CHAPTER IV

GENERAL THEORY
OF
DIELECTRIC PROPERTY
INTRODUCTION :-

A number of ferroelectric compounds and solid solutions of complex composition in the pervoskite and tungsten bronze families exhibit a characteristic, low frequency, dielectric dispersion and several unusual associated dielectric, optical and thermal properties [1-3]. A statistical treatment based on a postulated Gaussian distribution of local Curie temperatures associated with composition fluctuation has been given by Rolve [4].

The first ferroelectric crystal discovered was the Rochelle salt. Ferroelectricity of Rochelle salt was established by detailed studies by Valasek [5] who was the first to point out the analogy between the dielectric properties of Rochelle salt and magnetic properties of ferroelectric materials. It was due to this analogy with ferromagnetism that the phenomenon was named ferroelectricity by Muller [6].

The second ferroelectric crystal discovered by Bush and Scherrer [7] was potassium dihydrogen phosphate considered to be the only ferroelectric crystal.

Around 1943, Wainer and Saloman in United
State, in Russia Wul and Goldman and in Japan Orgaw, discovered independently the anomalous dielectric properties of barium titanate \((\text{BaTiO}_3)\). Since the discovery of ferroelectricity in \(\text{BaTiO}_3\) compounds with perovskite structure have been studied extensively. These studies have resulted in the discovery of many few substances. Jona and Shirane \([8]\) have given a table of seventy six ferroelectric crystals.

The first theoretical explanation of the properties of Rochelle salt was proposed by Kurchatov \([9]\). The first molecular theory of ferroelectricity, based on the actual crystal structure to explain the ferroelectric transitions in \(\text{KH}_2\text{PO}_4\) was proposed by Slater \([10]\), Bacon and Pease \([11]\) and Peterson et al \([12]\) verified this theory using the neutron diffraction. Muller \([13]\) put forward two phenomenological treatments of Rochelle salt which have proved very successful in co-relating its properties and have contributed much to the subsequent theories of ferroelectricity. Devonshire \([14]\) has proposed phenomenon logical theory of \(\text{BaTiO}_3\), which explains its behavior with remarkable success. Ferroelectricity studied on
the basis of lattice dynamical theory by Cochern [15] also lines statistical theory [16] have provided major understanding of ferroelectric phenomena.

4.1 DIELECTRIC PROPERTIES OF MATERIALS:

When a flat slab of any solid dielectrics placed in a uniform electric field $\mathbf{E}_0$ with its normal parallel to the field, the dielectric displacement $\mathbf{D}$ (in CGS units) is given by

$$\mathbf{D} = \epsilon_0 \mathbf{E}_0 = \epsilon \mathbf{E} = \mathbf{E} + 4\pi\mathbf{P} \quad \text{(4.1)}$$

Where $\mathbf{E}_0$ and $\mathbf{E}$ are the field strengths outside and in the dielectric, $\epsilon_0$ and $\epsilon$ are dielectric constants of the surrounding medium and of the dielectric material respectively, and $\mathbf{P}$ is the polarization (electric moment per unit volume). Since surrounding medium is usually air or vacuum, the dielectric constant considered to be unity. Ignoring spontaneous polarization, the general relation between $\mathbf{E}$ and $\mathbf{P}$ is

$$\mathbf{P} = n\mathbf{E} \quad \text{(4.2)}$$

Where $n$ is the dielectric susceptibility. In an isotropic cubic medium $\mathbf{P}$ is always parallel to $\mathbf{E}$, then all quantities in the above equation may be written as scalars. From equation (4.1) the
dielectric constant of an isotropic medium is defined as

\[ \varepsilon = \frac{E + 4\pi P}{E} \]

\[ \varepsilon = 1 + \frac{4\pi P}{E} \]

\[ \varepsilon = 1 + 4\pi n \]

\[ n = \frac{\varepsilon - 1}{4\pi} \]

These equations are perfectly general statistical descriptions of dielectric phenomena, in terms of quantities that are observable outside the dielectric. They involve no hypothesis concerning the molecular nature of polarization. The statement concerning the molecular nature and internal field are summarized below. The dielectric behavior of ferroelectric crystals depend on polarizability and internal field. For the remaining crystals there are no dielectric anomalies. The dielectric constants are nearly constant over wide ranges of temperature, field and frequency. Therefore, for such crystals, it is not necessary to refer molecular theory of polarization.

The actual field in a dielectric varies greatly from point to point, over distances comparable with molecular dimensions. The internal field is defined as that field in a very small
spherical cavity, from which the molecules have been removed. According to Lorentz equation,

\[ F = E + \tau \cdot P + E \left( 1 + \tau \cdot n \right) \quad 4.5 \]

Where \( E \) is statistical field in the dielectric, \( P \) is the polarization and \( \tau \) is the internal field constant. In an isotropic medium \( \tau = \frac{4\pi}{3} \). In the crystals of lower symmetry, it differs from \( \frac{4\pi}{3} \) but is of the same order of magnitude. It is usually considered as independent of temperature.

In the field \( F \) each molecule becomes polarized and acquires the dipole moment \( P \). The polarizability of an atom is defined by

\[ P = \alpha \cdot F \quad 4.6 \]

It is atomic property. But \( E \) depends on the manner in which the atoms are assembled in a crystal.

