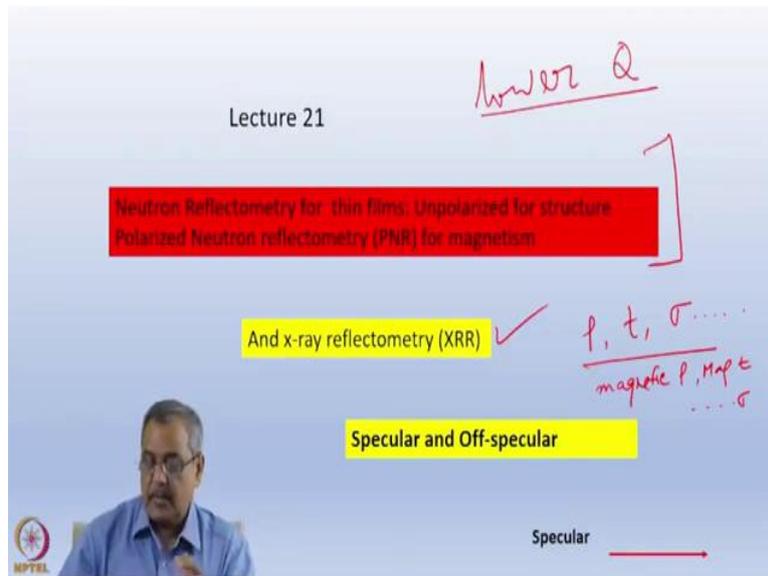


**Neutron Scattering for Condensed Matter Studies**  
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**Department of Physics**  
**Homi Bhabha National Institute**  
**Week 8: Lecture 21A**

**Keywords: Neutron reflectometry, XRR, Total external reflection, critical angle, SLD**  
(Refer Slide Time: 00:13)



From this lecture, we will start our discussion on Neutron Reflectometry. Till now, we have discussed mesoscopic structure studies using neutrons at low  $Q$  range. I have gone through the experiment that you can do using long wavelength neutrons, because you will be working at lower  $Q$  range or lower momentum transfer range.

Now, another leg of this mesoscopic structure study are thin films and multilayers where we will be using the technique of neutron reflectometry. This is an extremely important tool in hands of experimentalists at present, especially for magnetic thin films. Since the discovery of giant magneto-resistance a lot of work is going on in the field of thin films and their magnetism, interface coupling, interface magnetic moment, so on and so forth.

All these experiments or characterizations can be done using neutron reflectometry. Neutron reflectometry and x-ray reflectometry are close cousins as experiments, very similar and can be done on the same sample provided the scattering densities allow.

I will also be discussing x-ray reflectometry partly with you, and we will show that x-ray reflectometry and neutron reflectometry can be used for understanding mesoscopic structure of thin films in terms of density, thickness, interface roughness, etc. In addition, polarized

neutron reflectometry can be used for some parameters but also with the magnetic moment density in addition.

Magnetic moment density, magnetic layer thickness, magnetic roughness etc. can be studied using PNR. In the first part of my lectures, I will be discussing specular neutron and x-ray reflectometry, off-specular reflectometer is something which we will take towards the end.

(Refer Slide Time: 03:06)

Reflection from a mirror - specular  
 Reflection from a rough surface - off-specular

$\theta_i = \theta_r$   
 $\theta_i \neq \theta_r$

Lecture 21

Neutron Reflectometry for thin films: Unpolarized for structure  
 Polarized Neutron reflectometry (PNR) for magnetism

And x-ray reflectometry (XRR) ✓

Specular and Off-specular

Specular

*lower Q*

*$\rho, t, \sigma, \dots$   
 magnetic  $\rho, M, \mu, \dots$*

Let me quickly tell you, specular reflectometry is something in which we use Snell's law of reflection, where angle of incidence equals angle of reflection. In case off-specular reflectometry, we talk about diffuse reflection that means, the angle of incidence  $\theta_i$  is possibly not equal to angle of reflection  $\theta_r$ . So, in case of specular  $\theta_i = \theta_r$  and most of the time we will

be discussing specular neutron reflectometry and I will also take examples for off specular, which is also an interesting branch study when  $\theta_i \neq \theta_r$ .

