Fundamentals and Applications of Dielectric Ceramics

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Lecture - 35

First Order Phase Transition in Ferroelectric Materials

So welcome again to the new lecture of the course fundamentals and applications of dielectric ceramics. So, let us just briefly recap what we were doing in the last class.

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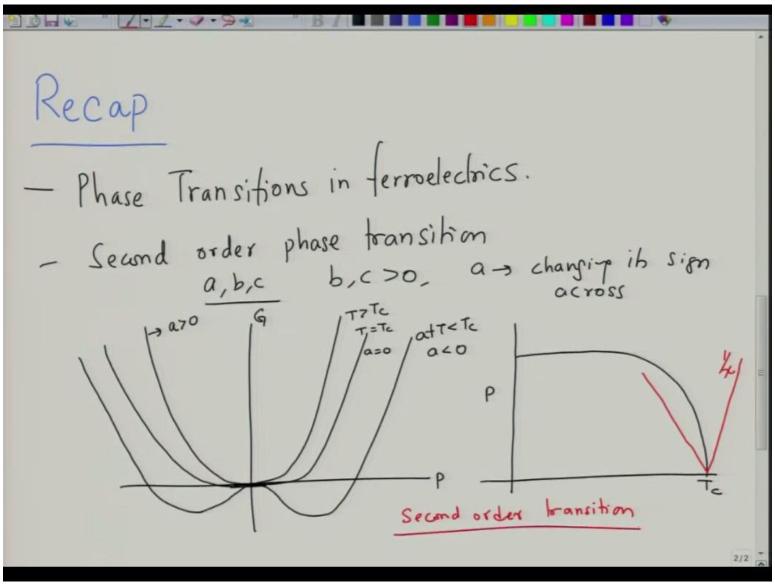

Recap

— Phase Transitions in ferroelectrics.

– Second order phase transition

a, b, c $b, c > 0$, $a \rightarrow$ changing its sign across

In the last class, we were looking at phase transitions in ferroelectrics. So, we started our discussion with second order phase transition where we found that you know in the free energy expression, you have three constants a, b, c and b and c being positive but a changing its sign across T_c. So, of course, these free energy plots can be plotted by choosing appropriate values of a, b, c.

So, when we plot them, what we find is that, when you plot free energy as a function of polarization for a being, so 'a' could be changing its sign from positive to negative. So, basically what happens is that in the first case, your 'a' is positive when it is, so when the temperature is, so this $a > 0$ at $T > T_c$ and when 'a' is negative, there are 2 maxima, so this is at $T < T_c$ when 'a' is negative.

And then in between of course since a changes its sign which means as a function of temperature, it must be zero somewhere and it turns out it is zero at $T = T_c$ when $a = 0$. So, this is the second order phase transition and when you plot polarization as a function of temperature because you know the parameters are the function of temperature as well. So, when you plot polarization as a function of temperature, it shows a gradual change up to a temperature T_c.

So, this is polarization and when you plot susceptibility, at T_c this is $1/\chi$, it has different slopes on the two sides of the transition but there is a sort of, there is no abrupt change in polarization or in susceptibility at transition temperature and this is also manifested as we will see in the entropy.

The entropy also does not change, in the second order there is no abrupt change in the first derivative of free energy that is entropy but the second derivative changes abruptly. So, this is basically second order transition and then we also looked at what is first order phase transition.