According to Kittel [16], the polarization in the crystal may be expressed as

\[ P = \sum_j N_j \cdot P_j = \sum_j N_j \cdot \alpha_j \cdot F(J) \quad 4.7 \]

Where \( N_j \) is the concentration, \( \alpha_j \) is the polarizability of atoms, \( j \) and \( F(J) \) is the local field at atom sites \( J \). Taking local fields as

\[ F = E + \left( 4\pi \cdot P \right) / 3 \]
\[ P = \sum_j N_j \cdot \alpha_j \left( E + \left( 4\pi \cdot P \right) / 3 \right) \]
\[ \quad 4.8 \]
\[ \quad 4.9 \]

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Hence the dielectric susceptibility is given by
\[ n = p/E = (\Sigma N_j \alpha_j) / \left[ 1 - (4\pi/3) \alpha_j \right] \]
\[ \left[ 1 - (4\pi/3) \alpha_j \right] \]
\[ \text{Since } \epsilon = 1 + (4 \pi \pi n) \]
In CGS units we will get
\[ \left[ (\epsilon - 1) / (\epsilon + 2) \right] = (4\pi / 3) \Sigma N_j \alpha_j \]
This is well known Clausius - Mossotti relation. This equation relates the dielectric constant to the electronic polarizability. But only for those crystals for which the Lorentz local field exists. The total polarizability is usually separated into three parts. (01) Electronic polarizability \( \alpha_e \) which is due to displacement of electrons within the atoms or ions. (02) Atomic polarizability \( \alpha_a \) which is due to displacement of atoms or ions within the molecules. (03) Dipolar polarizability \( \alpha_d \) which arises from molecules with a permanent electric dipole moment that can change orientation in an applied field. In heterogeneous material there is also an interfacial polarization which arises from the accumulation of charges at structural interfaces. This polarization is of practical importance because commercial insulating materials are usually heterogeneous.

The contribution to the polarization, made by \( \alpha_e \) and \( \alpha_a \) is called distortion polarization and
contribution to the polarization made by $\alpha_d$ is called orientation polarization. The electronic and atomic polarizabilities are independent of temperature and hence, the portion of the dielectric constant dependents on them is essentially independent of temperature.

The dipolar polarizability is a function of temperature. According to Debye's Theory [17], the dipolar polarizability per molecule in a weak field is given by

$$\alpha_d = \frac{P^2}{(3KT)}$$  \hspace{1cm} 4.12

Where $P$ is dipole moment of a polar molecule, $K$ is Boltzman's constant and $T$ is absolute temperature.

Each type of polarizability is a function of frequency of the applied field. At low frequency of applied field all type of polarization are equal to the value in the steady field. As the frequency of the applied field is increased, polarization no longer has time to reach its steady value. The orientation polarization is affected first, at normal temperature in liquids and solids with moderately small molecules, orientation polarization takes a time of the order of $10^{-12}$ to $10^{-10}$ sec to reach its equilibrium value. Consequently when the applied field has a frequency
$10^{10}$ to $10^{12}$ Hz, the orientation polarization fails to reach its equilibrium value. It is fall of polarizability from

$$\alpha_T = [\alpha_e + \alpha_a + \alpha_d]$$

$$\alpha_T = \alpha_e + \alpha_a$$

which gives rise to dielectric dispersion.

In the frequency region in which dielectric dispersion occurs, $\alpha_e$ and $\alpha_a$ remains unchanged, because the distortion polarization of a molecule takes much less time to reach its equilibrium value with applied field than the orientation polarization does.

At frequencies of which are comparable with natural frequencies of vibrations of atoms in the molecule $\alpha_a$ will take time to reach its equilibrium value and there will be further dispersion. This usually occurs in the infra-red regions of the spectrum. At frequencies corresponding to the electronic transition between different energy levels in the atom i.e. visible, ultra-violet and x-ray frequencies there, is fall of $\alpha_e$. The contribution of total polarizabilities are shown in figure 4.1.

The dielectric constant at optical frequencies is entirely due to the electronic polarizability.
FIGURE 4.1 SCHEMATIC REPRESENTATION OF FREQUENCY DEPENDENCE OF THE SEVERAL CONTRIBUTION TO THE TOTAL POLARIZABILITY.
The atomic and dipolar contributions are small at high frequencies. In the optical frequency range the dielectric constant is given by

\[
\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \sum N_j \alpha_j
\]

4.13

Where \( n \) is the refractive index which is related to the dielectric constant by the relation

\[
n^2 = \varepsilon
\]

4.14

If the frequency on the polarizabilities is taken into account the result is a progressive decrease in dielectric constant with increasing frequency. In each of the regions where dielectric dispersion occurs, there is a certain characteristic frequency \( \omega_0 / 2\pi \), defined by equation

\[
\omega_0 = \left( \frac{2K\tau}{b} \right) / b = 1 / t
\]

Where \( K \) is Boltzman's constant, \( T \) is absolute temperature, \( b \) is a fractional constant and \( t \) is the relaxation time. The dielectric constant begins to decrease at the beginning of the absorption band.

Absorption of energy which is found in the infrared and optical spectrum regions is due to natural vibrations of electrons, molecules, or the crystal lattice. In the range of optical frequencies there is anomalous dielectric
dispersion. The dielectric constant normally increases with increasing frequency.

