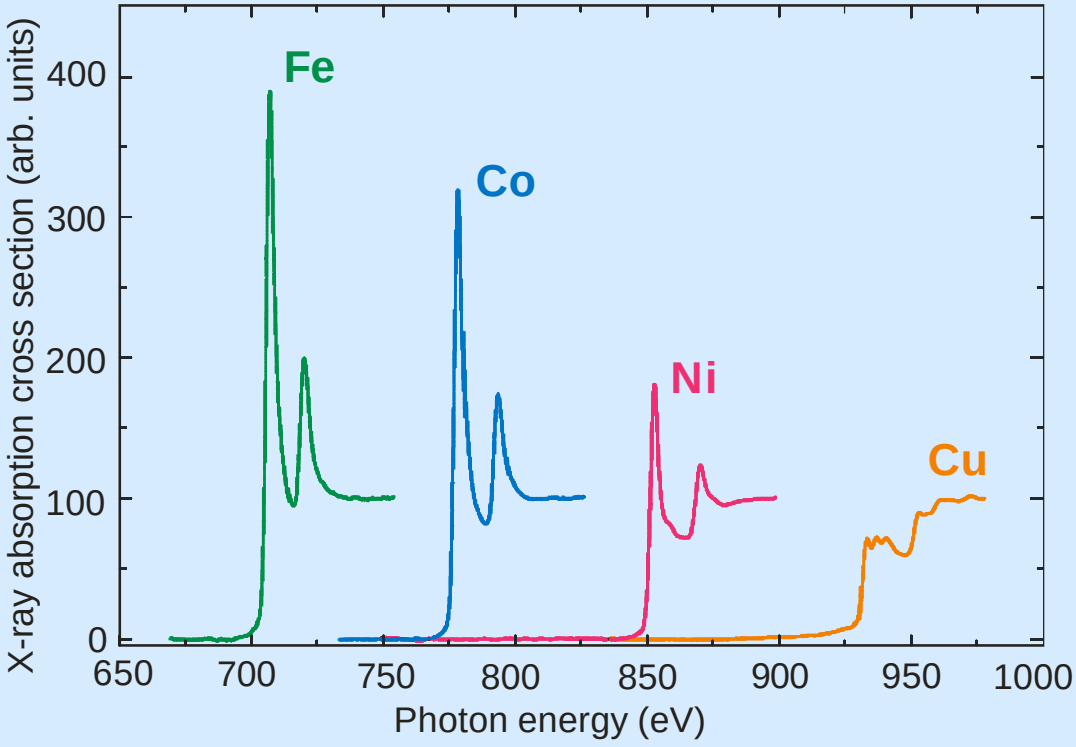
Lecture 5: X-ray Absorption Spectroscopy: Introduction

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



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

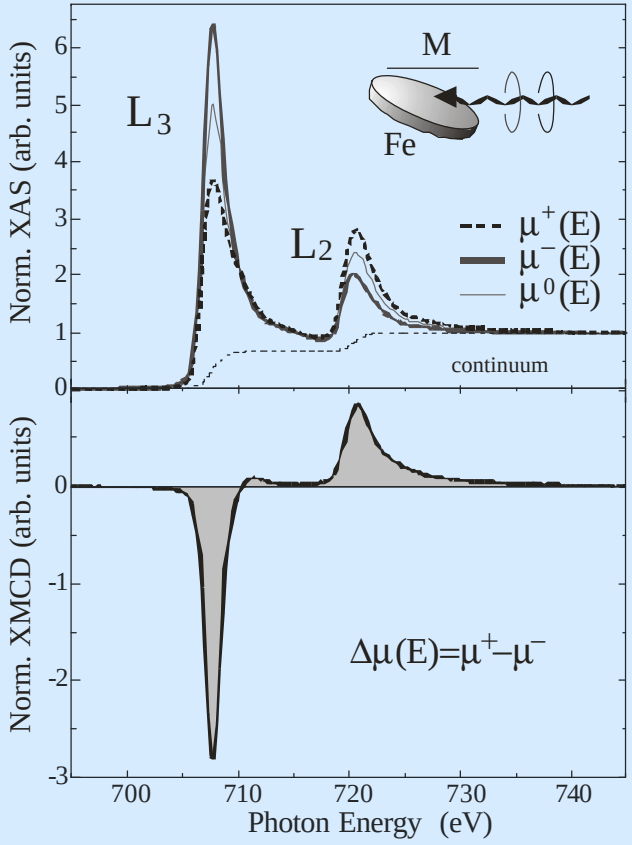
Note: the intensity of the 2p → 3d dipole transitions (E1) is proportional to the number of unoccupied final state (i.e. 3d- holes).

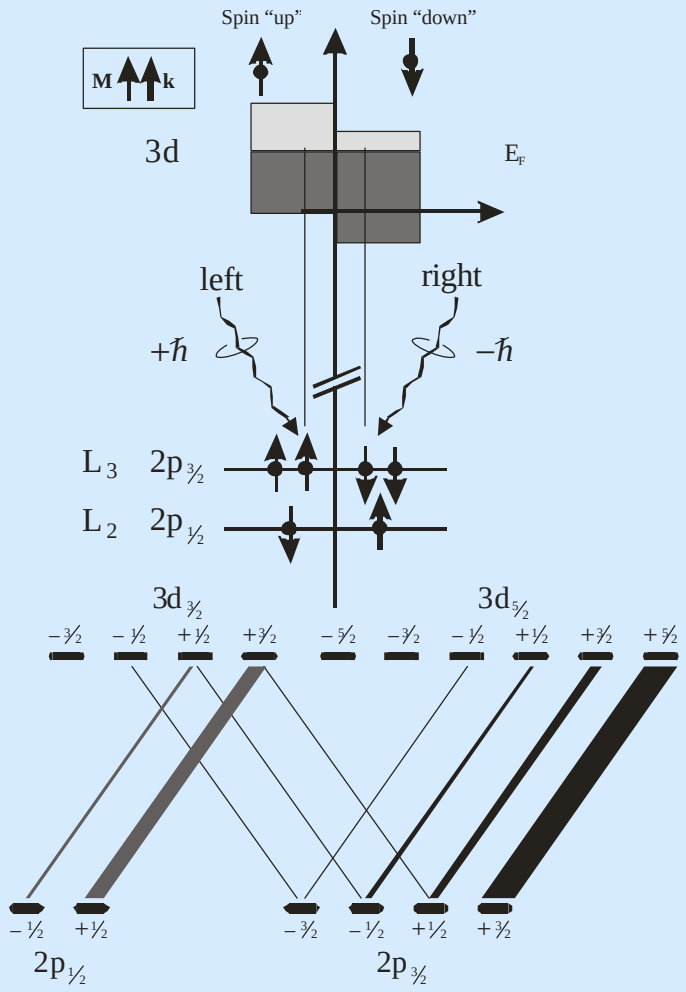
References

- 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).
- 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)



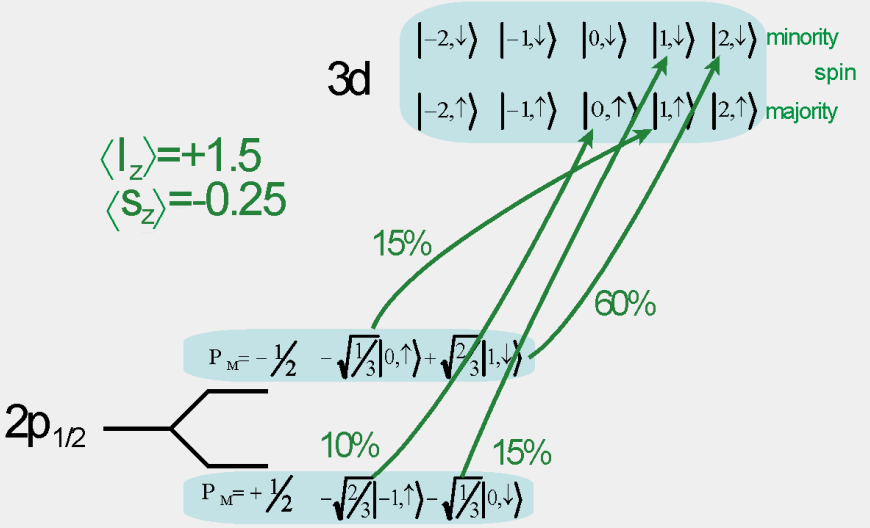


XMCD signal is a measure of the magnetization

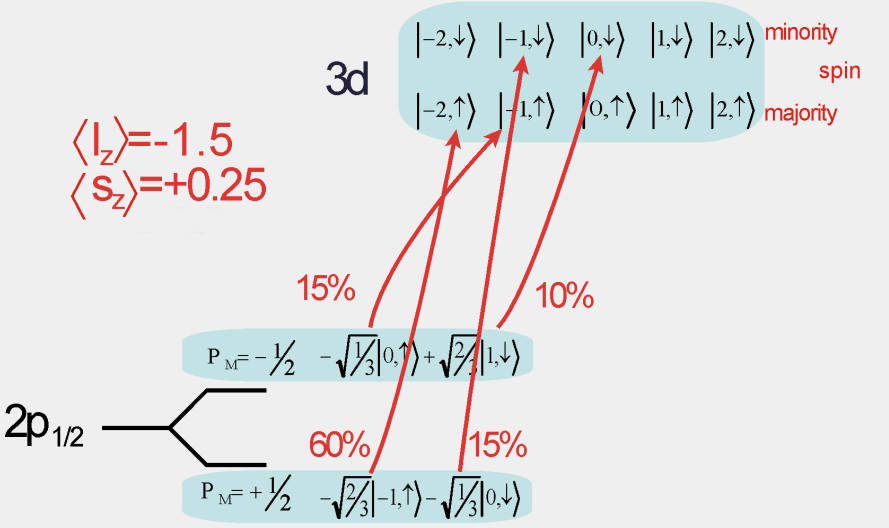
Many Reviews, e.g. H. Ebert Rep. Prog. Phys. **59**, 1665 (1996)

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

absorption of left circular pol. photon Δl=1, Δs=0

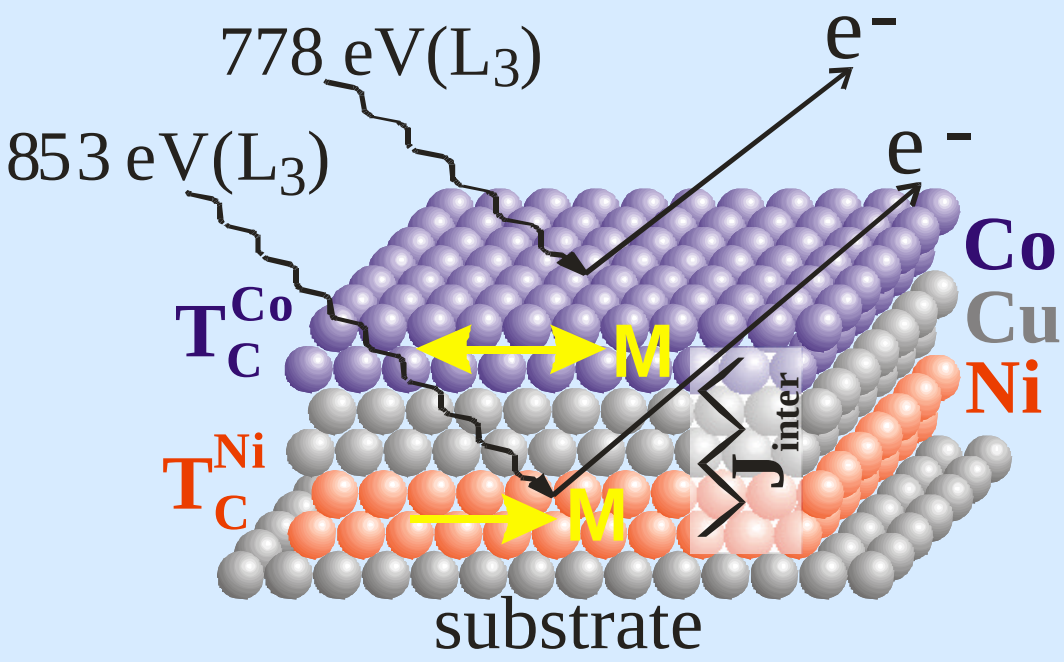


absorption of right circular pol. photon Δl=-1, Δs=0



There are many 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.

