Electroceramics
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Lecture - 27

So, again we are starting a new lecture. So, what we will do is that we will first just review the last lecture, and then move on into that new contents of this lecture.

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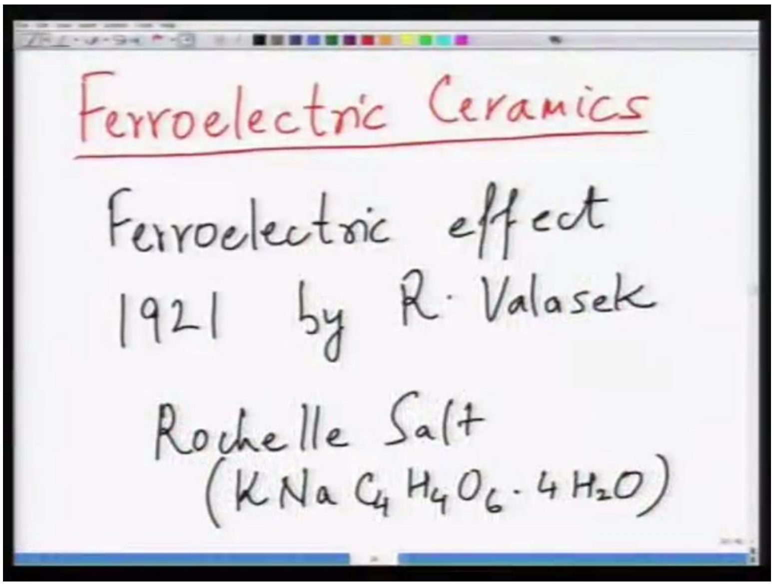

So, in the last class, we started discussion on ferroelectric ceramics. And ferroelectric ceramics as we discussed it was discovered in 1921, the effect ferroelectricity let to be more precise by Roger Valasek in Czech Republic on Rochelle salts. And following that there were many materials which were discovered, and of course most important of them happen to be titanates which are used for variety of technological applications.

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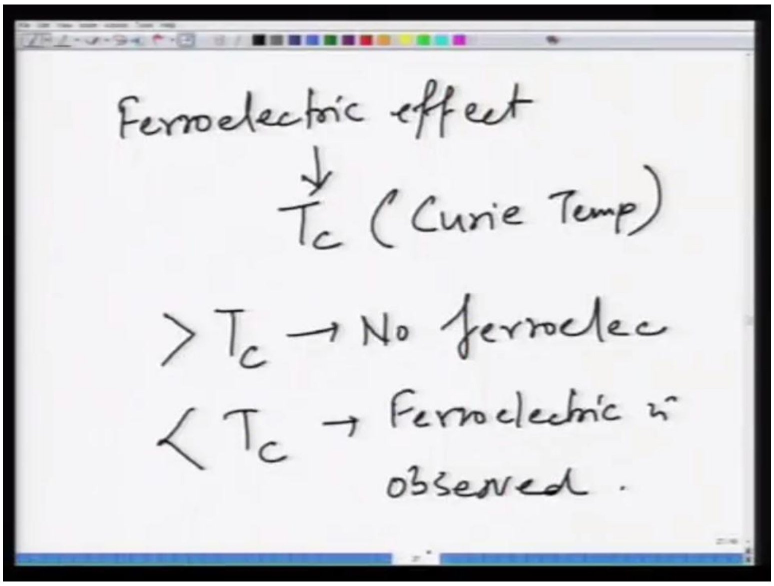

One of the important things about ferroelectric effect is, this effect goes through a critical temperature which is called as Curie temperature or T c. Now, below this temperature the material is in ferroelectric state while if a temperature is above T c the material does not show any ferroelectric effect.

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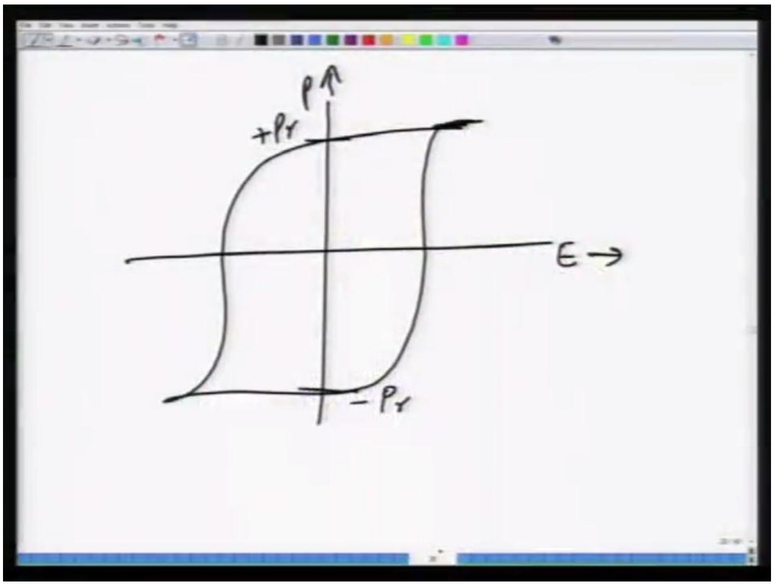

And basically, the ferroelectric effect is as you know it happens in non centrosymmetric materials with a unique polar axis. And the direction of that polar axis can be reversed as the field direction is reversed.

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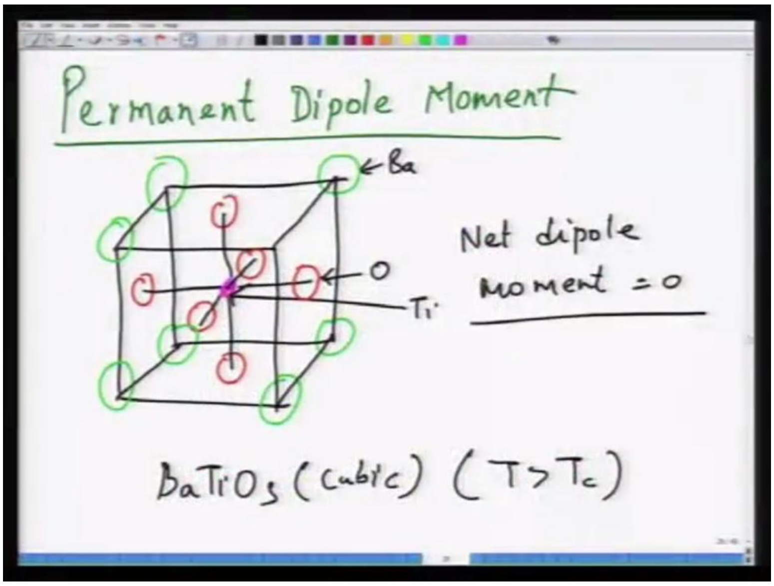

And then we looked at the example of barium titanate. So, in the cubic form one of the hypothesis is that or one of the easy ways to understand is that net dipole moment, it is z0. Now, this net dipole moment could be 0 first, because it is cubic second even if it is non centrosymmetric then which means it contains each unit cell contains a net dipole moment. All these dipole moment vectors cancel out each other because of thermal randomization.

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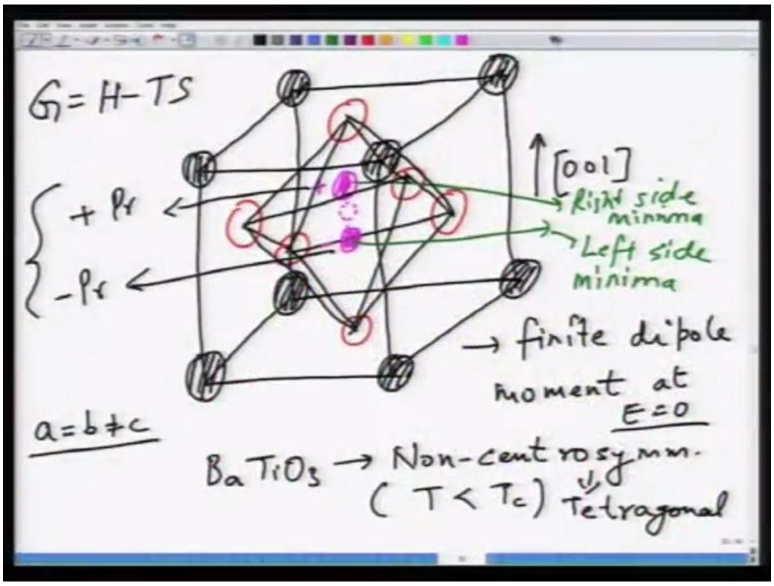

And in the ferroelectric effect the energetic requires this central titanium atom to be away from the centre position either shifted in the positive direction or negative direction along the z axis. And this gives rise to minima in the free energy polarization curve which are which correspond to plus P r and minus p r values. And this happens in the non centrosymmetric ferroelectric state of the material.

