Neutron Scattering for Condensed Matter Studies
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Week 10: Lecture 25A

Keywords: Off-specular reflectivity, Pitting corrosion, Height-height correlation function, Fractal dimension, Magnetic roughness, Hurst parameter

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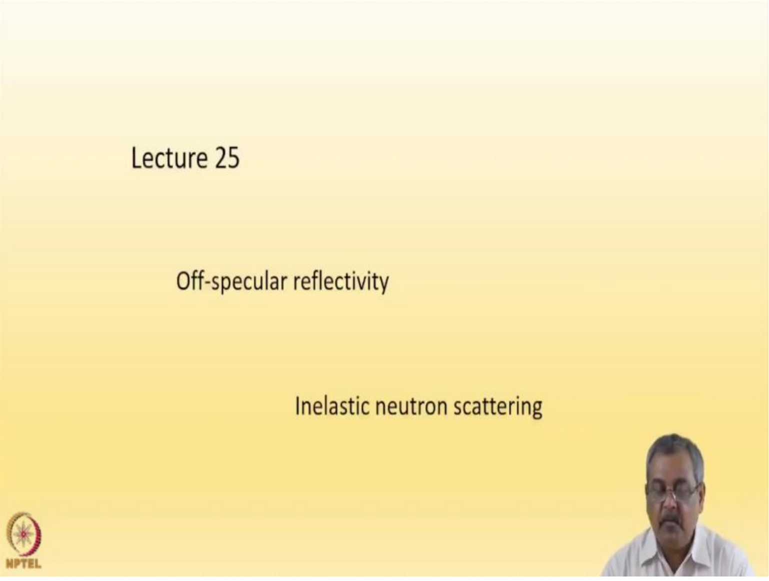

This lecture will have two modules. The first module will be the concluding section for neutron reflectometry, which is off-specular reflectivity and then we will switch over to inelastic neutron scattering from elastic scattering. Till now all our discussions were on elastic scattering related to structure and now we will switch over to inelastic neutron scattering for dynamics in materials.

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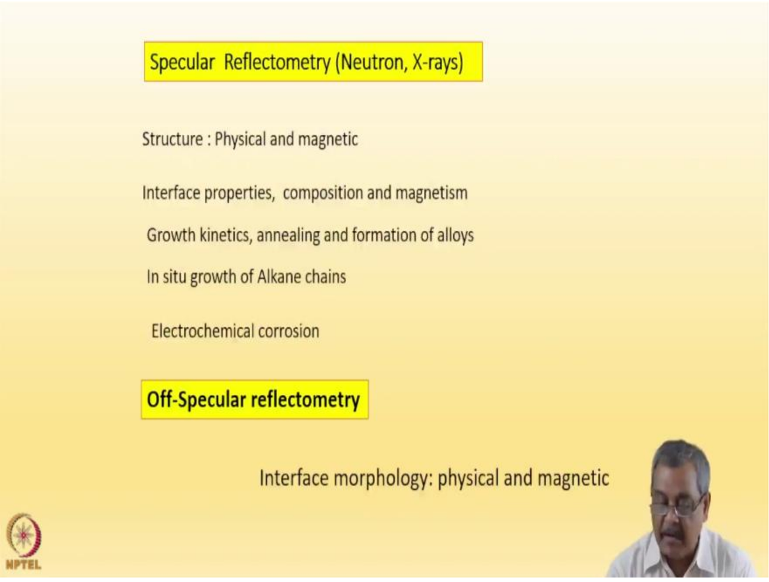

We had discussed specular neutron reflectometry for neutrons and x-rays and we saw that we can find out physical and magnetic structures, various interface properties (using this technique). We can study growth kinetics and formation of alloys. One example was on nickel aluminum alloy forming Al_3Ni. You can also study in-situ growth (of films) when the source is strong with large number of neutrons. The last part of this series is off-specular neutron reflectometry which can quantify interface morphology: physical and magnetic.

