Illuminating aspects of magnetism in nanoparticles and core/shell nanocomposites

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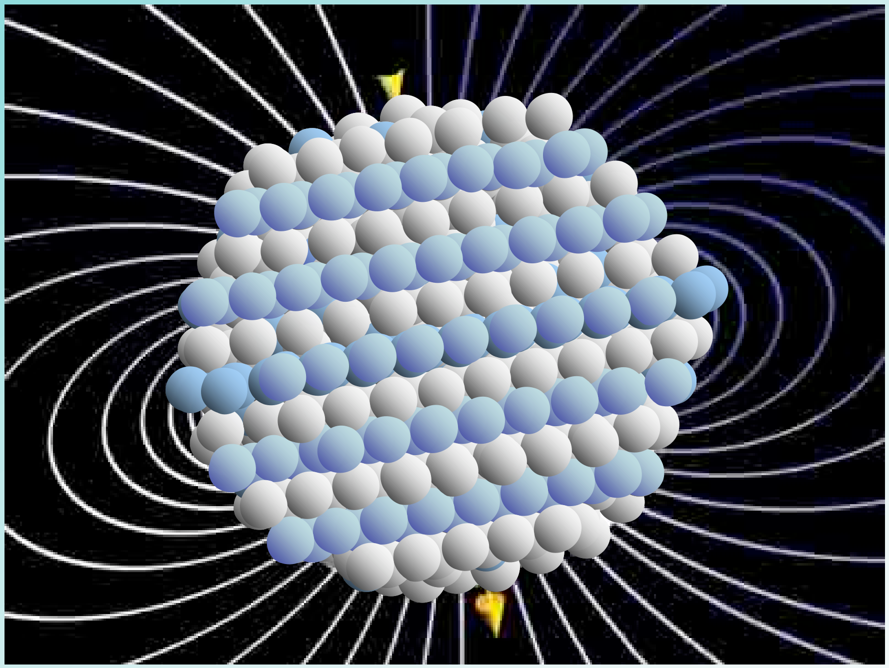


magnetic dipole
3 – 50 nm diameter

FePt ordered $L1_0$

Menue

- ***Aperitif***
- ***Hors d‘oeuvre***

Synthesis and magnetism

- ***Main course***

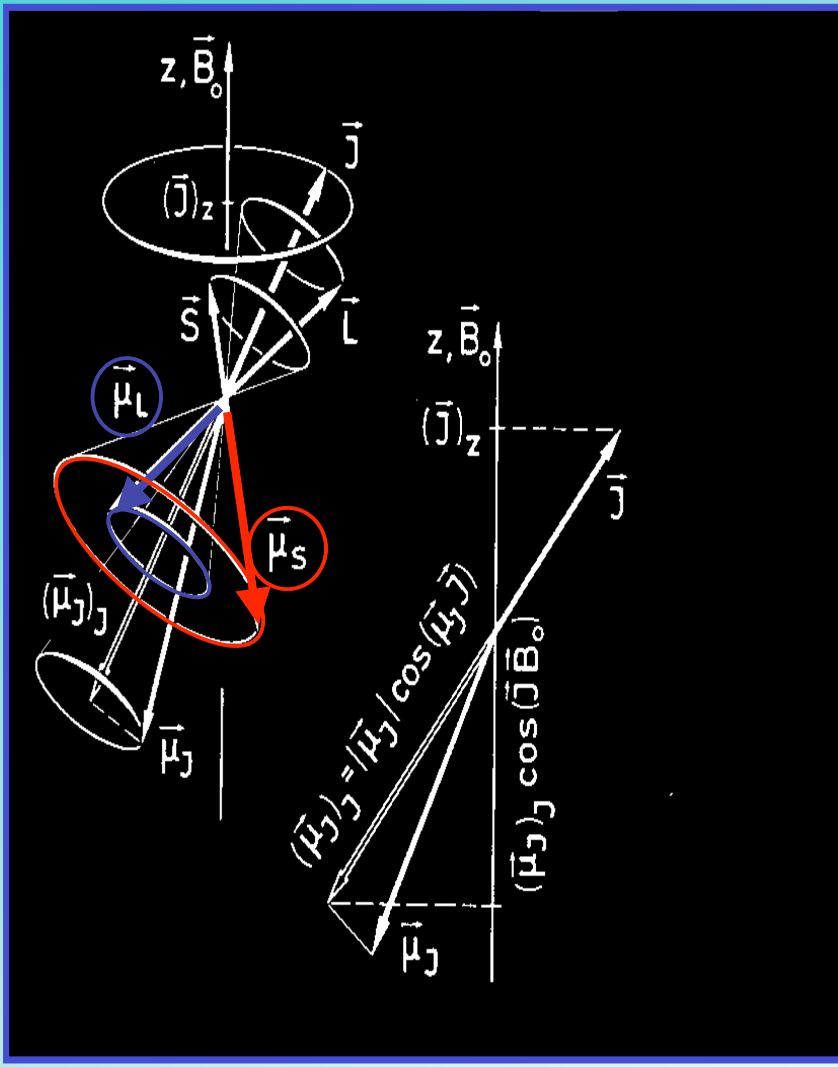
Fe_xPt_{1-x} nanoparticles (3-6 nm)
induced magnetic moment in Pt and interaction with Fe

CoO/Co nanoparticles (8- 12 nm)
„giant“ magnetic moments at interior interfaces

- ***Dessert***

functionalisation and hybrid magnetic nanocomposites
„luminescent magnetism“

Magnetic Orbital Moment



Magnetic Moment

Atom

$\mu_{tot} = g_J\, \mu_B\, [J(J+1)]_{-}$

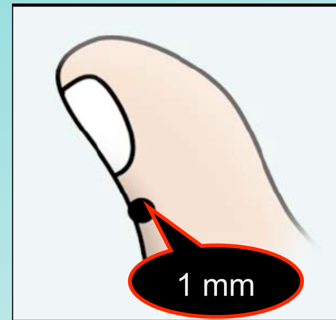
⇕

Solid state

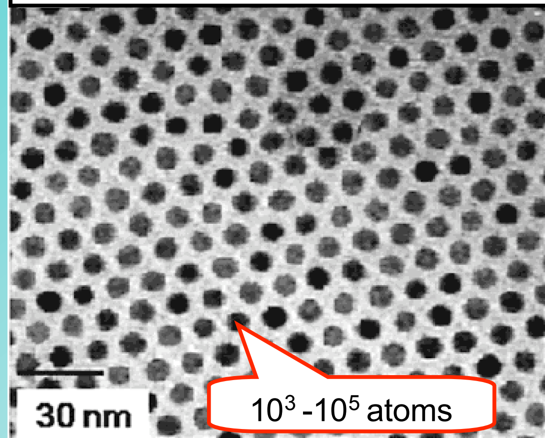
$\mu_{tot} = 2 \langle S_z \rangle + \langle L_Z \rangle$

“μ_S” + “μ_L”

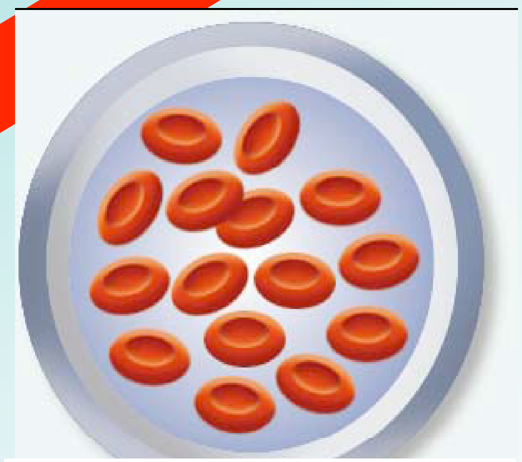
„Nanoparticle“: sizes



J. Phys. Chem. B ***105*** *(2001) 7913*

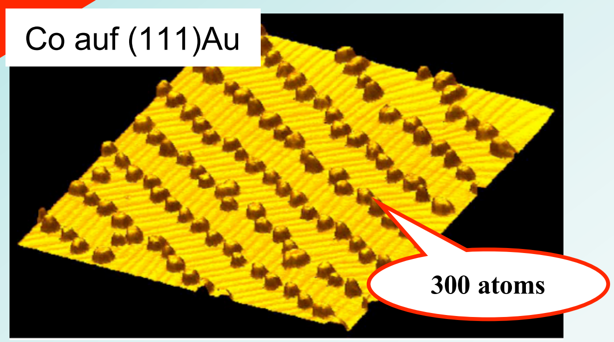


1 nm = 10 atoms
DNA = about 2.5 nm.



µm : Biological cells,

Co auf (111)Au



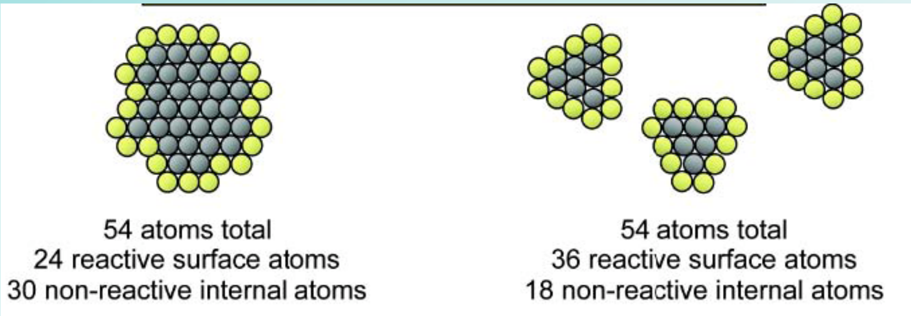
Nanoparticle in solution = colloid

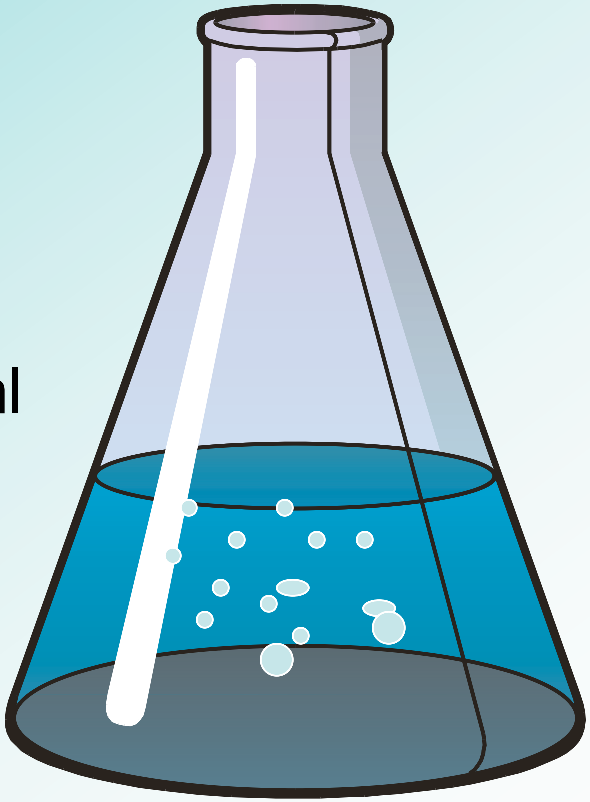
(greek: Kolla = glue , “Leim”)

Particle

diameters 5 –1000 nm
($10^5 – 10^{12}$ Molmass)

- surface/interface **IMPORTANT !**
  z.B. particle ∅ = 52 nm , $1.3 \cdot 10^{15}$ /ml
  => **11 m²/ml**

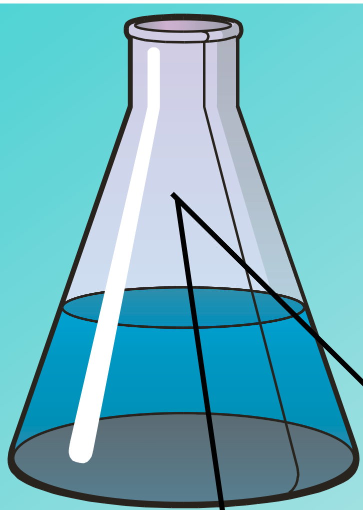


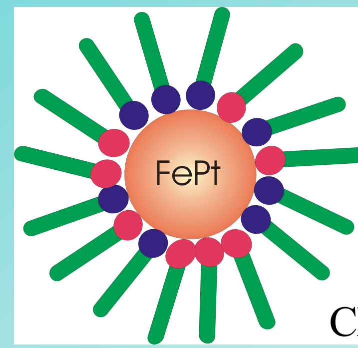


Synthesis

- Organometallic Chemistry

Synthesis (S. Sun et al., SCIENCE 287 (2000) 1989



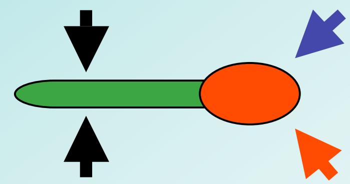


e.g. Fe and Pt

Types of surfactant used

$CH_3(CH_2)_7CH=CH(CH_2)_7C(=O)OH$

Oleic acid



Non-polar tail

Polar head

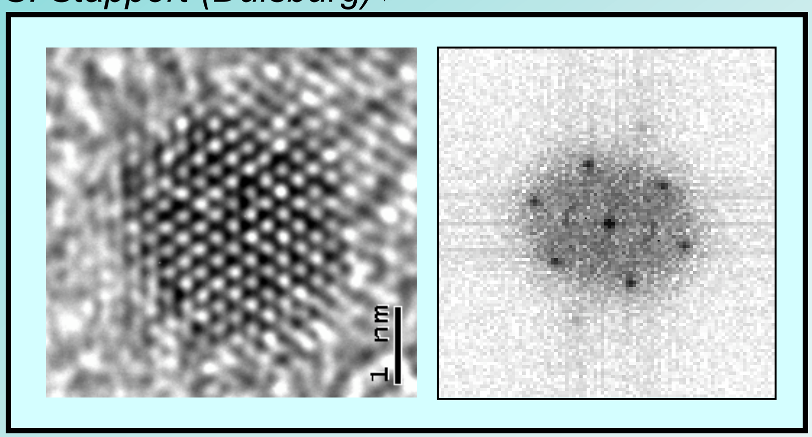
$CH_3(CH_2)_7CH=CH(CH_2)_7NH_2$

Oleylamine

HR-TEM

composition and size

S. Stappert (Duisburg)

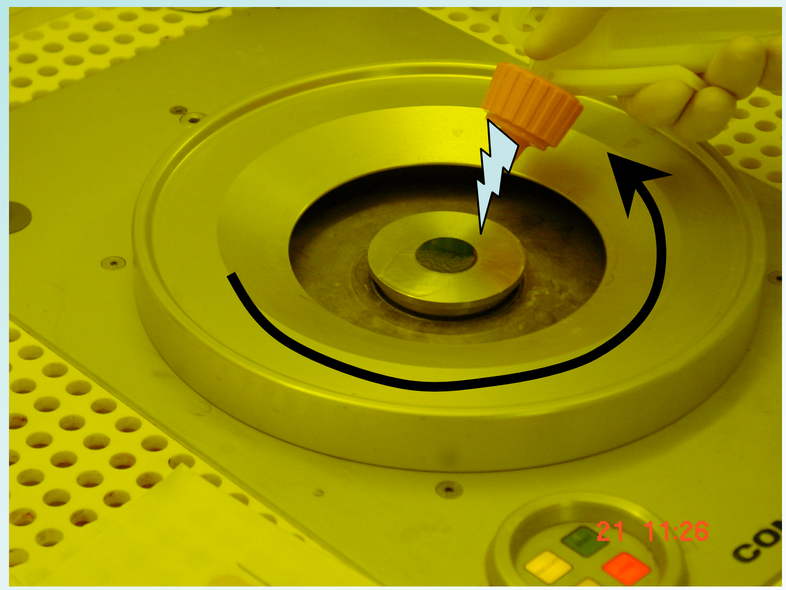


43 ± 3 % Fe	3.6 ± 0.1 nm
48 ± 2 % Fe	3.6 ± 0.1 nm
58 ± 3 % Fe	3.6 ± 0.1 nm
70 ± 3 % Fe	2.6 ± 0.1 nm

Two-dimensional Layers

by spin-coating on Si wafer
or "Self- Assembly"

