Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture –07
EPR instrumentations – I

Hello today we are going to discuss the basic EPR instrumentation whatever items are used to make an EPR spectrometer.

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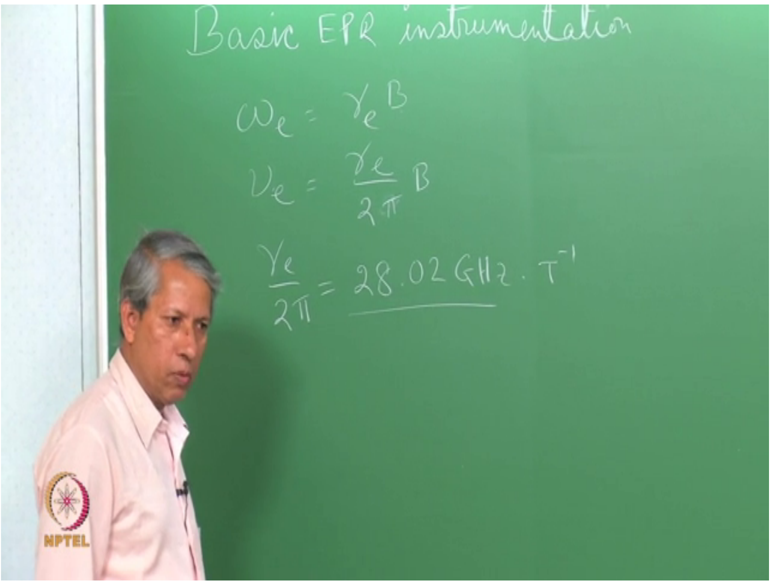

We have seen in earlier lecture that the Armour frequency of an electron is given by this is the Gyramor basic of electron is a magnetic field it is a frequency of precision. Now this gamma e gyromagnetic ratio gives a frequency in angular frequency unit that is radiant per second if you want frequency normal unit let us say nu e with gamma e by 2 pi B and we have seen the value of this gamma e by 2 pi is 28.02 Giga Hertz per tesla.

So, you see our typical frequency will be of the order of several gigahertz if the magnetic field is of the order of 1 tesla. This frequency comes in the microwave region, what do you need to have a spectrometer based on whatever you have understood about the principles of the EPR spectroscopy let us look at this slide here.

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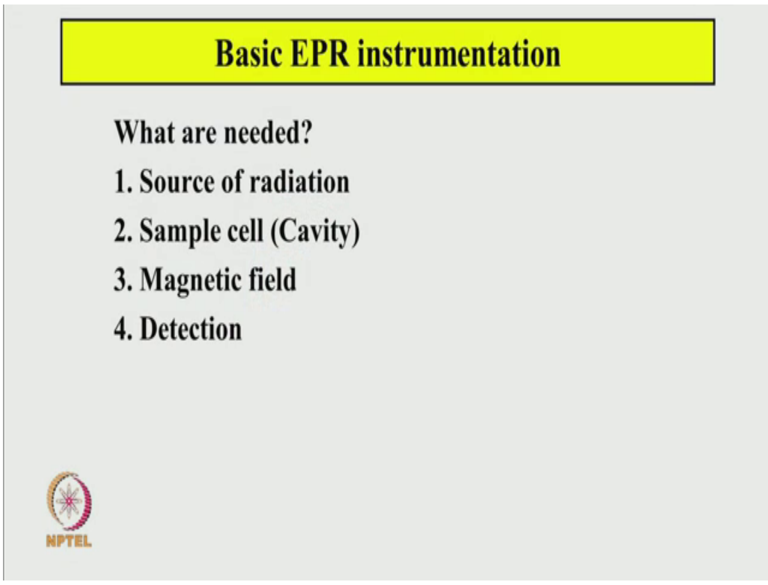

We need a source of radiation, then we need a sample cell to hold the sample which in this for per lense called a cavity, then you need a magnetic field, and also detection system

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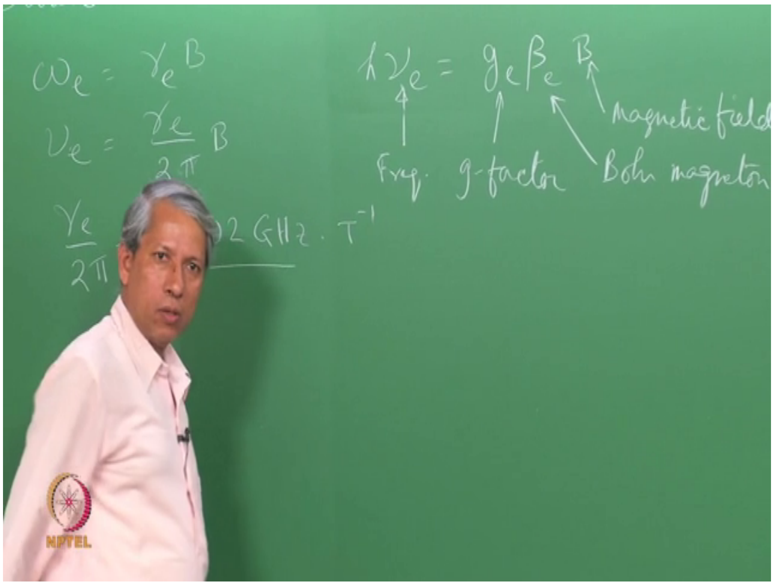

We also have seen a (Refer Time: 02:34) condition is given as h nu is equal to g e beta e B, this is the g factor, this is Bohr magneton and this is the magnetic field, this is the frequency of resonance, just now said that this frequency comes the microwave region for typical magnetic field of the order of a tesla. So, here once again to recapitulate or earlier understanding that we can either vary the frequency and keep the magnetic field constant or vary the magnetic field and keep the frequency constant both are possible in principle, but in practice it is almost always true that we vary the magnetic field and keep the microwave frequency constant will see several reasons why that is so.

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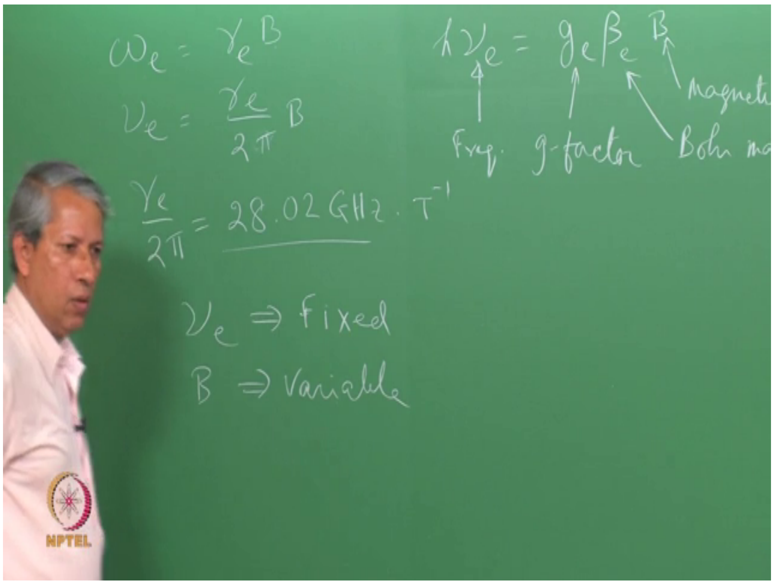

We need therefore, is fixed and B variable, how will a spectrometer look like a simplest possible spectrometer will look like this.

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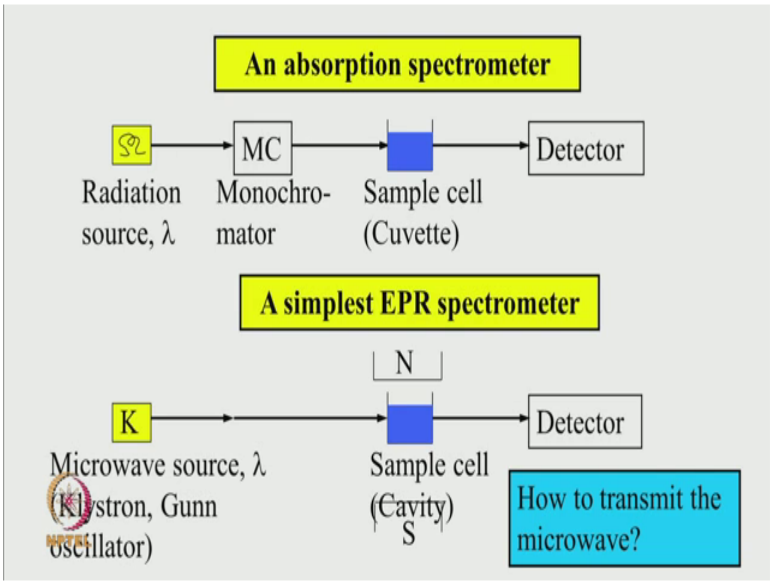

And here we are comparing a normal absorption spectrometer which you must have seen in a optical experiment for example, ultra guard visible spectroscopy, infrared spectroscopy or what not. They have source of radiation and they monochromator which you chooses a particular frequency then sample cell which normally call cuvette radiation goes to this and whatever comes out is measured on a detector, whenever the radiation absorbed by the sample at a given wavelength that change in the signal detector is an essence spectrum.