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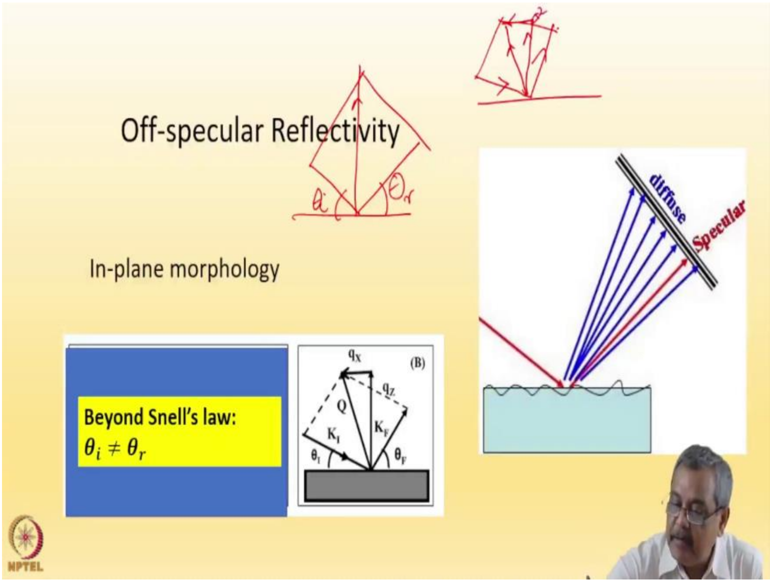

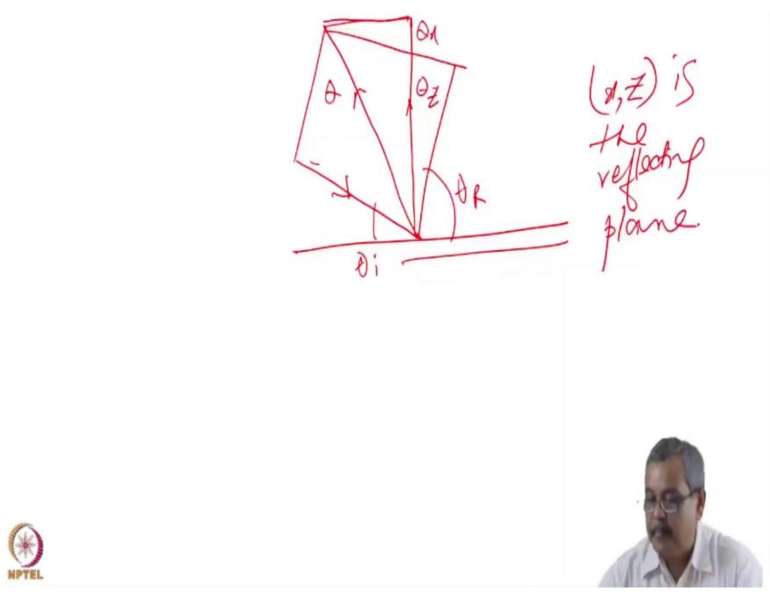

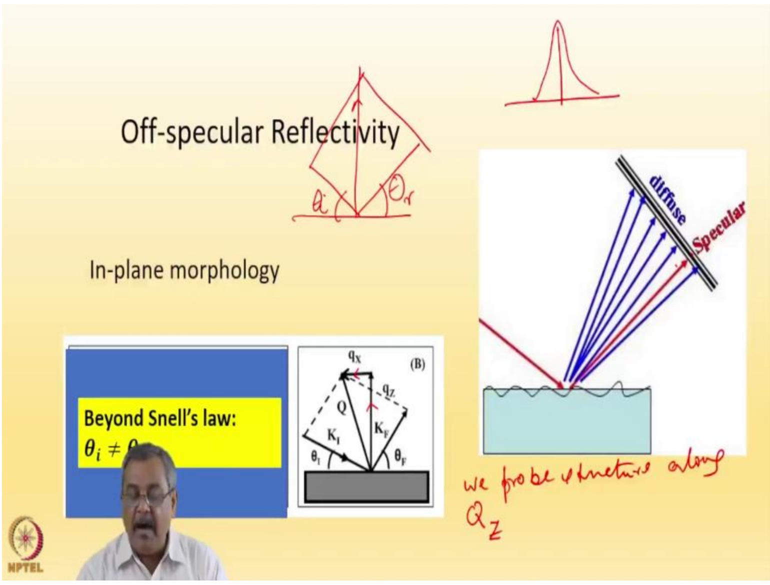

What do we mean by off-specular? So far, we have discussed reflectivity where the incident angle and the reflected angles were equal, but I can also do studies where the incident angle is not equal to the reflected angle. So far, the Q vector was normal to the surface of the film. Now you have a Q vector which is at an angle to the surface and I can have two components out of it, namely, Q_Z and Q_X.

