Fundamentals and Applications of Dielectric Ceramics

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Lecture - 33
Thermodynamics of Phase Transition in Ferroelectrics

Welcome again to the new lecture of the course fundamentals and applications of dielectric ceramics. So let us briefly recap what we have done in the last.

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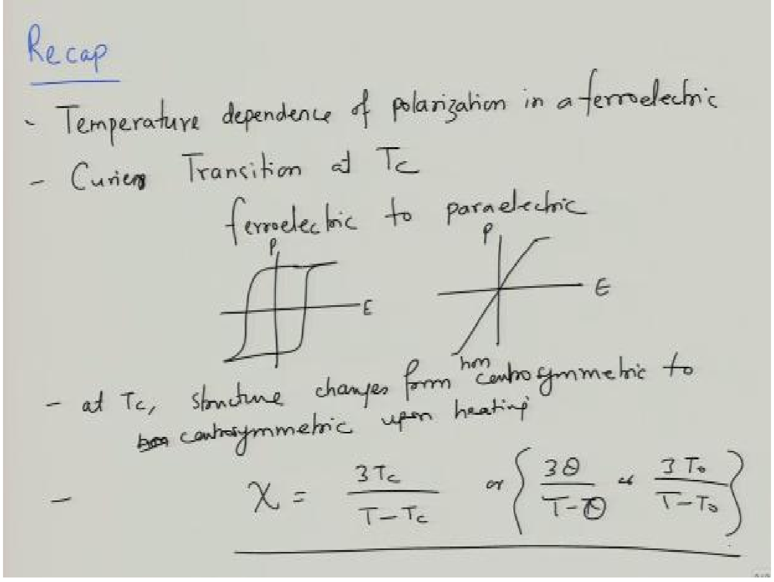

Recap

- Temperature dependence of polarization in a ferroelectric
- Curie Transition at T_c
  ferroelectric to paraelectric
- at T_c, structure changes form non centrosymmetric to centrosymmetric upon heating
- $\chi = \frac{3T_c}{T-T_c}$ or $\left\{\frac{3\theta}{T-\theta} \;\&\; \frac{3T_0}{T-T_0}\right\}$

So in the previous lecture we were looking at temperature dependence of polarization, in a ferroelectric material and we saw that ferroelectric materials undergo what we call as Curie transition at a temperature T_c which is called as Curie temperature and at this temperature when you heat the material the material transformers from ferroelectric to piezoelectric. So the hysteresis that you see at temperature lower than T_c it disappears.

And what we have is the more or less like a linear behaviour of polarization electric field curve. So at T_c structure also changes from centrosymmetric to non-centrosymmetric. Sorry non-centrosymmetric to centrosymmetric structure upon heating. So this is basically what it is and we also have this the material follows, the susceptibility follows Curie law. So the susceptibility shows behaviour as:

$$\chi = \frac{3T_c}{T - T_c}$$

In many books it is also written as:

$$\chi = \frac{3\theta}{T - \theta}$$

it is also written as:

$$\chi = \frac{3T_0}{T - T_0}$$

So it depends upon the type of book that you are following, but general this is the behaviour that susceptibility follows as a function of temperature. So basically you can see from here that as T approaches T_c the susceptibility tends to become very large and this is also manifested in dielectric constant.

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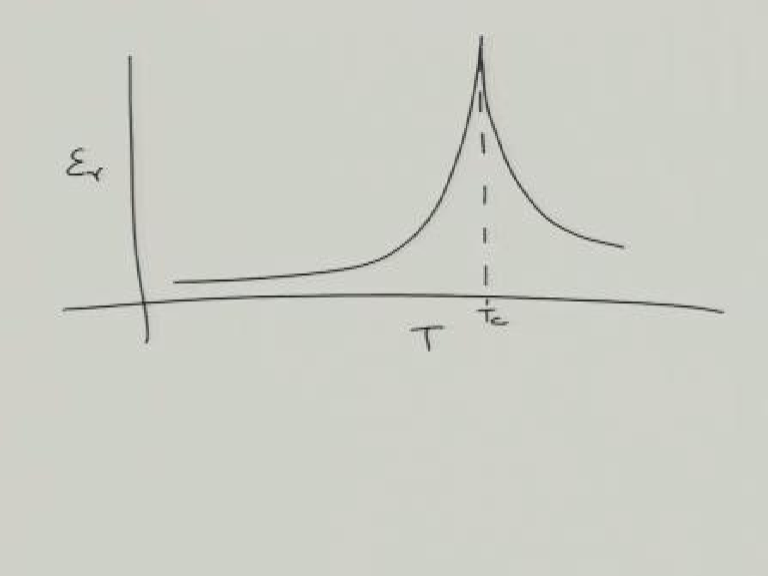

