



# A15. Circular dichroism in X-ray absorption spectroscopy and its application

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1. Introduction to NEXAFS and XMCD.
2. Element specific magnetizations in trilayers.
3. Determination of orbital- and spin- magnetic moments; XMCD sum rules.
4. Magnetic Anisotropy Energy (MAE) and anisotropic  $\mu_L$ .
5. New developments, outlook.

## See also other lectures

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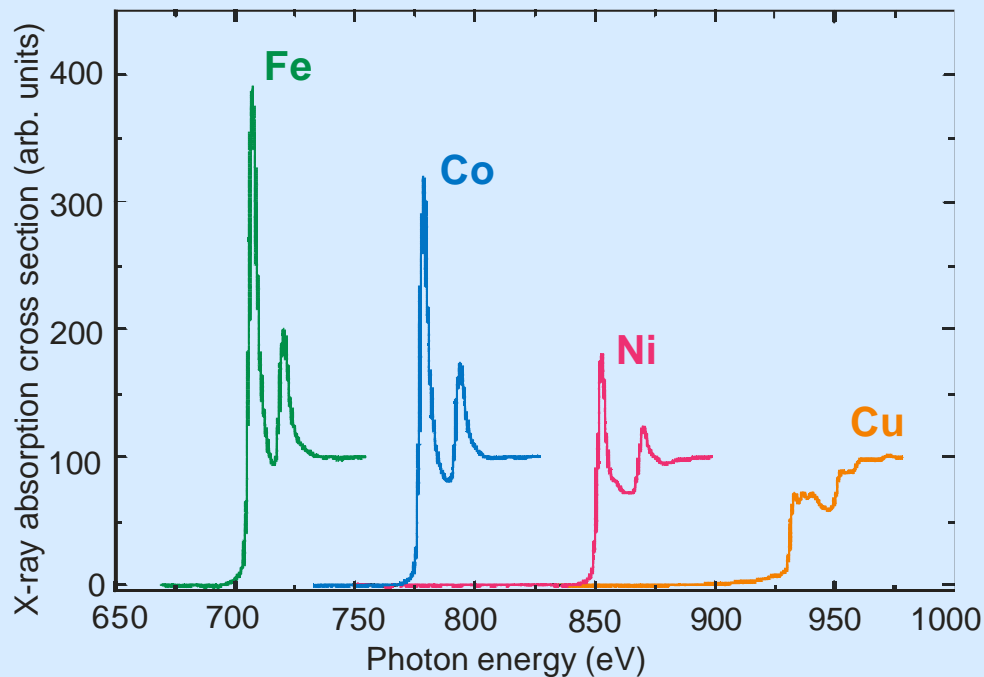
- 9 B. Lengeler X-ray absorption spectroscopy ...
- A 13 J. Vogel XAS: theoretical basis
- A14 Y. Joly XAS: the monoelectronic approach
- A'16 F. Sirotti Magnetic dichroism ...
- A'17 M. Sacchi Soft X-ray magnetic dichroism

This lecture see:  $\text{P}$  <http://www.physik.fu-berlin.de/~bab>  $\text{P}$  Lectures  $\text{P}$  Hercules 2007

- 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).
- J. Stöhr, H.C. Siegmann: *Magnetism*, Springer 2006
- 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).
- L-edges of 3d elements (... Mn, Fe, Co, Ni ...) and K-edges of 2p elements (... C, N, O ...) range between 100 and 1000 eV

# 1. Introduction: XAS

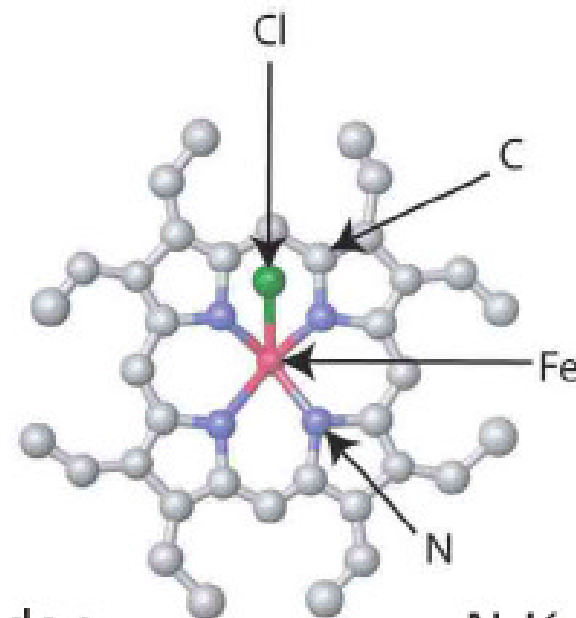
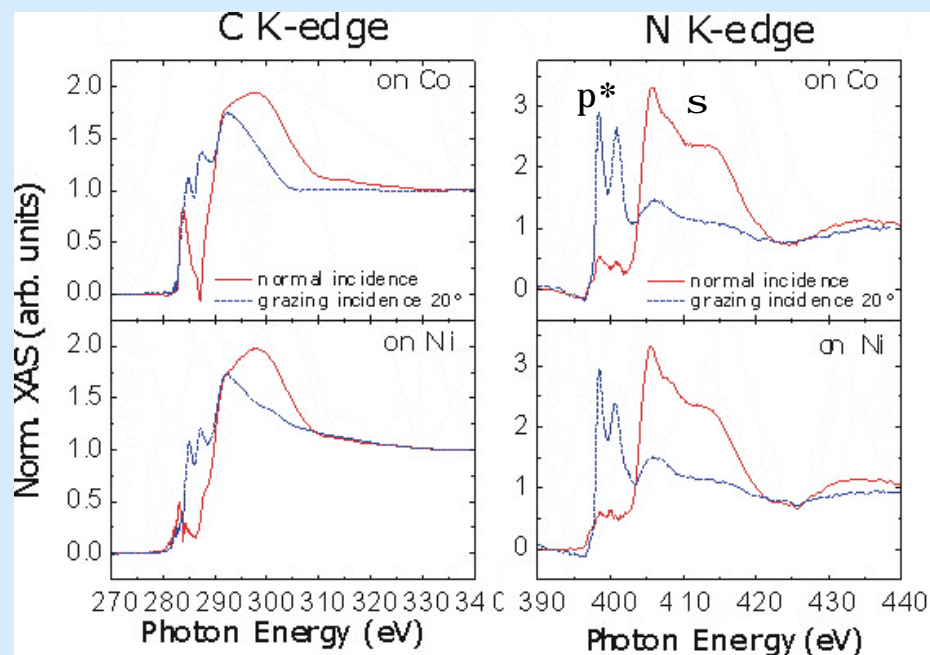
X-ray Absorption Spectroscopy is the most appropriate technique for element specific investigations.



$L_{3,2}$  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).

# XAS of 1 ML of Fe octaethylporphyrin on metal surface



Porphyrin molecule

Für einen  $3d^1$  Zustand mit  $MX_6$  Liganden ist die Energieaufspaltung in tetragonaler Symmetrie wie folgt gegeben:

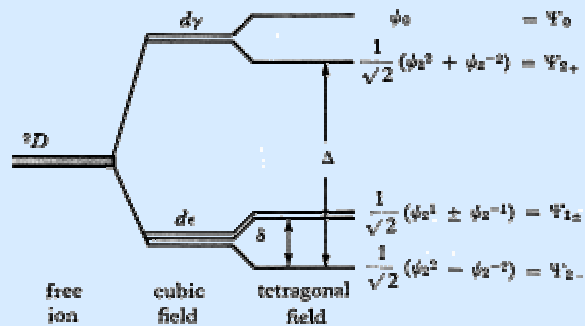


Fig. 3-4 Splitting of the  $^3D$  term by a tetragonally distorted cubic field.

3) Berechnen Sie für den Grundzustand

$$\psi_{2-} = (2)^{-1/2} \{ |2 \rangle - |-2 \rangle \} = |2 \rangle -$$

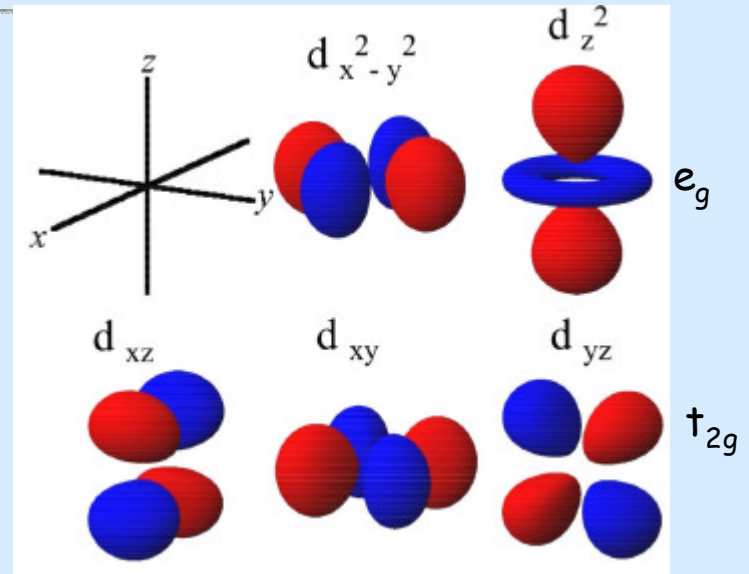
die Beimischung der angeregten Zustände durch  $\lambda L \cdot S$  und beachten Sie dabei, daß auch Spinzustände einzuführen sind (zweckmäßig  $\alpha|2 \rangle$  und  $\beta|-2 \rangle$  für Spin "up" and "down")

