Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture - 09
EPR instrumentation - III

Hello. We have discussed various components of an EPR spectrometer. Today, we are going to see how the whole spectrometer is made off. So, for that let us see a simplest possible EPR spectrometer that is shown here.

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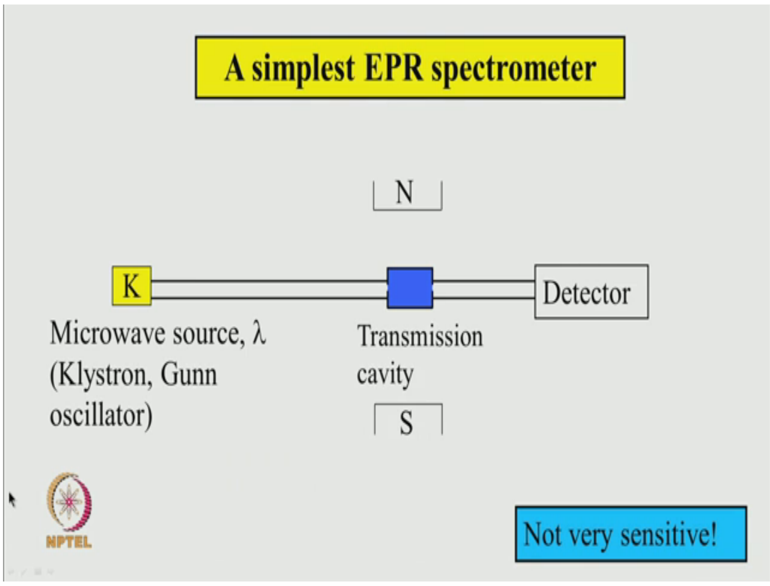

Micro power comes from some source, it could be a klystron oscillator or a Gunn oscillator sample is kept inside a transmission cavity. So, microwave enters through this iris and comes out again through a wave guide, it goes to a detector and this sample is kept in a magnetic field. So, by scanning the magnetic field one can see the spectrum.

But this is not a very sensitive spectrometer. As I said earlier, the queue of this transmission cavity is very low. So, in though such spectrometers were used earlier nowadays this set of spectrometers never used. So, we almost always use a reflection cavity whose queue is much higher. Now how is that used? So, we need to have the microwave coming from microwave from the klystron go to the cavity and when the power is reflected from the cavity it should not go back to the klystron it should go back to the detector. So, for that we use a special micro wave component called a circulator this is shown here.

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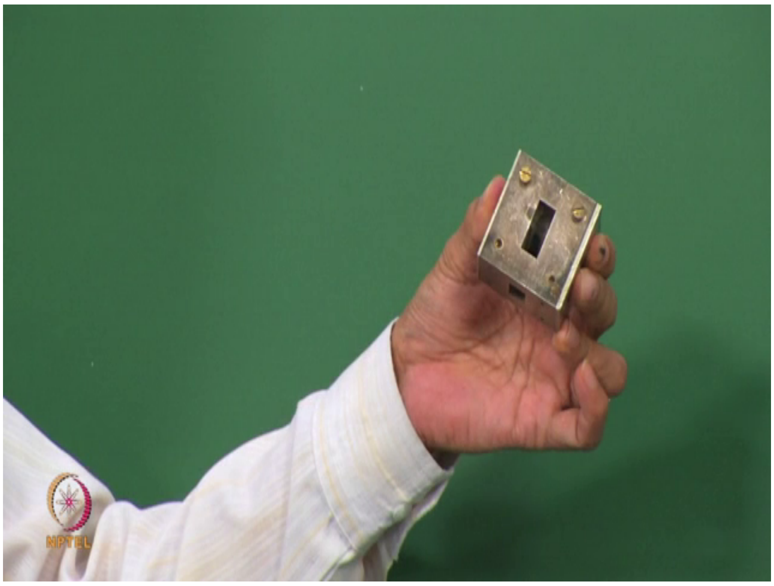

See, it has got 3 holes one here, here and there and they are all connected, if you see that this will through and through all there, but the property of this device is such that it is non reciprocating what do you mean by that for that.

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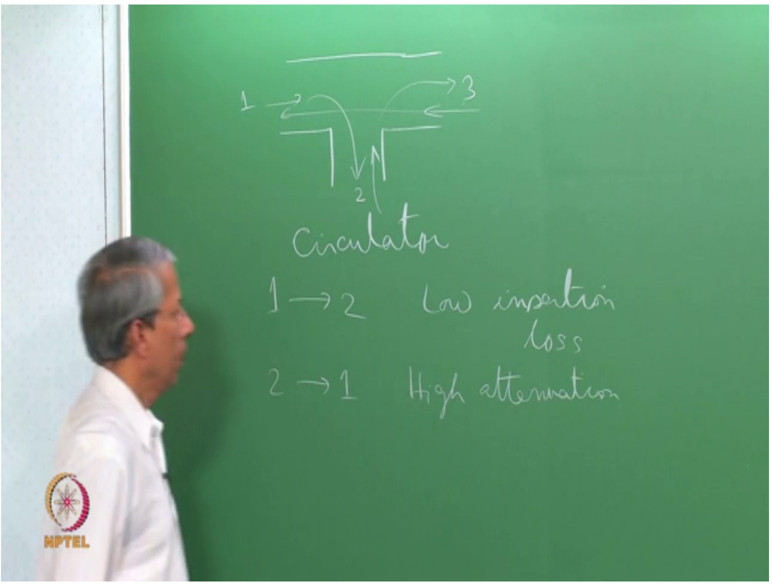

Let me draw the schematic diagram of this circulator here are 3 holes and we call them port; port number 1, 2 and 3; the way this circulator behaves is very interesting suppose the micro power is entering here.

Then even though internally they are all hallow spaces it cannot appear here, it has to appear here this is the power comes out, similarly, if the micro power enters here port number 2, then it will only appear at port 3 as an output. And similarly if the micro power entering the port number 3, then it cannot appear here it can only come here. So, this is the non reciprocating device that is property for the radiation to enter go from port 1 to 2 is not same as property for radiation one in test 2 to 1.

In other words 1 to 2, I may say this gives a low insertion loss, but 2 to one gives high attenuation same is to for the other pair of ports here this could be as little as point lesser 3 dv this could be as high as twenty degree. So, using these, we can make a spectrometer which will allow us to change the micro allow us to for the micro power to go from the klystron to the cavity in this fashion.

