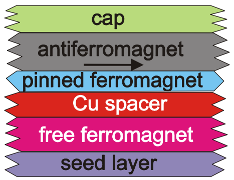
More Thin Film X-ray Scattering and X-ray Reflectivity

Mike Toney, SSRL

1. Introduction (real space – reciprocal space)
2. Polycrystalline film (no texture) – RuPt
3. Textured film: MnPt
4. X-ray Reflectivity
5. Summary
    - how do you get diffraction data from thin films
    - how to choose what to do (what beam line & scans)
    - what do you learn

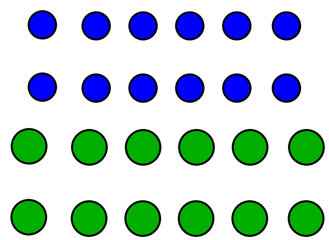


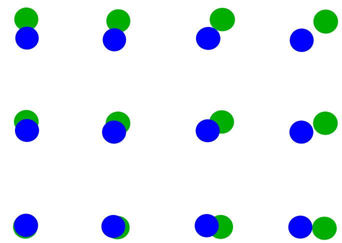
Real and Reciprocal Space

Real space

Reciprocal space

epitaxial film



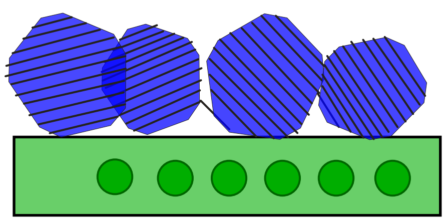


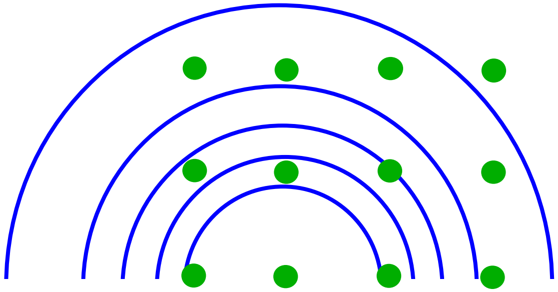
origin

spots

Arturas

"powder" film (polycrystalline)



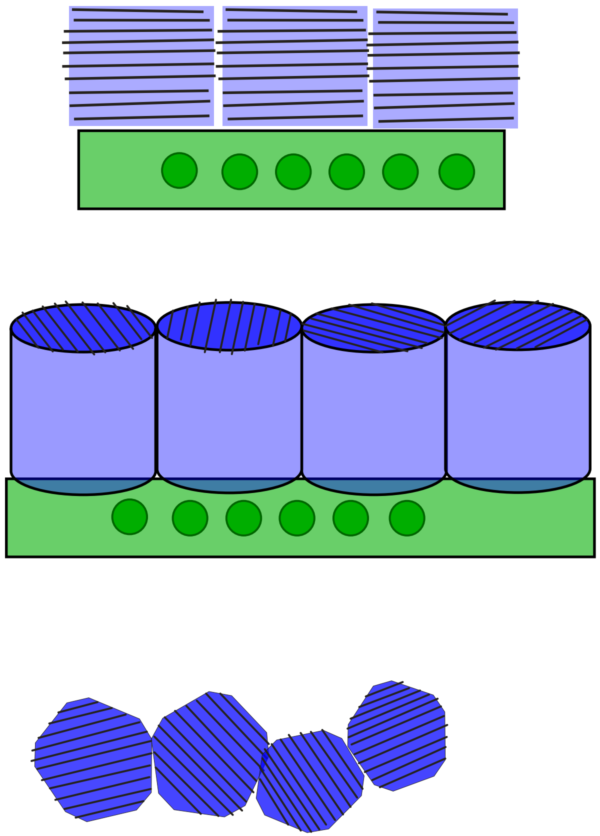


spheres

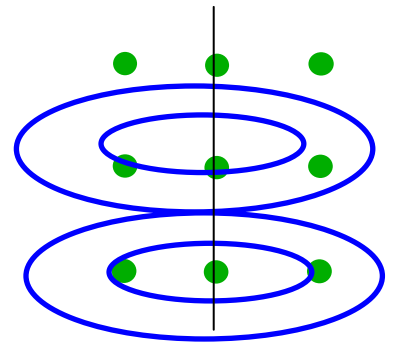
Real and Reciprocal Space

textured film

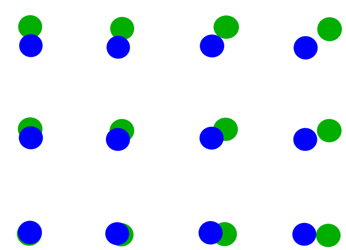
Real space



Reciprocal space



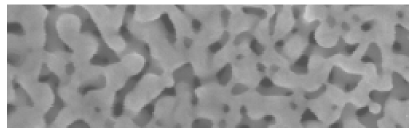
rings

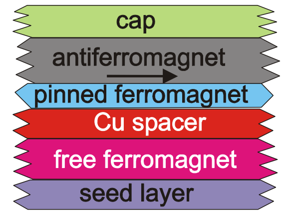


slice gives spots

differences in extent of texture

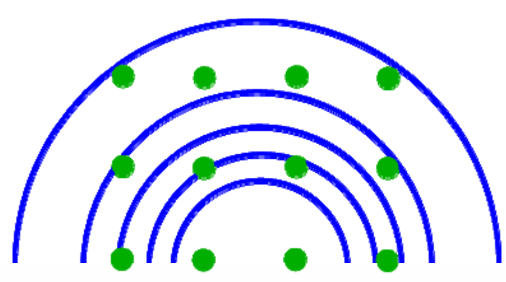
Thin Film Scattering

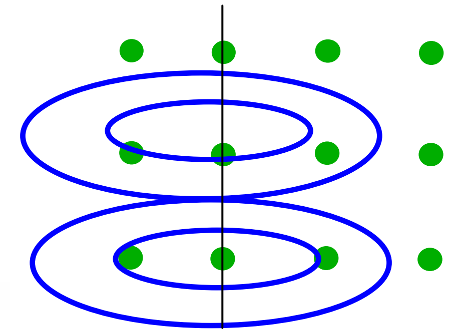




What do you do?

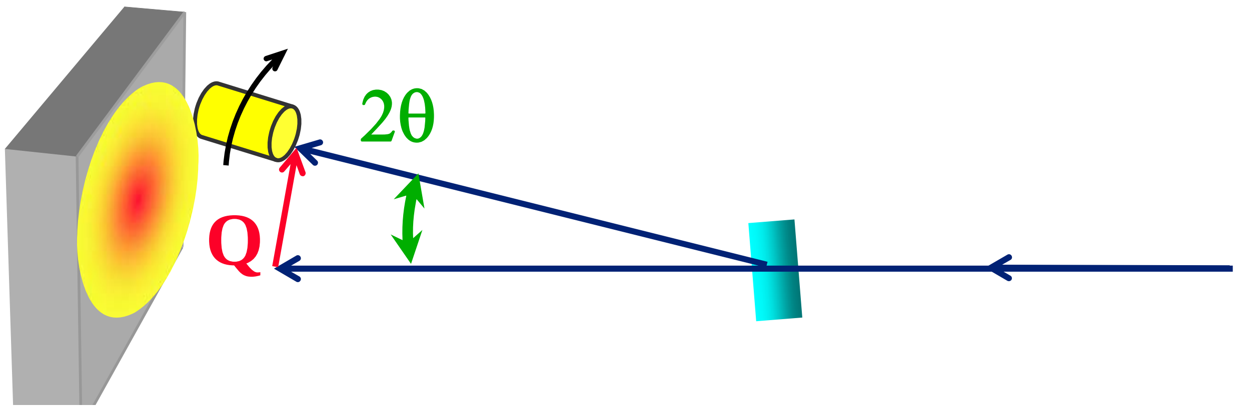
- what beam line? (2-1, 7-2, 11-3)
  - area vs point detector; flux; energy
- what scans? ("where" in reciprocal space)
  - what do you want to learn:
    - ➢ phase identification
    - ➢ lattice parameters
    - ➢ defects
    - ➢ texture
    - ➢ crystallite size
    - ➢ atomic structure

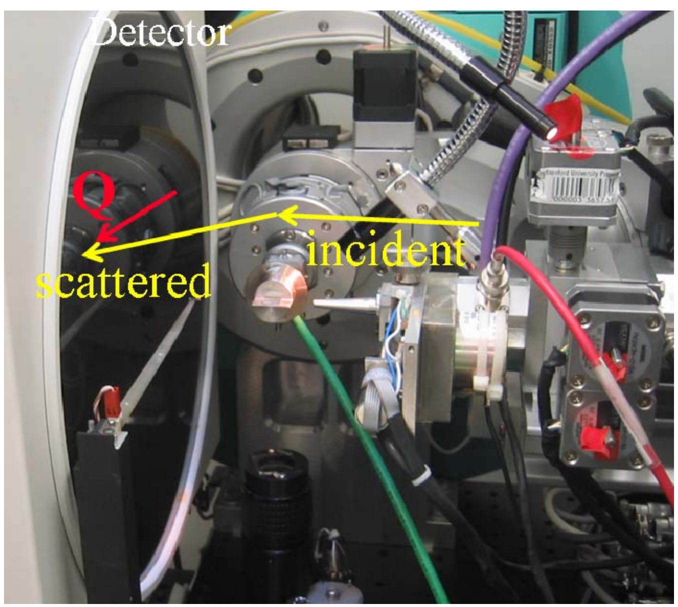


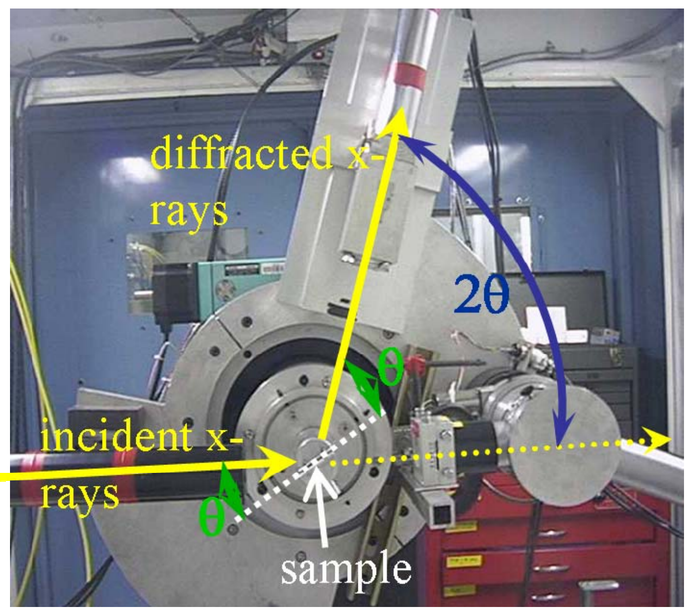


Thin Film Scattering

Two ways: Area detector & Point detector







RuPt Thin Films

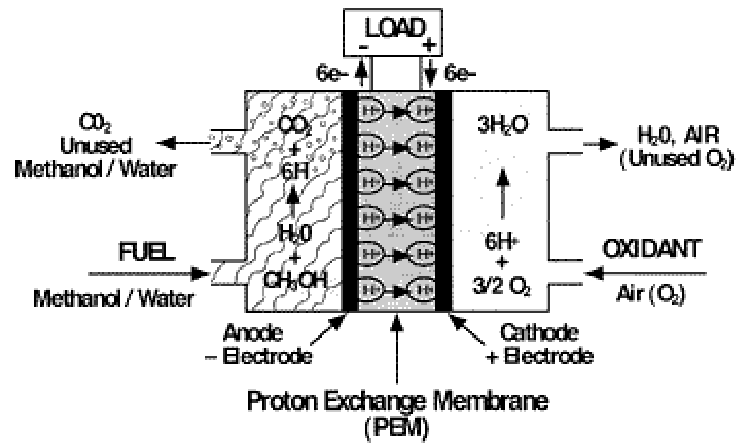
Direct Methanol Fuel Cell (DMFC)

- low operating temperature & high energy density
- low power applications (cell phones, PCs,)

DMFCCs Prototype Laptop Cartridge

RuPt alloys used as catalysts for DMFCs

- as nanoparticles, but also films
- catalytic activity of RuPt depends on composition and structure (hcp or fcc)



anode: $CH_3OH + H_2O \Rightarrow CO_2 + 6H^+ + 6e^-$

cathode: $3/2O_2 + 6H^+ + 6e^- \Rightarrow 3H_2O$

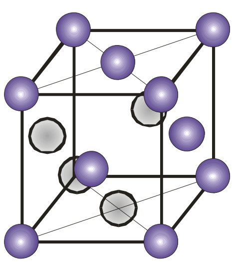
sum: $CH_3OH + 3/2O_2 \Rightarrow CO_2 + 2H_2O$

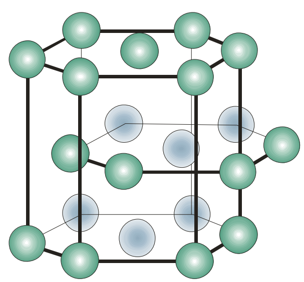
Hamnet, Catalysis Today **38**, 445 (1997)
Park et al., J. Phys. Chem. B **106**, 1735 (2002)

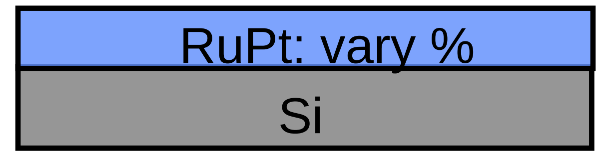
RuPt Thin Films

Goal: Correlate crystal structure of RuPt alloys to catalytic activity

Pt is fcc; Ru is hcp
fcc->hcp transition as Ru increases





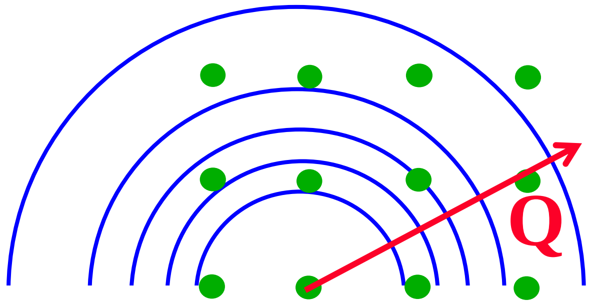


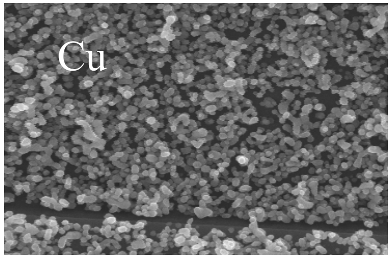
thin films of RuPt
rf sputtered
13 nm thick

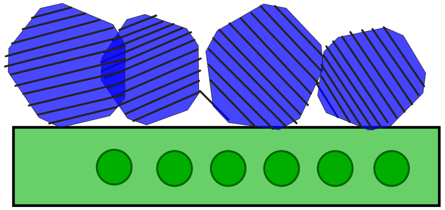
- T-W Kim, S-J Park, Gwangju Institute of Science & Technology, South Korea
- K-W Park, Y-E Sung, Seoul National University, South Korea
- Lindsay Jones, (SULI Internship)

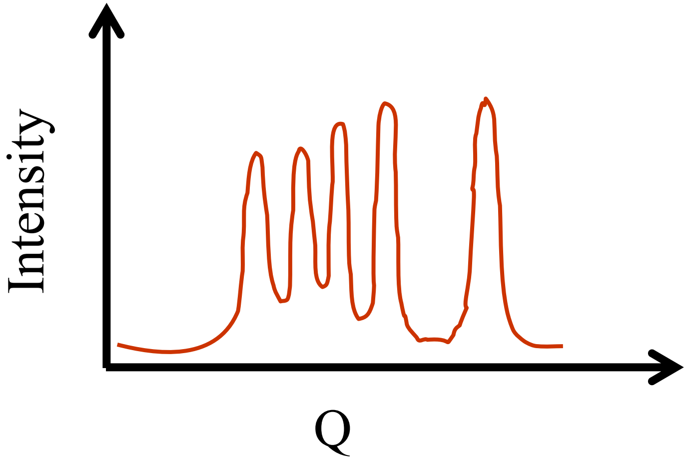
Polycrystalline (powder) film

"Powder": random orientation of many small crystals (crystallites)