(2 P)

4.) Berechnen Sie für den in  $\bar{U}3$  gefundenen neuen Grundzustand die anisotropen g-Faktoren

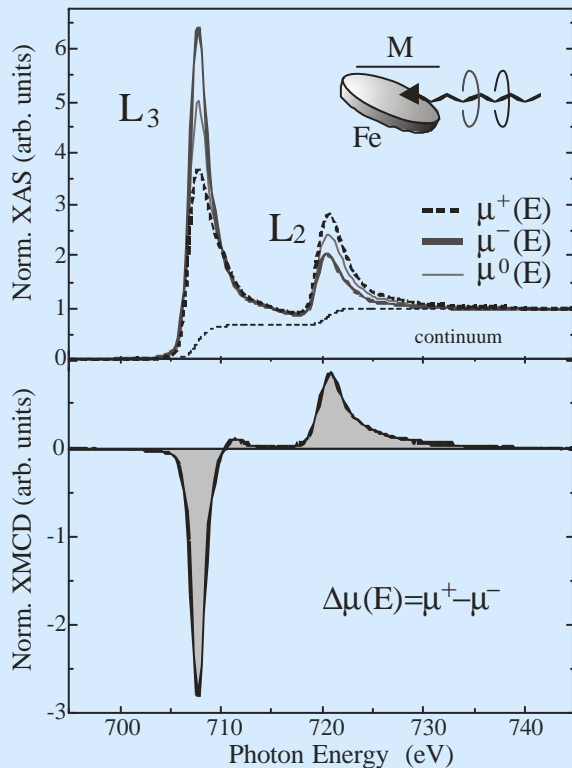
z.B.  $g_x - g_y$  durch "Einschalten" der Zeeman Ww:  $\mu_B(L + g_e S)H$

(3 P)

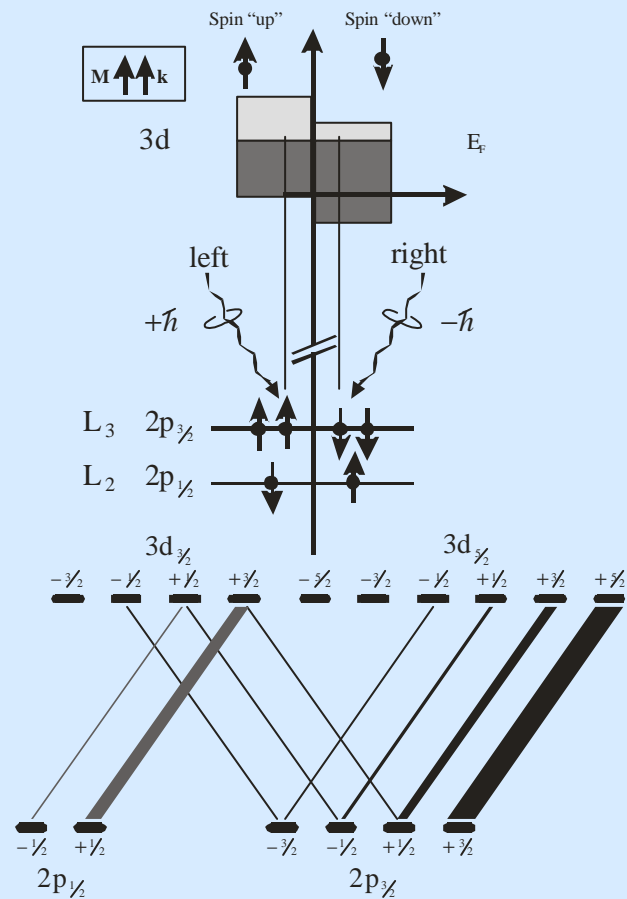


# X-ray Magnetic Circular Dichroism

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



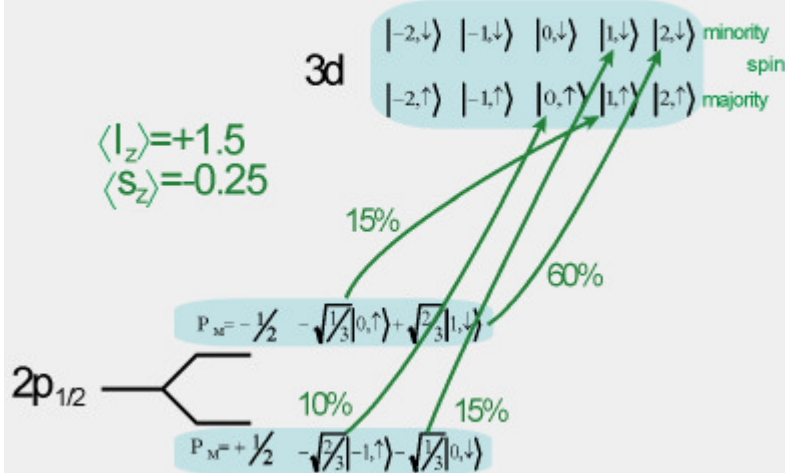
**XMCD signal is a measure of the magnetization**



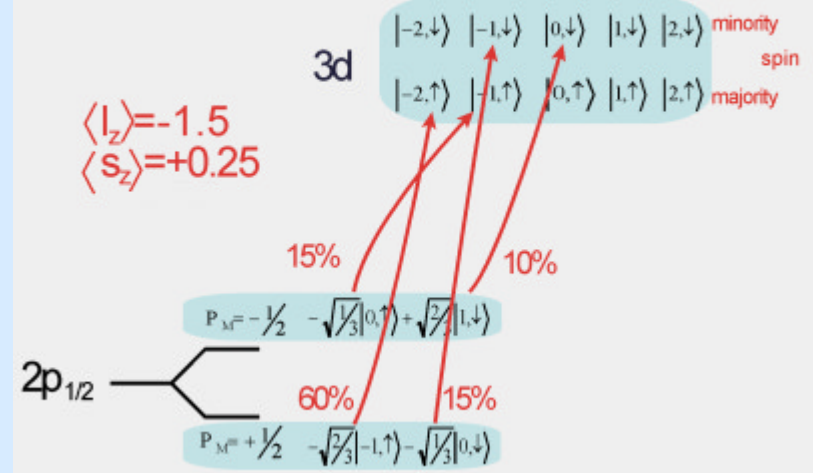
Many Reviews, e.g. H. Ebert Rep. Prog. Phys. **59**, 1665 (1996)

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

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



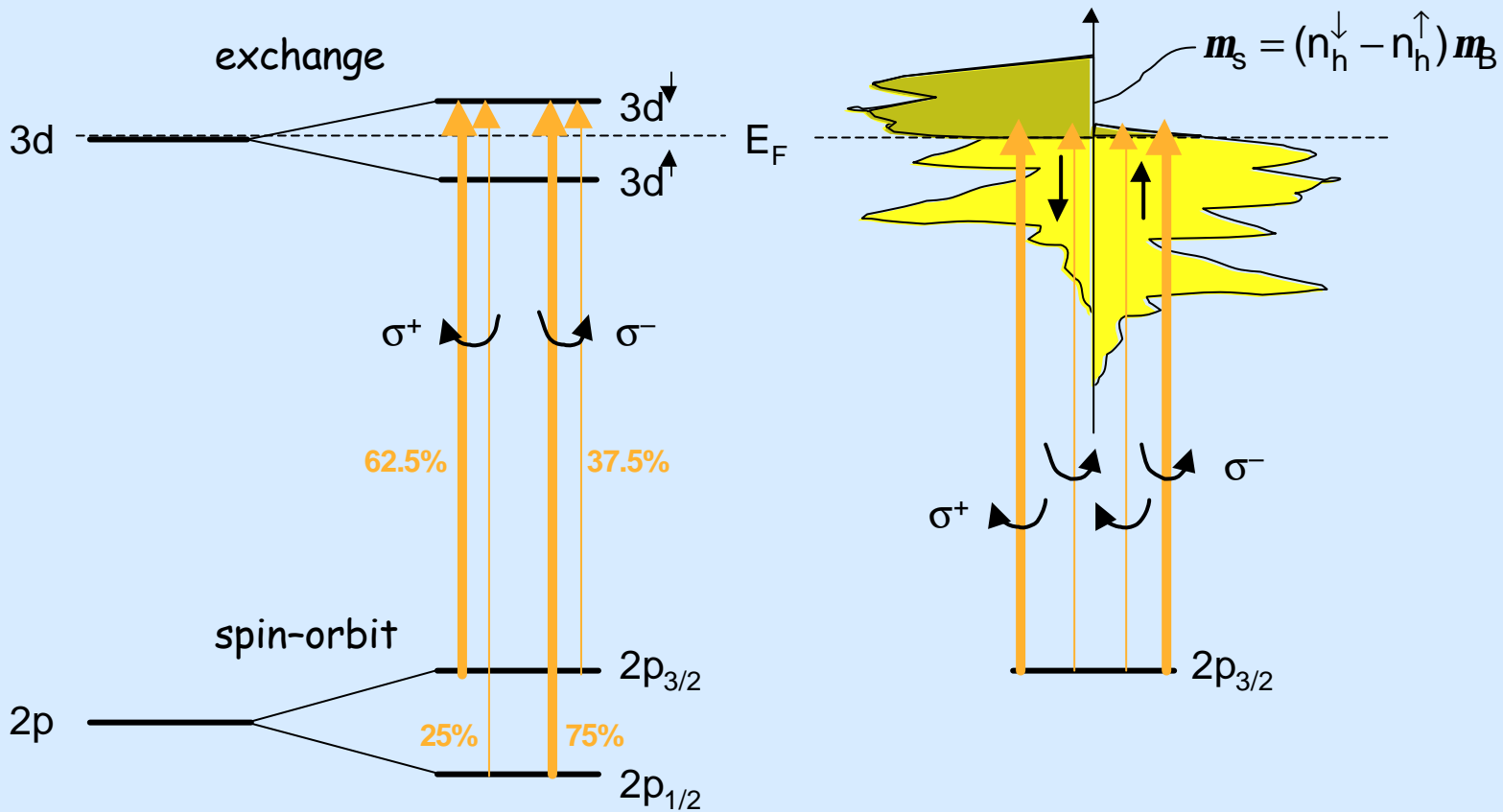
absorption of right circular pol. photon  $\Delta l=-1, \Delta s=0$



