



Magnetic anisotropy and orbital magnetism

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1. Introduction (tutorial)
2. Magnetic Anisotropy Energy (MAE)
3. Orbital magnetic moment μ_L
(which technique measures what?)

⇒ <http://www.physik.fu-berlin.de/~ag-baberschke>

1. Introduction

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 Energiedifferenz in tetragonaler Symmetrie wie folgt gegeben:

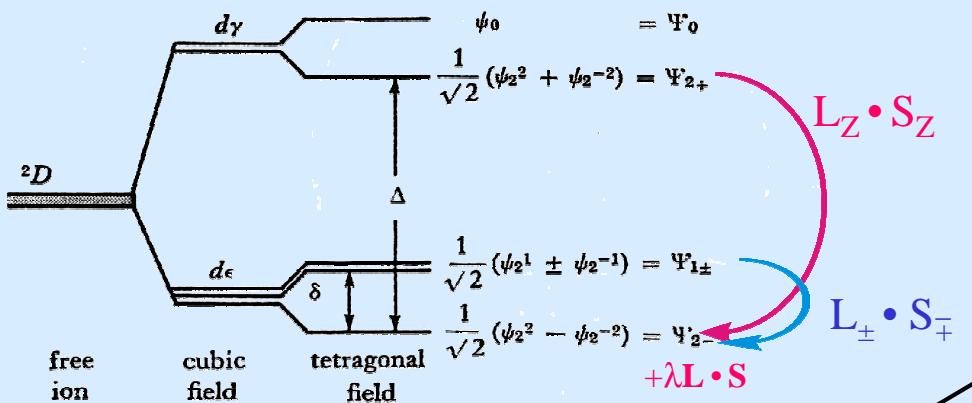


Fig. 3-4 Splitting of the 2D term by a tetragonally distorted cubic field.

3) Berechnen Sie für den Grundzustand

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

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.) Berechnen 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)

The orbital moment is quenched in cubic symmetry

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

but not for tetragonal symmetry

Orbital magnetism in second order perturbation theory

$$\mathcal{H}' = \mu_B \mathbf{H} \cdot \mathbf{L} + \lambda \mathbf{L} \cdot \mathbf{S}$$

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

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

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

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

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

$$S_x^2 + S_y^2 = S(S+1) - S_z^2 \quad \text{to give}$$

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

where

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

G.E. Pake, p.66

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

anisotropic $\mu_L \leftrightarrow \text{MAE}$

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

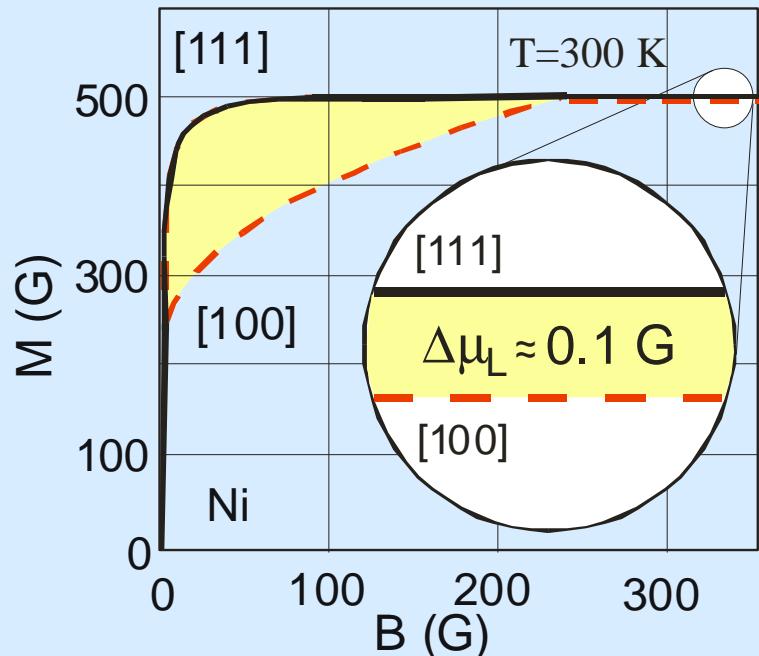


$$\text{MAE} \propto \frac{\xi_{LS}}{4\mu_B} \Delta \mu_L$$

Bruno ('89)

Magnetic Anisotropy Energy (MAE)

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



$$MAE = \int M \cdot dB \approx \frac{1}{2} \Delta M \cdot \Delta B \approx \frac{1}{2} 200 \cdot 200 G^2$$

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

$\approx 1 \mu\text{eV/atom}$ is very small compared to
 $\approx 10 \text{ eV/atom}$ 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 $\mu\text{eV/atom}$

uniaxial MAE (Co) 70 $\mu\text{eV/atom}$

Spin reorientation in bulk Gd

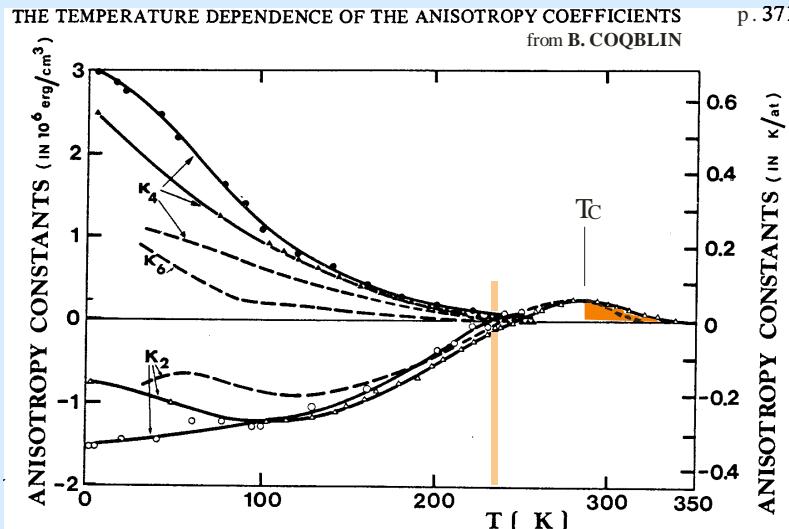


Fig. 160. Experimental values of the anisotropy constants κ_2 , κ_4 , and κ_6 versus temperature in Gadolinium. The circles (\circ for κ_2 , \bullet for κ_4) represent the data of Feron (Fig. 11 of Ref. 280), the triangles (Δ for κ_2 , \blacktriangle for κ_4) the data of Graham (Fig. 1 of Ref. 66) and the full lines connect respectively the data of Feron and those of Graham. The dotted lines give the data of Corner *et al.* (Fig. 5 of Ref. 70 modified by Ref. 661) for κ_2 , κ_4 and κ_6 .

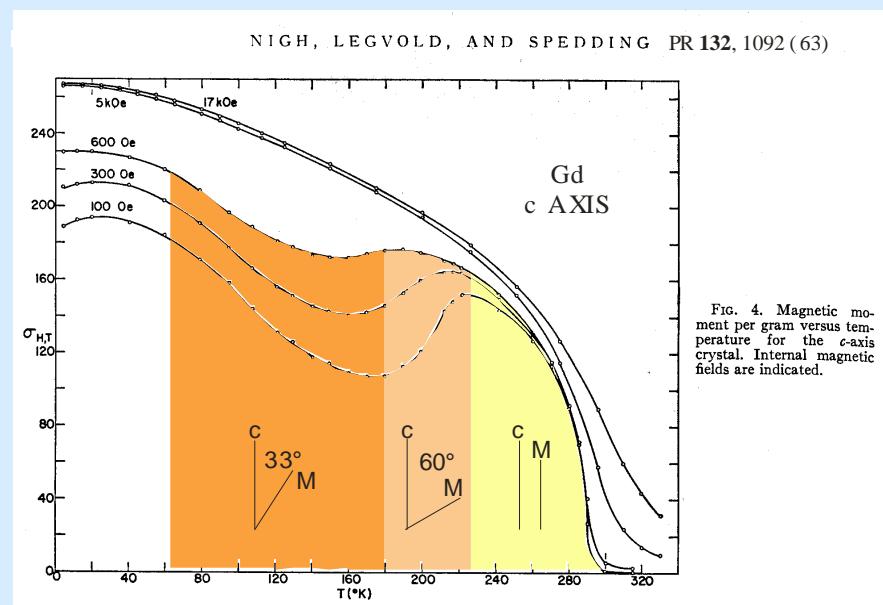


FIG. 4. Magnetic moment per gram versus temperature for the *c*-axis crystal. Internal magnetic fields are indicated.

Gd ist **not** isotropic, it has $K_2, K_4, K_6 \neq 0$

Note also finite MAE above T_C

Spin reorientation in bulk Ni und Co

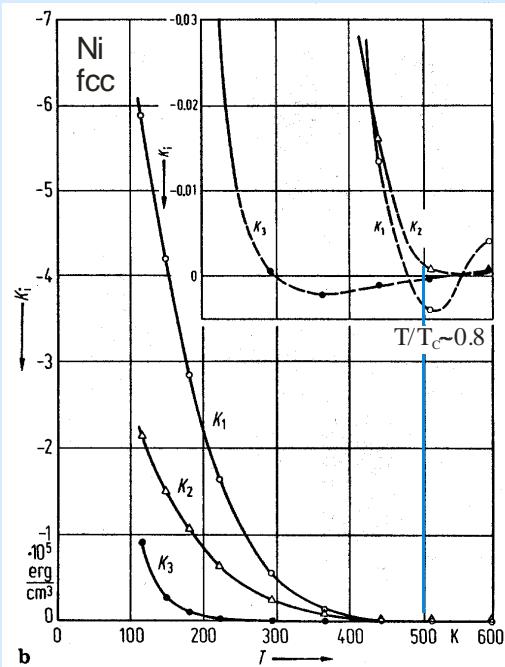


Fig. 7. Temperature dependence of magnetocrystalline anisotropy constants of Ni.(a) K_1 , 1: [68F1], 2: [74T1], 3: [77B2], 4: [77O1]. Solid line: calculation [77O1].(b) K_1 , K_2 , and K_3 . Accuracy of data is considerably reduced near T_c : dashed lines in the insert [68A1].(c) K_3 , 1 and 2: [76A1], 3: [69F2], 4: [77B2]. Solid line is to guide the eye through confidence limits [76A1].

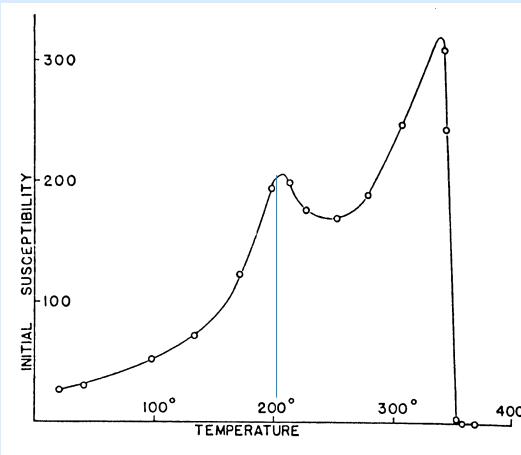


Fig. 6. The variation of the initial susceptibility with temperature in nickel.

$$\text{SRT for hcp Co}$$

$$\sin\theta = (K_2/2K_4)^{1/2}$$

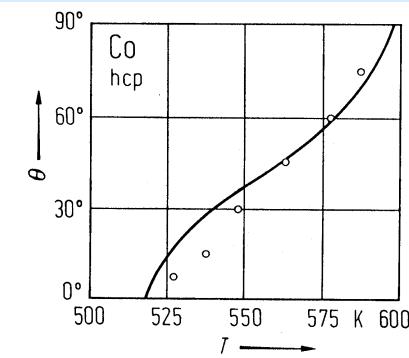


Fig. 5. Temperature dependence of the angle θ between the direction of spontaneous magnetization and the c axis of a single crystal of hcp Co [61B5]. Points: data. Curve: calculated from $\sin\theta = (-K_1/2K_2)^{1/2}$.

LB III, 19a, p.45

At the extremal value of K_2
a reorientation and second
maximum in χ appears

Superstarke Magnete intermetallischer Verbindungen der Seltenerdmetalle

Leistungssteigerung durch nanokristalline Strukturen

H. Kronmüller

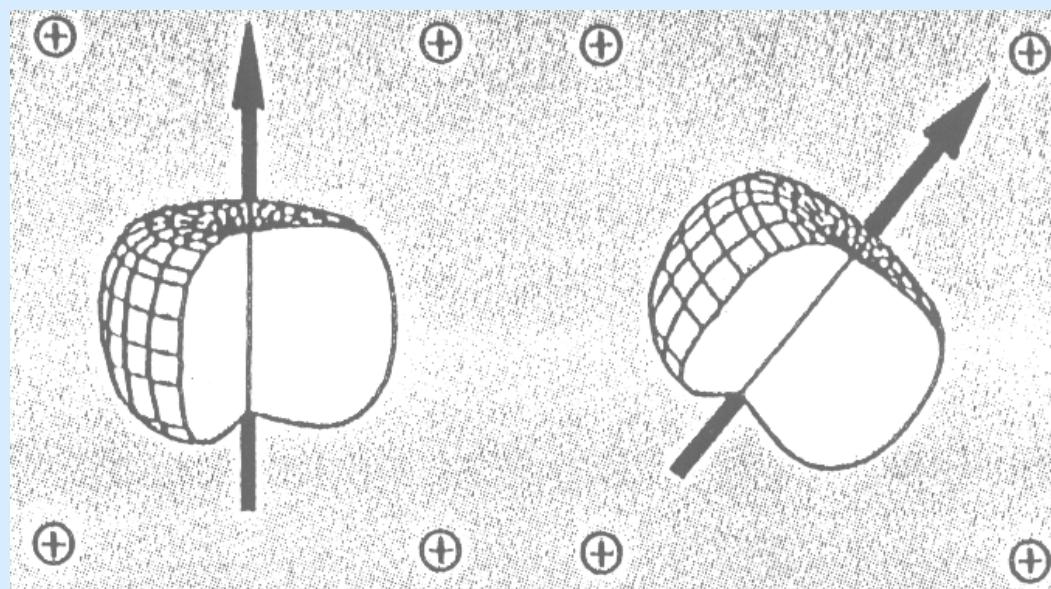


Abb. 3: Die Vorzugsrichtung des magnetischen Moments (*leichte Richtung*) der intermetallischen Seltenerdverbindungen hat ihre Ursache in der starren Kopplung zwischen magnetischem Moment (Pfeil) und Ladungsverteilung der 4f-Elektronen des Neodym. Bei einer Rotation des magnetischen Moments aus der c-Richtung (senkrecht) heraus dreht sich die anisotrope Ladungswolke mit. Da die Wechselwirkungsenergie zwischen 4f-Ladungswolke und Ladungswolken der benachbarten Ionen (⊕) dabei zunimmt, wird die leichte Richtung favorisiert.