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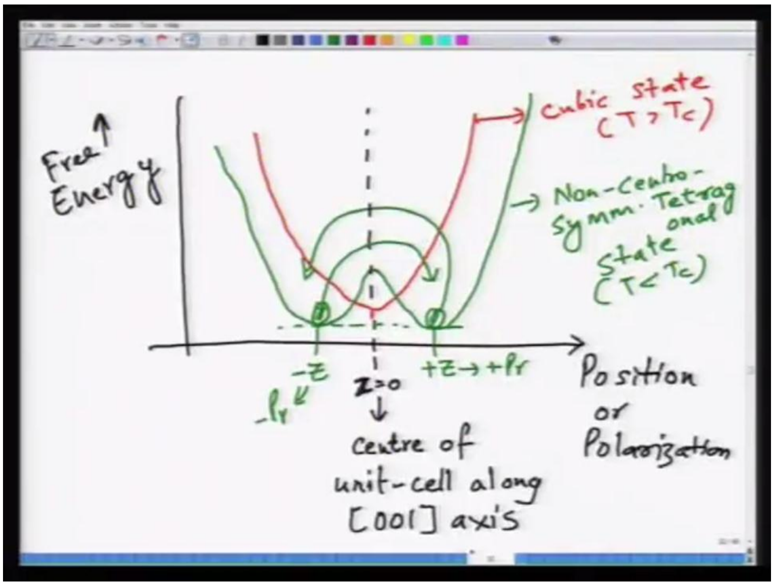

And this can be explained by this free energy composition, sorry free energy position or free energy polarization diagram. So, in the cubic or non ferroelectric state which is above T c, but here it shows only the free energy curve shows only 1 minima, and that happens at Z is equal to 0. And whereas, in case of non centrosymmetric materials in the ferroelectric state you have 2 minima which are away from each other. And this happens at titanium atom sitting at off centred position that is at minus z or plus z which correspond to plus P r and minus P r as I said before.

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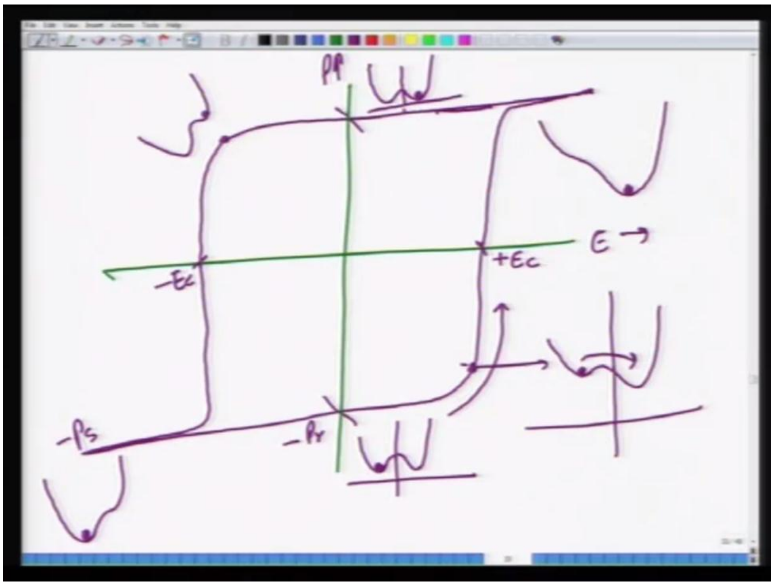

So, this gives rise to remnant polarization and then you can draw this how the energy wells change their shape? How the titanium atom moves from one side to another side as you switch the field? So, this can be drawn by tilting of energy wells as a function applied field.

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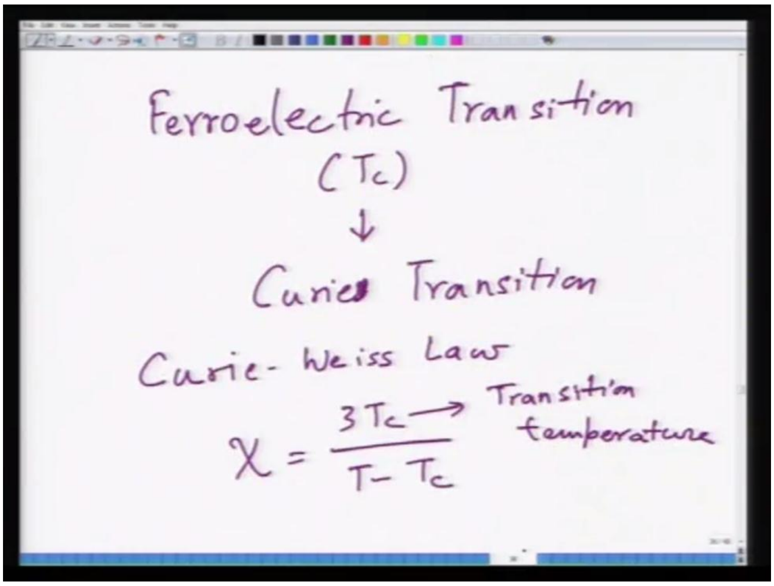

And then we looked at the ferroelectric transition follows the Curie-Weiss law which says that susceptibility is equal to 3 T c by 3 minus T c. And then we looked into the derivation of this expression by looking at molecular field theory. In this case, we took a local field which is given by clausius mossotti relationship. And then substitution of this and making some approximations near the T c such as N alpha divided by 3 epsilon naught equals to 1 or approaches is 1 which leads to very large susceptibilities as observed for electric materials, this gives you what is called as a expression for susceptibility near T c.

So, T c is defined as N C , C is the curie constant divided by 3 k epsilon naught, and N is the number of dipoles and so on. And so you get a expression for chi which is 3 T c divided by T minus T c, and this is how the ferroelectric transition looks like. So, you have this epsilon r or chi. So, when you start heating the material, material shows abnormally high electric constant or susceptibilities near the T c which again falls out in paraelectric state. So, what it how is it shown in terms of dipolar alignment is, in the ferroelectric state. You have a spontaneous alignment of dipoles overcoming the thermal randomization, while in paraelectric state dipoles even though each crystal may have a dipole moment, because of non centrosymmetric. It is still all these dipoles are randomly oriented with respect to each other and giving rise to zero polarization.

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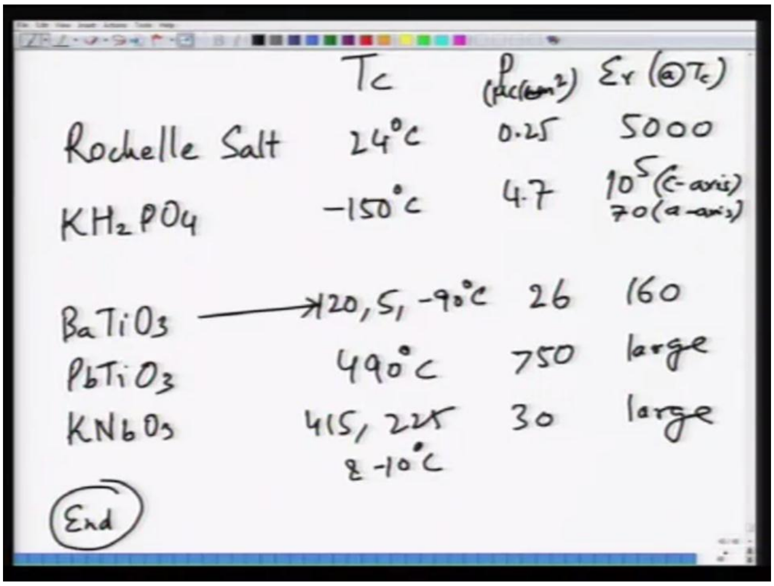

So, then we looked at certain materials with values of dielectric constant P r or and T c, and the stand out candidates of course, are titanates which are which have reasonably high T c as compared to other materials. And that is why they are more technologically more useful.