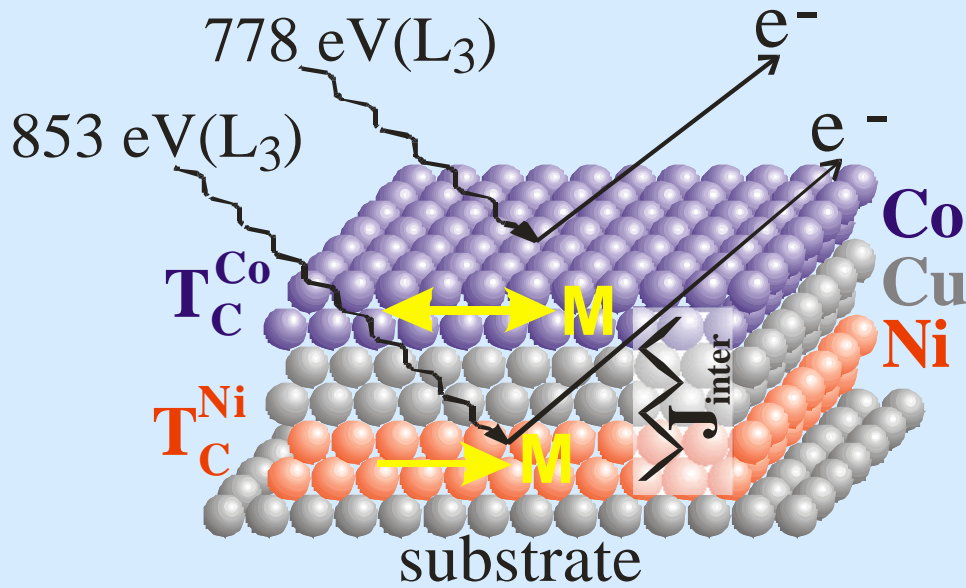
Reviews e.g.: Lecture Notes in Physics Vol. 466 by H. Ebert, G. Schütz



# X-ray magnetic circular dichroism (XMCD)



## 2. Element specific magnetizations in trilayers

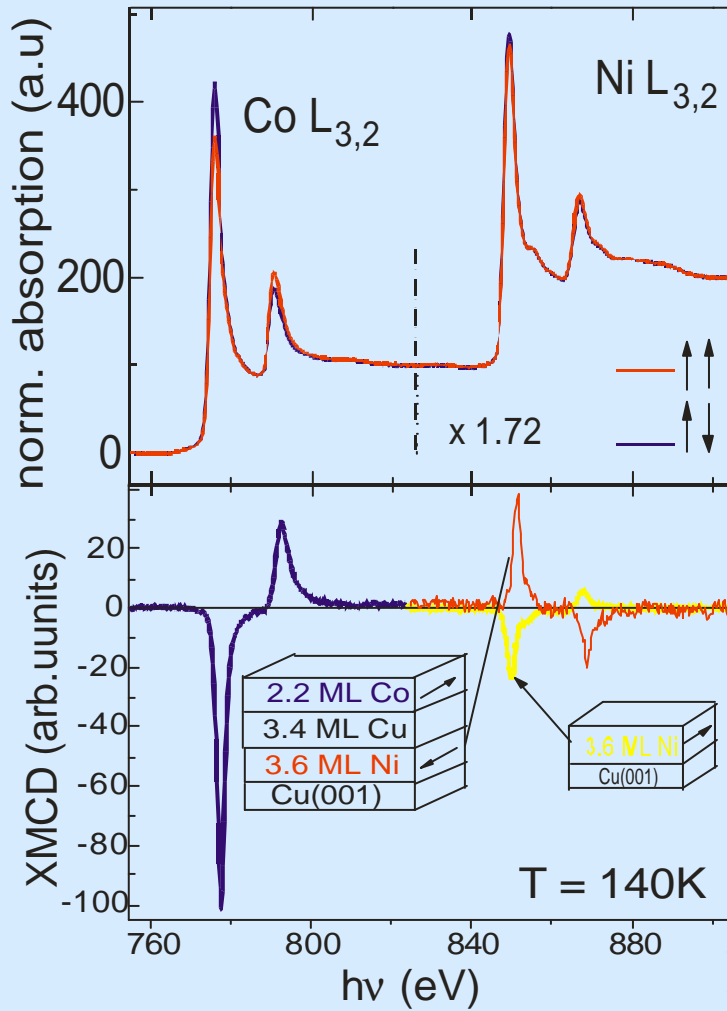


A trilayer is a prototype to study magnetic coupling in multilayers.

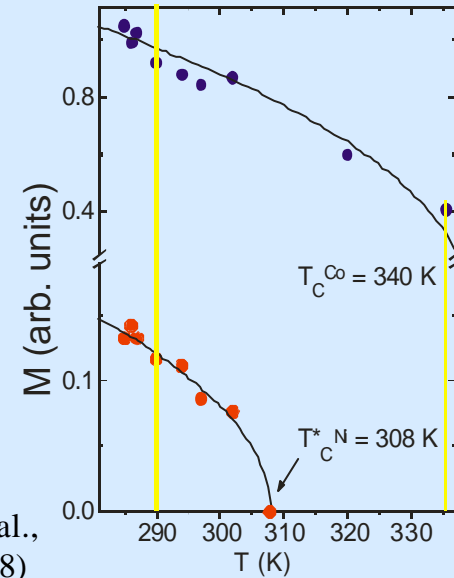
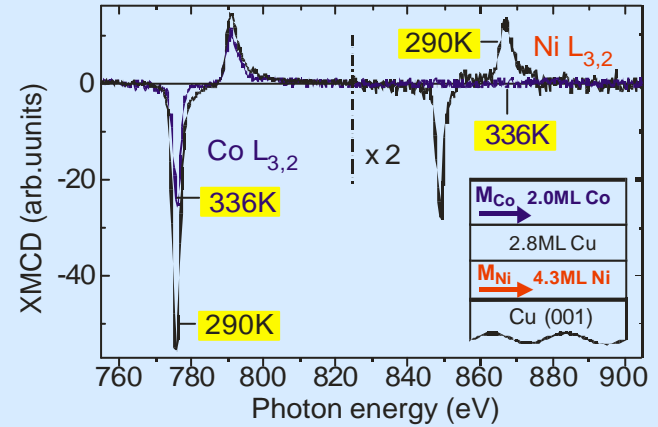
What about element specific Curie-temperatures ?

