompanied by some distortion of the unit cell and the domain walls are consequently in a state of strain; but the dimensional changes are relatively small. Though the domain walls act as interruptions in the regularity of the crystal, they are not regarded as grain boundaries between different crystals. A domain wall is instead, treated as a sub-grain within a single crystal. As soon as a single nucleus of the polarized phase is formed, the polarized phase begins to grow much faster in the direction of polarization than in the transverse directions. Because of this reason the growing domains are usually wedge-shaped. This was revealed by optical birefringence studies on $BaTiO_3$.

The ferroelectric domains are regarded as the electrical analogues of the ferromagnetic domains despite the fact that there are some interesting differences in their origin and growth. When the electric field is applied on a ferroelectric crystal, the number and size of domains that are polarized in the field increase. As a result of this

effect, upon the reversal of the field direction a hysteresis in the P versus E curve is observed.

4.6 Antiferroelectricity

Similar to ferroelectrics there is another group of solids, which has induced, ordered electric dipoles below a characteristic temperature but do not show spontaneous bulk polarization. In these crystals the neighbouring atomic lines are associated with antiparallel polarization because of which the bulk polarization of the crystal vanishes. Crystals exhibiting this property are called **antiferroelectric** crystals and the property is known as **antiferroelectricity**. The structural requirement for the ferroelectrics and antiferroelectric phases being common, a number of well-known antiferroelectric crystals are found to be isomorphous with some ferroelectrics. For example, ammonium dihydrogen phosphate (ADP) is isomorphous with potassium dihydrogen phosphate (KDP).

Perovskite type crystals are known to be susceptible to several types of deformation with almost equal energy difference between them. In many of them the coupling through the oxygen octahedral causes adjacent lines of basic cells to be polarized in opposite directions. Below a certain temperature the resultant deformation is such that the total energy in the antiparallel arrangement of adjacent lines of dipoles is lower, when compared separately to that in state of fully parallel arrangement of dipoles and to that in the state with no induced dipoles. Lead Zirconate ($PbZrO_3$) is a notable example of these perovskites. It shows to

Antiferroelectric phases, one each ferroelectric and paraelectric phases over different ranges of temperature.

PIEZOELECTRIC MATERILAS

5.1 Introduction to Piezoelectric materials

Piezoelectricity is the ability of certain dielectric crystals to produce a voltage when subjected to mechanical stress. The word is derived from the Greek*piezein*, which means to squeeze or press. The effect is reversible; piezoelectric crystals, subject to an externally applied voltage, can change shape by a small amount. The effect is of the order of nanometres, but nevertheless finds useful applications such as the production and detection of sound, generation of high voltages, electronic frequency generation, and ultra fine focusing of optical assemblies.

Pyroelectricity, the ability of certain mineral crystals to generate electrical charge when heated, was known of as early as the 18th century, and was named by David Brewster in 1824. In 1880, Pierre Curie and Jacques Curie brothers predicted and demonstrated piezoelectricity using tinfoil, glue, wire, magnets, and a jeweler's saw. They showed that crystals of tourmaline, quartz, topaz, canesugar, and Rochelle salt generate electrical polarization from mechanical stress. Quartz and Rochelle salt exhibited the most piezoelectricity. Twenty natural crystal classes exhibit direct piezoelectricity.

Piezoelectric materials

In addition to the materials listed above, many other materials exhibit the piezoelectric effect, including quartz analogue crystals like berlinite ($AlPO_4$) and gallium orthophosphate ($GaPO_4$), ceramics with perovskite or tungsten-bronze structures ($BaTiO_3$, $KNbO_3$, $LiNbO_3$, $LiTaO_3$, $BiFeO_3$, $NaxWO_3$, $Ba_2NaNb_5O_5$, $Pb_2KNb_5O_{15}$). Polymer materials like rubber, wool, hair, wood fiber, and silk exhibit piezoelectricity to some extent. The polymer polyvinylidene fluoride, ($-CH_2-CF_2-$)n, exhibits piezoelectricity several times larger than quartz. Bone exhibits some piezoelectric properties: it has been hypothesized that this is part of the mechanism of bone remodelling in response to stress.

Mechanism of piezoelectricity

In a piezoelectric crystal, the positive and negative electrical charges are separated, but symmetrically distributed, so that the crystal overall is electrically neutral.When a stress is applied, this symmetry is disturbed, and the charge asymmetry generates a voltage. A 1 cm cube of quartz with 500 lbf (2 kN) of correctly applied force upon it, can produce 12,500 V of electricity.

