Electroceramics
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Lecture - 28

So, again the start of new lecture, and we will just review the last lecture. So, in the last lecture, what we did was we looked at the thermodynamic point of view of ferroelectric phase transition. Now this is essential, because many, because ferroelectric phase transition is a phase transition, where not only you have change in the property, but also change in the structure or asymmetry of the material. And depending upon the type of phase transition, you see a different kind of behavior in the way properties change. So, basically in the state of equilibrium thermodynamic state of a ferroelectric material can be expanded in terms of you can write free energy expression that can be expanded in terms of parameters like electric field polarization stress and strain. So, assuming there are for instance, stress and electric field can be treated as external variables strain and polarization can be treated as internal variables. So, you can expand this free energy expression.

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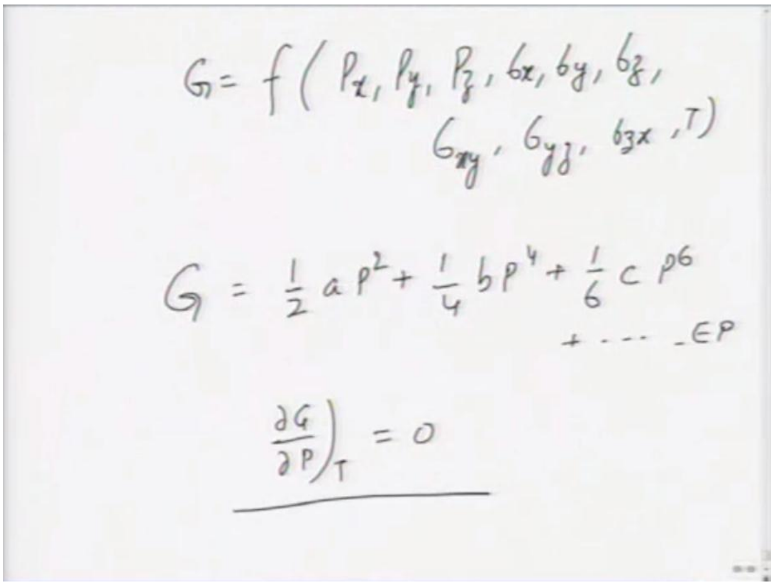

$$G = f(P_x, P_y, P_z, \sigma_x, \sigma_y, \sigma_z, \sigma_{xy}, \sigma_{yz}, \sigma_{zx}, T)$$

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

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

And this we wrote as G was function of P x P y P z components of polarization. And then you have sigma x sigma y sigma z sigma x x, sigma x y sigma y z and sigma z x and temperature. So, you can of course, write this in many parameters. So, in the context of ferroelectrics, we are writing this in terms of these parameters. Now, at a given temperature or let us say not even at a given temperature, but for unpolarized or unstrained crystal you can expand this for a ferroelectric as half a P square plus 1 by 4 b P 4 plus 1 by 6 c P 6 and so on and so forth minus EP.

So, this expression which is a simplified expression of course, we have removed parameters like, because in principle there could be parameters like electric magnetic field etcetera. So, we have got rid of them simply because we are only considering unstrained unstrained unpolarized ferroelectric crystal. So, in such a case this equation works well. And so, here we saw that a, b, c were the temperature dependent coefficients and P of course is the polarization, E is the electric field. Now, at equilibrium you have to minimize a free energy, free energy has to be minimized with respect to P. So, basically del G by del P at constant temperature has to be equal to 0, based on that we determine what is called as susceptibility? So, for such for a second order transition, we worked out the susceptibility.

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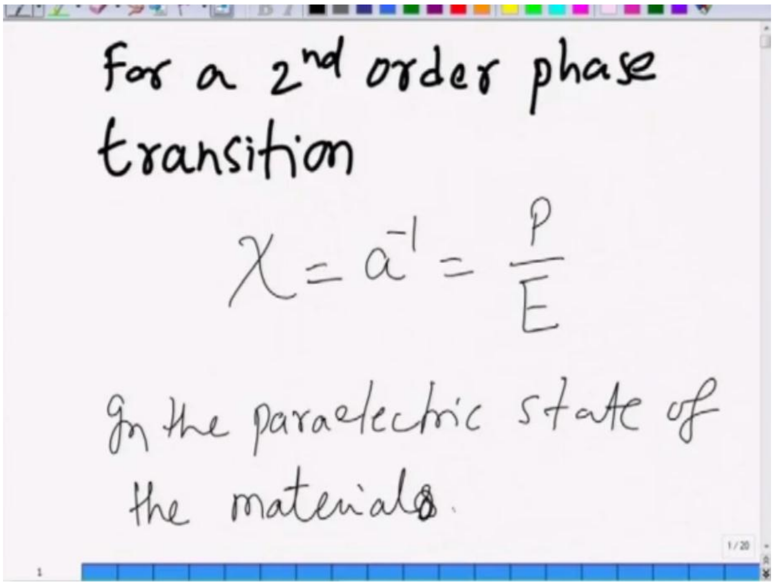

For a 2nd order phase transition

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

In the paraelectric state of the materials.

To come as chi was a inverse which was nothing but P by E and this is the classic equation that you got for normal material. So, this explains, this is the dependence of, this is the susceptibility above the transition temperature in the paraelectric state or in the unpolarized state. So, for a second order phase transition, we can write the susceptibility expression chi that is equal to a inverse and which is equal to nothing but P divided by E.

Now, this is basically a classic equation that you get for a ferroelectric material. Now, this is now mind you also; you should also note that this is the expression in the paraelectric state of the material. So, after the ferroelectric material has become paraelectric or non polar state of the material and one should also see, that this is when the size of a changes.

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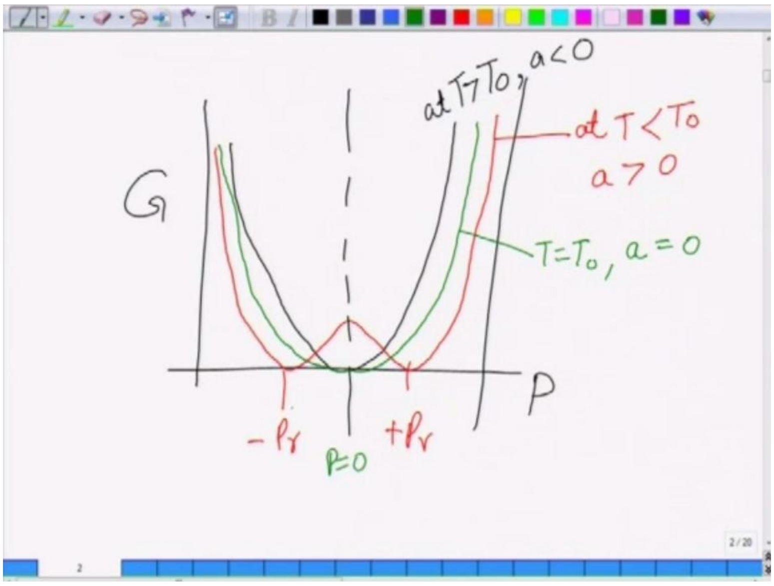

So, if I plot free energy versus polarization. So, at so this is a situation at T; T greater than T naught, and your basically a remains negative in this region. And what happens when you change the temperature? When you become? When you take into lower temperature, then the curve assumes; the shape like this and this gives you a curve like this, with the 2 minima’s at plus P r, minus P r on the left and plus P r on the right. And this happens at temperature T greater than T naught, and that is, where a is greater than 0.

So, you can see that a changes it sign at T; T is equal to T naught which is the transition temperature from negative to positive as you decrease the temperature from T above T naught to 2 below T below T naught, this should be below T naught T below T naught. So, this is the kind of phase transition that you get in the as a second order transition. So, if you and what will happen in case of let us say T which is equal to T naught at T equal to T naught, you will have a rather broader hump but, again with the only 1 minima. So, this will be at T is equal to T naught when a is equal to 0.

So, in summary what happens, when a in a second order phase transition a material at T greater than T naught shows only 1 minima at P is equal to 0. And when a is less than 0, when T is equal to 0 then, a is equal to 0 it again shows 1 minima a broad hump at P is equal to P naught. And then not the hump a shallow, a shallow sort of minima and then, as the temperature goes below T, T less than T naught when a changes it sign to positive. The free energy curve shows 2 minima 1 at minus P r, second at plus P r which are equidistant from the 0. So, this is the kind of nature of phase transition of second order. Now, what happens to polarization is.

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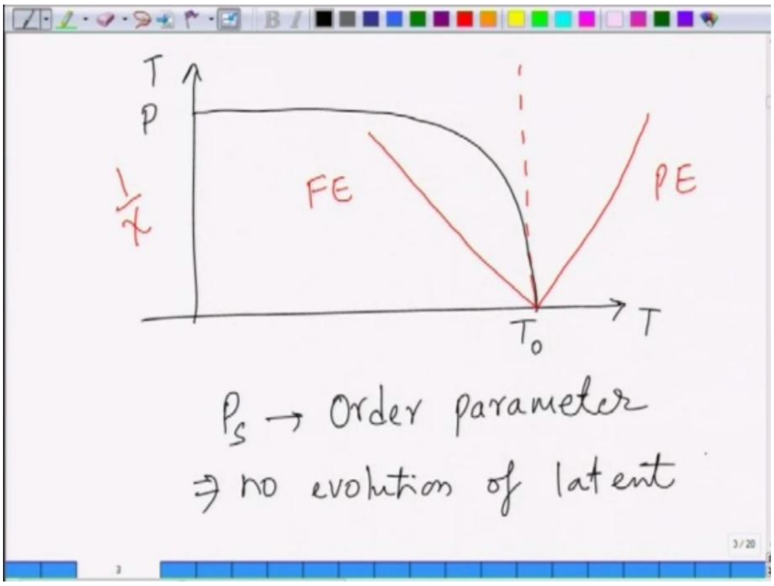

$P_s \rightarrow$ Order parameter

$\Rightarrow$ no evolution of latent

When you look at the polarization as a function of temperature, the polarization drops continuously as you reach T naught. So, this is the nature of phase transition that you this is the nature of polarization that you get in a material with a second order phase condition. And on top of this, if you project susceptibility as inverse of itself which is 1 over chi, and what you see is that 1 over chi goes like this in the ferroelectric state. And it goes like that in paraelectric state, and as we will see later on the slope of these 2 curves are different in these, ferroelectric and paraelectricare other way round. So, this is your ferroelectric state; this is your high temperature paraelectric state. So, essentially 1 over chi dips at T is equal to T naught before rising again in the ferroelectric region.

So, essentially in a ferroelectric material with the second order phase transition, you can call P or P s as a order parameter. And this order parameter does not show a discontinuity rather it drops gradually until T becomes equal to T naught, and what it means in terms of kind of phase transition you have? You have no evolution of latent heat, and in terms of free energy, what it means is that, if you remember the last class, in the last class we said.