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

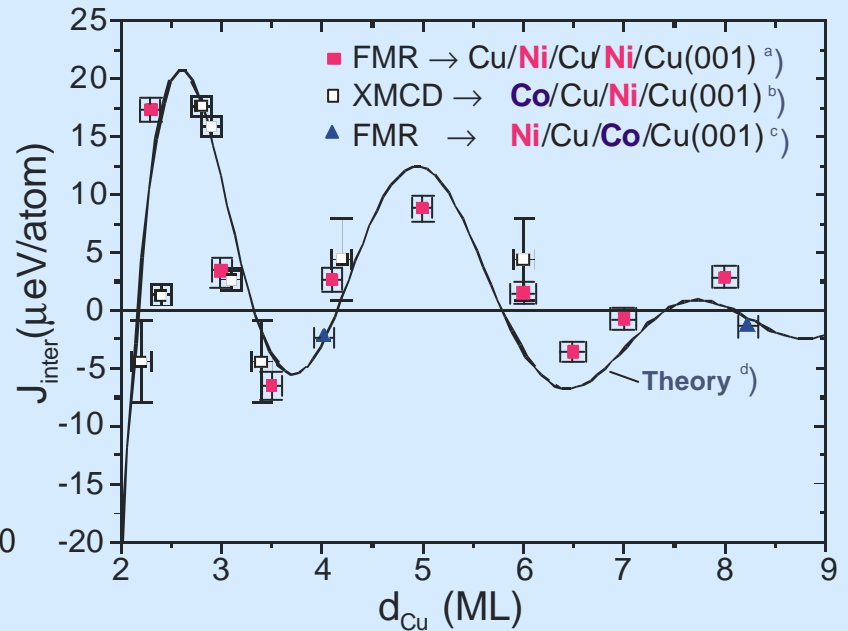
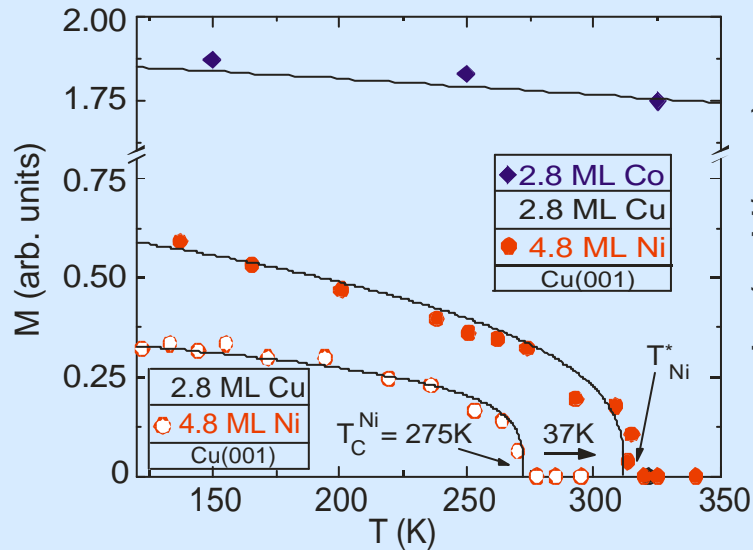
# Ferromagnetic trilayers



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



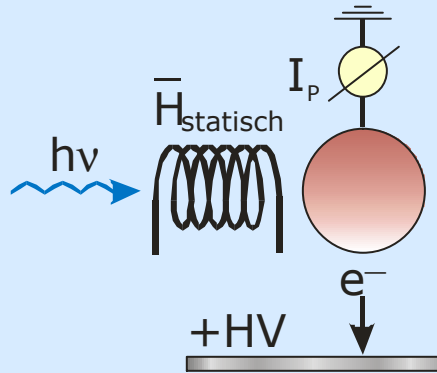
# Interlayer exchange coupling



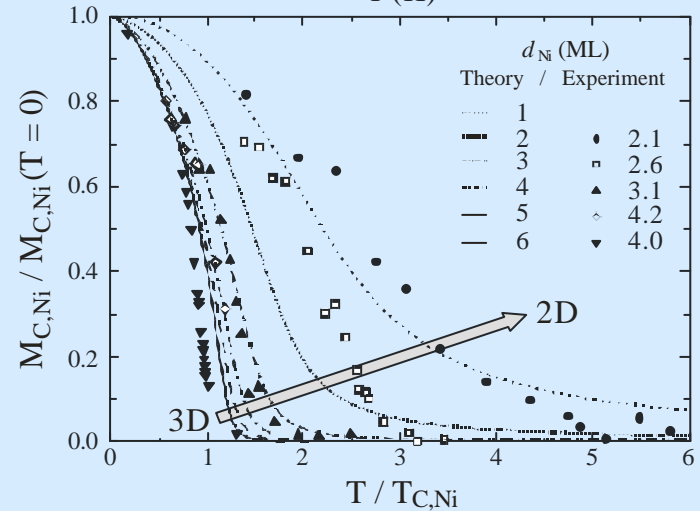
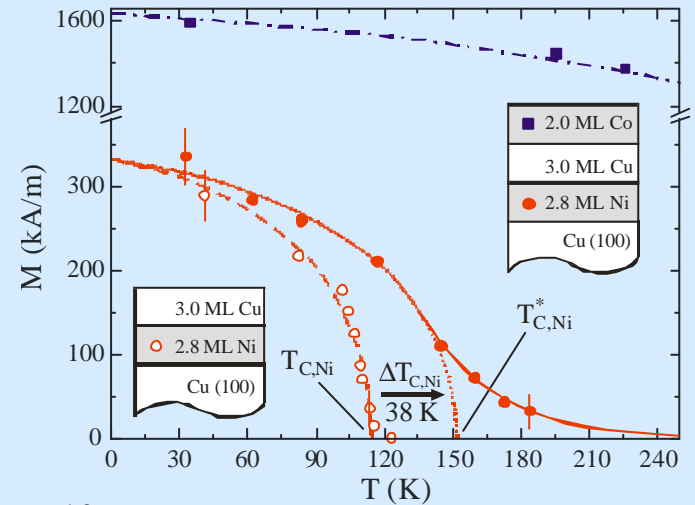
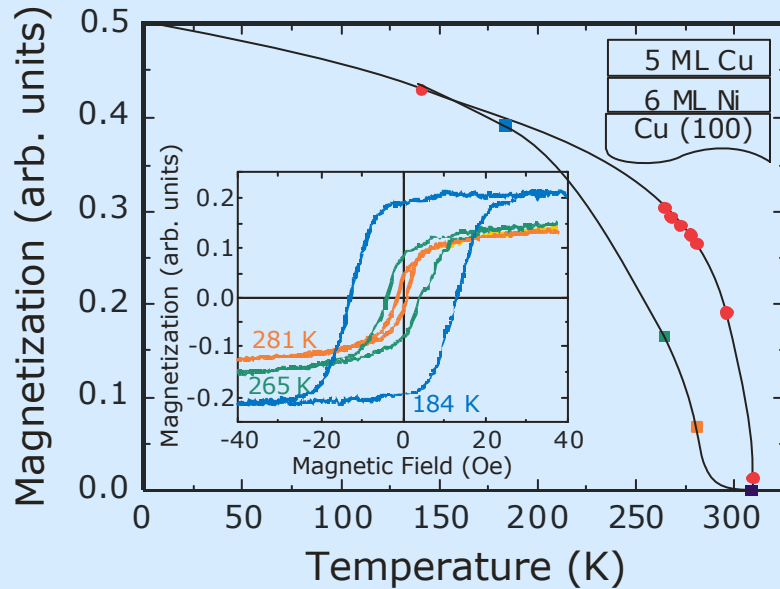
P. Pouloupoulos, K. B., Lecture Notes in Physics **580**, 283 (2001)

- 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



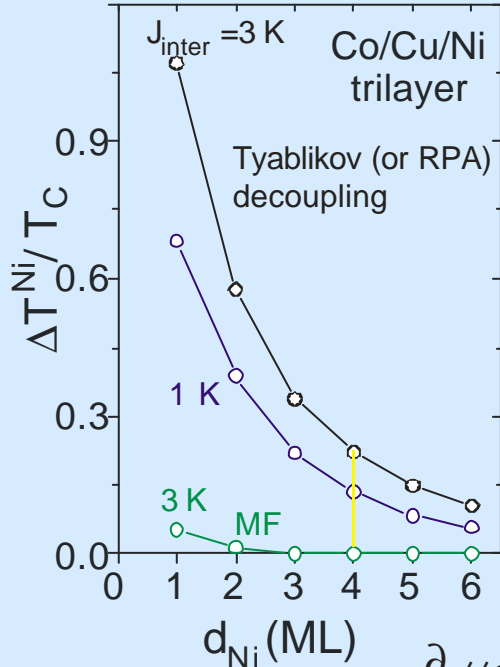
C. Sorg et al.,  
XAFS XII, June 2003  
Physica Scripta  
**T115**, 638 (2005)



# Enhanced spin fluctuations in 2D (theory)

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

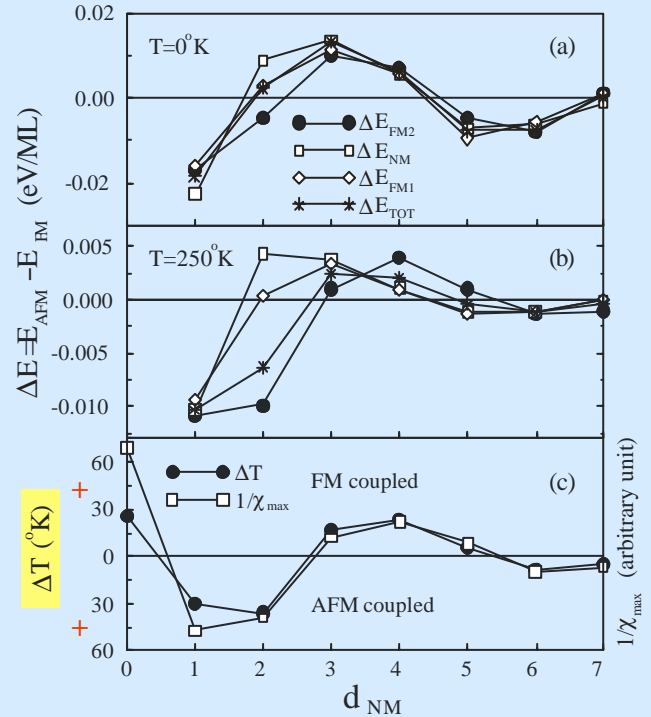
J.H. Wu et al. J. Phys.: Condens. Matter **12** (2000) 2847