(Discussion on the drawing) This is the reflecting surface where incident angle θ_i and reflected angle θ_R (or θ_F) are not equal. In this case this is the Q vector (not normal to surface). Now this Q vector can be split into two components, one is Q_Z which we are familiar with, but we also have a component which is parallel to the reflecting plane. We can call it Q_X. This is the case if X-Z is the reflecting plane.

In this picture you can see I have shown the surface and I have shown it with respect to a one-dimensional detector because in the instrument in Dhruva a one-dimensional detector is used so in that you have data on few channels because it (reflected data) cannot be in a perfect delta function because of instrumental resolution. A delta function reflection which follows Snell's law, means that $\theta_i = \theta_F$, on the detector. It will be broadened by instrumental resolution and give the specular peak. But beyond the specular peak we also have diffuse or off-specular reflectivity. To bring home the point what do we mean by off-specular reflectivity?

If you remember in olden days a movie projector used to project on a cloth screen, now that cloth screen is not a mirror. For a mirror, if we project the movie on a mirror you can only see it from certain angles but when we projected it on the cloth screen we could see the movie from any part of the movie theater because it was a diffuse scattering screen, a rough screen which was used to reflect diffusively.

Here also, because Snell's law is not valid (meaning beyond Snell’s law), we have reflected intensity beyond the specular peak. It is not a mirror like reflection and we have Q value which has got two components Q_Z and Q_X which I explained just now. Now the fact is that in any scattering experiment we probe structure along Q which was Q_Z for specular reflectivity. Now that we have a component which is along the surface plane, then it will also be able to probe the surface structure in terms of height-height correlation function on the surface.

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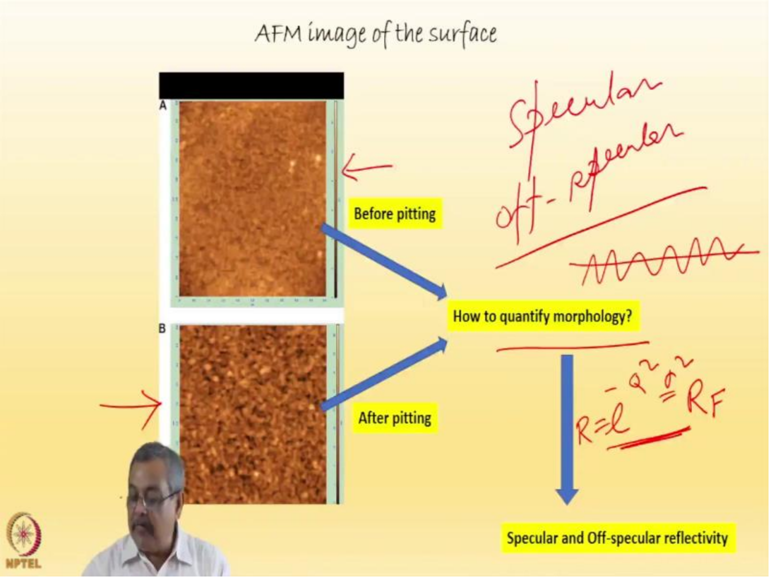

I will use one or two examples (for off-specular neutron reflectometry).

This is a nickel film which was intentionally taken through a corrosion process using sodium chloride and the images you see here, one is before pitting corrosion and other one is after pitting corrosion. We had done specular reflectivity from the surface and also did off-specular reflectometry and I will show you what (information) we get from these two (experimental techniques).

From the AFM picture you can see the surface structure is modified and granules are appearing on the surface after pitting corrosion. How to quantify the surface morphology? We can quantify the morphology with specular and off-specular (neutron) reflectivity.

We know that surface roughness has been characterized with a Debye–Waller like factor $e^{-Q^2\sigma^2}$ and this factor was multiplied with R_F to get the reflected intensity σ^2 gave the average roughness of an interface, not just the surface but (also) of an interface. This is the average fluctuation of the surface around a mean height. This was done in specular reflectivity.

