Magnetic X-rays versus Neutrons

- **what can we learn from scattering experiments when studying magnetism ?**

- **which probe to use to solve a given problem ? neutrons or synchrotron x-rays ?**

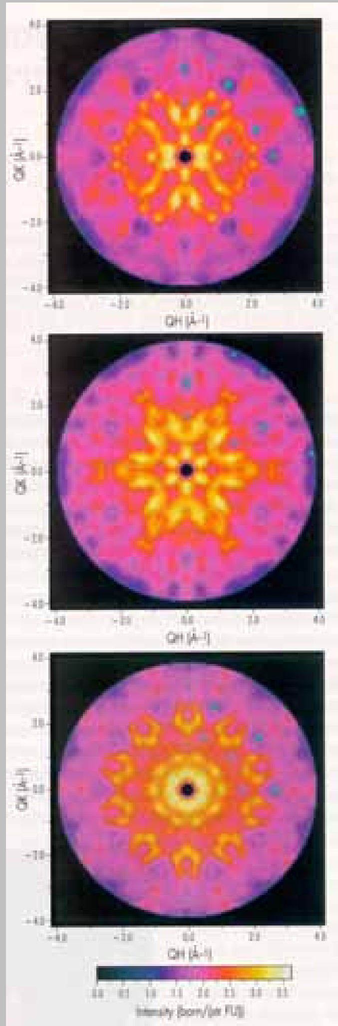
- **problems to be solved :**

  magnetic structures determinations

  observation of magnetic order

  origin of magnetic moments

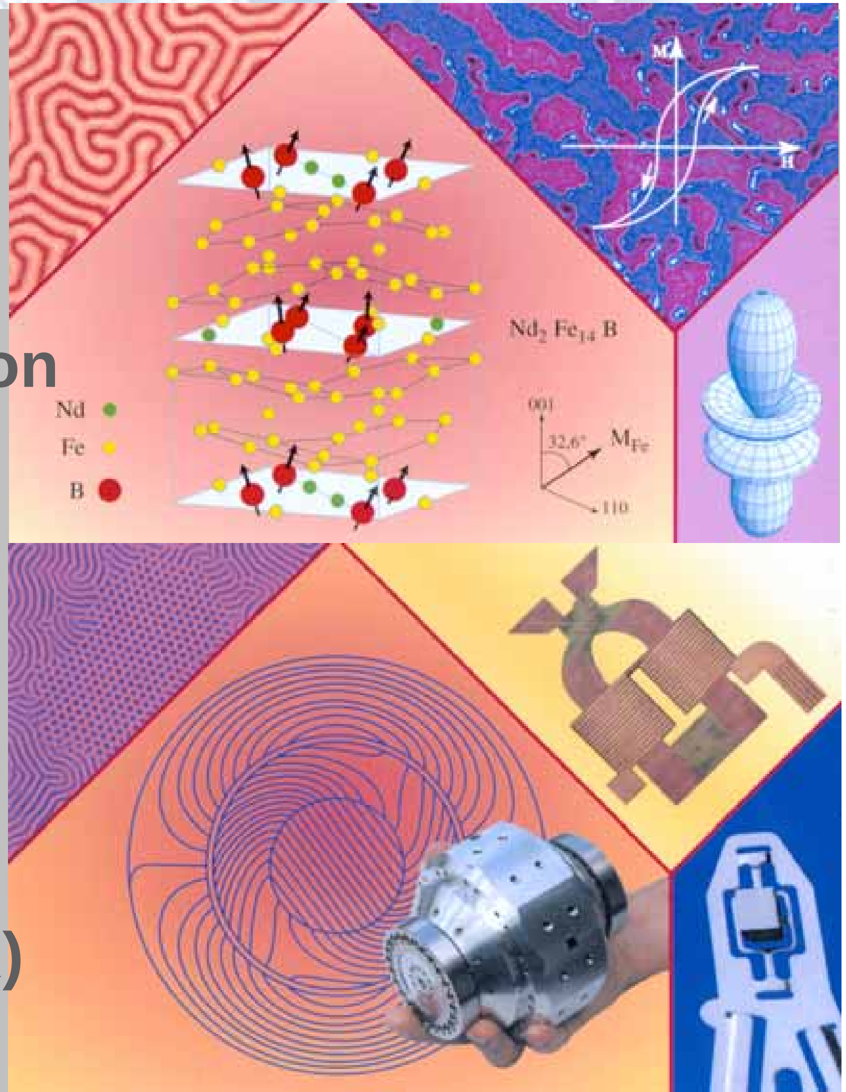
  complementary use n+x



T.J. Sato et al. 1998 ILL

Magnetic X-rays versus Neutrons

- **magnetism**
  - **basic and applied sciences**
- **several methods of investigation**
  - **bulk measurements**
    - **ordering temperature**
    - **type of ordering**
    - **anisotropy**
  - **microscopic measurements**
    - **scattering probes**
    - **local probes (muons, NMR)**
    - **microscopies**



PUG LLN team

Magnetic X-rays versus Neutrons

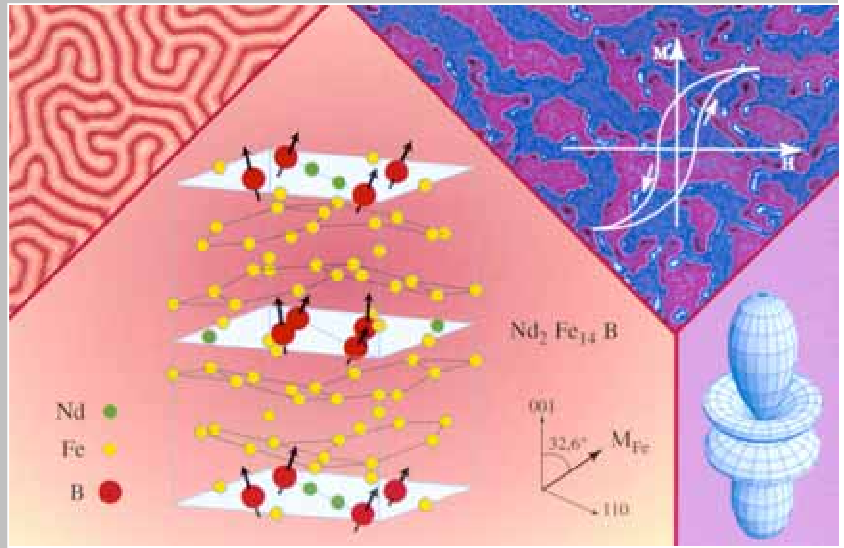
- **magnetic structures**

  arrangement of magnetic moments in solids

- **magnetic couplings :**

  magnetic excitations

  local anisotropy



- **origin of magnetic moments:**

  electronic shells

  form factors

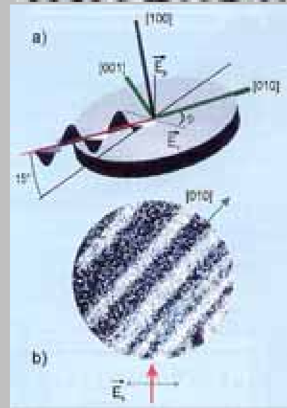
  origin of magnetisation *d*, *f*, *p*

Scattering methods

scattering versus real-space/real-time

- **real space images**

  comparison averaging / collecting data



- **real time (time-resolved) methods ?**

  relevant time scales

  electronic levels : < 10^{-18} sec

  electron-nuclei interactions : 10^{-15} sec

  fast chemical reactions : 10^{-12}-10^{-15} sec

  "magnetic" excitations : 10^{-12}-10^{-14} sec

  spin-flip : 10^{-12} sec

  domain rotations : around 10^{-9} sec

Time-resolved experiments

- ultra-fast time-resolved experiments : < 10^{-12} sec
  waiting for lasers!

- fast time-resolved experiments : 10^{-9}-10^{-10} sec
  stroboscopic experiments (pump-probe)
  white-beam x-rays experiments - imaging

- medium time-resolution : 10^{-3}-10^{-6} sec
  photon time-correlation - coherent x-rays

- slow dynamics - kinetics : 10^{-3} sec
  neutron & x-ray diffraction

Scattering methods

- **what is measured in scattering experiments?**

  correlations in space and time

  reciprocal space

  transformation into real space

- **what does it take to get a magnetic scattering probe?**

  magnetic sensitivity

  appropriate wavelength

  appropriate energy

  chemical and electronic sensitivity

- **neutrons, x-rays, polarised atoms, ...**

He* beams   M.Marynowsky et al. PRB 60, 6053 (1999)

Neutron scattering

- **neutron-nuclei interaction**

  Fermi length $b \approx 10^{-12}$ **cm**

- **magnetic interaction**

  spin 1/2

  total magnetic moment

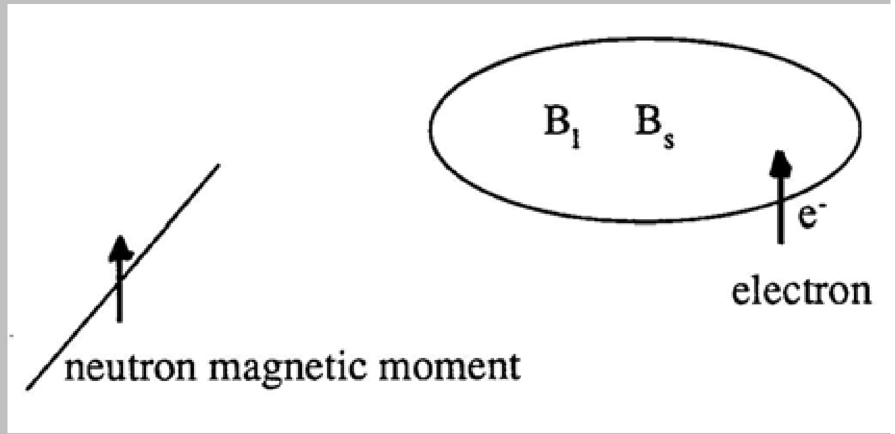
  $M \approx \langle L\rangle + 2\langle S\rangle$

  $g_n r_0 M/2 \approx 0.5\ 10^{-12}$ **cm**

  separation L/S difficult

  no chemical sensitivity

- **polarised neutrons (not for free!)**



$$a_m = \frac{g_n\ r_0}{2\mu_B}\left\{\hat{Q} \times \left(M(Q) \times \hat{Q}\right)\right\} \cdot \hat{\sigma}$$