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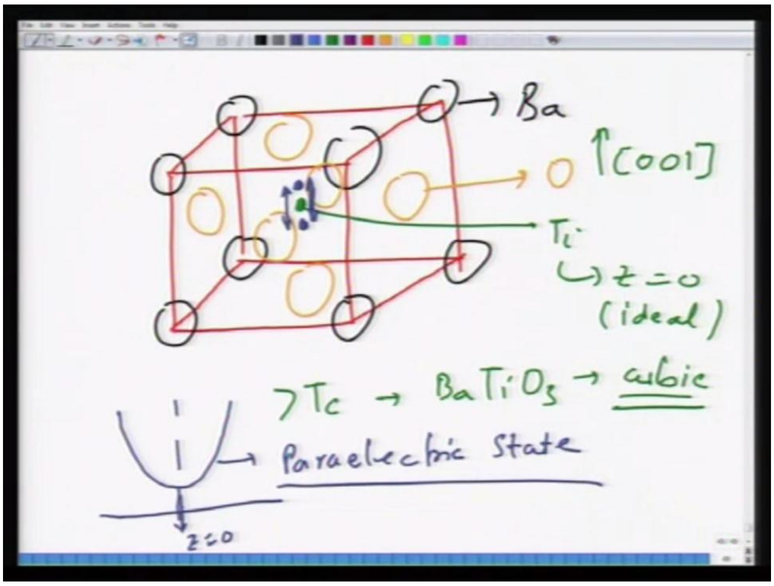

Now, one of the things that we discussed last time was, when you at barium titanium cubic in the centrosymmetric state for the sake of illustration we mention. So, if this is the unit cell of barium titanate. So, this is your barium atom, and then you have titanium atom, oxygen atom going. This is your oxygen atom, and then you have titanium atom sitting somewhere in the middle. So, ideally this titanium atom should sit if this is your 0 0 1 axis, titanium atom should sit as Z is equal to 0 ideal for a ideal perovskite.

Now, we said that in paraelectric state, we considered this Z to be sitting as Z is equal to 0 which is fine which is how it is assumed to be. Now, what it actually means is titanium atom, because the material is still is in non centrosymmetric state. So, even though at T is equal to T c barium titanate becomes cubic, but it is still is in non centrosymmetric state which means the titanium atom actually stays either in this position or in this position. But because of thermal randomizations, when you look across the material it is very difficult to discern whether titanium atom sits in this position or that position that is why in that average is taken as if it was sitting at the centre. So, if it was centrosymmetric of course, it would sit at the centre.

But even if it was non centrosymmetric, and showing zero polarization what it would mean is that it may be sitting in either of these two positions which are off centred. But it is very difficult to know from crystals to crystal, what is the exact location? Or you can say that the titanium atom keeps vibrating between these two positions, so because of symmetric vibration around this Z equal to zero position. The net polarization is taken as 0 and the free energy curve shows a minima. So, this minima basically corresponds to Z is equal to 0 in the paraelectric state. So, now what we will what we will do is that we will look at into the energetic of this ferroelectric transition, a little bit more carefully, because the nature of this free energy curve defines what kind of transition is it?

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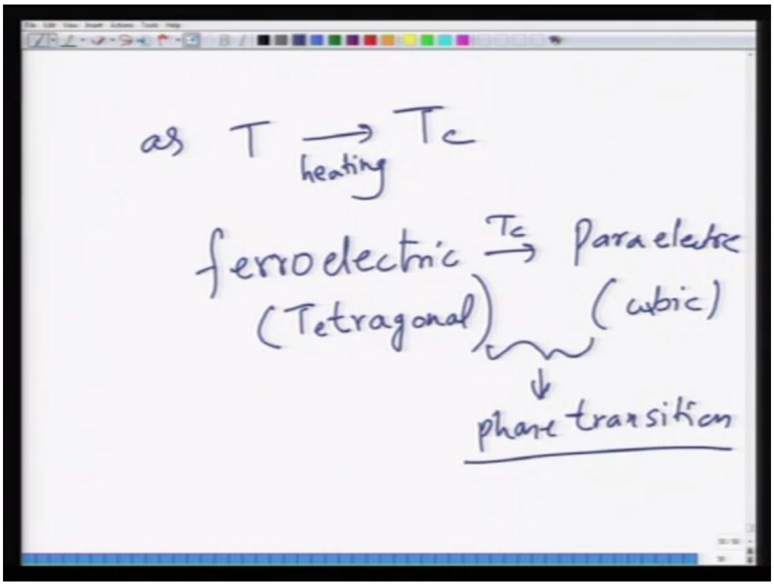

Because first of all you are seeing that as you as temperature goes to T c, T approaches the T c during heating material converts from ferroelectric to paraelectric. So, at T c it happens. Now, in ferroelectric state, we are saying that it has a for example, barium titanate, it has a tetragonal structure and here it has a cubic structure. Now, what it means is that there is a phase transition. So this corresponds to phase transition, and ferroelectricity in materials is often explained in terms of phase transition as well. And this phase transition could be either of first order or of second order. Now what is first order and what is second order, that we will look at in the while, but depending upon the nature of this transition, you can categorize ferroelectrics into 2, 2 of these categories.

And for this we will take help of what is called as there are different names given to this theory, but typically it is called as Landau theory. We will rely on Landau theory, although it was developed with the help of many other people. And we will take help of this Landau theory to understand this phase transition which is crucial in explaining the nature of ferroelectrics ferroelectric materials. Now, just another point before we go into this theory is as you change the temperature so for example, if you want to look at the temperature dependence.

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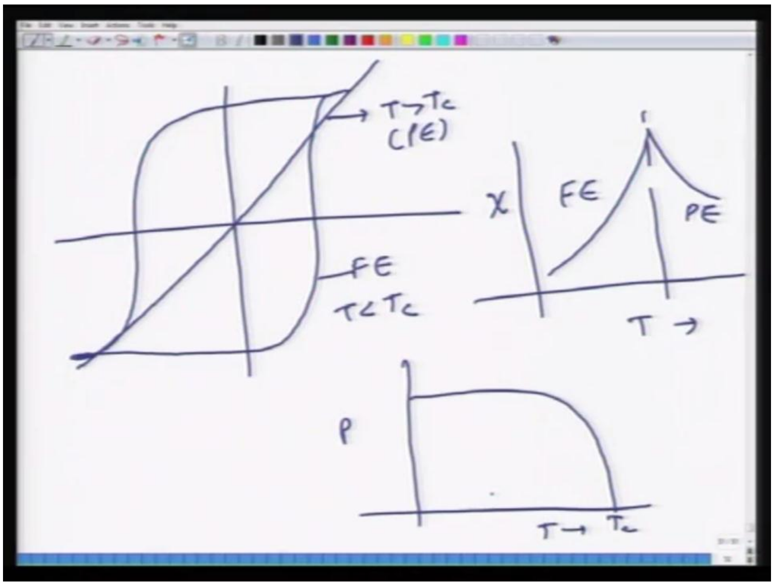

So, if I just plot. So, I have plotted dielectric constant verses temperature, it goes like this. So, this is your ferroelectric state and this is your paraelectric state. How does it look in terms of polarization verses hysteresis loop? So, a material is going to look like a ferroelectric. So, this is your ferroelectric state T is less than T c and at T greater that T c it is going to look something like this a linear dielectric. So, this is T greater than T c paraelectric state, which means this curve shrinks as it goes towards as it as it moves towards a T c.

Alternatively, as we will see from the phase a transition study is that the polarization goes this way near the T c. Now, how the polarization changes that is also a matter of concern, because that is related to that the nature of phase transition. In some cases you may have a abrupt change in the polarization near T c, in some cases you have a gradual change in the polarization near T c and that we will look at in while. So, what we will do is that we will.