In that spirit you can think of a simplest EPR spectrometer which will have a source of microwave radiation K radiation comes and falls on a sample which you call sample cell is call a cavity and this is kept in a magnetic field north and south and the transmitted radiation is detected by detector.

This is all very similar both the cases now in case of optical spectrometer we can change the direction of the light we can bend it, we can focus it using appropriate optical elements let us say you can use lens or mirror we can use any of this optical elements to bring the radiation to the sample and to the detector, but the trouble in EPR spectroscopy is the microwave radiation that is used here wavelength of this is pretty long.

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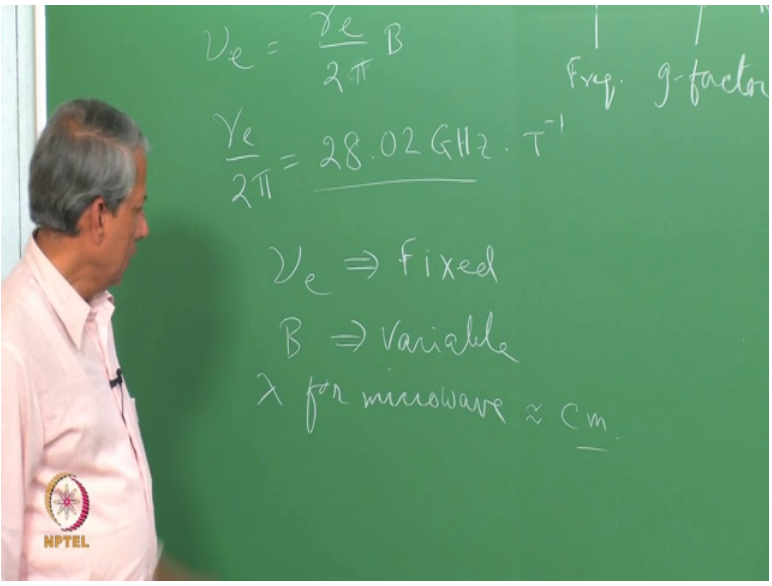

But, typical lambda for microwave is of the order of centimeter is in type of spectrum would normally use has a few centimeter wavelength, in that case it is very difficult to have an optical element to focus it only so big that when it goes through any element it gets diffracted very easily. So, you have a source of radiation let us say microwave comes from here and to very easily go all over, so compare to again here that I have got the radiation source from the optical element going to the monochromator and this radiation can be easily brought to the sample cell maybe with a lense or bend it in a mirror, but here radiation is coming out very easily gets spread out all over. So, whatever radiation comes out to the sample will be, small that the experiment will be very very difficult to perform.

The real problem is micro spectroscopy is how to transmit the microwave, for that there a certain tubes which are used to force the microwave to stay inside.

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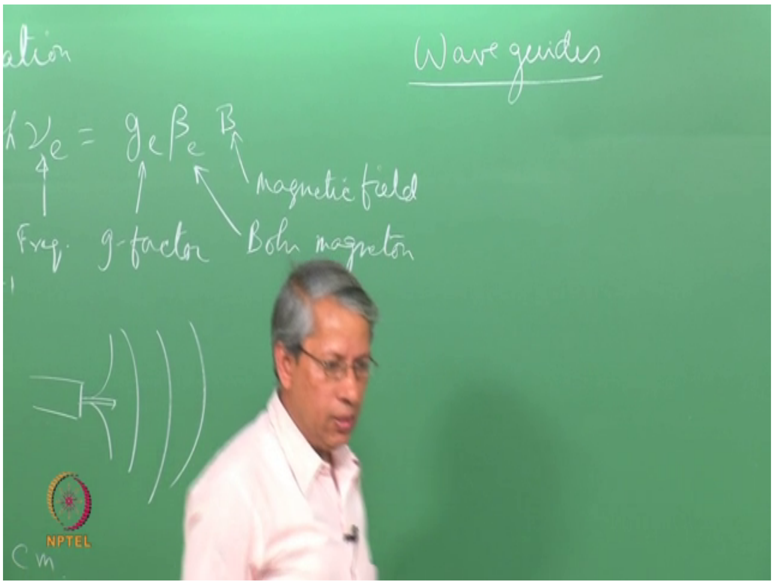

These tubes which carry microwave are called wave guides; here is an example see the rectangular tube here rectangular cross section.

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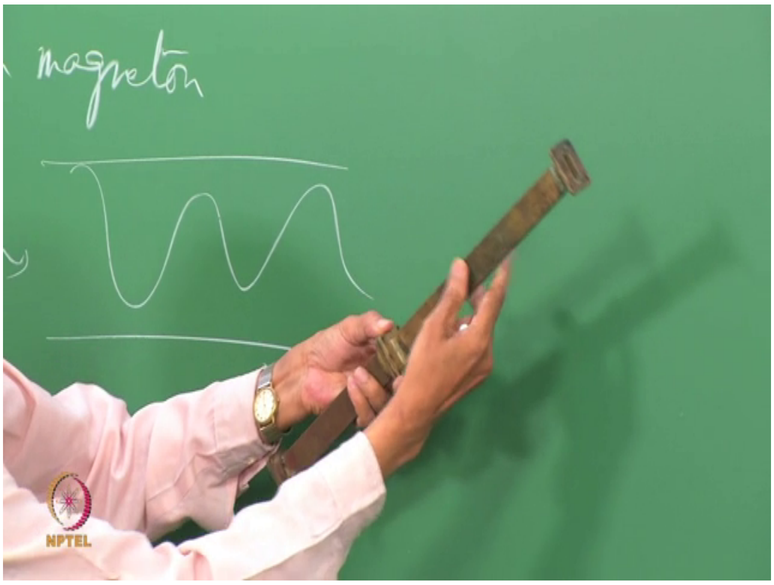

And the hole here through and through hole if you can see it, the hole is seen clearly, here the microwave enters here.

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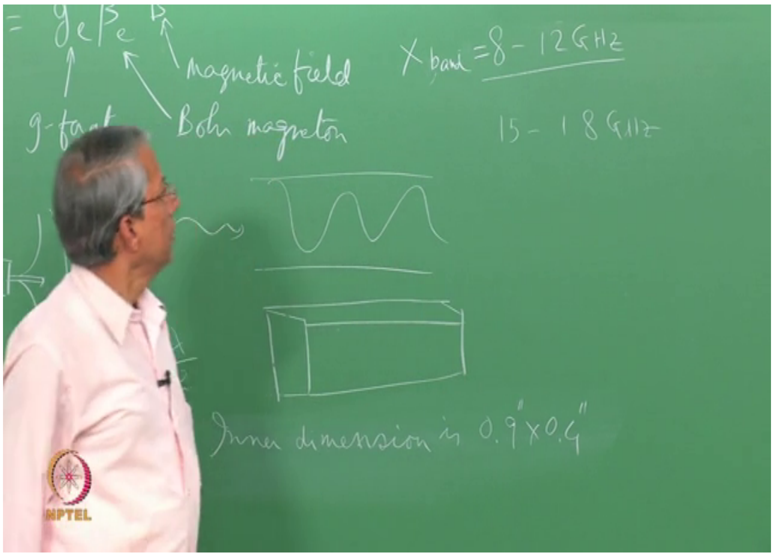

It is forced to stay inside this it does not come out, this tubes sometimes it is rectangular it could also cylindrical this tube circle waveguide because it guides the radiation inside it. So, whenever we need to bring the radiation one place to another place I can use different type of this waveguide elements for example, this a different length here one is bigger other is smaller, you can join these 2 to make a bigger waveguide these are their holes here and then these could be screwed appropriately to join, but often we need to bend the microwave radiation in case of optical experiment we use mirror of example, but here.