Neutron scattering

- inelastic neutron scattering possible

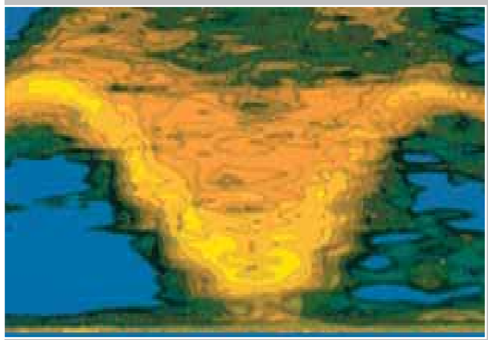
  incident energy : few meV up to 100 meV

  resolution 0.001-1 meV 10^{-9}-10^{-12} sec

  observation of collective modes (i.e. spin-waves)

  local excitations (crystal fields transitions)

  diffuse fluctuations



- intensity limited experiments flux at sample 10^8 n/cm^2/s

  sizeable sample volumes

  low spatial resolution - “large” beams

  restricted access to real-time mode

X-ray magnetic scattering

X-rays: weak relativistic interaction

Thomson scattering

electron charge

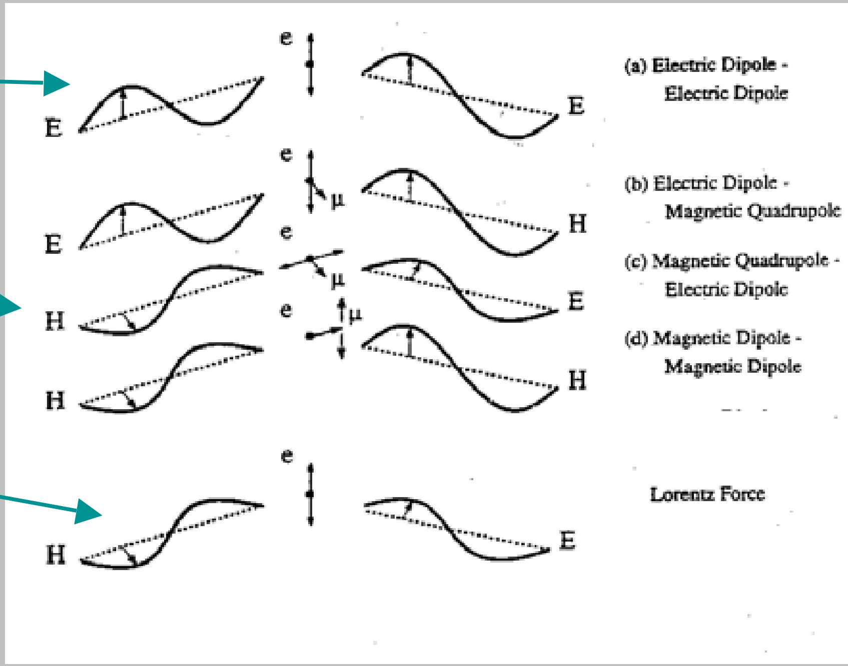
scattering amplitude $Zr_0 \approx 10^{-12}$cm

spin

(neutrons can see charges - Schwinger)

orbital momentum

X-ray polarisation effects



F. De Bergevin Acta Cryst. 1981)

weak scattering amplitude but flux at sample 10^{12} ph/mm²/s

and L/S separation

X-ray magnetic scattering

total scattering amplitude :

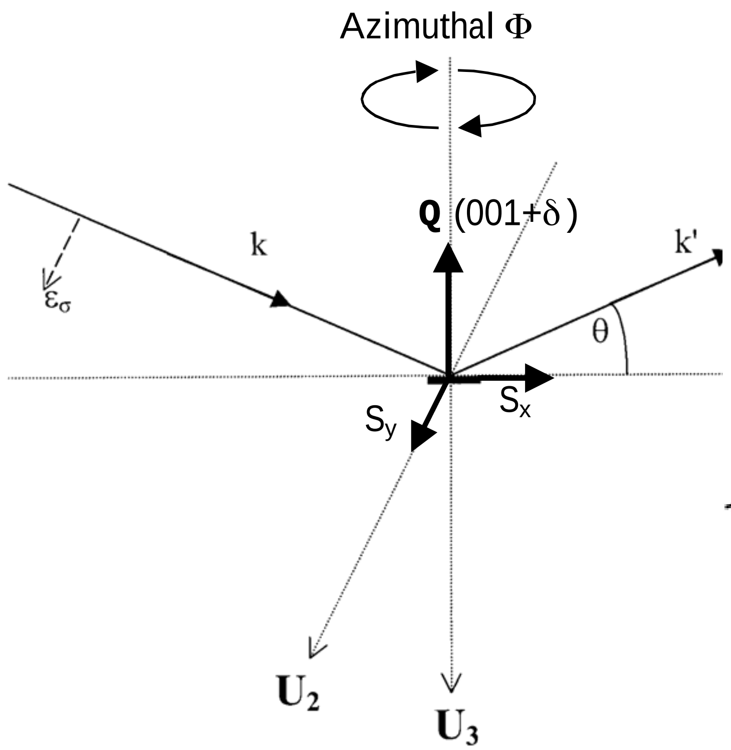
$$f_n(\vec{k},\vec{k}',\hbar\omega) = f_n^{\text{charge}}(\vec{Q}) + f_n^{\text{non-res}}(\vec{Q},\vec{k},\vec{k}') + f_n^{\text{res}}(\vec{k},\vec{k}',\hbar\omega) \qquad (1)$$

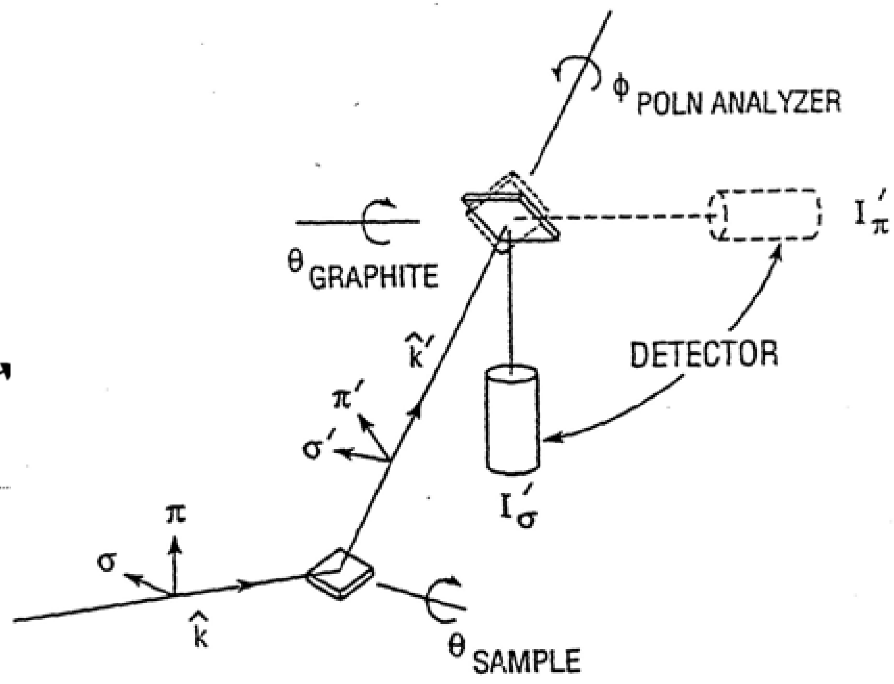
$$f_n^{\text{charge}}(\vec{Q}) = -\rho_n(\vec{Q})\,\hat{\varepsilon}.\hat{\varepsilon}' = -\rho_n(\vec{Q})\begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} \qquad (2)$$

$$f_n^{\text{non-res}}(\vec{Q},\vec{k},\vec{k}') = -i\,\frac{\hbar Q}{mc}\,2S \times$$

$$\begin{pmatrix} \cos\theta\,\hat{S}_2(Q) & \sin\theta\left[\cos\theta\,(\hat{S}_1(Q) - \frac{L_1(Q)}{S}) + \sin\theta\,\hat{S}_3(Q)\right] \\ \sin\theta\left[\cos\theta\,(\hat{S}_1(Q) + \frac{L_1(Q)}{S}) + \sin\theta\,\hat{S}_3(Q)\right] & \cos\theta\,(\hat{S}_2(Q) + 2\sin^2\theta\,\frac{L_2(Q)}{S}) \end{pmatrix}$$

Magnetic X-rays versus Neutrons





X-ray magnetic scattering

two main points

- **non-resonant magnetic intensities are weak and must be distinguished from charge scattering peaks (crystal structure)**

  intensity ratio around 10^{-6}

$$\frac{mc}{h} = 2.59\ \text{A}^{-1}$$

$$\frac{hQ}{mc} 2S \approx 10^{-3}$$

- **rotation of polarisation**

electrons are not at rest- they form bound states

any consequences?

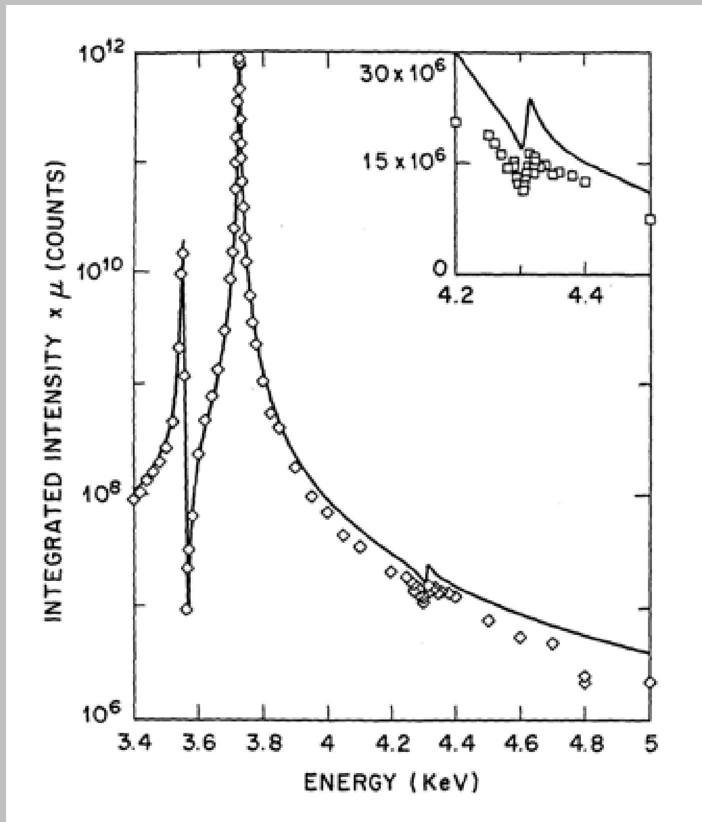
Resonant X-ray scattering

UAs simple antiferromagnetic Bragg peak

intensity as a function of photon energy

large resonant effects near absorption edges

enhanced intensities ~ 10^6 cts/s



McWhan et al. PRB 42, 6007 (1990)

Resonant X-ray scattering

resonant process : probe of excited states

scattering amplitude depends on the relative direction of the electrical field and the local quantization axis (magnetic moment, …)

atomic scattering factors are NOT spherical tensors

magnetic contrast : e$^-$ spin polarisation

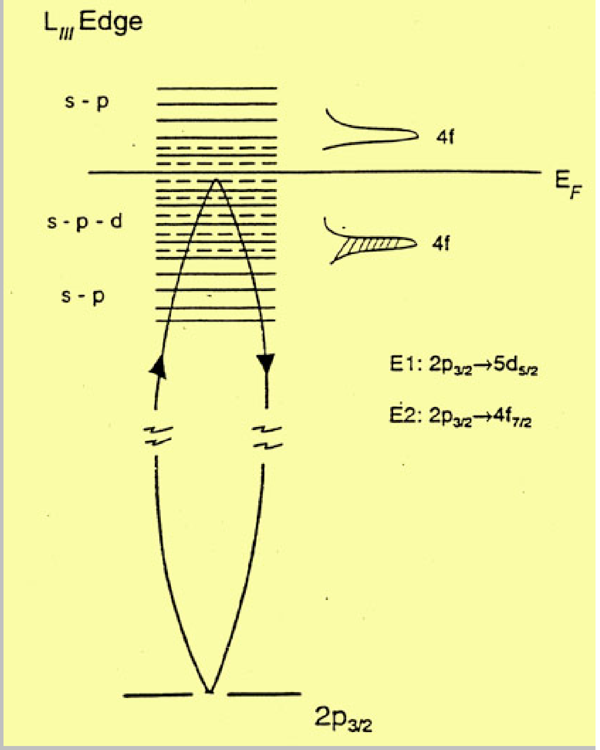
sensitivity to long range order

Bragg peaks in scattering

element selectivity

electronic shell selectivity

large intensities



J. Hannon et al. PRL (1988)

Resonant X-ray scattering

$$f_n^{\mathrm{res}}(k,k',\hbar\omega) = f_{E1}^{\mathrm{res}} + f_{E2}^{\mathrm{res}}$$