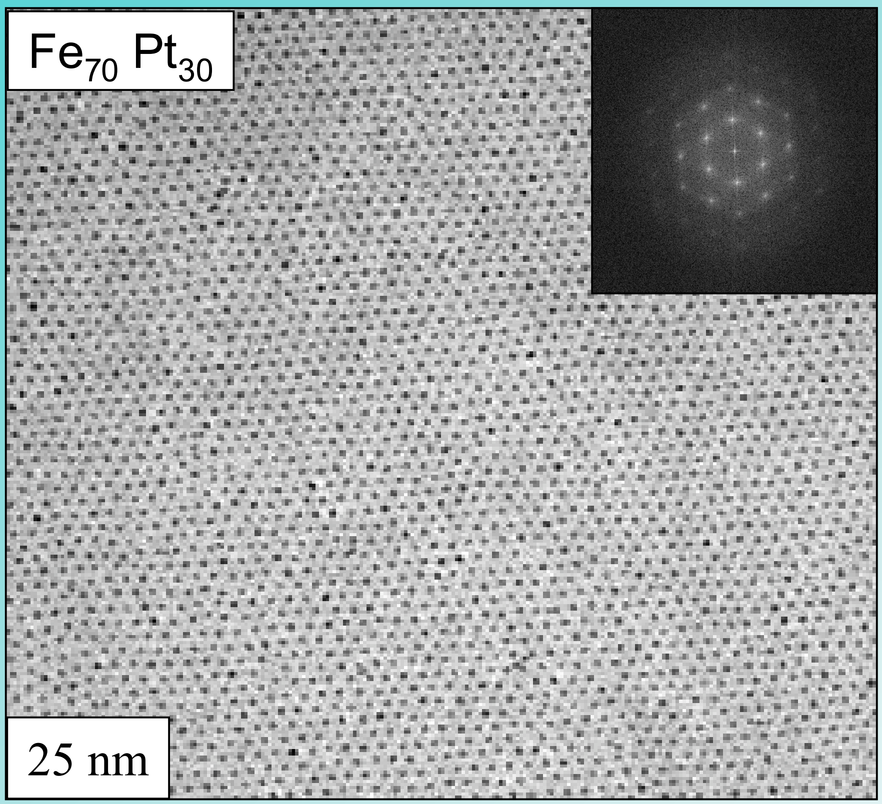
magnetic colloid $Fe_{60}Pt_{40}$



Spin-coating

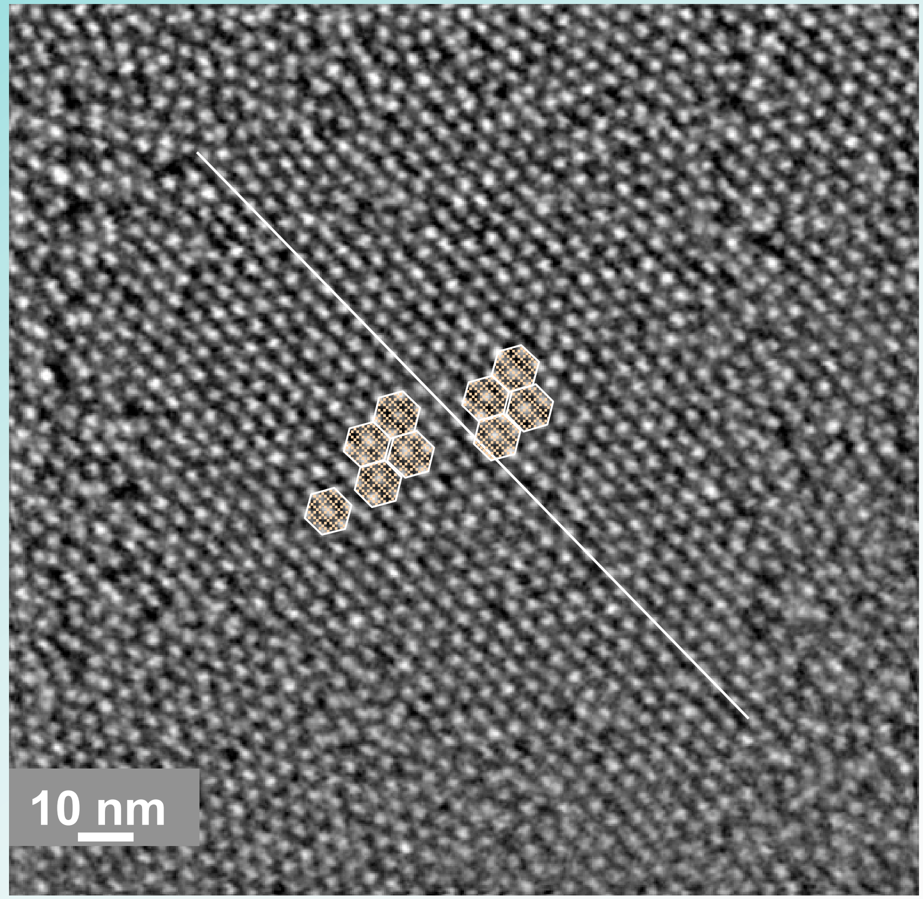
Self-assembly (10 Tb/inch^2)

one monolayer **of 3.6 nm** FePt particles



on amorphous carbon

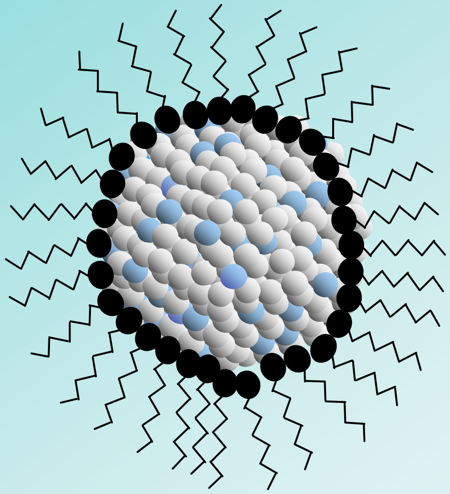
Secondary electron microscopy



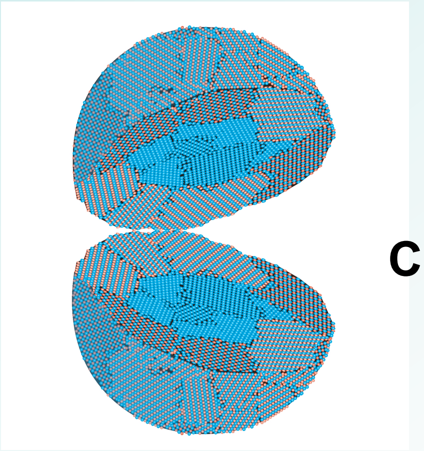
on Si wafer

Magnetism

- Superparamagnetism
- Magnetic Anisotropy
- Magnetic Orbitalmoment

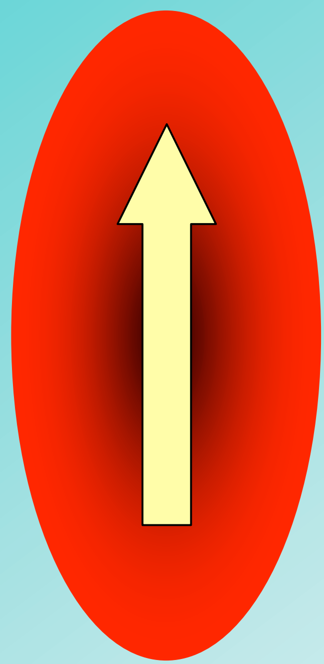


FePt



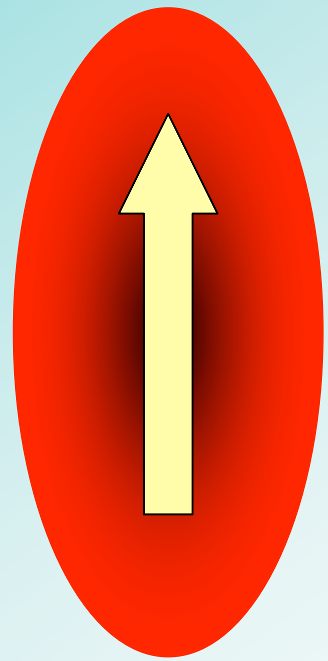
CoO@Co

Magnetic Nanoparticle



„blocked“

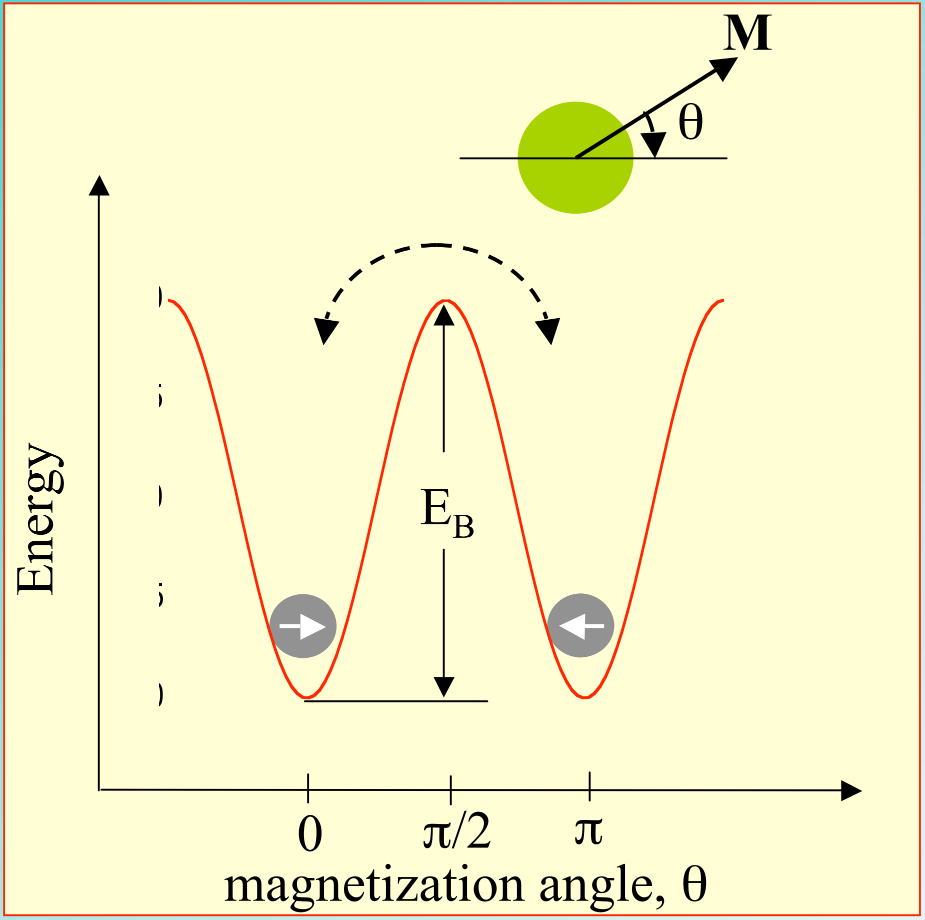
e.g. 300 K, Fe > ca. 16 nm



„superparamagnetic“

Depends on ***magnetic anisotropy*, *particle volume and temperature !***

Superparamagnetism
Instability of the Magnetisation for small Volumina !



$$E_B \cong K_u V$$

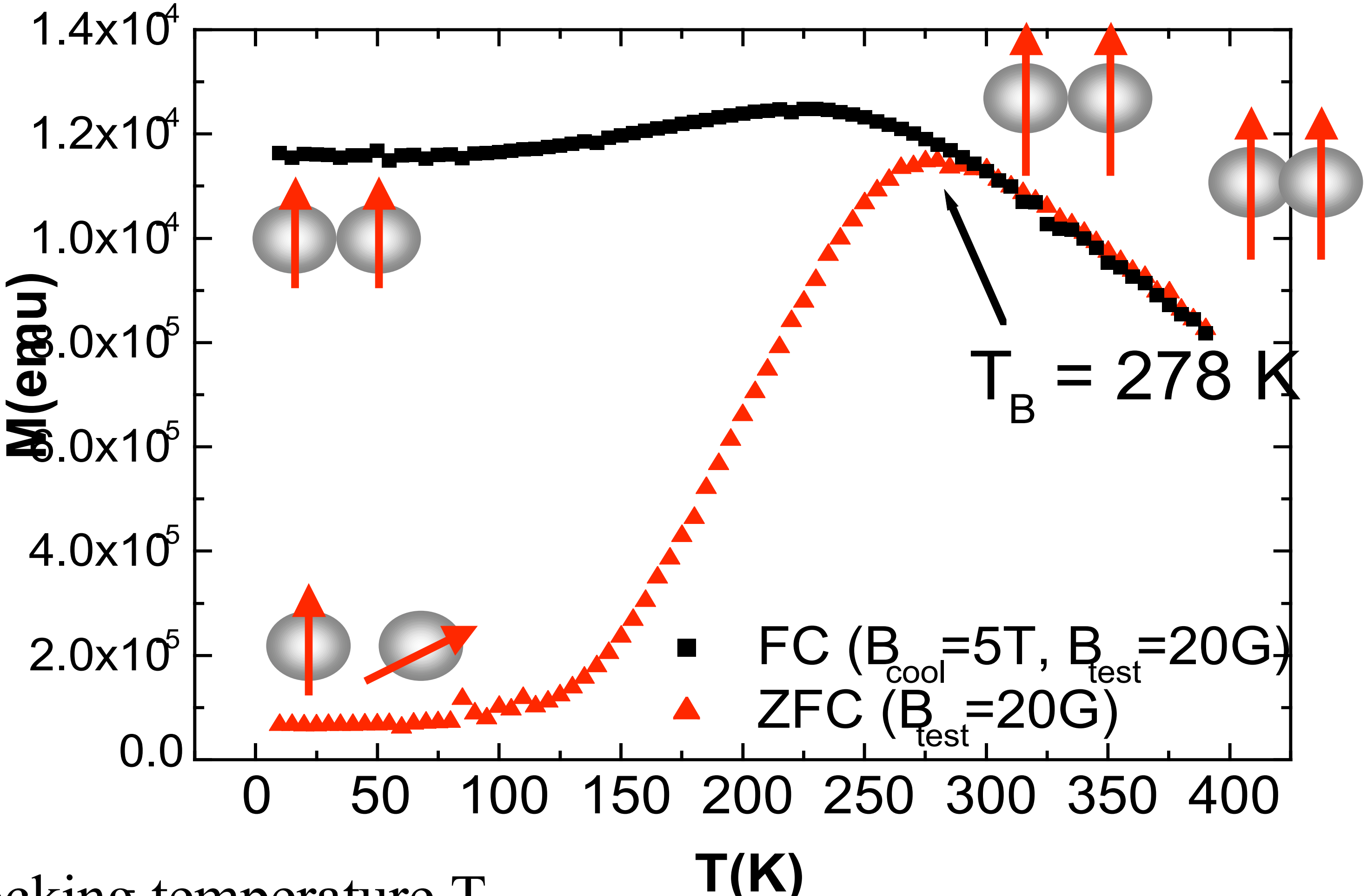
K_u anisotropy energy density
V particle volume

Volume → 0 (small)
stability $E_B \to 0$
unstable !

BIG PROBLEM !

Zero-field-cooled / field-cooled magnetization
11.4 nm Co assembly

„time window“: minutes



Blocking temperature T_B

Nanoparticle magnetism

Shape anisotropy
(dipole-dipole interaction)

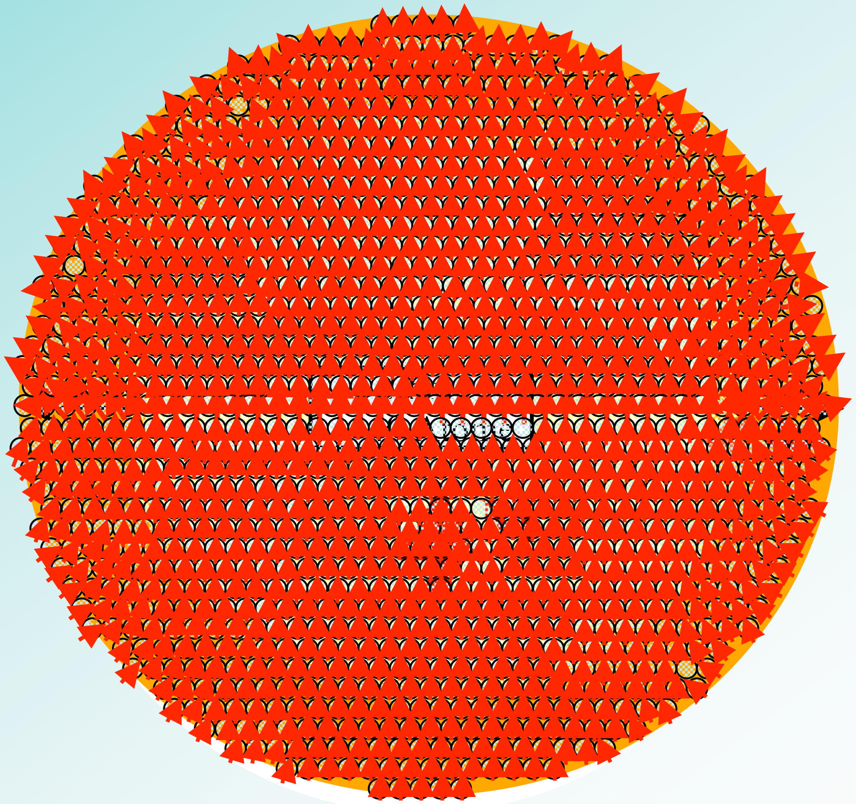
Magnetocrystalline anisotropy
(spin-orbit interaction)

Surface ≠ Volume ≠ Interface ≠ Step Anisotropy

Exchange anisotropy
(exchange interaction at FM/AFM interface)

↓

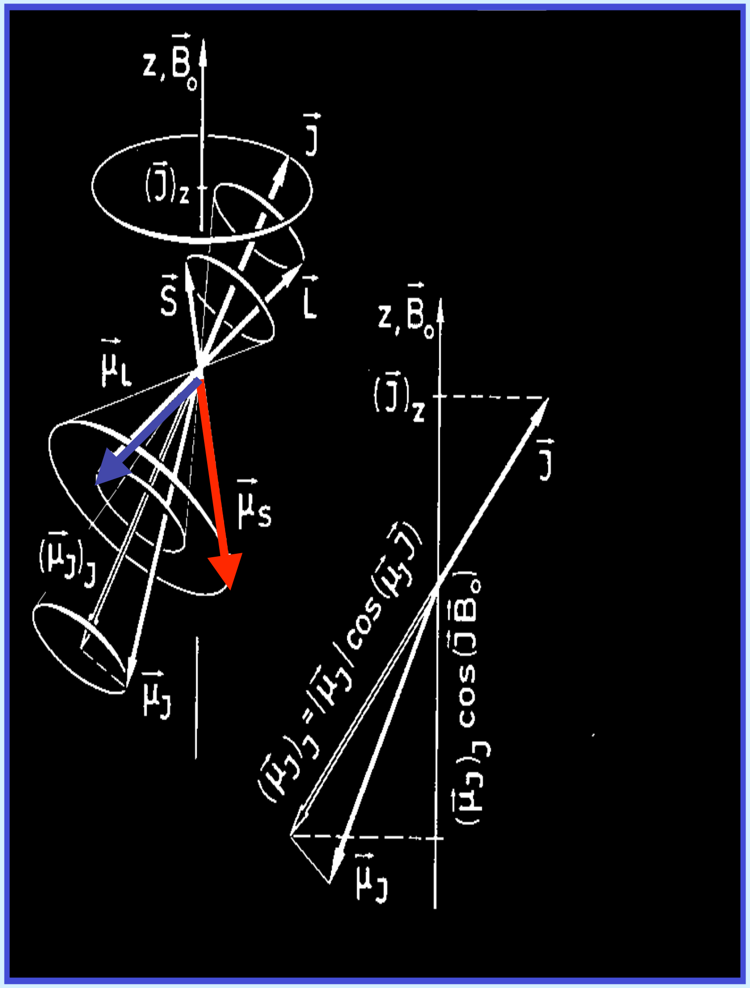
Effective magnetic Anisotropy K_{eff}



Complex, non-collinear spinstructure
Exchange energy ⇔ magn. Anisotropy

Magnetic Moment

$\mu_{tot}=g_J\mu_B[J(J+1)]^{-}$



Orbital Magnetism

Bulk: $\mu_{tot} = 2 \langle S_z\rangle + \langle L_Z\rangle$

"μ_S" + "μ_L"

$$\frac{\mu_L}{\mu_S}$$ Temperature independent !