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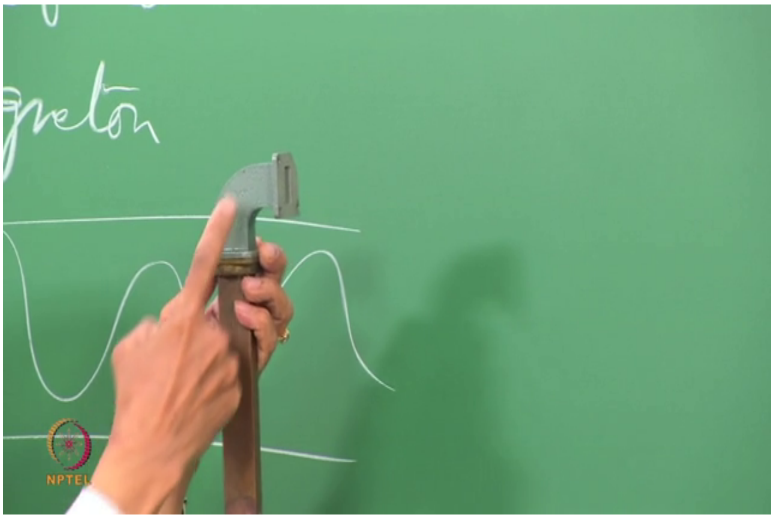

We have similarly an arrangement to bend it let us say here bends, we can have a microwave which is entering here it can bending in this way, that is possible so, but if you see here because rectangular nature the radiation will have certain polarization that is there will be specific orientation of the of the electric field and magnetic field inside this tube. So, when you want to change the orientation there also tube available which is called the twist here.

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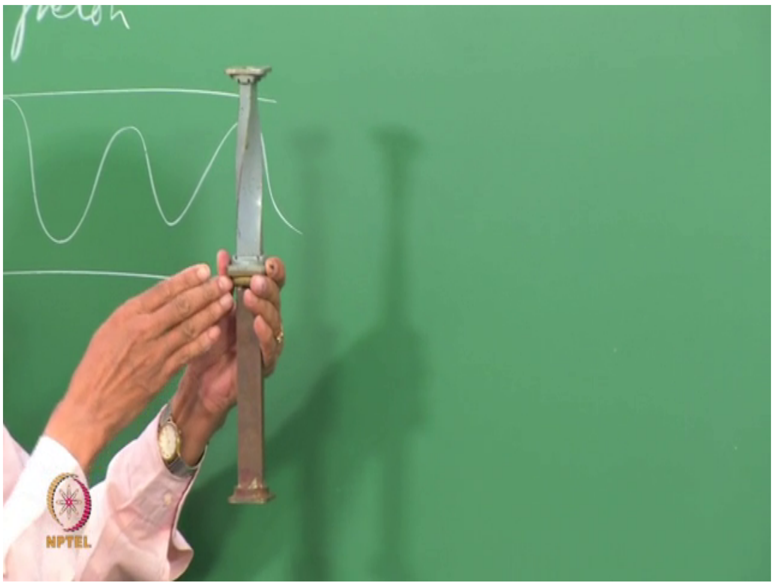

Again see the plain of the radiation enters here and gets twisted and then because perpendicular to that.

Naturally the wavelength of the radiation which is going through the tube has to enter or in another words the dimension of the waveguide which is here, this dimension decides what is of radiation can be carried by this waveguide. Now here the wavelength has to be smaller than that lambda by 2 has to fit here, any wavelength which is bigger than that cannot enter here and therefore, cannot be carried out by carried by this waveguide.

So, for example, I have another waveguide here you can see the dimension of these are this is different from that one you can see this is has smaller dimension that this one both ways is it narrower than this one here. This can carry microwave which frequencies higher than the frequency that is carried by this one, there is certain names given to this various frequency range is that can be carried in a different type of waveguide I have given you example of rectangular waveguide, but there are cylindrical waveguides also possible, but this particular one the inner dimension is you see that unit is inches which is very old fashioned because microwave technology came into be in sometime 1940s and there at that time this unit was very common and that has been continues then.

And the frequency that could be carried out by this waveguide range is from about 8 to 12 gigahertz this (Refer Time: 12:06) here.

We give certain letter code to different frequencies that this waveguide can carry similarly this one can carry a frequency which is some say 15 to 18 gigahertz higher frequency is carried out by this one with dimension smaller.

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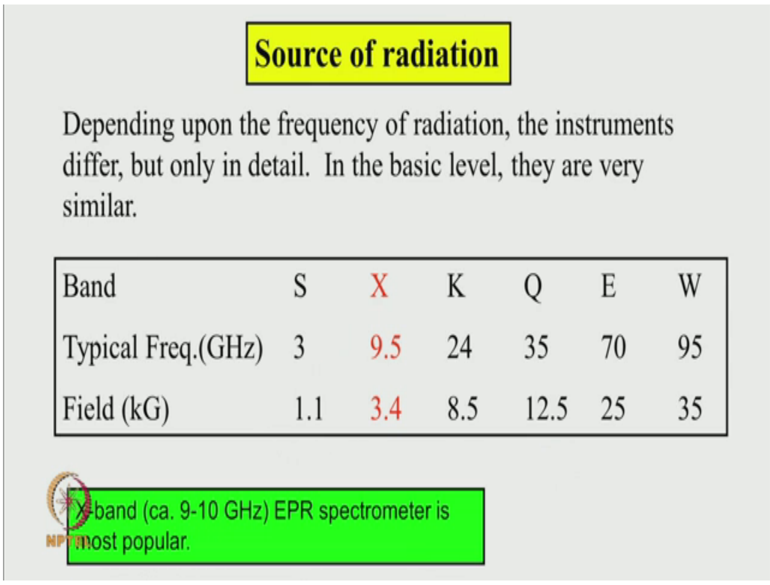

In next slide gives you various types of the micro frequency and what is the letter code for them, S X K Q E W they represent the frequencies 3 gigahertz here 9.5 and their other frequencies given here, this X band which is here this is called X band.

This is most popular frequency used in EPR spectroscopy and corresponding magnetic field is 3.4 kilo gauss.

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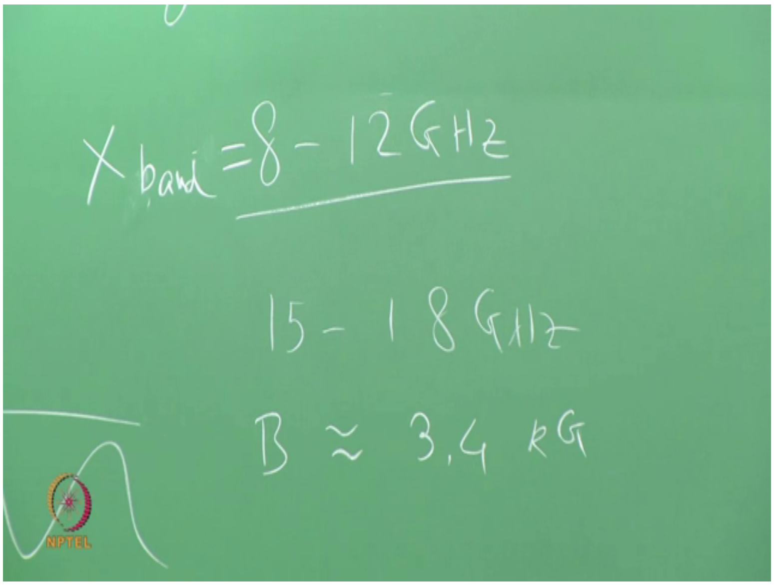

So, again in this table you see that various bands of frequencies one can have spectrometer and correspondingly magnetic field of course, be different X band is most popular Q band is also popular which works around 35 gigahertz micro frequency and requires magnetic field of 12.5 kilogauss when W value is also available what is the micro frequency goes of 95 gigahertz and works around 35 kilogauss of magnetic field once again X band is the most popular frequency.