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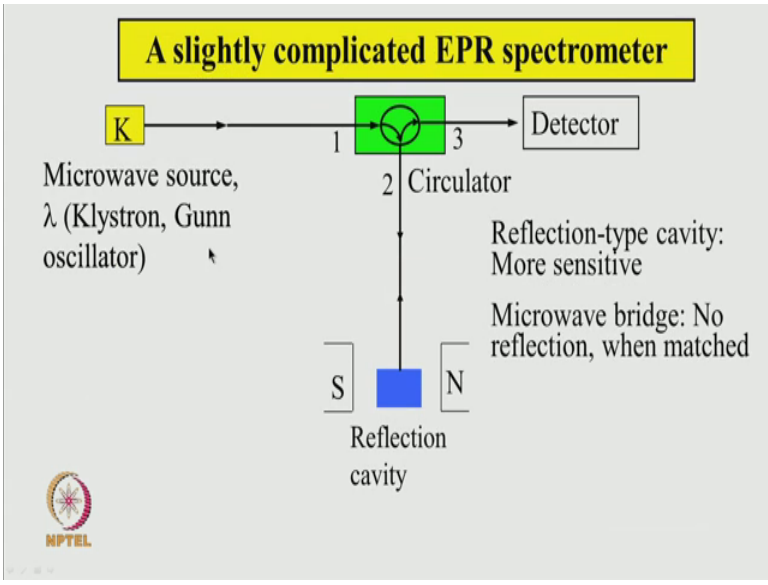

Let us see this is the circulator port number 1, 2 and 3 are connected in this fashion and klystron or the Gunn oscillator produces micro power which enter port number 1; this enters power enters from 1 to 2 and from this waveguide it goes to the cavity and cavity we reflection type it reflects the micro power and goes back here we are going back, it will not go to port number 1; instead to go to port number 3 and there we keep a detector.

So, the key of the cavity is much higher than the transmission cavity. So, it is more sensitive and the spectrometer works on the principle of reflection or micro wave from the cavity.

Now, we have seen that this reflection cavity forms standing wave and we can adjust the micro frequency such that it forms a standing wave and reflection from the cavity is minimum.

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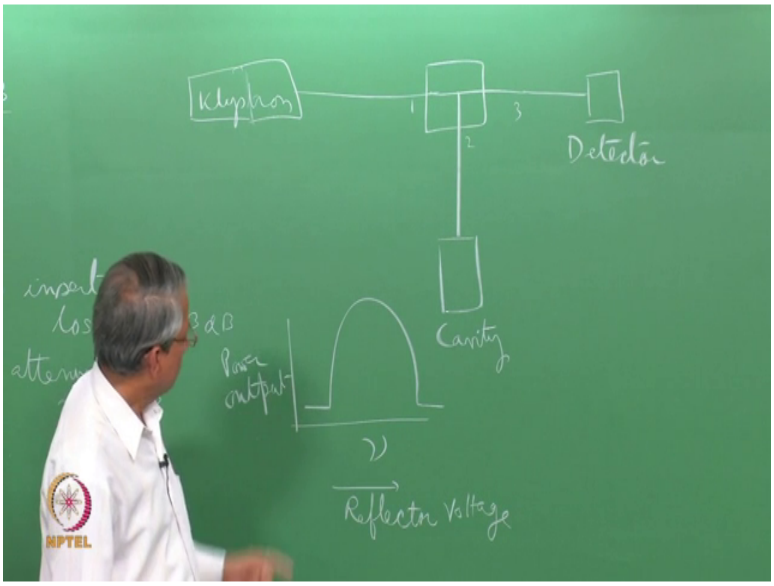

For the standing wave to form here, we have seen in the last lecture that the frequency of this must match the dimension of this things certain way and that to happen I must, therefore, first see that the microwave frequency from there is same as the characteristic frequency of these how do I find that out for that I start with varying the microbe frequency of the klystron by modulating its reflector voltage. So, that this gives out all sorts of frequency. In other words we try to see the mode of the klystron and we klystron mode we have seen that that would function of frequency power output has listed a pattern here. So, these are the possible frequencies that the klystron can give as a function frequency, but this can also be written in terms of the reflector of voltage because changing the voltage of the reflector changes the frequency.

So, what is done here is to continuous change the reflector voltage and see this mode on an oscilloscope then keep on changing the frequency such that the power that comes here will show a certain deep something like this kind that is at this frequency the cavity does not reflect. That means, that frequency the wave is formed and to explain that I have made a small animation here.

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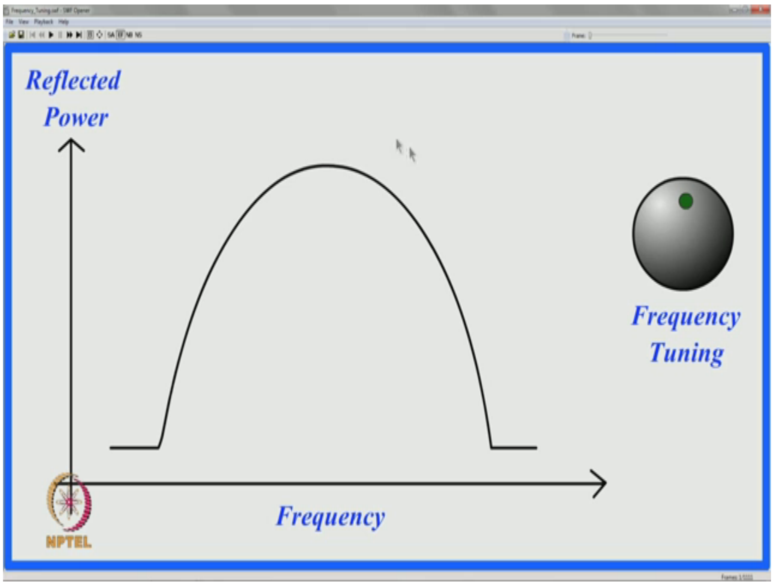

In this slide, let us say this is the frequency tuning norm if we turn this the frequency of the klystron is going to change what is shown here is the klystron mode the output of the micro power coming from the klystron as a function of frequency, but since same power is going to the cavity and cavity in general will have different resonance frequency complete power is reflected from the cavity. So, this is the mode of the klystron.

Now, let us start tune the frequency of the klystron and see that we get a pattern of this kind that the where the micro power is not reflected from the cavity here. So, it turning the frequency tuning knob and it is going through.