$$\frac{\mu_L}{\mu_S} = \frac{g-2}{2}$$

g : **g- factor**

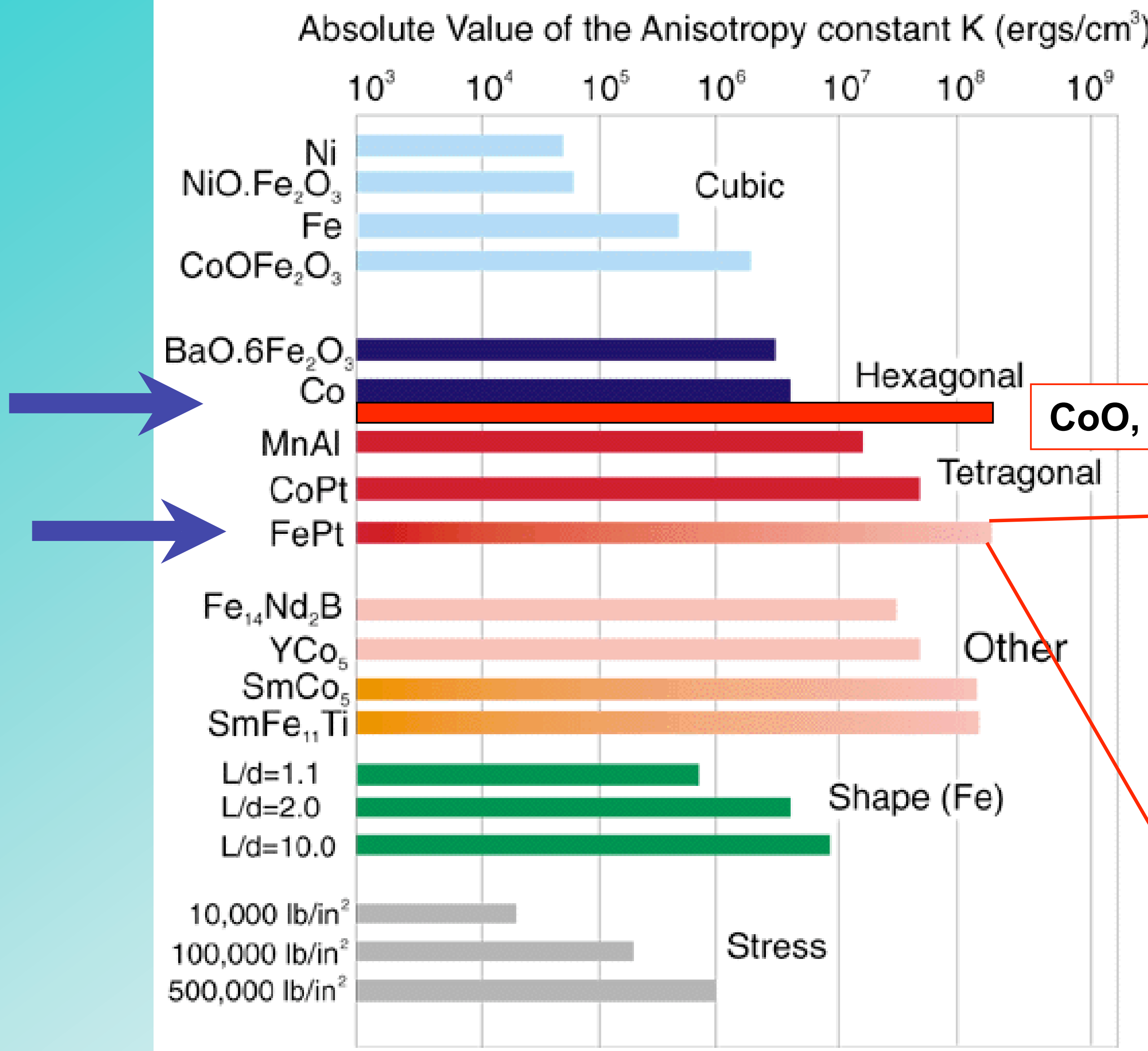
*M*agnetic *A*nisotropy *E*nergy :

$$MAE \approx -\alpha \frac{\lambda}{4\mu_B} \Delta\mu_L \quad , \quad \Delta\mu_L = \mu_L^{\perp} - \mu_L^{\parallel}$$

$$MAE = E_{[001]} - E_{[110]}$$

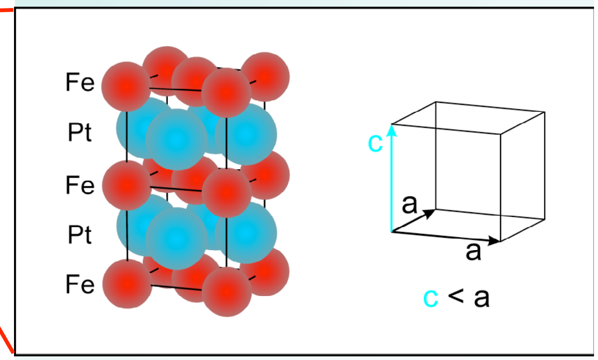
$$= - K_2 - 0.5\, K_{4\perp} + 0.25\, K_{4//}$$

Hard Magnetic Materials



CoO, 2.7x10^8

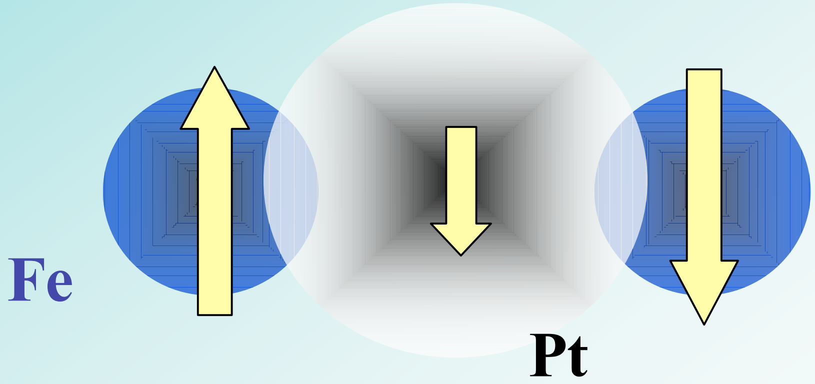
Figure courtesy of D. Weller, IBM, based on data taken from B. D. Cullity, *Introduction to Magnetic Materials,* Addison-Westley, Reading, MA, 1972, pg. 381, and T. Klemmer et al., *Scripta Metallurgica et Materialia* **33** (1995) 1793.]



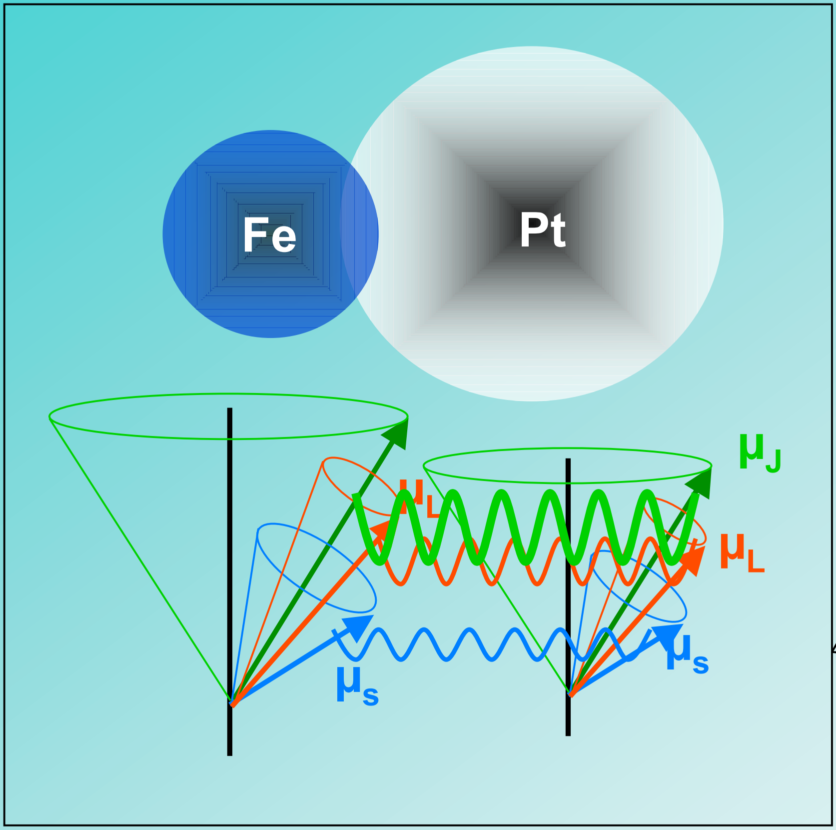
Exp.: 1.76 meV per FePt pair
4-10 10^7 erg/cm^3 , T_C=750 K
Theory:1.2-3.9 meV/cell

Nanoparticle Fe_xPt_{1-x}

- **Anti-** or Ferromagnetic ?
- Induced magnetic moment at Platinum ?
- Magnitude of magnetic moment (μ_L,μ_S) Fe, Pt ?
- Relative Orientation of magnetic moments ?



effective μ_L/μ_S in Fe_xPt_{1-x} ?



$$\frac{\mu_L^{eff}}{\mu_S^{eff}} = \frac{g-2}{2}$$

$$\frac{x\mu_L^{Fe} \pm (1-x)\mu_L^{Pt}}{x\mu_S^{Fe} \pm (1-x)\mu_S^{Pt}}$$!

„LS coupling“

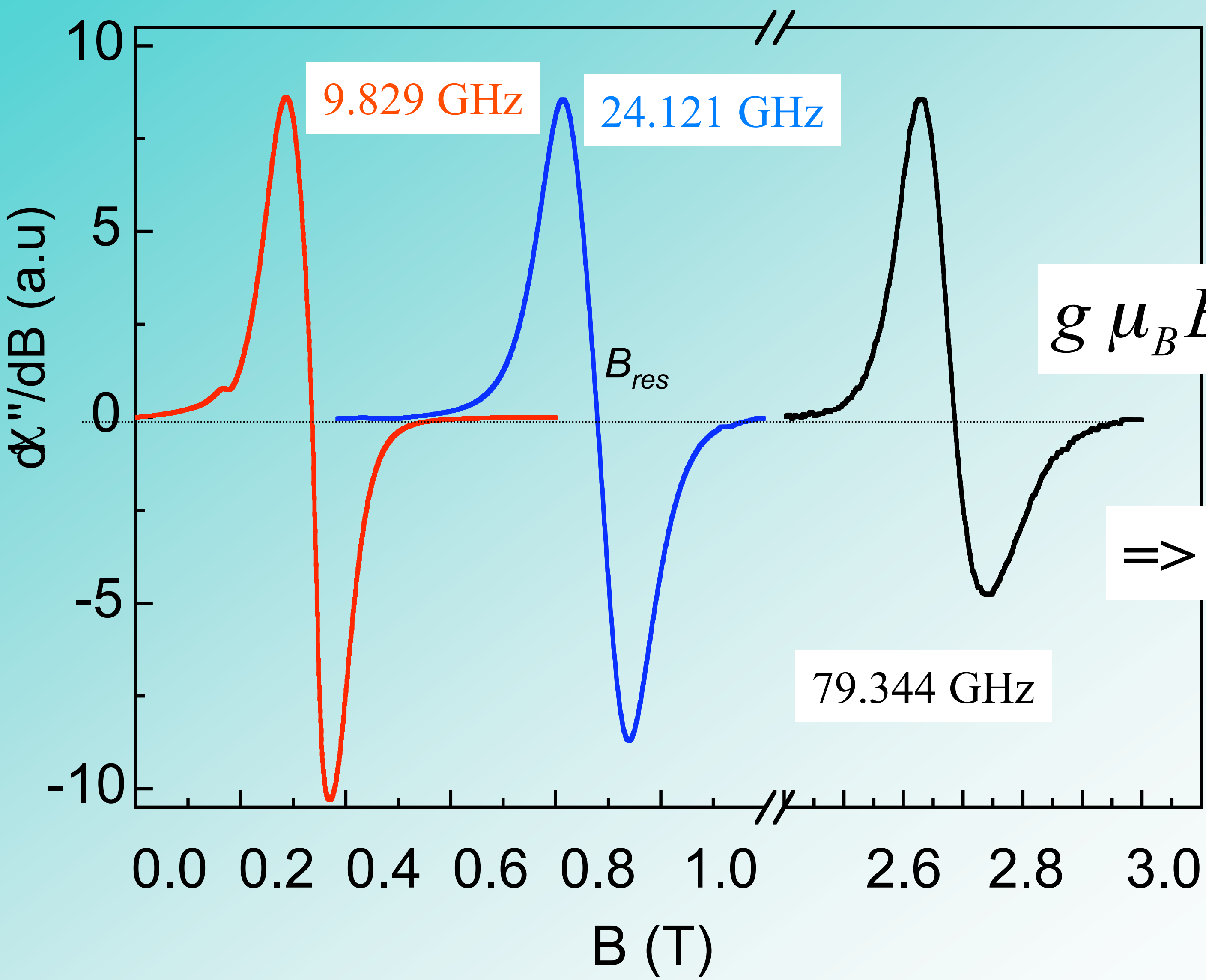
?

$$x\frac{\mu_L^{Fe}}{\mu_S^{Fe}} \pm (1-x)\frac{\mu_L^{Pt}}{\mu_S^{Pt}}$$

„jj coupling“

coupling scheme ?

Magnetic Resonance 3 nm $Fe_{73}Pt_{27}$

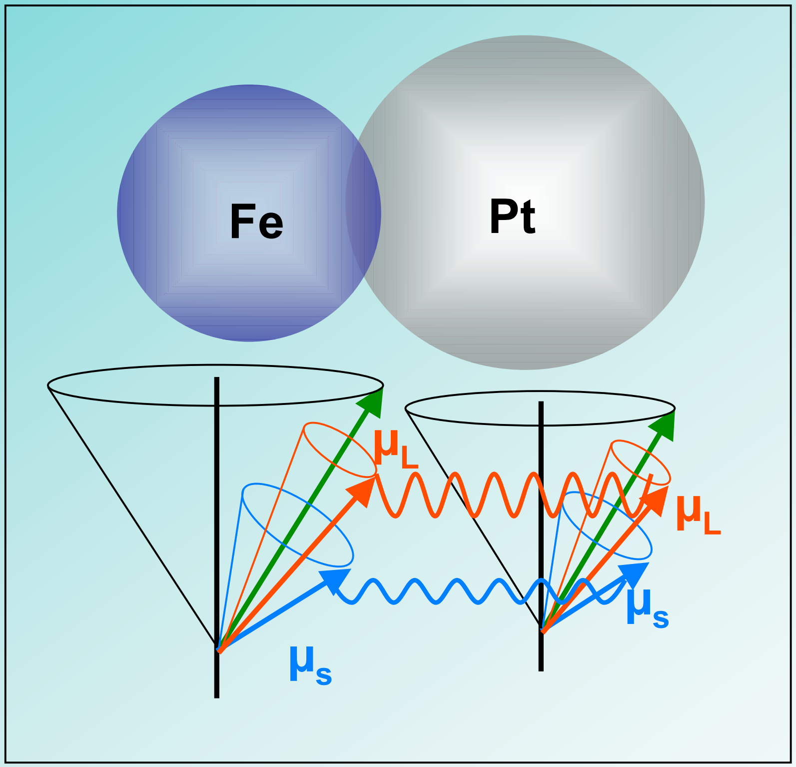


$$g\,\mu_B B_{res} = h\upsilon$$

=> g = 2.03

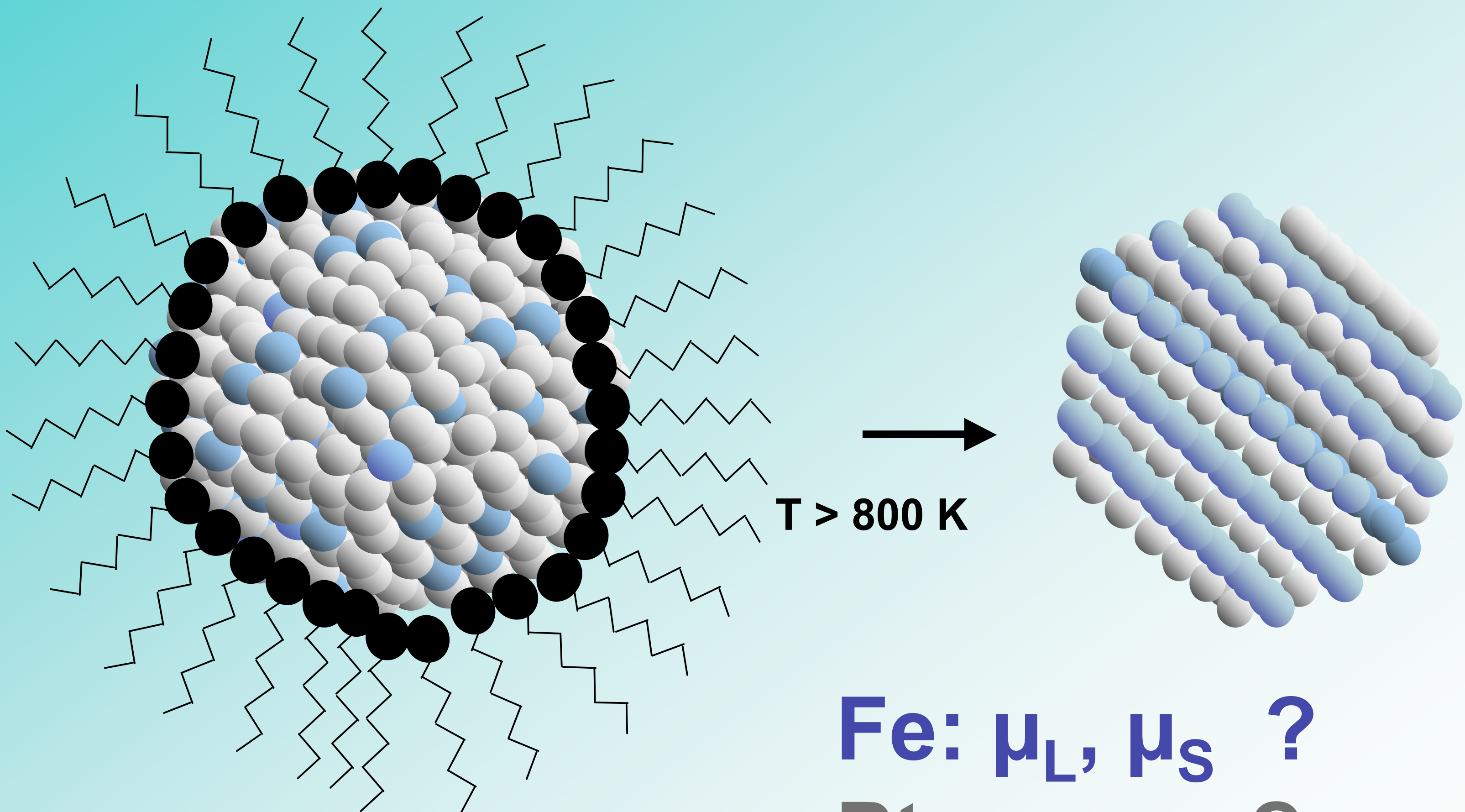
"LS" type coupling scheme

Induced orbital Pt moment couples to Fe orbital moment in disordered Fe_xPt_{1-x}