- **dipole resonances**

z : magnetization direction

$$f_{E1}^{res} = F^{(0)}\ \varepsilon'\cdot\varepsilon - i\ F^{(1)}\ (\varepsilon'\times\varepsilon)\cdot z + F^{(2)}\ (\varepsilon'\cdot z)(\varepsilon\cdot z)$$

$$= F^{(0)}\begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} - i\ F^{(1)}\begin{pmatrix} 0 & z_1\cos\theta + z_3\sin\theta \\ z_1\cos\theta - z_3\sin\theta & -z_2\sin 2\theta \end{pmatrix}$$

$$+ F^{(2)}\begin{pmatrix} z_2^2 & -z_2\left(z_1\sin\theta - z_3\cos\theta\right) \\ z_2\left(z_1\sin\theta + z_3\cos\theta\right) & z_1^2\sin^2\theta + z_3^2\cos^2\theta \end{pmatrix}$$

Resonant X-ray scattering

$$f_{E1}^{res} = F^{(0)}\ \varepsilon'\cdot\varepsilon - i\,F^{(1)}\,(\varepsilon'\times\varepsilon)\cdot z + F^{(2)}\,(\varepsilon'\cdot z)(\varepsilon\cdot z)$$

connection with absorption and spectroscopy - XMCD

Q=0 $\varepsilon' = \varepsilon$

linear polarisation **(real polarisation vectors)**

response quadratic in z

Cotton-Mouton effect

circular polarisation

response linear in z

circular dichroism **(see Faraday and MO Kerr effects)**

Resonant X-ray scattering

strength of resonance

order of transition   overlap integrals

spin-polarisation of intermediate states

elements	edge	transition	intermediate states	energy (keV)	wavelength (Å)	
3d	K	E1,E2	4p, 3d	7.112	1.743	$\approx 0.01\ r_0$
Fe	L3	E1	3d	0.707	17.54	$\approx 1\ r_0$
5d Pt	L3	E2	5d	11.65	1.072	
4f	L	E1,E2	5d, 4f	7.24	1.71	$\approx 0.1\ r_0$
Gd	M	E1	4f	1.22	10.2	$\approx 100\ r_0$
5f	L	E1,E2	6d, 5f	17.17	0.722	
U	M	E2	5f	3.74	3.32	$\approx 10\ r_0$

Magnetic scattering methods

neutrons	synchrotron x-rays
• spin 1/2 magnetic moment polarimetry large magnetic sensitivity	• high brilliance beams suited for surfaces and films
• mass moderate energy inelastic scattering	• chemical sensitivity • electronic shell sensitivity resonant process
• low brilliance beams low spatial resolution	• relatively weak magnetic sensitivity away from resonances • magnetic inelastic scattering not feasible

Choice of experimental methods

- **determination of magnetic structures/arrangements**

powder samples	neutrons
crystals	neutrons
surfaces	x-rays

- **origin of magnetic moments**

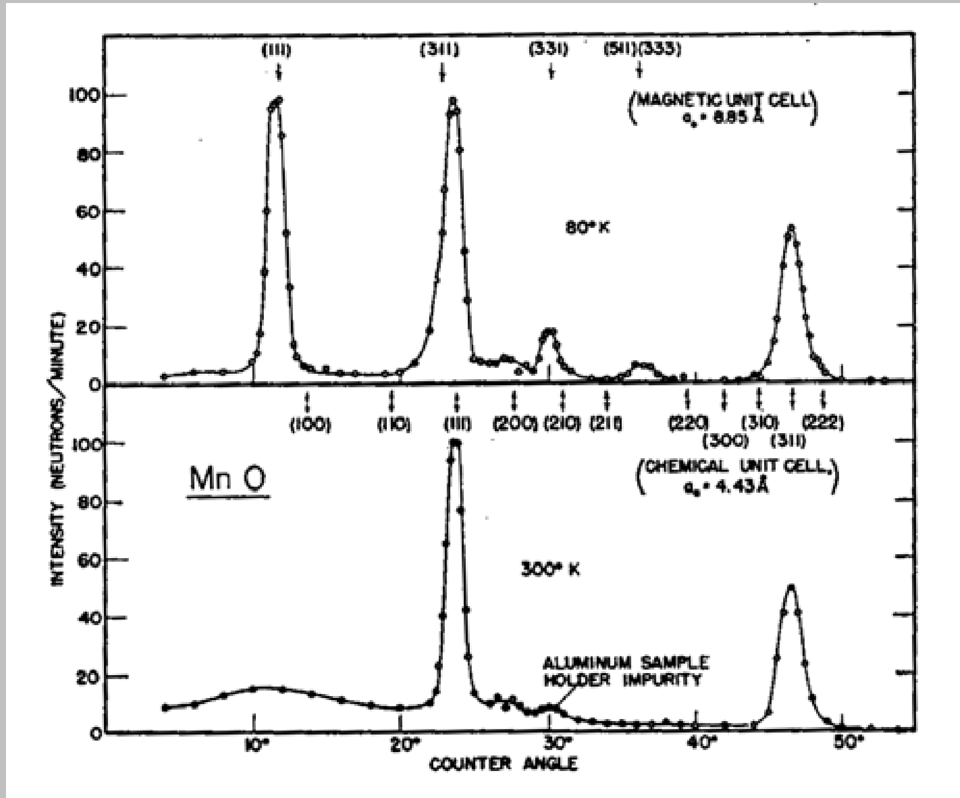
form factor/resonance	neutrons/x-rays
L/S	x-rays/ neutrons
hybridisation	x-rays

- **magnetic excitations** — neutrons

so far not possible with x-rays — not discussed here

Magnetic structure determinations

- **powder diffraction : Fourier components**
- **neutrons : unique tool for magnetic structure determination**
  - **powder diffraction**
  - **refinement on crystals**
- **necessary technique**
  - **used days and nights**
- **progress in instrumentation**
  - **faster acquisition**
  - **smaller sample volumes**



C.G. Shull at al PR 76, 1256 (1949)

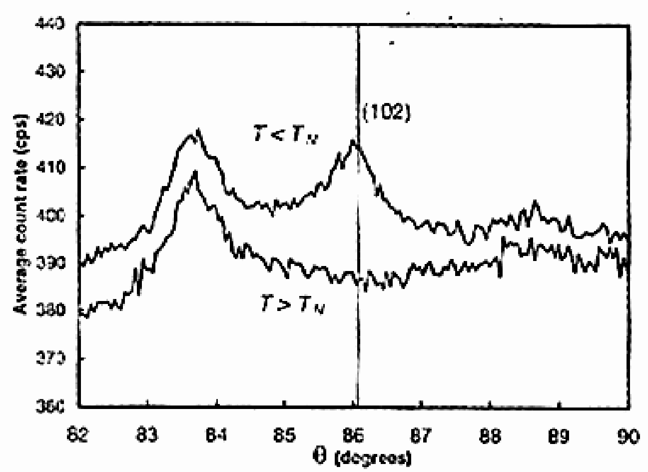
Magnetic structure determinations

only example from synchrotron

UO_2 powder

experiments at Daresbury

U M_4 edge



S.P. Collins et al. J. Phys. Cond. 7, L223 (1995)

Magnetic structure determinations

- **single crystals - once Fourier components are known!**

  scattering work with x-rays requires good single crystals

  neutrons are easier to handle

  low absorption and many more reflections

  exceptions Gd, B, GdB6 : M. Amara PRB 72, 64447 (2005)

  resonant x-ray magnetic scattering

  low energy photons - absorption

- **sample environment**

  cryostats magnets high pressure

  transmission / brilliance

- **heat load problems with x-rays**

Magnetic structure determinations

special case : resolution effects

magnetic diffuse scattering from

single quasicrystal

Zn_6-Mg_3-Ho_1 icosahedral

polarised neutrons

strong peaks near absent crystal Bragg peaks

antiferromagnetic correlations

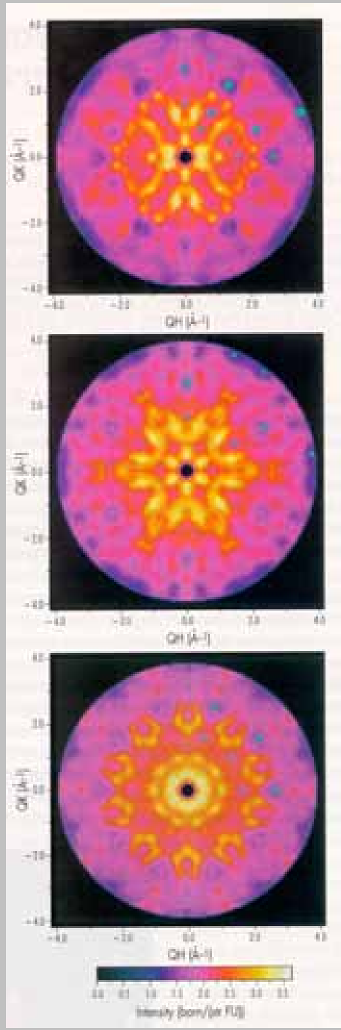
broad distribution in Q-space

neutron resolution in Q-space is adapted

2-fold

3-fold

5-fold



T.J. Sato et al. 1998 ILL

Magnetic structure determinations

special case : resolution effects

comparison neutrons/x-rays

scattering experiments

reciprocal space

magnetic ordering of Pr sites

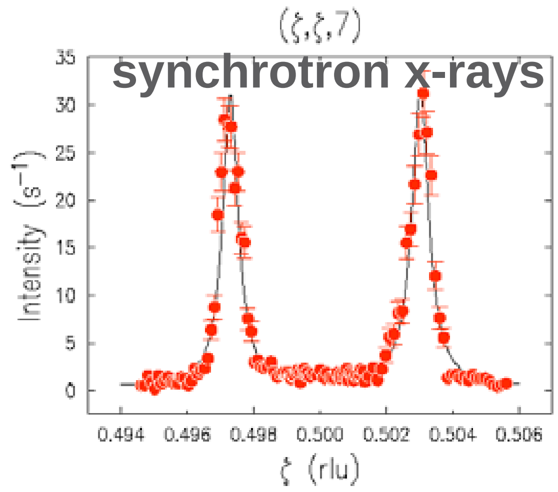
$PrBa_2Cu_3O_{7-\delta}$

IC modulation

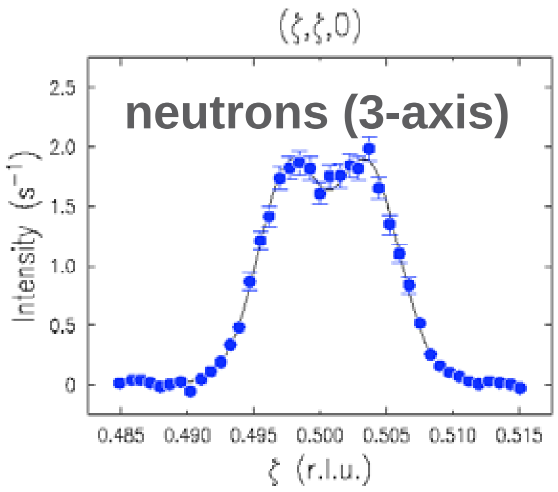
well ordered, ξ ≥ 900

long period, 600 Å

count rates !



