**Keywords: Reflected intensity, Kiessing oscillations, Parratt's formalism, Multilayers**

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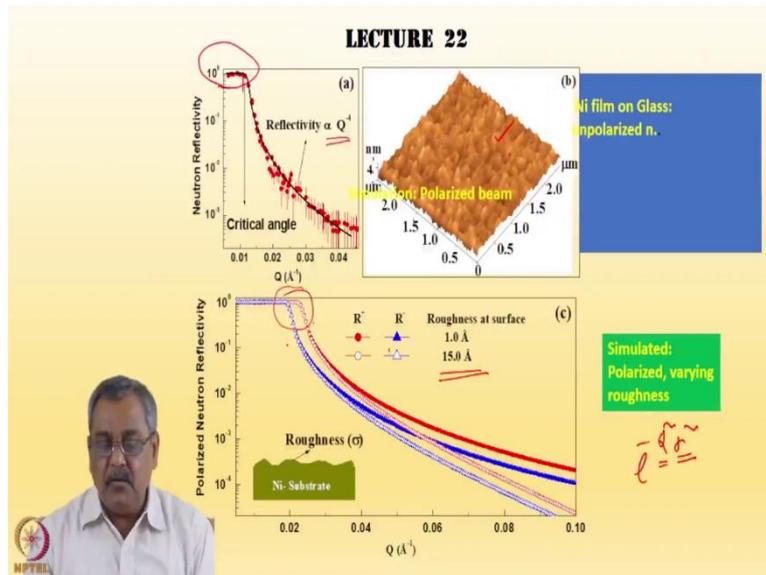
As I told you earlier that I can find out density of the film from the critical angle in general, and also the roughness of the film from the fall of the intensity profile. But usually, these films also have finite thickness and it is an important parameter that one would like to know.

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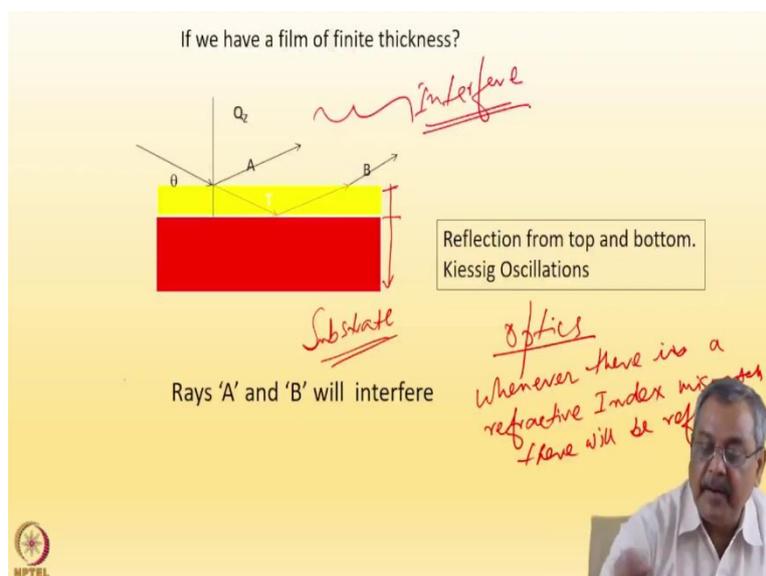
This is the schematic of a finite thickness film deposited on a substrate.

We know from optics that whenever there is a refractive index mismatch, there will be reflection of the incident beam. This is our daily experience even in our glass windows. Even if the window is transparent, you will find that, when you look at it carefully, you can see your image because there is a refractive index mismatch between air and the glass, you will have reflection. Same thing is true here. The whole phenomenon is taking place at grazing incidence, but the facts are same.

I have an incident beam which partially gets reflected from the surface and then you have a transmitted beam which gets reflected from the substrate and the film interface here. I have got one more reflected beam, and these two beams interfere. They will interfere and that interference pattern will be stamped on the reflectivity plot.

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So quickly, let me just tell you mathematically.

Let us evaluate the reflectivity from a finite thickness film. Let me just show it like this. This is a finite thickness film; this is the substrate. Reflectivity here is,

$$R = R_F \left| \int \frac{d\rho(z)}{dz} e^{iQz} dz \right|^2$$

This is a Fourier transfer of the density gradient in the z-direction. Here, Q is the wave vector transfer.

