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

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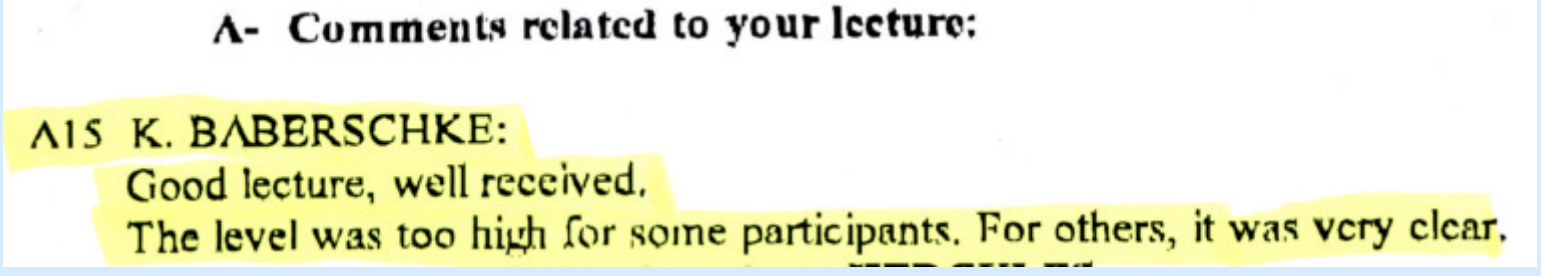
1. Introduction to NEXAFS and XMCD.
2. Element specific magnetizations in trilayers.
3. Determination of orbital- and spin- magnetic moments; XMCD sum rules.
4. Magnetic Anisotropy Energy (MAE) and anisotropic μ_L.
5. New developments, outlook.

See also other lectures

9	S.Pascarelli	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



A- Comments related to your lecture:

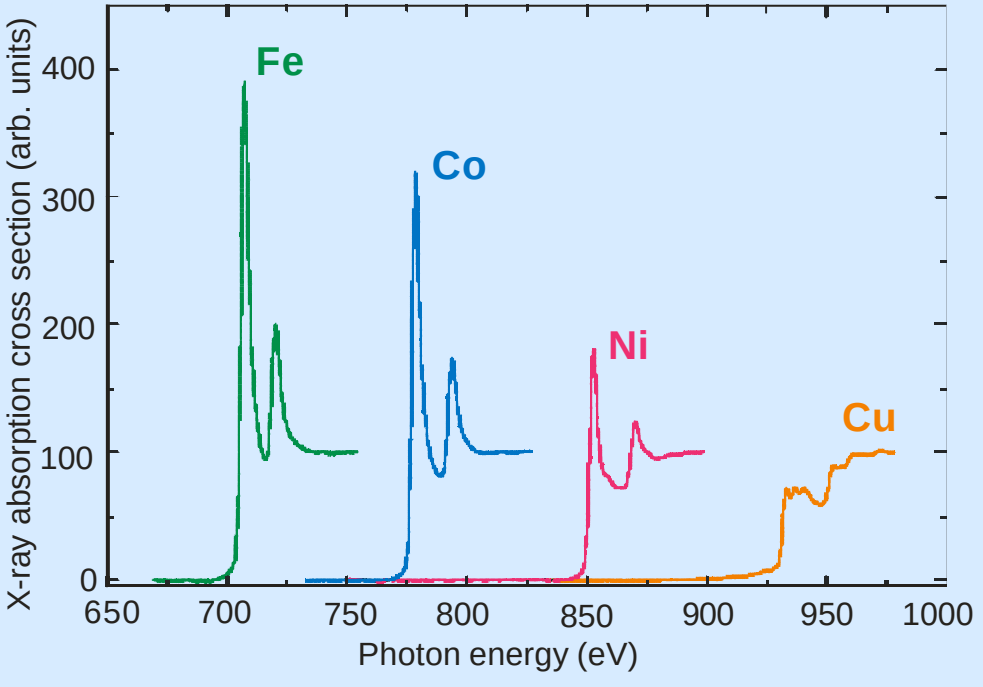
A15 K. BABERSCHKE:
Good lecture, well received.
The level was too high for some participants. For others, it was very clear.

This lecture see: Þ **http://www.physik.fu-berlin.de/~bab** Þ **Lectures** Þ **Hercules 2008**

- 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

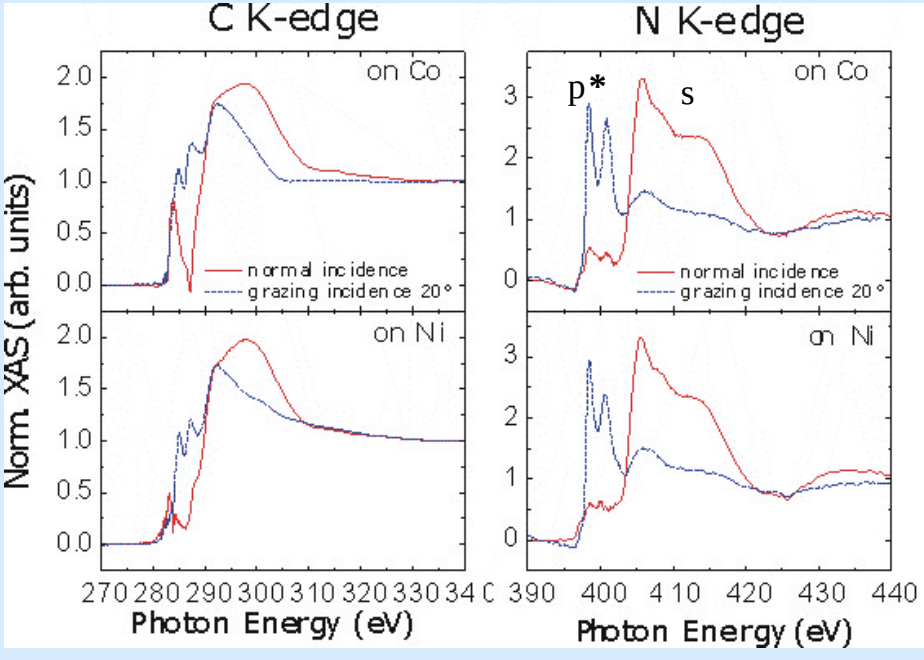
X-ray Absorption Spectroscopy is the most appropriate technique for element specific investigations.

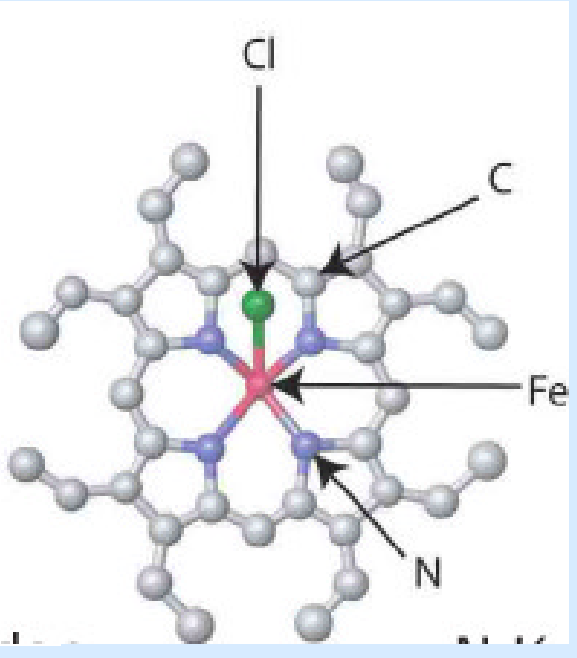


$L_{3,2}$ edges of 3d elements

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

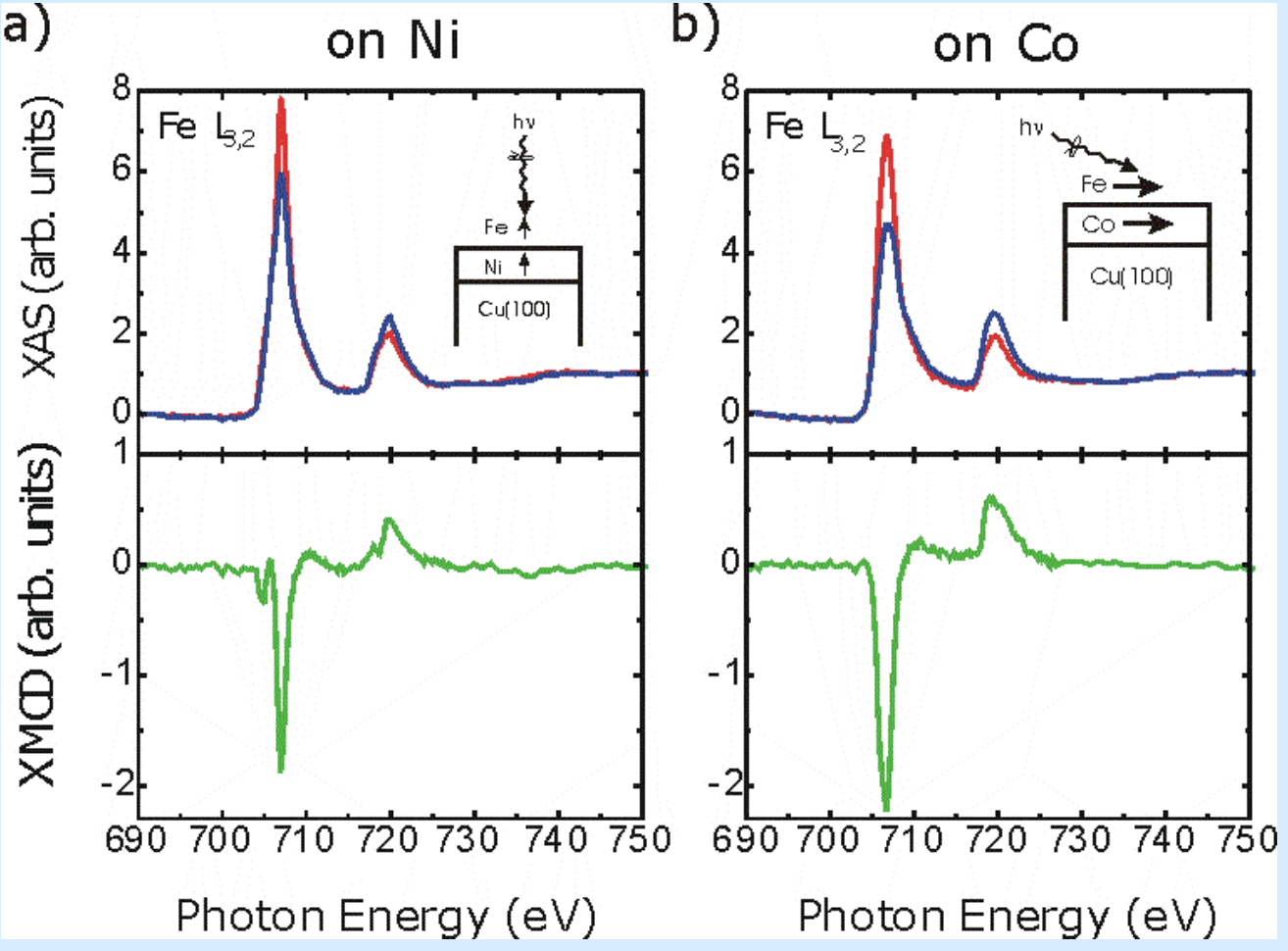
XAS of 1 ML of Fe octaethylporphyrin on metal surface