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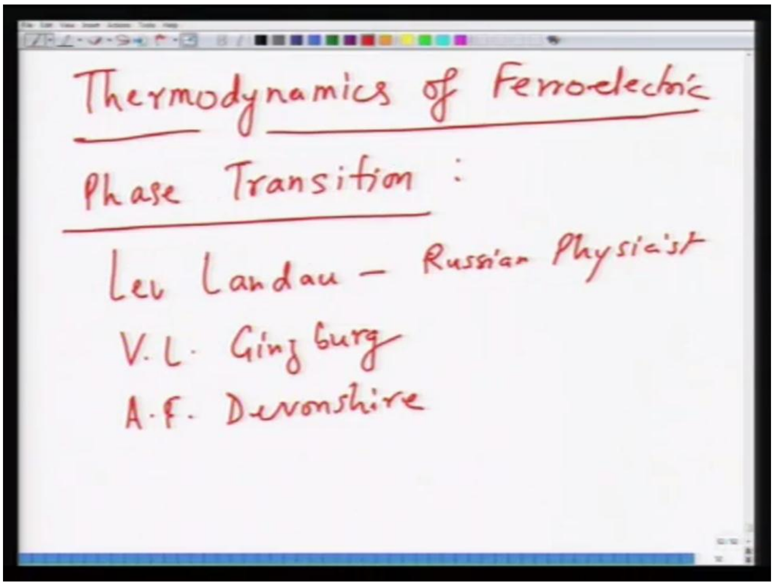

Now, look at what is called as thermodynamics of ferroelectric phase transition. Now, this is a very important topic. And this theory was developed by people like Lev Landau who was a Russian scientist, who was a Russian physicist along with or in those periods soviet physicist. And then Victor Ginzburg with contributions from devonshire who was a British physicist. So, basically and there are some other people who are involved in this theory, but these are the 3 main people who worked a lot in order to develop this concised theory of ferroelectric phase transitions. Basically, this theory the approach these guys took is based around calculating the free energy of the system, and then from this free energy expression trying to work out other thermodynamic parameters to predict the correct nature of phase transition. So, we will first write the first write the expression for free energy. And then we get into these parameters which these guys defined. So, now you need to know a bit of thermodynamics for this.

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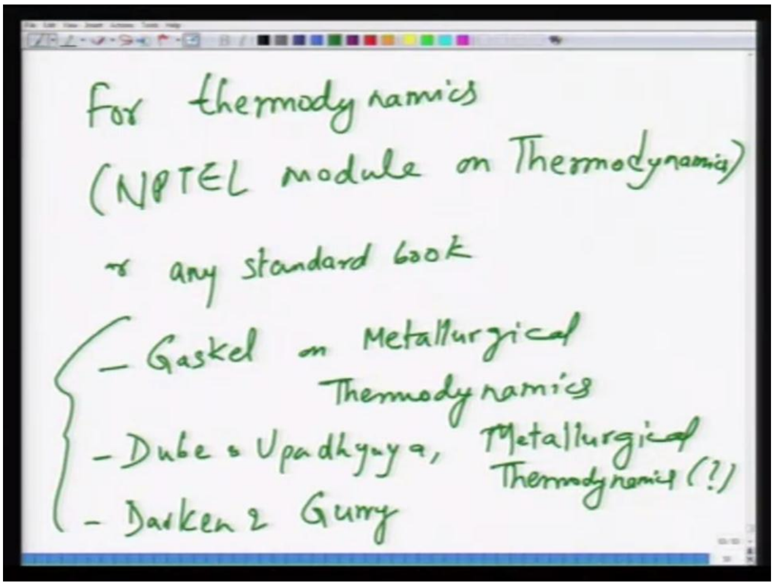

So, you can go to either thermodynamics module on NPTEL. So, basically you can refer to NPTEL module on thermodynamics or any standard book. So, for example, book by Gaskell on metallurgical thermodynamics or Dube and Upadhyaya. Again I forgot the title I think it is metallurgical thermodynamics, again check the title I am putting question mark here. And then another one is Darken and Gurry I think, and this is I think called as physical chemistry of materials something like that.

So, any of these 3 books you can just do the google search on these 3 books to get the right titles and everything. And then this must be available in the library in most institutes. So, follow any of these books or NPTEL module to get into the basics of thermodynamics. Now, basically you know thermodynamics basically if you look at the term thermo dynamics. So, it is basically related to effect of temperature and pressure on the state of material, so from the laws of thermodynamics; thermodynamic state of any material in the state of equilibrium. So, when the material is in the state of equilibrium then the thermodynamic state of that material can be defined in terms of number or variables.

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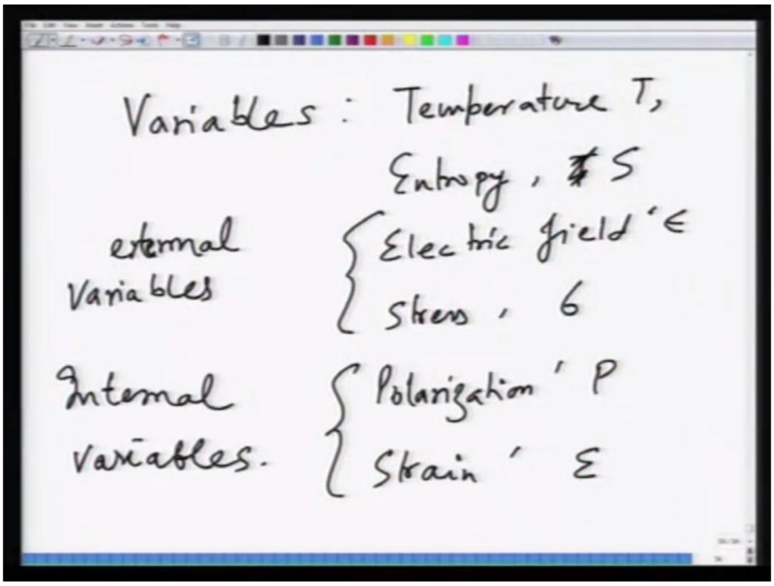

And these variables can be, so the variable which define the thermodynamic state can be temperature, it could also be entropy, it could be electric field in case of ferroelectrics, it could be stress sigma, and many other parameters in the contrast. In the case of ferroelectrics, what we are interested is in this should be S entropy, so temperature, entropy, electric field, stress, polarization and strain.

So, essentially we know that ferroelectrics are switched across the temperature. So, that is why temperature is very important variable entropy determines the state of disorder in any system and in the end affect the free energy expression. So, as a result entropy is an important factor, however for ordered system unless you have a phase transition, you can work a way around. And then you have electric field, and stress which you take as external variables, because you apply them there are stimuli. So, these are called as external variables. And then you have a polarization in strain, and these are the result as a these are you can say these are out come as a result of application of external variable, that is why these are called as internal variables.

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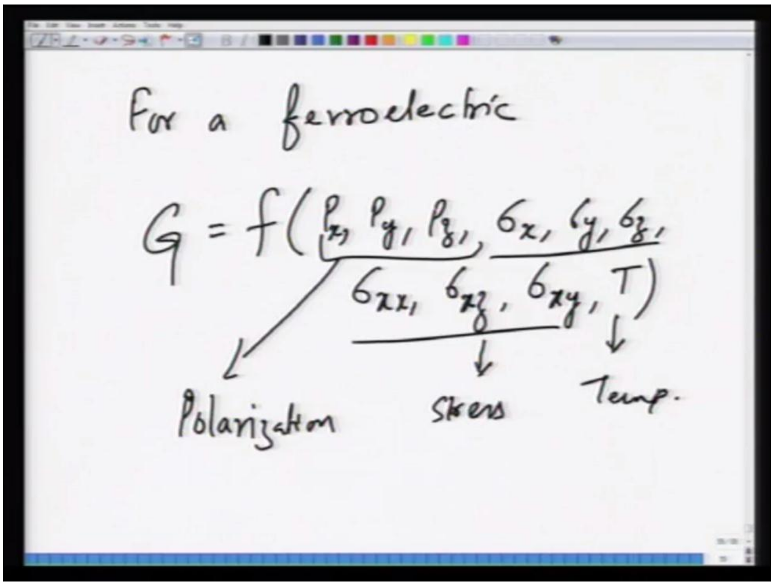

So, for a ferroelectric system for a ferroelectric material, I can write the free energy as let us say free energy is G then it is a function of polarization components of polarization you have P x; you have P y and you have P z. And then the components of stress sigma x sigma y sigma z, and you have sigma x x sigma, I am taking only the uniaxial ferroelectrics so sigma x z and sigma x y and then you have temperature. Now, we have ignored for instance, in this case, the entropy the strain, and the polarization, and the electric field, because each of them.

Because polarization is related to electric field, sigma is related to epsilon and T is related to entropy. So, we can work our way around with these. So, these are the, with these 10 variables. So, these are the components of polarization, and these are the components of stress and this of course, is temperature. So, now, we can get the independent variables in thermal equilibrium at the free energy minima. So, what we need to work out is around free energy minima.