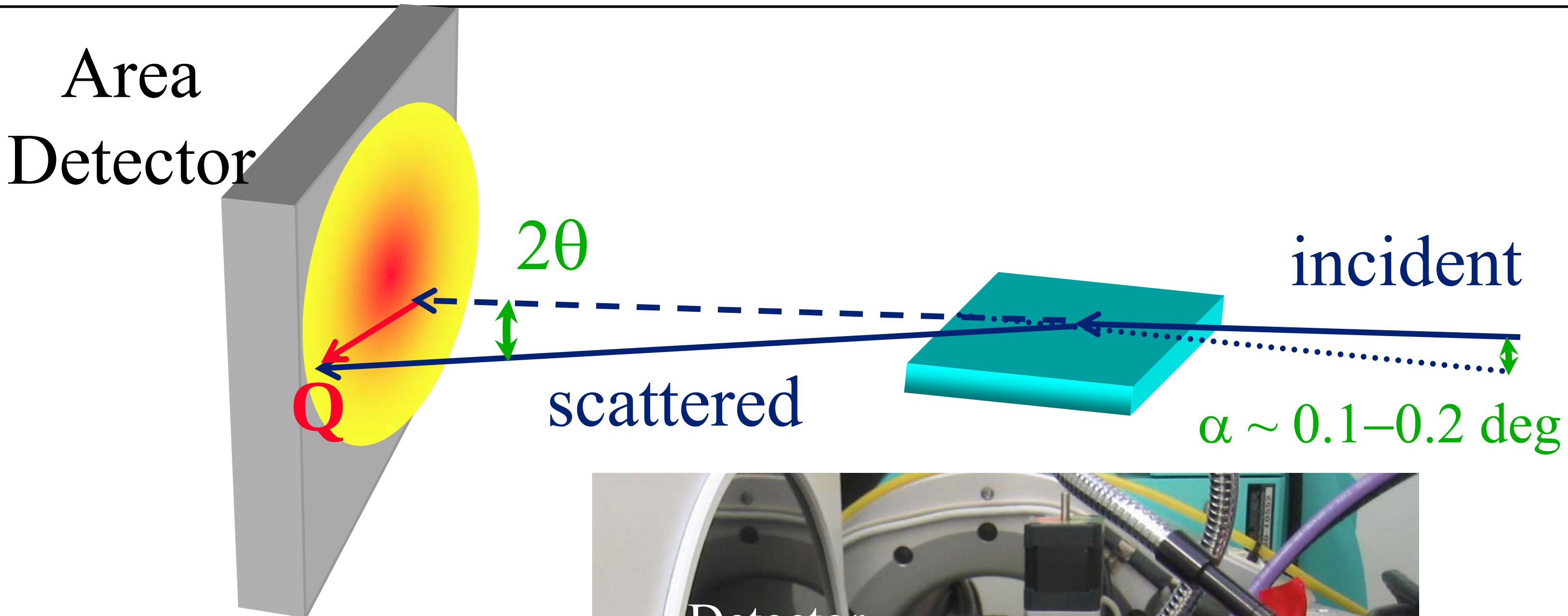




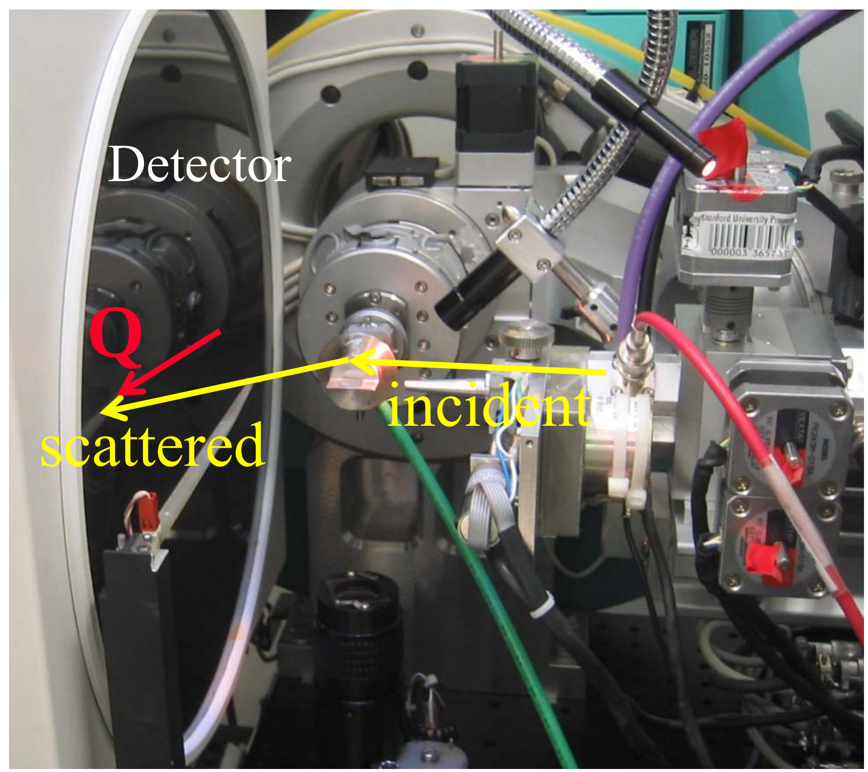




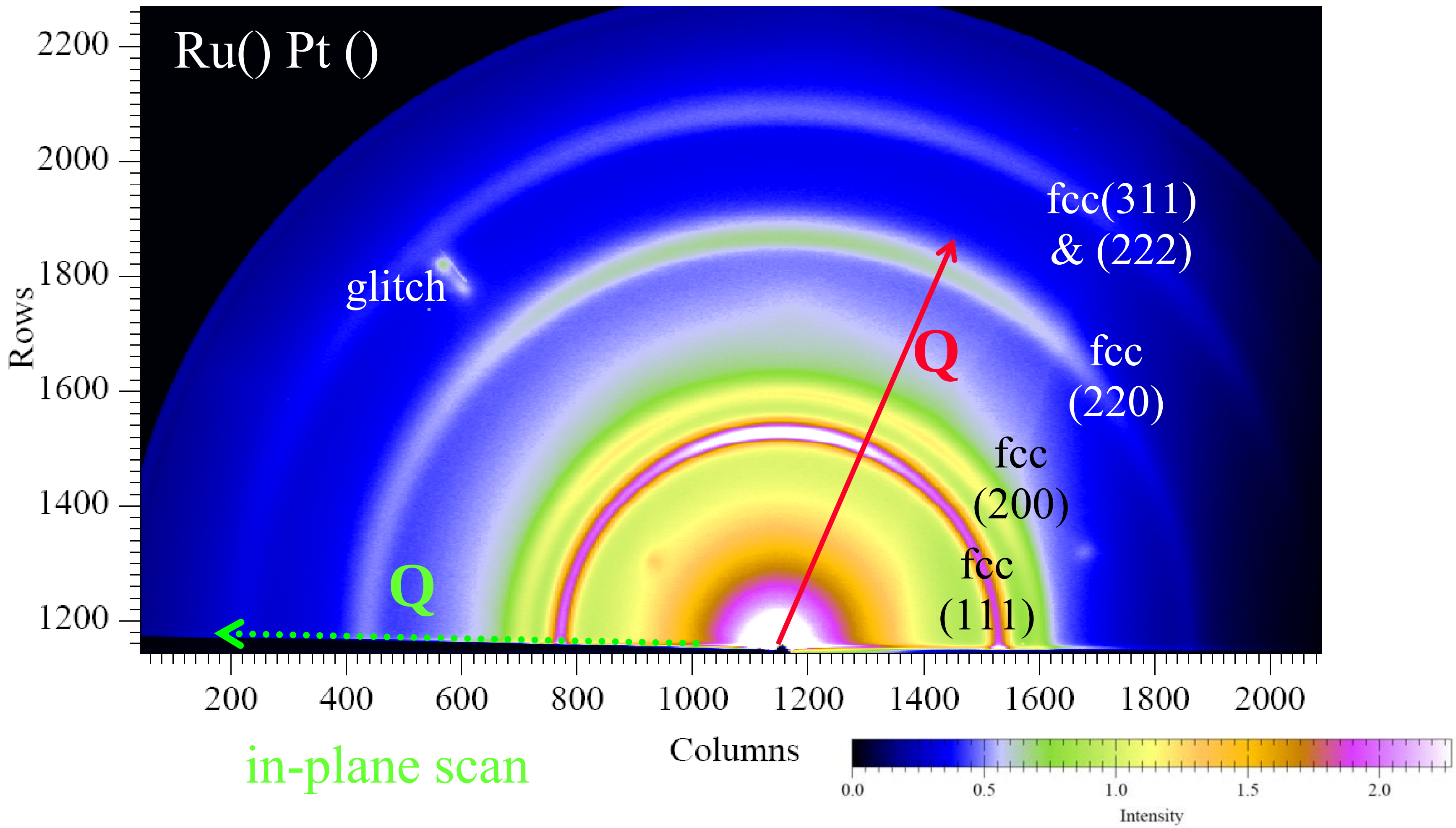
RuPt Thin Films



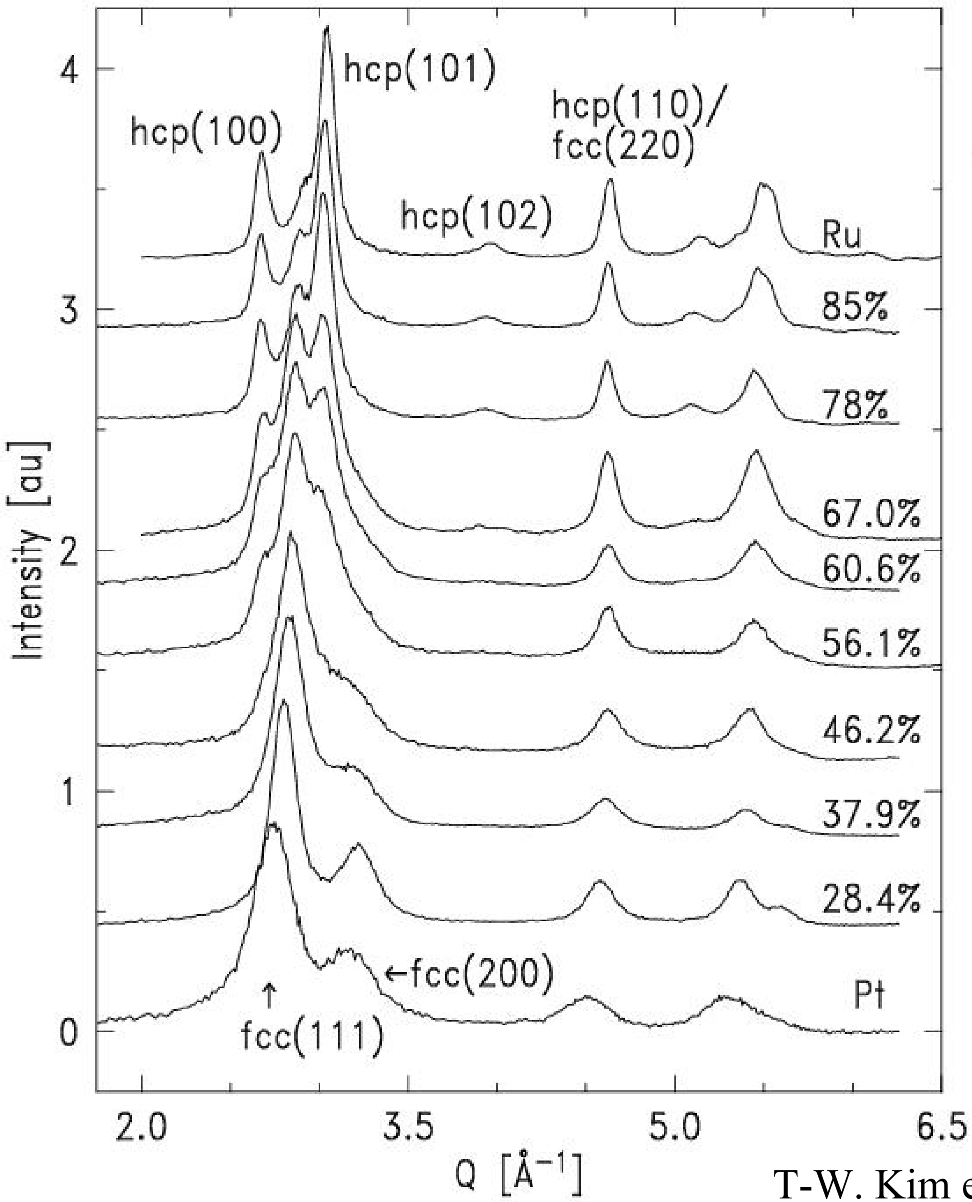
Beam line
11-3

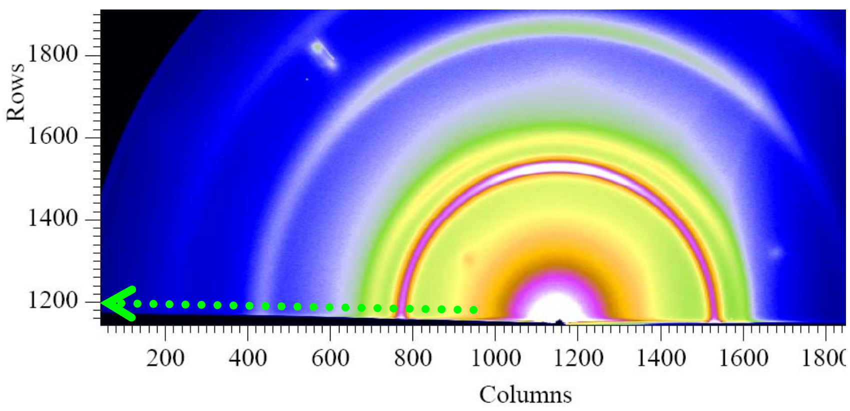


RuPt Thin Films



RuPt Thin Films: diffraction



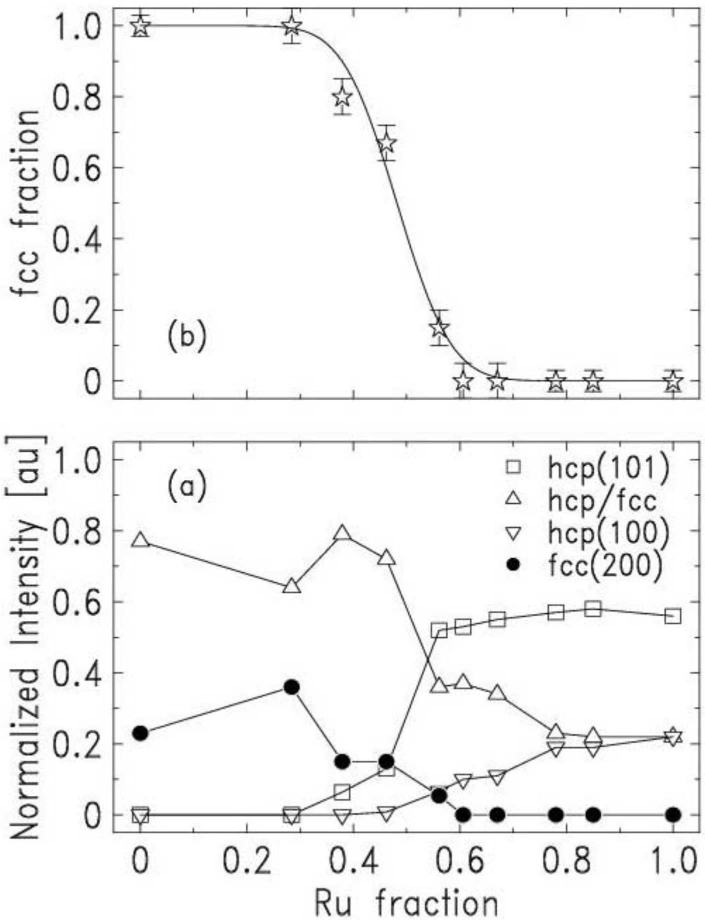


Increasing Ru => transition from fcc to mixed fcc/hcp to hcp

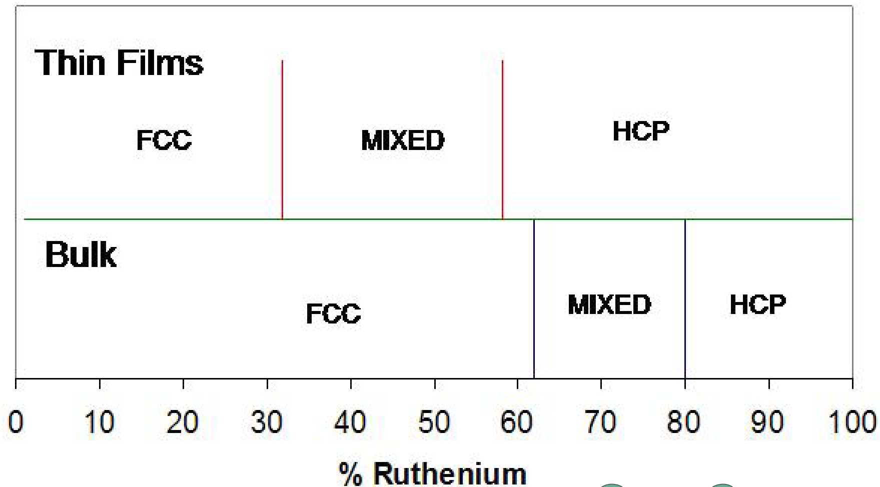
T-W. Kim et al., J. Phys. Chem. B **109**, 12845 (2005)