So when you measure the dielectric constant, so dielectric constant versus temperature shows a maxima, abnormal increase at temperature T_c. This is what we did in the last couple of lectures. Today we will look at the thermodynamics of phase transition in ferroelectric material.

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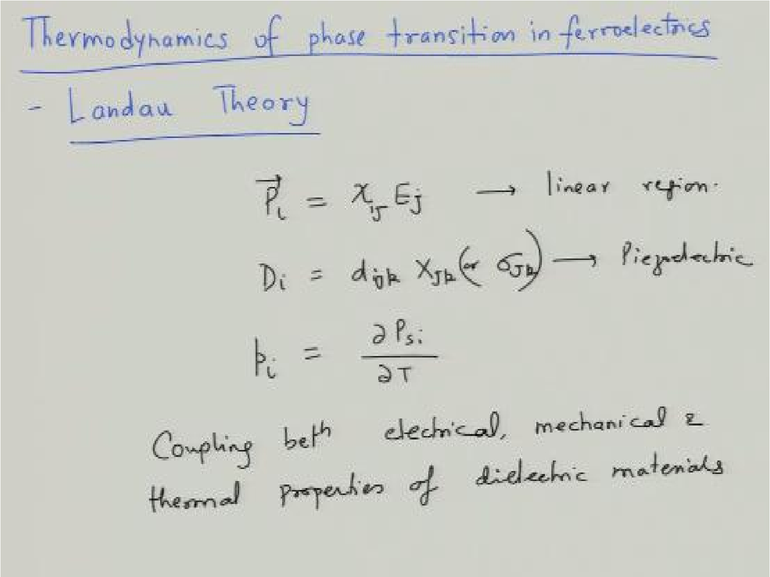

Thermodynamics of phase transition in ferroelectrics

- Landau Theory

$$\vec{P}_i = \chi_{ij} E_j \longrightarrow \text{linear region.}$$

$$D_i = d_{ijk} X_{jk} (\text{or } \sigma_{jk}) \longrightarrow \text{Piezoelectric}$$

$$p_i = \frac{\partial P_{si}}{\partial T}$$

Coupling betn electrical, mechanical & thermal properties of dielectric materials

So this relies on what we call as Landau theory. So according to Landau theory, we have seen in the past lecture that, you know the polarization when you apply, so the polarization can be related to electric field through susceptibility. So this is susceptibility, so this is at least for linear region. Basically you apply electric field, external electric field needs to change in the charge density in a polar material that is polarization.

And similarly, when you apply stress you can change the charge density. So:

$$D_i = d_{ijk} X_{jk}$$

so this is what is piezoelectric effect that we have seen. And then similarly, we also saw the pyroelectric coefficient that was, so change in spontaneous polarization as a function of temperature gives you the pyroelectric coefficient:

$$p_i = \frac{\partial P_{s,i}}{\partial T}$$

So there are many couplings like this, so basically what we looked at was coupling between electrical, mechanical and thermal properties of dielectric materials and these are special dielectric. So piezoelectricity shown by what we call as non-centrosymmetric material, pyroelectricity shown by non-centrosymmetric and polar materials, whereas ferroelectricity shown by non-centrosymmetric polar and in which polarization is reversible those kind of materials. Now what we do is that now, we first realise what is a free energy.