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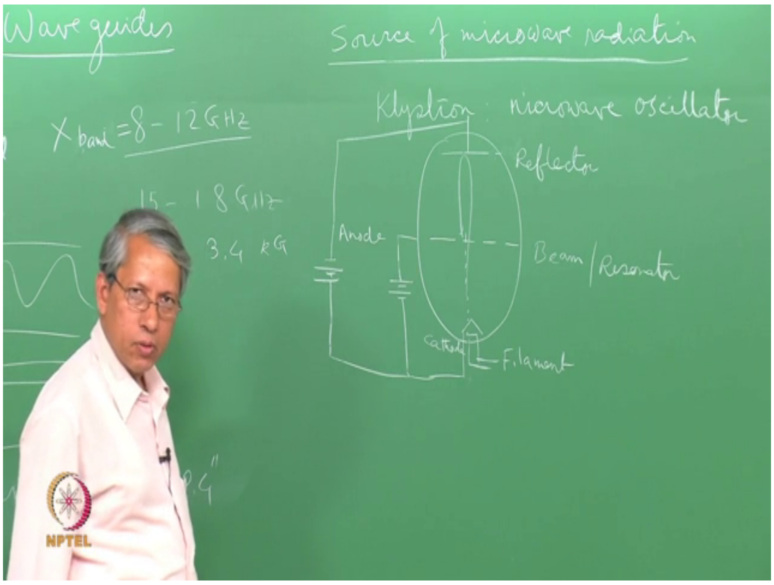

Next is the source of microwave radiation most common source of microwave radiation is microwave oscillator called Klystron it is a vacuum tube inside which electrons are made to undergo acceleration and deceleration and a very simplistic way the inside part of the klystron looks like this there is a filament which is heated and is produces electron now there is a cathode here and there is this is called cathode, this is called anode and this electrons are accelerated through this anode at a very high positive potential and then there is a another electrode here which is called the reflector and this is kept at negative potential with respect to cathode.

So, what is happening here electrons are emitted by the filament this accelerated by the positive anode and goes through this and then reflected by the negative potential we applied here. So, electron sort of goes up and comes down this should the motion it has it of course, a very simplistic picture the model is because of this acceleration deceleration electron that experiencing that produces a microwave radiation this anode is also called the beam or the resonator, the frequency of oscillation here decides the frequency of the microwave that comes out.

To change them up frequency one can change the physical distance between this beam and the reflector this gap is change there, that changes the transit time of the electron from here to there and back here, that changes the frequency of time period and changes the frequency oscillation also the frequency oscillation can be changed by changing the reflector voltage if we increase or decrease that will also change the transit time between these 2 and that can also change the frequency of oscillation. Now, here depending upon the Lipitor voltage and the beam voltage the output is going to come now the wave klystron behaves not all voltages are allowed here in other words the microwave will come out for only for certain allowed voltages of the reflector that is decided by the physical dimension of this. So, we can plot the output of the radiation as a function of the frequency the frequency of the microwave can plotted here.

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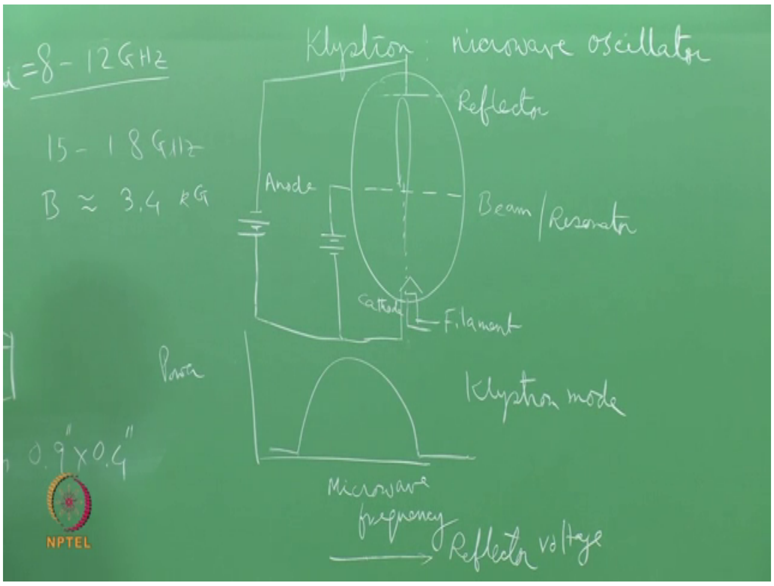

The function of power then the wave the klystron waves it does not give constant output power wave function frequency usually it looks like this something like this now microwave frequency as I said earlier is decided by the physical dimension between these 2 it also decided by the reflector voltage. If I keep the dimension constant keep on varying the reflector voltage the frequency going to change. So, this may X is could absolute we written in terms of the reflector voltage now they here you see then that when the reflector voltage is this and this there is no output of microwave only when the reflector voltage is certain allowed value from this to this the microwave power comes out. This behavior is characteristic of the klystron and you call this figure that is output power as a function of the reflector voltage is called klystron mode.

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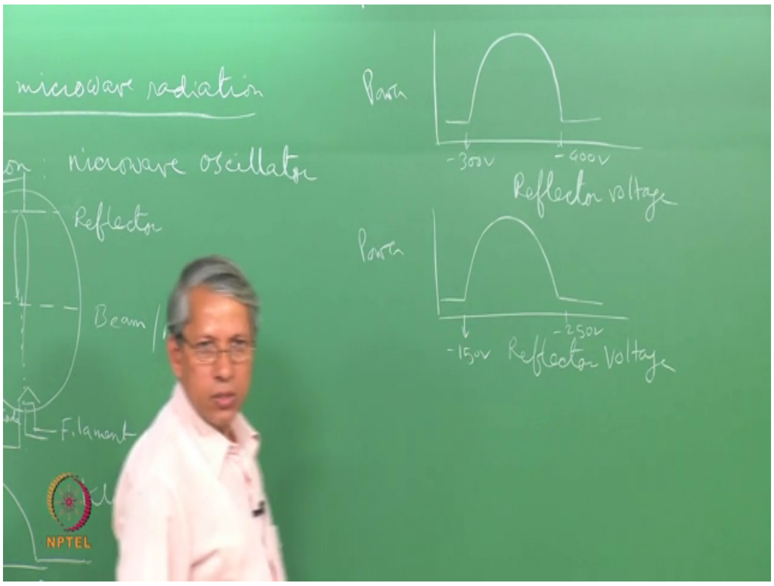

Now, klystron can have more than one mode what do mean by that .

It may look like this for a certain range of voltages let us say this could be minus 300 to minus 400 volt that is be that is from that is from here to here just for sake of more understanding that is the microwave power from the klystron has this set of shape when the reflector voltage goes from minus 300 to minus 400 volt.

In other words if the voltage because more negative it turn that there is no output or say becomes less negative than that there is no output, but it is possible that for same setting of this one and get another output of this kind there is similar this might be let us say minus 150 volt this will minus 250 volt. So, this is very similar if again the voltage because more negative than minus 250 there is no output a less than minus 150 then there is no output, this is second mode the another mode here that a way a klystron gives more than one mode, now for normally chooses that mode which gives the maximum power this would be maximum that voltage is chosen here for operation of the klystron .

Now, other than klystron more modern micro source that is being used in the EPR spectrometer is called a solid state device and that is called a Gunn oscillator this is a solid state solid state device unlike klystron which is actually based on vacuum tube everything.

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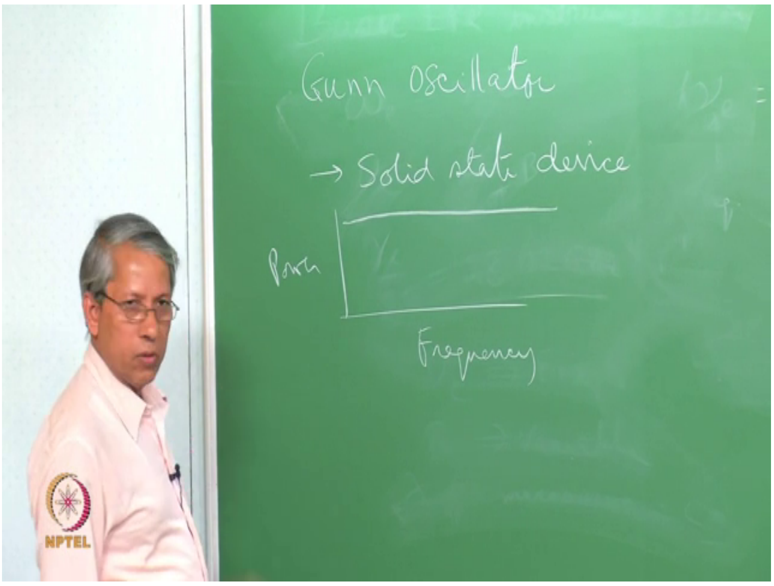

That is happening here is inside a in a vacuum tube this has no such thing a solid state device what electrons are meant to oscillate because of certain gunn effect we do not go into detail, but we only distinguish the behavior of this versus that one important difference is that the gunn out oscillator output has a function of frequency is almost constant, that way there is main difference, here in here I said the reflector voltage changes microwave frequency to the certain extent here we also see early the voltage that we applied to the gunn oscillator diode that also changes the frequency of the microwave. The next item in the spectrometer is the sample holder or the cavity.

