

Neutron Scattering for Condensed Matter Studies

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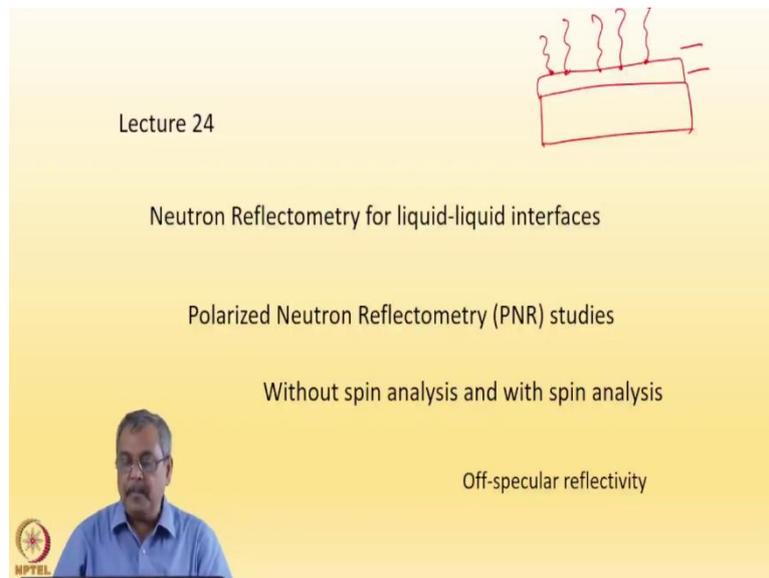
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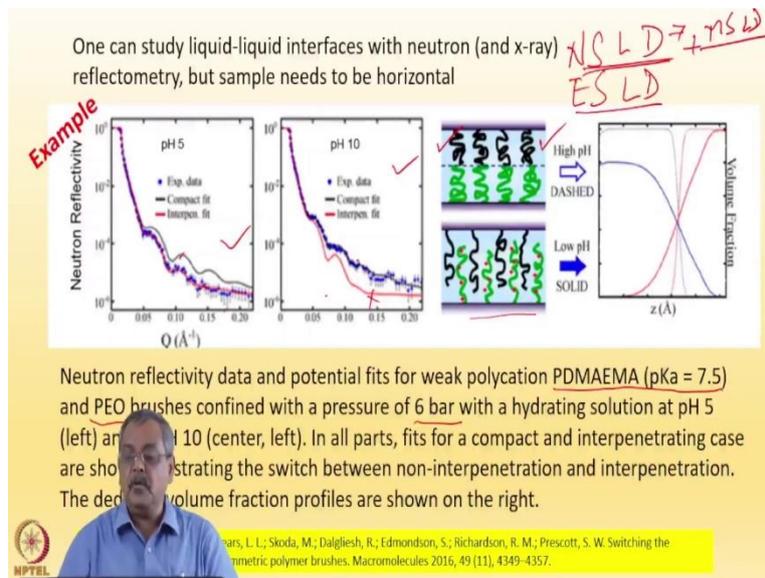
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In the last lecture, I discussed with you, how we could interpret the alloy composition in a Ni/Al multilayer. Though we used PNR but there it was more of physical density (and alloy composition) determination. Before I go on to Polarized Neutron Reflectometry magnetic studies, which is the most interesting thing for the condensed matter researchers, I must briefly mention you about neutron reflectometry for liquid-liquid interfaces.

This is a branch of studies which has gained popularity in last 20 years or so, where we study the interface between two liquids or interface between liquid and air with various chemicals. For example, we can study interfaces of a liquid possibly with surfactants sticking out from them. I use this example, because we ourself have studied this using SANS technique (discussed earlier). Similar studies in reflectometry for these interfaces are very much popular presently. Such studies have become, so much in demand that there are dedicated neutron reflectometers, often unpolarized neutron reflectometers, where you can have physical density profiles for proteins, on liquids or polymers on some kind of interfaces. I will use only one example to highlight the role of these studies.

