X-ray based characterization of thin films and multilayers

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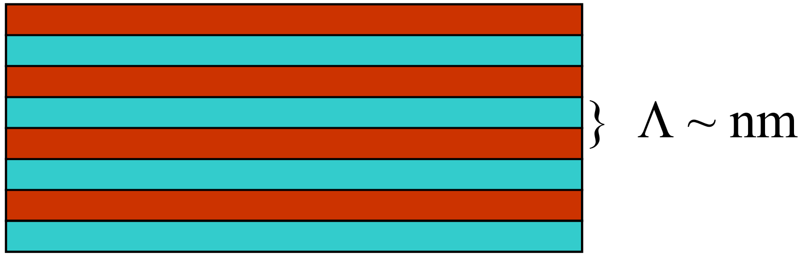
Multilayer Nanostructures:



As the thicknesses of individual layers decrease and become comparable to the characteristic length scale of a given physical property, that particular property can get modified drastically, e.g,

Electronic properties	-	Fermi wavelength (semiconductor quantum well)
Magnetic properties	–	exchange length (PMA multilayers)
Optical properties	–	wave-length of the radiation (x-ray mirrors, AR Coatings)
Electrical properties	-	electron mean free path (GMR multilayers)

A phenomenal development in the field over the last 2-3 decades has occurred due to developments in the field of thinfilm deposition techniques, enabling a precise control on the quality as well as structural parameters of the layers.

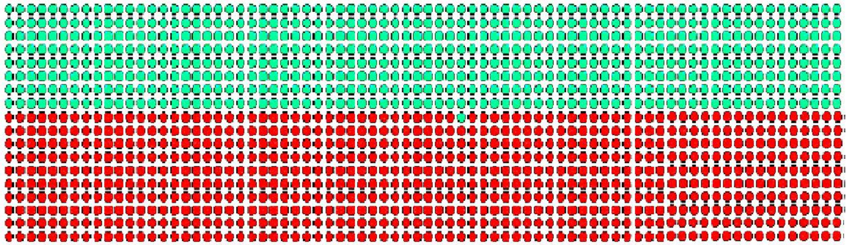
Suitable structural characterization techniques have played an equally important role in developments in this field

Structural parameters of interest

1. Film/layer thicknesses.
2. Film density
3. Interface roughness
4. Inter-diffusion
5. In-plane correlations
6. Vertical correlations

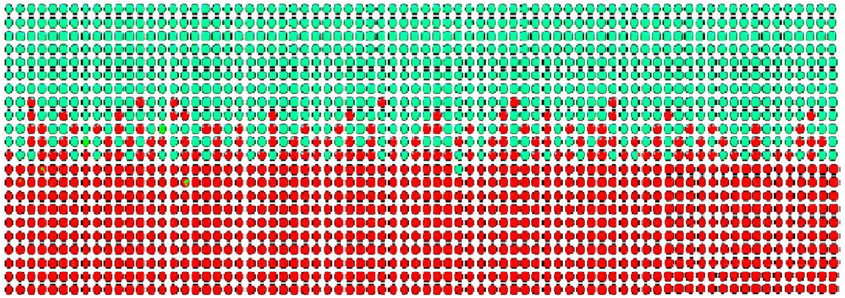
1. Elemental Concentration
2. Short range order
3. Phase analysis

Interface between two layers plays an important role in determining the physical properties of the multilayer structure



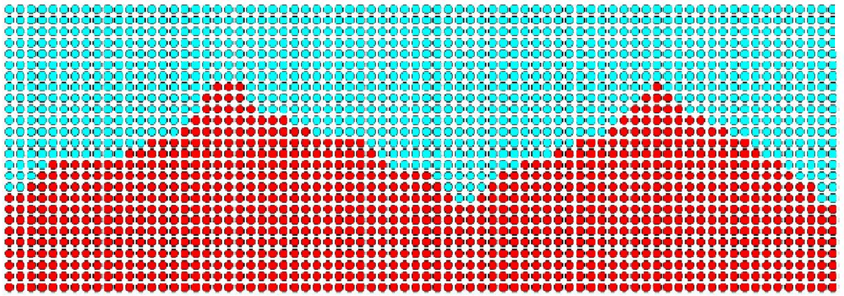
Ideal Interface:

- perfectly sharp and flat



Diffused Interface:

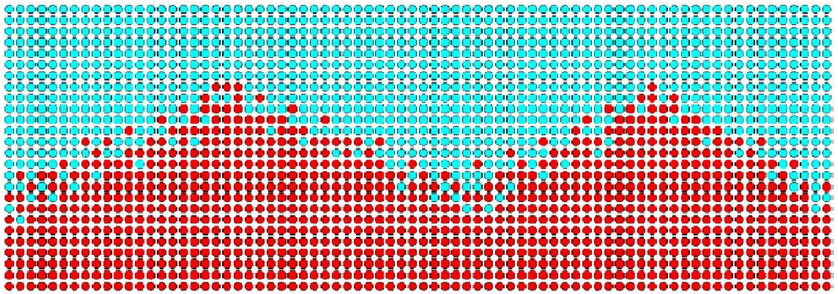
- Concentration gradient across the interface
- Characterized by the thickness of the intermixed region, d



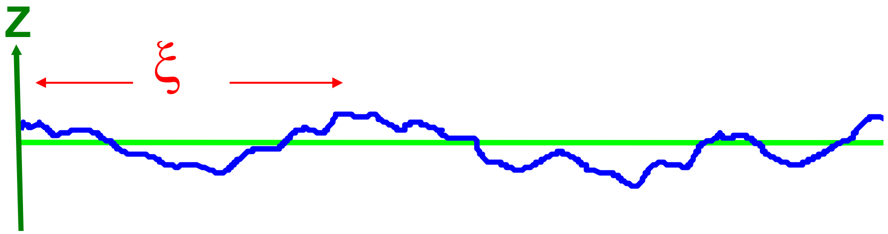
Rough Interface:

-Height of the interface varies from point to point in x-y plane

-Characterized by σ, ξ,h



Real Interface:



- If we define the average interface z_0 as

$$z_0 = \iint z(x,y)\,dx\,dy \;,$$

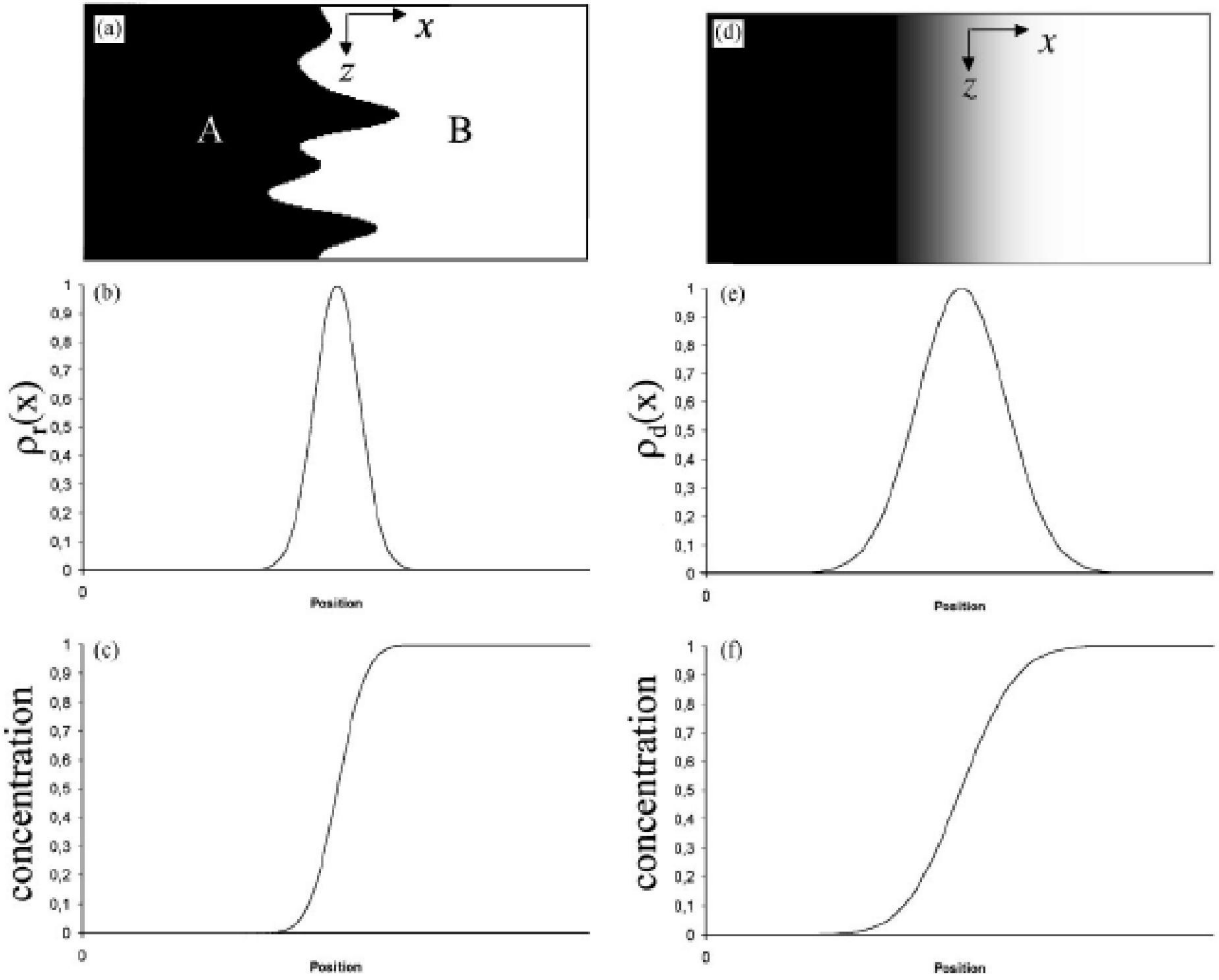
$$\rho(z) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left\{ \frac{-(z-z_0)^2}{2\sigma^2} \right\}$$

the **roughness** σ is defined as the rms deviation of the height of the interface from the average interface z_0

$$\sigma^2 = \iint [z(x,y)-z_0]^2\,dx\,dy$$

In the case of multilayers, the total roughness can be devided into correlated and uncorrelated parts:

$$\sigma^2_{tot} = \sigma^2_{cor} + \sigma^2_{uncor}$$


(a)
x
z
A
B
(b)
$\rho_r(x)$
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
Position
(c)
concentration
Position
(d)
x
z
(e)
$\rho_d(x)$
Position
(f)
concentration
Position

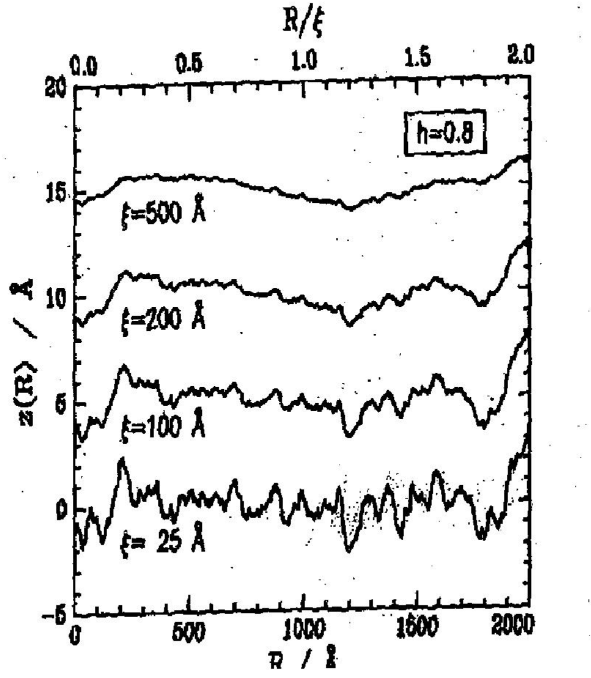
- The distribution of height in the x,y plane is characterised by the height-height correlation function

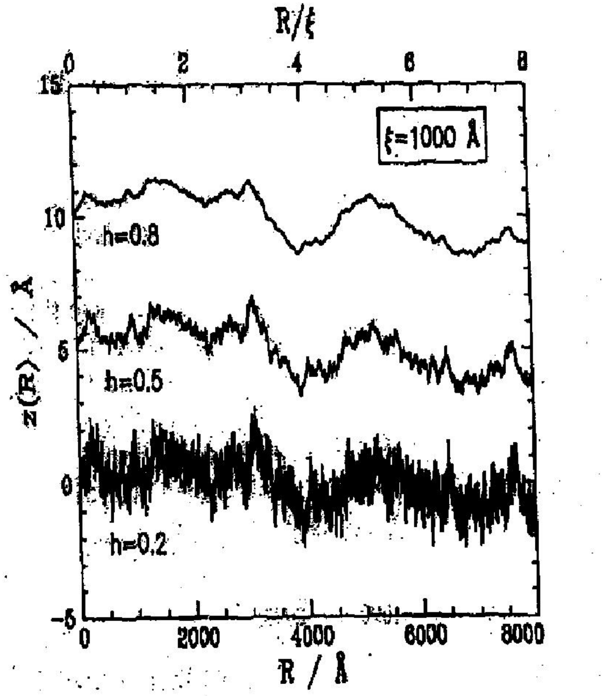
$$C(x,y) = \langle z(0,0)z(x,y)\rangle$$

