

Infrared Spectroscopy for Pollution Monitoring
Prof. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science–Bangalore

Lecture-11
Interaction of electromagnetic radiation with matter

Greetings to you, we are starting our next session that is interaction of a matter with electromagnetic radiation. Yesterday we had talked a little bit about it and then we had discussed about the reflection of radiation also.

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When radiation crosses an interface between media differing in refractive index reflection always occurs. For a beam entering an interface at right angles the fraction reflected is given by,

$$\frac{I_r}{I_o} = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2}$$

where,
 I_o is intensity of the incident beam and
 I_r is the reflected intensity and
 n_1 & n_2 are the refractive indexes of the two media.

And then I had shown you this slide where the reflection laws are presented.

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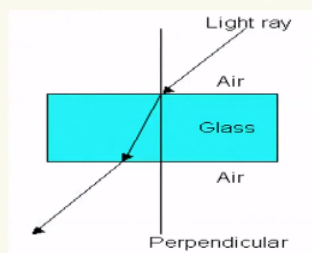
REFLECTION OF RADIATION

Mirrors reflect the radiation falling on them without any loss of the incident radiant power. Hence they are used as optical components of a spectrometer. Concave mirrors reflect the radiation as well as concentrate the reflected radiation at its focal point.

So, earlier I had explain to you that this is the equation governing the reflection, so when radiation crosses an interface between media in different reflect having different refractive index, reflection always occurs for abeam entering an interface at right angles the refraction reflected. We normally give it as a ratio, that is reflected ratio, reflected intensity of the reflected radiation and I_0 is the intensity of the incident radiation. The ratio is given by $\frac{n_2 - n_1}{n_2 + n_1}$ whole square where n_1 and n_2 are the refractive indexes of the 2 media.

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REFRACTION PHENOMENA

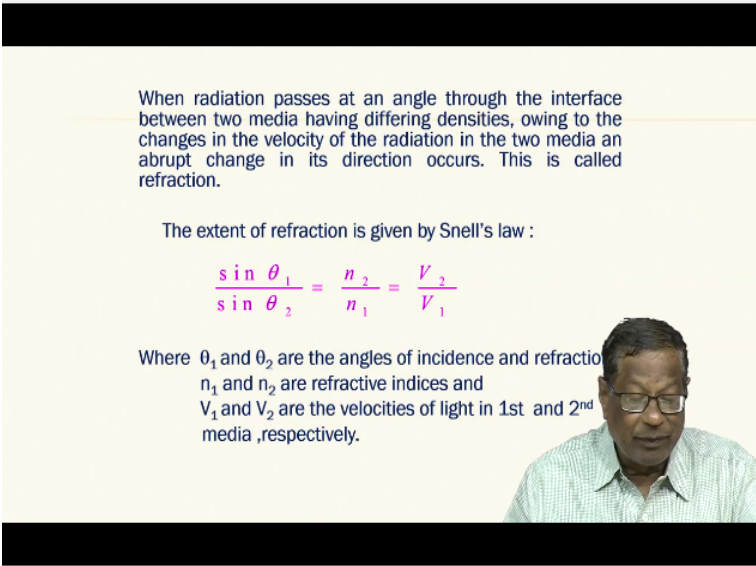


So, this is the figure I had shown you yesterday also you can imagine that the light ray is coming at slanted angle which is not exactly perpendicular to the media. I have shown you media is a glass here and it comes from the air a passes through the glass and exists at the other end. But

you can see that it bends a little bit depending upon the refractive index of the sample. So, whenever we design a spectrophotometer or spectrometer we have to take care of all these aberrations.

And then fix the optical diagram, so that the radiation from the source reaches the detector properly. So, that is why we are doing all these kind of exercises, so that this is refraction phenomena I have already this is the refraction phenomena.

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When radiation passes at an angle through the interface between two media having differing densities, owing to the changes in the velocity of the radiation in the two media an abrupt change in its direction occurs. This is called refraction.

The extent of refraction is given by Snell's law :

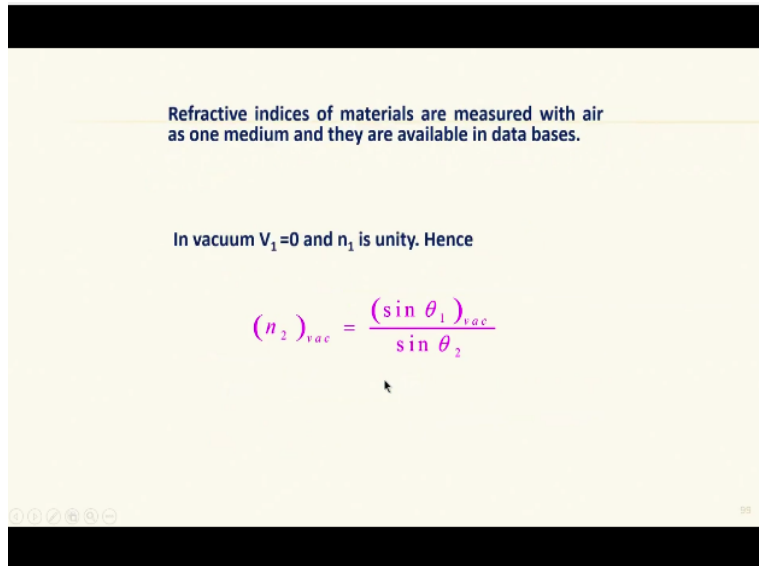
$$\frac{\sin \theta_1}{\sin \theta_2} = \frac{n_2}{n_1} = \frac{V_2}{V_1}$$

Where θ_1 and θ_2 are the angles of incidence and refraction, n_1 and n_2 are refractive indices and V_1 and V_2 are the velocities of light in 1st and 2nd media, respectively.

And the refraction phenomena when you can be defined has when the radiation passes at an angle through the interface between 2 media having different densities itself, owing to the changes in the velocity of the radiation in the 2 media and abrupt change in its direction occurs. So this is called refraction, so the extent of refraction is given by Snell's law that is $\sin \theta_1 / \sin \theta_2$ is equal to n_2 / n_1 that is also reflected in the velocities of the 2 beams a radiation in the 2 media.