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

$$S_i^z S_j^+ \approx \underbrace{\langle S_i^z \rangle S_j^+}_{\text{RPA}} - \langle S_i^- S_i^+ \rangle S_j^+ - \langle S_i^- S_j^+ \rangle S_i^+ + \dots$$

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



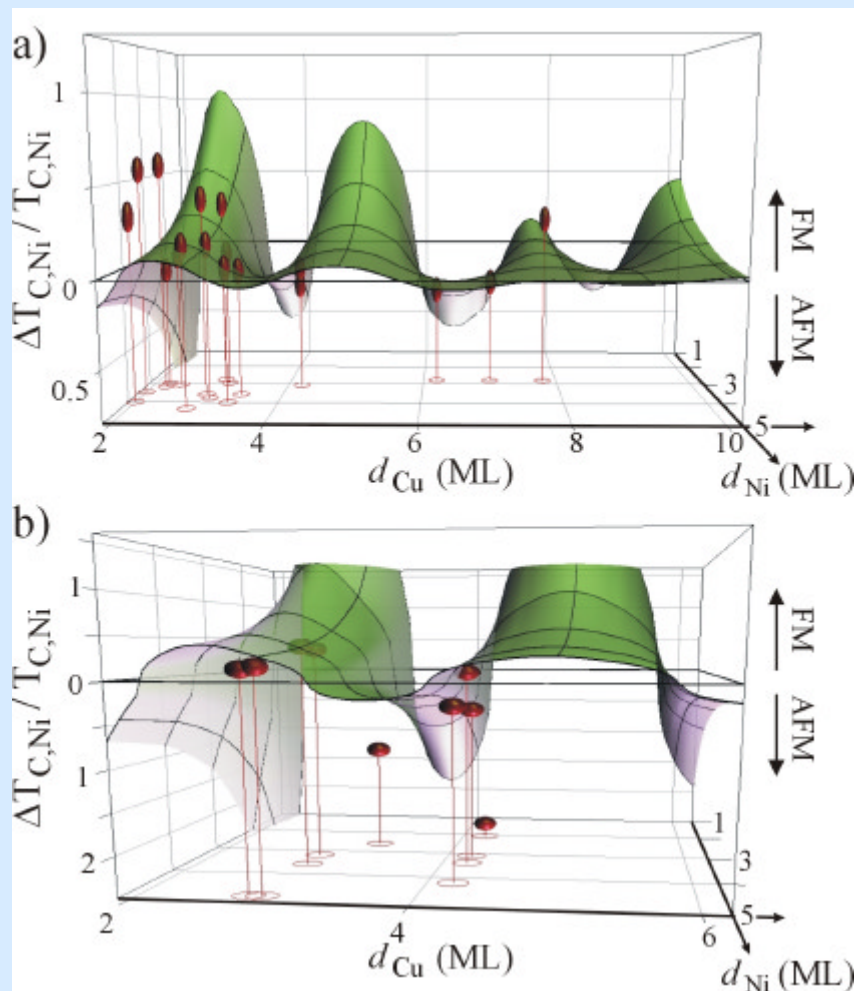
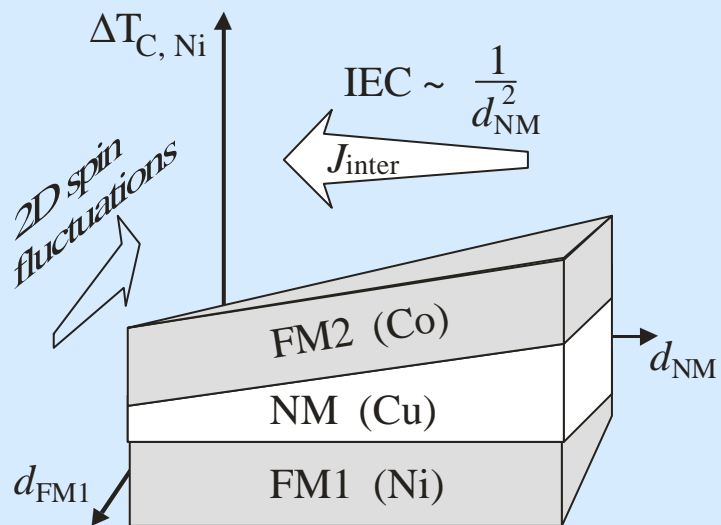
Single band Hubbard model:

Simple Hartree-Fock (Stoner) ansatz is insufficient

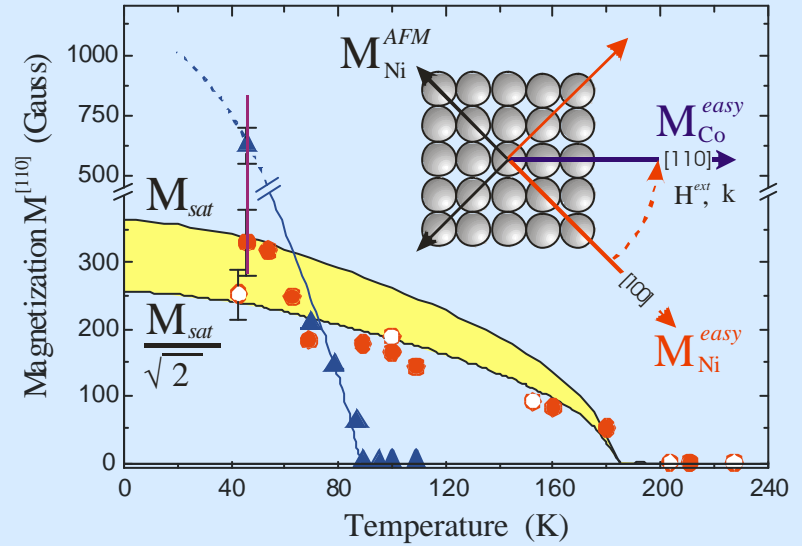
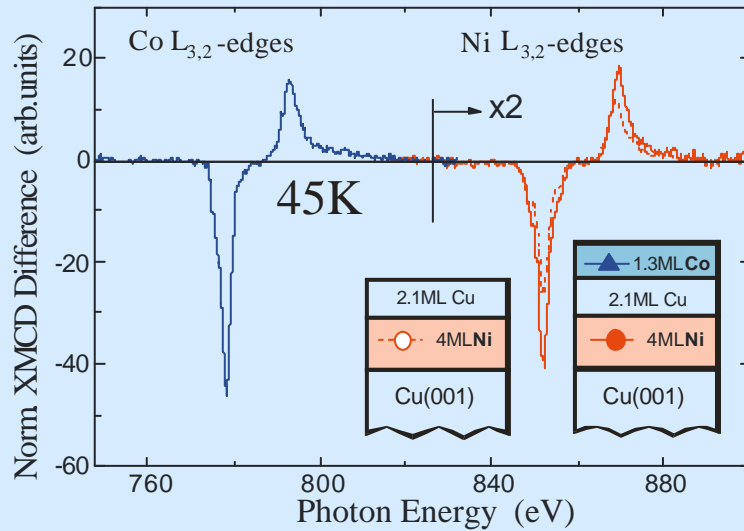
Higher order correlations are needed to explain  $T_C$ -shift

# Evidence for giant spin fluctuations

PRB 72, 054447, (2005)



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

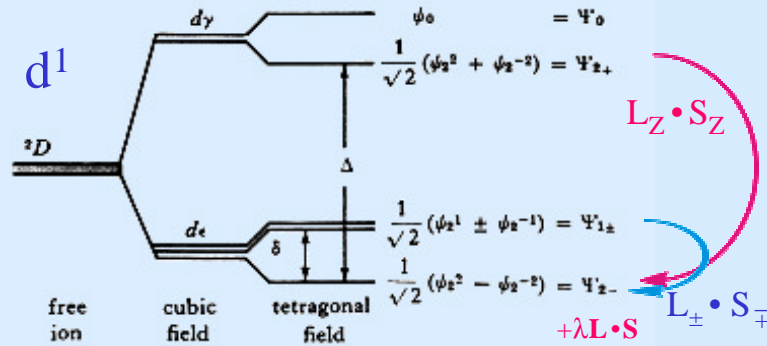


Two order parameter of  $T_C^{\text{Ni}}$  and  $T_C^{\text{Co}}$   
 A further reduction in symmetry happens at  $T_C^{\text{low}}$



# 3. Orbital magnetism in second order perturbation theory

effective Spin Hamiltonian



Splitting of the  ${}^2D$  term by a tetragonally distorted cubic field.

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

The orbital moment is quenched in cubic symmetry

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

but not for tetragonal symmetry

$$\mathcal{H} = \sum_{i,j=1}^3 [\beta g_e (\delta_{ij} - 2\lambda \Lambda_{ij}) S_i H_j - \lambda^2 \Lambda_{ij} S_i S_j] + \text{diamagnetic terms in } H_i H_j \quad (3-23)$$

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

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

$\langle 0 | \mu_0 \mathbf{H} \cdot \mathbf{L} | n \rangle \quad \langle n | \lambda \mathbf{L} \cdot \mathbf{S} | 0 \rangle \quad \langle 0 | \lambda \mathbf{L} \cdot \mathbf{S} | n \rangle \quad \langle n | \lambda \mathbf{L} \cdot \mathbf{S} | 0 \rangle$

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

to give

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

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

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)

# Determination of orbital- and spin- magnetic moments

Which technique measures what?