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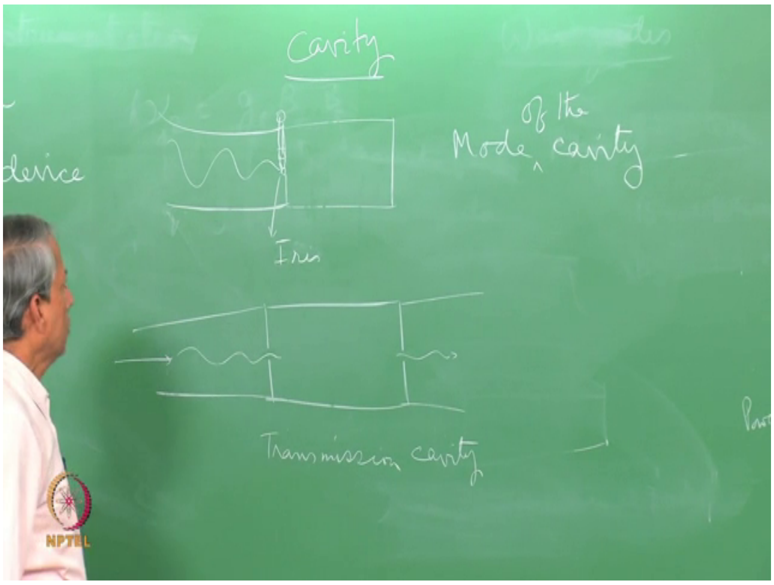

Now, cavity is a rectangular box or it could be cylindrical box, but the sample is kept, but important function of this is to ensure that the sample sees the magnetic field of the microwave radiation and not the electric field which you have seen earlier that is the magnetic dipole transition which is what we observe in EPR spectroscopy.

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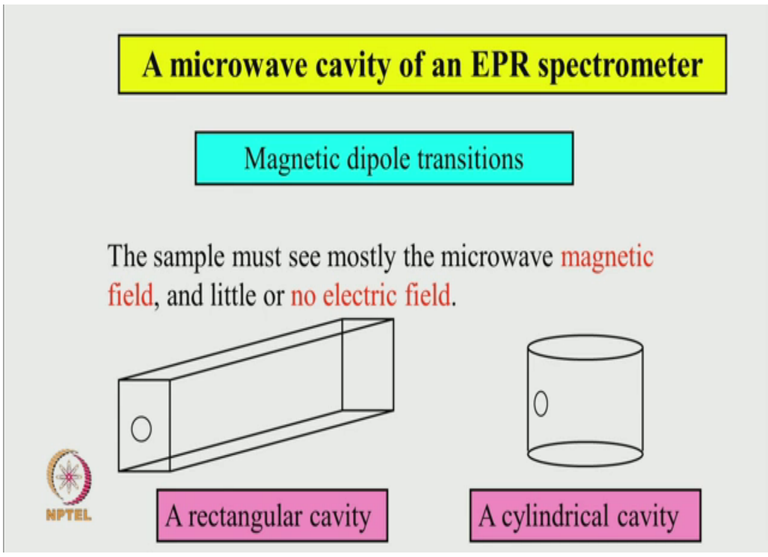

Microwave cavity functions a very important role it ensures that a magnetic dipole transition is taking place in the sample in the sample in other word sample must see mostly the microwave magnetic field and little or no electric field because microwave also can cause electric field transition and that is not what you are trying to look at.

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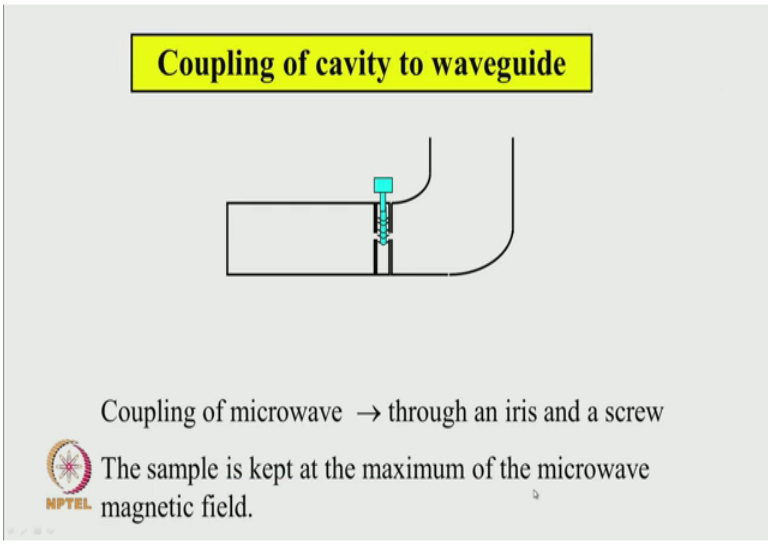

So, 2 designs are given here this is called rectangular cavity and a cylindrical cavity and then there is a hole kept here we call Iris hole and the wave guide can enter along the microwave to enter here through this hole, that is the way the wave guide is couple to the rest of the microwave circuit and easily one uses a screw here right.

By inserting a screw the appropriate depth one can cause a proper matching of the microwave radiation to the cavity as it is shown here this green object is the screw and you can see the hole through which the microwave can enter here.

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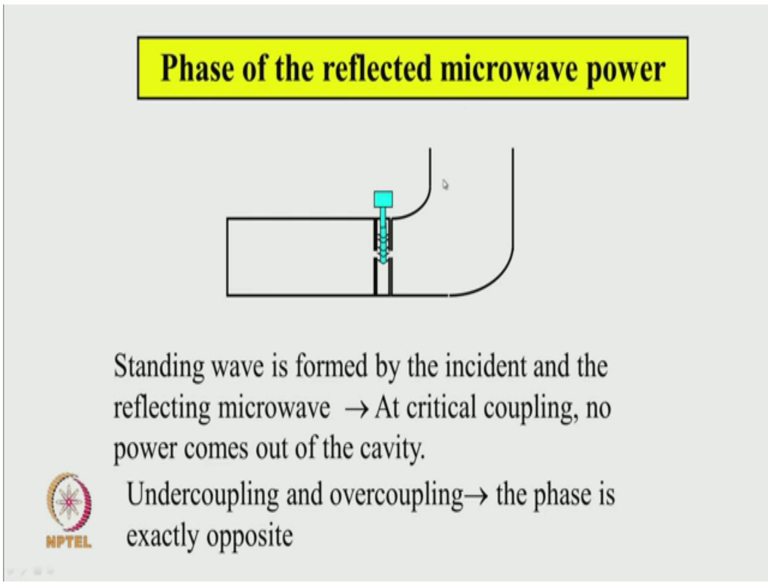

Now one can have a cavity which looks like this small hole here, another of small hole here and the radiation this wave guide radiation enters here goes through this and through this iris goes to the cavity and again goes out here, sample could be kept somewhere here this is called a transmission cavity and the cavity we have shown in this picture here is the radiation comes from here goes to this hole and then gets reflected to the back and then goes out again, this is called a reflection cavity.

So, will see that reflection cavity is a lot more useful cavity than this one as I have said earlier the sample must see the maximum of the microwave magnetic field and not the electric field and the way this cavity helps doing that is to form a sudden pattern of the radiation inside this and some places there will be electric field maximum and some other place there will be magnetic field maximum and that is called the mode of the cavity mode.

This mode will depend on the dimension of this cavity and although wavelength that enters here now to understand what a mode is it will be good to take a example of common microwave device that you almost all of us use and that is the microwave oven.