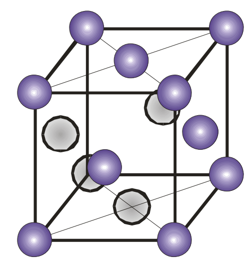
RuPt Thin Films

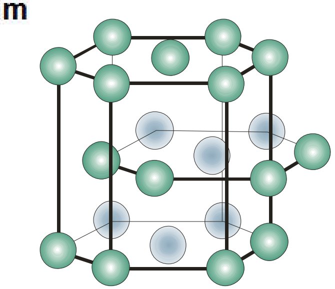
Use peak intensities to quantify phases



Thin Film Phase Diagram



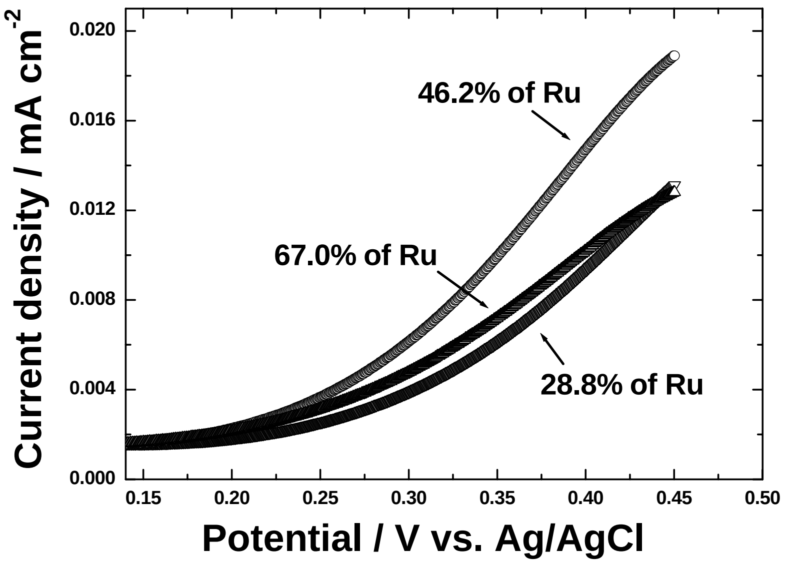


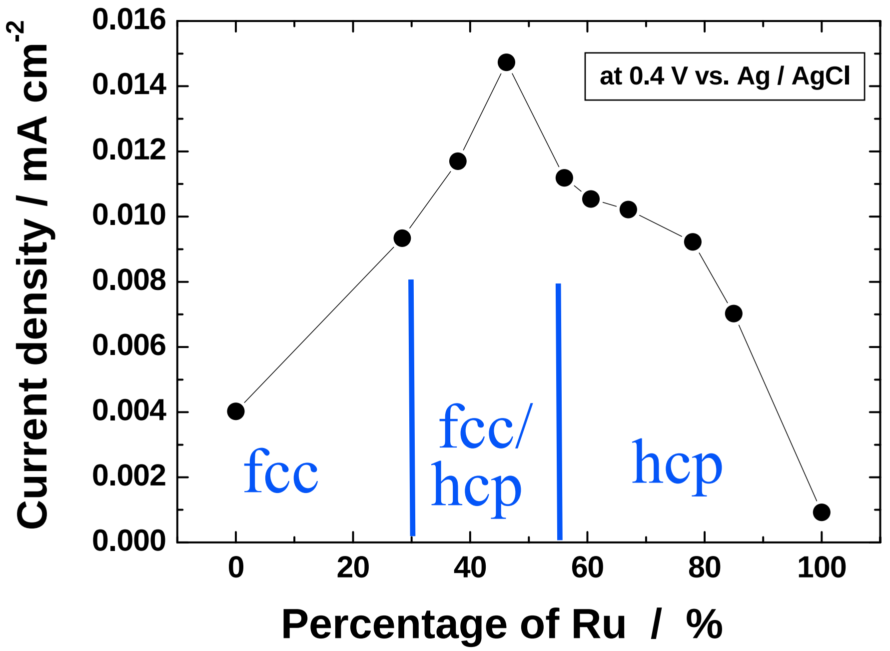


Thin film different from bulk, due to sputter deposition

Kinetics do not allow equilibrium

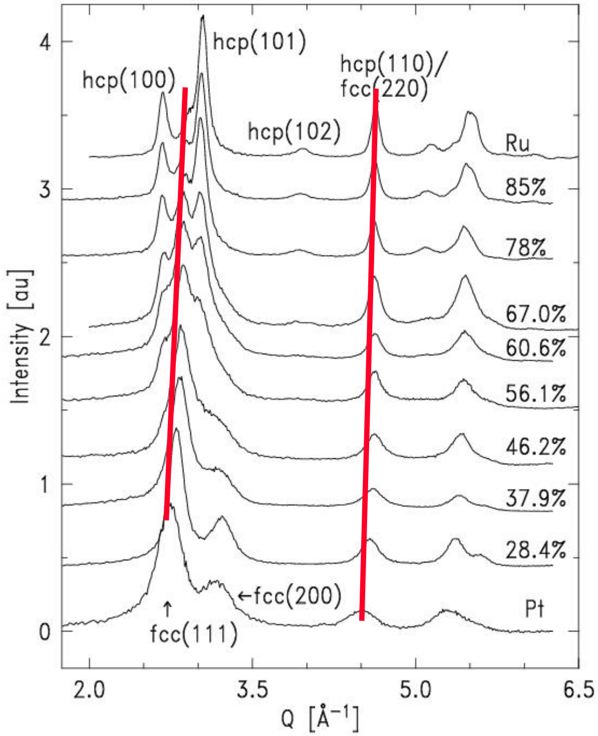
RuPt Thin Films

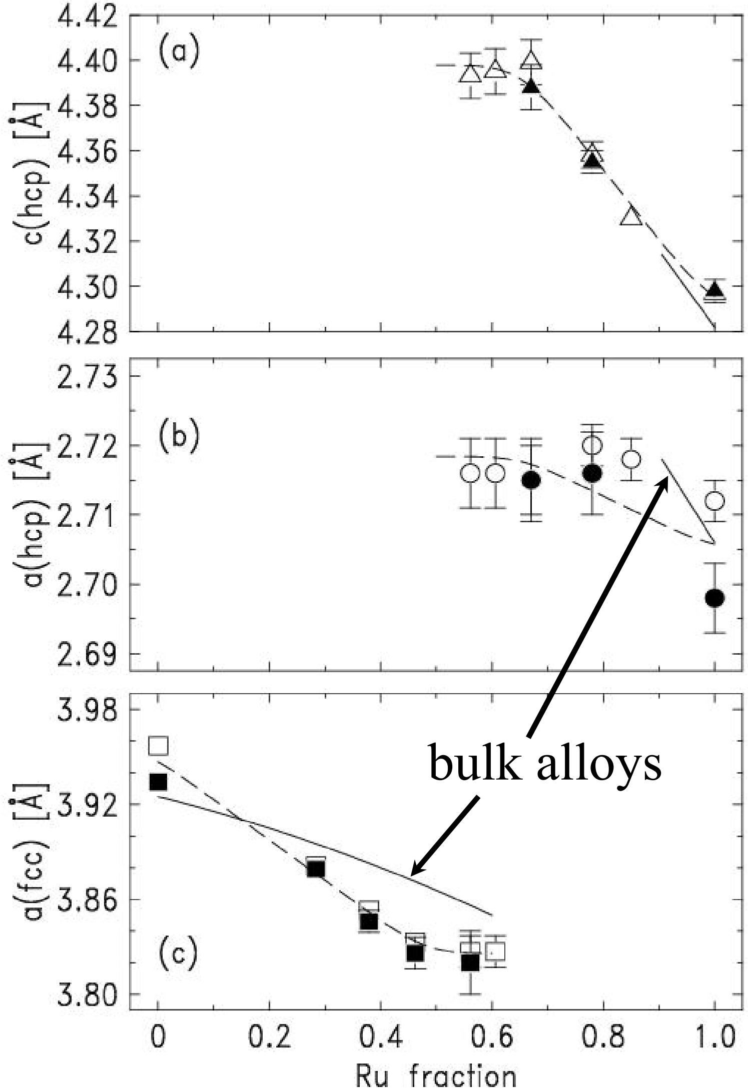




- composition dependent activity similar to pure fcc alloys
- hcp RuPt does not adversely affect activity
- may be manifestation of surface properties (similarity of fcc(111) and hcp(002)

RuPt Films: Lattice Parameters



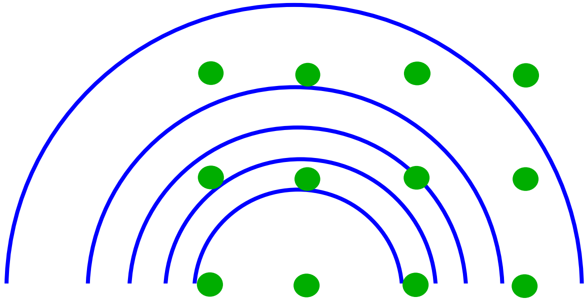


- Accurately determine lattice parameters
- Cannot use bulk alloy lattice parameters to get composition

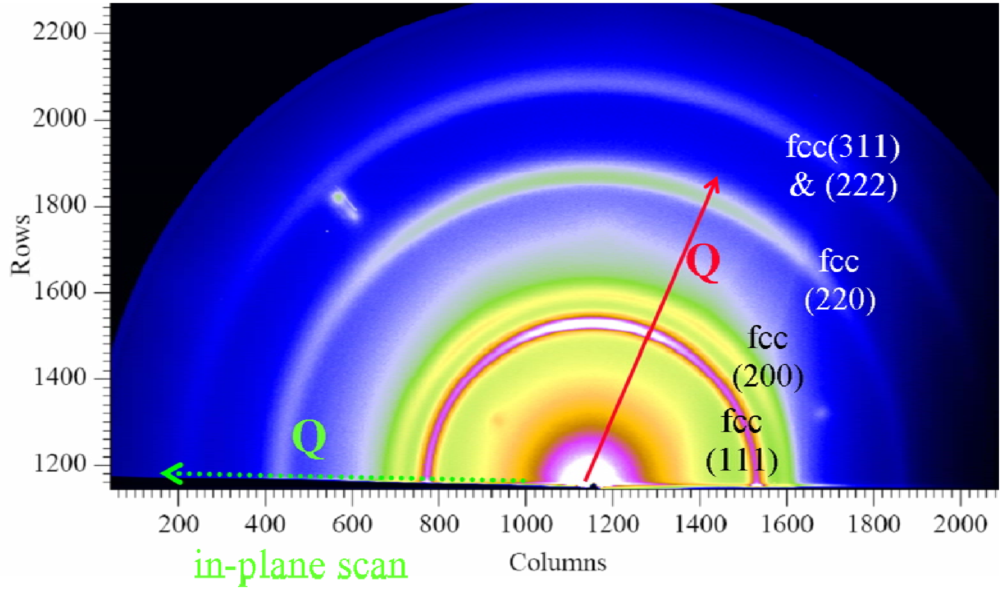
Summary: polycrystalline

RuPt films:

- ➢ phase identification (hcp, fcc)
- ➢ lattice parameters (strain)
- ➢ no strong texture
- ➢ crystallite size