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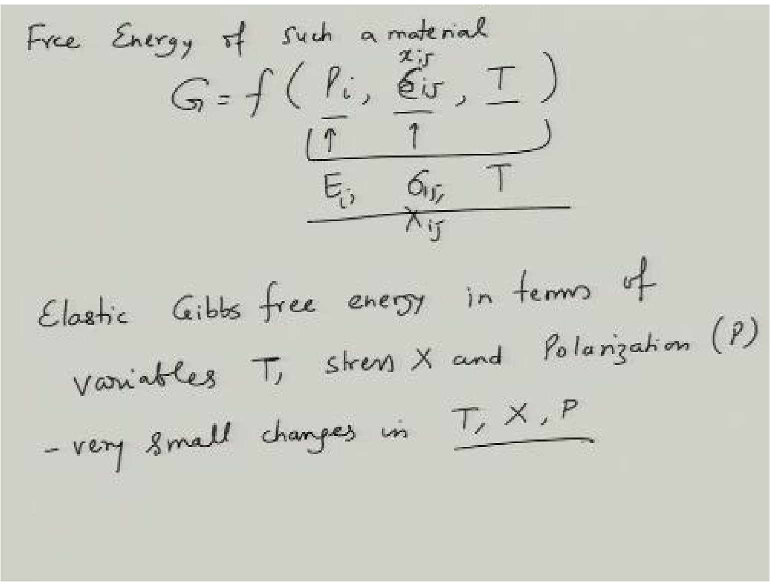

Free Energy of such a material

$$G = f(\underline{P_i}, \underline{\overset{x_{ij}}{\epsilon_{ij}}}, \underline{T})$$

$$\underbrace{\uparrow \quad \uparrow \qquad}$$

$$E_i, \quad \sigma_{ij}, \quad T$$

$$X_{ij}$$

Elastic Gibbs free energy in terms of variables T, stress X and Polarization (P)

- very small changes in $\underline{T, X, P}$

So free energy of ferroelectric let us say of such a material where these properties are coupled. It is expressed by, so free energy is a function of polarization. So you can take three components of polarization P_x, P_y, P_z, that is polarization. It is also component of stress. So σ_x to σ_y to σ_z. So basically instead of writing this we can just write function of P_i, so where P could be 1, 2, 3 and then you have σ_{ij}.

So stress tensor and then of course temperature and then free energy is also affected by what we call as electric, so now this is polarization is the generally what we measure after applying electric field, stress is something which you can apply or measure after you have application of electric field or application of strain, then you have thermal response. So basically when we apply electric field, we can measure polarization.

When we apply stress we can measure restrain or vice versa and similarly, when we apply electric field we can measure stress or when we apply stress we can measure the polarization and so on and so forth. So this is how it sort of couples these properties. So you can do legendre transform to related to really the stimuli, so a stimuli in this case would be E.

And you can write this in terms of E, σ and T or you can write this in terms of P, ε and T or it could be x_{ij} or it could be X_{ij} . So there are various ways of writing this Curie question that we saw in earlier. So now let us write a little bit detailed free energy equation. So let us say we wright elastic Gibbs free energy in terms of variables, temperature, stress X and polarization.

So now we talk of ferroelectric mostly in terms of polarization instead of D, the charge density because polarization and D are interchangeable. So instead of D we will use P, which is more common quantity and we assume very small changes in T, X and P. So the free energy expression turns out to be.

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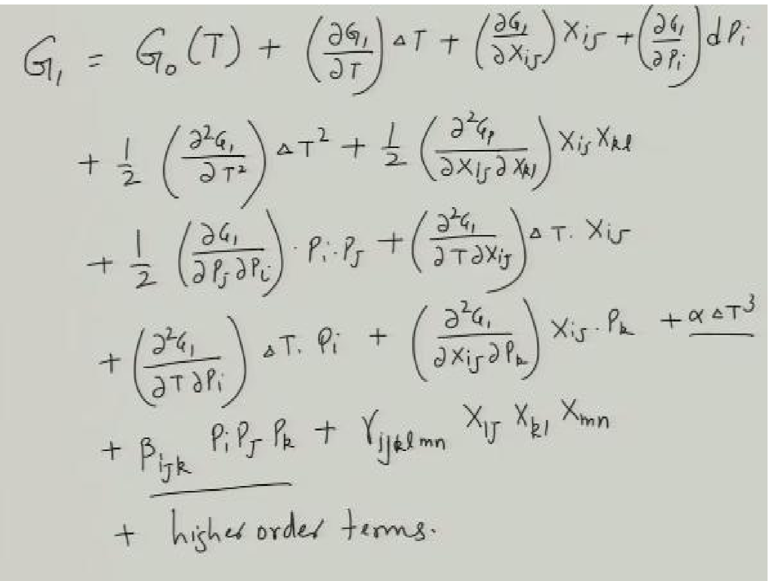