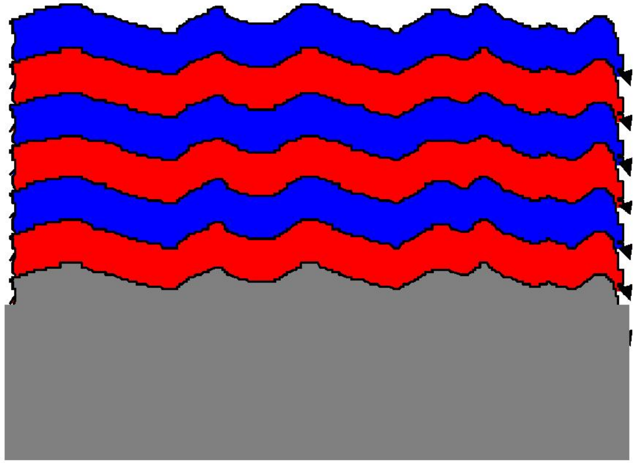
$C(x,y)$ can be approximated by an exponential correlation function

$$C(x,y) = \sigma^2 \exp(-|R|/\xi)^{2h}$$

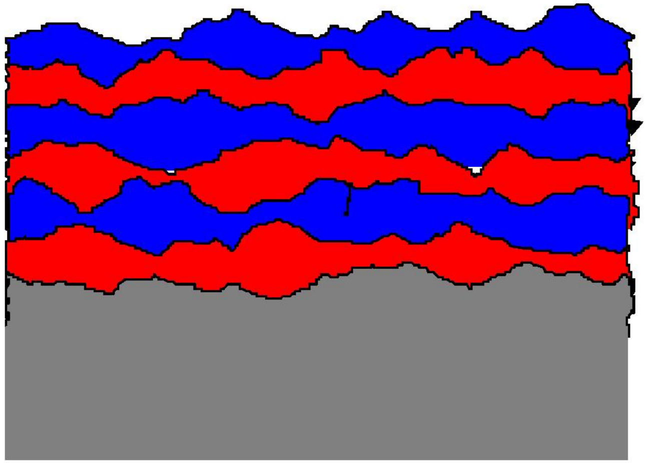
where $R=(x2+y2)^{1/2}$, ξ is the lateral correlation length and $0<h<1$ is jaggedness parameter



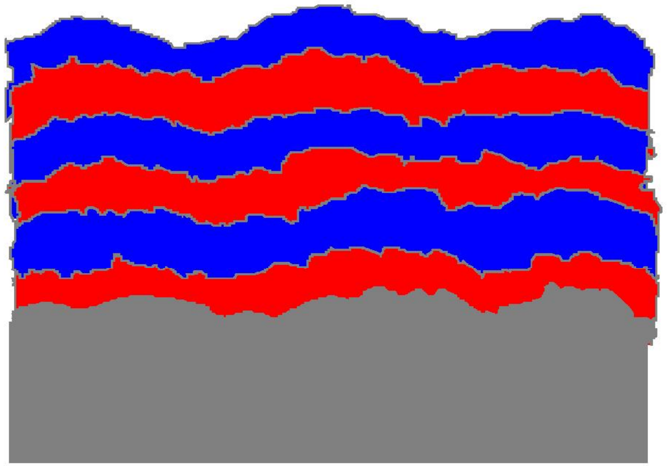




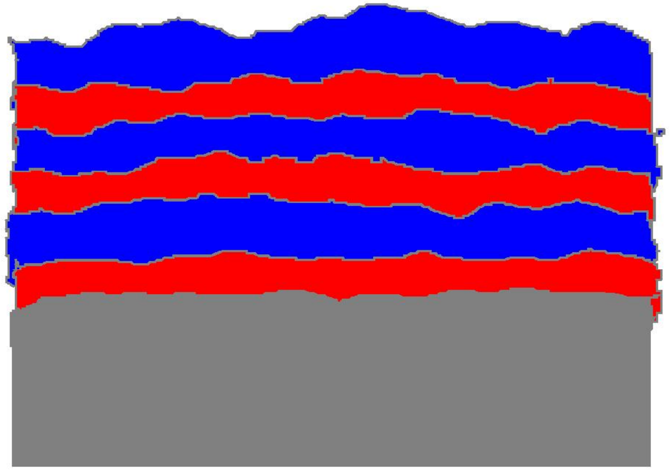
Correlated roughness



Uncorrelated roughness



partially correlated roughness



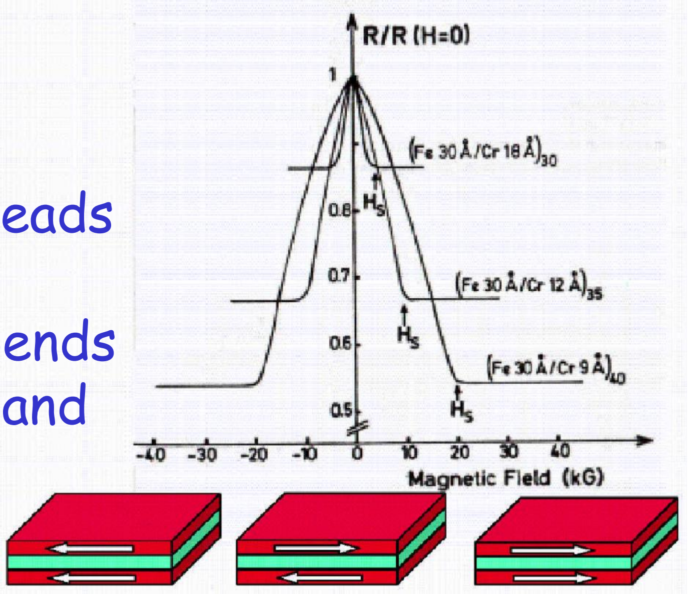
cumulative roughness

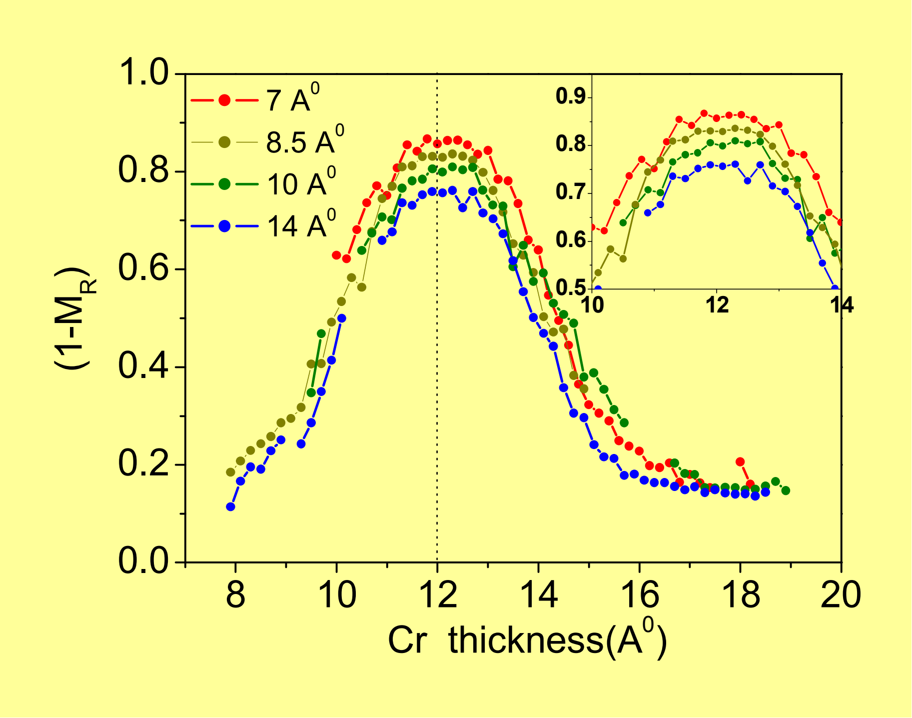
GMR multilayers

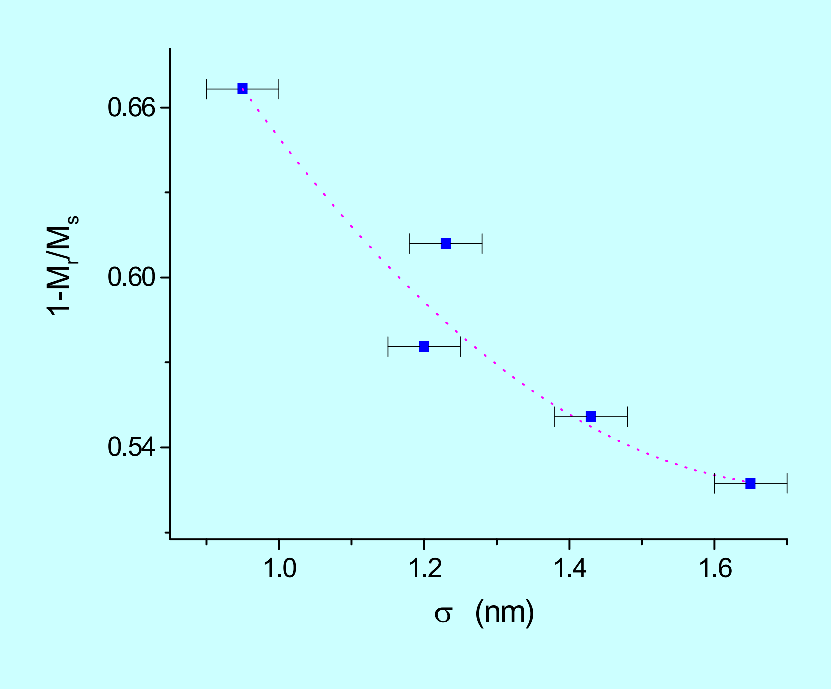
(Fe/Cr ; Co/Cu)

Used in non-volatile memories; read-write heads

Strength of antiferromagnetic coupling depends upon the thickness of spacer layer (e.g. Cr) and the interface roughness





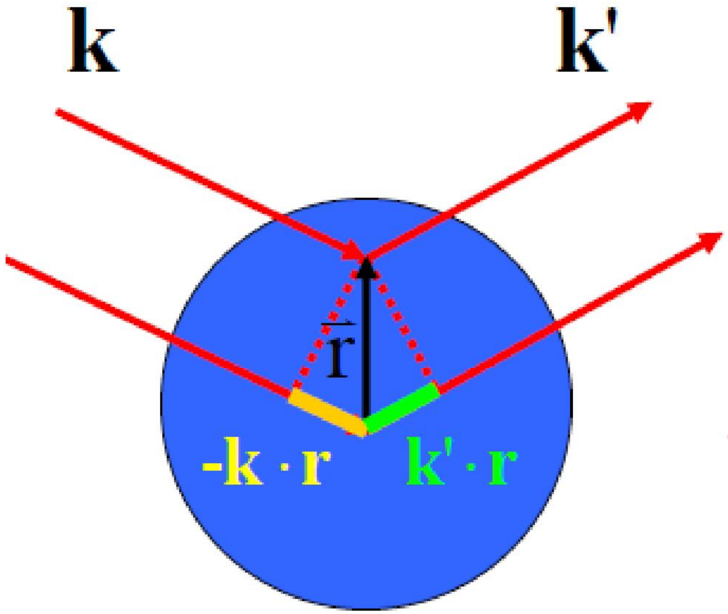


- X-rays are powerful probe for studying atomic scale structure:

•X-ray scattering (WAXS, SAXS)	long range order
•X-ray fluorescence	elemental analysis
•XAFS	local-order (element specific)
•Nuclear resonance scattering	local order/magnetism of a
•(of synchrotron radiation)	given element (isotope)

X-rays are highly penetrating radiation, which makes them useful for studying buried structures. But this penetration depth also makes an X-ray beam inherently less useful as a spatially localized probe.

X-rays scattered by an atom

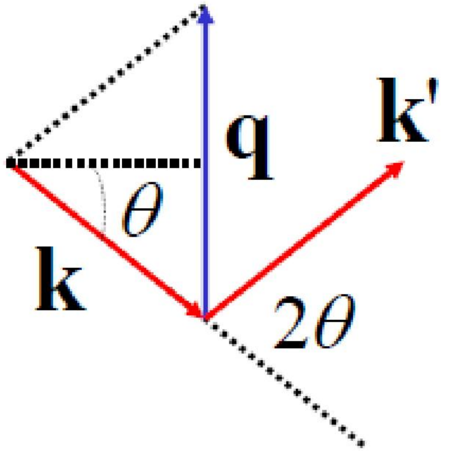


$$\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}}$$

Momentum transfer (in units of $\hbar$)

$$\mathbf{q} \equiv \mathbf{k}' - \mathbf{k}$$

elastic scattering $|\mathbf{k}| = |\mathbf{k}'| = k$



$$|\mathbf{q}|^2 = |\mathbf{k}' - \mathbf{k}|^2$$
$$q^2 = k^2 - 2kk'\cos 2\theta + k^2$$
$$= 2k^2(1 - \cos 2\theta)$$
$$= 4k^2 \sin^2\theta$$
$$q = 2k\sin\theta$$

A volume element $d^3\mathrm{r}$ at $\mathbf{r}$ will contribute an amount $-r_0\rho(\mathbf{r})d^3\mathrm{r}$ to the scattered field with a phase factor $\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}}$.