As an example, I might tell you the reflection from a mirror that we see every day is specular and reflection from a movie screen is off specular, because in a movie screen the image is seen from all angles, so, there is nothing like an angle of incidence and angle of reflection equality. Whereas in case of a mirror, you can see the image only when you are at a position where you are satisfying angle of incidence equals the angle of reflection. This is the broad difference between specular and off-specular reflection. I will be discussing initially the specular reflectometry.

(Refer Slide Time: 05:34)

This requires a suite of spectrometers:

Neutron Scattering Facilities at DHRUVA

Reactor Hall

Guide Tube Laboratory

NPTEL

Basics Of Neut. Scatt., Workshop on nuclear... Malaysia 07

Neutron Guides

Triple axis

Mag. Diffr.

Single x-axis Diffr.

Power Diffr. With PSD

Reactor Block

FDS

University-DAE

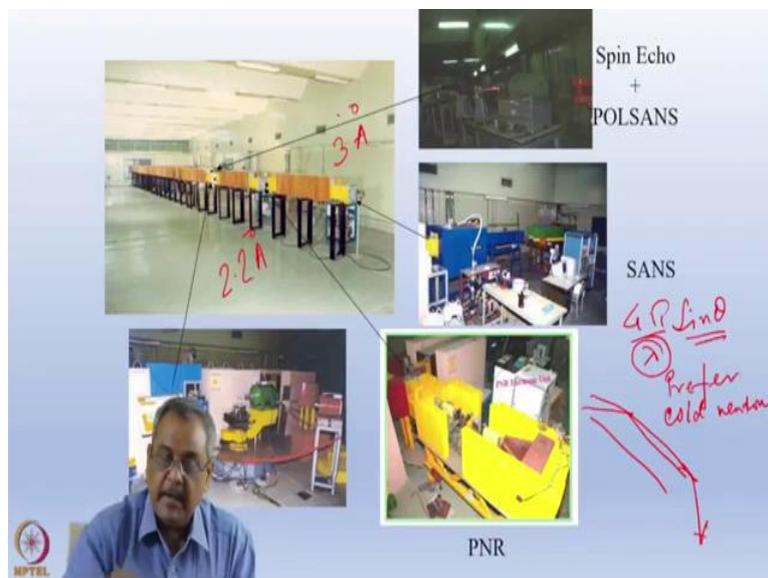
Large Q  
Powder diff.  
Liquid  
and  
amorphous

Large Q  
45 lines

NPTEL

But before I get into the discussion, I want to point out to you the small difference between experiments in the reactor hall and experiments in the guide halls. Please note that, so far, we have been discussing large- $Q$  experiments and large momentum transfer experiments. We have discussed powder diffraction, we have discussed single crystal diffraction, magnetic diffraction and also diffraction from liquid and amorphous systems. Liquid and amorphous spectrometer is on the other side of the reactor block in the photograph of Dhruva reactor hall. In all of these, the  $Q$  ranges are relatively large. Broadly I can categorize that the experiments which you do inside the reactor hall are in the large  $Q$  range. As  $Q = \frac{4\pi \sin \theta}{\lambda}$ , we use shorter  $\lambda$ .