Piezoelectric materials also show the opposite effect, called **converse piezoelectricity**, where application of an electrical field creates mechanical stress (distortion) in the crystal. Because the charges inside the crystal are separated, the applied voltage affects different points within the crystal differently, resulting in the

distortion.The bending forces generated by converse piezoelectricity are extremely high, of the order of tens of meganewtons, and usually cannot be constrained. The only reason the force is usually not noticed is because it causes a displacement of the order of a few nanometres.

Requirements for a crystal to show piezoelectricbehaviour were discussed in the previous Lesson. We showed earlier that all ferroelectrics are piezoelectrics and that its converse is not true. For example, quartz is piezoelectric but it does not possess the ferroelectric property.

The foremost condition for a crystal to piezoelectric is the absence of the centre of symmetry. a simple two-dimensional ionic crystal with no centre of symmetry.It is evident that a compressive force **F**decreases the electric dipole moment(hence the polarization) and a tensile force **F** increases the same. This is essentially the piezoelectric effect. We must appreciate that the displayed crystal could well be a ferroelectric crystal.

Next we take up another example to show how the symmetry of a non-centrosymmetric crystal controls firstly the magnitude and direction of polarization when the crystal is stressed and secondly the crystal dimensions when the crystal is polarized.   Consider a molecule of hypothetical ionic solid which at equilibrium has three electric dipoles of equal magnitude distributed over 360^0at an interval of 120^0. The molecules belong to the point group 3m and its net dipole moment is zero. But if the molecule together with the crystal is stressed or compressed along a direction

parallel or antiparallel to one of the three directions of the dipole moment, a net dipole moment would appear. Similarly, a molecule may be distorted by an electric field applied along one of the three arrows. The electric field produces an elongation or contraction of the crystal along the field direction and a length change of opposite sign in the lateral direction. An applied field that is perpendicular to one of the three dipole directions in Fig. 1. finds itself perpendicular to a mirror plane of symmetry and, therefore, is rendered ineffective in changing the crystal dimensions.
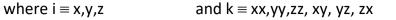
Because of lack of centre of symmetry and complex structure of piezoelectrics, their electrical behaviour under strain or strain behaviour under an electric field is not isotropic in nature. Nevertheless, a simple picture of the phenomena can be presented in a schematic one-dimensional notation by the following equations:

$$P = \sigma d + \varepsilon_0 E \chi :; \qquad e = \sigma s + Ed$$

where P is the polarization, σ the stress, d the piezoelectric strain constant, ε_0 the permittivity of free space, E the electrical field, χ the dielectric susceptibility, e the strain and s the elastic compliance constant.

In real crystals, however, the tensile, compressional or shear strains produced by an electrical field may develop in different directions and depend on the crystal orientation and the field direction in view of this fact the piezoelectric strain constants, that form a third rank tensor, are defined as

$$d_{ik} = \left(\frac{\partial e_k}{\partial E_j} \right)_{\sigma}$$

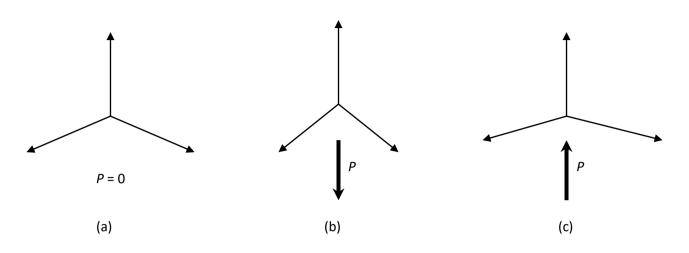where i $\equiv$ x,y,z   and k $\equiv$ xx,yy,zz, xy, yz, zx

Fig. 1 (a) Directions of polarization (b) A vertical tension or a horizontal compression causing
(c) A vertical compression or a horizontal tension causing a net polarization

Depending on the application and the desired behaviour, a crystal is cut so as to have the parallel faces of the crystal in a specific orientation. An X-cut is defined as a section cut from the crystal such that the x-axis of the crystal is perpendicular to parallel crystal faces. In order to obtain certain desirable properties the crystals are sometimes given oblique cut that is cut at angles is different from 90 degrees with the principal axes.

5.2 Electrostriction

It is appropriate to discuss a more universal phenomenon of deformation in crystals that is caused by an applied electrical field. It refers to the deformation in ionic crystals and the effect is commonly known ***electrostriction***.

