



Magnetic dichroism in XAS and its application

Klaus Baberschke

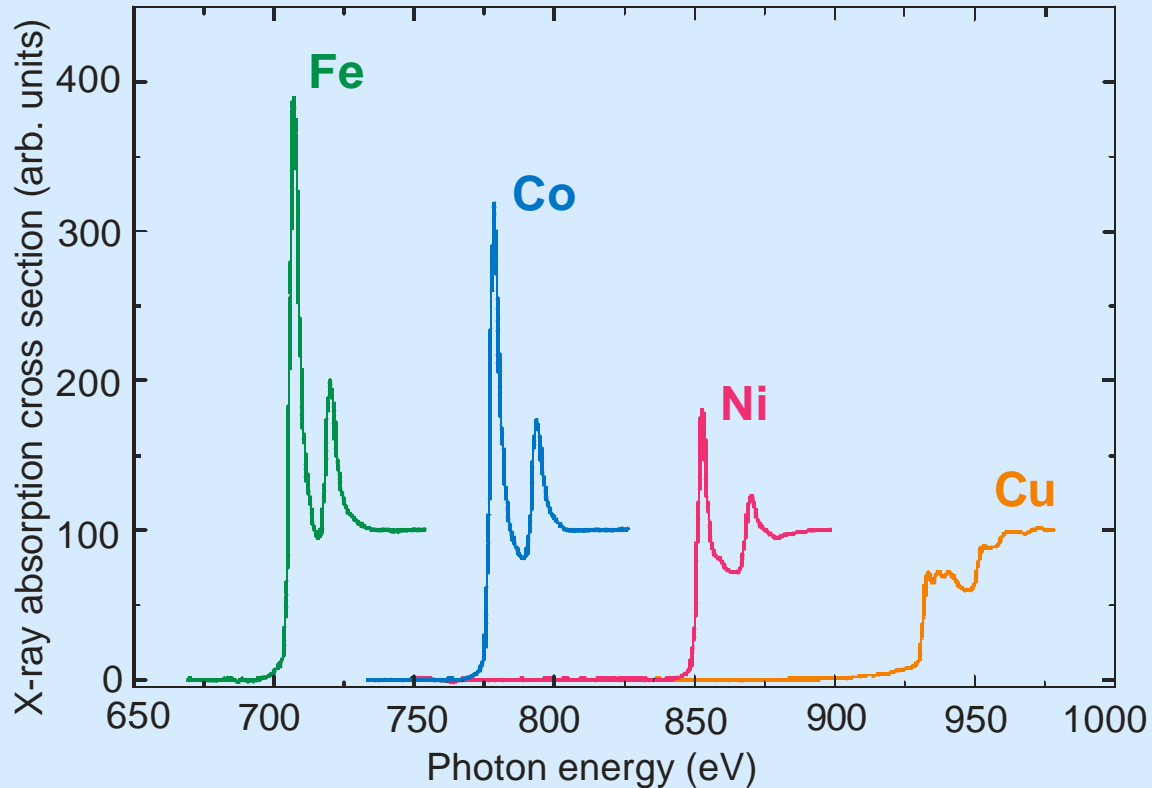
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1. Introduction.
2. Element specific magnetizations in trilayers.
3. Determination of orbital- and spin- magnetic moments;
XMCD sum rules.
Magnetic Anisotropy Energy (MAE) and anisotropic μ_L .
4. Induced magnetism at interfaces.
5. New developments, outlook

1. Introduction: XAS

X-ray Absorption Spectroscopy is the most appropriate technique for element specific investigations.



$L_{3,2}$ edges of 3d elements

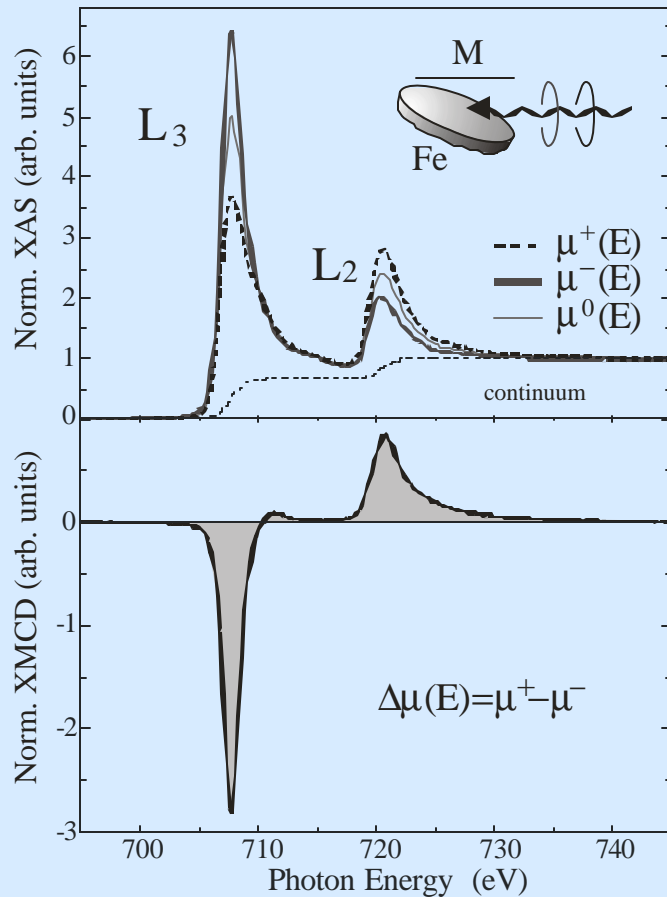
Note: the intensity of the $2p \rightarrow 3d$ dipole transitions (E1) is proportional to the number of unoccupied final state (i.e. 3d- holes).

Appendices/References

- In this lecture we will **not** discuss the equipment/apparatus, but rather focus on application of XAS in magnetism.
- Concerning XAS-technique there exist many review articles e.g.
J. Stöhr: *NEXAFS Spectroscopy*, Springer Series in Surface Science **25**, 1992;
H. Wende: *Recent advances in the x-ray absorption spectroscopy*, Rep. Prog. Physics **67**, 2105 (2004).
- See also lectures A13 J. Vogel; A14 Y. Joly;
A'15 (Trieste) F. Sirotti; A''15 (Saclay) M. Sacchi.
- In the soft X-ray regime (VUV) one needs to work in vacuum. For nanomagnetism one wants to prepare and work anyway in UHV (*in situ* experiments).

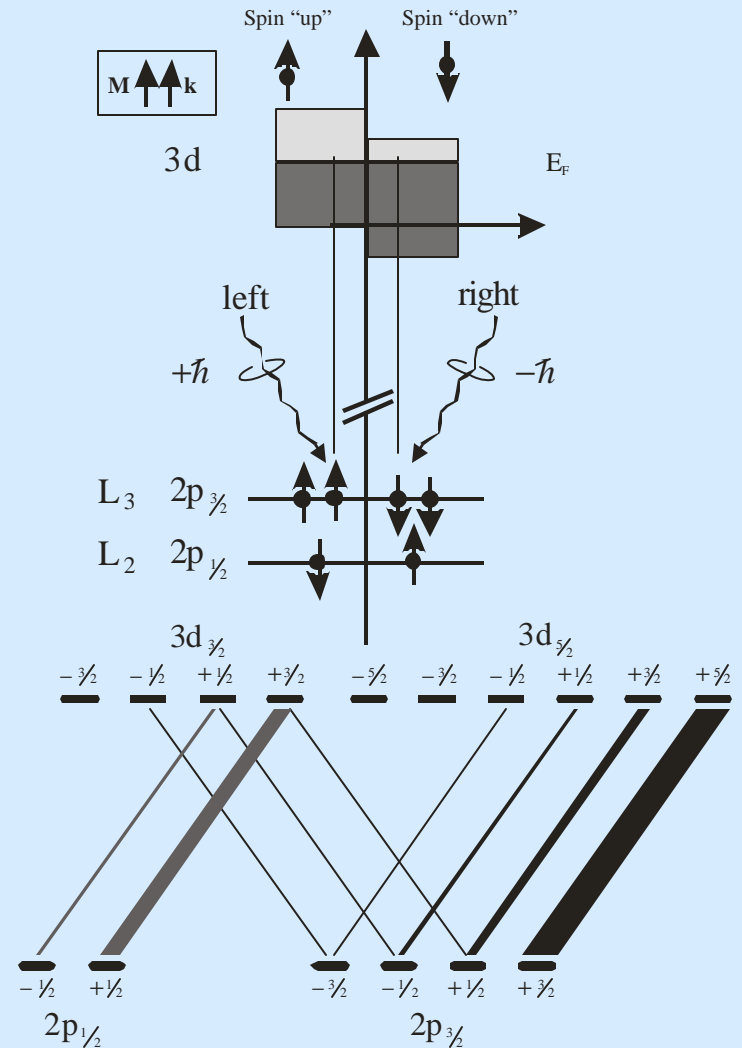
X-ray Magnetic Circular Dichroism

Faraday – effect in the X-ray regime (Gisela Schütz, 1987)



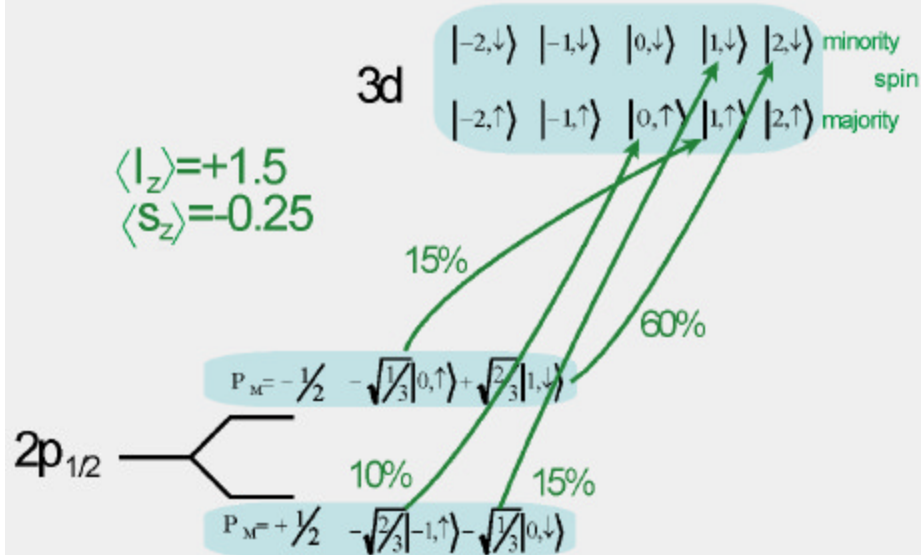
XMCD signal is a measure of the magnetization

Many Reviews, e.g. H. Ebert Rep. Prog. Phys. **59**, 1665 (1996)

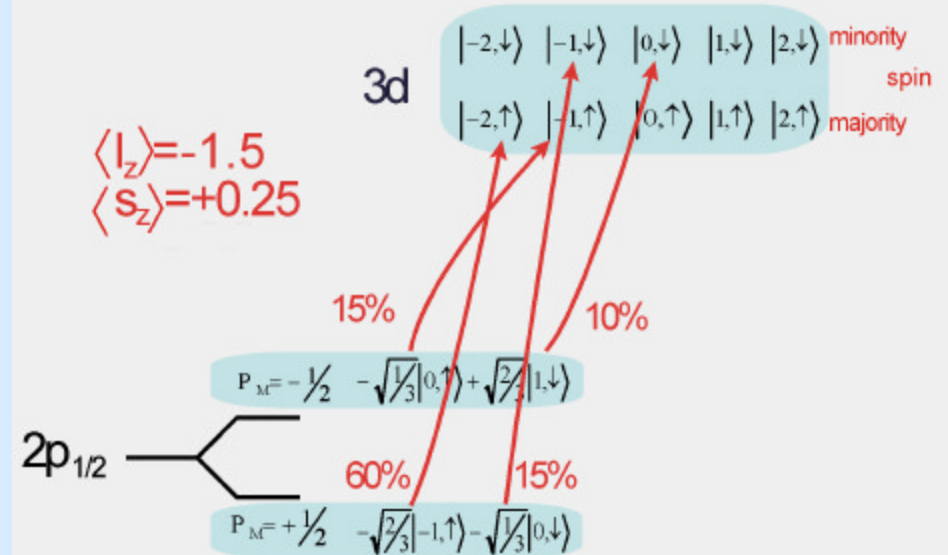


The origin of MCD (after K. Fauth, Univ. Würzburg)