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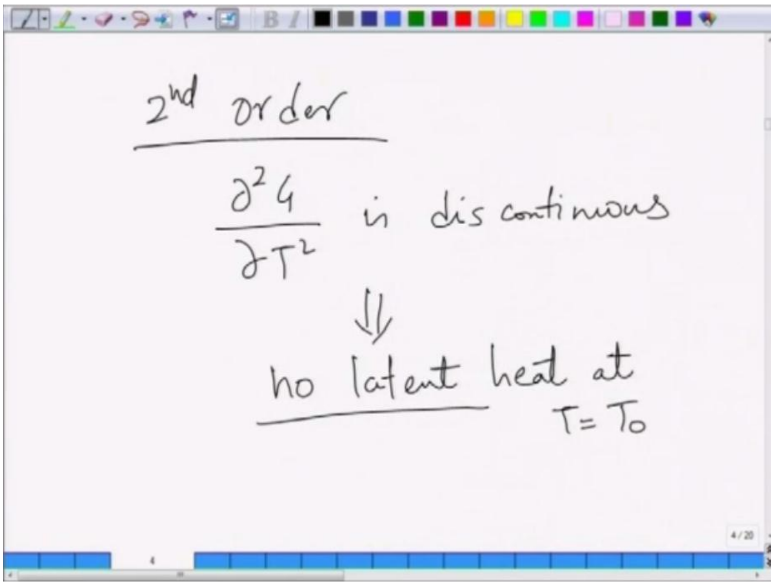

2nd order

$$\frac{\partial^2 G}{\partial T^2} \text{ is discontinuous}$$

$$\Downarrow$$

no latent heat at $T = T_0$

That in a second order phase transition, the second derivative of free energy is discontinuous, and which is what we looked at in the specific heat, so when the first derivative is continuous, second derivative is continuous, it may it is characterized as a second order phase transition. And this essentially means what I said earlier, that there is no latent heat involved at the transition. So, what now we will look at so, so far what we have is a qualitative understanding of semi quantitative understanding of second order phase transition. What now, we will do is that, we will look at them.

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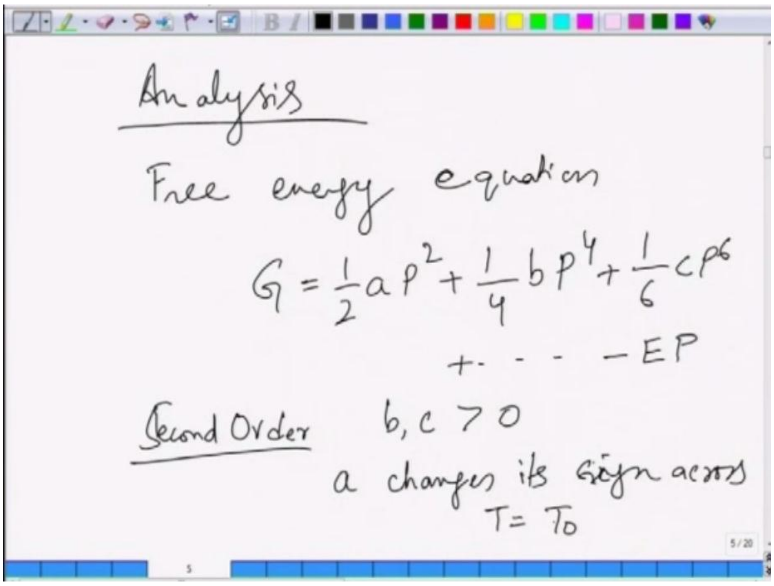

Analysis

Free energy equation

$$G = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \cdots - EP$$

Second Order $b, c > 0$

a changes its sign across $T = T_0$

Second order phase transition in terms of its analysis or quantitative analysis. So, basically what we are going to do is that, we are going to look at a susceptibility in the ferroelectric region and susceptibility in the paraelectric region. So, for that now we again get back to the free energy equation. So, free energy equation for a polar material can be written as G is equal to half a P square plus 1 over 4 b P 4 plus 1 over 6 c P 6 minus of plus higher order terms minus of E P, here P is the polarization a and b and c are the parameters or constants you can say, we change their sign as a function of temperature or we change their sign as a type of transition, and E is the electric field and P is the polarization and G is the total free energy.

Now, transition of course occurs for a second order transition you know, so if you want to go into details of this equation, you can go get back to the last lecture. But in this case what happens is that b c are greater than 0 and a changes its sign across T is equal to T naught which is the transition temperature for a second order phase transition for electric material.

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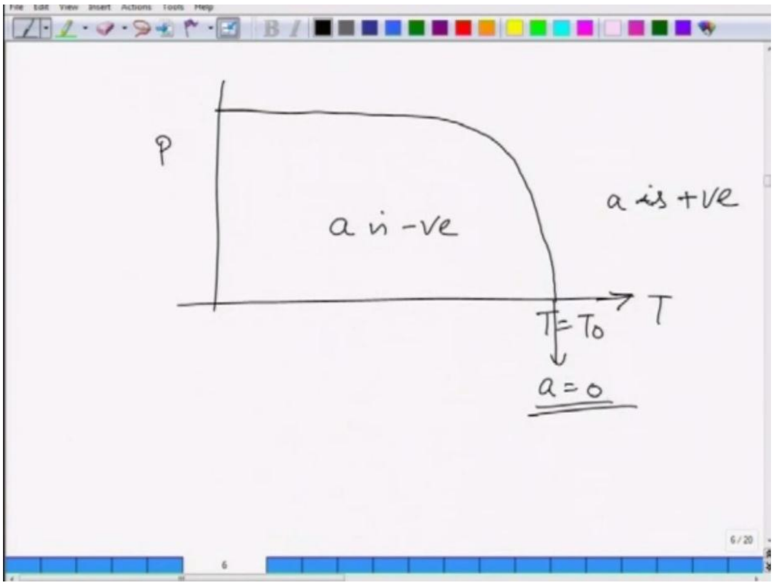

So, again I will just plot the polarization versus temperature which is like this, or rather its little bit something like that, T is equal to T naught. And this is your P; this is the temperature axis, and in this region a is negative, and in this region a is positive. So, it is essentially the sign of a which changes upon the transition and remember that b and c are positive in case of second order transition. And at T is equal to T naught a is equal to 0, as it changes its sign now assuming.

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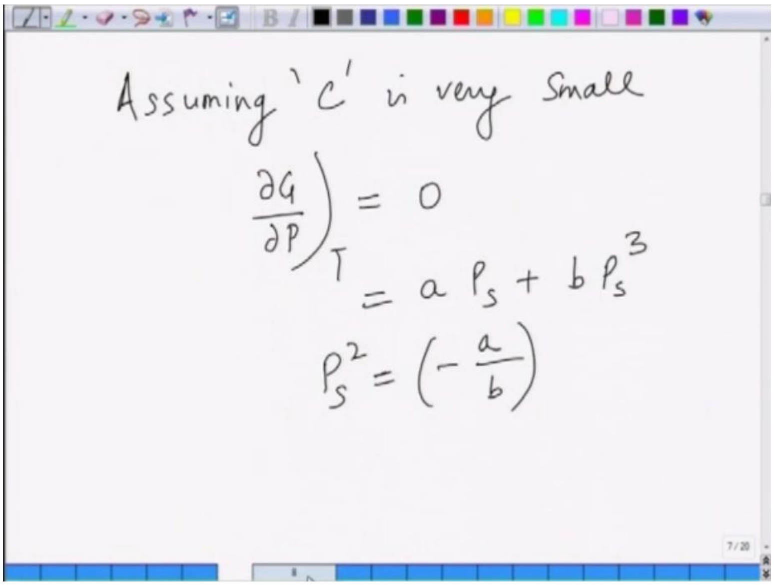

Assuming 'c' is very Small

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

$$= a P_s + b P_s^3$$

$$P_s^2 = \left(-\frac{a}{b}\right)$$

Assuming that c is very small. So, once you make this assumption c is very small, and then you can write this del G by del P at constant temperature to be equal to 0. And this is nothing but from the free energy expression, you can get it a P s plus b P s square, cube. And this will give you P s square to be equal to minus of a by b. Part of this we already did in the previous lecture. So, you can again so in some sense this is nothing but recap of the previous lecture until this point. Now, since P is a continuous function and C v is or specific heat is discontinuous which means second derivative of free energy is discontinuous. This is how it looks like. Now, what is susceptibility above and below T naught?

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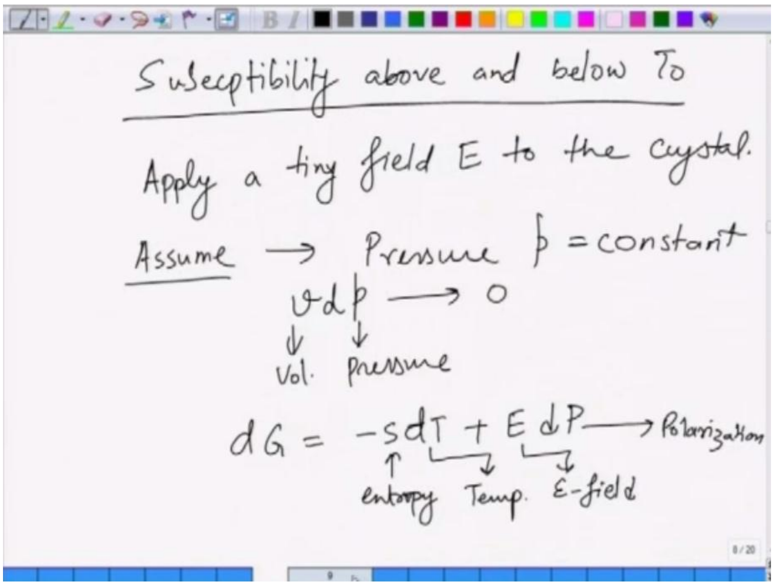

Susceptibility above and below T_0

Apply a tiny field E to the crystal.

Assume → Pressure p = constant

$$\underset{\text{Vol.}}{v}\,d\underset{\text{Pressure}}{p} \longrightarrow 0$$

$$dG = -\underset{\text{entropy}}{s}\,d\underset{\text{Temp.}}{T} + \underset{\text{E-field}}{E}\,dP \longrightarrow \text{Polarization}$$

So, first let us susceptibility above and below T naught which is the transition temperature. So, for this first apply a tiny field E to the crystal and of course, assume 0 pressure or pressure is constant, not 0 pressure, but assume that pressure is constant, pressure p is equal constant. And what basically it is that, is that in, the free energy term if you take the partial differentiation, then there is a term v d p; where v is nothing but volume and this small p is nothing but pressure. And since pressure is constant, this term becomes equal to 0. As a result the free energy term d G is nothing but minus of s d T plus E d P here s is your entropy; T is temperature E is electric field. And this P is nothing but polarization. So, do not confuse this E d P term with v d p term here p and P are different. So, this small p is pressure and capital P is the polarization.