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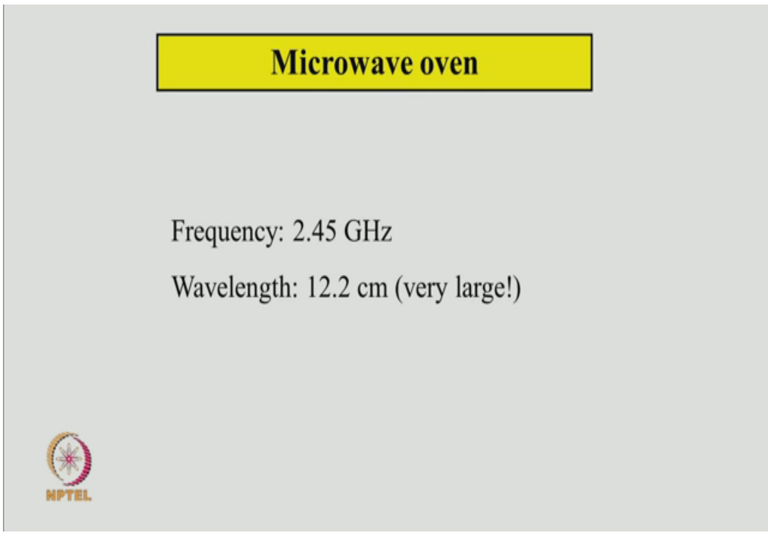

The microwave frequency used in a micro oven is 2.45 gigahertz and the corresponding wavelength is 12.2 centimeter approximately. So, you see this a really larger wavelength comparable to the food stuff that is used there and micro oven we cook food or we rather warm food by placing it in the box and that box is certain as a turn table, this gives moving it, the whole box is actually cavity that we have here.

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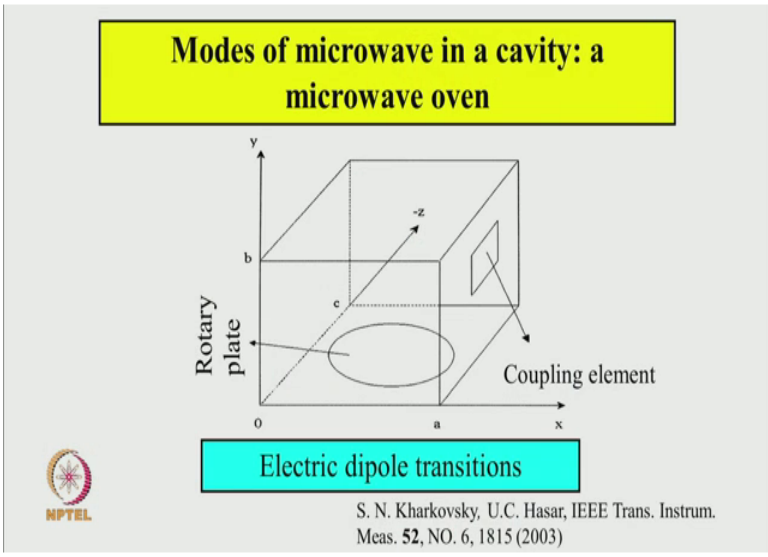

And how does it form a mode, here this is the rectangular box which is the microwave oven and if you see carefully usually at the top right corner there is a rectangular sort of element there through which the radiation from the microwave generator enters and it stays inside and this is a rotating plate now for cooking the food it is electric dipole transition that is used here that is most of the polar molecule the water for example, the most polar molecule that absorbs micro radiation undergoes rotational transition and then high rotational frequency it causes the heating, it is electric dipole transition.

So, here to find out what the electric field is maximum one can do a smaller experiment to remove the rotating plate that keep a very thin layer of let us say papad for example, or some thermal paper which changes it is color from white to black when it is hot and then run the micro oven for a sometime then what will happen because it is not turning wherever the electric field maximum at that place maximum heating will take place and the color of the paper will change or a papad may become charred. So, here the experiment which is done and reported in this paper given in this here.

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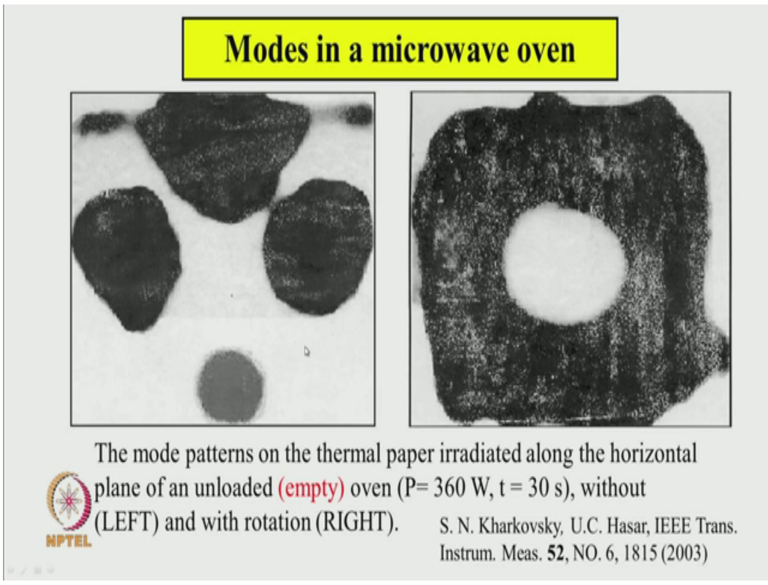

So, modes in a micro oven what is done here is that the turntable was removed and thermal paper escaped and a empty oven was around at 360 watt power for 30 seconds without the rotation and with rotation. Now here you see the with these 4 places maximum heating took place and no heating in this region see in other words the way the electric field was forming more inside the box is these 4 places the maximum electric field receivers there, that is also reason why it has to be rotated otherwise the food in this quite region will not get cooked, turntable job is to cook the food informally. So, when you turns this informally whole surface becomes hot, you can do the experiment very easily by using papad for example. Now this is an empty oven in other words in this language this is a empty cavity and shows the more pattern of electric field now if you put a sample here the sample is called load a 100 ml of water was kept here a load is written there.

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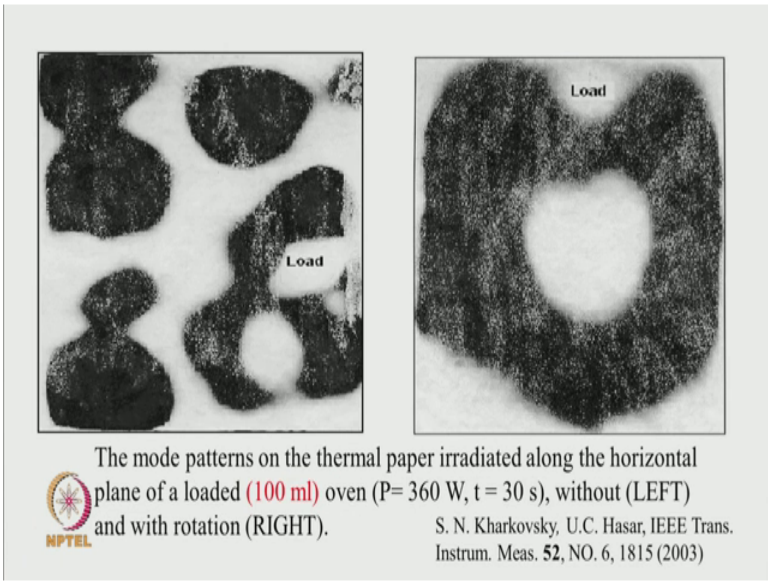

Here again the same experiment was done where the turntable was removed and you see that mode pattern has changed compare once again here empty cavity and this 4 regions has the maximum electric field intensity now just place a little bit of water here immediately the more pattern is changed. That is the important lesson for us that if you do anything to the cavity whenever you place the sample or put some sample to you or solvent this is going to disturb the cavity and change it is mode patterned, here after placing water again we turn the turntable and then see very inform late hits here, this shows the electric field forms sudden standing away pattern or a refluxing cavity this is very important.