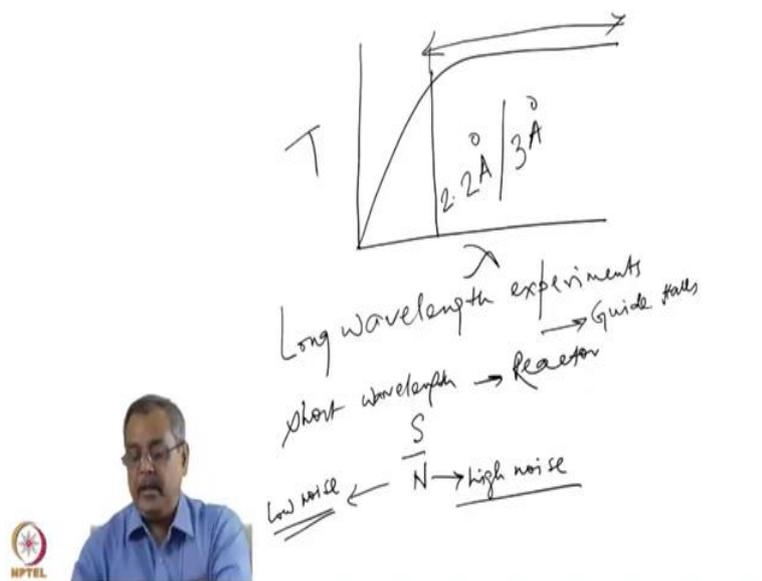
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And for the guide hall we have reserved experiments which are done at low  $Q = \frac{4\pi \sin \theta}{\lambda}$ , so at small angle and with longer wavelength. Why so? Because, these guides that you see they transport neutrons through total external reflection just like a mirror and the guides prefer to transport cold neutrons or neutrons which have wavelength longer than typical thermal neutrons in the higher energy.

This particular guide, it has got a critical angle of critical wavelength of 2.2 Å. And there is a guide on the other side in which it is 3 Å.

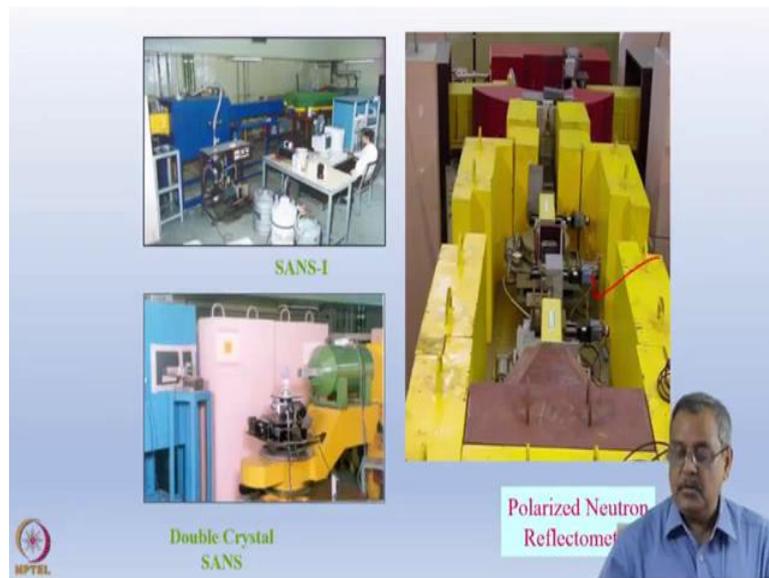
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Transmission of the guide depends on  $\lambda$  if it is a curved guide as shown in figure where critical wavelength is  $2.2 \text{ \AA}$  for one guide and  $3 \text{ \AA}$  for another guide in Dhruva. So, it is better to do experiments using neutrons in this range using the guide hall. In general, everywhere this partitioning you will find that the long wavelength experiments are done in guide halls and short wavelength experiments in reactor hall. There are also exceptions to this. There are thermal guides transporting thermal neutrons. , It is always preferable to go to the guide hall because of a very good signal to noise (for neutrons) ratio.