Free energy density of MAE, K

(intrinsic, after subtraction of $2\pi M^2$)

tetragonal [e.g. Ni, Co, Fe (001) / Cu (001)]:

$$\begin{aligned} E_{\text{tetr}} &= -K_2 \alpha_z^2 & -\frac{1}{2} K_{4\perp} \alpha_z^4 - \frac{1}{2} K_{4||} (\alpha_x^4 + \alpha_y^4) + \dots & (B. Heinrich et al.) \\ &= -K_2 \cos^2\theta & -\frac{1}{2} K_{4\perp} \cos^4\theta - \frac{1}{2} K_{4||} \frac{1}{4} (3+\cos 4\varphi) \sin^4\theta + \dots & (Bab et al.) \\ &= (K_2 + K_{4\perp}) \sin^2\theta & -\frac{1}{2} (K_{4\perp} + \frac{3}{4} K_{4||}) \sin^4\theta - \frac{1}{8} K_{4||} \cos 4\varphi \sin^4\theta + \dots \\ &= K_2' \sin^2\theta & + K_{4\perp} \sin^4\theta + K_{4||} \cos 4\varphi \sin^4\theta + \dots & (\text{traditional}) \end{aligned}$$

hexagonal [e.g. Ni (111), Gd (0001) / W (110)]:

$$E_{\text{hex}} = k_2 \sin^2\theta + \frac{1}{2} k_{2||} \cos 2\varphi \sin^2\theta + k_4 \sin^4\theta + k_{6\perp} \sin^6\theta + k_{6||} \cos 6\varphi \sin^6\theta + \dots$$

$$K = k_2 Y_2^0 + k_{4m} Y_4^m + \dots \quad \text{Legendre polyn. (B. Coqblin)}$$

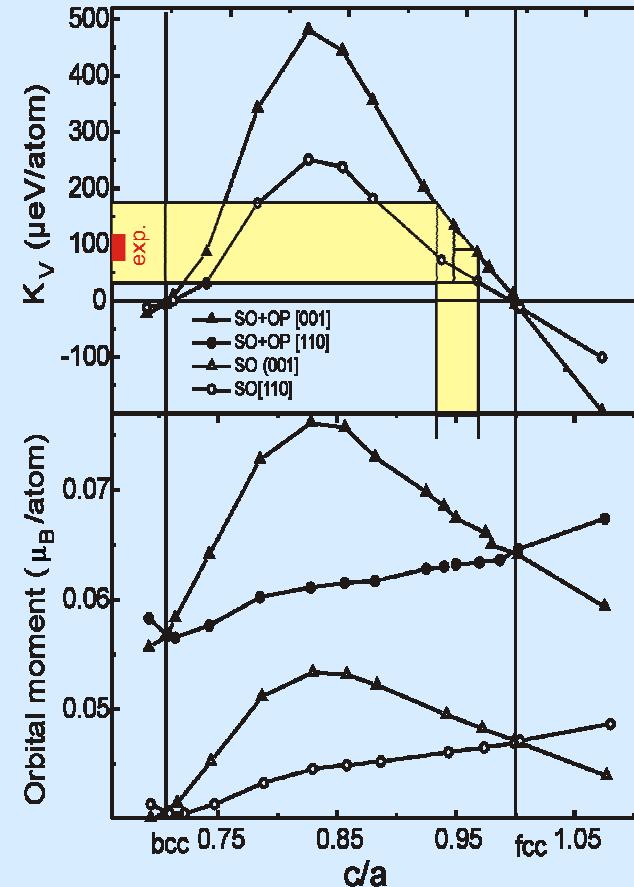
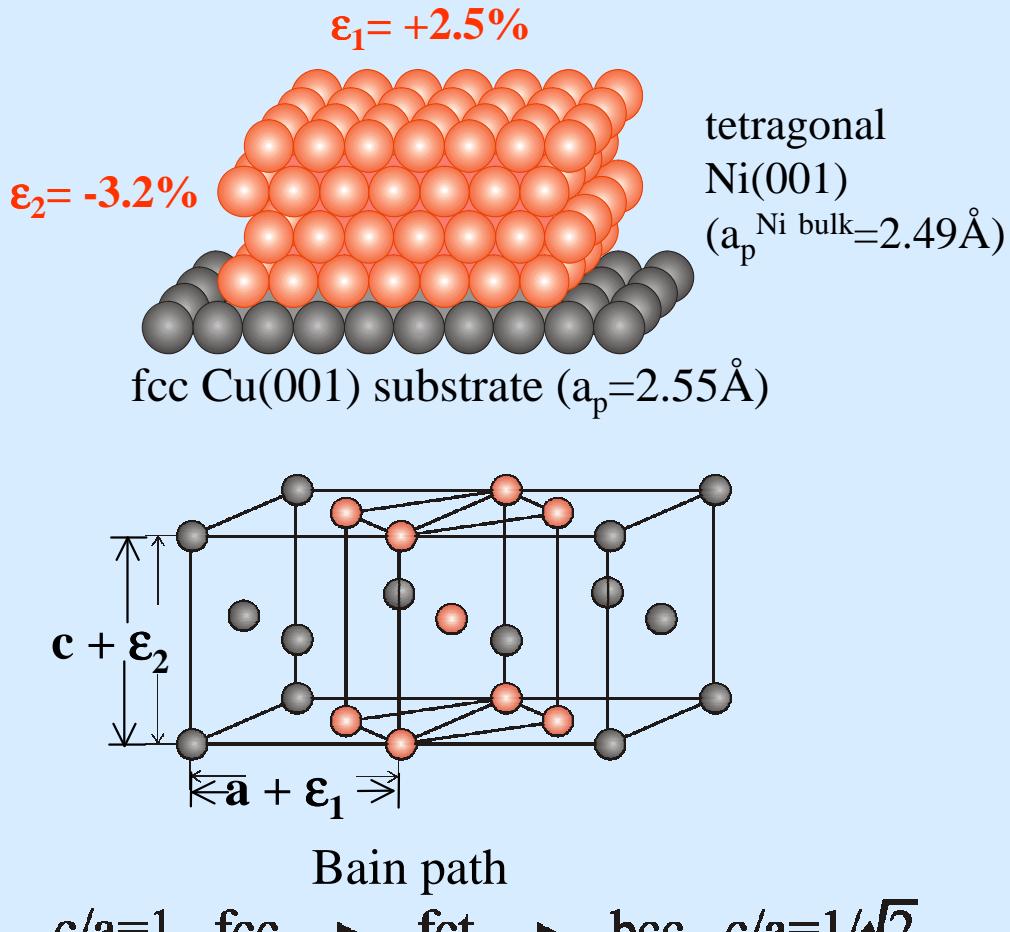
each K_i has a „volume“ and „surface“ contribution

$$K_i = K_i^v + 2K_i^s/d$$

2. Magnetic Anisotropy Energy (MAE) in ultra thin films

There are only 2 origins for MAE: 1) dipol-dipol interaction $\sim (\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})$ and
2) spin-orbit coupling $\lambda \vec{L} \cdot \vec{S}$ (intrinsic K or ΔE_{band})

Growth of artificial nanostructures
bcc, fcc \rightarrow tetragonal, trigonal



Structural changes by $\approx 0.05 \text{ \AA}$ increase MAE by 2-3 orders of magnitude ($\sim 0.2 \rightarrow 100 \mu\text{eV/atom}$)

O. Hjortstam, K. B. et al. PRB **55**, 15026 ('97)
R. Wu et al. JMMM **170**, 103 ('97)

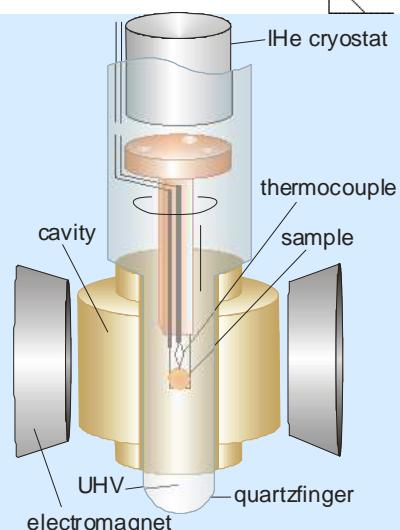
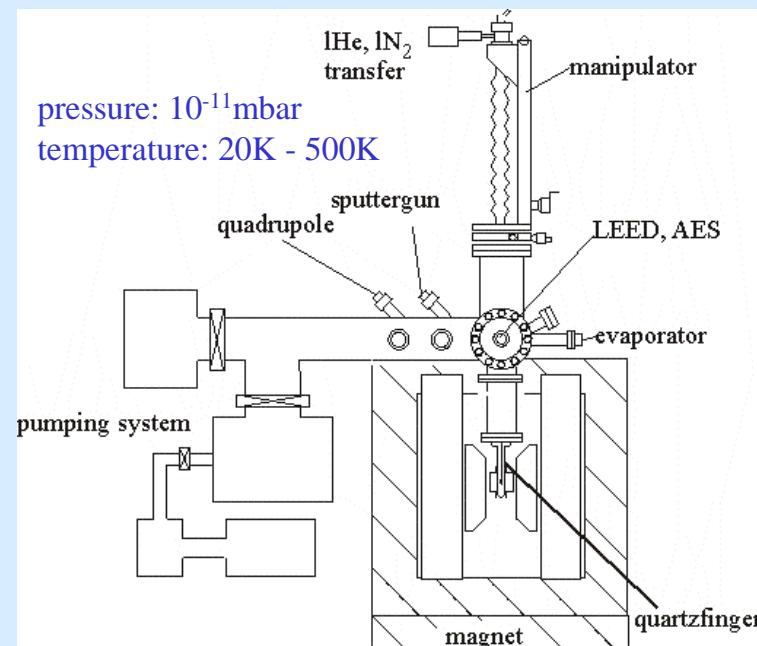
FMR in ferromagnetic nanostructure

In situ UHV-FMR set up

VOLUME 58, NUMBER 5

PHYSICAL REVIEW LETTERS

2 FEBRUARY 1987



M. Zomak et al.,
Surf. Sci. **178**, 618 (1986)

J. Lindner, K.B.
J. Phys.: Cond. Matt **15**, R193 (2003)

Ferromagnetic Order and the Critical Exponent γ for a Gd Monolayer: An Electron-Spin-Resonance Study

M. Farle and K. Baberschke
Institut für Atom- und Festkörperphysik, Freie Universität Berlin, D-1000 Berlin 33, Federal Republic of Germany
(Received 18 September 1986)

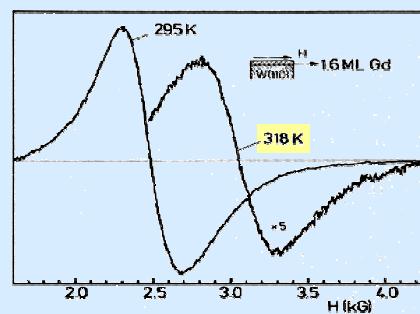


Fig. 4. ESR spectra for the new 1.6 ML sample (not cited in [2, 3]). Note the significant change in intensity and resonance field from 16 to 39 K above T_c .

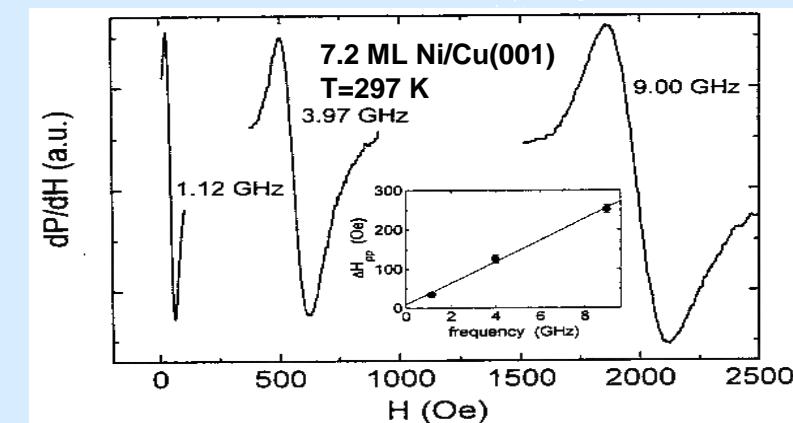
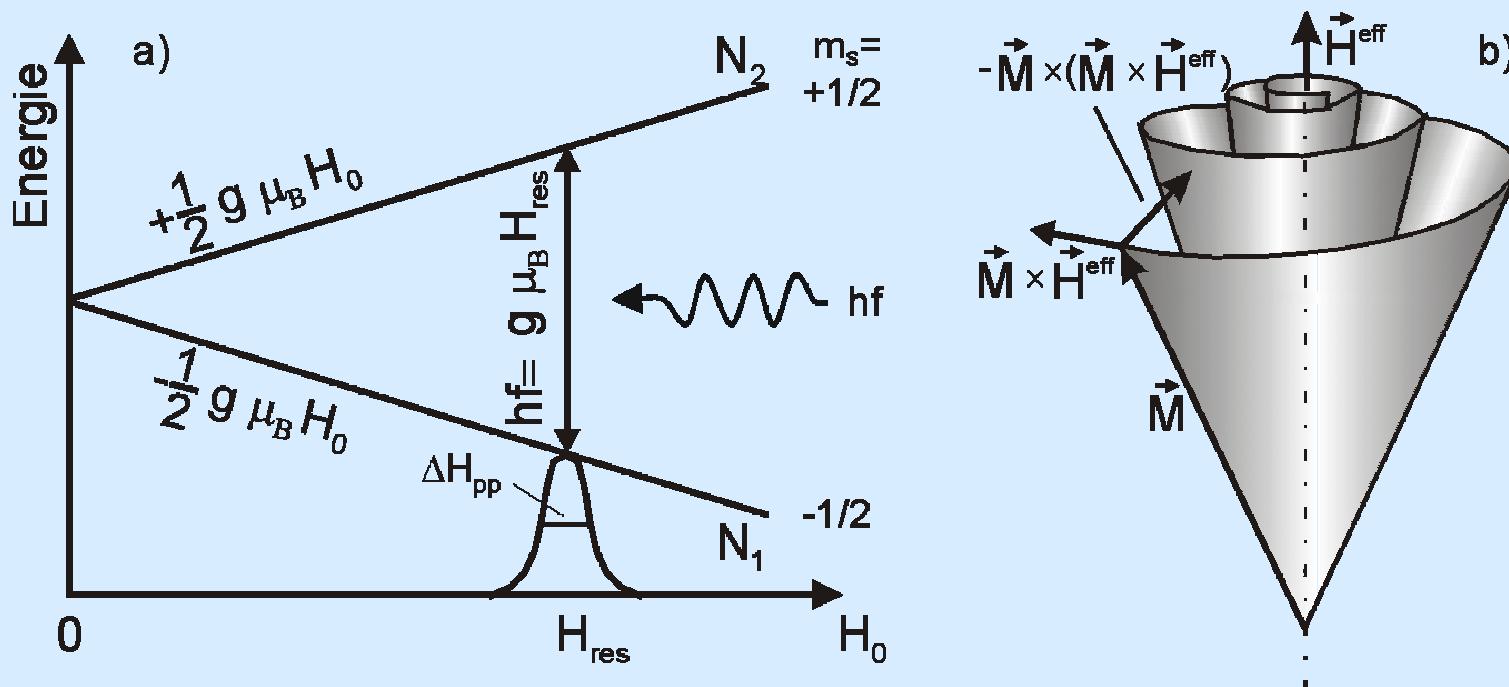


Fig. 5. Area of the ESR signal as a function of temperature for 80 Å (●), the new 1.6 ML (○), and the 0.8 ML (△). The insert shows the same data for a 18 μm thick Gd foil (bulk). Solid lines are guides to the eye. The 1.6 and 0.8 ML have a vertical gain factor of 20 and 44 with respect to 80 Å. The insert is not to scale.

Magnetic resonance (ESR, FMR)

Landau-Lifshitz-Gilbert-Equation

$$\frac{1}{\gamma} \frac{\partial M}{\partial t} = -(M \times H_{eff}) + \frac{G}{\gamma^2 M_S^2} \left(M \times \frac{\partial M}{\partial t} \right)$$



Determination of g-Tensor components

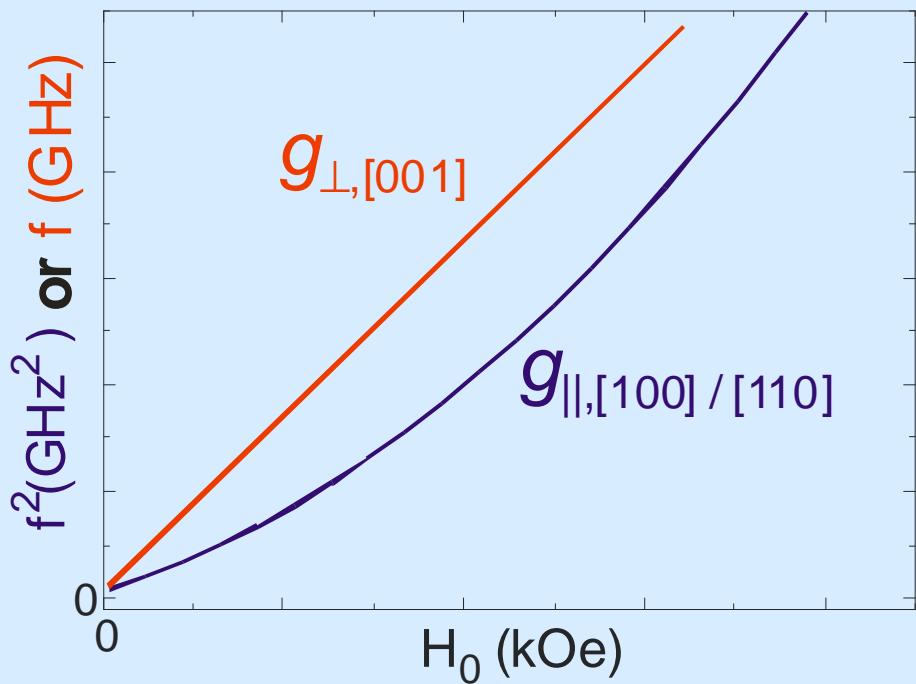
$$\frac{\omega^2}{\gamma_{\parallel, [100]}^2} = H_{0,[100]}^2 + H_{0,[100]} \left(4\pi M - 2 \frac{K_2}{M} + \frac{4K_{4\parallel}}{M} \right) + 2 \frac{K_{4\parallel}}{M} \left(4\pi M - 2 \frac{K_2}{M} + \frac{2K_{4\parallel}}{M} \right)$$

$$\frac{\omega}{\gamma_{\perp, [001]}} = H_{0,\perp} - 4\pi M + \frac{2(K_2 + K_{4\perp})}{M}$$