$\mu_L, \mu_S$  in UHV-XMCD

$\mu_L + \mu_S$  in UHV-SQUID

$\mu_L / \mu_S$  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)

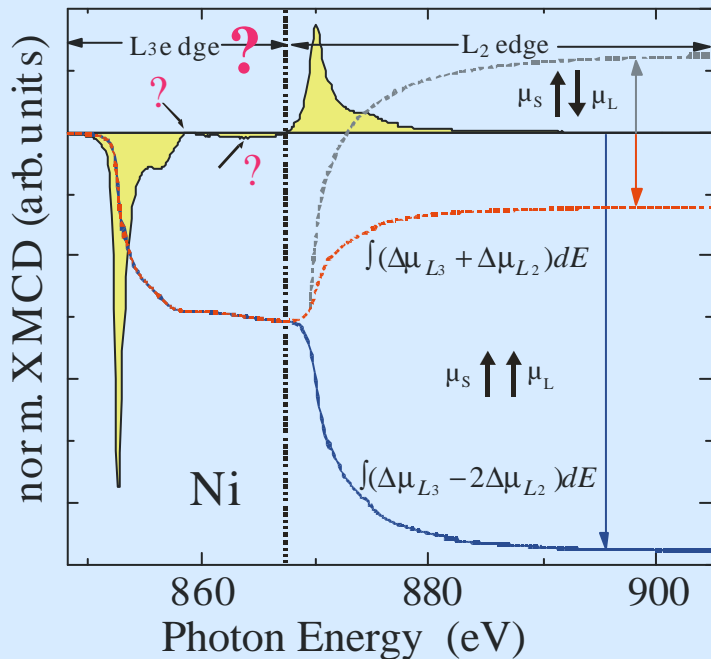
*per definition:*

- 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

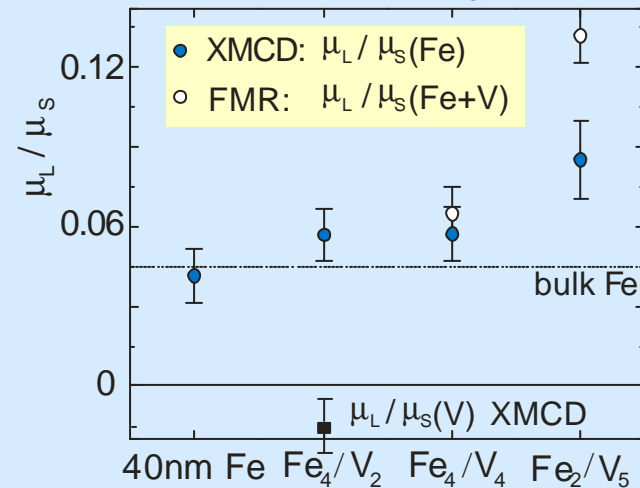
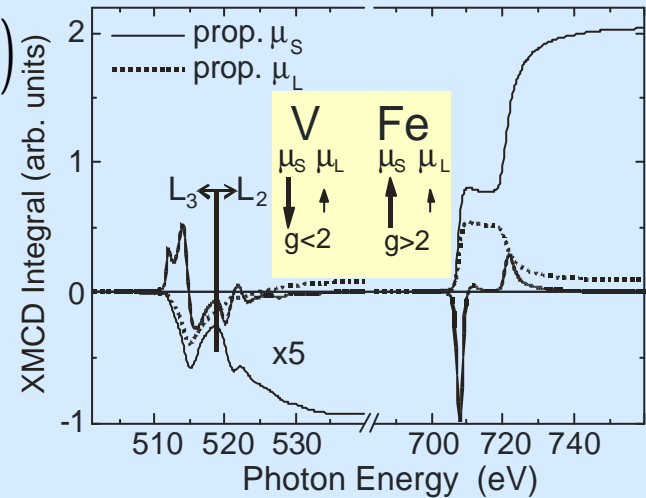
# Orbital and spin magnetic moments deduced from XMCD

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

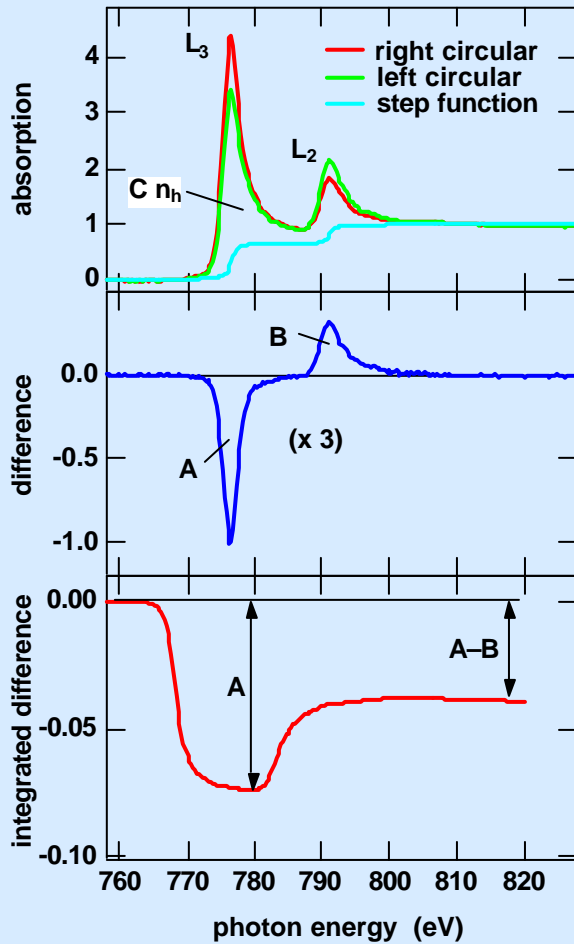
$$\int (\mu_{L3} + \mu_{L2}) dE = \frac{N}{2N_h^d} \langle L_Z \rangle^d$$



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







## 1. Summenregel:

$$m_s = -\frac{1}{C}(A+2B) m_B$$

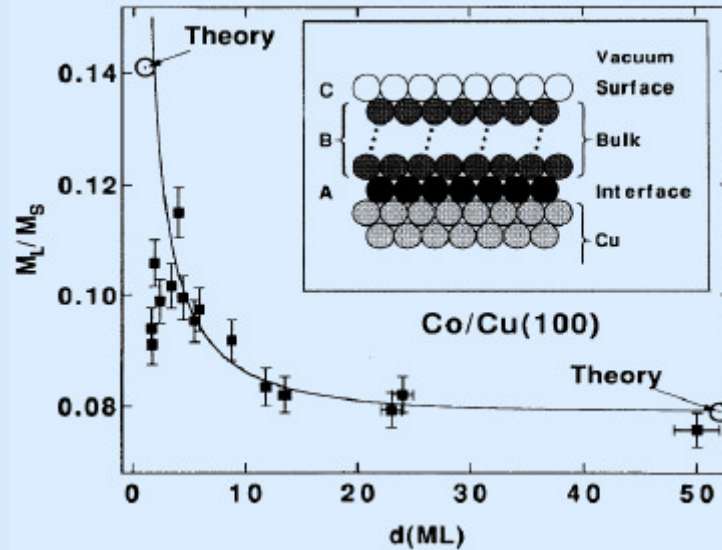
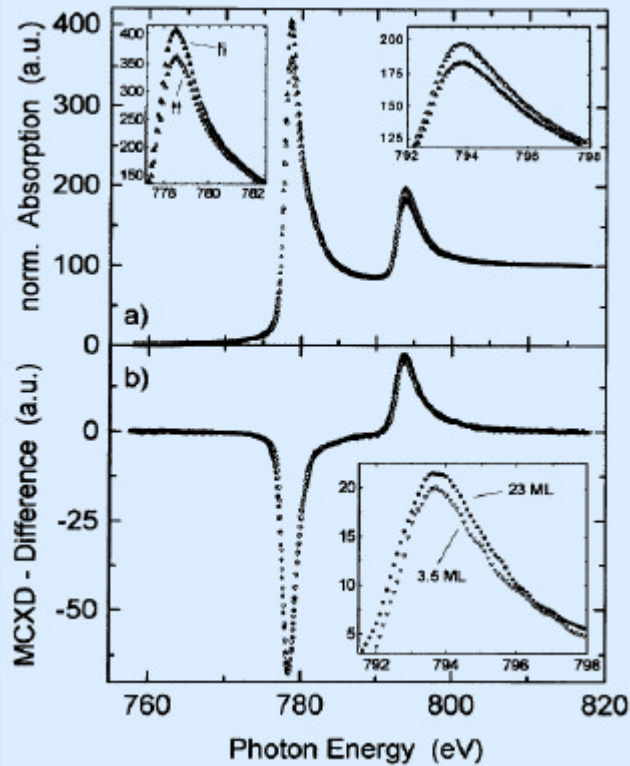
(P. Carra et al., PRL 70 (1993) 694)

## 2. Summenregel:

$$m_\ell = -\frac{2}{3C}(A-B) m_B$$

(B. T. Thole et al., PRL 68 (1992) 1943)