So we have here $\sin \theta_1 / \sin \theta_2$ is equal to n_2 / n_1 that is also equal to V_2 / V_1 where θ_1 and θ_2 are the angles of incidence and refraction, n_1 and n_2 are the refractive indices, V_1 and V_2 are the velocities of the light in the first and second media respectively okay.

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Now refractive indices of materials would be different because by nature every material is different. So, refractive index of air is different and some other gases are different, glasses different, quartz is different, water is different like that there are several materials which are having different refractive indices. But normally the measurement is done with air as 1 medium and the other has the test medium.

So, the refractive indices of different materials as compared with the air are available in the databases. So whenever we want to design a prism or something like that. We had to see what are the refractive indices of the media whether it is glass or quartz or something like that. So in vacuum velocity is change in velocity that is velocity 0 and n_1 is unity. So, we can write instead of n_1/n_2 we can write n_2 vacuum is equal to $\sin \theta_1$ vacuum / $\sin \theta_2$.

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SCATTERING OF RADIATION

Momentary absorption of radiant energy by atoms, ions or molecules followed by reemission of the radiation in all directions is known as scattering. Particles having comparable dimensions to that of the incident radiation removes most of the reemitted radiation by destructive interference except those traveling in the original direction. A very small fraction of the radiation is transmitted at all angles from the original path and its intensity increases with particle size.

Scattering by molecules or aggregates having smaller dimensions than the incident radiation is called Rayleigh scattering.



So such a calculations are possible whenever we want to design optical table for the infrared radiation to pass through the different parts of the instrument. Then we should know a little bit about scattering of radiation, so here momentary absorption of radiant energy by the atoms, ions and molecules normally they are followed by reemission of the radiation in all directions, that is known as scattering, suppose I have a small particle radiation comes.

It will scatter the radiation it is the very well known phenomena and experience by all, for example in the room where you are sitting if there is a light source it just does not travel in straight line and leave the remaining parts dark is not. So, the remaining parts are also illuminated because the incident radiation falls on the particulates air etc., and then gets reflected in different directions not necessarily in the direction of propagation.

So, that is known as scattering and what makes the scattering phenomena universal because it is observed whenever there are atoms, whenever ions and whenever there are molecules in these things are always there in the air. And then there will be particulates in the air, so all these things when they fall on the particles reemission of the radiation occurs in all directions. And particles having comparable dimension to that of the incident radiation see here we are assuming that the wavelength that the electromagnetic radiation is like a particle Corpuscular theory.

And a like photon the size of the photon having a comparable dimension to the particles present in the media then it removes most of the reemitted radiation by destructive interference except those travelling in the original direction. So a very small fraction of the radiation is transmitted at all angles from the original path and its intensity increases with the particle size. So, what we are talking here is if the particles are very small of the size comparable the scattering will be minimum that is the bottom line.

So scattering by molecules are aggregates having still smaller dimensions than the incident radiation is called as Rayleigh scattering. There are 3 different kinds particle is having equal almost same size and particle is having smaller size than the electromagnetic radiation that is the amplitude. We are talking about the amplitude of electromagnetic radiation, the amplitude is measured in distance, so the particle size also can be measured in distance.

So, we are talking about the interaction of equal, equal in size particles, smaller particles and bigger particles. So, scattering by molecules are aggregates having smaller dimension is called as Rayleigh scattering okay. Then larger molecules scatter radiations in different quantities again but that 2 in different directions this is called as Mie scattering and when the scattered radiation is also cotised to some extent like those occurring in the vibrational in the level or rotational energy levels etc. The transitions in the molecules as a consequence of polarization process it is called Raman's scattering.

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Larger molecules scatter radiations in different quantities in different directions. This is called as Mie Scattering.

When the scattered radiation is quantized like those occurring in vibrational energy level transitions in molecules as a consequence of polarization process, it is called as Raman Scattering.

This slide contains two paragraphs of text. The first paragraph defines Mie Scattering as the scattering of radiation by larger molecules in different directions and quantities. The second paragraph defines Raman Scattering as the scattering of radiation that is quantized due to vibrational energy level transitions in molecules, which is a result of a polarization process.

So, this is the Raman's scattering in terms of contestation which one the Nobel Prize for Professor Raman in 1931. So, Raman's scattering is also a very typical of several materials and we need to know now-a-days there is a separate branch of science for the identification differentiation of particles and chemicals etc. by Raman's spectral.

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POLARIZATION OF RADIATION

Ordinary radiation consists of a bundle of electromagnetic waves in which vibrations are equally distributed among a huge number of planes centered along the path of the beam.

Viewed end on it looks like an infinite set of electric vectors fluctuating from zero to a maximum amplitude A .

This slide features a title 'POLARIZATION OF RADIATION' in green. Below the title, there are two paragraphs of text. The first paragraph describes ordinary radiation as a bundle of electromagnetic waves with vibrations equally distributed among many planes along the beam's path. The second paragraph describes the appearance of this radiation when viewed from the end, comparing it to an infinite set of electric vectors fluctuating between zero and a maximum amplitude A . A small video inset of a man speaking is visible in the bottom right corner of the slide.

So, that we are not going to study Raman's spectra right now or not in this course anyway. And but it is good to know that the radiation scattering is a phenomena occurring everywhere it occurs inside the instrument. And this scattering is of no use in general because the scattered light does not reach the detectors 100%. So in their instrument we want the scattering to be minimum.

So, the optical path should be very precise and there should not be many particles in between the source and the detector that is air particles and things like that+we also want the if they are there it should be minimum usually most of the instruments do have about 1 to 5% of scattering whatever you do however dark system you make still there will be a you cannot make an instrument without joints.

So, there will be some parts to be joint together etc. and if you observe any machine you will see that it is composed of several components and which are joint together by either screws or press fit or something like that. So, they cannot altogether stop these scattering of the radiation and instruments are no exception to this rule. So, it is not possible humanly to eliminate scattering totally but it is possible to minimize.

We can paint the inside of a spectrophotometer black, so that it absorbs all other radiations etc., but the best one can achieve is about no 1% of scattering, less than that it makes the instrument very costly may not be worth it. But more than that means there is some problem with respect to the sensitivity that is the minimum quantity that can be detected or determined in presence of high scattering that is the little bit of a problem anyway.