Porphyrin molecule

XAS / NEXAFS and XMCD at Fe in OEP



20110 Ü **Übung zur Festkörperphysik II** **SS 1998**

Baberschke
Farle
Bovensiepen

Ausgabe: 28.04.98 Abgabe: 08.05.98

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

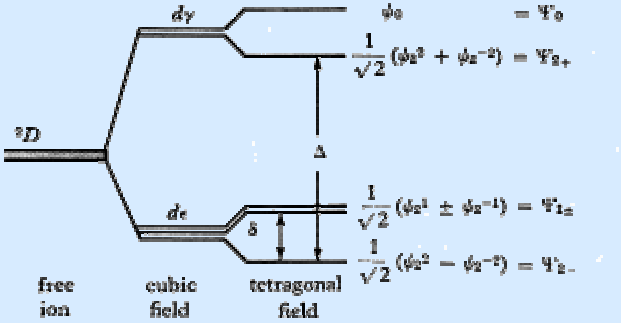


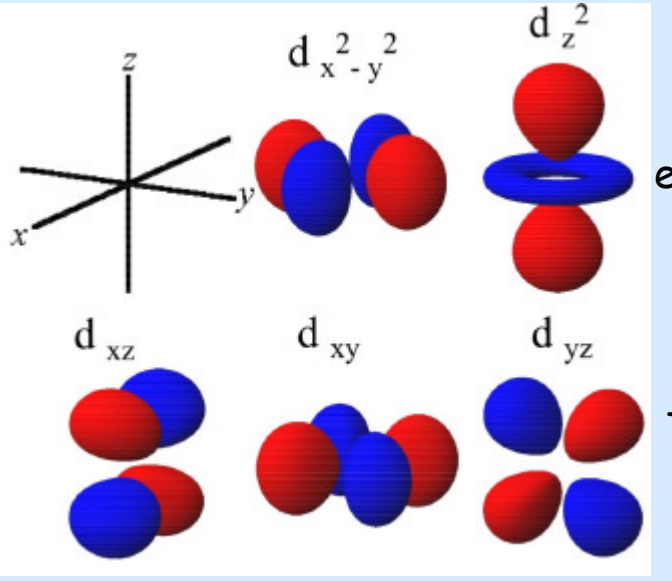
Fig. 3-4 Splitting of the ^2D term by a tetragonally distorted cubic field.

3) Berechnen Sie für den Grundzustand

$$\Psi_{2-} = (2)^{-1/2}\{|2> - |-2>\} = |2->$$

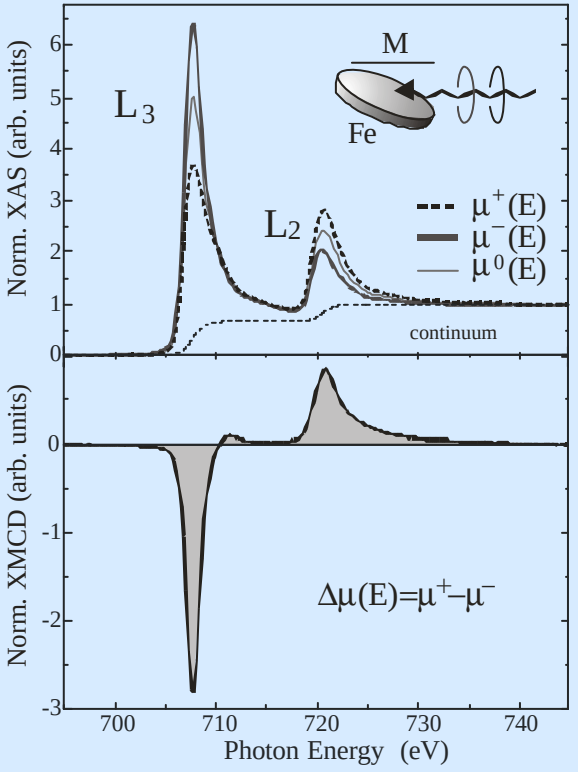
die Beimischung der angeregten Zustände durch $\lambda L \cdot S$ und beachten Sie dabei, daß auch Spinzustände einzuführen sind (zweckmäßig $\alpha|2->$ und $\beta|2->$ für Spin "up" and "down") (2 P)

4.) Gerechnen Sie für den in Ü3 gefundenen neuen Grundzustand die anisotropen g-Faktoren g_z, $g_x = g_y$ durch "Einschalten" der Zeeman Ww: $\mu_B(L+g_eS)H$ (3 P)

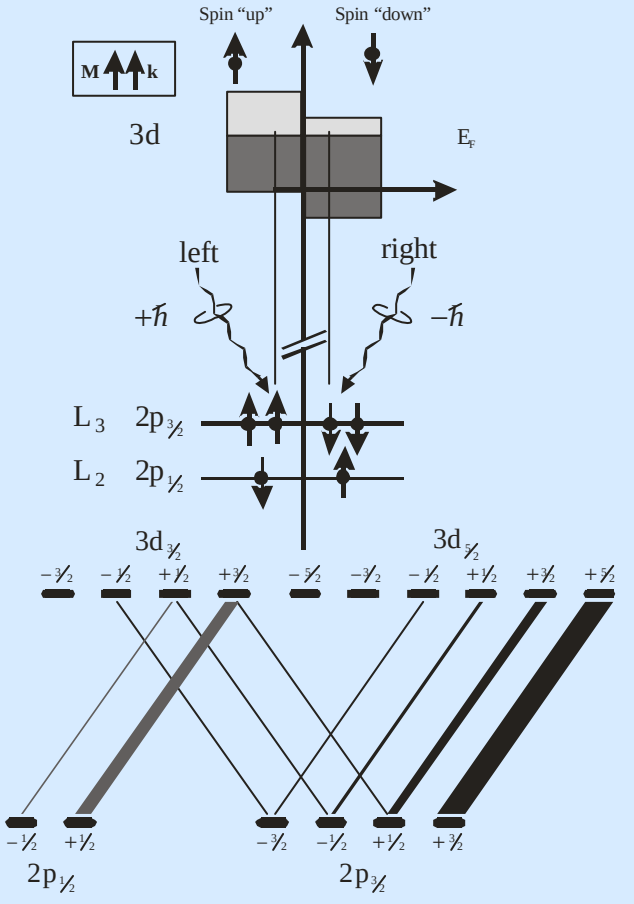


X-ray Magnetic Circular Dichroism

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

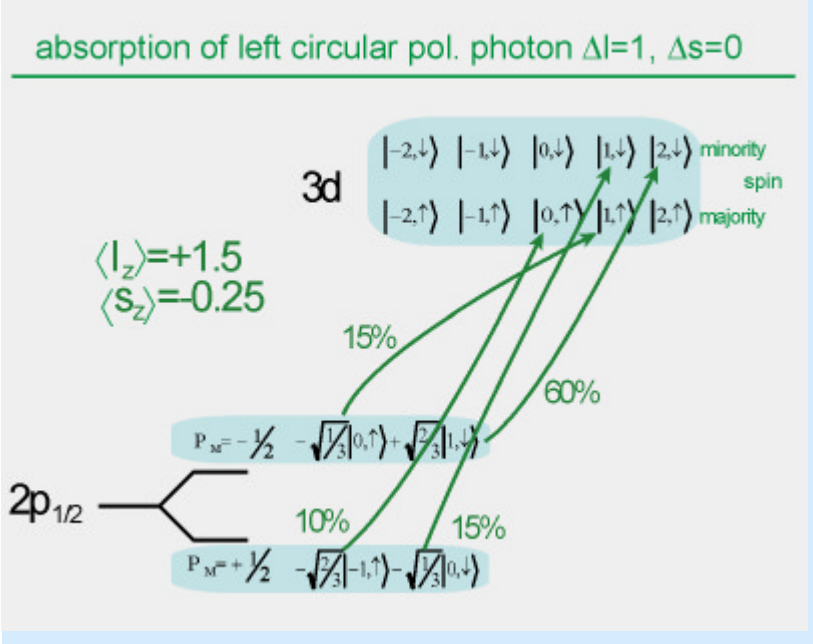


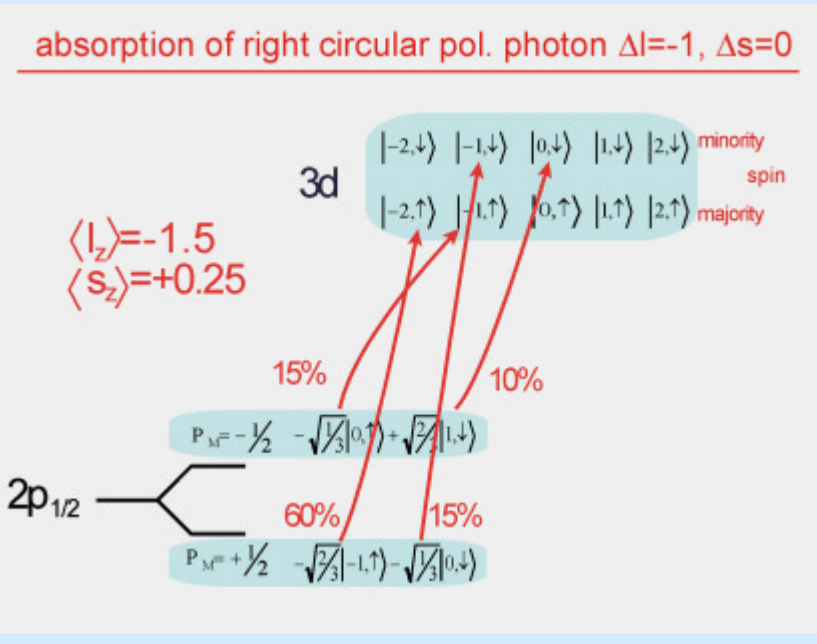
XMCD signal is a measure of the magnetization