Now if I have a film of constant density of thickness L then we will have two delta functions in the density gradient. This is the film and this is its density and you can see that one delta

function will be at the film-air interface, and the other delta function will be at the film-substrate interface for the density gradient.

Let me plot the density (ρ) vs depth (z) profile for a uniform density thin film deposited on a substrate. This is a film-air interface where the film starts and there is a substrate. This is the density for the substrate, this is the density for the film, and air has got a refractive index 1. If I differentiate this density, $\left(\frac{d\rho}{dz} \right)$ and plot it with respect to z then we have one delta function at air-film interface and another one at film-substrate interface. So, we have two delta functions, and this L is the thickness of the film. In that case,

$$R = R_F \left| \int (\delta(0) + \delta(L)) e^{iQz} dz \right|^2$$

$$R = R_F [1 + e^{iQL}]$$

This will be my reflected intensity, if I have a film of finite thickness.

Now from here you can see whenever $QL = 2\pi$ then $[1 + e^{iQL}] = 2$, and when $QL = \pi$ then $[1 + e^{iQL}] = 0$, and so there are oscillations in reflected intensity and whenever $QL = 2\pi$, you will have a peak in the reflected intensity. This is what I wanted to show you.

So, $R = R_F [1 + e^{iQL}]$ because there are two delta functions and the reflections are taking from the top and the bottom of the film. And, there will be oscillations in intensity and the oscillation width in Q space is given by $\Delta Q = \frac{2\pi}{L}$ and whenever 'Q' is $\frac{2\pi}{L}, \frac{4\pi}{L}, \frac{6\pi}{L}$ etc. it will give oscillations. So, the ΔQ between the oscillations will be a signature of the thickness of the film.

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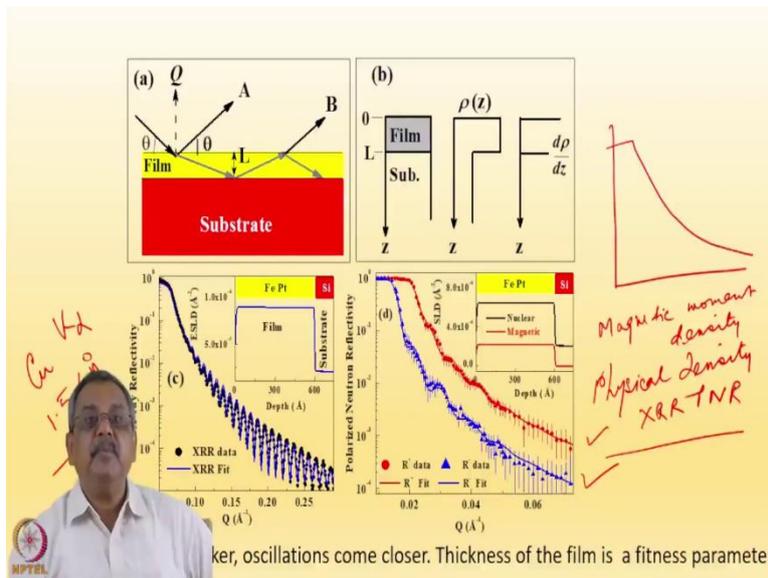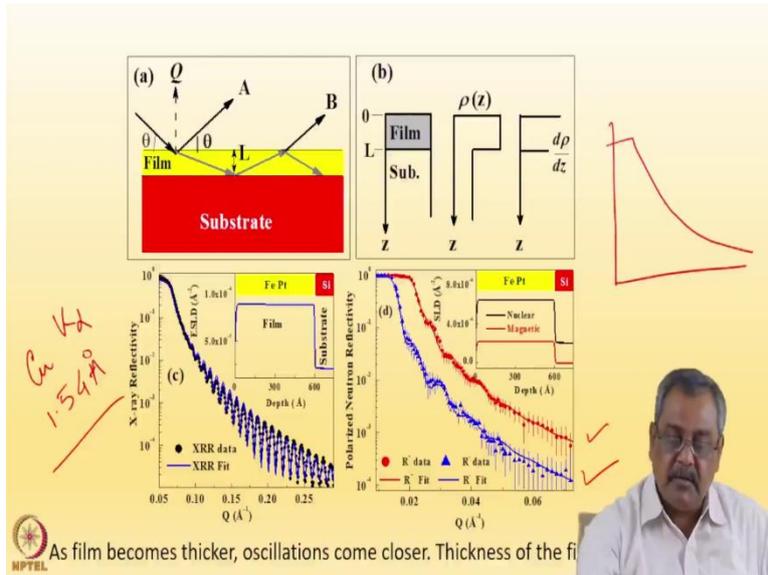
Now, I will show you some experimental data.