$$G_1 = G_0(T) + \left(\frac{\partial G_1}{\partial T}\right)\Delta T + \left(\frac{\partial G_1}{\partial X_{ij}}\right)X_{ij} + \left(\frac{\partial G_1}{\partial P_i}\right)dP_i$$

$$+ \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial T^2}\right)\Delta T^2 + \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial X_{ij}\partial X_{kl}}\right)X_{ij}X_{kl}$$

$$+ \frac{1}{2}\left(\frac{\partial G_1}{\partial P_j \partial P_i}\right)\cdot P_i \cdot P_j + \left(\frac{\partial^2 G_1}{\partial T \partial X_{ij}}\right)\Delta T.\, X_{ij}$$

$$+ \left(\frac{\partial^2 G_1}{\partial T \partial P_i}\right)\Delta T.\, P_i + \left(\frac{\partial^2 G_1}{\partial X_{ij}\partial P_k}\right)X_{ij}\cdot P_k + \underline{\alpha \Delta T^3}$$

$$+ \underline{\beta_{ijk}}\, P_i P_j P_k + \gamma_{ijklmn} X_{ij} X_{kl} X_{mn}$$

$$+ \text{higher order terms.}$$

So free energy expression G_1 can be written as:

$$G_1 = G_0(T) + \left(\frac{\partial G_1}{\partial T}\right)\Delta T + \left(\frac{\partial G_1}{\partial X_{ij}}\right)X_{ij} + \left(\frac{\partial G_1}{\partial P_i}\right)dP_i + \ldots\ldots\ldots\ldots$$

So this is the first order change that you make on the basis of temperature, the stress and the polarization. Now you need to take the second order term. So far we did not consider the second order terms, but we need to do the second order comes, which is nothing but Taylor expansion.

$$\begin{aligned}
G_1 = G_0(T) &+ \left(\frac{\partial G_1}{\partial T}\right)\Delta T + \left(\frac{\partial G_1}{\partial X_{ij}}\right)X_{ij} + \left(\frac{\partial G_1}{\partial P_i}\right)dP_i \\
&+ \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial T^2}\right)\Delta T^2 + \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial X_{ij}\partial X_{kl}}\right)X_{ij}X_{kl} \\
&+ \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial P_j \partial P_i}\right)P_i P_j + \frac{1}{2}\left(\frac{\partial^2 G_1}{\partial T \partial X_{ij}}\right)\Delta T.X_{ij} \\
&+ \left(\frac{\partial^2 G_1}{\partial T \partial P_i}\right)\Delta T.P_i + \left(\frac{\partial^2 G_1}{\partial X_{ij}\partial P_k}\right)X_{ij}P_k + \alpha \Delta T^3 \\
&+ \beta_{ijk} P_i P_j P_k + \gamma_{ijklmn} X_{ij} X_{kl} X_{mn} + higher-order\ \ terms
\end{aligned}$$

So this is the first interdependence of so you have first derivative $\partial G/\partial X$ and after that you make a change in temperature and then so this is the interdependent term. Then second interdependent term will be it could be between temperature and polarisation. So this could be ΔT into P_i right and then third term is $\partial^2 G_1$, ∂X_{ij}, ∂P_k and this is X_{ij} into P_k and then we can have various other terms.

We have alpha ΔT cube which is the volume expansion term and then we have $\beta_{ijk}P_iP_jP_k$. This is the third order term. So now we take the third order term. So this is the third order term, this is the third order term and then we take $\gamma_{ijklmn}X_{ij}X_{kl}X_{mn}$ plus other higher order terms. So this is massive equation, so basically what are these terms.