absorption of left circular pol. photon $\Delta l=1, \Delta s=0$

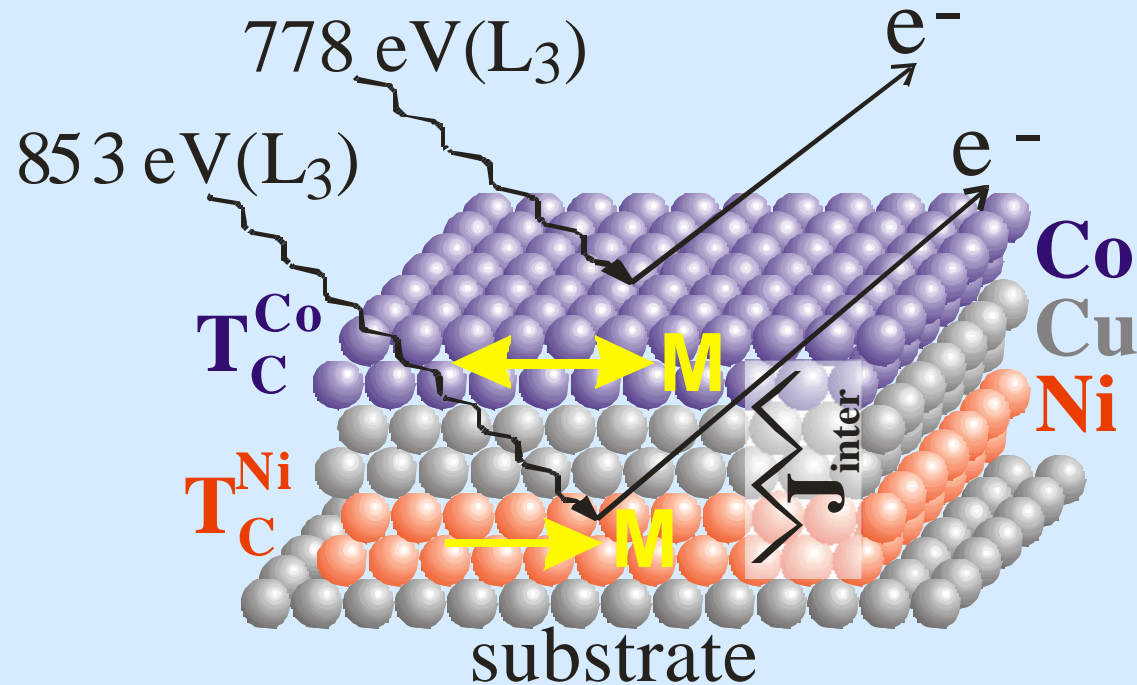


absorption of right circular pol. photon $\Delta l=-1, \Delta s=0$



Reviews e.g.: Lecture Notes in Physics Vol. 466 by H. Ebert, G. Schütz

2. Element specific magnetizations in trilayers

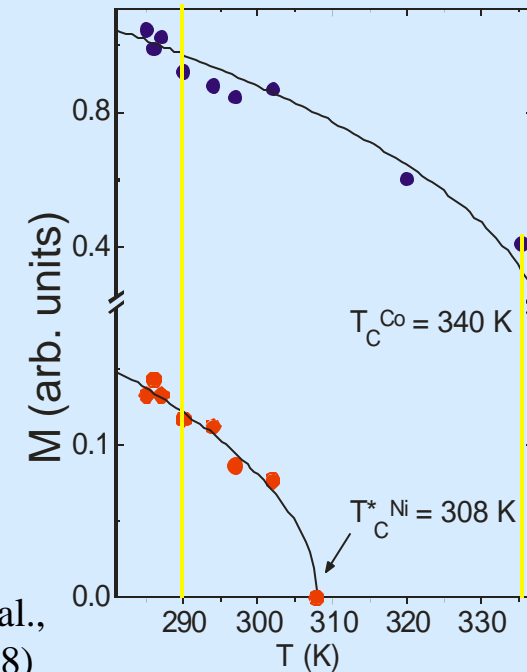
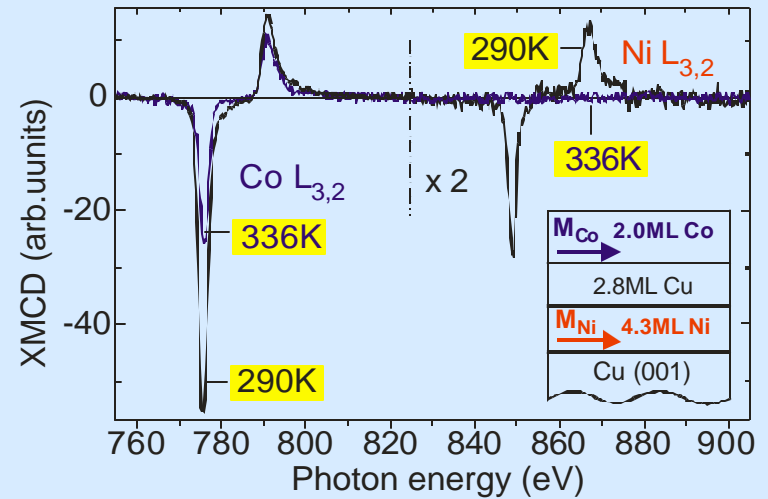
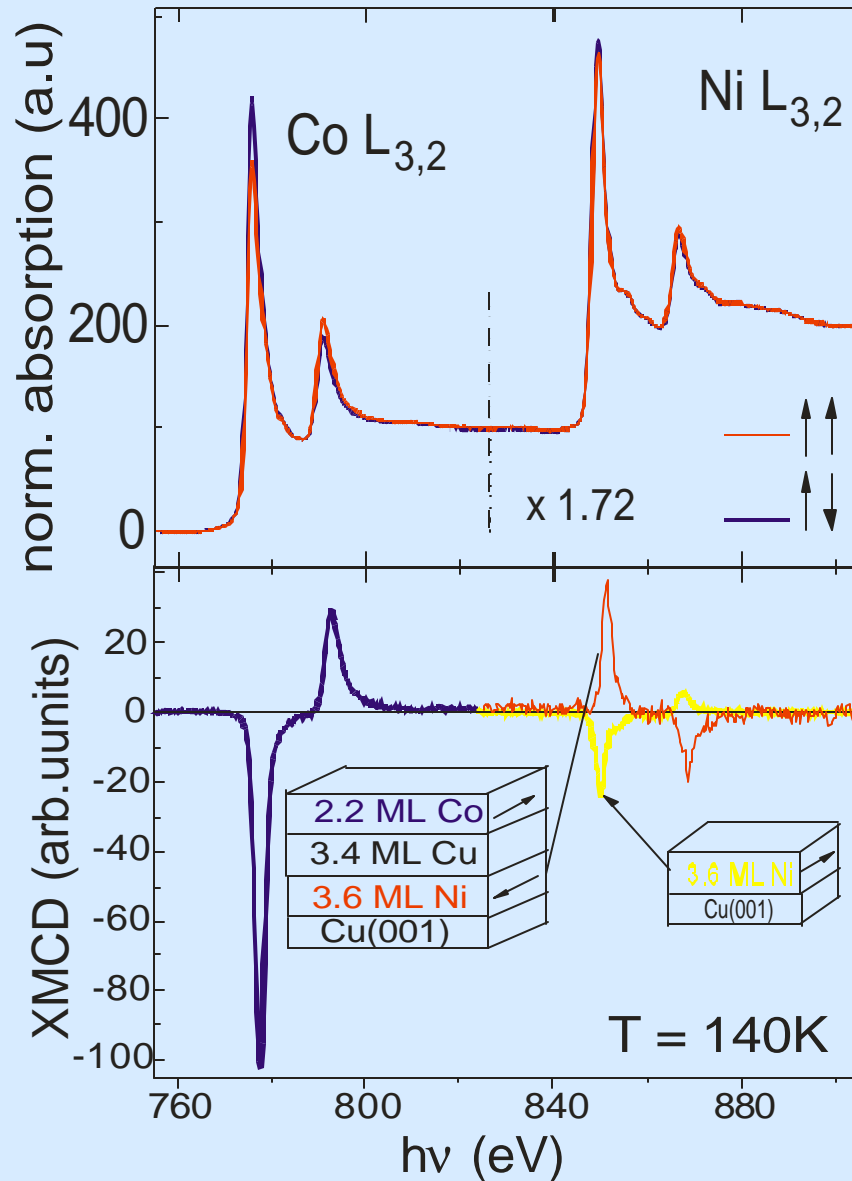


A trilayer is a prototype to study magnetic coupling in multilayers.

What about element specific Curie-temperatures ?

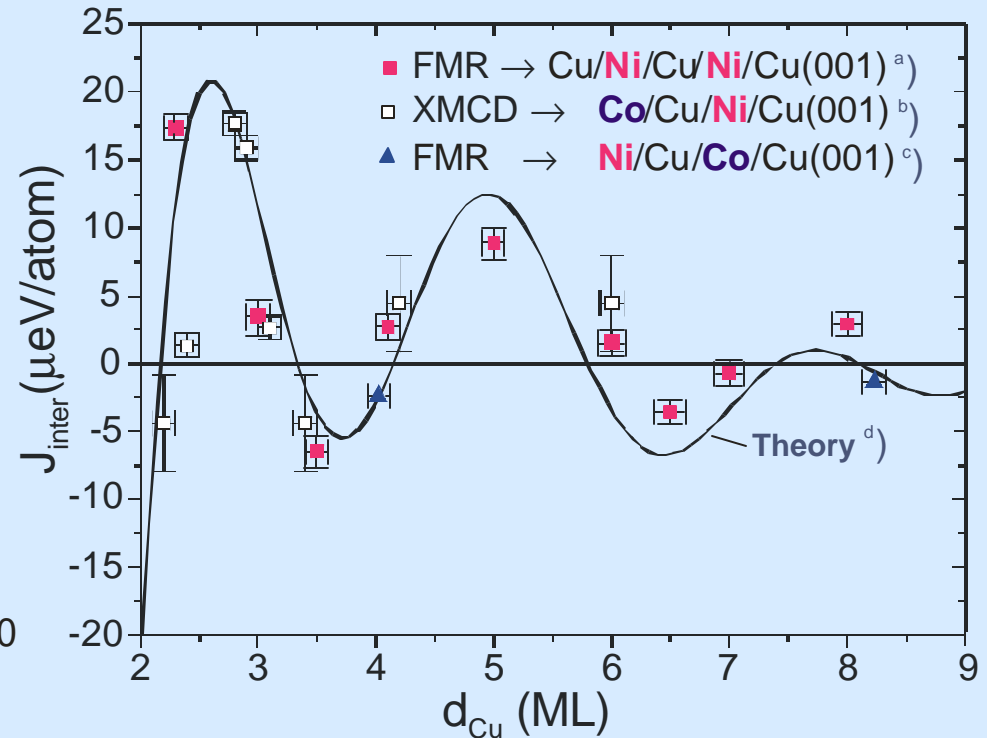
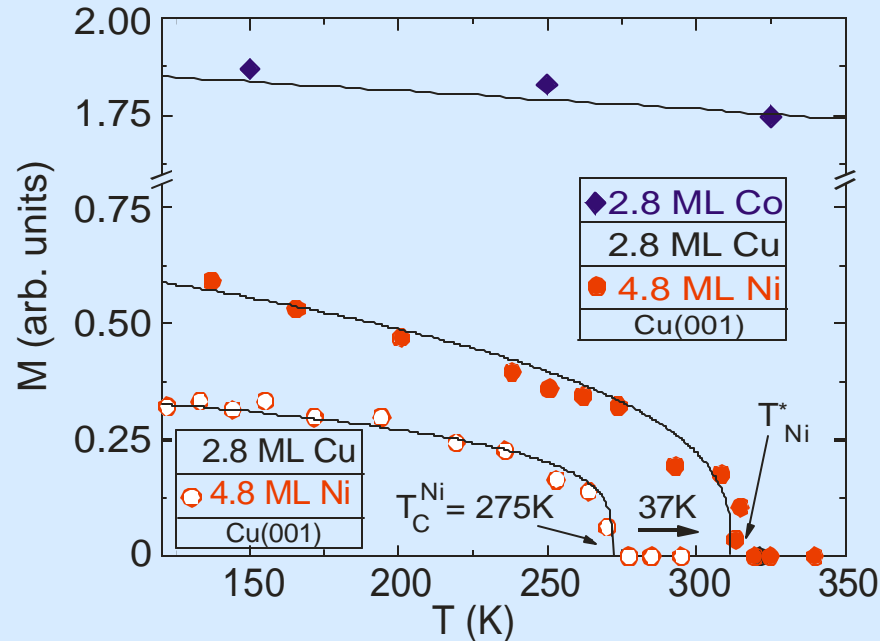
- Two trivial limits: (i) $d_{\text{Cu}} = 0 \Rightarrow$ direct coupling like a Ni-Co alloy
(ii) $d_{\text{Cu}} = \text{large} \Rightarrow$ no coupling, like a mixed Ni/Co powder
- BUT** $d_{\text{Cu}} \approx 2 \text{ ML} \Rightarrow ?$

