General properties of ferroelectric materials

In many respects analogous to the magnetic behavior of ferromagnetic materials, ferroelectric solids are so called because they are spontaneously polarized, i.e., it is polarized in the absence of an 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.
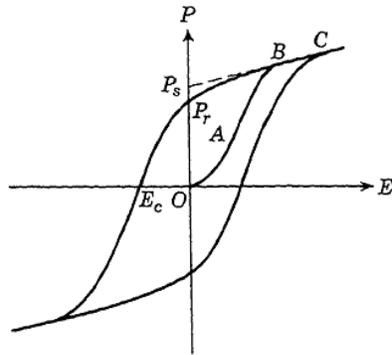
On the basis of the domain concept, the occurrence of hysteresis in the P versus E relationship can be explained as follows: With reference to Figure, let us consider a crystal which initially has an over-all polarization equal to zero, i.e., the sum of the vectors representing the dipole moments of the individual domains vanishes. When an electric field is applied to the crystal, the domains with polarization components along the applied field direction grow at the expense of the "antiparallel" domains; thus the polarization increases (OA). When all domains are aligned in the direction of the applied field (BC), the polarization saturates and the crystal has become a single domain.

The extrapolation of the linear part BC to zero external field gives the spontaneous polarization P_s. Thus, when we speak of "spontaneous polarization" we have in mind the polarization within a single domain and not the over-all polarization of a crystal. When the applied field for a crystal corresponding to point B in Figure is reduced, the polarization of the crystal decreases. But for zero applied field there remains the remnant polarization P_r where P_r refers to the crystal as a whole. The field in opposite direction required to make the polarization zero again is called the coercive field E_c.

A necessary, but not sufficient, condition for a solid to be ferroelectric is the absence of a center of symmetry. In total there are 21 classes of crystals which lack a center of symmetry; the classes are based on the rotational symmetry of crystals. Of these 21 classes, 20 are piezoelectric, i.e., these crystals become polarized under influence of external stresses. Ten out of the 20 piezelectric classes exhibit pyroelectric effects. These pyroelectric crystals are spontaneously polarized. However, the polarization is usually masked by surface charges which collect on the surface from the atmosphere; when the temperature of such a crystal is altered, the polarization changes and this change can be observed, hence the name pyroelectricity. The ferroelectric materials are part of the group of spontaneously polarized pyroelectrics. However, they have the additional property that the polarization can be reversed by an applied field.

Crystal class	Centro symmetric Point groups		Noncentrosymmetric Point groups				
			Polar		Non-polar		
Cubic	m3	m3m	none		432	$\bar{3}$ m	23
Tetragonal	4 or m	4 or mmm	4	4mm	$\bar{4}$	$\bar{4}$ 2 m	22
Orthorhombic	mmm		mm2		222		
Hexagonal	6 or m	6 or mmm	6	6mm	$\bar{6}$	$\bar{6}$2m	622
Trigonal	$\bar{3}$	$\bar{3}$ m	3	3m	32		
Monoclinic	2 or m		2	m	none		
Triclinic	$\bar{1}$		1		none		
Total Number	11 groups		10 groups		11 groups		

The ferroelectric properties of a ferroelectric disappear above a ***critical temperature* T$_c$**; this temperature is called the ferroelectric Curie temperature. Associated with the transition from the ferroelectric to the nonferroelectric phase are anomalies in other physical properties. Thus for a first-order transition, there will be a latent heat; for a second-order transition the specific heat will exhibit a discontinuity. We should also mention that the spontaneous polarization in the ferroelectric state is associated with spontaneous electrostrictive strains in the crystal; thus the ferroelectric structure has a lower symmetry than the nonpolarized state. At the transition temperature a change in crystal structure is therefore observed.

Classification and properties of ferroelectrics

Ferroelectric crystals may be classified into two main groups, ***order-disorder*** and ***displacive***. One may define the character of the transition in terms of the dynamics of the lowest frequency ("soft") optical phonon modes. If a soft mode can propagate in the crystal at the transition, then the transition is displacive. If the soft mode is only diffusive (non-propagating) there is really not a phonon at all, but is only a large amplitude hopping motion between the wells of the order-disorder system. Many ferroelectrics have soft modes that fall between these two extremes.

Order-disorder class: The order-disorder class of ferroelectrics includes crystals with hydrogen bonds in which the motion of the protons is related to the ferroelectric properties.

Example: Rochelle Salt ($NaKC_4H_4O_6 \cdot 4H_2O$); Potassium dihydrogen phosphate (KH_2PO_4)
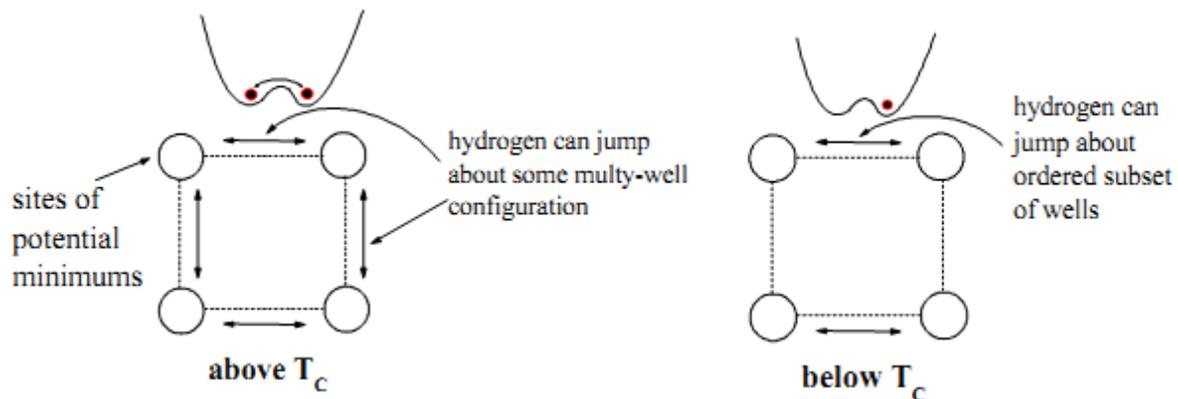
Note: Neutron diffraction data show that above the Curie temperature the proton distribution along the hydrogen bond is symmetrically elongated. Below the Curie temperature the distribution is more concentrated and asymmetric with respect to neighboring ions, so that one end of the hydrogen bond is preferred by the proton over the other end, giving a polarization.