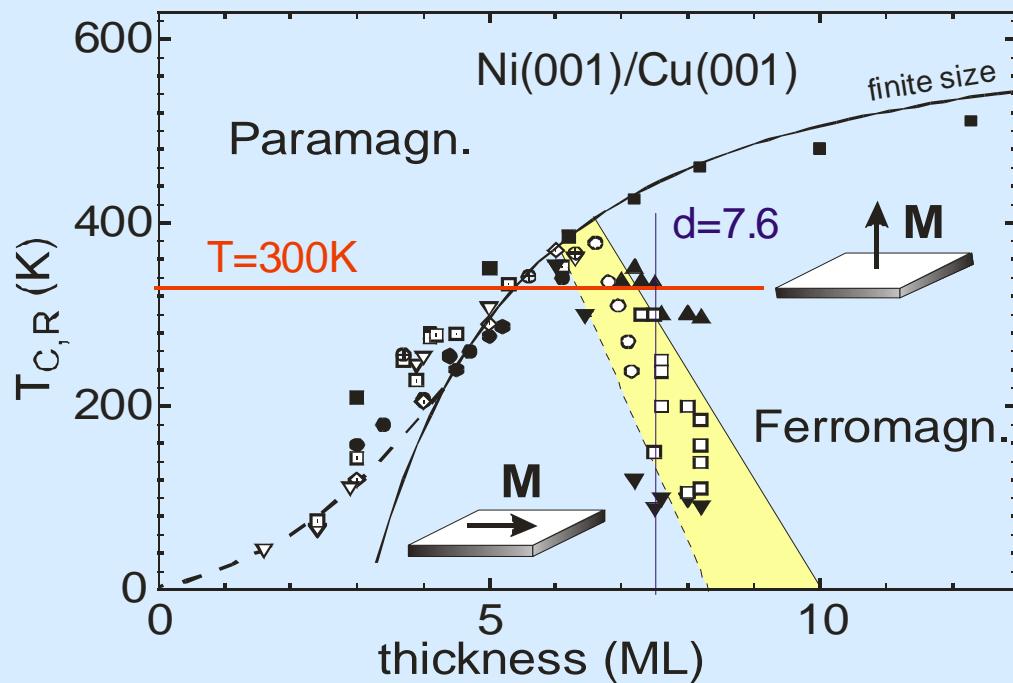
with $\gamma = \frac{g \cdot \mu_B}{\hbar}$

$$\frac{\mu_1}{\mu_s} = \frac{g-2}{2}$$

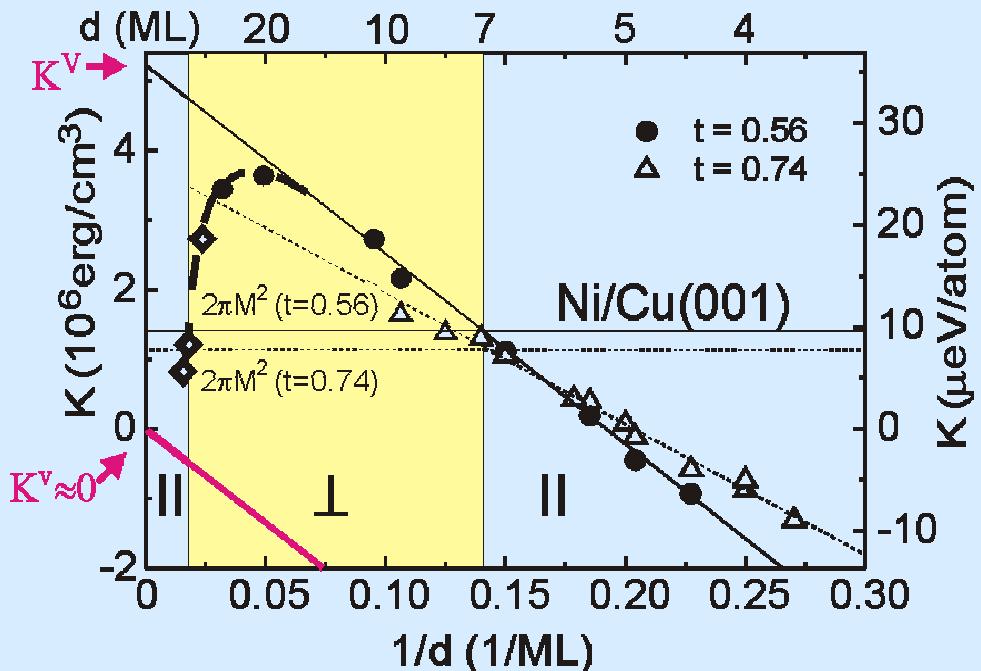
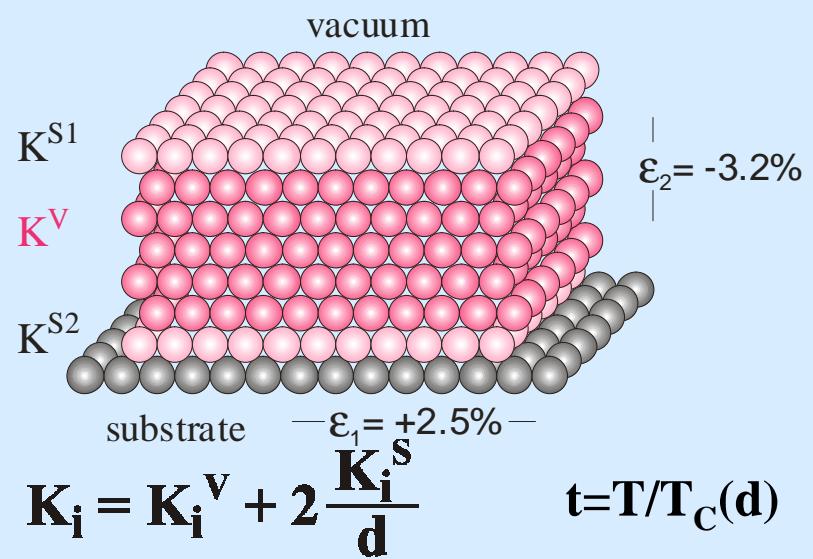
C. Kittel, *J.Phys. Radiat.* **12**, 291 (1951)

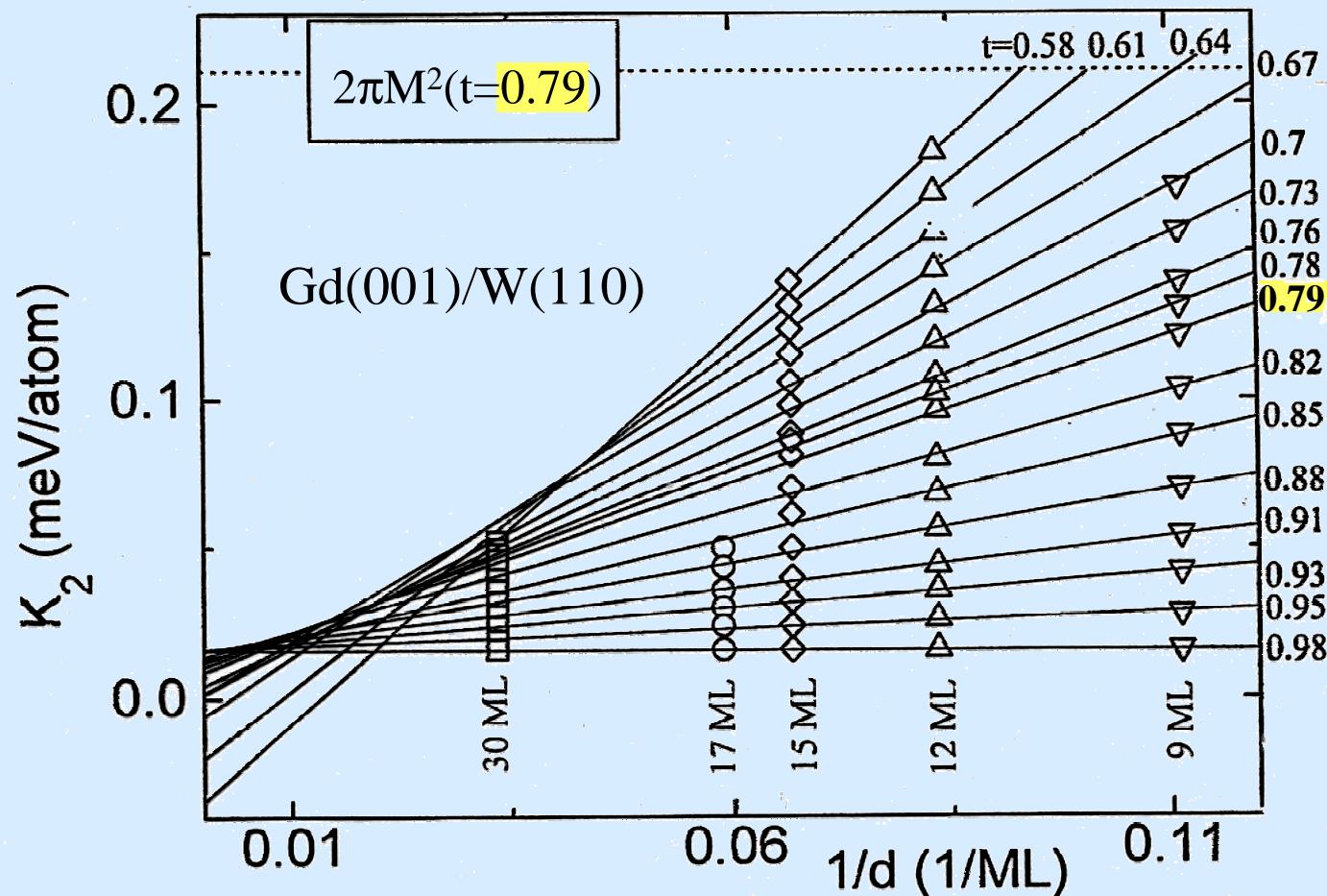


For thin films the Curie temperature can be manipulated



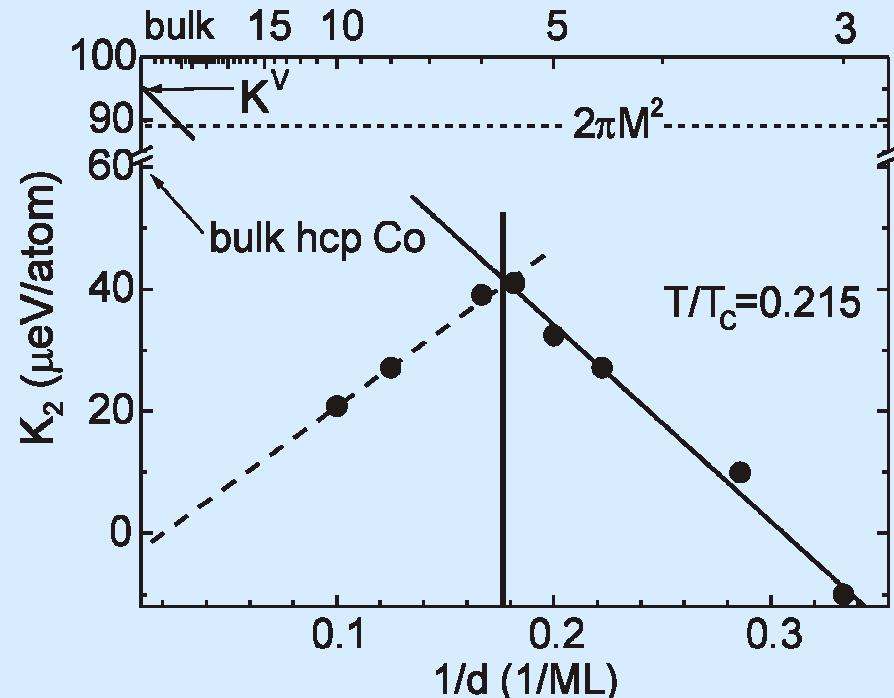
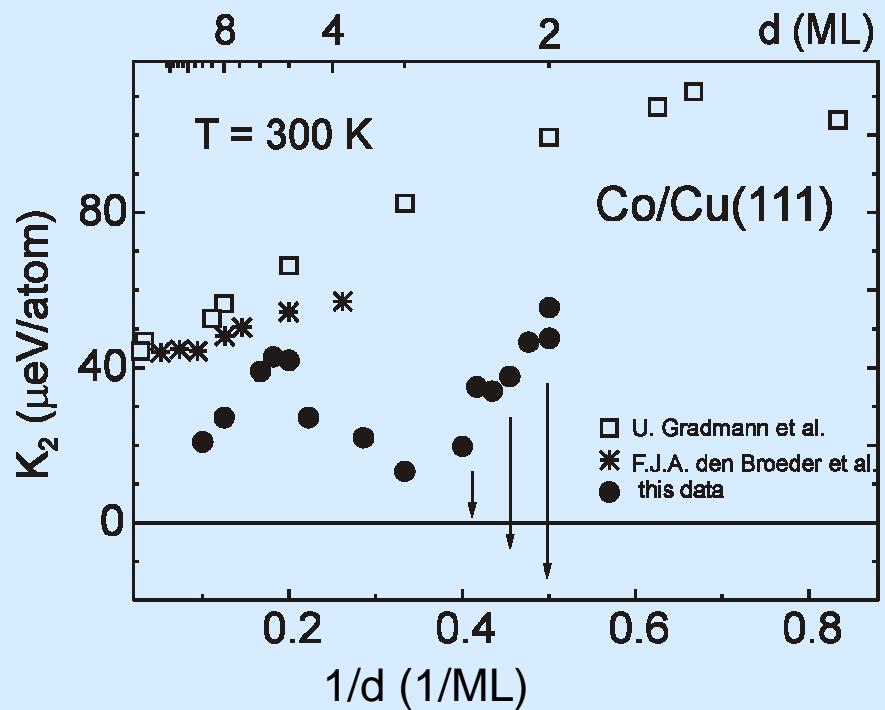
P. Poulopoulos and K. B.
J. Phys.: Condens. Matter **11**, 9495 (1999)





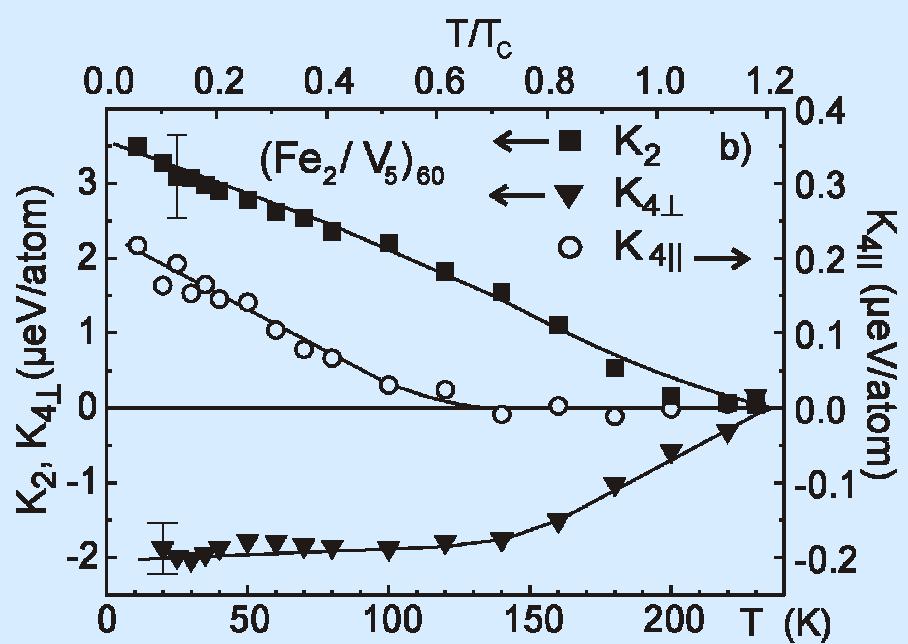
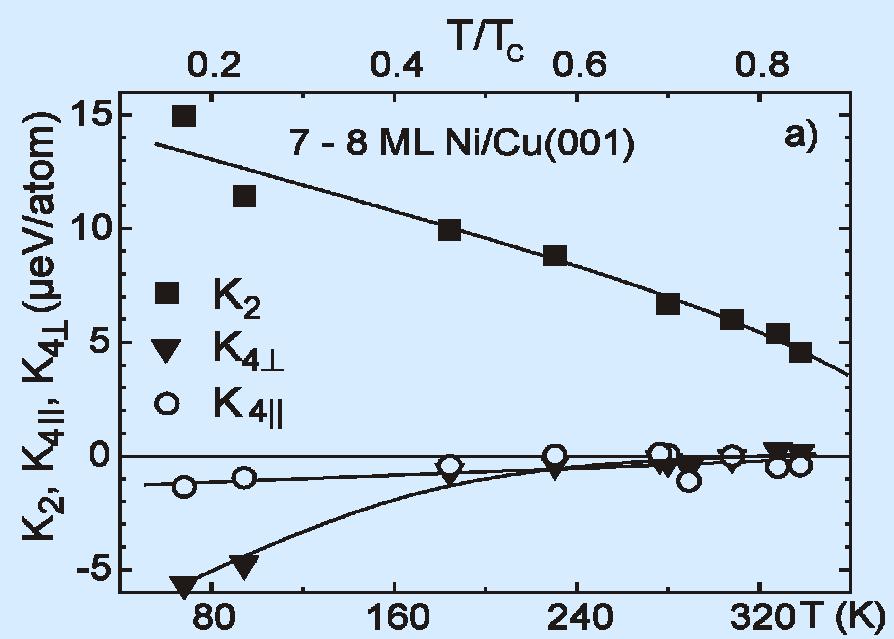
G. André et al., Surface Science **326**, 275 (1995)
 K. Baberschke and M. Farle, J. Appl. Phys. **81**, 5038 (1997)

