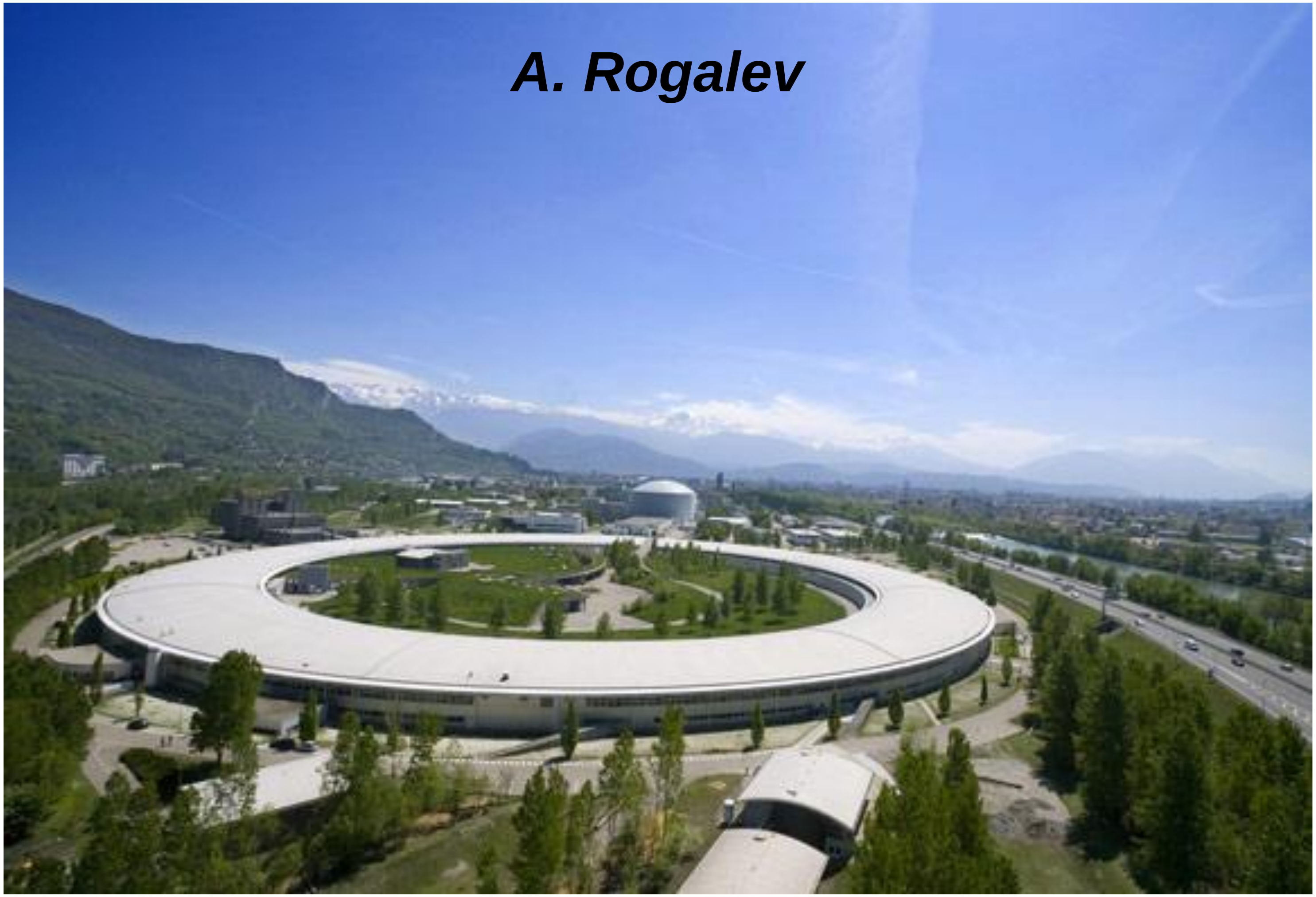
ESRF | The European Synchrotron

Magnetism and X-ray dichroism



A. Rogalev

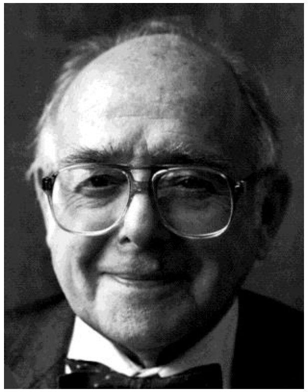
OUTLINE

- Introduction to X-ray Magnetic Circular Dichroism
- Experimental aspects: ID12 beamline at the ESRF
- Selected Results
  - ☐ Single molecular magnets
  - ☐ Orbital magnetic moment in actinides
- Conclusions

Nobel Prize in Physics 1994: B. N. Brockhouse and C. G. Shull

Press release by the Royal Swedish Academy of Sciences:

"Neutrons are small magnets…… (that) can be used to study the relative orientations of the small atomic magnets. ….. *the X-ray method has been powerless and in this field of application neutron diffraction has since assumed an entirely dominant position.* It is hard to imagine modern research into magnetism without this aid."



Cliff Shull

1994
Nobel Prize
in Physics

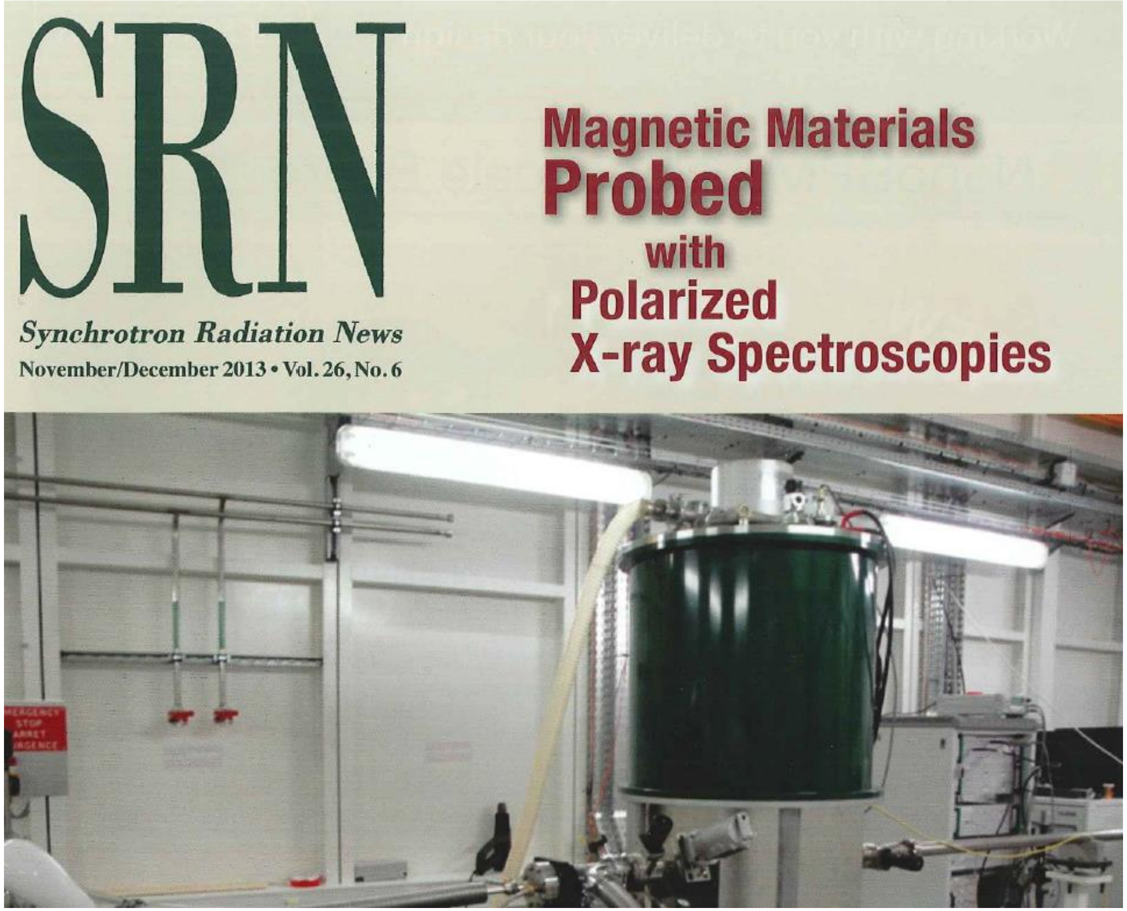
Bert Brockhouse

The Agilent Technologies Europhysics Prize for outstanding achievement in condensed-matter physics in 2000:
P. Carra, G. Schütz and G. van der Laan

"for their pioneering work in establishing the field of magnetic X-ray dichroism. …it is possible to obtain information about the material that cannot be obtained with traditional measurements."

Nowadays:

X-ray magnetic circular dichroism (XMCD) is considered to be one of the most important discoveries in the field of magnetism research in the last two decades. It is hard to imagine modern research into magnetism without the aid of X-ray spectroscopy.



SRN

Synchrotron Radiation News

November/December 2013 • Vol. 26, No. 6

Magnetic Materials Probed with Polarized X-ray Spectroscopies

“Magnetism,
as you recall from physics class, is a powerful force that causes certain items to be attracted to refrigerators.”

- Dave Barry

APPLICATIONS OF PERMANENT MAGNETS

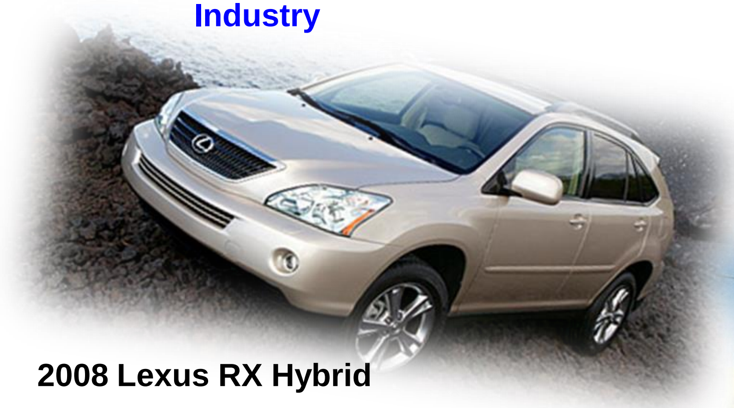
Magnetic resonance Imaging

High-Efficiency Motors for Energy-Efficient Homes

Computing and communication technologies

Rare Earth permanent magnets help make technologies more effective and more efficient.

Industry



2008 Lexus RX Hybrid

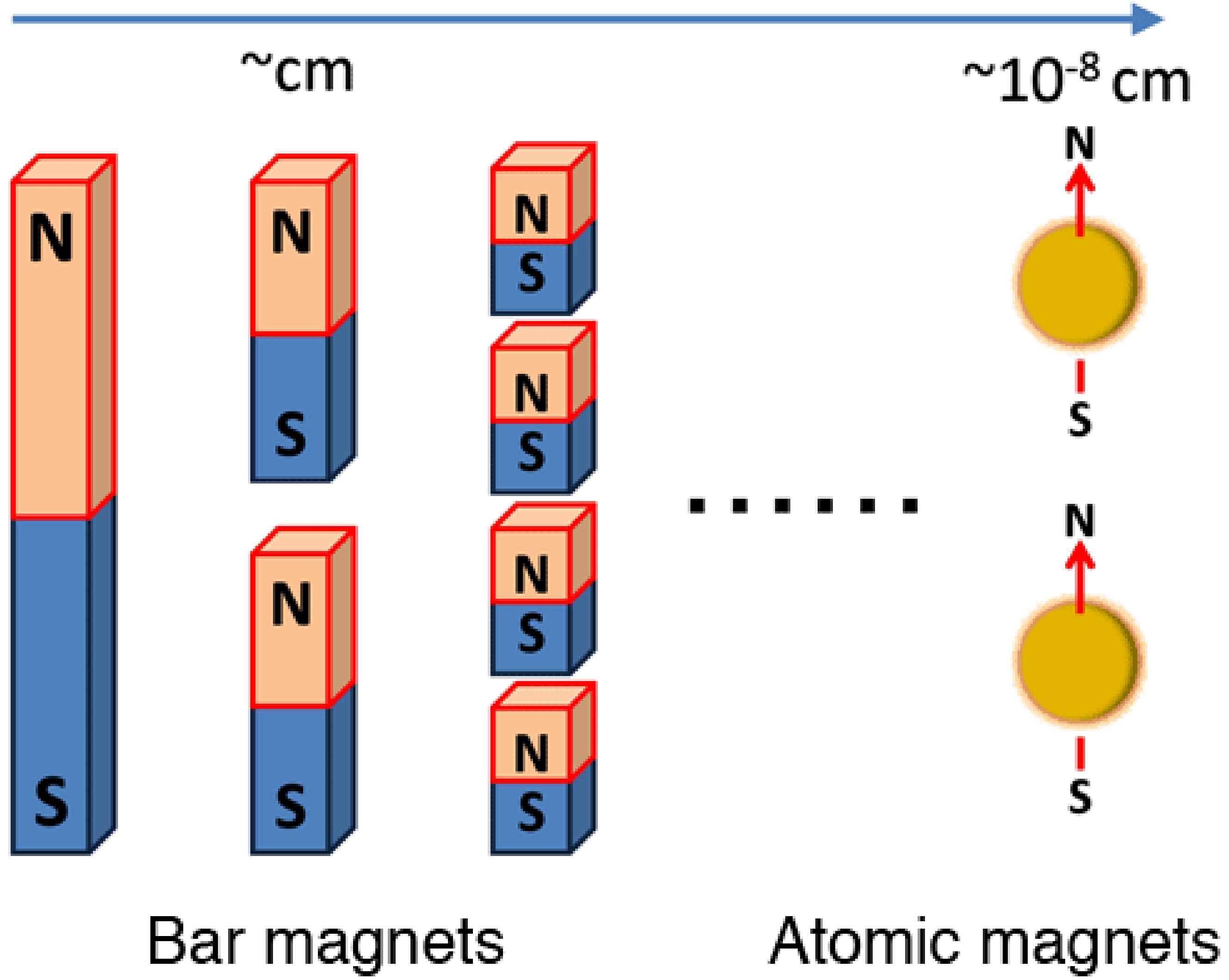
1118 magnets *(inc. 2.9kg of Nd-Fe-B)*

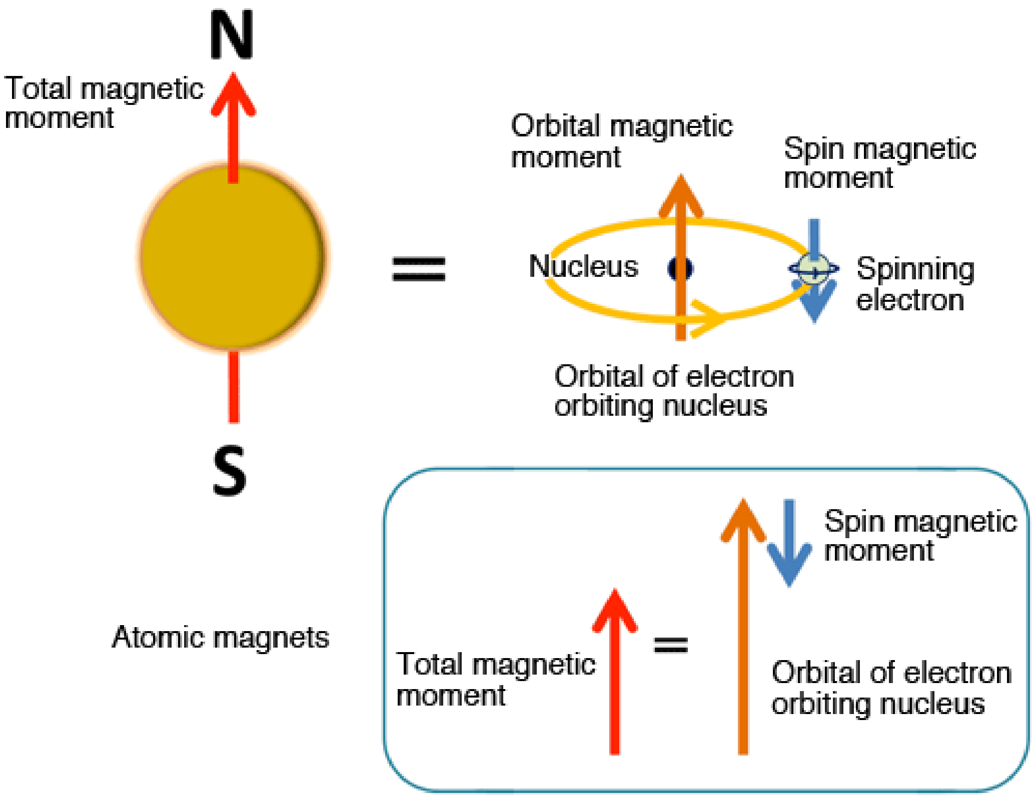
Clean Energy

Aerospace

direct-drive wind turbines require ~ 600 kg of permanent magnet material to produce 1 megawatt of electric power

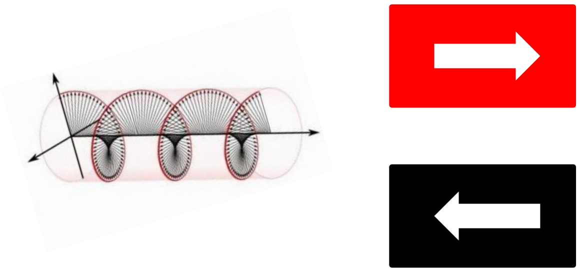
Dividing a magnet

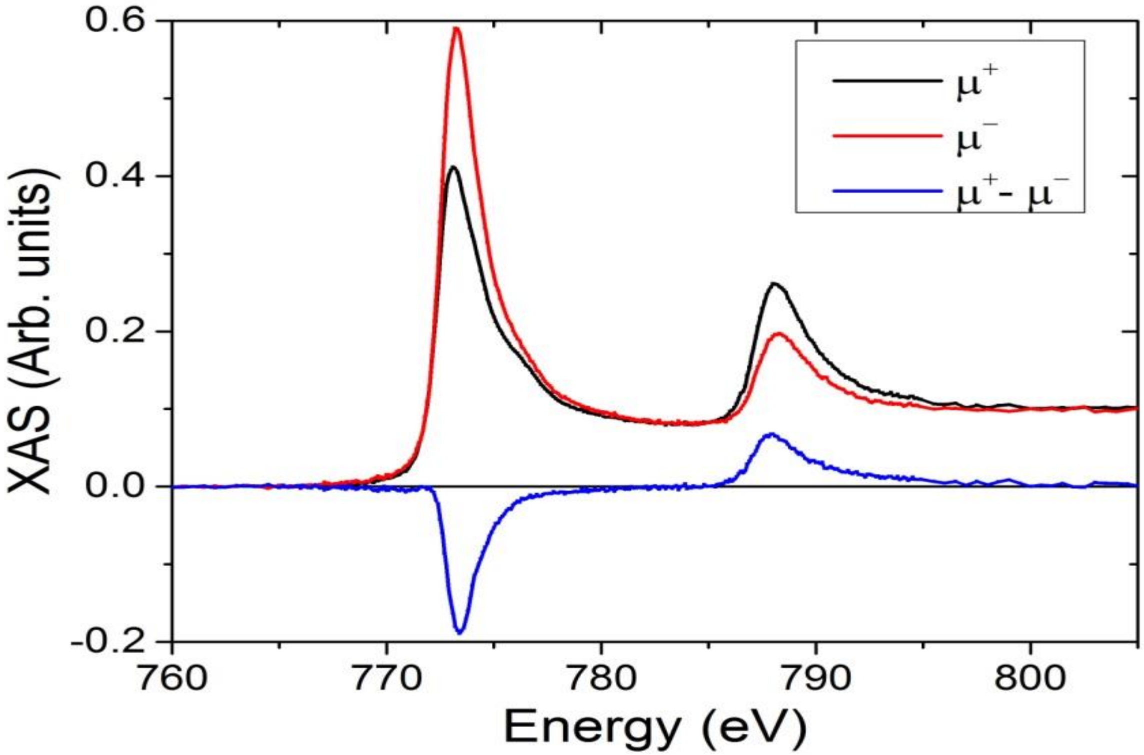




Spin and orbital magnetic moments are coupled via spin-orbit interaction, which is the key ingredient in magneto-optics, magnetocrystalline anisotropy, magnetic chirality, etc

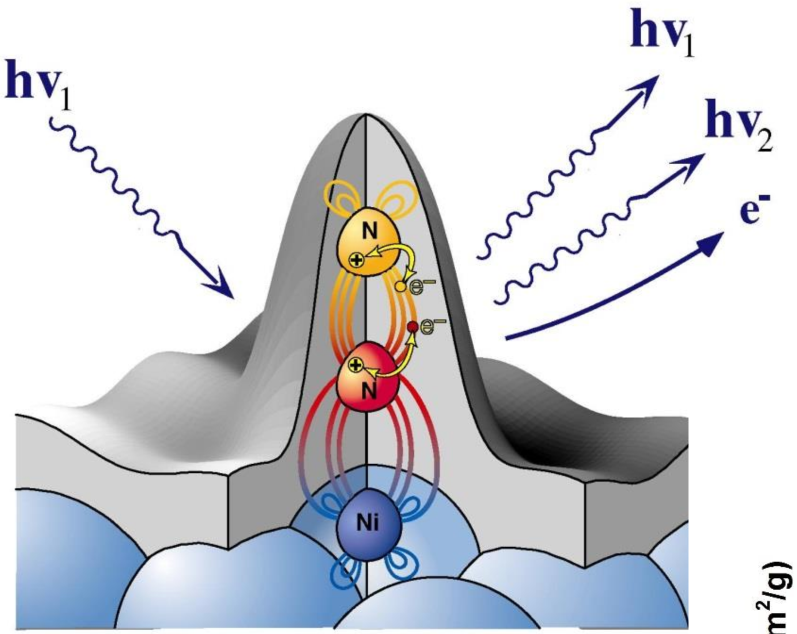
The experimental technique capable to measure separately SPIN and ORBITAL moments of an atom is X-ray Magnetic Circular Dichroism (XMCD)





Difference in absorption cross-section of circularly polarized X-rays for sample magnetization either parallel or antiparallel to the X-ray wavevector