Displacive class: The displacive class of ferroelectrics includes ionic crystal structures closely related to the perovskite structures.

Example: $BaTiO_3$. It has cubic structure above T_C, below T_C lattice structure is changed. Ba^{2+} and Ti^{4+} ions displaced relatively to the O^{2-} ions, which is the root of spontaneous polarization.
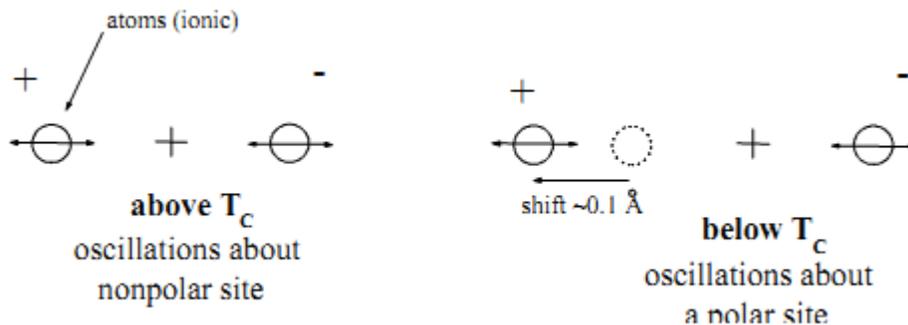
Rochelle Salt: Rochelle salt has the peculiar property of being ferroelectric only in the temperature region between -18°C and 23°C, i.e., it has two transition temperatures. In the region above 23°C and below **−1**8°C it crystallizes in the orthorhombic structure. In the ferroelectric phase the crystal is monoclinic. The spontaneous polarization occurs along the direction of the original orthorhombic a-axis. Thus Rochelle salt has only one polar axis and two possible polarization directions (+and − along the a-axis).
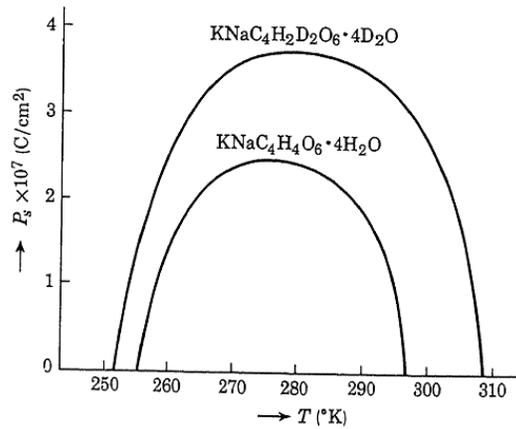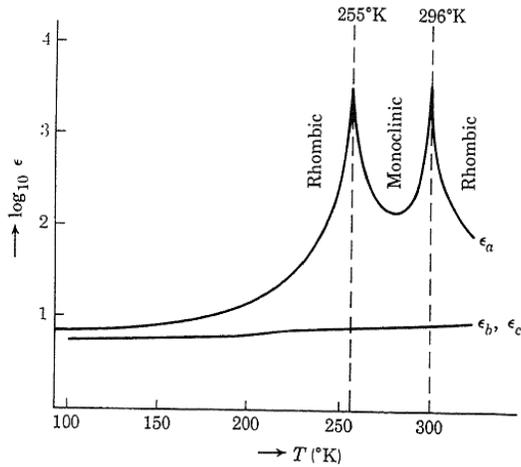
Note that the replacement of hydrogen by deuterium has a marked influence on the magnitude of the spontaneous polarization and on the temperature range over which the material is ferroelectric.

Potassium dihydrogen phosphate, KH₂PO₄: In contrast with Rochelle salt, KH_2PO_4 has one Curie temperature, $T_c = 123°K$. Above the transition temperature it has a tetragonal structure (3 mutually perpendicular axes a, a, c); below T_c it is orthorhombic (3 mutually perpendicular axes a, b, c). The c-axis is the spontaneous polarization direction.

Barium titanate (BaTiO₃): $BaTiO_3$ is the most important and most thoroughly studied representative of the perovskites. In the nonpolarized phase it has cubic symmetry. The Ba^{2+} ions occupy the corners of a cube, the oxygen ions are located at the centers of the faces, and the Ti^{4+} ion is at the center.
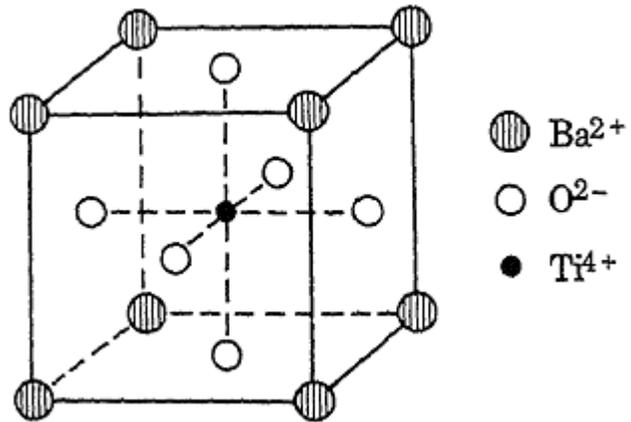
Below the Curie temperature, the direction of the spontaneous polarization and the crystal structure vary in the following fashion:

Temp. region (°K)	Dir. of pol.	Structure
278–393	[001]	tetragonal
193–278	[011]	orthorhombic
<193	[111]	rhombohedral