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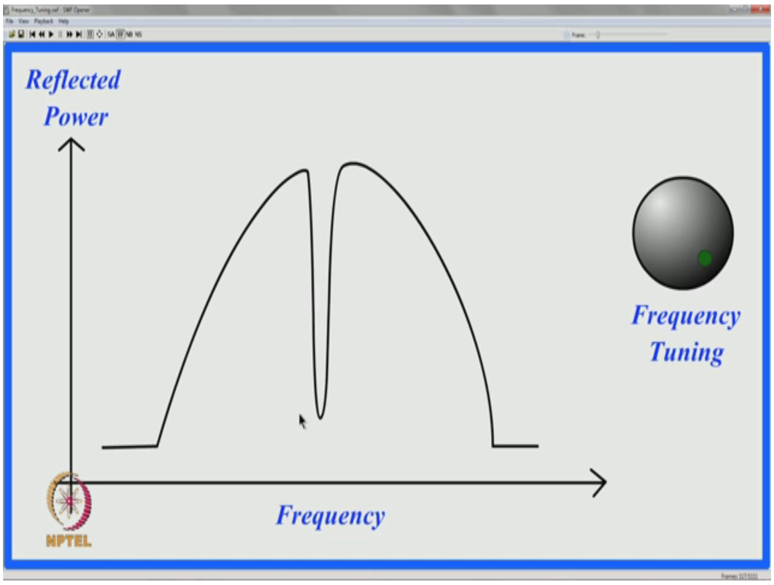

And then here the deep is same. So, these frequency therefore, corresponds to the frequency of the cavity now depending upon the voltage this can be anywhere in the profile of the klystron mode for example, here this frequency of the cavity it does not change what is changing is the condition of oscillations of the klystron. So, as I change the reflector voltage the position of the frequency here appears to change, but keep in mind that cavity frequency does not change if the klystron that giving out that voltage that is here that voltage is changing. So, we could in principle work anywhere in this profile here, but what is done is that we try to get the maximum micro power out from the klystron. So, we try to work at the top of the mode how to do this.

Let us say it is gone all the way down there. So, you have to go back and then try to bring the; this de cavity dip as it is called to the peak of this somewhere here where their maximum outcomes are expanding here. So, this is the place I must give the klystron frequency note here that though much of the micro power is absorbed by the cavity reflection is small nevertheless this is not completely 0 here this bottom of this thing is not touching 0. That means, again at that frequency some micro power is getting reflected from the cavity we can improve on this.

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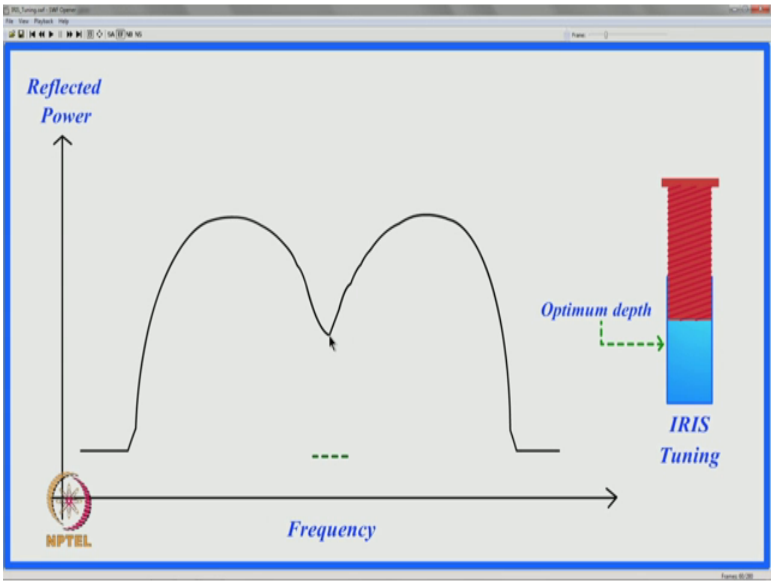

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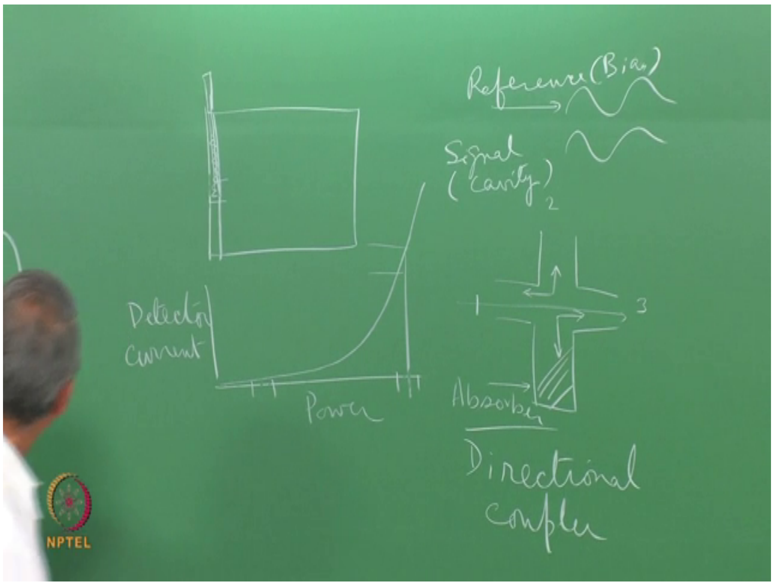

So, that the matching is such that very little power is reflected for that what you do is the cavity has iris tuner the cavity has a tiny screw in front of this iris hole by adjusting the position of the screw one can match the micro free that is coming from the klystron entering the cavity and that is reflected from the cavity that can be matched. So, the reflection is minimum, but to see that I have again put another animation here.

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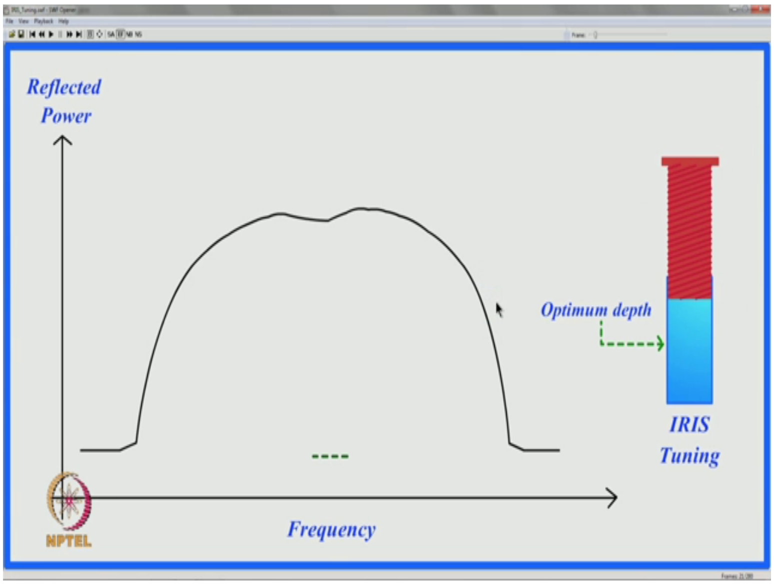

So, let us say the tune screw is quite far and cavity is not matched properly and this is the tune screw. So, one in red; now, I try to insert that screw slowly inside and this is small deep that you see here is the place where cavity is trying to retain the micro power inside it always run this one here.

So, here the cavity tune screw is gently inserted and see how the deep is increasing deep is increasing means less and less power is getting reflected from the cavity here.