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For this, I have chosen a study of liquid-liquid interfaces with neutrons. Such interfaces can also be studied with x-rays, but in case of neutrons the interesting thing is that we can play with the D_2 and H_2 ratio in the solution. Or if it is water substrate on which we spray these chemicals (then use H_2O/D_2O mixture), so that I can get a very good contrast. That is the advantage with neutrons.

Here, I am showing you an example of nuclear reflectivity data for weak polycation PDMAEMA, poly(2-(dimethylamino)ethyl methacrylate), and poly polyethylene oxide (PEO) brushes and how they interpenetrate at the interface! These studies are important because protein spread or protein unfolding on such medium are of interest for biological studies. In this example, they have been stabilized with a hydrating solution at pH-5 and pH-10. We know that pH is the negative logarithm of hydrogen density, and pH-7 is a neutral solution. So, pH-10 is alkaline, and pH-5 will be acidic. This whole experiment was done at a pressure of 6 bar

We have two data sets of unpolarized (neutron) reflectometry. If you look at this schematic or the cartoon on the right-hand side, you can see that there are two possible configurations at the interface for PDMAEMA and PEO. One is that they do not interpenetrate, they do not mix and the other one, if they mix that the brush is interpreted. The first data is at pH-5, and you can see that the fit without penetration and with penetration have been attempted, and the fit with interpenetration of the brushes gives a better fit and that means at pH-5 for these two brushes spread on a hydrating solution allow interpenetration.

But when we go to pH-10, then it switches from interpenetration to no penetration mode. Here, no interpenetration (of brushes) gives a much better fit.

This is an example where we measure scattering length density (SLD) profile. This is what we measure in all neutron and x-ray reflectometer experiments. The scattering length density profile is a nuclear density, if it is an unpolarized beam and so we call it NSLD, and in case of x-ray it is electron scattering length density or ESLD, and if the system is magnetized or it has got magnetic moment, then with this NSLD for neutrons, we also add one magnetic scattering length density (MSLD).

This is the only example I am using, where organic and biological samples (NSLD) at the interfaces (are studied) and their properties with respect to their spreading into each other. Penetration from one medium to another medium can be studied using (unpolarized) neutron reflectometry or neutron reflectivity. Now, I will get into polarized neutron reflectometry.

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PNR can be done in 2 modes. With no polarization analysis of the reflected beam and with polarization analysis of the reflected beam

Polarized Neutron Reflectometry

NCNR, NIST

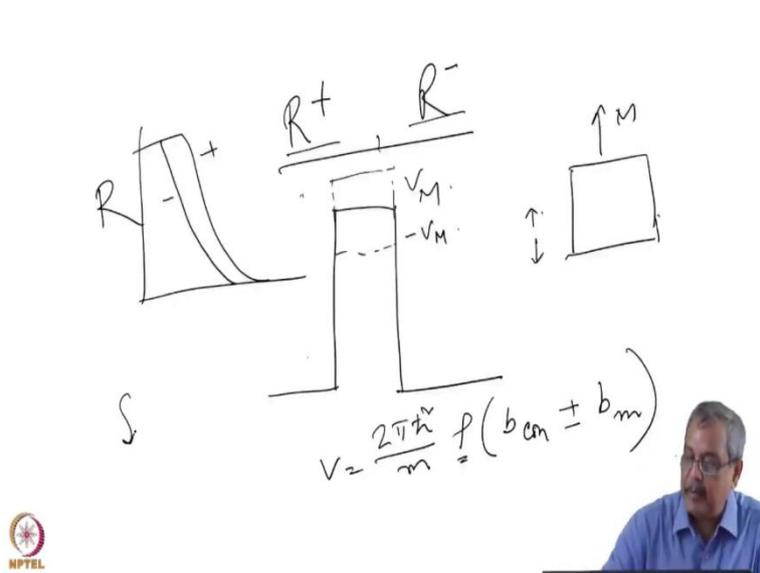
https://www.researchgate.net/publication/260835573_Determination_of_the_effective_transverse_coherence_of_the_neutron_wave_packet_as_employed_in_reflectivity_investigations_of_condensed_matter_structures_Part_1_Measurements/figures?to=1

DHRUVA

Polarized neutron reflectometry, PNR, as the name suggests that this needs a beam which is polarized. This instrument can be operated in two modes; one with no polarization analysis and with polarization analysis. I will first talk about (experiments) without polarization analysis and then with polarization analysis.