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

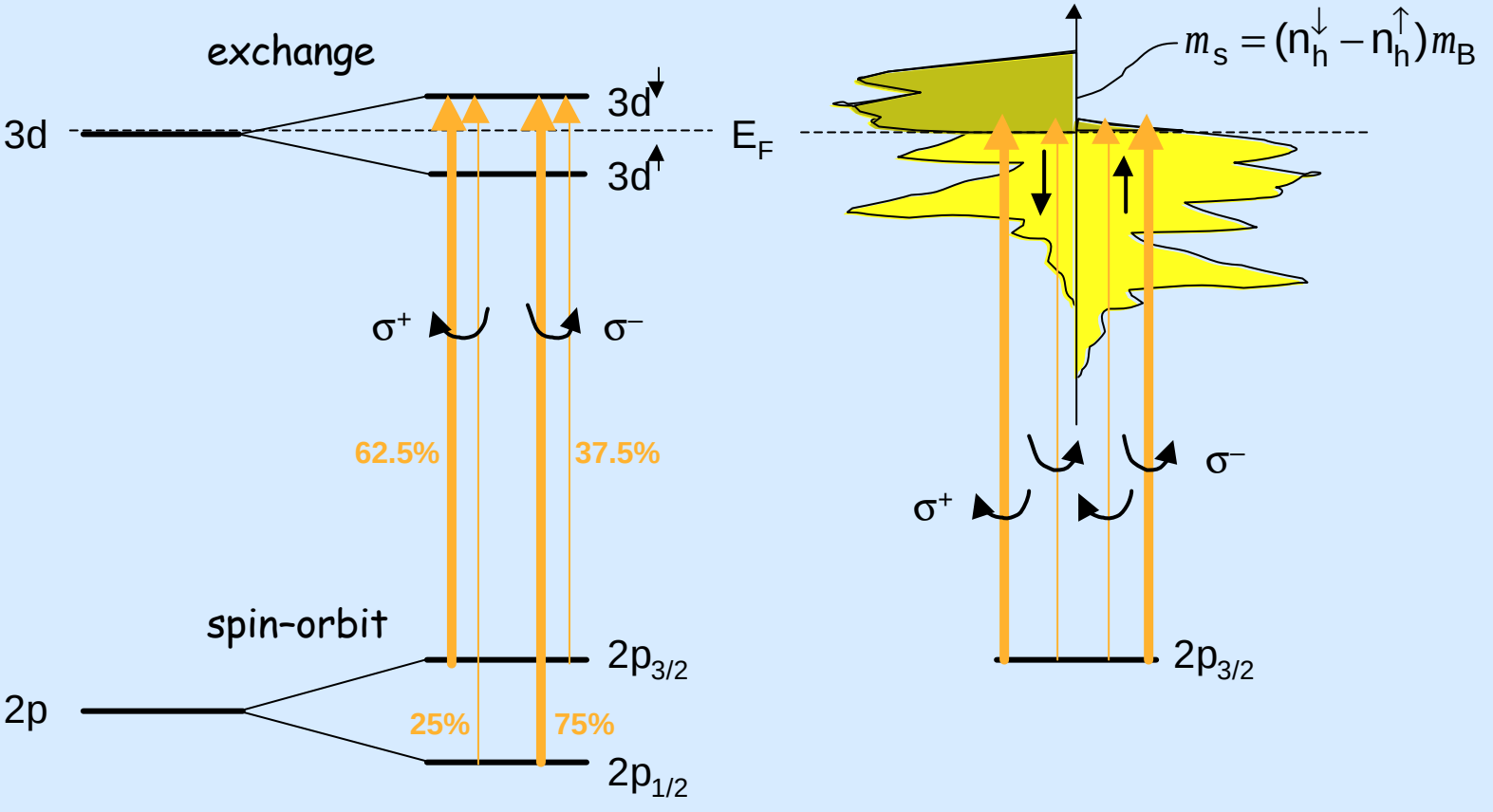
The origin of MCD (after K. Fauth, Univ. Würzburg)



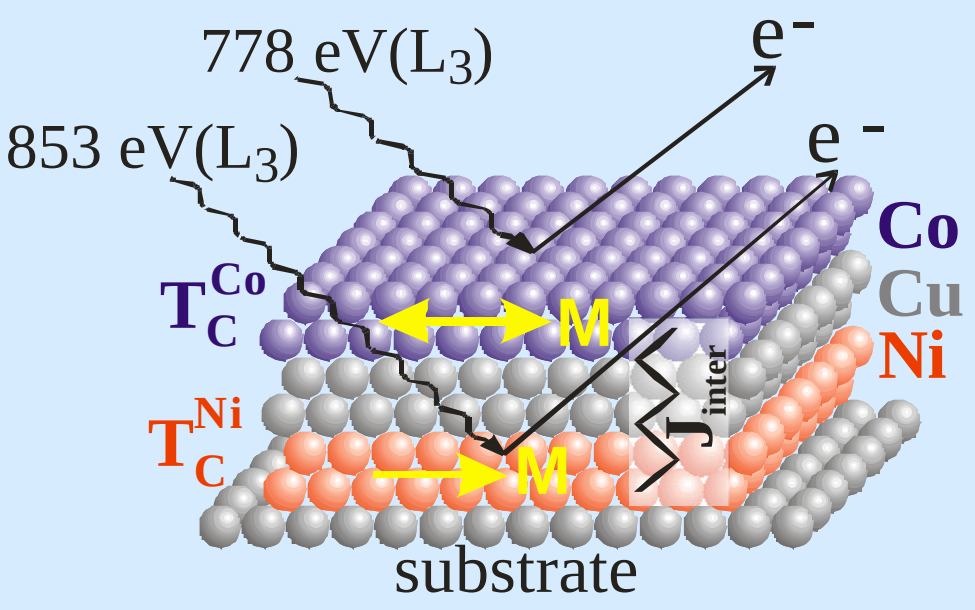


Reviews e.g.: Lecture Notes in Physics Vol. 466 by H. Ebert, G. Schütz

X-ray magnetic circular dichroism (XMCD)



2. Element specific magnetizations in trilayers



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

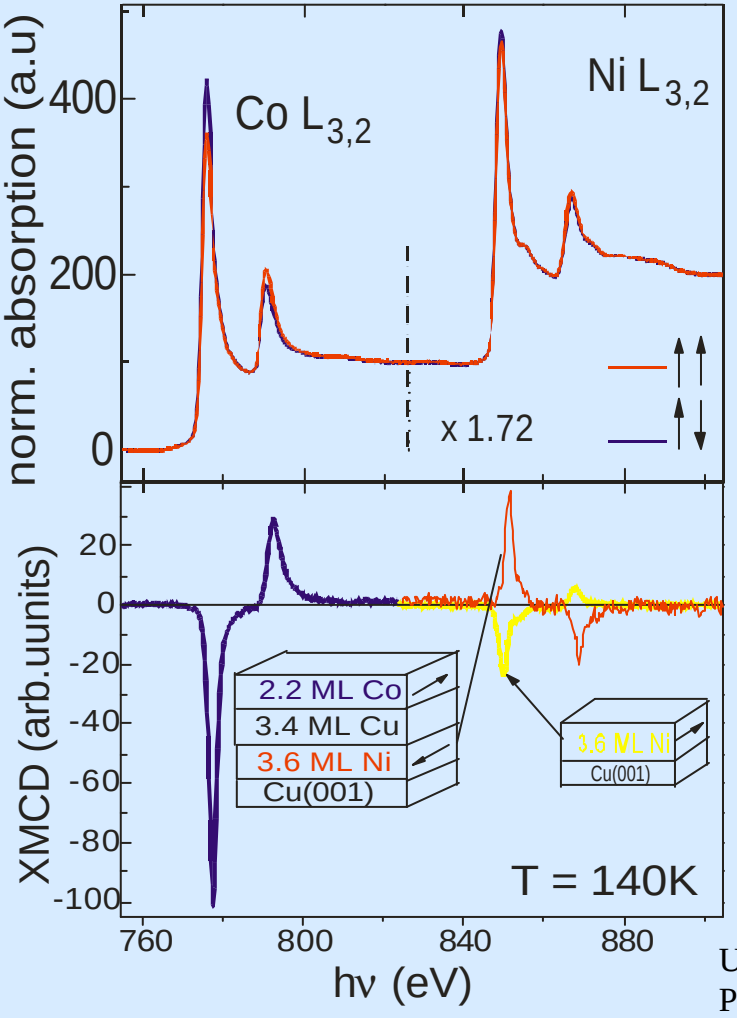
What about element specific Curie-temperatures ?

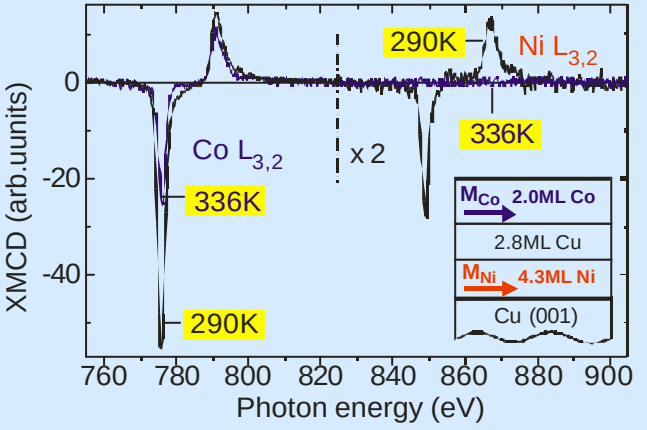
Two trivial limits: (i) $d_{Cu} = 0 \Rightarrow$ direct coupling like a Ni-Co alloy

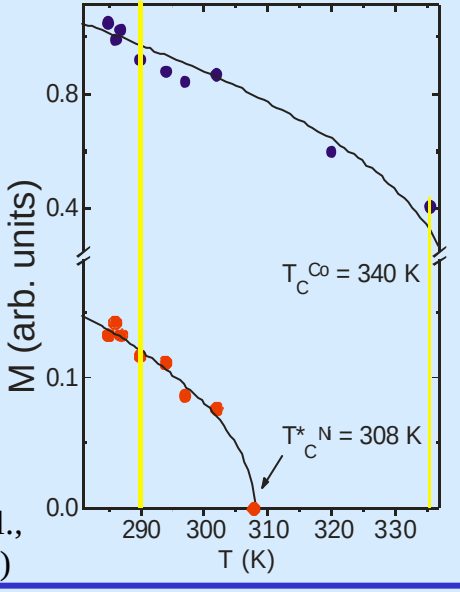
(ii) d_{Cu} = large $\Rightarrow$ no coupling, like a mixed Ni/Co powder