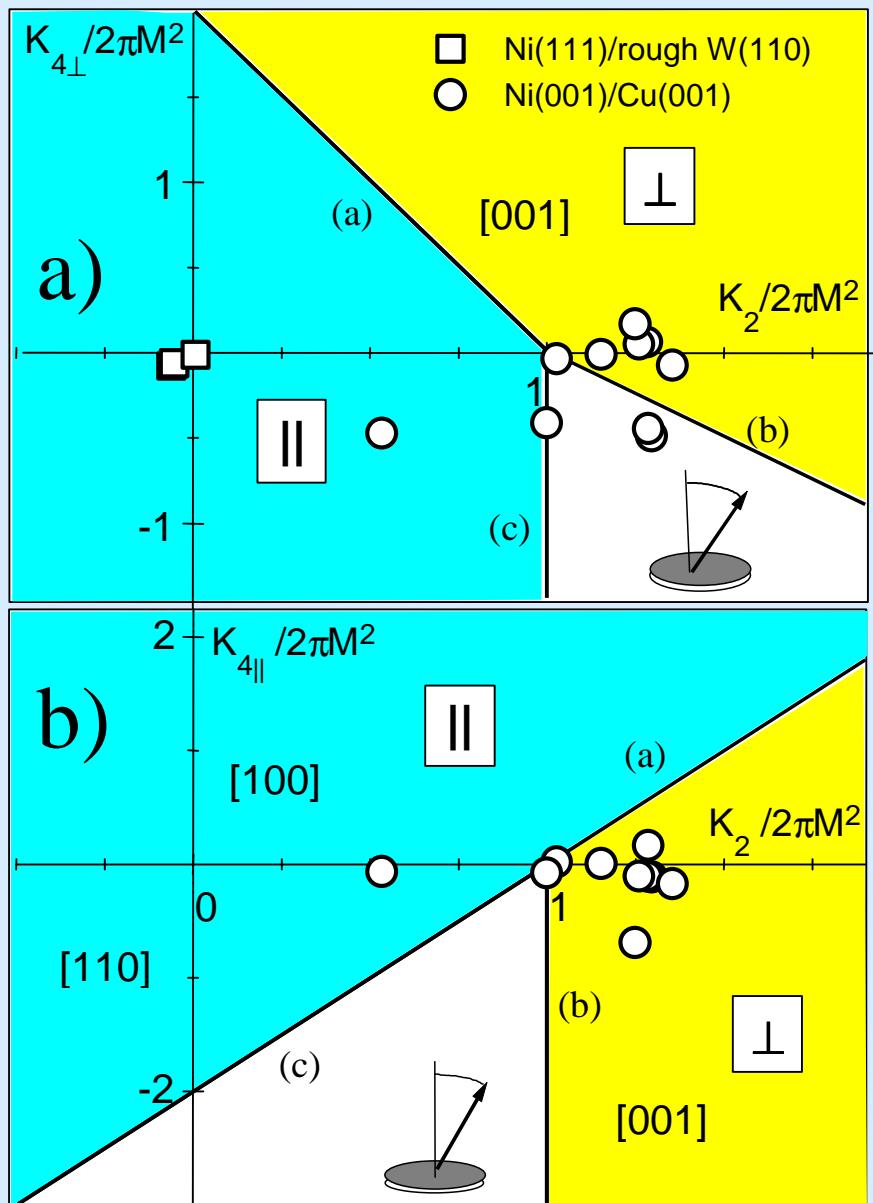
K is temperature dependent $\Rightarrow K(T/T_C)$



M. Farle et al., Surf. Sci. **439**, 146 (1999)

If d changes also $T_C(d)$ shifts
taking this into consideration we found for all systems a $1/d$ dependence

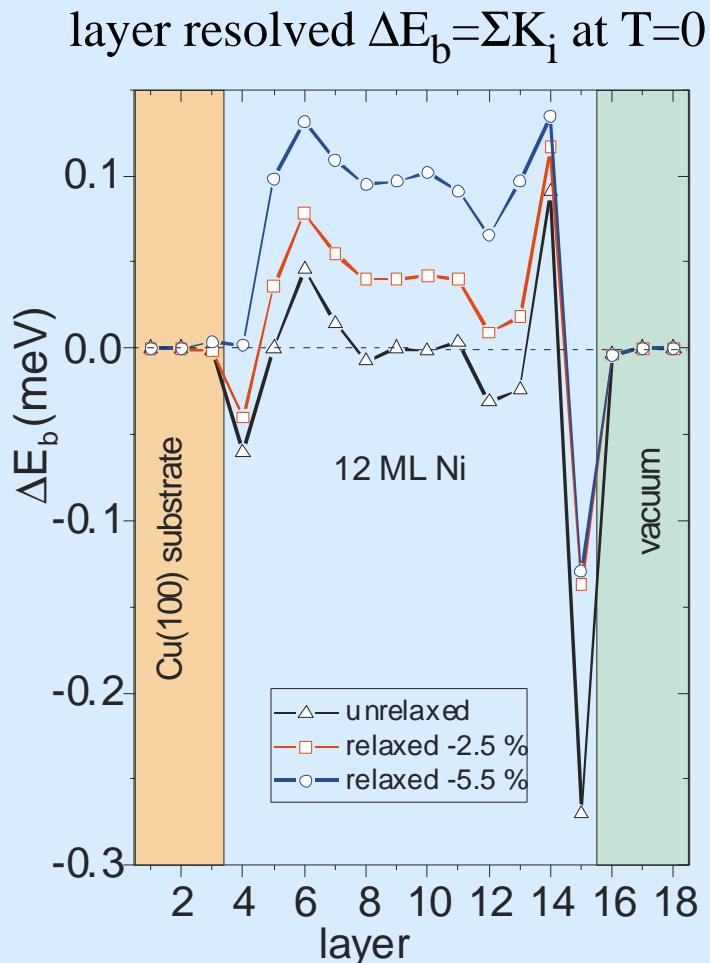




A. Berghaus, M. Farle, Yi Li, K. Baberschke
Absolute determ. of the mag. anisotropy of ultrathin Gd and Ni/W(110).
 Second Intern. Workshop on the Magnetic Properties of Low-Dimensional Systems.
 San Luis Potosi, Mexico, Proc. in Physics **50**, 61 (1989)

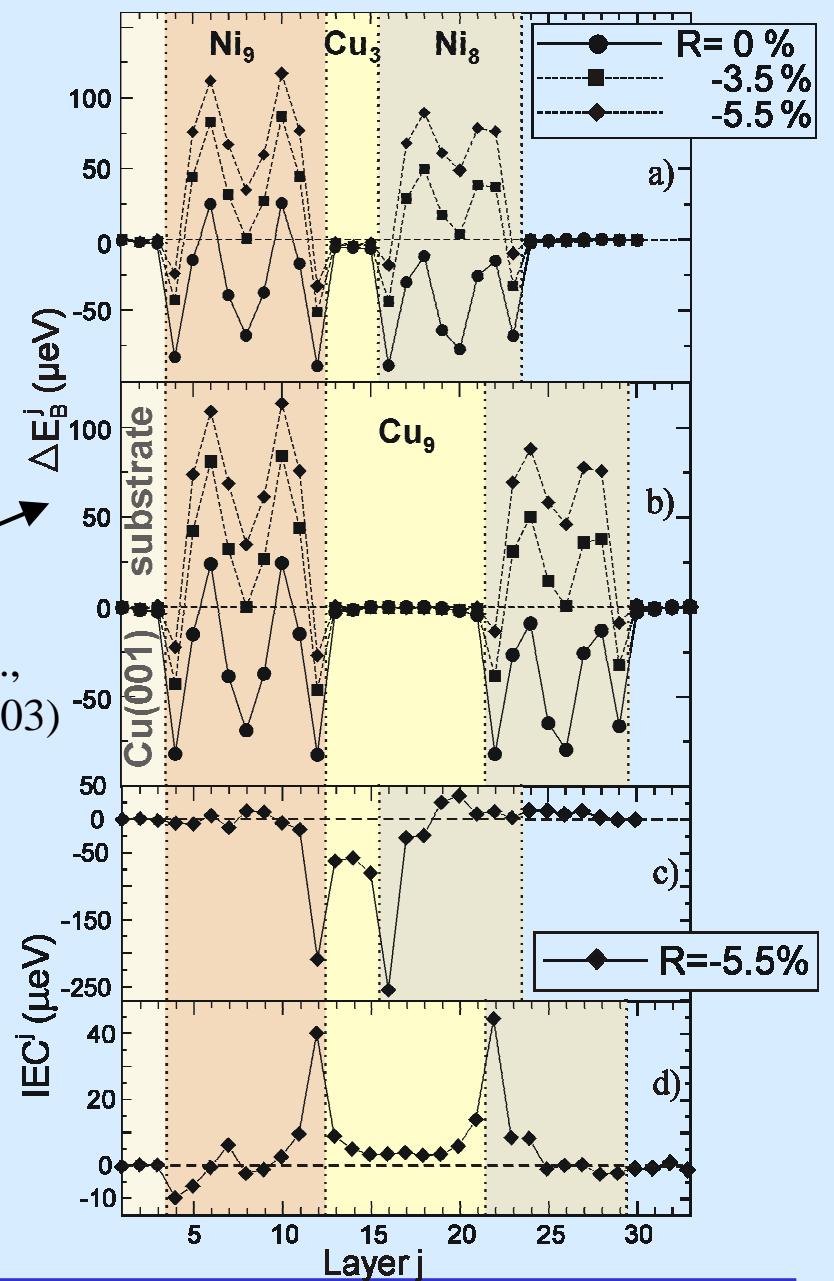
M. Farle et al., PRB **55**, 3708 (1997)

SP-KKR calculation for right fcc and relaxed fct structures



C. Uiberacker et al.,
PRL **82**, 1289 (1999)

R. Hammerling et al.,
PRB **68**, 092406 (2003)



The surface and interface MAE are certainly large (L. Néel, 1954) but count only for one layer each. The inner part (volume) of a nano-structure will overcome this, because they count for n-2 layers.

Summary of Chap. 2

- Historical names like „crystalline“ or „magnetoelastic“ anisotropy energy should not be used in nanostructures. It is all SO interaction, or better, a fully relativistic treatment (full potential, etc.).
- Atoms at edges, steps have different K-values.
- Small changes in the local structure \sim few/100 Å may change the MAE dramatically.
- In most cases K depends on the reduced temperature $t=T/T_C(d)$.
- The experiments measure in most cases the sum of dipole and intrinsic (bandstructure) K.
- The dipole term may not be $2\pi M^2$ (see PhD thesis, Farle 1989).

3. Orbital magnetic moment μ_L

Which technique measures what?

μ_L / μ_S in UHV-FMR

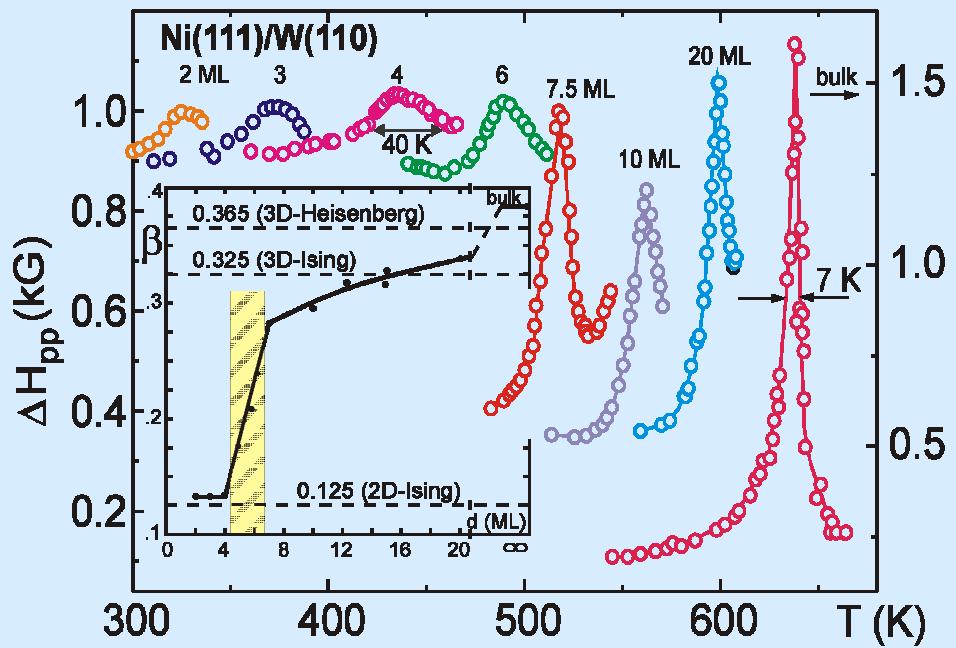
μ_L, μ_S in UHV-XMCD

$\mu_L + \mu_S$ in UHV-SQUID

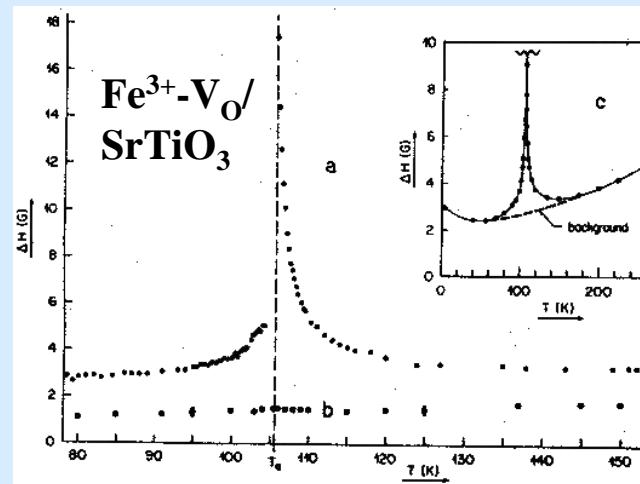
per definition:

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

FMR/ESR line width at the phase transition



Yi Li, K. B., PRL **68**, 1208 (1992)



Th.v. Waldkirch, K.A. Müller, W. Berlinger, PRB (1973)

Thermodynamics of thin ferromagnetic films in ...