Scattering amplitude: $$-r_0 \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r} = -r_0 f^0(\vec{q})$$

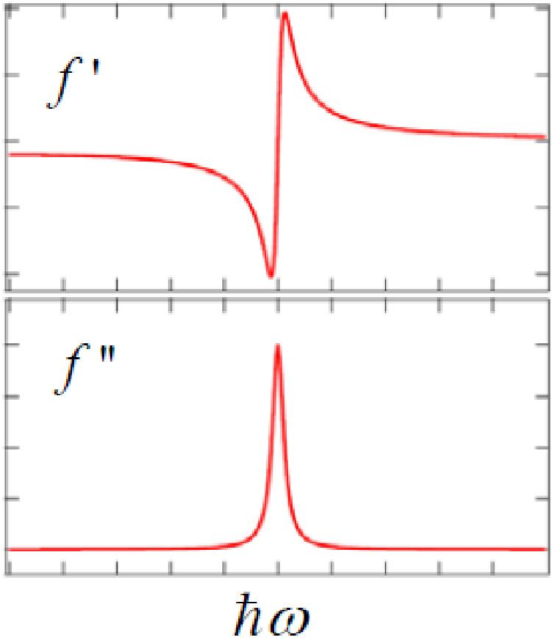
Atomic scattering factor $$f^0(\vec{q}) \equiv \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

$q \to 0,\quad f^0(\vec{q}) = Z$ (the number of electrons in the atom)

All of the different volume elements scatter in phase; each electron contributes -r_0 to the scattered field.

f^0 is independent on photon energy $\hbar\omega$; it is the scattering amplitude in units of $-r_0$.

f^0 is the Fourier transform of the charge distribution.



$$f = f\,' + i\,f\,''$$

$$f\,' = \frac{\omega_s^2(\omega^2-\omega_s^2)}{(\omega^2-\omega_s^2)^2+(\omega\Gamma)^2}$$

$$f\,'' = -\frac{\omega_s^2\,\omega\Gamma}{(\omega^2-\omega_s^2)^2+(\omega\Gamma)^2}$$

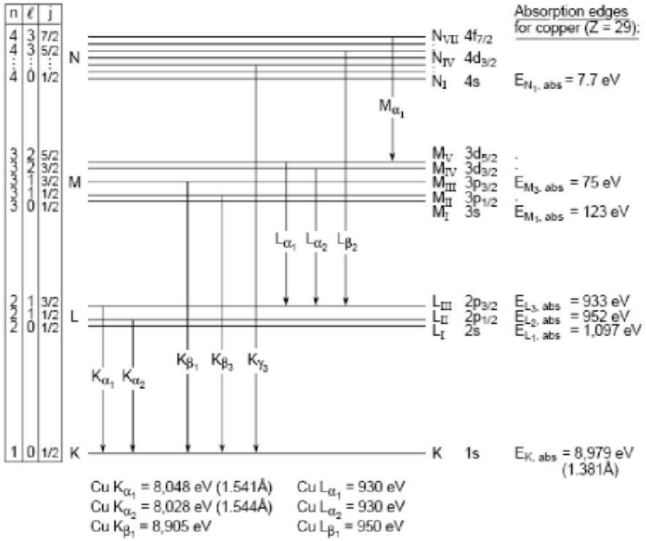
Absorption

$$\sigma = -\frac{4\pi}{k}\,\mathrm{Im}(f)$$

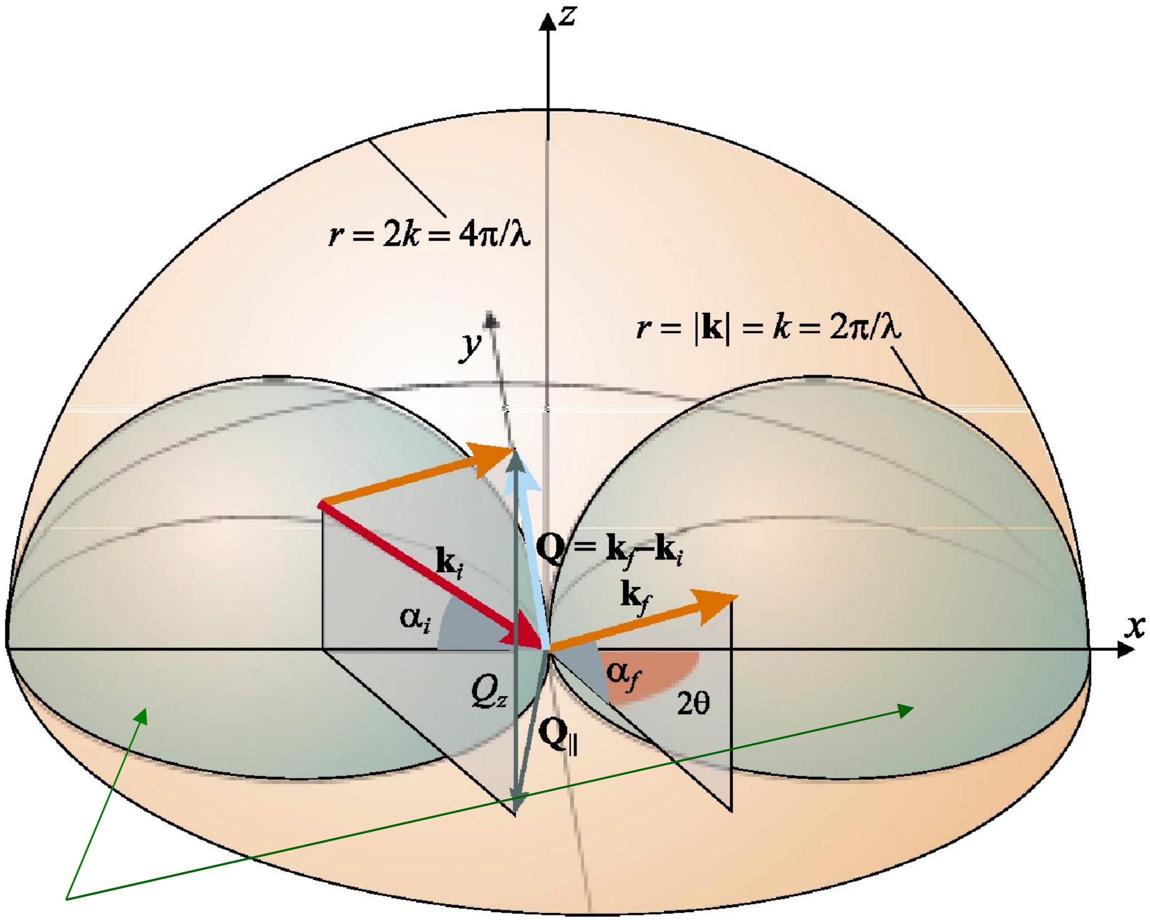
Resonant scattering

As the photon energy $\hbar\omega$ approaches the binding energy of one of the core-level electrons,

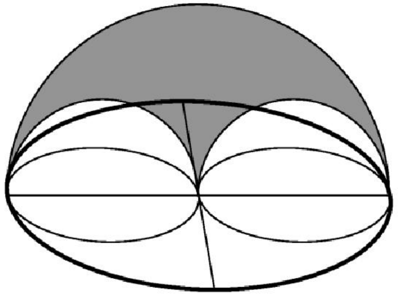
$$f_s(\mathbf{q},\hbar\omega) = f^{\,0}(\mathbf{q}) + \underbrace{f\,'(\hbar\omega) + i\,f\,''(\hbar\omega)}_{\text{dispersion corrections}}$$



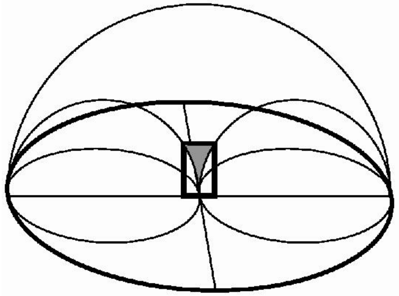
Accessible Q range in x-ray scattering from thin films



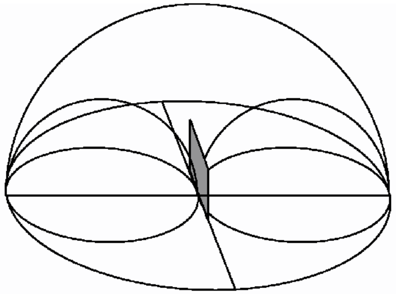
Laue zones



XRD



XRR



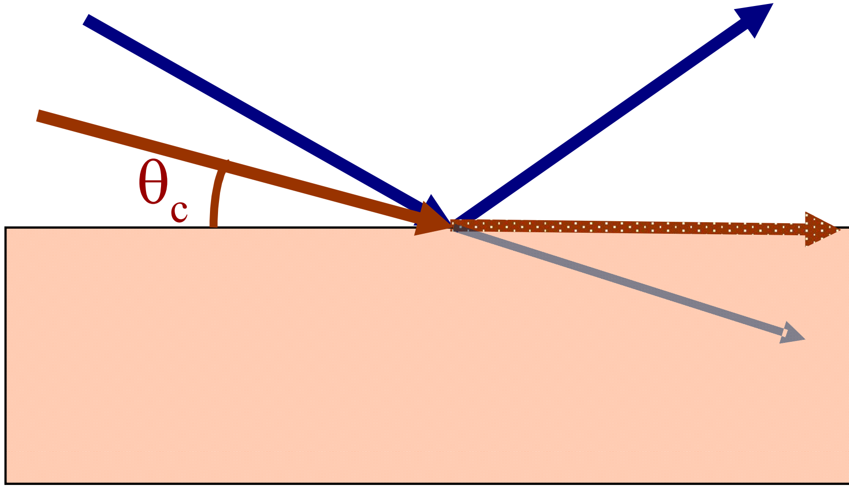
GISAXS

accessible length scale d~1/Q

X-ray Reflectivity

$Q \sim 0.5\ \mathrm{nm}^{-1}$

$d \sim 10\mathrm{nm}$



$$r = \frac{k_z - k'_z}{k_z + k'_z}.$$

$n = 1 - \delta + i\beta$

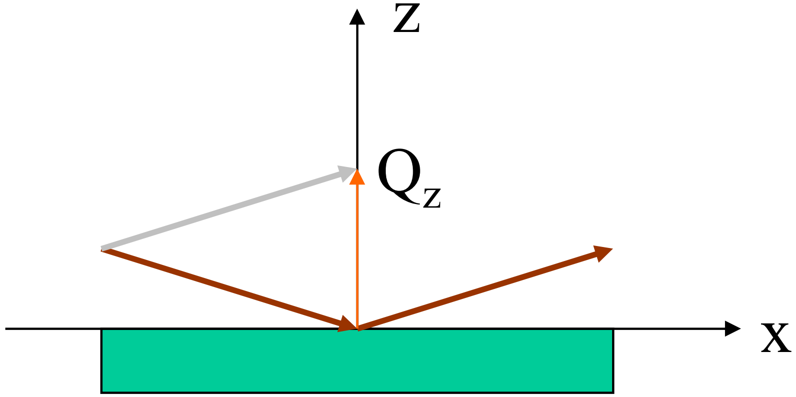
$$\delta = \frac{\lambda^2}{2\pi} r_e \rho_e$$

$\sim 10^{-5}$

$$\beta = \frac{\lambda}{4\pi} \mu_x.$$

$\sim 10^{-6}$

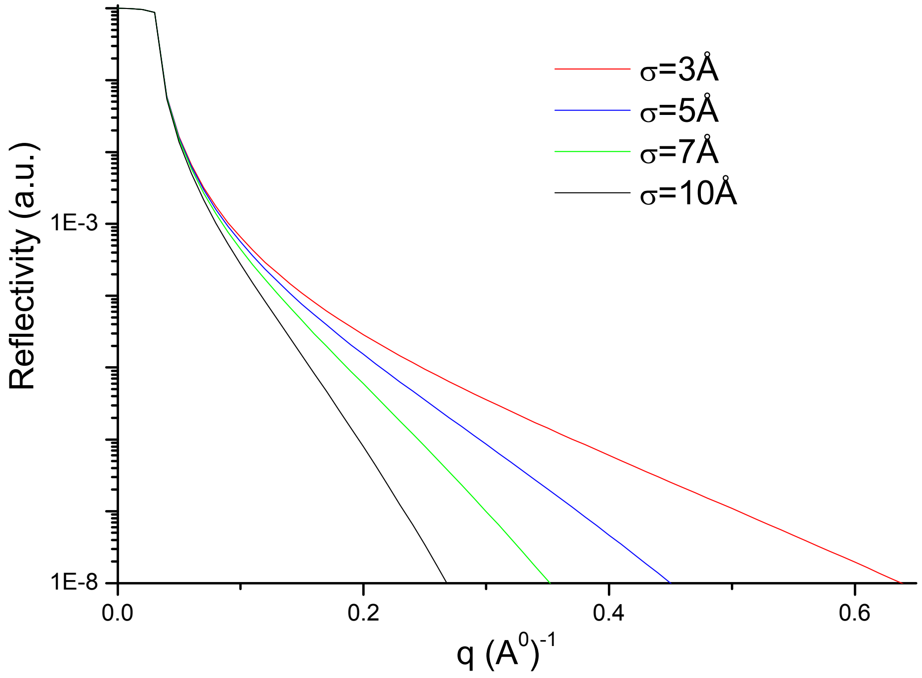
$\theta_c = \sqrt{(2\delta)} = \lambda(r_e\ \rho_{el} / \pi)^{1/2} \sim 0.5^0$