This is an FePt film that I had measured. In the schematic you can see that there is the reflection from the top interface and reflection from the bottom interface. In the left bottom XRR profile is shown while on the right bottom there is the polarized neutron reflectivity profile for this film.

There are several things that needs to be explained here. One is that in case of XRR you can see the Keissing oscillation and the data is obtained using Cu-Kα radiations with wavelength 1.54 Å. For infinite thickness film it should have been flat curve without oscillations, but here you see the oscillations. This is the schematic of the FePt film where the film is of finite thickness, and is deposited on silicon substrate, and you can see the finite thickness of the film

gives you this Kiessing oscillations, and from the fitting of this data you can get thickness of the film here.

For the same film, when you use polarized neutron reflectometry, you will have different critical angle for up and down neutrons along with the Kiessing oscillations which will be visible on the falling edge of the reflected intensity. There are no Kiessing oscillations below critical angle because below critical angle the film, the radiation does not penetrate the medium. So, you cannot see any kind of oscillations below critical angle. But above critical angle, because your beam is now penetrating the film you have got these two components, and these are the polarized beam intensities together with the thickness signature as Kiessing oscillations on the falling edge of the reflectivity pattern.

By fitting this, we can get physical density from both XRR and PNR because XRR gives electron density which can be taken back to physical density, and PNR gives nuclear plus magnetic moment density which can also be taken back to physical density. We can get magnetic moment density only from PNR. I get interface roughness from both of them. All these parameters have been extracted for these experiments. And usually, when you make a film and before you take it to polarized neutron reflectometry, it makes sense to do the XRR on the same film, provided it is a high-Z material film, not a biological film which has got a hydrogenous or deuterium-based material. Because in that case XRR will not give you anything.
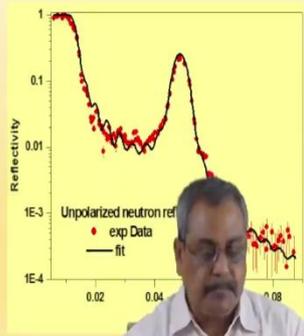
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So now I will go one step ahead.
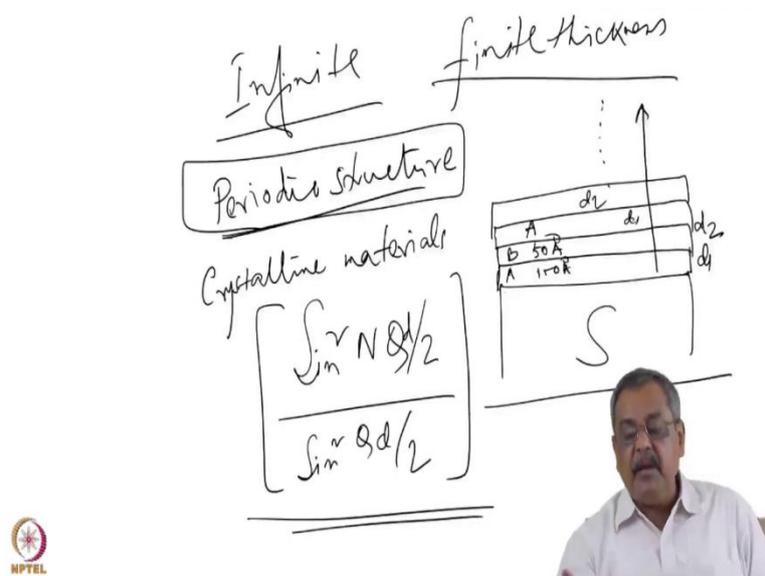
Till now I talked about infinite medium which gives you Fresnel reflectivity, and I also talked finite thickness film. Now what about a film which is actually a repetition of layers! Often, we study such films. The film will look somewhat like this. Let us say, this is a substrate. I will call this layer A of certain thickness $d1$, then layer B of certain thickness $d2$, then again layer A of $d1$ thickness and layer B of $d2$ thickness, and then I continue like this for maybe some 10 or 20 such layers. We often call such systems as thin film heterostructures. In this direction (Z direction), it is a periodic structure. Typical, let me say A can be ~ 100 Å, B can be ~50 Å, so on and so forth.