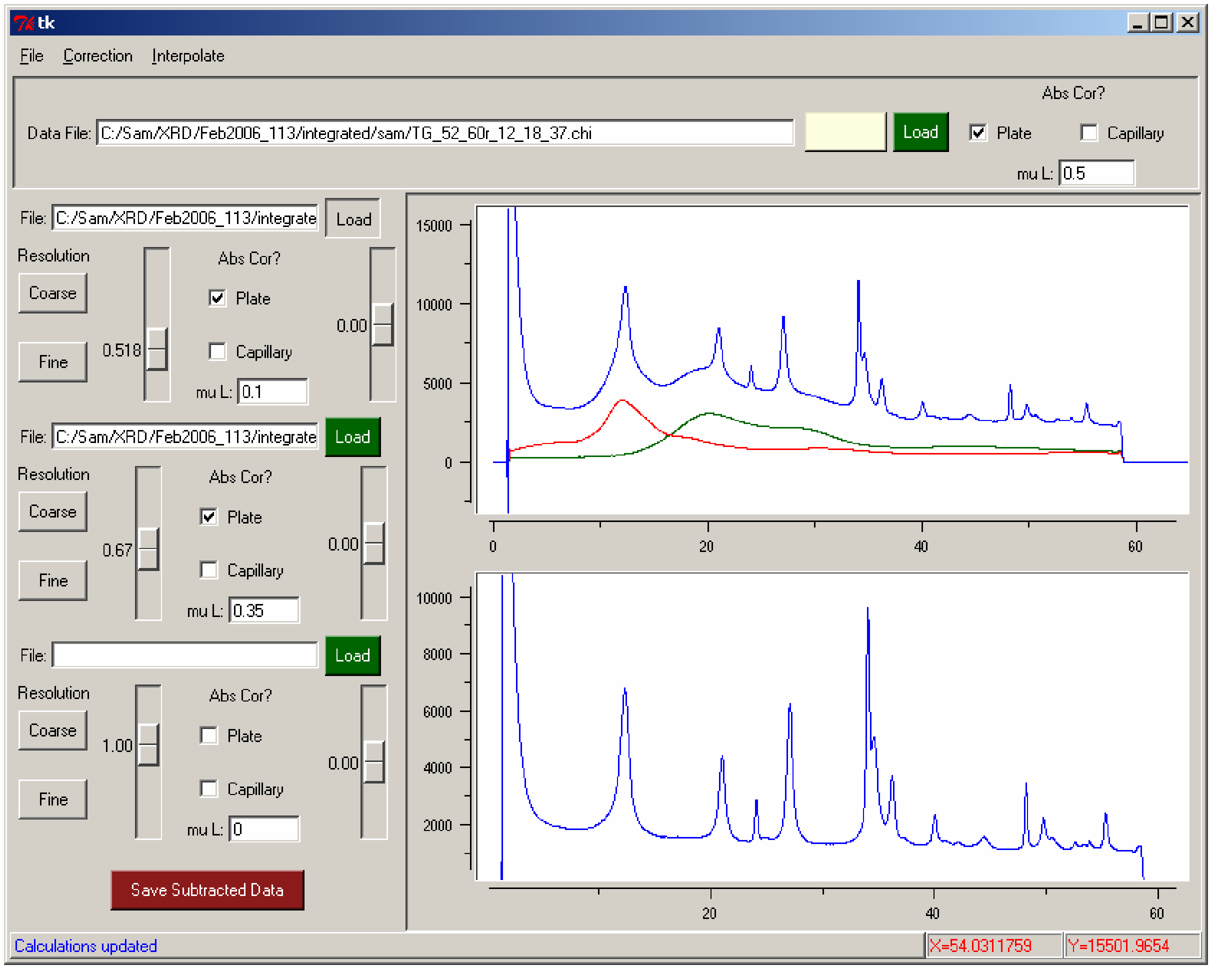
- Area detector
- Point detector



Scan choice straightforward

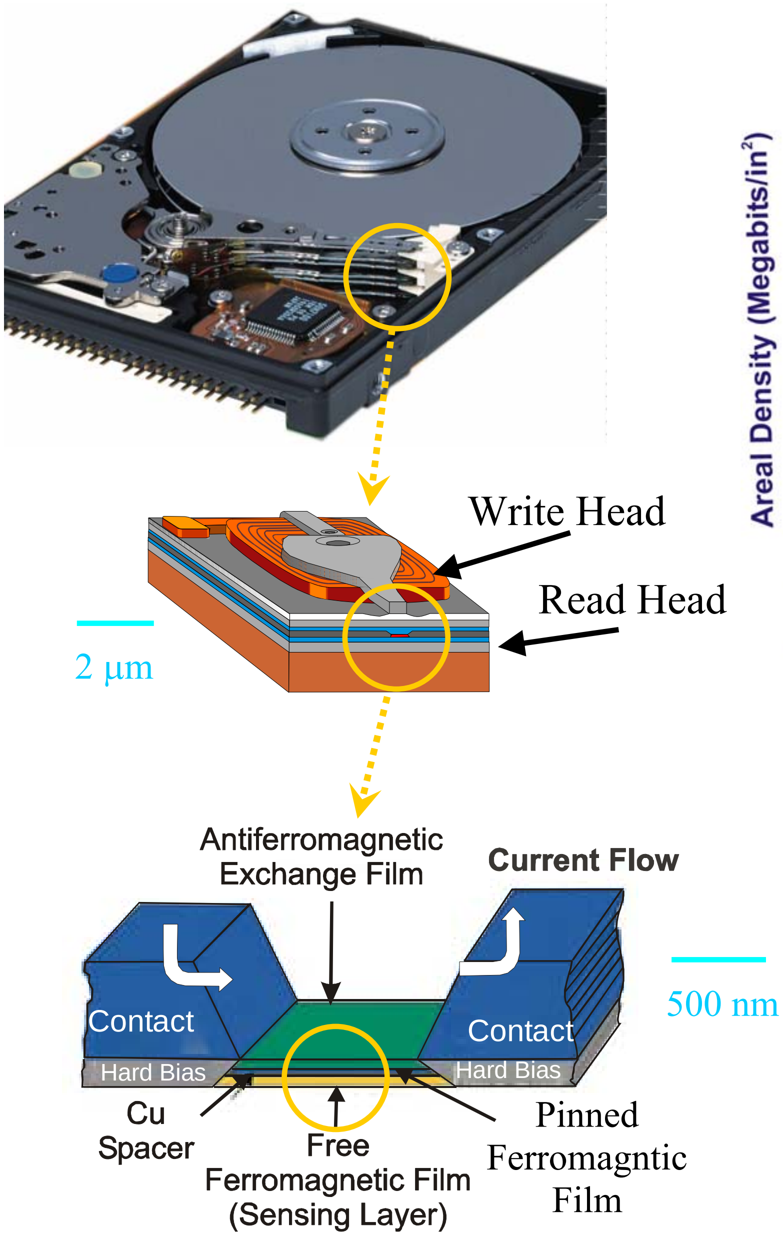
XRD - BS

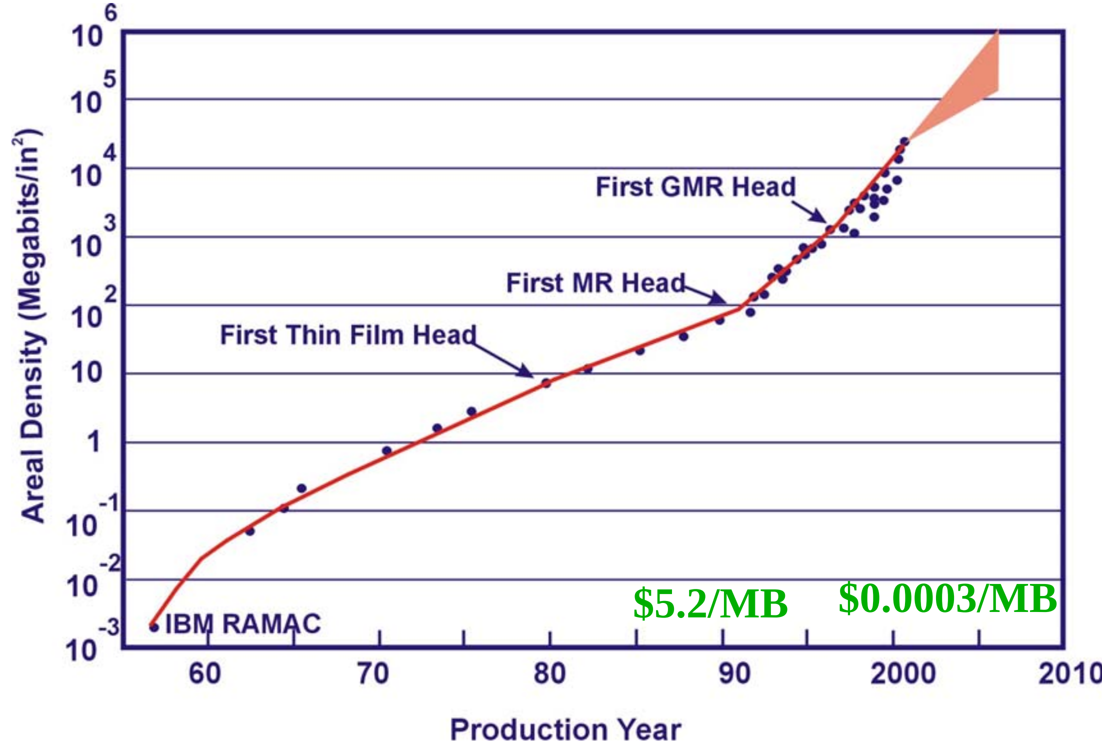
- GUI for removal of background and thickness corrections
  - http://www-ssrl.stanford.edu/~swebb/xrdbs.zip
  - http://www-ssrl.stanford.edu/~swebb/xrdbs.htm (coming soon)



Sam
Webb

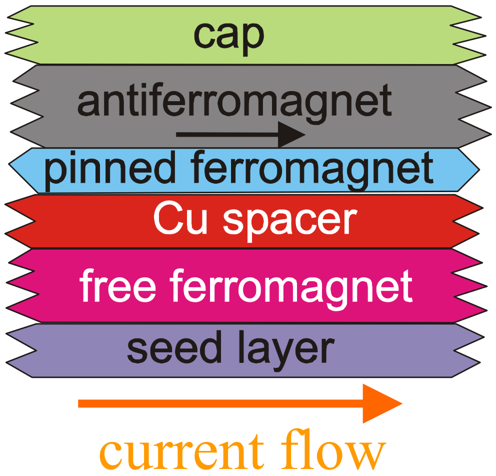
Thin Films for Magnetic Recording

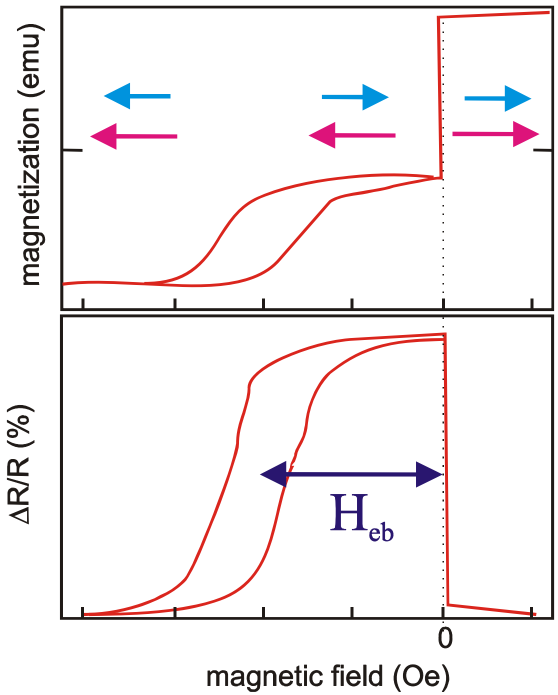




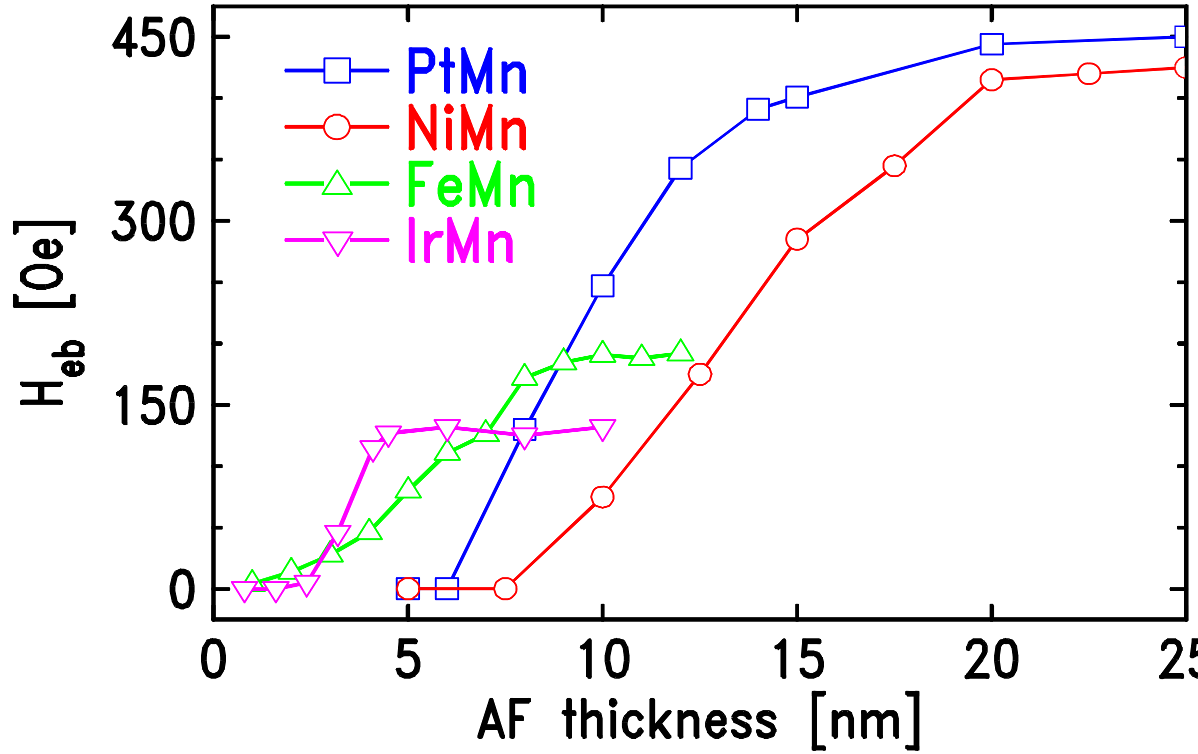
Tsann Lin and Daniele Mauri, Hitachi Global Storage
Mahesh Samant, IBM

Thin Films for Magnetic Recording





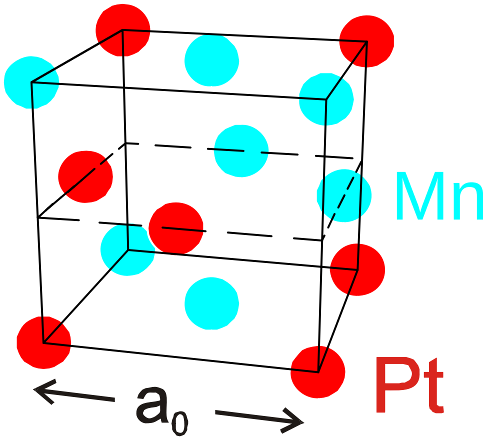
Exchange bias (H_{eb})



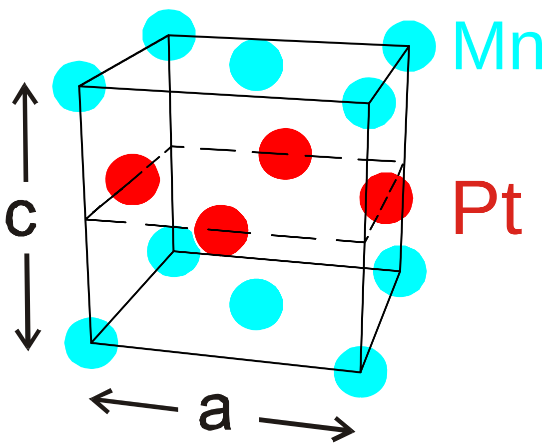
- Understand this behavior (for MnPt)

Toney, Samant, Lin, Mauri, Appl. Phys. Lett. **81**, 4565 (2002)

MnPt Films: chemical order



chemically disordered
fcc structure
not antiferromagnetic



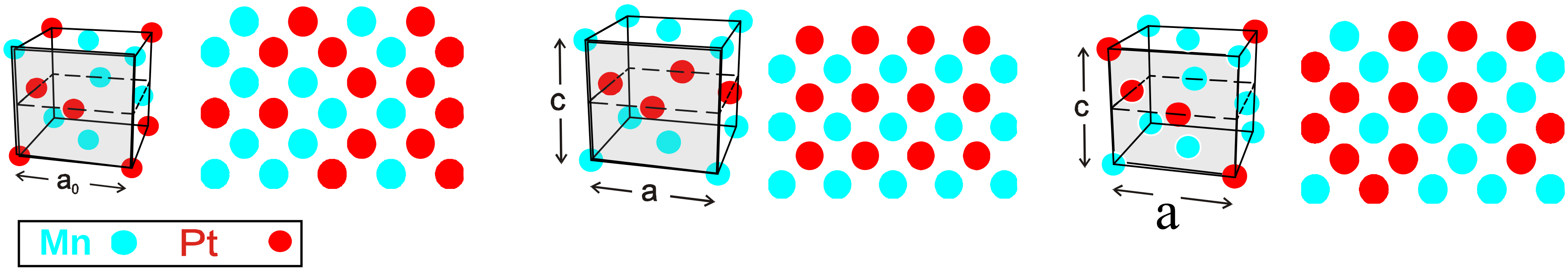
chemically ordered
$L1_0$ structure (face centered tetragonal)
$c/a = 0.92$
antiferromagnetic (T_N = 700-800^o C)

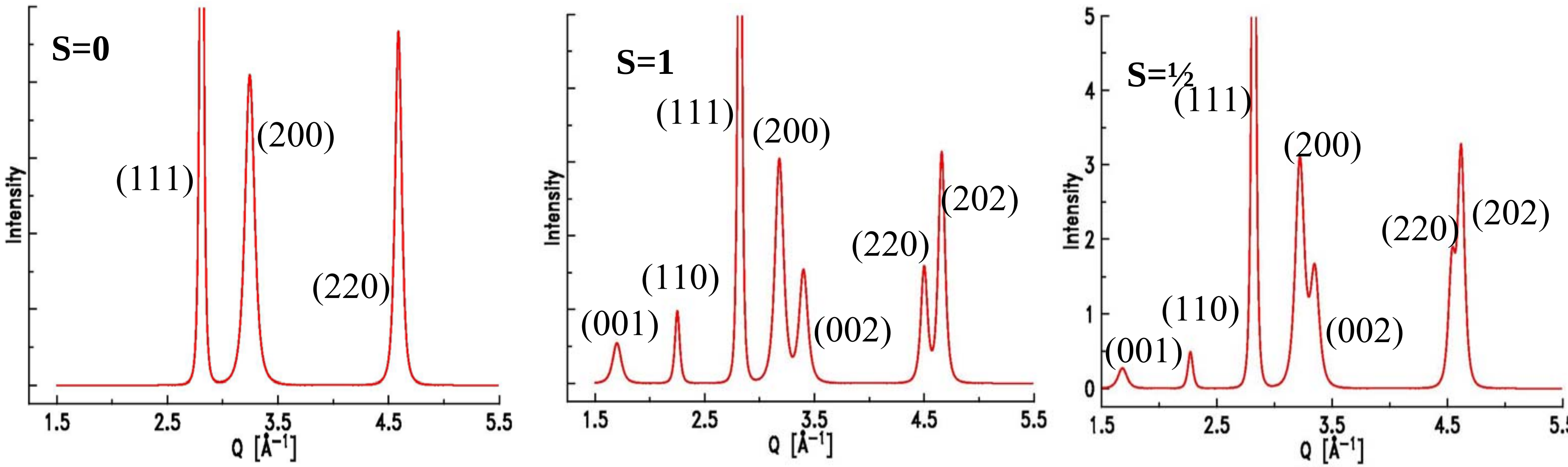
Cebollada, Farrow & Toney, in *Magnetic Nanostructures*, Nalaw, ed. 2002