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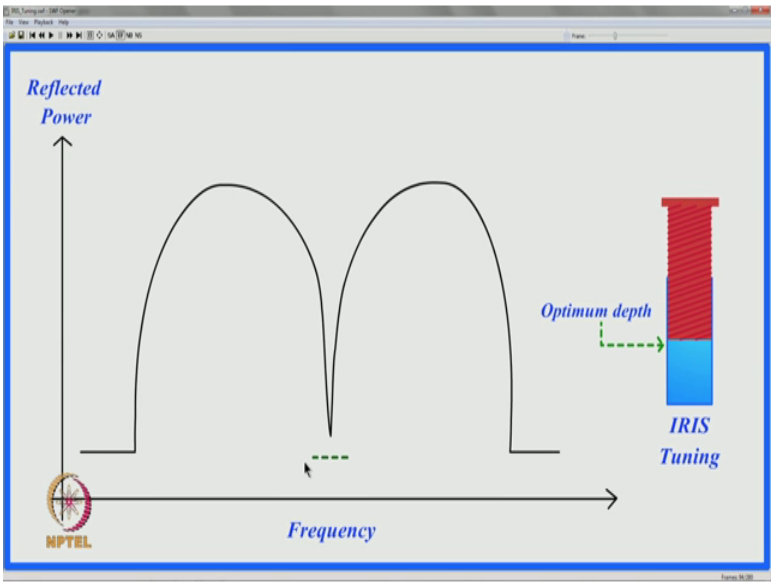

So, almost this is the 0 level, here reflection will be almost 0. So, here it almost touched 0 now if we go beyond that this will further start reflecting micro power. So, this position where it goes to the bottom most is called a critically matched cavity or critically coupled cavity.

The cavities critically coupled to the waveguide that allows the microwave to come in do it once more. So, if you go beyond the critical coupled condition micro power will be further reflected start from here. So, I am try to tune it by adjusting the depth of the micro screw slowly going down and down. So, here it is trying to go to 0; this is 0.

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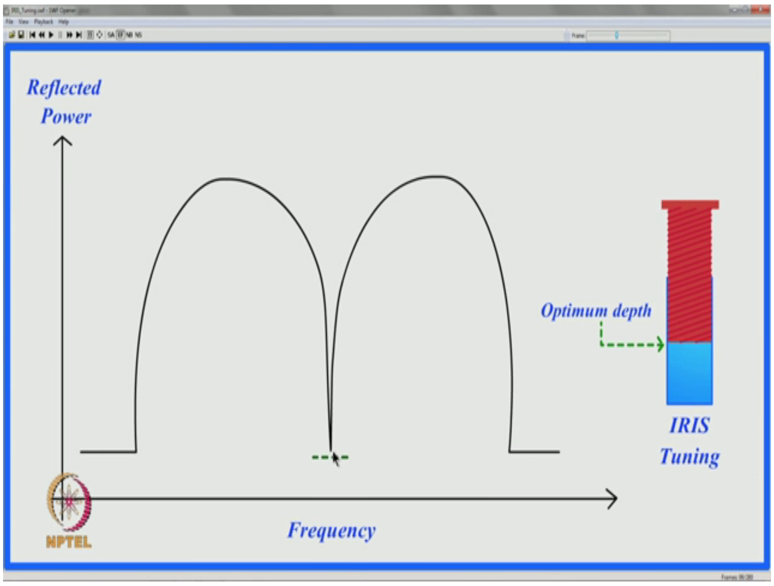

So, this is called the critically couple cavity. So, we try to work almost here if it is under coupled then the cavity dip.

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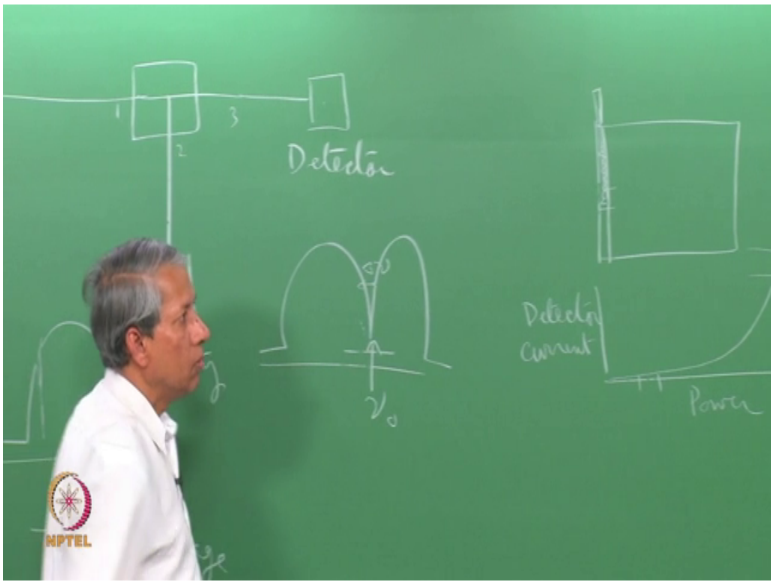

Let us should this is the critical couple condition. So, it just about to touch this bottom most position is called the slightly under coupled cavity and if it is it goes beyond that and again comes out that is called over coupled cavity

In a either case, the reflective power will be slightly finite that is it is not going to be exactly 0, it will be exactly 0 if it is critically coupled. So, this is going beyond critical couple. So, it is become over coupled long power is getting reflected. So, this is the spectrometer now where let us say, we have achieved the critical couple or very nearly critical couple condition. So, the very little micro power is getting reflected and happening in the detector.

Now, this is fine, but not good enough because the detector diode has very little power that falls on it we saw in the last lecture that the characteristic of the detector depends on the power that falls on it in this fashion current which looks something like this. So, when it is very small it is very insensitive and somewhere here is more sensitive that we saw in our last lecture. So, we want to have a sensitive spectrometer. So, there is small change in microwave, because of the EPR absorption can be detected much more conveniently this should be as high as possible for a small change of micro power that here versus here more the detector voltage is possible. So, here we can bias the detector diode such that it has to work here we like to work somewhere here.

Now, one way to do is to instead the working at critical couple condition or very nearly critical couple condition we deliberately mismatch it. So, that always some microwave power comes from here and fall from the detector that is possible, but there though it is possible and sometimes it is done it is not the very desirable arrangement because we are deliberately losing the sensitivity by spoiling the matching here. So, instead what is done here is that we take micro problem the klystron directly and to another path we try to bring it here and call it a bias power and that is done in the shown in the next slide.