R.P. Erickson & D.L. Mills PRB **44**, 11825 (91)

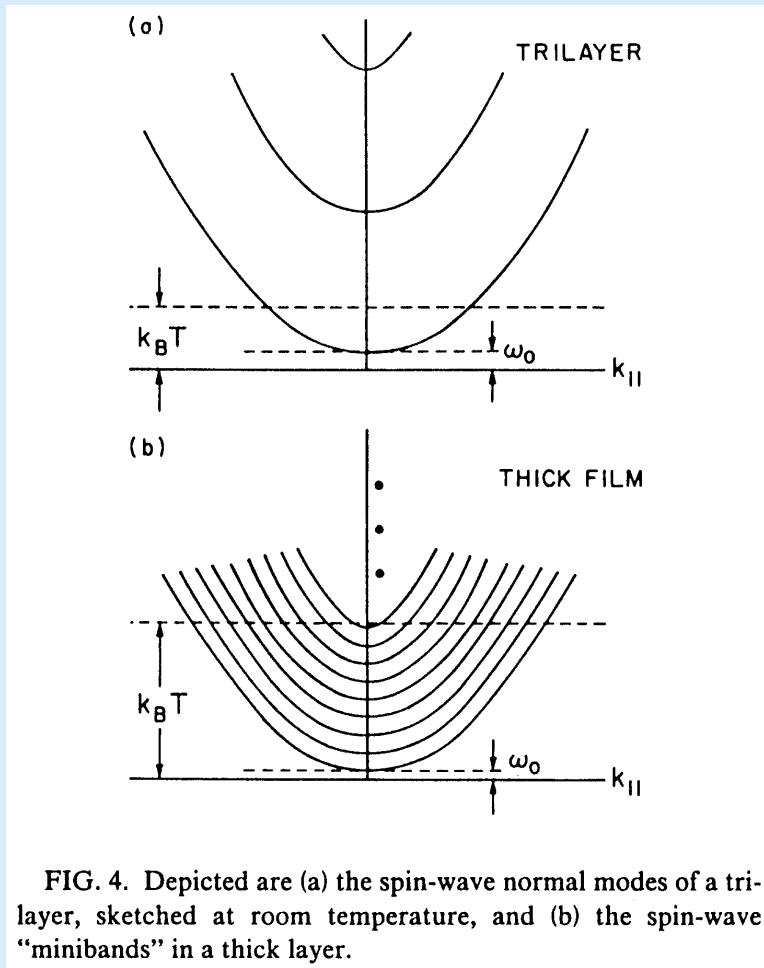


FIG. 4. Depicted are (a) the spin-wave normal modes of a trilayer, sketched at room temperature, and (b) the spin-wave "minibands" in a thick layer.

$$\text{Spin wave branches} = \omega_0 + \frac{1}{2} D \left\{ k_{||}^2 + \left[\frac{\pi}{Nd} \right]^2 \right\} \quad d: \text{spacing} \quad N: \text{layers}$$

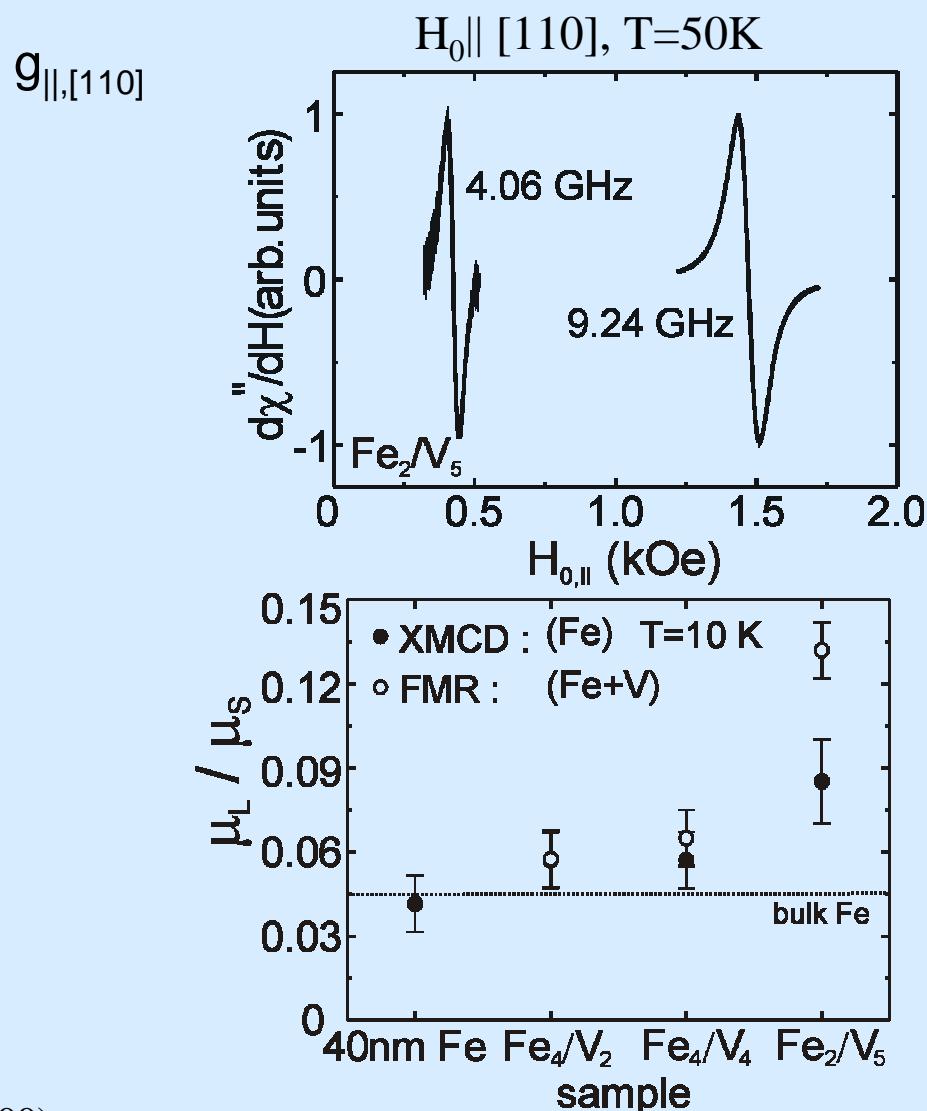
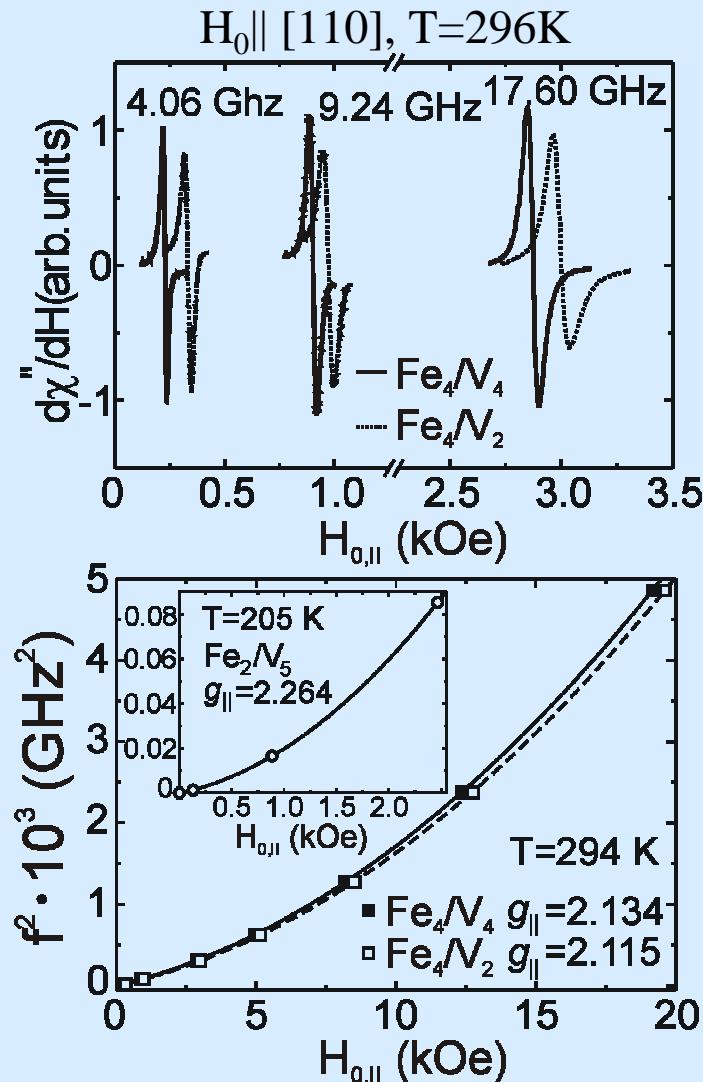
“A criterion for a crossover from quasi 2D to 3D is...”

$$N_C = \sqrt{\frac{\hbar D}{kT}} \cdot \frac{\pi}{d} \quad D: \text{stiffness const.}$$

$$\text{Ni: } \hbar D \approx 4 \cdot 10^{-1} \text{ eV}\text{\AA}^2; \quad d = 2.03 \text{\AA}$$

$$T = 300 \sim 500 \text{ K} \Rightarrow N_C \approx 6 - 5 \text{ layers}$$

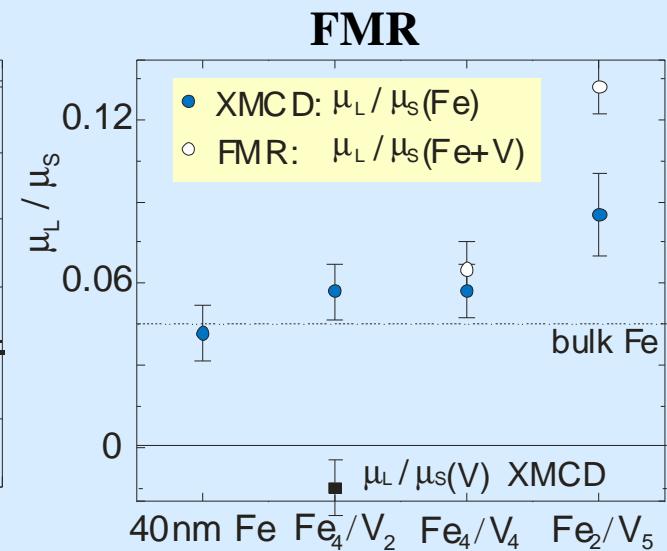
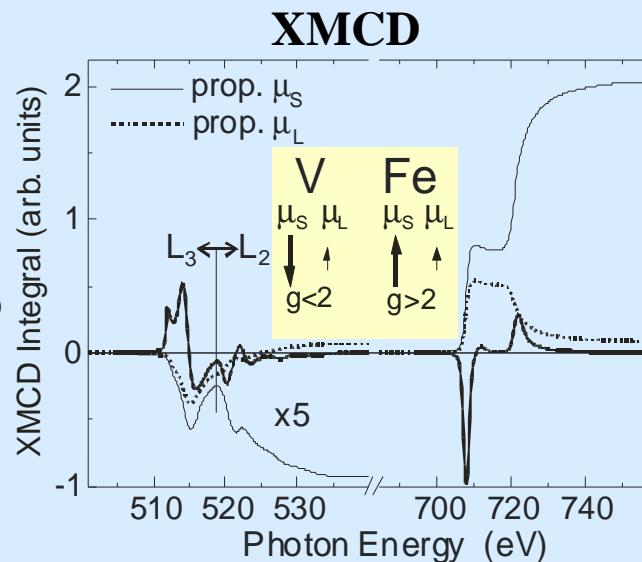
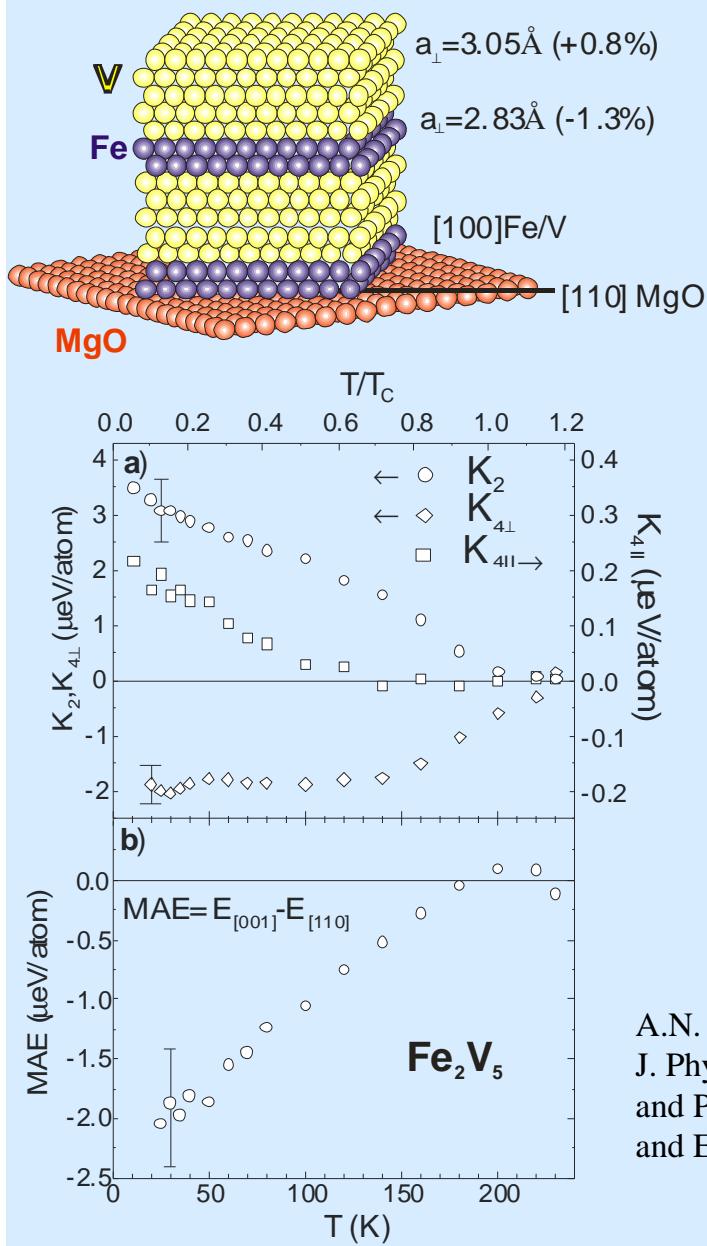
FMR in Fe_n/V_m superlattices



A.N. Anisimov et al., Phys. Rev. Lett. **82**, 2390 (1999)

A. Scherz et al., Phys. Rev. B **64**, 180407(R) (2001)

Ferromagnetic resonance on Fe_n/V_m(001) superlattices



$$\frac{\mu_L}{\mu_s} = \frac{g-2}{2} \quad (\text{Kittel'49})$$

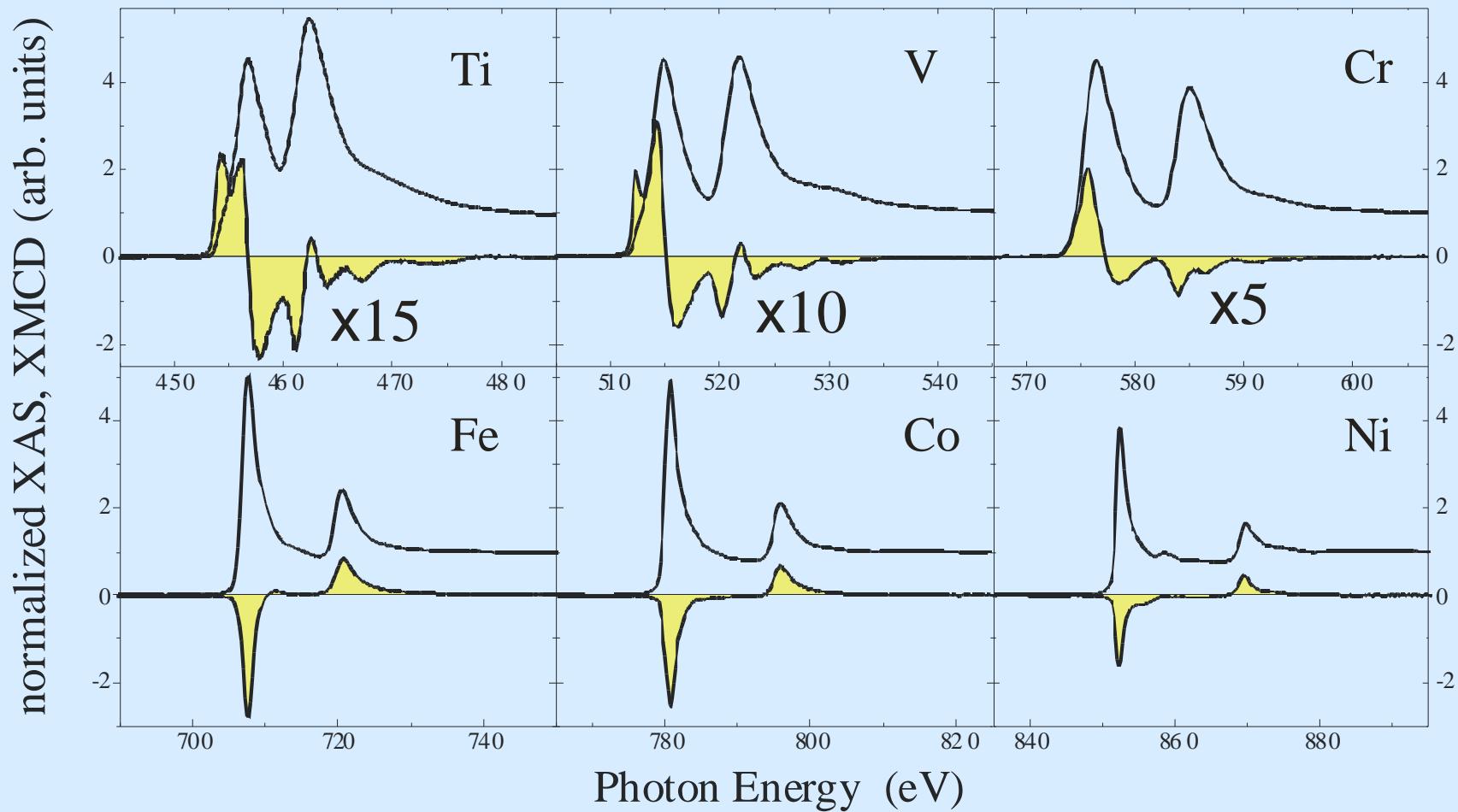
In solids g and μ_L are tensors

bcc (001) Fe ₂ /V ₅ superlattice					
g_{\parallel}	g_{\perp}	μ_L/μ_s	$\mu_L(\mu_B)$	$\mu_s(\mu_B)$	MAE $\mu\text{eV/atom}$
2.264	2.268	0.133	0.215	1.62	-2.0
bcc Fe-bulk					
2.09	2.09	0.045	0.10	2.13	-1.4