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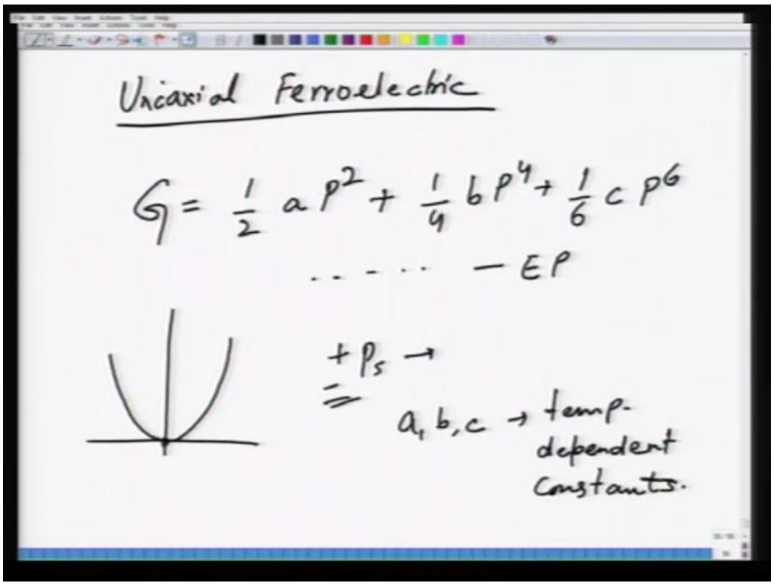

Now, consider the case of a uniaxial ferroelectric. Now, for a free for a uniaxial ferroelectric, we can ignore the stress field, and you can expand the free energy expression in terms of only polarization. So, this free energy expression G can be written as half P square plus 1 by 4 b P 4 plus 1 by 6 c P 6 and this goes on and on minus of E p. Now, this is this we have taken because the free energy of a unstrained crystal near the origin has to be equal to 0 for a unpolarized and unstrained crystal. So, basically it is like this. So, you have a free energy like this. So, near the origin it has to be equal to 0. So, when there is no strain, there is no polarization the G is equal to 0. And we have taken only the positive only then even powers.

So, that is because you have two states plus minus P s states, and these two states are equivalent states. So, if you put if you take the odd components, in that case the free energy of those two states become unequal which is not fine, because the free energy of both the states have to be equal. So, as a result you have to only take the even powers negative powers have to be, odd powers have to omitted, because they give rise to two different free energy states. And that is not permitted and here a b c are temperature dependant constants. And of course, E is the electric field I think everything is everything else is explained here. So, what now I am going to do now is that I need to now find the equilibrium.

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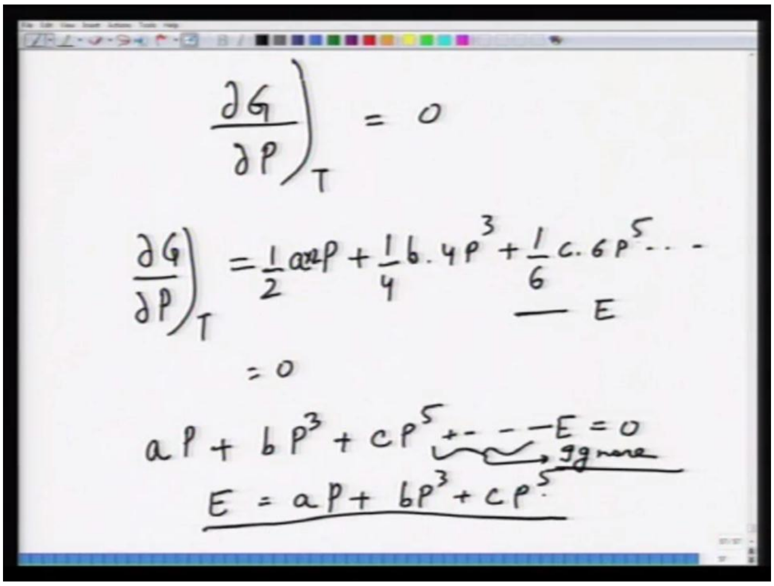

Now, at the equilibrium this del G by del P at constant temperature is equal to 0. So, I need to make one of the variables constant I have made temperature constant. And I am taking the equilibrium by making del G by del P equal to 0. Now, what it means is that, so if you go to the expression G was equal to 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 E P. So, what I am differentiating this equation. So, I get del G by del P at T as a P. So, basically half a P square in. So, basically that get differentiated to half a into 2 P plus 1 by f4 b into 4 p cube plus 1 by 6 c into 6 p's 5 and so on and so forth minus of minus of E and this is equal to 0.

So, what basically it means is that a P plus b P cube plus c P 5 minus of E is equal to 0 or E is equal to a P plus b P cube plus c P 5, if I ignore these ignore the higher power terms So, then I write this E as a function of polarization equal to a P plus b P cube plus c P 5. And now these a b c are temperature dependant constants, and their sign varies as a function of temperature. And so it depends whether you are below T c or above T c and that will determine the state of the material.

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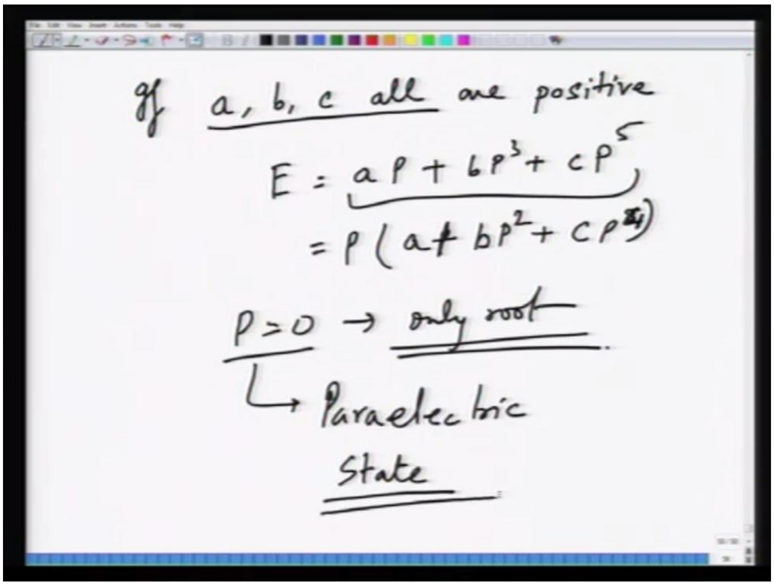

So, if the let us say a, b, c all are positive, if that is the case then the only route if you look at the expression now, E is equal to a P plus b P cube plus c P 5. So, if this was true a, b, c all positive. Then in this expression if you take P into a, a plus b P square plus c P 5 c P 4, sorry then P is equal to 0 is the only route, and this determines the state if P is equal to 0 is the only route at del G by del P is equal to 0. Then this refers to the state which is called as a paraelectric state of the material.

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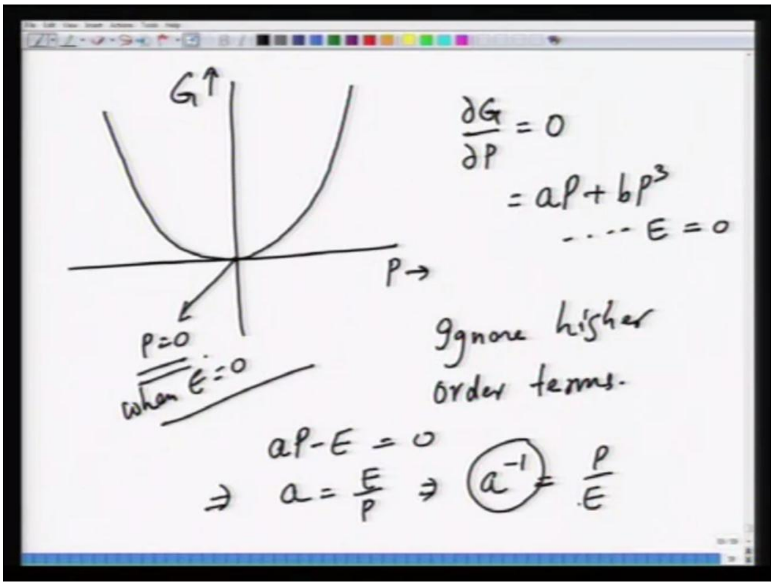

And, this is determined by if you now plot the free energy versus polarization then; this refers to the state like this. So, this is your G and this is P is equal to 0 and P is equal to 0 when of course, E is equal to 0. I forgot to mention that here P is equal to 0 is the only route when E is equal to 0. So, this determines the state of equilibrium when E is equal to 0 then P is equal to is. Now, if P is equal to 0. So, this determines the paraelectric state. Now, if we ignore the higher power terms, so now, del G by del P was equal to 0 and this was given as P multiplied by a P.