So now having no one know so much about the scattering we are going to talk about polarization of radiation. So, polarization I think many of us know we have seen the effect of polarization in our day to day life whenever you see 2 pictures imposed on one another especially in TVs and movie halls. If you are looking at the screen you will that 1 picture is imposed on another quite often.

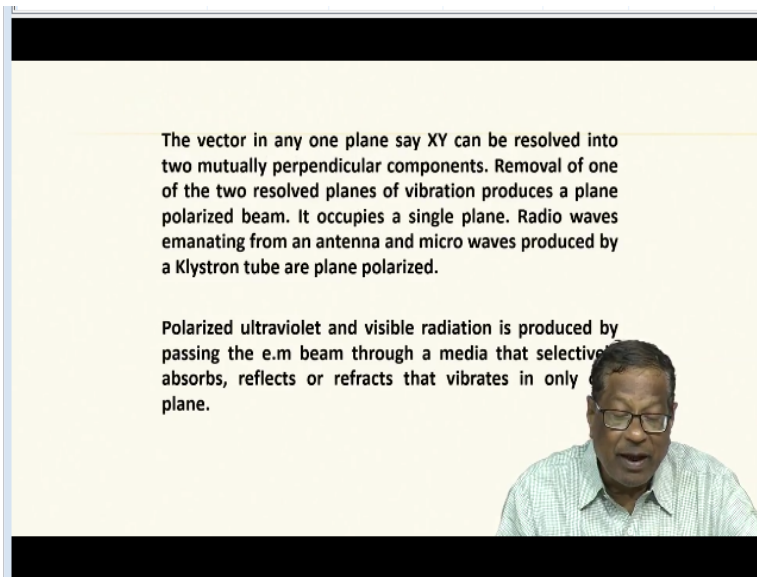
So that is all effect of polarization, so ordinary radiation usually consist of electromagnetic waves in which vibrations are equally distributed among a huge number of planes centered along the path of the beam. Here what I am trying to tell you is explain to you the phenomenon of polarization, so what I am trying to tell you is ordinary radiation. It consist of bundle of electromagnetic waves in which vibrations are there in all sides of the propagation okay.

So, there are huge number of planes centered along the path of the beam in general. So, 1 is electromagnetic wave, another is you know electric field 1 is magnetic field like that even those fields there will be slight variations and there will be a bundle of electromagnetic field around the propagation path of the radiation, that is what I am trying to tell you. So, viewed end on how does it look like then. It looks like a infinite set of electric vectors fluctuating from 0 to a maximum amplitude that is we can denote it by A.

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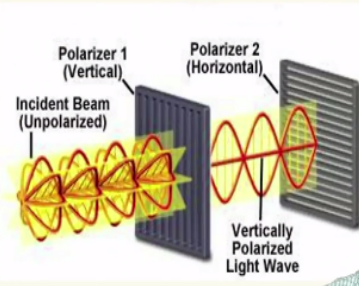
The vector in any one plane say XY can be resolved into two mutually perpendicular components. Removal of one of the two resolved planes of vibration produces a plane polarized beam. It occupies a single plane. Radio waves emanating from an antenna and micro waves produced by a Klystron tube are plane polarized.

Polarized ultraviolet and visible radiation is produced by passing the e.m beam through a media that selectively absorbs, reflects or refracts that vibrates in only one plane.



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POLARIZATION OF LIGHT WAVES

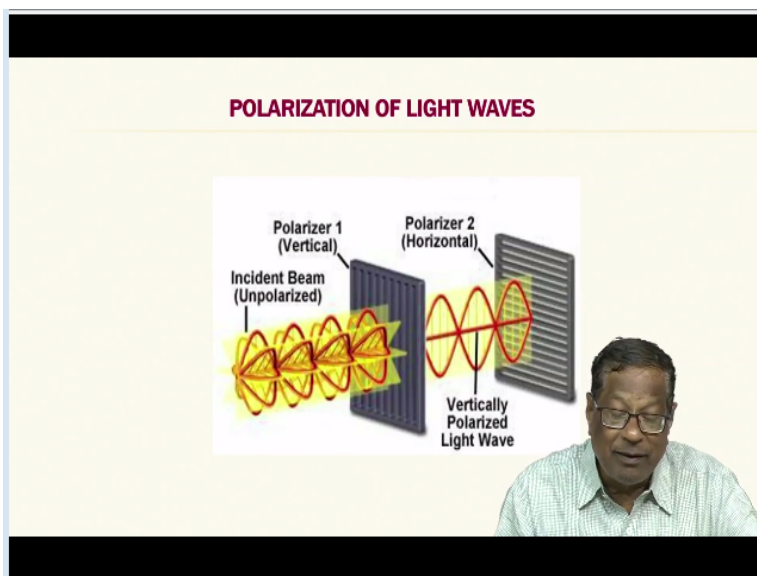


Incident Beam (Unpolarized)

Polarizer 1 (Vertical)

Polarizer 2 (Horizontal)

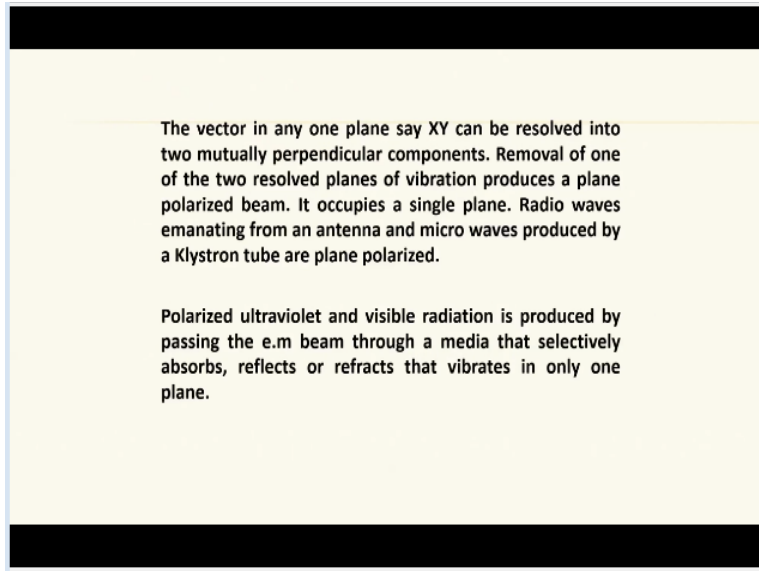
Vertically Polarized Light Wave



And this is how it looks okay, so here I have an incident beam unpolarized on the left side. So, you can see here there are number of planes amplitudes but all those amplitudes are not only

perpendicular to the plane of propagation. But they are also oriented in different planes, so this is what we normally see in unpolarized light. So, polarization of a, so you said there are number of planes that are present along electric field and magnetic field oriented in different directions in the space along the propagation field okay.