This is a periodic structure but the length scales are very different from what you have seen for crystalline materials at atomic level. But this periodic structure is also similar to a crystal, I call it a pseudo-crystal or you can call it a crystal at mesoscopic length scale and if there is a one-dimensional crystalline structure with N number of such layers, you will have intensity

$$I \propto \frac{\sin^2 NQd/2}{\sin^2 Qd/2}$$

And as N goes to infinity, this goes to a Bragg peaks. So, this synthetic crystal should also give me Bragg peaks in reflectivity profile. Since this structure is at larger length scale (compared to atomic distance in crystals), hence this Bragg peak will come at lower Q. Here, I must remind you that I have shown you crystallographic structure for magnetic flux lattice using small angle neutron scattering. That was very similar to a Laue experiment which you do with crystalline materials ordered at atomic level but the Laue pattern (of vortex lattice) was seen at low Q
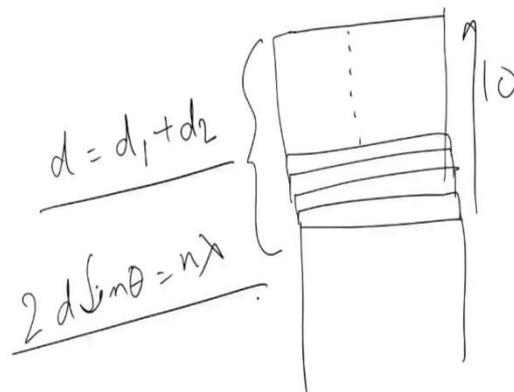
region because vortex lattices are very large in length scale (compared to atomic arrangement in crystals). I have taken another example here, where if I grow such bilayers of thin films, periodic in nature, then I will see Bragg peaks.

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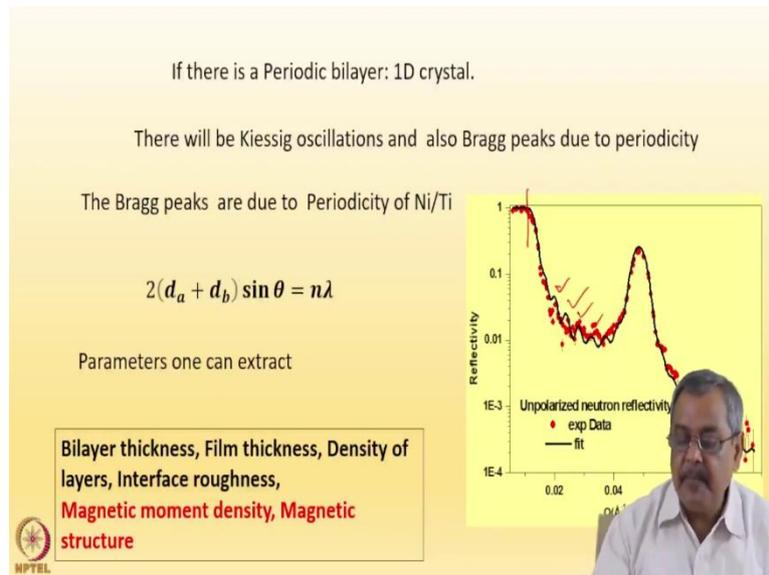
This is the unpolarized neutron reflectometry data from a Ni/Ti film where Ni and Ti are deposited one above another and we have got 10 such bilayers so that we have a periodic bilayer crystal with 10 bilayers. Here, you can clearly see the critical angle and Kiessing oscillations arising due to the finite total thickness of the film.

Apart from Kiessing oscillation, signifying the total thickness of the film, we also observe Bragg peak due to the periodicity of the bilayers with the thickness of bilayer $d = d1 + d2$. satisfying the Bragg's condition $2d \sin \theta = n\lambda$. In present case, we see only one Bragg peak, Kiessing oscillations and the critical angle. We can fit this and get the structural information including the magnetic moment density in the nickel layers, the interface roughnesses and the magnetic structures.