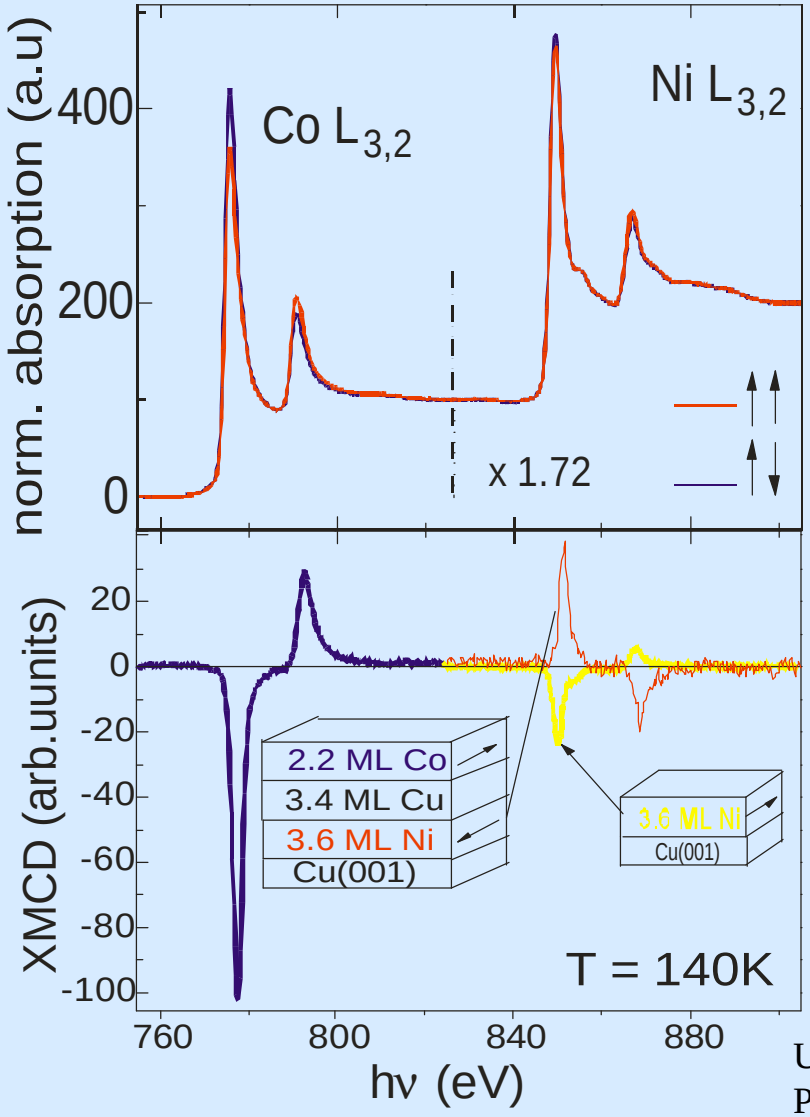
What about element specific Curie-temperatures ?

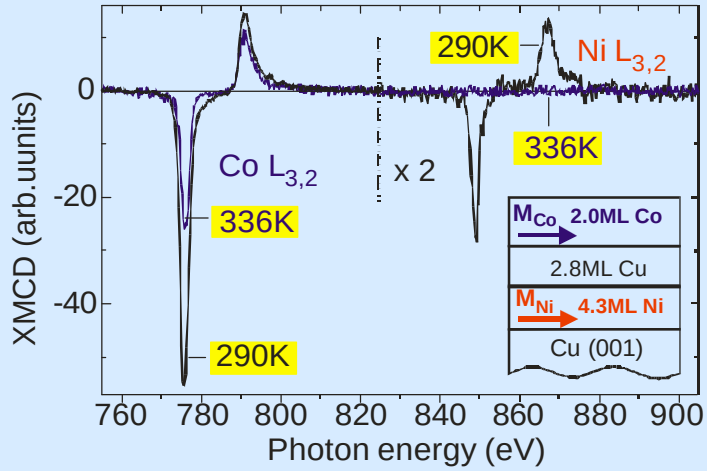
Two trivial limits: (i) $d_{Cu} = 0 \Rightarrow$ direct coupling like a Ni-Co alloy

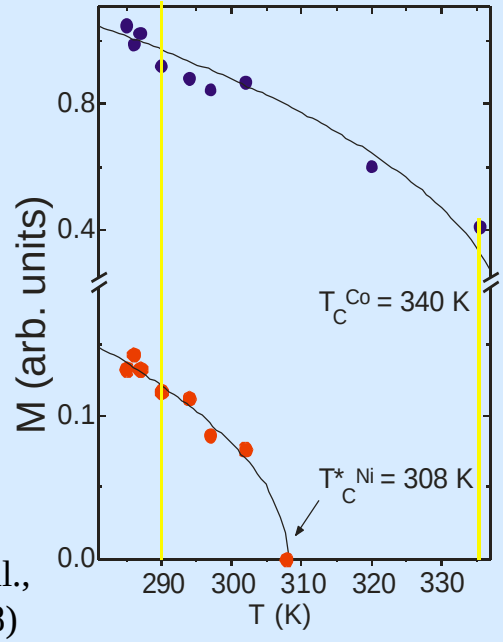
(ii) d_{Cu} = large $\Rightarrow$ no coupling, like a mixed Ni/Co powder

BUT $d_{Cu} \approx 2$ ML $\Rightarrow$ **?**

Ferromagnetic trilayers

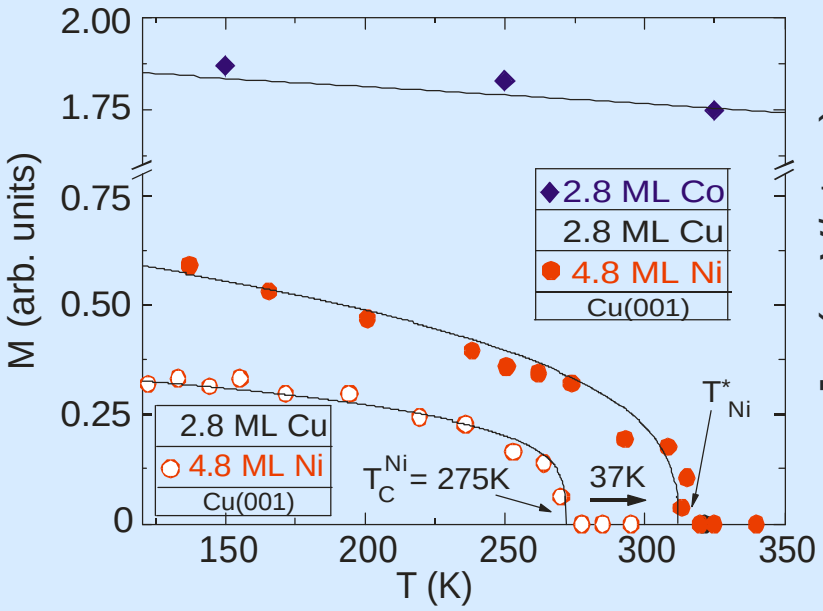


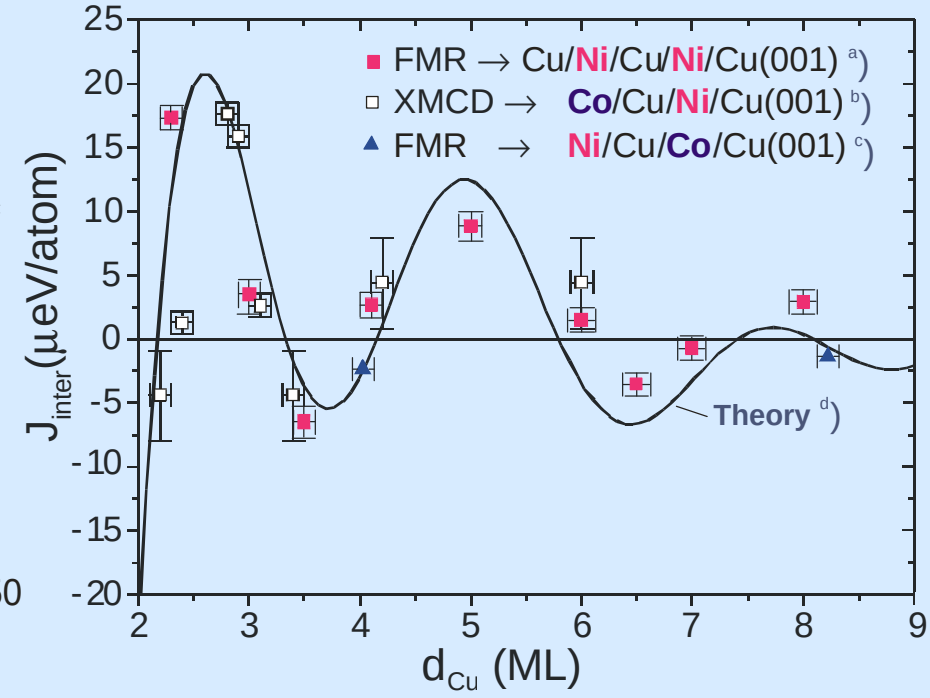




U. Bovensiepen et al.,
PRL **81**, 2368 (1998)

Interlayer exchange coupling

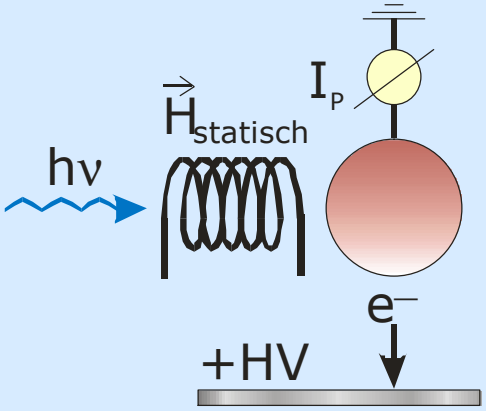




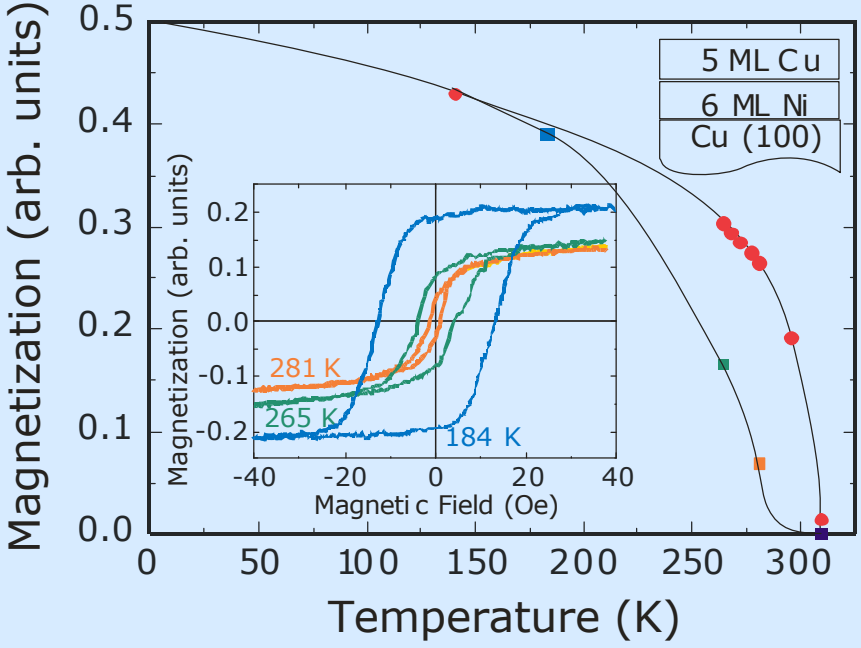
P. Poulopoulos, K. B., Lecture Notes in Physics **580**, 283 (2001)