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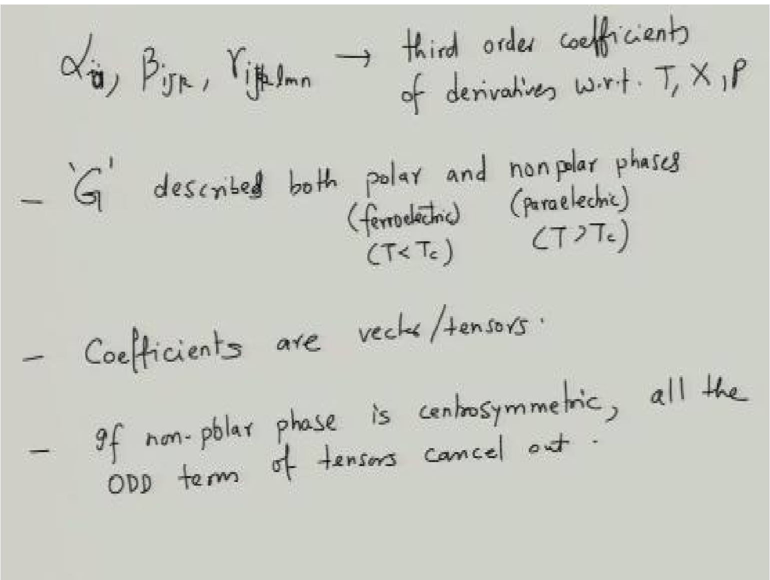

α_{ij}, β_{ijk}, γ_{ijklmn} → third order coefficients of derivatives w.r.t. T, X, P

- 'G' described both polar and nonpolar phases
  (ferroelectric) (paraelectric)
  ($T < T_c$) ($T > T_c$)
- Coefficients are vector/tensors.
- If non-polar phase is centrosymmetric, all the ODD term of tensors cancel out.

These terms are α_{ijk}, β_{ijk} and γ_{ijklmn}, these are third order coefficients right of derivatives with respect to temperature, with respect to stress and with respect to polarization right. These are the three, so here we assume that G, the free energy describes both polar and nonpolar phases. So polar will mean that it is ferroelectric phase and nonpolar will mean paraelectric phase.

So this is $T < Tc$, and this is $T > Tc$ right and then all the coefficients as we see they are tensors, or vector/tensors depending upon the coefficients and of course if nonpolar force if non polar what will happen if non polar phase is centrosymmetric which means displacement positive direction will cancel the displacements in negative direction as a result all the odd terms will cancel out each other.

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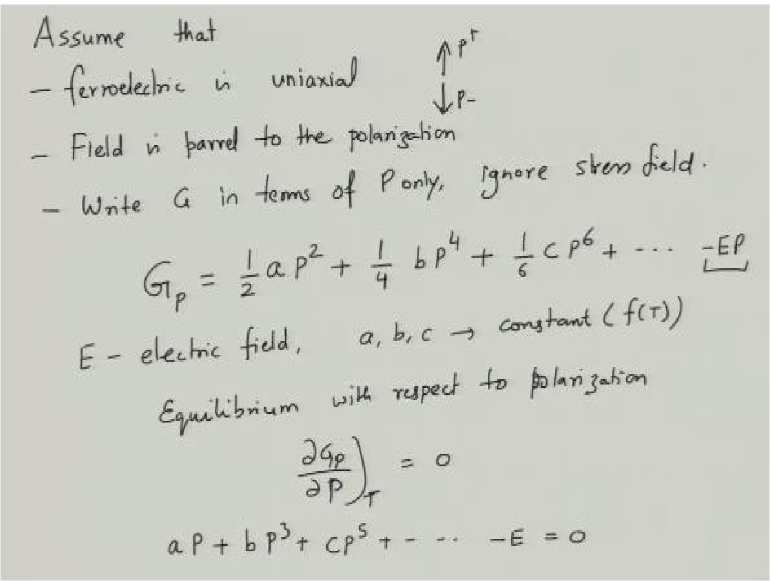

Assume that

- ferroelectric is uniaxial $\uparrow P^+$ $\downarrow P^-$
- Field is parrel to the polarization
- Write G in terms of P only, ignore stress field.

$$G_p = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \cdots \underbrace{-EP}$$

E - electric field, a, b, c → constant (f(T))

Equilibrium with respect to polarization

$$\left.\frac{\partial G_p}{\partial P}\right)_T = 0$$

$$aP + bP^3 + cP^5 + \cdots - E = 0$$

So we imagine that our ferroelectric is, assume that ferroelectric is uniaxial which means polarization either is in this direction or in that direction, there are no multi-component polarization vectors, which might complicate the situation. So this is P^+ this will be P^- and the field is applied parallel to the polarization, just for the sake of simplicity. So basically we want to write a expression for free energy of a crystal.