Ferromagnetic trilayers



U. Bovensiepen et al.,
PRL **81**, 2368 (1998)

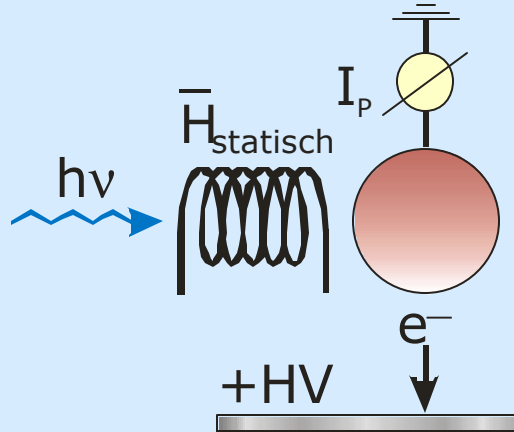
Interlayer exchange coupling



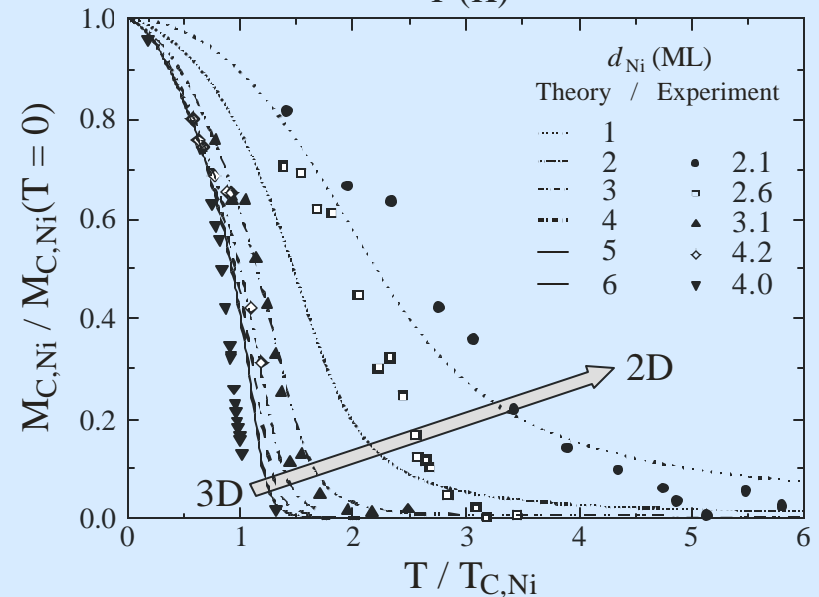
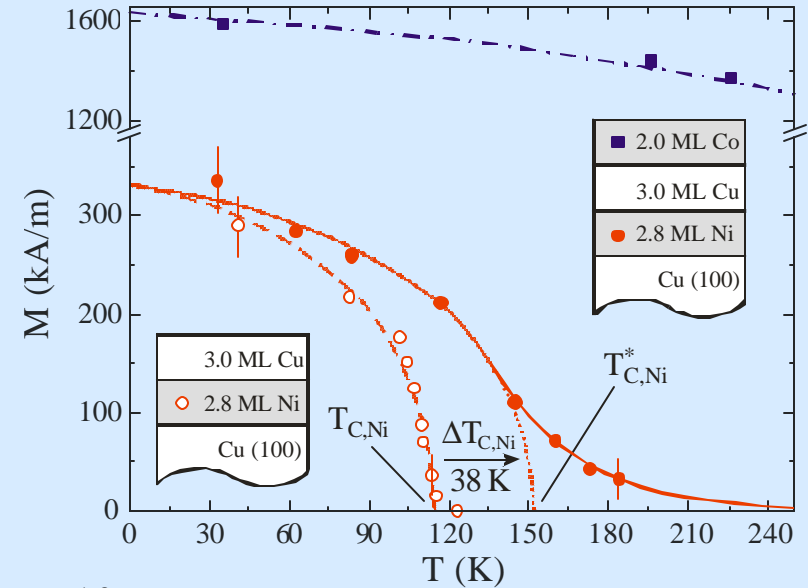
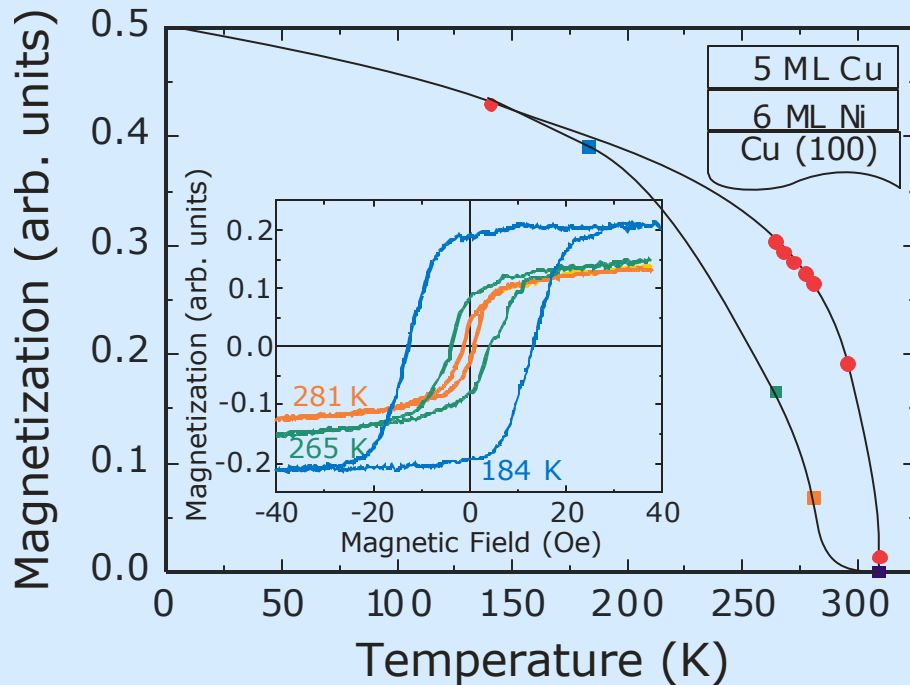
P. Pouloupoulos, K. B., Lecture Notes in Physics **580**, 283 (2001)

- a) J. Lindner, K. B., J. Phys. Condens. Matter **15**, S465 (2003)
- b) A. Ney et al., Phys. Rev. B **59**, R3938 (1999)
- c) J. Lindner et al., Phys. Rev. B **63**, 094413 (2001)
- d) P. Bruno, Phys. Rev. B **52**, 441 (1995)

Remanence and saturation magnetization



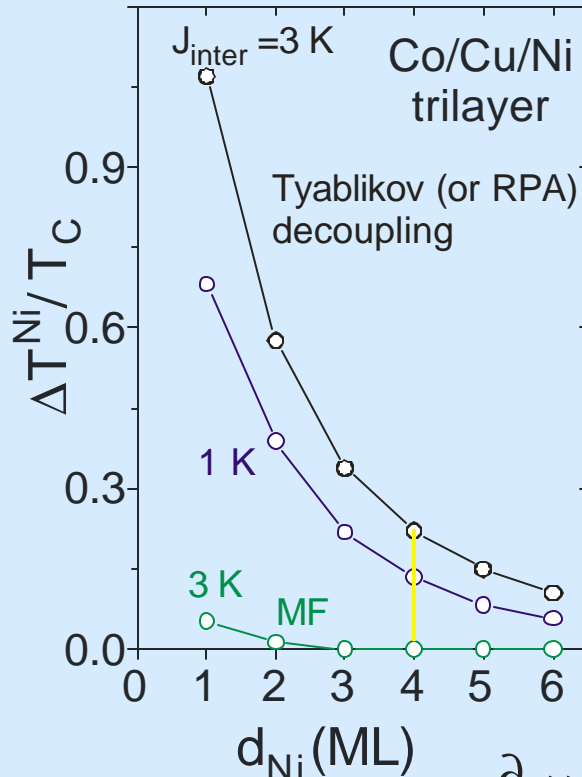
C. Sorg et al.,
XAFS XII, June 2003
Physica Scripta
T115, 638 (2005)



Enhanced spin fluctuations in 2D (theory)

P. Jensen et al. PRB **60**, R14994 (1999)

J.H. Wu et al. J. Phys.: Condens. Matter **12** (2000) 2847

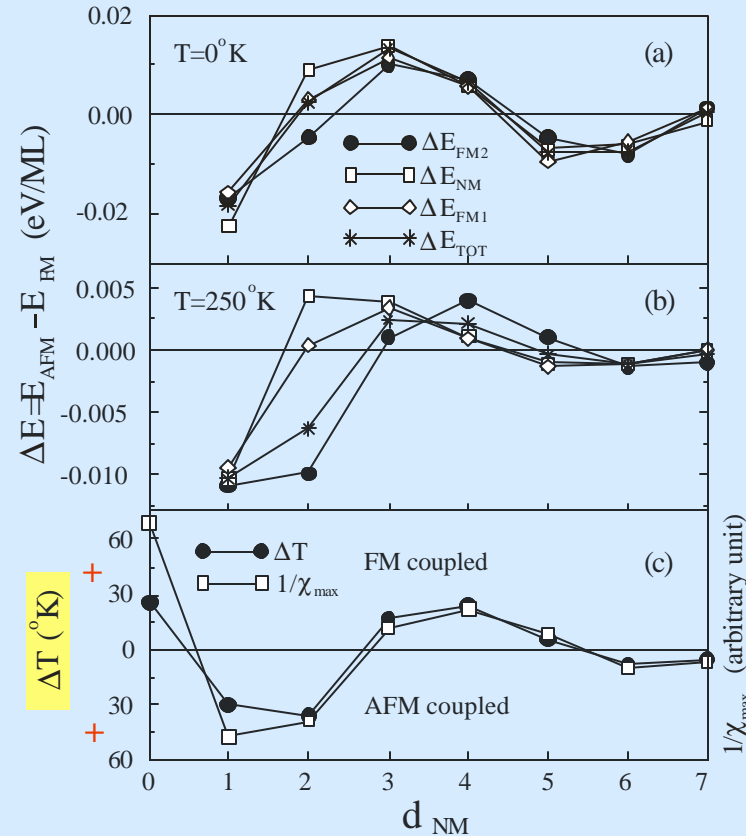


Spin-Spin correlation function $\frac{\partial}{\partial t} \langle \langle S_i^+ S_j^- \rangle \rangle \rightarrow$

$$S_i^z S_j^+ \approx \langle S_i^z \rangle S_j^+ - \langle S_i^- S_i^+ \rangle S_j^+ - \langle S_i^- S_j^+ \rangle S_i^+ + \dots$$

← RPA →

$\langle S_i^z \rangle S_j^+$ mean field ansatz (Stoner model) is insufficient to describe spin dynamics at interfaces of nanostructures



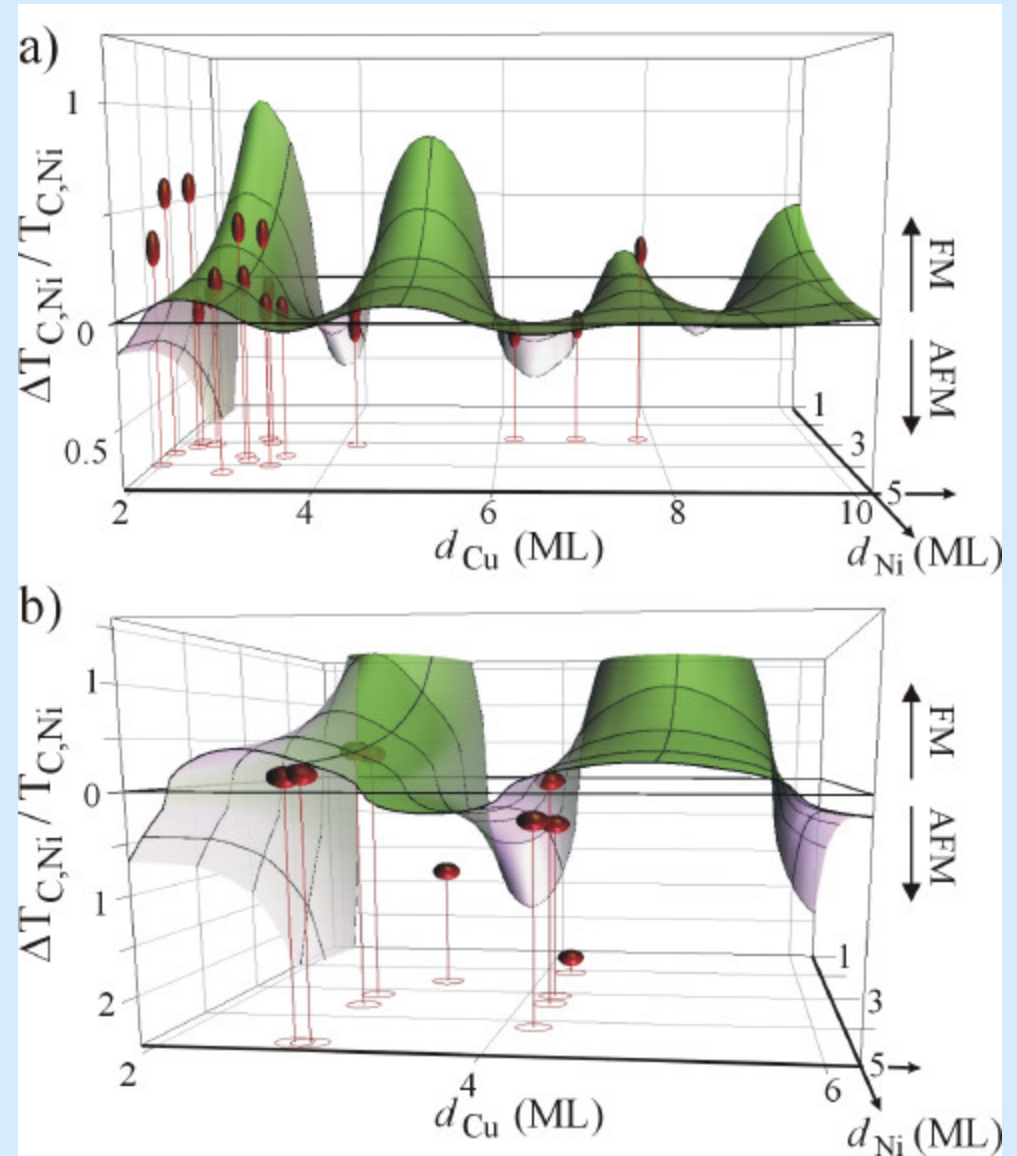
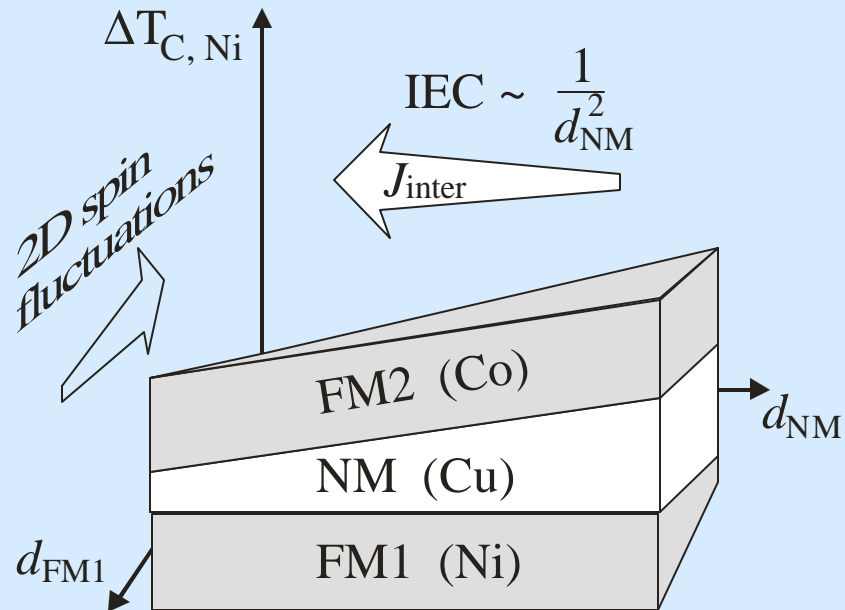
Single band Hubbard model:

Simple Hartree-Fock (Stoner) ansatz is insufficient

Higher order correlations are needed to explain T_C -shift

Evidence for giant spin fluctuations

PRB 72, 054447, (2005)



3. Determination of orbital- and spin- magnetic moments

Which technique measures what?

μ_L, μ_S in UHV-XMCD

$\mu_L + \mu_S$ in UHV-SQUID

μ_L / μ_S in UHV-FMR

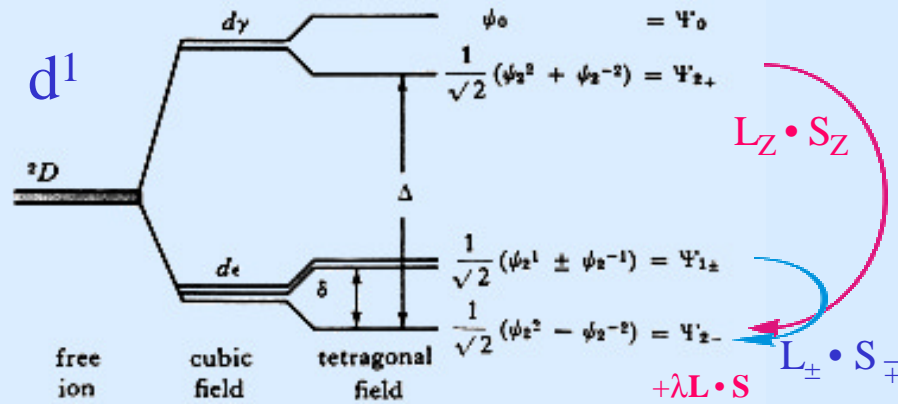
For FMR see: J. Lindner and K. Baberschke
*In situ Ferromagnetic Resonance:
An ultimate tool to investigate the coupling in
ultrathin magnetic films*
J. Phys.: Condens. Matter **15**, R193 (2003)

per definition:

- 1) spin moments are isotropic
- 2) also exchange coupling $\mathbf{J} \mathbf{S}_1 \cdot \mathbf{S}_2$ is isotropic
- 3) so called *anisotropic exchange* is a (hidden) projection of the orbital momentum into spin space

Orbital magnetism in second order perturbation theory

effective Spin Hamiltonian



Splitting of the 2D term by a tetragonally distorted cubic field.

$$y_{2-} \equiv (2)^{-1/2} \{ |2\rangle - |-2\rangle \} \equiv |2-\rangle$$

The orbital moment is quenched in cubic symmetry

$$\langle 2- | L_z | 2- \rangle = 0,$$

but not for tetragonal symmetry

$$\mathcal{H} = \sum_{i,j=1}^3 [\overbrace{g_{\text{exp}}}^{B_2^0 \rightarrow K_2^0} [\beta g_e(\delta_{ij} - 2\lambda\Lambda_{ij})] S_i H_j - \underbrace{\lambda^2 \Lambda_{ij}}_{\text{diamagnetic terms in } H_i H_j} S_i S_j] \quad (3-23)$$

where Λ_{ij} is defined in relation to states ($n > 0$) as

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle 0 | L_i | n \rangle \langle n | L_j | 0 \rangle}{E_n - E_0} \quad (3-24)$$

$\langle 0 | \mu_B \mathbf{H} \cdot \mathbf{L} | n \rangle \langle n | \lambda \mathbf{L} \cdot \mathbf{S} | 0 \rangle$
 $\langle 0 | \lambda \mathbf{L} \cdot \mathbf{S} | n \rangle \langle n | \lambda \mathbf{L} \cdot \mathbf{S} | 0 \rangle$

In the principal axis system of a crystal with axial symmetry, the $\underline{\Lambda}$ tensor is diagonal with $\Lambda_{zz} = \Lambda_{\parallel}$ and $\Lambda_{xx} = \Lambda_{yy} = \Lambda_{\perp}$. Under these conditions, \mathcal{H} of (3-23) can be simplified, since

$$S_x^2 + S_y^2 = S(S+1) - S_z^2$$

to give

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + D [S_z^2 - \frac{1}{3} S(S+1)] \quad (3-25)$$

where

$$\begin{aligned} g_{\parallel} &= g_e(1 - \lambda\Lambda_{\parallel}) \\ g_{\perp} &= g_e(1 - \lambda\Lambda_{\perp}) \\ D &= \lambda^2(\Lambda_{\perp} - \Lambda_{\parallel}) \end{aligned} \quad (3-26)$$

GE. Pake, p.66

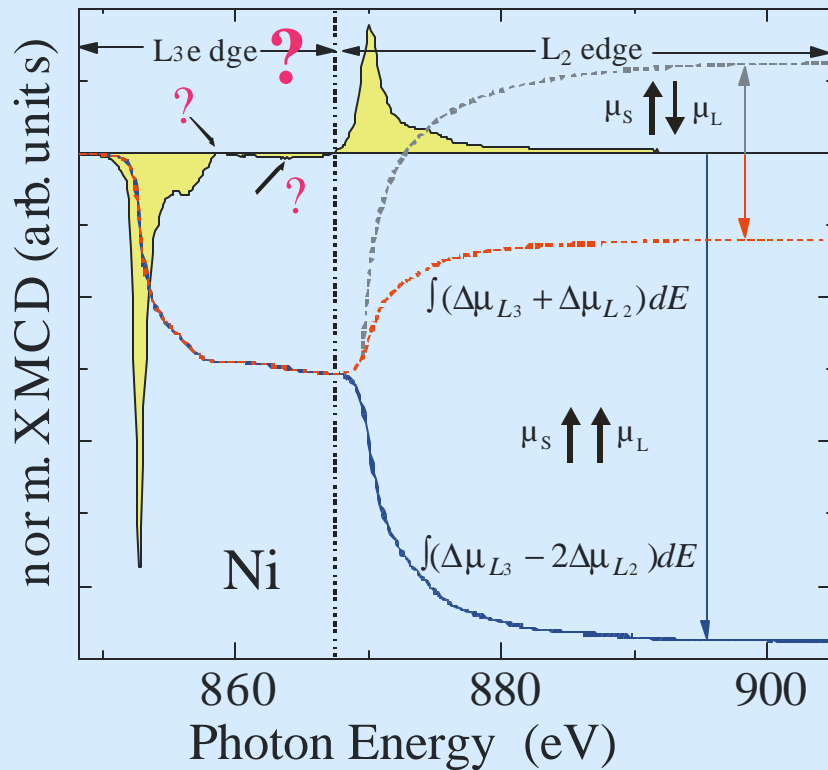
W.D. Brewer, A. Scherz, C. Sorg, H. Wende, K. Baberschke, P. Bencok, and S. Frota-Pessoa
Direct observation of orbital magnetism in cubic solids
 Phys. Rev. Lett. **93**, 077205 (2004)
 and

W.D. Brewer et al. ESRF – Highlights, p. 96 (2004)

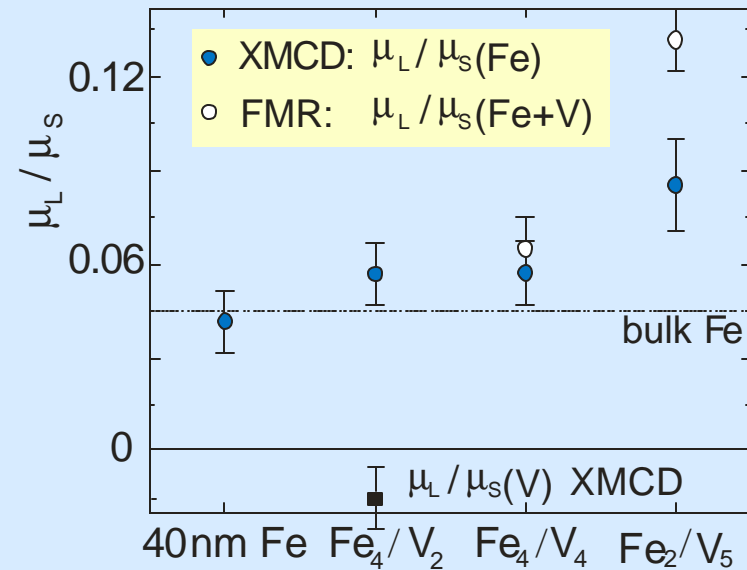
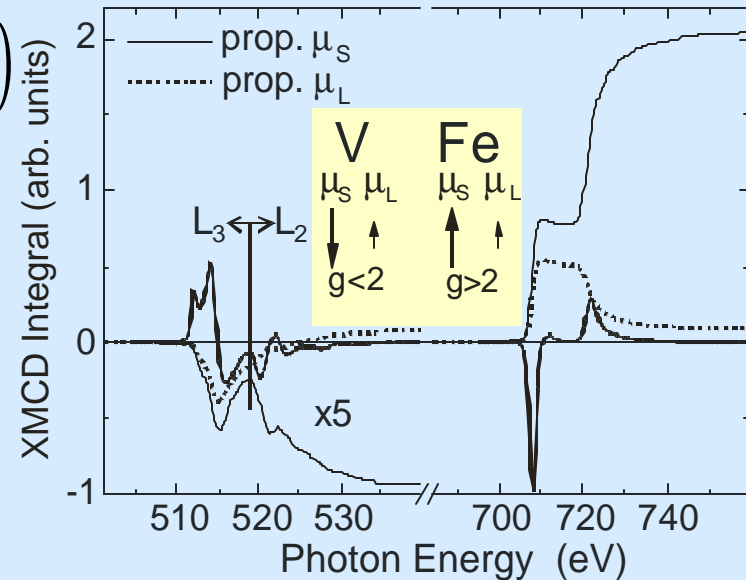
Orbital and spin magnetic moments deduced from XMCD

$$\int (? \mu_{L3} - 2 \cdot ? \mu_{L2}) dE = \frac{N}{3N_h^d} (2 \langle S_z \rangle^d + 7 \langle T_z \rangle^d)$$