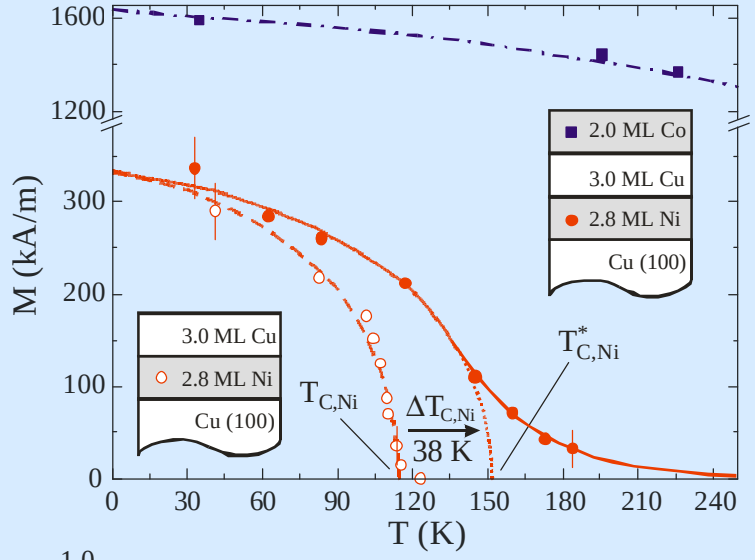
a) J. Lindner, K. B., J. Phys. Condens. Matter **15**, S465 (2003)
b) A. Ney et al., Phys. Rev. B **59**, R3938 (1999)
c) J. Lindner et al., Phys. Rev. B **63**, 094413 (2001)
d) P. Bruno, Phys. Rev. B **52**, 441 (1995)

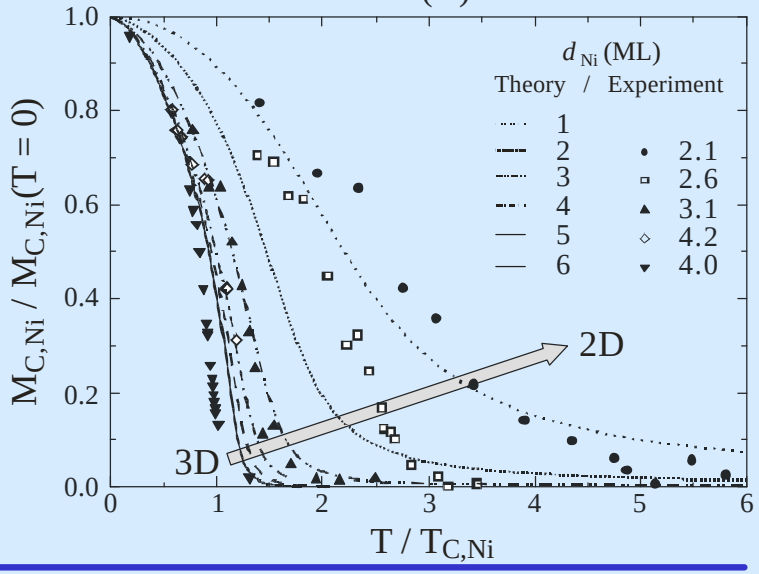
Remanence and saturation magnetization



C. Sorg et al.,
XAFS XII, June 2003
Physica Scripta 2005







PHYSICAL REVIEW B **70**, 212406 (2004)

Temperature-dependent magnetization in a ferromagnetic bilayer consisting of two materials with different Curie temperatures

J. Wu, G. S. Dong, and Xiaofeng Jin*
Surface Physics Laboratory, Fudan University, Shanghai 200433, China

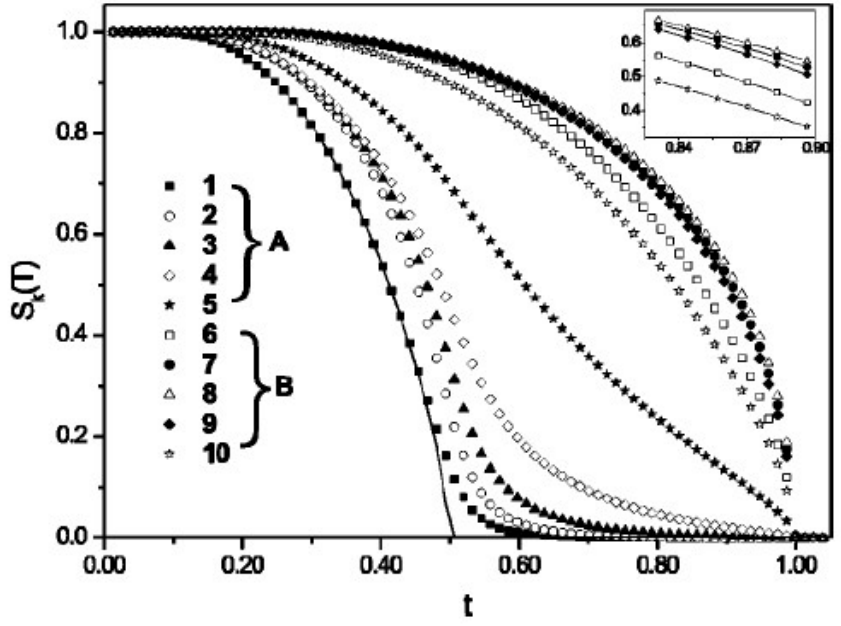
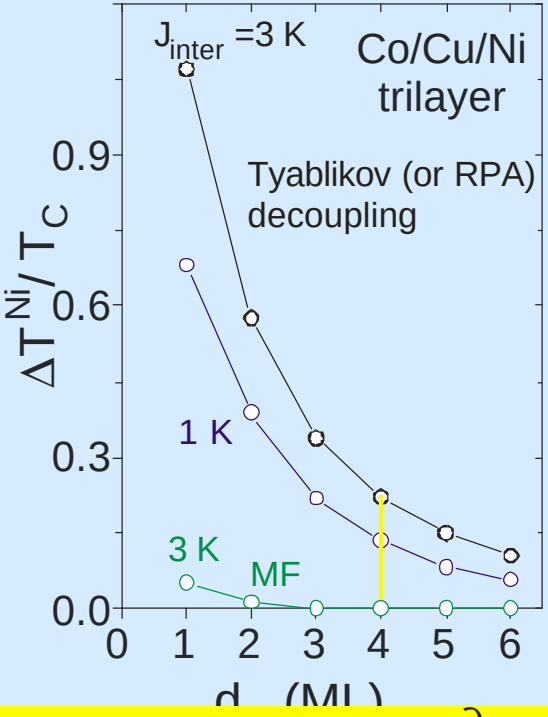


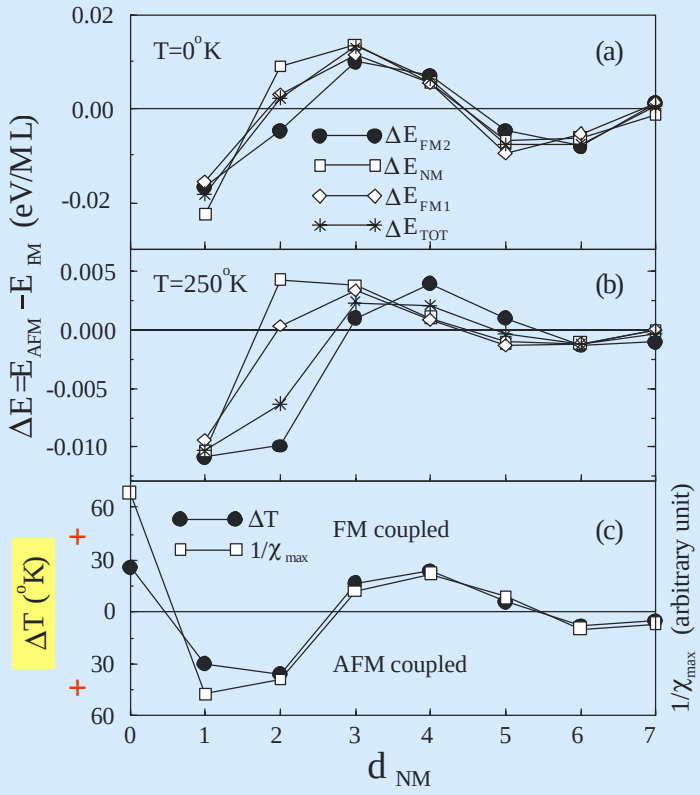
FIG. 3. Layer-dependent magnetization for a coupled bilayer with simple cubic structure. For any fixed temperatures, the layer-dependent curves of film *A* are ordered from the bottom as layers 1, 2, 3, 4, 5, respectively, while the curves of film *B* are ordered as layers 10, 6, 9, 7, 8, respectively. The solid line is the $S(T)$ curve of layer 1 in the uncoupled case.

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

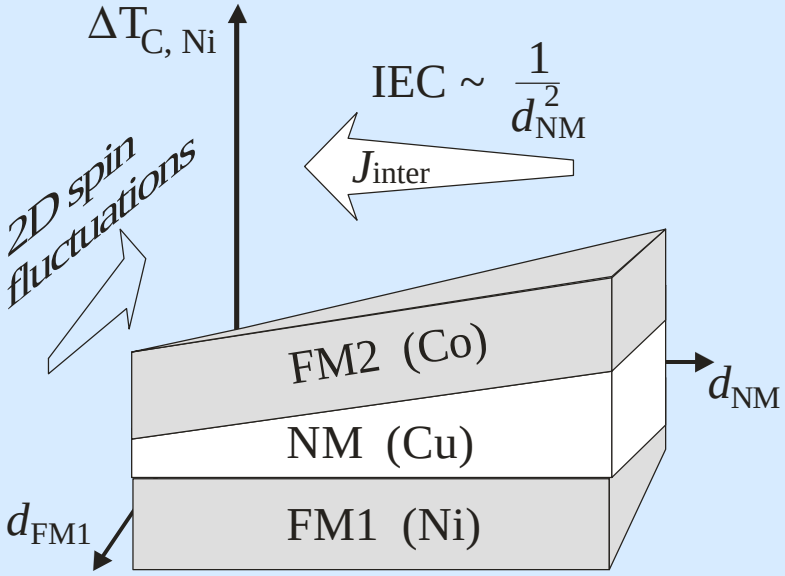
$$S_i^z S_j^+ \approx \langle S_i^z \rangle S_j^+ - \langle S_i^- S_i^+ \rangle S_j^+ - \langle S_i^- S_j^+ \rangle S_i^+ + \bullet\bullet\bullet$$