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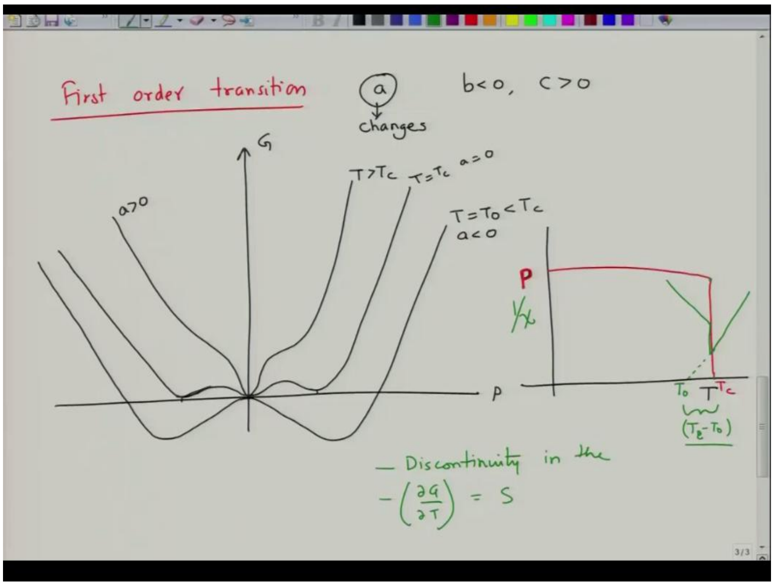

In the first order phase transition, what we saw was that now we took b < 0, c > 0 and sign of a changes and there we see that there is a range of temperature between which the free energy curve remains sort of unconventional. So, when you plot now free energy as a function of polarization, so G as a function of as a polarization, so at high temperatures let say at high temperatures, the polarization plot G.

So, this is at $T > T_c$ and it shows one minima which is the unpolarized state and then when you go to, so that is when $a > 0$. Now, when we plot at lower temperature, $T = T_0 < Tc$. So, at this temperature 'a' is negative.

So, this is let say at $T = T_c$ when $a = 0$ and this is the situation when we have three minimas. So, you can see there are two minimas corresponding to the polar phase and one minima corresponding to the nonpolar phase. So, this suggest that we have you know one nonpolar phase in coexistence with the polar phase between the temperature T_c and T_0 and it is only at T_0 the material stabilizes into perfectly.

So, this is polar state and this is manifested in polarization in a different way. So, when you plot polarization as a function of T in this case, what we see is that the polarization decreases and then it goes abruptly equal to zero at T_c but the susceptibility shows a different kind of behaviour. So, now when you plot susceptibility, it shows a discontinuity at temperature T_c.

And if you plot this extrapolation of this, this is the temperature T_0. So, the range T_c to T_0 within which you have coexistence of these two phases. In contrast, if you look for second order, in that case you can say $T_c = T_0$ but in this case you have T_0 and T_c which are different temperature, T_0 being lower than the T_c. Now, what is this manifested in? This is manifested in a discontinuity in susceptibility at T_c and sudden drop of polarization at T_c.

So, polarization has a finite value at this point and suddenly it drops to zero. So, which means there is a discontinuity. So, this is called as first order phase transition. This is also manifested in as we will see discontinuity in the first derivative that is:

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

So, in the second order phase transition, it is the second derivative that is discontinuous whereas in first order phase transition, the first derivative is discontinuous, that is the fundamental difference between the two.

So, we did some analysis of second order phase transition and we looked at the susceptibility parameters. Now, let us look at the first order phase transition again in little bit more detail.

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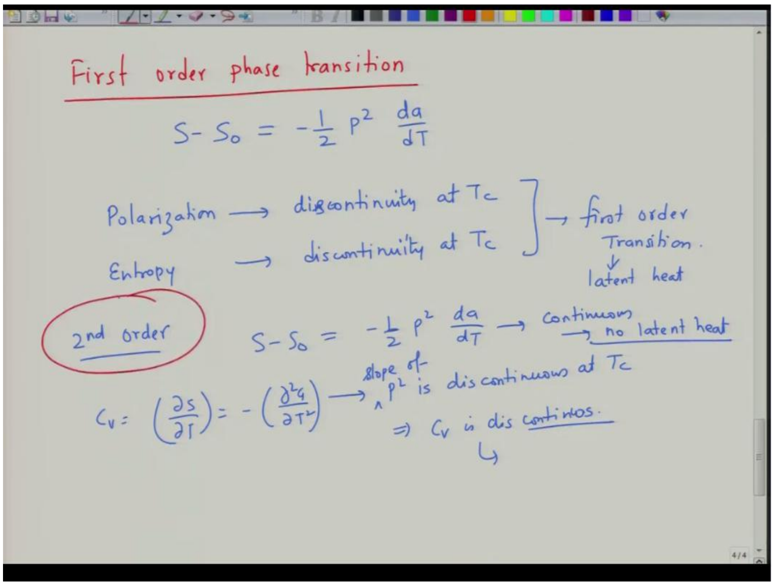