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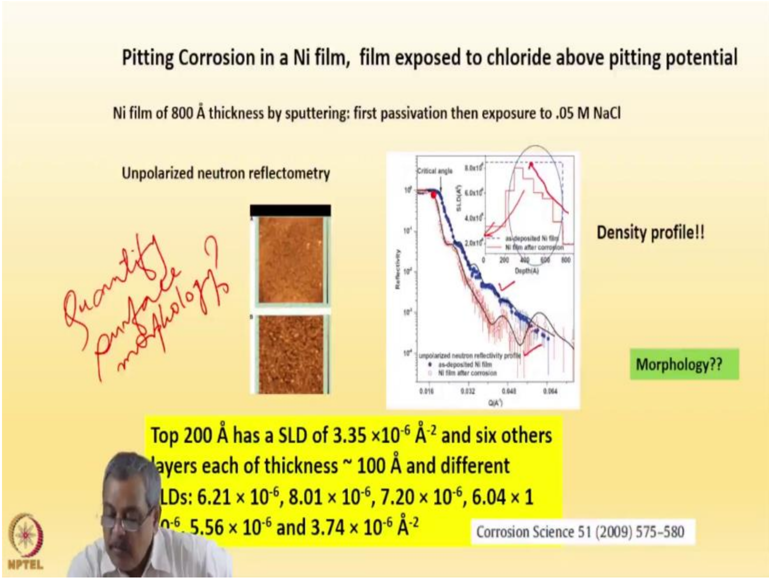

Now let us see how we do the characterization of the corrosion for this nickel surface. This nickel film was around 800 Å thick so approximately 0.1 micron which was first passivated and then exposed to 0.05 molar sodium chloride. We know that it causes corrosion. First, we did a specular reflectivity from which we can get the density profile (along depth). Interestingly here I show you two specular reflectivity patterns, one is as-deposited and one is after corrosion. Now one thing is clear, you can see that the critical angle is slightly less because there is a loss of density as the part of the film has been eaten away. Here the specular reflectivity profile was fitted with a six-layer model and you can see that each of the (virtual) layers was of around 100 Å thickness and with different scattering length densities because as we penetrate the film, we find that the film (layer) goes to higher density. Because the exposure to corroding fluid was on the surface so it penetrated and you can see that this is reflected in the density profile. These (densities of virtual layers) are shown as histograms.

These models tell us that as we go inside how the corrosion has changed the scattering length density profile. At the air and the film interface the corrosion is clear (from AFM) but now how to quantify the surface morphology!

One part is of course we can calculate the sigma for the surface and that is partial quantification (of surface morphology) but we can do a much finer work when we do diffuse neutron scattering.

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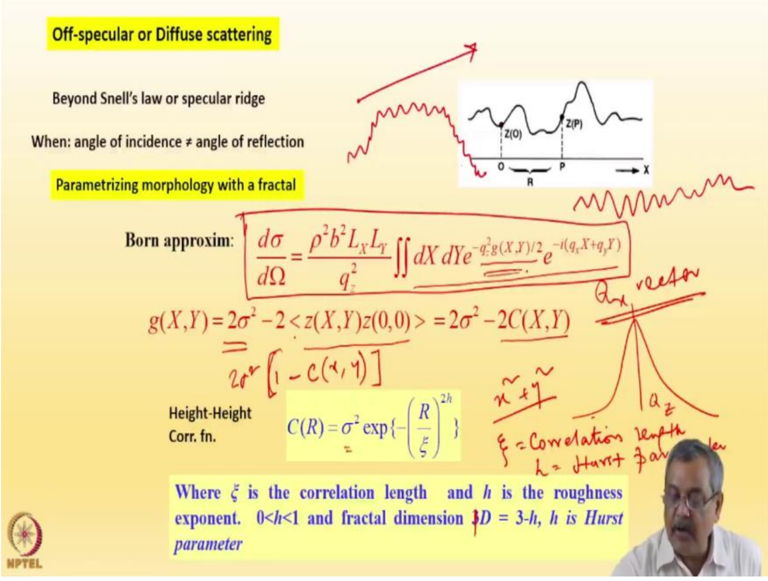

Now please look at this schematic, on the surface we have undulations like this and if I consider a mean or average surface below it then the height varies, depending on the roughness of the interface. This is along the Q_X vector that we defined earlier for off-specular reflectometry. Here the reflected intensity is given as a Fourier transform over X and Y of a height-height correlation function.