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

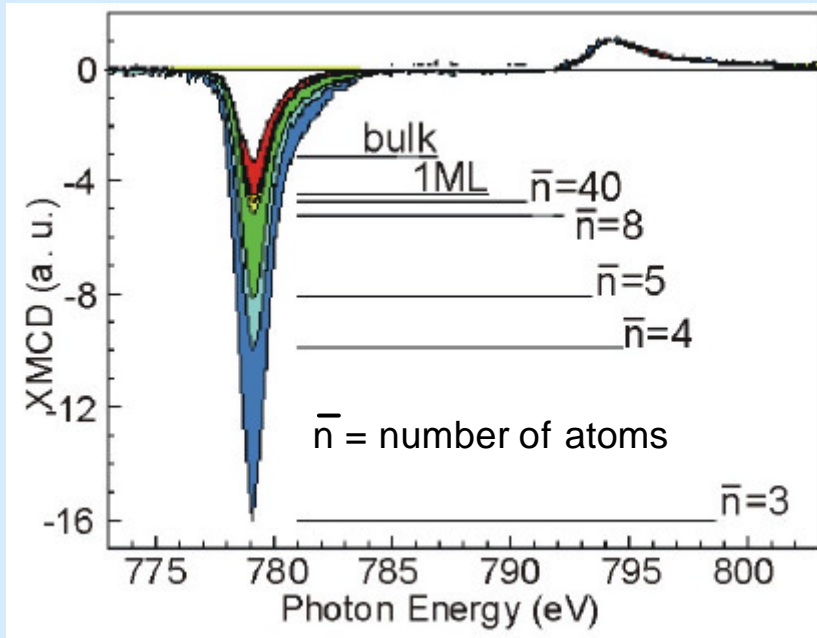


$$\left( \frac{M_L}{M_S} \right)_{\text{exp}} = \frac{Ae^{-D(d-1)/I} + B\sum_{n=3}^d e^{-D(n-2)/I} + C}{\sum_{n=0}^{d-1} e^{-nD/I}}$$

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

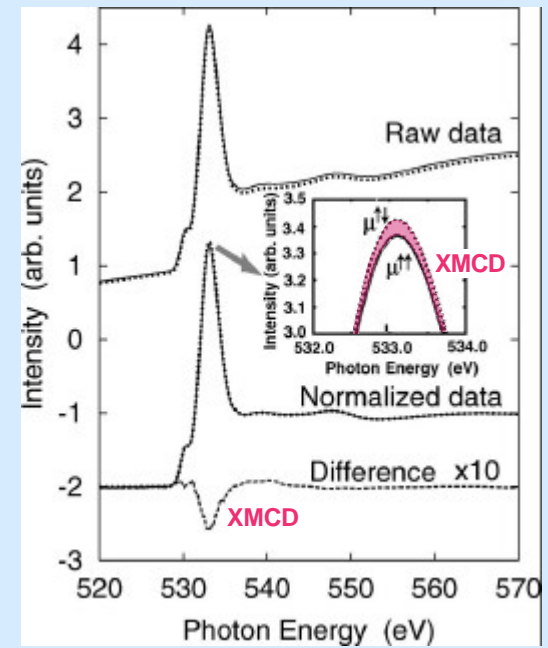
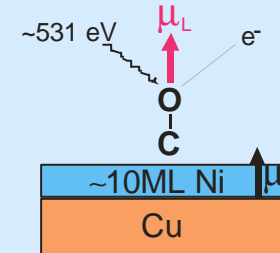
## Giant Magn. Anisotropy of Single Co Atoms and Nanoparticles

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



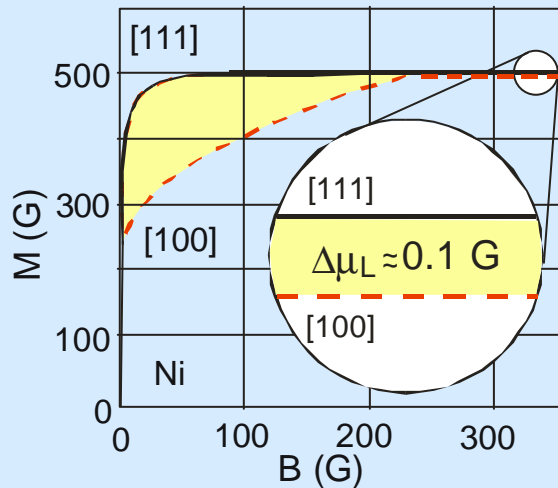
## Induced magnetism in molecules

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



## 4. Magnetic Anisotropy Energy (MAE) and anisotropic $\mu_L$

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



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

anisotropic  $\mu_L \leftrightarrow$  MAE

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



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

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

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

$\approx 1 \mu\text{eV}/\text{atom}$  is very small compared to  
 $\approx 10 \text{ eV}/\text{atom}$  total energy **but all important**

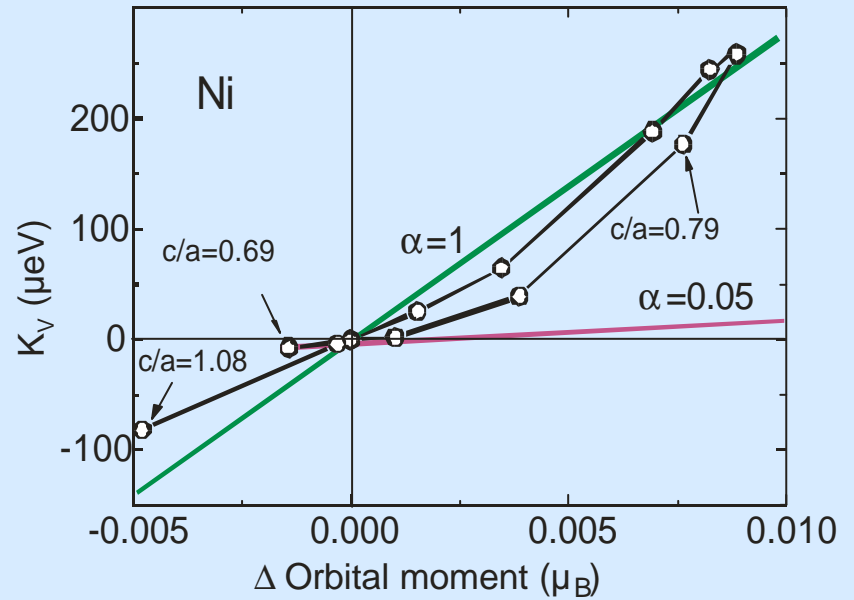
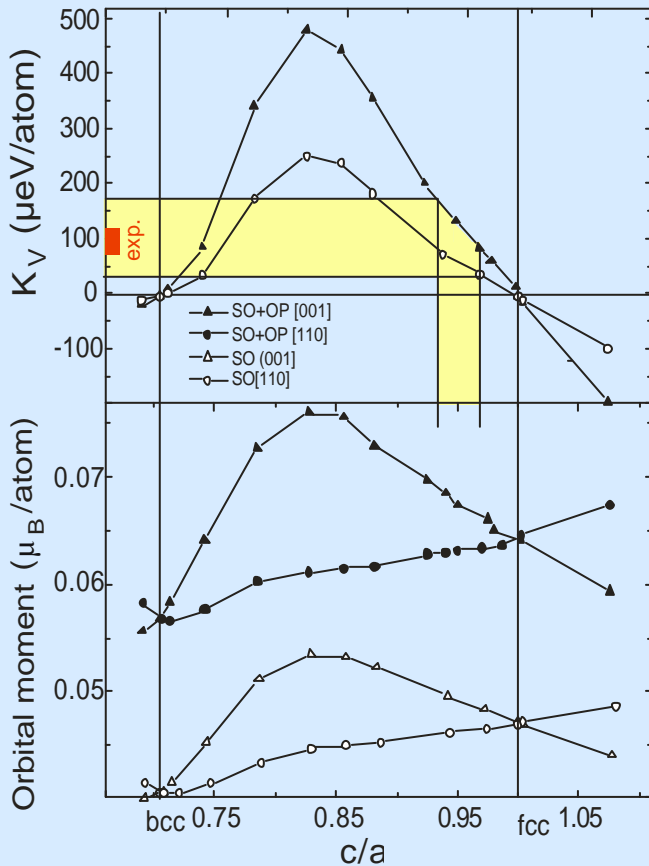
*Characteristic energies of metallic ferromagnets*

|                   |                                |
|-------------------|--------------------------------|
| binding energy    | 1 - 10 eV/atom                 |
| exchange energy   | 10 - 10 <sup>3</sup> 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)