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

Ferromagnetic trilayers

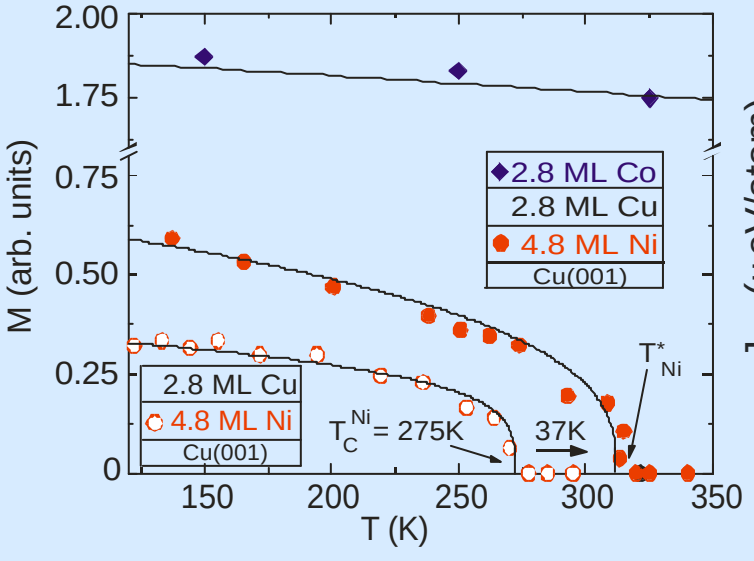


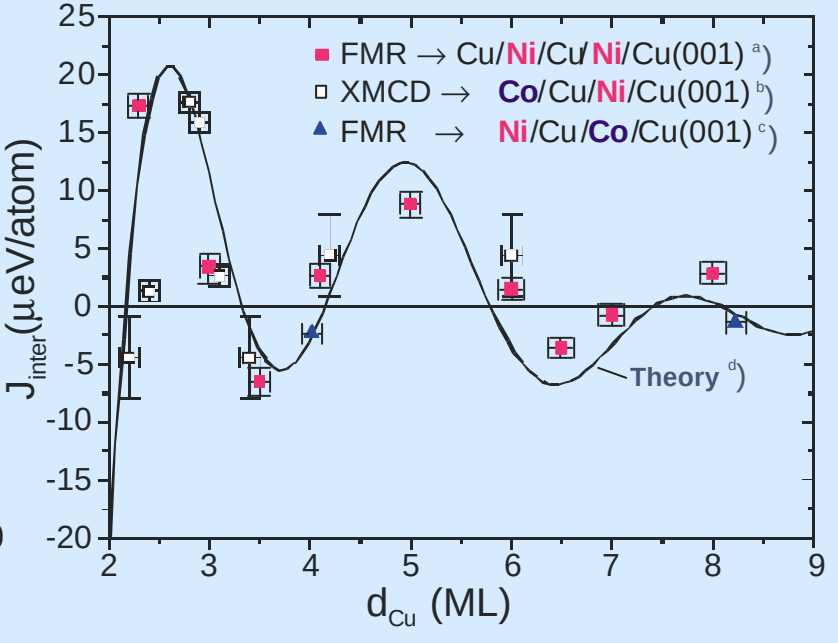




U. Bovensiepen et al.,
PRL **81**, 2368 (1998)

Interlayer exchange coupling

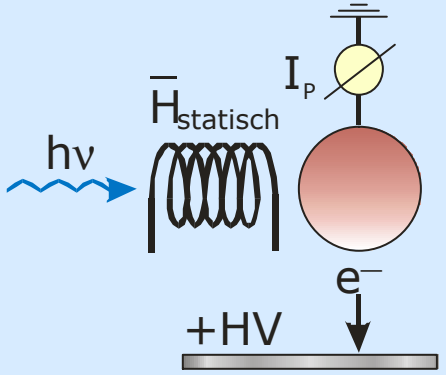




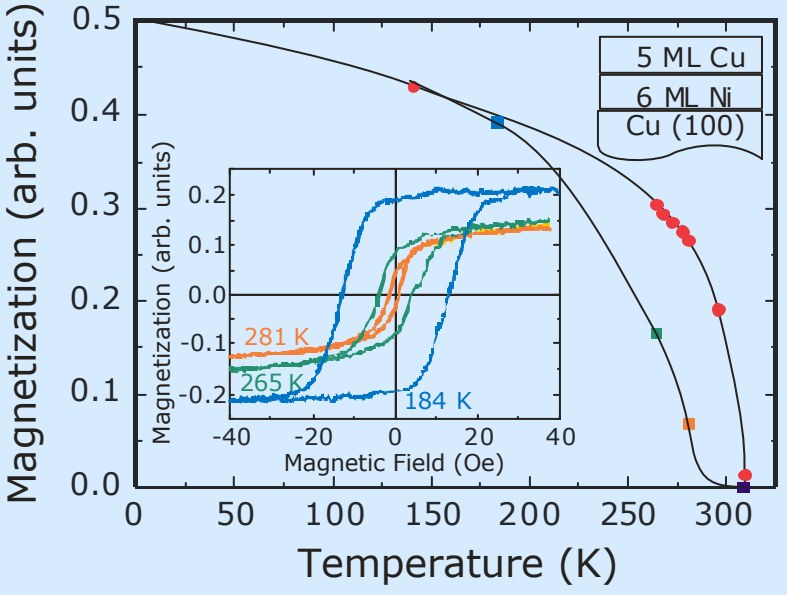
P. Poulopoulos, K. B., Lecture Notes in Physics **580**, 283 (2001)

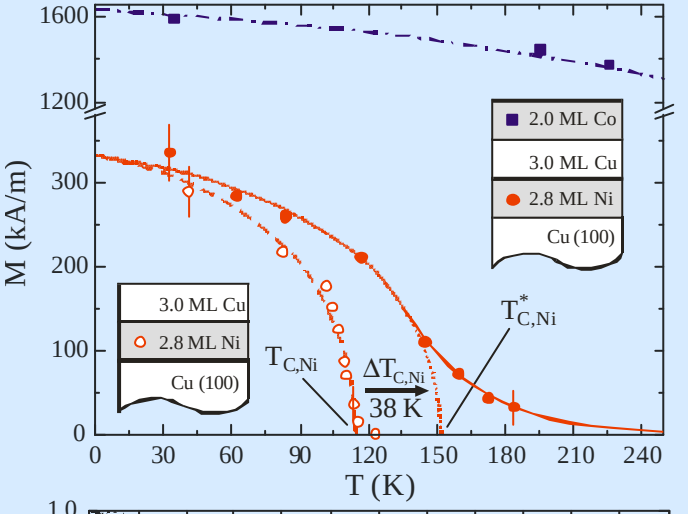
a) J. Lindner, K. B., J. Phys. Condens. Matter **15**, S465 (2003)
b) A. Ney et al., Phys. Rev. B **59**, R3938 (1999)
c) J. Lindner et al., Phys. Rev. B **63**, 094413 (2001)
d) P. Bruno, Phys. Rev. B **52**, 441 (1995)

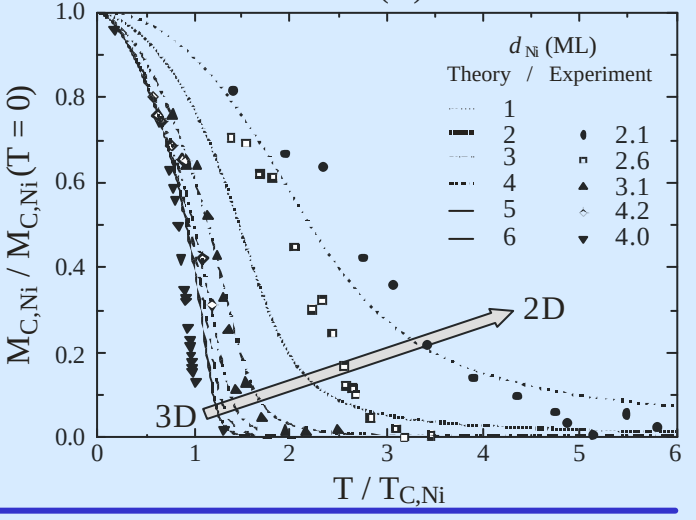
Remanence and saturation magnetization



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

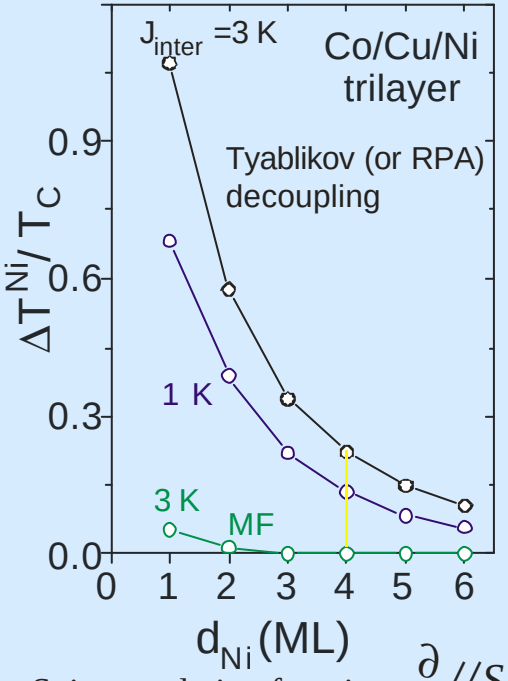






Enhanced spin fluctuations in 2D (theory)