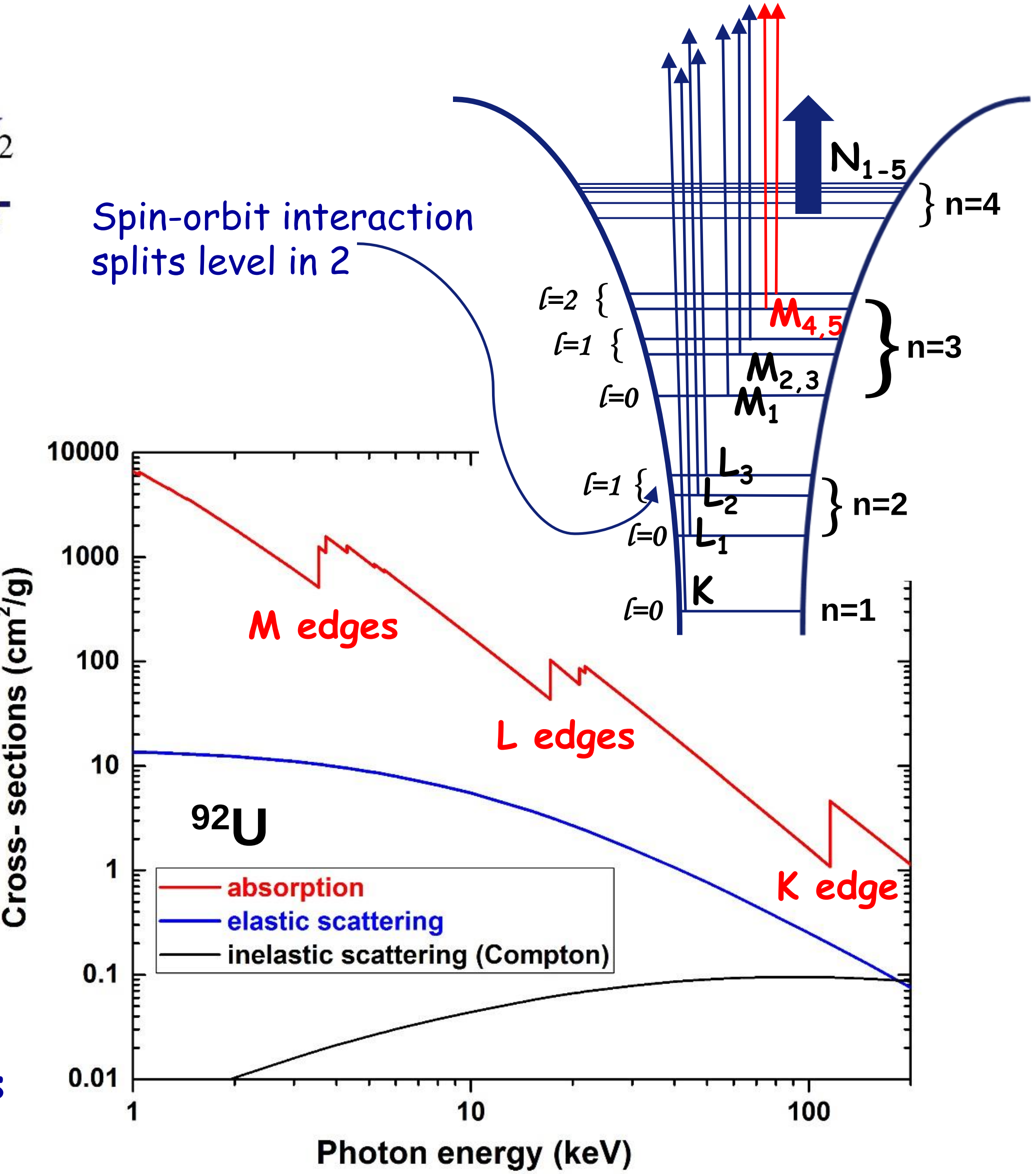
X-RAY INTERACTIONS WITH MATTER



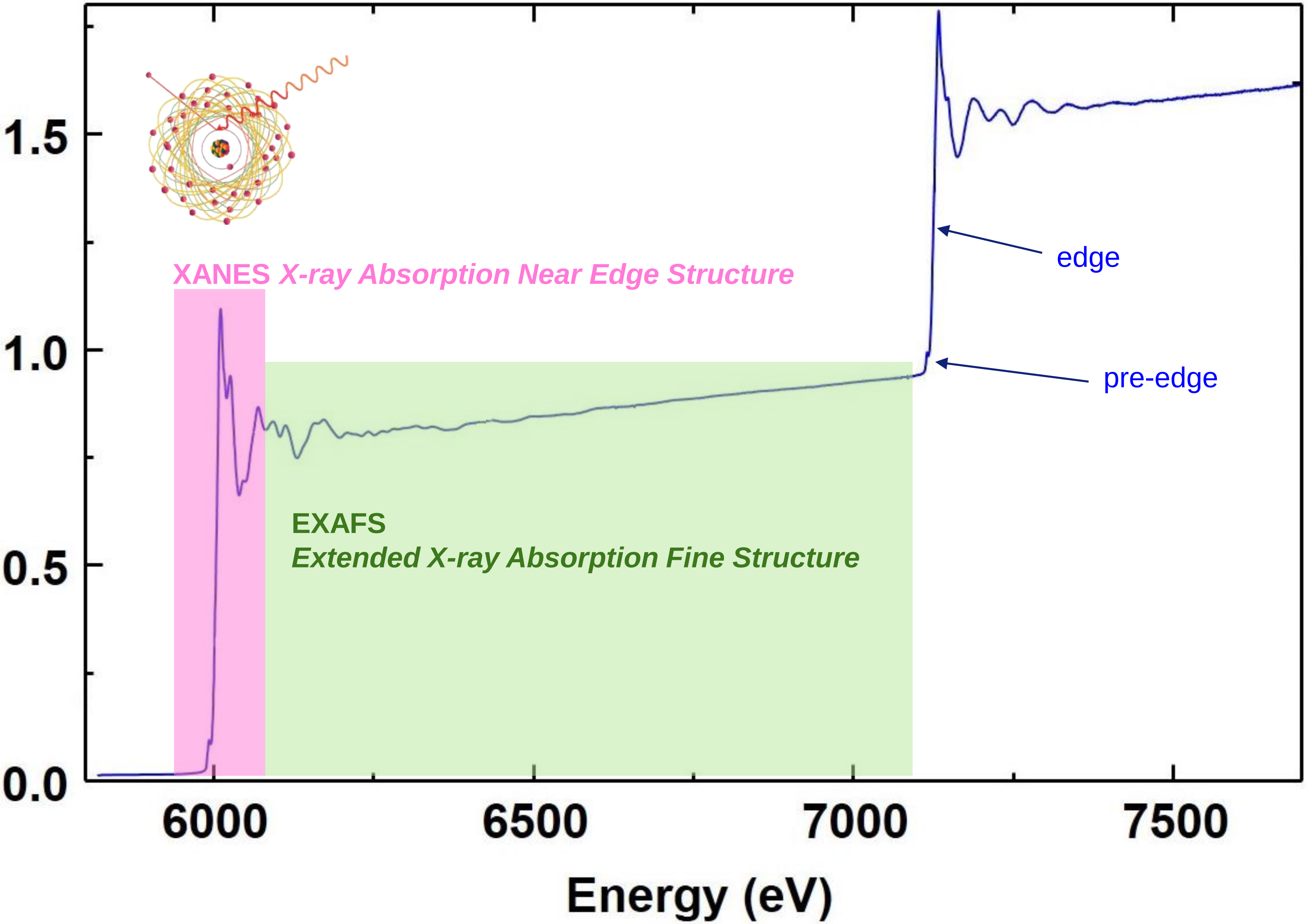
Photon could be

- absorbed (photoelectric effe
- elastically scattered
- inelastically scattered

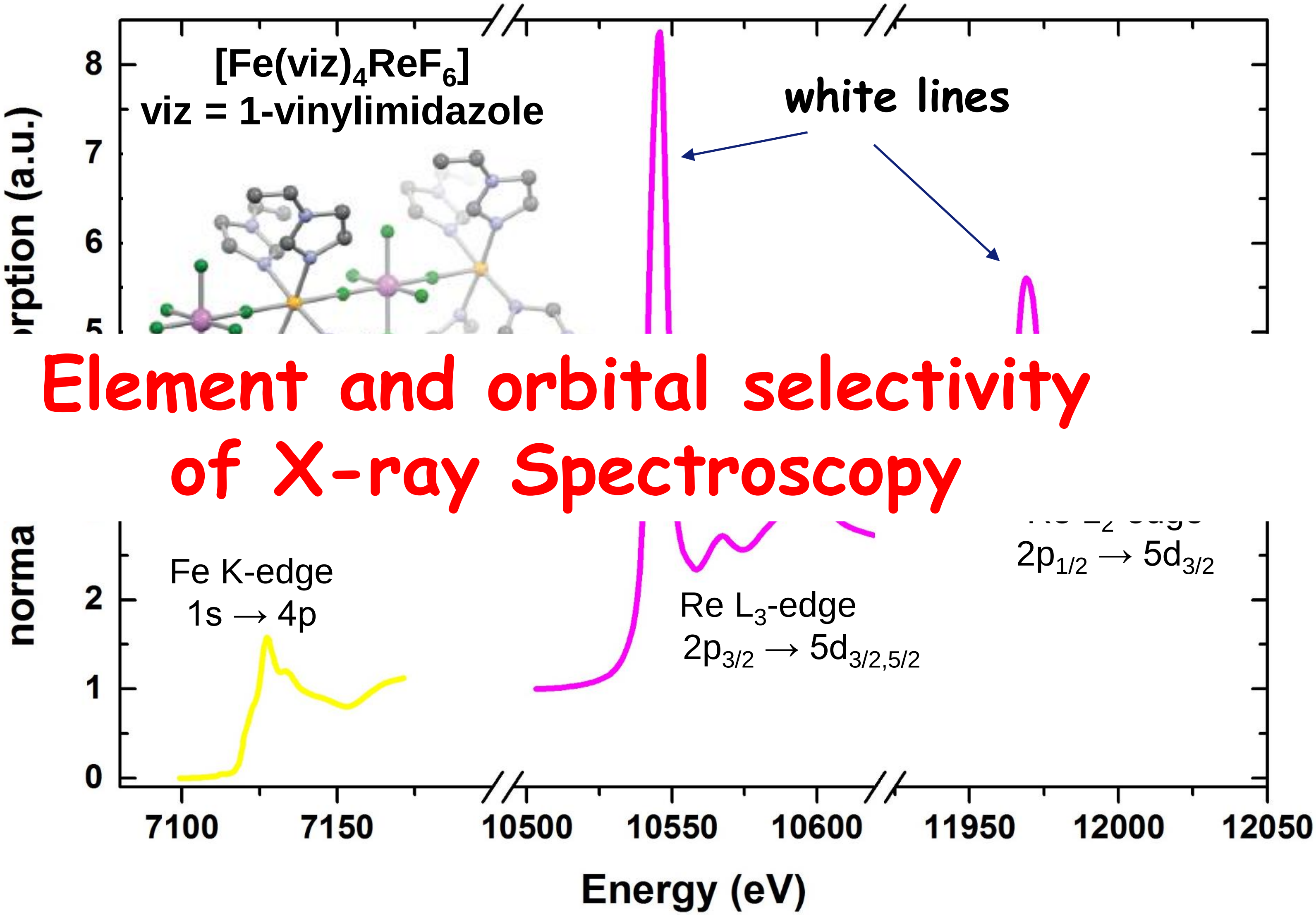
below 200 keV absorption dominates


Spin-orbit interaction splits level in 2

X-RAY ABSORPTION SPECTROSCOPY



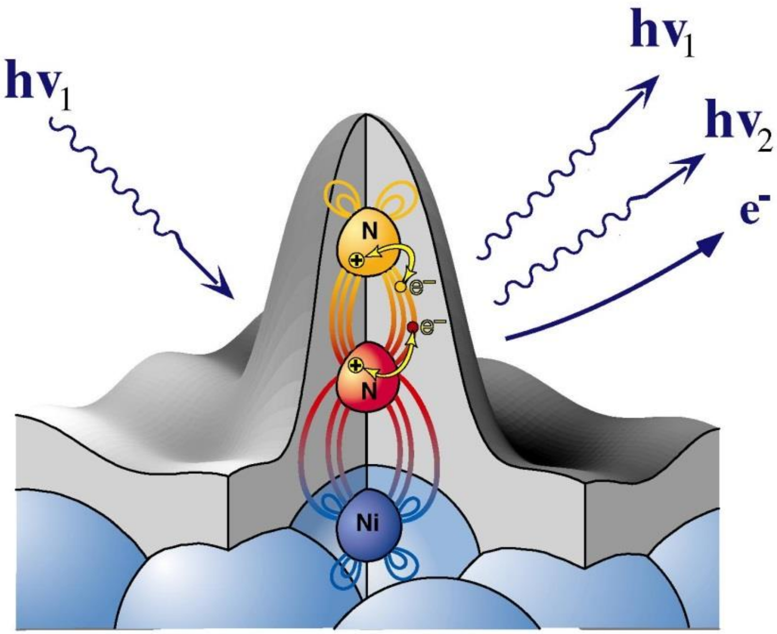
X-RAY ABSORPTION SPECTROSCOPY

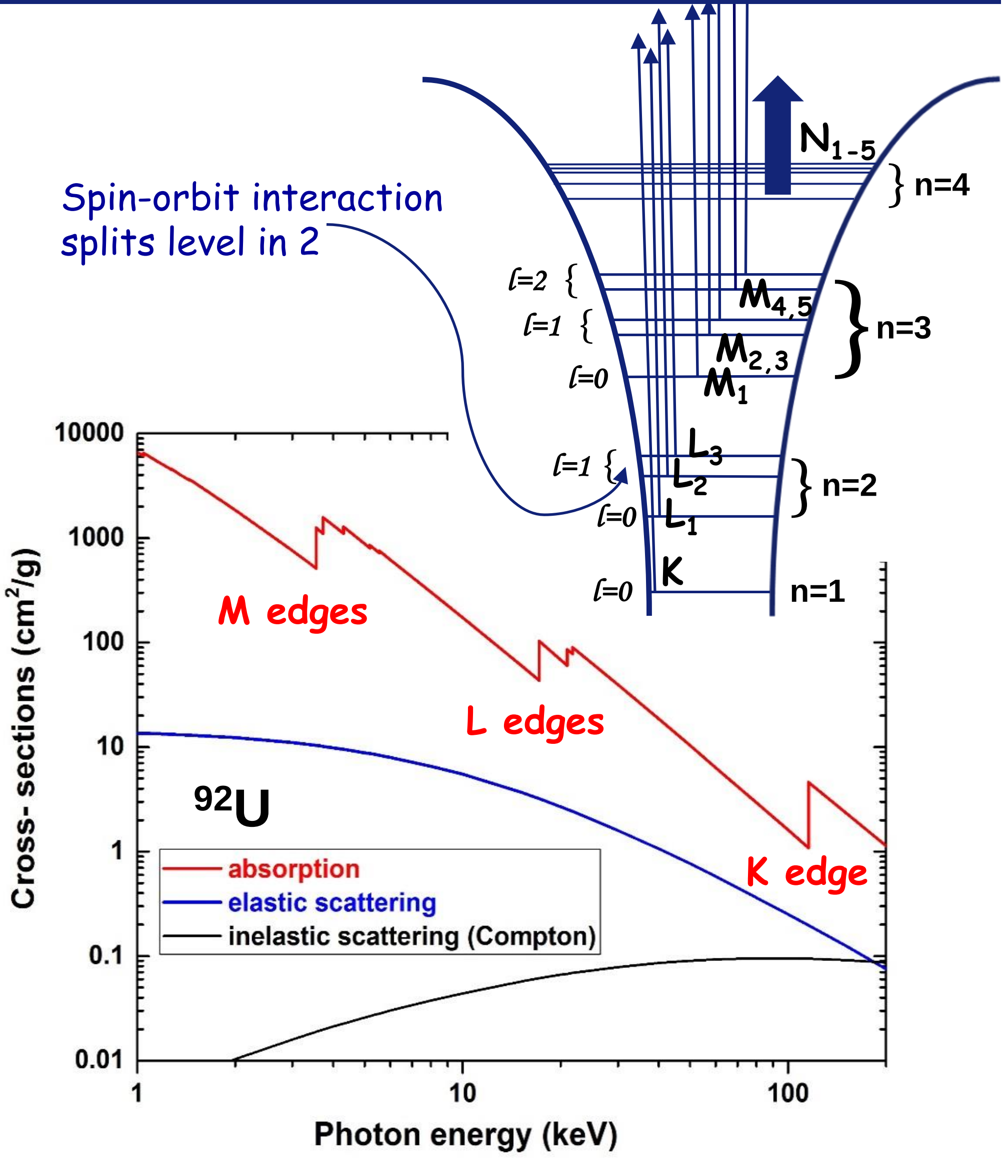


Element and orbital selectivity of X-ray Spectroscopy

In the early days of XAFS, absorption edges taken with use of photographic plates, appeared as unexposed bands on the plate (developed in negative), or “white lines”

X-RAY INTERACTIONS WITH MATTER



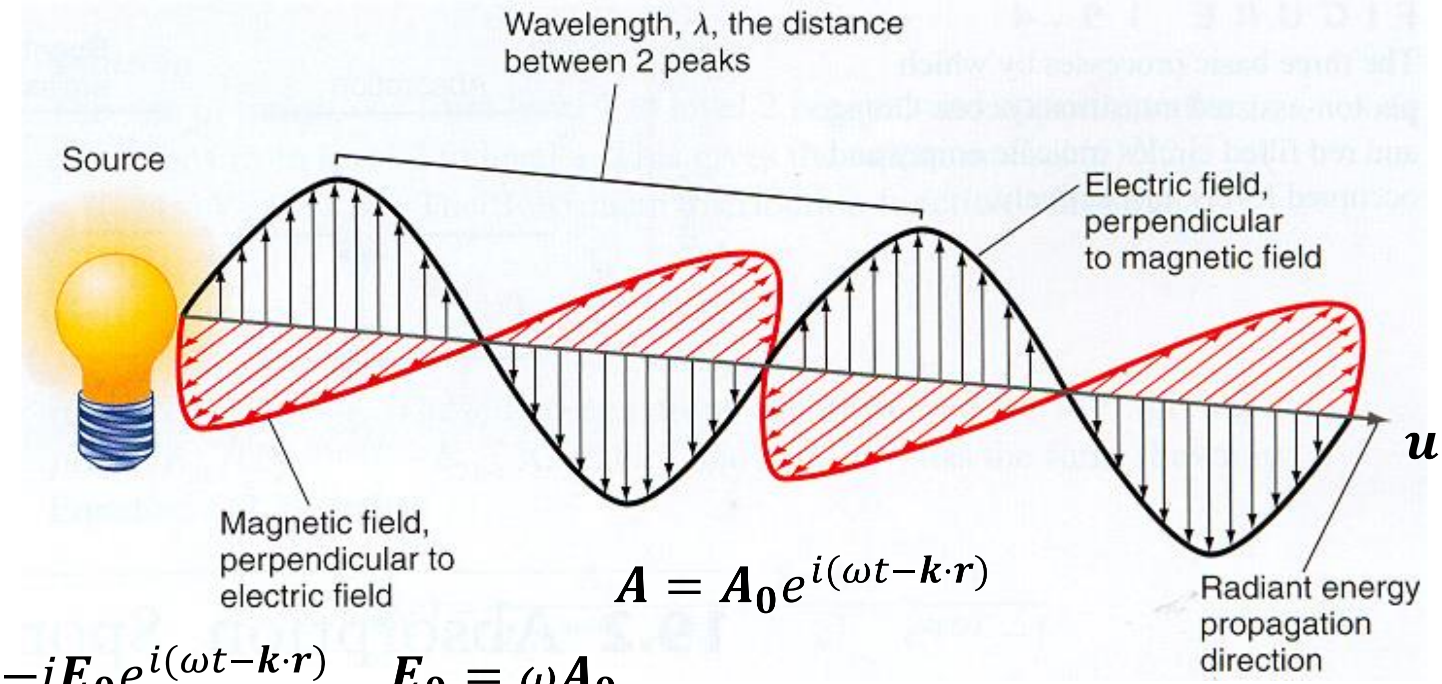

Spin-orbit interaction splits level in 2

Photon could be

- absorbed (photoelectric effect
- elastically scattered
- inelastically scattered

For magnetism research, the key word - **POLARIZATION**

REMINDER: LIGHT AS A EM FIELD



$$\boldsymbol{A} = \boldsymbol{A_0} e^{i(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})}$$

$$\boldsymbol{E} = -i\boldsymbol{E_0} e^{i(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})} \qquad \boldsymbol{E_0} = \omega \boldsymbol{A_0}$$

$$\boldsymbol{B} = -i\boldsymbol{B_0} e^{i(\omega t - \boldsymbol{k}\cdot\boldsymbol{r})} \qquad \boldsymbol{B_0} = \boldsymbol{k} \times \boldsymbol{A_0}$$

with the wave vector $\boldsymbol{k}$ such that $k^2 = \frac{\omega^2}{c^2} \qquad \boldsymbol{k} = \frac{2\pi}{\lambda}\boldsymbol{u} = \frac{\omega}{c}\boldsymbol{u}$

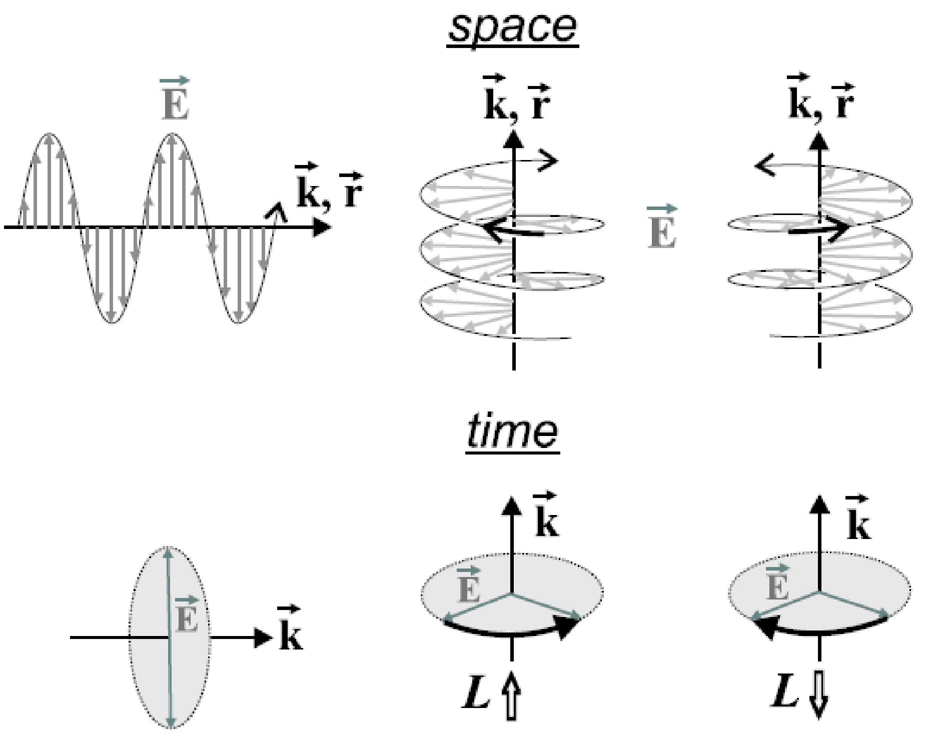
when $\boldsymbol{k}$ along z: $\boldsymbol{A_0} = \begin{pmatrix} A_{0x} e^{i\varphi_{0x}} \\ A_{0y} e^{i\varphi_{0y}} \\ 0 \end{pmatrix}$:

$\varphi_{0x} = \varphi_{0y}$ **linearly polarized light**

$A_{0x} = A_{0y}$
$\varphi_{0x} - \varphi_{0y} = \pm 90°$ **circularly polarized light**

POLARIZATION OF LIGHT

Linear polarization | Left circular polarization | Right circular polarization



Polarization vector $\boldsymbol{\epsilon} = \frac{\boldsymbol{E}}{E_0}$

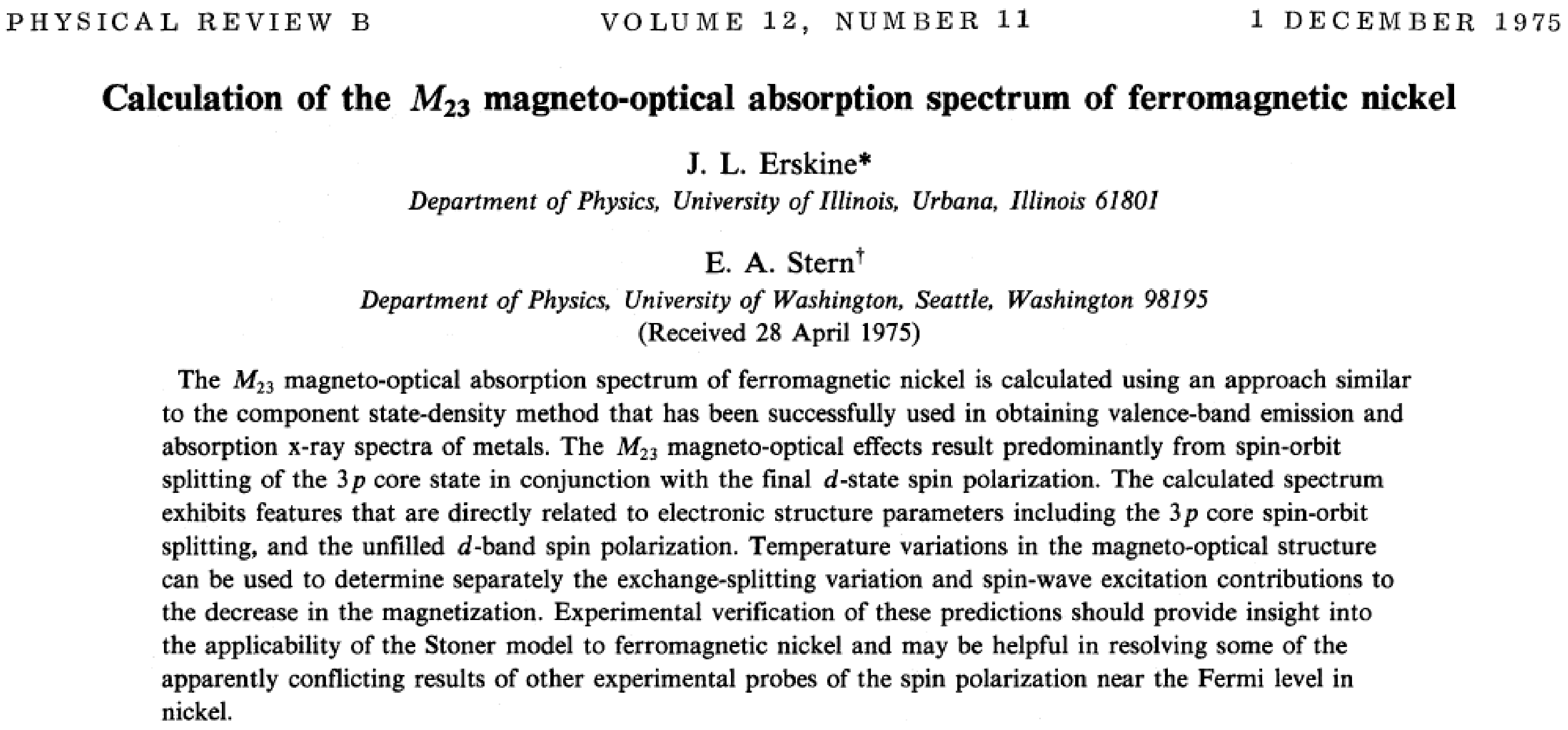
$\boldsymbol{k}$ // z

$$\epsilon = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \epsilon = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix} \qquad \epsilon = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}$$

Note: the phase conventions are highly variable

X-RAY MAGNETIC CIRCULAR DICHROISM

The first serious approach to the problem of absorption of circularly polarized X-rays



PHYSICAL REVIEW B VOLUME 12, NUMBER 11 1 DECEMBER 1975

Calculation of the M_{23} magneto-optical absorption spectrum of ferromagnetic nickel

J. L. Erskine*
Department of Physics, University of Illinois, Urbana, Illinois 61801

E. A. Stern[†]
Department of Physics, University of Washington, Seattle, Washington 98195

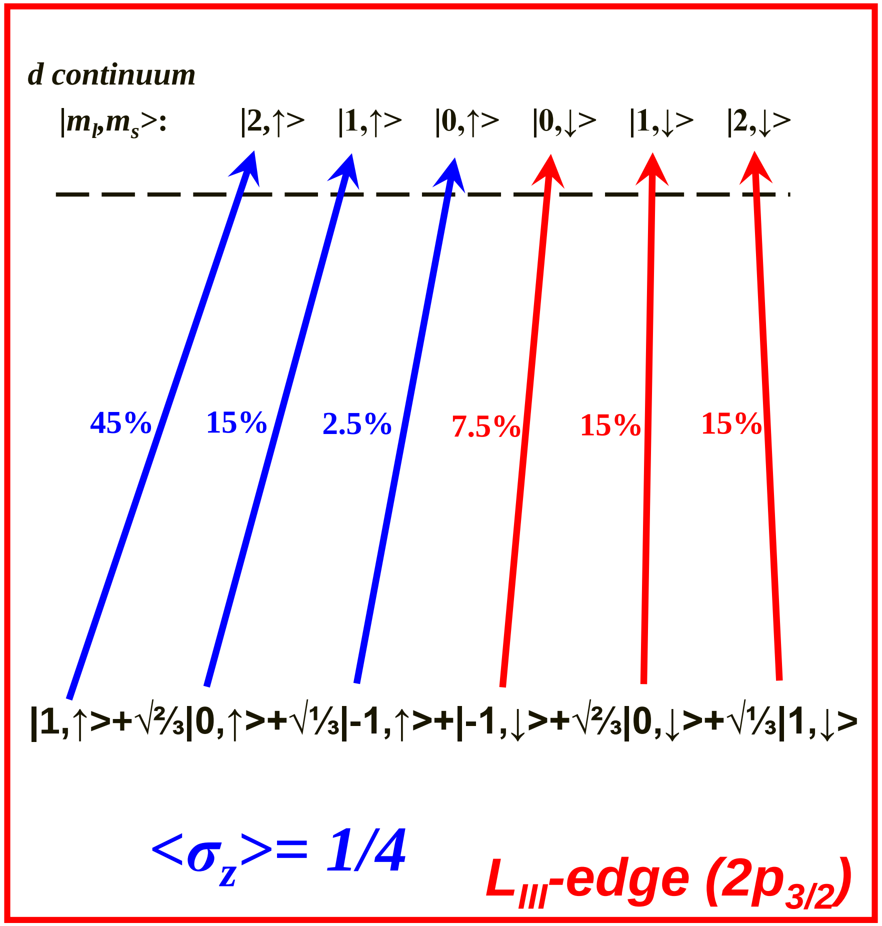
(Received 28 April 1975)

The M_{23} magneto-optical absorption spectrum of ferromagnetic nickel is calculated using an approach similar to the component state-density method that has been successfully used in obtaining valence-band emission and absorption x-ray spectra of metals. The M_{23} magneto-optical effects result predominantly from spin-orbit splitting of the $3p$ core state in conjunction with the final d-state spin polarization. The calculated spectrum exhibits features that are directly related to electronic structure parameters including the $3p$ core spin-orbit splitting, and the unfilled d-band spin polarization. Temperature variations in the magneto-optical structure can be used to determine separately the exchange-splitting variation and spin-wave excitation contributions to the decrease in the magnetization. Experimental verification of these predictions should provide insight into the applicability of the Stoner model to ferromagnetic nickel and may be helpful in resolving some of the apparently conflicting results of other experimental probes of the spin polarization near the Fermi level in nickel.