First order phase transition

$$S - S_o = -\frac{1}{2} P^2 \frac{da}{dT}$$

Polarization → discontinuity at T_c

Entropy → discontinuity at T_c

] → first order Transition. ↓ latent heat

2nd order

$$S - S_o = -\frac{1}{2} P^2 \frac{da}{dT} \rightarrow \text{continuous} \rightarrow \text{no latent heat}$$

$$C_v = \left(\frac{\partial S}{\partial T}\right) = -\left(\frac{\partial^2 G}{\partial T^2}\right) \rightarrow$$ slope of P^2 is discontinuous at T_c

$\Rightarrow$ C_v is dis continos.

So, we get back to first order phase transition. So, for the first order phase transition, we first see the change in entropy. The change in entropy is nothing but:

$$S - S_0 = -\frac{1}{2} P^2 \frac{da}{dT}$$

Now, since polarization is discontinuous at, so we know that polarization shows a discontinuity at T_c.

If polarization shows a discontinuity, then obviously entropy will also show discontinuity at T_c. So, basically we will have entropy also showing discontinuity at T_c and this is what is basically first order transition. In the second order what happened was, if you recall second order in second order the entropy will, the term will be the same:

$$S - S_0 = -\frac{1}{2} P^2 \frac{da}{dT}$$

but there P is continuous which means S is continuous.

Now, when you take the derivative of this:

$$C_V = \left(\frac{\partial S}{\partial T}\right) = -\left(\frac{\partial^2 G}{\partial T^2}\right)$$

Now, P^2 actually becomes discontinuous. So, P^2 is discontinuous, slope of P^2 square is discontinuous at T_c which means your C_v is discontinuous.

So basically in this sense there is a change in entropy, there is a discontinuity in entropy which means you have latent heat of transformation. There is since entropy is continuous, there is no latent heat involved. So, in some sense you can say the first order transition is more of a destructive transform, of a transformational where lot of rearrangement takes place, just like liquid solid kind of transformation.

Whereas in second order the transformation is more gradual as a result the free energy curve will also show some sort of continuity in two phase regions and the slopes being equaled in the both regions, as a result there are no discontinuity in the entropy out of free energy. There are no sudden changes in the free energy as a result there is no sudden kink in or discontinuity in the entropy. So, this is what it is in terms of phase transition. If you look at first order in little bit more detail.

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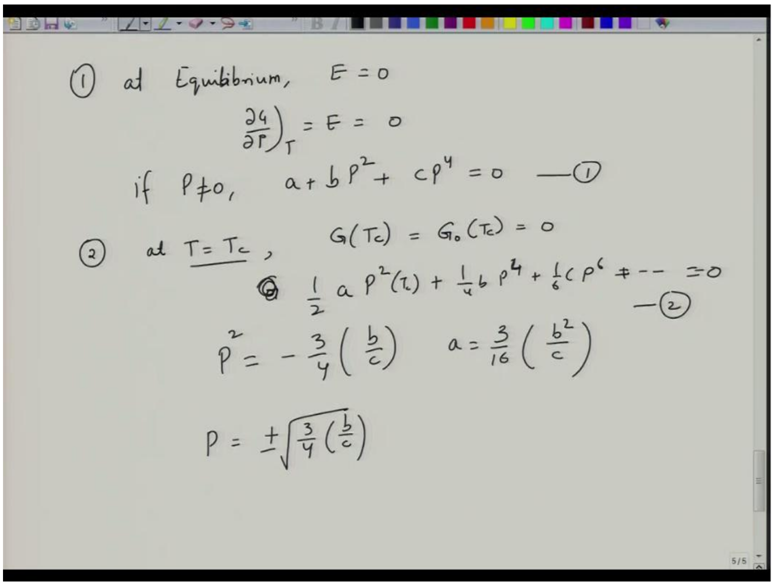