4.2 COMPLEX DIELECTRIC CONSTANT :-

A macroscopic of the electrical properties of a dielectric is provided by complex dielectric constant

\[ \varepsilon^* = \varepsilon' - j \varepsilon'' \quad 4.15 \]

Where \( \varepsilon' \) is the real part and \( \varepsilon'' \) is the imaginary part of \( \varepsilon^* \). The significant variable on which \( \varepsilon^* \) depends in the decreasing order of importance are the frequency, the temperature, the pressure and the intensity of the applied field. Since both \( \varepsilon' \) and \( \varepsilon'' \) are frequency dependent, the phase angle is frequency dependent. The phase lag between the polarization and the applied field leads to an absorption of energy in the dielectric.

4.3 FERROELECTRIC MATERIAL AND THEIR CHARACTERISTICS PROPERTIES :-

Ten out of thirty two crystal classes are polar i.e. they are both piezoelectric and pyroelectric. These crystal classes are represented by 1, 2, m, mm, 4, 4mm, 3, 3mm, 6 and 6mm. Polar crystals have the property that

\[ \iiint \varphi(x) \ F \ dx \ dy \ dz < 0 \]

Where \( \varphi(x) \) is combined nuclear and
electronic charges density. Such crystals possess a spontaneous electric polarizations $P_s$ in the absence of an external electric field. Ferroelectric crystals possess an additional property that polarization can be reversed by the application of an electric field. Thus ferroelectric crystals can be considered as a subgroup of pyroelectrics. It is a necessary condition for a ferroelectric crystal to belong to any one of the ten polar classes, in its ferroelectric phase but not a sufficient condition as reversibility of the polarity must also occur. A ferroelectric crystal is thus defined as pyroelectric crystal with reversible polarization. The polar structure of a ferroelectric crystal is a slightly distorted non-polar structure, and this fact gives rise to reversibility of the polarization.

With increasing temperature ferroelectricity usually disappears above a certain temperature called the transition temperature. Jona and Shirane [34], Kittel [16] and Kanzig [18], $T_C$ denotes the transition temperatures and is called the Curie temperature, while $T_0$ denotes the characteristic temperature appearing in the Curie Wiess law.

At the transition temperature, the
substance undergoes a phase transition from the polar state into the non-polar state. As a rule, the low temperature phase is polar. The phase transition can be of the first order or of a higher (usually second) order.

A first order transition is that in which there is a discontinuous change of volume and energy, the energy release as latent heat in very narrow temperature range. The second-order transition is that which there is no discontinuity in the change in volume and energy. Thus in second order transition there is no release of latent heat, but the expansion coefficient and the specific heat show anomalies extending over a finite temperature range. Other properties, such as, the polarization, show discontinuity in a first-order change but not in a second-order change. At the transition point the dielectric constant generally shows a peak, and above the transition point, it obeys the Curie Weiss Law. The Piezo-electric, elastic and electro-optic properties show a similar anomalous behavior.

The Properties possessed by most of the ferroelectric crystals can be summarized as:
1. They exhibit a dielectric hysteresis loop
between polarization and applied electric field below a certain critical temperature called as ferroelectric Curie temperature.

2. They have a ferroelectric domain structure which may be visible in polarised light.

3. They have a high dielectric constant along the polar axis, which is a function of temperature and rises to a peak value at the Curie temperature. Above this temperature, its falls of obeying the Curie Weiss law.

4. They posses a Pseudo - Symmetric structure. In the ferroelectric phase the structure belongs to the polar class.

5. They have a transition at the Curie temperature to form structure of higher symmetry.

6. The Curie temperature is raised by application of a baising field, or a hydrostatic pressure.

7. They show piezoelectric and pyroelectric properties below the Curie temperature.

8. There is a sudden appearance of surface charges at the transition.

4.4 CLASSIFICATION OF FERROELECTRICS :-

The phenomenon of ferroelectricity has been discovered in a large number of crystals. As investigations in recent years have shown that
ferroelectricity is a more common phenomenon than had been considered for a long time, a satisfactory classification of all materials was difficult. However, classifications have been proposed according to the following criteria.

1. Crystal - Chemical classification :-

   According to this classification, the ferroelectric compounds are divided into two groups
   (i) Hydrogen bonded crystals, such as $\text{KH}_2\text{PO}_4$ Rochelle salt, triglycerine sulphate etc.
   (ii) The double oxides, such as $\text{BaTiO}_3$, $\text{KNbO}_3$, $\text{Cd}_2\text{Nb}_2\text{O}_7$, $\text{PbNb}_2\text{O}_6$, $\text{PbTa}_2\text{O}_6$ and etc.

2. Classification according to the number of directions allowed to the spontaneous polarization:

   This classification also divides the ferroelectric crystals into two groups. The first group includes, those ferroelectrics that can polarize along only one axis such as Rochelle salt and related tartarates $\text{KH}_2\text{PO}_4$-type ferroelectrics, $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{BeF}_4$, Colemanite $\text{CaB}_3\text{O}_4(\text{OH})_3 \cdot \text{H}_2\text{O}$, Thiourea, Glycine sulphate and Glycine salient. The second group includes those ferroelectric which polarize along several axes that are equivalent in non-polar phase such as, $\text{BaTiO}_3$ type ferroelectric, $\text{Cd}_2\text{Nb}_2\text{O}_7$, $\text{PbNb}_2\text{O}_6$, the ferroelectric alums etc.
Both classes show piezoelectric effect in the polarized phase. Ferroelectric of the second class often have transitions points below their Curie temperature at which the spontaneous polarization changes in magnitude and direction. This classification is particularly useful for the study of ferroelectric domains.