Two-step model

TWO STEP MODEL OF XMCD

Absorption of a right circularly polarized photon electric dipolar transitions $p \rightarrow d \ (\Delta m_l = +1; \Delta m_S = 0)$



d continuum

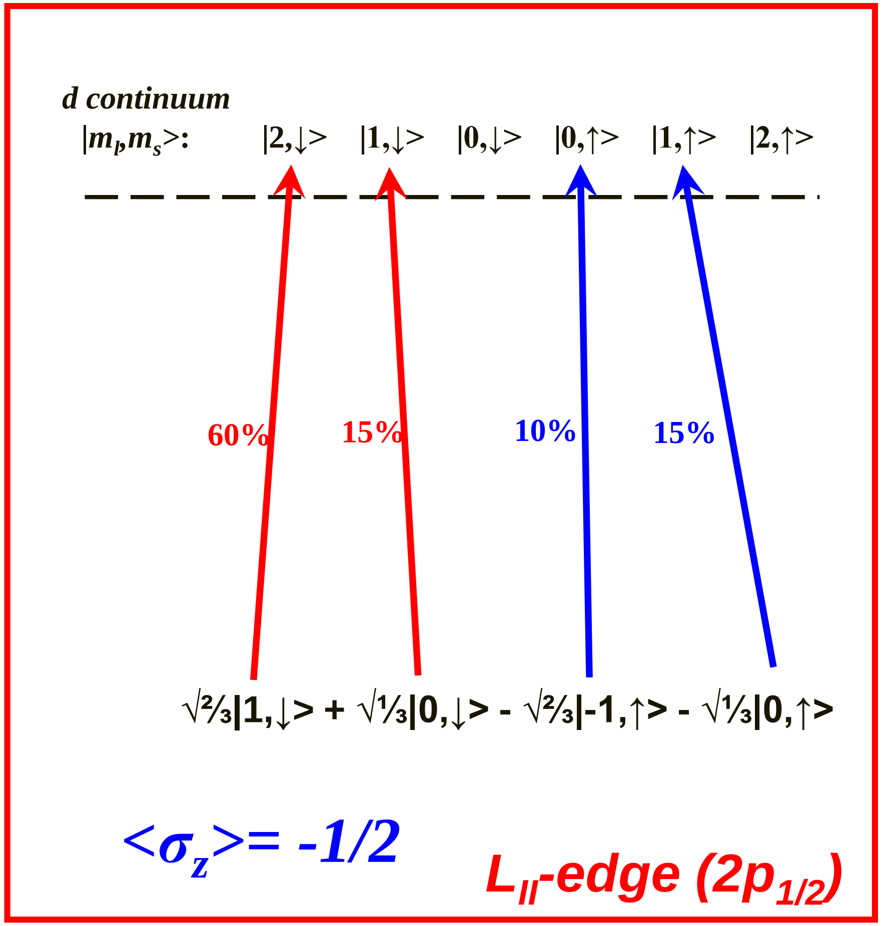
$|m_l,m_s>$: |2,↑> |1,↑> |0,↑> |0,↓> |1,↓> |2,↓>

45% 15% 2.5% 7.5% 15% 15%

|1,↑>+√⅔|0,↑>+√⅓|-1,↑>+|-1,↓>+√⅔|0,↓>+√⅓|1,↓>

$<\sigma_z>= 1/4$

L_{III}-edge ($2p_{3/2}$)



d continuum

$|m_l,m_s>$: |2,↓> |1,↓> |0,↓> |0,↑> |1,↑> |2,↑>

60% 15% 10% 15%

√⅔|1,↓> + √⅓|0,↓> - √⅔|-1,↑> - √⅓|0,↑>

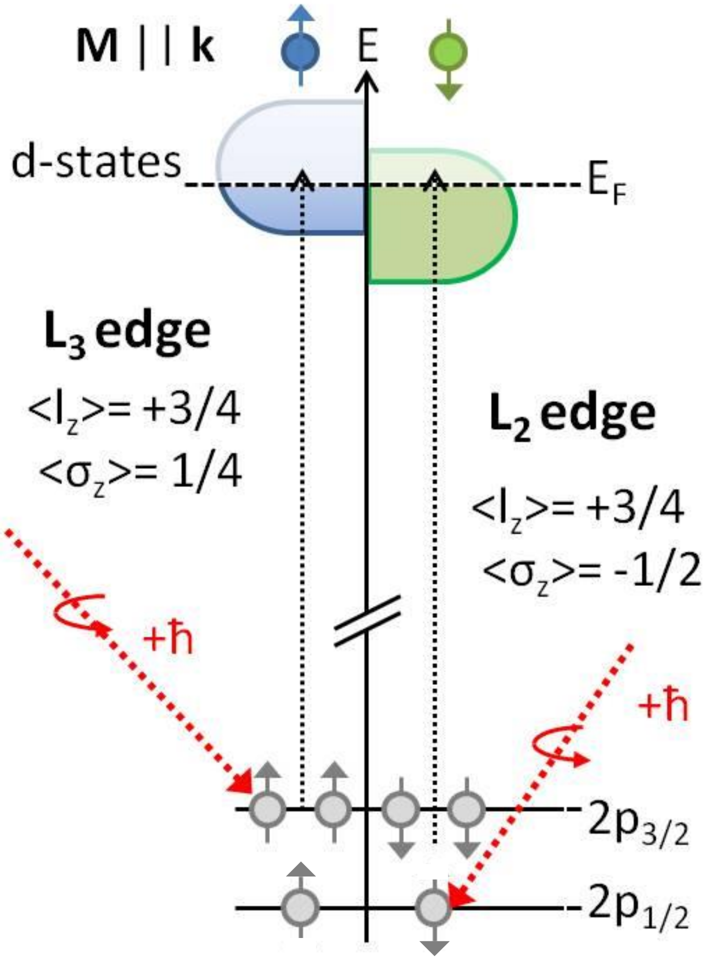
$<\sigma_z>= -1/2$

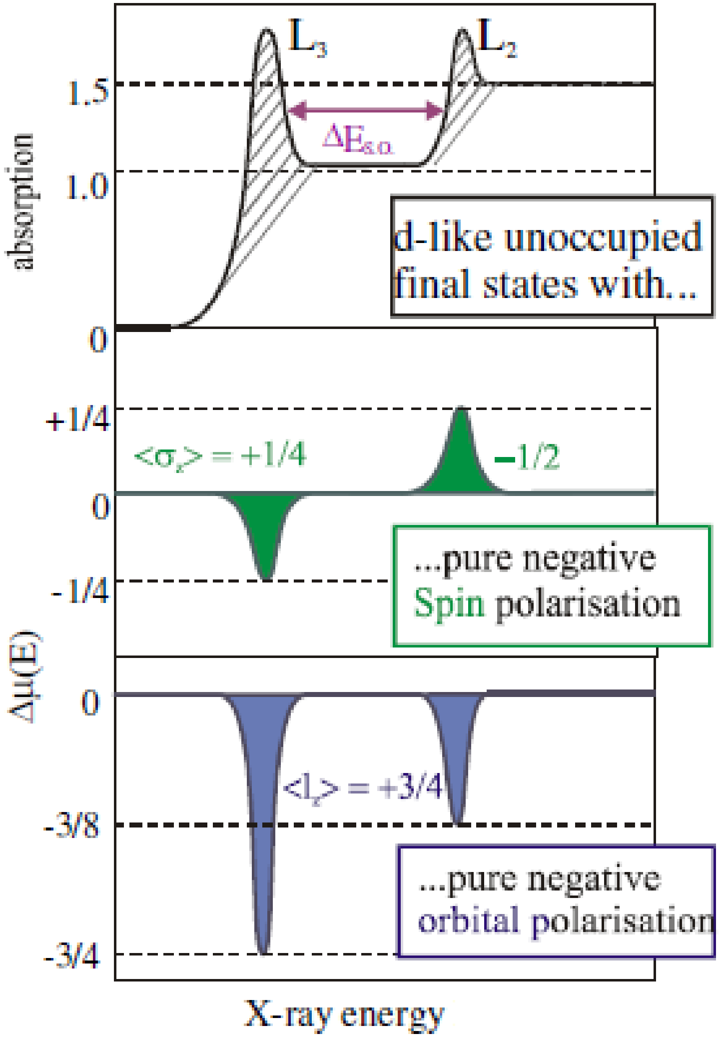
L_{II}-edge ($2p_{1/2}$)

Excited photoelectrons are spin polarized

TWO STEP MODEL OF XMCD

Exchange splitting of the valence band is driving the second step





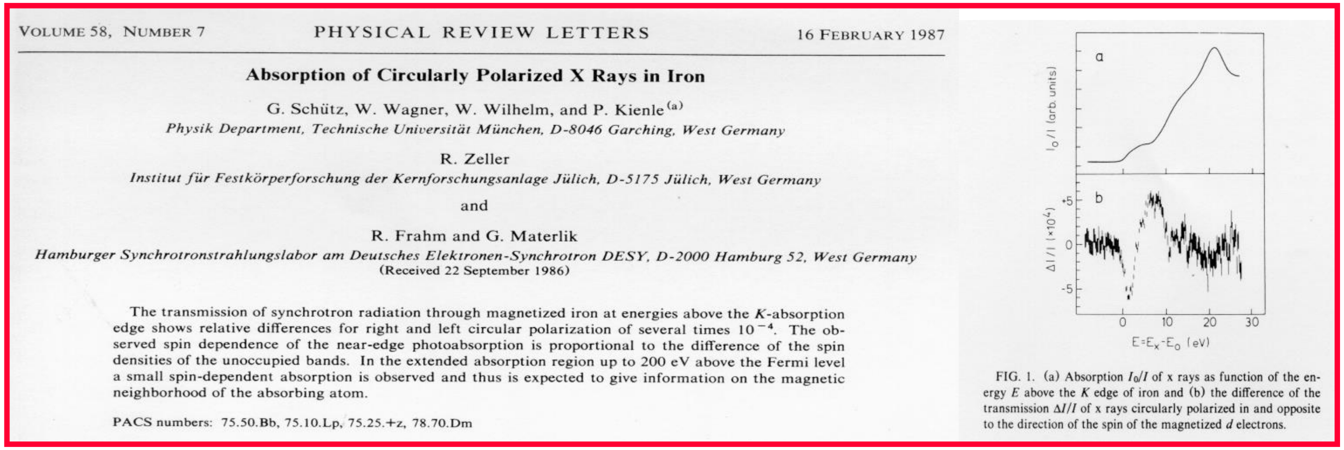
d-like unoccupied final states with…

…pure negative Spin polarisation

…pure negative orbital polarisation

FIRST EXPERIMENTAL OBSERVATIONS

First experimental evidence



VOLUME 58, NUMBER 7 PHYSICAL REVIEW LETTERS 16 FEBRUARY 1987

Absorption of Circularly Polarized X Rays in Iron

G. Schütz, W. Wagner, W. Wilhelm, and P. Kienle$^{(a)}$
Physik Department, Technische Universität München, D-8046 Garching, West Germany

R. Zeller
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5175 Jülich, West Germany

and

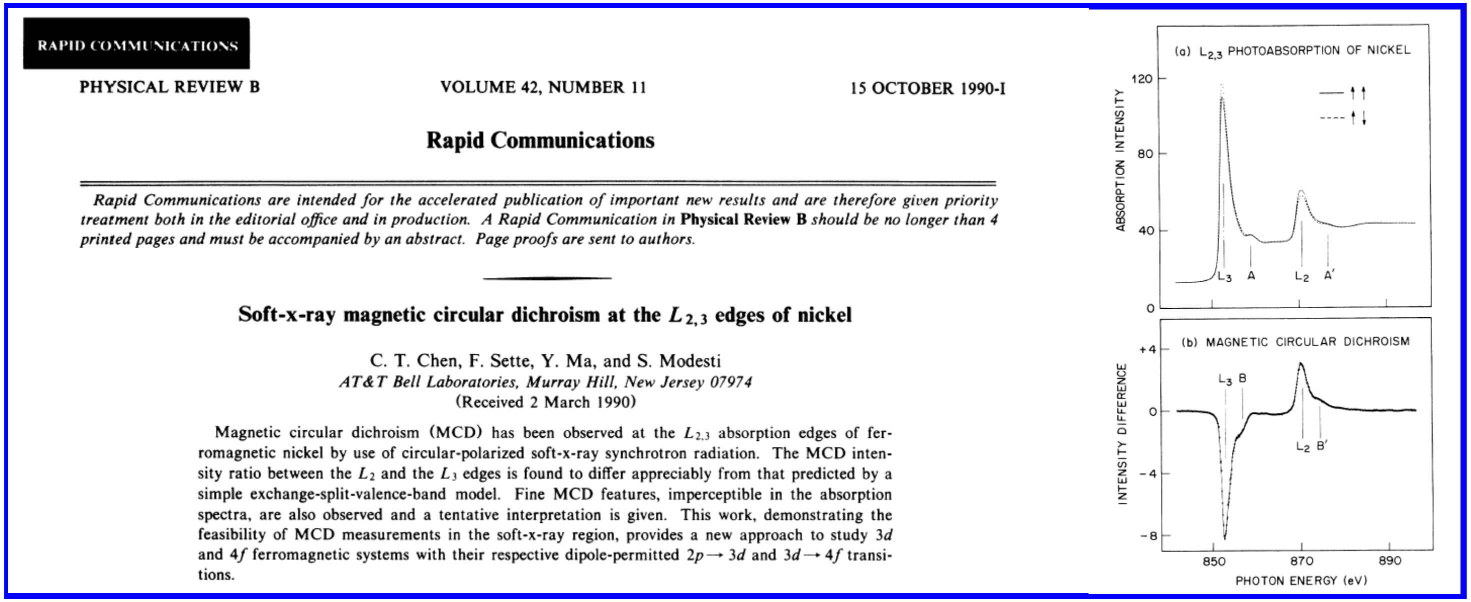
R. Frahm and G. Materlik
Hamburger Synchrotronstrahlungslabor am Deutsches Elektronen-Synchrotron DESY, D-2000 Hamburg 52, West Germany
(Received 22 September 1986)

The transmission of synchrotron radiation through magnetized iron at energies above the K-absorption edge shows relative differences for right and left circular polarization of several times 10^{-4}. The observed spin dependence of the near-edge photoabsorption is proportional to the difference of the spin densities of the unoccupied bands. In the extended absorption region up to 200 eV above the Fermi level a small spin-dependent absorption is observed and thus is expected to give information on the magnetic neighborhood of the absorbing atom.

PACS numbers: 75.50.Bb, 75.10.Lp, 75.25.+z, 78.70.Dm

FIG. 1. (a) Absorption I_0/I of x rays as function of the energy E above the K edge of iron and (b) the difference of the transmission $\Delta I/I$ of x rays circularly polarized in and opposite to the direction of the spin of the magnetized d electrons.

XMCD is a new approach to study ferromagnetic system



RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 11 15 OCTOBER 1990-I

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than 4 printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

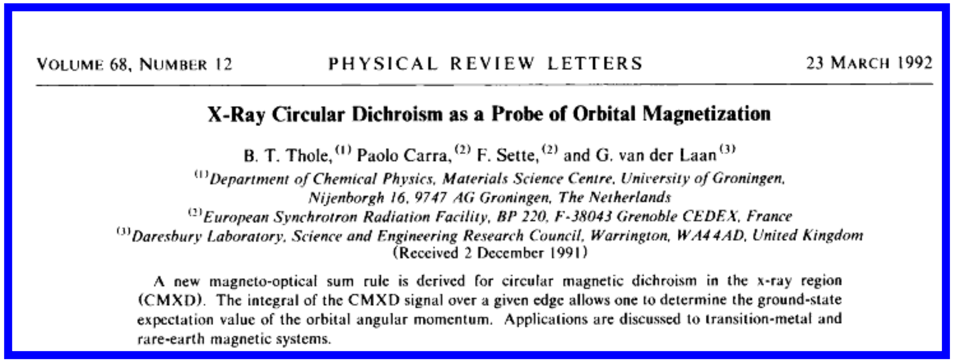
Soft-x-ray magnetic circular dichroism at the $L_{2,3}$ edges of nickel

C. T. Chen, F. Sette, Y. Ma, and S. Modesti
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 2 March 1990)

Magnetic circular dichroism (MCD) has been observed at the $L_{2,3}$ absorption edges of ferromagnetic nickel by use of circular-polarized soft-x-ray synchrotron radiation. The MCD intensity ratio between the L_2 and the L_3 edges is found to differ appreciably from that predicted by a simple exchange-split-valence-band model. Fine MCD features, imperceptible in the absorption spectra, are also observed and a tentative interpretation is given. This work, demonstrating the feasibility of MCD measurements in the soft-x-ray region, provides a new approach to study $3d$ and $4f$ ferromagnetic systems with their respective dipole-permitted $2p \rightarrow 3d$ and $3d \rightarrow 4f$ transitions.

XMCD SUM RULES

Sum rules relate experimental XMCD spectra to the spin and orbital moments



VOLUME 68, NUMBER 12 PHYSICAL REVIEW LETTERS 23 MARCH 1992

X-Ray Circular Dichroism as a Probe of Orbital Magnetization

B. T. Thole,(1) Paolo Carra,(2) F. Sette,(2) and G. van der Laan(3)
(1)*Department of Chemical Physics, Materials Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*
(2)*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France*
(3)*Daresbury Laboratory, Science and Engineering Research Council, Warrington, WA4 4AD, United Kingdom*
(Received 2 December 1991)

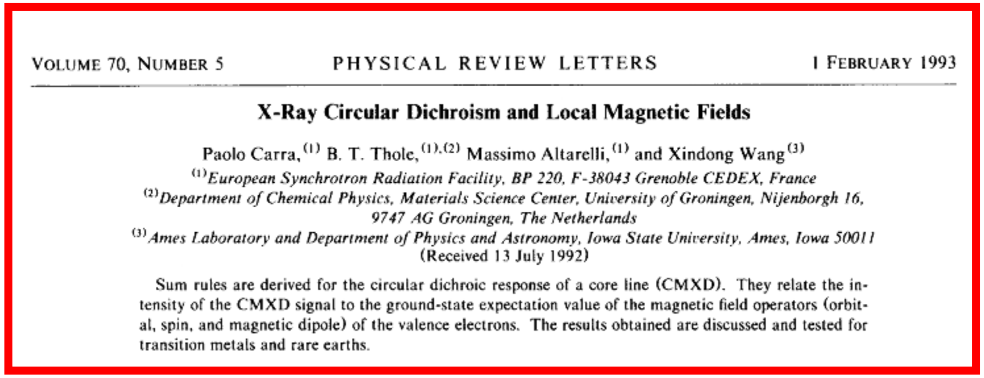
A new magneto-optical sum rule is derived for circular magnetic dichroism in the x-ray region (CMXD). The integral of the CMXD signal over a given edge allows one to determine the ground-state expectation value of the orbital angular momentum. Applications are discussed to transition-metal and rare-earth magnetic systems.

Orbital sum rule

$$\int_{j^+ + j^-} (\mu^+ - \mu^-) = \frac{2l(l+1)}{l(l+1)+2-c(c+1)} \times C \times \langle L_z \rangle$$

Spin sum rule

$$\int_{j^+} (\mu^+ - \mu^-) - \frac{c+1}{c} \int_{j^-} (\mu^+ - \mu^-) = C \times [A\langle S_z \rangle + B\langle T_z \rangle]$$



VOLUME 70, NUMBER 5 PHYSICAL REVIEW LETTERS 1 FEBRUARY 1993

X-Ray Circular Dichroism and Local Magnetic Fields

Paolo Carra,(1) B. T. Thole,(1),(2) Massimo Altarelli,(1) and Xindong Wang(3)
(1)*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France*
(2)*Department of Chemical Physics, Materials Science Center, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*
(3)*Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011*
(Received 13 July 1992)

Sum rules are derived for the circular dichroic response of a core line (CMXD). They relate the intensity of the CMXD signal to the ground-state expectation value of the magnetic field operators (orbital, spin, and magnetic dipole) of the valence electrons. The results obtained are discussed and tested for transition metals and rare earths.

$$T = \sum_i (s_i - 3r_i(r_i \cdot s_i)/r_i^2)$$

$$C = \frac{1}{n_h} \int_{j^+ + j^-} (\mu^+ + \mu^- + \mu^0)$$ *- X-ray absorption cross section per hole;*

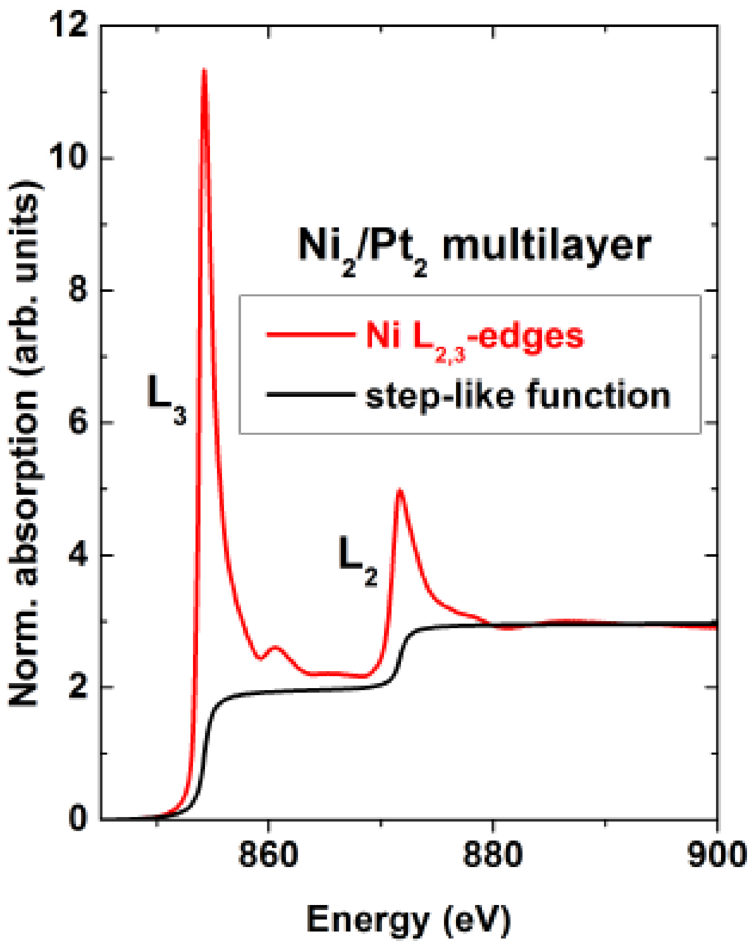
$$A = \frac{l(l+1) - 2 - c(c+1)}{3c}$$

$$B = \frac{l(l+1)[l(l+1) + 2c(c+1) + 4] - 3c(c-1)^2(c+2)^2}{6c \cdot l(l+1)}$$

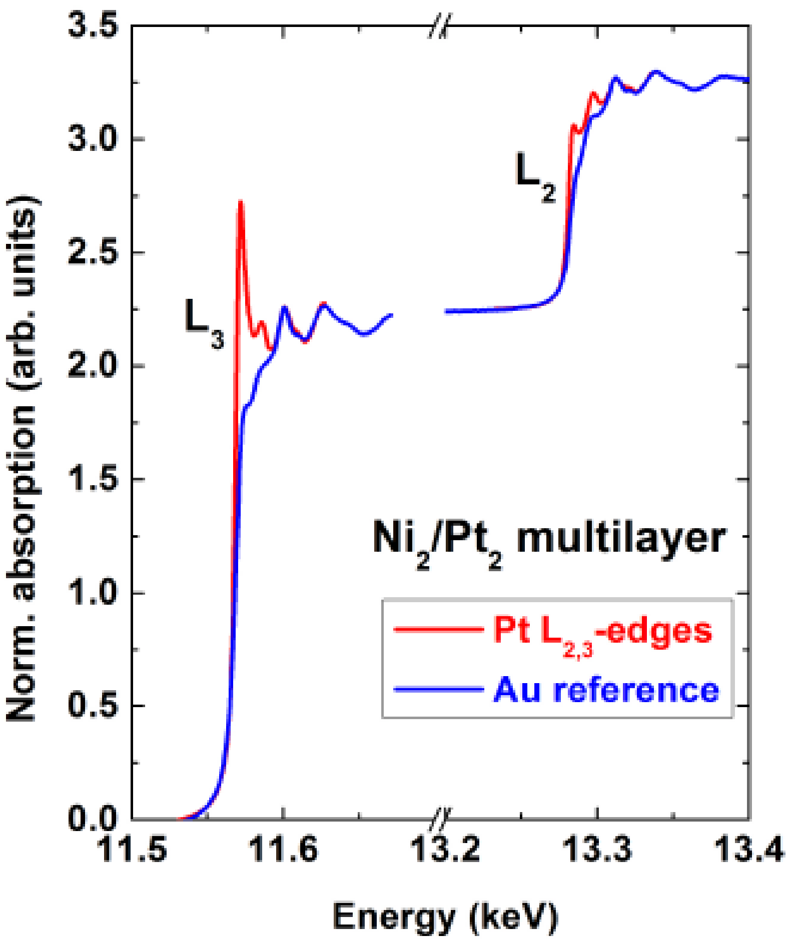
CHARGE SUM RULE

integrated whitelines intensity is measure for number of holes in the valence band => valence state