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



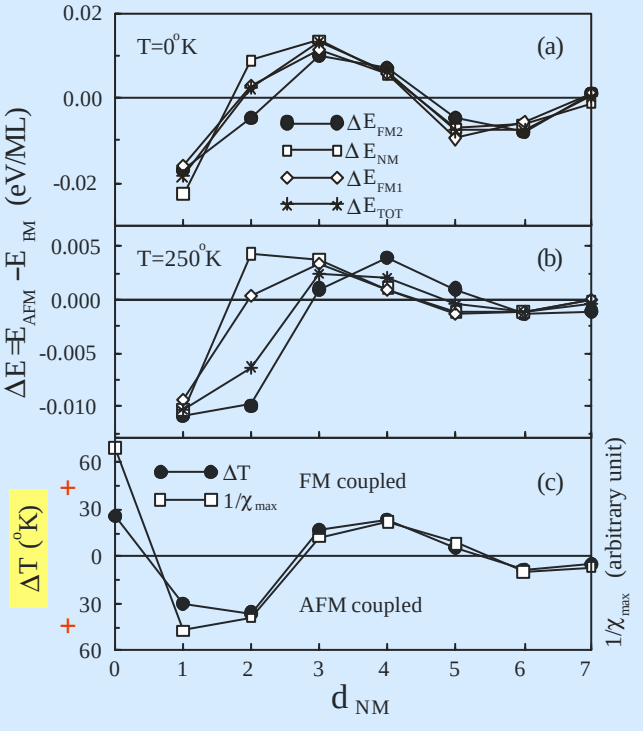
Spin-Spin correlation function $\frac{\partial}{\partial t}\langle\langle S_i^+ S_j^- \rangle\rangle \rightarrow$

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

RPA

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

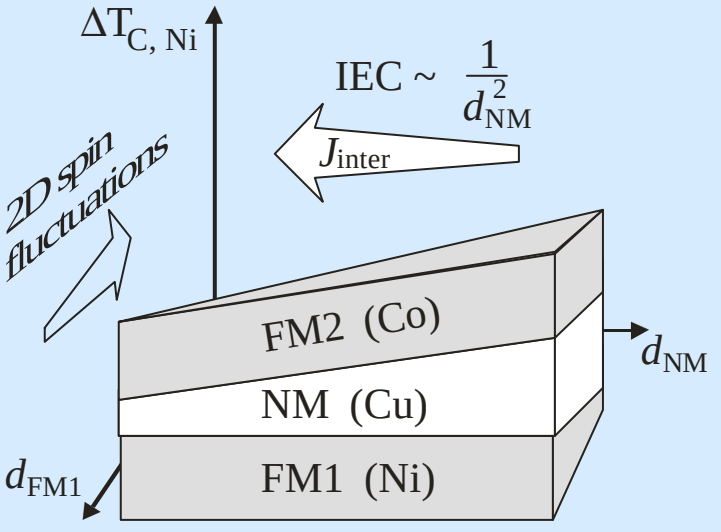
J.H. Wu et al. J. Phys.: Condens. Matter **12** (2000) 2847

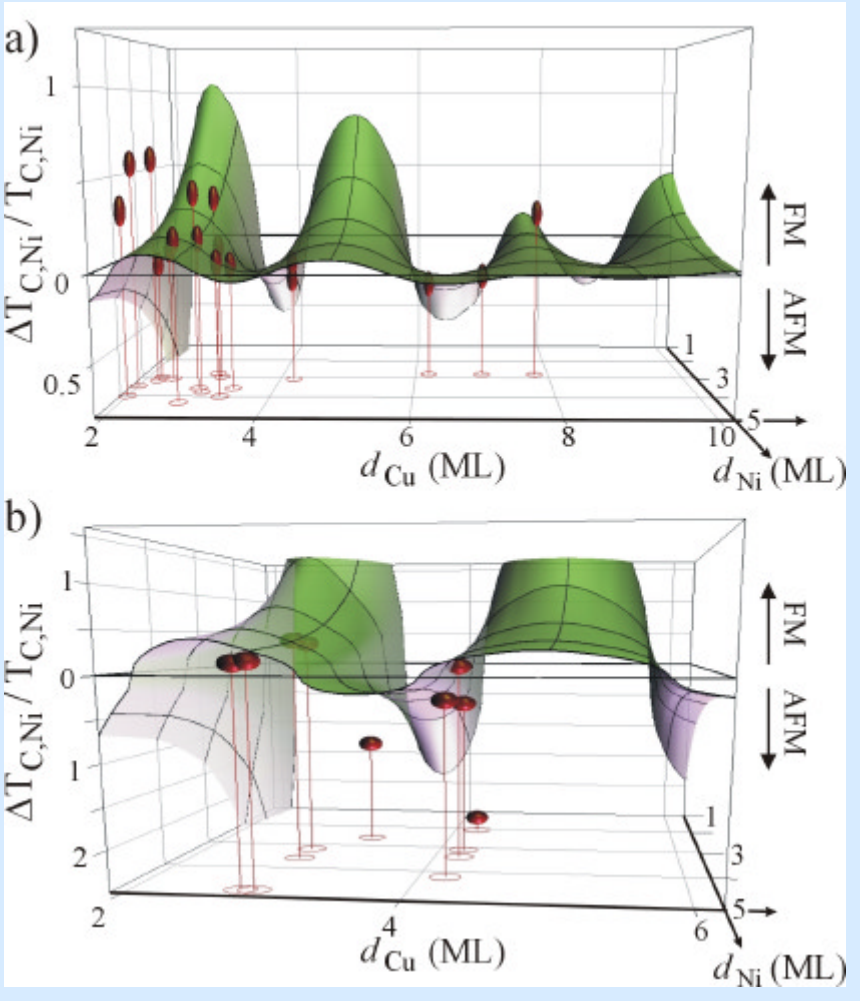


Single band Hubbard model:
Simple Hartree-Fock (Stoner) ansatz is insufficient
Higher order correlations are needed to explain T_C-shift

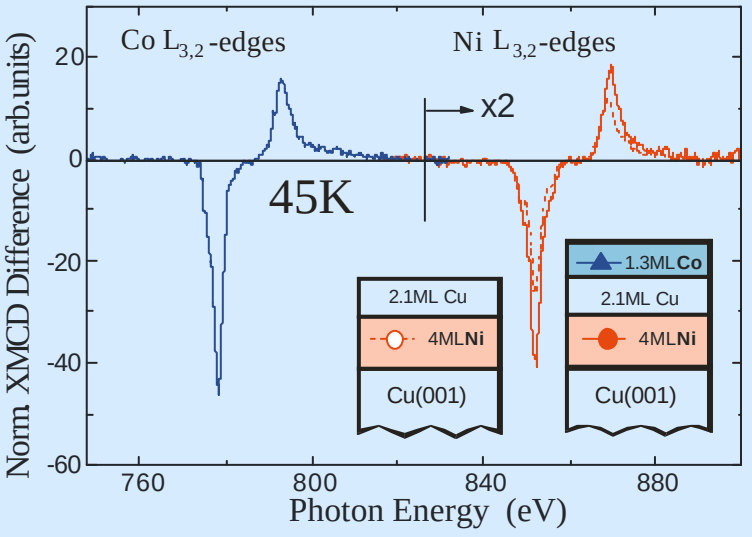
Evidence for giant spin fluctuations

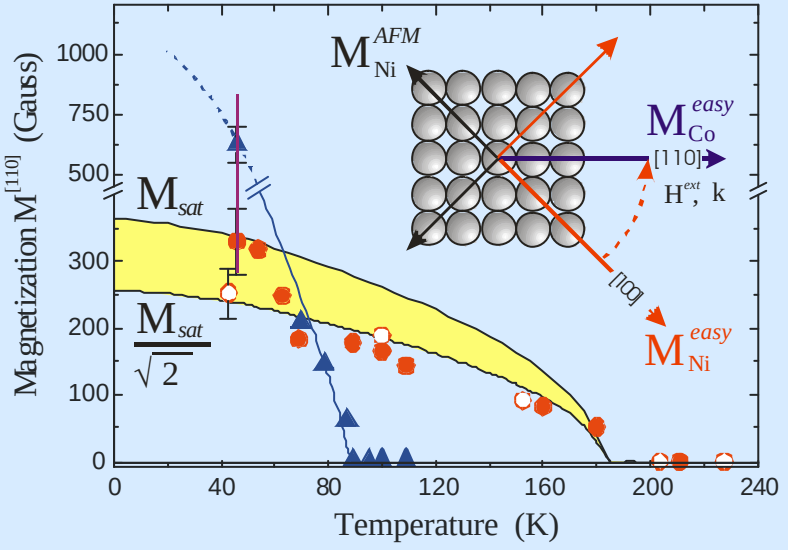
PRB **72**, 054447, (2005)





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

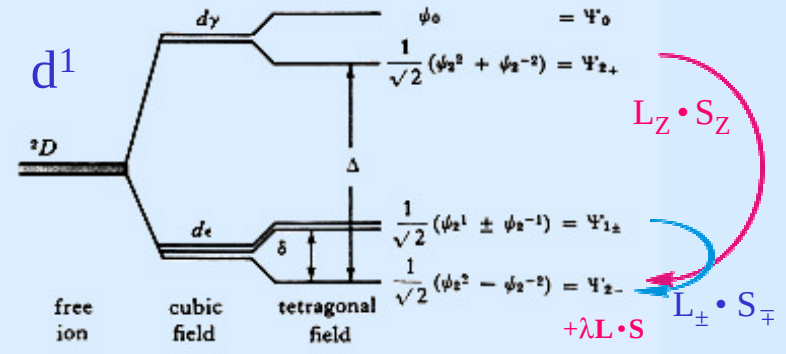




Two order parameter of T_C^{Ni} and T_C^{Co}
A further reduction in symmetry happens at T_C^{low}

3. 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

$$\langle 2\text{-} | L_Z | 2\text{-} \rangle = 0,$$

but not for tetragonal symmetry

$$\mathcal{H} = \sum_{i,j=1}^{3} [\beta g_e(\delta_{ij} - 2\lambda\Lambda_{ij})S_i H_j - \lambda^2\Lambda_{ij}S_i S_j]$$

g_{exp} ; $B_2^0 \rightarrow K_2^0$

+ diamagnetic terms in $H_i H_j$ (3-23)

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

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

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

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

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

where

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

G.E. 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?