So, let us just go back, and see what it was so del G by del P was a P and so on. And so forth minus E to be equal to 0. So, a P plus b P cube so on. And so forth minus E was equal to 0. So, if you ignore, these ignore these higher order terms. Now, what it means is that, that a P minus E is equal to 0. And what it means is that a to be equal to E by P or a to the power minus 1 is equal to P by E. And what does it mean a inverse in nothing but and P by E or we have not included epsilon naught here. So, if you include epsilon naught for a free space permeability, this becomes your susceptibility.

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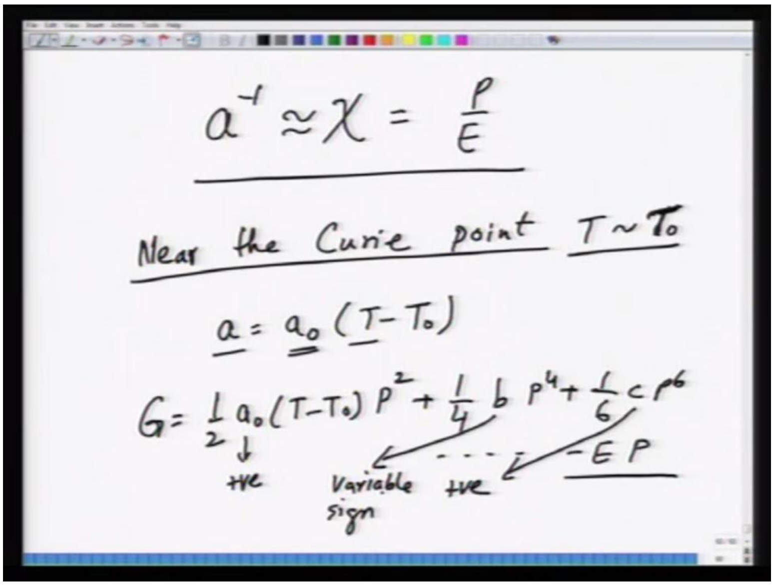

So, inverse of a is actually is equal to susceptibility and that is given as P by E. So, this is the same expression as you get for linear dielectrics. So, now near according to this Landau devonshire as it is called Landau devonshire theory near the Curie point. So, which means now here, so far we have known the Curie point as T c. Now, here we will introduce another term T naught, because as we will see subsequently that depending upon the phase transition, you may have 2 values; one is T naught and another is T c. So, here we introduce this thing T naught, it is T naught, it is not tau. So, near T is equal to T naught, we can assume this a to be equal to a naught into T minus T naught. And as a now, you can see that so here a is dependent upon temperature, but a naught is not. So, as a result, this a naught is always positive.

So, this G expression now becomes equal to half of a naught into T minus T naught multiplied by P square plus 1 by 4 b P 4 plus 1 by 6 c P 6 and so on and so forth minus of E P. So, here a naught is positive, and c is positive and depending upon the c sign of b. So, it could be variable sign, and depending upon the sign of b as a function of temperature you will have a phase transition.

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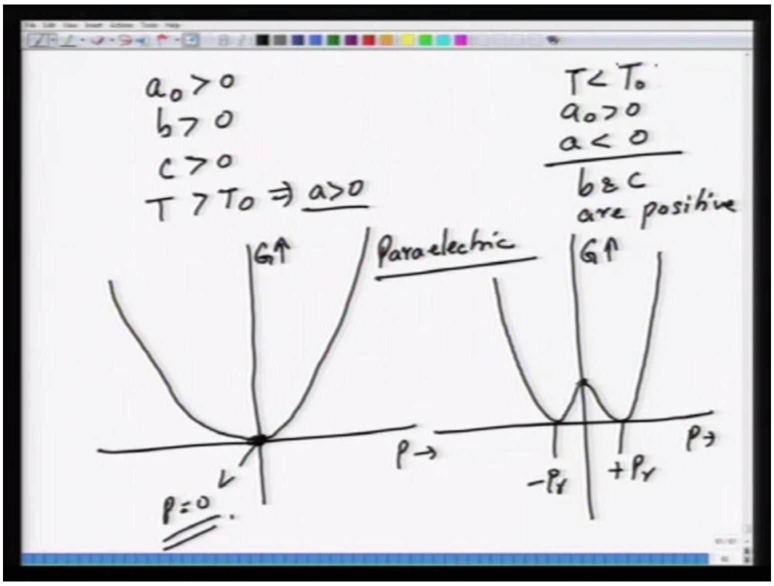

So, what you have is so for b is equal to 0 for a naught is equal to 0, b is equal to 0 and c is equal to 0. And this is the condition, when t is greater than T, T naught then and what it would mean is that basically a is also greater that 0. Then if you plot the free energy verses polarization plot, it goes like this. So, this is your G, this is your P, and you have a let me draw the line little bit more accurately. So line should pass here. So, this is the point which is P is equal to 0. And this refers to what is called as a paraelectric state as we just now saw.

However, when T is less than T naught since a naught is greater than 0, the a becomes less than 0. And what it also means is that both b and c are positive so if both b and c are positive. Then you again plot the free energy verses polarization, then you get 2 minima's. So, this looks like this. So, you have 1 minima, 2 equivalent minima's, and this is polarization; this is free energy. So, this is plus P r; this is minus P r, and this is the state for P is equal to 0. And this is what the ferroelectric state is. So, what you have here is at T less than T c depending upon the sign of a now b and c I am holding both positive. The sign of b change in the sign of b determines whether you have a what kind of phase transition is it.

But basically what you have for b and c both being positive only the sign of a changing as a function of temperature. You have a ferroelectric state at T less than T naught where you have 2 minima's equivalent minima's at plus, and minus P r. And another minima in the paraelectric state at P is equal to 0. So, these two states are called as paraelectric and ferroelectric states. So, now, what we will do is that we will have a look at dependence of b on the phase transitions. So, this particular phase transition when…

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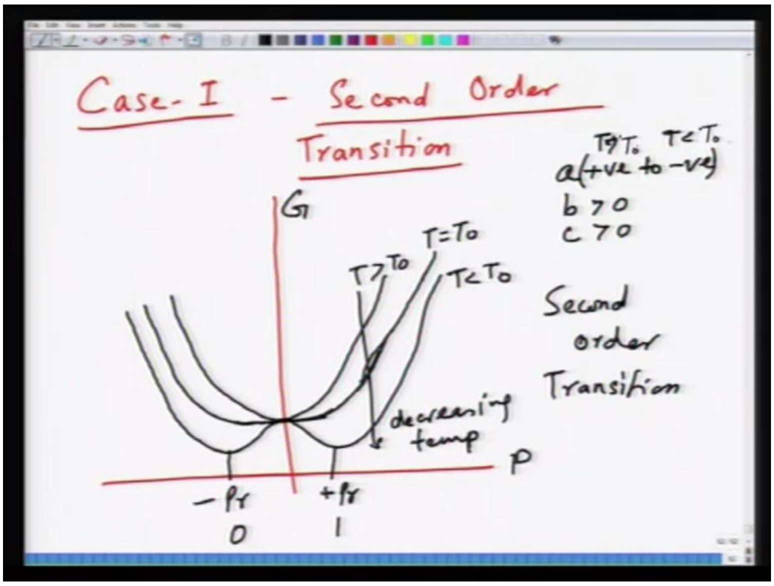

So, we will take the case one; which is called as second order transition which is essentially. So, what you have is, when you plot free energy verses polarization so this is G verses P. Now, you know the conditions. So, you have expression of G in which you have a b and c. So, b is greater than 0, c is greater than 0 and a changes its sign from positive to negative as temperature. Now, you can see a naught into T minus T naught so when T greater than T naught to T less than T naught. So you have a situation. So, this is this will of course, correspond to T greater than T 0. So, and you will have T less than T 0 and T is equal to T 0 will also be somewhere it will be a, this will be T is equal to T naught with a much more flatter bottom because. So, this is a case of what is called as a second order transition.