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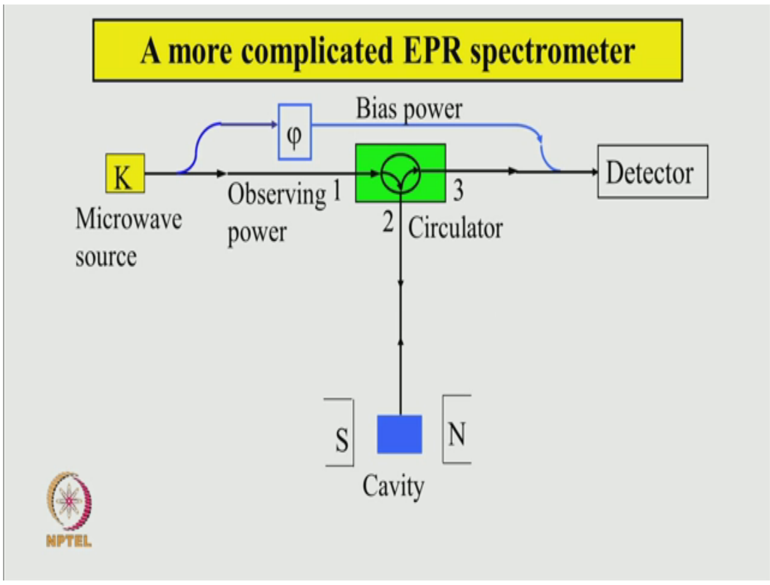

So, you see here in the blue line some part of the microwave is taken here and it is passed through a phase shifter the phi stands for phase shifter and this comes here and then it falls in the detector, we call this as bias power. So, that is by design we can bias the detector to work at a place where ever you want in this fashion. So, this taking a micro power from the waveguide is done through a type of device which is shown here this is called a directional coupler.

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So, here you see that one waveguide is as through and through hole here and other one has got a hole here, but it is blocked at this end and also it has got a arrow of this kind.

Let me draw this blocked here and the arrow has this sort of arrangement here. So, essentially it has got 3 ports; let us call it 1, 2, 3.

The way it works is that micro power is entering here will appear at port number 3, but a part of that will be coupled to this side and how much of this will couple depend on the construction on the other hand the power that is entering here and of course, come here, but a part of that will get coupled to this path, but here is blocked and also here or inside that we have put on material which observes the microwave.

So, this does not reflect. So, this type of coupler which couples microwave in a directed way that is if n power enters here and only in this direction it gets coupled here is called a directional coupler. So, this is the direction of coupler say power entering here will get coupled here and its entering here it will come here and get absorbed. So, this is the directional coupler which is shown here.

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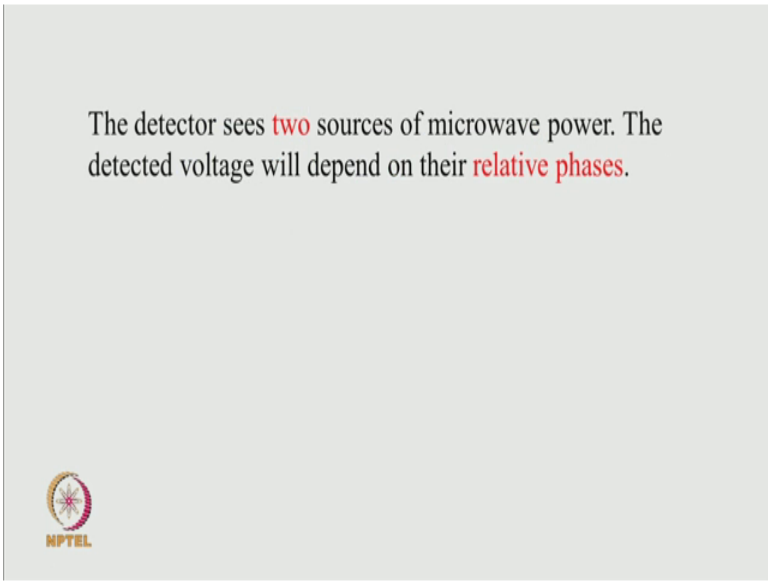

So, with this we can adjust the bias, but here you see that the detector sees microwave power coming from 2 sources one is from the bias path and other from the cavity. So, if they do not have the same phase then they will try to interfere in a destructive fashion. So, we must have some way to both the some way to have that this 2 radiation have the same phase now that is done by changing the phase of the reference power we got the bias for that comes through the bias arm also, where you want to work here how much power we want to use to bias it.

So, that is also important because in the arbitrary amount of power may not be the optimum value because noise is also increases as the; this bias power increases. So, for that we need to have a few more microwave element in the spectrometer here now.

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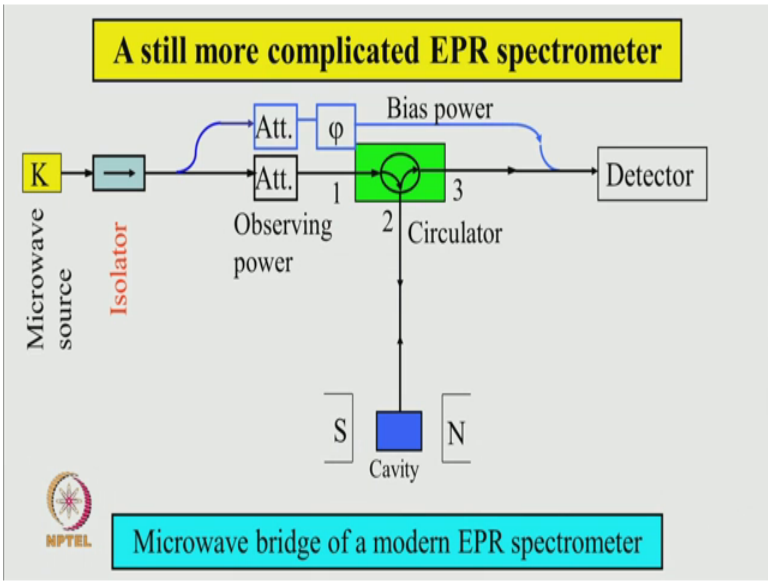

So, let us go through once again that microwave power comes from the klystron or my or Gunn oscillator, then it goes to this main path for absorbing power and I have got attenuator here which can be adjusted to enable me to have any desire amount of micro wave power to come to the sample to this path this is a directional coupler. Again attenuators put there, so that I can decide how much of bias power is necessary and that phase of the bias power is changed by the phase shifter here.

And then this is for allowed to come to the detector we have also put a isolator here and its job is to make sure that microwave radiation goes only along this direction any reflection from this direction or here is blocked by this one. So, that this radiation does not reach the microwave source and was interference and this of course, the cavity is kept in the magnetic field and this completes the spectrometer and that is the way a modern appear spectrometer looks like.