BaTiO$_3$ has three ferroelectric phases. As the spontaneous polarization sets in at 393°K, the crystal expands in the direction of polarization (c-axis) and contracts perpendicular to it (a-axis).
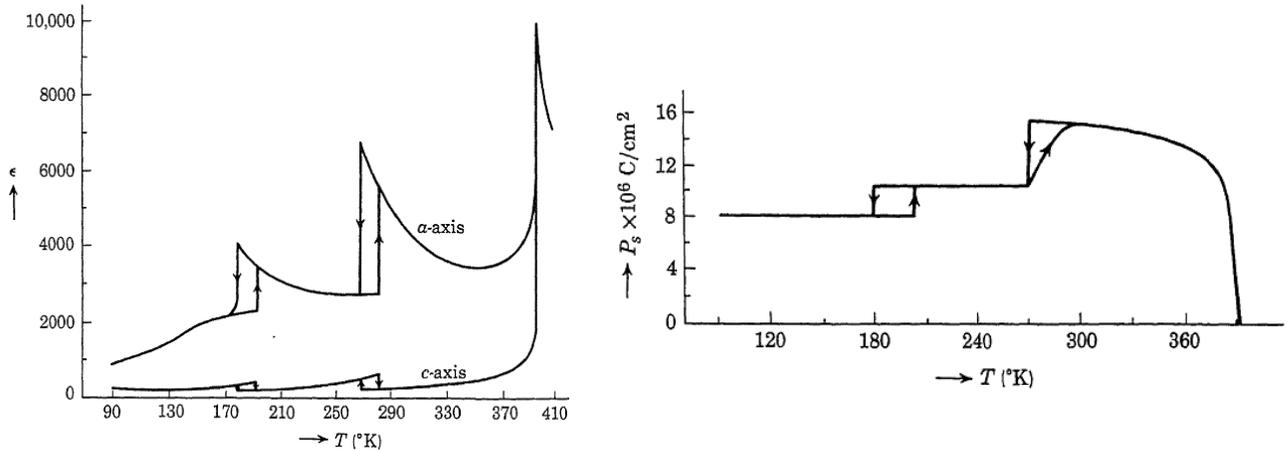
Polarization catastrophe

We may speak of a polarization catastrophe in which for some critical condition the polarization becomes very large. Considering the local field approximation, we find the dielectric constant,

$$\varepsilon = \frac{1 + \dfrac{2}{3\varepsilon_0}\sum_i n_i\alpha_i}{1 - \dfrac{1}{3\varepsilon_0}\sum_i n_i\alpha_i}$$ where α_i being function of temperature

could lead to the divergence of ε at a certain temperature with the critical value, $1 - \dfrac{1}{3\varepsilon_0}\sum_i n_i\alpha_i = 0.$ This is the condition for a polarization catastrophe. Expansion of small deviations linear in temperature around critical value gives

us $\dfrac{1}{3\varepsilon_0}\sum_i n_i\alpha_i = 1 - \dfrac{(T-T_0)}{C}$, where $(T-T_0) \ll 1.$ When T

approaches T_0, we find $\varepsilon_r \approx \dfrac{C}{(T-T_0)} \to \infty.$

In a polarization catastrophe the local electric field caused by the ionic displacement is larger than the elastic restoring force, thereby giving an asymmetrical shift in the positions of the ions. Higher order restoring forces will limit the shift to a finite displacement. This idea can be apprehended by considering LST relation: $\dfrac{\omega_T^2}{\omega_L^2} = \dfrac{\varepsilon(\infty)}{\varepsilon(0)}.$ Here, $\varepsilon(\infty)$ is the high frequency dielectric constant and $\varepsilon(0)$ being static dielectric constant. ω_T is the frequency TO (transverse
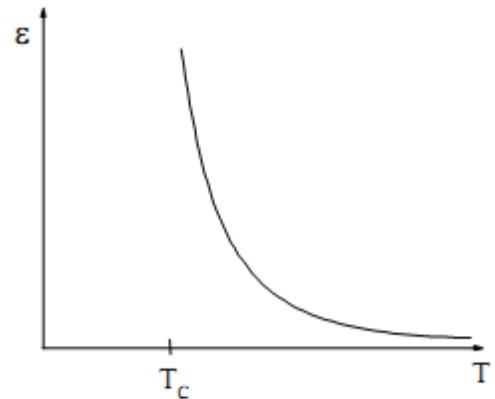
optical) phonon and ω_L, the LO (longitudinal optical) phonon frequency. The relation $\varepsilon(0) \approx \dfrac{C}{(T-T_0)}$ gives the values of $\omega_T \propto \sqrt{(T-T_0)}$ when T approaching towards T_0. In the condition of polarization catastrophe $(T \to T_0)$ the frequency of TO phonon decreases drastically.
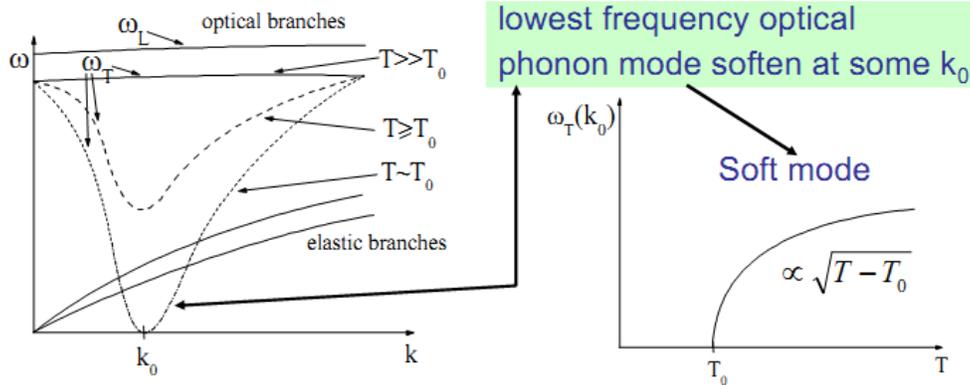
The dipole theory of ferroelectricity

The existence of spontaneous polarization in general requires a physical model in which the dipole moments of the different unit cells are oriented along a common direction. This brings ferroelectrics in the class of cooperative phenomena, the cooperation between the different unit cells in this case consisting of a tendency for a given unit cell to have its dipole direction parallel to that of its neighbors.