① at Equilibrium, $E = 0$

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

if $P \neq 0$, $a + bP^2 + cP^4 = 0$ — ①

② at $\underline{T = T_c}$, $G(T_c) = G_0(T_c) = 0$

$$\frac{1}{2} a P^2(T_c) + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \dots = 0$$

— ②

$$P^2 = -\frac{3}{4}\left(\frac{b}{c}\right) \qquad a = \frac{3}{16}\left(\frac{b^2}{c}\right)$$

$$P = \pm\sqrt{\frac{3}{4}\left(\frac{b}{c}\right)}$$

5/5

If you want to work out the susceptibility parts in both regions, then we know that first condition is that at equilibrium, we can take E = 0 and we know that:

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

So, if $P \neq 0$, in that case, you can write this expression as:

$$a + bP^2 + cP^4 = 0$$

This is the first equation that you will get. Secondly, at $T = T_c$, $G(T_c)$ will be equal to:

$$G(T_c) = G_0(T_c) = 0$$

The free energy of phases should be equal.

So, as a result, we can write the G expression as:

$$\frac{1}{2}aP^2(T) + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + ... = 0$$

If you ignore the higher order terms using these two equations, you can determine the polarization as:

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

$$P = \pm\sqrt{\frac{3}{4}\left(\frac{b}{c}\right)}$$

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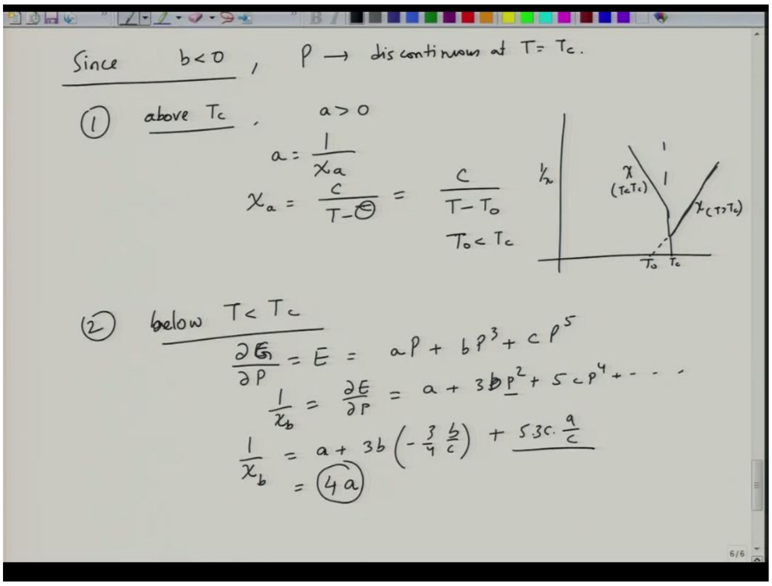

Since $b < 0$, $P \rightarrow$ discontinuous at $T = T_c$.

① above T_c, $a > 0$

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

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

$$T_0 < T_c$$

② below $T < T_c$

$$\frac{\partial G}{\partial P} = E = aP + bP^3 + cP^5$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3b\underline{P^2} + 5cP^4 + \cdots$$

$$\frac{1}{\chi_b} = a + 3b\left(-\frac{3}{4}\frac{b}{c}\right) + \underline{5 \cdot 3c \cdot \frac{a}{c}}$$

$$= \boxed{4a}$$

So, since we know that since we have assumed in the beginning that b < 0, then P becomes discontinuous at T = T_c. So, now we need to consider the susceptibility before and above T_c and if you do simple analysis at above T_c, a > 0 and a is equal to:

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

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

So, in this paramagnetic region, it will remain the same as earlier. This is the paramagnetic susceptibility. So, if you look at the plot of susceptibility $1/\chi$, so this will go like this and it will go up to T_0, where this T_0 is little smaller than T_c and then below T_c we can work out what is $(\partial G/\partial P)$. this is equal to E and this will be:

$$\frac{\partial G}{\partial P} = E = aP + bP^3 + cP^5$$

$$\frac{1}{\chi_b} = \frac{\partial E}{\partial P} = a + 3bP^2 + 5cP^4 + ...$$

$$\frac{1}{\chi_b} = a + 3b\left(-\frac{3}{4}.\frac{b}{c}\right) + 5.3c.\frac{a}{c} = 4a$$

So, in this region, it will go as 4a. So, that is what this susceptibility will be. So, in the first case, you will have a slope of 4 and in the second case you will have slope of 1. We just have to replace the value of 'a' there.

So, in general if you just wanted to look at the phase transitions, so ferroelectric phase transition, so as we said that second order phase transition is more common for materials like Rochelle salt and KH_2PO_4 etc., whereas first order phase transition is more common in materials like barium titanate etc, perovskite material show generally first order phase transition.

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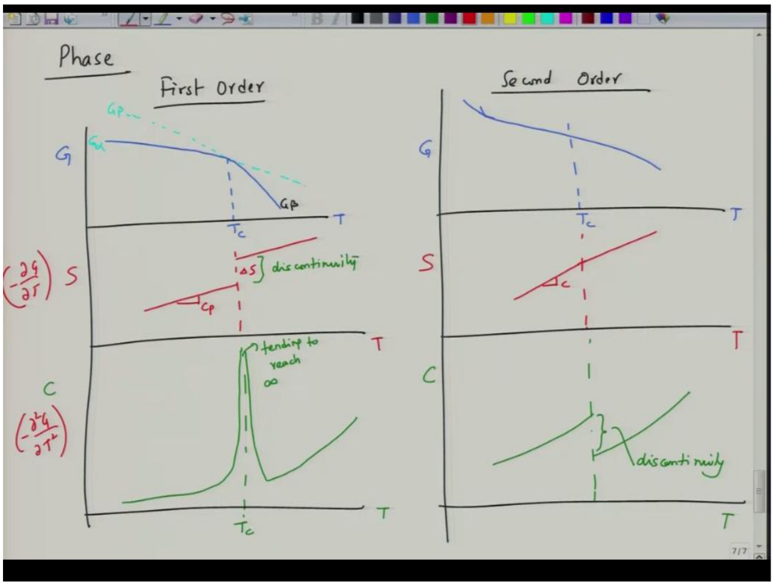

If you generally wanted to know about the phase transitions, the order of as we said the first order phase transition has a discontinuity in the first derivative of free energy. Second order phase transition will have a discontinuity in the second derivative of free energy. The first derivative remains continuous. So, if you plot this, now in a general sense, so let us say we make a column of first order and then we make a column of second order.

And let us just make the plots of these quantities. So, in the first one, we plot G versus T. So, when you plot G versus T, so let say you will have variation like this. So, this is the temperature T_c at which the transformation is occurring. So, you can consider this name as if this is the free energy plot of one phase let say G alpha and this is the phase we plot of another phase which is G beta.

So, you will see that free energy plots intersect each other at some point, so this is the free energy plot of one phase and this is the free energy plot of another phase. So, the first phase is plot continuous in this region in this fashion. So, this is G alpha and the second phase plot will go in this region as which is G beta.

Alpha beta could be considered as ferroelectric phase and paraelectric phase. So, you can see in this below T_c alpha is stable and above T_c beta is stable. So, this is first order phase transition. In the second order what you will see generally is that the free energy will be little bit sort of continuous along transition. So, let us say this is the transition temperature T_c, the free energy will show sort of they will have common slope at this point whereas in this case, the slopes are different.

Now, if you plot the entropy as a function of temperature, let us use the different color, so let say we plot entropy S versus T as a function of temperature. We will see that in this case, entropy is nothing but:

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

So, in this case, the entropy will show a discontinuity. So, this is ΔS which is correspondent to latent heat. So, the slope will be given as C_p specific heat and in this case we will see a sort of variation in the slope.