A.N. Anisimov et al.
J. Phys. C **9**, 10581 (1997)
and PRL **82**, 2390 (1999)
and Europhys. Lett. **49**, 658 (2000)

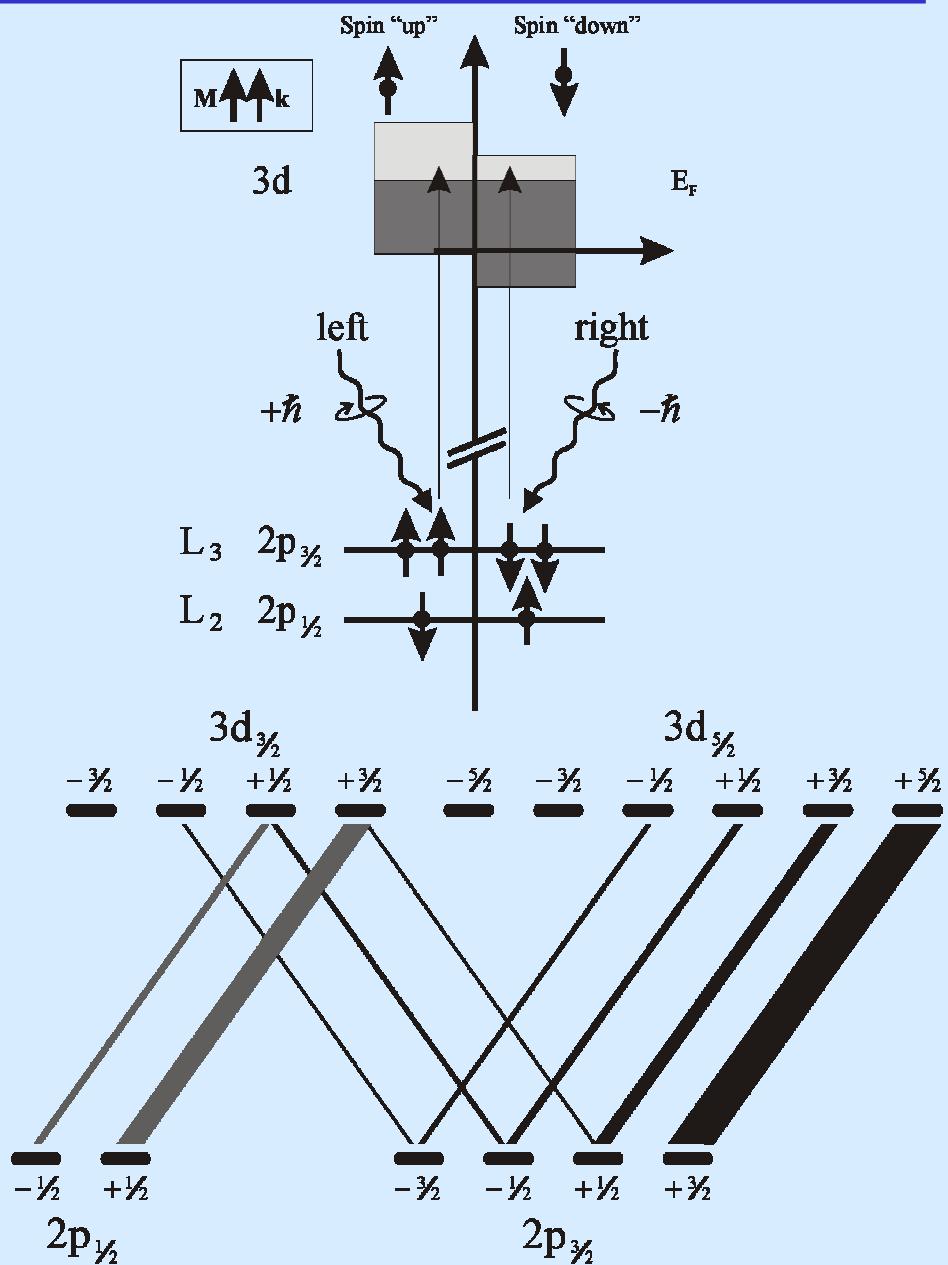
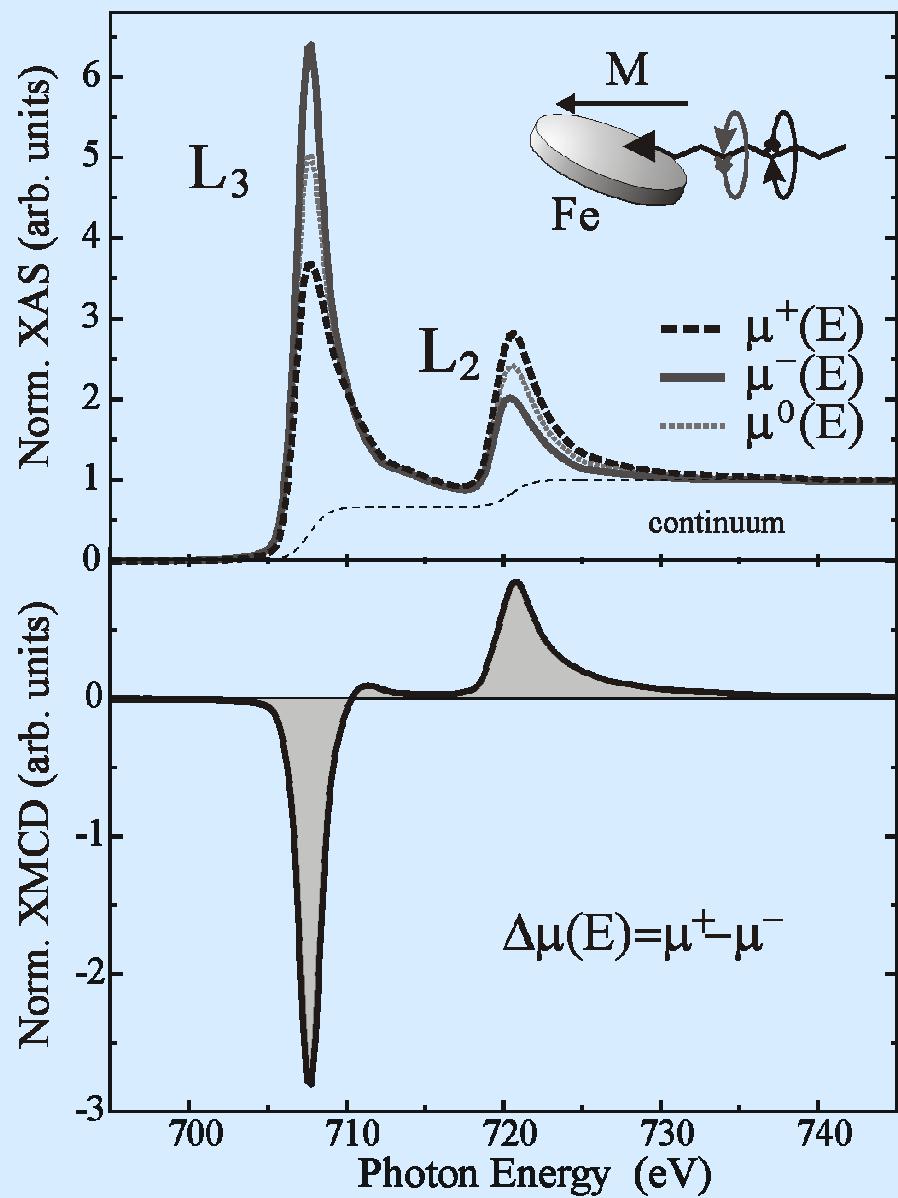
$L_{3,2}$ XAS and XMCD of 3d TM's

Sc Ti V Cr Mn Fe Co Ni Cu Zn



A. Scherz et al., XAFS XII June 2003 Sweden, Physica Scripta;
A. Scherz et al., BESSY Highlights p. 8 (2002)

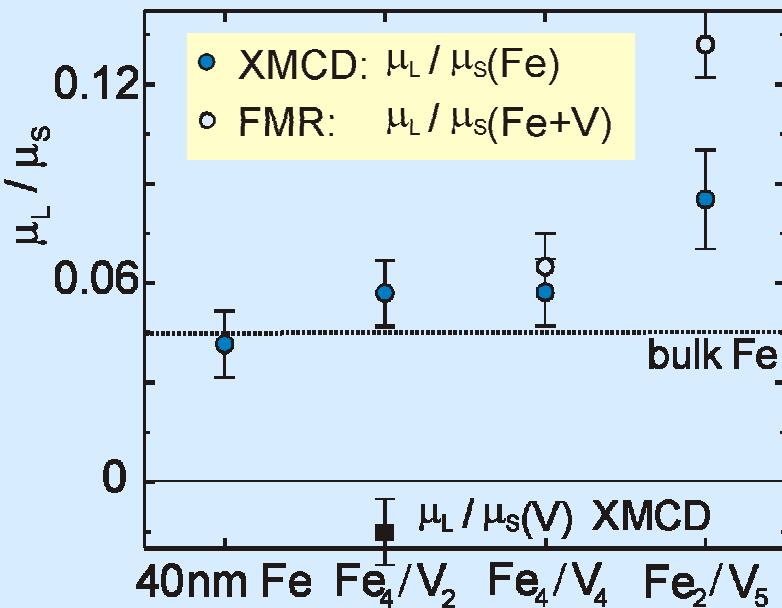
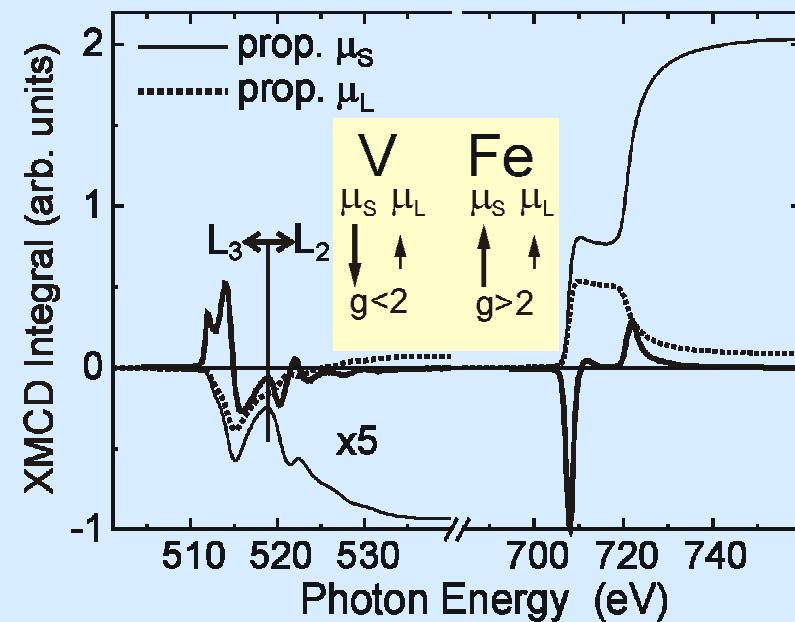
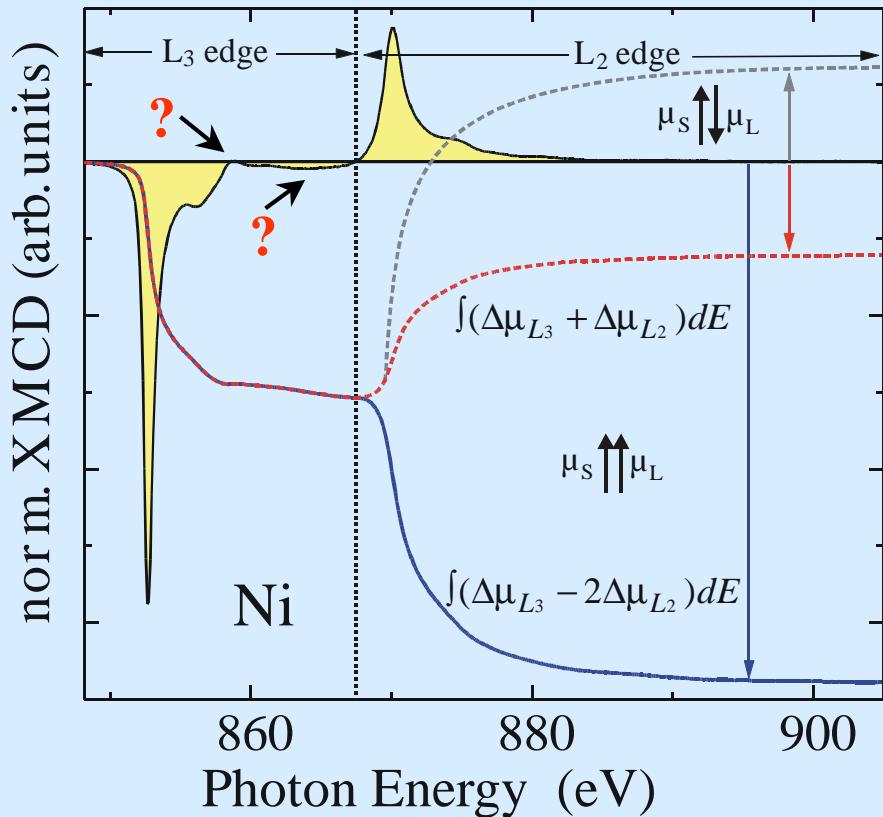
X-ray Magnetic Circular Dichroism



Orbital and spin magnetic moments deduced from XMCD

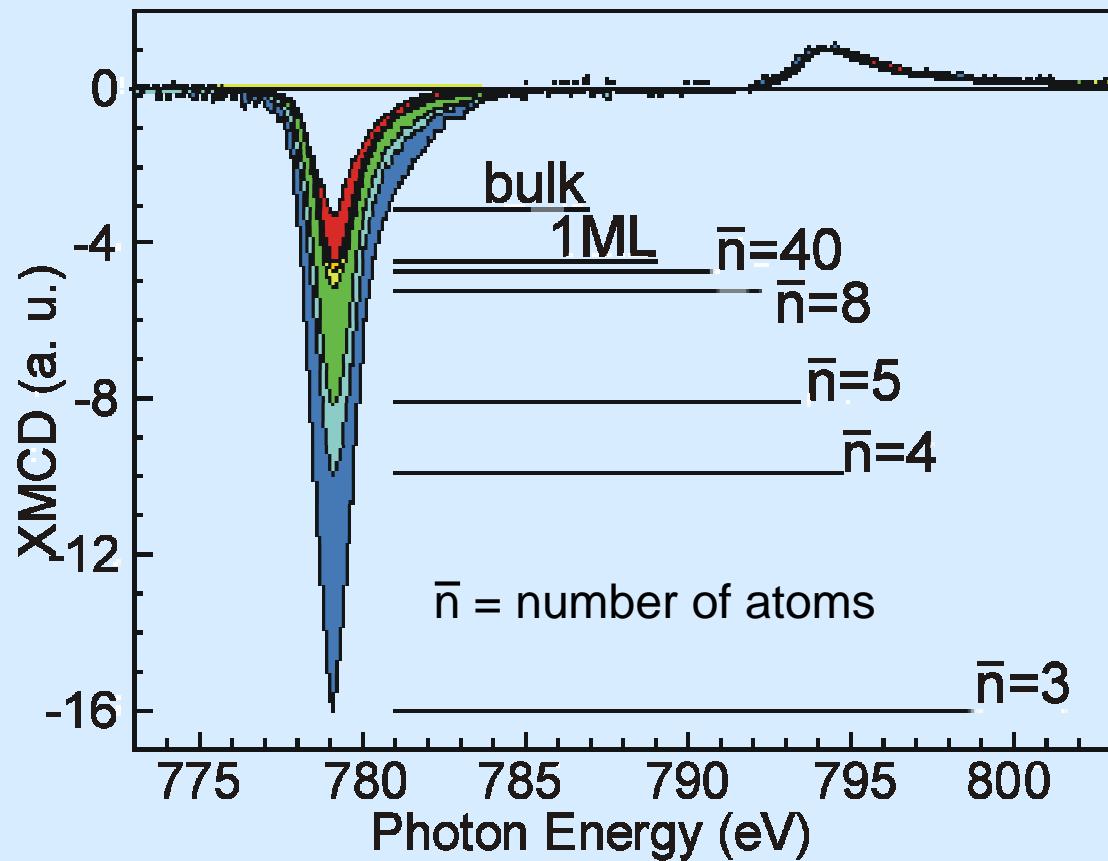
$$\int (\Delta \mu_{L_3} - 2 \cdot \Delta \mu_{L_2}) dE = \frac{N}{3N_h^d} (2\langle S_z \rangle^d + 7\langle T_z \rangle^d)$$

$$\int (\Delta \mu_{L_3} + \Delta \mu_{L_2}) dE = \frac{N}{2N_h^d} \langle L_z \rangle^d$$