Electrostriction is a property of all electrical non-conductors, or dielectrics that produces a relatively slight change of shape, or mechanical deformation, under the

application of an electric field. Reversal of the electric field does not reverse the direction of the deformation.

In the first approximation the deformation of piezoelectric crystal is proportional to applied electrical field and the stress induced polarization varies linearly with the strain produced. But in ionic crystals, which do not have to be necessarily piezoelectrics, the strain is much smaller and proportional to the square of electrical field. We can understand the origin of electrostriction by appreciating that dipoles created by the applied electrical field would interact with each other. The inline dipoles attract each other with a repulsive poles acting perpendicular to the direction of the polarization.

Let p denote the moment of a dipole and r the separation between two inline dipoles. The value of the electric field caused by a dipole at its in-line neighbour may be written as

$$E = \frac{1}{4\pi\varepsilon_0}\frac{2p}{r^3}$$

The energy of a dipole in the field U(r) and the corresponding attractive force F are related as

$$F = -\frac{dU(r)}{dr}$$

and $\qquad$ Ur) = - p.E

These relations yield

$$F = -\frac{1}{4\pi\varepsilon_0}\frac{6p^2}{r^4}$$

Similarly, we can find that the repulsive force is given by

$$F = \frac{1}{4\pi\varepsilon_0}\frac{3p^2}{r^4}$$

Since p = αE, the attractive force can be expressed as

$$F = -\frac{1}{4\pi\varepsilon_0}\left(\frac{6\alpha^2}{r^4}\right)E^2$$

To a first approximation the strain or deformation u may be assumed to follow the Hooke's law and then

$$u = -\frac{F}{k}$$

where k is the usual force constant in the direction of the in-line dipoles. The above relation, we get

$$U = \frac{1}{4\pi\varepsilon_0}\left(\frac{6\alpha^2}{kr^4}\right)E^2$$

Thus, there will occur a compression in the field direction and an extension perpendicular to the field direction. The above treatment holds for permanent dipoles as well on account of the effective dipole moment being proportional to the electric field.

5.3 Applications of piezoelectric crystals

It may be recalled all ferroelectrics are piezoelectrics, though the conversion is not true.As a result, ferroelectric materials have been frequently used in many applications that are based on the principle of piezoelectricity. But, because of importance of properties such

as mechanical and thermal strength the use of certain piezoelectric crystals becomes inevitable.

Piezoelectric crystals are used in numerous ways:

High-voltage sources

Direct piezoelectricity of some substances like quartz, as mentioned above, can generate thousands of volts (known as high-voltage differentials).

- Probably the best-known application is the electric cigarette lighter: pressing the button squeezes an piezoelectric crystal, and the high voltage thus produced ignites the gas as the current jumps over a small spark gap. The portable electrical sparkers used to light gas grills or stoves work the same way.

- A similar idea being researched by the **Defense Advanced Research Projects Agency** (DARPA) in the USA in a project called *Energy Harvesting*, which includes an attempt to power battlefield equipment by piezoelectric generators embedded in soldiers' boots.

- A piezoelectric transformer is a type of AC voltage multiplier. Unlike a conventional transformer, which uses magnetic coupling between input and output, the piezoelectric transformer uses acoustic coupling. An input voltage is applied across a short length of a bar of piezoceramic material such as PZT, creating an alternating stress in the bar by the inverse piezoelectric effect and

causing the whole bar to vibrate. The vibration frequency is chosen to be the resonant frequency of the block, typically in the 100 kilohertz to 1 megahertz range. A higher output voltage is then generated across another section of the bar by the piezoelectric effect. Step-up ratios of more than 1000:1 have been demonstrated. An extra feature of this transformer is that, by operating it above its resonant frequency, it can be made to appear as an inductive load, which is useful in circuits that require a controlled soft start.

Sensors

- To detect sound, e.g. piezoelectric microphones (sound waves bend the piezoelectric material, creating a changing voltage) and piezoelectric pickups for electrically amplified guitars.

- Piezoelectric oscillators are used to convert mechanical pulses into electrical ones and vice versa. The crystal in these devices works as a transducer. The acoustic pulses are used in underwater search (sonars) and other applications. The acoustic pulses are generated by the piezoelectric transducers excited by electrical fields in almost all search cases. The generation of ultrasonic waves is invariably accomplished by exploiting the above principle.

- Piezoelectric microbalances are used as very sensitive chemical and biological sensors.