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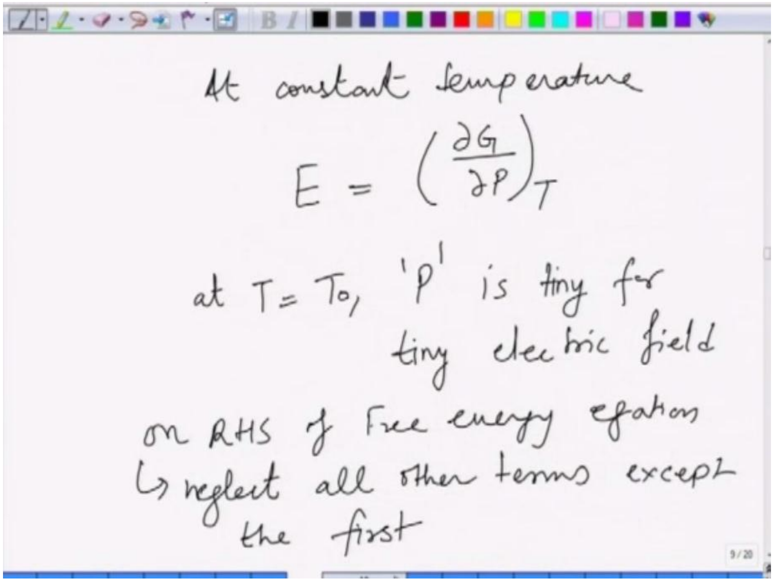

At constant temperature

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

at $T = T_0$, 'p' is tiny for tiny electric field

on RHS of Free energy eqation

↳ neglect all other terms except the first

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Now at constant temperature, I can write this electric field to be del G by del P. So, E becomes equal to del G by del P at constant temperature. Now, above so rather, let me say at T is equal to T naught or above T is equal to T naught as well, this polarization P is tiny for tiny electric field and that make sense. If your electric field is very small p is got to be very small. So, in the free energy expression on the right hand side of the expression, neglect all the terms. So, on right hand side of free energy equation, neglect all other terms except the first one, and then what you get is.

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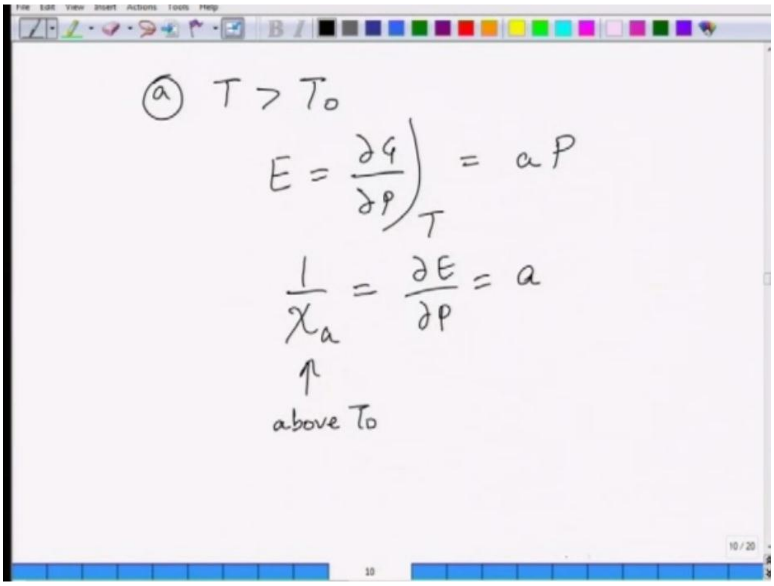

ⓐ $T > T_0$

$$E = \left.\frac{\partial G}{\partial P}\right)_T = aP$$

$$\frac{1}{\chi_a} = \frac{\partial E}{\partial P} = a$$

↑ above T_0

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At T greater than T naught since E is equal to del G by del P at constant temperature, this is nothing but equal to a P. So, the previous in the previous case we wrote an expression for E is nothing but del G by del P. Now, here what we are doing at T greater than T naught, if you ignore the higher order terms what you get is a E is equal to a P. So, this is nothing but E divided by P is nothing but 1 over susceptibility. So I can define this as chi a which is susceptibility above T naught and this is your del E by del P and del E by del P I have taken in these terms, because both E and P are very small. And this is nothing but equal to a. So, now from the curie law what.

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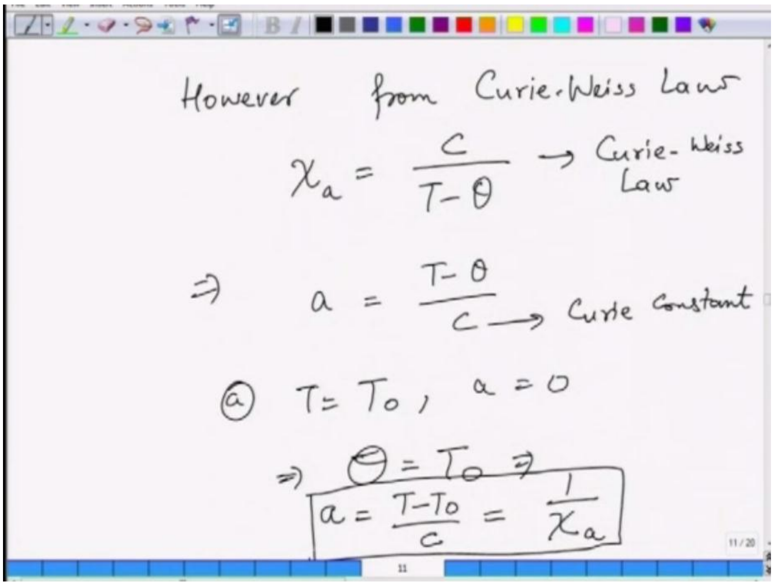

However from Curie-Weiss Law

$$\chi_a = \frac{C}{T-\theta} \rightarrow \text{Curie-Weiss Law}$$

$$\Rightarrow \quad a = \frac{T-\theta}{C} \quad C \rightarrow \text{Curie Constant}$$

@ $T = T_0, \quad a = 0$

$$\Rightarrow \theta = T_0 \Rightarrow \boxed{a = \frac{T-T_0}{C} = \frac{1}{\chi_a}}$$

However from Curie law, we know that chi a is equal to C divided by T minus some temperature theta. And this is nothing but your Curie-Weiss law; even here it should be Curie-Weiss law. I will just write it again. So, what basically it does is, if you compare this expression with the previous expression it gives you the value of a. So, this leads to a to be equal to T minus theta divided by C, where C is nothing but Curie constant. And this theta now we are going to determine the theta what is this theta? So, at we know that at T is equal to T naught your a is equal to 0, as a result since now enter the T naught. So, what you get is theta to be equal to T naught.

So, as a result now, what this leads to is that, a is equal to T minus T naught divided by C which is nothing but your chi a. So, this is the expression which is valid in the region T greater than T naught. Now, what we will do is that we will determine the expression.

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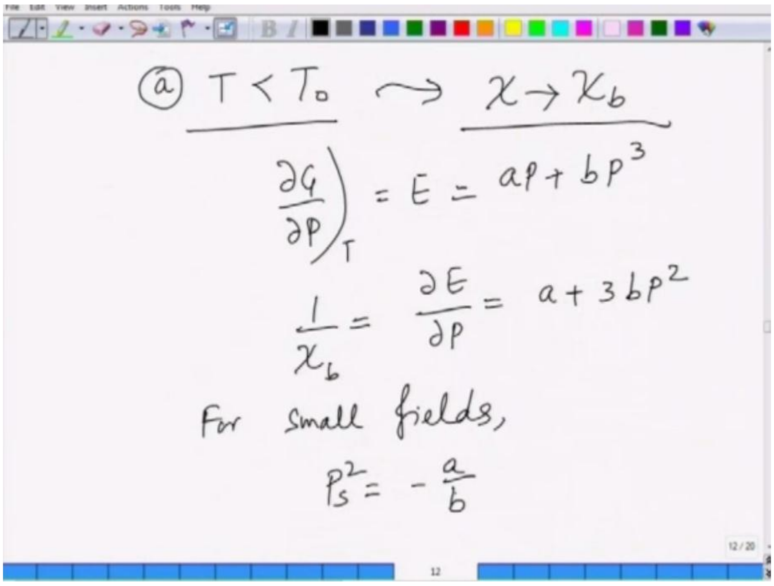

ⓐ $T < T_0 \rightsquigarrow \chi \to \chi_b$

$$\left.\frac{\partial G}{\partial P}\right)_T = E = aP + bP^3$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3bP^2$$

For small fields,

$$P_s^2 = -\frac{a}{b}$$

For susceptibility at T less than T naught, and at these temperatures chi is defined as chi b. So, so again we write the free energy expression del G by del P is equal to E at constant temperature a P plus b P cube. In this case we do not ignore the higher order terms, and now what we get is 1 over chi b is equal to del E by del P and this becomes a plus 3 b P square. And since, here we have taken the term first and second term and neglected all the other terms. So, for small fields, I can from the previous analysis I know that P s square is equal to minus a by b from the, from previous slide.

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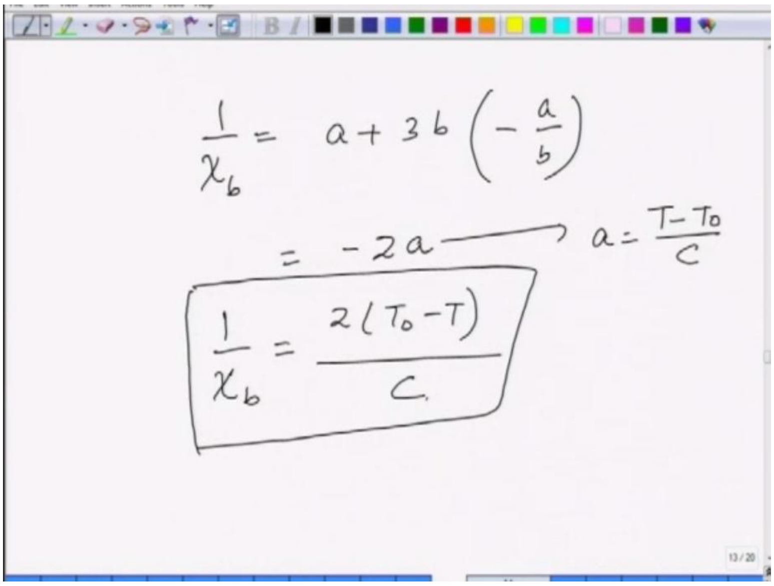

$$\frac{1}{\chi_b} = a + 3b\left(-\frac{a}{b}\right)$$

$$= -2a \longrightarrow a = \frac{T - T_0}{C}$$

$$\boxed{\frac{1}{\chi_b} = \frac{2(T_0 - T)}{C}}$$

So I can write the expression for 1 over chi b to be equal to a plus 3 b. Now, P square is nothing but minus of a by b, and this becomes equal to minus of 2 a. So, alternatively you can write this 1 over chi b to be equal to 2 into T naught minus T divided by C. So, this is your susceptibility variation this is because why, how this comes is because a you know is equal to T minus T naught divided by C. So, you can see how the susceptibility changes? So, susceptibility above susceptibility below T naught is equal to 2 into T 1 over chi is equal to 2 into T naught minus T divided by C.