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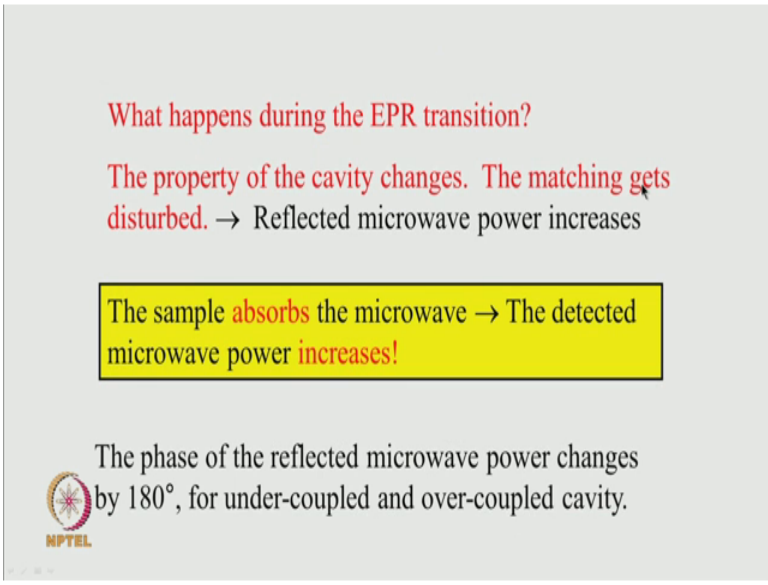

Now, what happens during EPR transition the property of the cavity changes the matching gets disturbed what is the matching is what matching means that we have seen that reflection for the microwave cavity is very very small and that matching get disturbed; so little bit of micro power is reflected. So, you see this is a bit of a come funny situation that when the sample absorbs microwave power then the detector actually sees that more power is falling on it unlike a conventional absorption spectrometer digital detector will see less power when the sample absorbs, but here the way we set up the spectrometer is that when the sample observes microwave the detector sees is more power.

We understand why because it is based on this matching of the cavity to the microwave frequency such that very little power is the steady state condition where no absorption takes place another important thing is that the coupling besides the phase of the power that is reflected from the microwave cavity.

So, let us say this is the reference power or the bias power and this is the signal from the cavity. So, when you go from here very nearly critical couple condition to over couple condition the phase of the micro power that goes from the cavity actually become opposite. So, it becomes this type of thing. So, what is usually done is that we do not work at all under in the over coupled condition we always optimum coupling is done. So, that goes very near to the critical coupling, but not quite workable condition. So, that the actual phase is decided once and for all.

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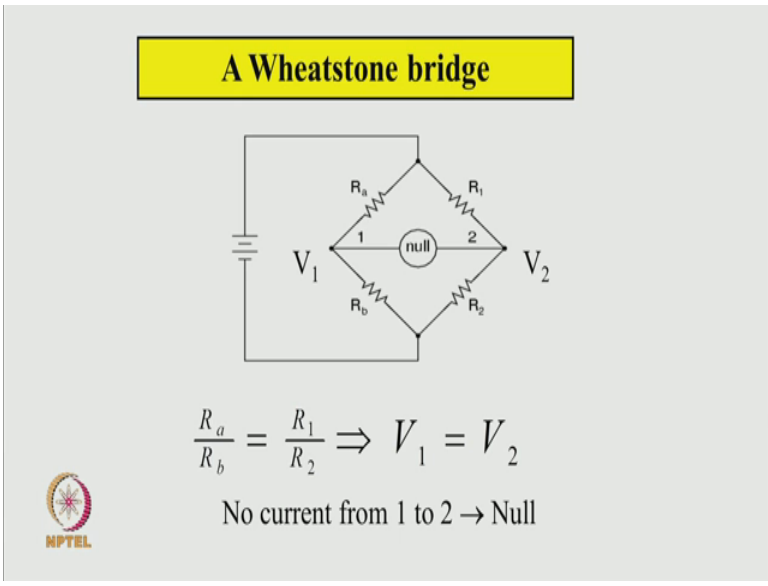

Now, why does it happen that phase changes an analogy is probably useful here, let us see the Wheatstone bridge here this four resistances R a, R b plus R 1, R 2 are arranged in this fashion and connected to a battery here now here if the ratio R a and R b; this R a by R b is equal to R 1 by R 2 and voltage V 1 is exactly equal to V 2. So, there is no current going through this and we say that that this bridge has reached null condition.

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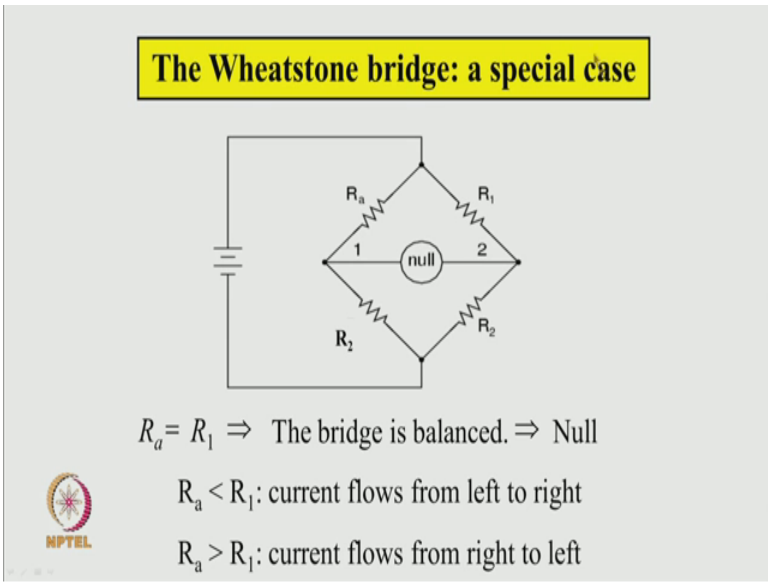

Now, let us say special type of Wheatstone; Wheatstone bridge where this R 2 here also R 2 here that is resistance value for these 2 are same in that case the bridge is balanced when R a will be equal to R 1, then again the current flowing through this will be 0 and we say the bridge is balanced and null is condition is achieved. Now if R a is less than R 1 the current will flow from left to right and if R a is greater than R 1 the current flows from right to left.

So, the direction of current is exactly opposite depending upon whether this is more than this or less than this in a similar fashion when the bridge is balanced in a slightly over coupled or under coupled the phase of microwave changes exactly by 180 degree in this fashion here.