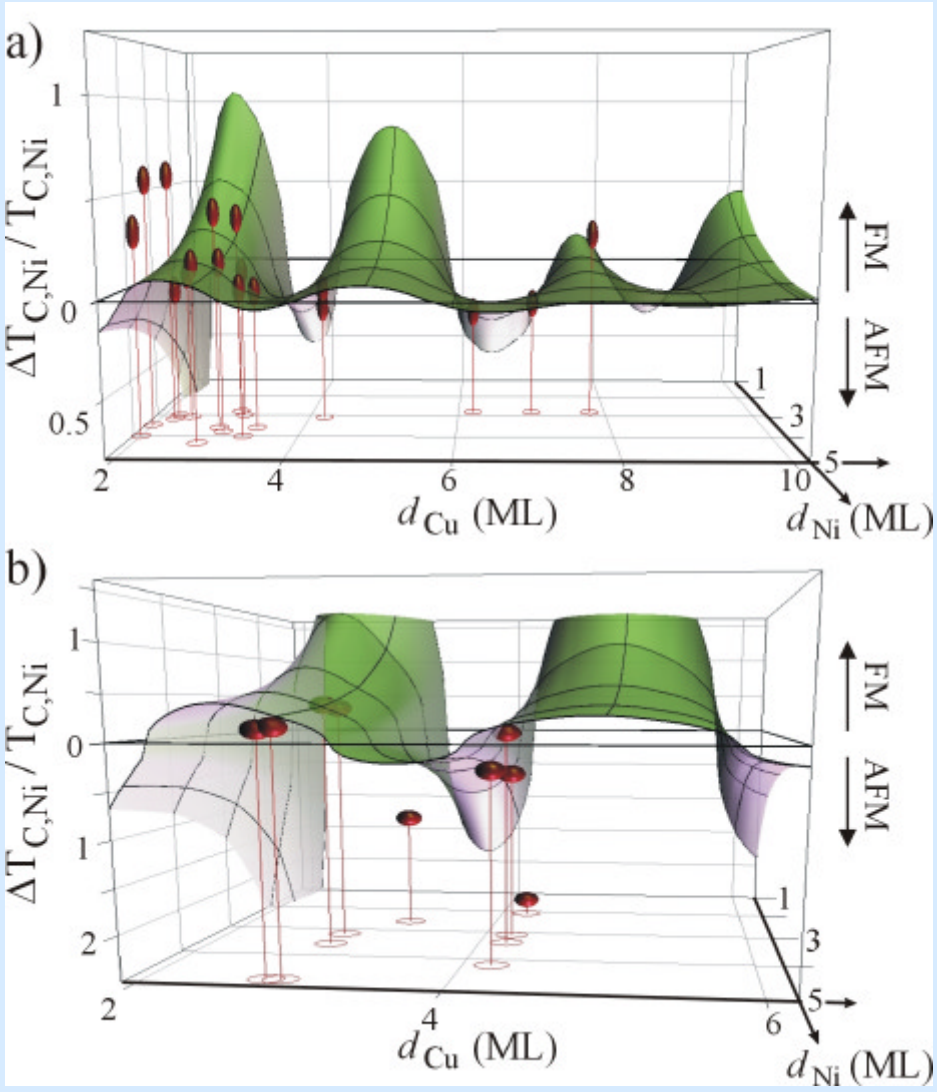
RPA

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

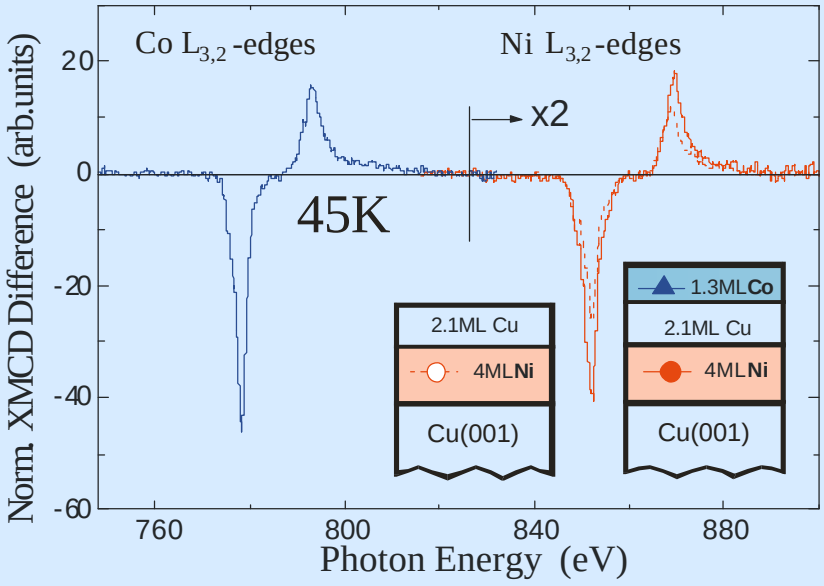
Single band Hubbard model:
Simple Hartree-Fock (Stoner) ansatz is insufficient
Higher order correlations are needed to explain T_C-shift

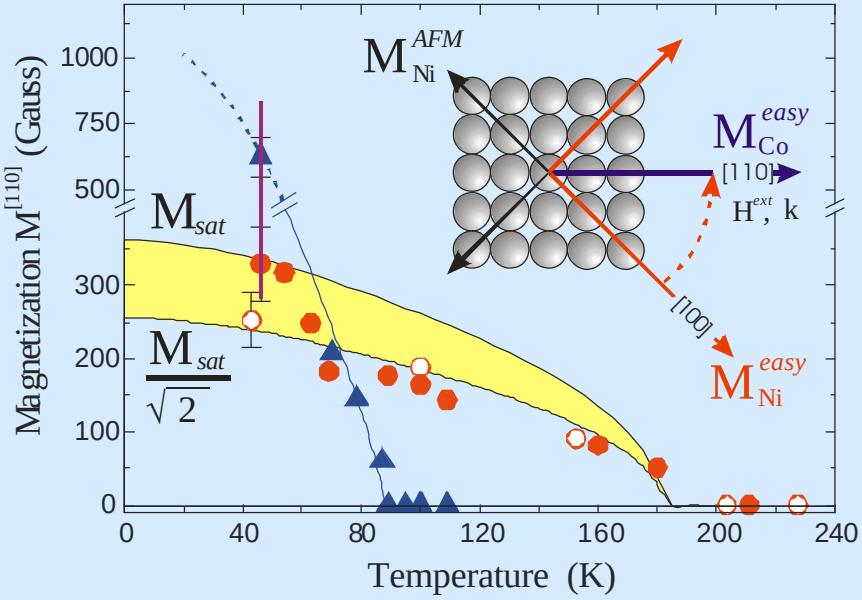
Evidence for giant spin fluctuations (PRB **72,** 054447 (2005)





Crossover of $M_{Co}(T)$ and $M_{Ni}(T)$





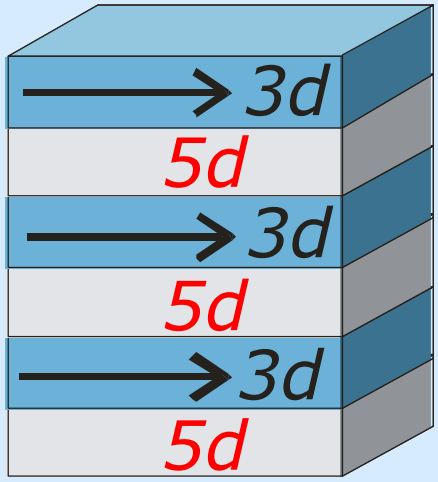
Two order parameter of T_C^{Ni} and T_C^{Co}
A further reduction in symmetry happens at T_C^{low}

Element specific XMCD, induced magnetism

Periodic alternation of ferro and non-magnetic layers

A large fraction of atoms are located at the interface

2 Dimensional systems



* **Full layer resolved magnetic profile in Ni/Pt multilayers**

→ **Soft and hard XMCD**

Probe the Interface Magnetism

Fe/V A. Scherz *et al.*, Phys. Rev. B66, 184401 (2002)

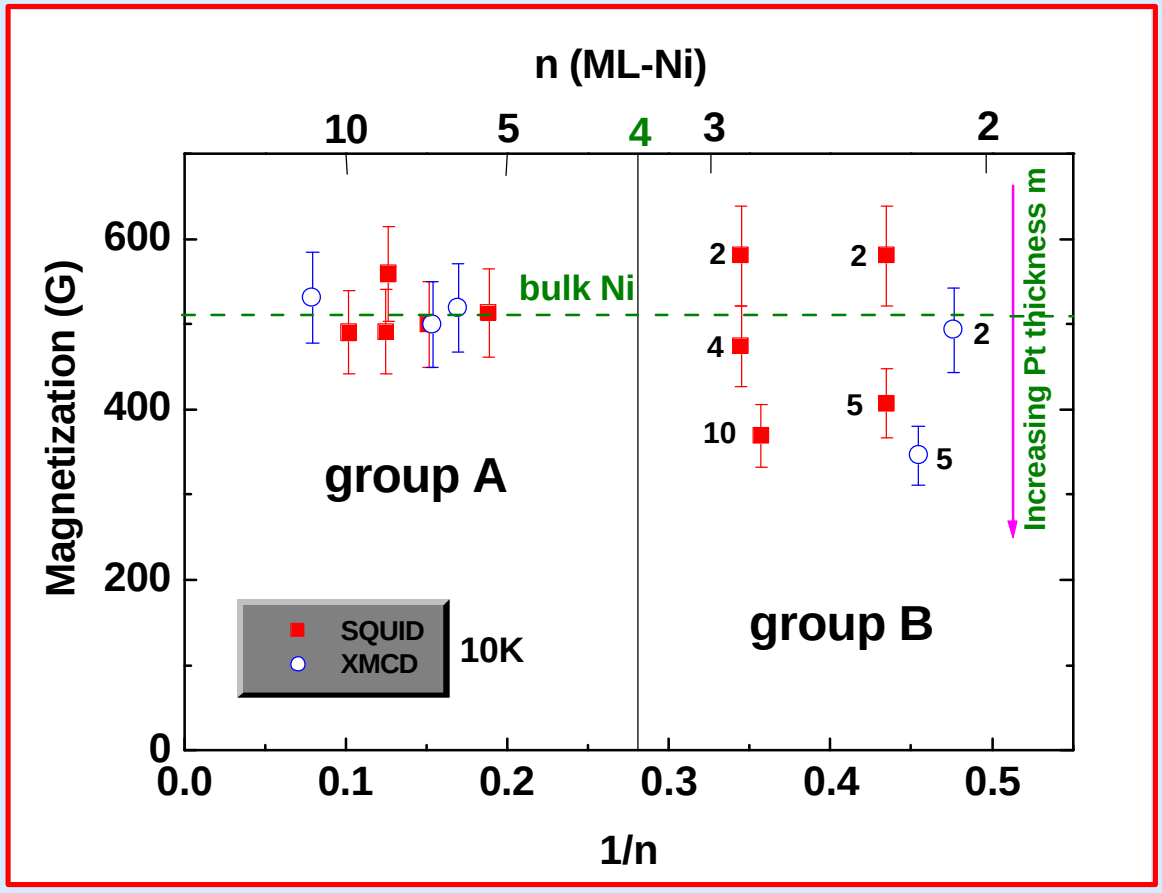
* **Focus on the *5d* induced magnetic moments**

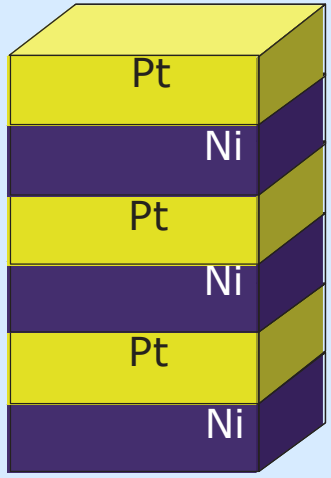
Systematics: the induced magnetism in 5*d* Series *(orbital magnetism)*