Specular Reflectivity

$K_{x,y}=0$

Yields electron density profile along z direction (averaged over x-y plane

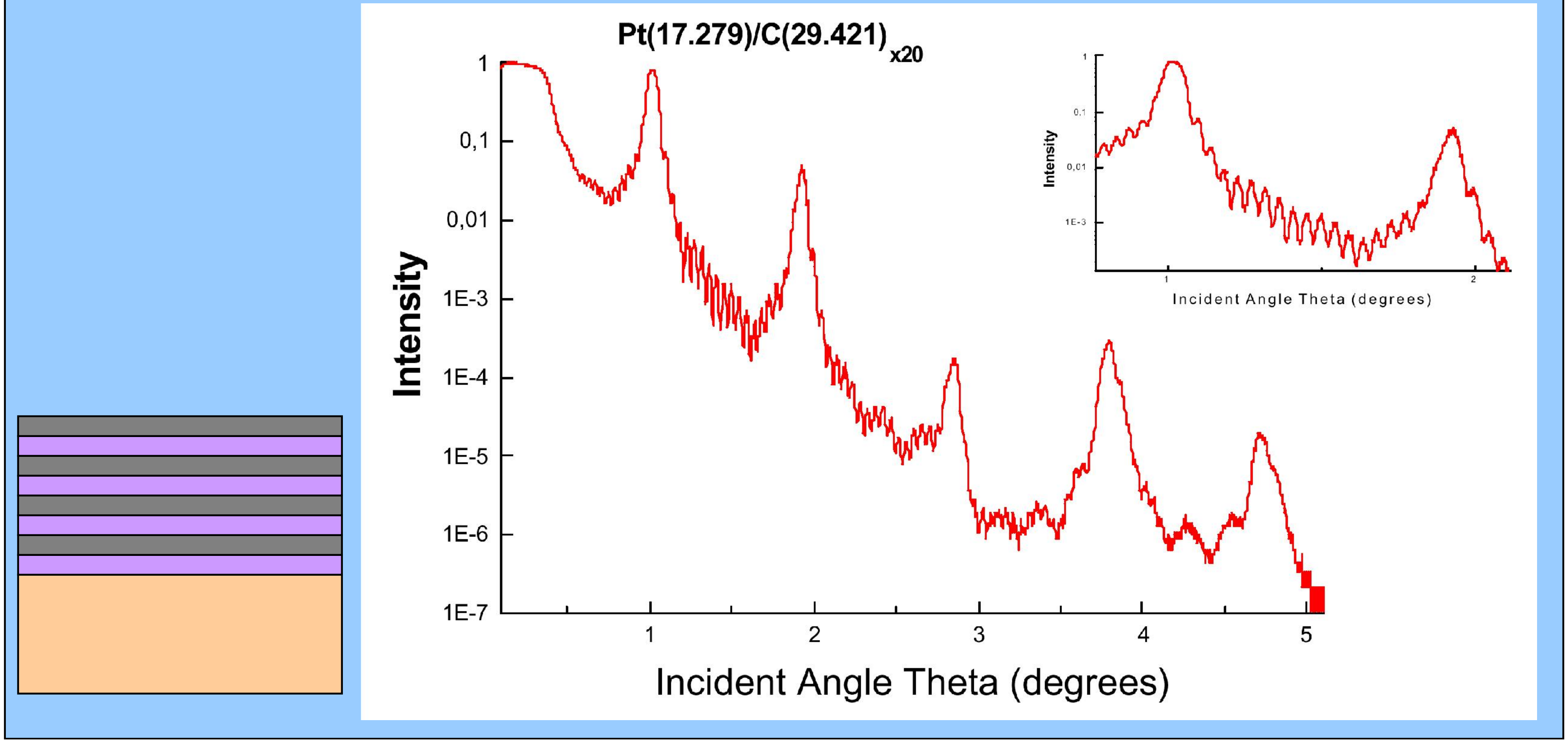


Fressnel reflectivity

$$R_F = |r|^2$$

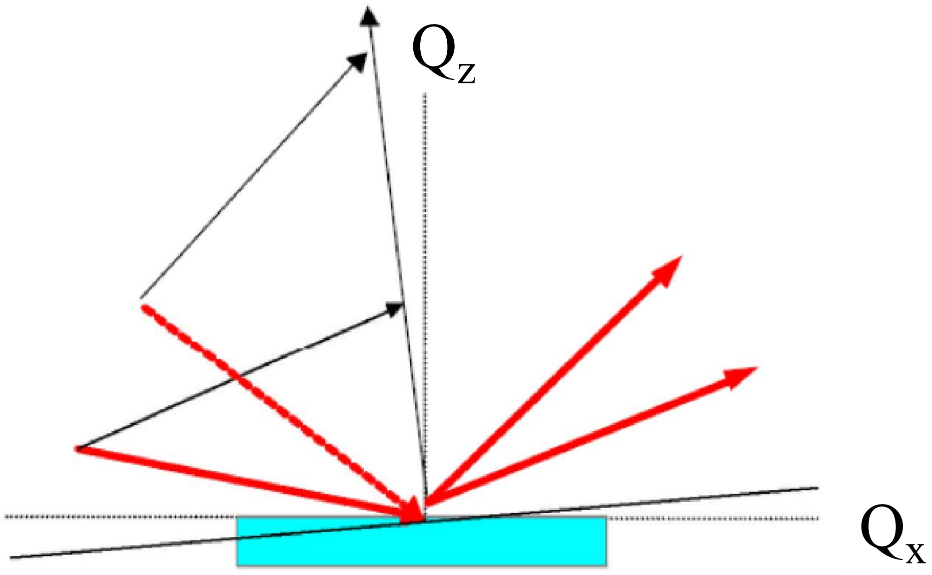
$$r = \frac{k_z - k'_z}{k_z + k'_z}.$$

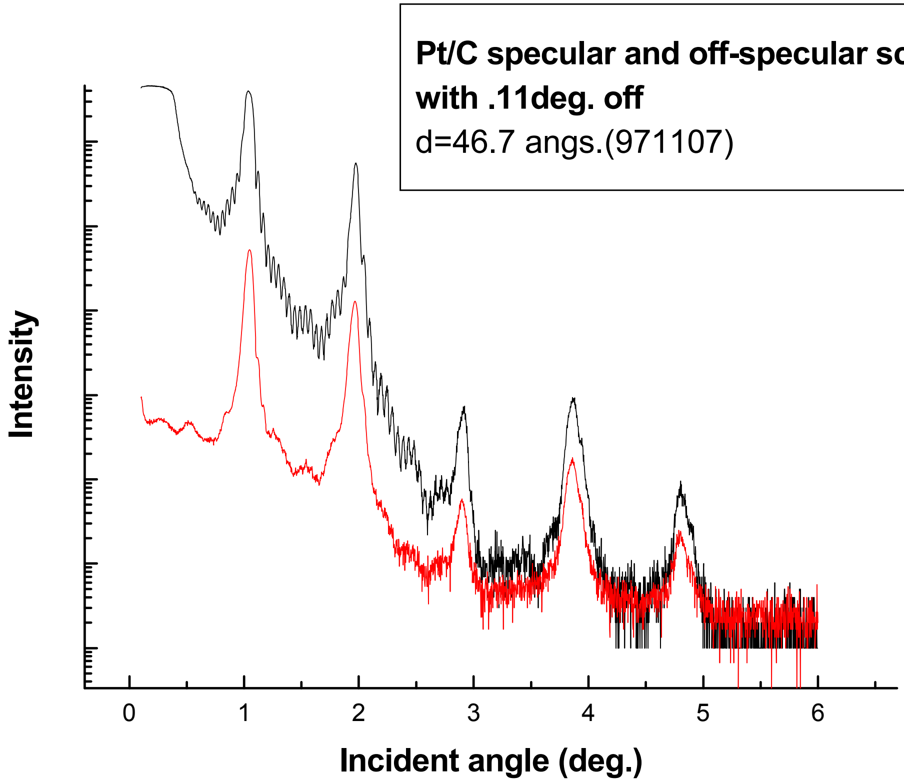
$$r_{rough} = r_{ideal}\, e^{-2k_z k'_z \sigma^2}$$

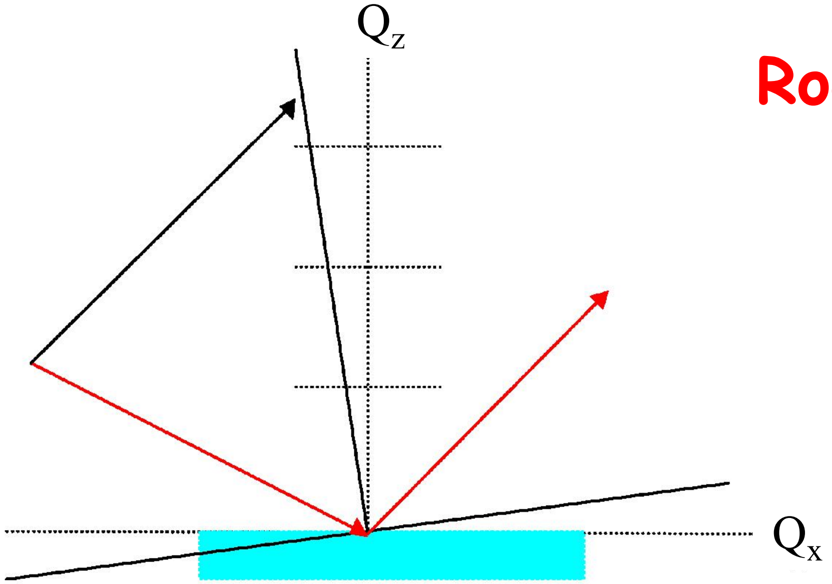

Pt(17.279)/C(29.421)$_{x20}$
Intensity
1
0,1
0,01
1E-3
1E-4
1E-5
1E-6
1E-7
1
2
3
4
5
Incident Angle Theta (degrees)
Intensity
1
0,1
0,01
1E-3
1
2
Incident Angle Theta (degrees)

Off-Specular Scan:

- offset Δω is kept fixed

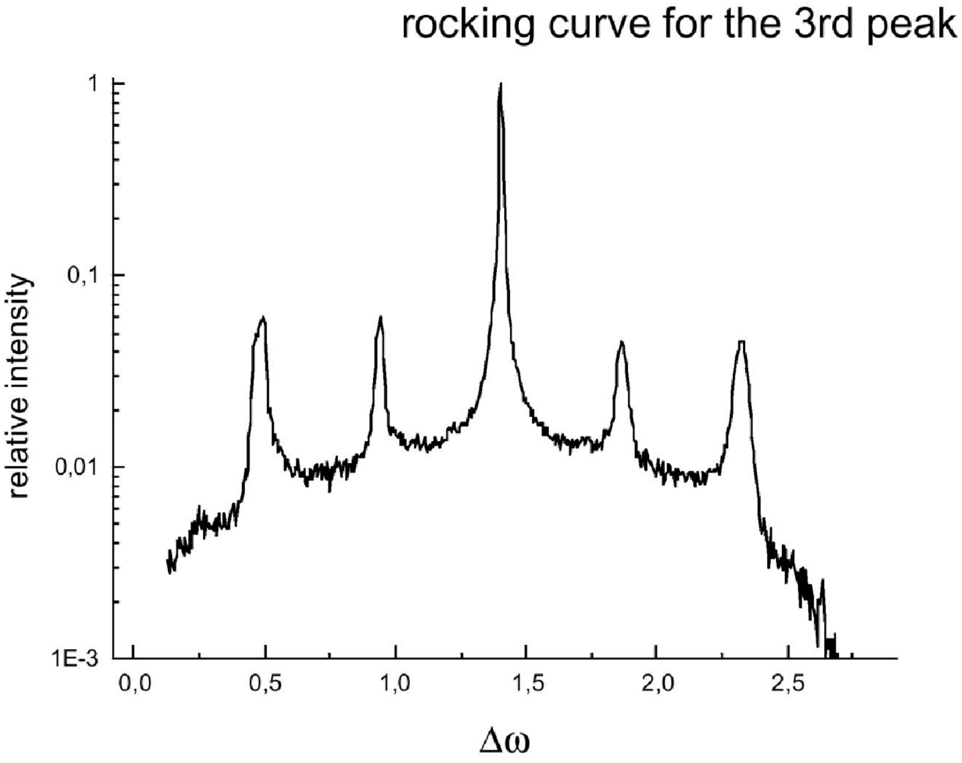


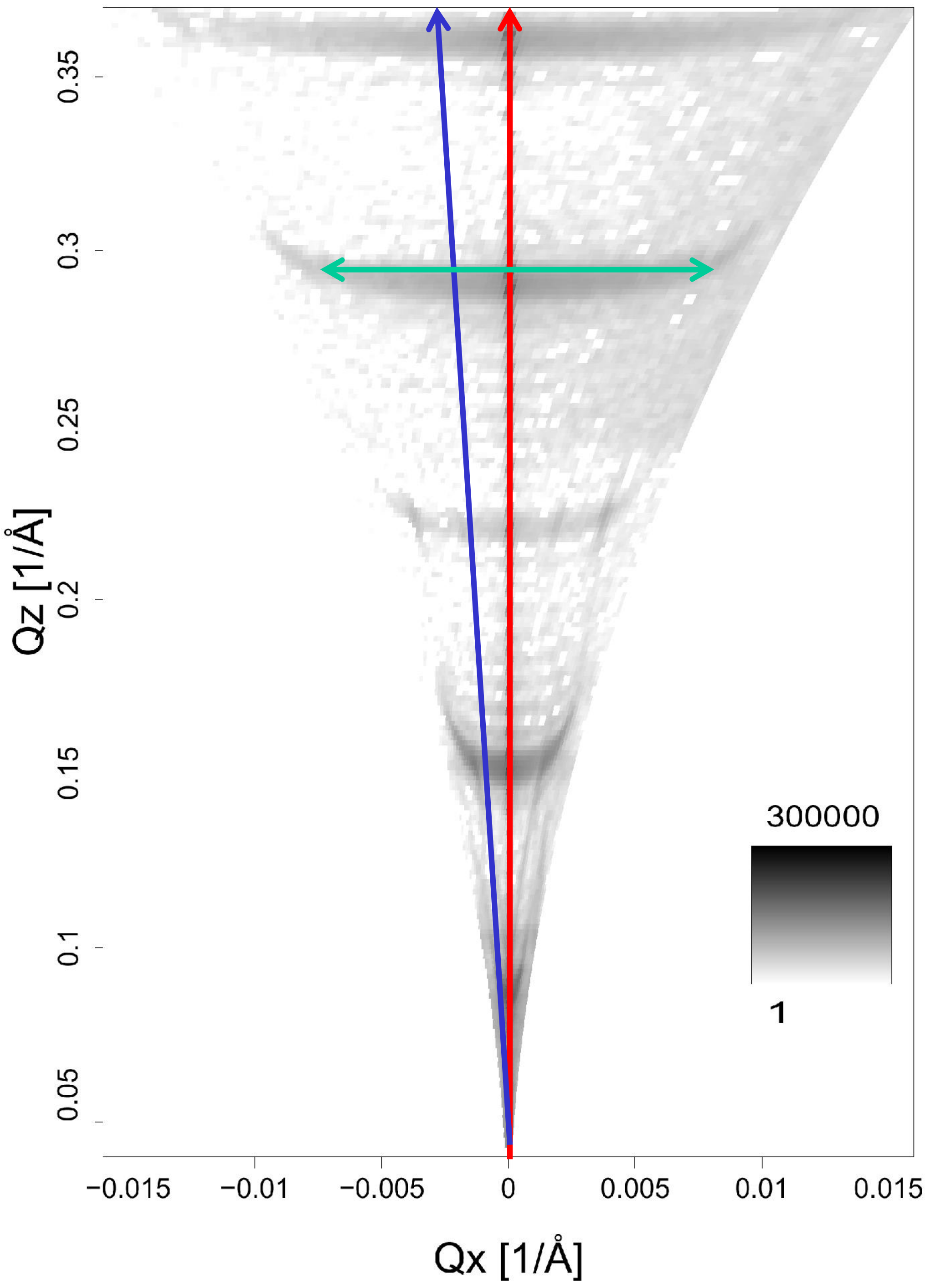




Rocking Curve:

- Magnitude of Q is kept fixed
- Its direction is rotated so that Q_x varies


rocking curve for the 3rd peak

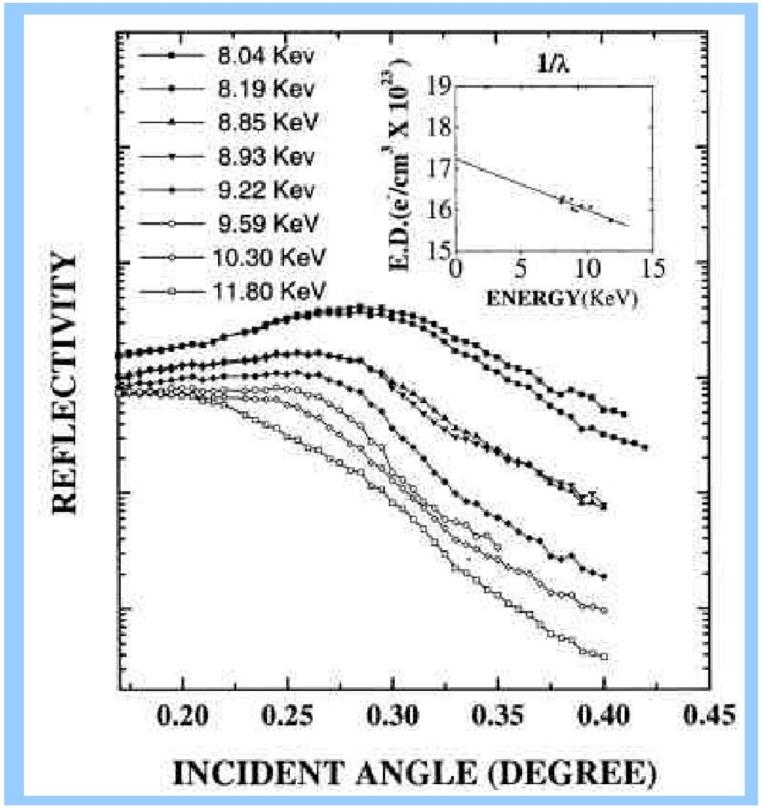


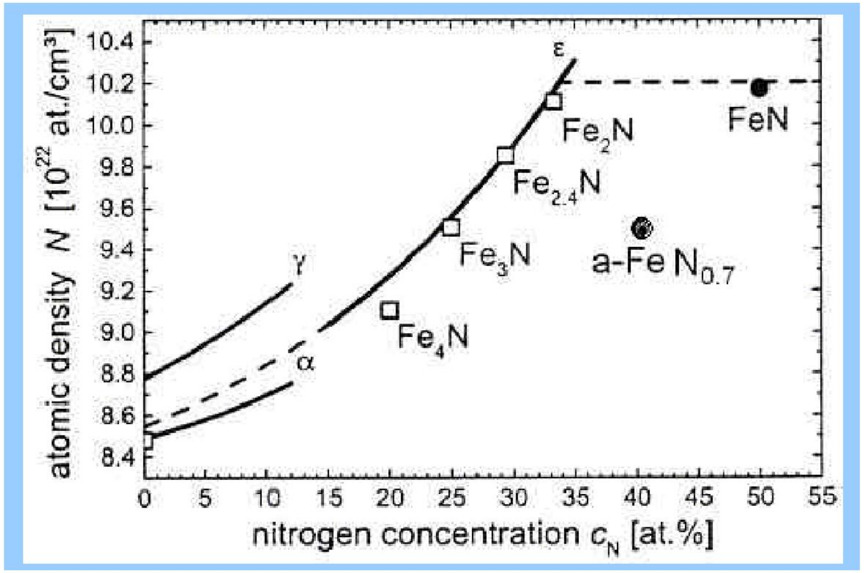
-Specular scan

-Off Specular scan

-Rocking curve

Amorphous Iron-Nitride Film:





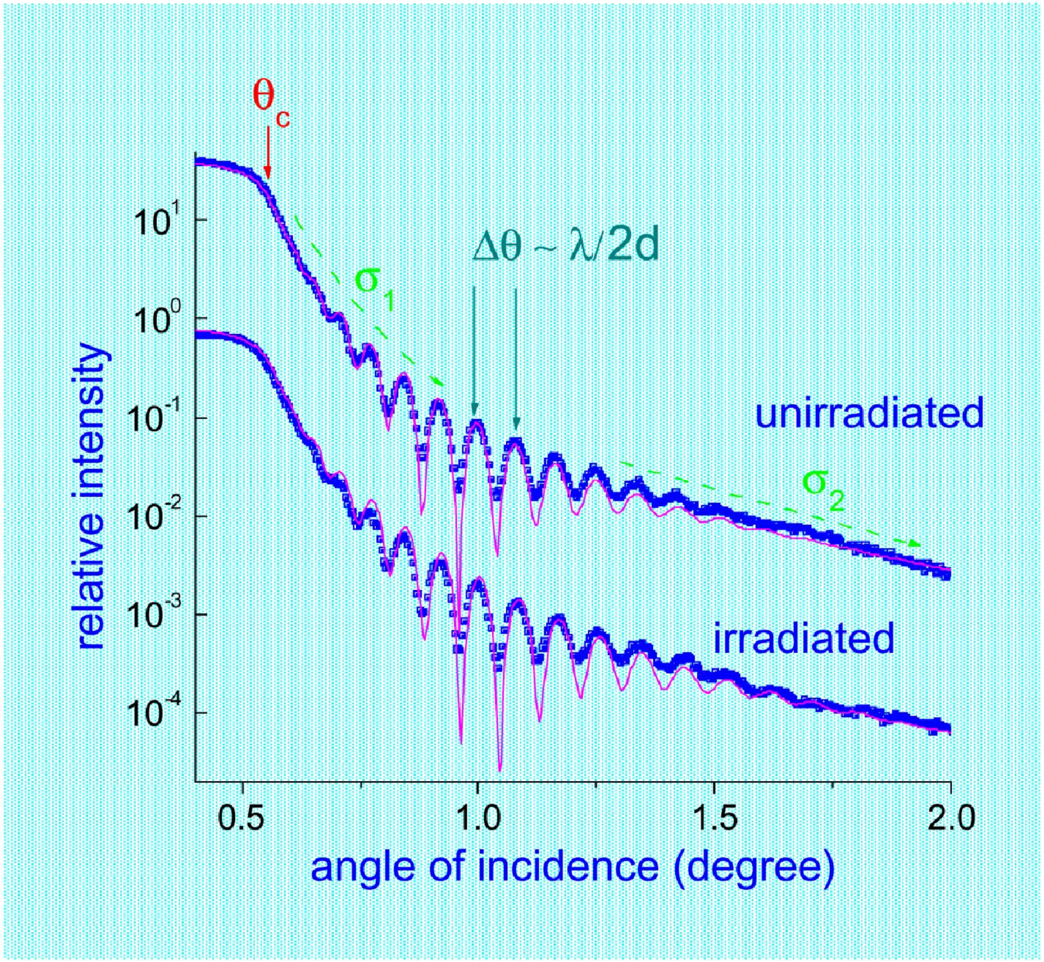
$$\theta_c = (2\delta)^{1/2} = \lambda(r_e \rho_{el} / \pi)^{1/2}$$

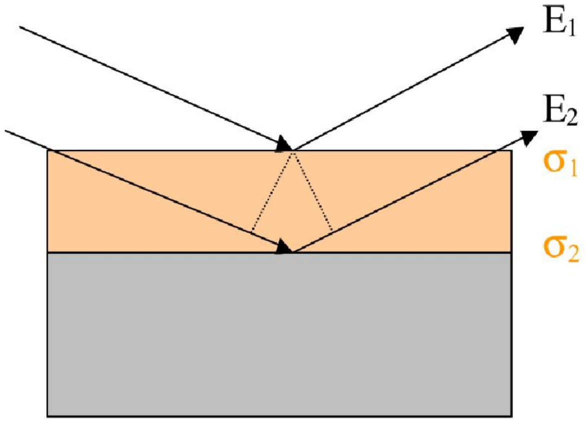
$FeN_{0.7}$

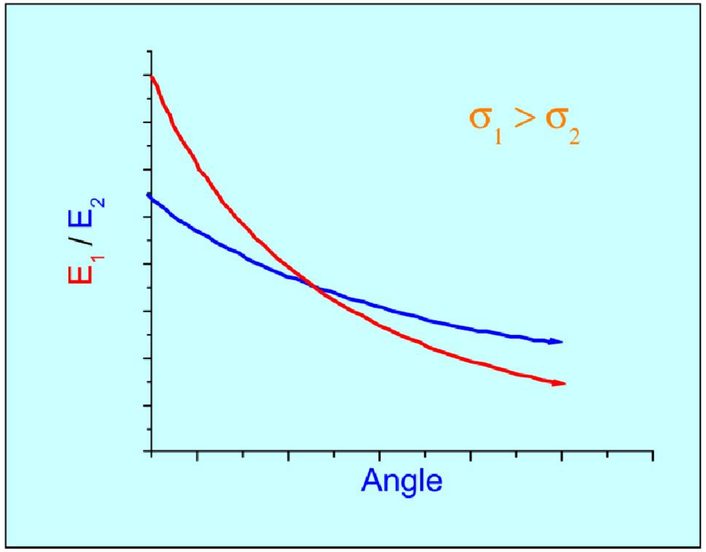
Electron Density: $(17.2\pm0.3)\times10^{23}$ e/cm^3

Mass Density: 6.2±0.2 gm/cm^3

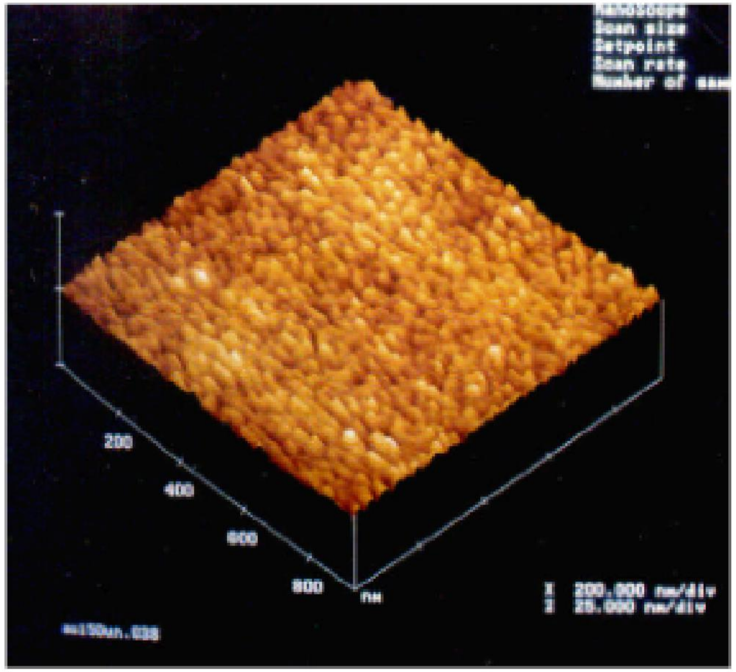
Gold film on float glass substrate:







designated Film thickness (Å)	Irradiation Dose (ions/ cm^2)	Layer	t_0 (Å)	t_i (Å)	σ_0 (Å)		σ_i (Å)	
					XRR	AFM	XRR	AFM
150	10^{12}	Au	152±1	152±1	11.0±0.5	9.0±0.5	10.0±0.5	9.0±0.5
		Glass	∞	∞	3.5±1.0	-	3.5±1.0	-
	10^{13}	Au	156	149	11.5	9.0	11.0	8.0
		Glass	∞	∞	4.0	-	4.0	-
450	10^{12}	Au	455	455	14.0	11.5	13.0	9.0
		Glass	∞	∞	3.5	-	3.5	-
	10^{13}	Au	454	450	14.0	11.5	12.5	8.0
		Glass	∞	∞	3.0	-	3.0	-

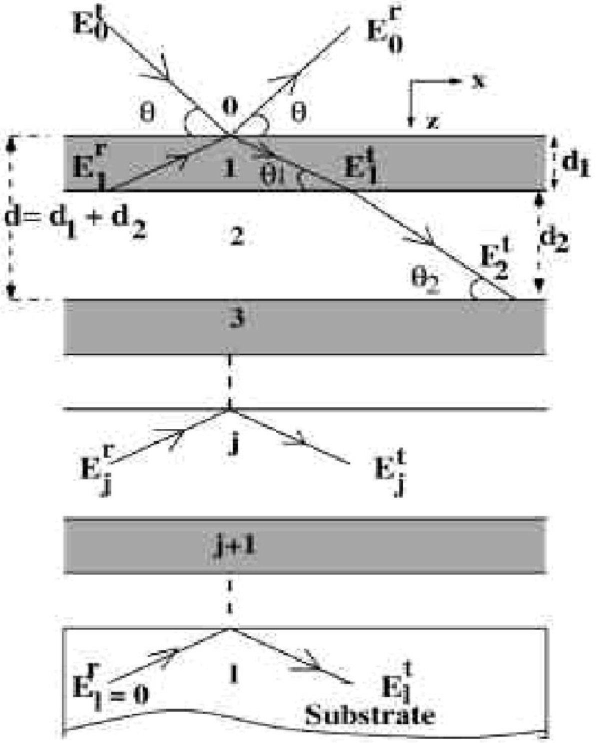


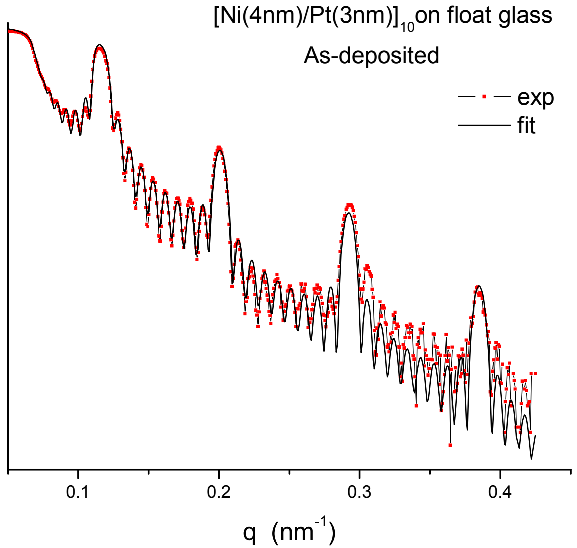
Sputtering rate:
150Å film: 410±80 atoms/incident ion
450Å film: 235±80 atoms/incident ion