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So, the vector in any 1 plane say xy can be resolved into 2 mutually perpendicular components we have already seen that. So, removal of 1 of the resolved planes of vibration produces the plane polarized beam that means in general there are sort of you know when the propagation is going on like this I have the amplitude, electric field as well as magnetic field suppose I remove the electric field.

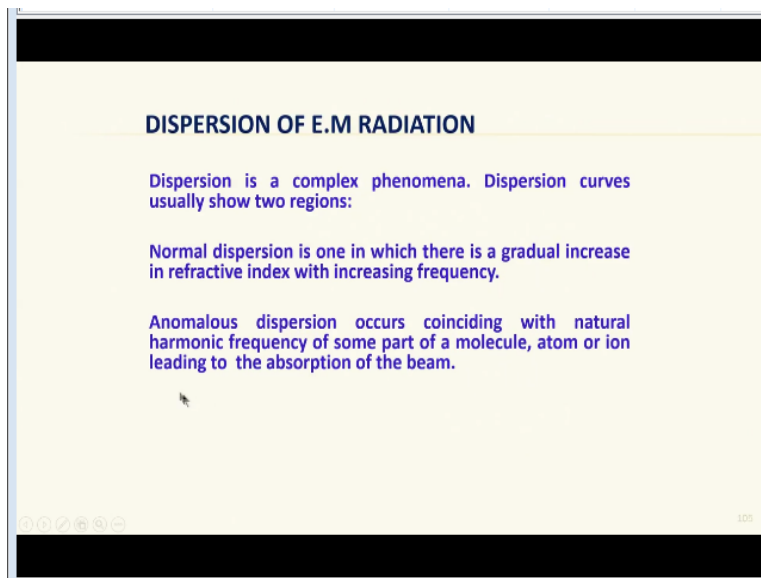
Then what I have here is what comes out I put a barrier to stop the electric field to come from coming and then only the magnetic field will be there oriented parallel to the propagation of incident by a beam. Similarly if I remove the magnetic field there will be only vertical propagation. So, that means the radiation that comes out after the interference will be more disciplined we can say.

So, polarized they all occupy why a single plane and radio waves emanating from an antenna and micro waves produced by a klystron tube are usually plane polarized. If you wish to more about it you can take a look at how the antenna, radio waves and other things are emanating from a

radio station etc. The information is available in the YouTube or Google or whatever it is, so polarized ultra violet and visible radiation is normally produce by passing e.m beam through a media that selectively absorbs, reflects or refracts refraction that vibrates in only 1 plane.

So, that is the how we understand, so here I do this I have a barrier here to stop all these Happ hazard planes. And then vertical barrier I have introduce, so I am getting only 1 beam horizontal. So, this is vertically polarized light beam and depends upon your perception okay vertically or horizontally how you look at it.

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And then now I want to talk to you about dispersion but dispersion is little bit of a complex phenomena dispersion curves usually show 2 regions. One is normal dispersion in which there is gradual increase I have discuss this earlier also a little bit okay. So, anomalous dispersion occurs coinciding with natural harmonic frequency of some part of a molecule that means the dispersion curve will not be changing uniformly there will be abrupt changes that is what anomalous dispersion occurs.

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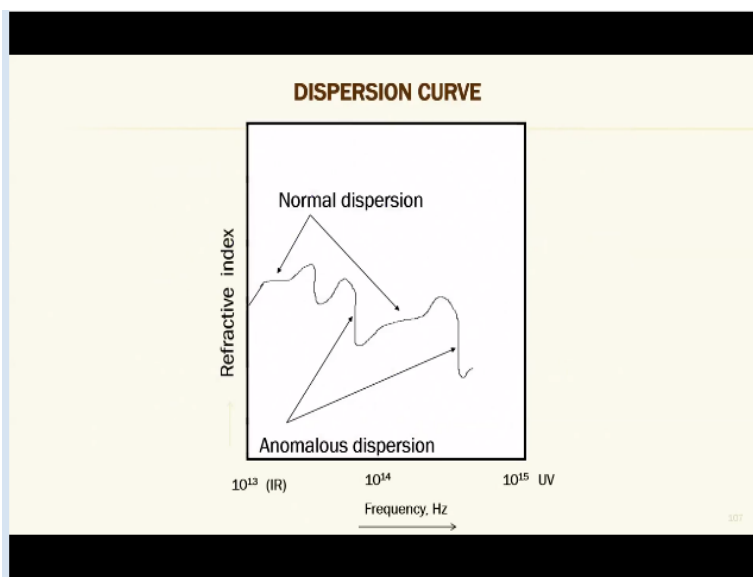
In spectroscopy, dispersion curves are important for optical components such as lenses. Most suitable components for the manufacture of lenses are those in which refractive index should be high and constant. This results in reduced chromatic aberrations.

For the fabrication of prisms refractive index should be large but also highly frequency dependent.

So, the in spectroscopy we want dispersion curves to be sort of you know ordered and disciplined. We want uniform change in the dispersion instead of abrupt changes, so dispersion curves are important for optical components such as lenses or even mirrors. And then most suitable components for the manufacture of lenses are those in which refractive index should be very high and constant also throughout the media.

So this results in reduced chromatic abrasions, so the fabrication of prisms refractive index should be as large as possible. But also it is normally our experience is it is frequency dependent.