Calculating Reflectivity for a layered structure: Parratt's formalism

To evaluate the reflectivity profile of a film with 'N' layers

$$\chi^2 = \sum_i \left(\frac{E_M(Q)}{M} - E_i^{exp} \right)^2$$

Now, the case is that how do we calculate the reflectivity or how do we fit the reflectivity profile for a periodic bilayer or a periodic material, a single film, a bilayer or any thin film structure that we want to study.

I had talked to you about Rietveld fitting regarding crystalline structure. In Rietveld refinement, we start with an assumed structure of the crystalline solid and then keep refining that till we come to a model which fits my experimental data. Then I discussed with you about liquid or amorphous solids and there also we start with a model structure, a three-dimensional model, and then we kept modifying it till we got a good fit with the experimental data.

So, basically, I am always starting with a model in real space, then finding out the experimental data in Q space for all the experimental points, and then I compare it with the experimental data and keep refining the model for chi-square minimization (χ^2). So, I always start in the real space, produce the data or rather the data that corresponds to the model in Q space, and then compare it with the experimental data. And try to reduce the error bar. Here also, in reflectometry, we go to similar exercise. Here to generate the reflectivity pattern, of a layered structure, we use Parratt's formalism.

This is a very robust formalism introduced by Parratt's together, with possibly, the first most famous reported data, which I have mentioned earlier, on X-ray reflectometry. Parratt's formalism can be equally applied to X-rays and neutrons to generate the reflectively pattern of a model layered structure.

The model layer structures, it looks somewhat like this, you have a substrate on which you grow your film. It can be a bilayer or it can be a single layer, it can be aperiodic, it can be a trilayer or whatever. And any layer is signified by its thickness. In this case, how do we evaluate the reflectivity profile of a film with the N layers?

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For neutrons wavefunction 'ψ' and its derivative 'dψ/dZ' at every interface are continuous

$$a_{n-1}\psi_{n-1} + a_{n-1}^{-1}\psi_{n-1}^R = a_n^{-1}\psi_n + a_n\psi_n^R$$

$$(a_{n-1}\psi_{n-1} - a_{n-1}^{-1}\psi_{n-1}^R)q_{n-1} = (a_n^{-1}\psi_n - a_n\psi_n^R)q_n$$

$$a_n = e^{-iq_n d_n/2}$$
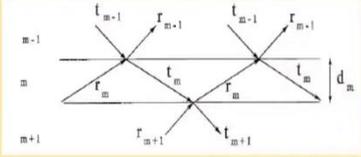
I will briefly introduce you to Parrett's formalism.

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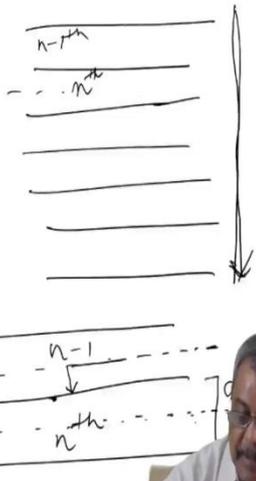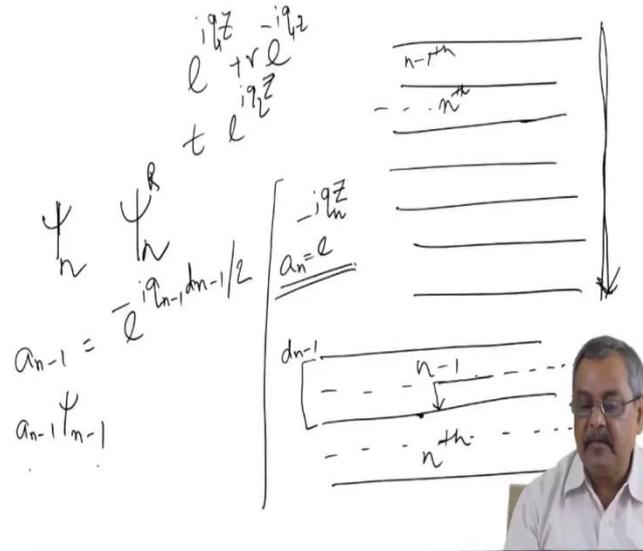
Earlier, I discussed with you about the reflectivity at only one interface. Now, I have got a number of layers, so, I have to do the same exercise layer by layer. Let me consider the nth and the n-1th layer in this multi-layer stack. My layer number is going up as I go inside the thin film heterostructure.