A.F. Starace, Phys. Rev. B5, 1773 (1972)



F. Wilhelm, et al. Phys. Rev. Lett 85, 413 (2000)

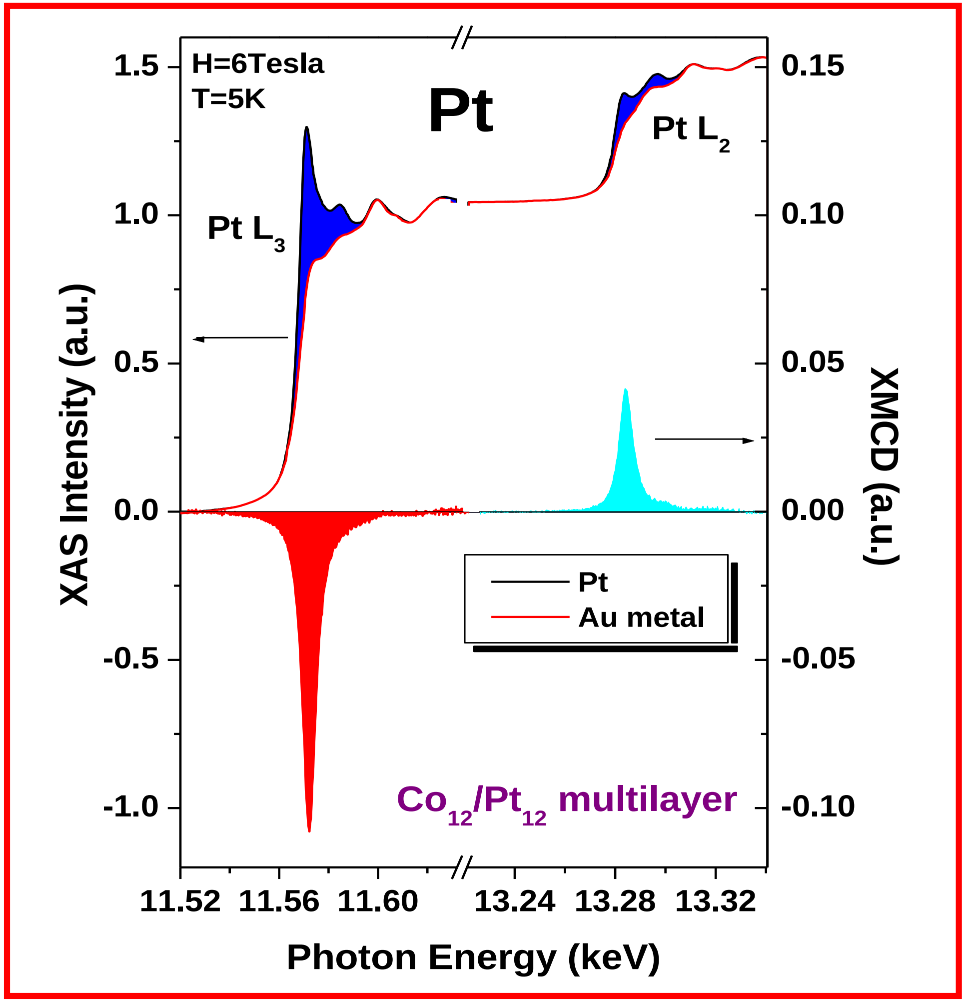


A. Rogalev et al. Lect. Notes Phys. 697, 71(2006)

APPLICATION OF THE XMCD SUM RULES FOR THE $L_{2,3}$ EDGES

integrated spectra related to spin and orbital magnetic moments in the ground state

B.T Thole et al., Phys. Rev. Lett. 68,1943 (1992)
P. Carra et al. Phys. Rev. Lett. 70, 694 (1993).



$$\langle L_z \rangle = -\frac{4}{3} \cdot C \cdot (A + B)$$

$$\langle S_z \rangle - 7\langle T_z \rangle = -2C \cdot (A - 2B)$$

$$\frac{\langle L_z \rangle}{\langle S_z \rangle - 7\langle T_z \rangle} = \frac{2}{3} \cdot \frac{(A + B)}{(A - 2B)}$$

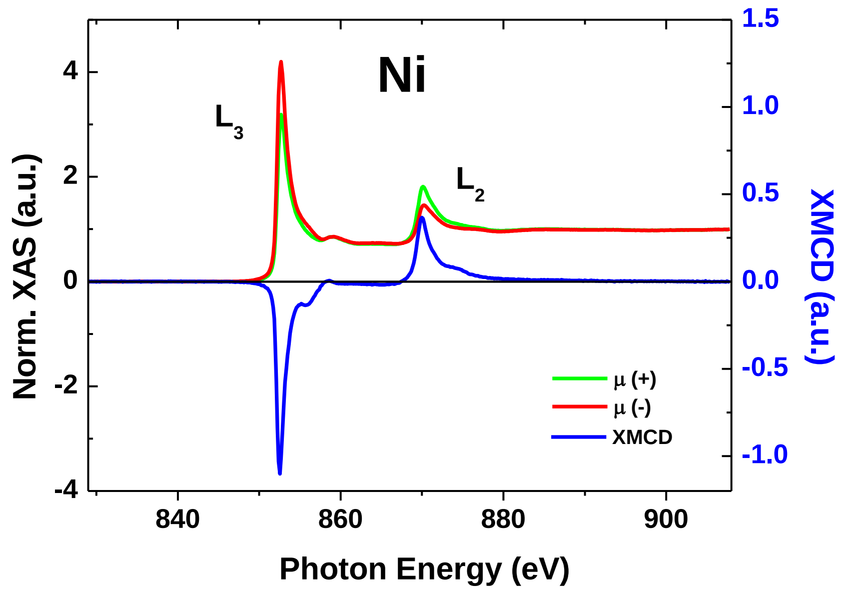
in the case of $L_{3,2}$ absorption edges

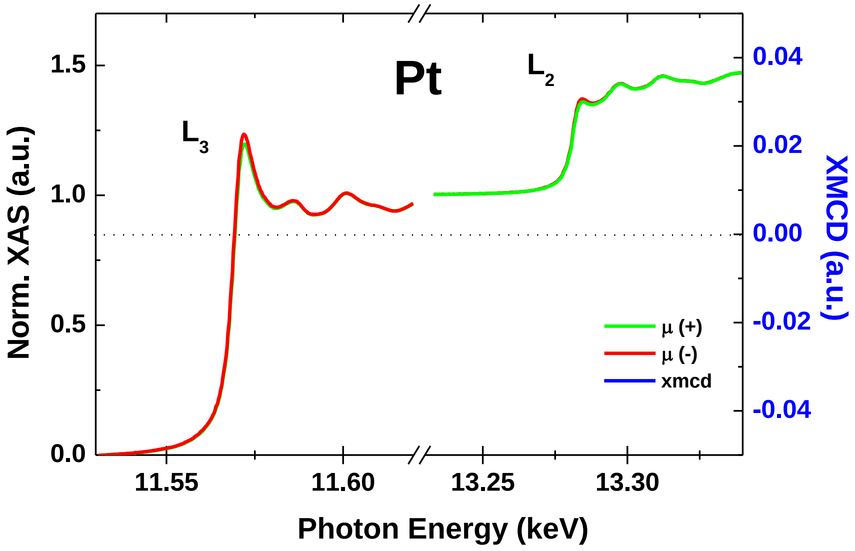
$$C = \frac{(n_h^{Pt} - n_h^{Au})}{A}$$

A ~ integrated intensity of transitions into unoccupied *d* band

n_h^d = number of holes in *d* band

ELEMENT SELECTIVITY OF XMCD

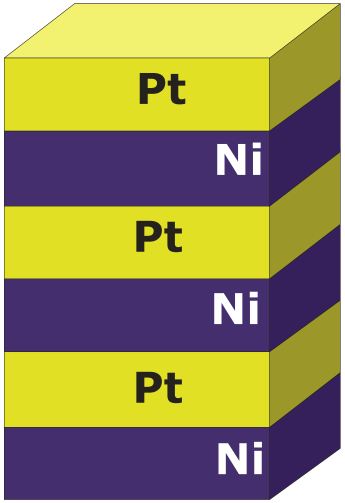




Ni_2 / Pt_2 multilayer

F. Wilhelm et al., Phys. Rev. Lett., 85, 413 (2000)

T ~ 10K
H = ± 5 T



RESULTS

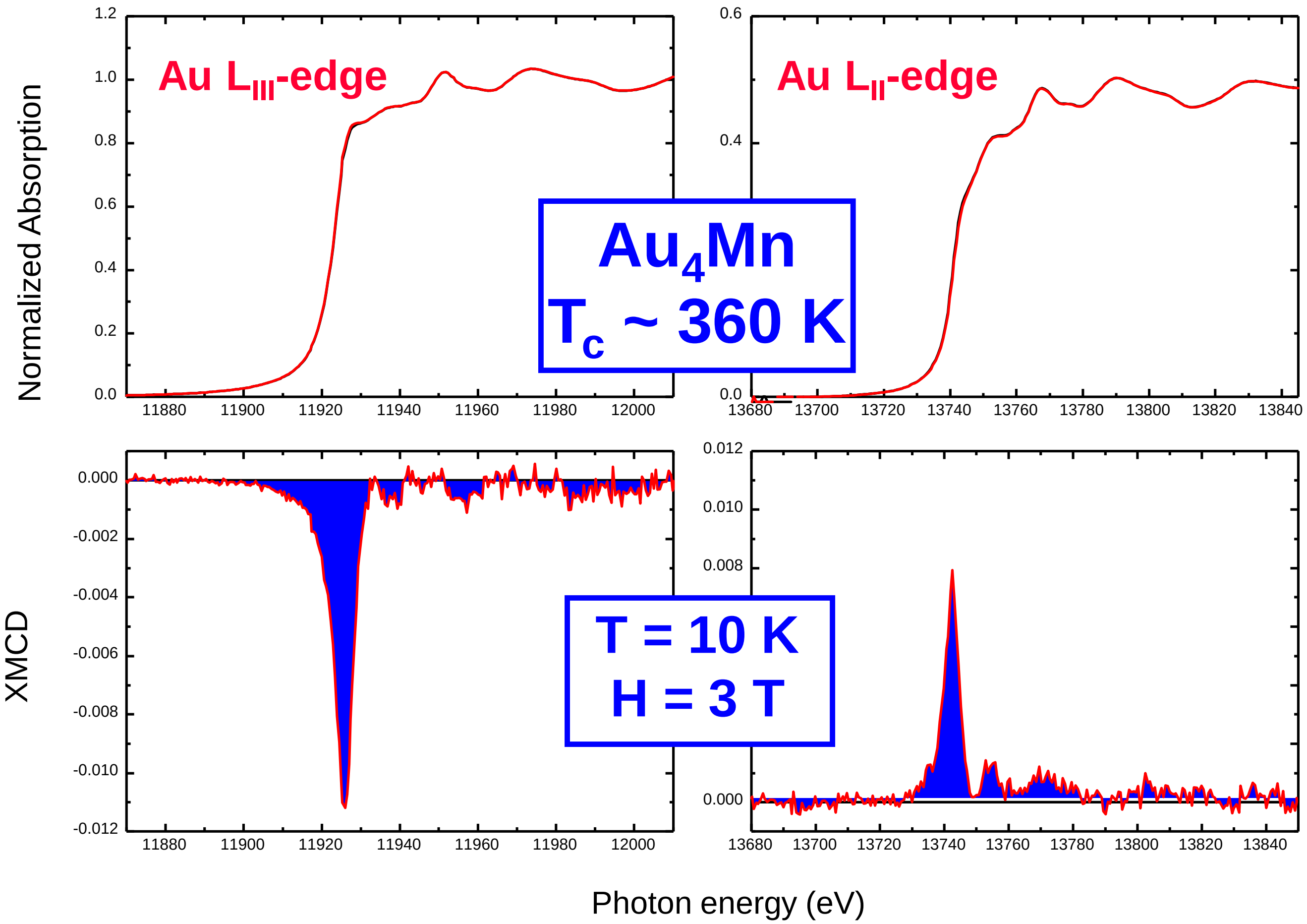
- **Ni magnetic moments:**

  μ_S^{3d}=0.35 μ_B/atom
  μ_L^{3d}=0.038 μ_B/atom

- **Pt induced magnetic moments:**

  μ_S^{5d}=0.14 μ_B/atom
  μ_L^{5d}=0.03μ_B/atom

SENSITIVITY OF XMCD

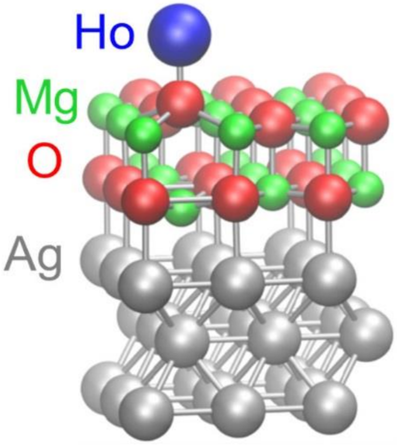


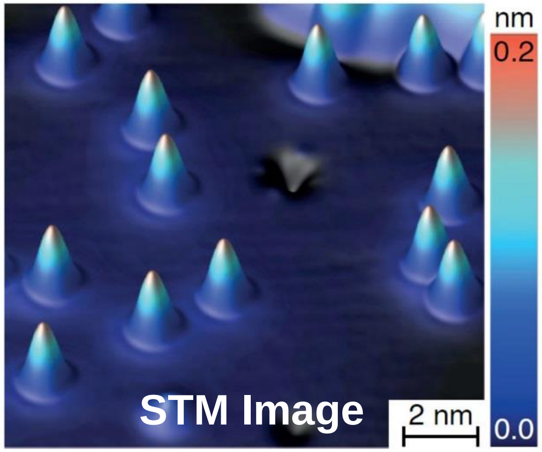
$\langle S_z \rangle = 0.0353(5)\mu_B$ $\langle L_z \rangle = 0.0054(5)\mu_B$ (per Au atom)

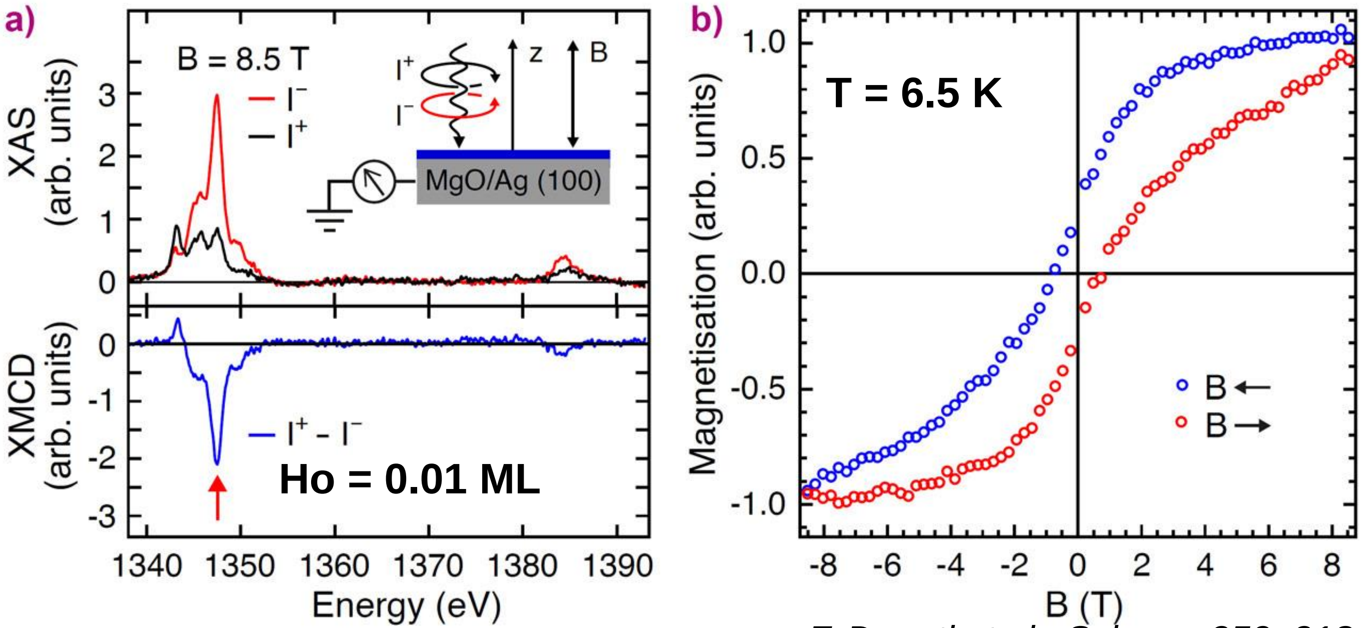
To compare with $4.15\mu_B$ per Mn atom

SENSITIVITY OF XMCD: A SINGLE SURFACE-ADSORBED ATOM

Ho atoms on a two-monolayer-thick MgO film deposited on Ag(100)



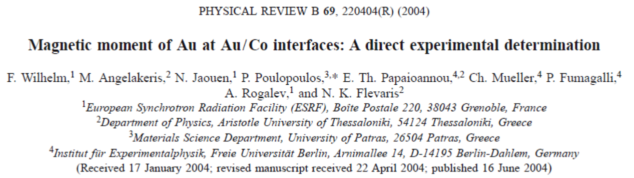




ESRF ID32

F. Donati et al., Science 352, 318-321 (2016)

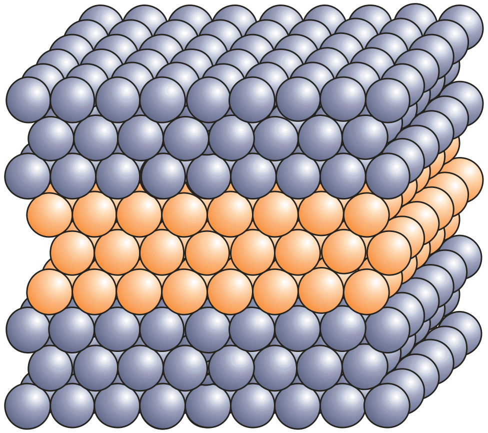
INDUCED MAGNETISM ON GOLD ATOMS

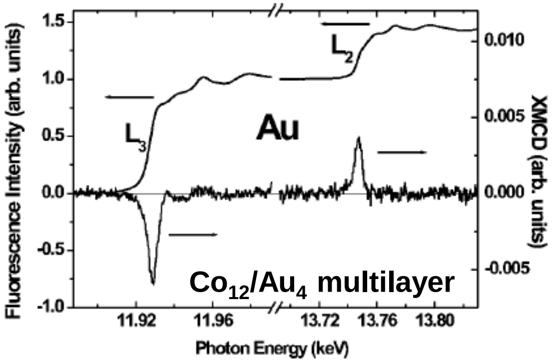


PHYSICAL REVIEW B **69**, 220404(R) (2004)

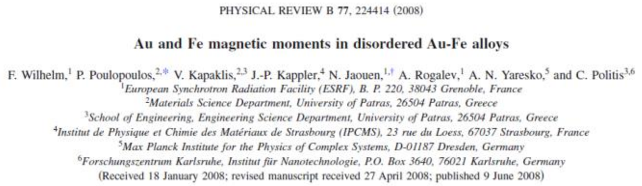
Magnetic moment of Au at Au/Co interfaces: A direct experimental determination

F. Wilhelm,[1] M. Angelakeris,[2] N. Jaouen,[1] P. Poulopoulos,[3,*] E. Th. Papaioannou,[4,2] Ch. Mueller,[4] P. Fumagalli,[4]
A. Rogalev,[1] and N. K. Flevaris[2]
[1]*European Synchrotron Radiation Facility (ESRF), Boîte Postale 220, 38043 Grenoble, France*
[2]*Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*
[3]*Materials Science Department, University of Patras, 26504 Patras, Greece*
[4]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany*
(Received 17 January 2004; revised manuscript received 22 April 2004; published 16 June 2004)





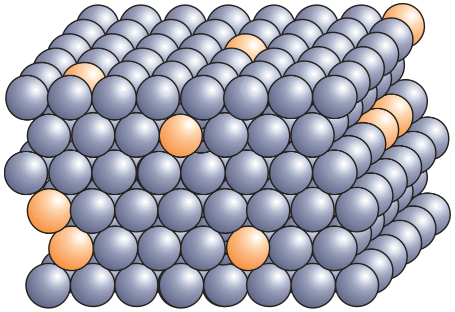
$\mu_{tot}^{Au} \approx 0.031\mu_B/atom$

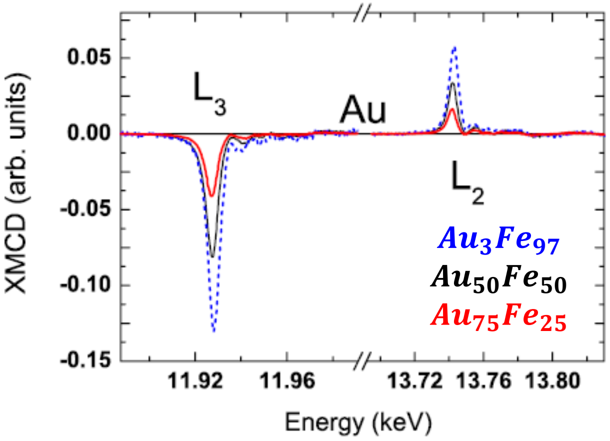


PHYSICAL REVIEW B **77**, 224414 (2008)

Au and Fe magnetic moments in disordered Au-Fe alloys

F. Wilhelm,[1] P. Poulopoulos,[2,*] V. Kapaklis,[2,3] J.-P. Kappler,[4] N. Jaouen,[1,†] A. Rogalev,[1] A. N. Yaresko,[5] and C. Politis[3,6]
[1]*European Synchrotron Radiation Facility (ESRF), B. P. 220, 38043 Grenoble, France*
[2]*Materials Science Department, University of Patras, 26504 Patras, Greece*
[3]*School of Engineering, Engineering Science Department, University of Patras, 26504 Patras, Greece*
[4]*Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), 23 rue du Loess, 67037 Strasbourg, France*
[5]*Max Planck Institute for the Physics of Complex Systems, D-01187 Dresden, Germany*
[6]*Forschungszentrum Karlsruhe, Institut für Nanotechnologie, P.O. Box 3640, 76021 Karlsruhe, Germany*
(Received 18 January 2008; revised manuscript received 27 April 2008; published 9 June 2008)

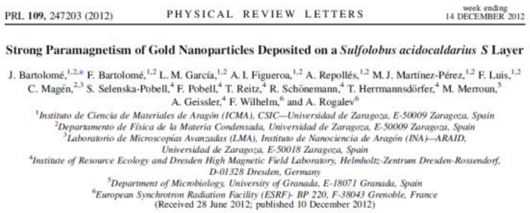




$\mu_{tot}^{Au} \approx 0.33\mu_B/atom$

$\mu_{tot}^{Au} \approx 0.197\mu_B/atom$

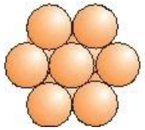
$\mu_{tot}^{Au} \approx 0.099\mu_B/atom$

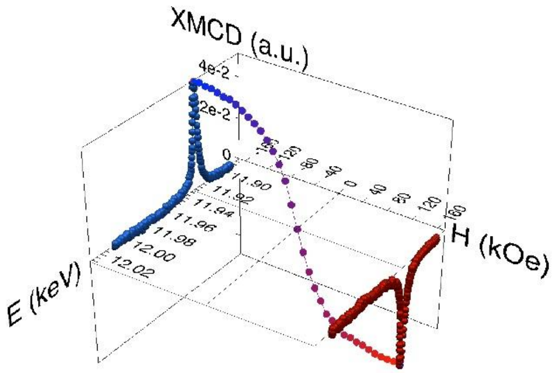


PRL **109**, 247203 (2012) PHYSICAL REVIEW LETTERS week ending 14 DECEMBER 2012

Strong Paramagnetism of Gold Nanoparticles Deposited on a *Sulfolobus acidocaldarius S* Layer

J. Bartolomé,[1,2,*] F. Bartolomé,[1,2] L. M. García,[1,2] A. I. Figueroa,[1,2] A. Repollés,[1,2] M. J. Martínez-Pérez,[1,2] F. Luis,[1,2]
C. Magén,[2,3] S. Selenska-Pobell,[4] F. Pobell,[4] T. Reitz,[4] R. Schönemann,[4] T. Herrmannsdörfer,[4] M. Merroun,[5]
A. Geissler,[4] F. Wilhelm,[6] and A. Rogalev[6]
[1]*Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC—Universidad de Zaragoza, E-50009 Zaragoza, Spain*
[2]*Departamento de Física de la Materia Condensada, Universidad de Zaragoza, E-50009 Zaragoza, Spain*
[3]*Laboratorio de Microscopías Avanzadas (LMA), Instituto de Nanociencia de Aragón (INA)—ARAID,*
Universidad de Zaragoza, E-50018 Zaragoza, Spain
[4]*Institute of Resource Ecology and Dresden High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf,*
D-01328 Dresden, Germany
[5]*Department of Microbiology, University of Granada, E-18071 Granada, Spain*
[6]*European Synchrotron Radiation Facility (ESRF)- BP 220, F-38043 Grenoble, France*
(Received 28 June 2012; published 10 December 2012)