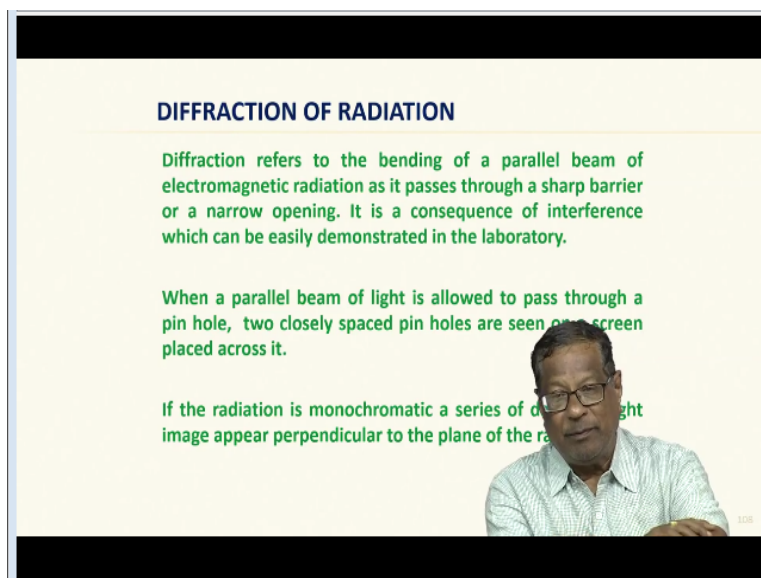
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So, this is the figure of dispersion for quartz and you can see that here I have plotted frequency here 10 rise to 13, 14 and 15. This is the refractive index but what is coming out these if it is this is all normal dispersion but anomalous dispersion is here see it is keeps on gradually increasing okay. And then it keeps on gradually decreasing, here the slope is different okay these things should not be there as for as possible okay.

So, this is known as anomalous dispersion because if the material is of uniform dispersion it should be just like this or it should keep on increasing depending on the thickness.

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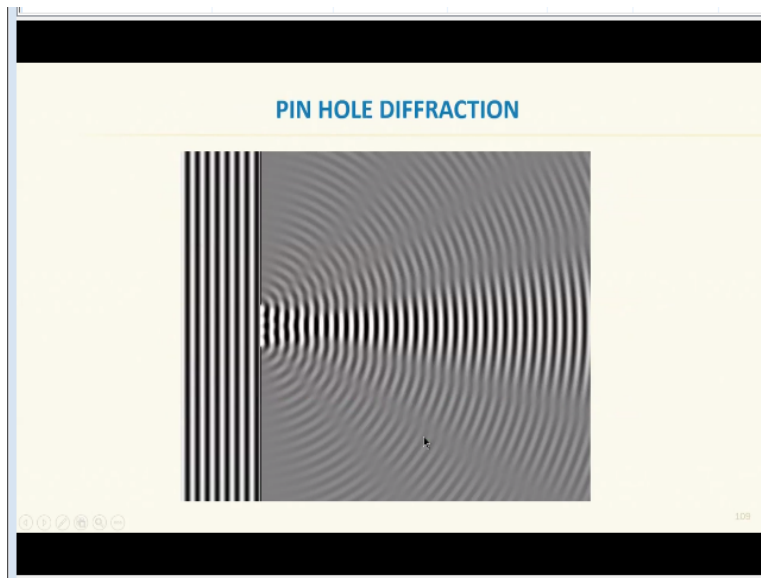
So, another phenomena that you should know about the interaction is diffraction interaction of e.m radiation with matter. So, diffraction refers to the bending of the parallel beam of electromagnetic radiation as it passes through a sharp barrier or a narrow opening. It is a consequence of interference which can be demonstrated in the laboratory it can be destructive it can be constructive interference also.

So, what is important is when a parallel beam of radiation like this falls and allow to pass through a small pin hole 2 closely spaced pin holes I play a make it in on the screen allow them to pass through, so then on the screen suppose I place a screen on the back side of the pin hole what do I see, I see dark and bright stripes. So, if the radiation is monochromatic that is having a

single wavelength all the radiation should have a single wavelength that is known as monochromatic radiation.

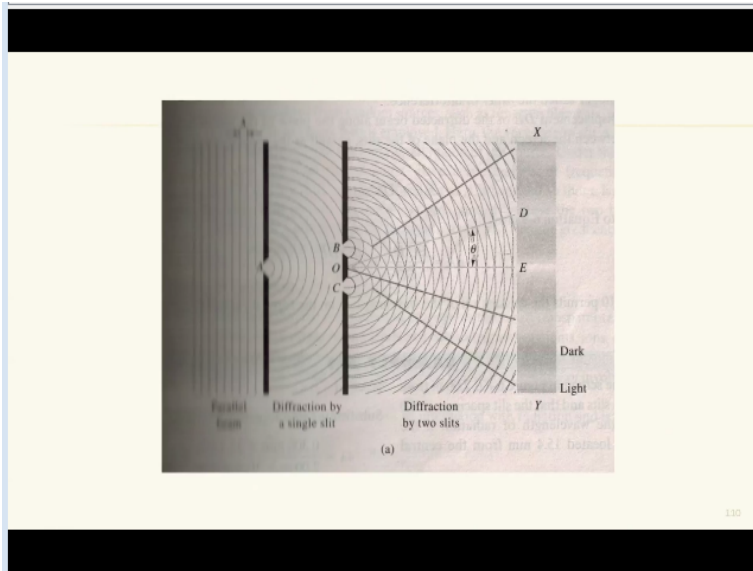
So monochromatic radiation if I use a series of dark and light images appear perpendicular to the plane of radiation.

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I will show you the figure here like this, this is a pin hole here. This is a screen radiation is coming out like this. And then I have this is the media the white lines you see on the left side of this figure is the media and the radiation comes out like this. But what you see on the screen after this pin hole is you will see bright patch small dark patch bright patch small like this they are all differing in intensity this is known as pin hole diffraction okay.