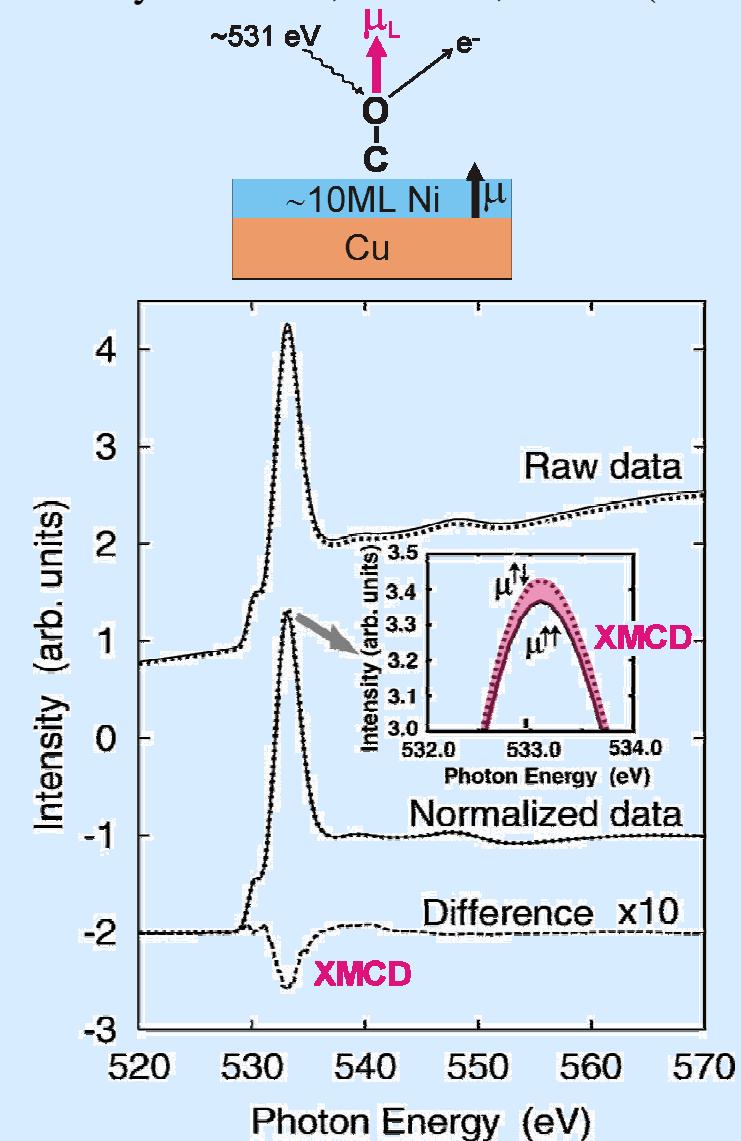
Giant Magn. Anisotropy of Single Co Atoms and Nanoparticles

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

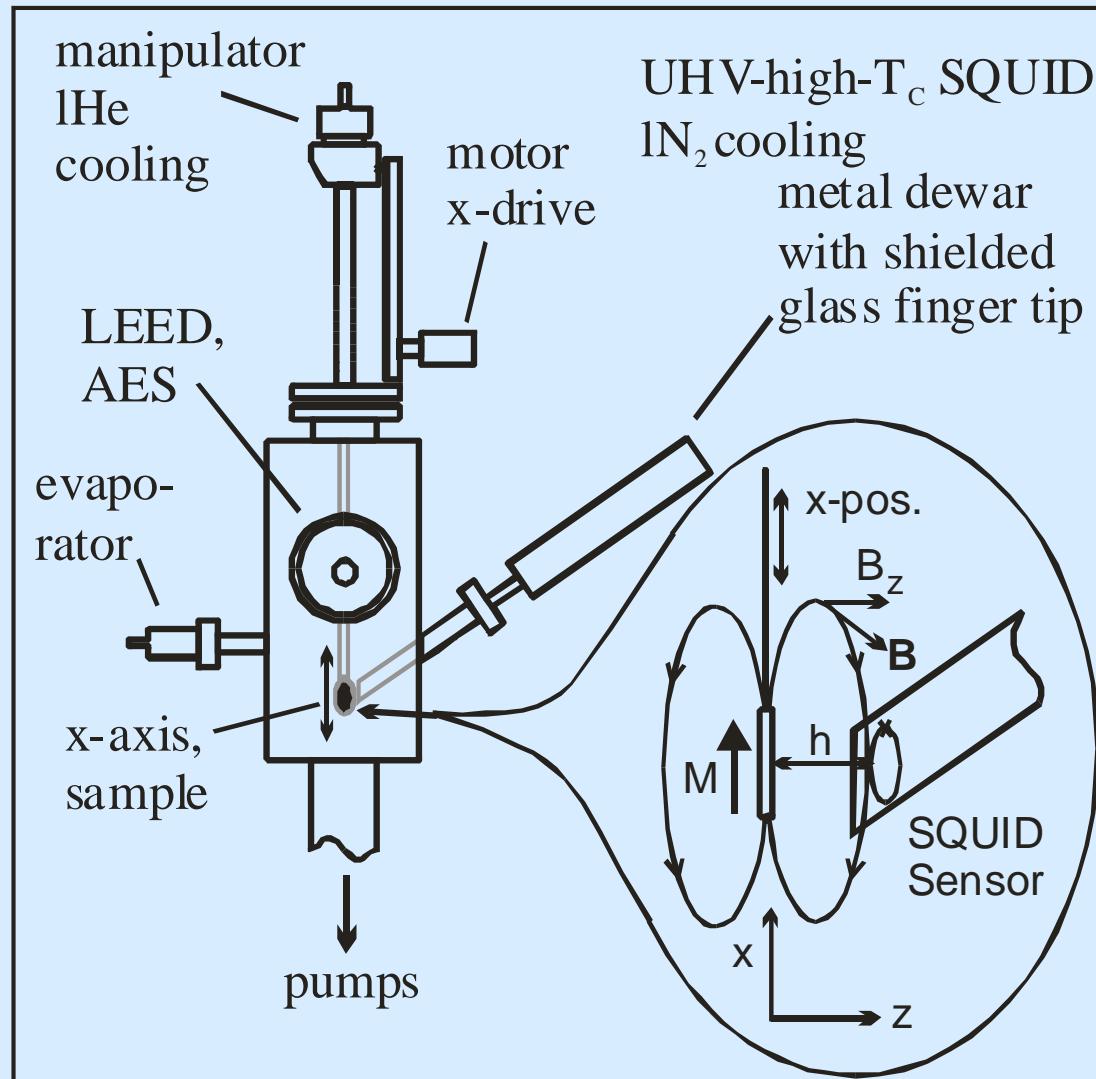


Induced magnetism in molecules

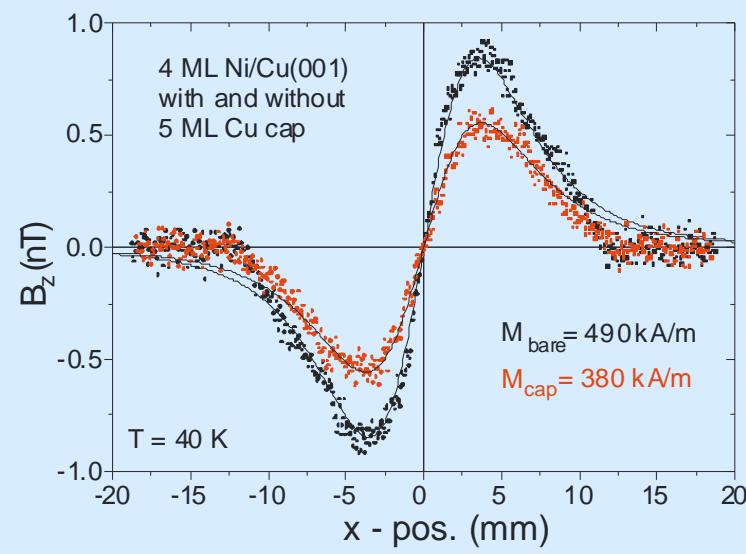
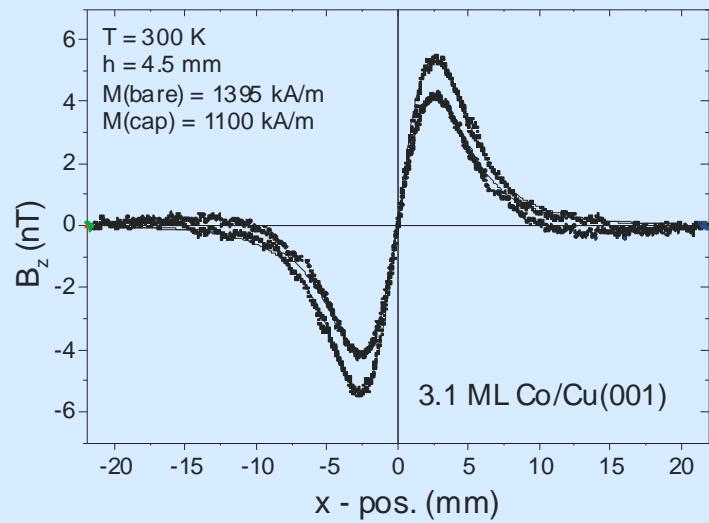
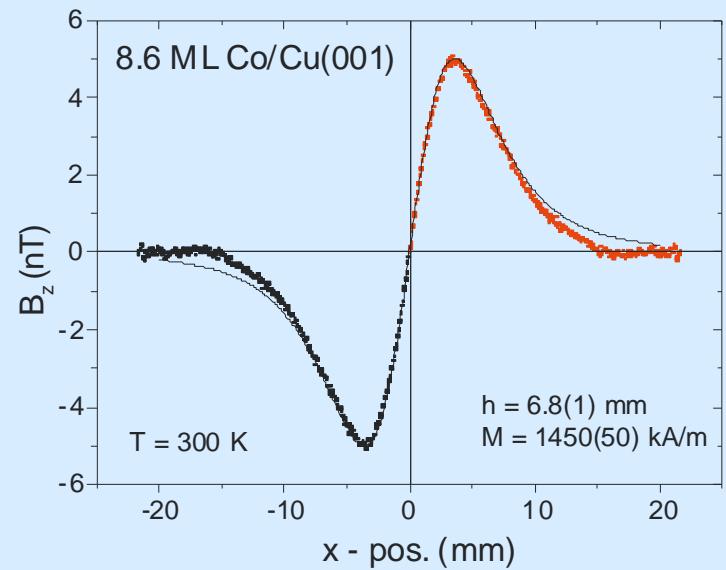
T. Yokoyama et al., PRB **62**, 14191 (2000)



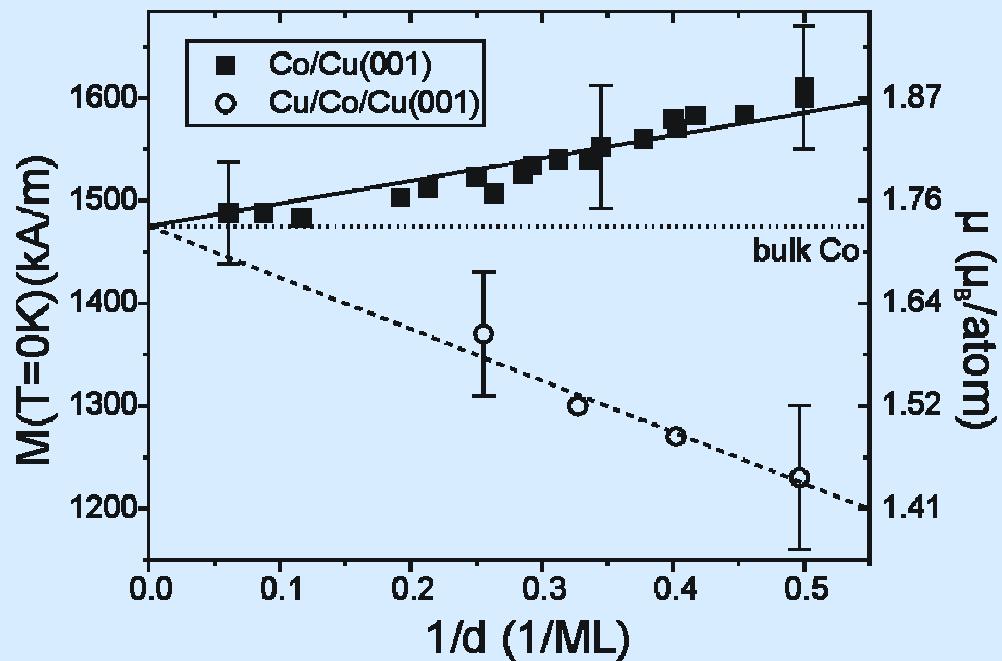
Design of the UHV-SQUID magnetometer



Sensitivity



UHV-SQUID measurements



Theory:

Hjortstam et al., PRB **53**, 9204 (1996)
Pentcheva et al., PRB **61**, 2211 (2000)

$$m_{\text{tot}} = m_{\text{vol}} + \frac{m_{\text{surf}} + m_{\text{inter}} - 2}{d} \quad (\text{linear with } 1/d)$$

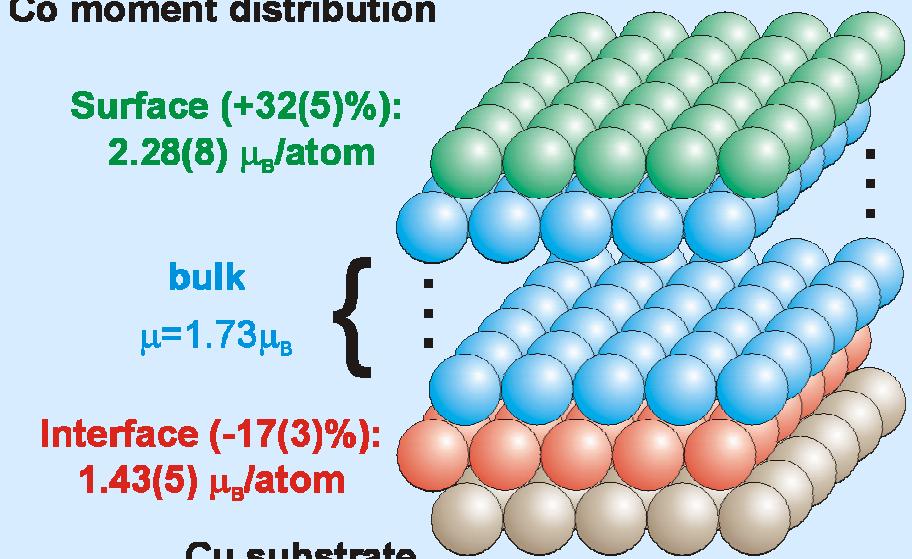
Co moment distribution

Surface (+32(5)%):
 $2.28(8) \mu_B/\text{atom}$

bulk
 $\mu = 1.73 \mu_B$

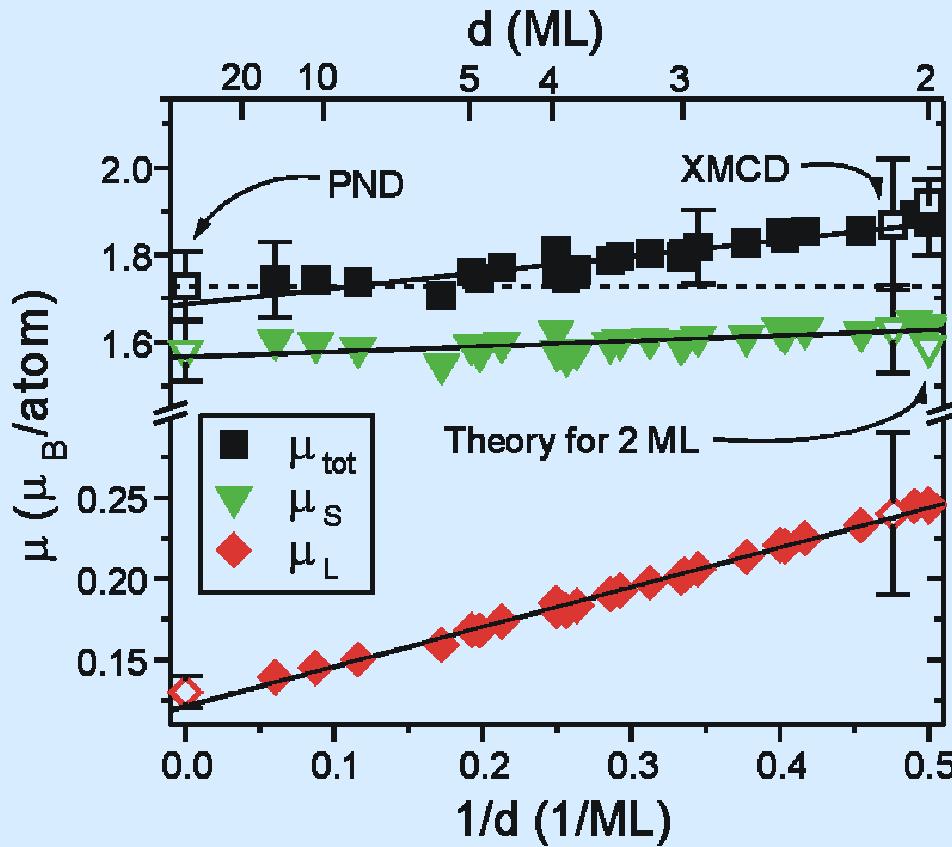
Interface (-17(3)%):
 $1.43(5) \mu_B/\text{atom}$