Q_Z is along the average Z value because the broadening of the peak due to off-specular reflectivity happens at a certain value of Z component or of Q_Z. g(X, Y) (we call it height-height correlation function) here is very interesting, given as

$$g(X,Y) = 2\sigma^2 - 2\langle z(X,Y)z(0,0)\rangle = 2\sigma^2 - 2C(X,Y)$$

here, $\langle z(X,Y)z(0,0)\rangle$ the correlation function for heights at arbitrary distance. In general, for a two-dimensional surface height at (X, Y) with respect to an (arbitrary) origin $C(X,Y) \equiv C(R)$, here $R^2 = X^2 + Y^2$ if I have both the components, *'x'* and *'y'*. Origin has nothing specific about it because we have an ensemble average, so we can set the origin anywhere and look for this correlation function. That is how the ensemble average is obtained. Correlation function $C(R)$decays with distance R, $C(R) = \sigma^2 \exp\left\{-\left(\frac{R}{\xi}\right)^{2h}\right\}$. This empirical formula we obtain for a fractal structure of the interface. Here ξ is a correlation length on the surface and h is known as Hurst parameter which gives the fractal dimension of the surface.

A fractal dimension is basically where the surface such that if I try to measure a length on it, it does not change linearly if we change the scale of measurement. It follows other power laws.

It is like India's coastline or the surface embedded by a tree branches. So basically, the surface roughness is characterized by its fractal dimensionality. The fractal dimension $D = 3 - h$. If it is a two-dimensional surface and $h = 1$ then $D = 2$. That means it will be a flat two-dimensional surface. But often you find $h < 1$, if h goes to 0 then basically the embedded fractal surface though is supposed to be 2-dimensional it reaches almost a 3 dimensional.

And as h gets smaller and smaller it goes to more and more fractal dimensionality and as h becomes closer to 1 it is closer to 2-dimensionality. That means a smooth surface will have h=1 and a it is a rough surface if h has a value which is less than 1. With this much of introduction let me just mention to you that this is what we will be trying to fit to the experimental data by fitting a height-height correlation function in the Fourier t space *('Q_x')*.

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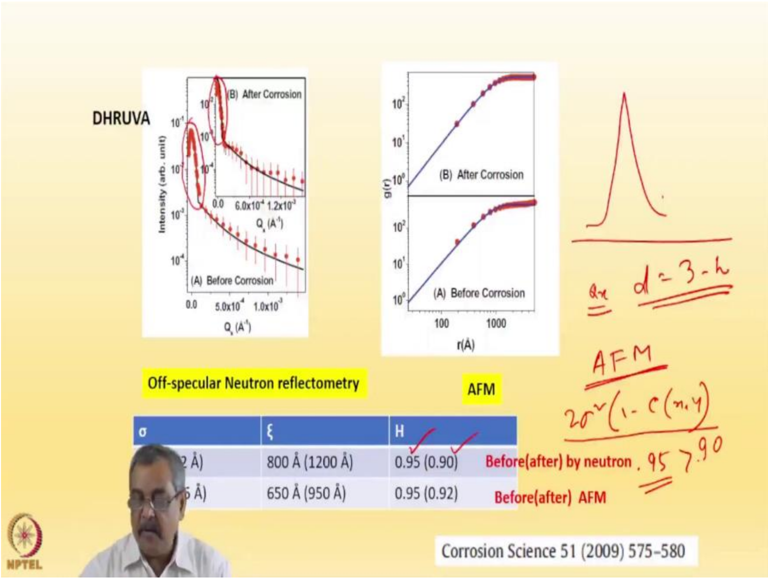