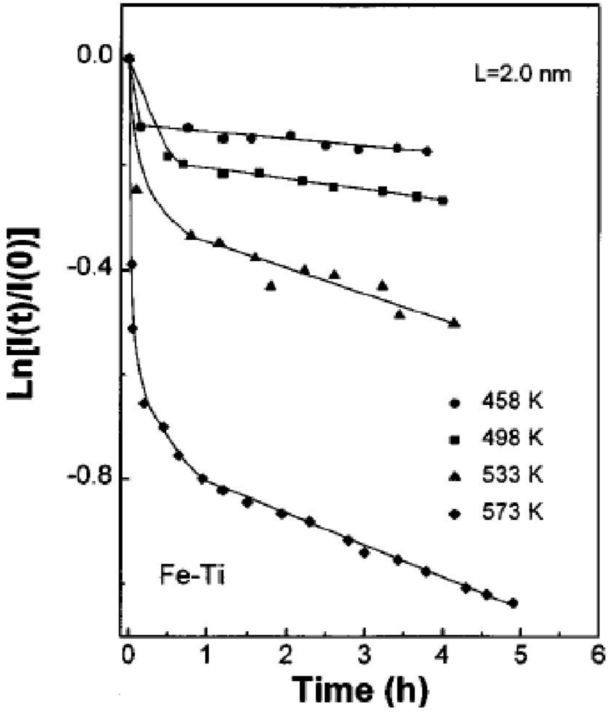
XRR gives a higher rms roughness as compared to AFM
- due to larger area probed by XRR (mm^2) as compared to AFM (μm^2)

X-ray reflectivity for interfacial diffusion:

$$n = 1 - \delta - i\beta$$
$$= 1 + (\lambda^2/2\pi)\Sigma\rho_i f_{0i}$$







$$\ln\left(\frac{I(t)}{I_0}\right) = -\frac{2\pi^2 n^2}{\lambda^2} L_d^2$$

L_d – diffusion length

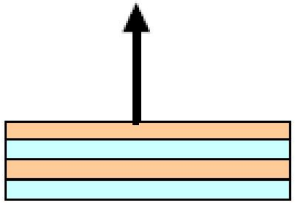
λ - periodicity of the multilayer

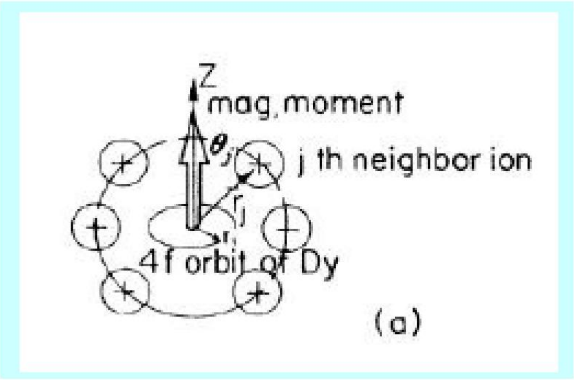
n – order of the Bragg peak

$$L_d = \sqrt{2Dt}$$

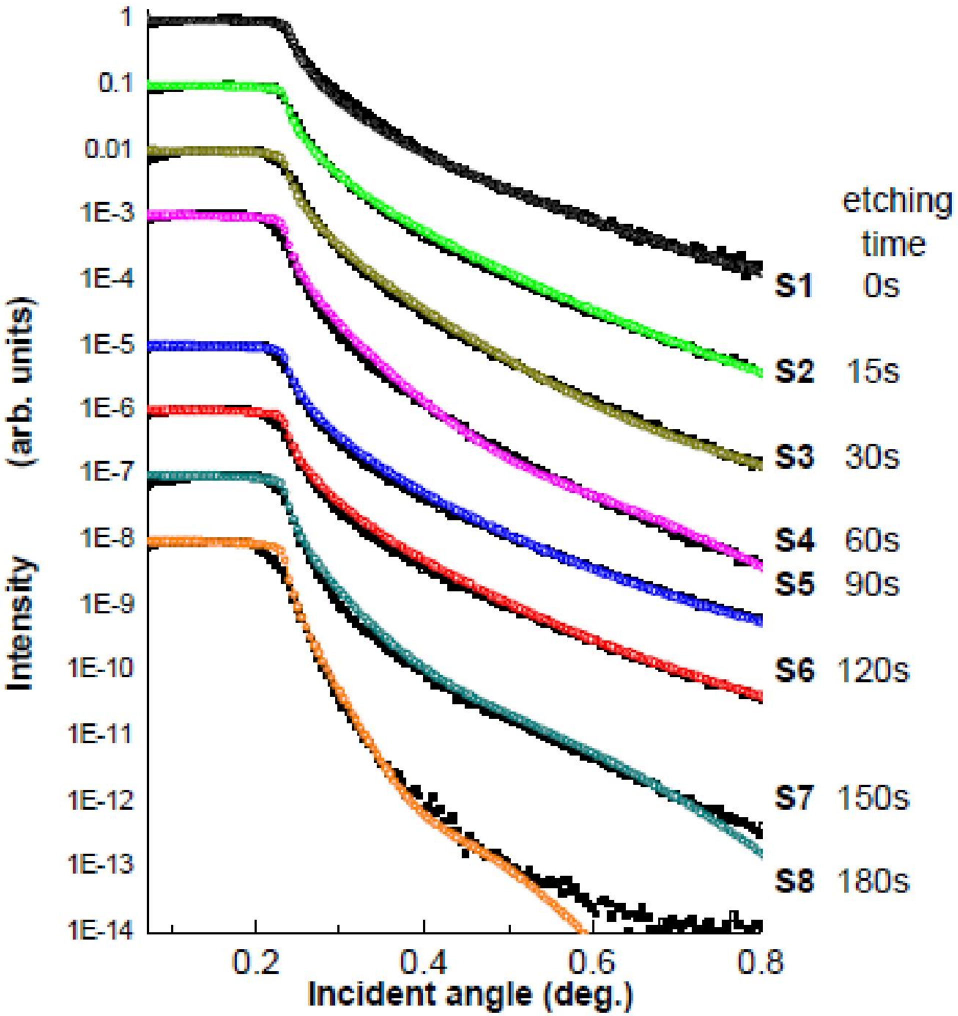
Fe/Tb Multilayer:

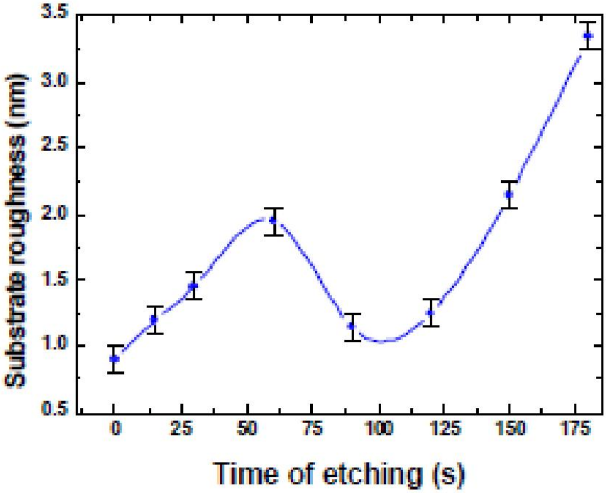
- It is generally believed that the single-ion anisotropy coupled with anisotropic Fe-Tb bonds at the interfaces is the origin of the PMA in this system
- State of the interface should affect the PMA





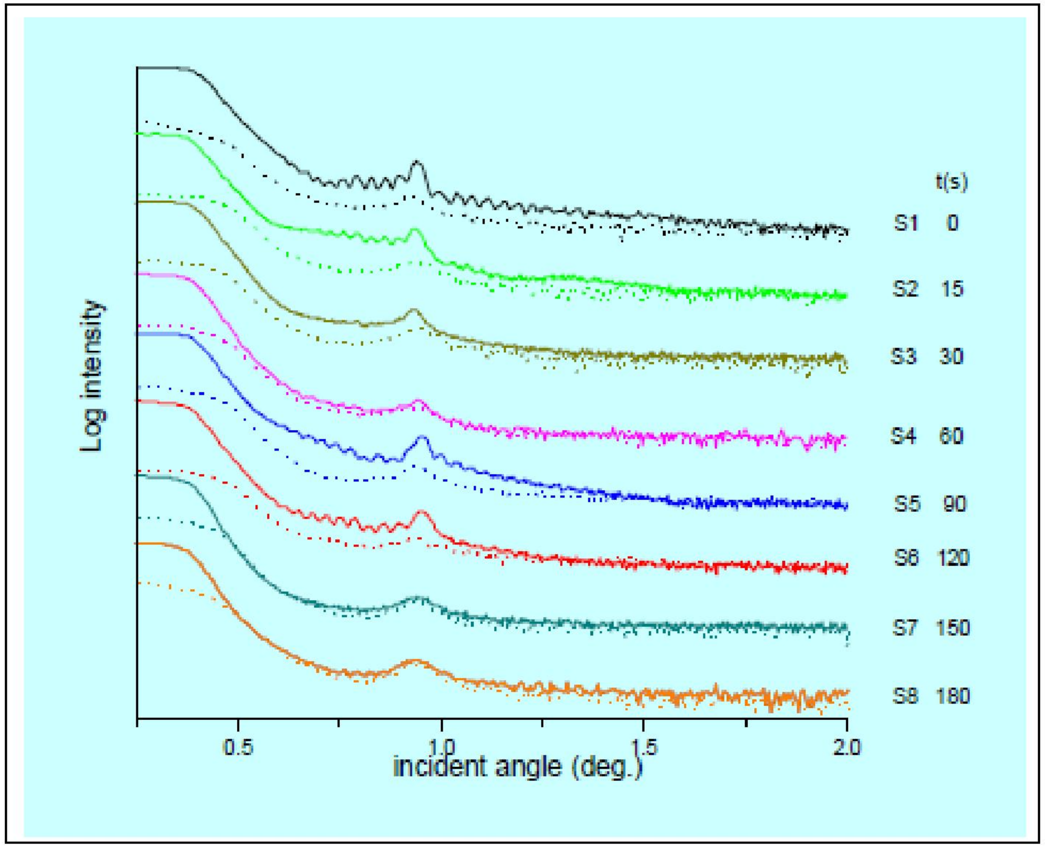
Float Glass etched in dilute HF:





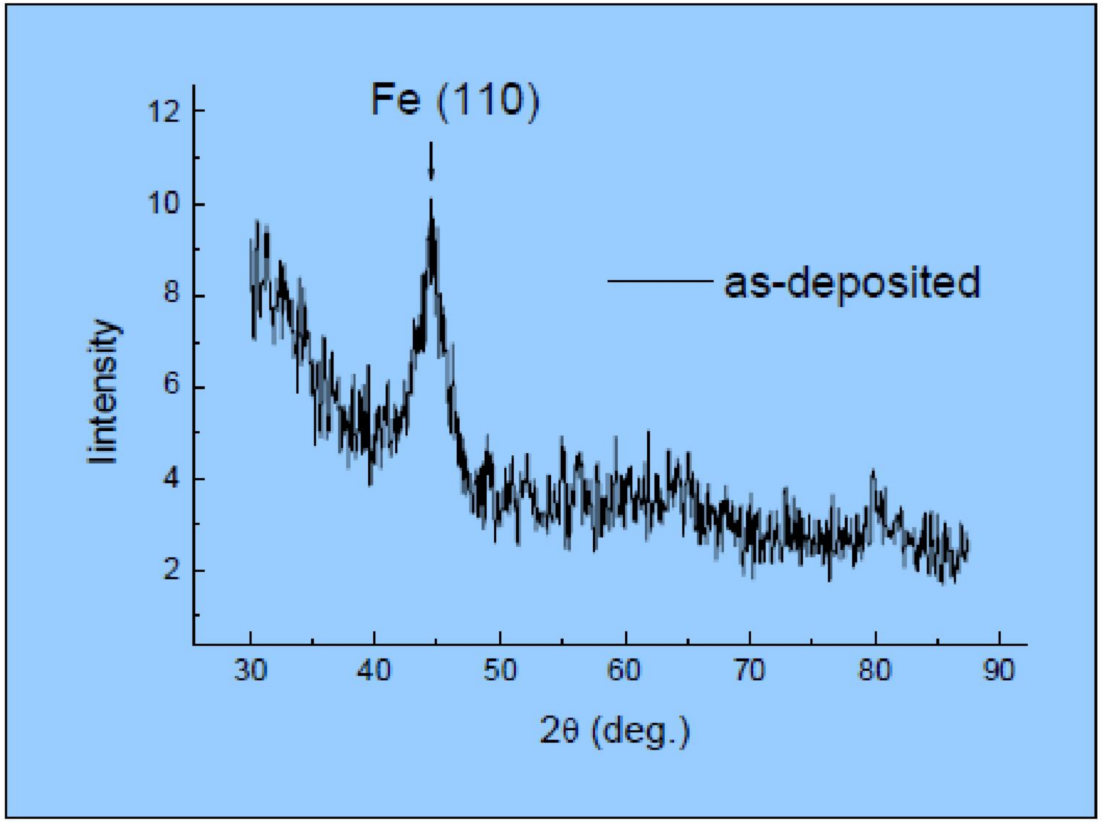
X-ray reflectivity:

Si (substrate)/[Tb 2nm/ Fe 3nm]x20

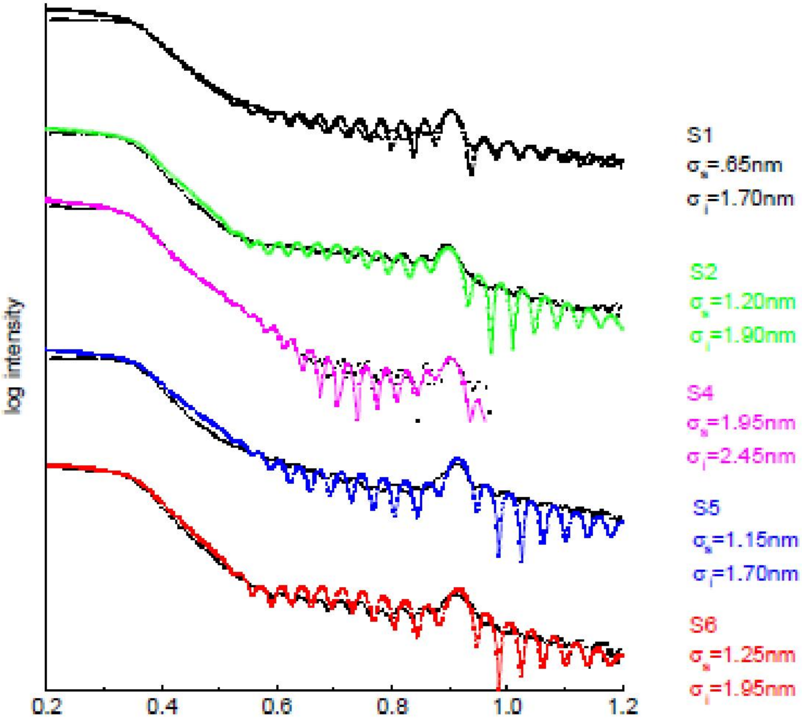


- **major part of the roughness is correlated** *(even when specular reflectivity is zero, off-specular reflectivity shows clear Bragg peak)*
- **there is substantial uncorrelated roughness** *(no total thickness oscillations)*

XRD:

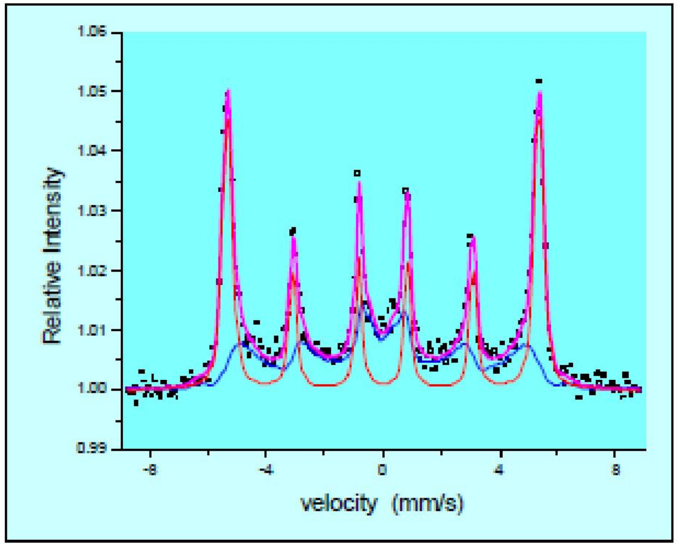


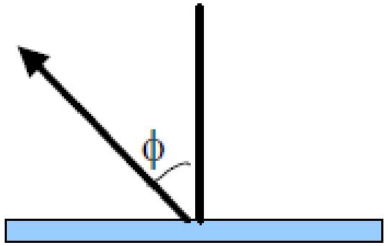
-Fe layer is crystalline



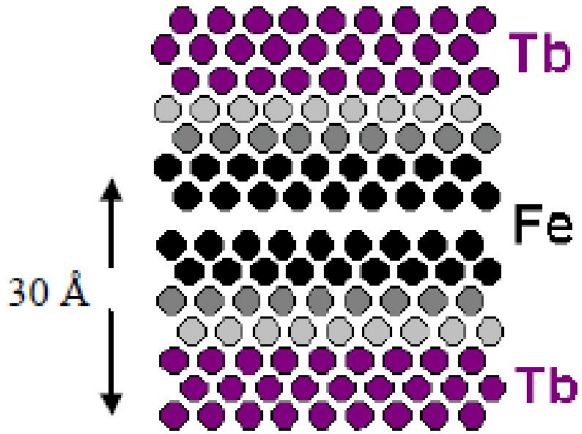
Sample	$\sigma_{substrate}$ (nm)	$\sigma_{interface}$ (nm)	$(\sigma_i^2 - \sigma_s^2)^{1/2}$ (nm)
S1	0.95±0.05	1.70±0.05	1.41±0.07
S2	1.20	1.90	1.47
S3	1.45	-	
S4	1.95	2.45	1.48
S5	1.15	1.70	1.25
S6	1.25	1.95	1.49
S7	1.45	-	
S8	3.35	-	

Mössbauer Measurements in Fe/Tb Multilayer:

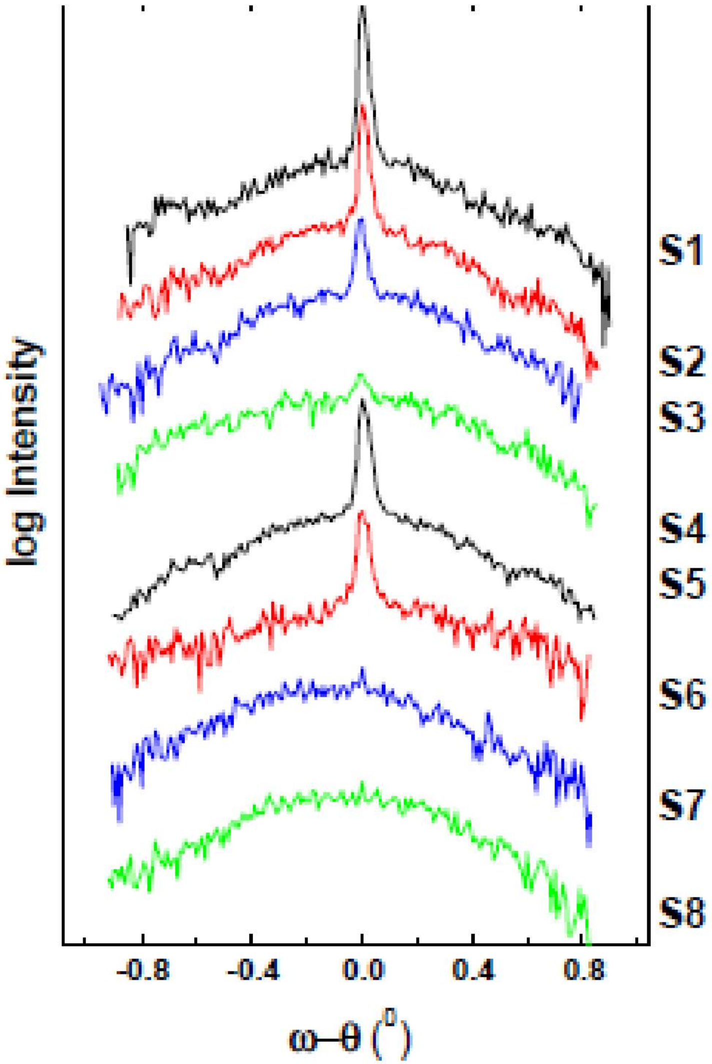


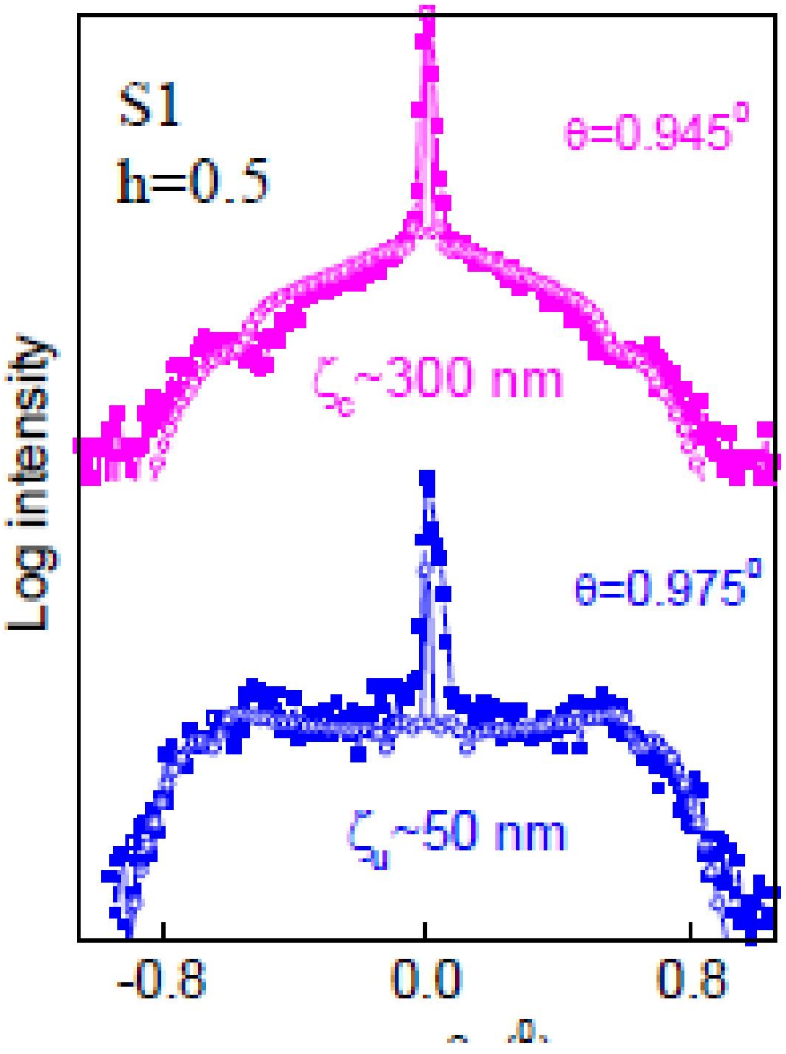


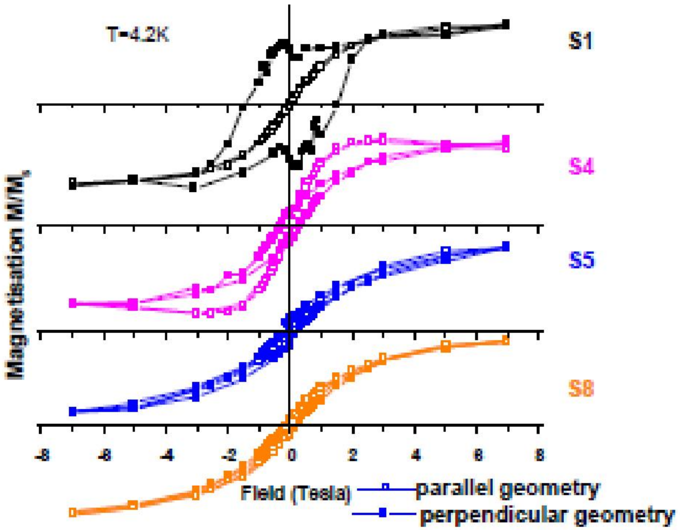
Sample	t	A_{oxide}	Parameters of the α-F component			φ
	(s)	(%)	$\langle B_{hf}\rangle$ (T)	ΔB_{hf} (T)	A_{α} (%)	(degree)
S1	0	2±2	32.7 ±0.3	0.7 ±0.5	44±2	42± 3
S4	60	5	32.8	0.6	46	43
S5	90	7	32.7	0.8	51	41
S8	18	6	32.3	1.0	48	50

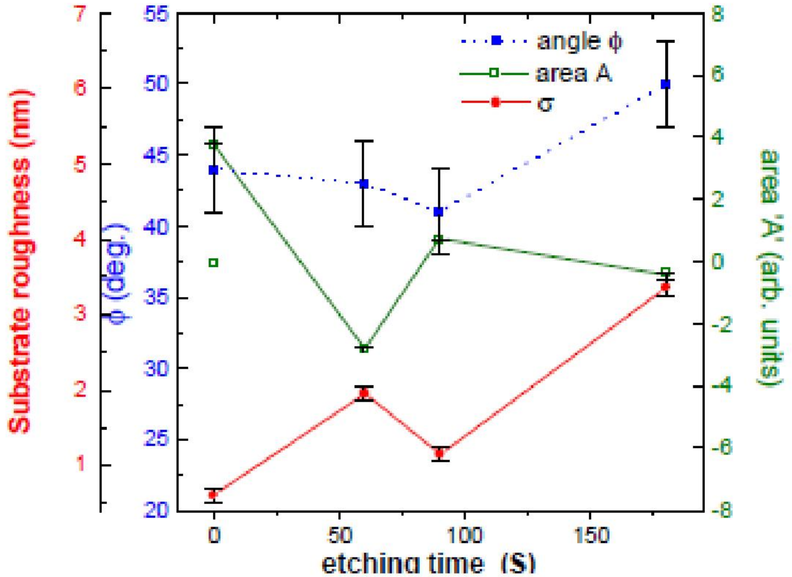


- Tb nn or nnn causes Fe hyperfine field to reduce
- 55% of Fe atoms in a layer have Tb nn or nnn
- Even for perfactly sharp inerfaces, two monolayers (~3 Å) of Fe on each interface have reduced field
  (i.e. 20% of a 30 Å thick Fe layer)
- Rest of the area under the broad sextet (35%) is due to interdiffusion at the interfaces
  (equivalent to ~5 Å of Fe on each interface)
- Taking composition of interdiffused layer to be $Fe_{0.5}Tb_{0.5}$, thickness of interdiffused layer at an interface is ~10 Å


log Intensity
S1
S2
S3
S4
S5
S6
S7
S8
-0.8
-0.4
0.0
0.4
0.8
ω−θ (°)