And whatever we do when we want to calculate the value of various independent variable, we need to minimise the free energy with respect to that variable. When you want to calculate something at equilibrium then free energy value must be minimum for that particular variable just like we do it defect concentration many other thing definitely should get minimised for that particular variable.

So now we would like to expand this free energy equation in terms of polarization only and we will ignore other terms. So we will just look at the polarization for uniaxial ferroelectric term, ferroelectric and ignore the stress fields. So we write G in terms of P only, ignore stress fields and this is not wrong because you have a uniaxial ferroelectric. So we are not considering any other directions as such and it is a unstrained crystal.

So let us say we write the ferroelectric G_p as:

$$G_p = \frac{1}{2} aP^2 + \frac{1}{4} bP^4 + \frac{1}{6} cP^6 + ... - E.P$$

So we write this expression for free energy that is in terms of polarization only, the negative E.P which is the product of electric field and polarisation which is the depolarizing energy for a ferroelectric.

Because in ferroelectric when you have polarization aligned in one direction and there is an opposing force which is the depolarizing energy which one should depolarize the material and we take even powers only because energy is same for +P$_s$ or -P$_s$ direction and the other term cancel out each other as we just discussed earlier for a nonpolar centrosymmetric phase.

So here E as we see is the electric field and a, b and c constants, which are function of temperature. They are temperature dependent. So this is a simplified equation of course you can write a complicated equation, but you can see that we have written that equation just in terms of polarization ignoring the stress field and let us say you want to now find out where is the minimum of energy with respect to polarization.

So equilibrium with respect to polarization is achieved by minimising the free energy. So we say that:

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

So if we do that then this expression can be:

$$aP + bP^3 + cP^5 + ... - E = 0$$

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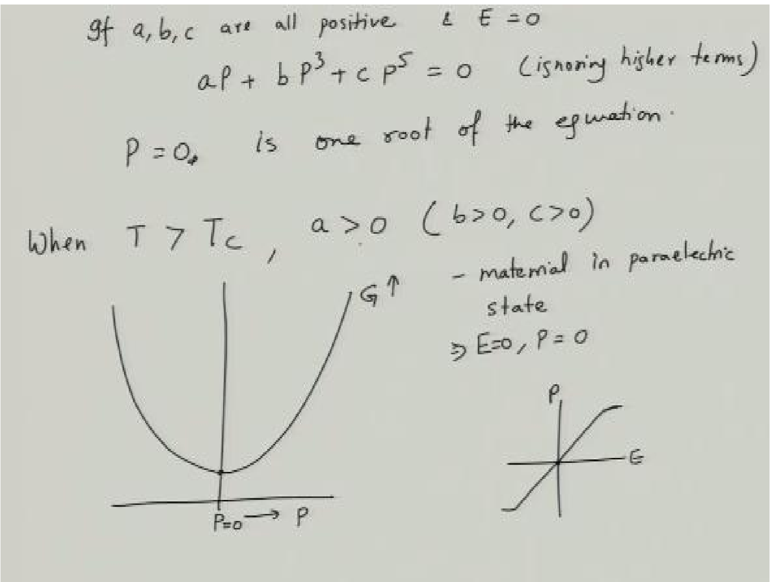

If a, b, c are all positive & $E = 0$

$aP + bP^3 + cP^5 = 0$ (ignoring higher terms)

$P = 0$, is one root of the equation.

When $T > T_c$, $a > 0$ ($b > 0$, $c > 0$)

- material in paraelectric state

$\Rightarrow E = 0, P = 0$

So assuming that first, if a, b, c are all positive because we do not know the value of a,b,c yet. So we are saying that right now assuming that if a b c are all positive then of course you can see that and let us say if E = 0, then we can say that:

$$aP + bP^3 + cP^5 = 0$$

ignoring higher terms and that is correct because we assume the change in the polarization is small and as a result higher order terms will not play significant role.