3. **Classification according to the existence of lack of center of symmetry in the point group of their non-polar phase:**

   The first group includes those ferroelectric that are piezoelectric in the unpolarized phase, such as Rochelle salt and related tartarates, \( \text{KH}_2\text{PO}_4 \) type ferroelectrics. The second group includes those ferroelectric, which are not piezoelectric in the unpolarized phase, such as \( \text{BaTiO}_3, \text{Cd}_2\text{Nb}_2\text{O}_7, \text{PbNb}_2\text{O}_4, \text{Colemanite CaB}_3\text{O}_4(\text{OH})_3 \text{H}_2\text{O} \) etc. This classification is particularly useful for the thermodynamic treatment of the ferroelectric transitions.

4. **Classification according to the nature of the phase change occurring at the Curie point:**

   According to this classification the ferroelectric crystals are divided into two groups order - disorder group and displacive group.
The order - disorder group of ferroelectrics includes crystals with hydrogen bonds. Such as KH$_2$PO$_4$ and isomorphous salts, triglycine sulphate and probably some of the alums. The ferroelectrics in this group undergo a transition of the order disorder type. In these crystals the motion of the protons is related to their ferroelectric properties as in KH$_2$PO$_4$ [19], Bush et al [20] and Mayer and Bjorkstam [21].

The displacive group of ferroelectrics includes ionic crystals whose structures are closely related to the perovskite and illmenite structures, such as BaTiO$_3$ and most of the double oxide ferroelectrics. The simplest ferroelectric crystal of this group is GeTe, Pawlay et al [22], with the sodium chloride structure. This classification is practically equivalent to that which is done on the basis of the existence of permanent or induced dipoles in the non-polar phase of the crystals.

5. Classification according to the predominant nature of the atomic displacement required by polarity reversal :-

Abrahams and Kere [23] have examined the properties of ferroelectric crystals into three
classes, according to the predominant nature of the atomic displacements required by polarity reversal.

The one dimensional class includes these ferroelectric crystals in which the atomic displacement vector and all loci (L) followed by the atoms, during reversal, are linear and parallel to the polar axis. These are restricted to the point group: 2, 2mm, 3, 3m, 4, 4mm, 6 and 6mm. The well known examples are BaTiO₃, PbTiO₃, KNbO₃, LiNbO₃, BiFeO₃, SbSiO₃.

The two dimensional class includes those ferroelectric crystals in which the atomic displacement vector or the actual loci (L) followed by atom during reversal lie in parallel plane containing the polar direction. These are five point group that satisfy the strict symmetry requirements for this class: m, mm2, 4mm, 3m and 6mm. Examples of such ferroelectrics are BaCO₃F₄, BaZnF₄, BaMnF₄, BaNiF₄, HCl, Ca(NH₂)₂, NaNO₂.

The three dimensional class includes those ferroelectric crystals in which the individual displacement vector and the loci (L) followed by the atom during reversal, have essentially random orientations. Three dimensional ferroelectric contains one or more of the following structural
features, discrete tetrahedral or molecular ions, hydrogen bonds or boron-oxygen frameworks. Examples of this type of ferroelectric are \( \text{B-Gd}_2(\text{MO}_4)_3 \), \( \text{(NH}_4\text{)}_2\text{SO}_4 \), \( \text{KH}_2\text{PO}_4 \), \( \text{CaB}_3\text{O}_4(\text{CH})_3 \), \( \text{H}_2\text{O} \).

4.5 GENERAL DIELECTRIC BEHAVIOUR OF FERROELECTRICS:

In the measurement of dielectric constant of a ferroelectric the frequency and the field strength must be specified because it depends on both frequency and field strength. At low frequencies the piezoelectric deformations can follow the periodic changes of the applied a.c. field hence one measures the dielectric constant of mechanically unconstrained "Free" crystal. At frequencies well above mechanical resonance frequencies of the crystal, the piezoelectric deformations are prevented by interial effects. Hence, measures the dielectric constant of clamped crystal. In non-piezoelectric crystals, such as \( \text{BaTiO}_3 \), above the Curie point the two dielectric constants are identical. But in strongly piezoelectric crystals, such as \( \text{KH}_2\text{PO}_4 \), they can differ by several orders of magnitude.

Megaw [24] has pointed out in the case of a ferroelectric, we should distinguish between the following definitions of susceptibility.
(1) The overall susceptibility $P_C/E_C$, the ratio of the values of $P$ and $E$ at the tip $C$ of the hysteresis loop in figure 4.2.

(2) The differential susceptibility, the slope $dp/de$ at any point.

(3) The initial or small signal susceptibility, the slope $(dp/de)_{E=0}$ of the curve $OA$ at the origin.

(4) The saturation susceptibility, the slope $dp/de$ at $c$.

If the material is already taken round the hysteresis loop, the initial susceptibility is that measured at $F$.

It can be shown to be equal to the slope for small fields applied to a new specimen.

It is seen from the figure (4.2) that the overall susceptibility is much greater than the saturation susceptibility. The saturation susceptibility is measured by applying a d.c. biasing field which is too large and to allow reversal of polarization by the testing ac field.

With the increase of temperature above $80^\circ C$, the hysteresis loop of most of the ferroelectric changes it's shape and in the vicinity of the transition temperature the loop becomes narrow, indicating increase in the susceptibility. For the
FIGURE 4.2 SCHEMATIC REPRESENTATION OF FERROELECTRIC HYSTERESIS LOOP THE COERCIVE FORCE IS $O D$. 
square loop of a true single crystal the sides close together into a vertical line at the transition temperature, showing that the susceptibility has become infinite.