And in the in the previous expression susceptibility is nothing but 1 over chi a is equal to T minus T naught divided by C. So, you can see the difference now between these 2 plots. So, they have different signs of slopes and which is nothing but sign of a changes as a function of temperature across the transition. So, essentially just to summarize in a second order transition, what you have is; you have polarization which is varying continuously until T naught and the…

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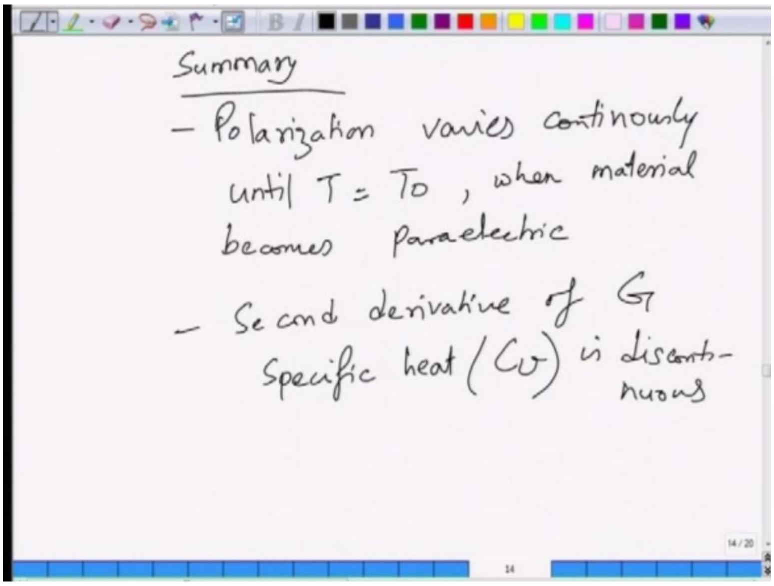

Summary

- Polarization varies continously until $T = T_0$, when material becomes Paraelectric
- Second derivative of G
  Specific heat (C_V) is discontinuous

So, polarization varies continuously just to summary until T is equal to T naught when material becomes paraelectric. So, below T is equal to T below T naught material is ferroelectric above T naught its paraelectric. And also the second derivative of G is discontinuous not it is, it is not the first derivative rather second derivative of G is discontinuous. And what basically it means is that your specific heat is discontinuous.

So, basically specific heat C v is discontinuous at T c and polarization drops continuously until T naught. So, this is the summary of your second order phase transition. So, what we will do now is that we will now shift to.

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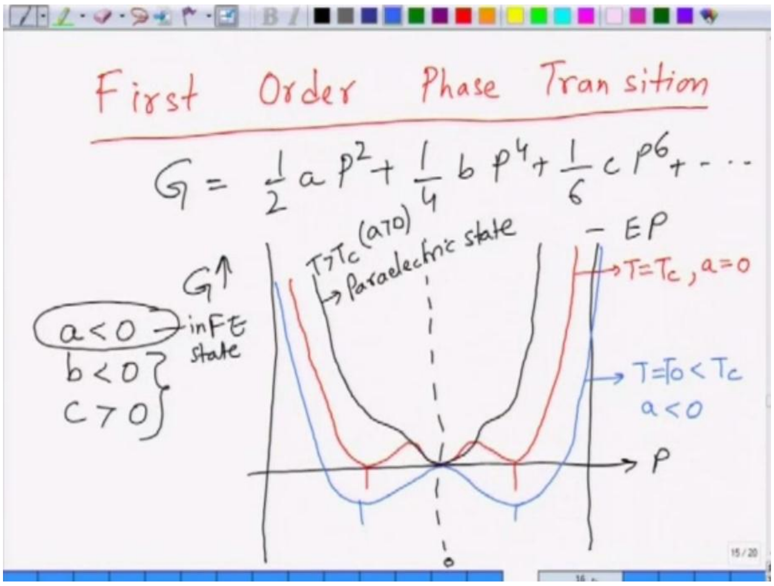

First Order Phase Transition

$$G = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \dots - EP$$

We will now look into other kind of transition which is called as first order transition. Now, this is a transition which is of quite significance in case of ferroelectric materials, because as we will later on see that most of the materials that we, that we observe in daily life ferroelectric materials. They order they follow first order transition rather than second order phase transition that we just now discussed. Now, in case of first order transition what happens is so again I will write the free energy expression first just to remind you what it is? So, G is nothing but a half a P square plus 1 over 4 b P 4 plus 1 over 6 c P 6 plus higher order terms minus of E P.

So, this is your free energy expression. Now, what happens in this case is, if I draw the plot of G versus P. So, this is G and this is your P, let us say your mid point is somewhere here, this is your 0, let me just take this line little bit further up so that I can make the plot completely. So, this is your P line. Now what happens is that in this, in this phase transition we will first look at the qualitative picture. So, in this case your a is less than 0, b is less than 0, but c is greater than 0. So, these are the two things which are different and sign of a change as a function of temperature. So, note the difference in the in the in the sign of b and c as compared to the second order transition.

So, let me just now plot the different plots. So, what happens at lower at higher temperature? At higher temperature the picture is something like this. So, this is let us say at a temperature T greater than T c and at which your a is greater than 0. So, here I have written a is less than 0, but this a is less than 0 in the ferroelectric state. So, however at T greater than a temperature T c now, mind you in the previous second order transition we have talked only about a temperature called as T naught not T c. But here we will see that both T c and T naught will come into picture and the story about these will come in a few slides from this point. So, T is at T greater than T c, both b and b is negative c is positive, but a is positive and this is basically your paraelectric state.

Now, the next thing is at some temperature which I will show which temperature. So, at now, what you see this is the kind of difference that you see in case of first and second order transition. So, at a temperature T is equal to T c when a is equal to 0 the plot shows apart from a minima at P is equal to 0. You also see 2 minima at finite value of P, and these this is the characteristic of second order, first order phase transition which is very different from second order phase transition, because you see 3 minima's; 1 at p is equal to 0 another 2 at plus minus P equidistant from 0.

And then, when you further lower the temperature, what happens is that your free energy plot looks like that, and this it this is at temperature T is equal to T naught. But at some temperature lower than T c, and this is where what you see is 2 minima just like you get in case of ferroelectric state and here your a is negative. So, you can see at T greater than T c, your a is positive material is in ferroelectric paraelectric state. At T less then T c, your a is negative and your material is in ferroelectric state, but in between these 2 temperatures which is in between T greater than T c and T is equal to T naught which is lower than T c. There is a state at T is equal to T c at which you see presence of 3 minima; 1 minima at p is equal to 0, another 2 minima at plus minus P. So, this is the kind of.

So, essentially what happens is that between these 2 temperatures T c and T naught? There is a problem material does not really remember which way to go. So, we will see what it is in the next few slides? But this is the key difference that we that we observe in the first order phase transition in comparison to in comparison to the second order phase transition.

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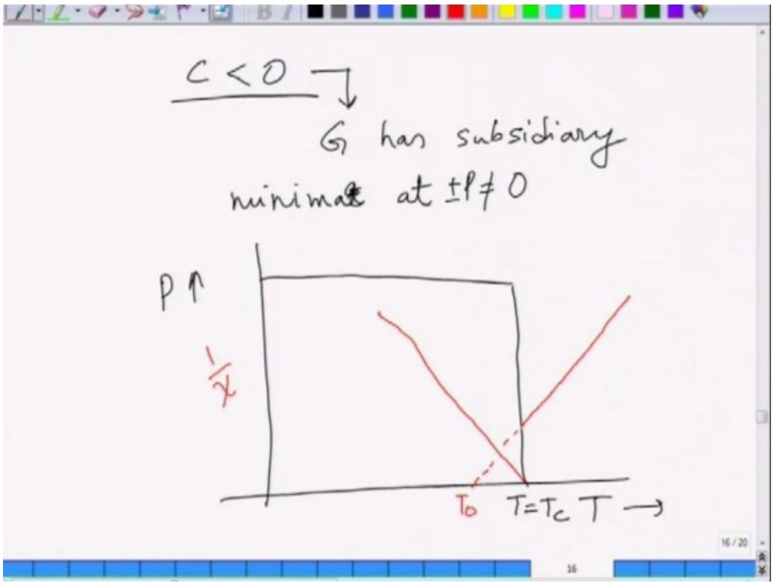
$C < 0$

G has subsidiary minima at $\pm P \neq 0$

So, basically the major difference is C greater than 0 and C is nothing but the term from this particular point which is the 1, 1 over 6 c P 6. So, this term being 0, what it does is basically the free energy G has subsidiary minima, minima at P is equal to P is not equal to 0 plus minus P not equal to 0 apart from in addition to P is equal to 0.

So, as you lower the temperature, the sign of a changes, and then you lower the temperature further and the material then remains, then retains the state which we were familiar with. So, let me just now go through the detailed analysis of this. So, basically what happens in terms of polarization as here? So, the previous plot is free energy plot, but what happens in terms of polarization? So, polarization as you know is the order parameter as a function of temperature, the polarization in this case drops suddenly at T is equal to T c and what happens to susceptibility is even more funny. So, the susceptibility which is 1 over chi it goes it goes like this, with intercept coming at a temperature T naught, and the other part of susceptibility goes like that. So, what basically you see that there is a discontinuity in the susceptibility at T is equal to T c.

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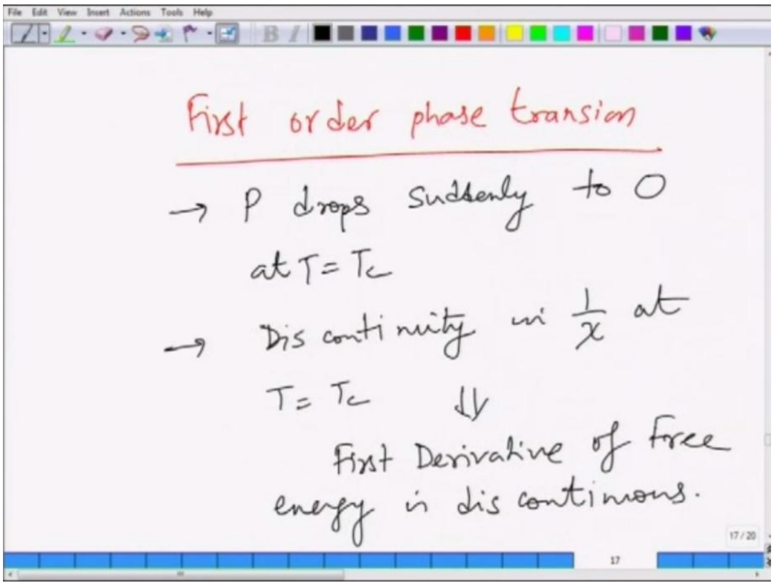

First order phase transion

→ P drops suddenly to 0 at $T = T_c$

→ Dis continuity in $\frac{1}{\chi}$ at $T = T_c$

$\Downarrow$

First Derivative of free energy is dis continous.