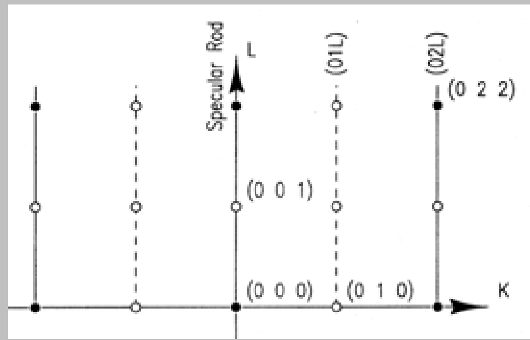
J.P. Hill et al. PRB 1999



Magnetism at surfaces

surfaces

x-rays well suited



resonant magnetic scattering

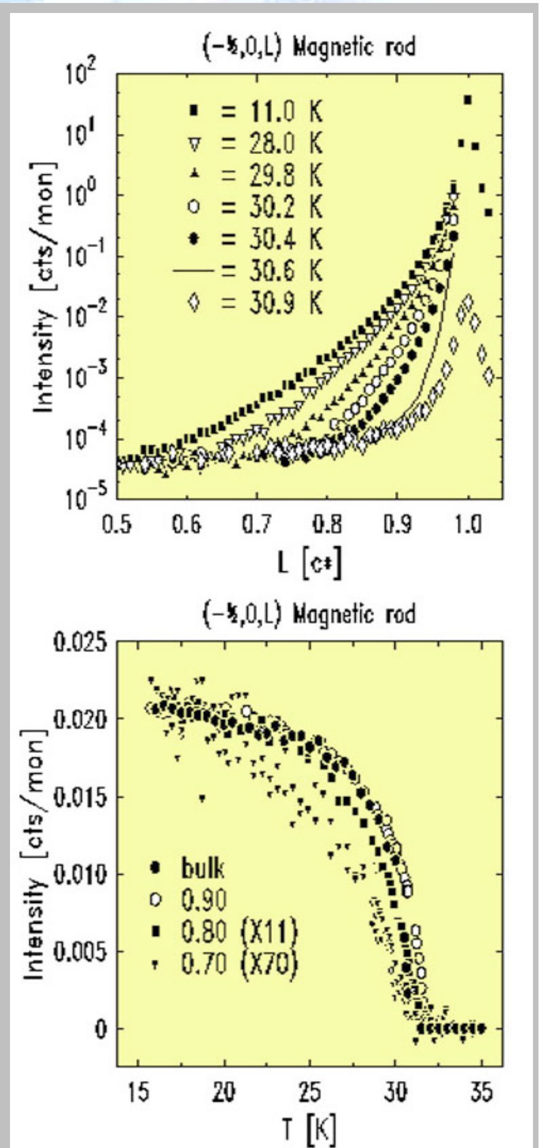
at low photon energy

absorption length is short (500-5000Å)

UO_2 U M-edge

observation of magnetic order at surfaces

phase transitions



G. Watson et al. 1999

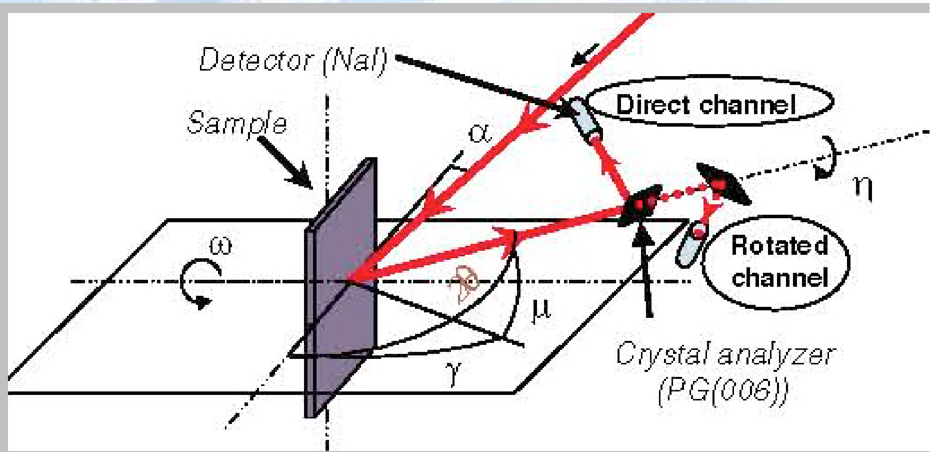
Magnetism at surfaces

NiO

non-resonant scattering

grazing incidence scattering

A. Barbier et al. PRL 93, 25708 (2004)

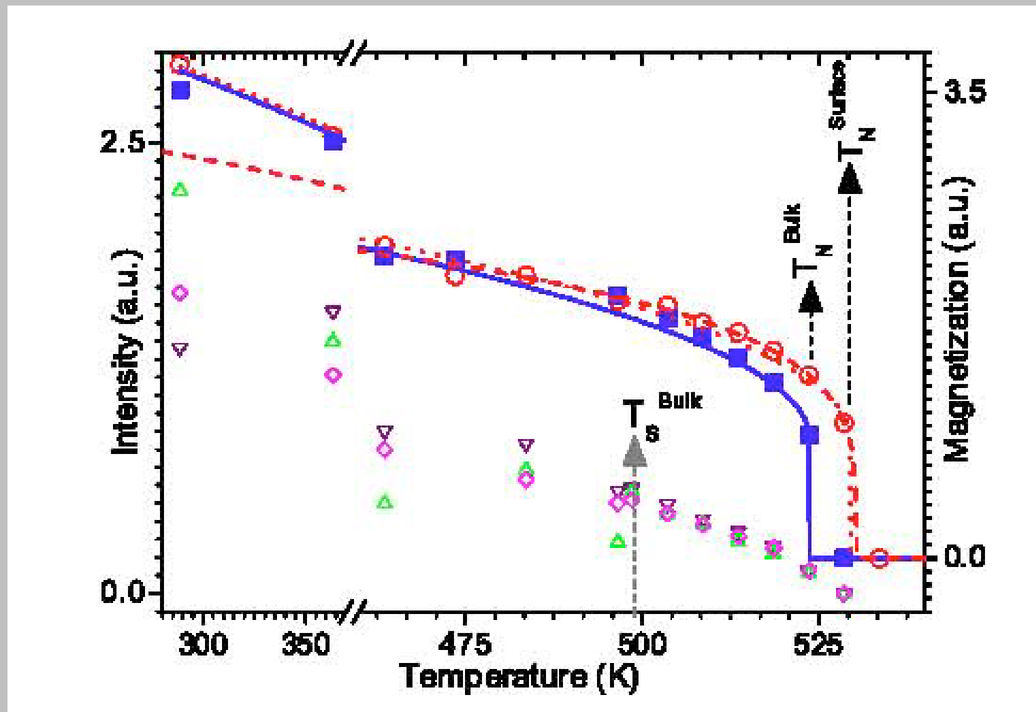


depth sensitive

surface ordering

well-defined 2D order

Melting of S-domains



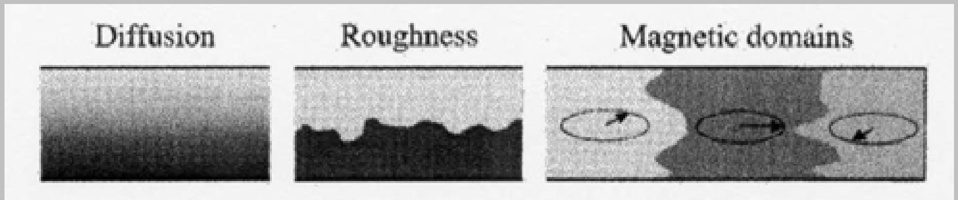
Magnetism near surfaces

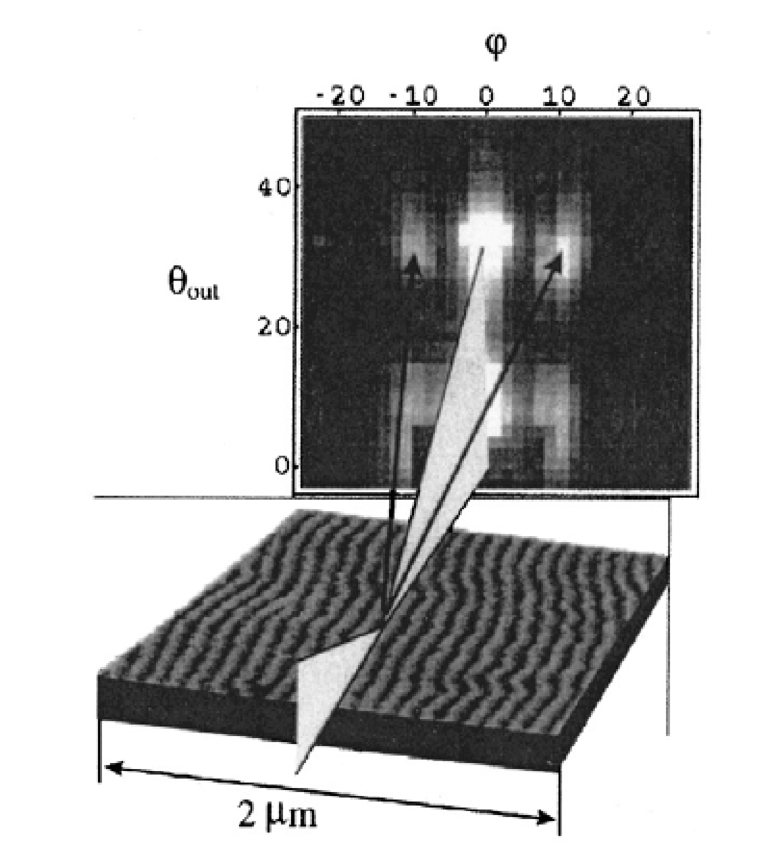
real interfaces are not sharp

effects of underlying “skin”