It can be seen in a qualitative way that the dielectric constant measured for small applied fields will show some kind of anomaly at the transition temperature. It is very large in the neighborhood of the transition temperature. For some ferroelectric, the temperature dependence of the dielectric constant above the transition temperature, measured for small applied low frequency fields, can be represented fairly accurately by Curie - Weiss law.

\[ \varepsilon = 4C / (T-T_0) \]  

In certain ferroelectrics which undergo a transition of second - order the Curie - Weiss temperature \( T_0 \) practically coincides with the transition temperature \( T_C \). But the First-order transition \( T_0 \) is lower than the transition temperature.

The Curie constant \( C \) of a ferroelectric containing water of crystallization or short hydrogen bonds is generally of the order of magnitude \( 10^2 \) \(^0\)K (For \( \text{KH}_2\text{PO}_4 \) \( 4C = 3.25 \times 10^3 \) \(^0\)K )
Where as the oxygen octahedra-type ferroelectric have a Curie constant of about $10^4$ $^0\text{K}$. (For $\text{BaTiO}_3$
$4C = 1.6 \times 10^5$ $^0\text{K}$). Models may be set up to explain the observed values of C. For example for a substance containing similar dipoles, each of which has two positions of equilibrium corresponding to opposite orientation of the dipoles as in $\text{KH}_2\text{PO}_4$, it can be shown that the Curie constant should be of the order of magnitude $10^2$ $^0\text{K}$.

4.6 SPONTANEOUS POLARIZATION :-

The existence of dielectric hysteresis loop indicates reversible spontaneous polarization $P_s$. The experimental methods for observation of the hysteresis loop on the screen of a Cathod Ray Oscillograph are based on the Sawyer and Tower circuit [25]. Linear extrapolation from the saturation region to zero field gives the spontaneous polarization $P_s$. The intercept of the loop on the P-axis represents the remanant polarization $P_r$ and the intercept OD on the E axis gives the coercive field. The total polarization of the ferroelectric saturation field OM is represented by the intercept OL.

The main defect of the Sawyer and Tower circuit is the phase difference introduced between
the applied field and the polarizatiorion of the crystal because the impedance of the crystal is variable. This circuit has been modified by Mueller [13b]. The circuits which are commonly used similar in principle to the modified circuit.

Other method which are commonly used for measuring the magnitude of $P_s$ are polarity reversal technique Glass [3], and pyroelectric measurement using calibration for scaling. The last technique is also used to study the temperature dependance of $P_s$ for measurement of pyroelectric.

The nature of the temperature dependence of $P_s$ is governed by the type of phase transition. In ferroelectric crystal which undergoes of first order transition, $P_s$ suddenly falls to zero at the transition temperature. The transition [26] in BaTiO$_3$ is an example of the first-order transition. In a ferroelectric crystal which undergoes a second order phase transition, $P_s$ decreases contineously and becomes zero at the transition temperature called as Curie temperature. The transition in triglycine sulphate, Jona and Shirne [8] is an example of a second order transition.

4.7 THEORIES OF FERROELECTRICITY :-

In view of a number of properties of
ferroelectric, which make them attractive for technological applications, numerous attempts have been made to explain ferroelectricity. The theories proposed so far are not completely satisfactory, and the one which is most promising is due to Cochran based on lattice dynamics. A description of the thermodynamic theory of ferroelectricity, and a brief review of the model theories are given below.

4.7.1. THERMODYNAMIC THEORY OF FERROELECTRIC CRYSTALS:-

A thermodynamic theory is very general in its scope. It is independent of any particular model and thus it leads to quite general conclusions. Although such a theory does not provide the physical mechanism which gives rise to ferroelectric properties of given material, it provides a mathematical framework which can be used in connection with any particular model. The pioneer work in formulating a thermodynamic theory, for the case of Rochelle salt has been done by Mueller [13] and Cady [27]. The theory can be applied to \( \text{KH}_2\text{PO}_4 \) type ferroelectrics.

The thermodynamic treatment of \( \text{BaTiO}_3 \) type ferroelectric is somewhat different, since these
crystals have more than one ferroelectric axis and are not piezoelectric in the paraelectric phase. A thermodynamic theory of such ferroelectric has been developed mainly by Devonshire [14] and Ginzburg [28]. The theory is based on the following assumptions.

(1) The free energy of a ferroelectric is a function of temperature, stress and polarization.

(2) The polarized phases are regarded as a slightly distorted unpolarized phases. Therefore, in all polarized phase the crystal is described by the same free energy function.

(3) The anomalous piezoelectric and elastic properties are considered to be a result of the anomalous dielectric behaviour. Thus the coefficients of $P^2$ in free energy function bear the significant temperature dependence.

(4) The second order piezoelectric coefficients i.e. the electrostrictive coefficients are of main importance because the crystal is not piezoelectric in the unpolarized state.

(5) The free energy function contain three components of the polarization vector.

Thus the free energy of the crystal is expressed by the elastic Gibb's function
\[ G_i = U - T*S - X_i X_i + E_m*P_m \]  

4.17

Where \( U \) is the internal energy of the crystal under external stress, \( T \) is the temperature, \( S \) is entropy, \( X_i \) is the \( i^{th} \) component of mechanical strain, \( E_m \) is the \( m^{th} \) component of electric stress (Electric field) and \( P_m \) is the \( m^{th} \) component of electrical strain (polarization).