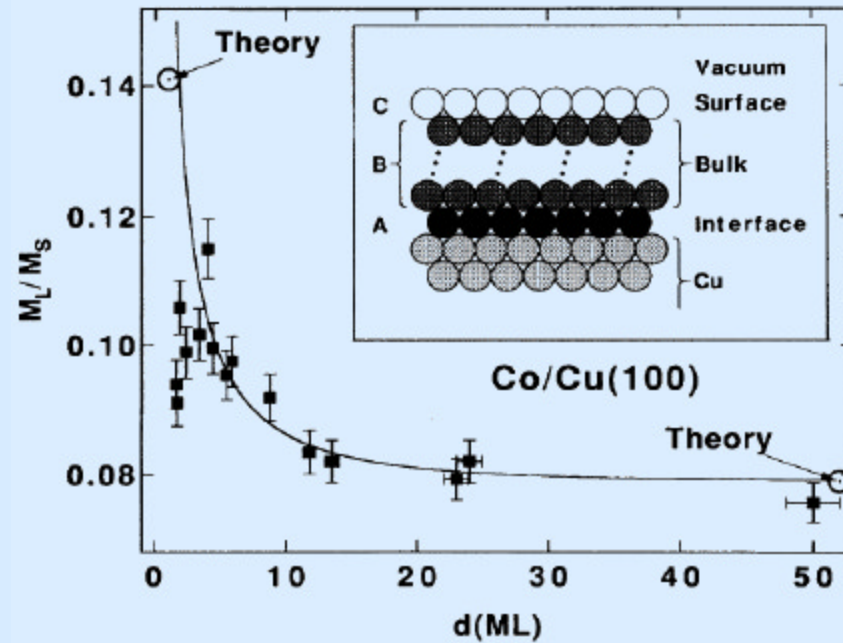
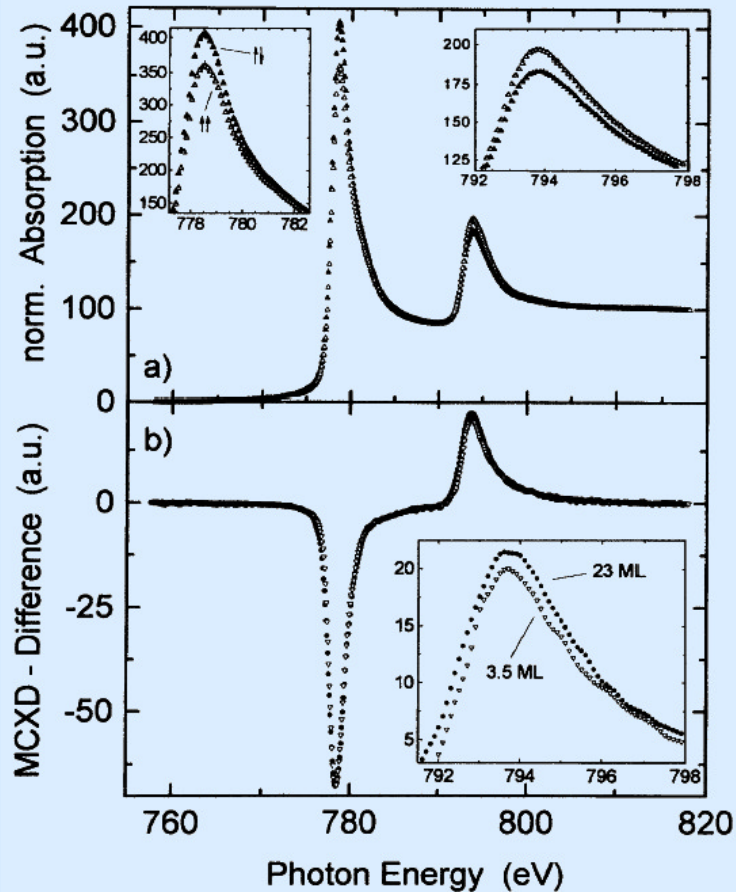
$$\int (? \mu_{L3} + ? \mu_{L2}) dE = \frac{N}{2N_h^d} \langle L_z \rangle^d$$



H. Ebert Rep. Prog. Phys. **59**, 1665 (1996)



Enhancement of Orbital Magnetism at Surfaces: Co on Cu(100)

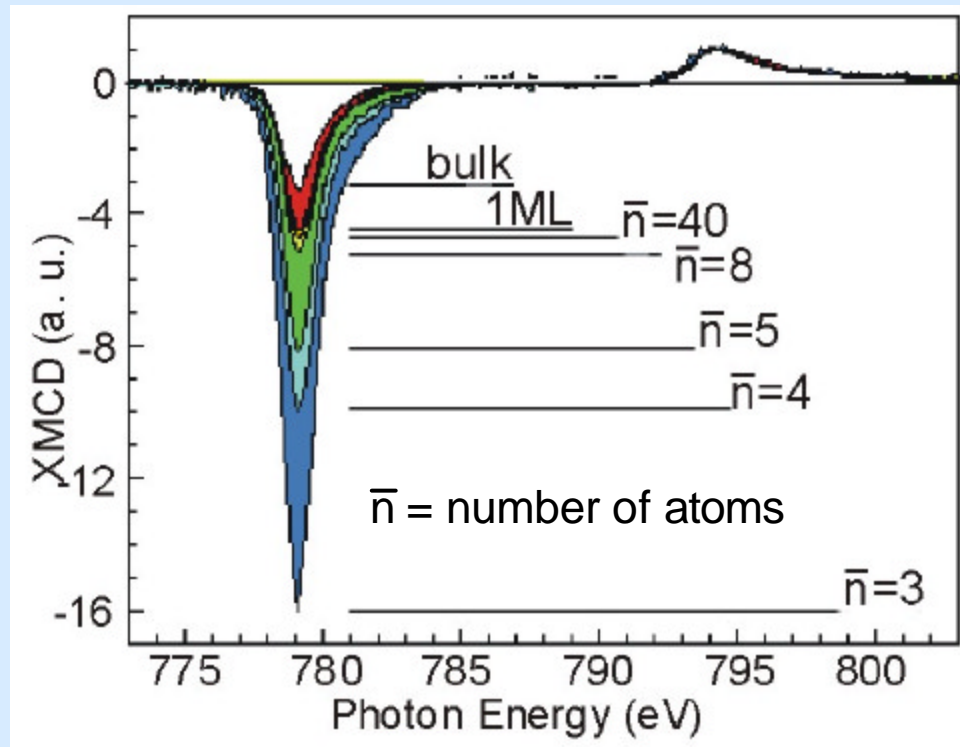


$$\left(\frac{M_L}{M_S} \right)_{\text{exp}} = \frac{Ae^{-D(d-1)/I} + B\sum_{n=3}^d e^{-D(n-2)/I} + C}{\sum_{n=0}^{d-1} e^{-nD/I}}$$

M. Tischer et al., Phys. Rev. Lett. **75**, 1602 (1995)

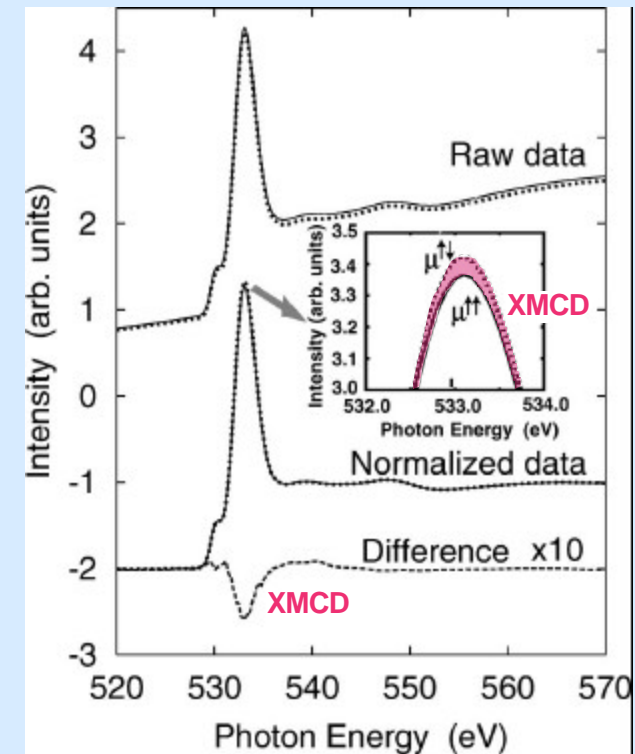
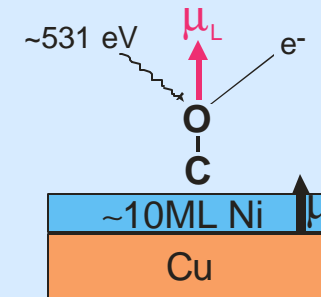
Giant Magn. Anisotropy of Single Co Atoms and Nanoparticles

P. Gambardella et al., Science **300**, 1130 (2003)



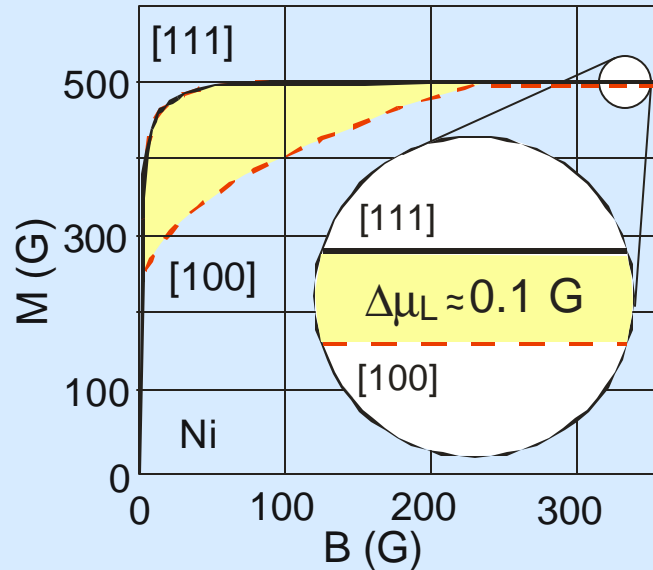
Induced magnetism in molecules

T. Yokoyama et al., PRB **62**, 14191 (2000)



Magnetic Anisotropy Energy (MAE) and anisotropic μ_L

1. Magnetic anisotropy energy = f(T)
2. Anisotropic magnetic moment \neq f(T)



$$MAE = \frac{1}{2} M \cdot dB \sim \frac{1}{2} M \cdot B \sim \frac{1}{2} 200 \cdot 200 \text{ G}^2$$

$$MAE \sim 2 \cdot 10^4 \text{ erg} / \text{cm}^3 \sim 0.2 \text{ } \mu\text{eV} / \text{atom}$$

$\approx 1 \mu\text{eV}/\text{atom}$ is very small compared to

$\approx 10 \text{ eV}/\text{atom}$ total energy **but all important**

$$g_{\parallel} - g_{\perp} = g_e \lambda (\Lambda_{\perp} - \Lambda_{\parallel})$$

anisotropic $\mu_L \leftrightarrow$ MAE

$$D = \frac{\lambda}{g_e} \Delta g$$



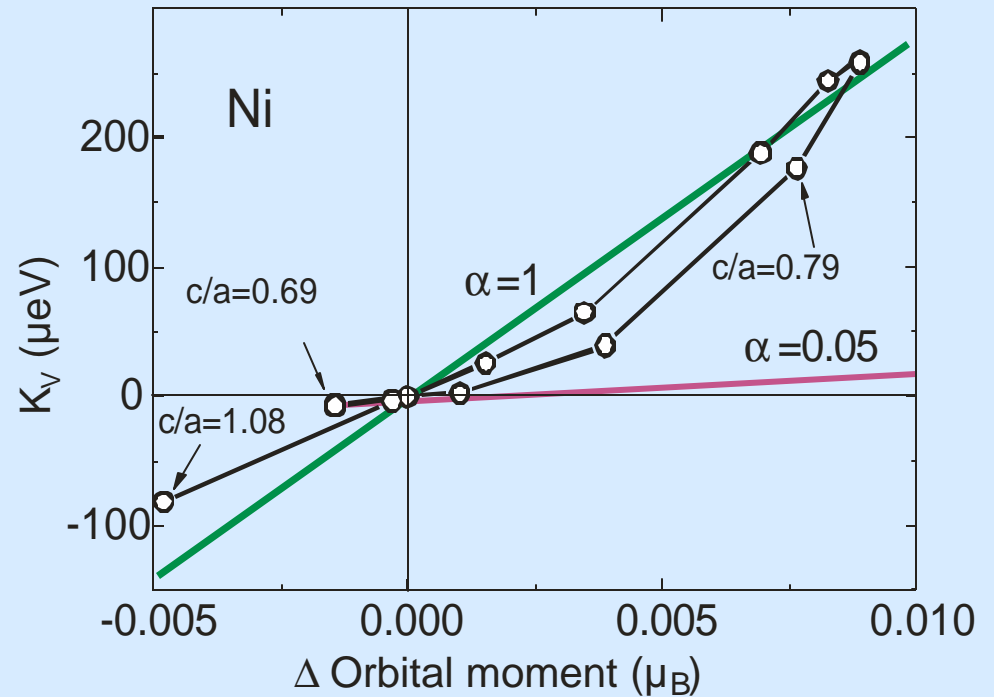
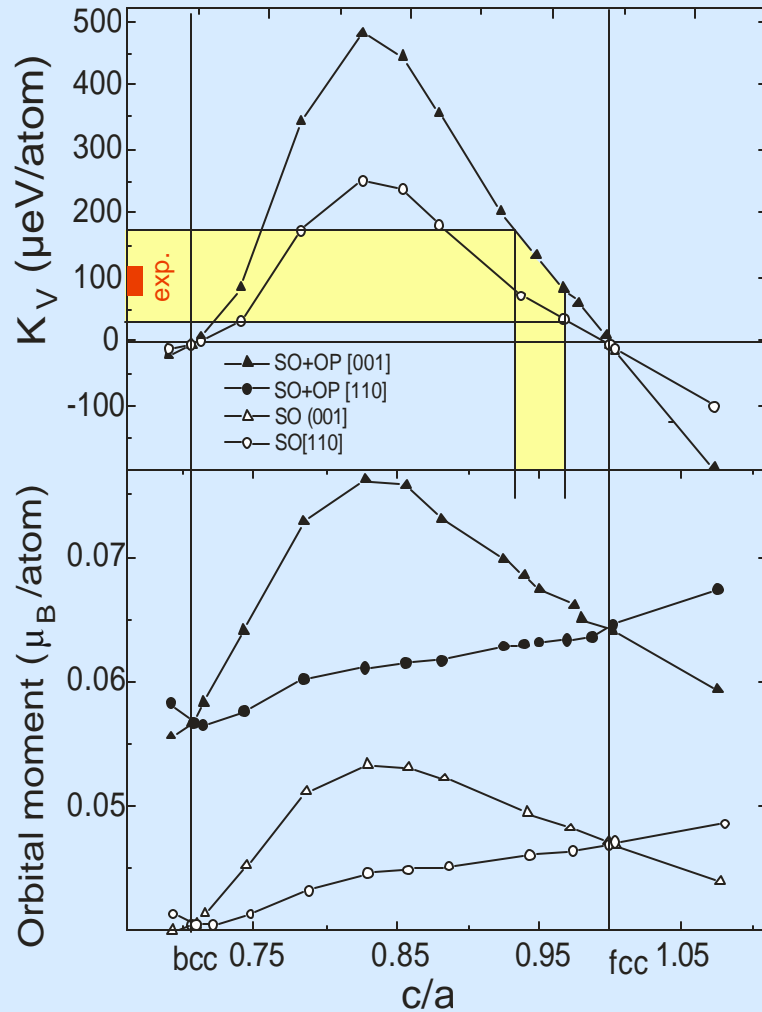
$$MAE \propto \frac{\chi_{LS}}{4\mu_B} \Delta\mu_L \quad \text{Bruno ('89)}$$