-Magnetic moments of W, Ir and Pt in multilayers

Comparison with *5d* impurities in Fe matrix

Magnetization per Ni-volume: SQUID - XMCD





Group A (n > 4ML Ni) ⟹ **Bulk-like behaviour**

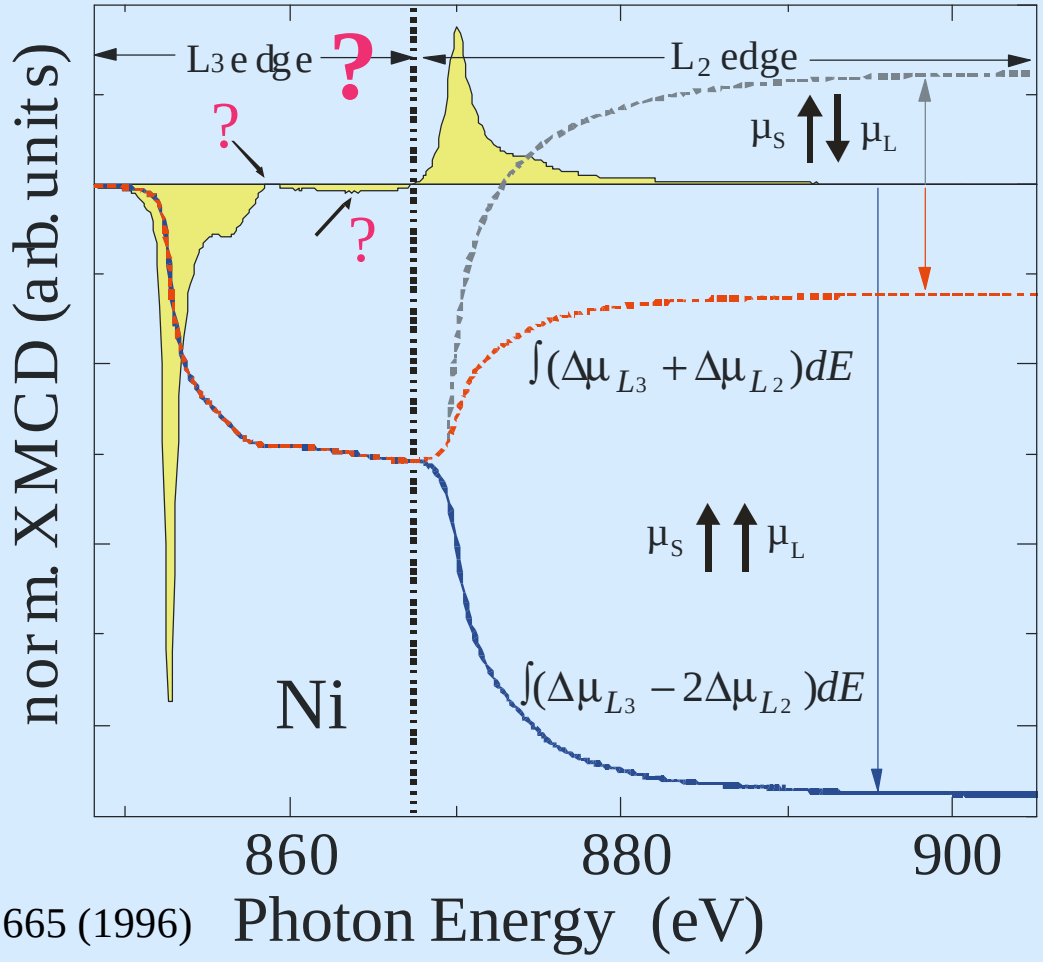
Group B (n < 4ML Ni) ⟹ **Depends on Pt thickness**

No 1/n dependence for Ni/Pt multilayer (predicted by MOKE) !

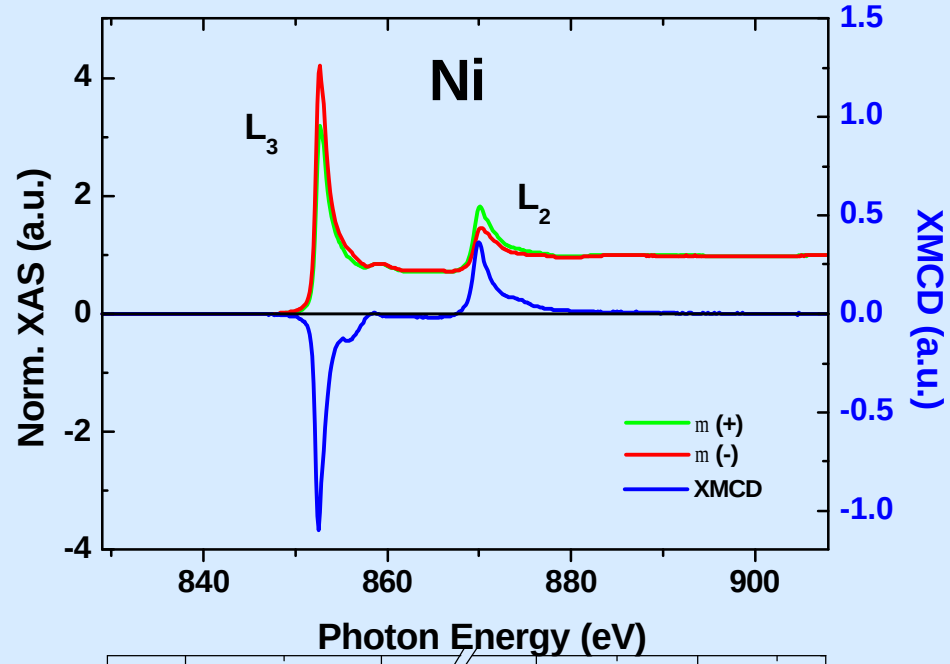
Orbital and spin magnetic moments deduced from XMCD

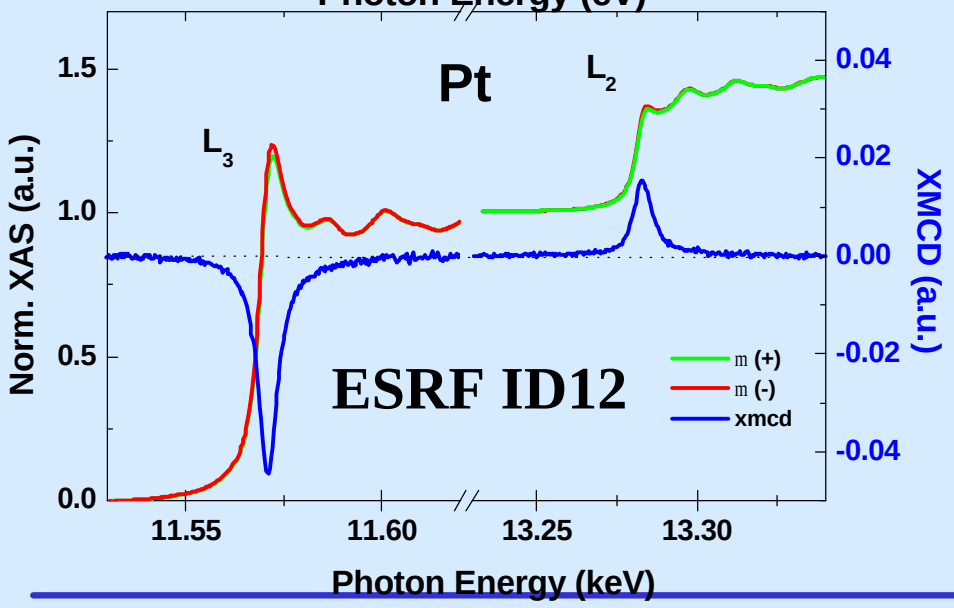
$$\int (?\,\mu_{L3} - 2\cdot ?\,\mu_{L2})\,dE = \frac{N}{3N_h^d}\left(2\langle S_z\rangle^d + 7\langle T_z\rangle^d\right)$$

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



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





Ni_2 / Pt_2 multilayer

$T_C \sim 300K$

Low Temperature Measurements

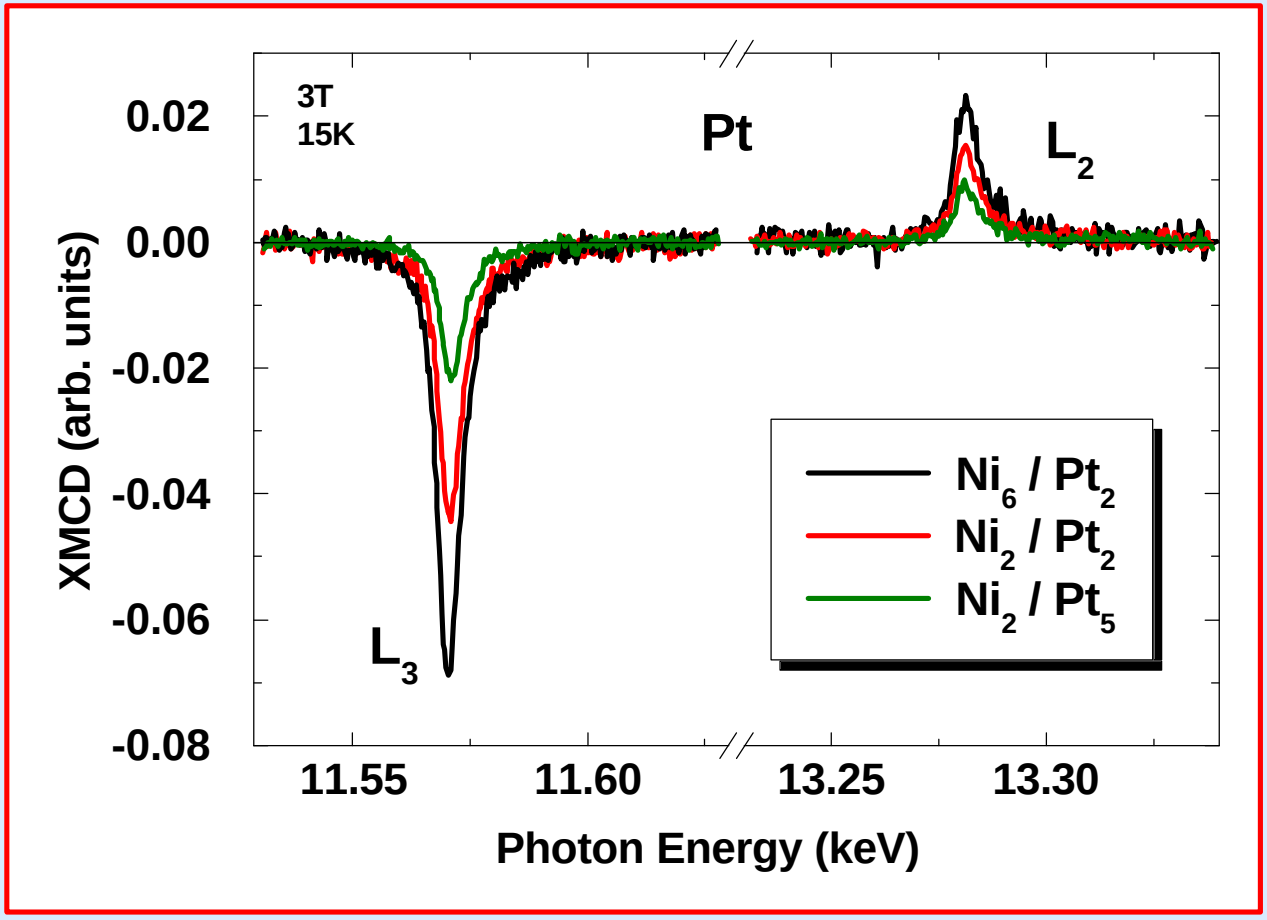
10K

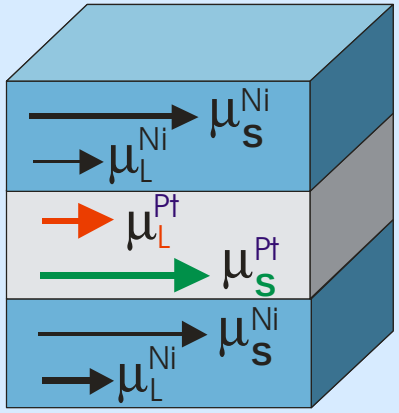
- **No 'dead Ni layers' at the interface**
  - $m_S^{Ni}=0.35\ m_B$/atom
  - $m_L^{Ni}=0.038\ m_B$/atom
- **Strong induced magnetic moments in Pt**
  - $m_S^{Pt}=0.14\ m_B$/atom
  - $m_L^{Pt}=0.03 m_B$/atom

Contrary to Kim *et al.*:

Sputtering methods (1-2 ML Ni 'dead' layers at the interfaces)

Pt XMCD as a function of Ni and Pt thickness





Via the magneto-optical sum-rules for Ni_6/Pt_2

$\langle L_z \rangle = 0.056(3)\ \mu_B$

$\langle S_z \rangle = 0.24(1)\ \mu_B$

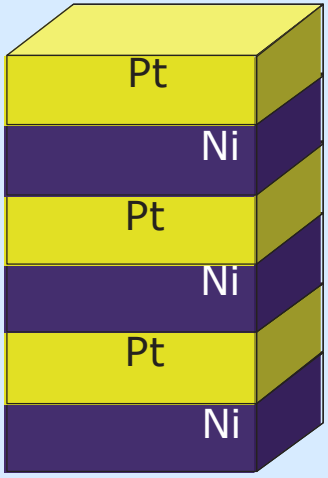
(per Pt atom)