So, something like that, so you will have, there will be no discontinuity but the slope will change and the slope again will be C, the specific heat. Now, coming to the next one, if you now plot the C at this transition it will be massive divergence in specific heat at T_c whereas in this case if you plot C versus T, the C versus T will show a discontinuity. So, there will be a discontinuity but in this case we will have it nearly goes to infinity.

So, there is a huge so sort of tending to reach infinity of very high values. So, in this case, in first order, you see a discontinuity in entropy or first derivative of free energy. So, first derivative discontinuous in first order, second derivative discontinuous in second order.

So, this is the whole summary of phase transitions of ferroelectrics. If you are really interested to know about ferroelectric phase transition, in fact the Landau theory, then please read the paper which is in journal *Advances in Physics, 3 (10), page 85 - 130, 1954 by A. F. Devonshire*, beautiful paper

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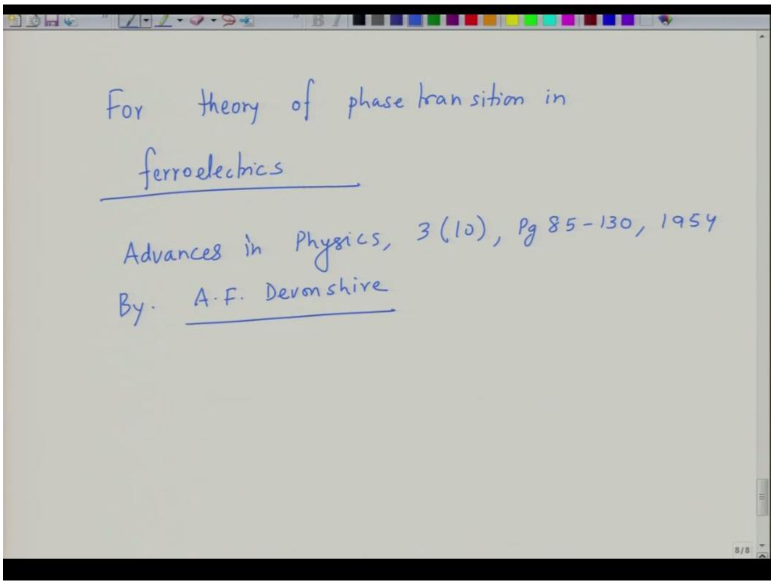

For theory of phase transition in ferroelectrics

Advances in Physics, 3 (10), Pg 85-130, 1954

By. A.F. Devonshire

This narrates the whole phase transitions in, different kinds of phase transitions in ferroelectrics. So, we unfortunately cannot go into so many details because the limitation of this course but we hope this has given you a brief idea about what kind of phase transitions that occur in these materials.

Now, let us go into the next topic of ferroelectrics having seen what kind of phase transitions occur in ferroelectrics. Now, let us look at how do ferroelectric materials switch, what is the reason of hysteresis in the ferroelectric materials.

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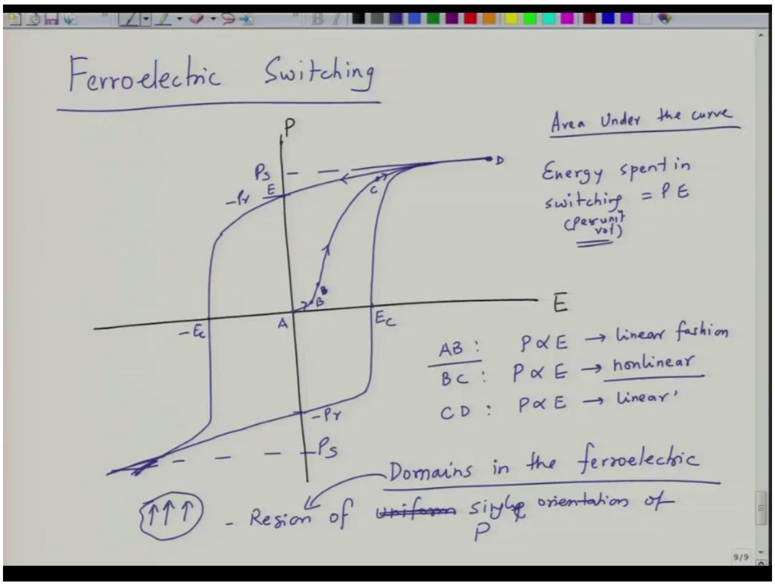