off-specular scattering

neutrons and x-rays



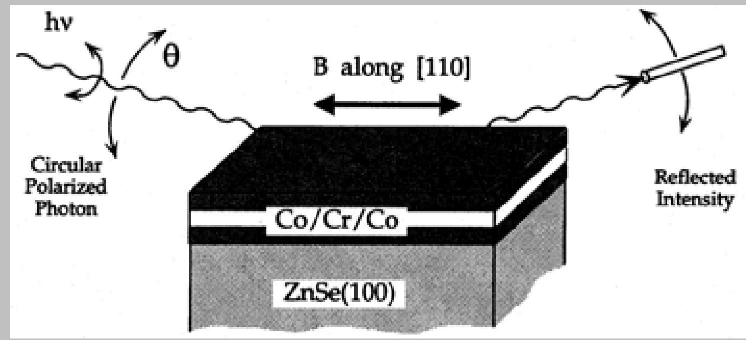


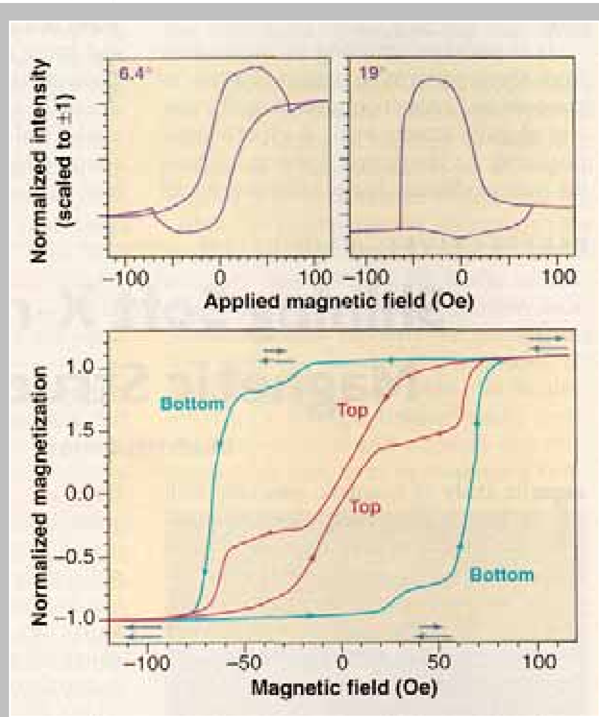
Magnetism near surfaces

- thin films and devices
  depth sensitivity reflectivity
  domain correlations
  RXMS specular scattering
  circular polarisation
- trilayer Co(35Å)/Cr(35Å)/Co(50Å)

- element sensitivity
  Co L_3 edge

  angular dependence
  coupling between layers (Cr)





U. Hillebrecht et al. Science 284, 2099 (1999)

Magnetism near surfaces

- **lateral effects**
- **off-specular signal**

polarised neutron reflectivity

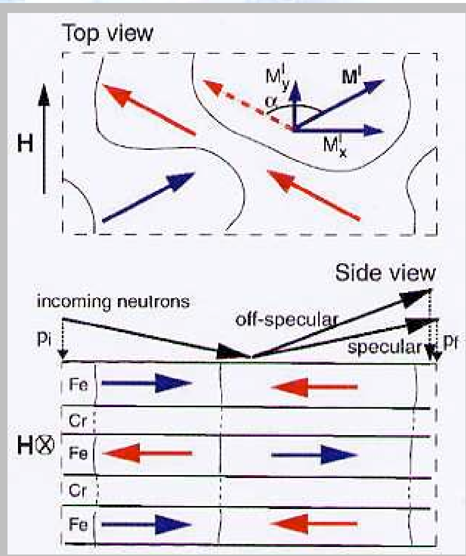
multilayers [Cr(9Å)Fe(58Å)]

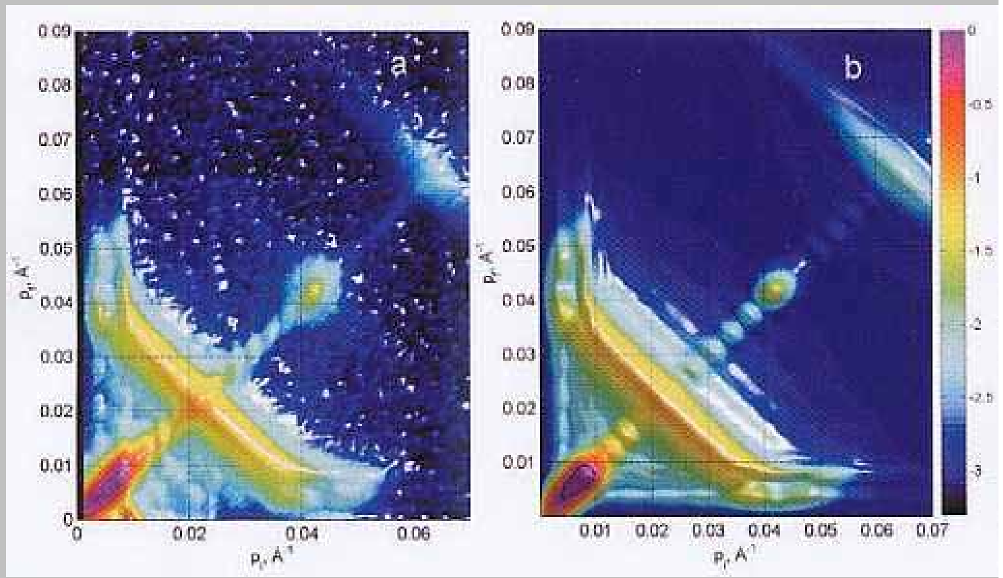
exchange bias

disorder of antiferromagnetic objects

columns through layers

average size 3000Å





H.J. Lauter et al. Appl.Phys.Lett.
74, S1557 (2002)

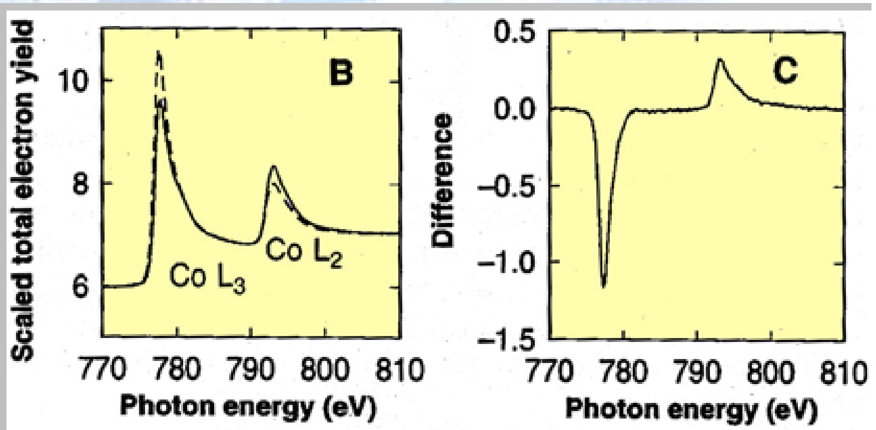
Magnetic arrangements imaging

XMCD

soft x-ray range (low energy)

circular x-ray polarisation

element sensitivity



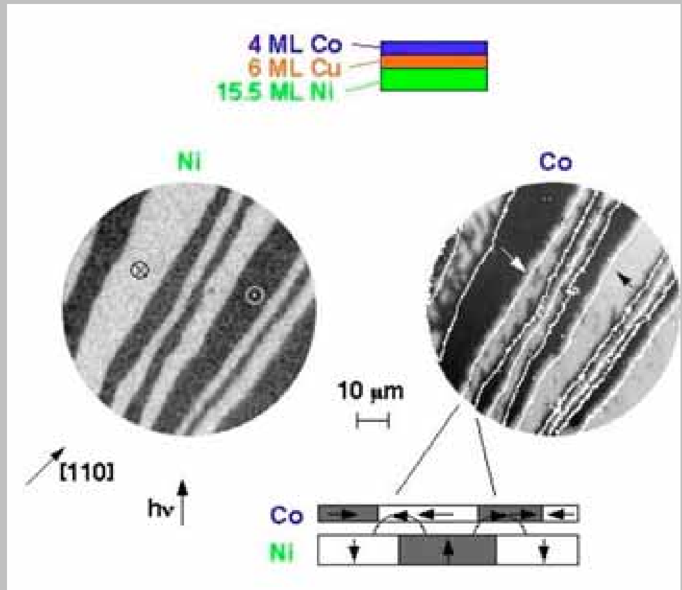
XMCD & PhotoElectron Emission Microscopy PEEM

imaging of magnetic domain/walls

Co/Cu/Ni trilayer

coupling mechanism through domain wall stray fields

importance for thin film technology



W. Kuch et al. PRB 67, 214403 (2003)

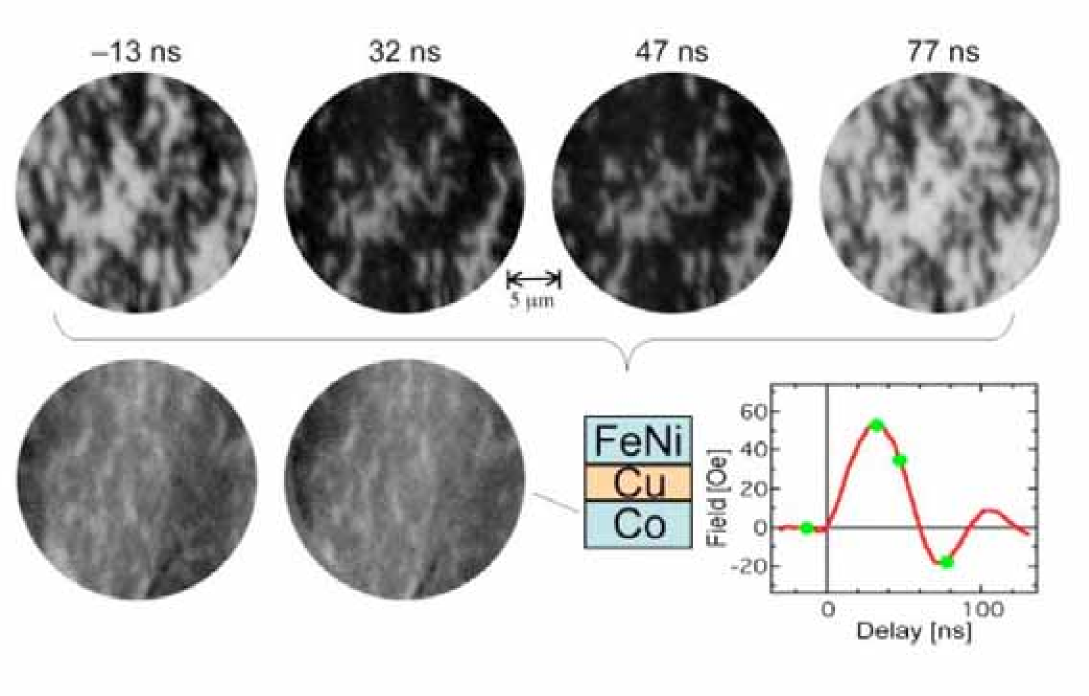
Magnetic arrangements imaging

imaging in real-time

D. Neeb et al. J.Phys.:Cond. Matter 17 S1381 (2005)

pump and probe

synchronized of magnetic field pulses



FeNi/Cu/Co trilayer

in-plan field pulses

soft layer domains change

hard layer domains unchanged

W. Kuch et al. Applied Phys. Lett., 85, 440 (2004)

Magnetic structure determinations

- structure determination
  - powder diffraction neutrons
    - Fourier components
    - moments directions
- details in magnetic structures
  - resolution effects neutrons/x-rays
  - absorption
- imaging x-rays
- surfaces x-rays
- “skins” neutrons and x-rays

Origin of magnetic moments

- which electrons carry magnetic moments ?
  - which atoms ?
  - which electronic bands ? symmetry ?