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

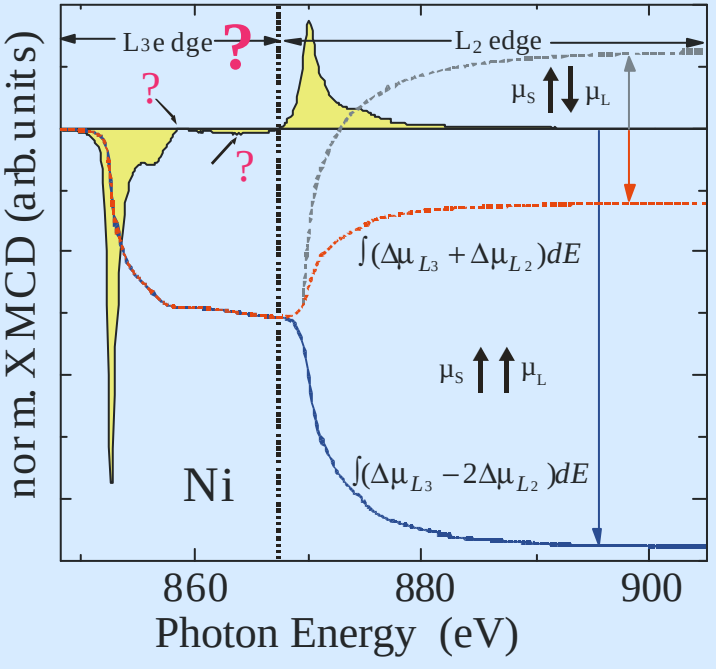
2) also exchange coupling $\mathbf{J}\,\mathbf{S}_1 \cdot \mathbf{S}_2$ is isotropic

3) so called ***anisotropic exchange*** is a (hidden) projection of the orbital momentum into spin space

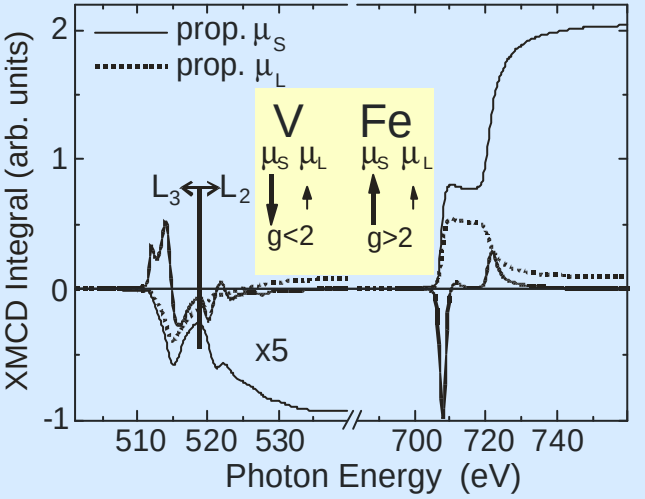
Orbital and spin magnetic moments deduced from XMCD

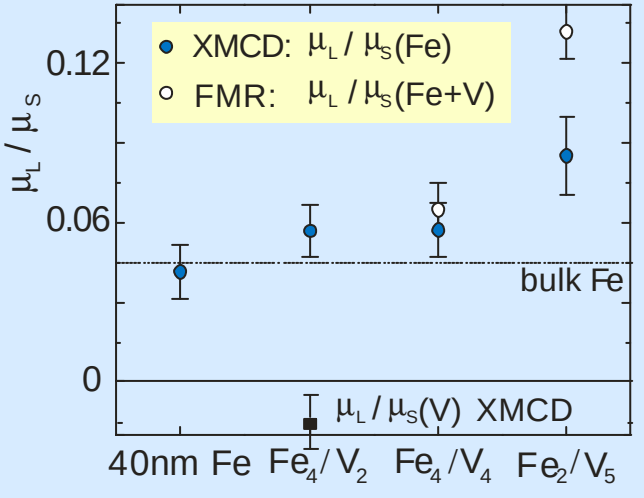
$$\int (?\,\mu_{L3} - 2\cdot ?\,\mu_{L2})\,dE = \frac{N}{3N_h^d}\left(2\langle S_Z\rangle^d + 7\langle T_Z\rangle^d\right)$$

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



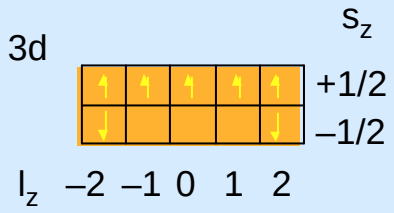
H. Ebert Rep. Prog. Phys. **59**, 1665 (1996)

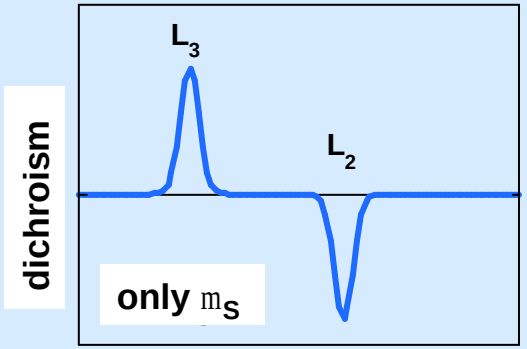




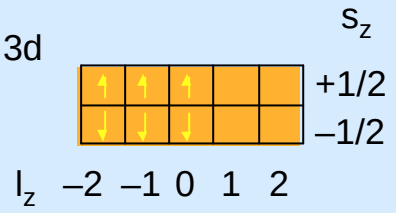
Sum rules

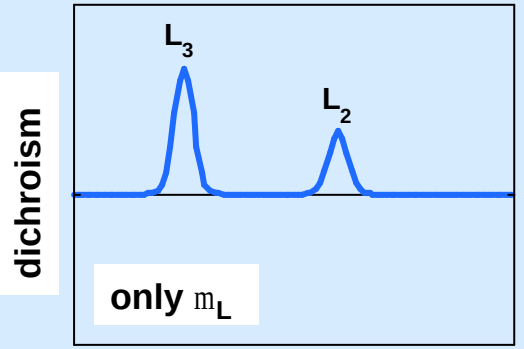
spin moment only

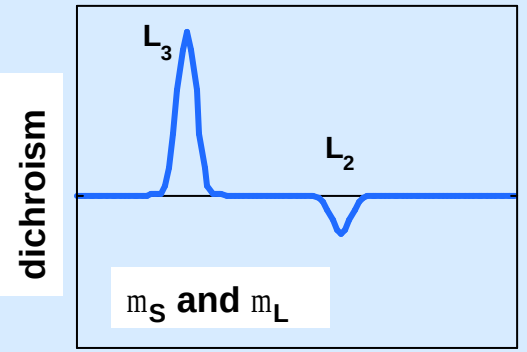


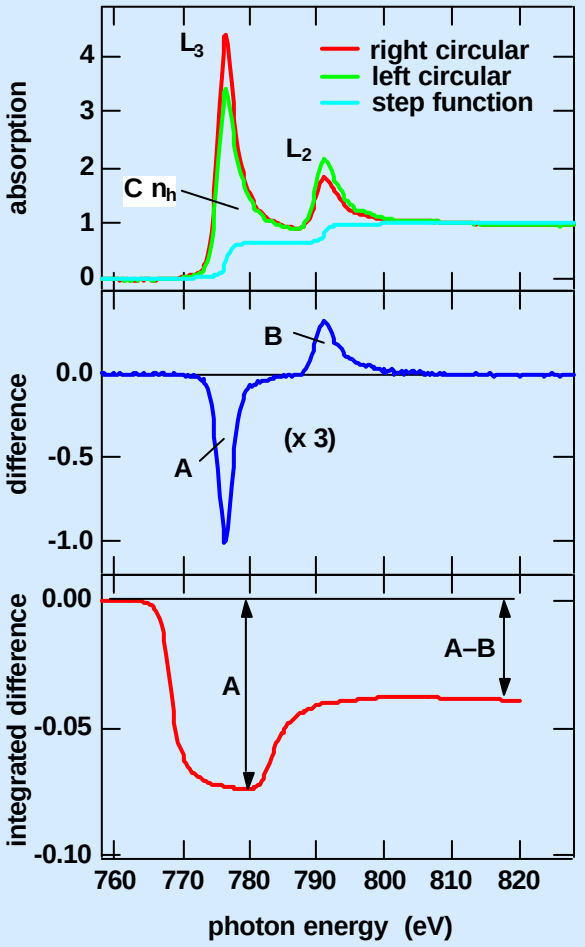


orbital moment only









1. Summenregel:

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

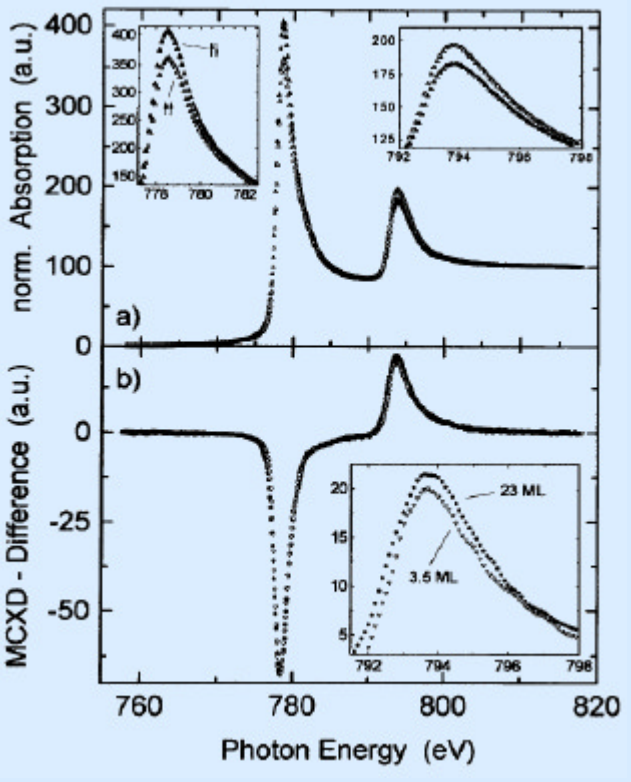
(P. Carra et al., PRL 70 (1993) 694)

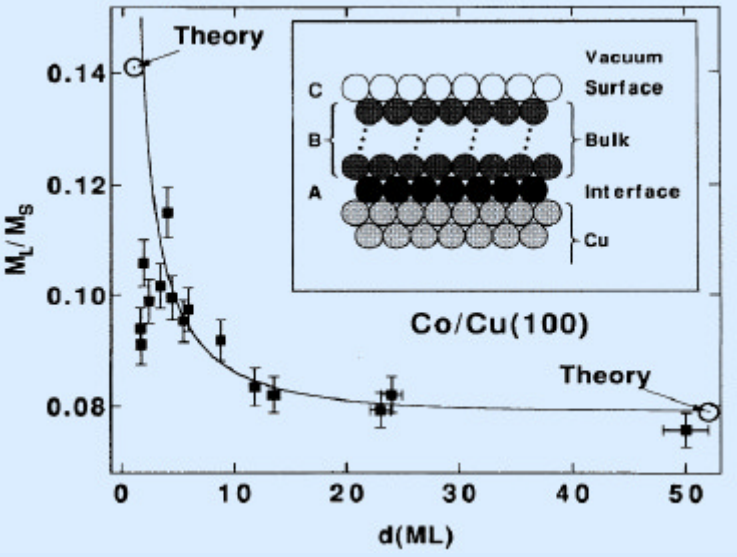
2. Summenregel:

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

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

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



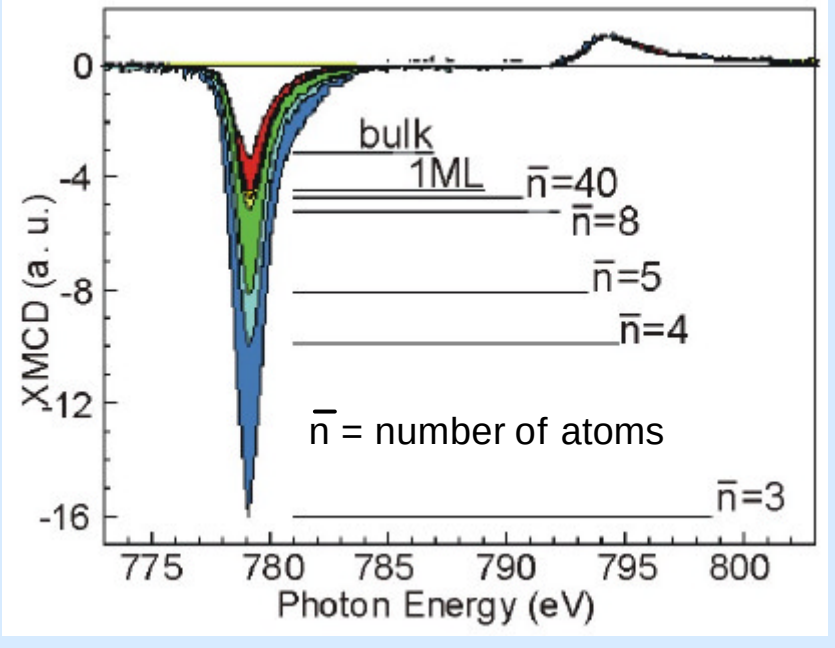


$$\left(\frac{M_L}{M_S}\right)_{\text{exp}} = \frac{Ae^{-D(d-1)/l} + B\Sigma_{n=3}^{d} e^{-D(n-2)/l} + C}{\Sigma_{n=0}^{d-1} e^{-nD/l}}$$

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

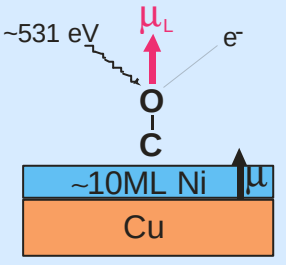
Giant Magn. Anisotropy of Single Co Atoms and Nanoparticles

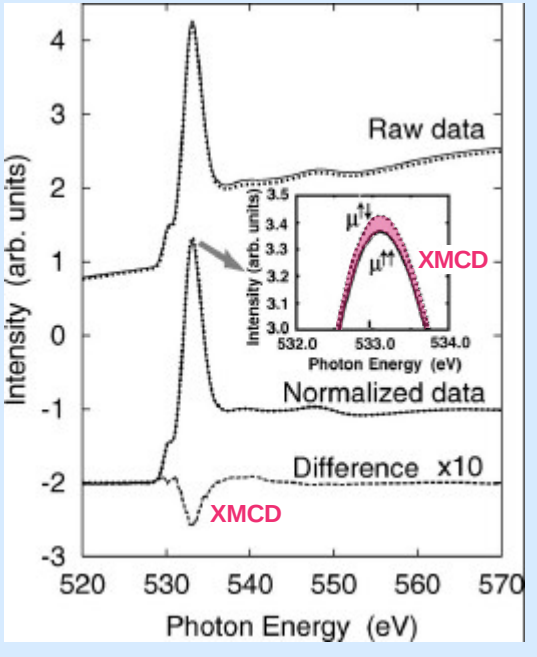
P. Gambardella et al., Science **300**, 1130 (2003)



Induced magnetism in molecules

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

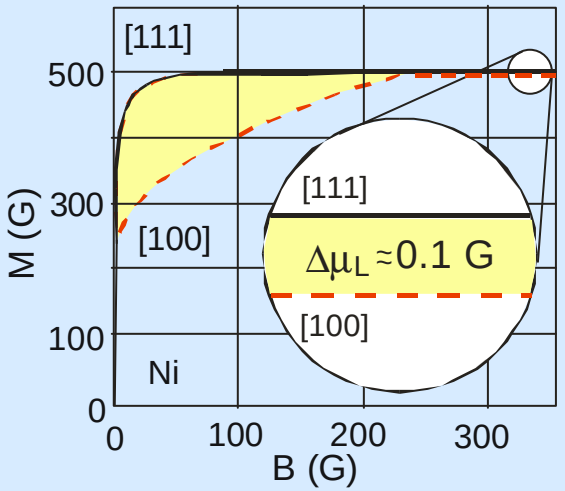




4. Magnetic Anisotropy Energy (MAE) and anisotropic μ_L

1. Magnetic anisotropy energy = f(T)

2. Anisotropic magnetic moment ≠ f(T)



MAE = ?M·dB ~ ½ ?M·?B ~ ½ 200 · 200 G^2

MAE ~ 2·10^4 erg / cm^3 ~ 0.2 µeV / atom

≈ 1µeV/atom is very small compared to
≈ 10 eV/atom total energy but all important

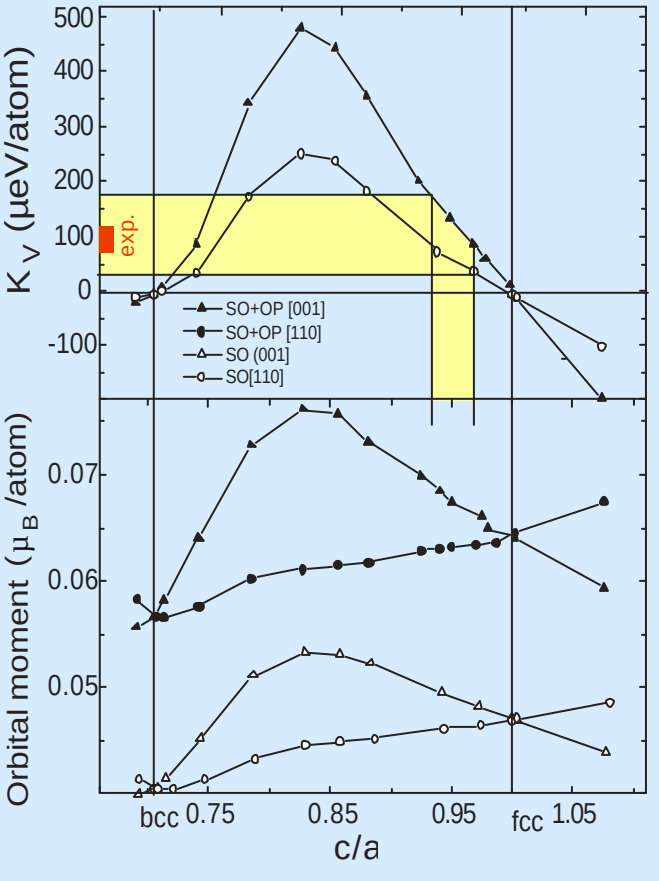
Characteristic energies of metallic ferromagnets

binding energy	1 - 10 eV/atom
exchange energy	10 - 10^3 meV/atom
cubic MAE (Ni)	0.2 µeV/atom
uniaxial MAE (Co)	70 µeV/atom

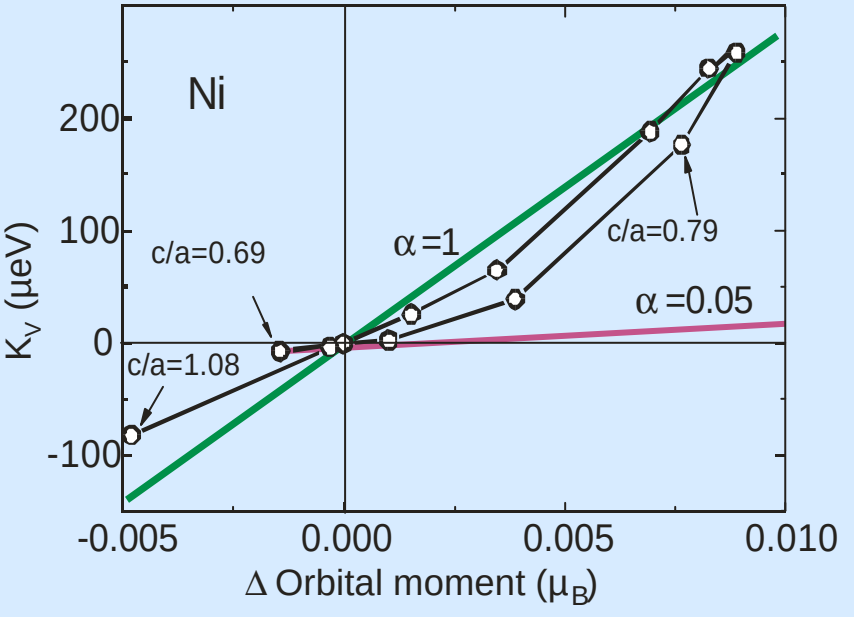
K. Baberschke, Lecture Notes in Physics, Springer **580**, 27 (2001)

Magnetic Anisotropy Energy MAE and anisotropic μ_L

anisotropic μ_L $\leftrightarrow$ MAE



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

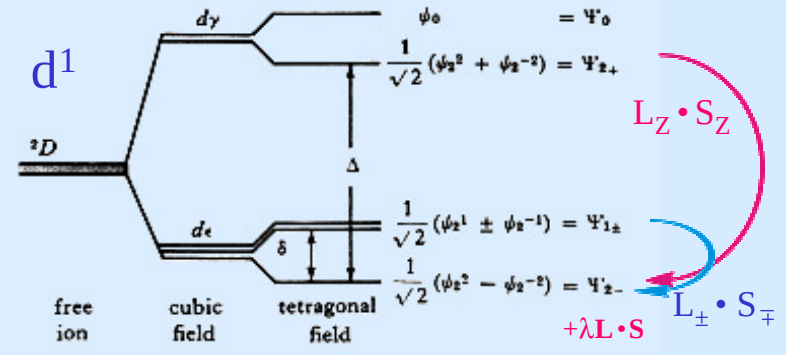


$$D = \frac{\lambda}{g_e}\Delta g; \quad g_{||} - g_{\perp} = g_e\lambda(\Lambda_{\perp} - \Lambda_{||})$$

$$\updownarrow$$

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

effective Spin Hamiltonian



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

$$\mathcal{H} = \sum_{i,j=1}^{3} [\beta g_e(\delta_{ij} - 2\lambda\Lambda_{ij})S_iH_j - \lambda^2\Lambda_{ij}S_iS_j]$$

g_{exp} ; $B_2^0 \rightarrow K_2^0$

+ diamagnetic terms in H_iH_j (3-23)