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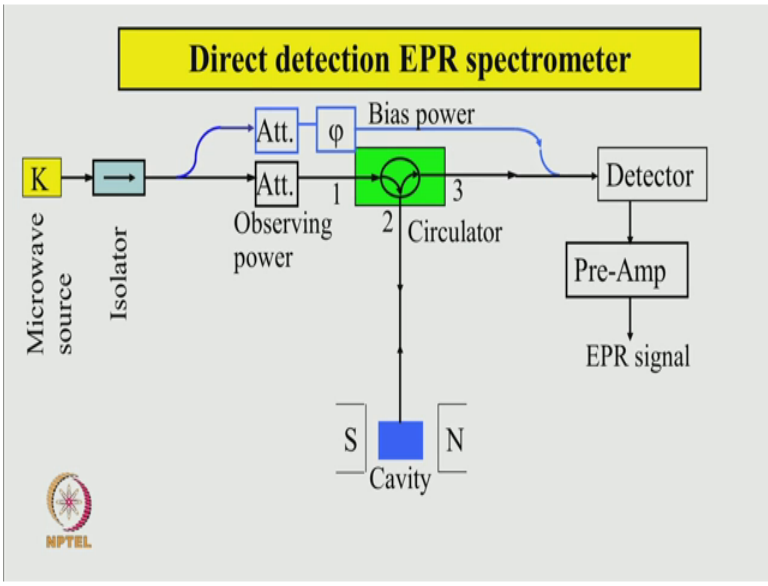

So, this is what we have got so far is called the direct detection EPR spectrometer; the detector signal that is generated by the detector now is passed through broadband preamplifier. And we can get the EPR signal to get the signal is scan the magnetic field I record this output as a function of magnetic field.

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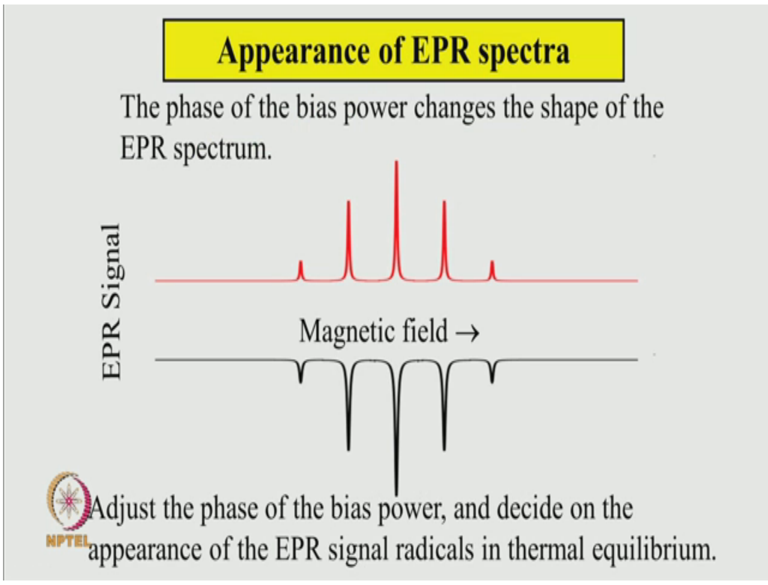

So, the spectra will look like this. So, this is some hypothetical radical gives five line and this set of pattern there now the appearance of this will depend on what bias power see if you change the phase of the bias power which is the reference power by hundred it will be then the detector signal changes sign. So, it can change from maybe this to this. So, you have to adjust a bias power and decide what sort of signal we want to replace a take order on display. So, we are often dealing with a signal which comes from a radical which are in thermal equilibrium. So, we get an absorptive signal because in thermal equilibrium that lower level has got slightly more population than the higher level. So, there will be net absorptive signal.

So, whether this is called absorptive representation or this is absorptive representation that one has to decide once and for all, but the appearance will depend on the phase of the bias power what will also depend on the cavity matching.

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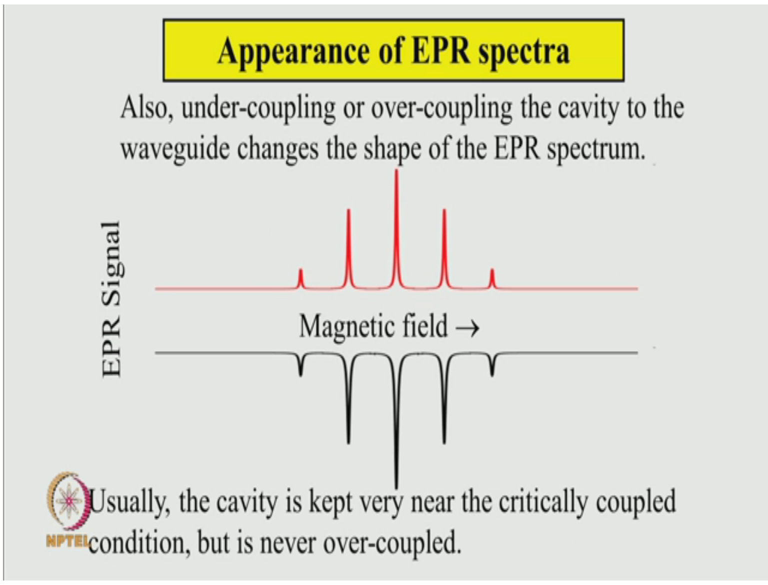

For the under coupling or over coupling that will also change the phase of the power that comes out from the cavity. So, again the appearance the signal will be dependent on whether cavity is critically coupled under coupled or over coupled.

But in practice we never work under over couple condition, we work under just a little bit less than critical coupled condition.

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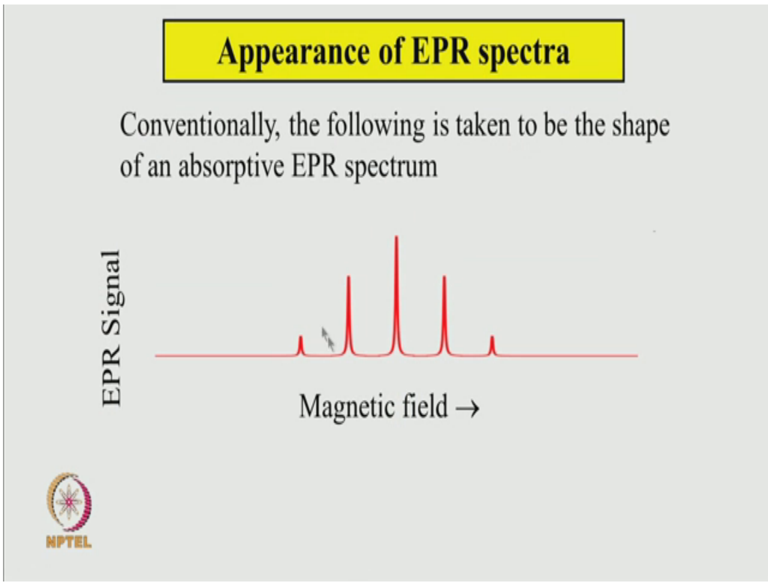

So, conventionally for an absorptive spectrum this is the shape that we have taken to be the true shape of the spectrum; it is just convention.