Let me just highlight the interface between (n-1)th and n^{th} layers. So here at this interface, I have to do exactly what I did earlier for a single layer. Assume that thickness of (n-1)th and n^{th} layers are d_{n-1} and d_n respectively. At the center of the nth layer, I consider that there are two parts of the wave function like this, one is $\psi_n(forward)$ and another one is $\psi_n^R(reflected)$ where the suffix n represents that I am talking about the nth layer. For such a structure, I am considering the interface between n^{th} and n-1th layers. Now let me just talk about a phase factor, $a_n = e^{-iq_n z}$. This phase factor comes because I have assumed ψ_n at the center of the layer. So, at the interface,

$$a_{n-1}\psi_{n-1} + a_{n-1}^{-1}\psi_{n-1}^R = a_n^{-1}\psi_n + a_n\psi_n^R$$

where ψ_{n-1} is at the center of the n-1th layer so I have to take this ψ_{n-1} forward by $e^{-iq_{n-1}d_{n-1}/2}$ because it moves $d_{n-1}/2$ with respect to the center of the layer. Here, phase factor is $a_{n-1} = e^{-iq_{n-1}d_{n-1}/2}$. I considered only z-component and assumed that xz-plane is the reflection plane. So, if ψ_{n-1} is at the center of the n-1th layer and if I take it forward then it becomes $a_{n-1}\psi_{n-1}$. Now with this, I need to add the reflection amplitude just like I did before. The reflected beam has to be moved back. So, it will be $a_{n-1}^{-1}\psi_{n-1}^R = e^{iq_{n-1}d_{n-1}/2}\psi_{n-1}^R$.

Now, consider the interface of (n-1)th and nth layers, then considering the continuity of wave function across the interface we have,

$$a_{n-1}\psi_{n-1} + a_{n-1}^{-1}\psi_{n-1}^R = a_n^{-1}\psi_n + a_n\psi_n^R$$

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Now from the continuity of the differential of wavefunction across the interface, we get

$$(a_{n-1}\psi_{n-1} - a_{n-1}^{-1}\psi_{n-1}^R)q_{n-1} = (a_n^{-1}\psi_n - a_n\psi_n^R)q_n$$

where the phase factor basically takes care of propagating the beam from the center of the medium to the interfaces. With this, I got two equations.

Now, I know that the reflectivity at the n-1th and nth interface is given by $\frac{\psi_n^R}{\psi_n}$. I have to solve

above two equations to get this.

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To solve these equations, I have to just add and subtract them. I am not doing the algebra part here rather; the results are more interesting.

I get a parameter $R_{n-1,n}$ which is written as,

$$R_{n-1,n} = a_{n-1}^4 \left| \frac{R_{n,n+1} + F_{n-1,n}}{1 + R_{n,n+1} F_{n-1,n}} \right|$$