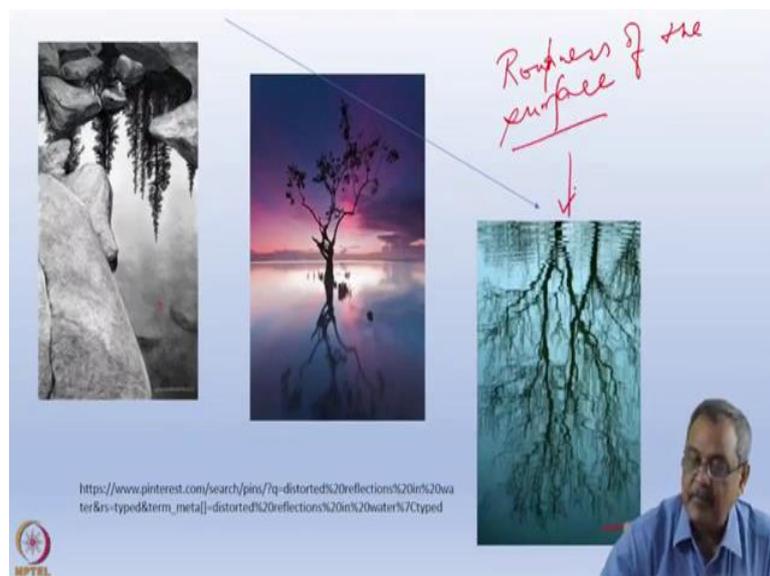
In case of the reactor hall, the signal to noise ratio is poorer because we have high noise from background neutrons, whereas, in case of a guide hall you have low noise from low number of background neutrons and signal to noise ratio improves. So, it is preferable to do experiments in the guide hall in general, but because guides transport long wavelength neutron preferably, the low  $Q$  or long wavelength experiments are preferred to be set up in the guide hall.

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I will go back to reflectometry. This is the reflectometer in Dhruva, I will also discuss other reflectometry instruments all over the world and what kind of studies we can do with them.

(Refer Slide Time: 10:27)



Let us come back to reflection. Reflection is a phenomenon, which is our daily experience. I have just shown you some photographic image of reflection of trees in water. Now, you can see as I travel from here to here, one qualitative comment that I can make is that the water surface is smooth here and slightly less smooth here and rough here. So, I can talk about roughness in a qualitative term for the surface. So, from the reflection, I can make a qualitative comment about the surface: whether the surface is more rough or less rough.



(Refer Slide Time: 11:37)

These are optical reflections visible to the eye

Neutrons and x-rays can also be reflected

Neutron and x-ray reflectometry can determine structural, magnetic information of thin films and interfaces at mesoscopic length scales → 100 Å, 1-10 Å, 10 Å

Only at near-grazing incidence and that's why difficult

The slide features a light blue background with black text. A red lambda symbol is written above the second line. The word 'structural' is underlined in red. Handwritten red annotations include '100 Å', '1-10 Å', and '10 Å' with arrows pointing to the text. A small circular logo is in the bottom left, and a headshot of a man in a blue shirt is in the bottom right.

Different from optical reflections that are visible to the naked eye, neutrons and x-rays can also be reflected. Because neutrons have a De Broglie wavelength  $\lambda$  and x-rays are electromagnetic waves, so, both of these are waves and reflection is a property of wave refraction. They can be reflected, refracted, but with certain constrictions that I will come to.

Neutron and x-ray reflectometry both can determine structure. Categorically for magnetic structure one uses polarized neutron reflectometry data. This determination is done on thin films and interfaces at mesoscopic length scales. I will talk about a film which maybe 100 Å thick and may have magnetic moment density. Roughness maybe 1 to 10 Å. These are quantifying parameters at a mesoscopic length scale. But both these experiments are at near grazing incidents to the plane of a film. And that is why it is difficult.

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① A narrow beam  $\sim 10^{-10}$

② Alignment of the sample in the beam

These are optical reflections visible to the eye

Neutrons and x-rays can also be reflected

Neutron and x-ray reflectometry can determine structural, magnetic information of thin films and interfaces at mesoscopic length scales

$100 \text{ \AA}$ ,  $10 \text{ \AA}$   
 $1 - 10 \text{ \AA}$

Only at near-grazing incidence and that's why difficult

What can one say about x-rays and neutrons?

Röntgen on reflection of x-rays

"The question as to the reflection of the X-ray may be regarded as settled, by the experiments mentioned in the preceding paragraph, in favor of the view that no noticeable regular reflection of the rays takes place from any of the substances examined Other experiments, which I here omit, lead to the same conclusion.1"

"On a New Kind of Ray, A Preliminary Communication"  
December 28, 1895 in Würzburg Physico-Medical Society

Re-discovered in 1954 and re-established as a technique

Before I get into this, let me just quickly tell you that what is the difficulty. We have seen that in case of small angle, we use a very narrow beam, and the sample is in transmission mode, whereas, in case of x-ray and neutron reflectometry, we have a thin film mostly on a substrate and I have to put it in a reflection mode in a narrow beam. The beam is narrow because the average angle with respect to the surface is of the order of 10s of arc minutes to maybe a degree and the incident beam can be as narrow as a few arc minutes.