The differential form of this function is

\[ d(G_i) = -S*dT + X_i*dX_i + E_m*dP_m \]  

4.18

The index \( i \) can take six values. For compressions or expansions \( i. = 1, 2, 3 \) and for shear \( 4,5,6 \). For a stress free crystal \( X=0 \). The function \( G_i \) can be expanded in powers of polarization with temperature dependent coefficients. Let the crystal be ferroelectric for the temperatures below the transition temperature \( T_c \). For simplicity, it is assumed that in the ferroelectric region the spontaneous polarization occurs along only one axis. Let \( G_{10} \) be the free energy of the unpolarised crystal. Devonshire [14] found that it was necessary to consider the terms up to \( P^6 \). Thus an expansion of the free energy for \( X=0 \) is given by the equation,

\[ G_1 - G_{10} = \frac{1}{2} X_0 P^2 + \frac{1}{4} \beta P^4 + (1/6) \tau P^6 \]  

4.19

It is assumed that \( P \) is total polarization.
and derivative of $G_1$ with respective to $P$ is the externally applied electric stress.

The significant temperature dependence is contained in the coefficient $X_0$.

The meaning of $X_0$ can be seen from the following consideration. Let a small electric field $E$ is applied to the crystal. Then under zero pressure from equation 4.18 we have,

$$dG_1 = -SdT + E dP$$

4.20

So,

$$E = (dG_1/dP)_T$$

4.21

Above the transition temperature the polarisation is small for small applied fields. Therefore for $T > T_C$ all terms except that first on the right hand side of above equation may be neglected. Therefore, we have,

$$E = (dG_1/dP)_T = X_0 P$$

4.22

The dielectric constant and the susceptibility along the polar axis are given by

$$dE/dP = 4\pi / (\epsilon - 1) = 1/n$$

4.23

so, From above equation

$$X_0 = 4\pi / (\epsilon - 1) = 1/n$$

4.24

This equation shows that the coefficient $n$ is equal to the reciprocal of the susceptibility. However, in this temperature range the susceptibility and the dielectric constant along the polar axis are given
by the Curie-Weiss law

\[ n = \left( \epsilon - 1 \right) / 4\pi = C / \left( T - T_C \right) \]  

so that

\[ X_0 = \left( T - T_C \right) / C \]

Where \( C \) is the Curie constant and \( T_C \) is the Curie-Weiss temperature.

Hence equation 4.19 may be written in the following form.

\[ G_1 - G_{10} = \frac{1}{\epsilon} \left[ \left( T - T_C \right) / C \right] P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \tau P^6 \]

From equations 4.22 and 4.27 we get, equations for the applied field and the dielectric constant.

\[ E = \left( dG_1 / dP \right)_T = \left[ \left( T - T_C \right) / C \right] P + \beta P^3 + \tau P^5 \]

\[ 1/n = \left[ 4\pi / \left( \epsilon - 1 \right) \right] = \left[ \left( T - T_C \right) / C \right] + 3\beta P^2 + 5\tau P^4 \]

(a) **Spontaneous Polarization** :-

In the thermal equilibrium \( dG_1 / dP = 0 \), so that the spontaneous polarization \( P_S \) for zero applied electric field satisfies the equation

\[ 0 = X_0 P_S + \beta P_S^3 + \tau P_S^5 \]

It follows that the values of \( P_S \) which give maxima or minima values of \( G_1 \) are given by

\[ P_S = 0 \]

and

\[ X_0 + \beta P_S^2 + \tau P_S^4 = 0 \]

Also differentiating equation no 4.19 and rearranged we have,

\[ d^2 G_1 / dP^2 = X_0 + 3 \beta P^2 + 5 \tau P^4 \]
If $X_0$, $\beta$ and $\tau$ are all positive $P_S = 0$ gives a positive values of $d^2G_1/dP^2$, Therefore $P_S = 0$ will correspond to the only minimum of free energy and in this case spontaneous polarization would not occur. However, if as a result of temperature dependence the co-efficient $X_0$ becomes negative, $G_1$ would be maximum for $P_S = 0$ because in this case $d^2G/dP^2$ is a negative quantity. When $X_0$ is negative equation 4.32 gives at least one non vanishing value of $P_S$ for which $d^2G_1/dP^2$ would be a positive quantity. This shows that in this case $G_1$ would be minimum, i.e. spontaneous polarization would occur consequently, continuous variation of $X_0$ from positive to negative values changes a stable paraelectric state ($X_0 > 0$) to a stable ferroelectric state ($X_0 < 0$). At the transition temperature $T_c$ between these states we have $X_0 = 0$.

Two particular cases are considered below for discussing the properties in the vicinity of the transition temperature.