The essential point in the dipole theory is that the internal field E_i which tends to orient a given dipole is assumed to be of the form, $E_i = E + \gamma P$ \hfill (1)

where E is the externally applied field, P is the polarization, and γ is the internal field constant. This expresses the cooperation between the dipoles, because the larger P, the larger E_i and the stronger the tendency for the dipole under consideration to align itself in the direction of the polarization of its surroundings.

As long as one is far away from saturation of the polarization, one may write,

$$P = N\mu\langle\cos\theta\rangle = N\left(\mu^2/3kT\right)E_i \tag{2}$$

where N is the number of dipoles per unit volume.

From Eqs. (1) & (2),

$$\chi = P/E = N\left(\mu^2/3kT\right)\left(E_i/E\right) = \frac{N\left(\mu^2/3kT\right)E_i}{E_i - \gamma P} = \frac{N\left(\mu^2/3kT\right)}{1-\left(\gamma P/E_i\right)} = \frac{N\left(\mu^2/3kT\right)}{1-\left(\gamma\left(N\left(\mu^2/3kT\right)E_i\right)/E_i\right)}$$

$$\Rightarrow \chi = \frac{N\left(\mu^2/3kT\right)}{1-\left(N\gamma\mu^2/3kT\right)} = \frac{\theta/\gamma T}{1-\theta/T} = \frac{\theta/\gamma}{T-\theta}. \tag{3}$$

Here, $\theta = N\gamma\left(\mu^2/3k\right)$ is the extrapolated Curie temperature and θ/γ being Curie constant.

To show that Eq. (1) also leads to spontaneous polarization, we make use of the Langevin expression, which allows for saturation effects.

This gives $P = N\mu\langle\cos\theta\rangle = N\mu L\left(\mu E_i/kT\right) = N\mu L\left(\mu(E+\gamma P)/kT\right).$ (4)

$L(x)$ is the Langevin function. To show Eq. (1) indeed leads to the possibility of spontaneous polarization. Putting $E = 0$ in Eq. (4), we may write $P/N\mu = P/P_{sat} = L(x)$ (5)

Where $x = \mu\gamma P/kT$ or $P/N\mu = \left(kT/N\mu^2\gamma\right)x.$ (6)

$N\mu = P_{sat}$ represents evidently the saturation polarization corresponding to complete alignment of the dipoles.
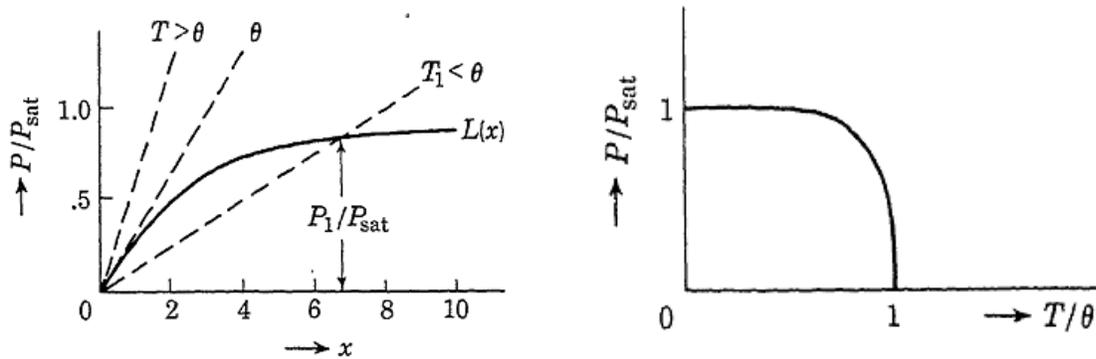
The fully drawn curve represents the Langevin function. The slope of $L(x)$ at the origin is 1/3. However, *P/Psat* should also satisfy Eq. (6), which corresponds to a set of straight lines passing through the origin, the slope of the lines being given by $kT/N\mu^2\gamma$. Thus the solution for P/P_{sat} corresponding to the temperature T_1 is determined by the intersection of $L(x)$ and the line of slope $kT_1/N\mu^2\gamma$. It is observed that as T decreases, the slope of the straight line Eq. (6) decreases and the solution *P/Psat* approaches unity. Also, when the temperature is higher than a critical value determined by $kT_c/N\mu^2\gamma = 1/3$ or $T_c = N\mu^2\gamma/3k = \theta.$ (7)

In other words, there is no spontaneous polarization for $T \succ \theta.$

Note: *One may **conclude the assumption** for Eq. (1) for **a model of freely rotating dipoles** accounts for: (a) the Curie-Weiss law above the Curie temperature; (b) the possibility of spontaneous polarization below the Curie temperature; (c) qualitatively the correct temperature behavior of P/Psat versus temperature in the ferroelectric region.*

Estimation of extra specific heat (discontinuity in specific heat) from dipole theory

An anomalous peak in the specific heat as function of temperature observed for ferroelectrics in the vicinity of the Curie temperature. We try to find the relation between the internal field constant γ appearing in the above theory and the appearance of anomalous peak in specific heat. In the completely ordered state, when all dipoles are aligned in parallel, the energy of a given dipole in the field of all others is equal to $-\mu\gamma P_{sat}$ as we know, the energy of a dipole μ in a field E is given by $-\mu \cdot E$. Thus the energy of polarization in the ordered state is per unit volume equal to $-N\mu\gamma P_{sat}/2$, where the factor of ½ is introduced because for each pair of dipoles the energy is counted twice. Now, as the temperature is increased to above the Curie temperature, the spontaneous polarization decreases to zero. It is evident that an "extra" amount of heat must be supplied to the crystal to bring about the transition from the completely ordered to the completely disordered state. Let C_e represent the extra specific heat per unit volume; we may then write

$$\int C_e(T)dT = N\mu\gamma P_{sat}/2 = \gamma P_{sat}^2/2$$

(8)

Thus, if $C_e(T)$ and P_{sat} are known from experiment, Eq. (8) allows one to calculate the internal field constant γ.