Let me show you the experimental setups, this is the one at DHRUVA, this setup is at NCNR NIST. You can see that there is a polarizer in both the instruments (before sample), and after the sample there is a (spin) analyser (at NIST). Here also there is an Fe/Si analyser.

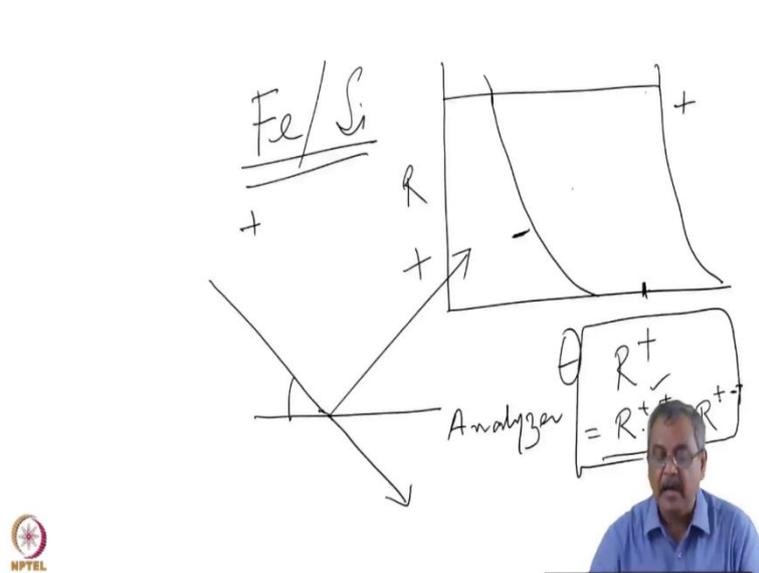
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In case of without polarization analysis, we measure R^+ and R^- . If this is the magnetic sample with this magnetization direction, then I have two reflectivity, one where the neutron beam (spin) is parallel to the magnetization in the sample, and the other one is antiparallel to the magnetization in the sample. R^+ and R^- corresponds to these two cases, respectively.

Now, if you remember as I had earlier discussed with you, for R^+ , nuclear potential is added with one magnetic potential while for R^- magnetic potential is subtracted from the nuclear potential. Hence, the total potential here is given by $V = \frac{2\pi\hbar^2}{m} \rho (b_{coh} \pm b_{mag})$ and then because of this we also have two different critical angles (for up and down neutrons) as potential dictates the critical angle of reflection for that particular neutron (spin). So, in the reflectivity plot, we observe different critical angles for R^+ and R^- .

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Let me just remind you that these polarizers are often (neutron) supermirrors. As I already told you that in NIST beamline Fe/Si supermirror is used as polarizer. If we observe supermirror's reflectivity then we find that critical angle is large for one spin direction of neutrons while it is much smaller for other neutron spin and if I take a reflection at an angle which is between these two critical angles, then I can get a fully polarized beam. This is the principle of polarization, and in the reflected beam, using the same principle, if I put an analyser of the same supermirror at an angle which is again between these two critical angles, then I will get only one particular spin reflected into the beam, and the other (spin) will be transmitted.

Actually, $R^+ = R^{++} + R^{+-}$ where R^{++} is the non-spin flip component and R^{+-} is the spin flip component (of reflectivity) and we get both of these together if we do not carry out the polarization analysis. However, if we want to do the analysis, then I will get two reflections separately. R^{++} is non-spin flip, because plus goes as plus, and R^{+-} is spin flip as plus goes as minus. I will come to it later.