(b) Second - Order Transition :-

If the coefficients $\beta$ and $X_0$ are positive and varies from positive to negative as the temperature is lowered we obtain free energy curves as shown in figure 4.3(a). The corresponding
spontaneous polarization as function of temperature is shown in figure 4.3(b). Assuming that \( \tau \) is negligible the spontaneous polarization is obtained from equation 4.30

\[
X_0 P_s + B P_s^3 = 0 \quad 4.33
\]

so, that either \( P_s = 0 \) or

\[
P_s^2 = \left( \frac{X_0}{B} \right) = \frac{(T-T_0)}{(C B)} = \frac{(T_0-T)}{(C B)} \quad 4.34
\]

For \( T < T_C \) the only real root of equation 4.33 is at \( P_s = 0 \) because \( C \) and \( B \) are positive. Thus \( T_0 \) is the Curie temperature. For \( T > T_C \) the spontaneous polarization is given by

\[
P_s = \left[ \frac{(T_C-T)}{(C B)} \right]^{1/2} \quad 4.35
\]

This equation shows that \( P_s \) is a continuous function of temperature below \( T_C \) and it decreases continuously to zero at \( T_C \) [Figure 4.3]. This transition is of a second order type. For second order transition the susceptibility and the dielectric constant above the Curie temperature \( T_C \) are given by

\[
n = \left[ \frac{(\varepsilon-1)}{4\pi} \right] = \frac{C}{(T-T_C)} \quad 4.36
\]

Below \( T_C \) the transition temperature on expression for the susceptibility and the dielectric constant is obtained as follows. Assuming that the fifth term in the equation 4.28 and 4.29 is negligible we obtain,

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FIGURE 4.3(a) SCHEMATIC REPRESENTATION OF THE FREE ENERGY AS FUNCTION OF POLARIZATION FOR VARIOUS VALUES OF X FOR A SECOND-ORDER TRANSITION.

FIGURE 4.3(b) SCHEMATIC REPRESENTATION OF THE SPONTANEOUS POLARIZATION AND RECIPROCAL SUSCEPTIBILITY NEAR THE TRANSITION TEMPERATURE $T_c$ FOR A SECOND-ORDER TRANSITION.
\[ S - S_0 = - \frac{1}{2} P^2 dX_0/dT = - \frac{1}{2} P^2 d \left( \frac{T - T_0}{C} \right) / dT \]

\[ S = S_0 - \frac{1}{2} P_s^2 / C \quad \text{(4.41)} \]

Since \( P_s \) is a continuous function of temperature is second order transition and since the slope of \( P_s^2 \) has discontinuity at \( T - T_c \), there should be a discontinuity in the specific heat at the transition temperature.

(c) First order transition:

It has been seen that the condition for the occurrence of spontaneous polarization is that \( X_0 \) should be negative. If at the same time \( S \) is positive, there is a second-order transition. Let us consider the case for which \( S \) is negative and \( X_0 \) is positive and varies from positive to negative values as the temperature is lowered. In this case the free energy curves are shown in fig. 4.4(a). A transition from the non-polarized state to a spontaneously polarized state will now occur when the minimum of the free energy corresponding to \( P_s = 0 \) become equal to the minimum associated with \( P_s \neq 0 \).

In the absence of an external field, the spontaneous polarization satisfies equation 4.30. At the transition temperature \( (T_c) \) the spontaneous polarization should satisfy equation
FIGURE 4.4(a)  SCHEMATIC REPRESENTATION OF THE FREE ENERGY AS FUNCTION OF POLARIZATION FOR VARIOUS VALUES OF X FOR A FIRST-ORDER TRANSITION.

FIGURE 4.4(b)  SCHEMATIC REPRESENTATION OF THE SPONTANEOUS POLARIZATION AND RECIPROCAL SUSCEPTIBILITY NEAR THE TRANSITION TEMPERATURE $T_C$ FOR A FIRST-ORDER TRANSITION.
4.30 and also the condition \( G_1 = G_{10} \). Therefore equation 4.19 we have,
\[
\frac{1}{2} X_0 P_s^2 + \frac{3}{4} \beta P_s^4 + \frac{1}{6} \tau P_s^6 = 0 \quad 4.42
\]

From equations 4.30 and 4.42 we find the relations
\[
P_s^2 = - \left( \frac{3}{4} \right) \frac{\beta}{\tau} \quad 4.43
\]
\[
X_0 = \left( \frac{3}{16} \right) \frac{\beta^2}{\tau} \quad 4.44
\]
\[
P_s^2 = 3 \left( \frac{X_0}{\beta} \right) \quad 4.45
\]

Equation 4.43 shows that the spontaneous polarization is discontinuous at the transition temperature, Fig. 4.3.(b). According to equation 4.41 the entropy will also be discontinuous at \( T_C \) and there will be a latent heat i.e. the transition is of the first order.

Let us consider the susceptibility and the dielectric constant on both sides of the transition temperature. As in the case of a second-order transition the susceptibility and the dielectric constant in the region above \( T_C \) again follow the Curie-Weiss law.
\[
n = \left[ \frac{(\varepsilon - 1)}{4\pi} \right] = \left[ \frac{C}{(T - T_0)} \right] \quad 4.46
\]
Where for first order transition \( T_0 < T_C \)

Below for transition temperature an expression for the susceptibility and the dielectric constant is obtained as follow.
For small applied fields, \( P = P_a \) so that from equation 4.30 we have,

\[
1/n = 4\pi/(\varepsilon - 1) = [(T - T_C)/C] + 3P_s^2 + 5TP_s^4 \quad 4.47
\]

From equation 4.43 and 4.45

\[
3P_s^2 = -(9/4)*(\delta^2/\gamma)
\]

\[
= -(9/4)*(16/3)*X_0
\]

\[
= -12*(T-T_0)/C
\]

and

\[
5P_s^4 = 15X_0 = 15[(T-T_0)/C]
\]

Substituting these values in equation 4.4 We have,

\[
1/n = 4\pi/(\varepsilon - 1)
\]

\[
= [(T-T_0)/C] -12[(T-T_0)/C] + 15[(T-T_0)/C]
\]

or

\[
1/n = 4\pi/(\varepsilon - 1) = 4[(T-T_0)/C]
\]

So

\[
n = (\varepsilon - 1) / 4\pi = C / 4(T-T_0) \quad 4.48
\]

From above equations it is seen that the reciprocal of the susceptibility in a first order transition is not zero at the transition temperature \( T_C \), but it is a positive quantity. Its temperature variation just above and just below \( T_C \) is shown in figure 4.4(b).