Objections against the dipole theory

In connection with Rochelle salt, the following objections may be raised against the dipole theory.

(i) In the vapor, H_2O has a dipole moment of 1.85 Debye units; if we assume this to be the same in Rochelle salt, one calculates for the maximum spontaneous polarization $P_{sat}= N\mu = 1.52 \times 10^{22} \times 1.85 \times 10^{-18} = 28120$ esu. The experimental value is about 750 esu which is smaller by a factor of nearly 40.

(ii) Furthermore, the dipole theory does not predict the existence of two Curie points, as observed for Rochelle salt.

(iii) A much more serious objection against the dipole theory is of a theoretical nature and refers to the use of the internal field given by Eq. (1). In fact, if the dipole theory based on Eq. (1) were correct, a large number of polar liquids should also be ferroelectric; we know, on the other hand, that ferroelectric materials are rare. On considering the concept of reaction field, it is finally observed that γ is not a constant but that it depends on the dielectric constant in such a manner that as ε increases, γ decreases.

Note: *Let us consider a spherical cavity of molecular radius inside a dielectric in the absence of an external field. Suppose a dipole μ is located at the center of the cavity. The dipole will polarize the surrounding material and this in turn will produce a "reaction field" inside the cavity. If the dielectric is homogeneous, it can be shown that the reaction field E, is homogeneous and parallel to the dipole μ. It is evident that the reaction field does not exert a torque on the dipole. If one now applies to this system a homogeneous external field E and calculates the internal field by the Lorentz method, a part of the internal field is contributed by the time average of the reaction field; this part is equal to $E_r<cos\ \theta>$ where θ is the angle between μ and E and, as said above, does not produce a torque on the dipole. To find the actual field strength tending to orient the dipole, one must subtract the reaction field component in the external field direction. By putting this value it is observed that γ is not a constant but that it depends on the dielectric constant in such a manner that as ε increases, γ decreases.*

Curie-Weiss Law for a nondipolar solid

We have seen that the dipole theory led to a Curie-Weiss law for the susceptibility above the Curie temperature with an expression of the type Eq. (1) for the internal field. But it is also pointed out that the internal field could not be considered the field producing a torque on the dipoles. On the other hand, the objection of Onsager was that electronic and ionic displacements are not referred in dipole theory. In this section it will be shown that in case the dielectric constant of a material is large compared with unity, a Curie-Weiss law may be obtained which is solely due to electronic and ionic displacements.

For the sake of argument, let us assume that, for a particular nondipolar solid, the Clausius-Mosotti expression holds

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\alpha}{3\varepsilon_0} = \beta N \qquad (9)$$

Here N represents the number of unit cells per cm^3 and α represents the total polarizability per unit cell assuming that α is independent of temperature.

As long as ε is of the order of 10 or smaller, any changes in N resulting from thermal expansion do not affect the value of ε to any great extent. On the other hand, if $\varepsilon \gg 1$, the left-hand side of Eq. (9) approaches unity and it is observed from Figure that small variations in βN may lead to large changes in the dielectric constant. In order to determine the temperature coefficient of ε, we differentiate Eq. (9) with respect to T,
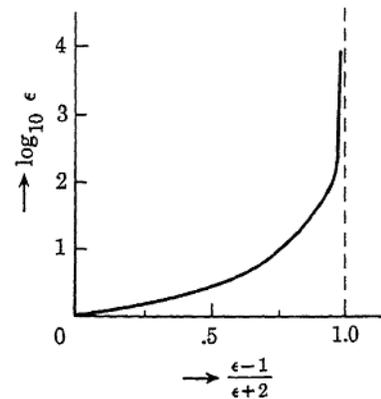
$$\frac{(\varepsilon+2)-(\varepsilon-1)}{(\varepsilon+2)^2}\frac{d\varepsilon}{dT}=\beta\frac{dN}{dT} \Rightarrow \frac{(\varepsilon+2)-(\varepsilon-1)}{(\varepsilon+2)^2}\frac{d\varepsilon}{\beta dT}=\frac{dN}{dT}$$

$$\Rightarrow \frac{(\varepsilon+2)-(\varepsilon-1)}{(\varepsilon+2)^2}\frac{d\varepsilon}{dT}\frac{N(\varepsilon+2)}{(\varepsilon-1)}=\frac{dN}{dT}$$

$$\Rightarrow \frac{3}{(\varepsilon+2)(\varepsilon-1)}\frac{d\varepsilon}{dT}=\frac{1}{N}\frac{dN}{dT}=3\lambda \qquad (10)$$

where $\frac{1}{N}\frac{dN}{dT}$ corresponds to volume expansion coefficient and λ is the linear expansion coefficient.

Making use of the fact that $\varepsilon \gg 1$, so that $(\varepsilon+2)(\varepsilon-1)\approx\varepsilon^2$, one obtains $\int\frac{d\varepsilon}{\varepsilon^2}=-\int\lambda dT$

or $\varepsilon=\frac{1/\lambda}{T-\theta}=\frac{C}{T-\theta}$. The last expression has indeed the form of the Curie-Weiss law; the Curie temperature θ enters as a constant of integration. It is of interest to note that the Curie constant is equal to the reciprocal of the linear coefficient of expansion. The variation of linear coefficient of expansion is controlled by TO phenomena in the range $\varepsilon \gg 1$.

Theory of spontaneous polarization of BaTiO$_3$

The existence of three transitions in BaTiO$_3$ to is based on the assumption that the displacement of oxygen ions is essential in the context of spontaneous polarization. Devonshire pointed out that the restoring force for small oxygen displacements in a direction perpendicular to the plane of four surrounding Ba^{2+} ions is probably small. This is the result of the fact that O^{2-} ions are tightly squeezed between Ba^{2+} ions.