$\mu_{tot}^{Au} \approx 0.051\mu_B/atom$

(T = 2.3K; H = 17 T)

OUTLINE

- Introduction to X-ray Magnetic Circular Dichroism
- **Experimental aspects: ID12 beamline at the ESRF**
- Selected Results
    - ☐ Single molecular magnets
    - ☐ Orbital magnetic moment in actinides
- Conclusions

XMCD EXPERIMENT

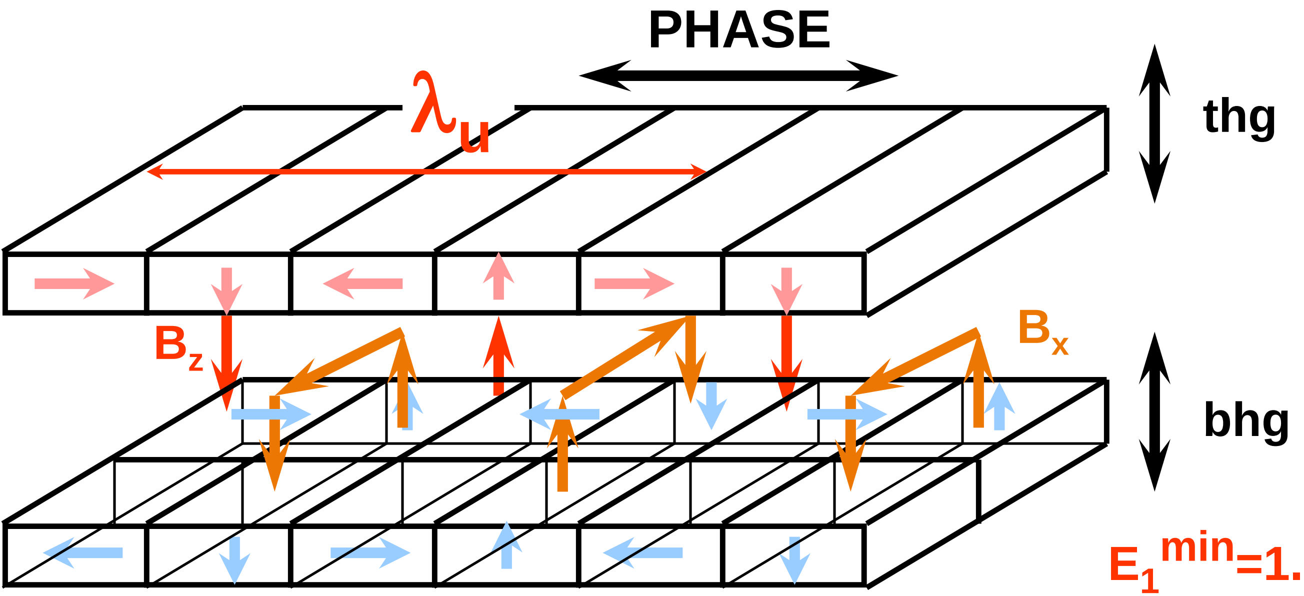
Quantity to measure: $\Delta\mu = \mu^{+} - \mu^{-}$

μ^{+}, μ^{-} => Absorption cross-sections for CP X-rays with
(+) helicity *parallel* to the sample magnetization
(-) helicity *antiparallel* to the sample magnetization

- ☐ **Source of monochromatic circularly polarized X-rays**
- ☐ **Magnetic field to magnetize a sample**
- ☐ **Highly performing X-ray detectors**

The best possible at the 3rd generation synchrotron radiation facilities

SOURCE OF CIRCULARLY POLARIZED X-RAYS



31 periods

λ_u = 52 mm

thg = 6.0 mm
(B_z=0.493 T)
bhg = 6.0 mm
(B_x=0.349 T)

E_1^{min}=1.7 keV, E_1^{max}=6.2 keV

*P. Elleaume, J. of Syn. Rad., **1**, 19-26 (1994)*

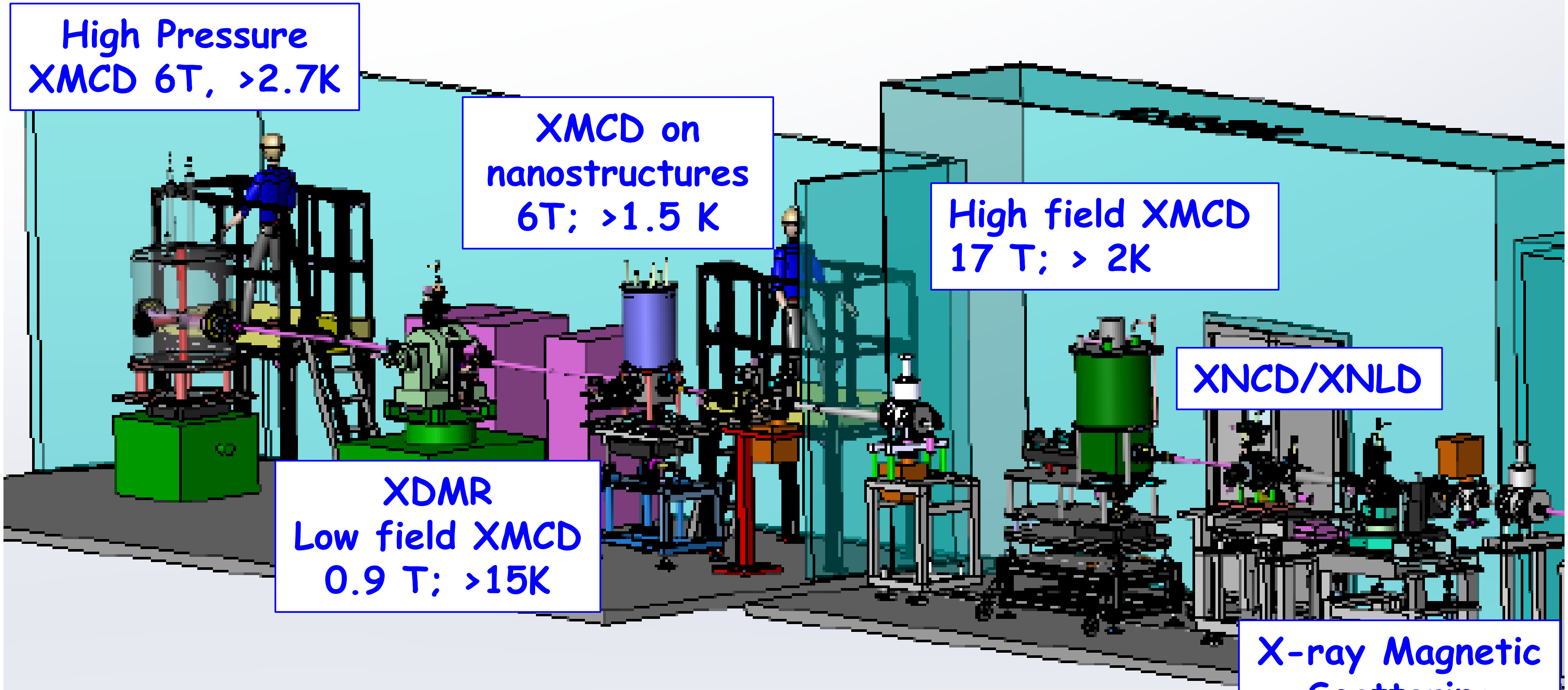
Flux: 10^{14} ph/s/0.1%bw

Full control of polarization: flipping time ~ 5 seconds

$B_x = B_z$

PHASE	$-\lambda_u/4$	0	$\lambda_u/4$	$\lambda_u/2$

ESRF BEAMLINE ID12



High Pressure
XMCD 6T, >2.7K

XMCD on
nanostructures
6T; >1.5 K

High field XMCD
17 T; > 2K

XNCD/XNLD

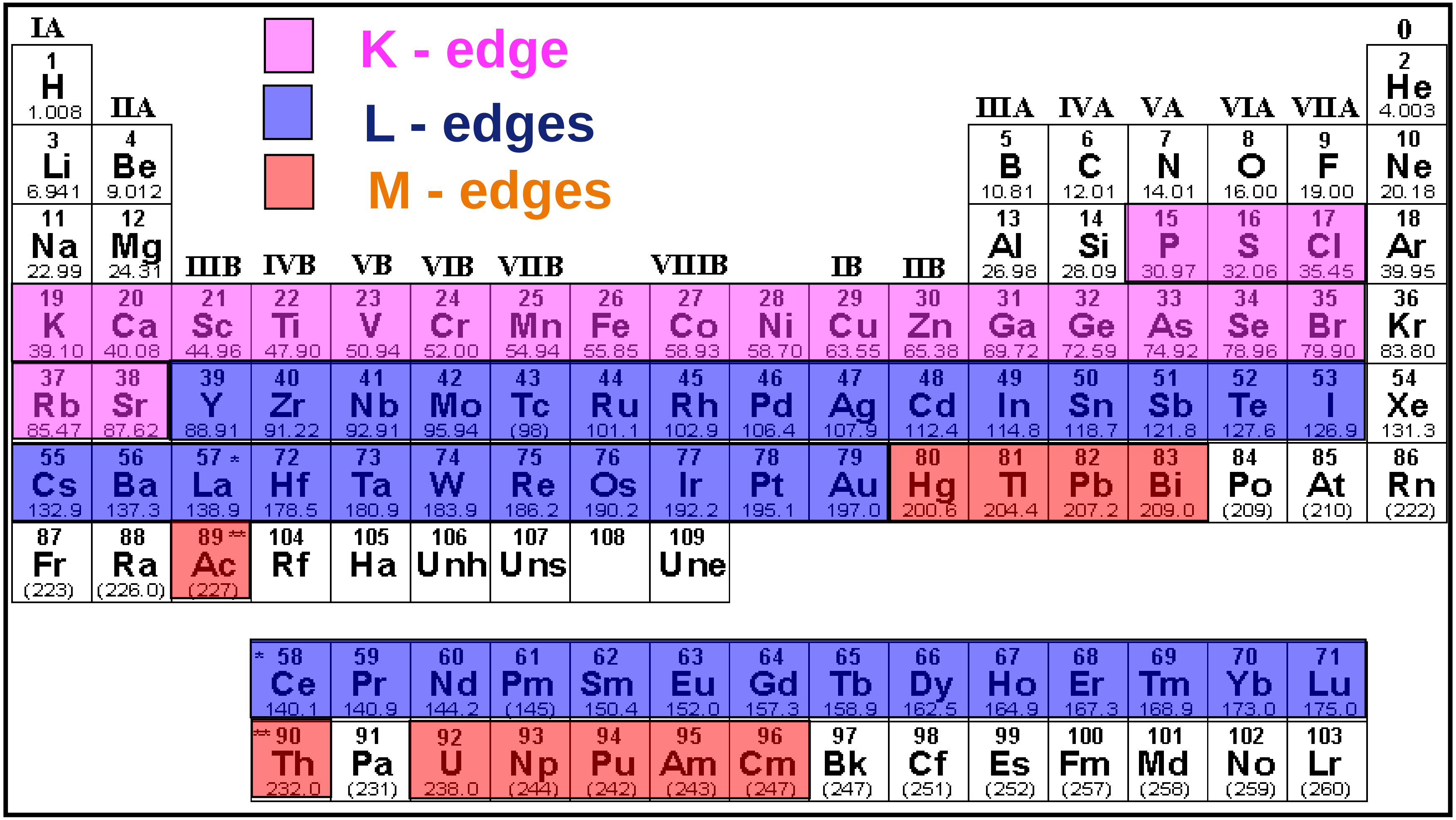
XDMR
Low field XMCD
0.9 T; >15K

X-ray Magnetic
Scattering
$0 < \Theta_B < 18^\circ$
0.6 T; >20K

Spot size 1μm(V) x 20μm(H) with
Be refractive lenses
over whole spectral range 2-15 keV

ESRF BEAMLINE ID12

2.05 keV - 15 keV



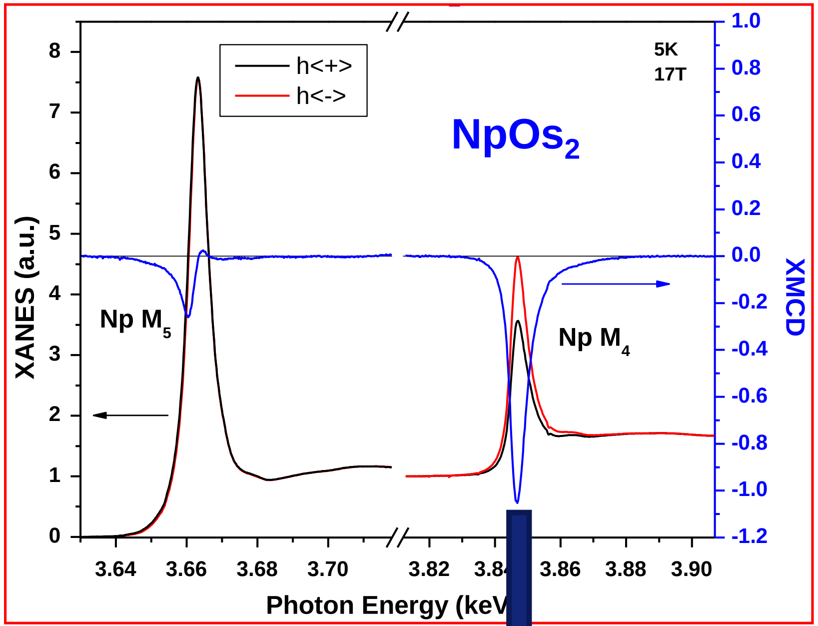
🟪 K - edge

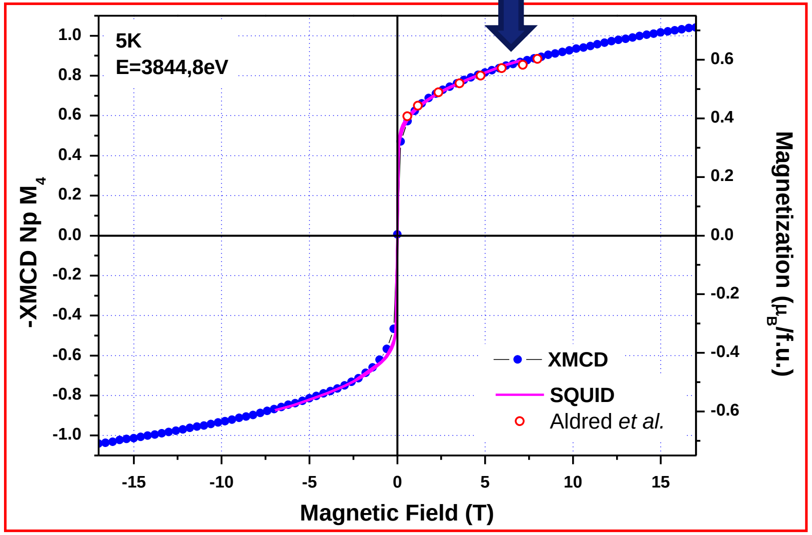
🟦 L - edges

🟥 M - edges

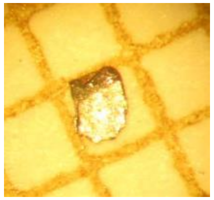
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	🟪 15 P 30.97	🟪 16 S 32.06	🟪 17 Cl 35.45	18 Ar 39.95
🟪 19 K 39.10	🟪 20 Ca 40.08	🟪 21 Sc 44.96	🟪 22 Ti 47.90	🟪 23 V 50.94	🟪 24 Cr 52.00	🟪 25 Mn 54.94	🟪 26 Fe 55.85	🟪 27 Co 58.93	🟪 28 Ni 58.70	🟪 29 Cu 63.55	🟪 30 Zn 65.38	🟪 31 Ga 69.72	🟪 32 Ge 72.59	🟪 33 As 74.92	🟪 34 Se 78.96	🟪 35 Br 79.90	36 Kr 83.80
🟪 37 Rb 85.47	🟪 38 Sr 87.62	🟦 39 Y 88.91	🟦 40 Zr 91.22	🟦 41 Nb 92.91	🟦 42 Mo 95.94	🟦 43 Tc (98)	🟦 44 Ru 101.1	🟦 45 Rh 102.9	🟦 46 Pd 106.4	🟦 47 Ag 107.9	🟦 48 Cd 112.4	🟦 49 In 114.8	🟦 50 Sn 118.7	🟦 51 Sb 121.8	🟦 52 Te 127.6	🟦 53 I 126.9	54 Xe 131.3
🟦 55 Cs 132.9	🟦 56 Ba 137.3	🟦 57 * La 138.9	🟦 72 Hf 178.5	🟦 73 Ta 180.9	🟦 74 W 183.9	🟦 75 Re 186.2	🟦 76 Os 190.2	🟦 77 Ir 192.2	🟦 78 Pt 195.1	🟦 79 Au 197.0	🟥 80 Hg 200.6	🟥 81 Tl 204.4	🟥 82 Pb 207.2	🟥 83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226.0)	🟥 89 ** Ac (227)	104 Rf	105 Ha	106 Unh	107 Uns	108	109 Une									
			🟦 * 58 Ce 140.1	🟦 59 Pr 140.9	🟦 60 Nd 144.2	🟦 61 Pm (145)	🟦 62 Sm 150.4	🟦 63 Eu 152.0	🟦 64 Gd 157.3	🟦 65 Tb 158.9	🟦 66 Dy 162.5	🟦 67 Ho 164.9	🟦 68 Er 167.3	🟦 69 Tm 168.9	🟦 70 Yb 173.0	🟦 71 Lu 175.0	
			🟥 ** 90 Th 232.0	91 Pa (231)	🟥 92 U 238.0	🟥 93 Np (244)	🟥 94 Pu (242)	🟥 95 Am (243)	🟥 96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)	

HIGH FIELD XMCD END-STATION





H < ± 17 Tesla, T > 2.0 K



Typical sample size
0.65mm X 0.80mmx0.12mm

Aldred et al., ***PRB10, 1011(1974)*** ***Wilhelm et al.***, ***PRB 88, 024424 (2013)***

X-ray Magnetic Circular Dichroism is a unique tool to study microscopic magnetic properties

- Element-specific and orbital-selective magnetometry tool
- Sensitive to the electronic structure (valence state, symmetry,…)
- Possibility to extract Spin and Orbital magnetic moments of absorbing atoms only
- Small size samples (focusing the x-ray beam)
- Single crystals, polycrystalline and amorphous materials, thin films, nanoparticles, monolayers, ad-atoms, …

OUTLINE

- Introduction to X-ray Magnetic Circular Dichroism
- Experimental aspects: ID12 beamline at the ESRF
- Selected Results
  - ☐ Single molecular magnets
  - ☐ Orbital magnetic moment in actinides
- Conclusions

MAGNETIC STRUCTURES

classical

nanoscopic

quantum

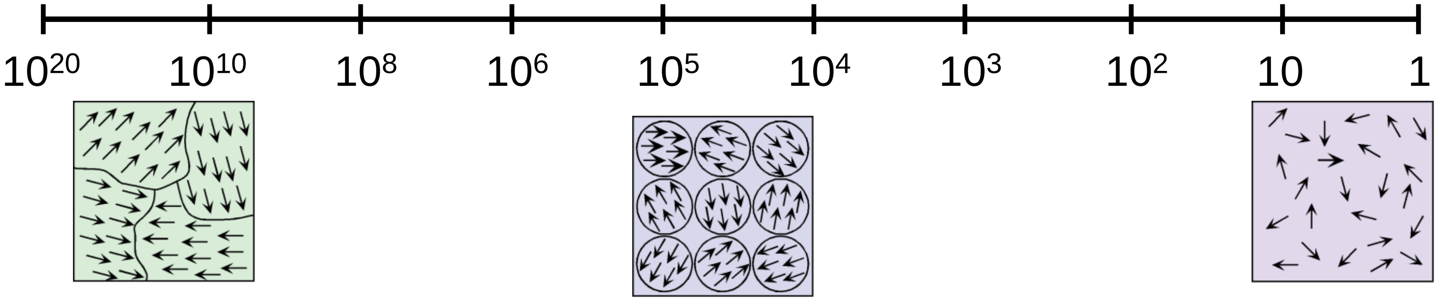
permanent magnets

micro-particles

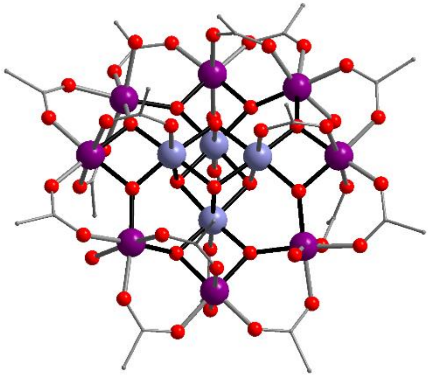
nano-particles

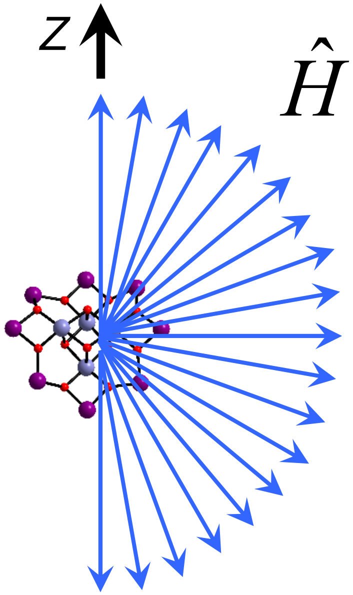
clusters

Paramagnets and Single-molecule magnets



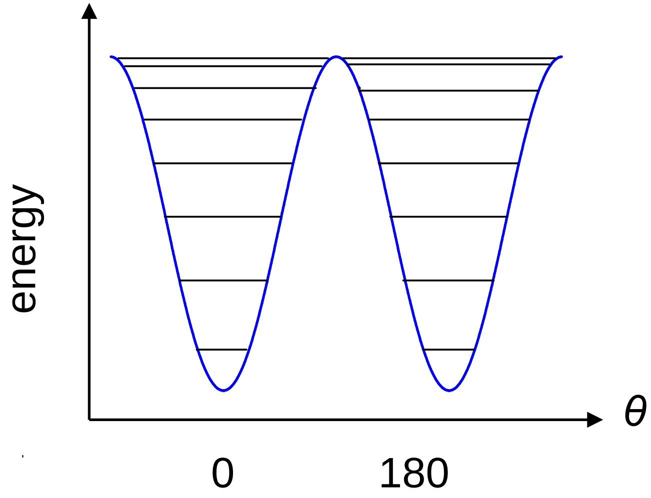
$Mn_{12}ac$





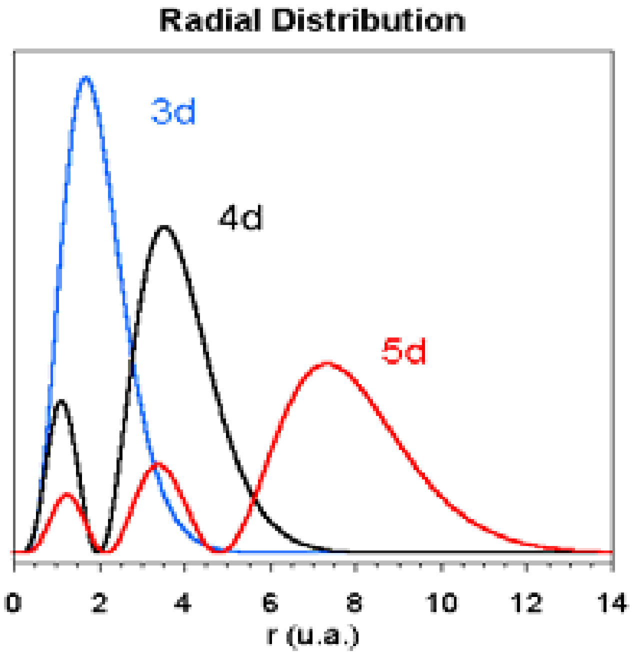
$$\hat{H} = D\hat{S}_Z^{\,2}$$

$$\tau(T) = \tau_0 \exp\{\Delta_{\mathrm{eff}} /(k_B T)\}$$

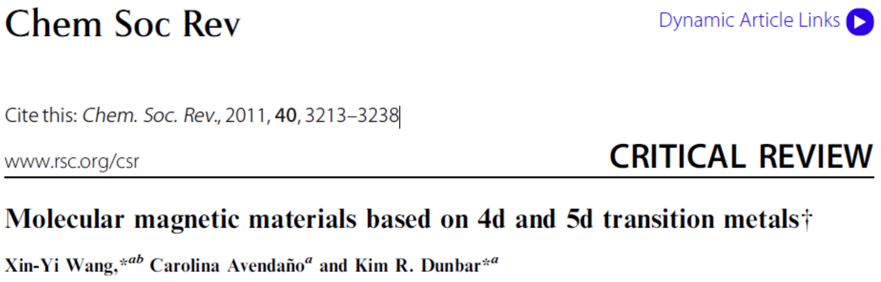


Low temperature!