So, the first order phase transition, 1 P drops suddenly or abruptly to 0 at T is equal to T c discontinuity in 1 over chi at T is equal to T c. And from the free energy expression, if you know what is the relation of susceptibility to free energy? Then, you would realize what basically this means is that, that the first derivative of free energy is discontinuous. And this is the major difference between first and second order transition.

In case of second order transition your P, P dropped continuously until T is equal to T naught. But in this case P drop suddenly P abruptly drops to 0 at T is equal to T c and which is reflected in a discontinuity in 1 over chi which is susceptibility inverse at T is equal to T c. And thermodynamically what it means is that, the first derivative of free energy is discontinuous, whereas in case of second order phase transition it was the first derivative of free energy which was discontinuous these are the. So, this is these are the two major differences and this discontinuity; this first derivative of free energy being discontinuous signifies that there is evolution of latent heat. So, in some sense this transition is nothing but similar to your reconstruct transition which happens in liquid to solid kind of transformation. So, now what we will do is that.

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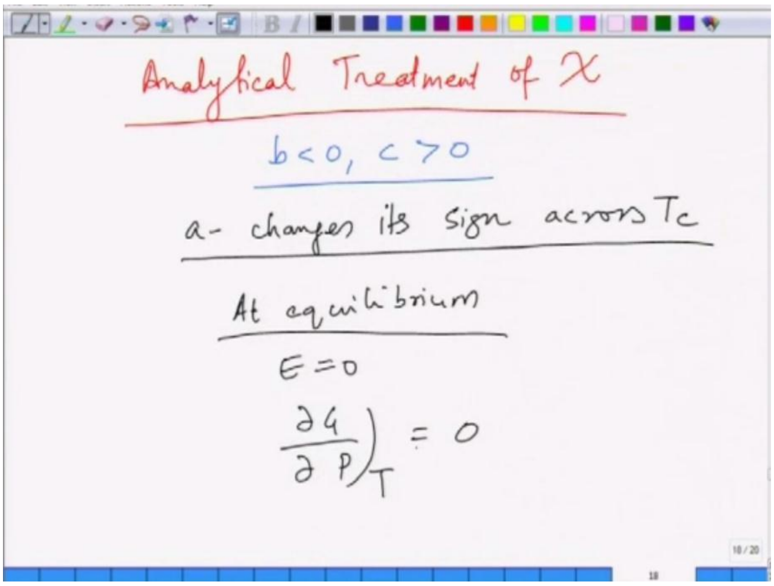

Analytical Treatment of χ

$b<0, \; c>0$

a- changes its sign across T_c

At equilibrium

$E=0$

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

We will look at analytical treatment of susceptibility of chi. So we will look at what chi is below and above T c. So, so basically again I will write that b is less than 0, c is greater than 0 for a first order phase transition and a change its sign across T c. And this we saw in the in this slide when a changes its sign from positive to negative as it G 1 from T greater then T c to T less then T c. So, basically now let me write at equilibrium. So, consider that equilibrium conditions consider electric field also to be equal to 0, if this is the case then del G by del P is equal to 0 and if this is the case then from the free energy expression.

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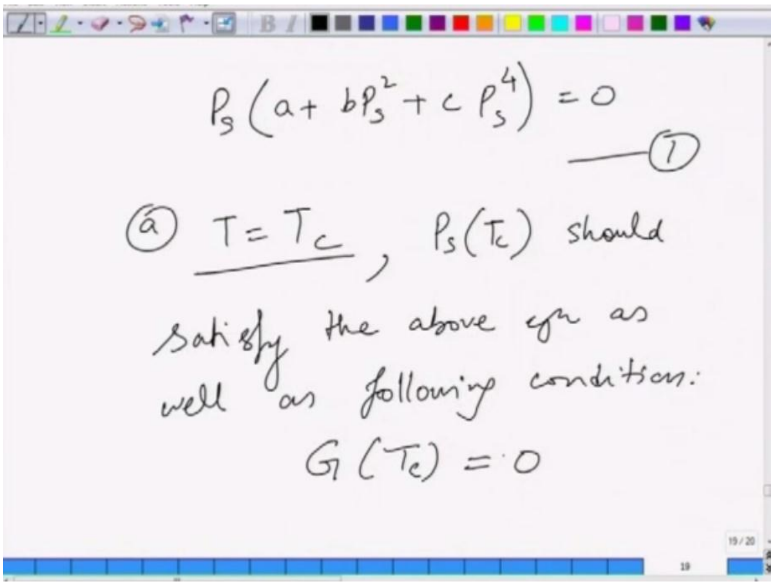

$$P_s\left(a + bP_s^2 + cP_s^4\right) = 0 \quad \text{——} ①$$

ⓐ $\underline{T = T_c}$, $P_s(T_c)$ should satisfy the above eqn as well as following condition:

$$G(T_c) = 0$$

You can write P s into a plus b P s square plus c P s 4 and ignoring higher order terms to be equal to 0. So, this derive so based on this condition, which is del G by del P at constant temperature to be equal to 0, you can obtain this expression from the differentiation of free energy expression. Now, at T is equal to T c, your P s at T c should satisfy the above equation as well as another condition which is as follows. And that condition is nothing but your G at T c has to be equal to 0. So, if this is the case.

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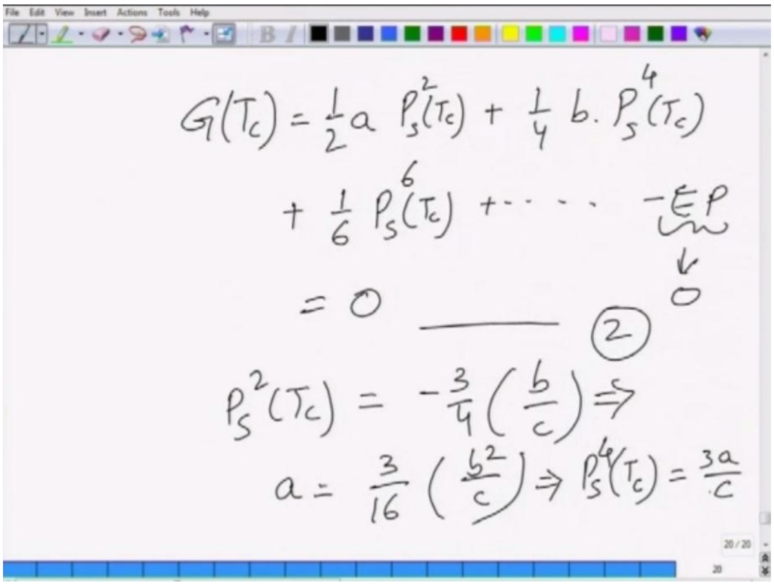

$$G(T_c) = \frac{1}{2}a\,P_s^2(T_c) + \frac{1}{4}b.\,P_s^4(T_c) + \frac{1}{6}P_s^6(T_c) + \cdots \underbrace{-EP}_{\downarrow\, 0}$$

$$= 0 \quad \text{——} ②$$

$$P_s^2(T_c) = -\frac{3}{4}\left(\frac{b}{c}\right) \Rightarrow$$

$$a = \frac{3}{16}\left(\frac{b^2}{c}\right) \Rightarrow P_s^4(T_c) = \frac{3a}{c}$$

So, you know that, so G at T c will become half of a P s at T c square plus 1 by 4 b into P s at T c to the power 1 by 4 plus 1 by 6 P s at T c to the power of 1 by 6 plus so on and so forth, and since E is equal to 0 this minus E P term is 0. So, I am since and this is equal to 0. So, if you take this as equation number 2 and the previous 1 as equation number 1, if you solve these 2 equations, you can get the answer for P s square T c which turns out to be minus of 3 by 4 b by c or and the value of a you determine is 3 over 16 b square divided by c. So, this so you can alternatively write this as P s to the power 4 T c will become 3 a by c. So, if this is the case. So, basically what you have is you have 3 non digital roots.

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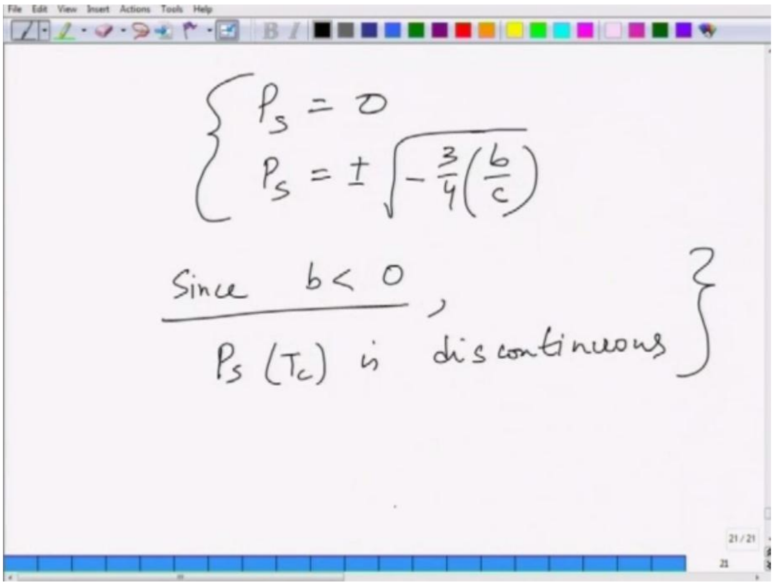

$$\begin{cases} P_s = 0 \\ P_s = \pm\sqrt{-\frac{3}{4}\left(\frac{b}{c}\right)} \end{cases}$$

$$\left.\begin{array}{l} \underline{\text{Since } b < 0}, \\ P_s(T_c) \text{ is discontinuous} \end{array}\right\}$$

One is at P s to be equal to 0 and another there is P s is equal to plus minus of minus 3 by 4 b by c. So, and of course, since b is your b is positive and c is negative. So, this term will become positive. So, as a result you have 3 minima’s in between at the, if you notice here. So, we had 3 minima’s at T is equal to T naught which is this minima; this minima and this minima. And these minima’s are nothing but at 1 at 0 and 2 at plus or minus root of minus 3 by 4 b divided by c. So, now, since b is less than 0 what this means is that P s at T c is discontinuous. So, this is the problem here since b is less than 0 the T c is discontinuous the P s is discontinuous as T is equal to T c. Now, what we do is that we now look at what is the expression for susceptibility.