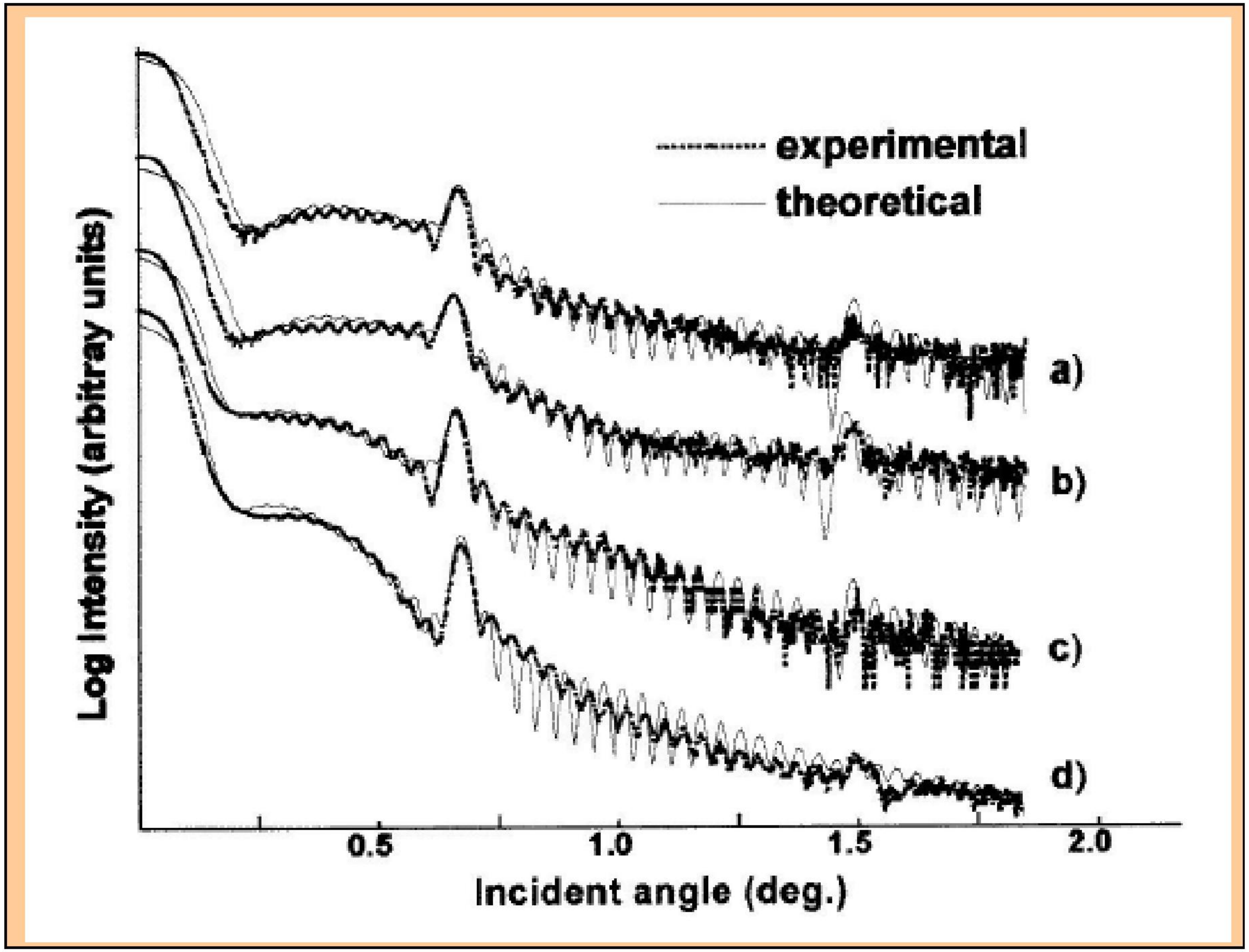

S1
h=0.5
θ=0.945°
ζ_c~300 nm
θ=0.975°
ζ_u~50 nm
Log intensity
-0.8
0.0
0.8





- PMA decreases with increasing interface roughness *(correlated part)*
- Dependence on roughness is rather weak

Swift heavy ion irradiation of Fe/Tb Multilayer:



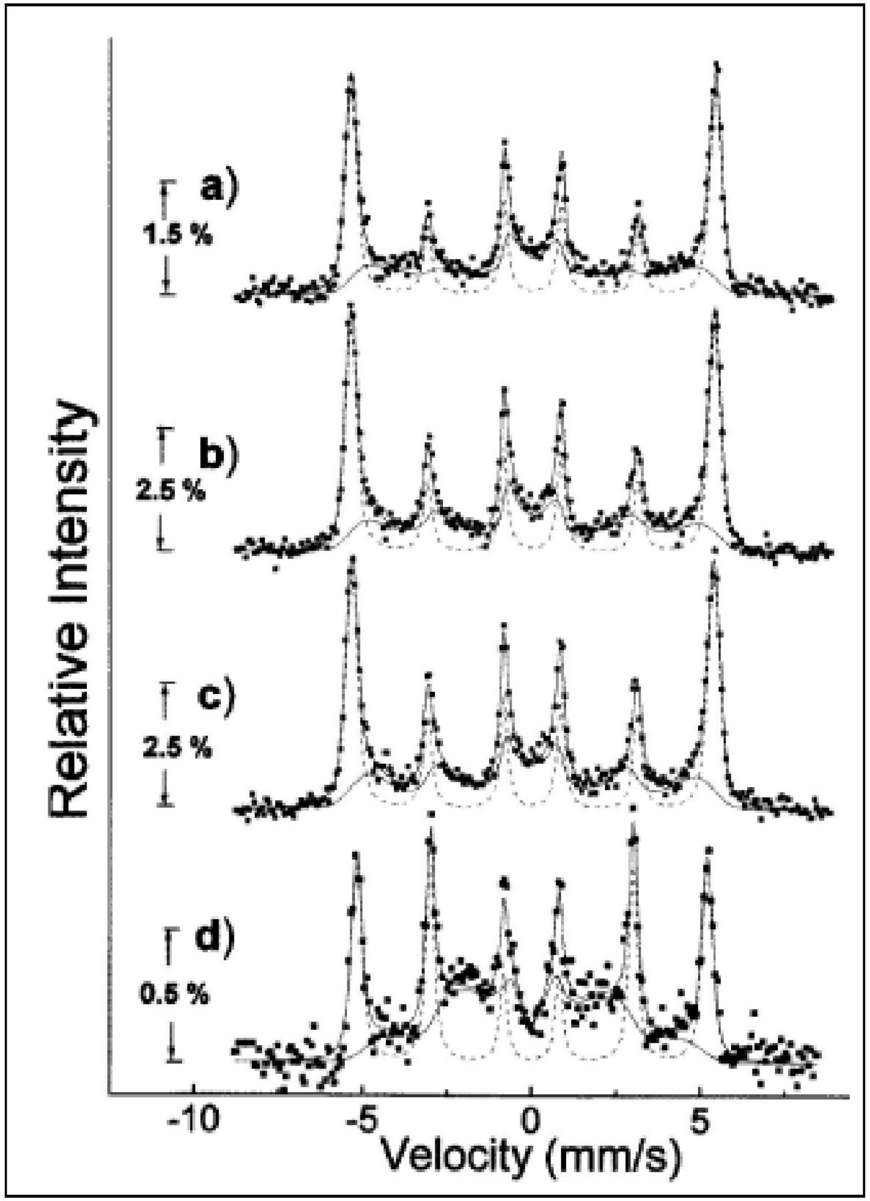
80 MeV Si

0.0 ions/cm^2

1.0E14 ions/cm^2

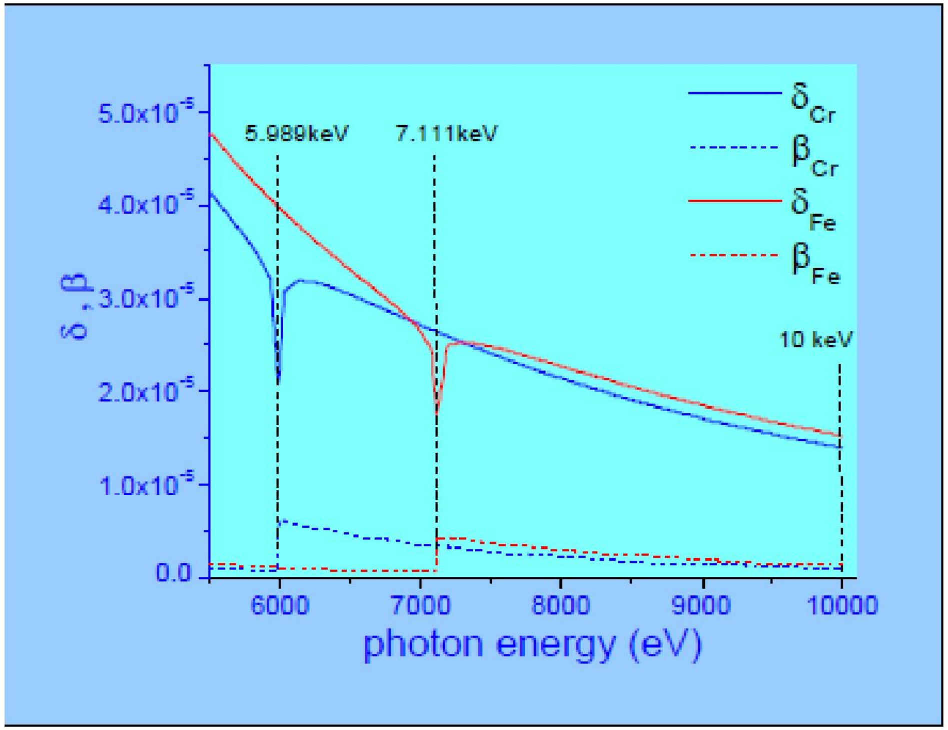
1.0E15 ions/cm^2

1.0E13 of
150MeV Ag



Sample	σ (A)	Rel. area	ϕ (deg)
a)	2.0	54±1	33.6±1
b)	2.5	55	36.1
c)	6.5	54	39.9
d)	10.0	47	62.2

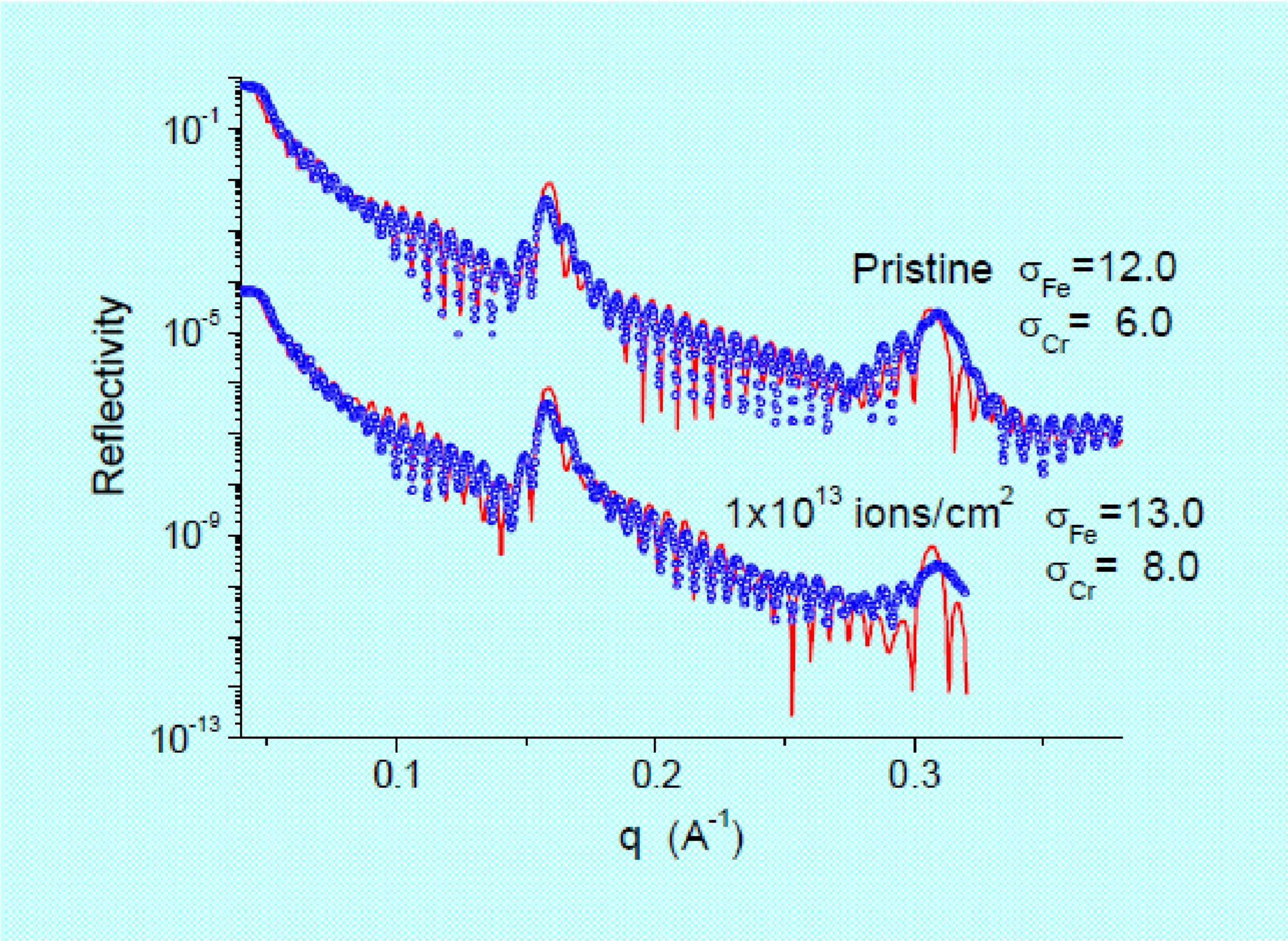
Anomalous x-ray reflectivity



$$n = 1 - \frac{r_e \lambda^2}{2\pi} \sum N_A f_A$$

$$f_A(E) = Z_A + \underbrace{f'_A(E) + i f''_A(E)}_{\text{Anomalous scattering factor}}$$

- Away from the absorption edges, contrast between Fe and Cr is low because $Z_{Cr} \sim Z_{Fe}$



-Roughness changes only by ~2 Å

-No change in interdiffusion (from Mössbauer measurements)