Characteristic energies of metallic ferromagnets

binding energy	1 - 10 eV/atom
exchange energy	10 - 10 ³ meV/atom
cubic MAE (Ni)	0.2 $\mu\text{eV}/\text{atom}$
uniaxial MAE (Co)	70 $\mu\text{eV}/\text{atom}$

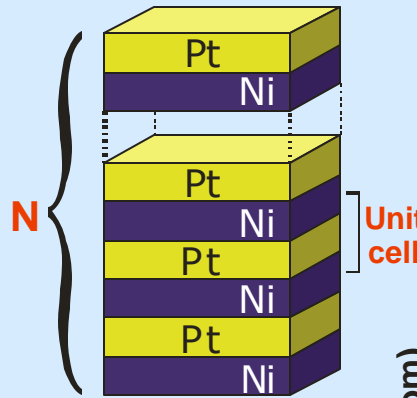
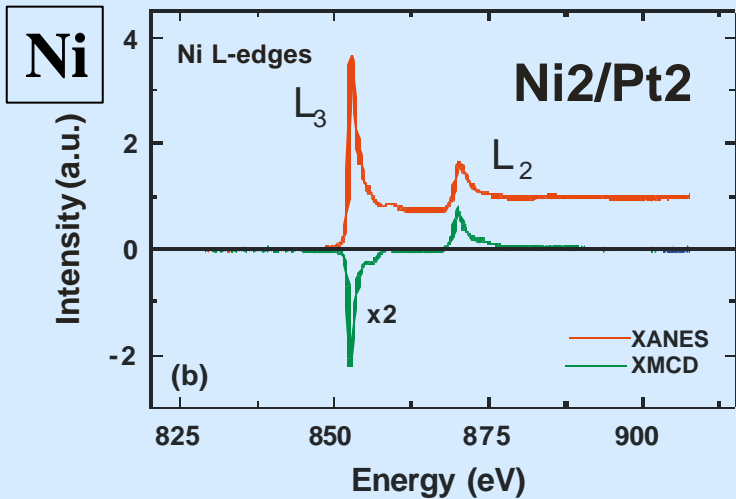
K. Baberschke, Lecture Notes in Physics, Springer **580**, 27 (2001)

Magnetic Anisotropy Energy MAE and anisotropic μ_L

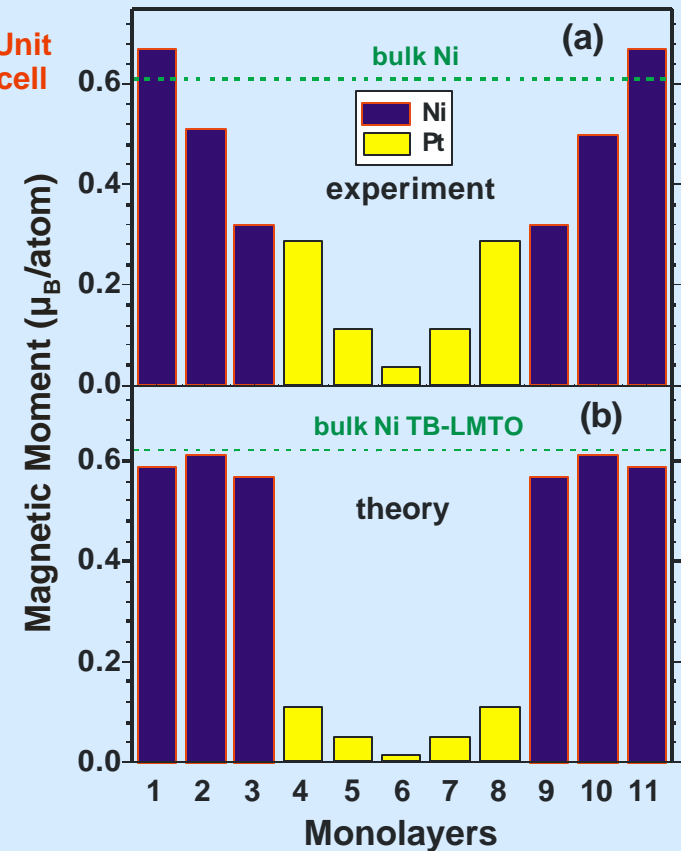


O. Hjortstam, K. B. et al. PRB **55**, 15026 ('97)

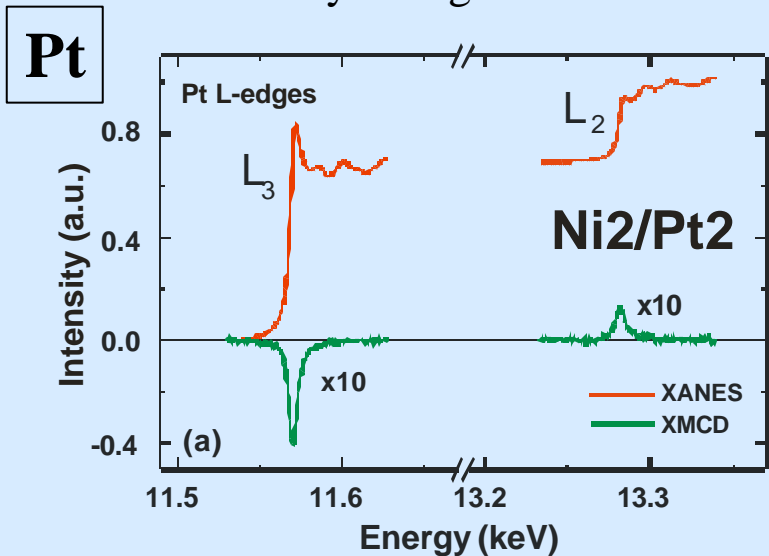
4. Induced magnetism at interfaces



Magnetic moment profile for a Ni₆/Pt₅ ML



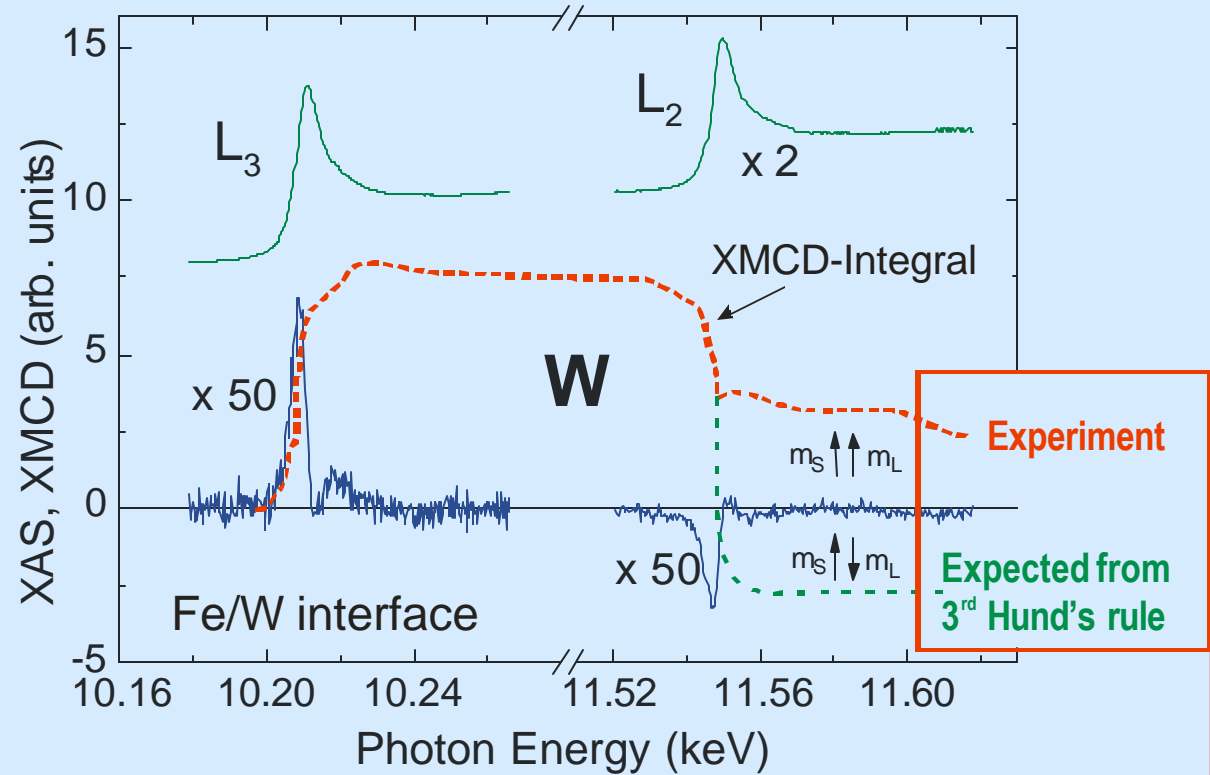
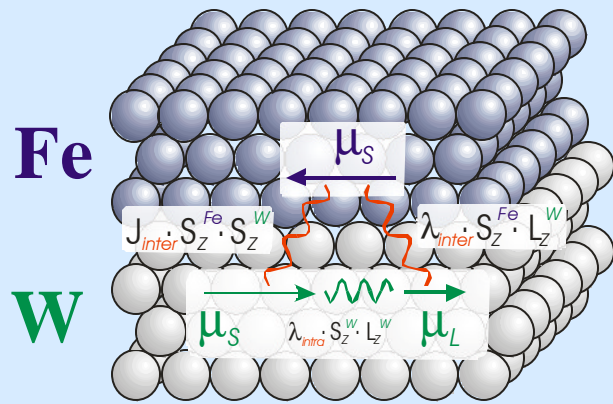
Ni and Pt carry a magnetic moment



No 'dead' Ni layers

F. Wilhelm et al. PRL **85**, 413 (2000) and ESRF Highlights 2000

Induced magnetism in 5d-transition metals breakdown of 3rd Hund's rule ?

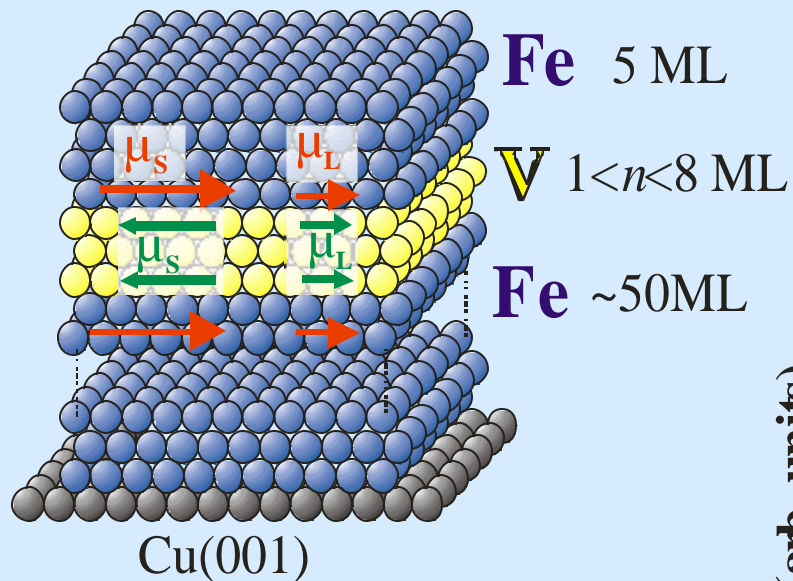


$$J_{inter} \cdot S_Z^{Fe} \cdot S_Z^{W} > \lambda_{inter} \cdot S_Z^{Fe} \cdot L_Z^{W} > \lambda_{intra} \cdot S_Z^{W} \cdot L_Z^{W}$$

alternatively: details of SP-DOS; hybridization

F. Wilhelm et al.,
Phys. Rev. Lett. **87**, 207202 (2001)

Fe/V/Fe(110) Trilayer



XMCD measurements:

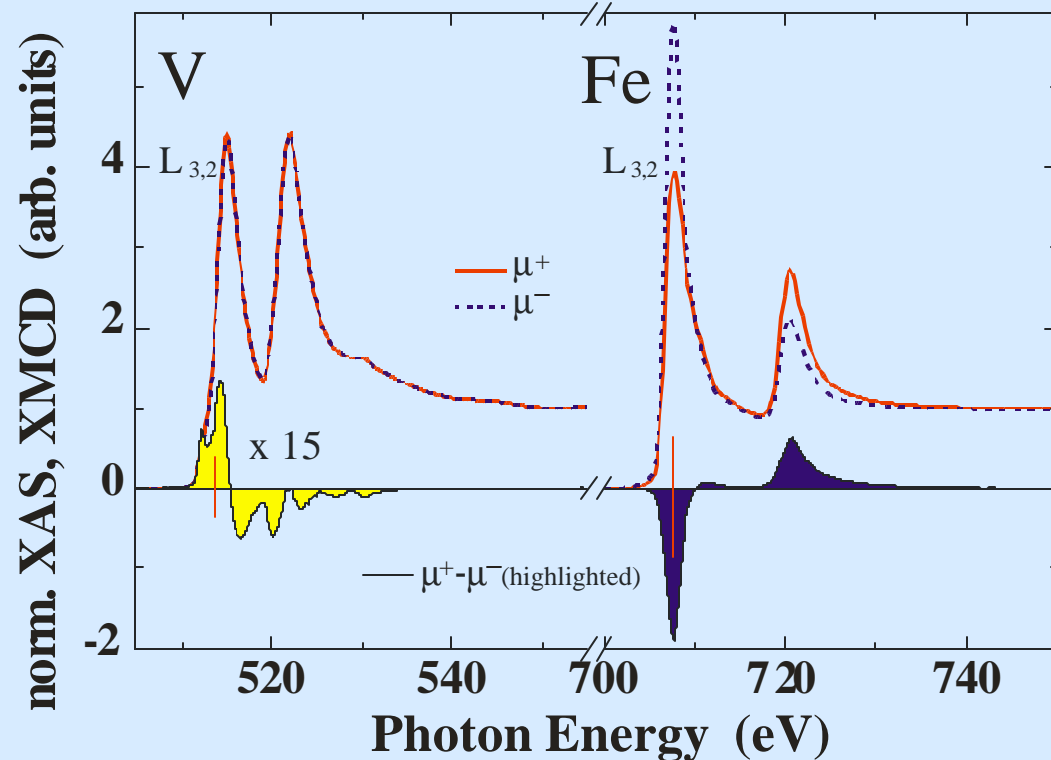
- BESSY II, third generation synchrotron source in Berlin
- Newly developed ‘gapscan’ mode: High degree of circularly polarized light and high photon flux

Advantages:

controlable growth

- annealing to reduce surface roughness
- preparation at 300 K

In-situ experiment, i.e. no capping layers



5. Full calculation of $\mu(E)$

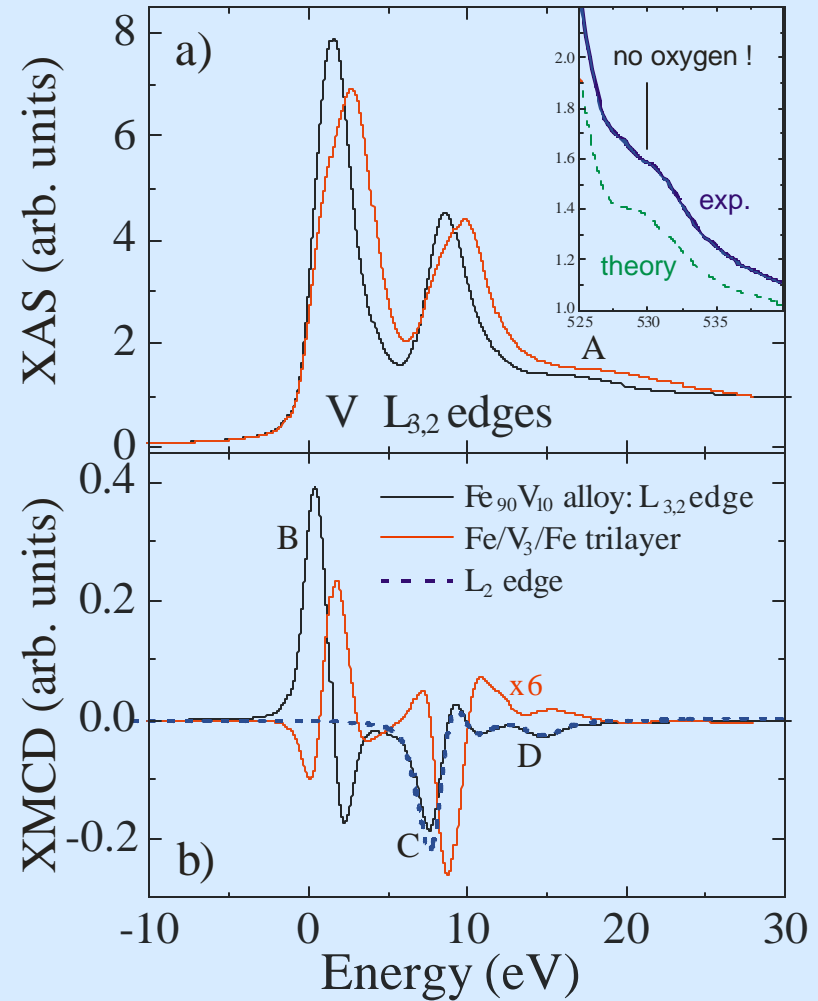
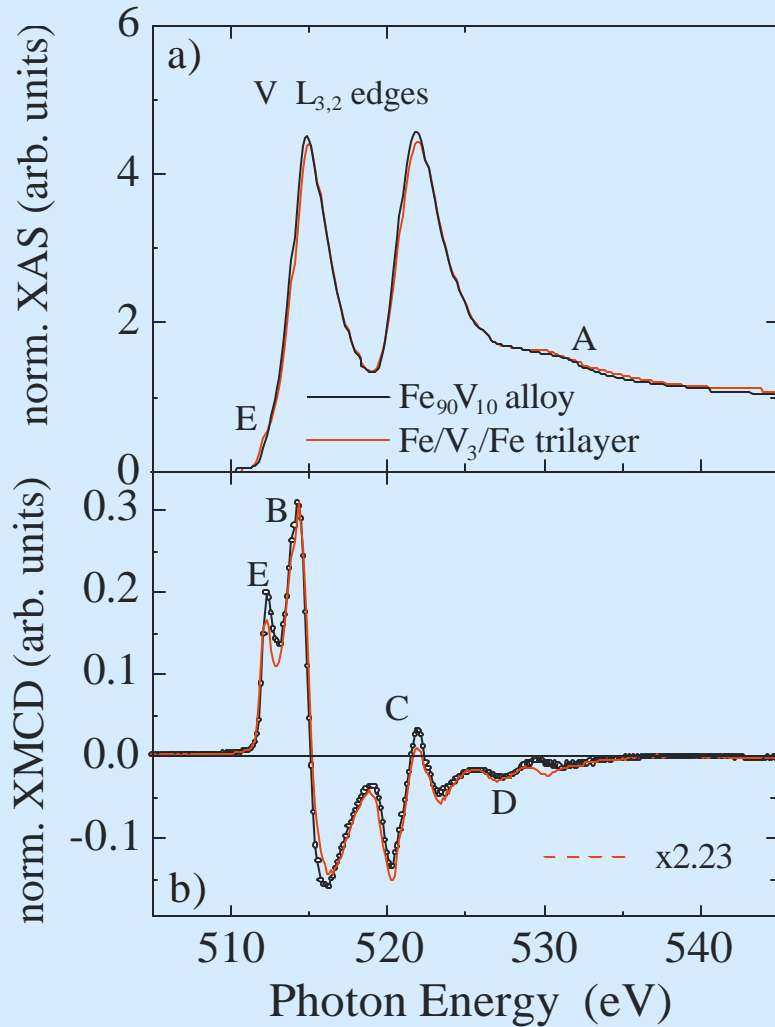
Experiment

A. Scherz et al.

PRB 66, 184401 (2002)

Theory

J. Minar, D. Benea, H. Ebert, LMU



Beyond sum rules: full calculation of $\mu(E)$

PHYSICAL REVIEW B 66, 184401 (2002)

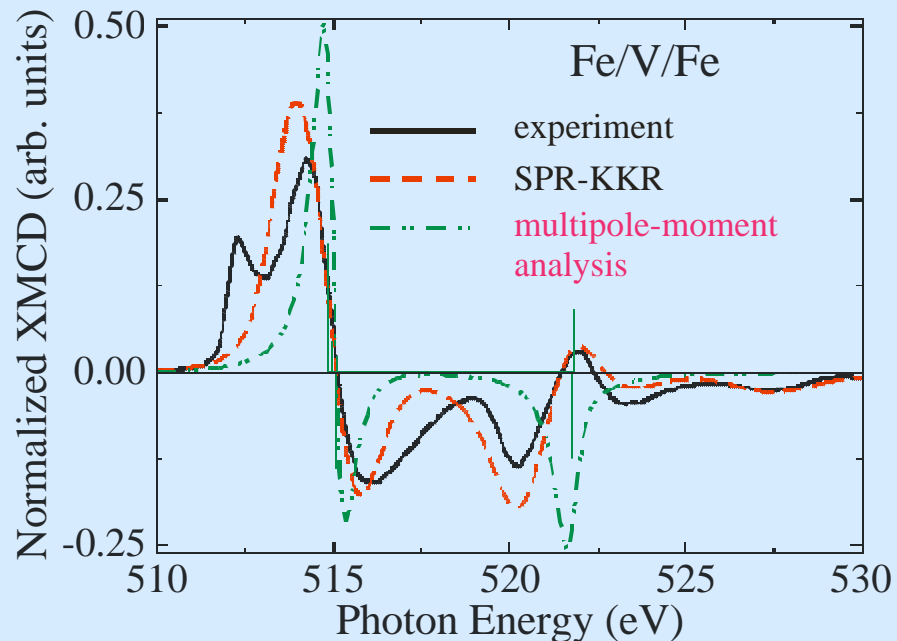
Relation between $L_{2,3}$ XMCD and the magnetic ground-state properties for the early 3d element V

A. Scherz,* H. Wende, and K. Baberschke

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

J. Minár, D. Benea, and H. Ebert

Physical Chemistry, Department of Chemistry and Pharmacy, University of München, Butenantstraße 5-13, 81377 München, Germany



Sum rules and beyond

* Gerrit van der Laan

Daresbury Laboratory, Warrington WA 4 4AD, UK

Abstract

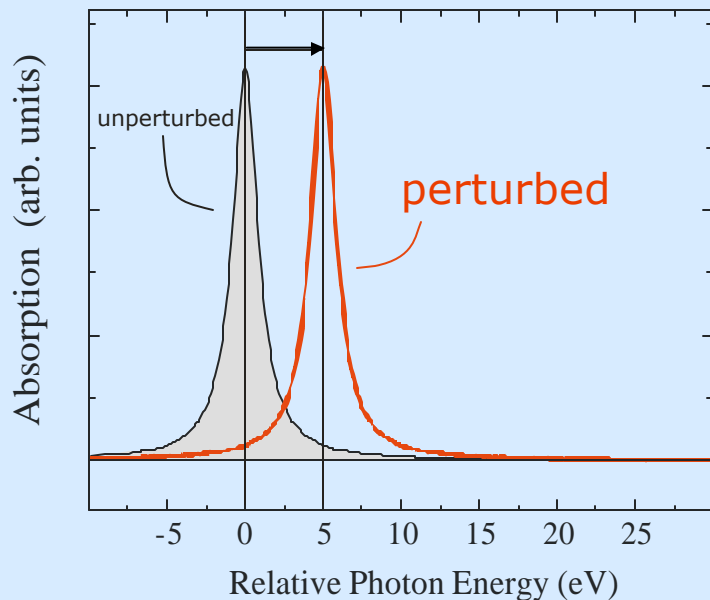
Sum rules relate the integrated signals of the spin-orbit split core levels to ground state properties, such as the spin-orbit coupling, magnetic moments and charge distribution. These rules give the zeroth moments of the spectral distribution. It is shown how this can be generalized to higher-moment statistical analysis

Journal of Electron Spectroscopy and Related Phenomena
101–103 (1999) 859–868

double pole approximation (time-dependent DFT)

single pole

Petersilka et al. PRL 76 (1996) 1212
Atoms ($^1S \rightarrow ^1P$)