The instrument needs a narrow beam, often much narrower than what we use in SANS instruments and alignment of the sample in the beam is very important. These are the difficulties because when you make a narrow beam you cut down the intensity of neutrons. So, you have lesser number of neutrons when you have such a narrow beam.

I need to align my sample in the beam means I have to bring it in a beam at a certain angle, so that I can see the reflected beam and the refraction angle itself also can be questioned unless we have means of answering that. One is the angle of reflection and second is how to bring the sample in the beam because the sample maybe 100 nm thick and it needs to be placed in the beam by moving the substrate.

These are the challenges with respect to a neutron/xray reflectometer. Historically, I feel like sharing this information with you because these are major techniques today, what one could say about x-ray and neutron reflectometry. The discoverer of x-rays was Roentgen, the first Nobel laureate in physics. You look at his comment in 1895. “The question as to reflection of the x-ray may be regarded as settled, by the experiments mentioned in the preceding paragraph, in favor of the view that no noticeable regular reflection of the rays takes place from any of the substrates examined. Other experiments, which I omit, lead to the same conclusion.”

He said that the x-ray cannot be reflected. This was December 28, 1895. That is the year when x-rays were discovered. But this technique (x-ray reflectometry) was rediscovered in 1954 and re-established as a technique.

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Historically, Fermi and Zinn, in 1946, were the first to present neutron reflectivity measurement for finding out coherent nuclear scattering cross-section of various materials. Approximately a decade later, the first report on x-ray reflectivity (XRR) for thin-film characterization from L. G. Parratt appeared. The reincarnation of neutron reflectometry (NR) as a useful tool for studying thin films and their magnetic structure is due to G. P. Felcher of Argonne National Laboratory in the 1980s

1. Fermi, E. and Zinn, W. (1946) Reflection of neutrons on mirrors. *Physical Review* 70: 103A
2. Parratt, L.G. (1954) Surface studies of solids by total reflection of x-rays. *Physical Review* 95 (2) 369



So far as neutron is concerned, historically, Fermi and Zinn in 1946 were the first to present neutron reflectometry measurements for finding out coherent nuclear scattering length. Why is it so? I will show you coherent nuclear scattering length can be found out using neutron reflectometry. And approximately a decade later, the first report on x-ray reflectivity, following the above comment by Röntgen, later in 1954, we get the classic paper by Parratt for surface studies of solids by total reflection of x-rays.

(Refer Slide Time: 17:49)

**Beginning of x-ray reflectometry**

**Analysis of the shape of the curve of reflected x-ray intensity vs glancing angle in the region of total reflection provides a new method of studying certain structural properties of the mirror surface about to several hundred angstroms deep. Dispersion theory, extended to treat number of stratified homogeneous media, is used as a basis of interpretation.**

L. G. Parratt, PHYSICAL REVIEW VOLUME 95, NUMBER 2, JULY 15, 1954

HPTEL

The slide features a light blue background. At the top, the title 'Beginning of x-ray reflectometry' is in black. The main text is in bold red font. A red oval highlights the citation 'L. G. Parratt, PHYSICAL REVIEW VOLUME 95, NUMBER 2, JULY 15, 1954'. A small HPTEL logo is in the bottom left, and a video feed of a man in a blue shirt is in the bottom right.

So, x-rays can be reflected shown in this classic paper, which is followed by almost entire thin film community those who attempted to do x-ray reflectometry for thin film characterization. Parratt in 1954 worked on analysis of the shape of the curve of reflected x-rays. So, basically Röntgen missed reflection of x-rays because he did not realize that the refractive index of x-rays is almost equal to one. I will come to it briefly.