One can associate three O^{2-} ions with each unit cell as six ions belong to two unit cells. They can be denoted by O$_x$, O$_y$, and O$_z$. When cooled from the region T > T$_c$, the cubic lattice contracts and at T$_c$ one of the three O^{2-} ions (say, O$_z$) is squeezed out of the plane of the Ba^{2+} ions. This produces a dipole moment per unit cell along z-axis. One of its parts is equal to *2ed$_z$* where *d$_z$* is the displacement of the O$_z$ ion relative to the plane of Ba^{2+} ions. At the same time, this allows a possible contraction of the lattice in the plane of the Ba^{2+} ions. The direction of polarization corresponds to the c-axis of the tetragonal structure and sets in along one of the cube edges at T$_c$. As the temperature is lowered further, O$_y$ and O$_x$ ions are successively squeezed out of their normal positions, leading to a polarization along a face diagonal [011] and a body diagonal [111], respectively.

Agreement with experiment

Experimentally it is found that in the tetragonal region the contraction of the lattice is proportional to the square of the polarization and satisfies the relation:

$$\Delta a/a = 1.2 \times 10^{-12} P^2 \tag{11}$$

where a is the cube edge just above the Curie point and Δa is the contraction in the tetragonal phase. Now, in the cubic phase, the sum of the radii of the Ba^{2+} and O^{2-} ions is equal to $a/\sqrt{2}$. We suppose now that the oxygen ion is displaced out of the plane of Ba^{2+} ions by an amount z and let it be assumed that the radii of the ions remain constant and that the oxygen and barium ions remain in contact. With reference to Figure it then follows that if $(a-\Delta a)$ is the new edge of the square of Ba^{2+} ions, we must have
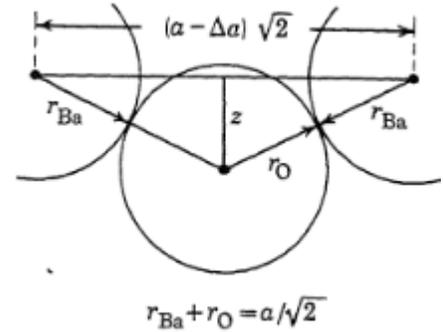
$$(a-\Delta a)^2/2 = a^2/2 - z^2$$

As long as $\Delta a/a \ll 1$, this yields $\Delta a/a = (z/a)^2$ (12)

The dipole moment per unit volume resulting only from the displaced oxygen ions is equal to $P_{O_z} = 2ez/a^3$ and it thus follows from Eq. (12) that

$$\Delta a/a = (a^4/4e^2)P_{O_z}^2 = 2.8 \times 10^{-12} P_{O_z}^2 \tag{13}$$

Both expressions are of the same form, and that if P_{O_z} represents two thirds of the total polarization, the agreement is quantitative.

Landau theory of Phase Transitions

A ferroelectric with a first-order phase transition between the ferroelectric and the paraelectric state is distinguished by a discontinuous change of the saturation polarization at the transition temperature. In the second-order transition the degree of order goes to zero without a discontinuous change as the temperature is increased. A thermodynamic theory has the advantage of being independent of any particular atomic model and thus leads to quite general conclusions. Such a theory does not provide the physical mechanism responsible for the ferroelectric properties of a given material.

Let us consider a solid which is ferroelectric for temperatures $T < Tc$; let the external pressure be zero and let there be no applied electric field. If the crystal is in equilibrium at a given temperature, the free energy of the crystal F should be a minimum. For simplicity we shall assume that in the ferroelectric region the spontaneous polarization occurs along a single axis; this would be the case for the Rochelle salt,

KH_2PO_4 and for the upper transition of $BaTiO_3$. Let F_0 represent the free energy of the unpolarized crystal; the free energy F of the polarized crystal may then be expanded as a power series in the polarization

$$F - F_0 = \frac{1}{2}c_1 P^2 + \frac{1}{4}c_2 P^4 + \frac{1}{6}c_3 P^6 + ... \tag{14}$$

The coefficients c are functions of temperature; the numerical factors are introduced for later convenience. Note that since we want the free energy to be the same for "positive" and "negative" polarization along the polar axis, only even powers of P are included. In thermal equilibrium, $\left(\frac{\partial F}{\partial P}\right)_T = 0$. The spontaneous polarization, thereby, satisfies the equation:

$$c_1 P_s + c_2 P_s^3 + c_3 P_s^5 + ... = 0 \tag{15}$$

It is observed that $P_s = 0$ is always a root of this equation and that and c_1, c_2, c_3 are all positive, the root $P_s = 0$ will correspond to the only minimum of the free energy and thus spontaneous polarization would not occur. However, if as a result of the temperature dependence the coefficient c_1 would become negative, F would have a maximum for $P_s = 0$ and there would be at least one nonvanishing value for P_s for which F would be a minimum, i.e., spontaneous polarization would occur.

Second-order transition:

If the coefficients c_1, c_2, c_3 are all positive and the value of c_1 varies from positive to negative as the temperature is lowered, one obtains free energy curves as illustrated in Figure. The corresponding spontaneous polarization as function of temperature is indicated in Figure.
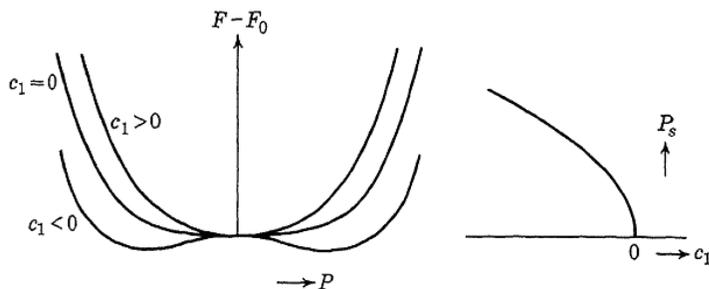
The transition temperature corresponds to $c_1 = 0$. Assuming in Eq. (15) that the term with c_3 is negligible, one obtains for the spontaneous polarization,

$$P_s^2 = -c_1/c_2. \tag{16}$$

P_s is a continuous function of temperature; a transition of this type is not associated with a latent heat but with a discontinuity in the specific heat and is called a *second-order transition*.