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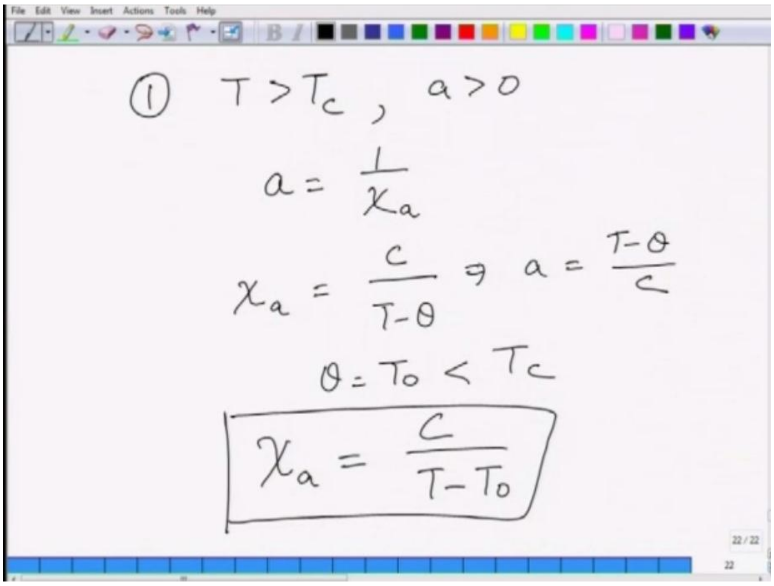

① $T > T_c$, $a > 0$

$$a = \frac{1}{\chi_a}$$

$$\chi_a = \frac{c}{T-\theta} \Rightarrow a = \frac{T-\theta}{c}$$

$$\theta = T_0 < T_c$$

$$\boxed{\chi_a = \frac{C}{T-T_0}}$$

So, first we look at the case of T greater than T c when a is positive and a we know is nothing but 1 over chi a and chi a, we are aware from Curie-Weiss law is equal to 1 c divided by T minus theta or rather I can write a to be equal to T minus theta divided by C. And so, basically T greater than c is nothing but paraelectric state. So, the treatment is similar to what we had in case of second order phase of transition? And this theta is nothing but T naught which is in a smaller than T c. So, you can determine what is chi a which is nothing but your chi a will be equal to c divided by T minus T naught. So, this is in the region T greater than T c.

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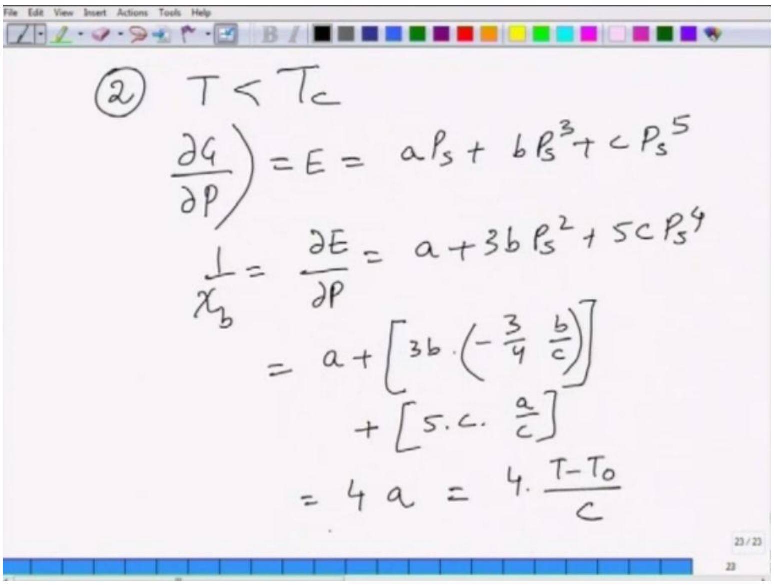

② $T < T_c$

$$\left.\frac{\partial G}{\partial P}\right) = E = aP_s + bP_s^3 + cP_s^5$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3bP_s^2 + 5cP_s^4$$

$$= a + \left[3b\cdot\left(-\frac{3}{4}\frac{b}{c}\right)\right]$$

$$+ \left[5.c.\frac{a}{c}\right]$$

$$= 4a = 4.\frac{T-T_0}{c}$$

Now, we look at second region which is T less than T c and here del G by we again go back to free energy equation del G by del P is equal to E. And this is equal to a P s plus b P s cube plus c P s 5. So, 1 over chi b in this region is del E by del P and this is nothing but a plus 3 b P s square plus 5 c P s 4. And if you now make the substitution for P s square which is which we know what it is? Then this will be a plus 3 b into minus of 3 by 4 b by c. So, for this you need to go to the previous slide and plus 5 into c into a by c. And this will give you 1 over chi b to be equal to 4 a. So, again you put in the value of a which is nothing but your 4 into T minus T naught divided by C. So, this will be your susceptibility in the region T less than T c.

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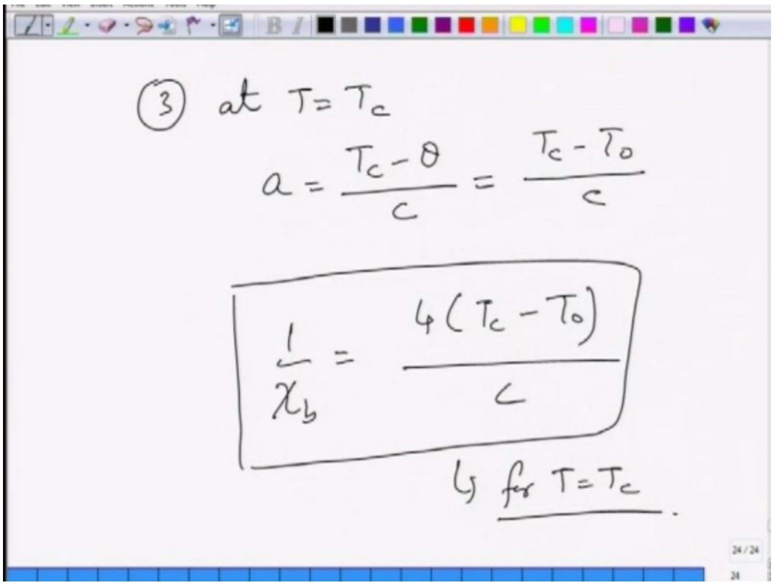

③ at $T = T_c$

$$a = \frac{T_c - \theta}{c} = \frac{T_c - T_0}{c}$$

$$\boxed{\frac{1}{\chi_b} = \frac{4(T_c - T_0)}{c}}$$

↳ for $T = T_c$.

And at T is equal to T c, a is equal to since T c minus theta divided by C your, so this is T c minus T naught divided by C, your 1 over chi will become. So, basically what I am doing is that I am just. So, just if I just plug it in into the previous expression then, 1 over chi b turns out to be 4 into T c minus T naught at divided by c. This is for T is equal to T c. Now, we can we have seen there are three different regions of susceptibility one is below T c, second is above T c and third is right at T c which is, so you see a discontinuity in T c discontinuity in the susceptibility at T is equal to T c which is different from what you basically saw in case of first sort of phase transition. So, now I will summarize or I will compare second and first order phase transition in case of second order.

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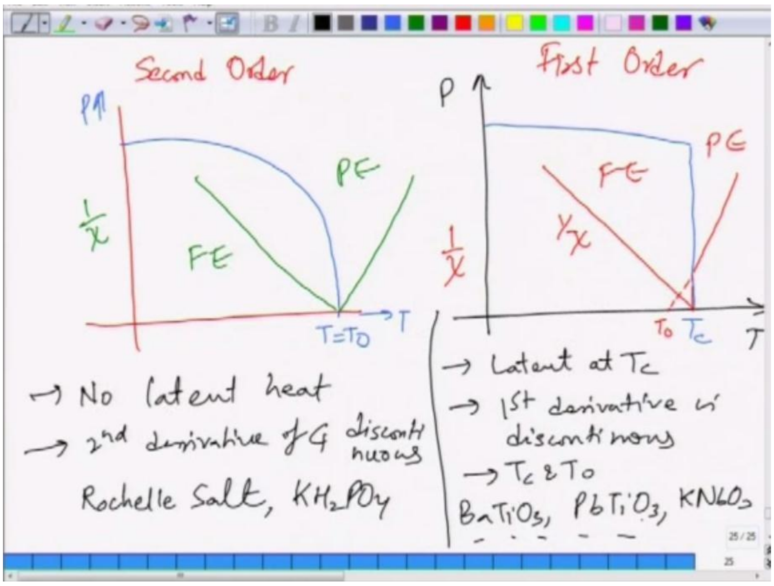

→ No latent heat

→ 2nd derivative of G discontinuous

Rochelle Salt, KH_2PO_4

→ Latent at T_c

→ 1st derivative is discontinuous

→ T_c & T_o

$BaTiO_3$, $PbTiO_3$, $KNbO_3$

So, let me just first write the second order and here we write first order, in case of a second order phase transition your polarization drops continuously this is not very continuous. So, I will just, I will just draw it. So, this is your T is equal to T naught. So, this is your P and this is your T, and the susceptibility goes susceptibility goes in a different sense so, 1 over chi which is the green curve. So, you will have 1 slope for this, another slope for that, and this will be a susceptibility behavior, and this will be your ferroelectric state, and this will be your paraelectric state.

In case of first order phase transition situation is slightly different. This is your temperature axis, polarization axis, the polarization goes bang suddenly. So, let me just draw it differently. So, it goes up to this point like that and then drops suddenly. This is your T c and the susceptibility goes as your, so this will have its intercept at T is equal to T naught and then, this will, you will have another part going like that. So, there will be a discontinuity in susceptibility. So, this is your 1 over chi. So, this is your ferroelectric state; this is your paraelectric, and the key differences are 1, no evolution of latent heat. So, i can just write it this case, no latent heat at T c at T naught and then, first second derivative of G discontinuous.

And examples of materials in this case are your Rochelle salt and K H 2 P O 4, not too many ferroelectrics follow this kind of phase transition. So, these are two specific characteristics, no latent heat evolution at T is equal to T naught, and second order of free energy is discontinuous. In this case you have latent heat at T c just like solid liquid phase transition, first derivative is discontinuous and between T c and T naught material does not remember itself and the example of materials are barium titanate, lead titanate.

Most of the common ferroelectrics that you see potassium niobate etcetera, etcetera. Most of them follow this first order phase transition. So, these are the critical differences between these 2 phase transitions. So, first order transition, second order transition basically is a thermo dynamic effect if you want to go into details of it you can again go into details of this in a any in I would prefer if you want to understand.