But if you can take care of the beam that has to be extremely narrow, and if you can take care of the angles that you can measure reflected x-ray (neutron) intensity. The paper by Parratt says analysis of the shape of the curve of reflected x-rays intensity versus glancing angle in the region of total reflection provides a new method for studying certain structural properties of the mirror surface about several 100 Å deep using dispersion theory. Extended to treat number of stratified homogeneous media, it is used as a basis of interpretation. This classic paper not only provides you the experimental results, but also with the formalism that we use even today to analyze or fit x-ray and neutron reflectometry data obtained from our instruments.

(Refer Slide Time: 19:19)

A unique **non-destructive** tool for thin film characterization

Refractive index for x-rays and neutrons can be written as  
(without absorption)

$$n = 1 - \delta$$

Where  $\delta \sim 10^{-5}$  for x-rays and  $\sim 10^{-6}$  for neutrons

The deviation of rays in a medium is small

*Handwritten note:  $n < 1$*




### X-ray Refractive indices

For x-rays, propagation is through Thomson scattering. This gives the refractive index for the electron cloud as:

$$n^2 = 1 - \frac{\omega_p^2}{\omega^2} \quad \omega_p \text{ Plasma freq.} \quad \omega_p = \frac{4\pi e^2 \rho_e}{m_e}$$

$\rho_e$  = electron number density =  $\sum N_i Z_i$

$$n = 1 - \frac{\lambda^2}{2\pi} \left( \frac{e^2}{m_e c^2} \right) \rho_e = 1 - \frac{\lambda^2}{2\pi} r_e \rho_e \quad r_e = \frac{e^2}{m_e c^2} = 2.818 \text{ fm}$$

$$n = 1 - \frac{\lambda^2}{2\pi} r_e [f + \Delta f] - i \frac{\lambda \mu}{4\pi} = 1 - \delta - i\beta$$

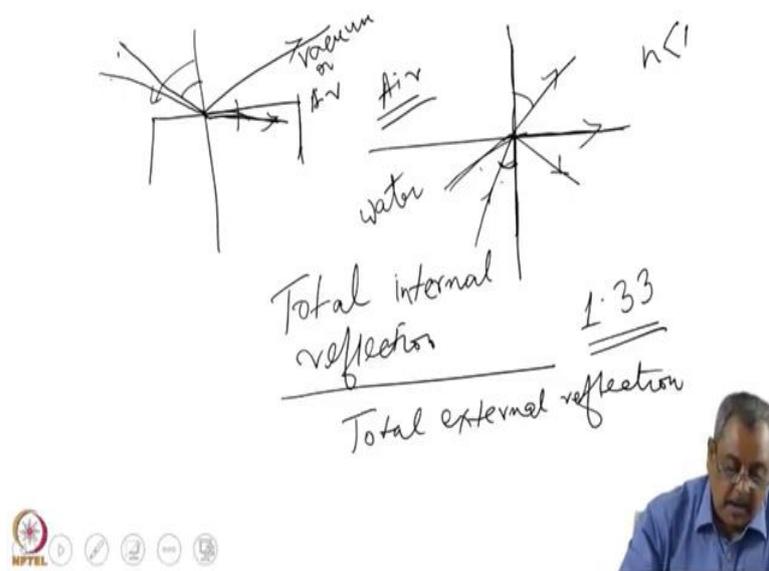
Including  $\mu$




X-rays and neutrons give us non-destructive tools for thin film characterization in form of reflectometry. As I mentioned earlier, the refractive index for x-rays and neutrons can be written as  $n = 1 - \delta$ . What is the value of the  $\delta$ ? I will come to in later part.

But I want to point out to you that this  $\delta$  is very small. So,  $n$  is marginally less than 1 for neutrons and x-rays and then what it means when we compare this with what I find in general optics.