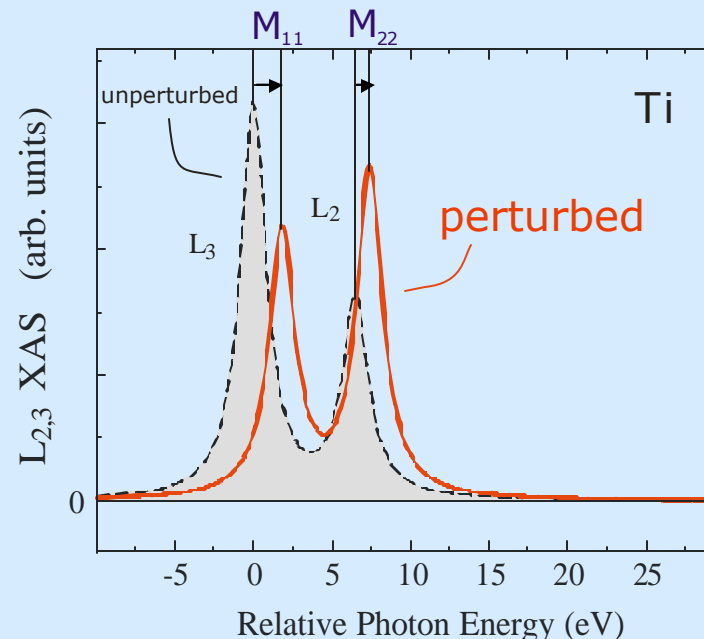
frequency-dependent perturbation

↓
ground-state density

⇓
linear response theory

double pole

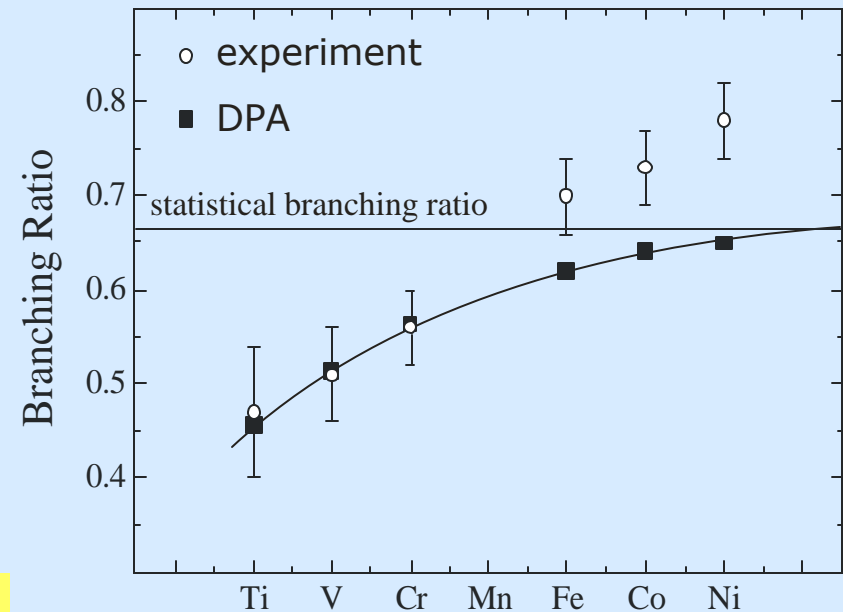
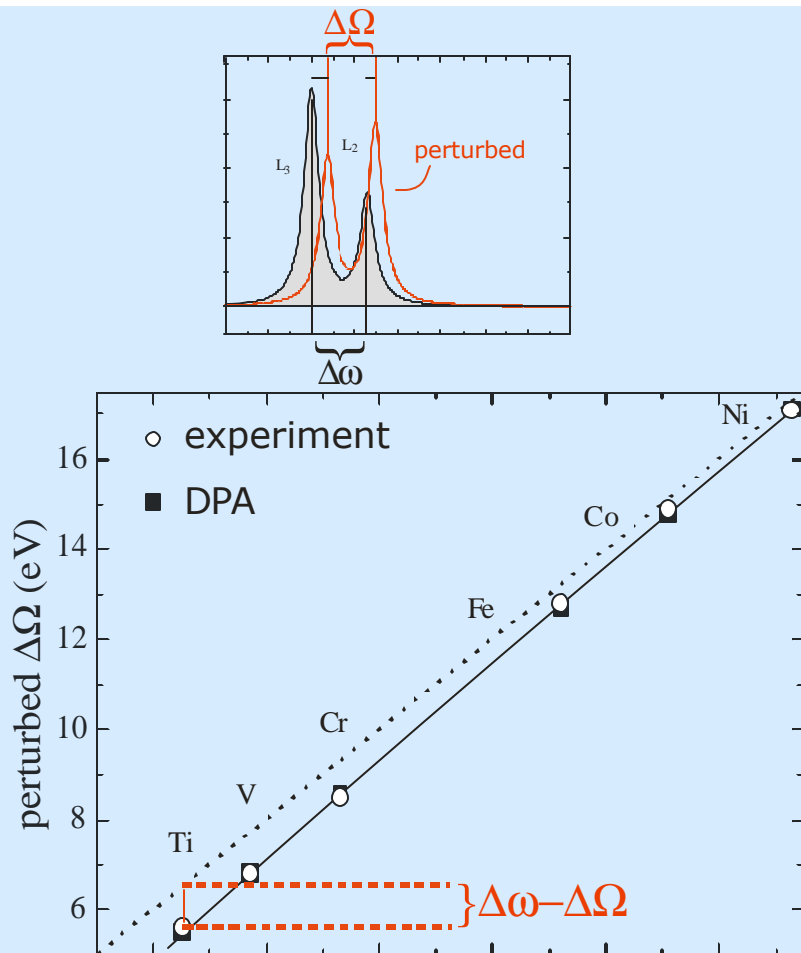
PhD thesis A. Scherz
 $L_{3,2}$ edges metals



- energy shift of perturbed resonances
- shift of spectral weight $L_3 \rightarrow L_2$ (branching ratio)

$$K(\mathbf{r}, \mathbf{r}', \mathbf{w}) = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \mathbf{w})$$

⇓ determine matrix elements



A. Scherz, et al.
Measuring the kernel of time-dependent density functional theory with X-ray absorption spectroscopy of 3d transition metals
 Phys. Rev. Lett. **95**, 253006 (2005)

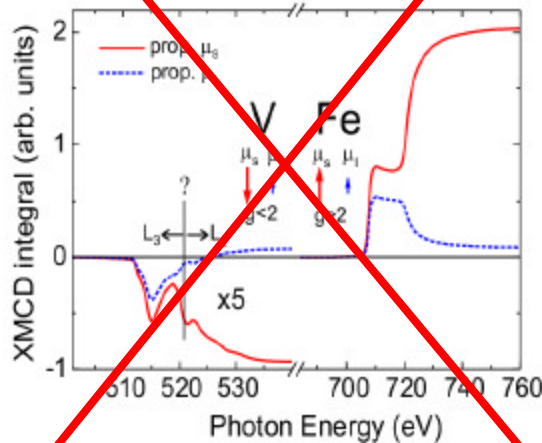
n_H

- ⇒ double pole model describes branching ratio for light 3d's
- ⇒ regime where sum rules fail

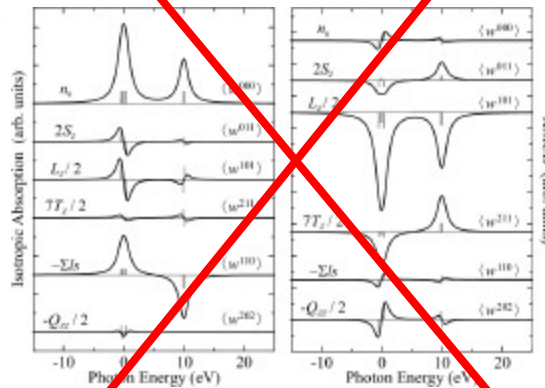
Summary

- gap-scan technique \Rightarrow systematic investigation of XAS, XMCD fine structure
- development double pole approximation
 \Rightarrow correlation energies (Ti: $M_{11}=3.07$ eV, $M_{22}=-0.56$ eV, $M_{12}=0.54$ eV)
- experiment \Rightarrow failure of spin sum rule \leftrightarrow core-hole interaction
- theory \Rightarrow correlation energies as input for theory
- \Rightarrow future ab initio calculations must include core-hole correlation effects

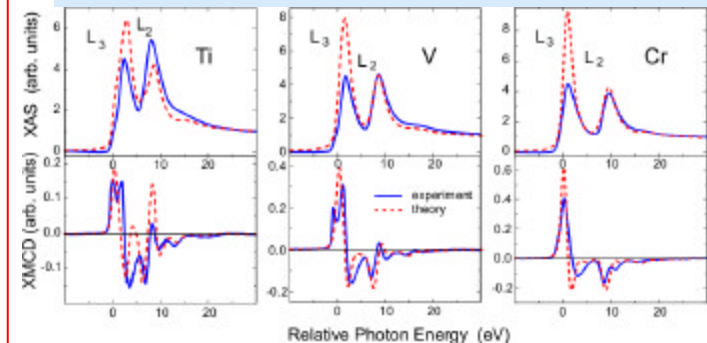
1) integral SR



2) MMA



3) calculation of full $\mu(E)$ ✓



see: Recent advances in x-ray absorption spectroscopy

H. Wende, Rep. Prog. Phys. **67** (2004) 2105-2181

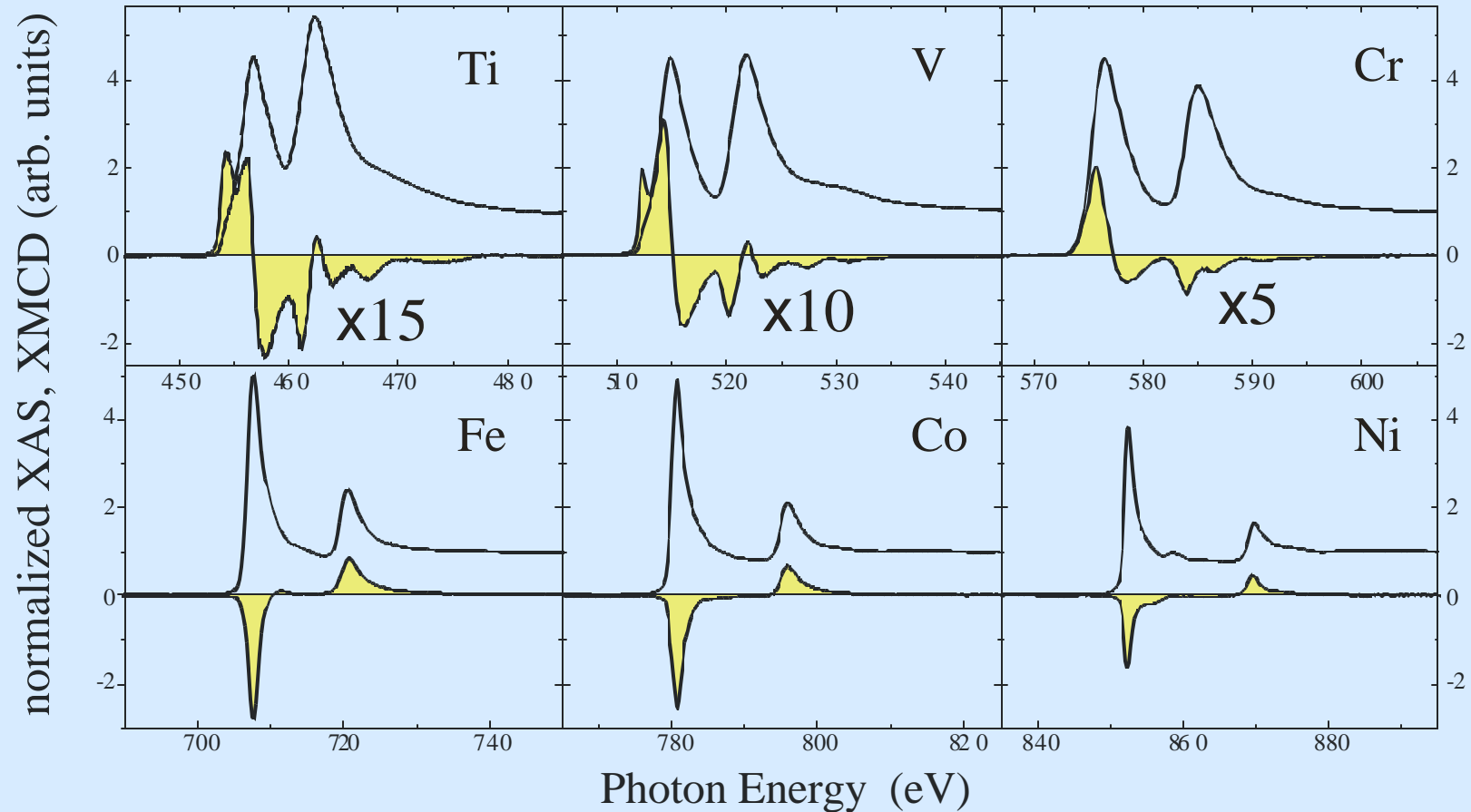
-
- All spectroscopic techniques do not restrict themselves to measure the intensity (area under the resonance) only.
i.e.: integral sum rules.
 - A resonance signal contains a resonance position, a width, an asymmetry profile, etc.
 - The optimum is given if theory can calculate the full profile of the resonance, in our case $\mu(E)$ i.e. the spectral density.

Recent advances in x-ray absorption spectroscopy

H. Wende , Rep. Prog. Phys. **67**, 2105 (2004)

L_{2,3} XAS and XMCD of 3d TM's

Sc Ti V Cr Mn Fe Co Ni Cu Zn



A. Scherz et al., XAFS XII June 2003 Sweden, Physica Scripta **T115**, 586 (2005)

A. Scherz et al., BESSY Highlights p. 8 (2002)

Conclusion, Future

During last few years: enormous progress in

- Theory:**
- calculate $\mu(E)$, spin dependent spectral distribution
 - full relativistic calculations
 - real (not ideal) crystallographic structures

- Experiment:**
- higher $\Delta E/E$, detailed dichroic fine structure
 - undulator, gap-scan technique, constant high P_C
 - element-selective microscopy, probe of “non-magnetic” constituents

- Future:**
- core hole effects:
 - change of branching ratio for early 3d elements
 - effect on XMCD unknown!
 - correct determination of $\Delta \mu_L$ and MAE with XMCD (x30)
 - correction for spin- and energy-dependence of matrix elements