Let us now consider the susceptibility of the crystal above and below the transition temperature. For this purpose it is necessary to apply a small electric field to

the crystal. Now, for a crystal under zero pressure in an applied field E, we may write according to thermodynamics, $dF = -SdT + EdP$.

Above the transition temperature the polarization will be small for small applied fields, and in this region we may neglect all terms on the right-hand side of Eq. (14) except the first. For $T > T_c$, $E = \partial F/\partial P = c_1 P$ and $1/\chi_a = \partial E/\partial P = c_1$ (17)

χ_a being susceptibility above the Curie temperature. The susceptibility in this temperature

range is given by the Curie-Weiss law $\chi_a = \dfrac{C}{T-\theta} \Rightarrow c_1 = \dfrac{T-\theta}{C}$, where C is the Curie constant.

Since the transition at $T = T_c$ corresponds to $c_1 = 0$, we have $\theta = T_c$ which leads to

$$c_1 = \frac{T-T_c}{C} = 1/\chi_a. \tag{18}$$

Similarly, in the ferroelectric region, we obtain,

$$E = \partial F/\partial P = c_1 P + c_2 P^3 \Rightarrow 1/\chi_b = \partial E/\partial P = c_1 + 3c_2 P^2 \tag{19}$$

χ_b being susceptibility above the Curie temperature.

For small applied fields, $P \approx P_s$ in this region, so that according to Eqs. (16) and (19) we have

$$1/\chi_b = c_1 + 3c_2\left(-c_1/c_2\right) = -2c_1 \tag{20}$$
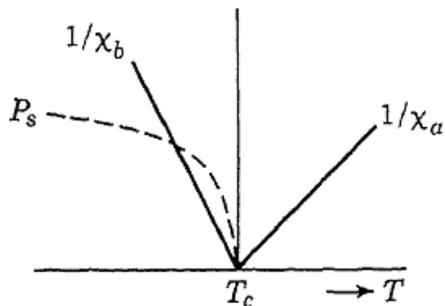
If we still assume the temperature dependence of c_1 on the ferroelectric side of T_c, we further obtain from Eqs. (19) and (20), $1/\chi_b = -2c_1 = -\dfrac{2\left(T-T_c\right)}{C}$ (21)

In connection with the entropy associated with spontaneous polarization, the entropy is

$$S = -\left(\partial F/\partial T\right)_P = S_0 - \frac{1}{2}P^2\left(\partial c_1/\partial T\right)$$

$$-\frac{1}{4}P^4\left(\partial c_2/\partial T\right) + \dots\dots$$

where S_0 is the entropy of the unpolarized crystal. To a first approximation, we may write

$$S - S_0 \simeq -\frac{1}{2}P^2\left(\partial c_1/\partial T\right) \tag{22}$$

Since P is a continuous function of temperature for the case under consideration and since the slope of P^2 has a discontinuity at $T = T_c$, there should be a discontinuity in the specific heat, but no latent heat, i.e., the transition is of the second order.

Dielectric constant in case of second-order transition: The dielectric constant can be simply

written as $\varepsilon = 1 + P/\left(\varepsilon_0 E\right)$. Above the transition temperature $E = c_1 P = \dfrac{\left(T-T_c\right)P}{C}$. So the

expression of dielectric constant is $\varepsilon = 1 + \dfrac{C}{\varepsilon_0 (T - T_c)}$. At $T = T_c$ the reciprocal of dielectric constant is zero.

First-order transition:

We have seen that spontaneous polarization requires the coefficient c_1 to be negative. Furthermore, we have seen that if at the same time c_2 is positive, a second-order transition results.

(a)

(b)
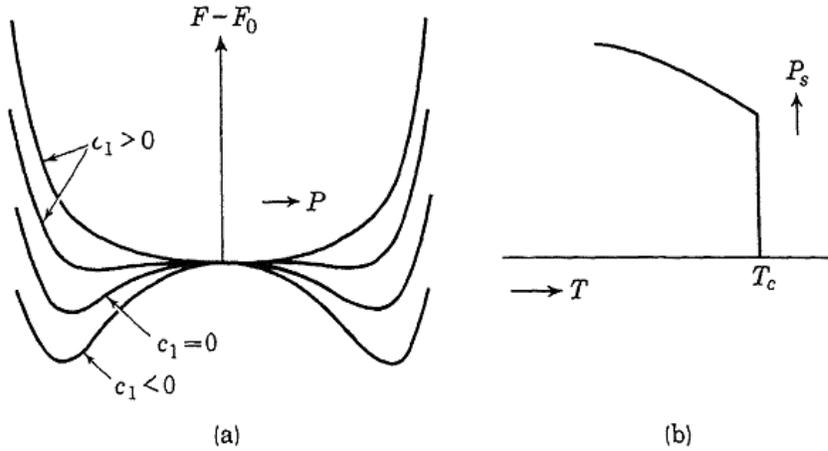
We shall now consider the case for which c_2 is negative and c_3 is positive. Under these circumstances it is possible for the free energy curves to have a minimum value for a nonzero value of the polarization to coexist with a minimum for $P_s = 0$. Assuming that c_1 varies from positive to negative values as the temperature is lowered, one obtains free energy curves of the type indicated in Fig. a.