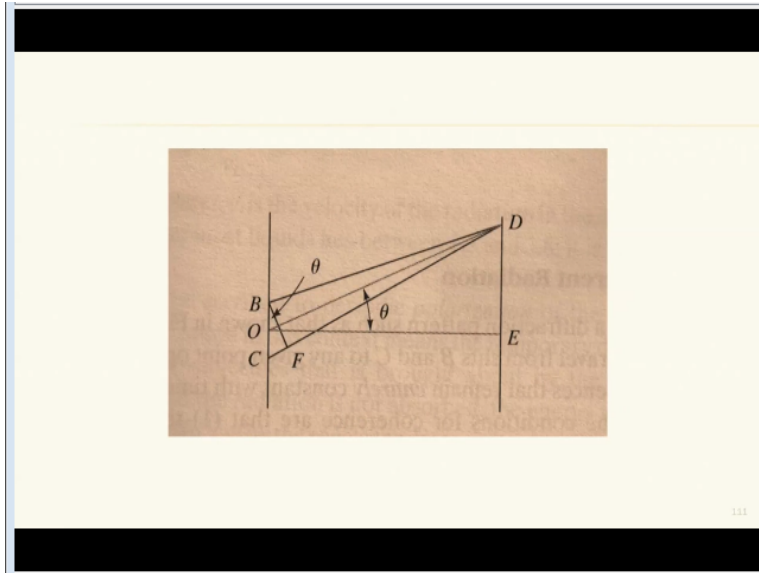
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Now if I have 2 pin holes like this here I have seen B, O, C 2 pin holes I have seen one is B, another is C, O is the midpoint what I see here is a number of crisscrossed interaction of the wave beams okay. And here I have on the left side the parallel beam, this is the parallel beam and diffraction by single slit will be like this dark patch white patch dark patch white patch, but if I do it with the 2's pin holes.

I get to see a series of interactions and if I catch it on the photographic plate. I see you can see I have shown it here that is X, D, E and then Y, this patch this is something like a photographic plate you can see dark patch, white patch, dark patch, white patch like that it will there will be a series of dark and white patches. You will be seeing this is the phenomenon of diffraction okay.

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Now we can show that this phenomenon of diffraction there will be the distance between bright and dark patches can be calculated depending upon the incident radiation as well as the distance between the 2 pin holes okay. So I will not going to details of this but you can see these things in (()) (24:26) also. You will see this phenomenon explained very nicely okay.

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In the above figure it can be shown that

$$\overline{CF} = \overline{BC} \sin \theta$$

For two beams to be in phase at D, it is necessary that \overline{CF} should correspond to the wavelength of the radiation. Hence

Reinforcement also occur at $2\lambda, 3\lambda$ etc. Hence,

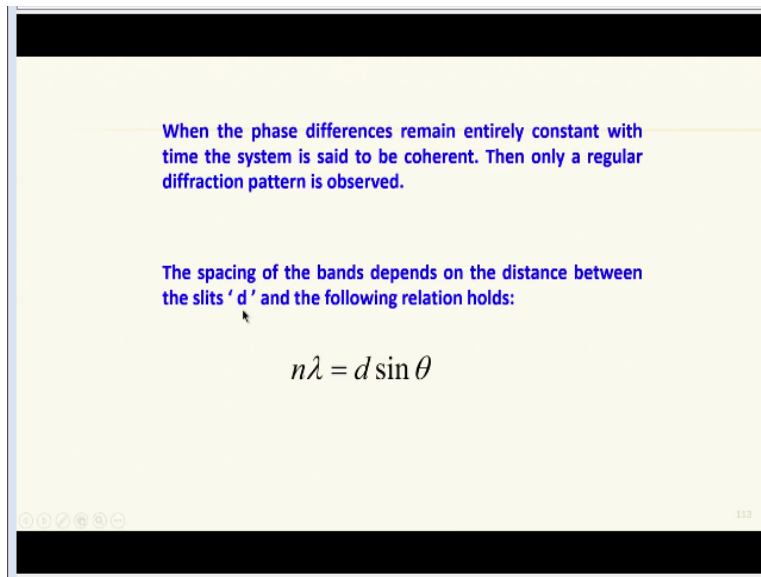
$$n\lambda = \overline{BC} \sin \theta$$

where n is an integer called the order of the interference.

Now I can show you that the in previous figure the distance between the 2 fringes can be I can show that C of is you call to $\overline{BC} \sin \theta$ for 2 beams to be in phase. We need to have this and reinforcement occurs at $2\lambda, 3\lambda$ etc., hence $n\lambda = \overline{BC} \sin \theta$ where n is the integer called the order of interference. So, I can except number of interference fringes.

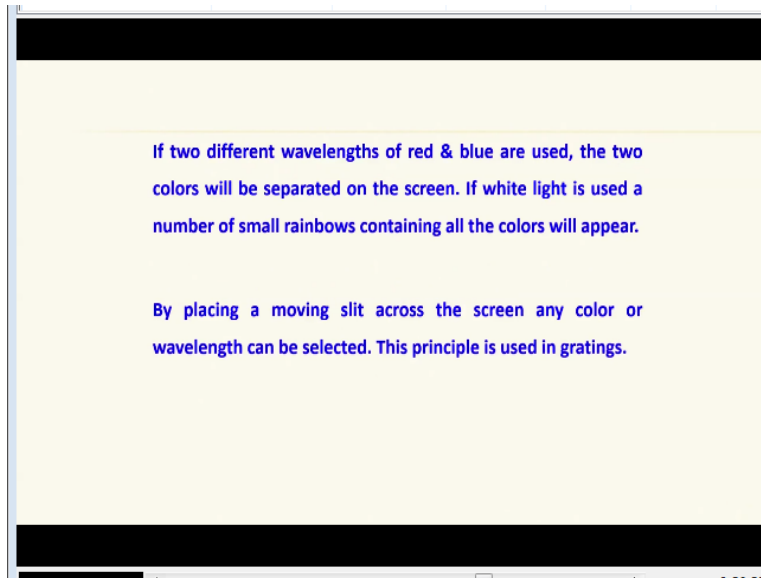
So, $n=, n+1, 2, 3, 4$ etc., so depending upon the number of pin holes and other things I have I get different construction constructive and destructive patterns. So when the phase difference is remain entirely constant which time the system is said to be coherent. You should remember this, so then only a regular diffraction pattern can be obtained. So what about the spacing then, the spacing of the bands depends upon the distance upon the distance between the slits that is denoted by d .

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And this following relation holds to determine the spacing between the 2 bands that is $n\lambda$ is equal to $d \sin \theta$, n is the order λ is the wavelength. These the distance between the 2 spacing and θ is the angle of incidence okay.