4.7.2 MODEL THEORIES OF FERROELECTRICITY :-

In order to explain the occurrence of spontaneous polarization in general it is necessary
to have physical model in which the dipole moment of the different unit cells are oriented along a common direction. Since a ferroelectric crystal is a very complicated molecular system, a rigorous theorotical treatment of a realistic model is very difficult. A number of scientist have proposed model theories of ferroelectricity. Most of the theories are applicable to a single case. Because of the importance of oxygen-octahedra ferroelectrics, a brief review of model theories. Which have been proposed to explain ferroelectric properties is given below.

In the model theory of BaTiO$_3$, Mason and Mathias [29] have suggested that the stable position for the Ti$^{4+}$ ion is not at the centre of the oxygen octahedra. Instead it is at any of the six position which correspond to slight displacement from the centre towards the oxygen ions. When the Ti$^{4+}$ ion is in any of these positions the unit cell would have a dipole moment. However, if any dipole theory were correct, a number of polar liquids would be ferroelectrics, which is not the case. Another disadvantage of this theory is that it is not possible to obtain good agreement with experimental calculations.
Jaynes [30] proposed a model in which oxygen ions are displaced rather than titanium ions. He has also proposed a theory in which dipole moments are not attributed to atomic displacements. Only the electronic states of the TiO$_6$ octahedra are considered. The theory is satisfactory for determining the entropy change. But it predicts an infra-red absorption line at 10 μ. Which was not detected.

Devonshire’s model theory [31] considers the dipole of an atom vibrating in the field of its neighbours. The dipole moment is not fixed in magnitude but depends on the displacement from equilibrium position.

Slater [10] has also proposed a model theory which is similar to that of Devonshire. In addition, he assumes that each atom has an electronic polarization and the titanium ion has an ionic polarization. The theory predicts that the direction of spontaneous polarization is along the axis, but this is a disadvantage when it is applied to some other structure.

Megaw [32] has suggested that directional covalent bonding is of primary importance in the ferroelectricity of PbTiO$_3$ and the
antiferroelectricity of PbZrO$_3$. The 110 displacements of the Pb ions in PbZrO$_3$ indicate that the Pb ion can displace in directions other than a fourfold axis, in which it remains in PbTiO$_3$ at all temperatures from the Curie point (490 °C) to that of liquid Helium. He points out that Zr ions may have directional covalency which would certainly influence that of Pb. The disadvantage with Megaw's theory is that the origin of ferroelectricity is attributed to abrupt changes in the character of bonds at each transition.

4.7.3 COCHRAN'S THEORY OF FERROELECTRICITY :-

Cochran [15] has proposed a lattice dynamical theory of ferroelectricity for certain crystals. The theory is based on the assumption that the ferroelectric phase transitions are the results of the instability of the crystal lattice with respect to one of the homogeneous transverse optical mode. If crystal is wholly or partly ionic, lattice vibrations are accompanied by polarization oscillations of equal frequency, which give rise to a local field interacting with the ions through long range coulomb forces. If for one particular mode of vibration, these long range forces are equal in magnitude but opposite in sign.
to the short range forces, the crystal becomes unstable for this mode. The dielectric constant, which is connected to the frequency of the critical model becomes extremely large, at the Curie temperature.

The theory provides an explanation of ferroelectric phase transition in diatomic crystals of the NaCl or CaCl-type. Cochran [15] has used the data on the lattice dynamics of diatomic crystals and his own experimental data on the dielectric properties of cubic crystals in an analysis of some characteristics of transition in BaTiO$_3$. He has estimated the dielectric constant and the spontaneous polarization $P_s$ of BaTiO$_3$, at the Curie temperature as $\epsilon = 1.4 \times 10^4$ and $P_s = 19.5$ $\mu$C/cm$^2$ respectively. Which are very close to the experimental values. The temperature dependence of the spontaneous polarization, calculated by Cochran is very close to the experimentally determined variation [26]. These results indicate that Cochran's theory explains quite satisfactorily many properties of BaTiO$_3$. Moreover, the parameters used in Cochran's calculations have reasonable values.

The most interesting new result of the theory is the prediction of the absolute values of the
frequency $W_t$ of the transverse optical mode with wave vector zero for perovskite type materials. This frequency has been estimated to be $W_t = (2 \text{ to } 3) \times 10^{11}$ CPS. for BaTiO$_3$. The frequency lies in the millimeter wavelength range. For this reason an experimental verification of the theory is difficult. Recently, investigation have been made in the infra-red part of the spectrum. Infrared studies by Ballantye [33] on BaTiO$_3$ above the Curie temperature, show that within the experimental error the results are in agreement with Cochran's theory. Similar results have also been reported in other perovskite ferroelectric. Cochran's theory is also supported by experimental observations that there is a fall of the frequency of the transverse optical mode as the Curie temperature is reached from above and that no dielectric relaxation occurs for several perovskite ferroelectrics upto $10^{11}$ CPS.
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