4D/5D IONS IN SINGLE MOLECULAR MAGNETS



$$\lambda = \tfrac{1}{2} m_e Z^4 \alpha^4 c^2 \frac{1}{n^3 l(l+\frac{1}{2})(l+1)}$$



Chem Soc Rev

Dynamic Article Links

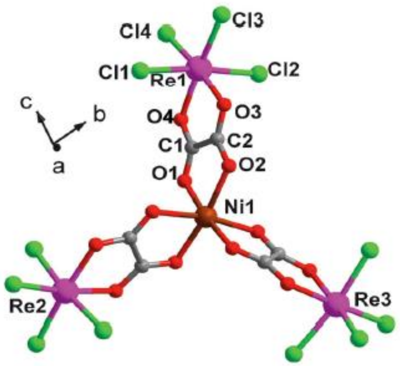
Cite this: *Chem. Soc. Rev.*, 2011, **40**, 3213–3238

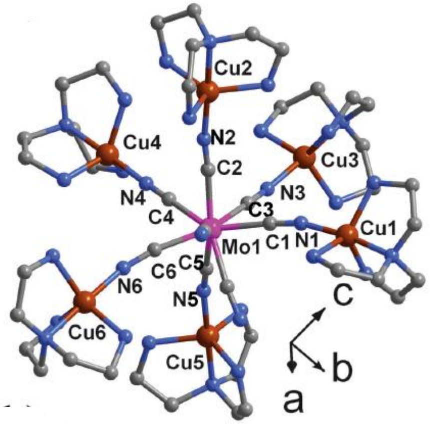
www.rsc.org/csr

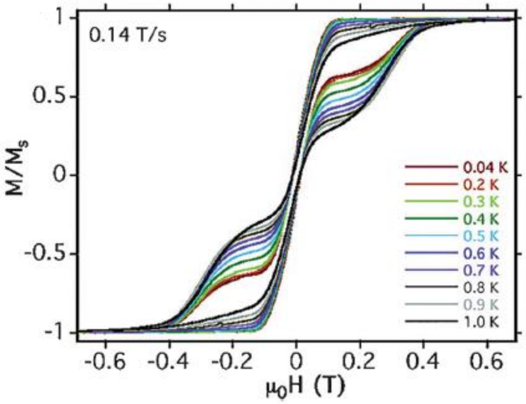
CRITICAL REVIEW

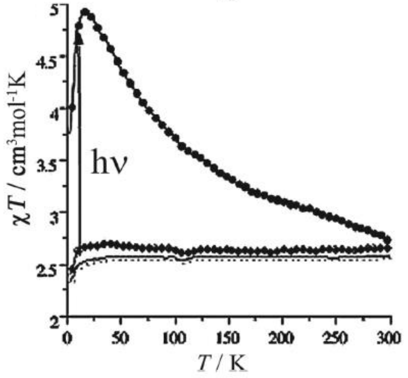
Molecular magnetic materials based on 4d and 5d transition metals†

Xin-Yi Wang,*[ab] Carolina Avendaño[a] and Kim R. Dunbar*[a]







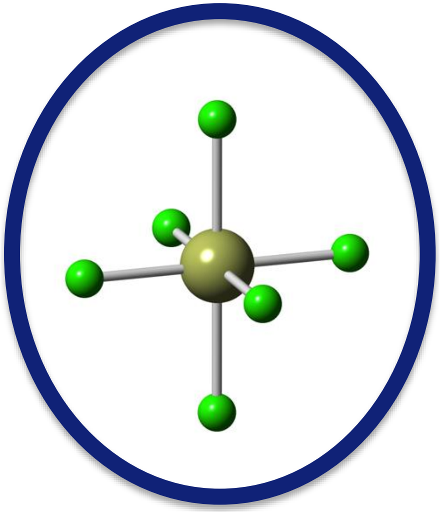


EXOTIC MAGNETIC PHENOMENA IN “IRIDATES”

$\{IrO_6\}^{8-}$

$[IrF_6]$

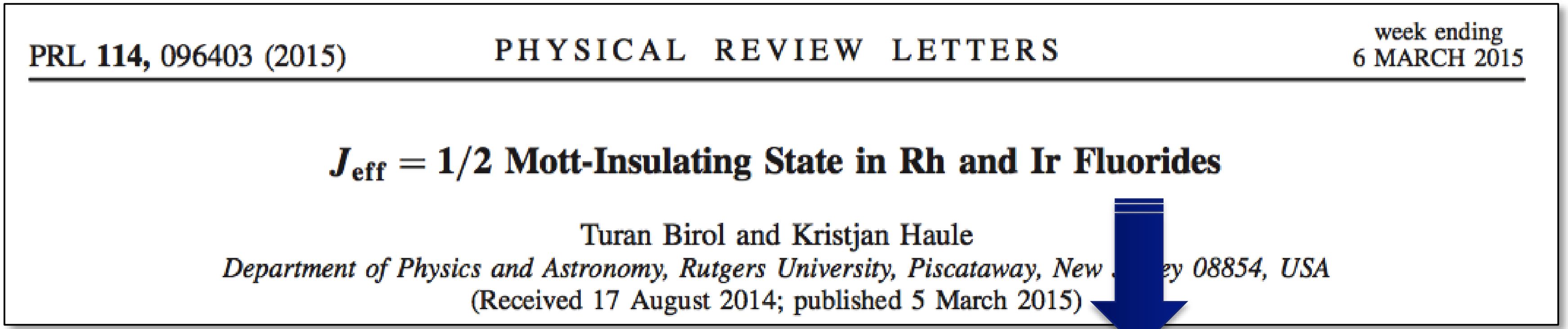
$Sr\ IrO_4$



Electronegativity
Mass and size
Redox-innocence
….

also:

(pyrochlores)
(honeycomb)
(hyperkagome)



PRL **114,** 096403 (2015) PHYSICAL REVIEW LETTERS week ending 6 MARCH 2015

$J_{\text{eff}} = 1/2$ Mott-Insulating State in Rh and Ir Fluorides

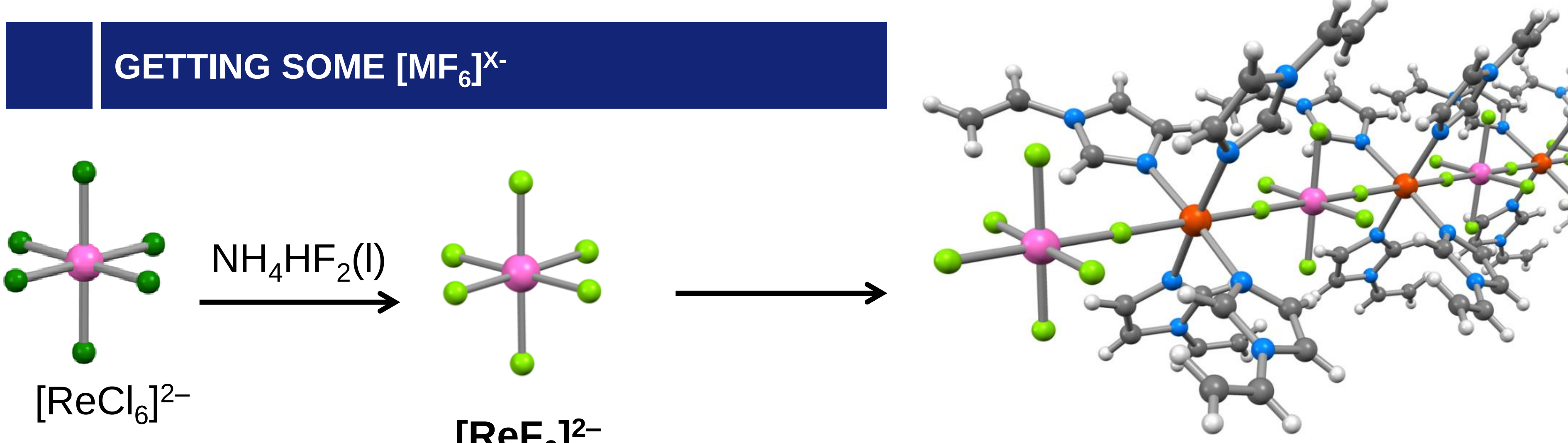
Turan Birol and Kristjan Haule
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA
(Received 17 August 2014; published 5 March 2015)

$[IrF_6]^{2-}$

Kim et al. *Phys. Rev. Lett.* **2008**, *101*, 076402
Kim et al. *Science*, **2009**, *323*, 132
Machida et al. *Nature* **2010**, *463*, 210
Modic et al. *Nat. Commun.* **2014**, *5*, 4203

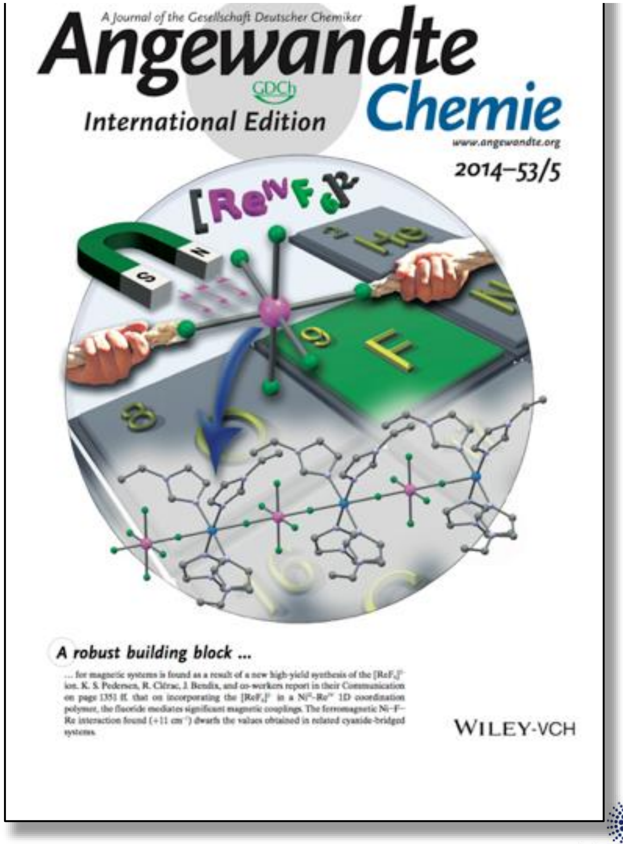
Chun *et al. Nat. Phys.* **2015**, *11*, 462
Chen *et al. Nat. Commun.* **2015**, *6*, 6593
Kim et al. *Nat. Phys.* DOI: 10.1038/NPHYS3503
Zhao et al. *Nat. Phys.* DOI: 10.1038/nphys3517

GETTING SOME $[MF_6]^{X-}$



$[ReCl_6]^{2-}$ $\xrightarrow{NH_4HF_2(l)}$ **$[ReF_6]^{2-}$** $\longrightarrow$

K. Pedersen et al, Angew. Chem. Int. Ed. **2014**, *53*, 1351



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

International Edition

GDCh

www.angewandte.org

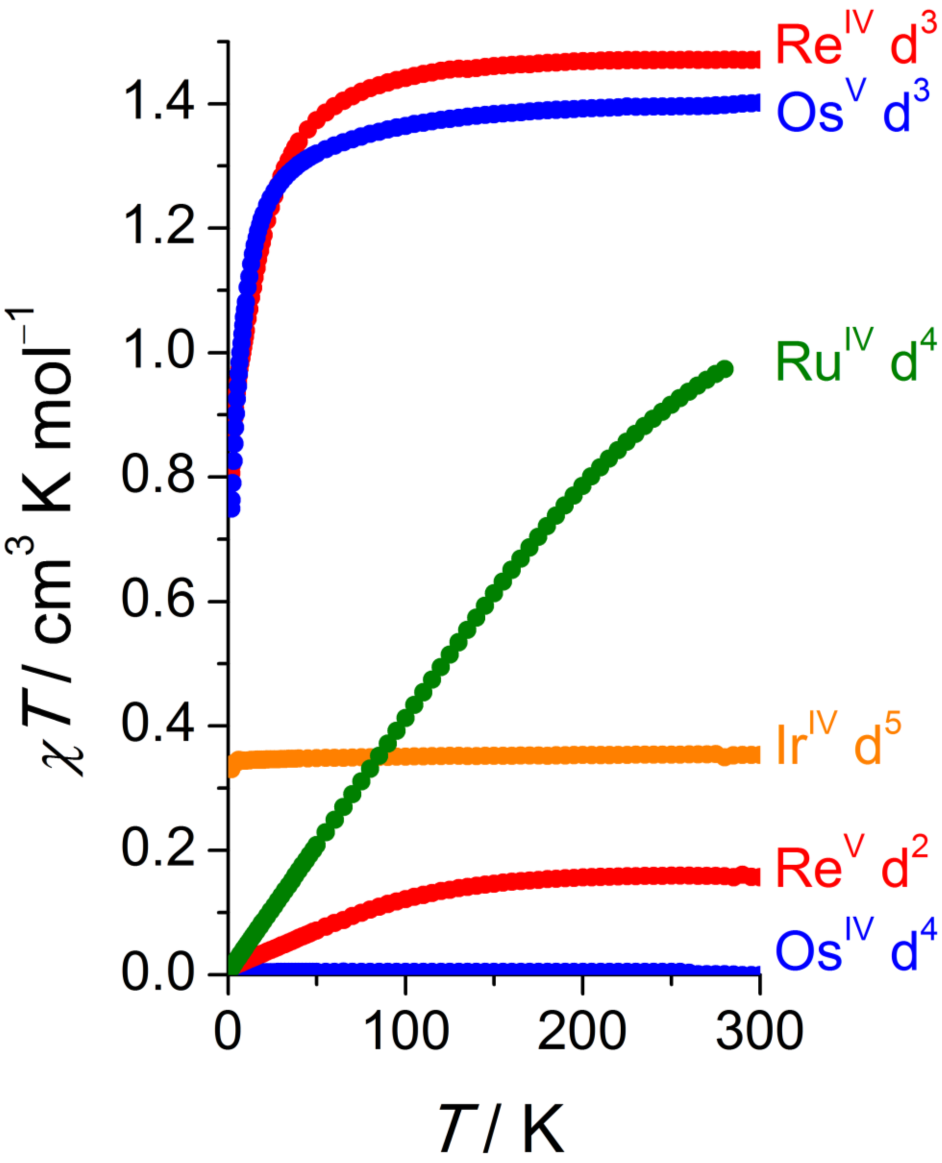
2014–53/5

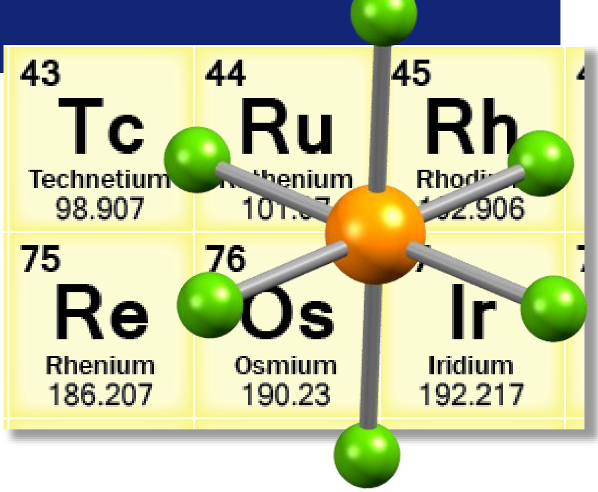
A robust building block ...

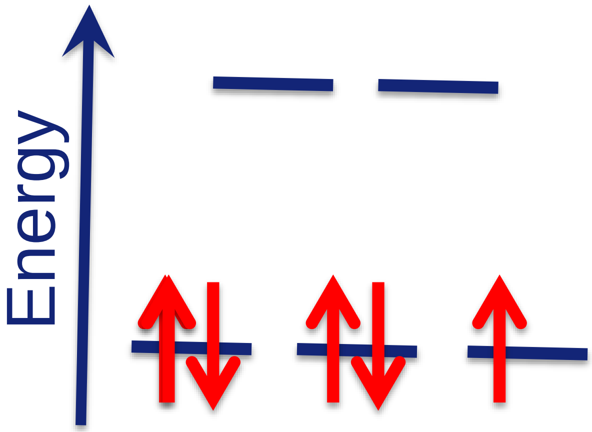
... for magnetic systems is found as a result of a new high-yield synthesis of the $[ReF_6]^{2-}$ ion. K. S. Pedersen, R. Clérac, J. Bendix, and co-workers report in their Communication on page 1351 ff. that on incorporating the $[ReF_6]^{2-}$ in a Ni^{II}–Re^{IV} 1D coordination polymer, the fluoride mediates significant magnetic couplings. The ferromagnetic Ni–F–Re interaction found (+11 cm^{-1}) dwarfs the values obtained in related cyanide-bridged systems.

WILEY-VCH

SOME INDICATIONS OF ORBITAL MAGNETISM

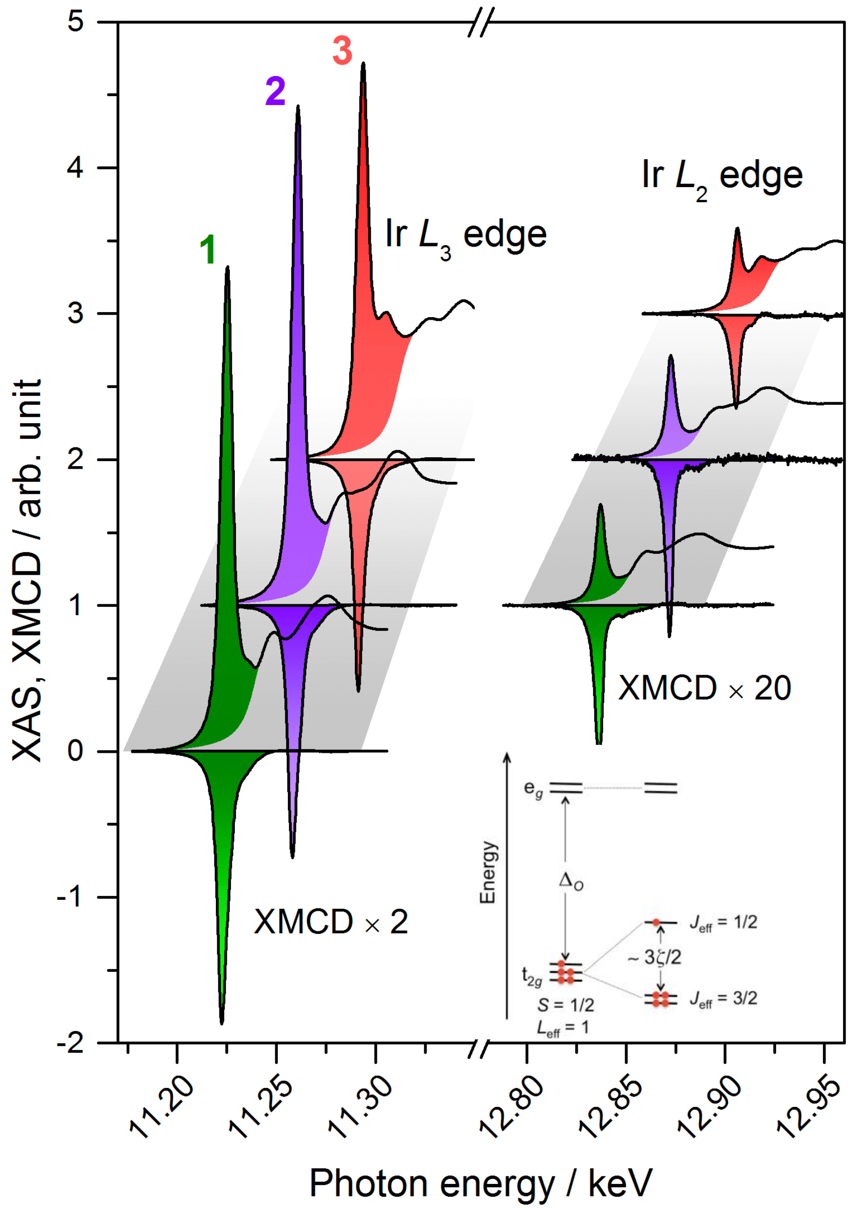






$$\chi T = \frac{g^2}{8} S(S+1)$$

XMCD OF $[IrX_6]^{2-}$ COMPLEXES



ARTICLE

Received 21 Mar 2016 | Accepted 7 Jun 2016 | Published 20 Jul 2016 DOI: 10.1038/ncomms12195 OPEN

Iridates from the molecular side

Kasper S. Pedersen[1,2,3,4], Jesper Bendix[5], Alain Tressaud[3,4], Etienne Durand[3,4], Høgni Weihe[5], Zaher Salman[6], Thorbjørn J. Morsing[5], Daniel N. Woodruff[7], Yanhua Lan[8], Wolfgang Wernsdorfer[8], Corine Mathonière[3,4], Stergios Piligkos[5], Sophia I. Klokishner[9], Serghei Ostrovsky[9], Katharina Ollefs[10,†], Fabrice Wilhelm[10], Andrei Rogalev[10] & Rodolphe Clérac[1,2]

$$\langle L_z \rangle \propto I_{L_3}^{XMCD} + I_{L_2}^{XMCD}$$

$$\langle S_{eff} \rangle \propto I_{L_3}^{XMCD} - 2 \times I_{L_2}^{XMCD}$$

	$[IrF_6]^{2-}$	$[IrCl_6]^{2-}$	Sr_2IrO_4
$\langle S_z \rangle$	0.13	0.15	0.15
$\langle L_z \rangle$	0.77	0.65	0.63

OUTLINE

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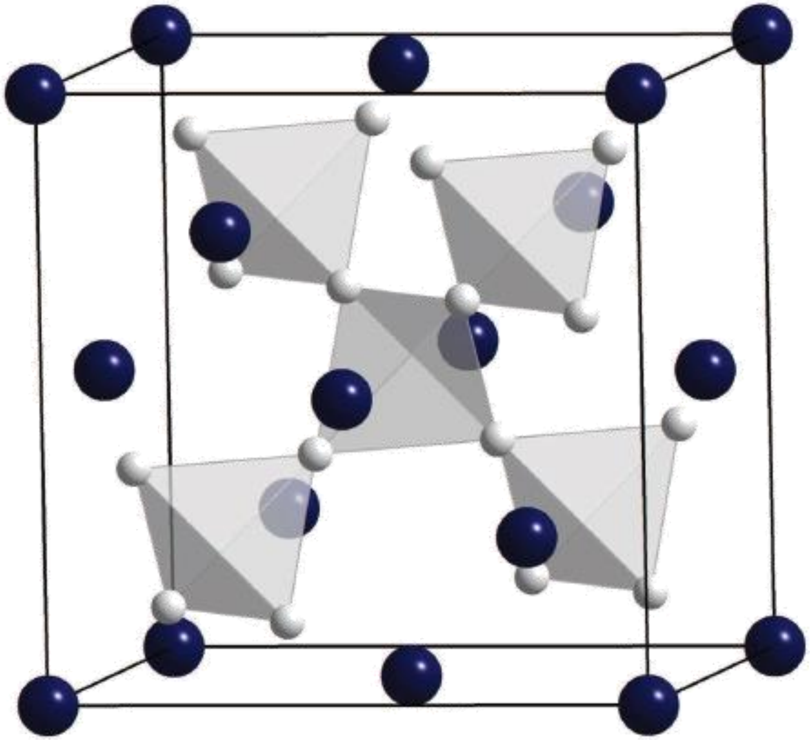
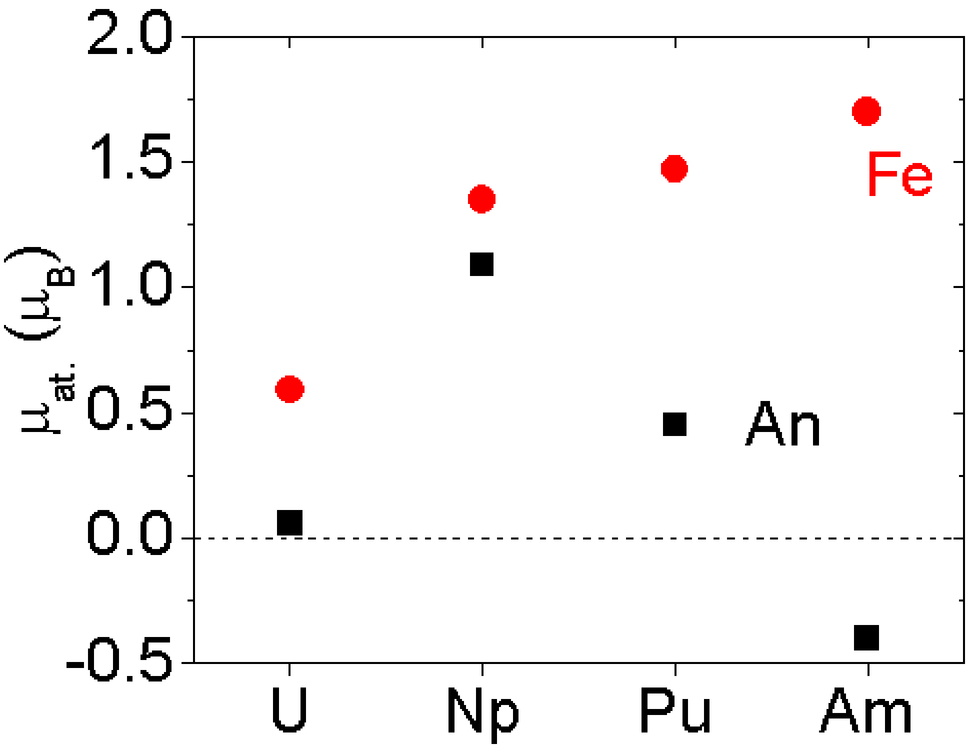
- Conclusions

THE ANFE$_2$ SYSTEM





Laves phase, C-15 structure, fcc unit cell

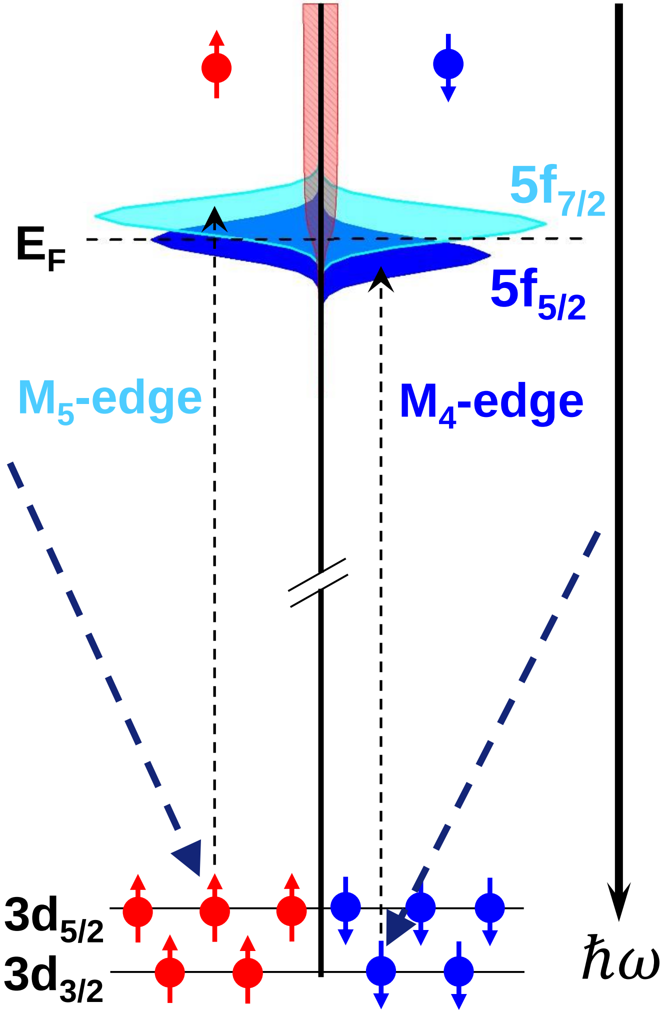
T$_C$s between 160 K (UFe$_2$) and ~700 K (AmFe$_2$)