This is the general assembly of a reflectometer with the analyser in place. Typically, in the reflected beam we need to put a polarization analyser to know the non-spin flip and spin flip components. Earlier, we were just measuring R^+ and R^- , that means we were not doing any spin analysis of the reflected beam; we were just impinging a beam which is either parallel to the magnetization in the sample or antiparallel, and measuring the reflected intensity

Now, as I told you earlier that V (potential) in a matrix form has got two components, one is (for) the (spin) plus component, (other)one is (for) the (spin) minus component,

$$V = \begin{bmatrix} V_+ \\ V_- \end{bmatrix} = \frac{2\pi\hbar^2}{m} \rho \begin{bmatrix} b_{coh} + b_M \\ b_{coh} - b_M \end{bmatrix}$$

Similarly, we have two critical angles for the polarized beam and are given by,

$$\theta_c^\pm = \lambda \sqrt{\frac{\rho(b_{coh} \pm b_M)}{\pi}}$$

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Without polarization analysis, one measures R^+ and R^-

Polarization of the neutron beam parallel (R^+) and antiparallel (R^-) to the sample magnetization. The up (+) and down (-) beams see different magnetic potentials.

$$V = \begin{bmatrix} V_+ \\ V_- \end{bmatrix} = \frac{2\pi\hbar^2}{m} \rho \begin{bmatrix} b_{coh} + b_M \\ b_{coh} - b_M \end{bmatrix}$$

$$\theta_c^\pm = \lambda \sqrt{\frac{\rho(b_{coh} \pm b_M)}{\pi}}$$

Schrodinger eqn.s for neutron propagation with spin parallel (+) or anti-parallel (-) to the magnetization

$$\frac{d^2\psi_+(Z)}{dZ^2} + \frac{2m}{\hbar^2} [E - V_+(Z)]\psi_+(Z) = 0$$

$$\frac{d^2\psi_-(Z)}{dZ^2} + \frac{2m}{\hbar^2} [E - V_-(Z)]\psi_-(Z) = 0$$

Parratt's Formalism




Now, we also have to consider the Schrodinger equation for propagation of these waves, and there are actually two equations, one for the up neutrons, the standard form of the Schrodinger equation, where V_+ is the potential and another one is for the antiparallel neutron where V_- is the potential. You can see the solutions are different and the critical angles will be different for the solutions.

Now also I use Parratt's formalism to calculate the model reflectivity pattern for up and down neutrons. And then do the fitting, in our case we use genetic algorithm but there are other fitting techniques which are used, to get the solution in form of reflectivity as a function of angle (or Q , momentum transfer) for the two polarizations.

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In this case one measures two reflectivity profiles for the up and down neutrons as a function of wavevector transfer, 'q_z' and one attempts to extract magnetic moment density profile as well as physical density profile from the data.

Asymmetry parameter $\frac{R^+(Q) - R^-(Q)}{R^+(Q) + R^-(Q)}$

Ni: 0.54 μ_B
Magnetic moment density

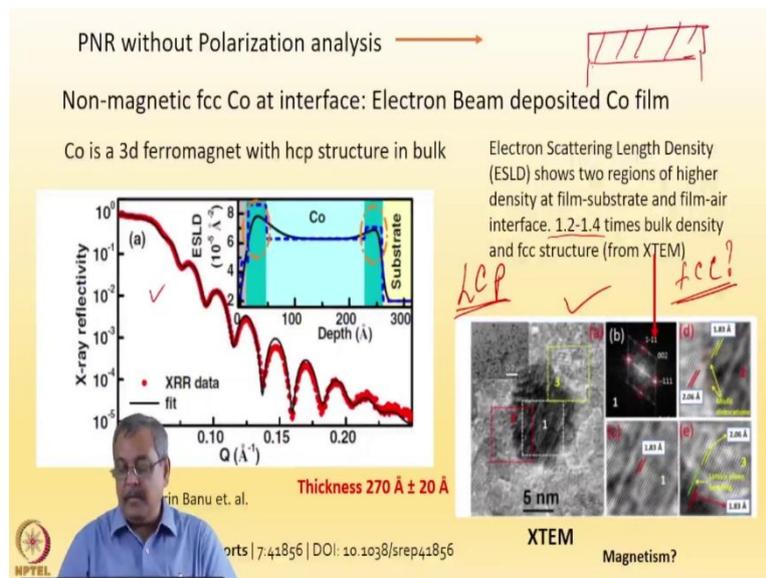
Phys.: Cond. Matt. 21 (2009) 055010 (6pp)