To compare with

0.49 μ_B per Ni atom

Results for Ni_n / Pt_m multilayers

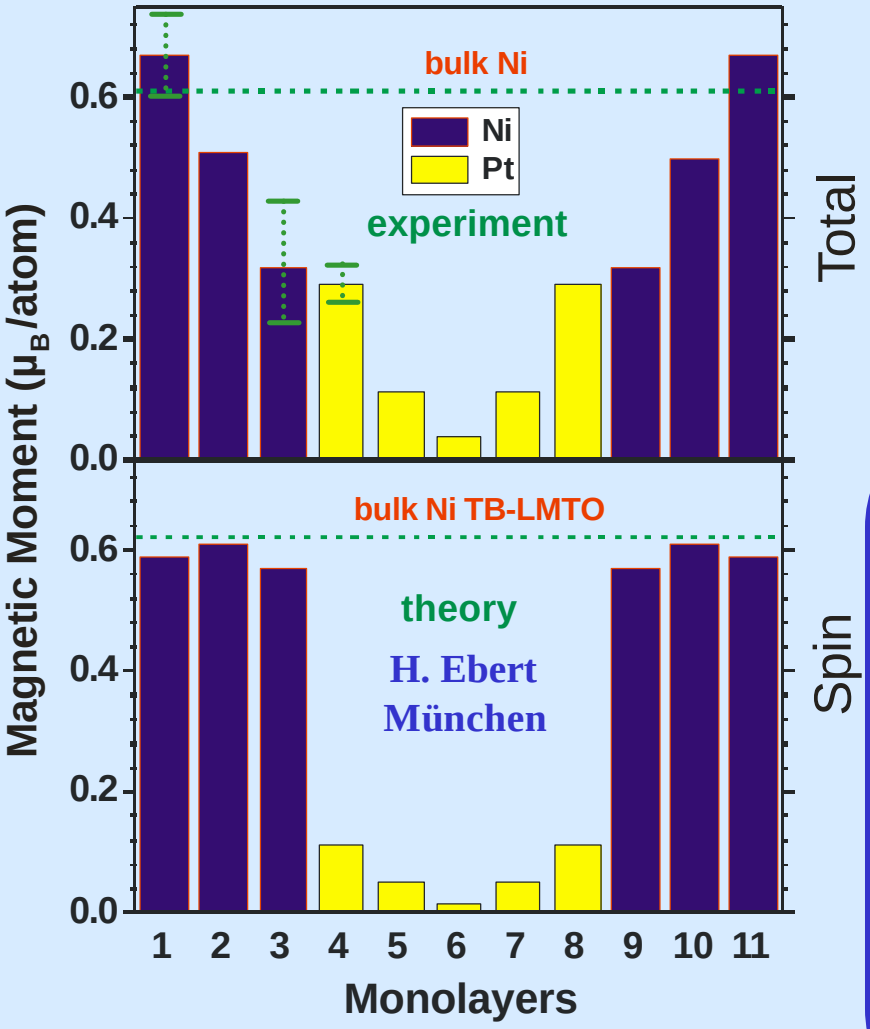
From Sum-Rules:

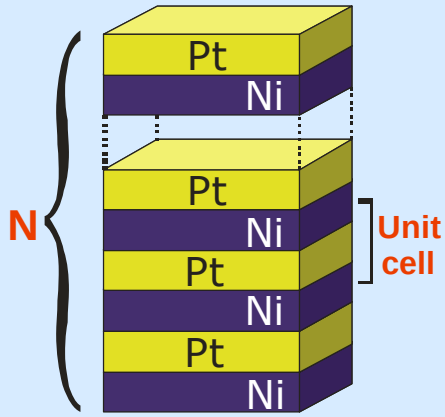


Ni *n* (ML)	Pt *m* (ML)	m_{Ni} (m_B/atom)	m_{Pt} (m_B/atom)	m_{tot} per Ni-volume (m_B/atom)
2	2	0.39	0.17	0.56
2	5	0.24	0.09	0.47
6	2	0.49	0.29	0.59
6	5	0.47	0.17	0.61
13	5	0.54	0.21	0.62
bulk Ni				0.61 (Kittel)

- Even samples with 2 ML of Ni separated by thicker Pt layers are magnetic. They would not be magnetic if alloyed (onset of ferromagnetism :>40 at. % Ni).
- No magnetically 'dead' Ni layers at the interfaces.
- **Strong polarization** of the Pt *5d* electrons. (contributes of about 10-50% to the magnetization)

Magnetic profile of a Ni_6/Pt_5 multilayer





Exp.

- **Atomic Interface exchange processes between Pt and Ni (could leads to alloyed region at the interface)**
- **Reduction of Ni moment, Pt unaffected**

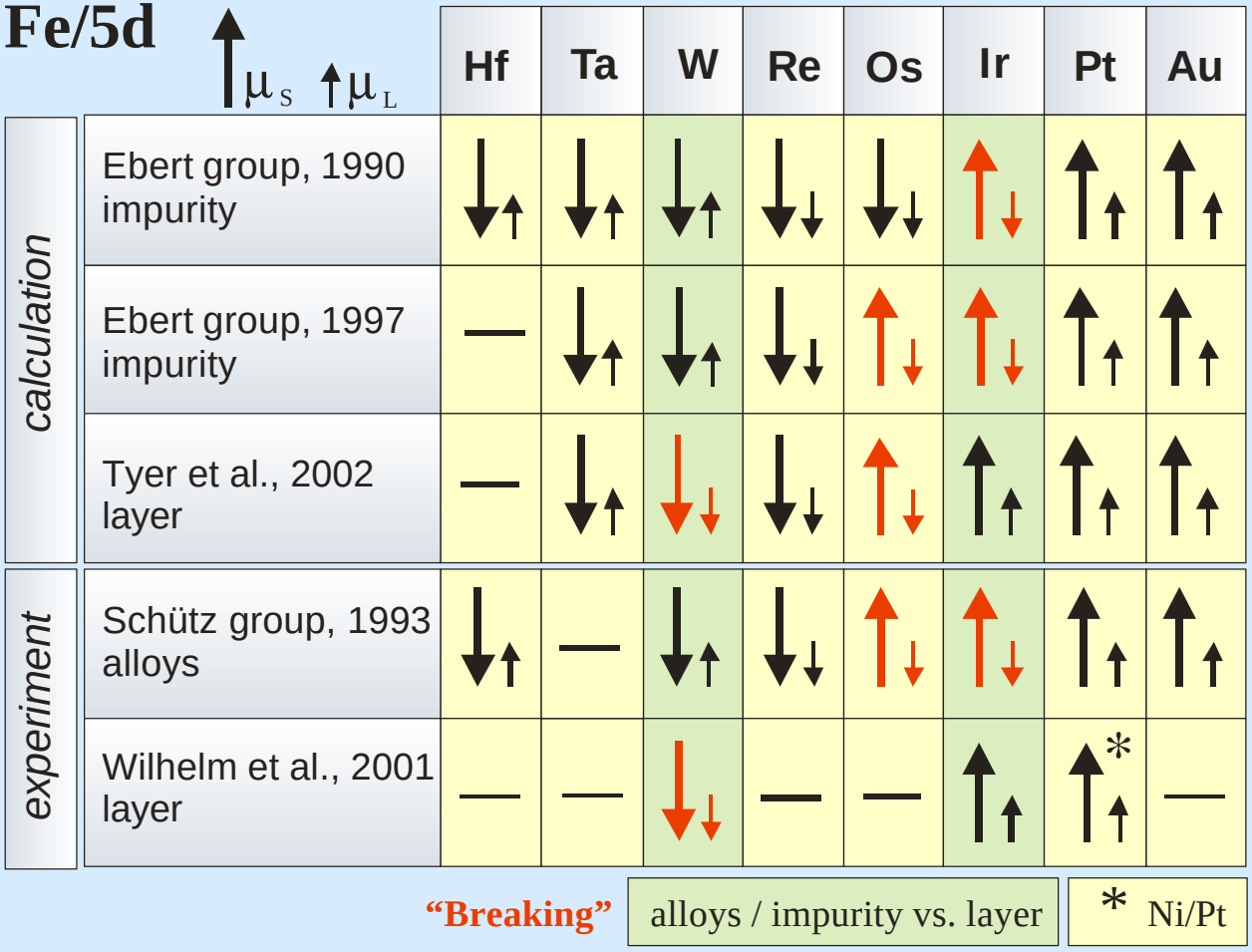
Theory

- **Lattice distortions neglected (1-5% in volume change 10% moment)**
- **Spin-only calculations (20% of orbital for Pt)**
- **S. Frota-Pessôa *et al.*, Phy. Rev. B66, 132416(2002) Ni and Pt profile well reproduced assuming only 25% interface intermixing**

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

P. Poulopoulos *et al.*, J. Appl. Phys. 89, 3874 (2001).

Calculation versus Experiment



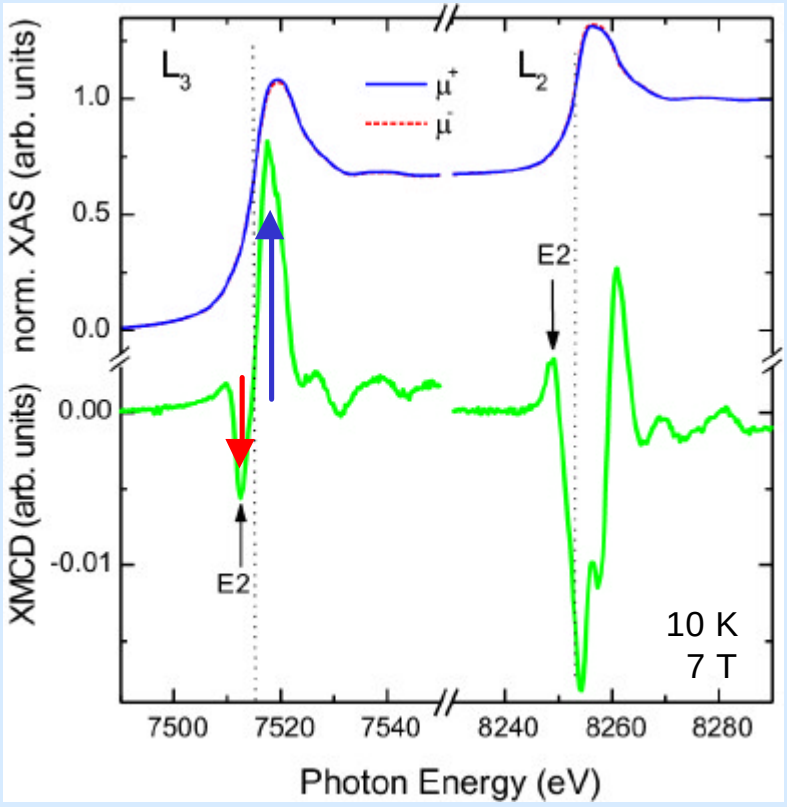
5c XMCD beyond integral sum rules

standard XMCD analysis fails (sum rules, MMA)
for important elements:

- rare earth metals
- light 3d transition metals

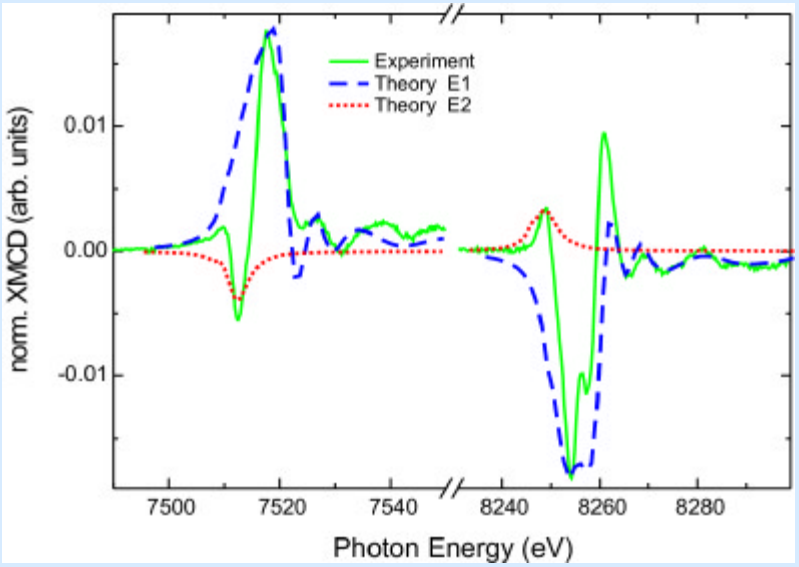
rare earth $L_{2,3}$ edge XMCD: Tb

ESRF: ID12



sum rule: 4f ↓ ↑ 5d

magnetometry: 4f ↓ ↓ 5d



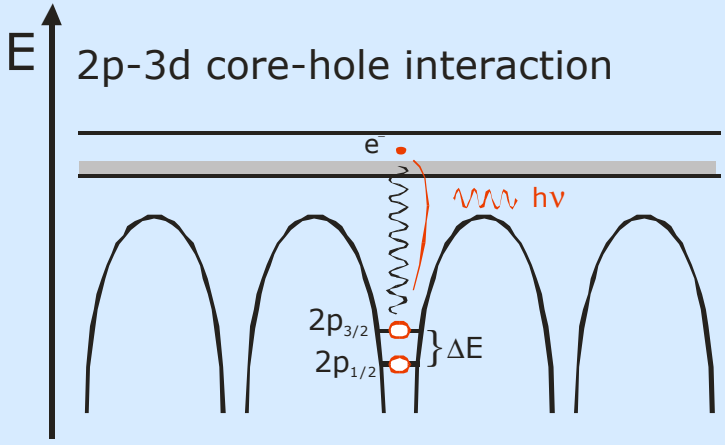
- E1 ($2p \rightarrow 5d$) and E2 ($2p \rightarrow 4f$) contributions
- spin-dependence of matrix elements

  Þ sum rules: wrong sign of 5d moment!

3d transition elements

influence of core-hole interaction on early 3d L-edge spectra

3d: Sc Ti V Cr Mn Fe Co Ni Cu Zn



effect of core-hole correlations

→ on isotropic spectra:

- Zaanen et al., PRB **32** (1985) 4905
- Schwitalla, Ebert, PRL **80** (1998) 4586
- Ankudinov, Nesvizhskii, Rehr PRB **67** (2003) 115120
- Teramura, Tanaka, Jo, J. Phys. Soc. Jap. **65** (1996) 1053: Mn, Fe, Co, Ni

But:

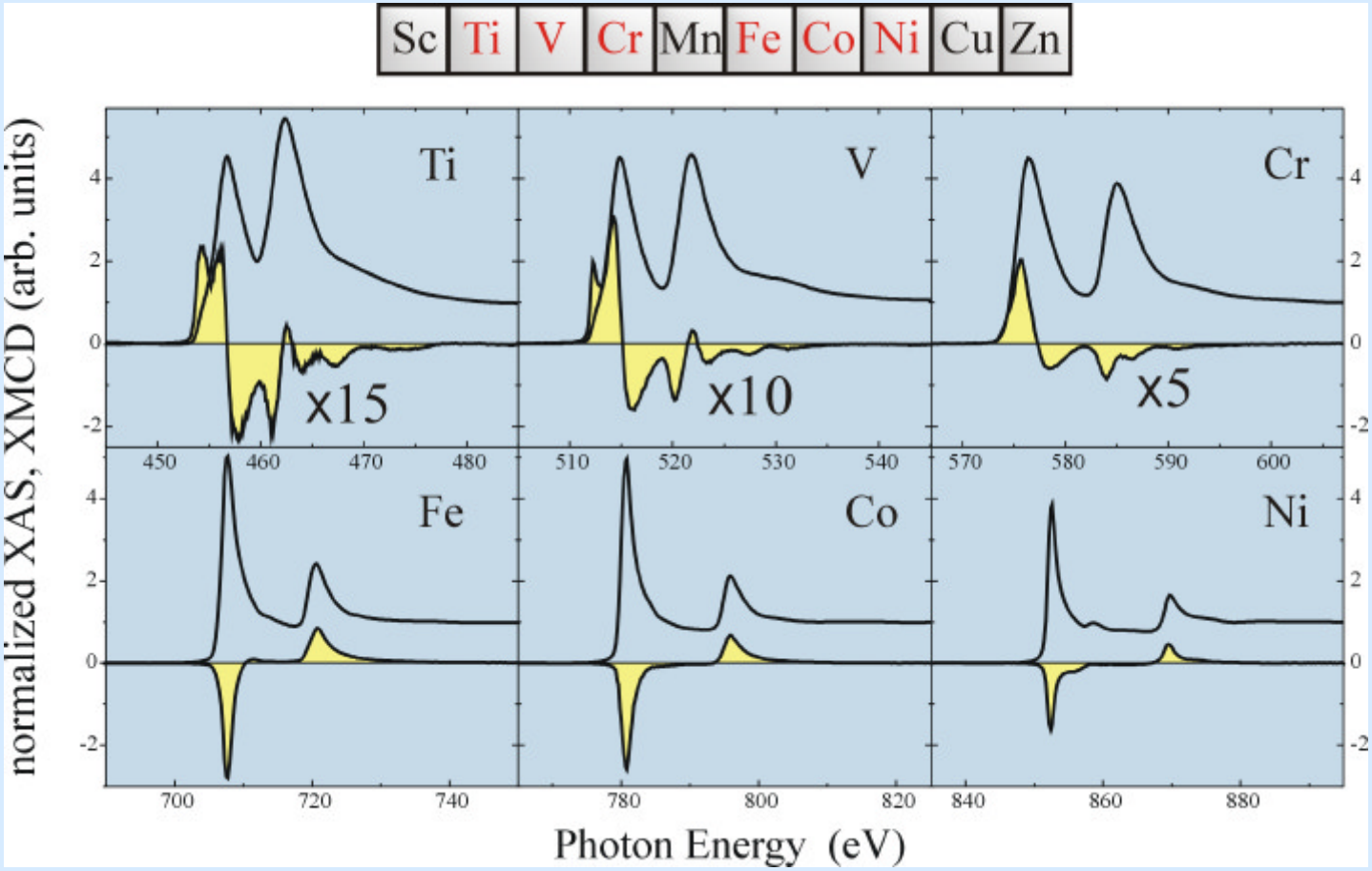
→ unknown on dichroic spectra of light 3d's (Ti, V, Cr)

early 3d: $\Delta E \approx$ core-hole correlation energy

$\Rightarrow$ identification of pure $2p_{3/2} \leftrightarrow 2p_{1/2}$ states not possible

$\Rightarrow$ mixing

gap-scan technique at BESSY II → XMCD spectra with detailed fine structure

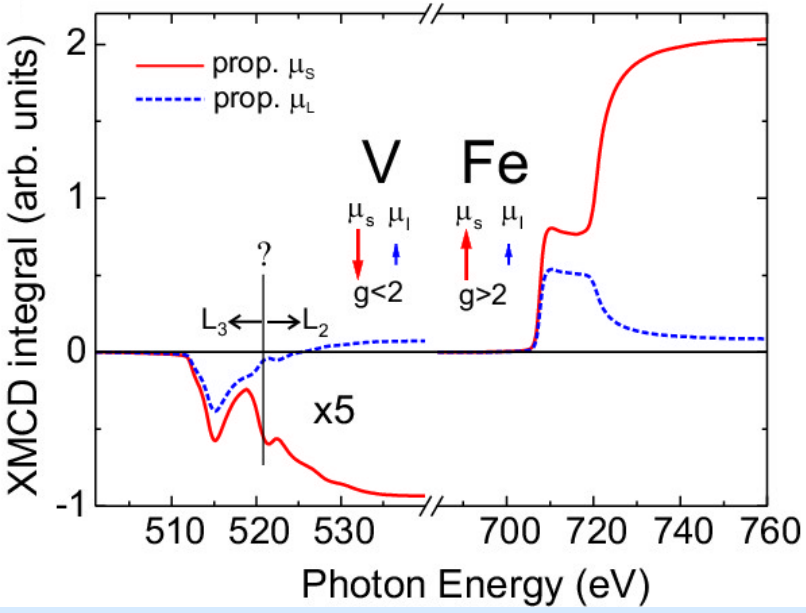


- A. Scherz PhD thesis FUB 2003
- A. Scherz, H. Wende, C. Sorg et al., BESSY-Highlights 2002, p. 8
- A. Scherz, H. Wende, K. Baberschke, Appl. Phys. A **78** (2004) 843

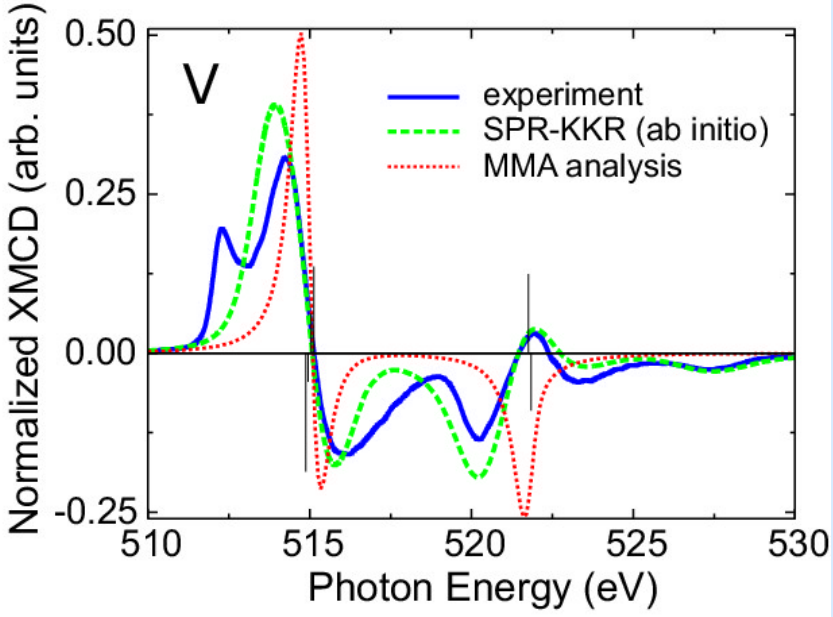
standard XMCD analysis fails for early 3d elements

A. Scherz, H. Wende, K. Baberschke, J. Minár, D. Benea, H. Ebert, PRB **66** (2002) 184401

integral sum rule analysis fails



multipole-moment analysis fails



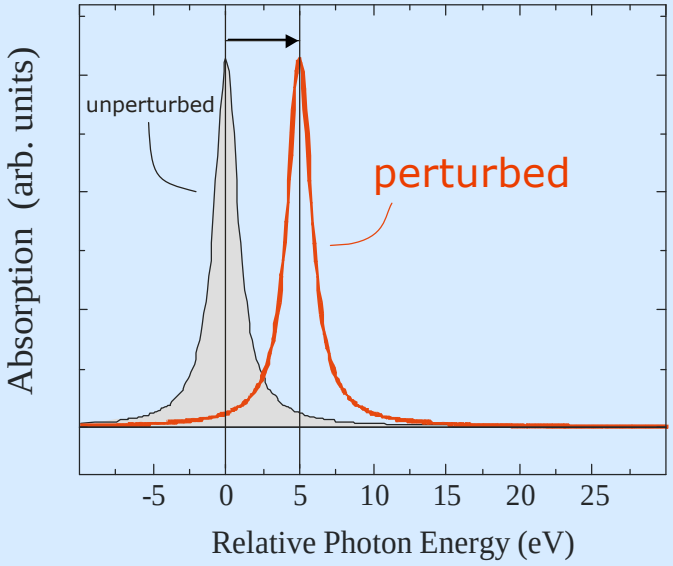
V: M. Sacchi et al PRB **60** (1999) R12569