Phys. Rev. B 69, 054417 (2004)
Europhysics Letters 70 (2005) 250

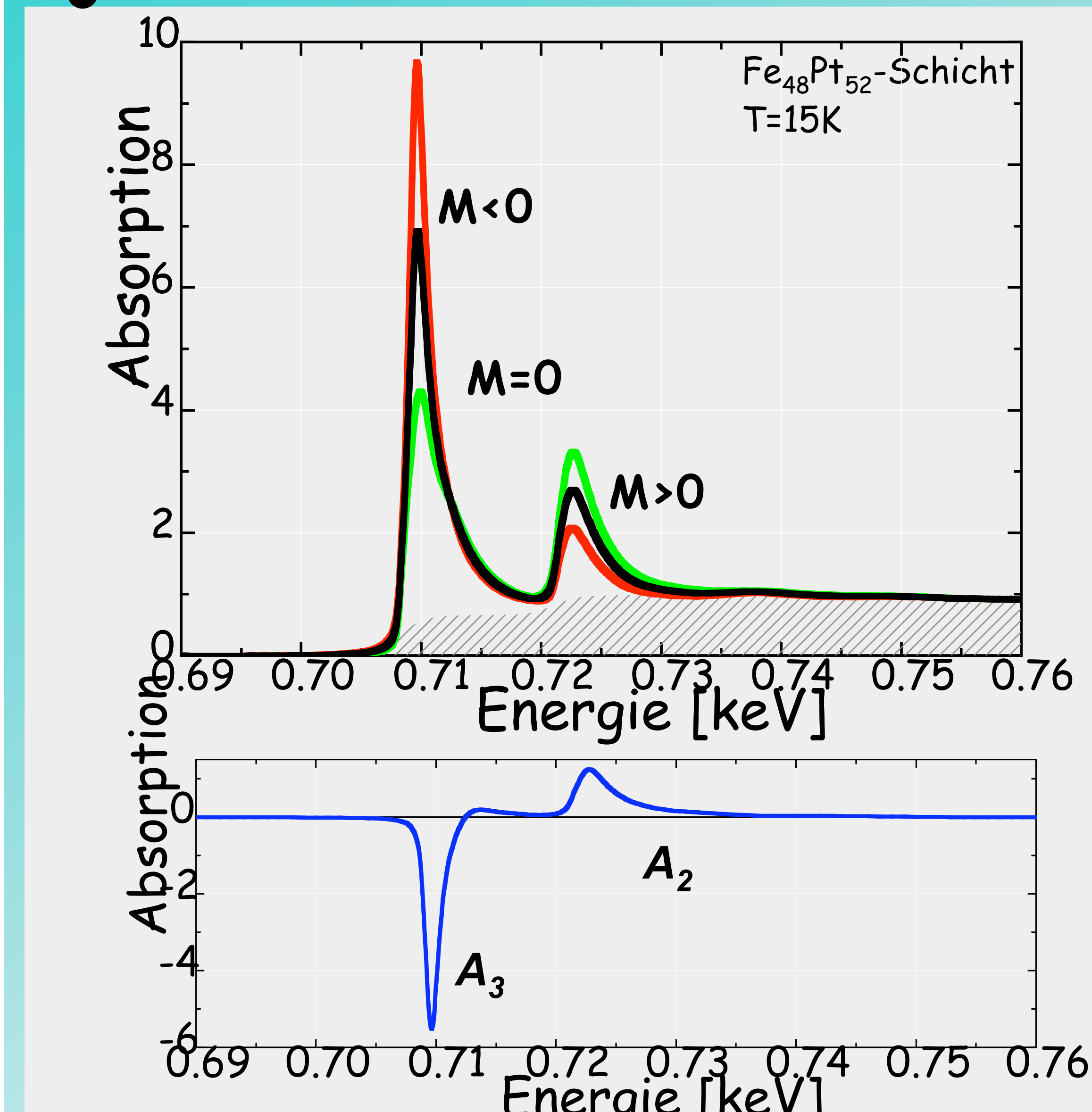
FePt : Influence of ligands and crystalstructure



Fe: μ_L, μ_S ?

Pt: μ_L, μ_S ?

X-ray magnetic circular dichroism, $L_{3,2}$-edges



$$\frac{s}{n_h} = \frac{-3A_3 + 2(A_3 - A_2)}{A_{iso}}$$

$$\frac{l}{n_h} = \frac{-A_3 + A_2}{A_{iso}}$$

$$\Rightarrow \frac{l}{s} = \frac{2}{3}\,\frac{A_3 - A_2}{A_3 + 2A_2}$$

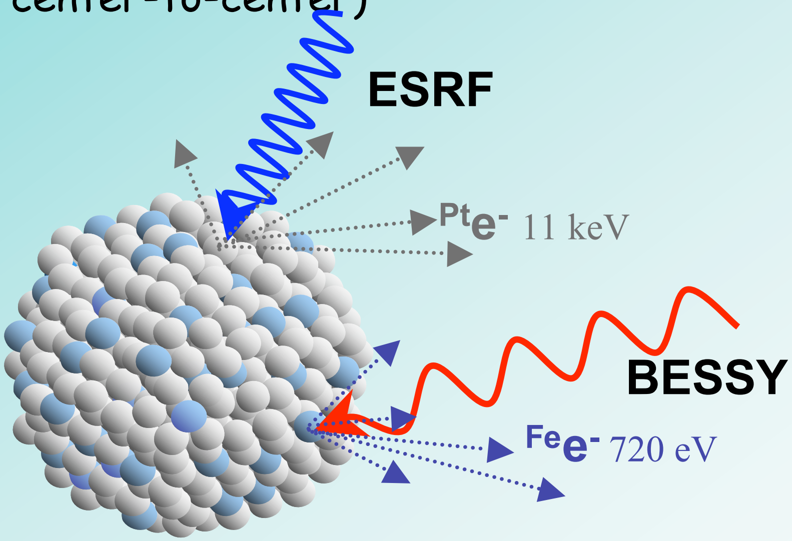
Difference M>0, M<0: „XMCD“

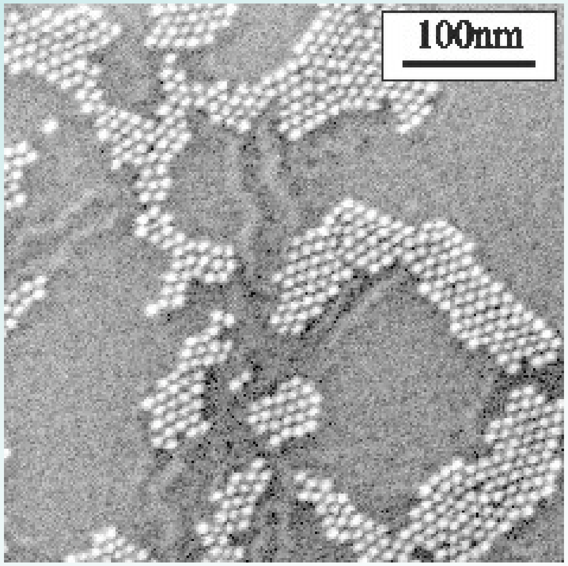
=>elementspezific M(H)

Sample morphology, FePt (6.3 nm)

As prepared particle

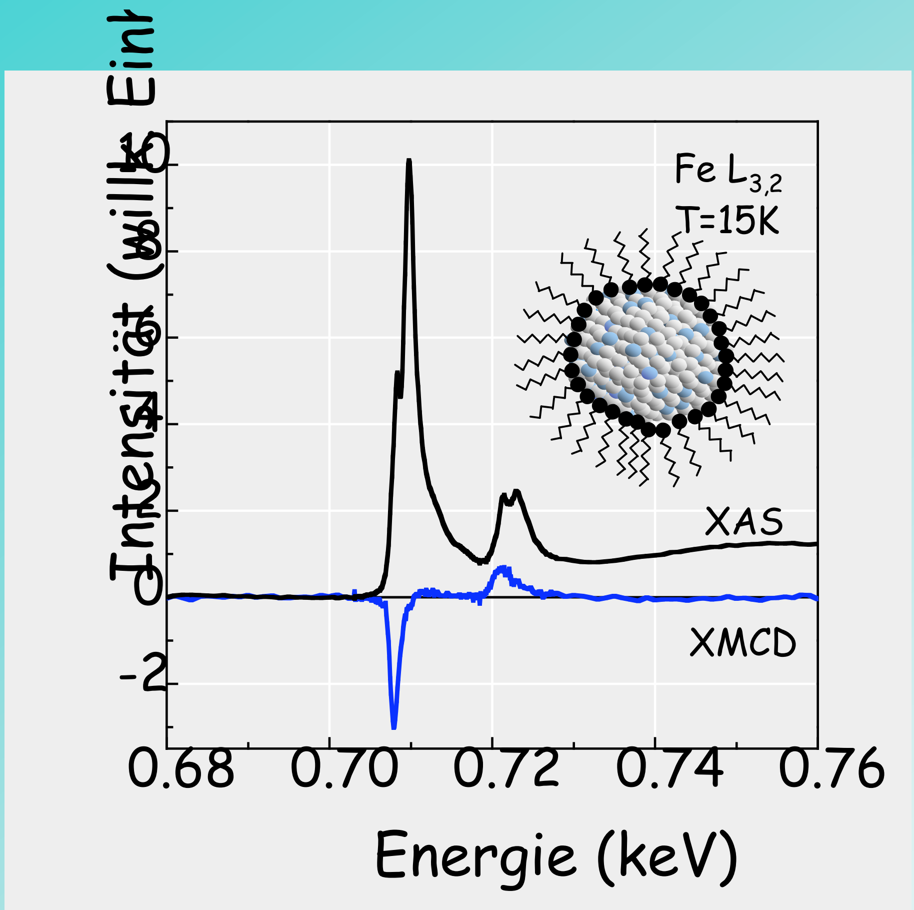
Fe-contents:	**(50 ± 3) at%**
Ligands:	**oleic acid, oleylamin**
structure:	**fcc, chem. disordered**
average diameter:	**6.3 nm, _ = 0.9nm**
Average distance: (in „islands" center-to-center)	**9 nm**





Chemical state FePt (6.3 nm)

As prepared particle



XAS => doublepeak-structure at L_3- and L_2-edge of Fe

-> particles (surface) oxidized

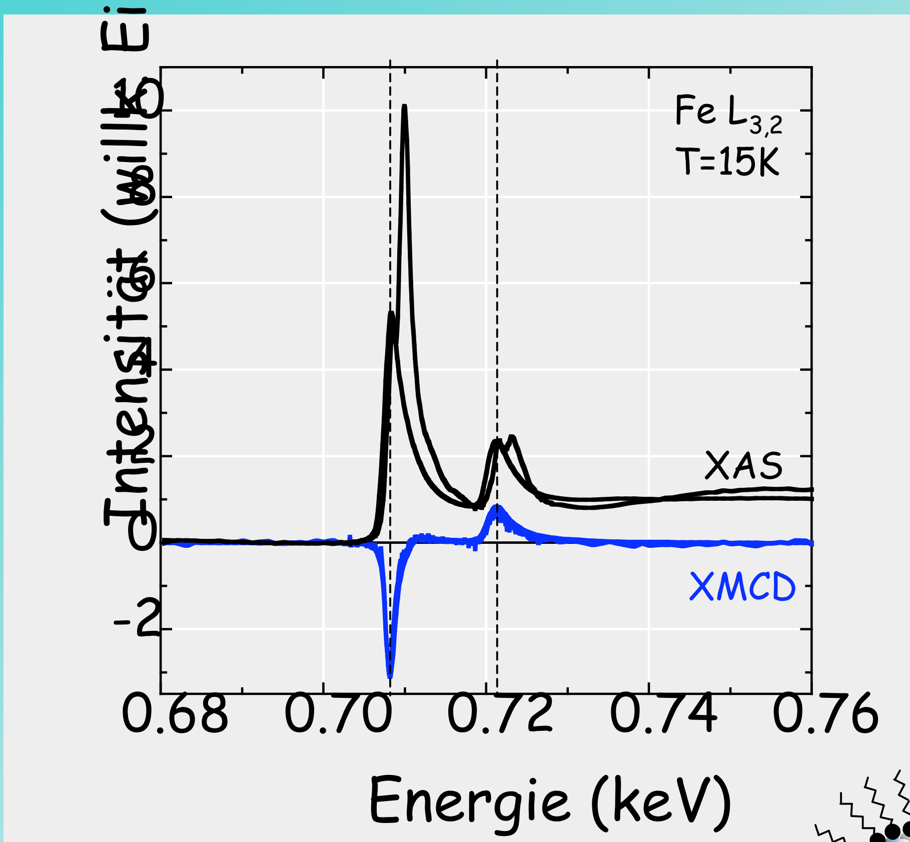
XMCD like metallic Fe

-> Fe-oxide antiferromagnetic (α-Fe_2O_3)

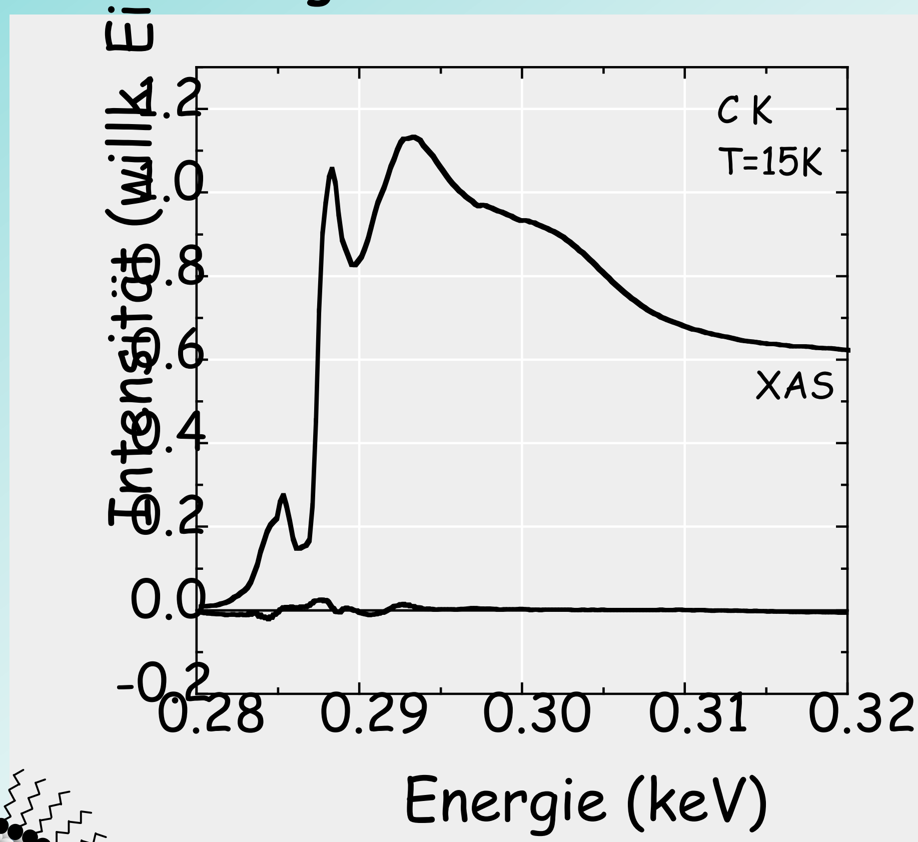
Plasma cleaning FePt

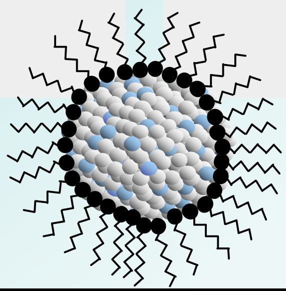
Particle after H-Plasma (5 Pa, 15 min at 300 K)