Cu substrate



A. Ney et al.
Europhys. Lett. **54**, 820 (2001)

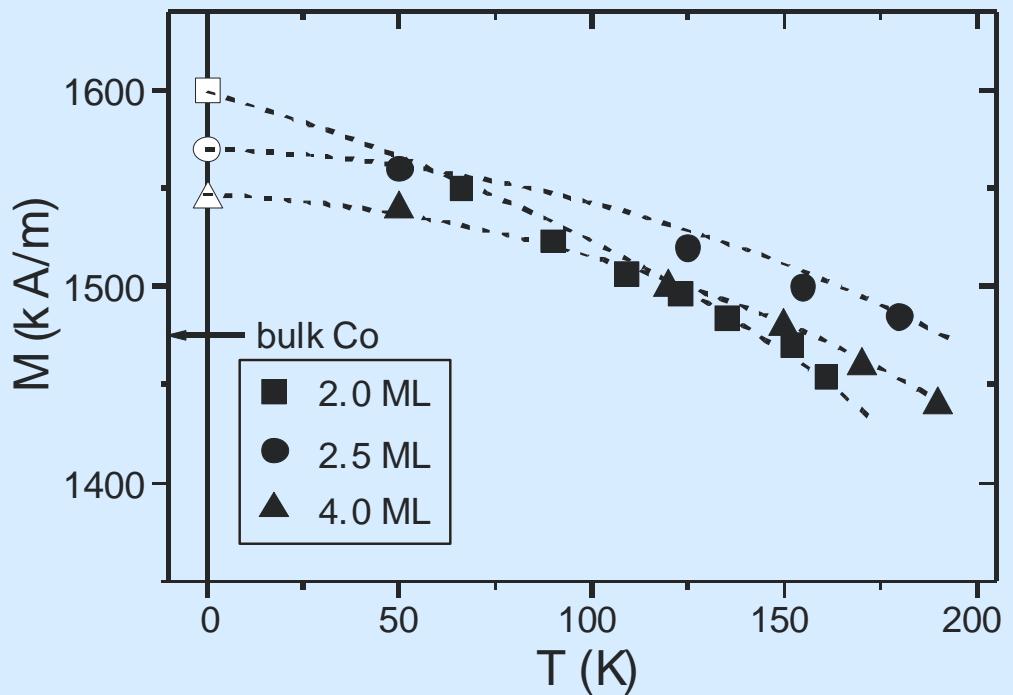
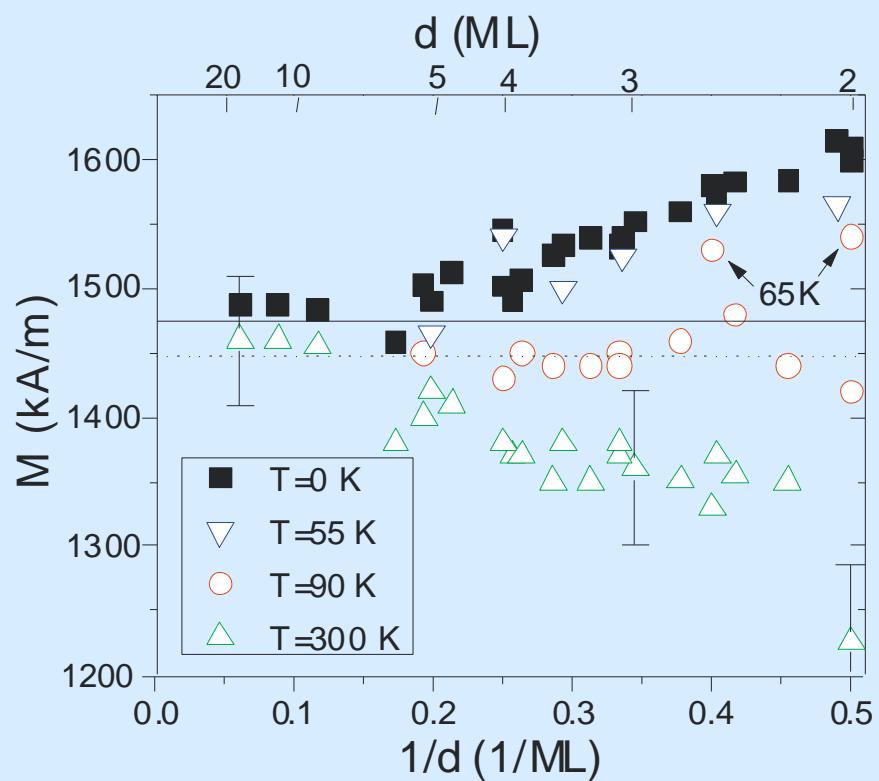
SQUID data deconvolution into spin (μ_s) and orbital (μ_L) moments



The total magnetic moment (squares) of Co/Cu(001) vs the inverse film thickness and its separation into spin (down triangle) and orbital (diamonds) contribution. The bulk value is indicated (dashed line). For comparison experimental results using PND and XMCD are given by the open symbols.

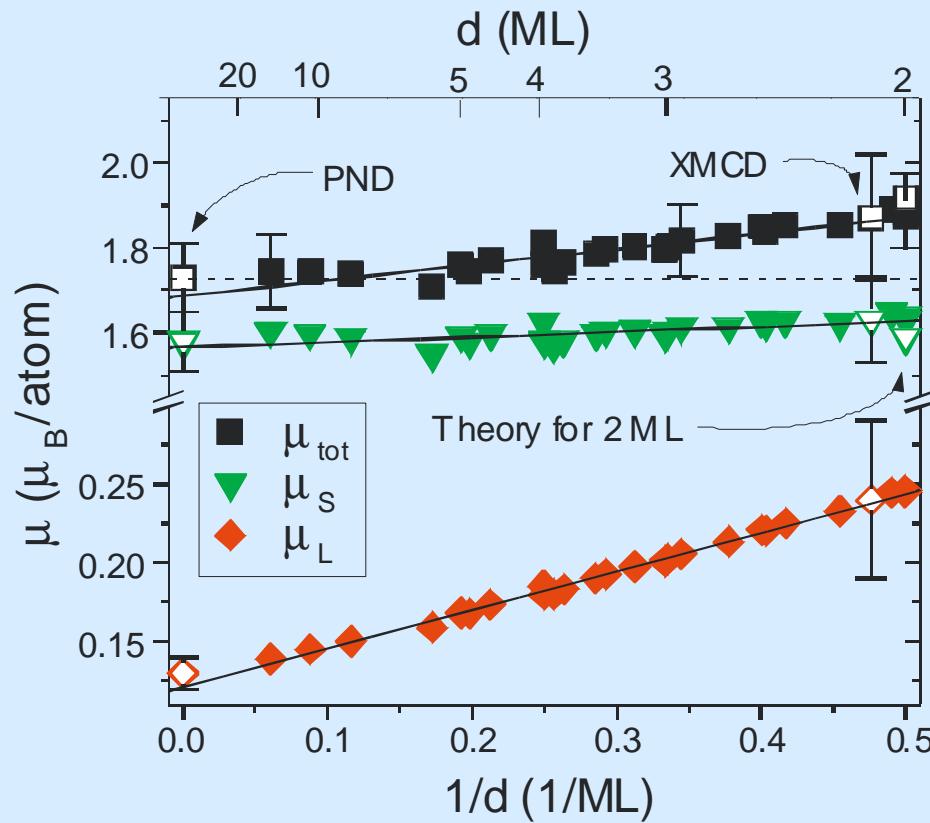
<http://www.dissertation.de/PDF/an452.pdf>

The effect of temperature



The magnetization of Co/Cu(001) vs the inverse film thickness at different temperatures.
The bulk values for 4K (full line) and 300K (dashed line) are indicated.

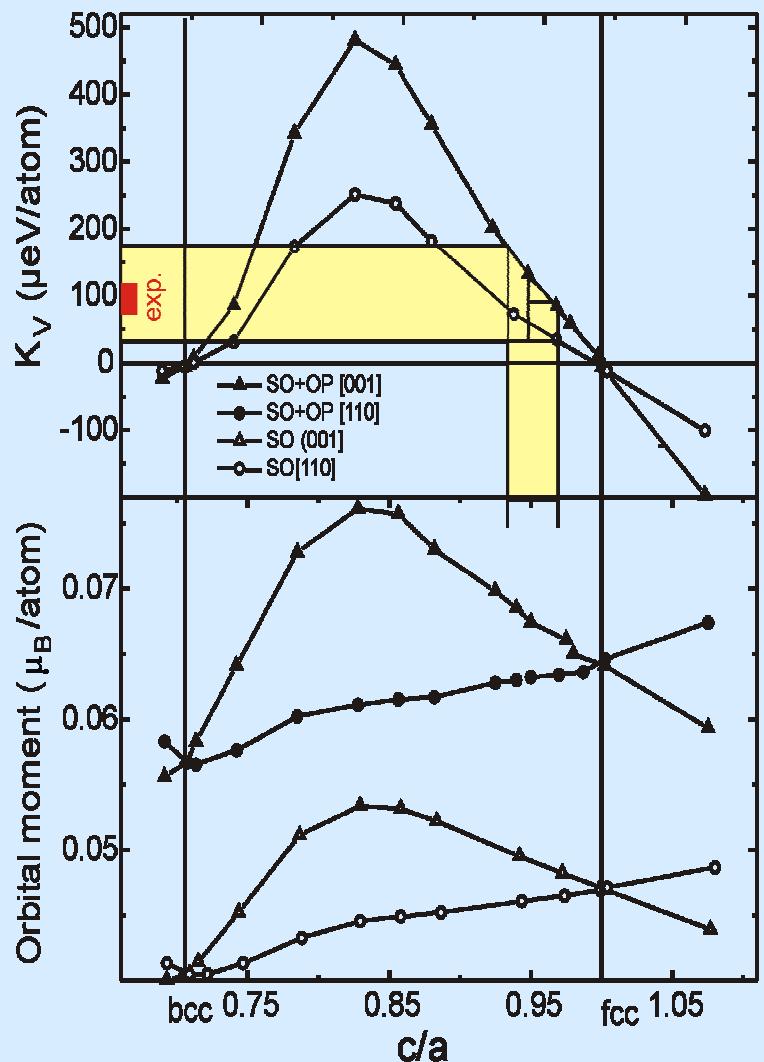
Deconvolution into spin (μ_s) and orbital (μ_L) moments



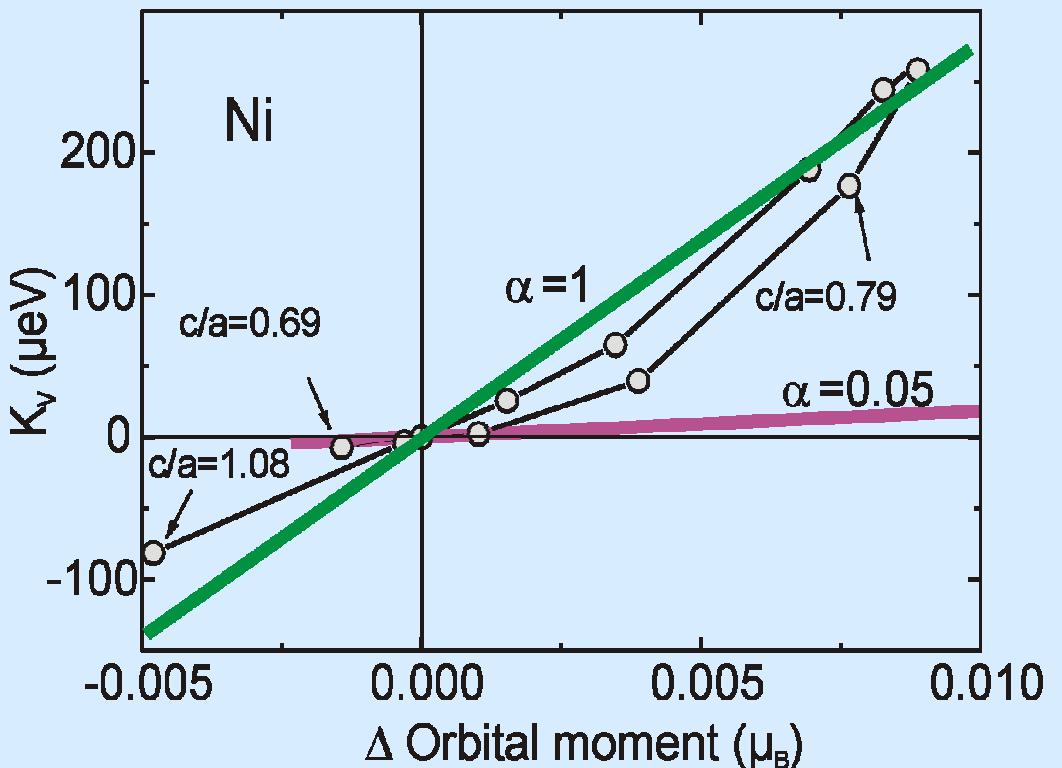
The total magnetic moment (squares) of Co/Cu(001) vs the inverse film thickness and its separation into spin (down triangle) and orbital (diamonds) contribution. The bulk value is indicated (dashed line). For comparison experimental results using PND and XMCD are given by the open symbols.

<http://www.dissertation.de/PDF/an452.pdf>

Combination of MAE and $\Delta\mu_L$



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



$$\text{The equ. } \text{MAE} = -\alpha \frac{\lambda}{4\mu_B} \Delta\mu_L \quad (\text{Bruno } `89)$$

is not strictly a linear relation

Summary of Chap. 3

- Different experiments measure different moments (μ_L and/or μ_S).
Not every number is a “spin moment“.
- FMR was little used, but determines unambiguously the ratio μ_L/μ_S (-if possible!).
- XMCD did use the sum rules very intensely. However, if one looks for small contributions of μ_L there are several pitfalls.
- To look at $\Delta\mu_L$ is even worse. At present there is still a mystery: if XMCD measures $\Delta\mu_L$ and calculates from this (via „Bruno formula“) the MAE, it becomes in most cases **to large by a factor 30**.
- SQUID measures in absolute units. But how do we normalize to moments / ion ?
Apparent enhanced moments appear if a fraction of the ions in a nanocluster do not contribute to the magnetization (oxidized, etc.)

Zusatz:

- 1) „magnetisches Moment“/Atom, gemessen in μ_B , ist temperaturunabhängig.
 - 2) Magnetisierung $M = \sum \mu_i$; maximaler Wert = Sättigungsmagnetisierung
 M ist $f(T)$ und verschwindet bei T_C, T_N .
 - 3) μ setzt sich aus μ_L und μ_S zusammen, μ_S ist isotrop, μ_L anisotrop (nicht sphärische Ladungsverteilung, Bahndrehimpuls) in Festkörper g-Tensor.
 - 4) Aus 3) resultiert MAE, (makroskopisch: Koerzitivfeldstärke).
Es gibt (nach meiner Kenntnis) keinen isotropen Heisenberg Ferromagneten – mindestens tritt die anisotrope Dipol-Dipol Ww. auf.
 - 5) $J\bar{S}_1 \cdot \bar{S}_2$ ist isotrop, koppelt nicht an den Ortsraum. $(\bar{\mu}_1 \cdot \bar{r})(\bar{\mu}_2 \cdot \bar{r})$ koppelt an \bar{r} und ist in der Regel anisotrop (siehe $\bar{l} = \bar{r} \times \bar{p}$).
- *) bei sogenannten anisotropen Austausch ist \bar{l} via $\lambda \bar{l} \cdot \bar{s}$ in einem effectiven Spinraum projiziert