where $R_{n,n+1} = a_n^2 \frac{\psi_n^R}{\psi_n}$ and $F_{n,n+1} = \frac{q_{n-1} - q_n}{q_{n-1} + q_n}$
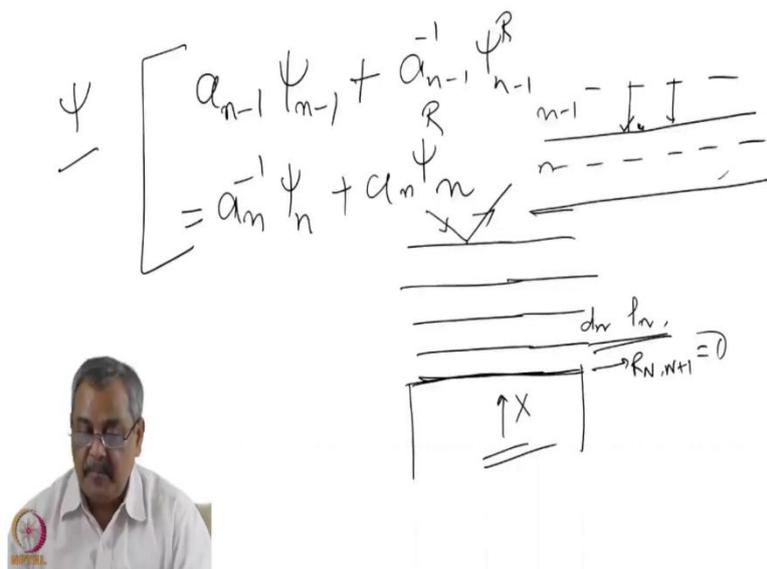
$F_{n,n+1}$ would have been the reflection amplitude if I had only n-1th and nth layers. $R_{n,n+1}$ is the reflectivity parameter. I have solved it but I have a problem here. You see this is a recursion formula for R, where I can go from layer to layer, and keep calculating $R_{n-1,n}$. And then by squaring, I can get the reflected intensity. But interestingly, to get $R_{n-1,n}$, I need $R_{n,n+1}$. That means to get the reflected intensity at the interface of n-1th and nth layers, I need that reflected amplitude at nth and n+1th layer. This is clearly a problem here.

How to get rid of this problem? Parratt made an excellent assumption and even today we do the same thing. Parratt assumed that whatever enters the substrate nothing comes back. It goes out from the bottom of the substrate. That means with your film going deep, you have a substrate which is very thick and whatever enters the substrate, nothing goes back.

That means, at the film-substrate interface, I can consider $R_{N,N+1} = 0$. I get nothing back from the bottom of the substrate. Here, N is the last layer in the substrate. The last layer is the Nth layer, whatever goes inside the substrate, nothing comes back. Once I put it here, I can keep

going up and keep calculating the reflected intensity for each and every layer, and ultimately, I can arrive at the film-air interface, provided I have made a model in which I have assigned density, thickness for each and every layer.

Now, I might have a sample which can even be a single layer and need not be a multilayer, but I can break it up into layers, and assign thickness, density, magnetic moment density for each and every (virtual) layer and for that, I can calculate the reflectivity at the film-air interface, what we measure actually. I take the whole stack and put it in the reflectometry instrument, and measure the reflected intensity. But assuming that $R_{N,N+1} = 0$, that means nothing comes back from the substrate, I start evaluating reflectivity. And with that, I can have a model, and I can have a model reflectivity pattern for that, which I can compare with the experiment.

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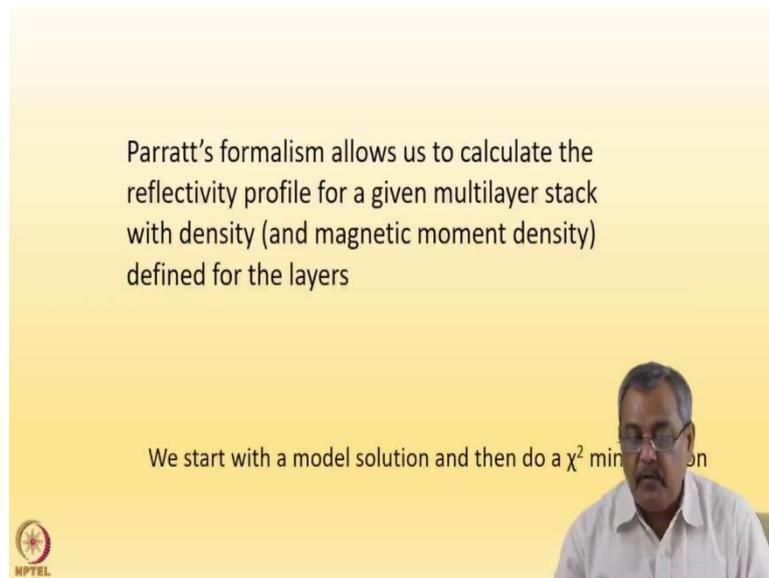
So, Parratt's formalism allows us to calculate the reflectivity profile for a given multilayer stack with density, together with (also) magnetic moment density if it is polarized neutron reflectometry, that defined for the layer. And now we can have a model solution. Then we go back to the same technique what we do for all other diffraction techniques. We try to do a chi-square minimization.

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I will take up in the next part, the data analysis and how we do it.