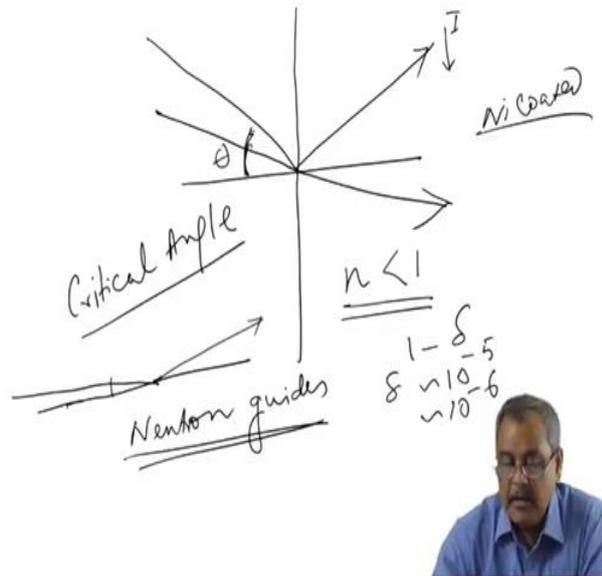
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You are familiar that water has a refractive index around 1.33 for optical rays. In case of optics, we use the angle with respect to the normal to the interface between the two mediums. If it is water to air, when light rays come out from water to air, it undergoes total internal reflection. That means as I keep increasing this incident angle, at some angle the refracted beam goes along the boundary and beyond that it reflects back inside the medium and it cannot come out from water. This is known as total internal reflection.

Just as opposite to this, if  $n < 1$  then the medium has a lesser refractive index compared to the vacuum or air. When the ray comes from vacuum inside the medium, just the same thing happens in the opposite direction at the interface for neutron (x-rays). It under undergoes a change in direction at larger angles. If this angle is smaller, then it undergoes total external reflection. So, because the refractive index is less than one, I have total external reflection.

(Refer Slide Time: 22:57)



A unique **non-destructive** tool for thin film characterization

Refractive index for x-rays and neutrons can be written as  
(without absorption)

$$n = 1 - \delta$$

$n < 1$

Where  $\delta \sim 10^{-5}$  for x-rays and  $\sim 10^{-6}$  for neutrons

The deviation of rays in a medium is small



### X-ray Refractive indices

For x-rays, propagation is through Thomson scattering. This gives the refractive index for the electron cloud as:

$$n^2 = 1 - \frac{\omega_p^2}{\omega^2} \quad \omega_p \text{ Plasma freq.} \quad \omega_p = \frac{4\pi e^2 \rho_e}{m_e}$$

$$\rho_e = \text{electron number density} = \sum N_i Z_i$$

$$n = 1 - \frac{\lambda^2}{2\pi} \left( \frac{e^2}{m_e c^2} \right) \rho_e = 1 - \frac{\lambda^2}{2\pi} r_e \rho_e \quad r_e = \frac{e^2}{m_e c^2} = 2.818 \text{ fm}$$

$$n = 1 - \frac{\lambda^2}{2\pi} r_e [f + \Delta f] - i \frac{\lambda \mu}{4\pi} = 1 - \delta - i\beta$$

Including ab



Let me point out right at the onset, unlike optics, in this case, I will consider the angle with respect to the surface and not with respect to the normal. That means, as I go from smaller angle with respect to the surface to larger angle, up to a certain angle the beam gets totally reflected. So, this is total external reflection and beyond a certain angle known as critical angle, it starts penetrating the medium and as the ray penetrates in the medium and the reflected intensity goes down.

So, please be aware of this fact that I am measuring the angle with respect to the surface and the refractive index  $n < 1$ . Actually, it is marginally less than one ( $1 - \delta$ ) where  $\delta$  is around  $10^{-5}$  for x-rays even lower for neutrons. So, this total external reflection takes place at an extremely small angle up to an angle known as  $\theta_c$  or critical angle, which is very small the beam gets totally reflected and this is the principle of neutron guides.

I showed you photograph of neutron guides earlier and today also, the neutron guide surface which is nickel coated float glass, it reflects the beam and allows it to travel in vacuum. We have to evacuate the nickel guides for allowing the neutron to travel. You can see it is similar to light traveling in an optical fiber through total internal reflection. In neutron guide it is total external reflection. Now, let us get back to the refractive index of x-rays. I will quickly try to give you how we derive the refractive index for x-rays.