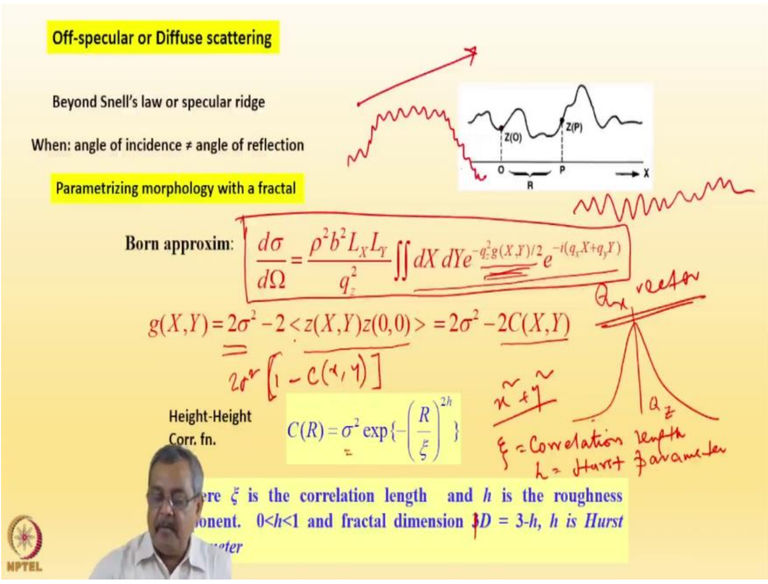

We did the experiment at Dhruva on the film which was taken through a pitting corrosion cycle. This is the Q_Z peak (encircled) around which we have collected the (off-specular) data. This is actually possible because it is a one-dimensional PSD and we can collect the data over a range of say Q_X (depending on PSD channel) because we considered Q_X as the deviation from specular reflectivity.

In this data you can see that the Q_X value is much smaller than the value of Q_Z what is shown there (in the plot) and that is why we can have a mean Q_Z value and the tail which depends on the height-height correlation function. By fitting these two before and after corrosion, we can see the change in surface morphology. I will just give you the parameters that we obtained from the fits. we fitted this for the height-height correlation function and what we found is σ (mean roughness) equal to 20 Å before and 22 Å after corrosion.

We had also compared it with the height-height correlation function that we obtained by using AFM (on the surface). This is AFM data on the right-side plot and because $g(X,Y) = 2\sigma^2 - 2\langle z(X,Y)z(0,0)\rangle = 2\sigma^2 - 2C(X,Y)$ where $C(X,Y)$ is an exponential function. As x, y goes to infinity we get a saturation value. So, this is what we expect to get when we measure the height-height correlation function from AFM data and this is what we get from the neutron off-specular reflection from the surface. Their matching is excellent, for example before corrosion the correlation length was 800 Å and after corrosion this increased to 1200 Å, from off-specular reflectometry. the AFM says it was 650 Å and 950 Å, before and after corrosion. Most importantly the fractality of the surface or the fractal dimension before corrosion was 0.95 and h has become smaller (0.90) after corrosion. So because of pitting corrosion the fractality of the surface has increased or rather dimension has gone more towards 3 dimensionality and the matching between the two data (PNR and AFM) are excellent.

But then the question might come if we can do the thing with AFM then why do off-specular neutron reflectometry? Answer comes from the fact that neutrons penetrate deep while with AFM we can do the height-height correlation function determination only on the surface of a film whereas in neutron reflectometry we can carry out experiments for hidden interfaces also, which is not possible by AFM.

This study was more of a comparative nature and the comparisons show that neutron reflectometry data and AFM data had an excellent matching. But now I will relate something which is possible only and only with neutrons and possibly this is a unique study which I am going to describe to you. It is a quite interesting study in off-specular neutron reflectometry.

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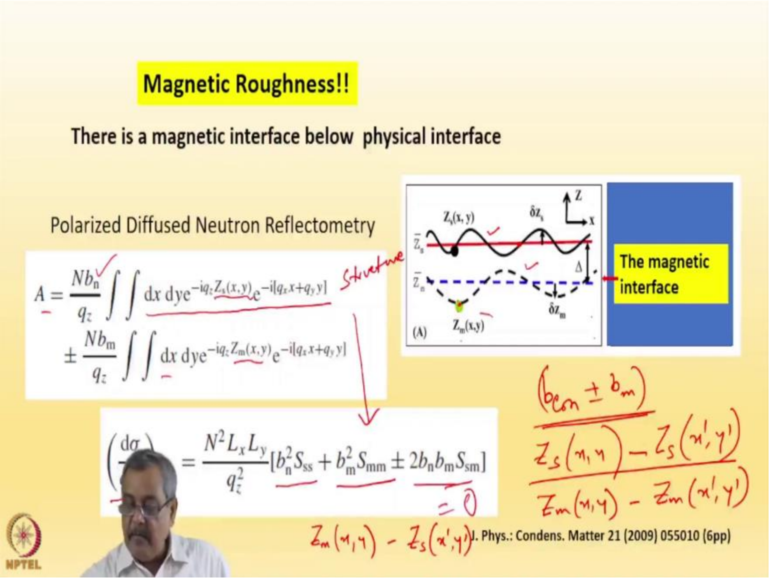