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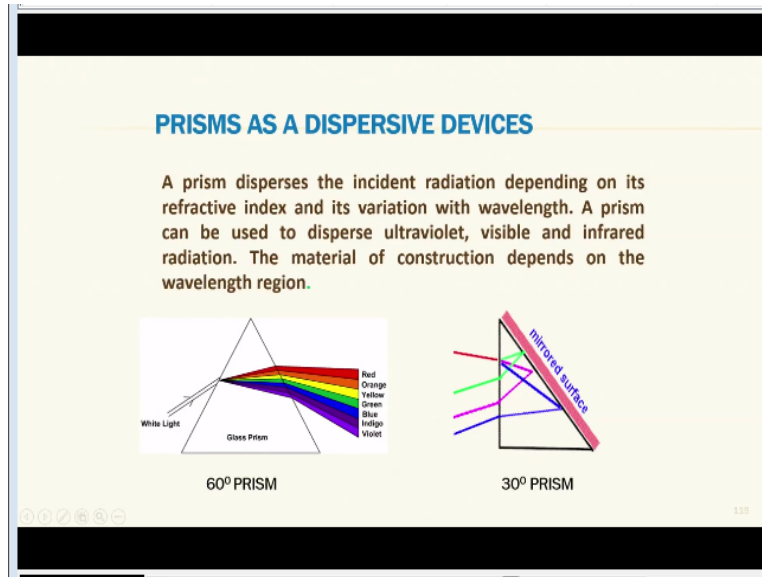
So, if 2 different wavelengths I use for example 1 red light and 1 blue light the 2 colors will be separated on the screen that is the beauty. You can see both blue and red patches on the screen, so but if I use a white light a number of small rainbows are containing all the colors fill out appears. So by placing a moving slit across the screen I can have any color or wavelength selected, this is the principle used in gratings.

Because in any spectroscopic technique what I need is an electromagnetic radiation of a specific wavelength. So, this specific wavelength how do I select, for example I have a source, source means a lamp it gives all kinds of wavelengths corresponding to infrared radiation or spectroscopic radiation. But I need to when I want to scan I need to have only 1 wavelength leaving stopping all other wavelengths reaching the sample.

So how do I select from a given source the correct wavelength which needs to be pass through the sample, that is done by gratings okay. So, what I do is I have show already shown you the picture that is this one, so here I have see I have shown you that you can get different colors. So, if I put my detector here it will detect only the radiation coming in this range, if I put a detector here.

For example it will show radiation coming through this that means I can choose different wavelengths from a diffraction grating to cover the entire range of the electromagnetic spectrum corresponding to infra red spectroscopy or this thing.

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So, essentially it works like this only for example here I have shown you a prism and here white light comes and then all other colors get separated. Because of the refractive index I put a screen here and if I put a hole here I will get red. If I put it here I will get orange, if I do it there I will get yellow, I put a hole here I will get blue color like that I can choose any color that comes out of the prism exactly same thing happens when I am using grating.

But in grating what happens is the wavelengths are more precise than the prisms, so we will see about gratings how they are made it certain some other contacts later. But essentially gratings and prisms do the same job okay. They separate the different wavelengths of the incident radiation and by placing a prism I separate and then I put a mechanical hole in front of the separate and radiation and pick up the exact wavelength whatever I need or I can make the slit move from one end to the other end.

And then scan the whole lot, so I have a choice of using a prism or a grating in a given instrument okay. So, then how does the prism work prism also works on the same principle. I have a prism here in this slide you can see this it disperses the incident radiation depending on its

refractive index and its variation with wavelength okay. So, that is the principle function of the prism, so a prism can be used to disperse I can disperse ultraviolet rays.

I can disperse visible rays, I can disperse infra red several other things also. So, to disperse these things I can use a prism or grating okay. Now the material of construction which material I should take glass prism quartz prism or polished iron prism. You know there are many prism, prism materials which have different characteristics, so the material of construction depends upon the wavelength region which we want to select.

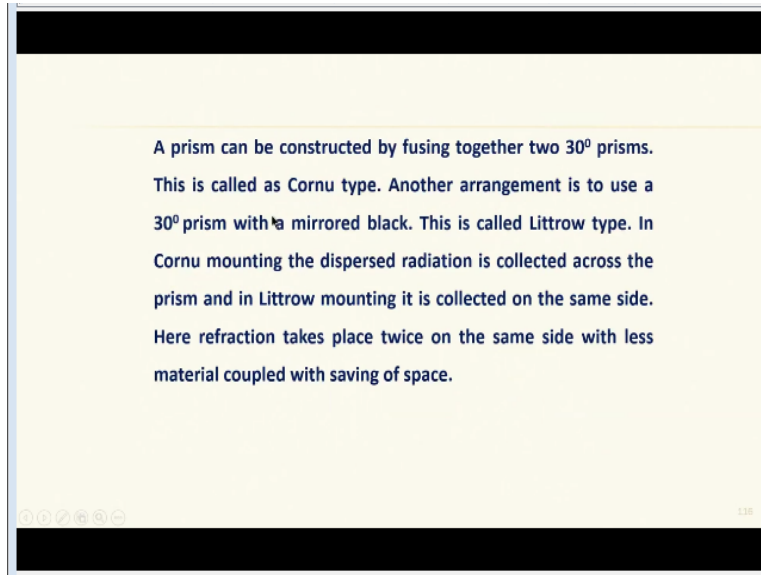
So here I am showing you 2 types of arrangement one is a prism with this is a 60 degree angle let us say. If this is a sort of isosceles triangle, so this is 60, this is 60, this is 60 okay all the 3 angles. And a prism is made like this and inside white radiation comes here then it separates into different materials, the extent of separation depends upon the material as well as its refractive index and I get the things like this here it is 60 degrees.

Now what I am going to do is another way that is I cut this into 2 parts this prism. So here I have cut and take an only one part. But I am going to put a mirror here okay that is what I have shown on the right side, so this is known as 30 degrees prism. Because if I cut this angle into 2 I get 30 degrees and then now I have a half prism in my hand. In this half prism the one part is rectangular remaining part is just like what it was earlier in this arrangement.

But I have a mirror edit here, so what happens any radiation that comes in goes here it is the mirror surface it cannot pass through it is reflected back and comes out on the same side, so you can see the difference between these 2 that is if I use an ordinary prism its 60 degree apex angle. I can get this same separation okay, on the other side of the light that comes that is coming in, it comes in at this angle.