Here, I am showing you an experimental example of a Ni film which is magnetic with a magnetic moment of around 0.54 μ_B/atom. I have shown here the plot of the reflectivity profile of the two spins, R⁺ and R⁻ reflected from the film. Often, we also take a recourse to a plot of an asymmetry parameter given by $\frac{R^+(Q) - R^-(Q)}{R^+(Q) + R^-(Q)}$. So, this asymmetry parameter joins the two reflectivity profiles in one and also joins the fit to both of them (in one plot) as I have shown here.

So, we have fitted reflectivity pattern using Parratt's formalism for the two spin components and this is the joint fit which shows that these oscillations are due to Kiessing oscillation and you can see the asymmetry parameters and the fit, and from the fit we could get the magnetic moment density in this medium.

When we do not do polarization analysis, what we get is magnetic moment density in the medium. This is at mesoscopic length scale. Now, with this much of introduction to experiments that are possible without polarization analysis of the reflected beam, I will use two examples to highlight the findings (of such studies).

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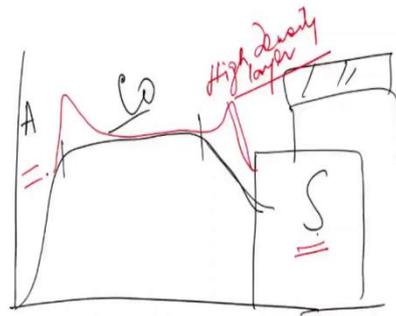


One of them is about a Co film which was deposited by electron beam deposition technique. Usually, for most of the samples, XRR is carried out prior to the neutron reflectometry or polarized neutron reflectometry, because with XRR it is possible to get very accurate result for the physical density as it is a high intensity technique.

We have also used XTEM, high-resolution cross-sectional TEM, to get the crystallographic structure at the interfaces. Study is never complete unless we marry several techniques together. Surely, PNR is an excellent tool, but I want to highlight this point that to get interesting results, we need to combine several techniques together.

Here, in the XRR data, you can see the Kiessing oscillations due to the thickness of the film and fit to the data gives me a physical density profile and gives us signatures of something, which needs to be probed further. What are those signatures?

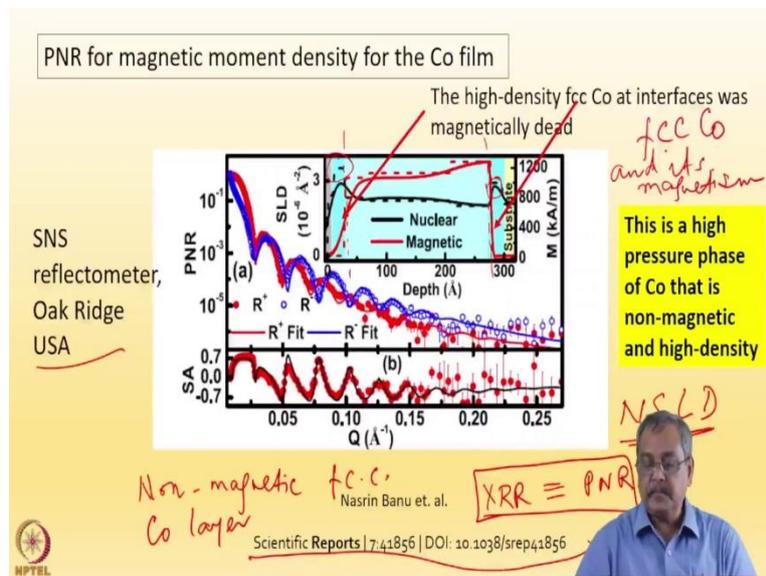
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If you look at the density profiles that have been fitted for the Co film what I would expect for such a single film is somewhat like this. If I consider the substrate density profile is this in some unit then Co film density should look somewhat like this. Because, generally, we have seen that the density at the surface is less and after some point (deeper) it goes to near bulk density. Similarly, due to inter-penetration or mixing between the substrate and the film, there is a lowering of density at the interfaces. But here what I found by XRR is something very interesting. Contrary (to our guess), we found higher density layers at two interfaces, one is at the substrate-film interface, the other one at the substrate-air interface. This is something which was not expected.