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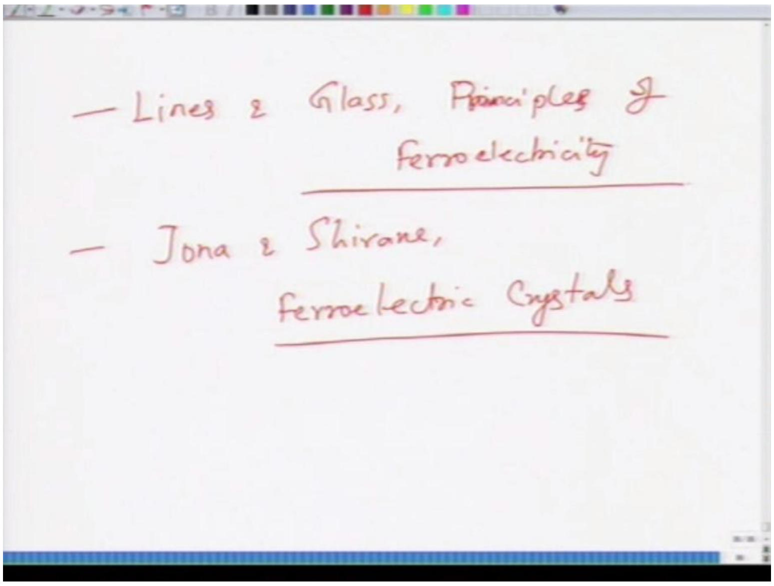

— Lines & Glass, Principles of Ferroelectricity

— Jona & Shirane, Ferroelectric Crystals

Then, go to this Lines and Glass Principles of Ferroelectricity. And you can also go through Jona and Shirane and it is ferroelectric crystals. So, this is about the ferroelectric transitions in the materials. So, we will finish the so we have finished what is? So, we have looked at ferroelectric materials so far.

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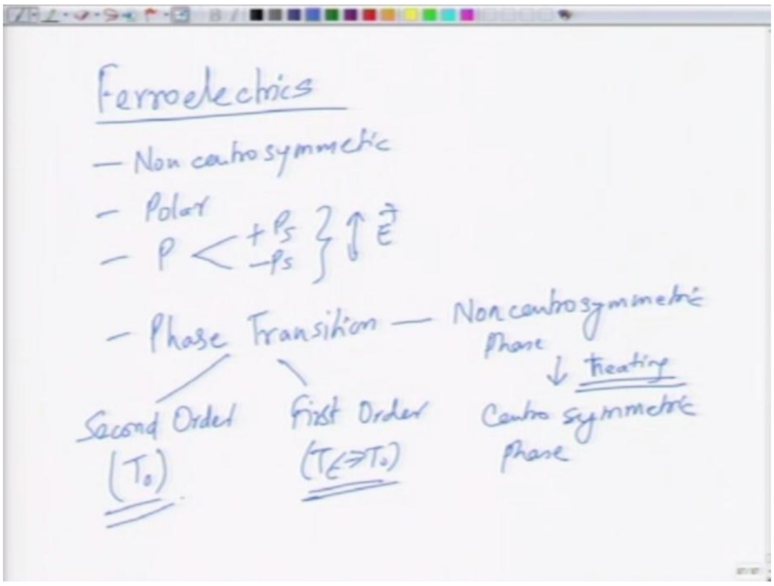

Ferroelectrics

— Non centrosymmetric

— Polar

— $P < \begin{matrix} +P_s \\ -P_s \end{matrix} \Big\} \updownarrow \vec{E}$

— Phase Transition — Non centrosymmetric Phase

↓ Heating

Centro symmetric Phase

Second Order (T_0)

First Order $(T_c \Rightarrow T_0)$

So, you have ferroelectrics and these ferroelectrics have qualities as have characteristics lie if they are non centrosymmetric, they are polar. And this polarization has 2 states plus P s and minus P s depending upon how you switch it? So, this is switchable as you change the polarity of electric field.

So, this is the difference and not only these three characteristics, it also undergoes a phase transition. So, this phase transition is from basically when you heat it, so it is from a non centrosymmetric phase to a centrosymmetric phase typically or you can say it goes from lower symmetry to higher symmetry as you as you heat the material. And this which means that it has a transition temperature and this transition temperature is very précised in case of second order transition.

So, in case of second order transition, you have a transition at T naught and this T naught defines the transition temperature. And in case of first order transition you have a transition at between T c and T naught, and it depends whether you cool it or whether you heat it. And the difference between these 2 transitions is that, in the second order transition the polarization drops continuously up to the transition. In the first order the polarization drops abruptly at the transition. So, there is a discontinuity in the polarization which is called as order parameter for the first order transition and it drops suddenly at the transition temperature. And this is also shown in the susceptibility of the first order transition which shows the discontinuity.

Another difference is in the second order transition you have discontinuity in the specific heat near the transition. But there is no evolution of latent heat. In case of first order you have discontinuity in the specific heat, but you also have evolution of latent heat. So, it is like liquid solid transition in some sense the first order transition in ferroelectrics. So, moving now away from the phase transitions now, what we look need to look at how the ferroelectric materials switch? So, we know that the ferroelectric material.

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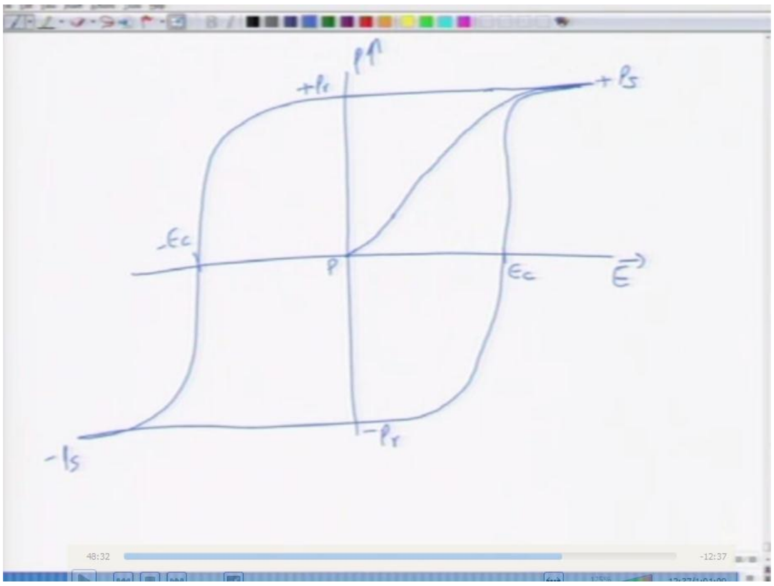

When you draw the hysteresis of ferroelectric when you pole a ferroelectric material, and you make a plot of polarization versus electric field and this shows a curve like this. So, this is your plus P r; this is your minus P r; this is your plus P s; this is your minus P s and this is your plus E c; this is your minus E c. Now a ferroelectric material typically now the question is why does it happen? Why does it happen and how does it happen? So, you when you start with the material which is virgin material which is as prepared material then, typically in ferroelectric materials for a poly crystal you start at zero polarization.

Now, as you start from zero polarization which means what it means is that net polarization of the material is 0 although locally it still is polar and that is for the reasons what I will show you in a while and then it is start increasing. So, it is it goes like this and then it goes like that. And once all the dipoles aligned in the direction of applied field it gets back to non-zero state and this process keeps happening. Now, what happens is basically in ferroelectric material you have anyway polarization.

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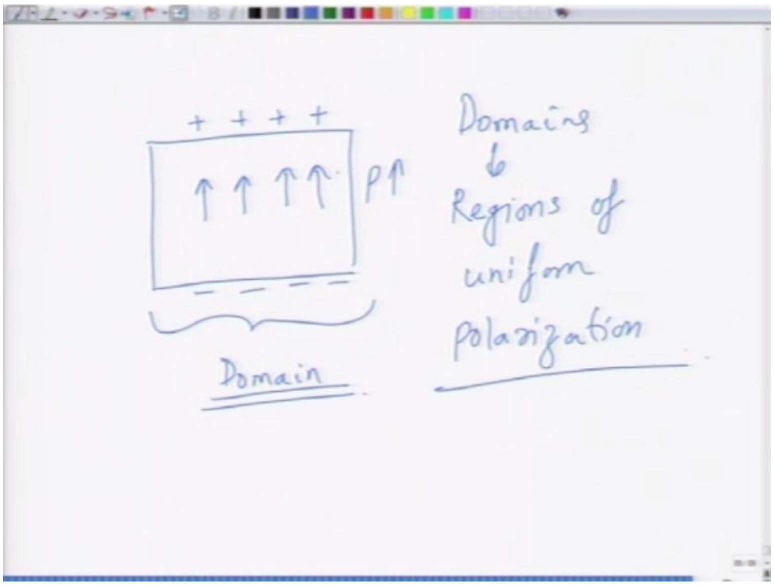

But these dipoles as we said earlier they are aligned in one direction when they are aligned in one direction. And this alignment when it extends over a region of the crystal then, this region which has a uniform alignment of dipoles is called as a domain. But the moment you form a domain you have these ends of the. So, if this is the P vector then, you have charge build up on the phases of this domain and this charge build up starts increasing the electro static energy. Now, this if this electro static energy goes up then that depolarizing field becomes high. So, the counter field which wants to turn this other way round that increases.

So, the question now is what is the extent of this region? The extent of that region is governed by what is the depolarizing field? So, it is the competition between the energy which aligns all the dipoles in one direction, and the depolarizing energy which defines the extent of this alignment. So, these regions of uniform polarization, so domains essentially are regions of uniform polarization and typically what you see in the ferroelectric materials is.

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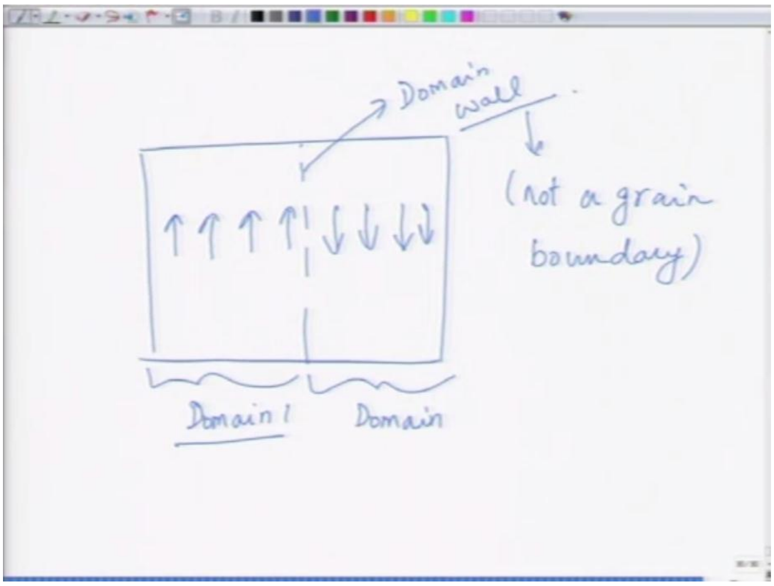

You have these domains which are separated by. So, you have one region. Now, mono domain status is not favorable for regions for reasons that we will see in a while it is because of energetic, because the energy of the system does not allow it to retain the mono domain state. So, you have 1 domain. So, this is domain 1 in which alignment of dipoles is in one direction. You have another domain which is domain 2 and which in which the alignment of dipoles is in another direction. And they are separated by a boundary which is called as domain wall. And this domain wall is not grain boundary, because here you are not changing the crystal orientation all you are changing is the domain or the polar vector and how it happens is.