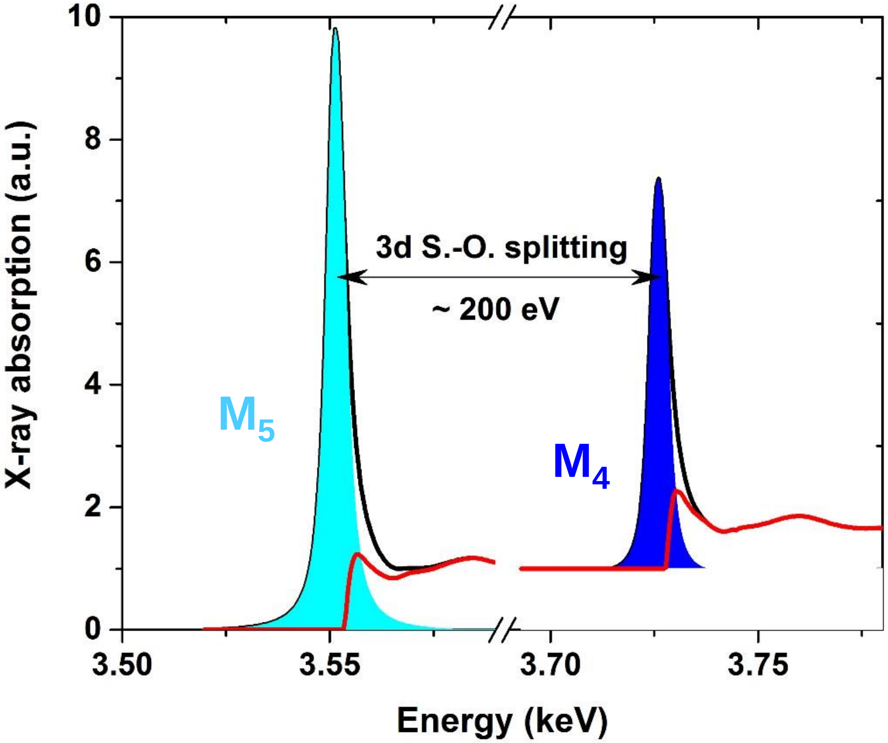
Easy magnetization direction: <111> (U,Np) or <100> (Pu,Am)

X-RAY ABSORPTION SPECTROSCOPY: SPIN-ORBIT SUM RULE

dipolar transitions

$$\Delta l = \pm 1; \Delta s = 0; \Delta j = 0; \pm 1$$

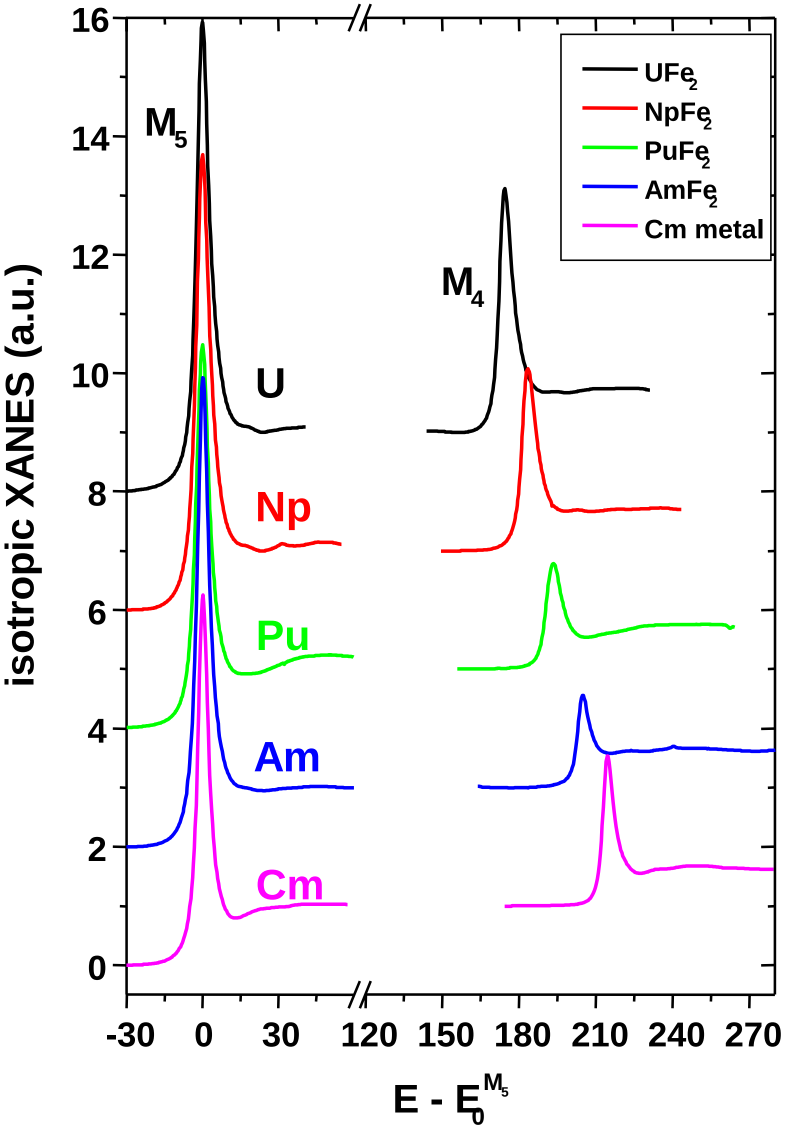




$$I_{M_5} + I_{M_4} \propto n_h^{5f}$$

$$B = \frac{I_{M_5}}{I_{M_5} + I_{M_4}} \qquad < l.s >= \frac{3}{2} n_h^{5f} \left(B - \frac{3}{5} \right) + \Delta$$

$M_{4,5}$ X-RAY ABSORPTION SPECTRA OF ACTINIDES



Intensity of the M_5 XANES spectra decreases from U to Cm

Intensity of the M_4 XANES spectra decreases from U to Pu but increases for Cm

SPIN-ORBIT SUM RULE:

$$< l.s > = -3/4n_h(2I_{M5}-3I_{M4})/(I_{M5}+I_{M4}) + \Delta$$

$$= 3/2\ n_{7/2} - 2\ n_{5/2}$$

Δ = -0.014, -0.010, -0.005, 0.000, +0.005, +0.015

for n_e^{5f} =2, 3, 4, 5, 6, 7

G. van der Laan, Phys. Rev. Lett. 93, 097401 (2004)

APPLICATION OF THE SPIN-ORBIT SUM RULE

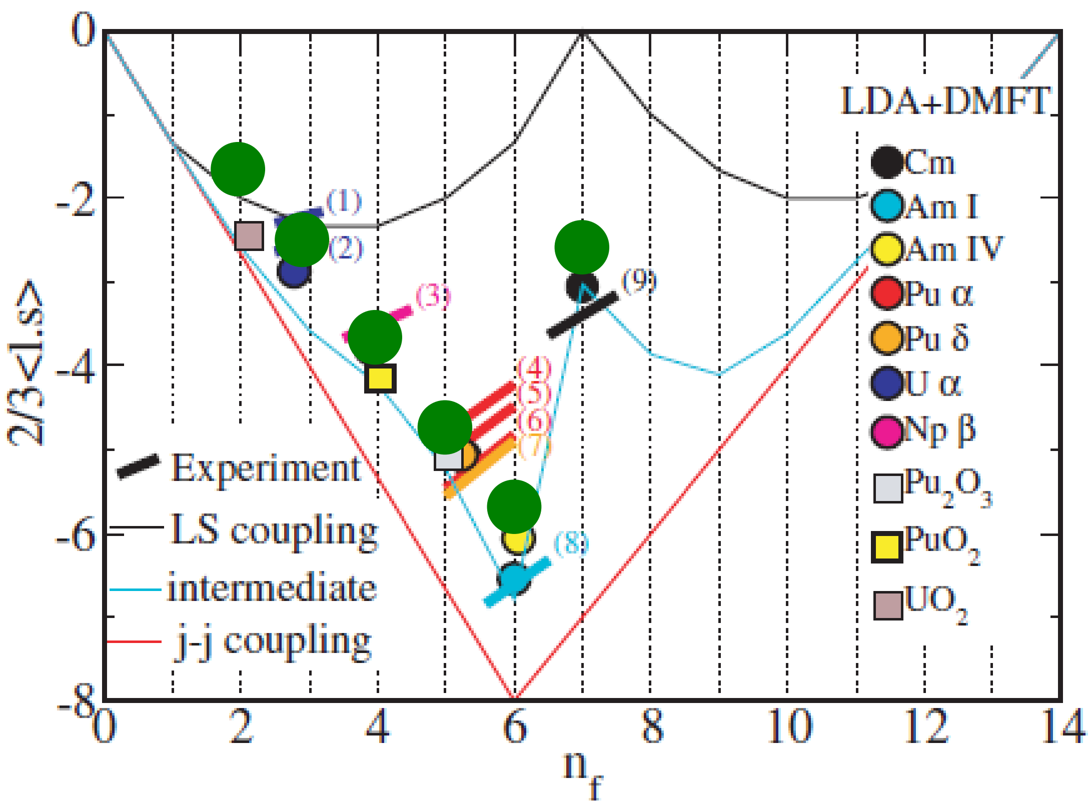
	B	n_e^{5f}	$2/3\langle l.s\rangle$	$n_{5/2}$	$n_{7/2}$
U^{4+}	0.65	2	-1.67	1.57	0.43
α-U^{3+}	0.687	3	-2.52	2.37	0.63
Np	0.742	4	-3.6	3.26	0.74
Pu	0.803	5	-4.56	4.10	0.90
Am	0.88	6	-5.56	4.95	1.05
Cm	0.735	7	-2.26	3.97	3.03

XANES spectra were measured on

- UO_2 for ionic state of U close to $5f^2$ configuration
- U/Fe multilayers, UFe_2 for $5f^3$ configuration
- $NpFe_2$ for $5f^4$ configuration
- $PuFe_2$ for $5f^5$ configuration
- $AmFe_2$ for $5f^6$ configuration
- Cm metal for $5f^7$ configuration

Uncertainty of a few %

APPLICATION OF THE SPIN-ORBIT SUM RULE



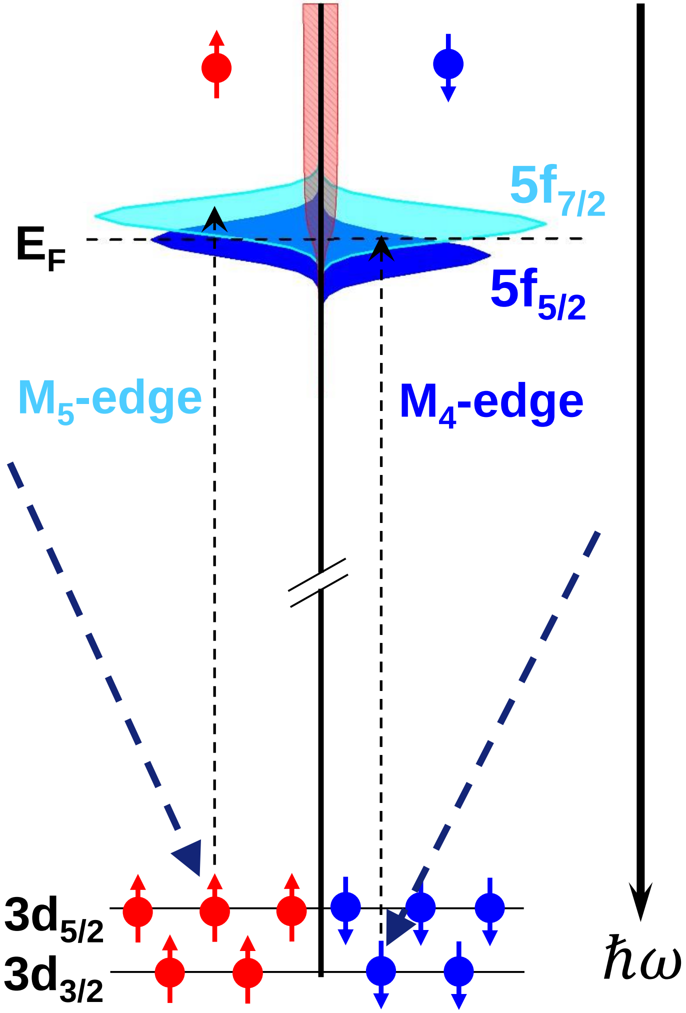
LDA+DMFT : J. H. Shim, K. Haule and G. Kotliar, Euro. Phys. Lett. 85, 17007 (2009)
Atomic multiplets: K. T. Moore and G. van der Laan, Rev. Mod. Phys. 81, 235 (2009)
Experiment: EELS and XAS (K.T. Moore and G. van der Laan)

5f states are well described with intermediate coupling scheme

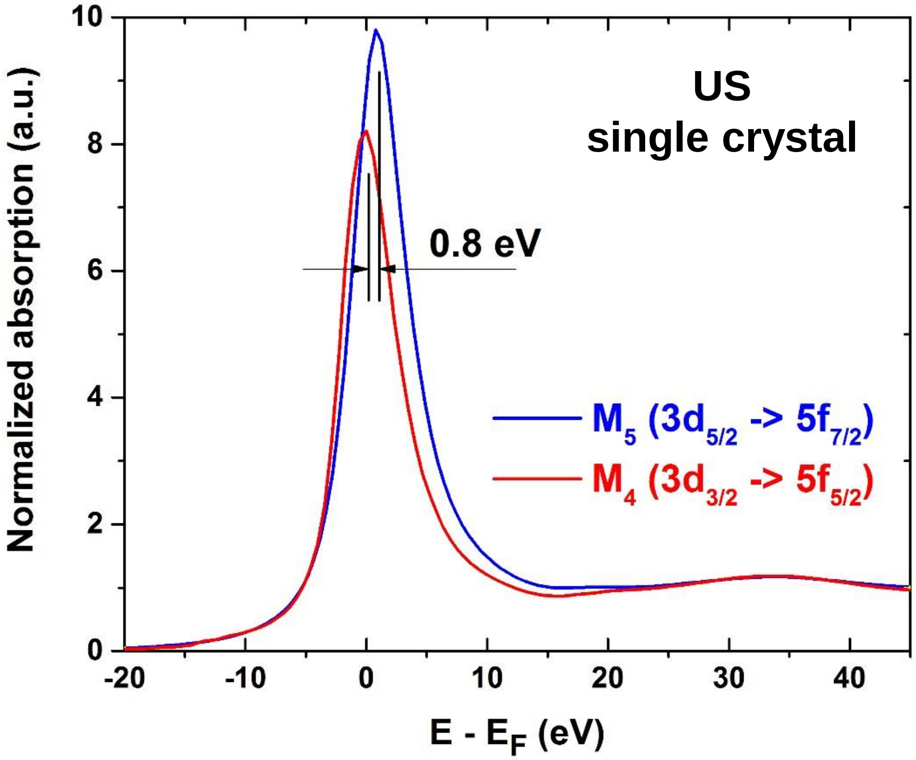
X-RAY ABSORPTION SPECTROSCOPY: SPIN-ORBIT SUM RULE

dipolar transitions

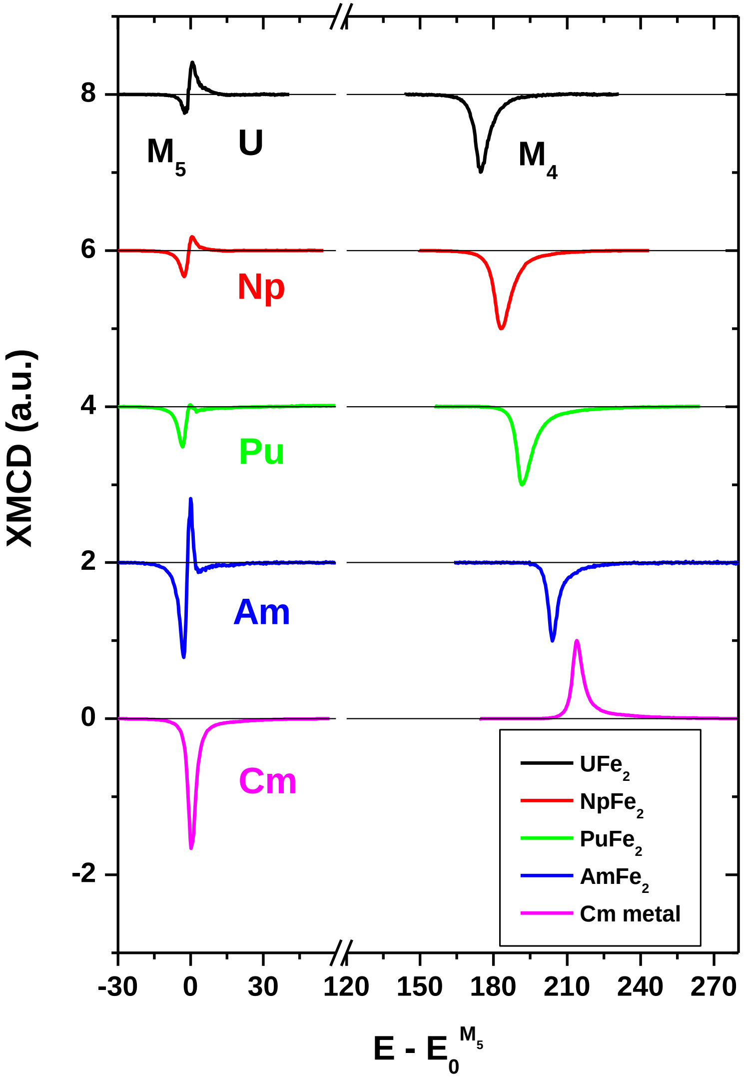
$$\Delta l = \pm 1; \Delta s = 0; \Delta j = 0; \pm 1$$



5f spin-orbit splitting



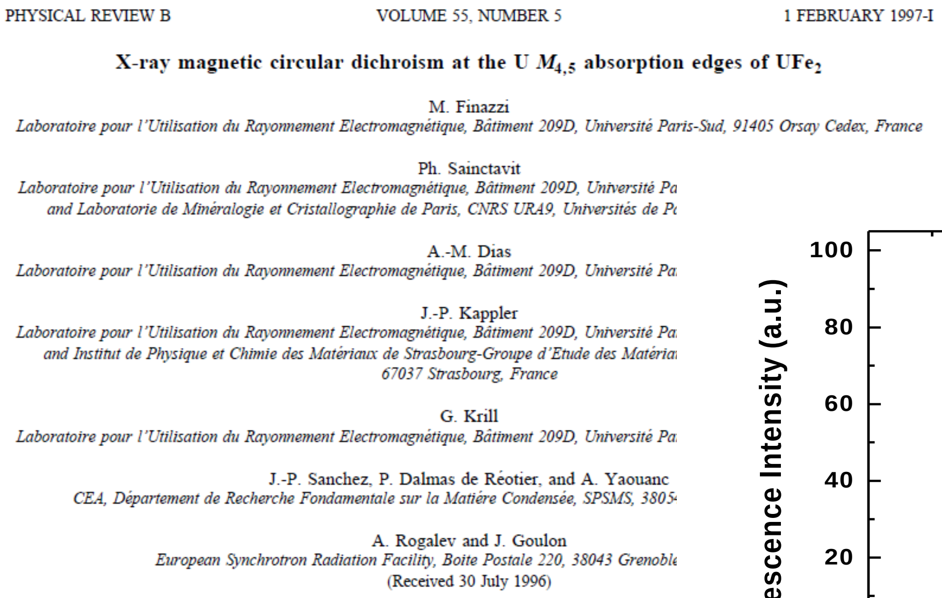
$M_{4,5}$ XMCD OF ACTINIDES



$M_{4,5}$ XMCD spectra normalized to unity at M_4

- **XMCD spectral shape at the M_5-edge has an asymmetric S shape for light actinides (U-Am) but becomes symmetric for Curium metal**
- **XMCD spectral shape at the M_4-edge has slight asymmetry on high energy side and negative for light actinides but changes the sign for Curium metal.**

$M_{4,5}$ XMCD OF ACTINIDES



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X-ray magnetic circular dichroism at the U $M_{4,5}$ absorption edges of UFe_2

M. Finazzi
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Paris-Sud, 91405 Orsay Cedex, France

Ph. Sainctavit
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Pa
and Laboratorie de Minéralogie et Cristallographie de Paris, CNRS URA9, Universités de Pa

A.-M. Dias
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Pa

J.-P. Kappler
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Pa
and Institut de Physique et Chimie des Matériaux de Strasbourg-Groupe d'Etude des Matéria
67037 Strasbourg, France

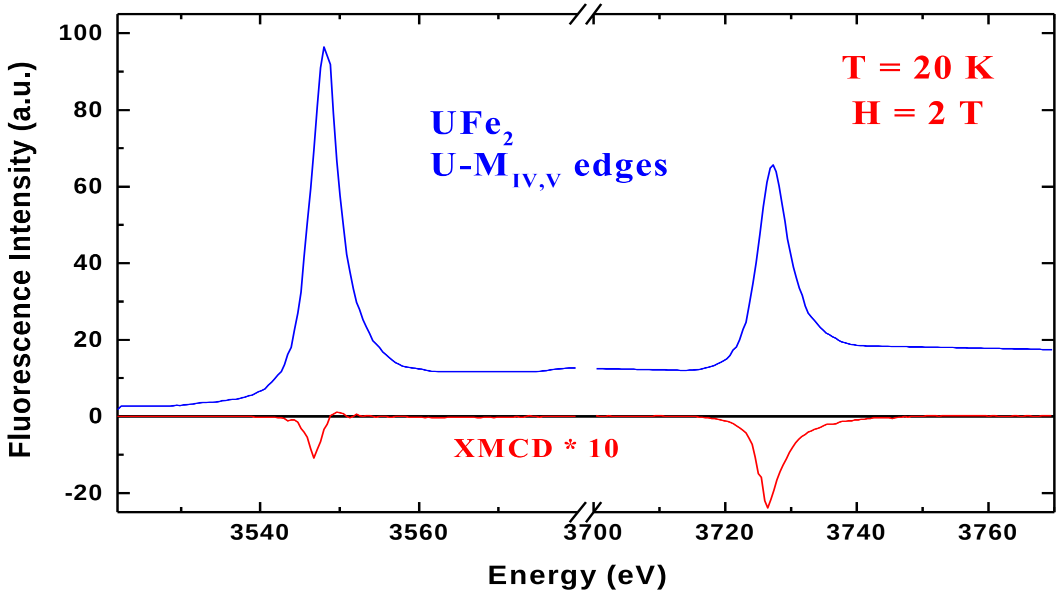
G. Krill
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université Pa

J.-P. Sanchez, P. Dalmas de Réotier, and A. Yaouanc
CEA, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS, 3805

A. Rogalev and J. Goulon
European Synchrotron Radiation Facility, Boite Postale 220, 38043 Grenoble
(Received 30 July 1996)

ferromagnet with $T_c = 160$ K

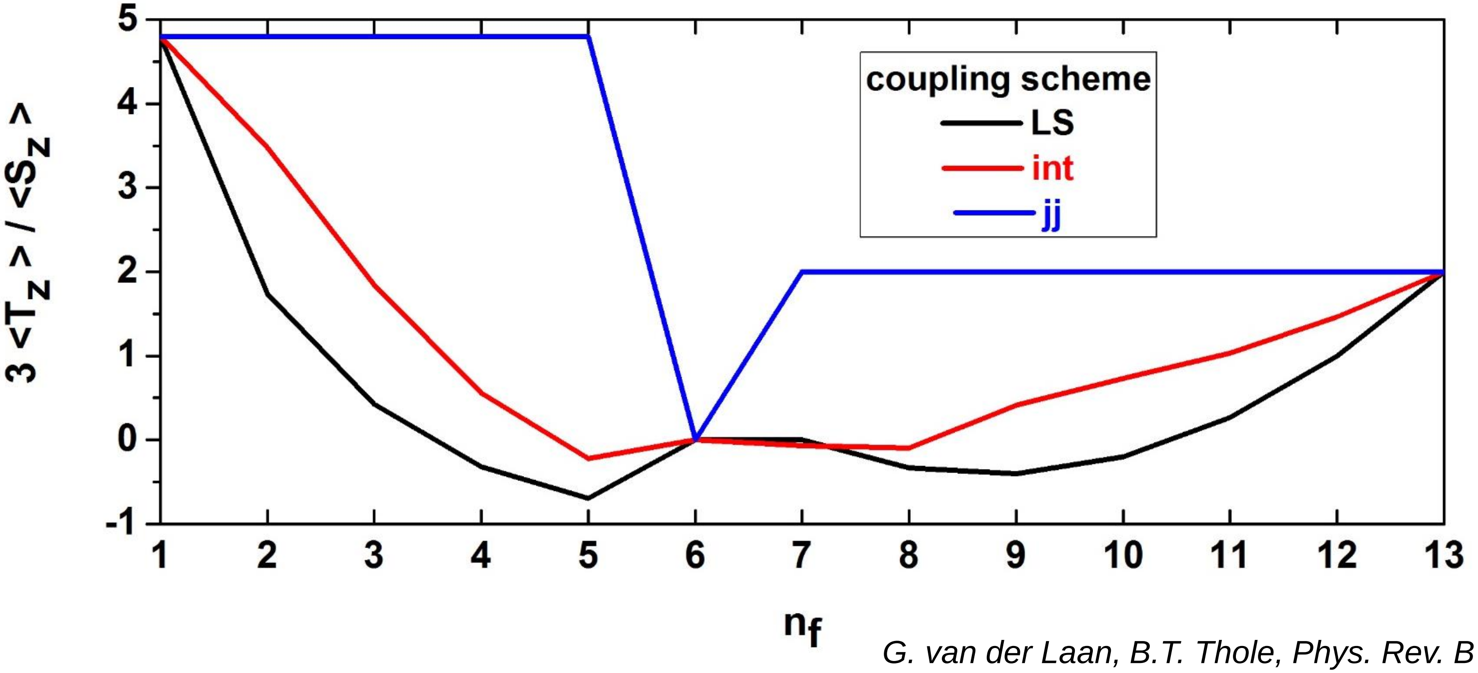
$\mu_{Fe} = 0.58\ \mu_B$ and $\mu_U \sim 0\ \mu_B$



	$\mu_L(\mu B)$	$\mu_S(\mu B)$	$-\mu_L/\mu_S$
XMCD	0.21±0.02	-0.20±0.02	0.97±0.05
Neutron	0.23±0.01	-0.22±0.02	1.05±0.05
Theory	0.47	-0.58	0.81

MAGNETIC DIPOLE TERM

$\langle T_z \rangle$ is a measure of a spin moment anisotropy induced either by a charge quadrupole moment or by the spin-orbit interaction



G. van der Laan, B.T. Thole, Phys. Rev. B 53, 14458 (1996)

There are no any direct measurements of this term (so far !!!)