We did XTEM in this region, and this is the region which we have highlighted here. And the fast Fourier transform of the XTEM pattern over here gives me an fcc structure. This is also an interesting phenomenon, because this is high density fcc structure with density at interface almost 1.5 times that of the bulk density (of Co), whereas bulk of the cobalt is a ferromagnet which is hcp.

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After this study, we took this sample to a neutron reflectometer at SNS, Oak Ridge. With this technique, I can study both physical density profile as well as its magnetism. The physical density profile that I will obtain from nuclear scattering length density is the same I obtained in XRR through electron scattering length density.

The polarized neutron reflectivity data shows the fits for the plus and minus polarized neutrons and this is the asymmetry parameter over a very large Q range almost up to 0.25 \AA^{-1} . You can see the high-density layers.

So, XRR and PNR both are able to identify this high-density layer and density determined from PNR turns out to be similar to what we found from XRR values. We have also obtained the magnetic density profile from the reflectometry data of R^+ and R^- . This is the asymmetry parameter (plot). Interestingly; the bulk of the Co has a positive magnetic scattering length density that means it is ferromagnetic, but if I look at the high-density layers at the interfaces, they are non-magnetic.

So, these experiments allow us to identify a non-magnetic fcc Co layer at the interfaces and this has been reported here. fcc and non-magnetic Co layer is an interesting observation, because it is known that under high pressure Co goes to non-magnetic high-density phase, but here when you study the film in reflectometer experiment, it is at ambient pressure and this same (high pressure) phase is obtained! We conjectured that due to grain boundary migration at the interfaces some grains got pressurized, and they turned into this fcc high density Co in this specific film, which is otherwise not seen in the bulk at ambient pressure. This one is a

very interesting result found using magnetic moment density from thin films (by neutron reflectometry).

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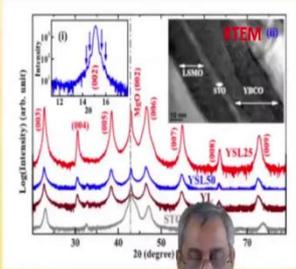
Coupling between a superconductor and ferromagnet: Cooper pair tunneling

A trilayer, $\text{YBa}_2\text{Cu}_3\text{O}_{7.6}$ (YBCO) (SC) / SrTiO_3 (STO) (I) / $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) (FM)

LASER beam deposition, tunneling geometry, substrate single crystal MgO

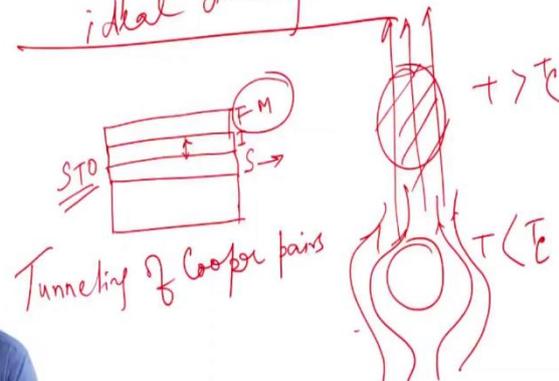
$T_{\text{curie}} = 290 \text{ K}$, $T_{\text{sc}} = 65 \text{ K}$, Highly oriented [001] structure from XRD

d-wave SC (001)



Surendra Singh et. al.
Appl. Phys. Lett. 116, 022406 (2020); doi: 10.1063/1.5134406