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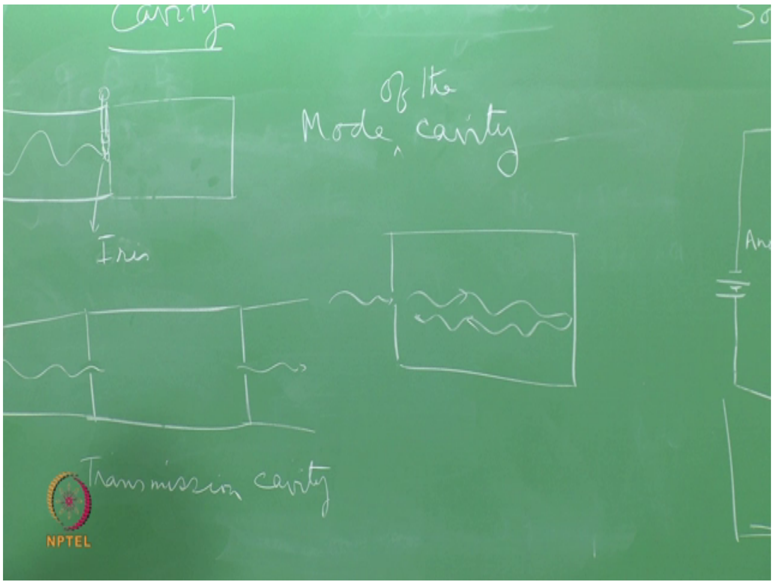

So, radiation enters here enters here and gets reflected this way, if the dimension has certain particular relationship to the wavelength of this radiation then it can forms standing away pattern see in that case the radiation will be stored inside and not come out of that not only that when the standing wave forms then depending upon the dimension of this certain places there will electric field which is maximum and other place magnetic field will be maximum.

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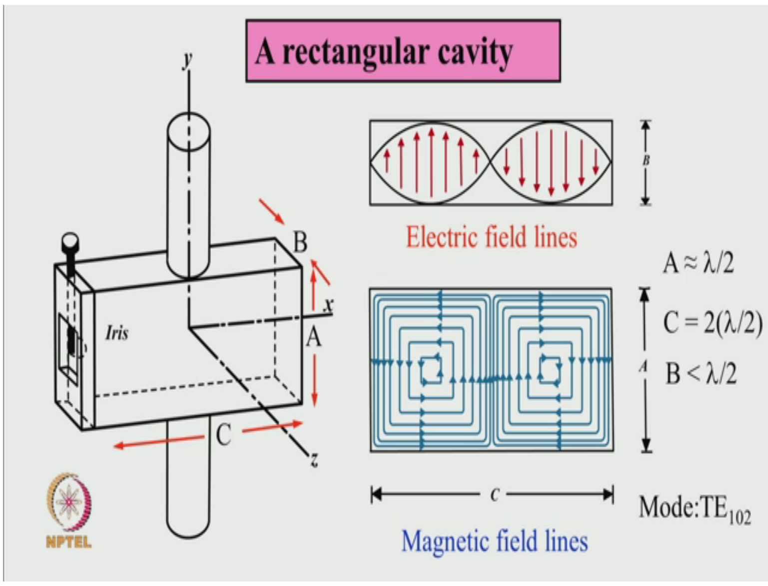

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Now, let us see what sort of more pattern this cavities have here it is a rectangular cavity dimension is given here then let us say a is the this border dimension of the waveguide.

This is the C B is the narrower dimension C is the longest dimension here and the iris hole and the coupling screw is shown on the left now for this electric waveguide radiation enters here gets reflected and comes out of this electric. If the wavelength has the certain relationship to the dimension here given by this let us say the dimension A this border surface is approximately equal to half of the wavelength and B is very narrow, it is less than half the wavelength, and C has the exactly twice the half wavelength in that case standing wave pattern will have this sort of mode electric field line shown here in red lines.

This will be forming the standing wave such that it will oscillate in this plane A B plane and value of the electric field is maximum here and here and minimum at the 2 surfaces and also in center of the cavity electric field is maximum. Similarly the magnetic field modes are given in the blue line magnetic field in intensity is maximum at the center also maximum in the wall and it is very small nearly 0 at the center here and the this center here, see if you now imagine this rectangular box that magnetic field has exactly maximum intensity here and the surface here and the surface there electric field has minimum intensity at the plane here and here and here. This particular mode you can see that how critical it is related to the wavelength of the microwave which you have working.

This mode is called T E 102 in this per lense of EPR spectrometer and T it stands for transverse electric radiation moving in this direction electric field is orthogonal to that that is oscillation of the electric field is perpendicular to the direction that is why it is called transverse electric and then one stands for that there how one half wavelength there this a dimension 0 half wavelength in B dimension, B dimension is so narrow that no half wavelength can fit here and C dimension has exactly twice the half wavelength, this rectangular cavity is called, therefore, transverse electric 102 mode.

Now you see how carefully this designed and we can easily figure out now where to place the sample we can place the sample right at the center of the cavity, in this 2 pipes here this can act as a sample holder right the center of the through the sample the electric field 0 and magnetic field maximum and that exactly what we need for magnetic dipole transition to take place.

So this is the placement for sample this sample is shown here this tube is here is a center similarly here the sample tube is here .

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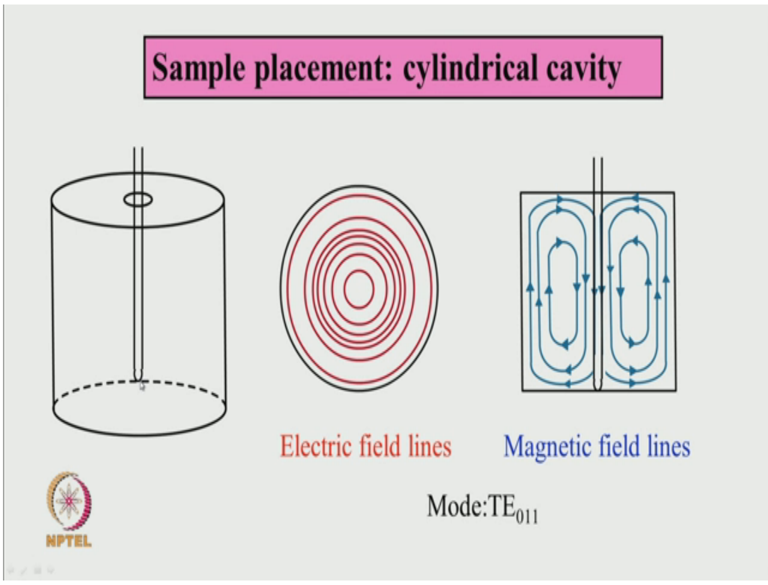

Other popular cavity is called a cylindrical cavity this is nothing, but a small cylinder now through which a radiation is couple through a one side iris here the electric field lines are circular in nature. So, here maximum electric field is approximately center of this and min minimum at the center and the magnetic field lines are shown in this dimension here is magnetic field lines are maximum at the center and this 2 walls and minimum at the here as well as here. Now this mode is called again T E because electric field lines are orthogonal to the direction of the propagation of the radiation transverse electric field and 0 1 stands for that there is 0 half wavelength along this circular direction and 1 half wavelength is this direction along the radius another half wavelength is along this particular direction.

The mode is T E 011, this is the cylindrical cavity here again the best place to place the sample particular experiment is the center of this because here magnetic field is maximum electric field is minimum, that is the way I have shown here sample placement is this center of the cylindrical cavity. So, both for rectical cavity or a cylindrical cavity only one particular frequency can form the standing wave inside this therefore, it cannot have a very well frequency EPR experiment. In fact, this is the single most important reason why EPR spectrometers are always constructed to work in a fixed frequency mode this is the reason, how will does a cavity store microwave inside there is a quantitative way of stating that in order to understand that let us guess.

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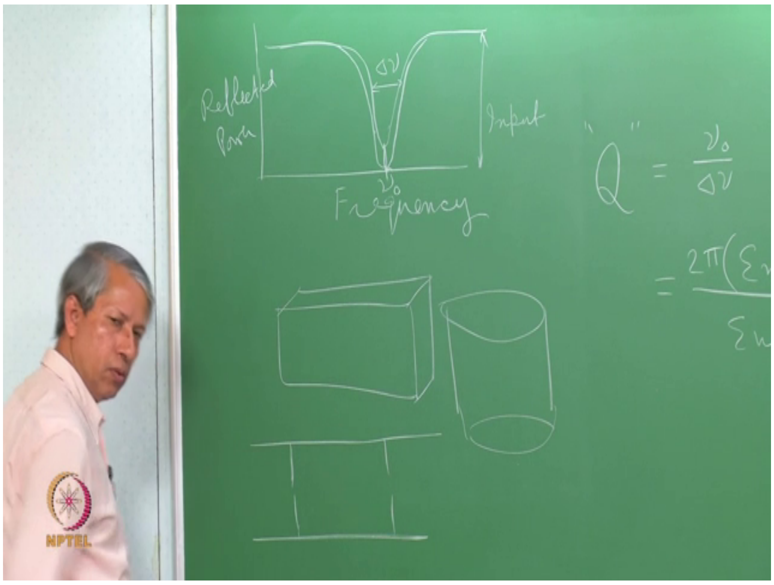

How the reflex from microwave form a cavity depends on the frequency of the microwave, this is the reflected power this cavity could be rectangular cavity or a cylindrical cavity. Let us say we have coupled the microwave and the frequency of the resonant frequency of the cavity and the microwave they are matching either here or here.