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Handwritten derivation on a whiteboard:

$$n^2 = 1 - \frac{\omega_p^2}{\omega^2} - \epsilon$$

X-rays interact with e-cloud

$$\omega_p^2 = \frac{4\pi e^2 n_e}{m_e}$$

$$n = 1 - \frac{1}{\omega^2} \left[ \frac{4\pi e^2 n_e}{m_e} \right]$$

$$= 1 - \frac{\lambda^2}{2\lambda_c^2} \left( \frac{Z}{A} \right) \left( \frac{N_A}{m_e c^2} \right) e^2$$

Additional notes on the right side of the whiteboard:

$$\lambda_c = \frac{hc}{m_e c^2}$$

$$\frac{\omega \rightarrow \lambda}{\omega^2} = \frac{hc}{\lambda^2}$$

$$\frac{e^2}{m_e c^2} = r_e$$

This is from our master's level course in plasma physics, the refractive index is given by  $n^2 = 1 - \frac{\omega_p^2}{\omega^2}$  where  $\omega_p$  is a plasma frequency and  $\omega$  is the frequency at which we are calculating the

refractive index. Now, x-rays interact with electron charge cloud to be precise. I can write down this plasma frequency as,  $\omega_p^2 = \frac{4\pi e^2 \rho_e}{m_e}$  and using this we can write,  $n^2 = 1 - \frac{4\pi e^2 \rho_e}{\omega^2 m_e}$ .

We know,  $\hbar\omega = h\nu = \frac{hc}{\lambda}$  and using this we can write,  $n = 1 - \frac{\lambda^2}{2\pi} \left(\frac{e^2}{mc^2}\right) \rho_e$ . It is by taking the square root of equation  $n^2 = 1 - \frac{\omega_p^2}{\omega^2}$  and assuming  $\frac{\omega_p}{\omega}$  is very small so that  $\left(1 - \frac{\omega_p^2}{\omega^2}\right)^{1/2}$  can be approximated to  $1 - \frac{1}{2} \frac{\omega_p^2}{\omega^2}$ . Now,  $\frac{e^2}{mc^2}$  is known as  $r_e$  classical electron radius with a value of 2.818 fm.

(Refer Slide Time: 28:45)

S.L.D

$$n = 1 - \frac{\lambda^2}{2\pi} \rho_e r_e$$

$\rho_e = \sum_i N_i Z_i$  = Electrons per unit volume

$$n = 1 - \frac{\lambda^2}{2\pi} \rho_e r_e$$



$$n^2 = 1 - \frac{\omega_p^2}{\omega^2} \quad | - \epsilon$$

X-rays interact with e-cloud

$$\omega_p^2 = \frac{4\pi e^2 \rho_e}{m_e}$$

$$n = 1 - \frac{1}{\omega^2} \left[ \frac{4\pi e^2 \rho_e}{m_e} \right]$$

$\hbar\omega = h\nu = \frac{hc}{\lambda}$   
 $\omega \rightarrow \frac{2\pi c}{\lambda}$

$$= 1 - \frac{\lambda^2}{2\pi} \left(\frac{e^2}{mc^2}\right) \rho_e = r_e = 2.818 \text{ fm}$$



Finally, I can write  $n = 1 - \frac{\lambda^2}{2\pi} r_e \rho_e$  where  $r_e$  is the classical electron radius and  $\rho_e$  is the electron density. Electron density for Co or Ni like atoms is given by,  $\rho_e = \sum N_i Z_i$  where  $Z_i$  is  $i^{\text{th}}$  atom charge number and  $N_i$  is number per unit volume. Since it is a sum over all the atoms, so, it need not be one type of atom. It can be many. Hence,  $\rho_e$  gives electrons per unit volume.

If you remember, similar thing I discussed with respect to SANS. I discussed SLD or scattering length density. We will come to something similar later. So, for x-rays it is  $n = 1 - \frac{\lambda^2}{2\pi} r_e \rho_e$ . This is the value of refractive index for x-rays. It depends on the electron density and the classical electron radius.