- structure factors : where scattering arises from!
  but model-dependent
- neutron scattering : magnetic form factors
  spin density maps
- x-ray scattering : resonant scattering
  chemical + electronic selectivity
  non-resonant scattering
  L/S

Origin of magnetic moments

- **magnetic form factors**

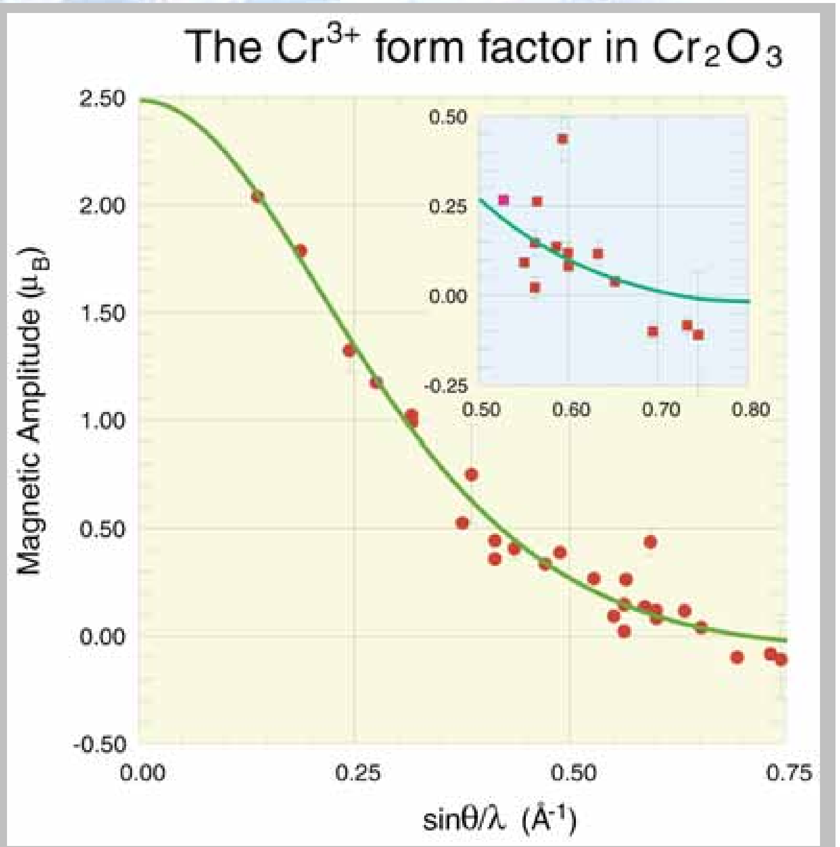
- **neutrons : the perfect tool**

  spherical polarimetry

  ^{3}He neutron spin filter

- **flipping ratio measurements**

$$R = \left(\frac{N+M}{N-M}\right)^2 \approx 1 + 4\frac{|NM|}{|N|^2}$$

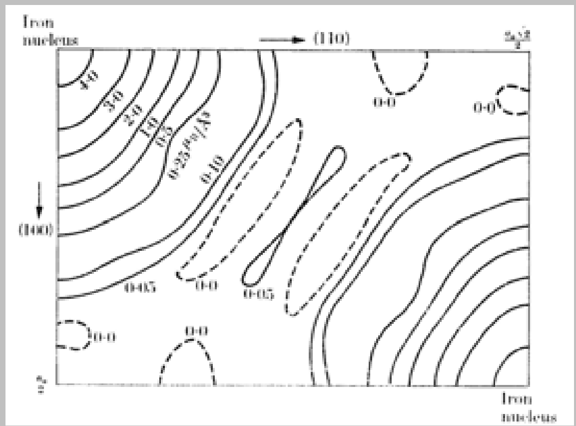


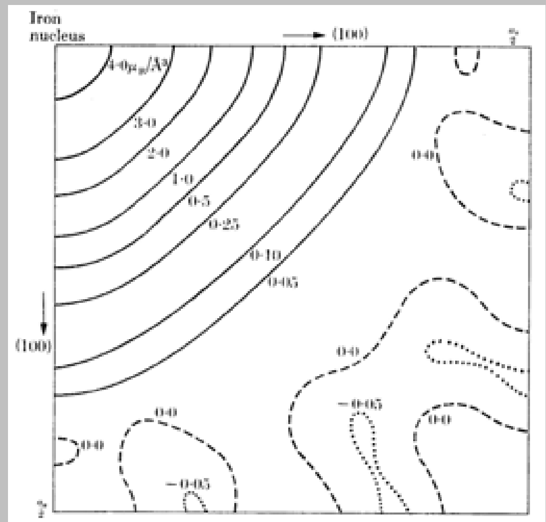
J. Brown et al. 1999

- **ferromagnets, saturated paramagnets**
- **antiferromagnets**

Origin of magnetic moments

- **spin density maps**





Iron

C. Shull et al. J. Phys Soc. Jpn 17, BIII, 1 (1962)

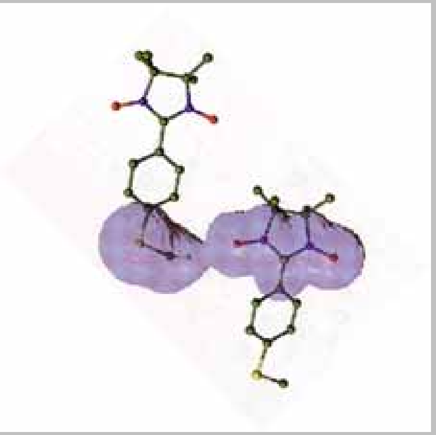
Origin of magnetic moments

- organic materials

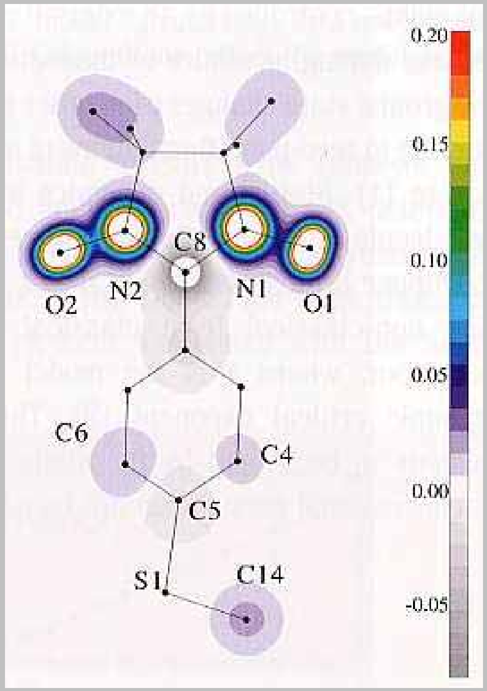
  molecular magnets

  high Tc ?

  couplings driven by radical and crystal packing



Nitrophenyl nitronyl nitroxide Tc=0.6K



S. Pillet et al. (2001)

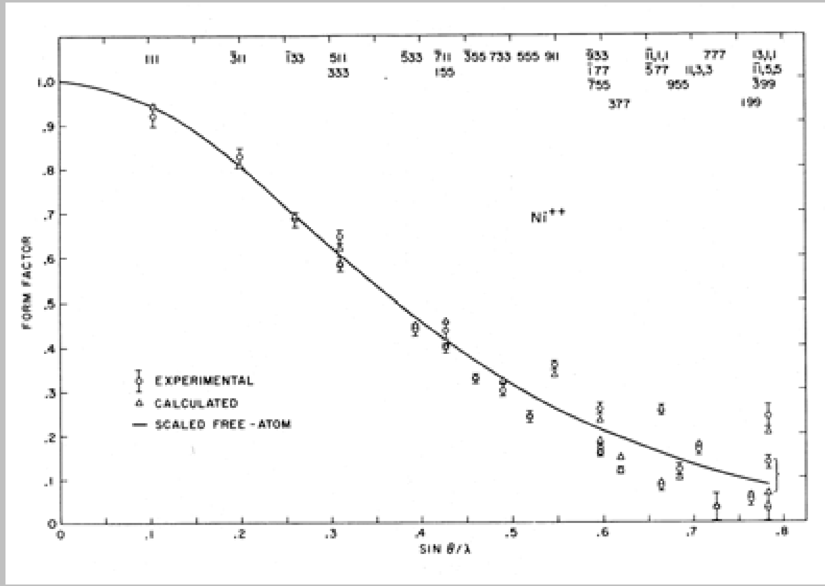
Origin of magnetic moments

- **L/S separation**

  magnetic form factor NiO

  H.A. Alperin PRL 6, 55 (1961)

  scaling factor in Q space



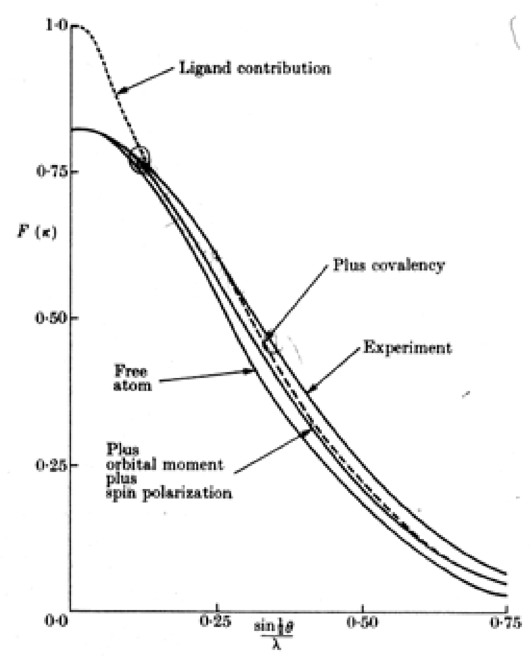


FIG. 7.27. Experimental and theoretical form factors for NiO.

inclusion of covalence and ligands

orbital momentum contribution ?