MnPt Films: chemical order

chemical order parameter (S): extent of chemical order

No chemical order: S=0 | Full chemical order: S=1 | partial chemical order: S=1/2

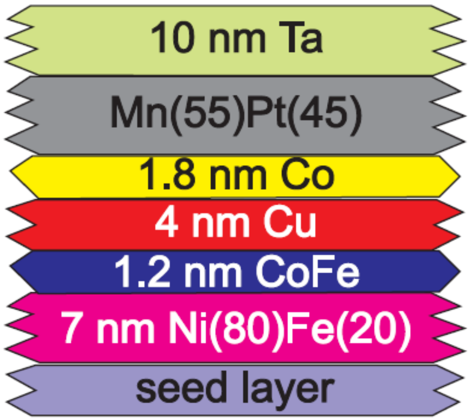




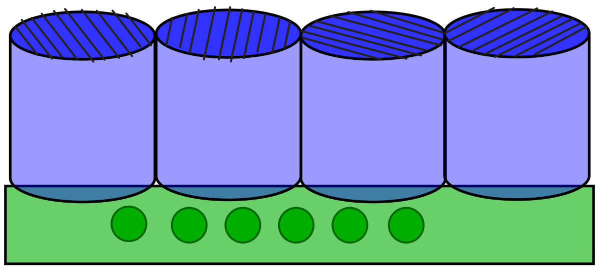
determine S from peak intensities (110)/(220) ratio

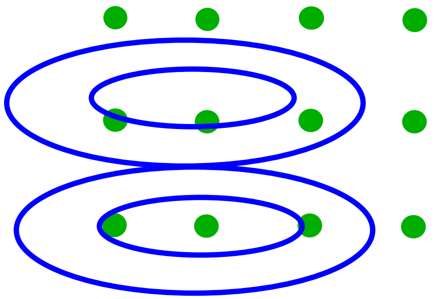
Cebollada, Farrow & Toney, in *Magnetic Nanostructures*, Nalaw, ed. 2002

Highly Textured Thin Films

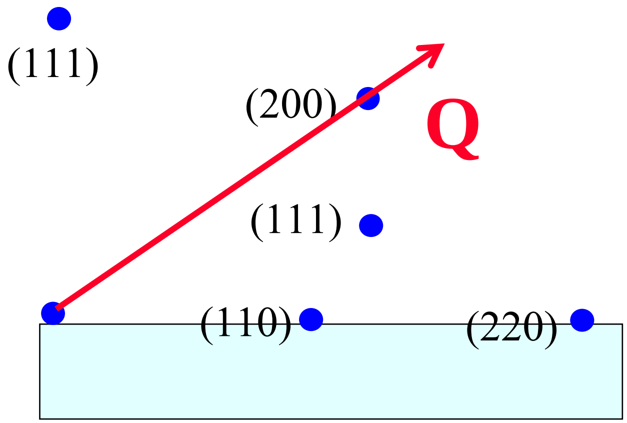


- sputtered
- annealed at 280C for 2 hours



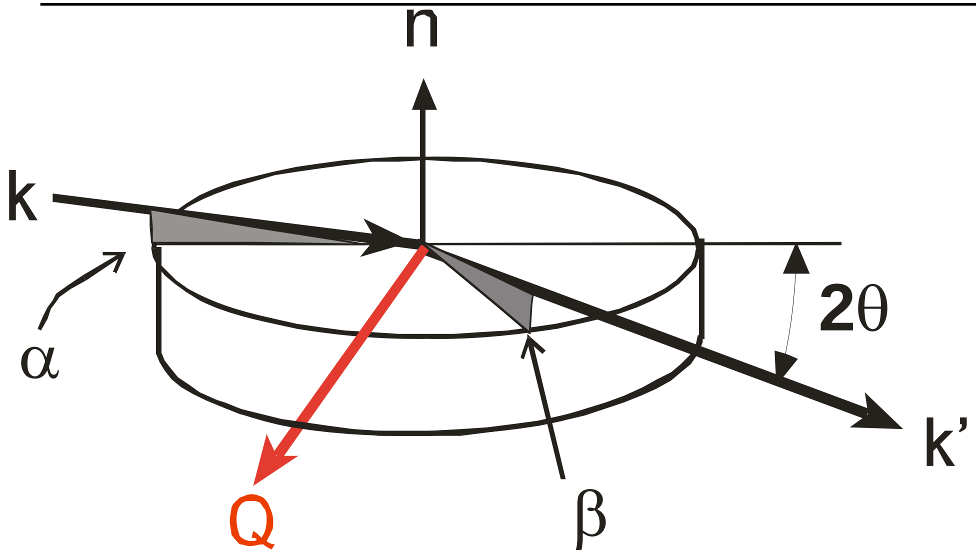


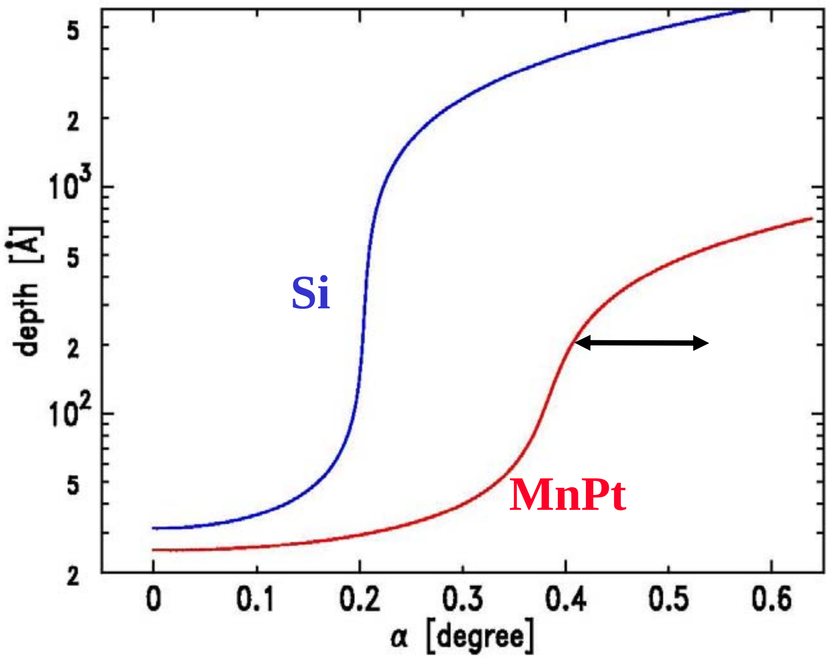
rings



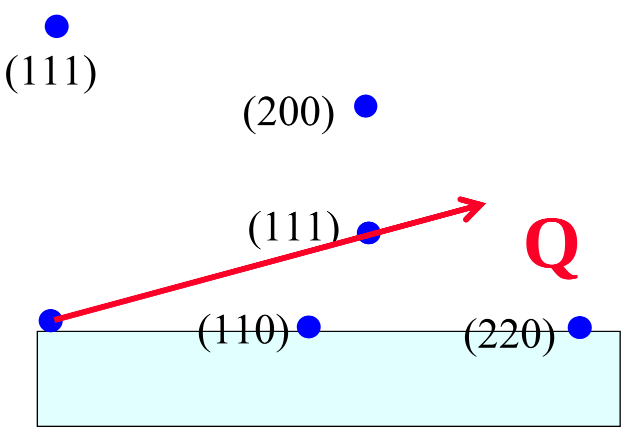
slice gives spots

MnPt Films: diffraction

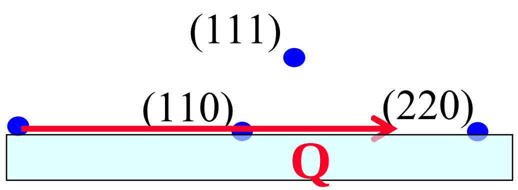


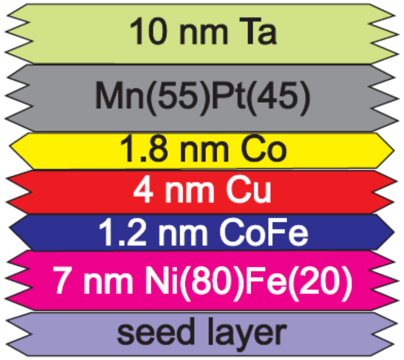


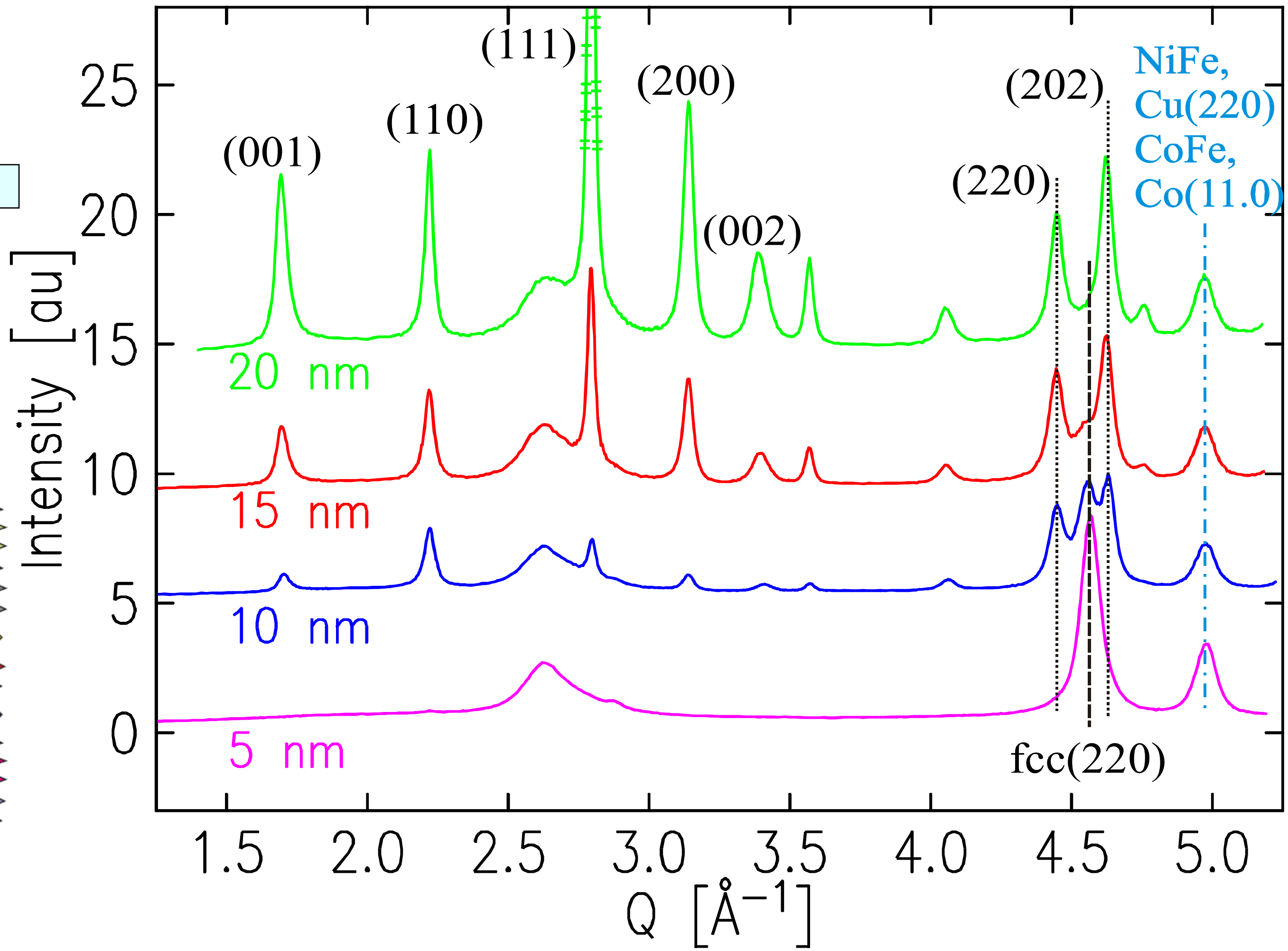
2θ is scattering angle
Q = scattering vector
Q = (4π/λ) sin θ
α = incidence angle
β = exit angle



MnPt Films: diffraction



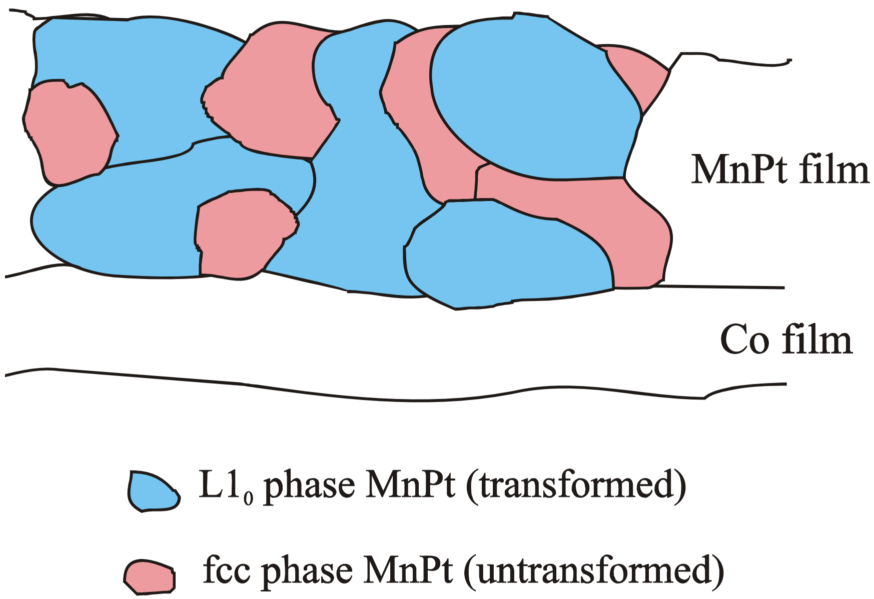


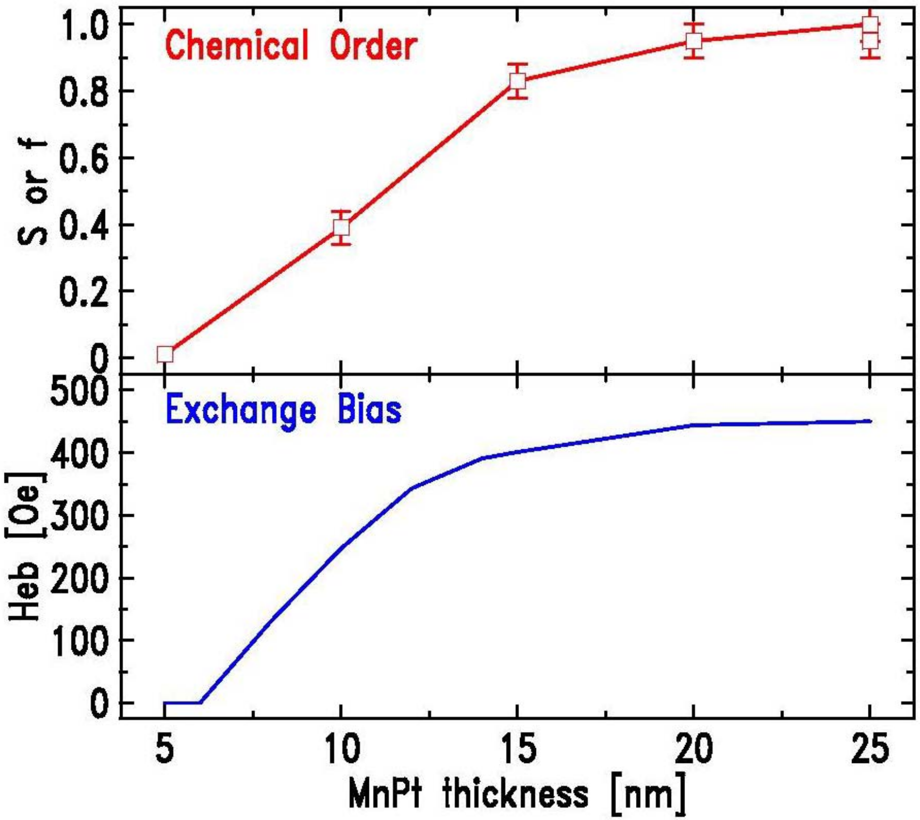


- increased thickness: the superlattice (001) and (110) peaks increase => more chemical ordering
- coexistence of fcc and $L1_0$