- The piezoelectric effect in synthetic poly vinyliden fluoride (PVF_2) is about five times stronger than that in quartz. Being flexible and easy to handle like ultrasonic transducers, the PVF_2 films are frequently used in applications such as monitoring blood pressure and respiration.

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

Actuators

As very high voltages correspond to only tiny changes in the width of the crystal, this width can be changed with better-than-micrometer precision, making piezo crystals the most important tool for positioning objects with extreme accuracy.

- Loudspeaker: Voltages are converted to mechanical movement of a piezoelectric polymer film.

- Piezoelectric elements can be used in laser mirror alignment, where their ability to move a large mass (the mirror mount) over microscopic distances is exploited to electronically align some laser mirrors. By precisely controlling the distance between mirrors, the laser electronics can accurately maintain optical conditions inside the laser cavity to optimize the beam output.

- A related application is the acousto-optic modulator, a device that vibrates a mirror to give the light reflected off it a Doppler shift. This is useful for fine-tuning a laser's frequency.

- Atomic force microscopes and scanning tunneling microscopes employ converse piezoelectricity to keep the sensing needle close to the probe.

Frequency standards

- Quartz clocks employ a tuning fork made from quartz that uses a combination of both direct and converse piezoelectricity to generate a regularly timed series of electrical pulses that is used to mark time. The quartz crystal (like any elastic material) has a precisely defined natural frequency (caused by its shape and size) at which it prefers to oscillate, and this is used to stabilize the frequency of a periodic voltage applied to the crystal.

- The same principle is critical in all radiotransmitters and receivers, and in computers where it creates a clock pulse. Both of these usually use a frequency multiplier to reach the megahertz and gigahertz ranges.

- Crystals shaped to have a prescribed mechanical resonance frequency are used as narrow band electrical filters. Only those electrical signals whose frequency is coincidence with the mechanical vibrational frequency pass through the crystal and all other are rejected.

- The piezoelectric materials are used as delay lines. When an electrical signal is converted into an acoustic one to one and of a quartz rod. The signal passes along rod as an acoustic wave, travelling at velocity of sound. At the other end acoustic may converted into an electrical signal. The initial signal is thus delayed. Such an arrangement is often used in communication devices.

Piezoelectric motors

- Types of piezoelectric motor include the well-known travelling-wave motor used for auto-focus in reflex cameras, inchworm motors for linear motion, and rectangular four-quadrant motors with high power density (2.5 watt/cm³) and speed ranging from 10 nm/s to 800 mm/s. All these motors work on the same principle. Driven by dual orthogonal vibration modes with a phase shift of 90°, the contact point between two surfaces vibrates in an elliptical path, producing a frictional force between the surfaces. Usually, one surface is fixed causing the other to move. In most piezoelectric motors the piezoelectric crystal is excited by a sine wave signal at the resonant frequency of the motor. Using the resonance effect, a much lower voltage can be used to produce a high vibration amplitude.

5.4 Applications of Piezoelectric materials

- Piezoelectricity is the ability of certain dielectric crystals to produce a voltage when subjected to mechanical stress.

- Pierre Curie and Jacques Curie brothers predicted and demonstrated piezoelectricity in 1880. They showed that crystals of tourmaline, quartz, topaz, canesugar, and Rochelle salt generate electrical polarization from mechanical stress.

- Piezoelectric materials also show the opposite effect, called converse piezoelectricity, where application of an electrical field creates mechanical stress (distortion) in the crystal.

- The foremost condition for a crystal to piezoelectric is the absence of the centre of symmetry.

- Depending on the application and the desired behaviour, a crystal is cut so as to have the parallel faces of the crystal in a specific orientation. *An X-cut is defined as a section cut from the crystal such that the x-axis of the crystal is perpendicular to parallel crystal faces*.

- Electrostriction is a property of all dielectrics that produces a relatively slight change of shape, or mechanical deformation, under the application of an electric field.

- Reversal of the electric field does not reverse the direction of the deformation.

- The compression will occur in the field direction and an extension perpendicular to the field direction.

- Piezoelectric crystals are used in high-voltage sources, sensors, actuators, frequency standards, piezoelectric motors etc.,

PREFACE

The present book deals with the studies on "**Insulating materials**".

Present book deals with advanced insulating materials, namely dielectrics, ferroelectrics and piezoelectric materials. I believe that the information furnished in this book will improve the easy way of understanding the importance of insulating materials in solid state. The main purpose of the book is link to academicians, professional and students.

I shall feel highly satisfied and amply rewarded in case the student community is benefitted to any substantial extent.