So, as you change the temperature from T greater than T naught. So, this is decreasing temperature. So, as soon as the material is less as soon as the temperature is less than T naught, you come across 2 subsidiaries minima's which are at plus P r and minus P r or you can say 1 0 state. And this gives rise to our characteristic ferroelectric loop which is like this.

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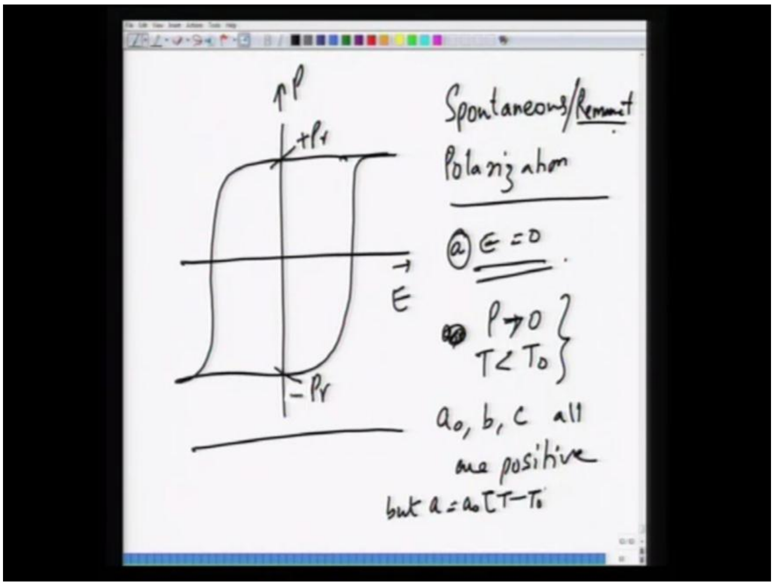

So, you have plus P r, and you have minus P r. This is your P; this is your E. However, this shape does not still tell you whether you have some other kind of phase transition. We will see, we will look at another phase transition, first order phase transition where the polarization hysteresis loop remains same. But the way the free energy composition the way the free energy polarization curve changes that is related that is different.

So, a spontaneous now, how do you determine the spontaneous polarization? Basically or let us say remnant polarization. So, this polarization basically the polarization at E is equal to 0. So, when you have and what you do is that you substitute E is equal to 0 in the previous equations. And retain only the two lowest order components, since you know that a naught. So, this is so your P is P is greater than 0, when T is less than T naught. So of course, the condition is only when T is less than T naught. So, you want to determine what P. So, you know that a naught b and c at T less than T c all are positive. But as you know that a is equal to a naught T minus T naught, a is less than 0.

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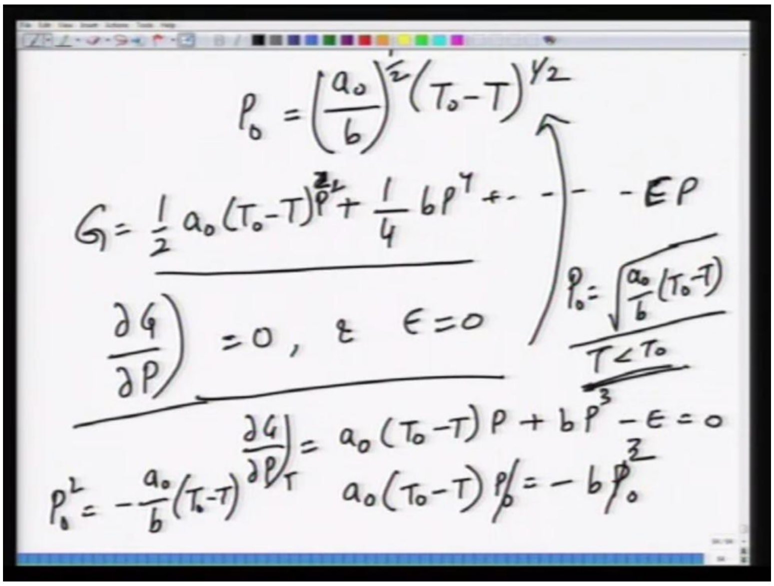

If this is the case then P naught becomes equal to, if you ignore all the higher order terms then P naught is equal to a naught divided by b into T naught minus T to the power half. So, because you know that G was equal to half of a naught to T naught minus T square plus 1 by 4 b, let me just look at the expression I am forgetting. So, your G was equal to half a P square plus so on and so forth, so a naught T minus T into P square, and this half will be P 4 plus minus of E into P. So, when E is equal to 0 then from this you can work out, because free energy you know that del G.

You again need to calculate what is del G by del P and that is of course, equal to 0, and insert and E is equal to 0. And this is going to give rise to this condition, where P naught will equal to a naught divided by b into t naught minus T to the power half. So, you can see del G by del P will be equal to a naught a naught P plus b P cube. And if you ignore the higher order terms this is equal to 0. So, if I take this to be equal to a naught into T naught minus T into P, that will be equal to minus of b P square and at. So, this is at E is equal to 0.

So, you can replace this P as P naught, and cube. And this P naught P naught will cancel each other. And what you will have is P naught square to be equal to minus of a naught divided by b into. So, basically you can say you can take this minus inside or you can just leave it like this and this P naught will be equal to route of a naught by b into T naught minus T. And since and this is fine. So, here also you should have half. So, what you will have is since T is less than T naught, this is a perfectly fine equation.

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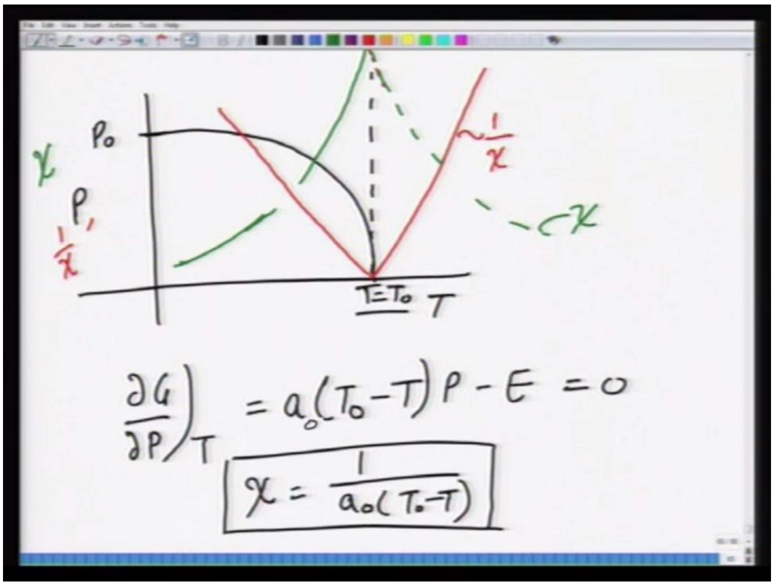

So, the P naught the polarization at 0 field for the second order transition is given as root of a naught divided by b multiplied by T naught minus T. And this of course, shows you that. So, when you plot now, the polarization as a function of temperature. So, you start with T naught and this T naught goes to 0 at T is equal to T naught. And now, you can also do the susceptibility. So, since you know that del G by del P was equal to a naught T naught minus T into P was equal to this 1. So, E so I can just now, so since I know that del G by del P was equal to a naught into T naught minus T into P plus, ignore the higher order terms. So, what you will have is minus of E which is equal to 0, and since you know that this was, and this is nothing but chi will be nothing but equal to.

So, chi will equal to P by E, this will be equal to 1 divided by a naught into T naught minus T. So, this will be chi, so if you now plot chi, this chi goes as then. Now, so if this is a T c. The 1 over in fact you have plot 1 over chi, and 1 over chi goes as this. So, this is your 1 over chi. So, P and 1 over chi typically you need to draw 1 over chi. In order to get it more appropriate, because chi will vary something like this. So, if you plot chi since, this is coming down the chi, chi goes abnormally high at temperature. So, determination of chi is rather impractical. So, 1 over chi gives a much better representation of behaviour of second order transition near the T c. So, that is why so this, this should be chi.

So, what it shows is basically for a second order transition in ferroelectric materials. The polarization drops gradually to 0 at T is equal to T naught susceptibility 1 divided by reciprocal of susceptibility 1 divided by chi dips at T is equal to it shows a sharp dip at T is equal to T naught. Before further rising when susceptibility reaches abnormally high values at temperatures which are closer to the transition temperature.