Toney, Samant, Lin, Mauri, Appl. Phys. Lett. **81**, 4565 (2002)

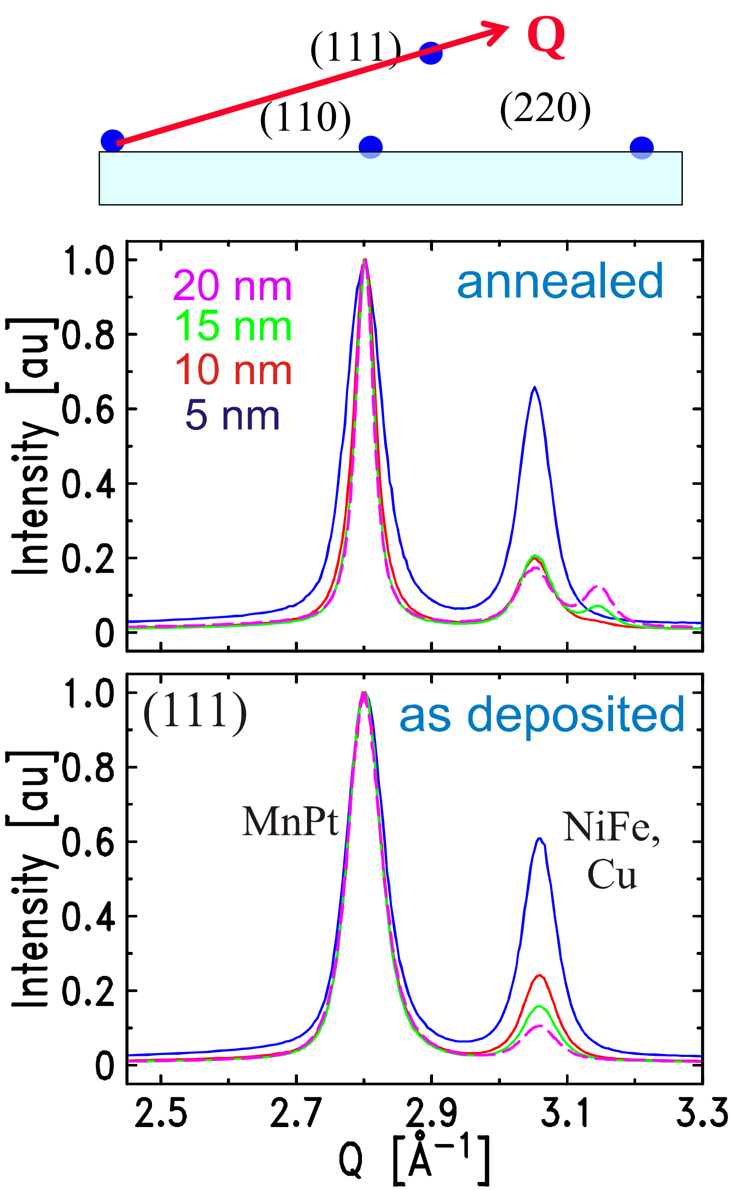
MnPt Film Structure

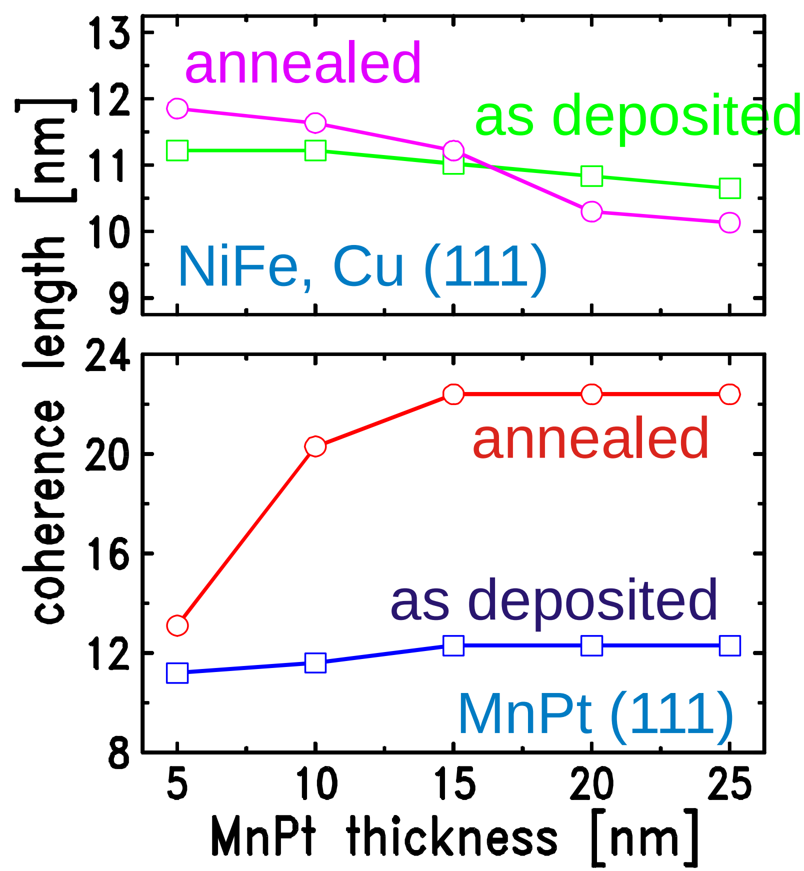




- coexistence of fcc and $L1_0$ MnPt (inhomogeneous)
- complete chemical order for highest H_{eb}

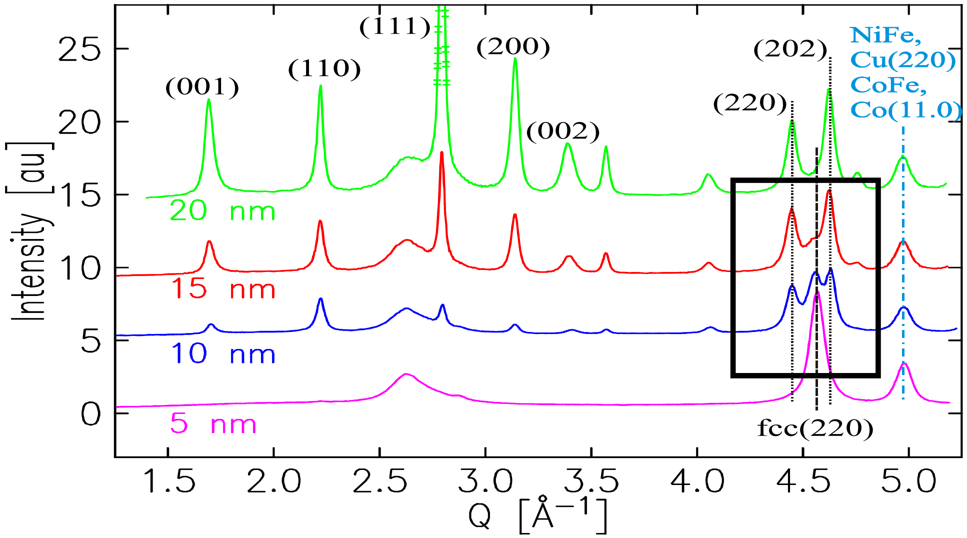
MnPt Films: crystallite size



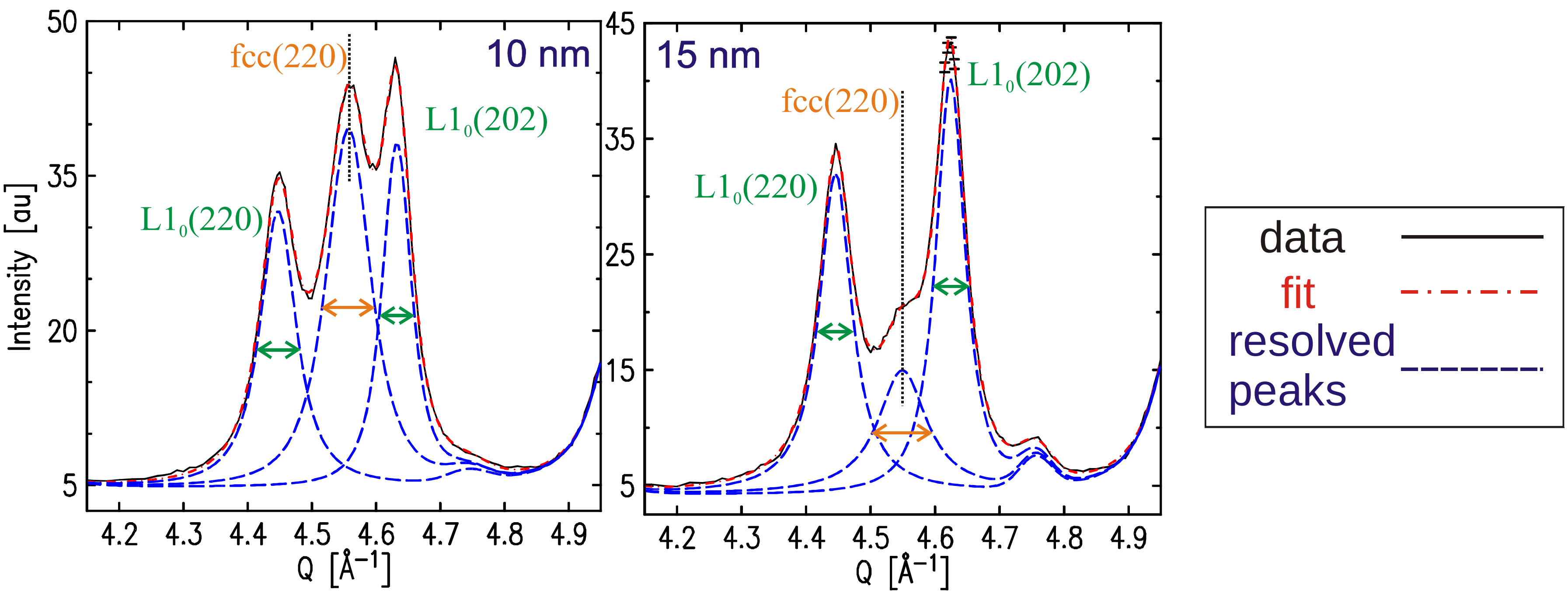


- more chemically ordered MnPt -> larger grains
- NiFe & Cu do not change much with annealing

MnPt Films: crystallite size

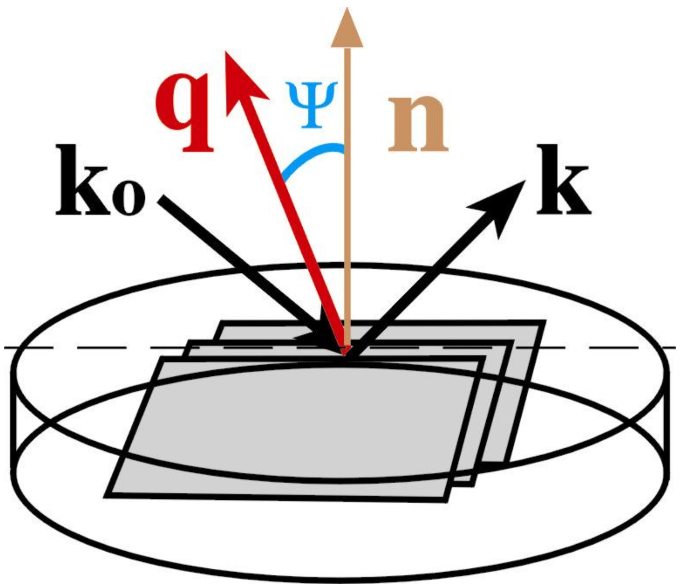


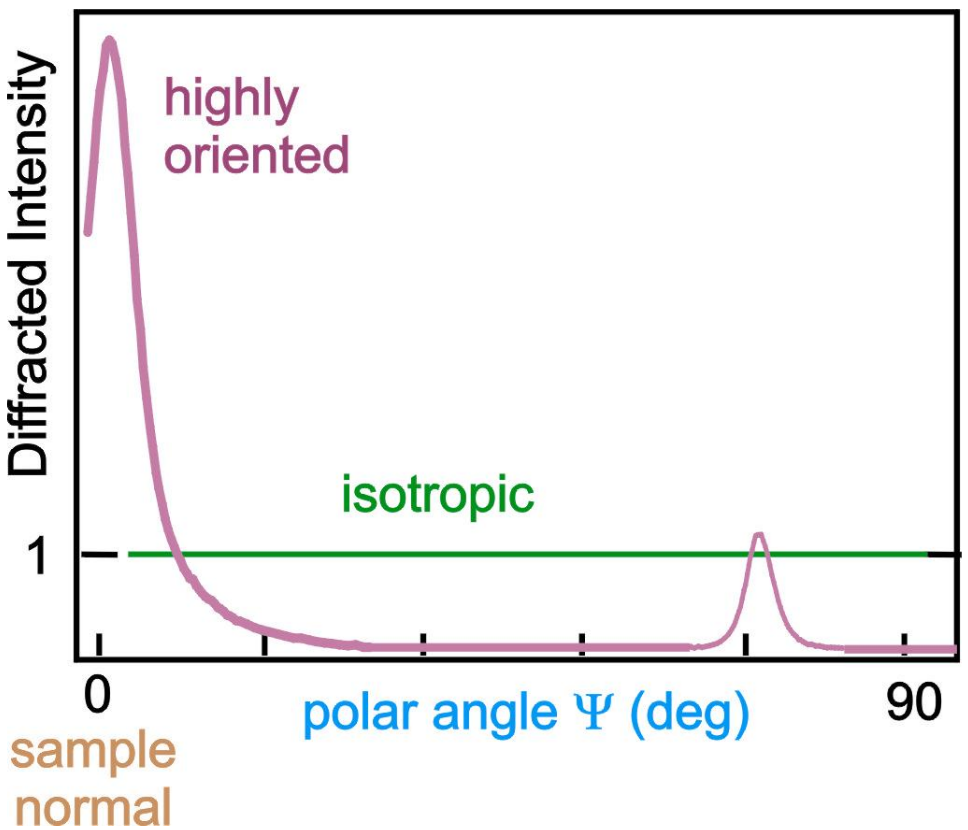
- ➢ $L1_0$ (transformed) regions have larger crystallite than fcc regions
- ➢ fcc regions close to unanneled crystallite size