But I on this side but my radiation collection should be on the other side here if I use only 30 degree prism 30 degrees apex angle. And mirror it on the other side the radiation will come here, go here travels the same path that means the distance travelled will be exactly same as this. If I mirror the one side, so this is no there are 2 different types of arrangements.

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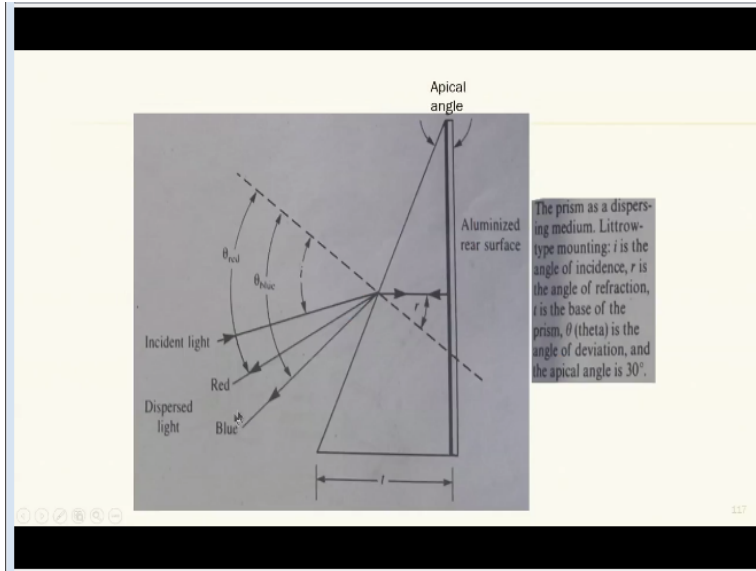


One is I can take two 30 degrees prisms if I take one more and fuse it here, I get 60 degree apex angle. So, a prism can be constructed by fusing two 30 degree prisms, this is called as cornu type, so try to remember this is cornu 60 degree prism is cornu type. And 30 degree prism is Littrow type another arrangement is to use 30 degrees prism mirrored black. This is called a Littrow type in cornu mounting the disperse radiation is collected across the prism.

And in Littrow mounting it is collected on the same side okay. So the only difference between the 2 cornu mounting and the Littrow mounting. So, in actual instrument in Littrow mounting refraction takes place twice on the same side with less material coupled with the saving of space. So in most of the analytical equipments or infrared spectrometers what I have is if you want to make the instruments smaller we would like it to be sort of Littrow mounting.

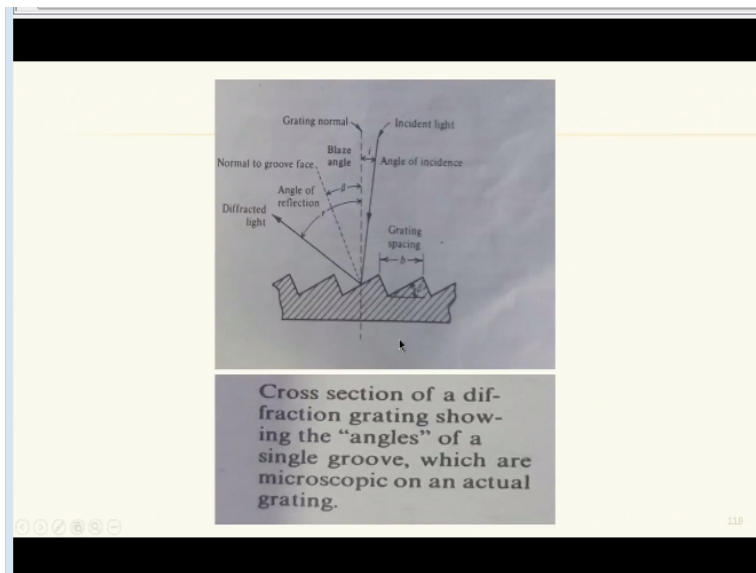
But if the instrument earlier in Russian models etc., instruments used to be huge because they will use bigger prisms and things like that and every instrument use to be taller and bigger than a human size. But now-a day's thanks to technology all these things have become table top, bench top, portable that is beauty of the instrument.

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So, this is another way of looking at the apical angle and this is the Littrow mountain. We can see that the radiation comes in and heats here and comes back and it gives you different red, blue like that different radiations.

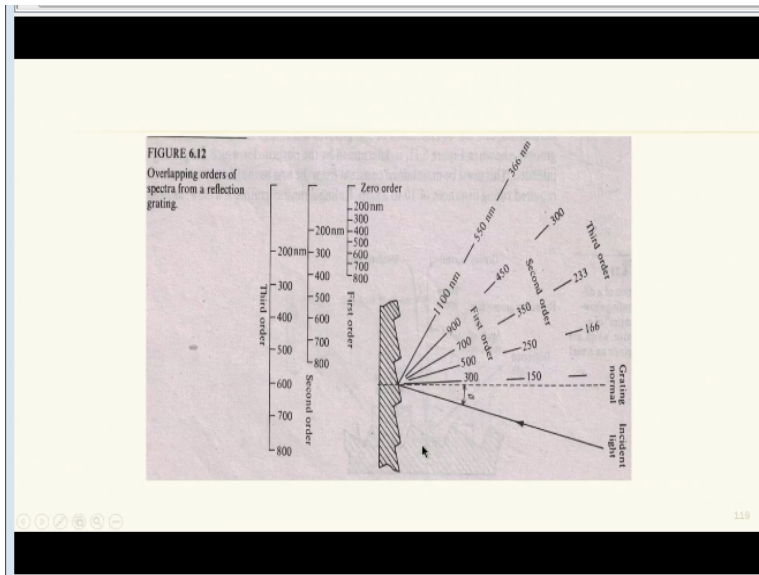
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So, this is a grating here you can see that the prism there are we can see here in this area figure there it looks like a boat now. But earlier it is essentially a collection of small small prisms. You can see the in the figure you can see small, small ridge like thing okay like this. There is one here, one here, on here 1, 2, 3, 4, 5 five ridges are there that means I have made 5 prisms here with the same in the same size.

So, this is the cross section of a diffraction grating showing the angles of a single grue which are microscopic on an actual grating okay.

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We will continue discussion in the next class.