Oxidefree



Ligand free



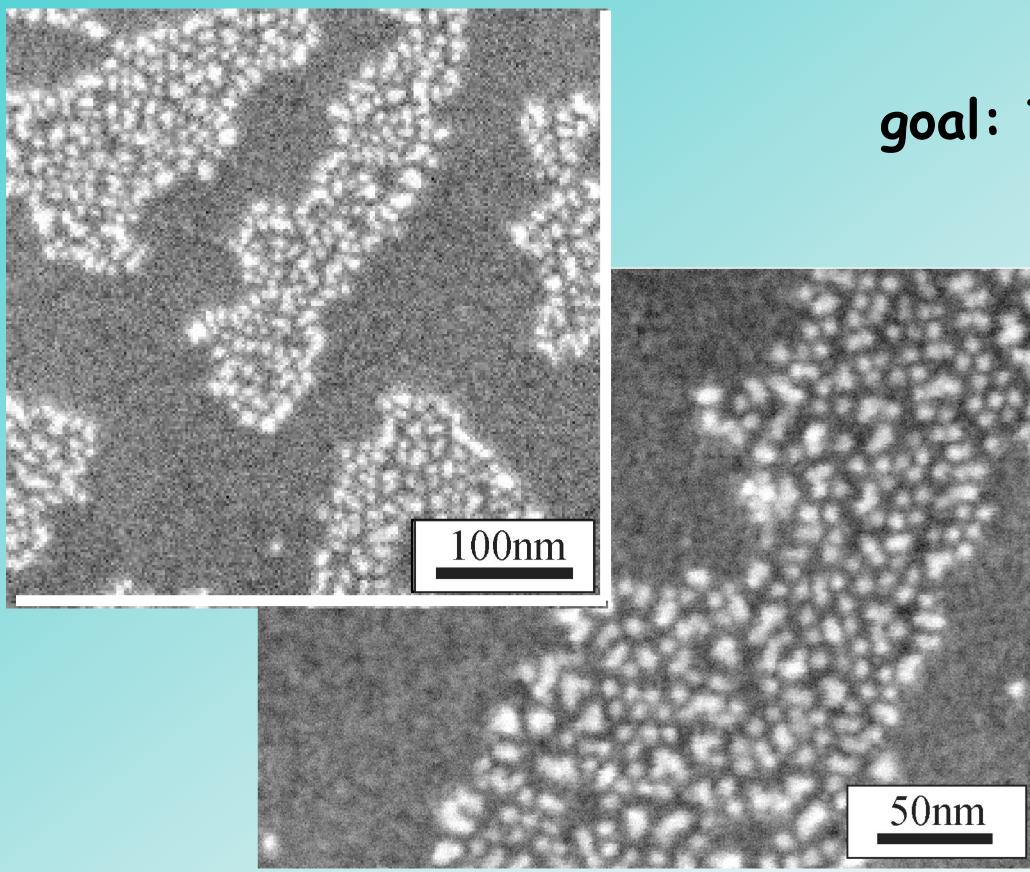


Structure and magnetic properties

Annealling FePt-Nanoparticles on Si-waver

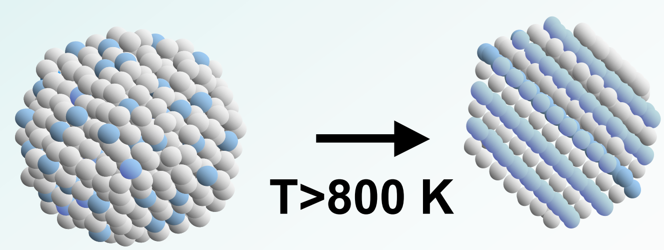
Parameter: 30min at 600°C
in H-Plasma at 6Pa

goal: Transformation into chemically
ordered $L1_0$-phase



Scanning Electron Microscopy

-> ca. 20% of particles
are agglomerates
of 2-4 nanoparticles

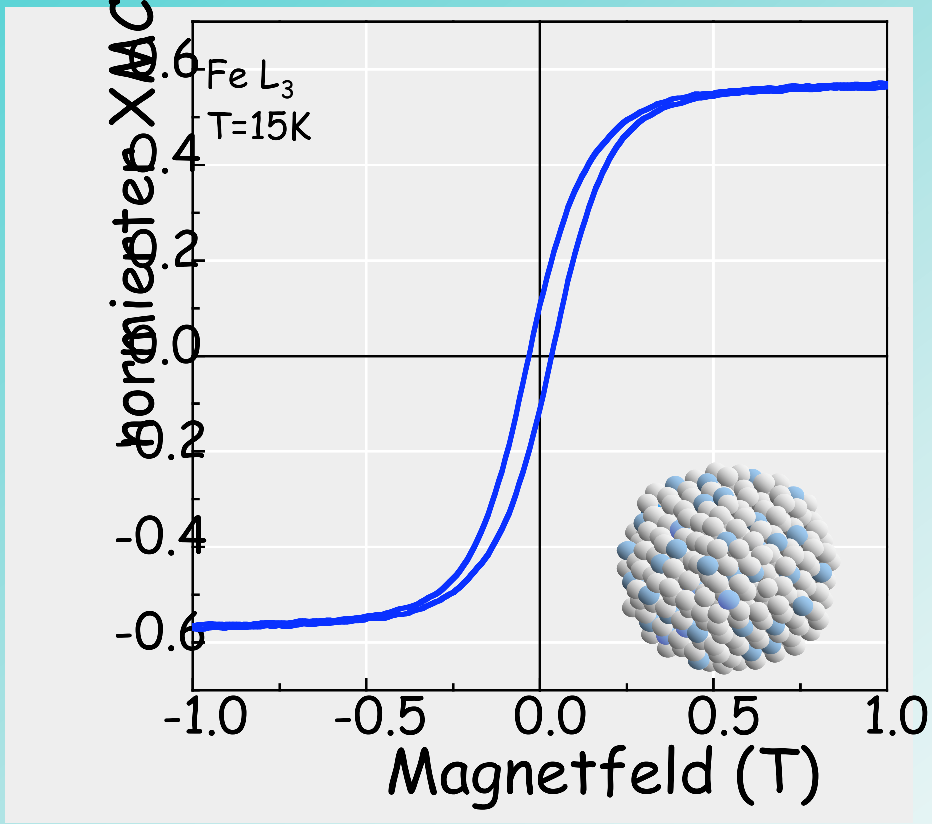


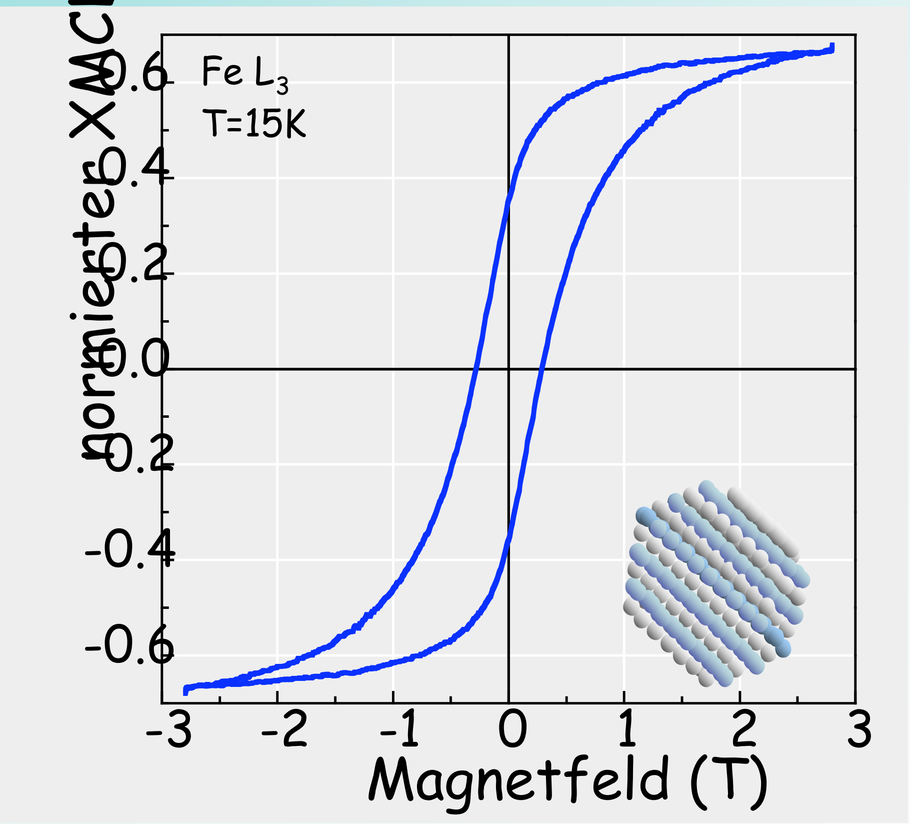
Elementspecific M(H)-loops

fcc, chem. disordered → annealed

H_c = (36 ± 2) mT

H_c = (292 ± 5) mT

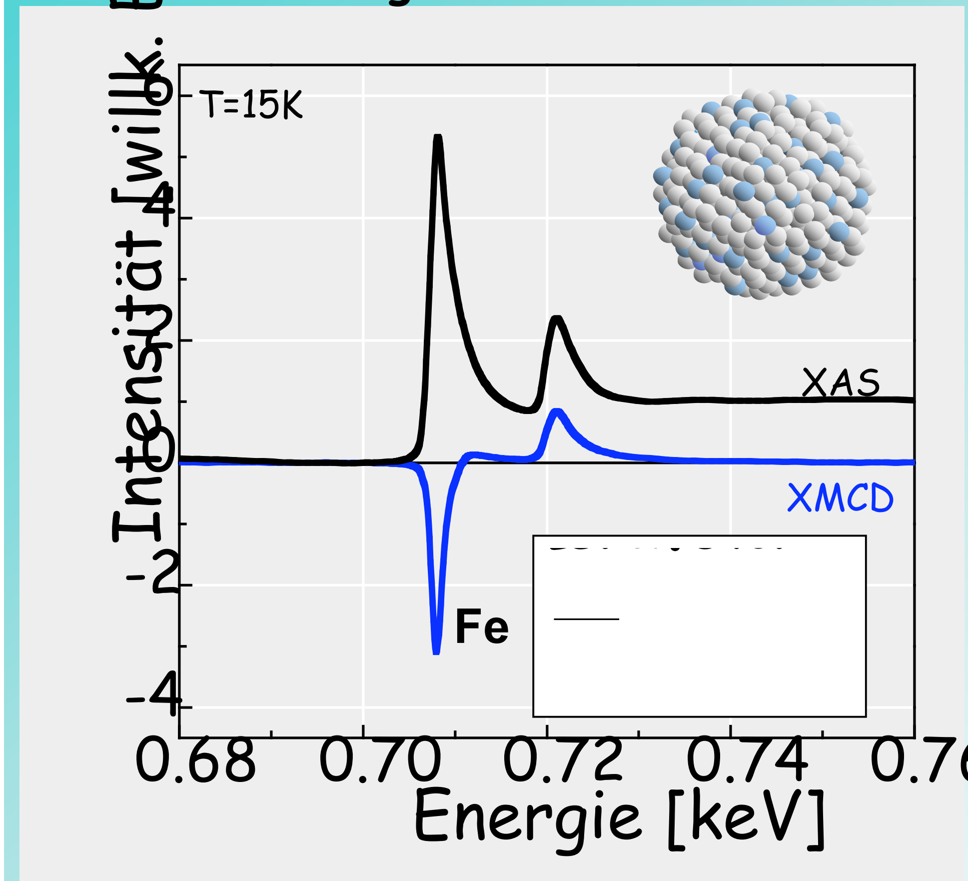




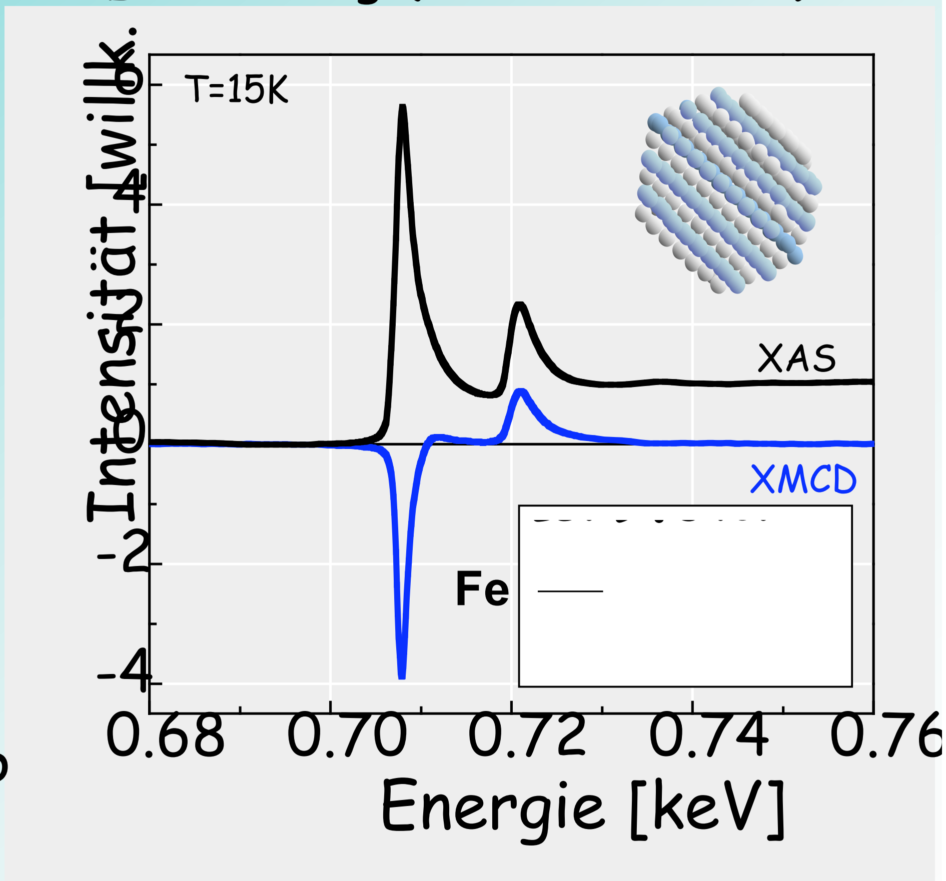
Magnetic Moments in FePt-Nanoparticles

Fe $L_{3,2}$-edges

Before annealing



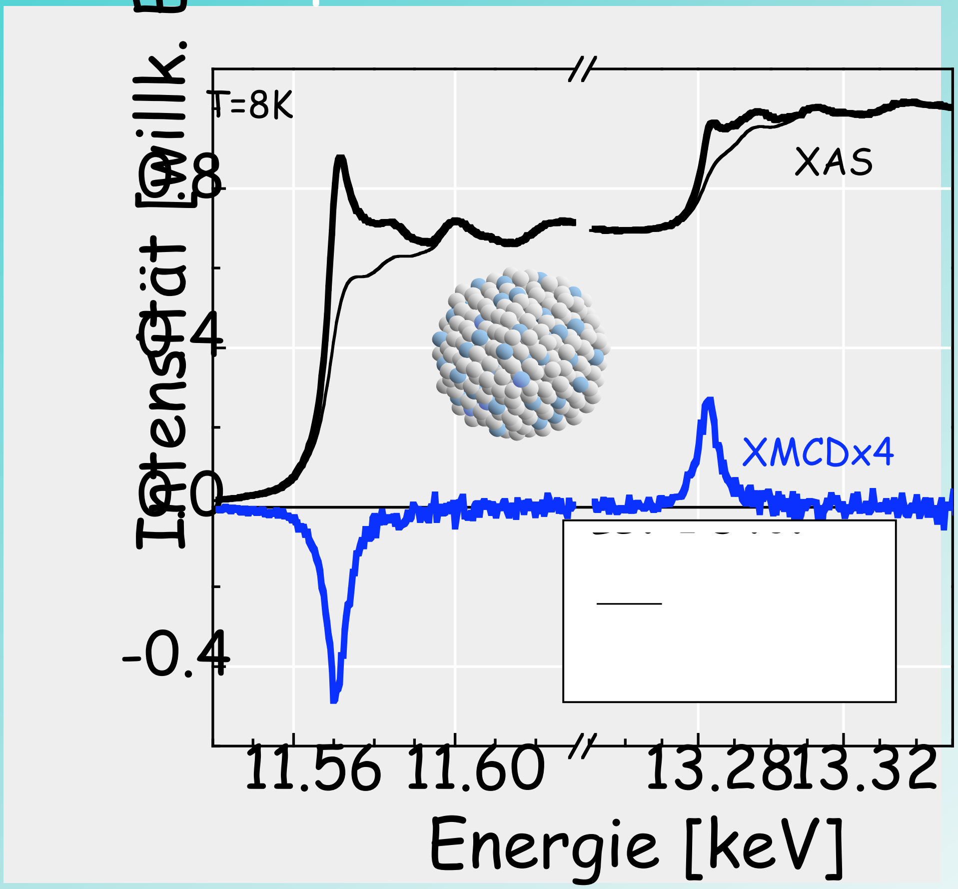
After annealing (30min at 600°C)



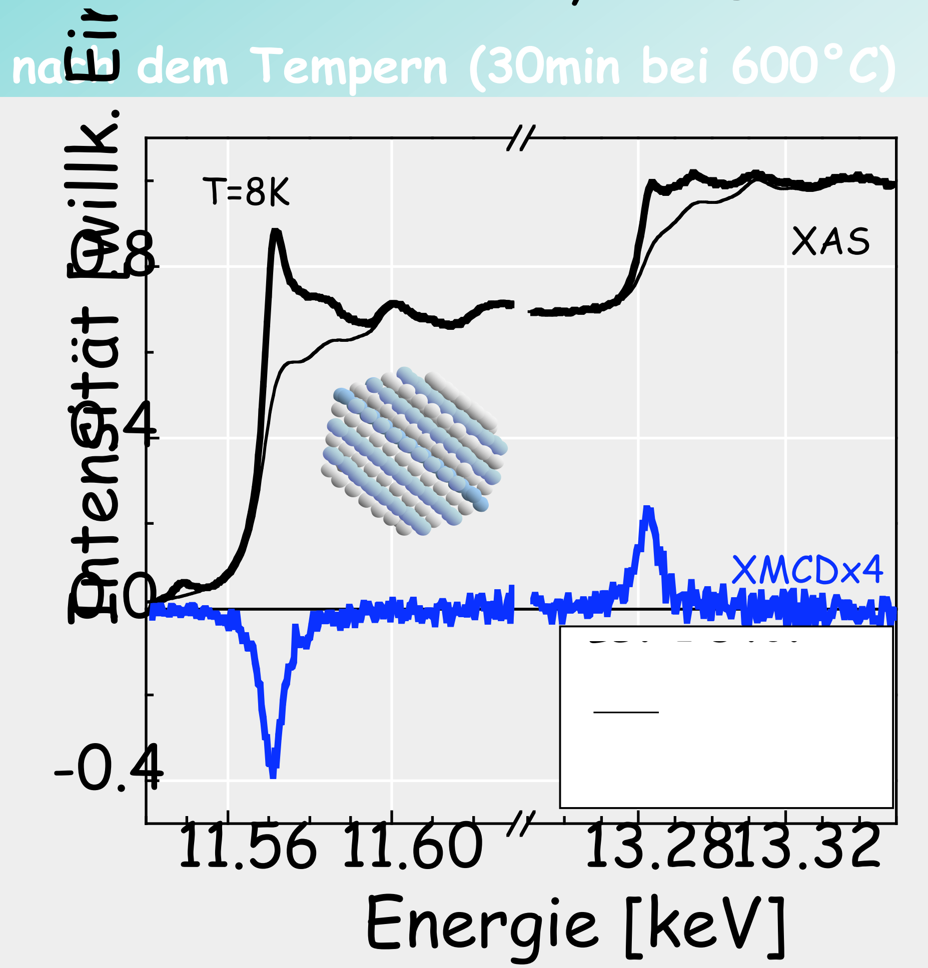
Magnetic Moments in FePt-Nanoparticles

Pt $L_{3,2}$-edges

vor dem Tempern



nach dem Tempern (30min bei 600°C)