W. Marshall and S.W. Lovesey

Theory Thermal Neutron scattering

X-RAY SCATTERING

total scattering amplitude :

$$f_n(\vec{k},\vec{k}',\hbar\omega) = f_n^{\text{charge}}(\vec{Q}) + f_n^{\text{non-res}}(\vec{Q},\vec{k},\vec{k}') + \cancel{f_n^{\text{res}}(\vec{k},\vec{k}',\hbar\omega)} \qquad (1)$$

$$f_n^{\text{charge}}(\vec{Q}) = -\rho_n(\vec{Q})\,\hat{\varepsilon}.\hat{\varepsilon}' = -\rho_n(\vec{Q})\begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} \qquad (2)$$

$$f_n^{\text{non-res}}(\vec{Q},\vec{k},\vec{k}') = -i\,\frac{\hbar Q}{mc}\,2S \times$$

$$\begin{pmatrix} \cos\theta\;\hat{S}_2(Q) & \sin\theta\left[\cos\theta\,(\hat{S}_1(Q) - \frac{L_1(Q)}{S}) + \sin\theta\;\hat{S}_3(Q)\right] \\ \sin\theta\left[\cos\theta\,(\hat{S}_1(Q) + \frac{L_1(Q)}{S}) + \sin\theta\;\hat{S}_3(Q)\right] & \cos\theta\,(\hat{S}_2(Q) + 2\sin^2\theta\,\frac{L_2(Q)}{S}) \end{pmatrix}$$

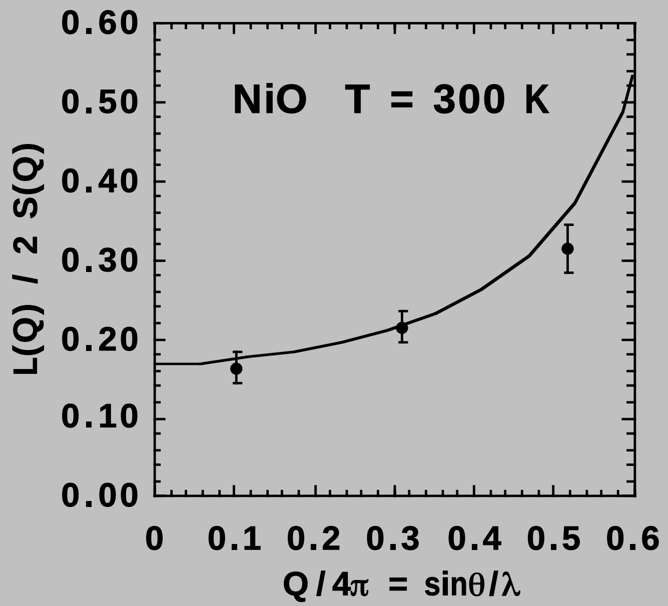
Origin of magnetic moments

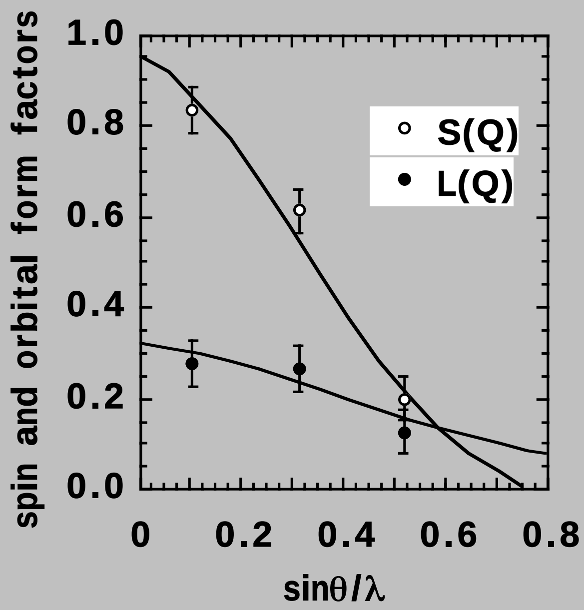
X-rays : no modelling of data

non-resonant x-ray scattering separation L/S

measure of orbital moment in NiO

V. Fernandez et al. PRB 57, 7870 (1998)

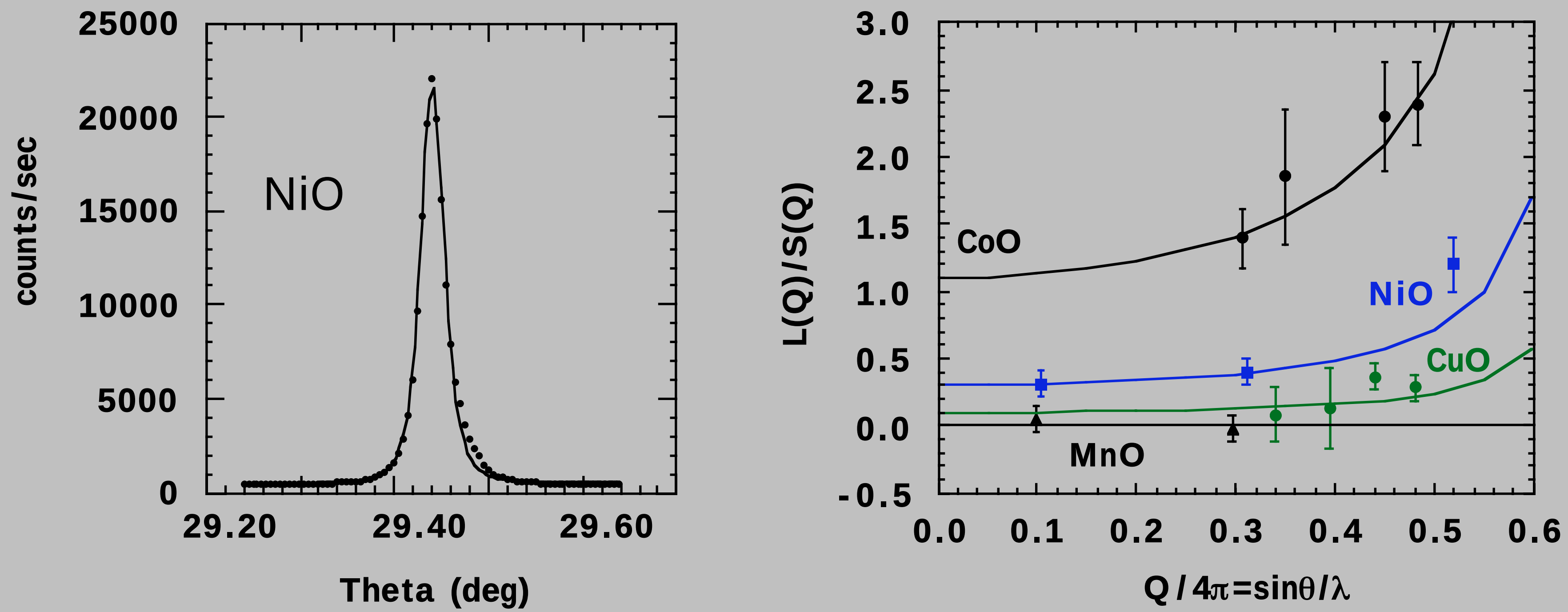




similar results on $NiFe_2O_4$ using XMCD   **G. van der Laan et al. PRB 1999**

Origin of magnetic moments

other oxides

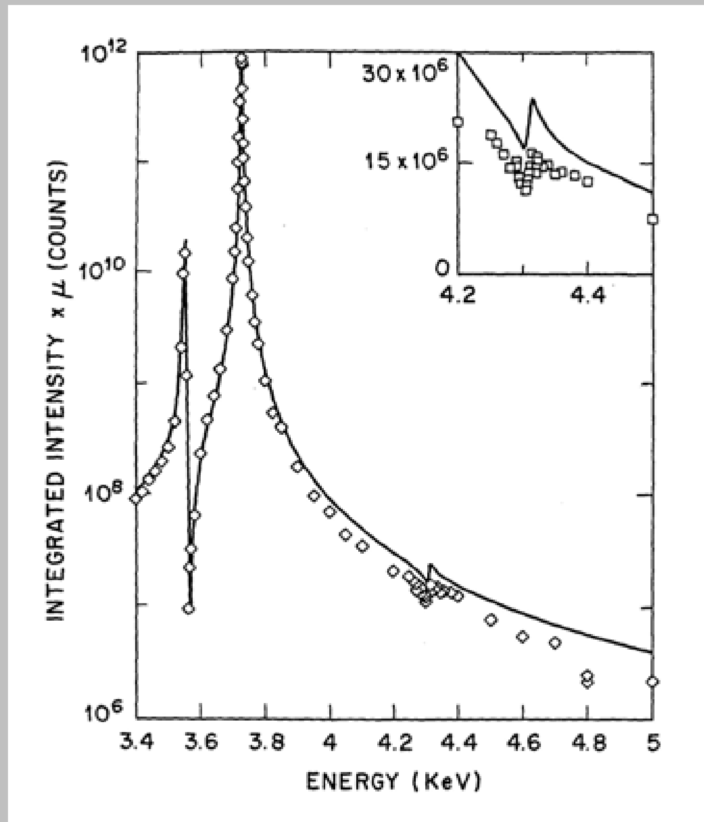


W. Neubeck et al. J.Phys.Chem.Solids 62, 2173 (2000)

large incident flux from synchrotron sources

Origin of magnetic moments

resonant effects have made x-ray scattering experiments popular



large resonant enhancements

in particular at M edges

D.B. McWhan et al. PRB 42, 6007 (1990)

Resonant x-ray magnetic scattering

- **important edges**

			typical edges		
elements	edge	transition	intermediate states	energy (keV)	wavelength (Å)
3d	K	E1,E2	4p, 3d	7.112	1.743
Fe	L3	E1	3d	0.707	17.54
5d Pt	L3	E2	5d	11.65	1.072
4f	L	E1,E2	5d. 4f	7.24	1.71
Gd	M	E1	4f	1.22	10.2
5f	L	E1,E2	6d, 5f	17.17	0.722
U	M	E2	5f	3.74	3.32

E1 $\Delta l = 1$

E2 $\Delta l = 2$

- **wide energy range**
- **limitations** **Bragg cut-off**

  absorption

  strength of the resonance

  E1 transition to the interesting e- levels

Resonant x-ray magnetic scattering

- **across series**

		3d series		
element	K edge (eV)	L1 edge (eV)	L2 edge (eV)	L3 edge (eV)
Sc	4492	498	403	399
Ti	4966	561	461	454
V	5465	623	520	512
Cr	5989	696	584	574
Mn	6539	769	650	639
Fe	7112	845	720	707
Co	7709	925	793	778
Ni	8333	1008	870	853
Cu	8979	1097	952	932
Zn	9659	1196	1045	1022