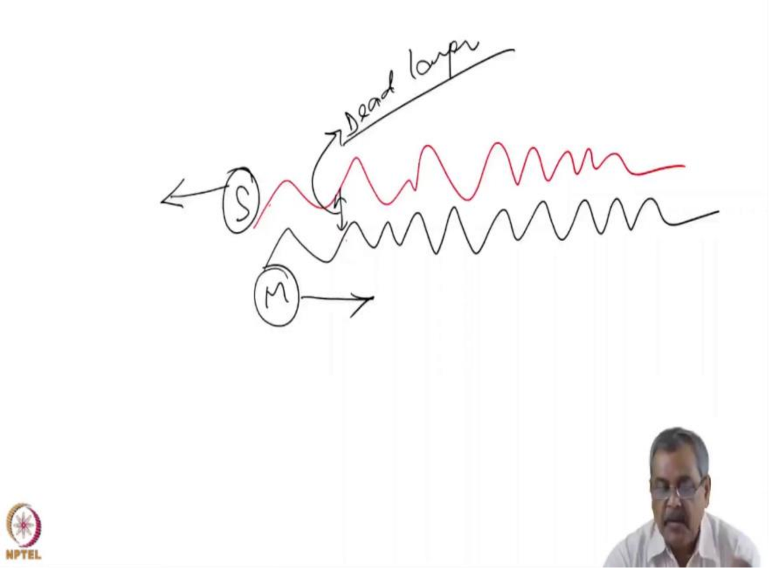

We attempted to measure magnetic roughness of an interface. What do we mean by magnetic roughness? Basically, if we have a magnetic film with an interface like this then a certain thickness of the surface is a magnetically dead layer and this is the magnetic interface and this is a physical interface. We attempted to do an experiment where we tried to get the height-height correlation function for the magnetic interface, also obtain the height-height correlation function for the physical interface and compare these two and the nature of these two interfaces.

Because we have a physical interface and the magnetic interface buried under it, we have now the scattering amplitude in terms of two height-height correlation functions. Please note it is similar to when I wrote $b_{coh} \pm b_{mag}$ when we describe the potential for specular neutron reflectometry of a magnetic sample. Here please see the scattering amplitude is equal to a part which is due to structural interface and we have another part which depends on the magnetic scattering length, otherwise same. This depends on the magnetic height-height correlation function.

Square of this gives me $\frac{d\sigma}{d\Omega}$. Here the term S_{SS} is structure-structure part that means structural height-height correlation function. Here it will be $Z_s(x, y) - Z_s(x', y')$, the two heights I will be correlating using a height-height correlation function. The other term S_{mm} is magnetic only that means this will be $Z_m(x, y) - Z_m(x', y')$ involving a magnetic height-height correlation function. Along with this we will also have an interference term which gives me the height-height correlation function between these two interfaces where we will have a term $Z_m(x, y) - Z_s(x', y')$. So, it reflects how the height of the magnetic interface over here is correlated to the height of the physical interface. Hence, we have three terms here: subscript *ss* corresponds to physical surface correlations only, *mm* corresponds to magnetic surface correlations only and physical surface-magnetic surface interference correlation term represented as *sm*.

So, if there is no correlation between the magnetic surface and the physical surface then the third term (*sm*) will go to 0. Then we will get the height-height correlation function of the structural surface and the magnetic surface or interface. Now let us see what we obtained experimentally.

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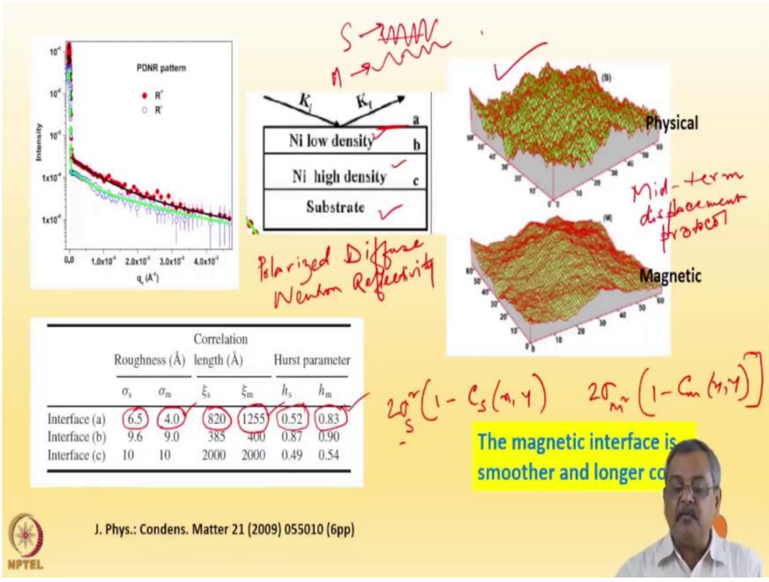