One can estimate $\langle T_Z \rangle$ *via* combination of XMCD with Neutron scattering, magnetic Compton scattering or SQUID measurements

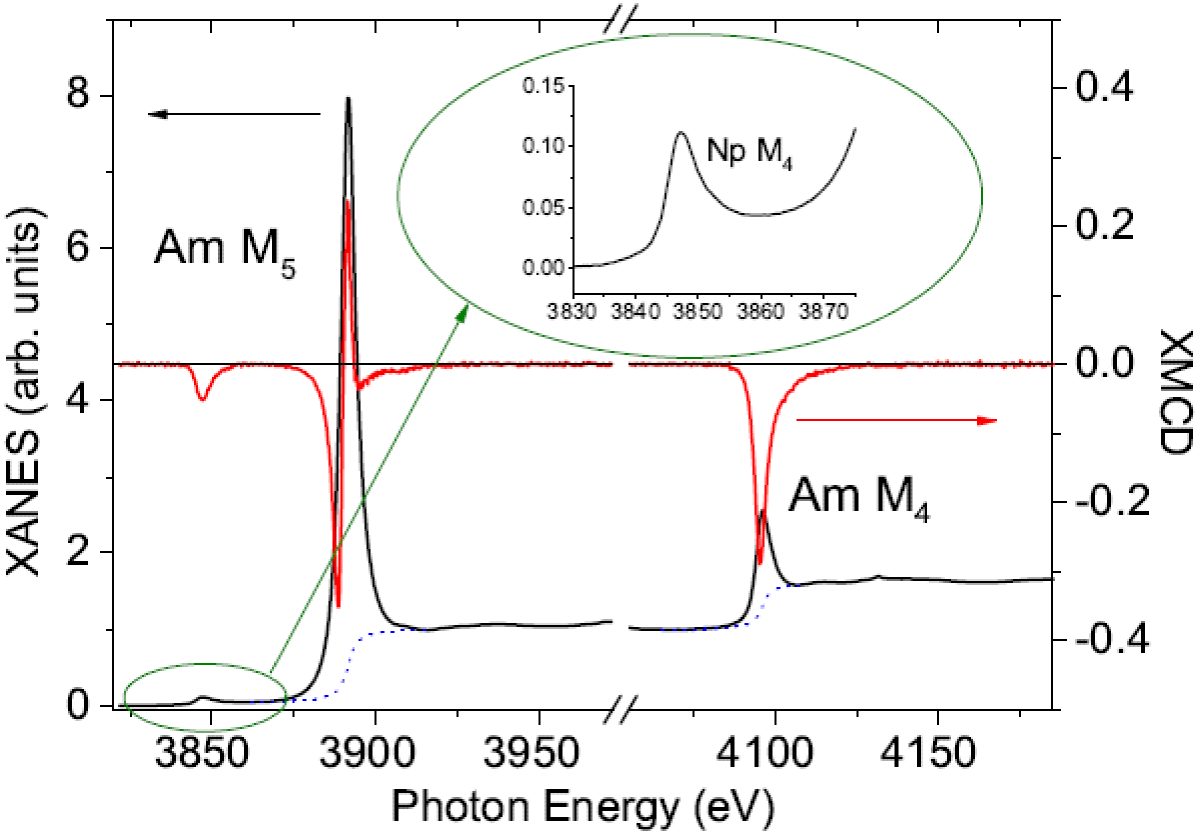
XMCD IN AMFE$_2$

Sum rules analysis:

$\langle L_z \rangle = -0.44(5)$
$\langle S_z \rangle + 3\langle T_z \rangle = -0.135(15)$
$\langle J_z \rangle = \langle L_z \rangle + \langle S_z \rangle = 0$

$\mu_L = -\langle L_z \rangle = +0.44\ \mu_B$
$\mu_S = -2\langle S_z \rangle = -0.88\ \mu_B$
$3\langle T_z \rangle = -0.57$

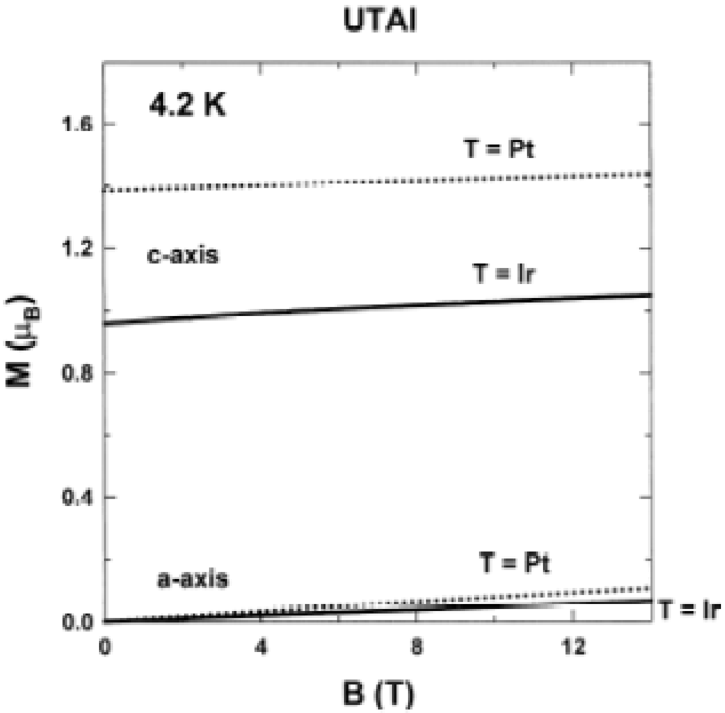
Calculated: (with $H_{int} = 180$ T)
$\mu_L = -\langle L_z \rangle = +0.47\ \mu_B$
$\mu_S = -2\langle S_z \rangle = -0.94\ \mu_B$
$3\langle T_z \rangle = -0.51$

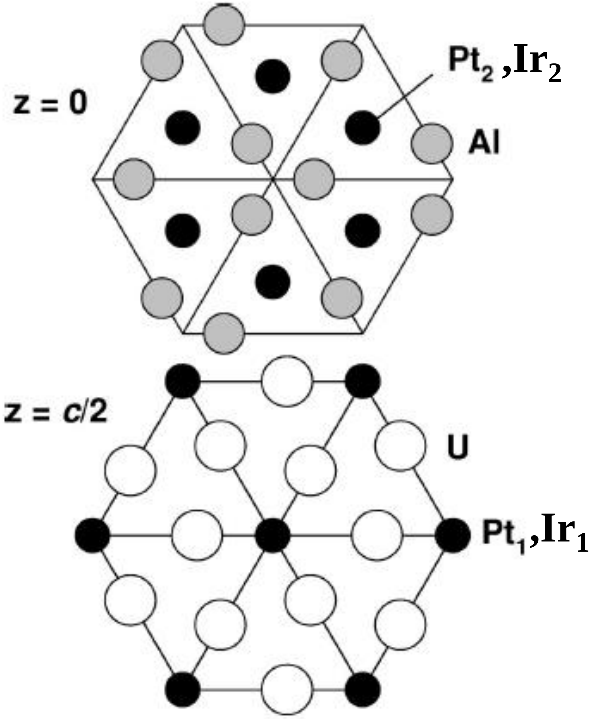


MAGNETISM IN UTX TERNARY COMPOUNDS

Both are ferromagnets

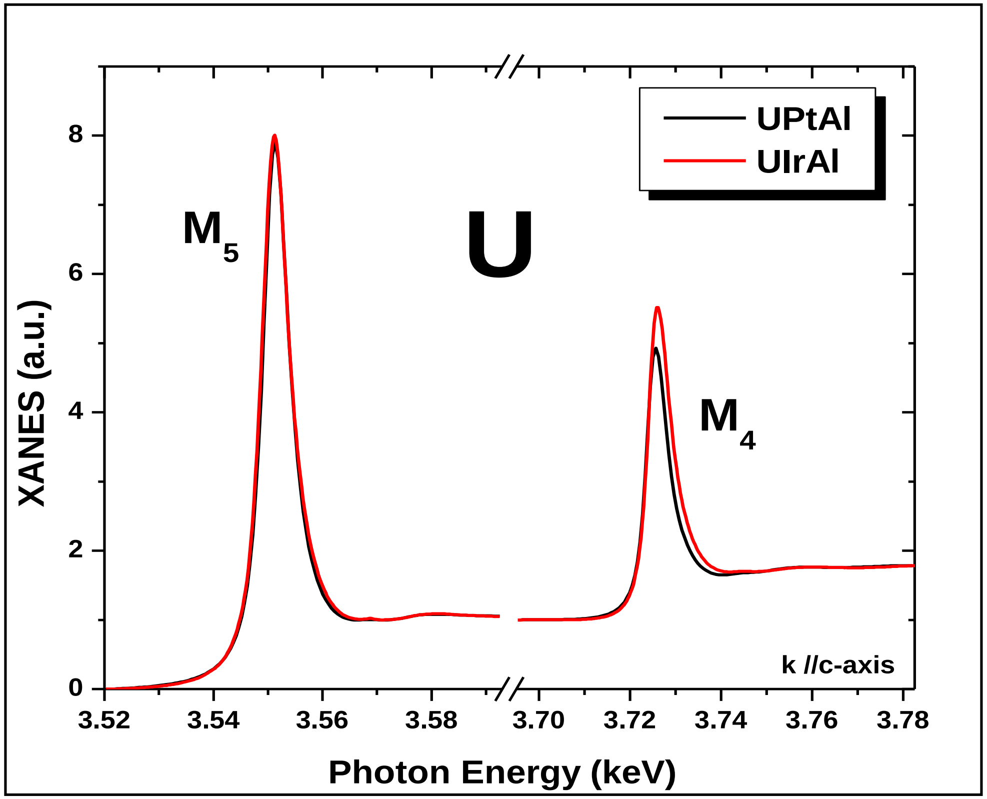
- **UIrAl ($\mu_{TOT} = 0.98\ \mu_B$) T_C=64K**
- **UPtAl ($\mu_{TOT} = 1.38\ \mu_B$) T_C=43K**





A.V. Andreev, J. Alloys Compd. 336, 77 (2001)

U $M_{4,5}$ XANES SPECTRA IN UTX CRYSTALS



Isotropic spectra are similar at M5-edge

M4-edge XANES shows that there are more $5f_{5/2}$ holes in UIrAl

Different expectation value of the 5*f* spin-orbit interaction per hole

U valence state in UIrAl seems to be U^{4+} whereas in UPtAl it is U^{3+}

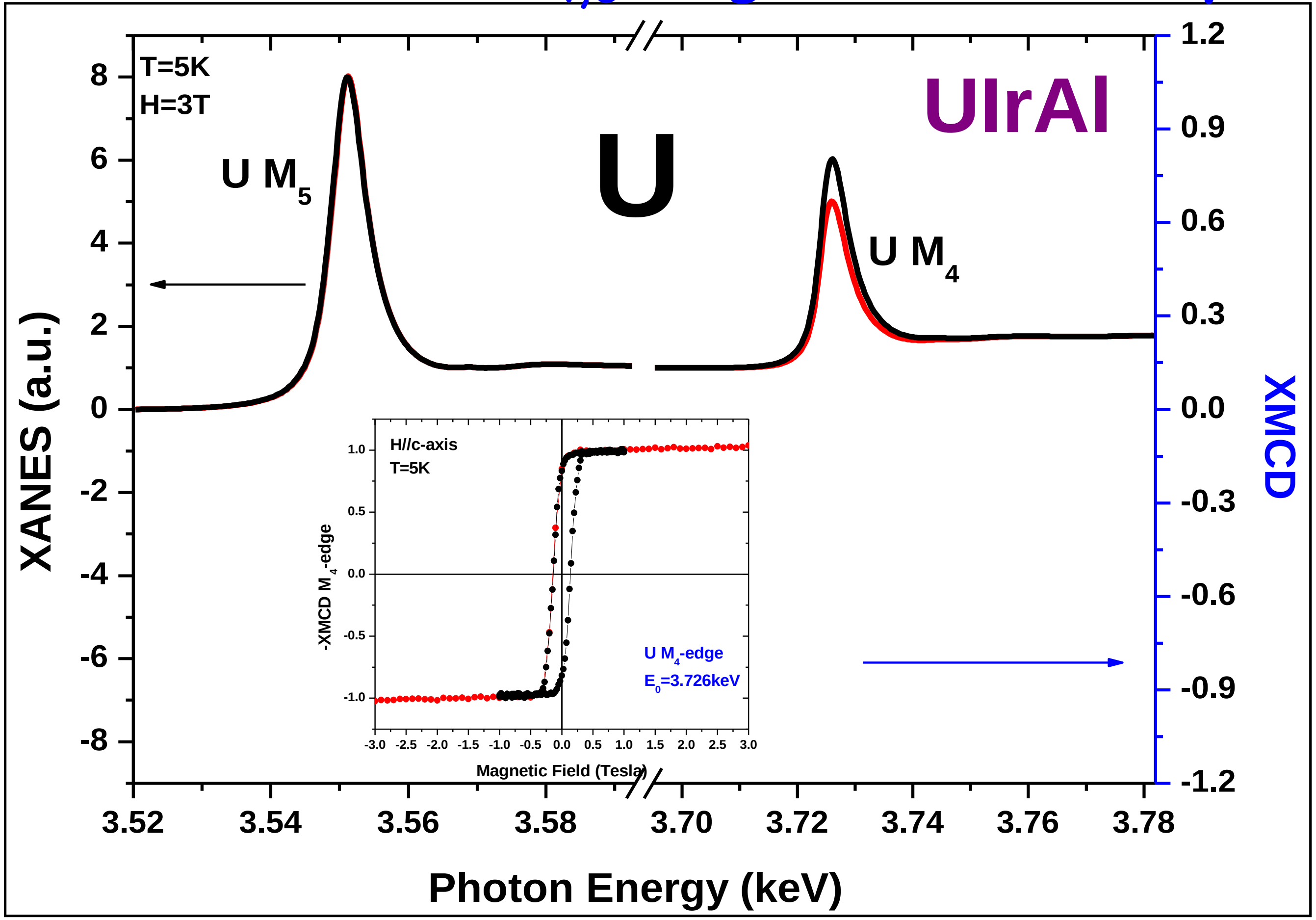
Exp. error bars ~%

	B	$2\langle l.s\rangle/(3.n_h^{5f})$ - Δ	n_e^{5f}	$n_{5/2}$	$n_{7/2}$
UIrAl	0.654	-0.135	2 (U^{4+})	1.62	0.38
			3 (U^{3+})	1.96	1.04
UPtAl	0.692	-0.230	2 (U^{4+})	2.11	-0.11
			3 (U^{3+})	2.42	0.58

for n_e^{5f} =2
Δ =-0.014

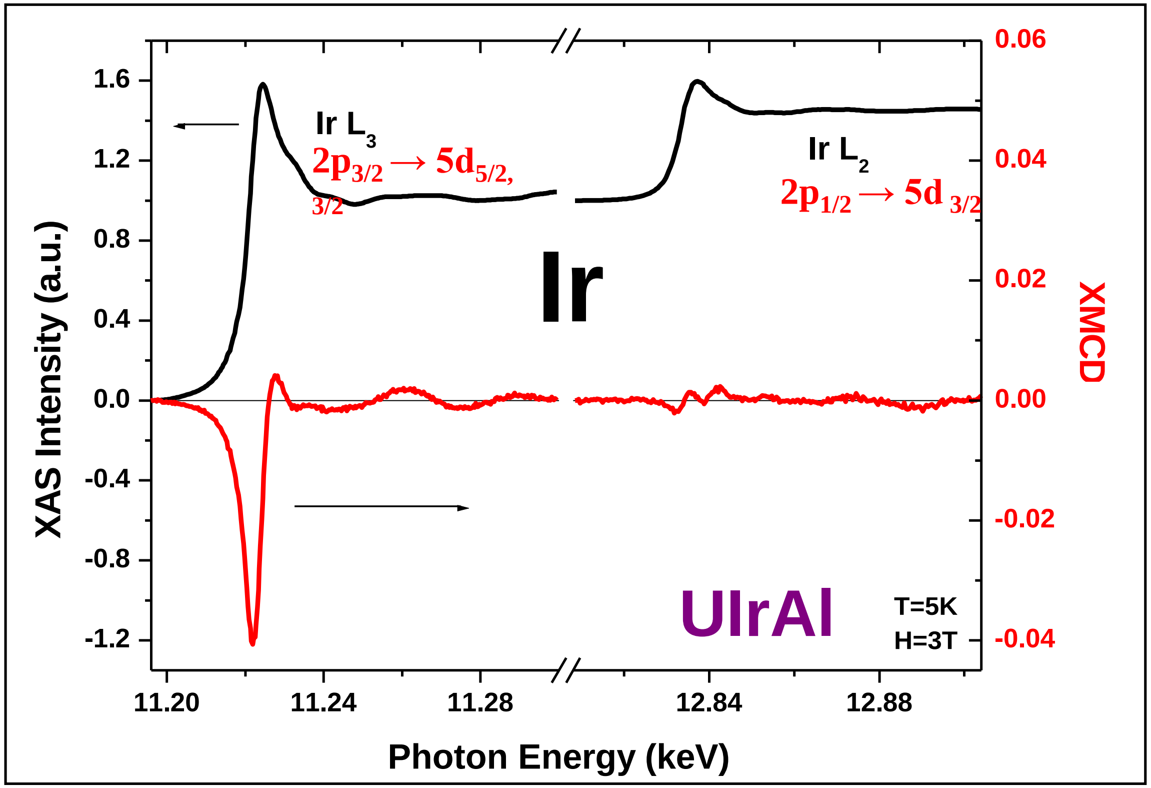
for n_e^{5f} =3
Δ =-0.010

XMCD at the U $M_{4,5}$-edges in UIrAl crystal



- ☐ Strong XMCD at the M4-edge
- ☐ s-like shape XMCD at the M5-edge
- ☐ element specific magnetization curves recorded at U similar to the macroscopic one

XMCD at the Ir $L_{2,3}$-edges in UIrAl crystal



- ☐ Strong XMCD at the L_3-edge
- ☐ Small XMCD at the L_2-edge
- ☐ Large Ir 5d orbital moment aligned parallel to the spin

$\mu_L^{Ir}(5d)$ (μ_B /atom)	$\mu_S^{Ir}(5d)$ (μ_B /atom)	$\mu_{tot}^{Ir}(5d)$ (μ_B /atom)	$\mu_L^{Ir}(5d)/\mu_S^{Ir}(5d)$
0.028	0.048	0.076	0.60

ANALYSIS COMBINING XMCD AND VSM MEASUREMENTS

- $M^{U}(5f) = 0.92\ \mu_B$ /U atom for $n_f = 2$ (U^{4+})
- $M^{U}(5f) = 0.62\ \mu_B$ /U atom for $n_f = 3$ (U^{3+})
- $M^{Ir}(5d) = 0.076\ \mu_B$ /Ir atom (sum over two Ir sites)

$$M_{total} = M^{U} + M^{Ir} = 0.996\ \mu_B$$

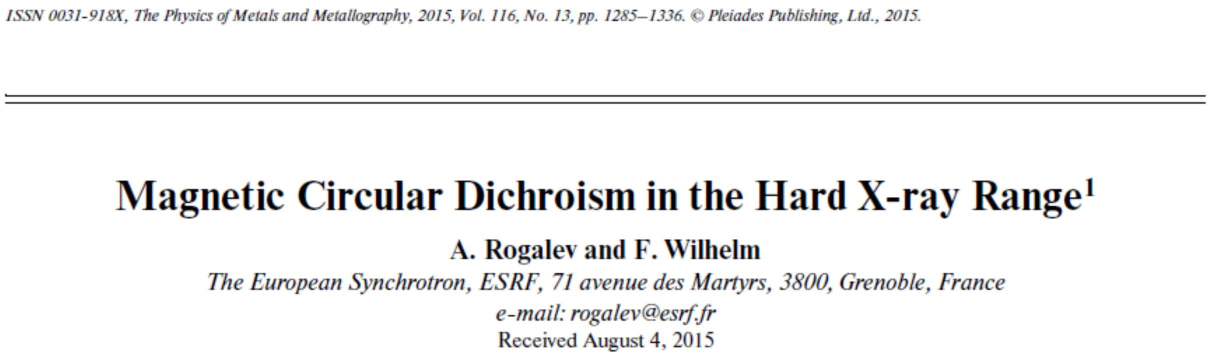
Al and U(*6d*) contributions are neglected

VSM Data: $M_{total} = 0.98\mu_B$ at 6 Tesla and 4.2K

MESSAGE TO TAKE HOME

XMCD

is very powerful spectroscopy tool
to unravel the microscopic origin of magnetism



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Magnetic Circular Dichroism in the Hard X-ray Range[1]

A. Rogalev and F. Wilhelm

The European Synchrotron, ESRF, 71 avenue des Martyrs, 3800, Grenoble, France

e-mail: rogalev@esrf.fr

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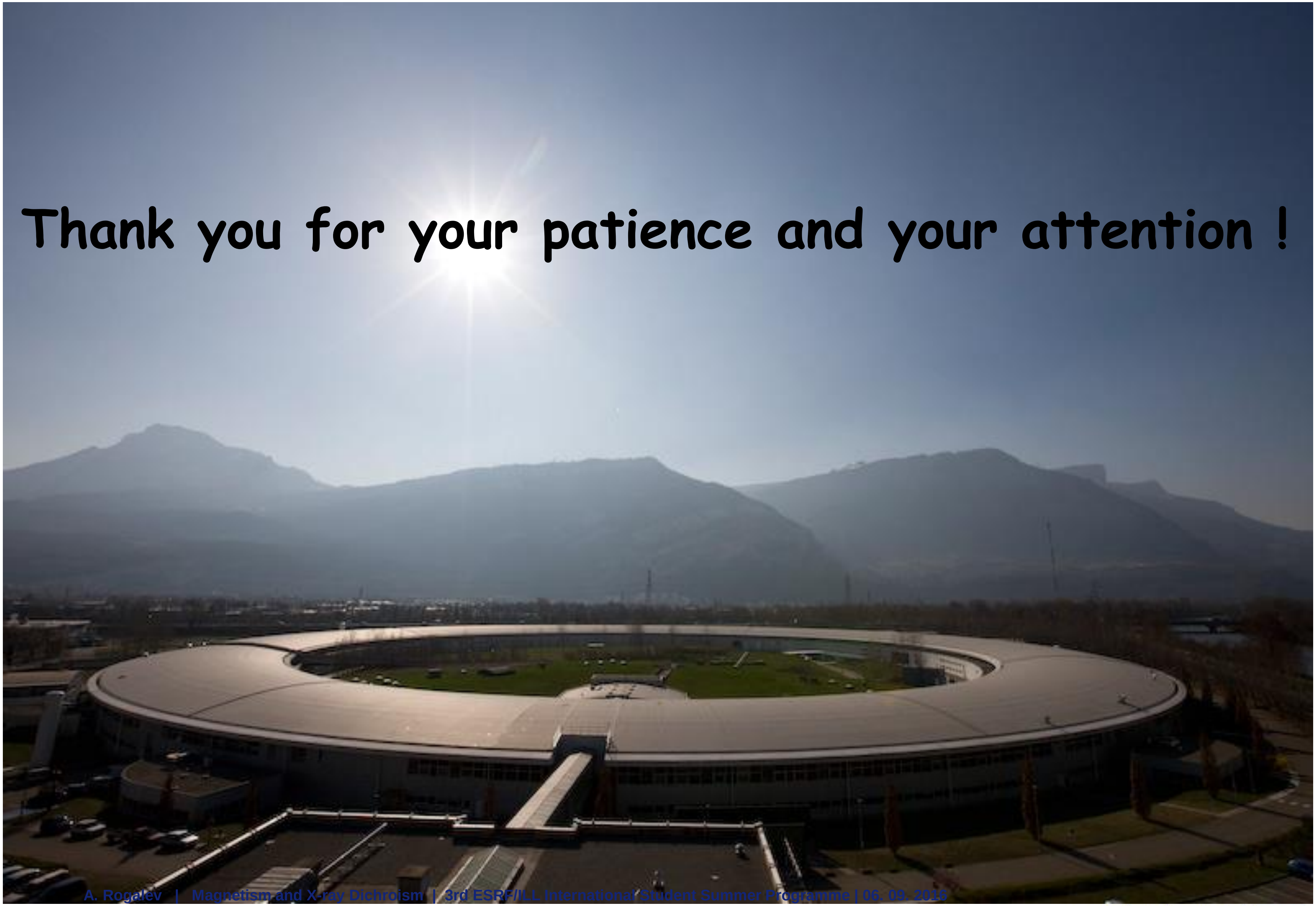
Review

X-ray magnetic circular dichroism—A versatile tool to study magnetism

Gerrit van der Laan, Adriana I. Figueroa

Magnetic Spectroscopy Group, Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom



Thank you for your patience and your attention !