So if that is true, if a,b and c are all positive and E = 0 then we can clearly see that P = 0 is one root. So add P = 0 there is certainly one minimization that will occur. So that is first lesson that we learn from this exercise. So basically we can say that at a temperature, so now when are these conditions met. These conditions a,b and c are positive are met, so when T is greater than a critical temperature Tc.

And a > 0 simultaneously b > 0, c > 0, in that case the free energy shows, so this is G versus P. So at P = 0, we have a free energy minimum. So basically for this condition we represent the material as material being, material is in paraelectric state and what it means is that when E = 0, P is also equal to zero and that is what it meant for a pyroelectric state this was our plot.

So this is P, this is E, saturates of course, but at E = 0, the P = 0 that is what root is and that is what the free energy minimum occurs. So this basically suggests that for a > 0, b > 0, c > 0, at $T > T_c$, the material is in paraelectric state with polarization P = 0 as a root. So now let us say in the above derivation that we did:

$$aP + bP^3 + cP^5$$

now let us say $E \neq 0$.

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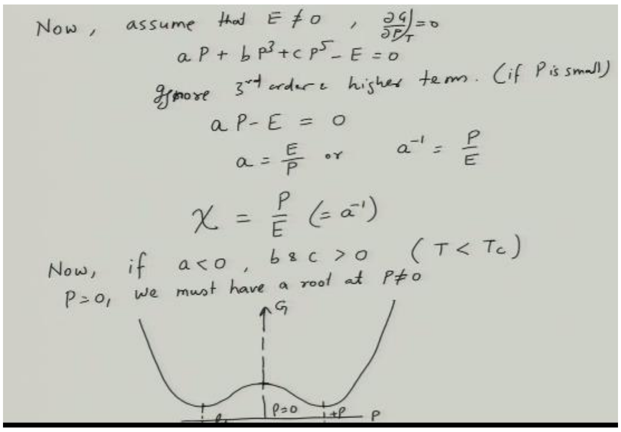

Now, assume that $E \neq 0$, $\left.\frac{\partial G}{\partial P}\right)_T = 0$

$$aP + bP^3 + cP^5 - E = 0$$

Ignore 3rd order & higher term. (if P is small)

$$aP - E = 0$$

$$a = \frac{E}{P} \quad \text{or} \quad a^{-1} = \frac{P}{E}$$

$$\chi = \frac{P}{E} \ (= a^{-1})$$

Now, if $a < 0$, $b \,\&\, c > 0$ $(T < T_c)$

$P = 0$, we must have a root at $P \neq 0$

Now let us say assume that $E \neq 0$, then we know that aP and then we said that:

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

So,

$$aP + bP^3 + cP^5 + \dots\dots\dots\dots\dots\dots - E = 0$$

this was the expression that we have. Now let us say we ignore third order and higher terms for a small polarization and we can write:

$$aP - E = 0$$

$$a = \frac{E}{P} \;\; or \;\; a^{-1} = \frac{P}{E}$$

P divided by E is nothing but the susceptibility. So this is susceptibility of a ferroelectric in the linear region that is:

$$\chi = \frac{P}{E} \;\; (= a^{-1})$$

Now on the other hand if we say, if we assume $a < 0$, but b and $c > 0$ and what did we say earlier, a,b and c all are temperature dependent. So which means something has happened to temperature because ‘a’ has changed it is sign. So if ‘a’ is positive for T temperature being greater than Tc then T must have gone below T_c for a being less than zero. So this condition is valid for T less than T_c.

So in this case if $a < 0$ and b and $c > 0$ then there should be, so not only $p = 0$ is a root, there should also be a root at P that is non zero. So we must have a root at $P \neq 0$. There should be some finite value. So this is expressed in this form schematically, we will do a detailed analysis little while. So this is G and this is P, so we have root here, that is $-P_r$, this is just write -P and +P.

And this is the maxima that we get at so we mean this is maxima or minima, we did not define it, we mean so here what we are getting is a maxima in G at $P = 0$ and minima in G are two values that is +P and -P and this condition is defined for $T < Tc$ and this is for $a < 0$ and b, c being positive and basically this is manifested in terms of in this fashion.