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

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

$< o|\mu_B H \cdot L|n > < n|\lambda L \cdot S|o >$; $< o|\lambda L \cdot S|n > < n|\lambda L \cdot S|o >$

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

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

where

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

G.E. Pake, p.66

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

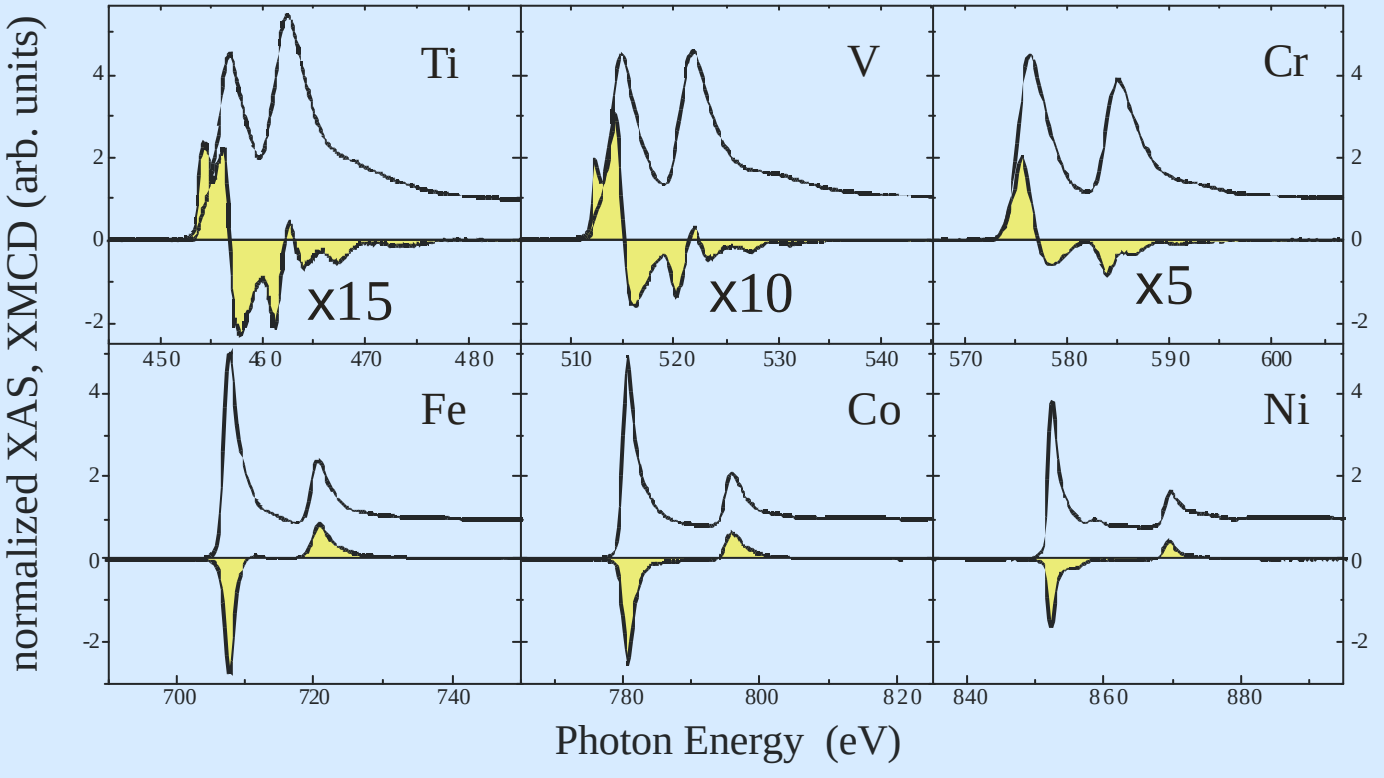
The orbital moment is quenched in cubic symmetry

$$\langle 2\text{-}|\, L_Z \,|\, 2\text{-}\rangle = 0,$$

but not for tetragonal symmetry

$L_{2,3}$ 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)

5. Full calculation of μ(E)

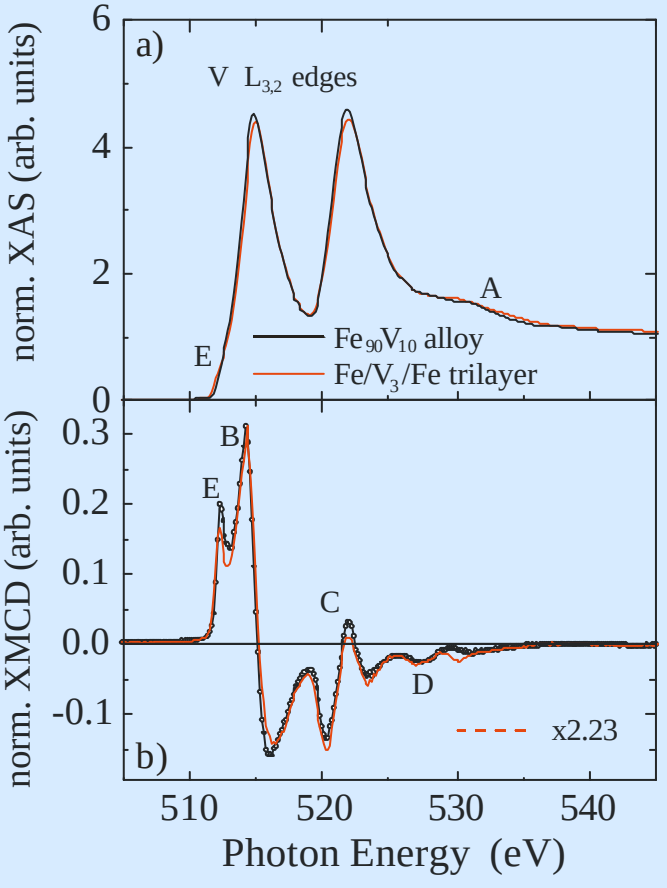
Experiment

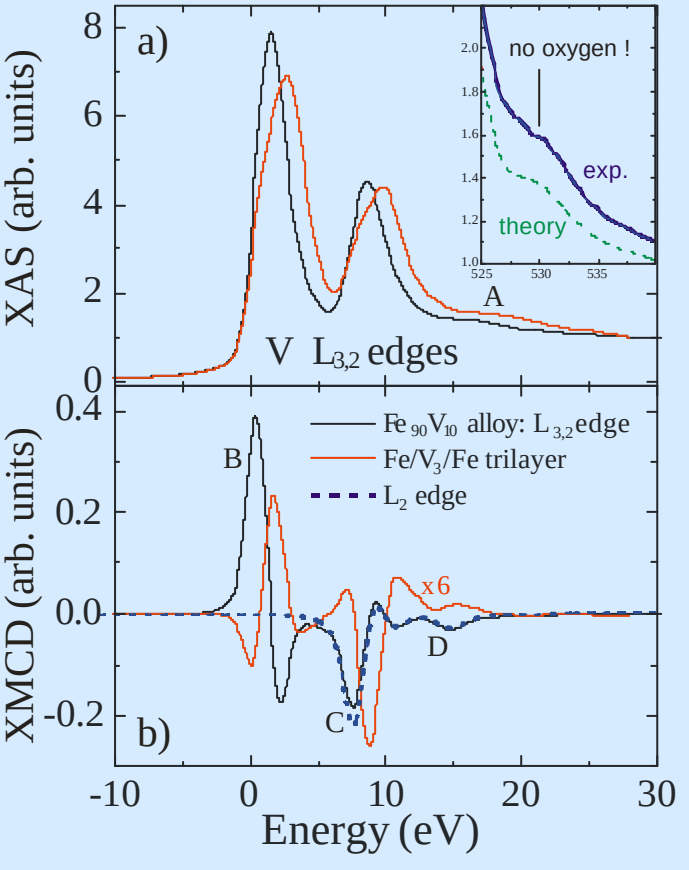
A. Scherz et al.

PRB **66**, 184401 (2002)

Theory

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

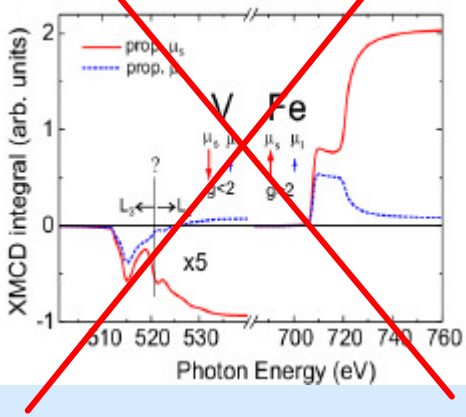




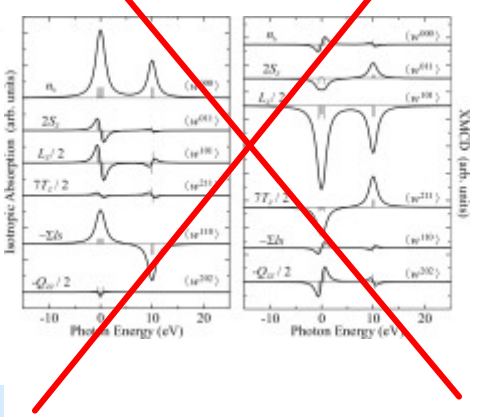
Summary

- 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

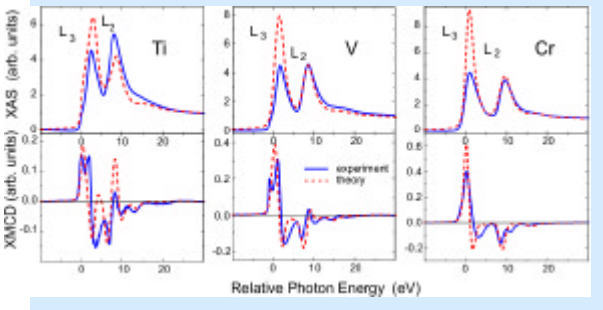
1) intergral SR



2) MMA



3) calculation of full μ(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 μ(E) i.e. the spectral density.
- In many calculations the matrix elements for the transition probability have been taken ≠ 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)
Handbook of Magnetism and Advanced Magnetic Materials (Wiley&Sons 2008)
Five volumes ; K. Baberschke Vol. 3

Conclusion, Future

During last few years: enormous progress in

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

Experiment:
- higher ΔE/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