Superconductors are ideal diamagnets



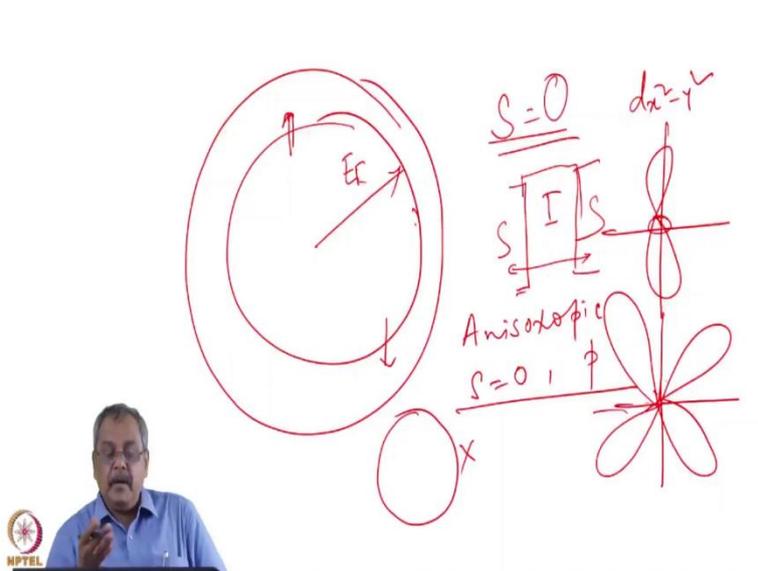
Tuning of Cooper pairs

Another interesting study is coupling between a superconductor and a ferromagnet. This is an ideal sample for polarized neutron reflectometry. Reason being that superconductors are ideal diamagnets, they repel any magnetic field. If a superconducting material is placed in a magnetic field and you go below the superconducting transition temperature, then, for a type I superconductor, it will expel the magnetic flux. That is why a superconductor is known as an ideal diamagnet.

And by measuring magnetic moment density, we should be able to identify the magnetism in a superconductor. Here, we have gone into a little more interesting aspect; we have got a trilayer

heterostructure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO)/ SrTiO_3 (STO)/ $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO). Here STO is an insulator and LSMO is ferromagnetic. This (structure) is a tunnelling geometry. That means we have a superconductor and a ferromagnet separated by a layer of insulating (layer of) STO. We are familiar with the fact that in case of superconductors, we have tunnelling of Cooper pairs.

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Now, what are Cooper pairs? In BCS theory, we know that electrons with opposite spin, on the Fermi couple with each other. So we have got spin 0 ($S=0$) Cooper pairs and it is (also) known that if we have two superconductors separated by an insulator in between then we can have two kinds of tunnelling. One is single particle tunnelling known as Giaever tunnelling and we also have Cooper pair tunnelling and based on this (phenomena) many experiments and many devices like SQUIDs are built.

We have built a trilayer where we have invoked this tunnelling geometry. All of these oxide layers are deposited by a laser beam. This superconductor deposited here has a superconducting transition temperature of around 65 K and LSMO deposited here has got Curie temperature of around 290 K which were determined from the bulk magnetization measurements.

Interestingly, in this case what we found from x-ray diffraction is a highly (0 0 l) oriented structure which you can clearly see from the peaks indexed here. We call this trilayer YSL. Similar results were obtained for YBSO/LSMO as well. Because of the crystalline (lattice) matching between these layers, we get a highly oriented film. There is a reason for me, telling you this, because the superconductor YBCO is a d -wave superconductor. As I told you earlier

that other conventional (BCS) superconductors have spin, $S = 0$, Cooper pairs and have got a spherical symmetry of the Cooper pair. But here, because it is a d -wave superconductor, the superconducting gap at fermi surface is anisotropic.

Cooper pair wave function here can have $d_{x^2-y^2}$ component which looks like this and d_{xy}, d_{yz}, d_{zx} which looks like this. So, the Cooper pair wave function is symmetric but not spherically symmetric here. The directionality in the deposited film should have something to say about the Cooper pair tunnelling and also the gap that you see in various directions in k -space (momentum space).

Now, let me get into the experiment of polarized neutron reflectometry on this highly oriented YBCO/STO/LSMO film, in which we have created a tunnelling junction and we want to see how the magnetization is affected by the superconducting transition temperature.