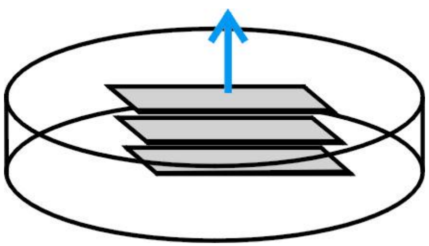
Texture in Thin Films

- Pole figure measures orientation distribution of diffracting planes

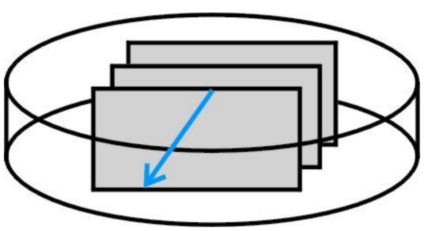




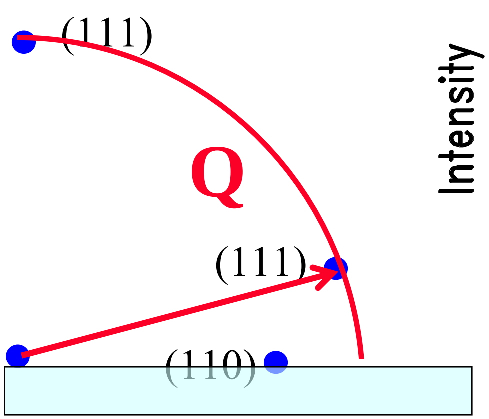
- Ψ = 0 deg planes along substrate

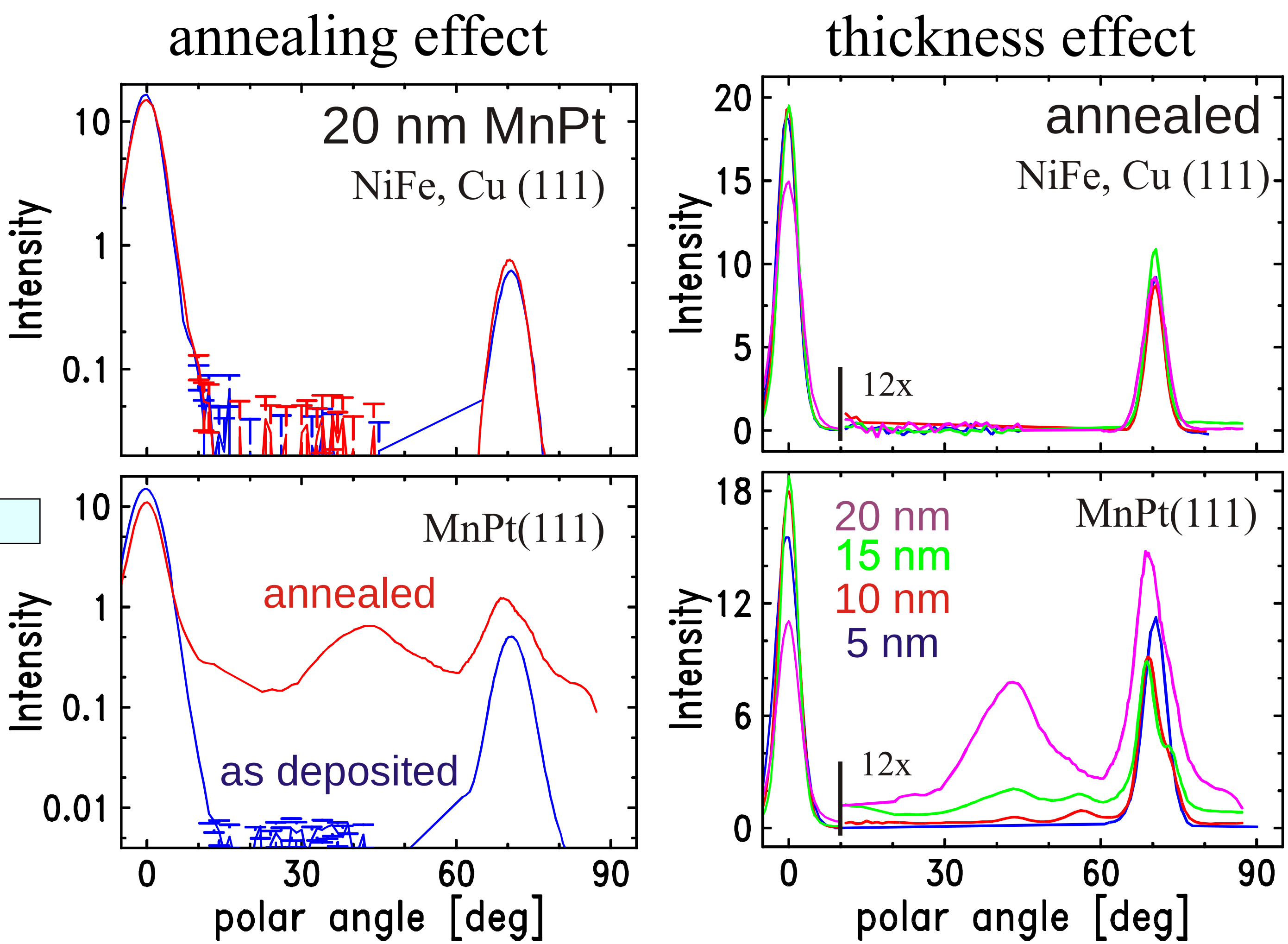


- Ψ = 90 deg planes ⊥ to substrate



MnPt Films: Texture

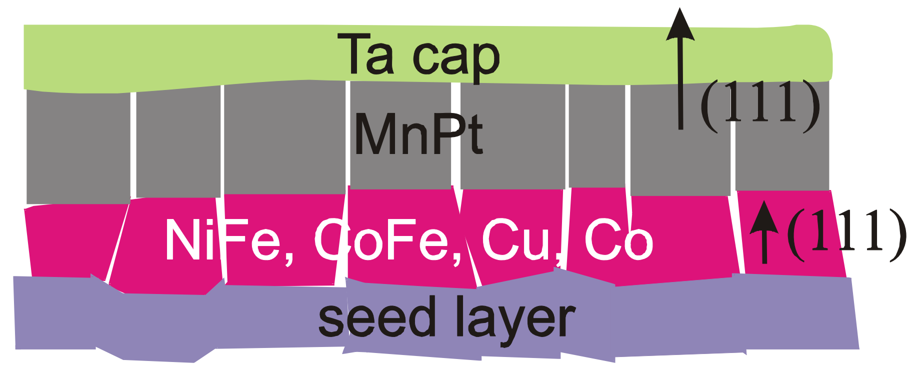




MnPt Films

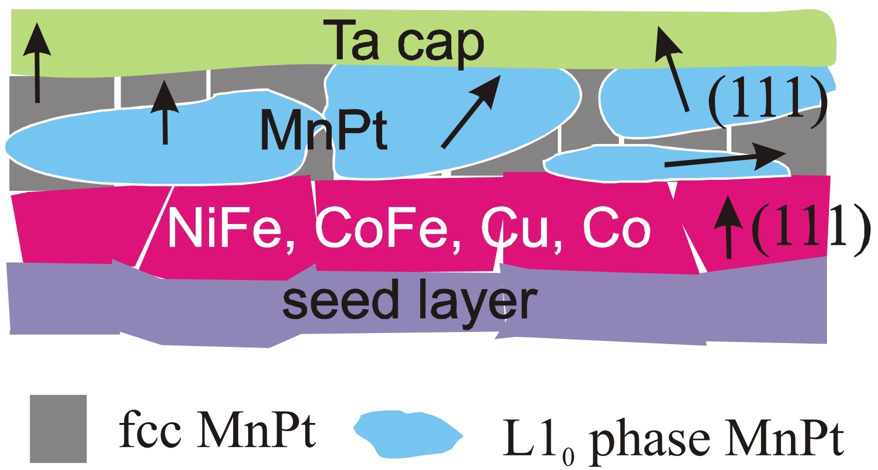
as deposited

- seed layer induces (111) growth in NiFe & Cu [(00.2) in hcp Co & CoFe] and columnar morphology
- MnPt follows (111) growth



annealed

- NiFe & Cu maintain (111) orientation [(00.2) in Co & CoFe]
- fcc MnPt keeps (111) orientation
- L10 MnPt:
  - ✓ some keeps (111) orientation
  - ✓ some becomes nearly isotropic
  - ✓ grain growth

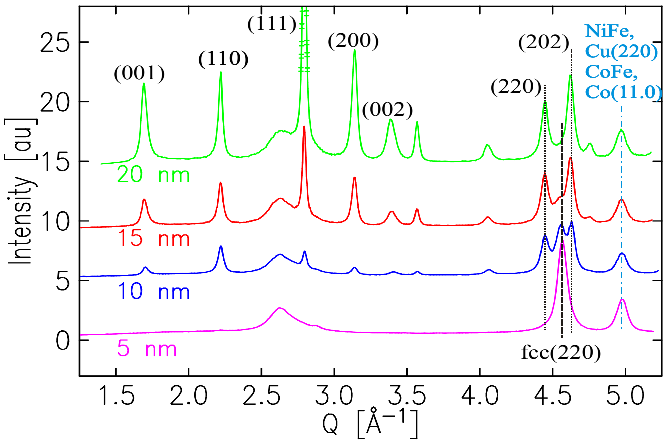


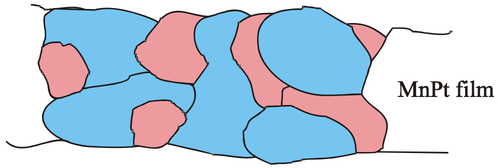
=> L1$_0$ MnPt forms by nucleation and growth

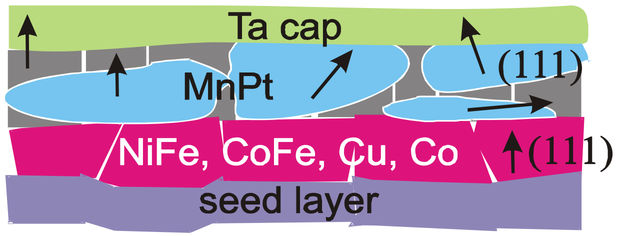
MnPt Films: Summary

- thin MnPt remains fcc => not antiferromagnetic and no exchange bias coexistence between fcc and $L1_0$ (inhomogeneous)
- need complete $L1_0$ order to get highest exchange
- no (<0.5 nm) fcc layer near interface
- grain growth and change in preferred orientation with development of chemical order

=> $L1_0$ forms by nucleation & growth



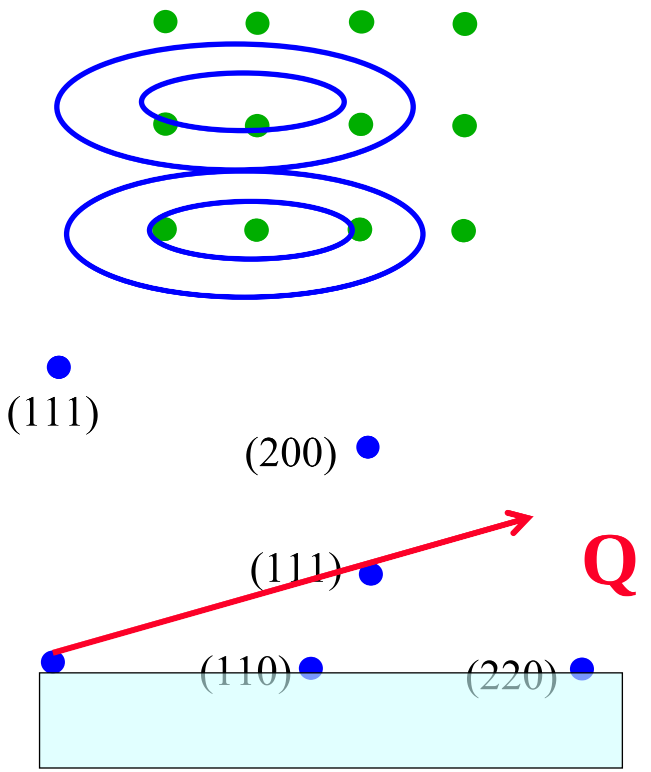




MnPt Thin Films: Summary

MnPt films:

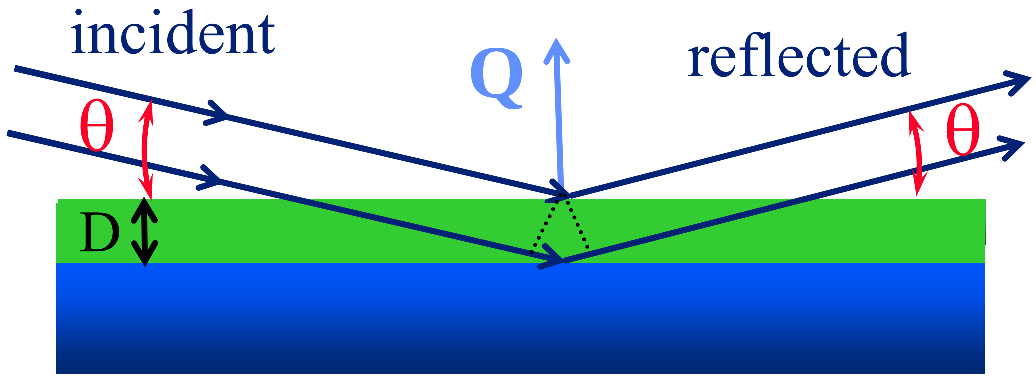
- phase identification ($L1_0$, fcc)
- lattice parameters (strain)
- texture
- crystallite size



- Area detector
- Point detector

- Scan choice requires knowledge of reciprocal space & what you want to learn
- Same is true for pentacene

X-ray Reflectivity



$Q = (4\pi/\lambda) \sin\theta$

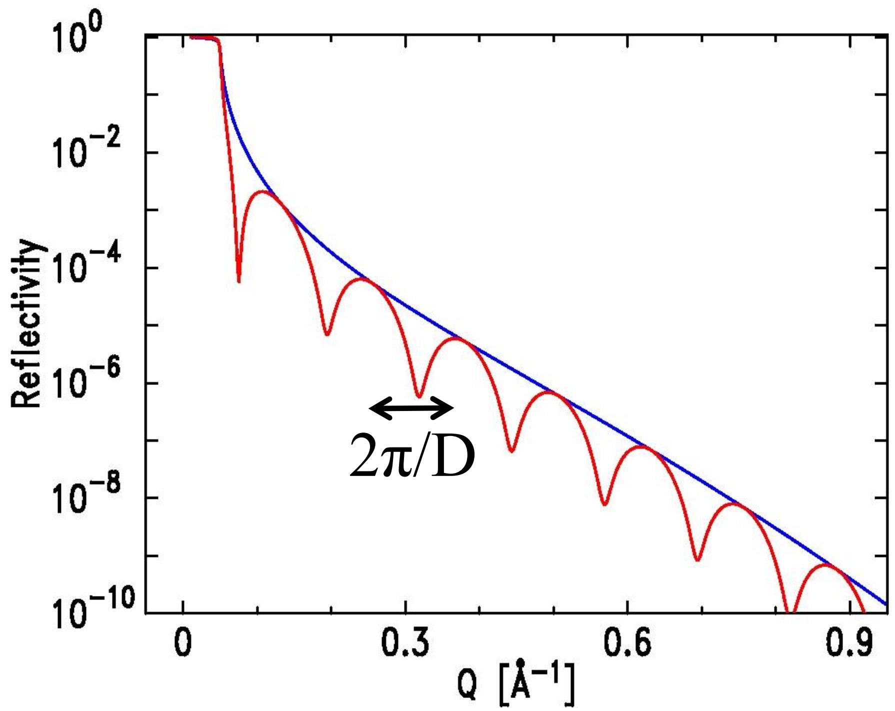
$Q < Q_c$: $R \approx 1$

$Q \gg Q_c$: $R \approx (Q_c/Q)^4$

R= reflectivity

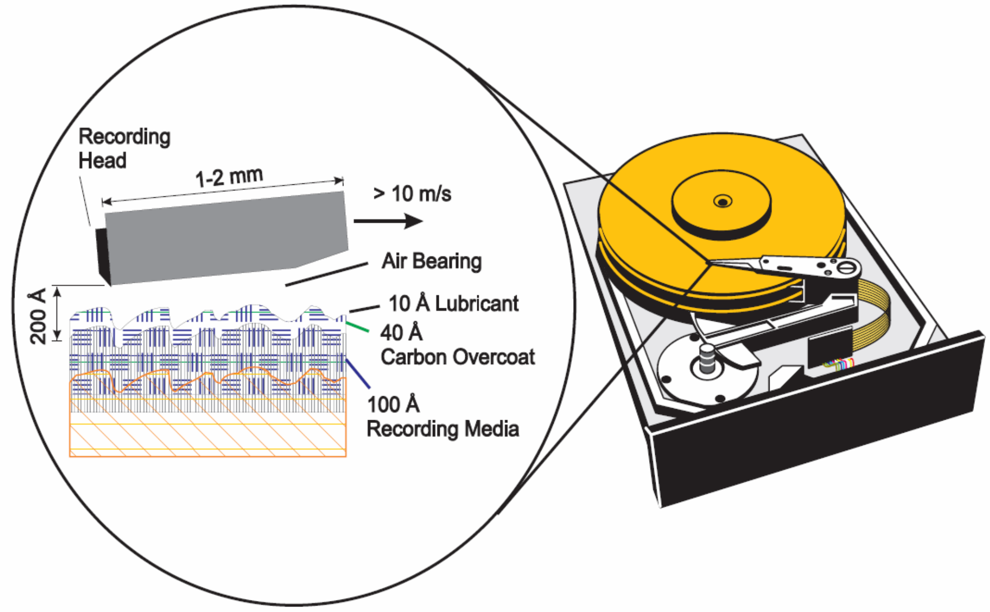
$Q_c \approx \sqrt{\rho_{e-}}$, electron density

$R \approx | r_1 + r_2 \exp(iQD)|^2$

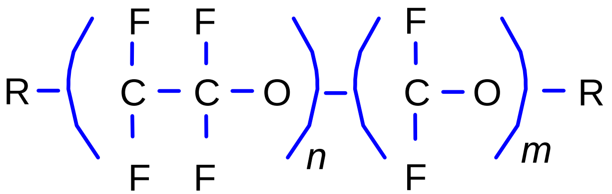


- Lu, Lee, Thomas, Acta Cryst. **A52**, 11-41 (1996).
- Tolan, "X-ray Scattering from Soft-Matter: Materials Science and Basic Research", Springer (1998).