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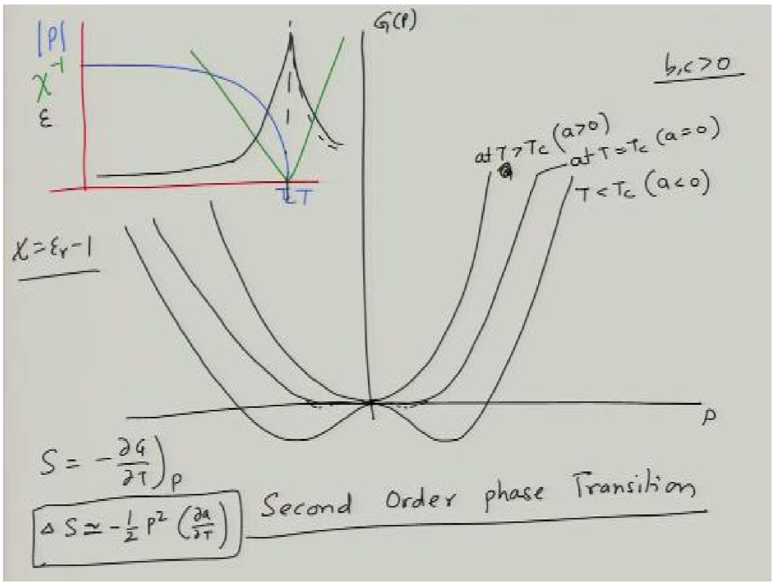

So if you now put the two curves together, if you now put the 2 curves together let us say we plot G as a function of polarization and this is polarization, the first thing that we drew was like this. This is the curve at $T > T_c$ when we have one root what happens when you decrease the temperature at $T < T_c$, we have a situation which is like this, which is at $T < T_c$.

So at this temperature $a > 0$, at this temperature $a < 0$ and b, c = 0 for all temperatures. So in between what happens if a is changing it is sign, it must go through zero, at this temperature is greater than zero, at this temperature is less than zero, it makes sense that ‘a’ will go through sort of change of sign at $T = T_c$, where $a = 0$ and that is where show a shallow sort of minima.

So there is a transition that takes place in the nature of free energy curve, this is just a little perturbation below c will give you two minima like this. So this is reflected in terms of polarization. So if you plot now polarization as a function of temperature, the polarization decreases gradually at a temperature called as T_c. So below T_c you have finite polarization.

Either you will have +P or -P, it is a uniaxial ferroelectric and both the states are equal. So you can write this as |P| and you can also plot another parameter that is susceptibility. So if you look at this expression and varies as P over E, but in the previous analysis that we did we will do temperature dependent analysis and we will see that susceptibility varies in this fashion.

So it as certain dependence at temperature of a P_c, $1/\chi$ decreases to zero at T_c and then again increases and in terms of dielectric constant what it would mean is that if you plot dielectric constant let us say ε_r, you will have divergence of dielectric constant at this value or even susceptibility, because $\chi = \varepsilon_r - 1$. So this kind of phase transition where susceptibility where there is a gradual change in the free energy plot, where the polarization is dropping gradually.

$1/\chi$ as you decrease the temperature first decreases and then increases and at T_c it goes to equal to zero, this kind of transition where there is no discontinuity in the susceptibility and there is not a sudden jump in polarization, this kind of transition is called a second order phase transition and if you calculate in this case you will not have a discontinuity in entropy for specific heat when you calculate for these materials.

So these are second order continuous phase transitions where susceptibility does not change abruptly at the transition or order parameter polarization is called as order parameter, the order parameter does not abruptly become equal to zero rather it goes to zero gradually and this is what it means in terms of since what happens in this case is the polarization can be related to entropy.

But you can relate the entropy as:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$\Delta S \cong -\frac{1}{2}P\left(\frac{\partial G}{\partial T}\right)$$

So when this is continuous which means the phase transition is second order. If there is a discontinuity you see, then it is a first order phase transition. If it is continuous then it is a second order phase transition.

So this is basically a second order phase transition, it is seen in material such as Rochelle salt, KH_2PO_4 etc, so we will stop here, we will look at the analytical treatment of different phase transition in the next lecture and we will also follow up with the discussion on the first order phase transition.