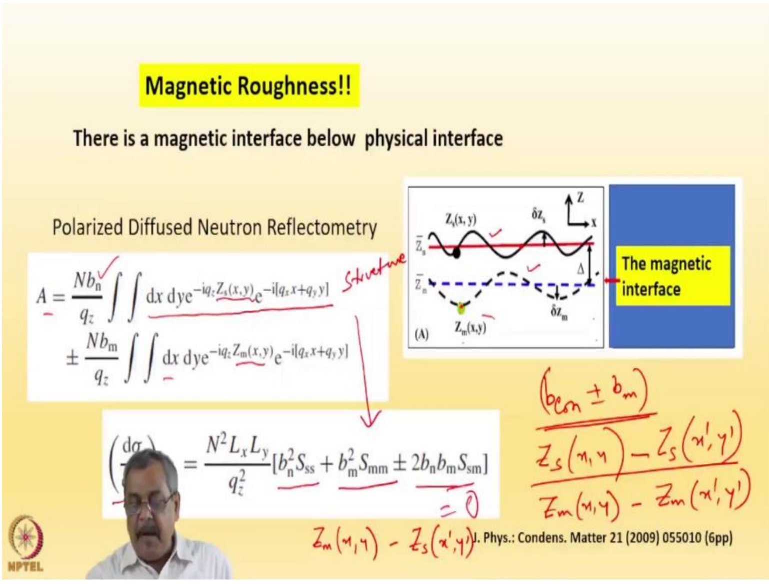

You know that the magnetic potential part can be added or subtracted depending on the polarization of the neutron beam, whether it is parallel or anti-parallel to the magnetization of the film. So, what we did was polarized diffuse neutron reflectivity or PDNR in brief. In this case we have gone one step ahead and not only we are doing off-specular neutron reflection, in addition we are doing off-specular reflection in the polarized mode. That means my probing (neutron) beam is up polarized and down polarized for this experiment with magnetized nickel film. I had earlier also shown you the specular reflectivity data fitted with three-layer model. We have a low-density layer, a high-density layer and on the substrate and what we are looking at is the air film interface here.

Actually, there is not only one interface but there is a physical interface and there is a magnetic interface below this and we try to fit the correlation function for both these interfaces. This is the data plotted in the log scale, so that you can clearly see the distinct difference between the R^+ and R^- data indicating that there is indeed off-specular magnetic reflection.

From this expression you can see that all the three terms are present and there is a difference. Otherwise, if this was not there then only for both of them, I will have *ss* and *mm* and then they will be identical. Since they are not identical that indicates that there is a difference and we obtained the parameters of the interfaces, namely *a*, *b* and *c*, from the fits to the PDNR data.

I will talk about the *a* interface. Please look at this interface which is of interest to us. Here first what we fitted is the σ value because we had height-height correlation function and if you remember it is $2\sigma^2 - 2C_s(X,Y)$ and $2\sigma^2 - 2C_m(X,Y)$, so, there are two correlation functions that I fitted.

At this interface, average structural roughness was larger than average magnetic roughness, the magnetic interface has a longer correlation length and the Hurst parameter (h) is much smaller for the structural surface compared to that for the magnetic interface. That means the magnetic interface is much more smooth and closer to 2-dimension than the structural interface and it is correlated over a much longer distance compared to the physical interface. Also, the magnetic interface has much smaller roughness compared to the physical interface. This actually is justified, because we know that height-height correlation for a magnetic interface should be dependent on the magnetic dipole-dipole interaction and this is supposed to be long range and, so, the magnetic interface is supposed to be much smoother because of long range interaction and weak interaction between the two height-height parts unlike the structural air- film interface.

We used mid-term displacement protocol to generate these two fractal surfaces. With the parameters obtained from the fits we generated the physical interface as well as the magnetic interface. You can visibly see the distinction between the two interfaces.

Hence, we can do polarized diffuse neutron reflectometry to obtain the difference between a magnetic interface and a physical interface and possibly this is a unique experiment which has not been done in many other places. With this I complete the module on structural studies using neutrons and in the next part I will start inelastic neutron scattering for dynamics.