In the absence of an external field we obtain from the equilibrium condition $(\partial F / \partial P)_T = 0$ and from Eq. (14) for the nonvanishing value of the spontaneous polarization the equation $c_1 - |c_2| P_s^2 + c_3 P_s^4 = 0$ (23)

A transition from the non-polarized state to a spontaneously polarized state will now occur when the minimum of the free energy corresponding to $P_s = 0$ becomes equal to the minimum associated with a nonzero value for P_s. So we can write that

$$F(P_s, T_c) = F_0(0, T_c) \Rightarrow \frac{1}{2} c_1 P_s^2 (T_c) - \frac{1}{4} |c_2| P_s^4 (T_c) + \frac{1}{6} c_3 P_s^6 (T_c) + \ldots\ldots = 0 \tag{24}$$

From Eq. (23), $\qquad c_1 = |c_2| P_s^2 - c_3 P_s^4$ (25)

Putting the value of c_1 in Eq. (24), we obtain

$$\Rightarrow \frac{1}{2} P_s^2 (T_c) \left[|c_2| P_s^2 - c_3 P_s^4 \right] - \frac{1}{4} |c_2| P_s^4 (T_c) + \frac{1}{6} c_3 P_s^6 (T_c) = 0$$

$$\Rightarrow \frac{1}{4} |c_2| P_s^4 (T_c) - \frac{1}{3} c_3 P_s^6 (T_c) = 0$$

$$\Rightarrow P_s^4(T_c)\left[\frac{1}{4}|c_2|-\frac{1}{3}c_3 P_s^2(T_c)\right]=0$$

Either $P_s=0$ or $P_s^2(T_c)=\dfrac{3|c_2|}{4c_3}$ \hfill (26)

It is evident that in this case the polarization jumps at the critical temperature from zero to some non-zero value, i.e., the polarization as function of temperature exhibits a discontinuity at $T=T_c$. According to Eq. (22), the entropy will also be discontinuous at $T=T_c$ and there will be a latent heat, i.e., the transition is of the first order.

Using the condition of Eq. (25) in Eq. (26),

$$c_1=|c_2|P_s^2-c_3 P_s^4=|c_2|\frac{3|c_2|}{4c_3}-c_3\left(\frac{3|c_2|}{4c_3}\right)^2=\frac{3|c_2|^2}{16c_3} \hfill (27)$$

Hence, $P_s^4=\left(\dfrac{3|c_2|}{4c_3}\right)^2=\dfrac{9}{16}\dfrac{|c_2|^2}{c_3}\dfrac{1}{c_3}=\dfrac{9}{16}\dfrac{16c_1}{3}\dfrac{1}{c_3}=\dfrac{3c_1}{c_3}$ \hfill (28)
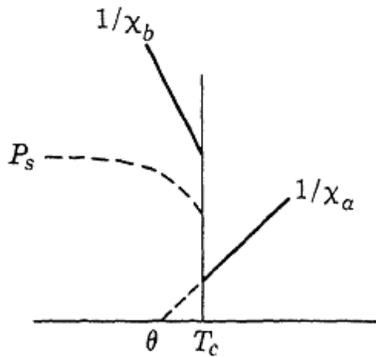
We now consider the susceptibility on both sides of the critical temperature. As in case of second-order transition, the coefficient c_1 in the region above the temperature T_c is again equal to $1/\chi_a$. In this region the susceptibility follows the Curie-Weiss law, so that $c_1=\dfrac{T-\theta}{C}=1/\chi_a$. \hfill (29)

We find also susceptibility below the critical temperature in following manner:

$$E=\partial F/\partial P=c_1 P-|c_2|P^3+c_3 P^5 \Rightarrow 1/\chi_b=\partial E/\partial P=c_1-3|c_2|P^2+5c_3 P^4$$

$$\Rightarrow 1/\chi_b=c_1-3|c_2|\frac{3|c_2|}{4c_3}+5c_3\frac{3c_1}{c_3}=16c_1-\frac{9|c_2|^2}{4}\frac{16c_1}{3|c_2|^2}=16c_1-12c_1=4c_1=4\frac{(T-\theta)}{C}$$

At the critical temperature c_1 is, according to Eq. (29), equal to $\dfrac{(T_c-\theta)}{C}$ and the susceptibilities just above and just below T_c are given by $1/\chi_a=\dfrac{T_c-\theta}{C}$ and $1/\chi_b=\dfrac{4(T_c-\theta)}{C}$.

Dielectric constant in case of first-order transition:

The expression of dielectric constant is $\varepsilon=1+\dfrac{C}{\varepsilon_0(T-\theta)}$. At $T\to\theta$ the reciprocal of dielectric constant is $\dfrac{(T-\theta)}{C}$. At $T=\theta$ the reciprocal of dielectric constant is zero. But the reciprocal of dielectric constant becomes $\dfrac{(T_c-\theta)}{C}$ at $T=T_c$.

Ferroelectric domains

In a ferroelectric crystal, it is likely that the alignment of dipoles in one of the polar directions extends only over a region of the crystal and there can be different regions in the crystal with aligned dipoles which are oriented in many different directions with respect to one another.

Regions of uniform polarization are called domains, separated by a boundary called domain wall. We should not confuse ferroelectric domain walls with the grain boundaries. Depending upon the grain size, one grain can have more than one or more domains. The types of domain walls that can occur in a ferroelectric crystal depend upon the crystal structure and symmetry of both paraelectric and ferroelectric phases. For instance, rhombohedral phase of lead zirconate titanate, $Pb(Zr,Ti)O_3$ has P_s vector along [111]-direction which gives eight possible directions of spontaneous polarization with 180°, 71° and 109° domain walls. On the other hand, a tetragonal perovskite like $PbTiO_3$ has P_s along the [001]-axis and here domain walls are either 180° or 90° domain walls.

Formation of the domains may also be the result of mechanical constraints associated with the stresses created by the ferroelectric phase transition e.g. from cubic paraelectric phase to tetragonal paraelectric phase in $PbTiO_3$. Both 180° and 90° domains minimize the energy associated with the depolarizing field but elastic energy is minimized only by the formation of 90° domains. Combination of both effects leads to a complex domain structure in the material with both 90° and 180° domain walls.

Why is there a domain wall?

The driving force for the formation of domain walls is the minimization of the electrostatic energy of the depolarizing field (E_d), due to surface charges due to polarization, and the elastic energy associated with the mechanical constraints arising due to ferroelectric-paraelectric phase transition. This electrostatic energy associated with the depolarizing field can be minimized by splitting of the material into oppositely oriented domains or compensation of the electrical charge via electrical conduction through the crystal.