Effect on magnetic moments

in 6.3 nm nanoparticle FePt

	Fe		Pt	
	—$_S$ [—$_B$]	—$_L$ [—$_B$]	—$_S$ [—$_B$]	—$_L$ [—$_B$]
Before annealing	2.48(7)	0.056(10)	0.41(1)	0.054(2)
After annealing	2.59(8)	0.240(18)	0.41(1)	0.042(2)
theoret. $L1_0$ *	2.50	0.064	0.41	0.020

After annealing: μ_L of Fe enhanced by <u>330%</u>

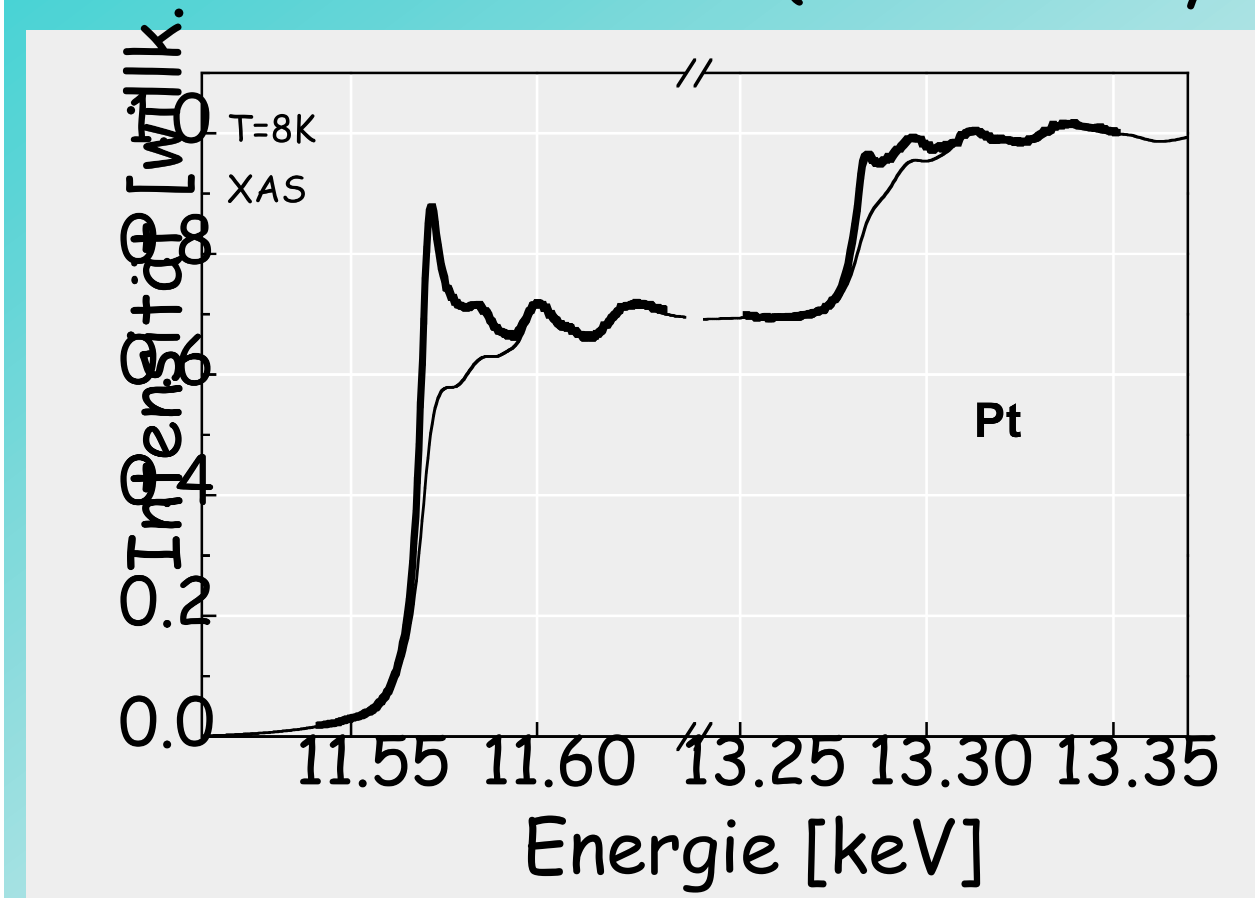
μ_L/μ_s^{Fe} increases by factor 4 (2% → 9.3 %)

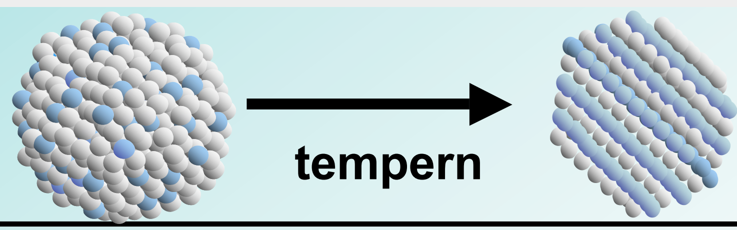
μ_L/μ_s^{Pt} changes from 13% → 10%

* Theory: I. Galanakis, M. Alouani, and H. Dreyssé, JMMM **242**, 27 (2002)

evidence for structural transformation

EXAFS (extended x-ray absorption fine structure)





Frequency of EXAFS-Oszillations →

Nearest neighbor distance

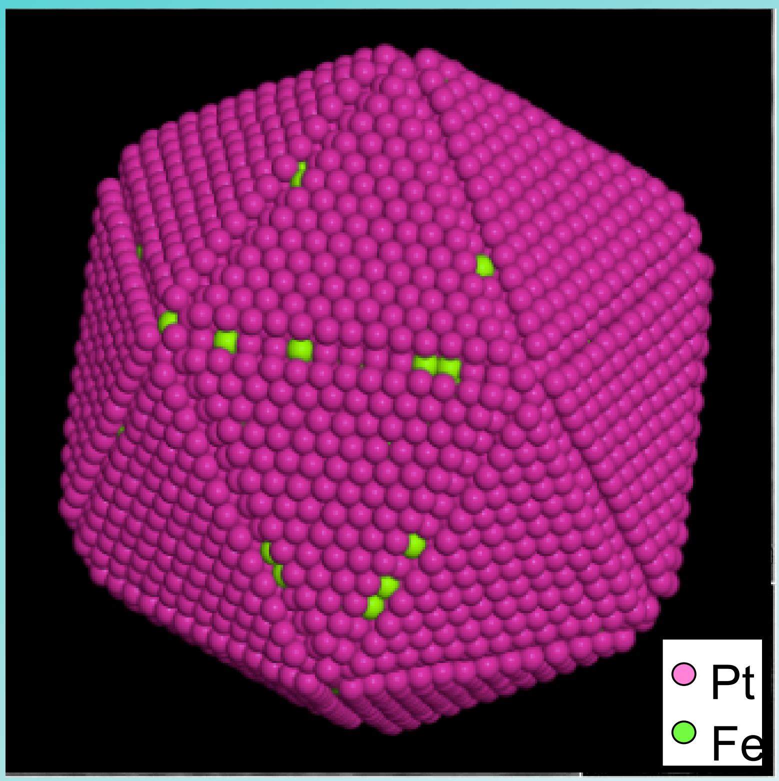
After annealing: decrease by factor

0.97 ± 2

theoret. value: 0.98 (bulk)

Layer resolved structural relaxation!

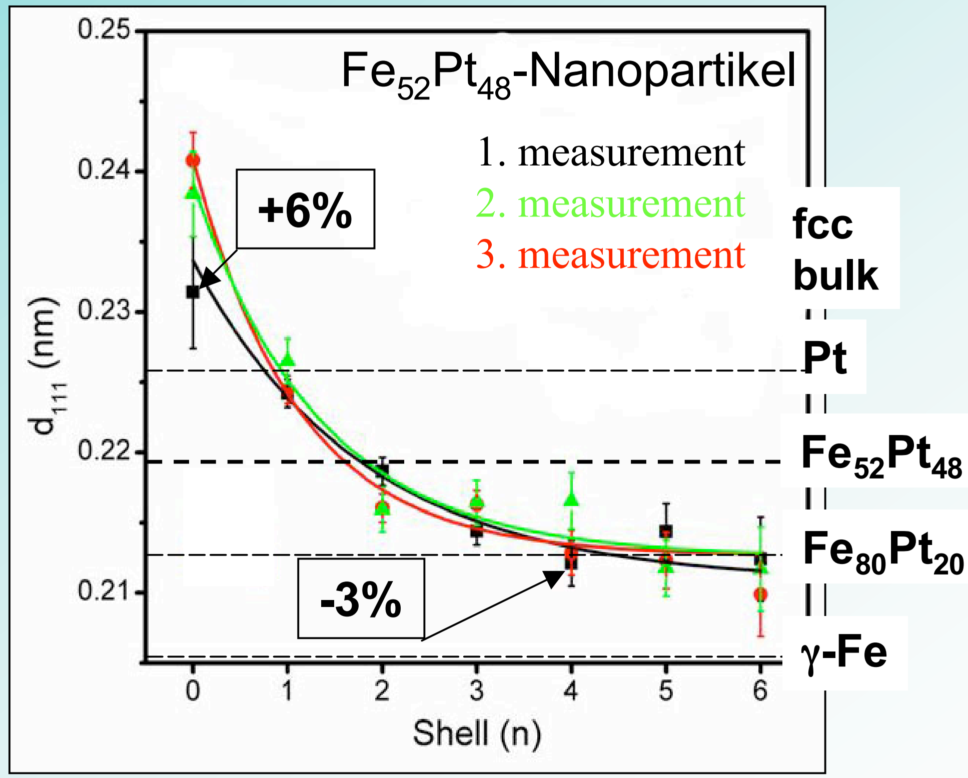
Layer resolved **magnetic** structure ?



Sub-Ångstrom-resolution of icosaeder FePt-nanoparticle: „focal series reconstruction"

Pt enrichment at surface

(Wang et al. submitted, NCEM, Berkeley)



„outside"→ „in "

Summary FePt

- Experiments on oxide/ligand free particles from colloidal suspensions
- No influence of organ. Liganden on surface oxidized measurable magnet. moments
- Struktural transformation in 6 nm FePt-Nanoparticles T > 800 K evidence by Pt - EXAFS-Oscillations
- Transformation associated with
  - Large enhancement of Fe-orbital moment (+330%)
  - Increase of coercive field by factor 8
  - Reductuin of induced Pt – orbital moment (-20%)

Core Shell Particles

„Co“ = CoO@Co

Synthesis

Structural Properties

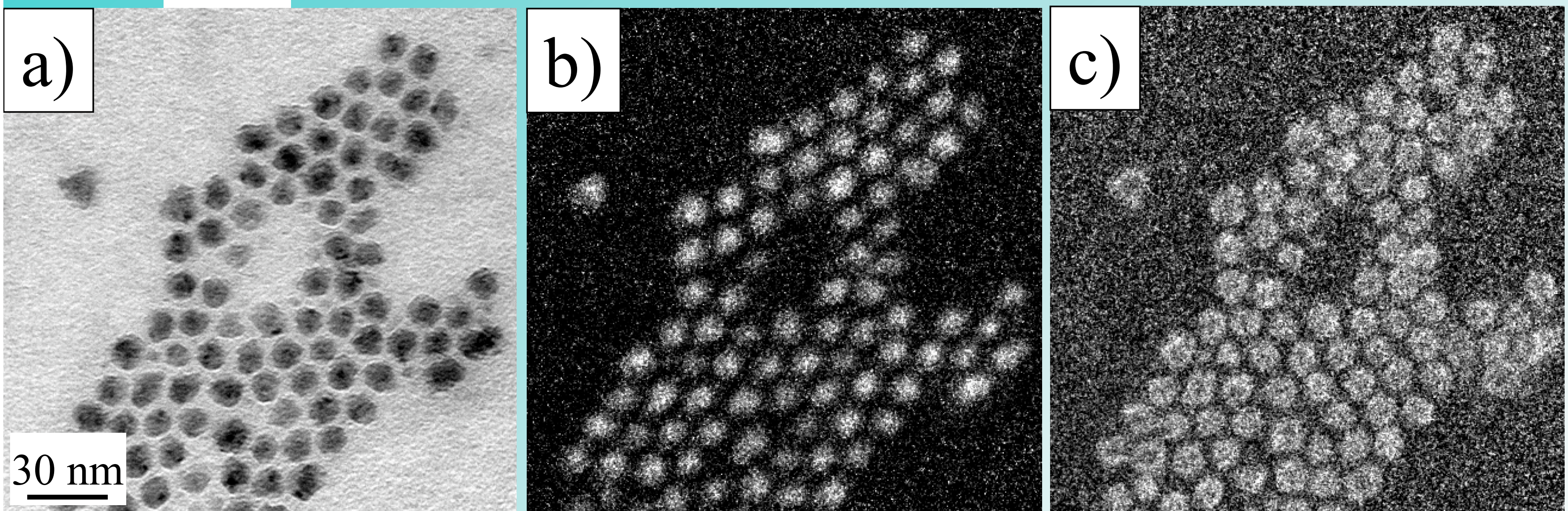
Chemical mapping

Some measurements with T. Radetic at (NCEM, Berkeley)

Chemical composition

of Co particles in a ligand shell

TEM | Co mapping | Oxygen mapping



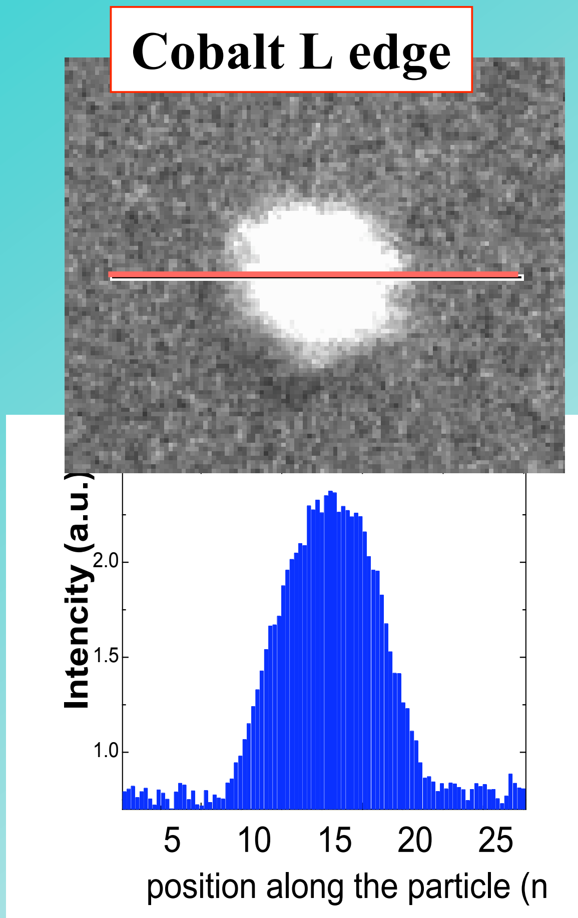
Cooperation with T. Radetic, U. Dahmen (NCEM, LBL Berkeley)

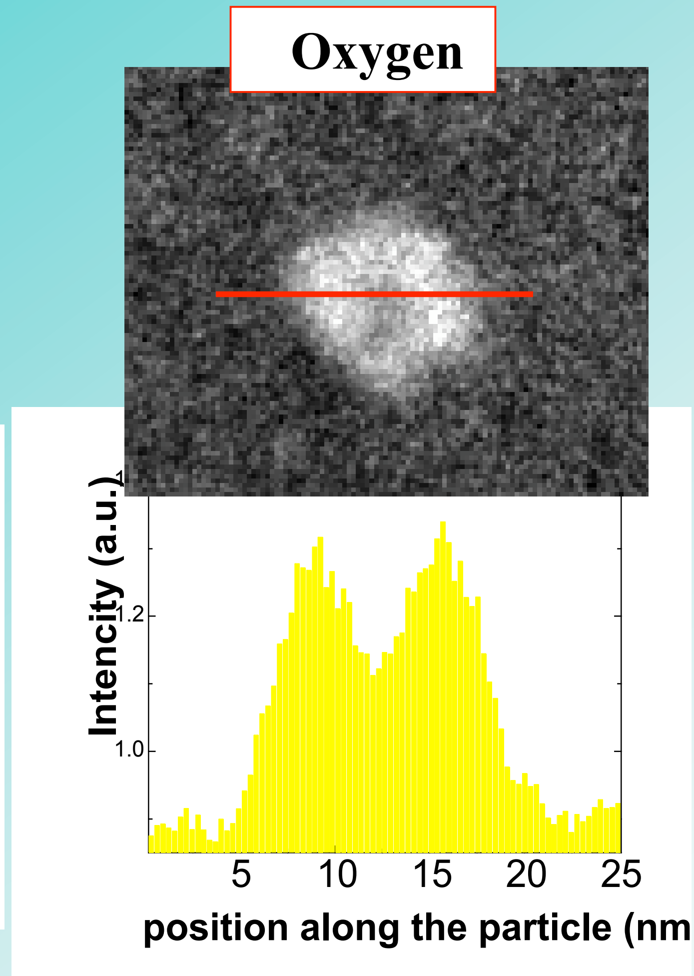
(a) TEM image of Co nanoparticles.
(b) Energy filtered images at the Co L_3-edge (~ 778 eV)
(c) Energy filtered images at the oxygen K-edge (~ 543 eV loss)

spatial resolution 0.28 nm
energy resolution 2.0 eV

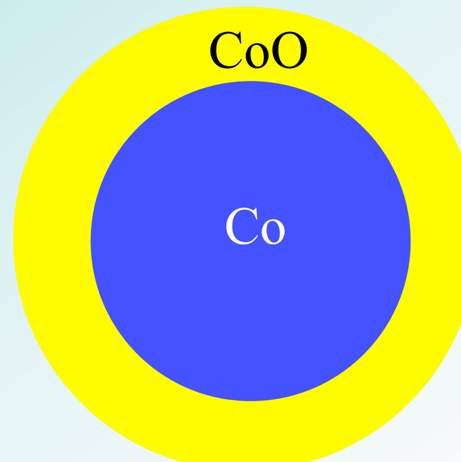
U. Wiedwald et al., J. Vac. Sci. Technol. A ***19*** *(2001) 1773*
M. Spasova et al., J. Magn. Magn. Mat. ***240*** *(2002) 40*