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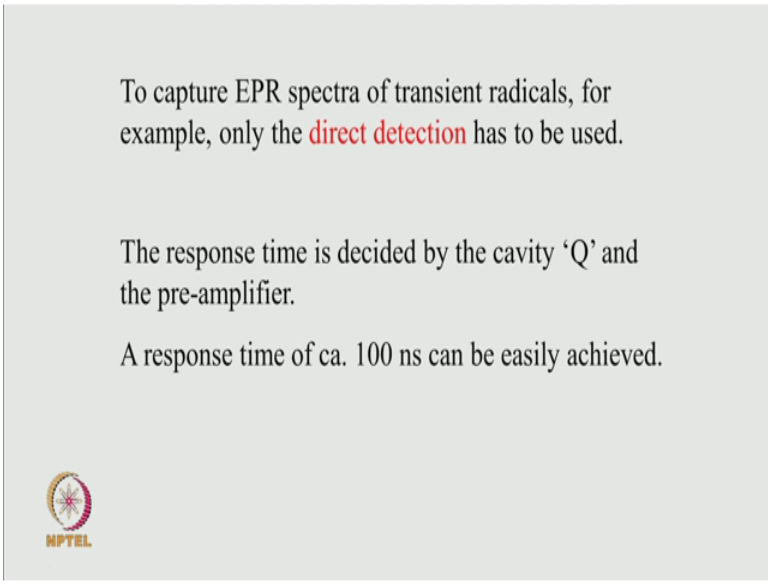

Now, this direct detection EPR spectrometer that that just now we described these does not have very high sensitivity nevertheless this has got very fast response time. So, when one interested in looking at transient radical for example, which does not live for long time then this directive spectrometer is used.

Transient radical can be created by a pulse laser light which leaves for radicals may leave for a few hundred nanosecond to maybe millisecond; those are not easy to capture sometimes also experiments involve pulse experiment that determines the spin lattice relaxation time for that the relaxation time of the order of micro second can be detected if the spectrometer is fast enough again the direct detection technique is used there to look at the signal the way we have described now. So, response time of the spectrometer is decided primarily by the cavity Q and the pre amplifier.

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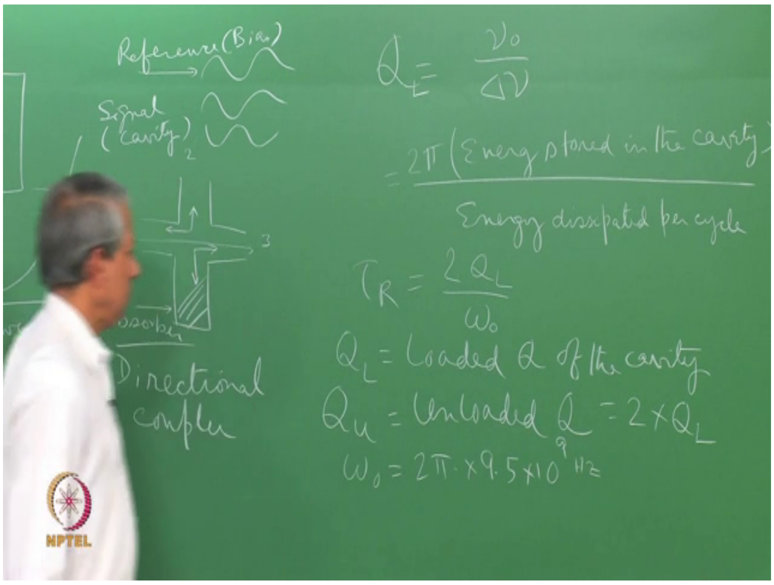

If the pre amplifier has a sufficiently broad bandwidth the response time of the spectrometer is decided by the key of the cavity. So, Q is defined to be nu 0 by delta nu where in this cavity mode this this is the delta nu and this is the nu 0. So, this is the Q this is also defined to be the same as the energy stored in the cavity divide by energy dissipated per cycle energy dissipated per cycle. So, the higher is the Q see it is going to store energy with a very little loss. So, higher Q cavity will be reluctant to reduce its energy. So, a Q which is very high the micro wave power inside the cavity does not change very rapidly.

What I am trying to arrive at is that to have a very fast responding spectrometer Q should be low or higher Q makes the spectrometer slower, but how is the relation now. So, if we say that response time of the spectrometer tau R and this relation Q is given by 2 times Q L by omega 0 this Q L is called the loaded Q of the cavity. Now loaded Q is a term, we have not used. So, far here whenever the cavity is connected to a waveguide and match to a microwave source what we measure in this fashion is actually the loaded Q of the cavity.

So, that is experimentally measured quantity and the way we measure is just this the electron that is used here is called unloaded Q; Q it has got more of a theoretical interpretation and it happens to be that this is 2 times Q L. So, we do not have much interest here just it has got some theoretical; why it should be twice of this one, but whatever see in practice is just the loaded Q that we measure experimentally. So, that is this Q given by this formula this is actually this is same as Q L here.

So, let us see an spectrometer. Let us say of this kind working in the x band as frequency omega 0 2 pi the nu which is let us say 9.5 into 10 to the power 9 hertz in this 9.5 gigahertz.

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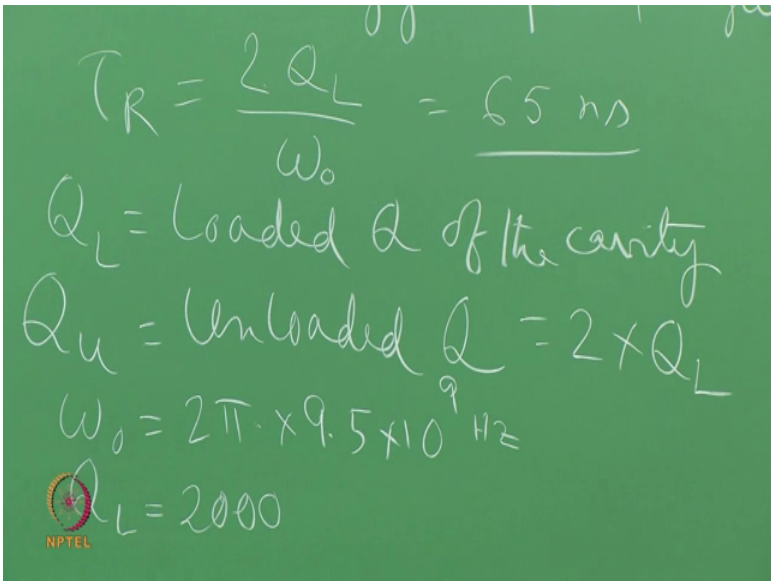

And Q L is typically set 2000; anyway 2000 or 3000 is the typical values of x band rectangular cavity.

So, if you put it here and then calculate the tau over comes out about 65 nanosecond. So, typically the signal which is changing somewhat slower than 65 nanosecond can be recorded by this spectrometer. So, it is here the higher the Q then becomes longer. So, that is same as what we had said that cavity Q is high, then is if you set of resist the change of microwave power inside the cavity.

With this, we have basically given the overall appearance of an direct detection EPR spectrometer. And in the next lecture, we will see how you can improve the sensitivity of this.