Ferroelectric Switching

Area Under the curve

Energy spent in switching (per unit vol) = PE

AB : $P \propto E$ → linear fashion

BC : $P \propto E$ → nonlinear

CD : $P \propto E$ → linear'

Domains in the ferroelectric

↑↑↑ - Region of ~~uniform~~ single orientation of P

So, as we saw earlier that so here we will look at ferroelectric switching. So, ferroelectric switching basically is manifested in as we saw earlier you make a plot between charge and electric field or charge density versus electric field or polarization versus electric field. So, this saturates at high fields.

And so what happens in this ferroelectrics is as we saw earlier, you have a hysteresis, the polarization at high fields is spontaneous polarization, polarization at zero field is remnant polarization and the values of these spontaneous polarization and remnant polarization, they are equal and opposite to each other and then polarization become zero at a field called as coercive field which is depicted at ± Ec which are symmetric with respect to each other for ideal system.

The area under the curve by the way is nothing but the energy that is spent in switching. So, energy spent in switching will be P x E energy per unit volume. So, this is nothing but µE divided by volume. So, this energy is basically spent in switching. So, the question is why do we get this kind of behaviour.

Now, what happens in these ferroelectrics? When you start from a virgin ferroelectric which has never been switched before, you start generally from origin, the polarization of a virgin ferroelectric is generally zero, polycrystalline ceramic and what happens is that initially when you start switching the ferroelectrics, it switches in sort of a linear fashion.

So, up to point B ferroelectrics are nonlinear ceramics but in the beginning from A to B the polarization changes as a function of electric field in a linear fashion. So, this is AB. Now, when you go from B and that is when you start again you start witnessing polarization increase much more rapidly than what a linear relation would suggest and massive increase in polarization happens and once you reach point C, after that increases linearly, so C to somewhere like you know D when it saturates there is a linear increase again

And then when you decrease the field, so after you have saturated, you have no more increase in the polarization that takes place. So, basically at very high fields, all the dipoles are aligned, you have nothing else left to be aligned and you will have very little increase in the polarization if you just increase the electric field by basically polarizing it more in terms of. So, electronic and ionic polarization will contribute but it will be very small amount of polarization.

So, basically it tends to saturation. Once it saturates, now if you start decreasing the electric field, so this is what you went about. Now, when you go back in this direction, what happens is polarization does not come back to zero instead it stays as a value called as remnant polarization. What is the reason for this?

Now, the reason for this why the polarization follows the behaviour A, B, C, D and then why does it follow a path DE instead of following DC BA is something whose regions lie in formation of what we call as domains in the ferroelectric material and as we will see in the next lecture, these domains are basically regions of uniform or rather we can write regions of single orientation of polarization.

So, in these regions called as domains which could be of certain shape, all the dipoles are aligned in one direction. So, this is a domain. It is not a grain boundary, you should not confuse with the grain boundary. The grain boundary is about the grain orientation, the crystalline orientation whereas in this case, we are not talking about crystalline orientation, we are saying that polar vector in these regions is aligned in one direction.

So, we will come back to microscopic mechanisms of this switching in the next lecture where we learn about domains, what domains are and how do domain switching lead to what we see in reality. So, we will stop here. What we have discussed is about more details of phase transitions. We have finished the phase transitions basically said that first order phase transition manifested in sudden drop of polarization, sudden change in susceptibility which is due to first derivative of energy being discontinuous at T_c.

Whereas second order phase transition is manifested in gradual drop of polarization around T_c, it goes to zero at T_c, susceptibility also goes to zero at $1/\chi$ goes to zero at T_c and in this case, the second derivative of free energy is discontinuous but first derivative is continuous.