So, basically so this domain wall first of all not a grain boundary and what it also means is that domain is not a grain. So, grain and domains are the two different terms, it is a different matter that 1 grain can be 1 domain, but domain and grain conceptually are extremely different. So, basically there are variety of domains, there are domains in various directions, so for a poly crystal.

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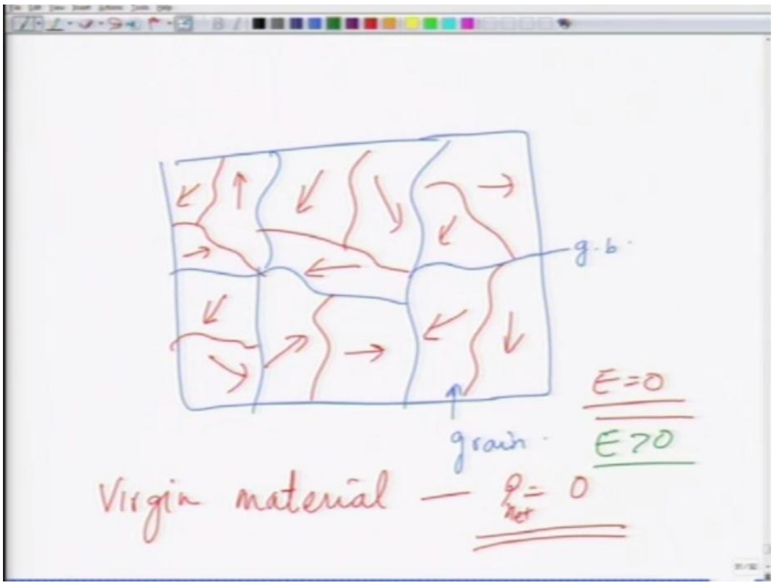

You have situation like this. So, this is your let us say a poly crystalline material now these are grains. So, this is your grain boundary and this is your grain, let us say this grain is big enough. So, you may have regions in this. Now I am going to use different color. So, you may have these different regions of different domains. So, let us say orientation of this domain is this one; this is as prepared material orientation of this domain is that this is this this is that this is this this is that this is that and so on and so forth. So, the orientation of domain walls orientation of polarization in the adjacent domains is restricted by the structure of the material although here it is looking much more random it is not that random. So, I will just come to that in a while so and you so on and so forth.

So, for a virgin material in a polycrystalline material which is as prepared all the domains are randomly distributed. So, even though the material microscopically is polar, the net polarization is equal to 0 when it is not poled. Now, when you start applying this electric field to this material when you start applying electrical field, so what happens is that now you have? So, you have grain boundaries like this and if you go to previous slide itself. So, when you so this is when E is equal to 0 now what happens when E becomes greater than 0, when E becomes greater than 0 then, all these domains which are unfavorably oriented they start. So, basically the in this case the ferroelectric the domain creation or the domain movement in the ferroelectric materials is slightly different. So, what happens is that basically new domains form which are aligned in the direction of applied field. So, you start forming new regions, new domains which are aligned in the direction of the applied field. And these domains grow as the field strength is increased at the expense of all these unfavorably oriented domains.

So, all the basically old domains are consumed and new domains form, which are conducive to the direction of applied field. And when the field is maximum and when all the domains when all when the alignment of dipoles in all the domains is in the direction of applied field that is where you have saturation. So, when E is very large then, saturation is achieved which means you have achieved a mono domain state, but this mono domain state is not favorable. So, when you bring the field back to back to E is equal to 0 then, all the domains get back to the same configuration which means giving rise to a zero polarization state.

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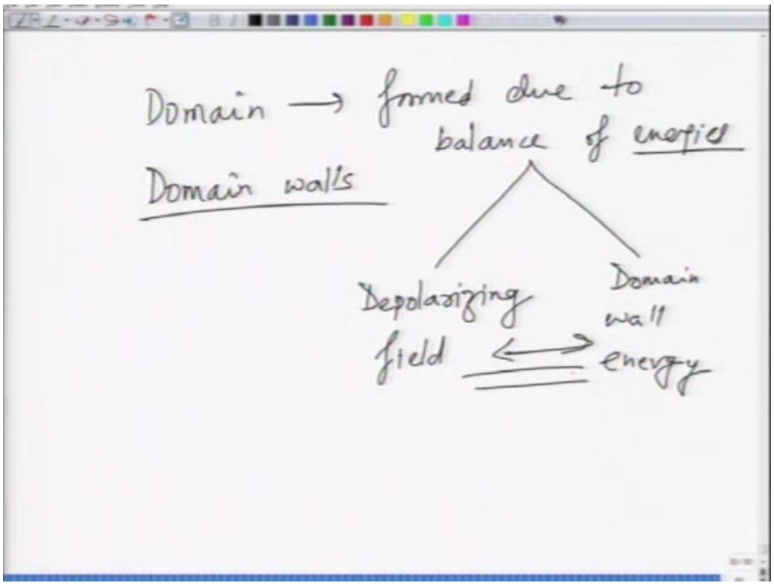

Domain → formed due to balance of energies

Domain walls

Depolarizing field ⟷ Domain wall energy

So, basically you have domains, you have domain walls. Domain walls are boundaries which separate the domains, and these domains are formed due to balance of energies and as I will show you the analyses, these energies typically are your depolarizing energy due to depolarizing field and domain wall energy. So, as so what basically is means that when you have a mono domain state now polarization is very high, but at the same time since you build up the charge at the end of diploes that depolarizing field becomes large. When the depolarizing field becomes large, it wants to turn the polarization in the other direction. But when you turn the polarization in other direction in some parts of the crystal you create these boundaries. And these boundaries are domain walls and these boundaries or domain walls are nothing but surfaces and surface is required energy. So, it is a competition between these two energies which determine what is the domain size and domain configuration going to be, so for instance in a material like you know barium titanate, lead titanate.

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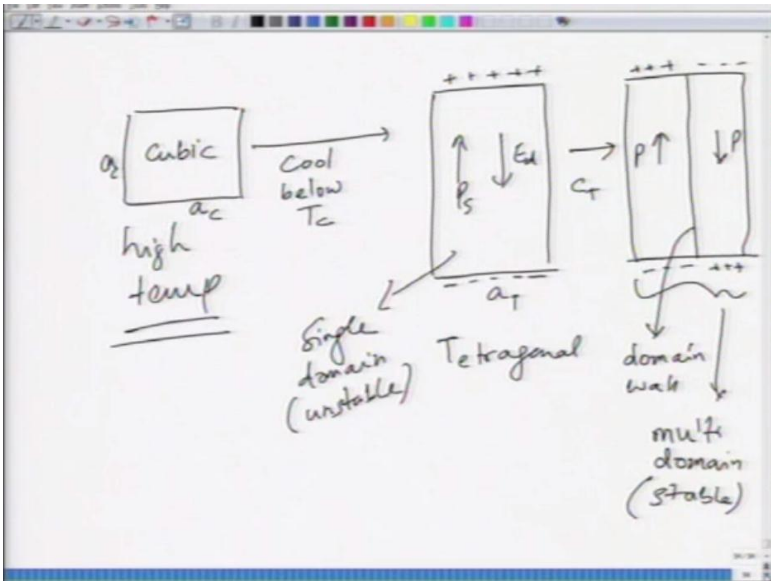

So, you have a cubic material; you start with a cubic state of the material from high temperature. So, this is high temperature cubic state. So, when you cool it cool below T c then, what happens is that the material transforms into tetragonal state. So, this is now tetragonal. So, here this was here it was a a .So, here it becomes a and c. So, a T and c T here it was a c and T c. So, here what happens is that when it becomes tetragonal it develops a polarization in this direction. So, you have build up of charges on the phases of the crystal correspondingly you have a depolarizing field which is called as E d now, this state being not. So, this is a mono domain state, but this stage is state is unstable.

So, what you get instead is you have polarization in this direction; you have polarization in this direction. So, here so the surface charge density goes down as a as a result you can see that the depolarizing field has disappeared. And this kind of domain boundaries this is this wall is called as domain wall. So, this was single domain unstable and this state is basically multi domain which is a stable configuration. And depending upon the type of the crystal structure you can have variety of domain walls so for instance for a.

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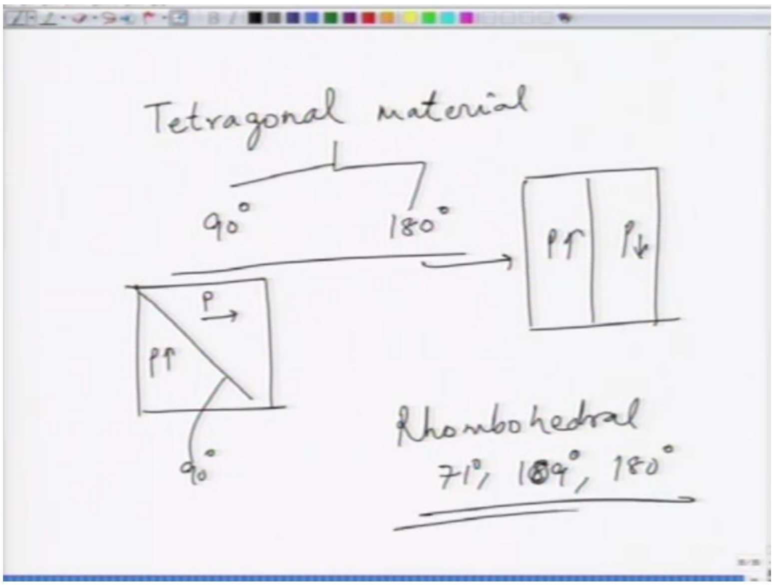

For a tetragonal material, domain walls are of 90 degree domain walls and 180 degree domain walls. So, what essentially it means is that, you can have domain walls like this. So, P so this is your 180 domain wall and 90 degree domain wall would mean, you have for instance a material like this so P in one direction and P in another direction. So, this is your 90 degree wall and for similarly, for materials like rhombohedral structure, you can have 71 degree domain wall, 109 degree, 109 degree domain wall and 180 degree domain wall. So, depending upon the crystal structure the configuration of domain walls will change.

So, in the next class, we will finish the lecture here; in the next class, what we will see is that we will look at the little bit analytical treatment of the domain wall, some pictures how the domains look like? And how the configuration of atoms at the domain wall boundary looks like? So, that you do not get confused with the grain boundary, it is slightly different from the, it is very different from the grain boundary, there is no change in the orientation of the crystal or a crystal orientation remains same, it is just the polar vector changes in one to another direction.

So, we will finish this lecture here. So, in this we have finished the phase transition. We looked at the first order phase transition in detail; we also looked at the remaining part of second order phase transition. And the crucial difference you must remember in the first order transition, the order parameter drops discontinuously near the T c, whereas in the first second order transition orders parameter varies continuously until the T c. And then, we started what is called as domain wall, domains and domain walls? And these domains are stable features inside the material simply, because mono domain state or alignment of polarization dipoles across the whole volume the material is not a stable state. So, we will have a little bit more discussion in the next lecture.

Thank you.