Distribution of Cobalt and Oxygen



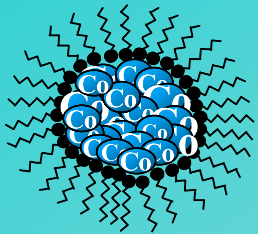


Core/shell particle



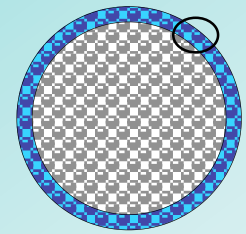
spherical with a Co core (∅ 7-8 nm) and a CoO shell (2 - 2.5 nm)

M. Spasova, et al., Mat. Res. Soc. Symp. Proc. 721 (2002) 195.



Magnetism

CoO@Co

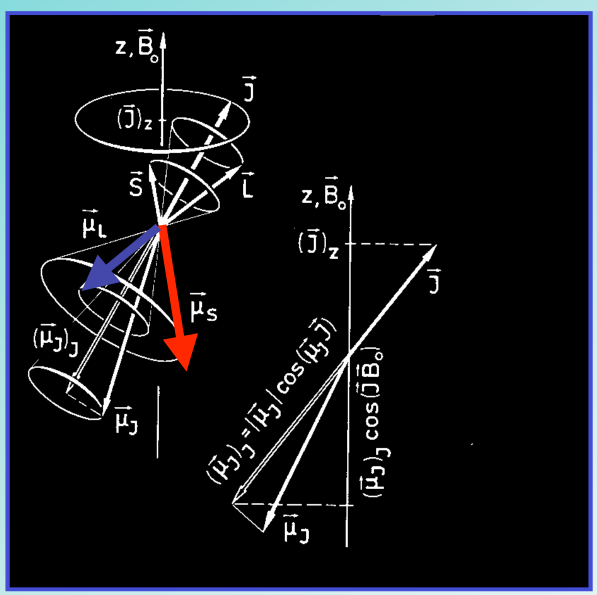


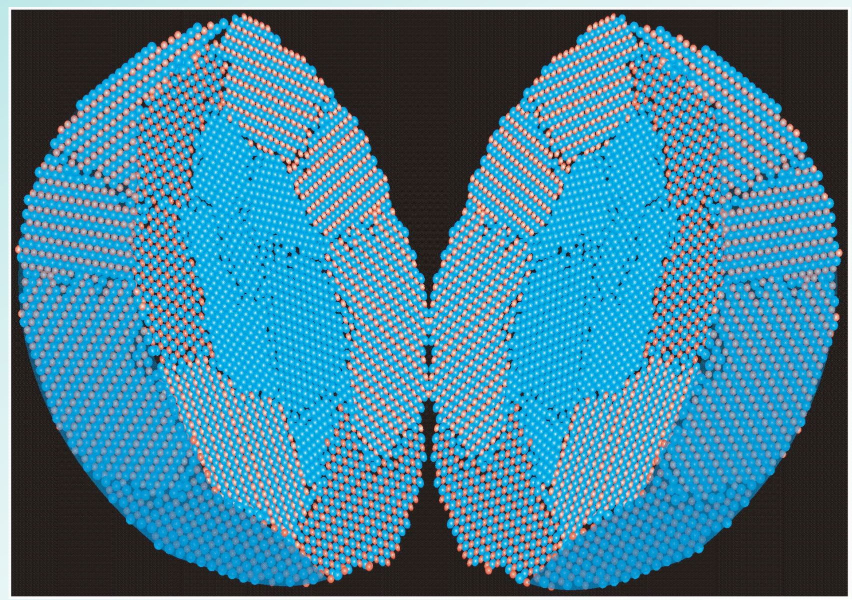
Magnetic Moment

Orbital Magnetism μ_L

Para/ferromagnetic resonance (FMR)

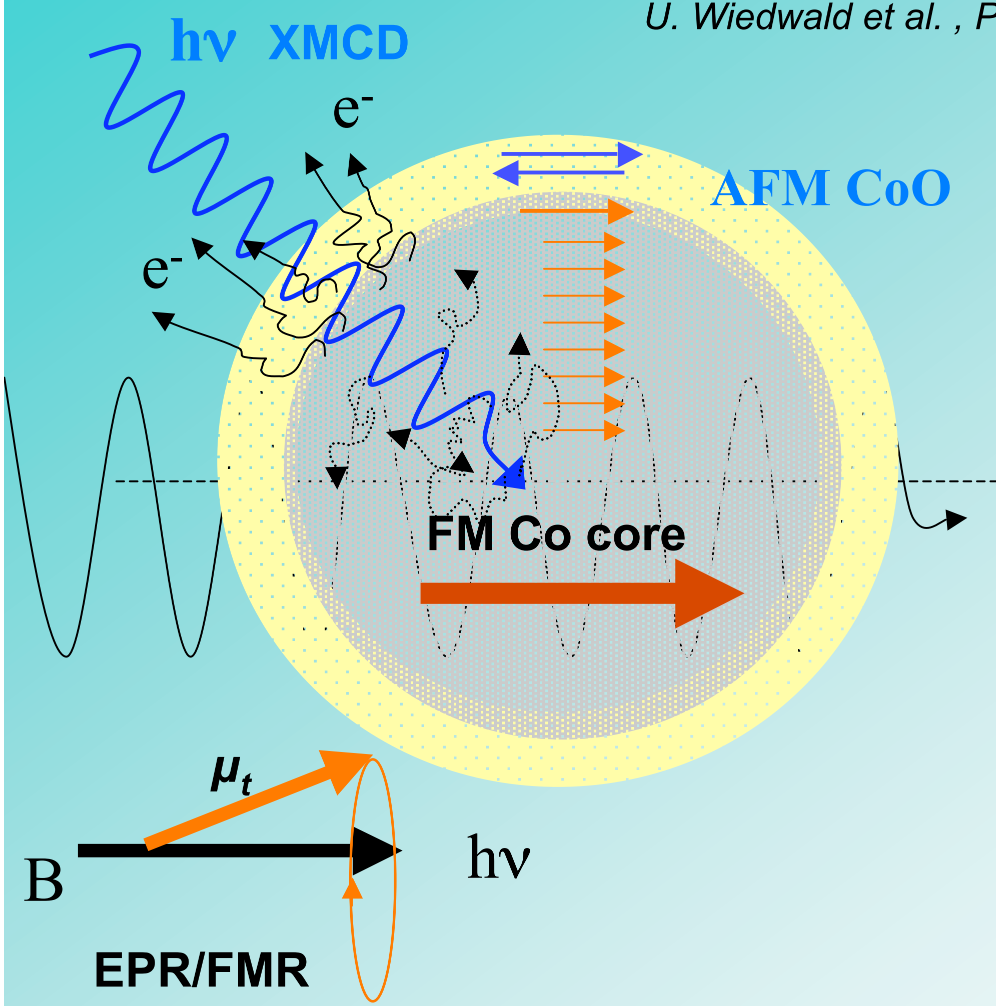
X-ray magnetic circular dichroism (XMCD)





11.4 nm Co XMCD and EPR/FMR

U. Wiedwald et al. , Phys. Rev. B ***68,*** 064424 (2003)



XMCD:

μ_L / μ_S = 0.24 ± 0.06

➔ 300 % enhanced!

fcc volume: μ_L/μ_S = 0.08

sampling depth:

XMCD : (app. 2 nm)

FMR (100 nm)

FMR:

g = 2.15 ± 0.005

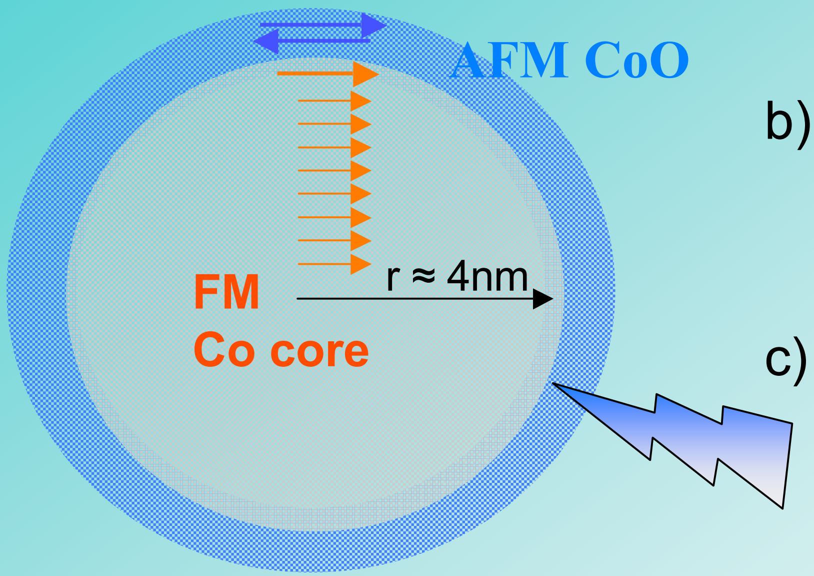
μ_L / μ_S = 0.075 = volume !

See also *M. Spasova et al, NATO Science Serie II. Mathematics, Physics and Chemistry, vol. 91 (2003) 173.*

RESULT

1-2 nm CoO @ 7- 9 nm Co core

Phys. Rev. B 68 (2003) 064424, Phase Transitions **78** (2005) 85–104



a) bulk like Co core

small μ_L/μ_S=0.08

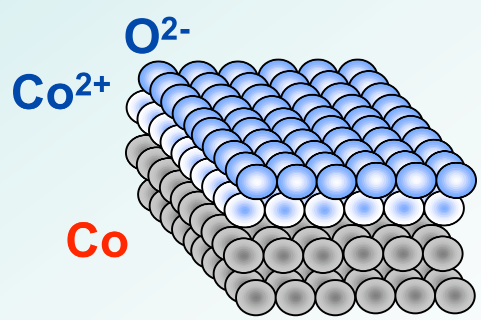
b) large orbital magnetism (Co^{2+}) at afm/fm interface

=> **„uncompensated moments“**

c) Model with app. 1 layer of interface moments at r = 4 nm

μ_L/μ_S=0.5 – 0.7, explains XMCD ratio

	Atom		bulk		
		μ_t (μ_B)	μ_t (μ_B)	μ_L (μ_B)	μ_L/μ_S
Co	$3d^7\ 4s^2$	6.62	1.72	0.13	0.08
Co^{2+}	$3d^7$	6.62	6.62	3	0.6-1

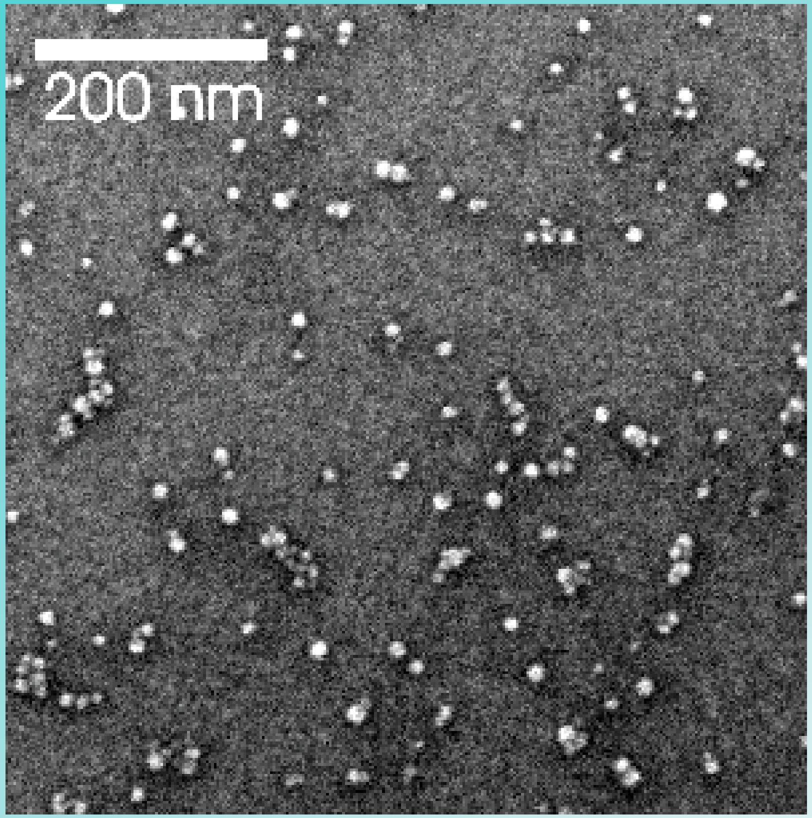


Surface Functionalization

some possibilities

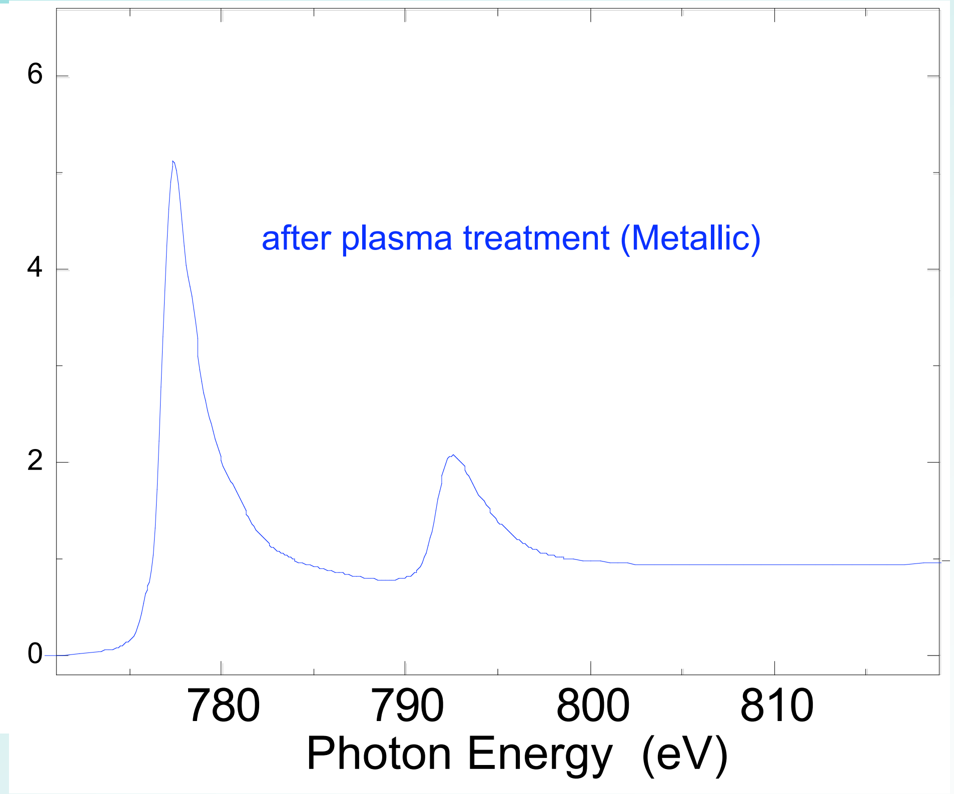
- Plasma cleaning
- Silica coating
- Exchange of ligands
  _ water based Fe_xPt_{1-x}
- Luminescent Magnetic Particles
- Layer-by-layer assembly

Plasma etching of CoO@Co



After plasma treatment

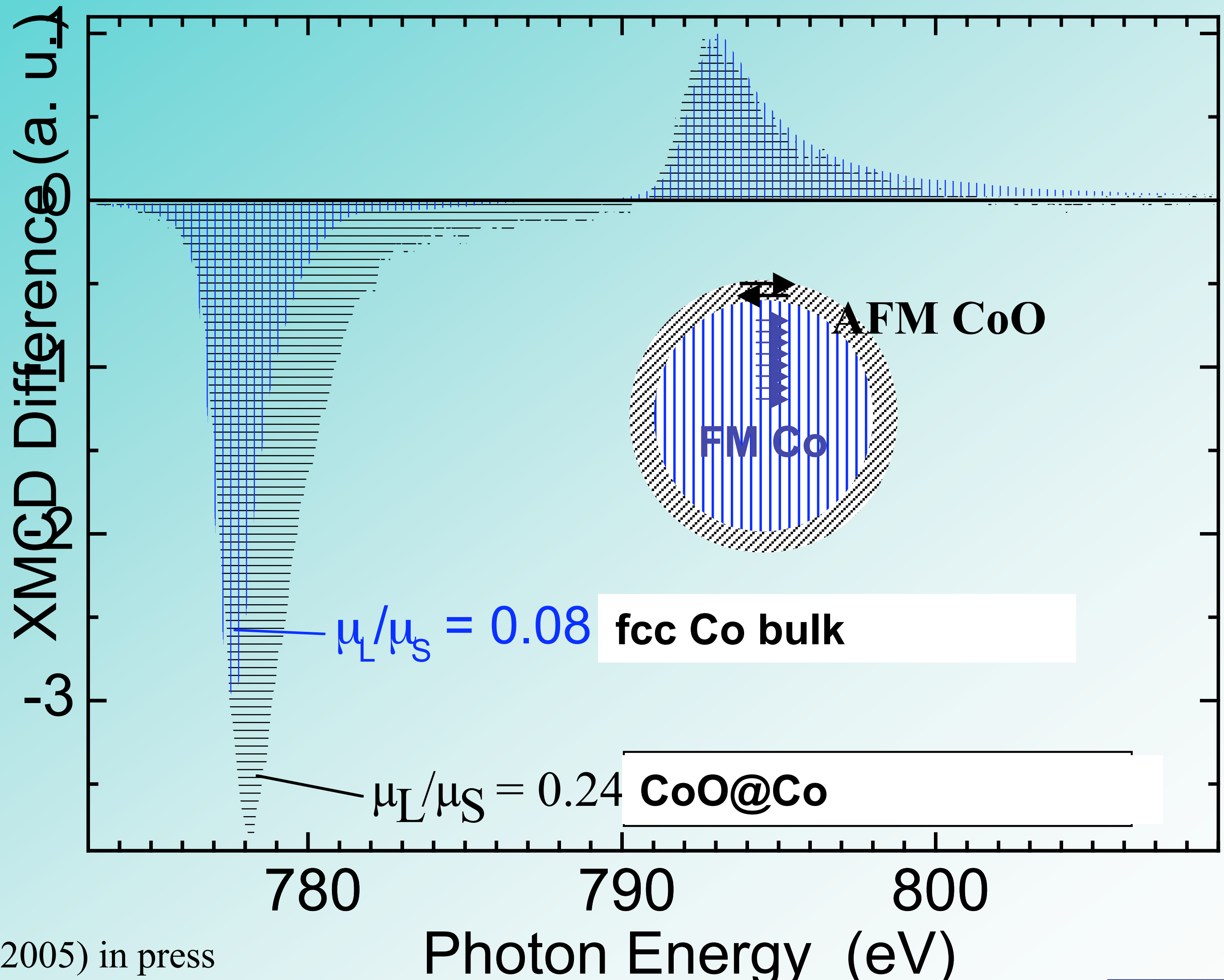
X-ray **A**bsorption **F**ine**S**tructure



no movement or agregation by plasma treatment

Magnetism after removal of oxygen

with H.-G. Boyen (Ulm) and K. Fauth (Würzburg, BESSY2)