Cr: E. Goering et al PRL **88** (2002) 207203

double pole approximation (time-dependent DFT)

single pole

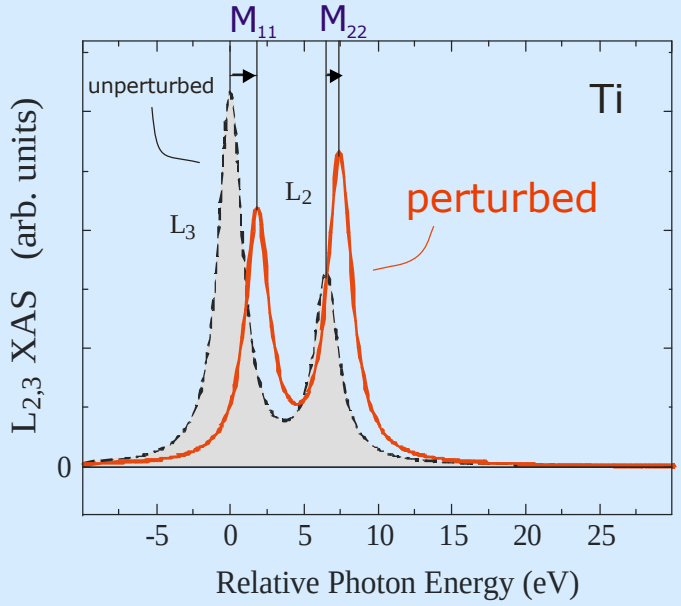
Petersilka et al. PRL 76 (1996) 1212
Atoms ($^1S \rightarrow {}^1P$)



frequency-dependent perturbation
↓
ground-state density
⇓
linear response theory

double pole

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

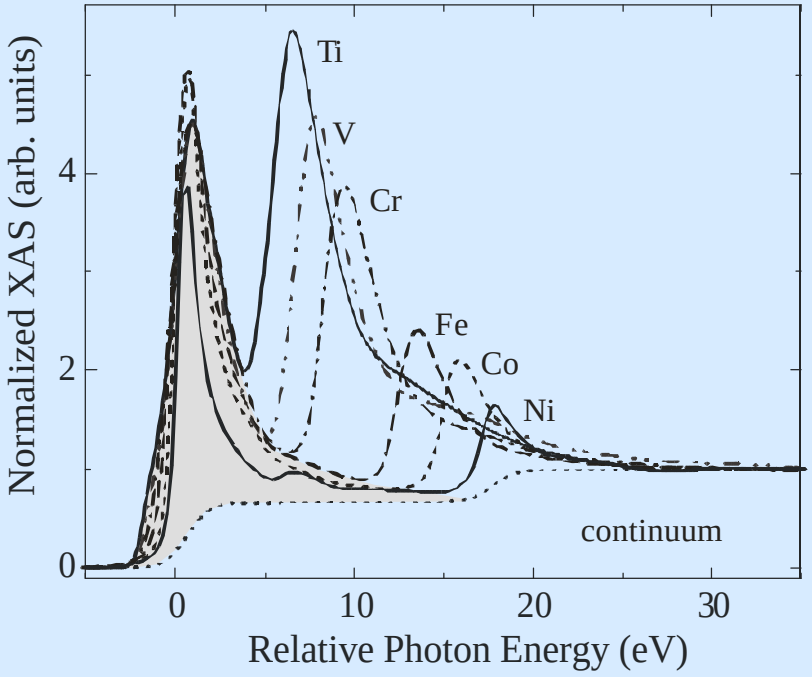


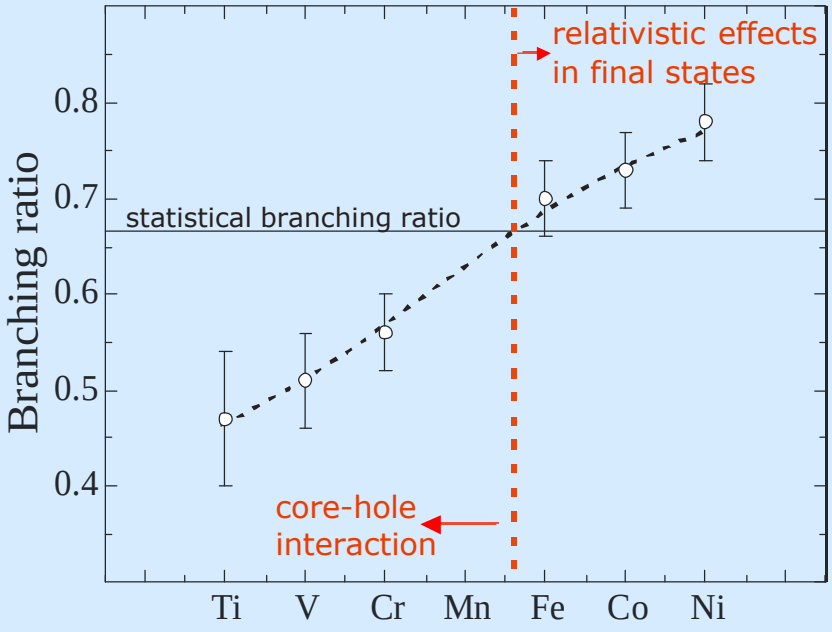
- energy shift of perturbed resonances
- shift of spectral weight $L_3 \rightarrow L_2$ (branching ratio)

⇓ determine matrix elements

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

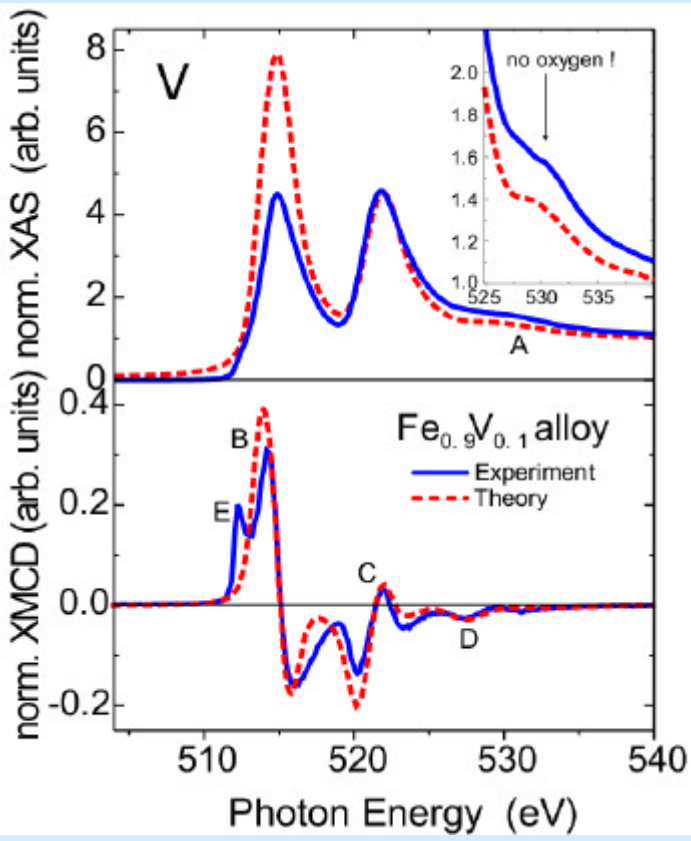
experimental determination of branching ratio

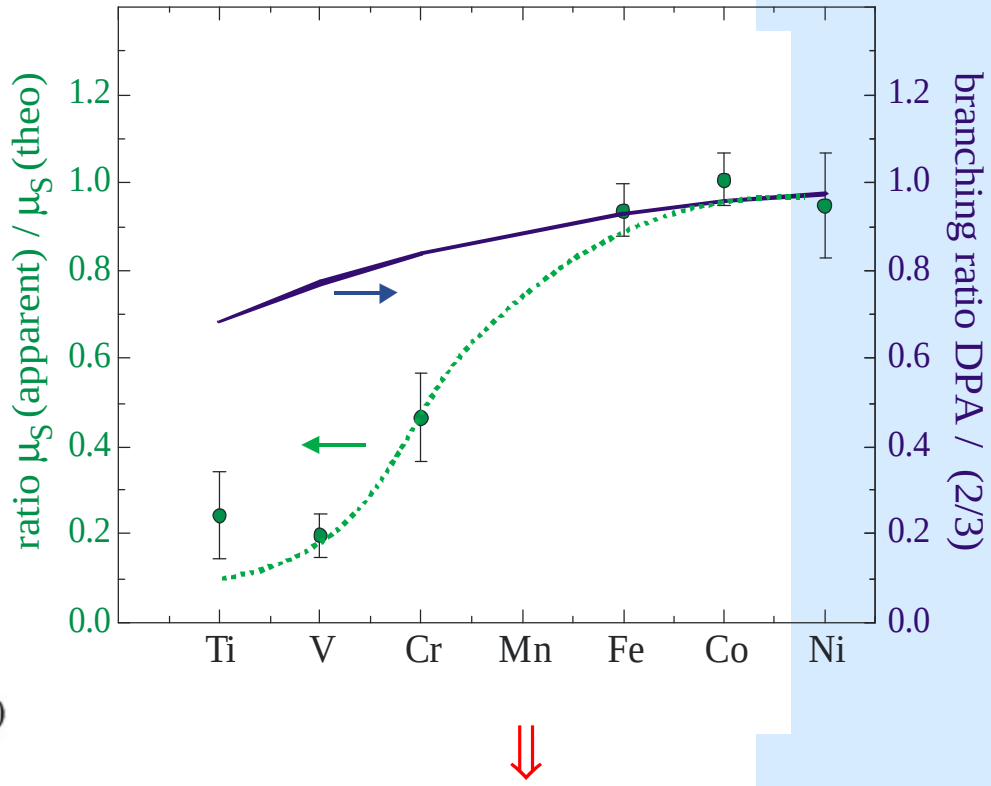




$$\text{branching ratio} = \frac{\text{Area L3}}{\text{Area L3 + Area L2}} \Rightarrow$$

branching ratio independent of:
- lifetime broadening
- experimental broadening





- theory Ebert, Minar → μ_S(theo)
- experiment + sum rule → μ_S(apparent)

- spin sum rule breaks down for strong correlation effects

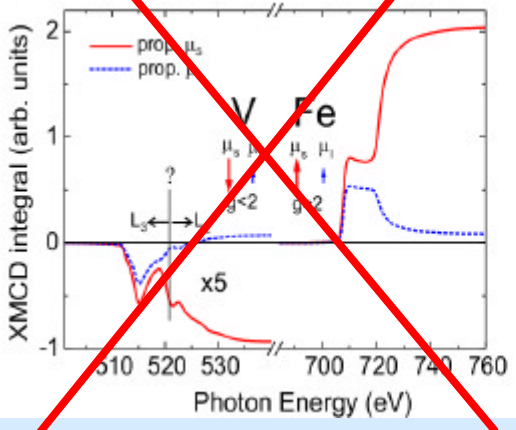
A. Scherz, H. Wende, C. Sorg, K. Baberschke, J. Minar, D. Benea, H. Ebert
Limitations of integral sum rules for early 3d elements
XAFS12 proceedings Physica Scripta **T115**, 586 (2005)

Conclusion

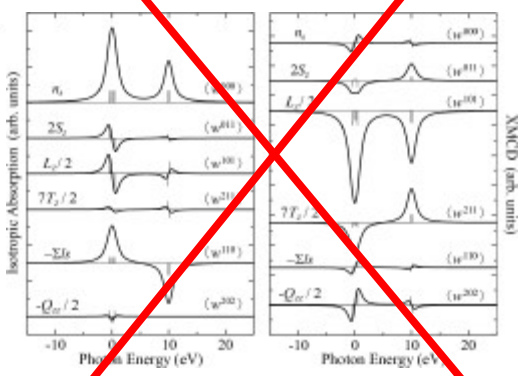
- gap-scan technique ⇒ systematic investigation of XAS, XMCD fine structure
- development double pole approximation
  ⇒ correlation energies (Ti: M_{11}=3.07 eV, M_{22}=-0.56 eV, M_{12}=0.54 eV)
  - experiment ⇒ failure of spin sum rule ↔ core-hole interaction
  - theory ⇒ correlation energies as input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

see review article: H. Wende, Rep. Prog. Phys. **67** (2004) 2105-2181

1) integral SR



2) MMA



3) calculation of full μ(E) ✓