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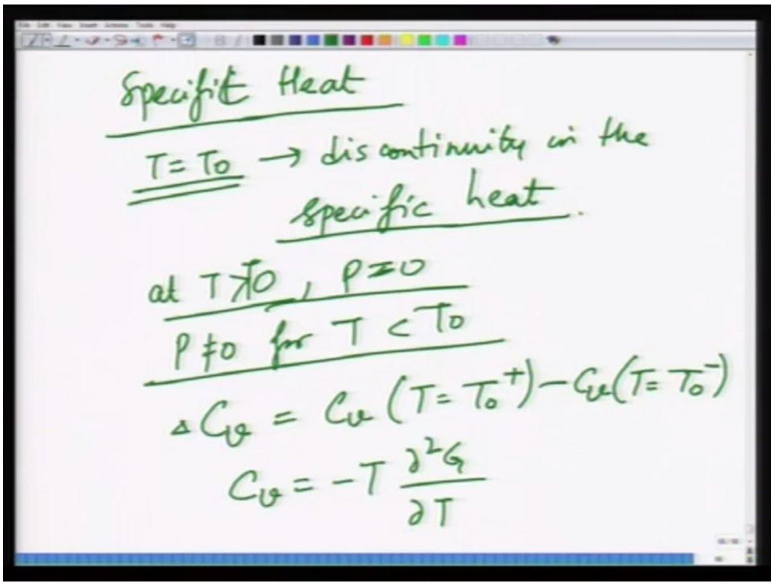

So, this is how you work it out. Now this transition you can also you can also show this transition by showing the specific heat. So, now thermodynamically those are the ways in which you can represent the phase transition in terms of. So, P is also called as order parameter. So, basically the order parameter goes gradually goes to 0 at T is equal to T c. But what is the other depiction? The other depiction can be written in terms of a specific heat, so basically at the transition temperature T is equal to T naught you have a discontinuity in the specific heat for a second order transition. Now, that we will see how?

So, basically at T greater than T naught you have P is equal to 0, if this was true then use the then you can and P is not equal to 0 for T less than T naught. So, your finite polarization for temperature less than T naught and this from this one can determine what is the specific heat? So, delta C v will be C v at so you can get delta C v near the transition. So, this will be C v at T is equal to T naught plus slightly higher than T naught minus of C v which is equal to and which is at T is equal to T naught minus. So, just within the vicinity of, so you are calculating the change in the specific heat in the vicinity of the phase transition, and since C v is given as minus of T del 2 G by del T square.

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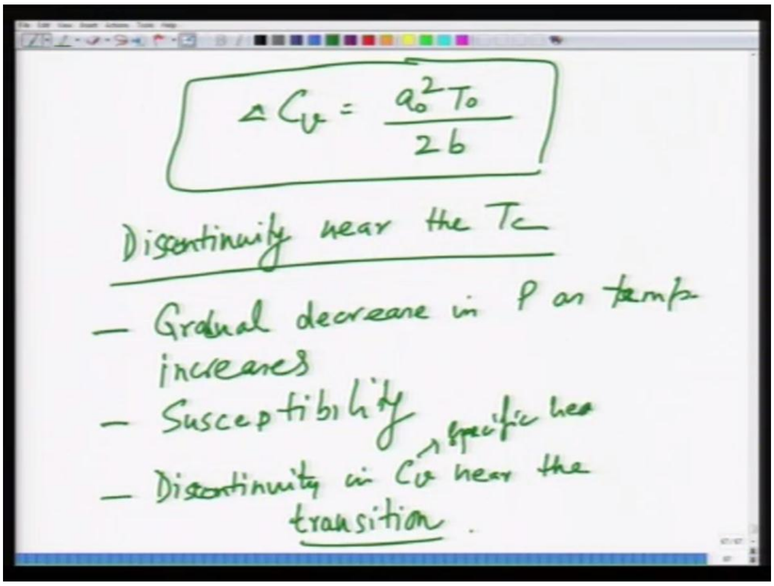

You can work out from the expressions of free energy, this delta C v is given as a naught square T naught divided by 2 b. And this basically shows discontinuity near the T c. Now this expression basically, since now, you have to know about this from the thermodynamic principles. So, that is why I said you need to go through the books of thermodynamics in order to get the thermodynamic relation, what is the free energy, what is the entropy, what is the enthalpy, what is specific heat, etcetera. And then you are able to, then you would be able to appreciate these expressions a little bit more.

So basically, now to summarise a second order phase transition is a phase transition in which you have gradual decrease of polarization near the transition temperature and it goes to 0 at the transition temperature. So, you have, so basically the features are gradual decrease in polarization as temperature increases before it falls down to 0 at T is equal to 0 and then you have susceptibility. So 1 over chi goes through a dip near the T c but it does not have any discontinuity near the T c on the other hand chi goes through very large values near the T c. And then another thing that is important is; the specific heat you have a discontinuity in the specific heat at the transition. So, this is how your second order transition is like remember for second order transition. All you are worried about is changing the sign of a. There is no change in the sign of b and c in the free energy expression. Now, what happens when the sign of b changes that is a that is the matter of different phase transition which is called as a first order transition and that we will look at in the next class.

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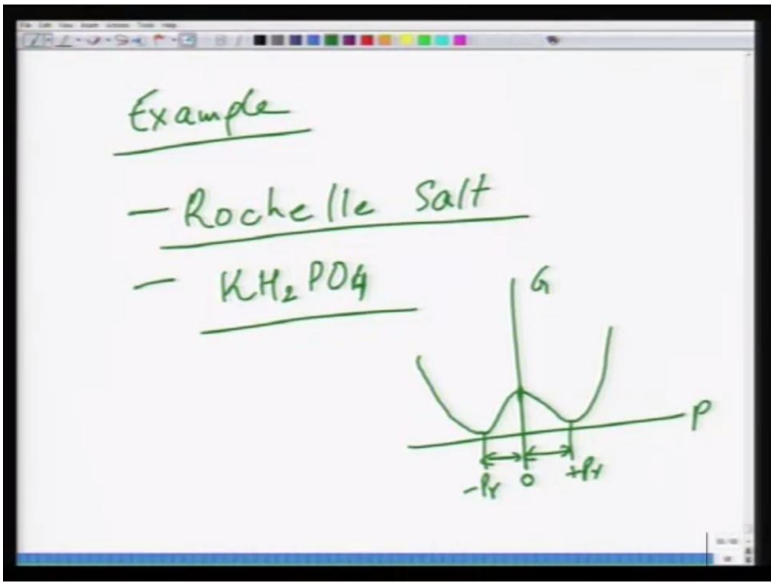

The example of the materials, examples of this material are for instance your Rochelle salt and potassium dihydrogen phosphate K H 2 P O 4, so there are few materials which show this second order transition. So, again just remind yourself about the nature of this transition. So, what you have to do basically, you start with the free energy expression. This free energy expression basically now a free energy expression can be derived in variety of in terms of variety of thermodynamic parameters.

So, here for a uniaxial ferroelectric we chose to expand this free energy in the terms of polarization in electric field. Now in order to work out the equilibrium state, you need to work out what is you need to minimise the free energy derivative at. You know at equilibrium so del G by del P is equal to 0 at constant temperature, and this gives you a state if all the constants were positive. Then this gives you a state where polarization is equal to 0 and that is the only route of the equation and this gives you a state which is called as a paraelectric state.

At temperature less than T is equal to T naught, then the situation changes because the sign of a changes. Because as we saw that a is equal to a naught T minus T naught, so as a temperature drops to T drops to temperature lower than T naught, then a becomes negative. The moment a becomes negative, your free energy composition curve changes, free energy polarization curve changes. And this is characterised by two minima's which are evenly spaced with respect to the subsidiary maxima at P is equal to 0. So, remember these 2 are evenly spaced, so whenever you draw this free energy polarization plot, so make sure these are evenly spaced with respect to this. So this, so if this is 0, this is plus P r, this is minus P r.

So, these 2 are evenly spaced minima's and this is characterised by as I said earlier gradual drop in the polarization abnormally high susceptibilities near the phase transition and a discontinuity in the specific heat near the transition. So, what we will do in the next class is, we will take up the case of first order transition before we complete this thermo dynamical analysis and moving in to another few more aspects of the ferroelectric materials.

Thank you.