So, for that condition correction, let us say we have coupled the microwave to this cavity or this cavity and the frequency of the microwave matches with the characteristic frequency of the cavity, at that time the cavity suppose to store the microwave without reflection at least the reflection should be minimum. So, let us say at the characteristic frequency of the cavity mu 0 let us say this is the reflection here, as the frequency of the microwave changes either this way or that way power is going to reflected from the cavity. This will be somewhere here and here see if we keep imaging that as the radiation of the micro frequency is higher and higher from the characteristic frequency of the cavity the reflection will be more of course, we have to keep the input for the cavity constant, the shape of the curve will be something like this.

So, when the microwave frequency is very far from the cavity written frequency the power that is reflected will be totally the input power that goes inside, this is the input power totally power gets reflected. So, here the quality of the cavity or how well it stores the microwave inside it without reflection is a is measured in terms of the narrowness of this profile, see if I call this delta nu then this quality of this cavity is universally called the Q value Q stands for quality; obviously, is defined to be this nu 0 by delta nu.

So, with definition it is obvious that the narrower the cavity higher will be the Q value, the Q value is a quantitative measure of the quality of the cavity it shows how will the microwave power is stored how will it is stored, if it is narrower then the say this is better cavity why is that.

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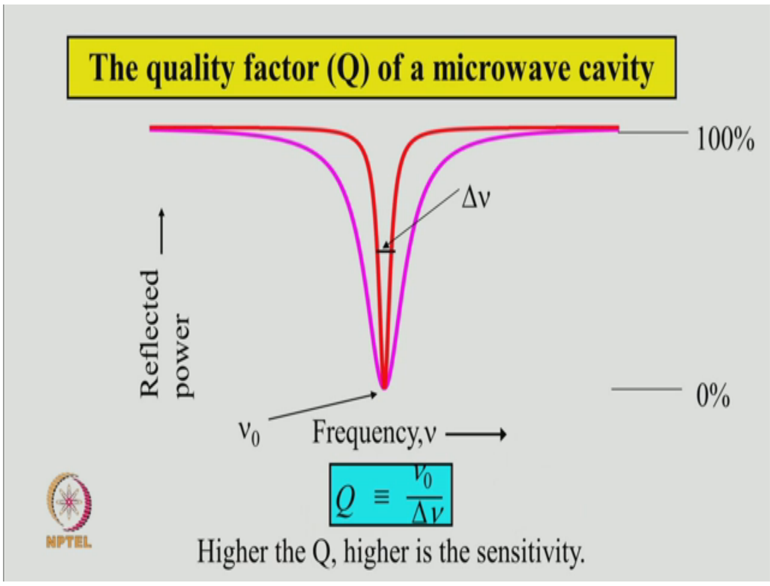

So, in this slide I have shown this reflection profile of a cavity for 2 different Q value, this shows the response of 2 different cavities the red one is sharper and the pink one is broader. So, delta nu for this is smaller than the pink one, as the Q is defined to be equal to nu 0 by delta nu this cavity with a red profile is sharper and higher is the Q higher is the sensitivity should be apparent from here. This is the place where the cavity is matched with the micro frequency, that let us say reflex is minimum 0 percent the maximum and this further will maximum away from the nu 0 now if there is any disturbance in the cavity or change in the in the characteristic property of the cavity then for small change this pink cavity for small change the reflection from the cavity will be much larger for the red profile than the pink profile.

Up to this for very small change in this frequency the red is going to reflect lot more than the pink one, any signal which depends on the reflection of the cavity will be more with the cavity has very sharper response, that way the sensitivity comes into the instrument the Q is also defined.

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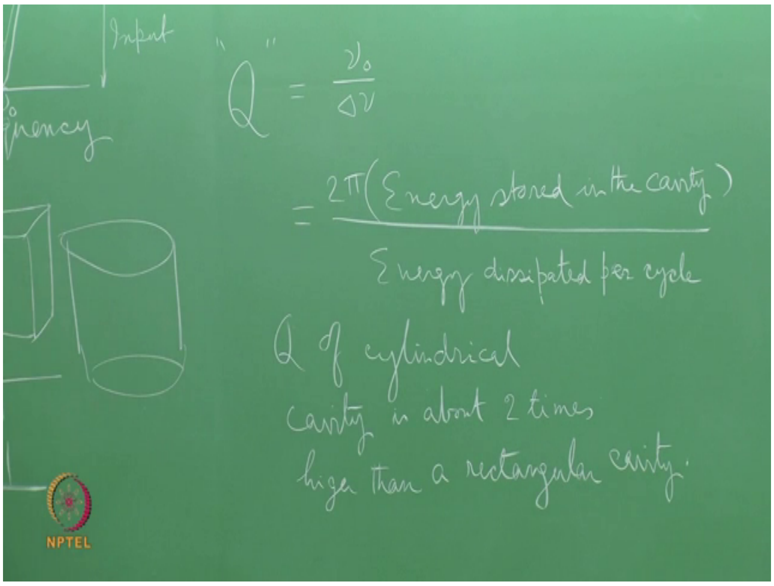

In this way that is how much power rather how much energy is stored in the cavity divided by energy dissipated per cycle, the higher the Q the lesser the amount of energy that is lost per cycle, it is stores energy much more efficiently if the Q is high. These 2 are actually equivalent definition; in a spectrometer the one which has a higher Q that cavity can store energy more efficiently. The spectrometer also becomes sensitive because any small disturbance in the cavity because of the absorption of microwave the reflection of the cavity will be correspondingly higher if the cavity is Q is also higher now here this 2 are reflection cavity and I also said earlier that transmission cavity. We are also used early it is by the Q of transmission cavities are much lower than Q one can get for in reflection cavity therefore, this is not a very sensitive cavity and therefore, these are not used anymore.

Reflection cavities can have much higher Q even between these 2 this is the rectical cavity and this is the cylindrical cavity, Q of cylindrical cavity is about 2 times higher than this one cavity is about 2 times higher than a rectangular cavity. The spectrometer that uses a cylindrical cavity will be about 2 times more sensitive than a spectrometer that uses a rectangular cavity. Let us summarize now what we have discussed in this class today we have discussed the following topics.

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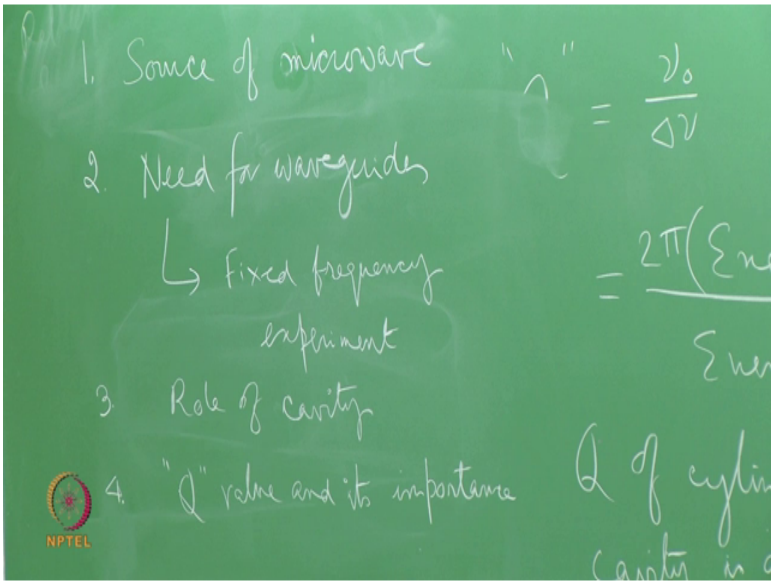

The source of microwave, need for waveguides and how it restricts the fixed frequency experiment, then we talked about the role of cavity and the and the Q value and it is importance will continue our discussion on the other components of an EPRspectrometer and see how at EPR spectrometer looks like afterwards in the subsequent lecture that is it.