- **valence state**

TmSe **Tm ions in 2 different configurations Tm^{2+} and Tm^{3+}**

Origin of magnetic moments

- **chemical selectivity**

  absorption edges

  alloys, compounds, intermetallics

  heteromagnetic multilayers, …

$U_{1-x}Np_xRu_2Si_2$

  antiferromagnetic system

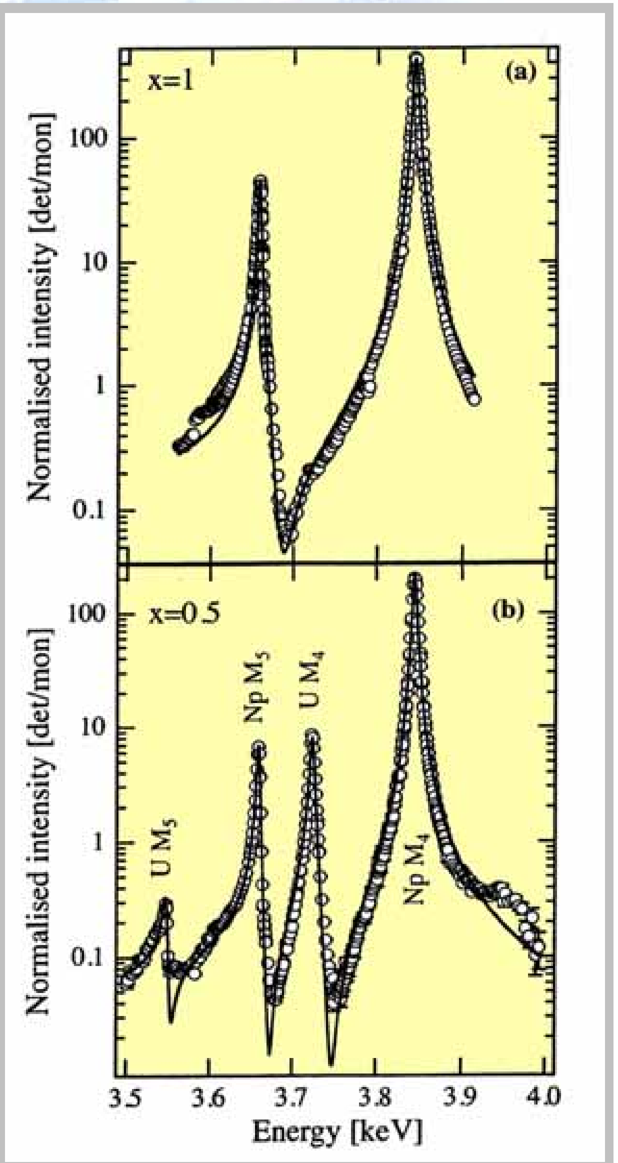
  incommensurate structure at x=0

  (neutron scattering)

  magnetic intensity at (00 4+q)

separation of U and Np response

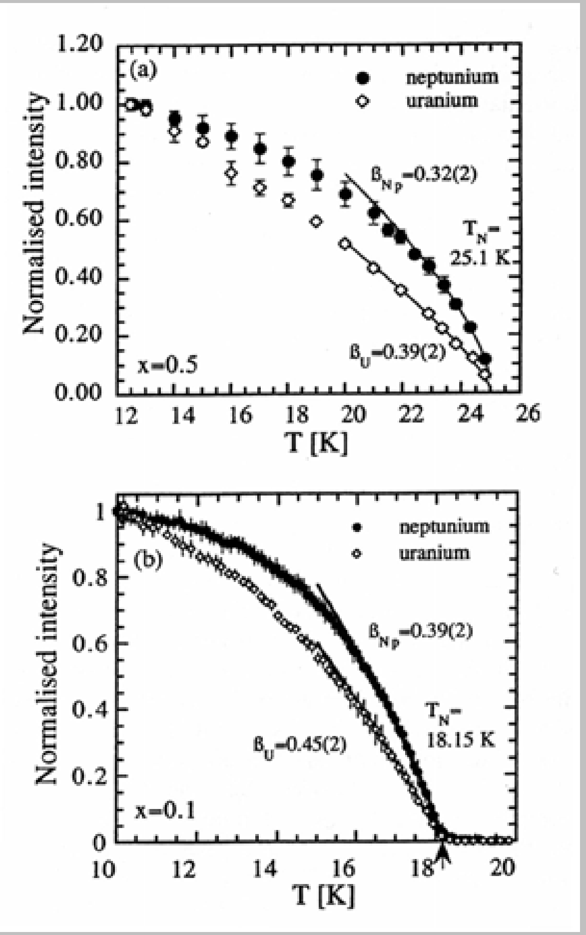
E. Lidström et al. PRB 61, 1375 (2000)



Origin of magnetic moments

element specific studies

Uranium is driven by Neptunium



- **studies : multilayers**

  C.T. Chen at al. PRB 1993

  Y.U. Idzerda PRB 1993 V. Chakarian et al. PRB 1996

  N. Ishimatsu et al. PRB 1999 Fe/Gd

- **induced moment on V in V/Fe ML**

  M. Sacchi et al. PRB 1999

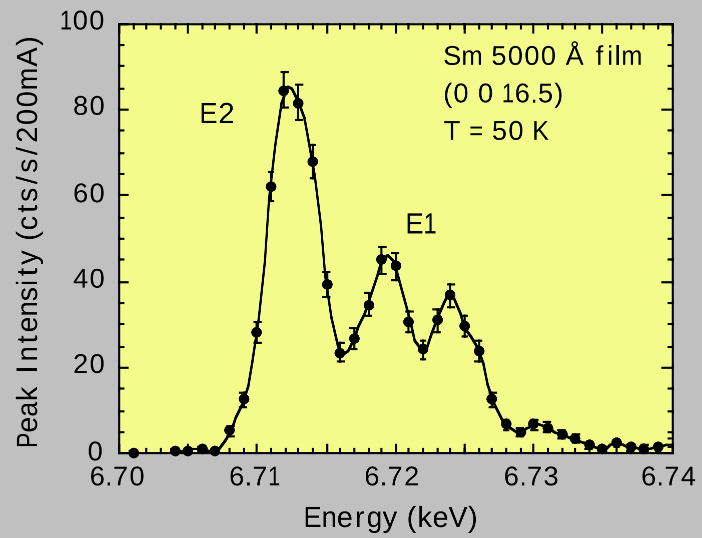
Origin of magnetic moments

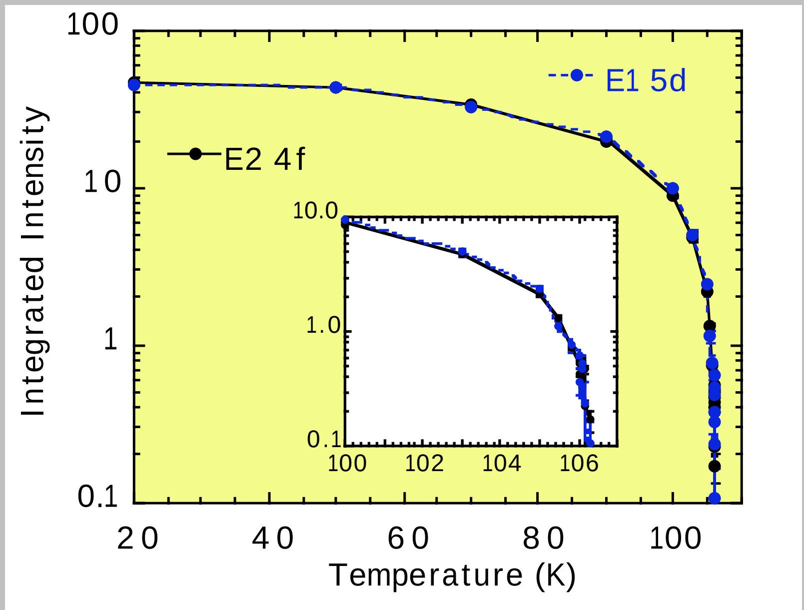
- **Samarium**

RXMS **E1 and E2**

5d and 4f

temperature dependence





A. Stunault at al. JMMM 226, 1116 (2001)

Scattering experiments

scattering probes have characteristic time scales

energy resolution !

- x-rays $\Delta E \approx 1$ eV

  fast fluctuations 10^{-15} sec

- neutrons $\Delta E \approx 0.001\text{-}0.2$ meV

  slow fluctuations $10^{-8}\text{-}10^{-12}$sec

- do we measure the same quantities ?

  itinerant systems/insulators

Magnetic X-rays versus Neutrons

NEUTRONS	SYNCHROTRON LIGHT
magnetic structure determination	imaging and time-dependence
polycrystals	devices
magnetisation densities	chemical selectivity
	electronic selectivity
magnetic excitations	surfaces
local collective	microcrystals (resonance)

Magnetic X-rays versus Neutrons

NEUTRONS FOR SCIENCE

- neutrons are magnetic
- x-rays are electronic

- well defined domains of excellence for neutrons and x-rays

  magnetic structure determinations/ imaging nano-objects

  excitations / origin of moments

- x-ray methods are relatively recent and will develop
- gains in neutron optics are expected

  new neutron sources are being prepared

  new x-ray sources are dreamed of

- one probe + another probe makes more than two probes

Magnetic X-rays versus Neutrons

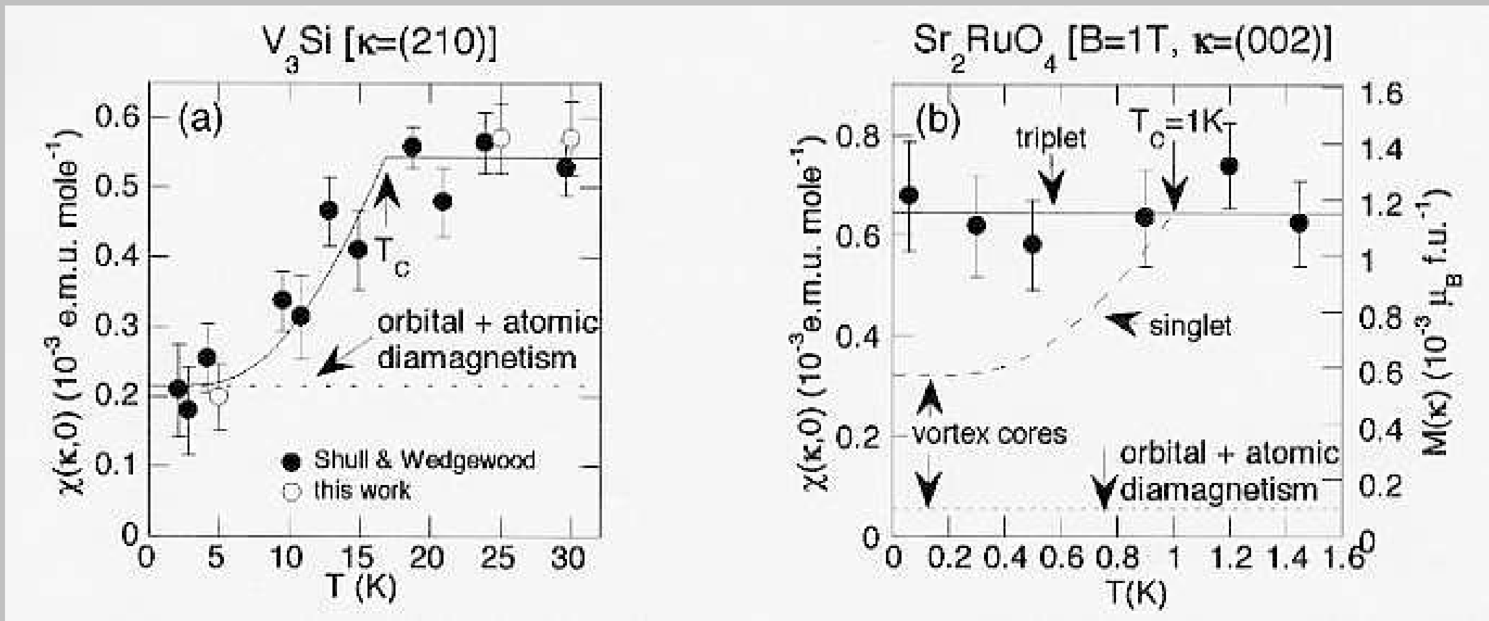
NEUTRONS FOR SCIENCE

ORIGIN OF MAGNETIC MOMENTS

- **are neutrons sensitive to electronic properties ?**

magnetic form factor

Fourier transform of magnetic electrons



J. Brown et al. 2002

Origin of magnetic moments

- important for magnet technology

- important for chemistry

- x-rays could be used at O, N absorption edges
  but wavelength is too long for diffraction

  only Q=0 experiments (absorption, dichroism, ..)
  no spatial information