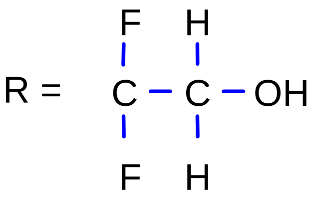
Lubricant Films



Fomblin Disk Lubricants:

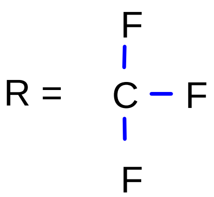


random co-polymer



Z-Dol

4700 g/mol



Z

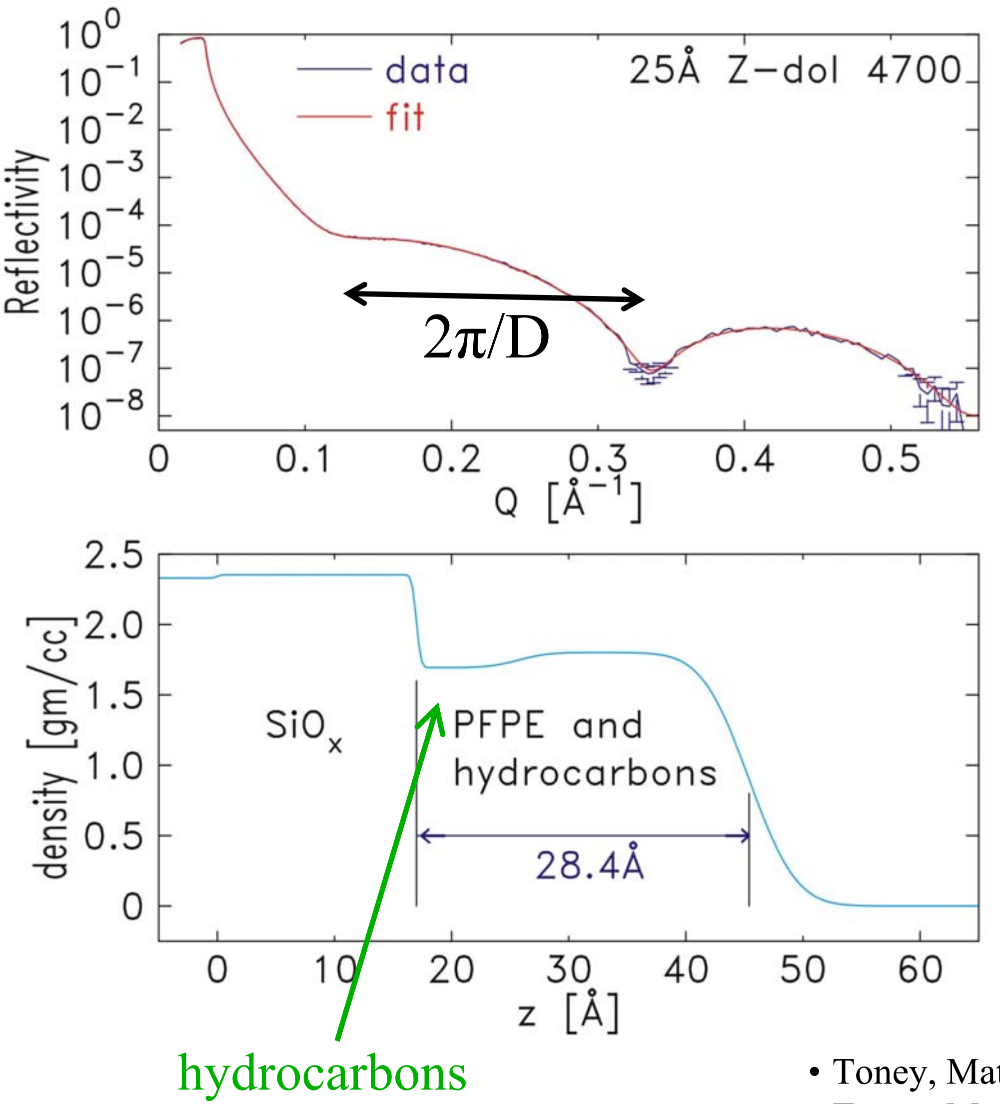
4600 g/mol

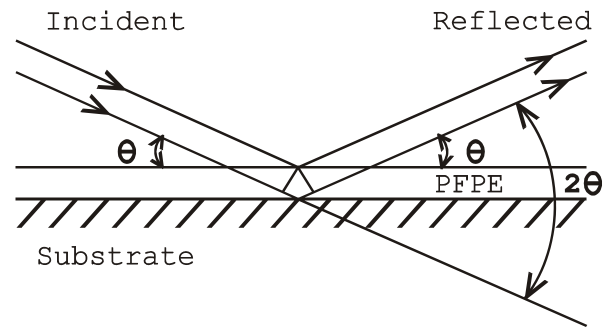
How thick is the lubricant?

What we did:

- use reflectivity to measure various thicknesses
- compare with 'established' methods

Lubricant Films: Thickness





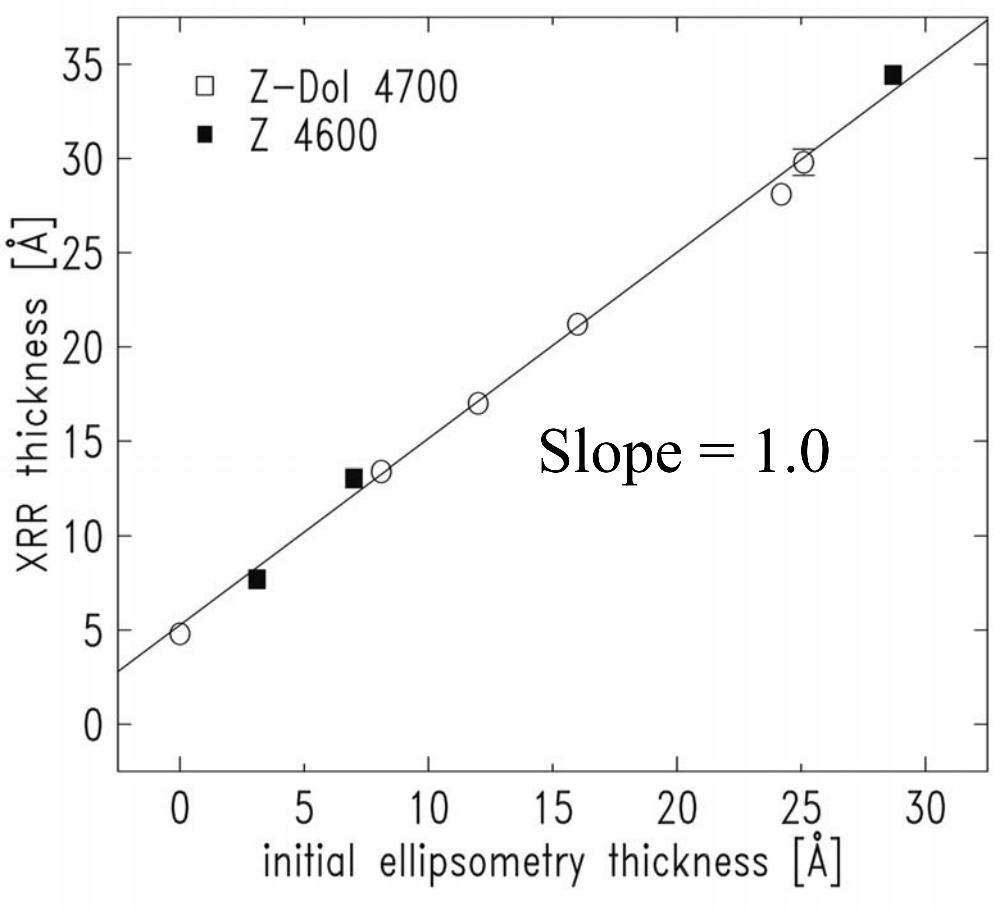
$$R \approx |\, r_1 + r_2 \exp(iQD)|^2$$

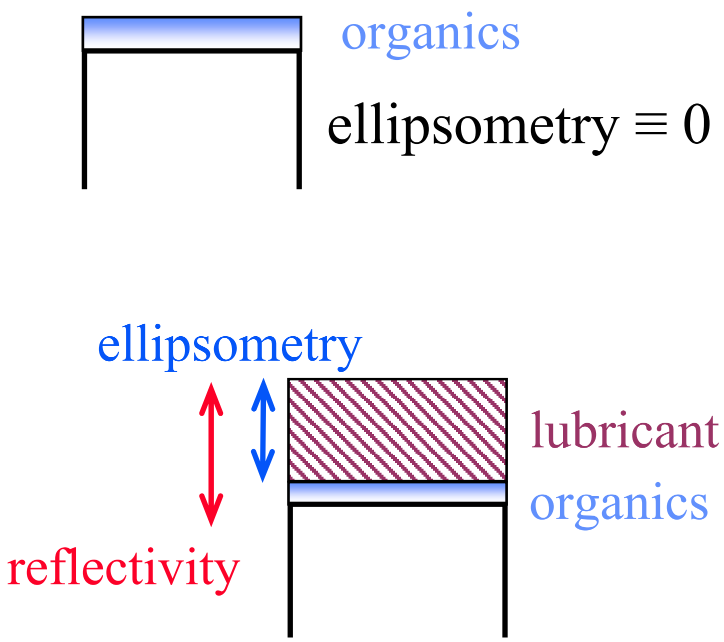
What can you learn?

- film thickness (accurate!)
- film density
- film roughness

• Toney, Mate, Pocker, IEEE Trans. Magn. **34**, 1774 (1998)
• Toney, Mate, Leach, Pocker, J. Coll. Inter. Sci. **225**, 119 (2000)

Lubricant Films: Thickness

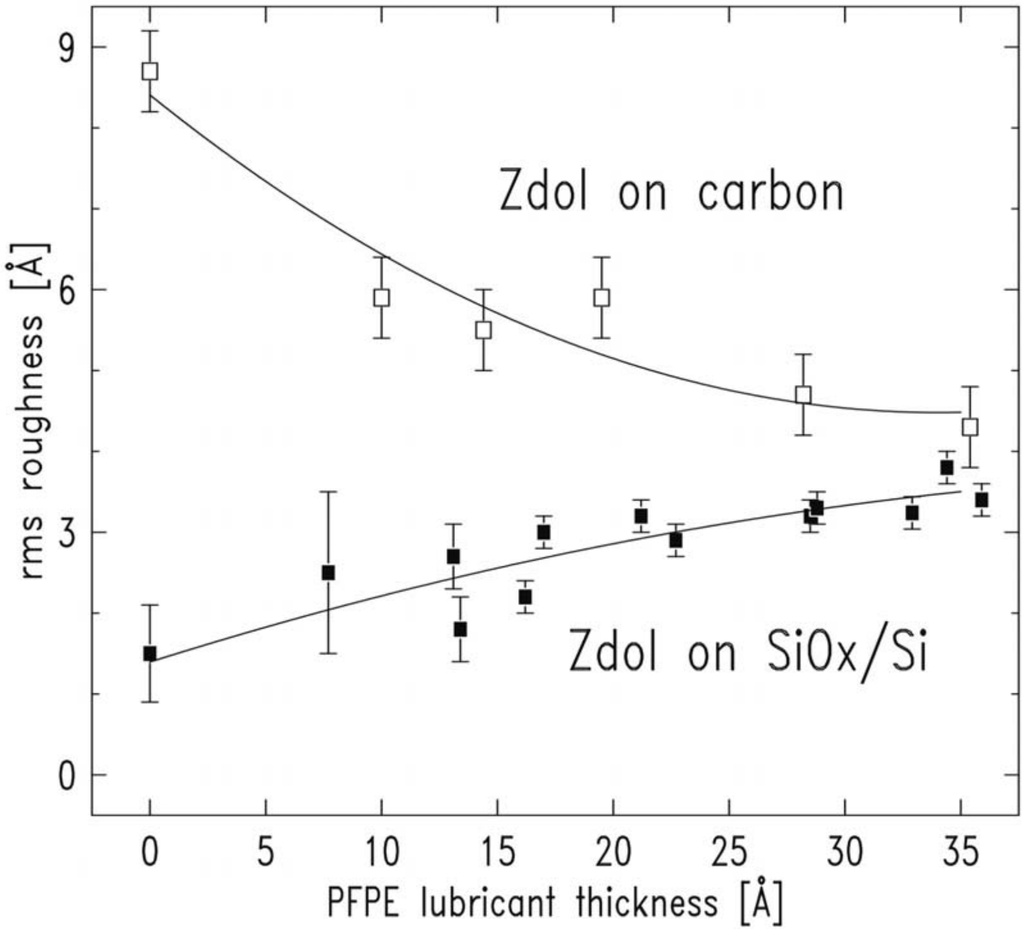




ellipsometry and ESCA can provide accurate thickness

- Toney, Mate, Pocker, IEEE Trans. Magn. **34**, 1774 (1998)
- Toney, Mate, Leach, Pocker, J. Coll. Inter. Sci. **225**, 119 (2000)

Lubricant Films: Roughness



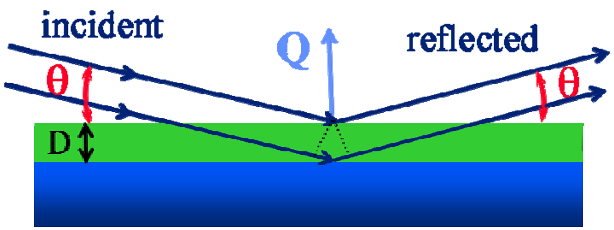
- lubricant smoothes carbon surface
- for thick films, roughness approaches limit due to molecular nature of lubricant molecule

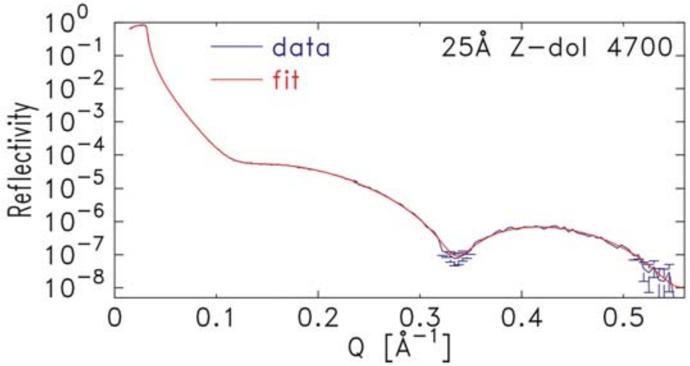
Toney, Mate, Leach, Appl. Phys Lett. **77**, 3296 (2000)

X-ray Reflectivity: Summary

What you can learn:

- ➢ accurate film thickness (Å resolution)
- ➢ film density
- ➢ film roughness
- ➢ surface morphology
- ➢ single and multiple layers

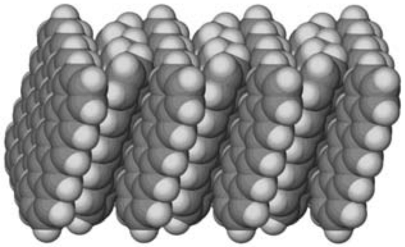


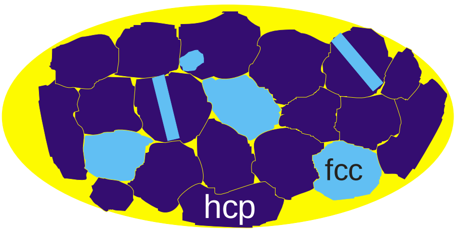


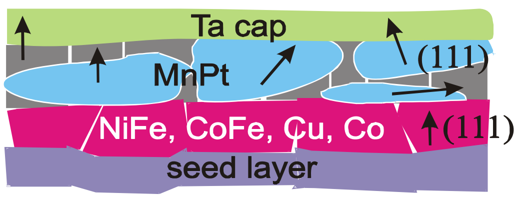
Summary

what do you want to learn:

- phase identification
- lattice parameters
- defects
- texture
- crystallite size
- atomic structure







What do you do?

- what beam line? (2-1, 7-2, 11-3)
    - area vs point detector; flux; energy
- what scans? ("where" in reciprocal space)