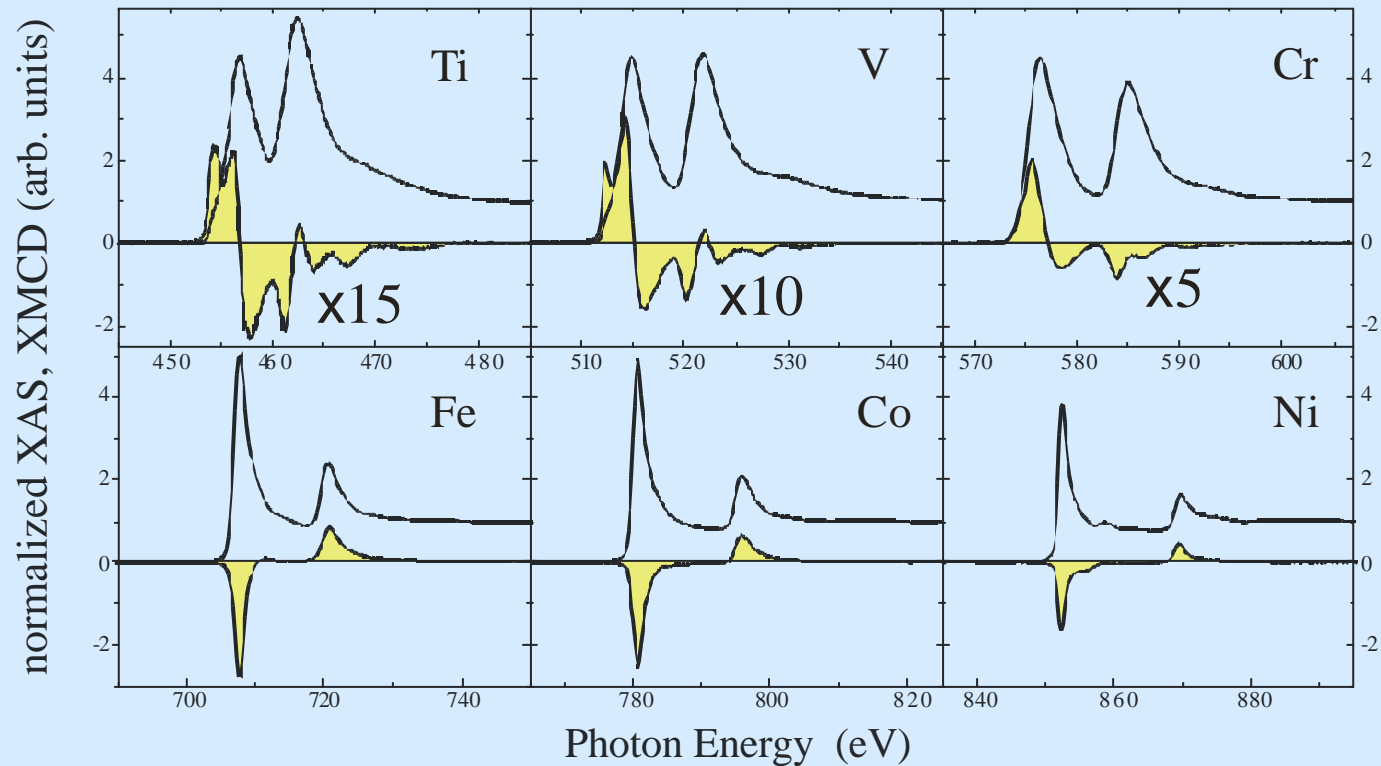
# Magnetic Anisotropy Energy MAE and anisotropic $\mu_L$



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

# L<sub>2,3</sub> 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)

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

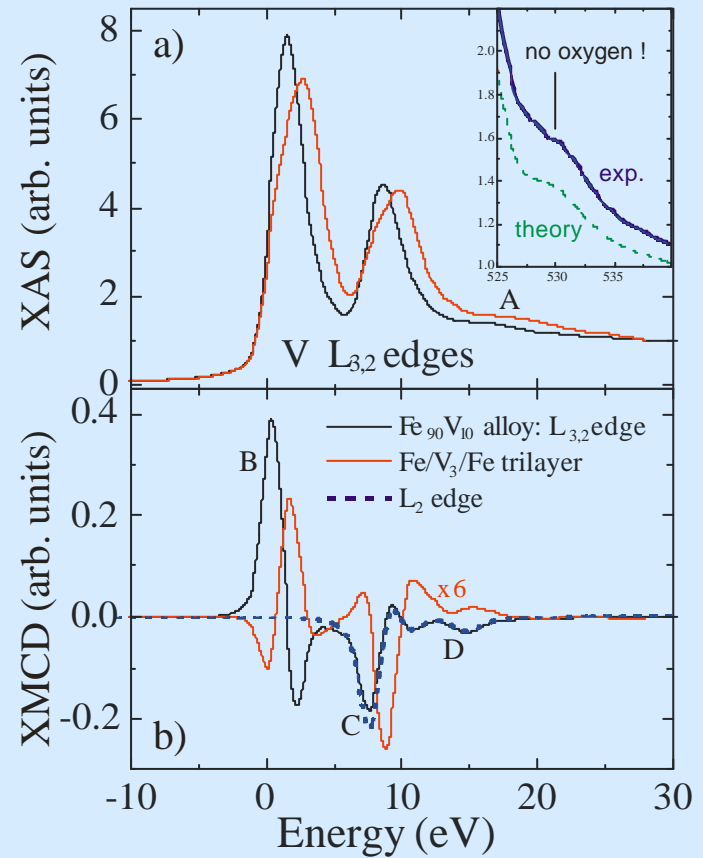
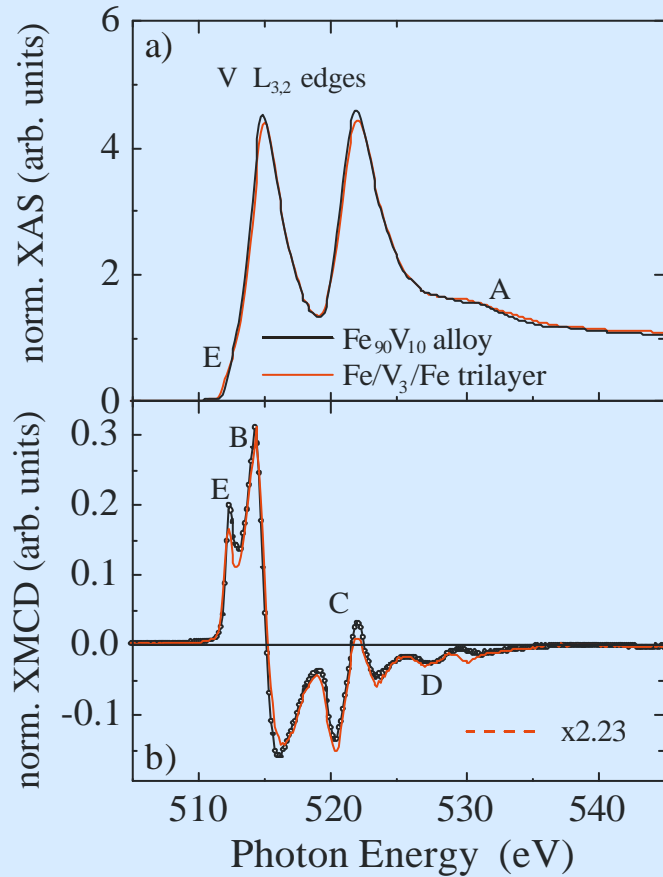
### Experiment

A. Scherz et al.

PRB **66**, 184401 (2002)

### Theory

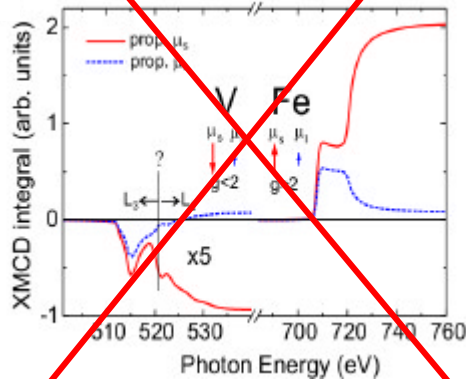
J. Minar, D. Benea, H. Ebert, LMU



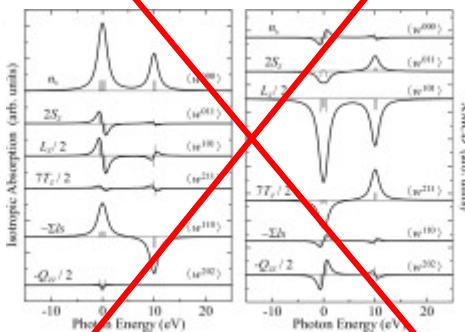
# Summary

- 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

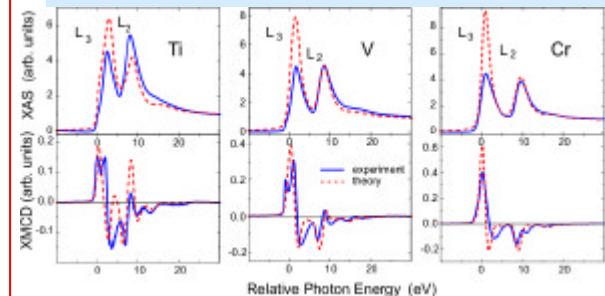
1) intergral SR



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.
  - In many calculations the matrix elements for the transition probability have been taken  $\neq f(E)$
  - now we have to pay attention even to the spin dependence  
A.L. Ankudinov, J.J. Rehr, H. Wende, A. Scherz, K. Baberschke  
*Spin-dependent sum rules for x-ray absorption spectra*  
Europhysics Letters **66**, 441 (2004)

***Recent advances in x-ray absorption spectroscopy***

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

# Conclusion, Future

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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