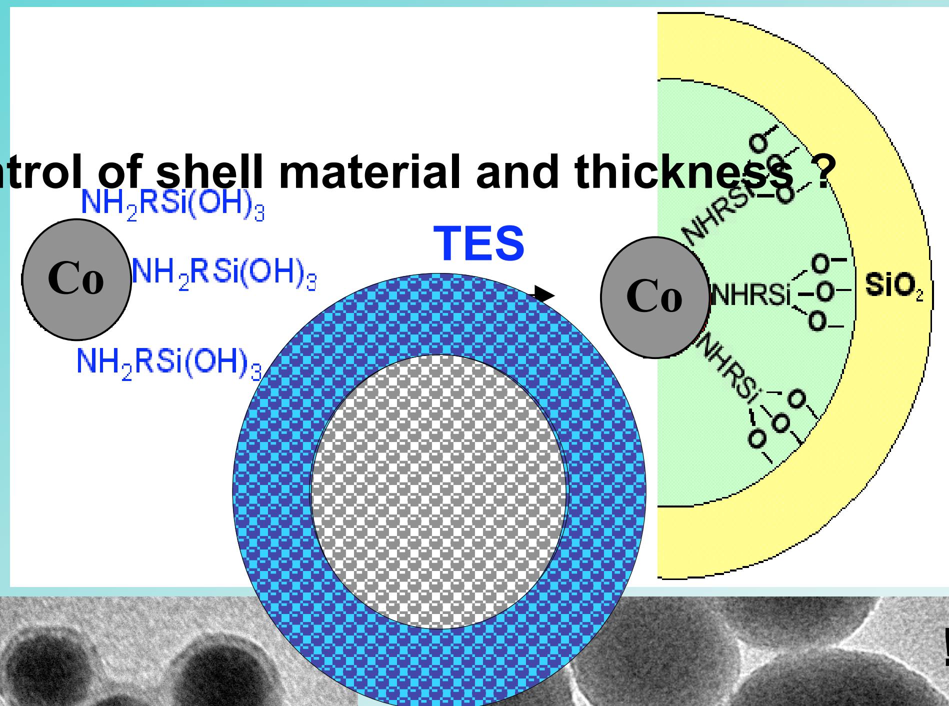
ChemPhysChem (2005) in press

Surface Functionalization
some possibilities

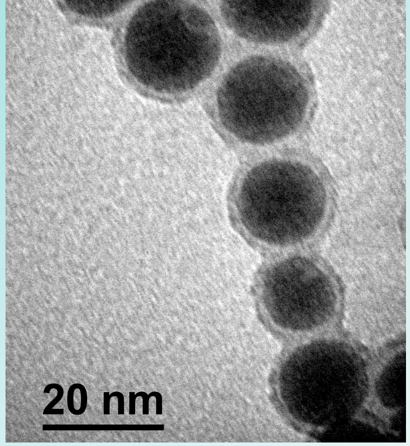
- Plasma cleaning
- **Silica coating**
- Exchange of ligands
  - _ water based Fe_xPt_{1-x}
- Luminescent Magnetic Particles
- Magnetic capsules

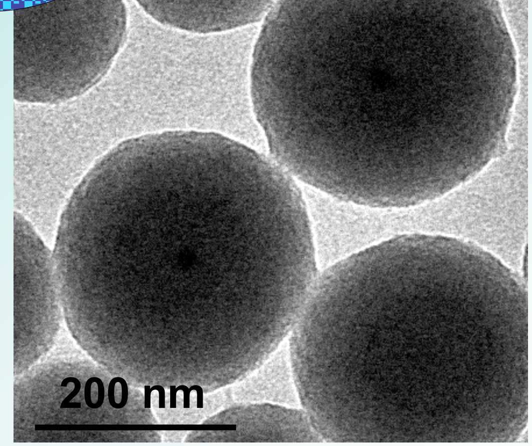
Silica coated Co Nanoparticles !

Control of shell material and thickness ?



Yes !





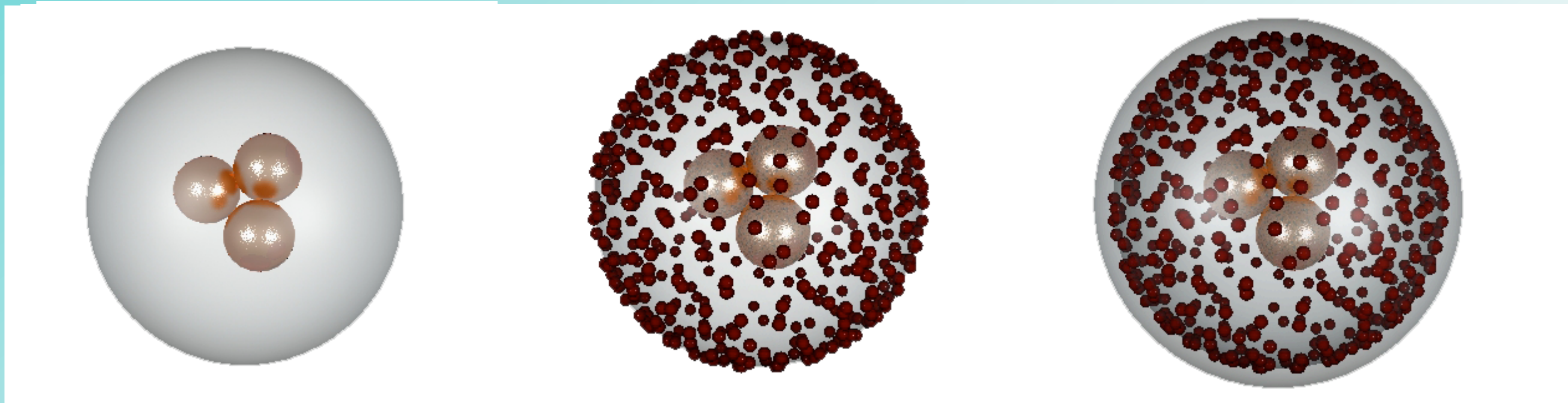
Tunable Shell !

Surface Functionalization
some possibilities

- Plasma cleaning
- **Silica coating**
- Exchange of ligands
  - _ water based Fe_xPt_{1-x}
- **Luminescent Magnetic Particles**
- Magnetic capsules

Luminescent Magnetic Particles

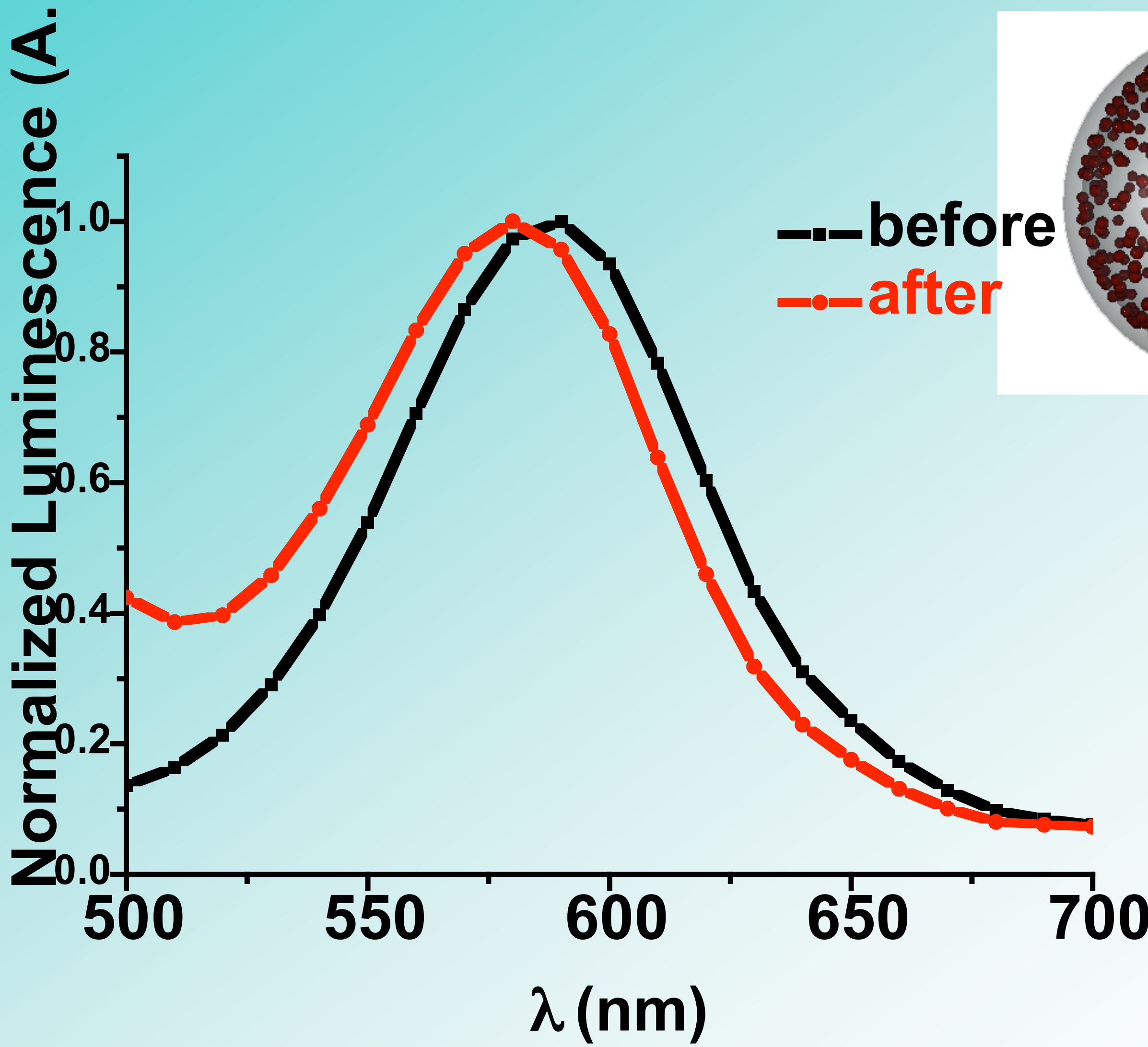
Magnetic core
Fe oxide particles in silica

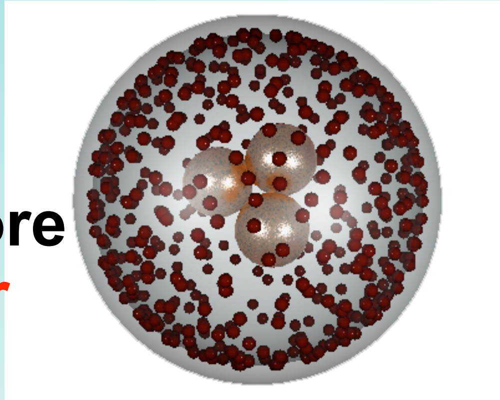


CdTe particles **Shell of Silica**

Adv. Funct, Mater. **15** (2005) 1036 ,
and Adv. Funct. Materials in press

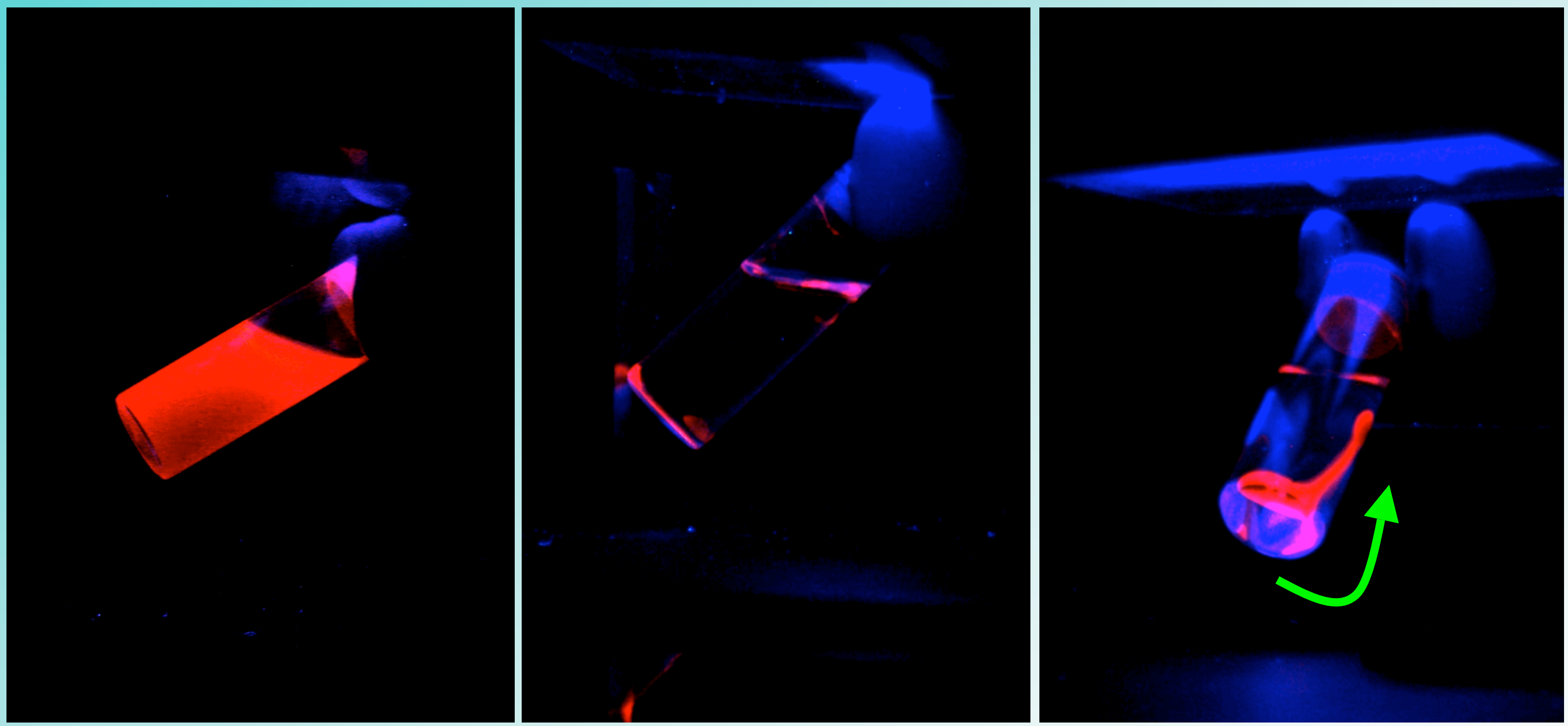
Luminescent Magnetic Particles





Magnetic Luminescent Spheres before and after deposition of an outer shell of SiO_2

Luminescent Magnetic Particles



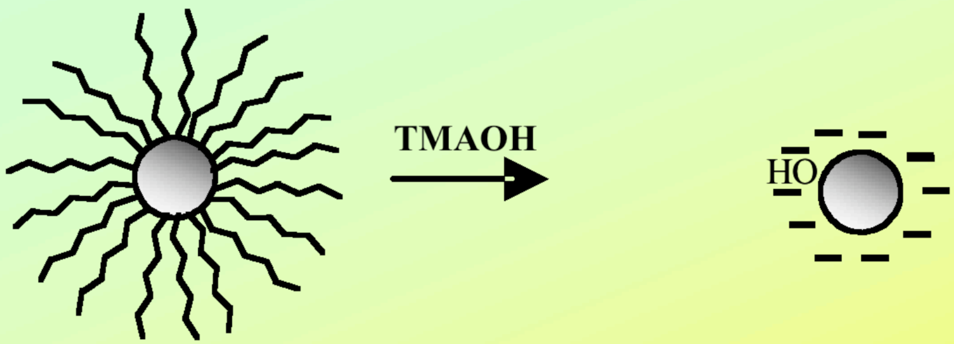
V. Salguerino-Maceira et al., Adv. Funct. Materials in press

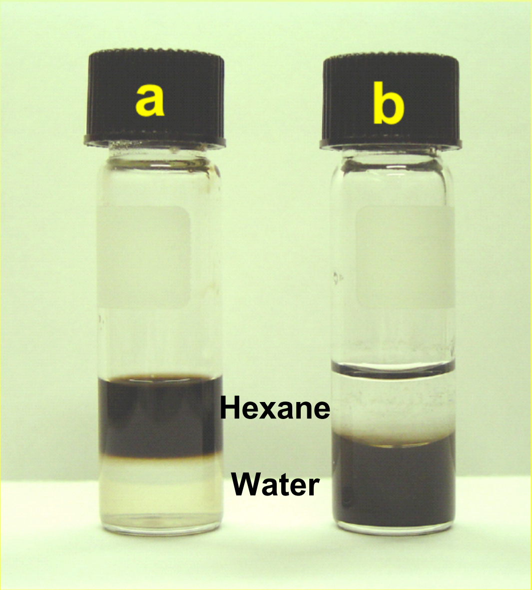
Surface Functionalization

some possibilities

- Plasma cleaning
- Silica coating
- **Exchange of ligands**
  _ water based Fe_xPt_{1-x}
- Magnetic capsules

Transfer of Fe_xPt_{1-x} Nanoparticles from hexane into water



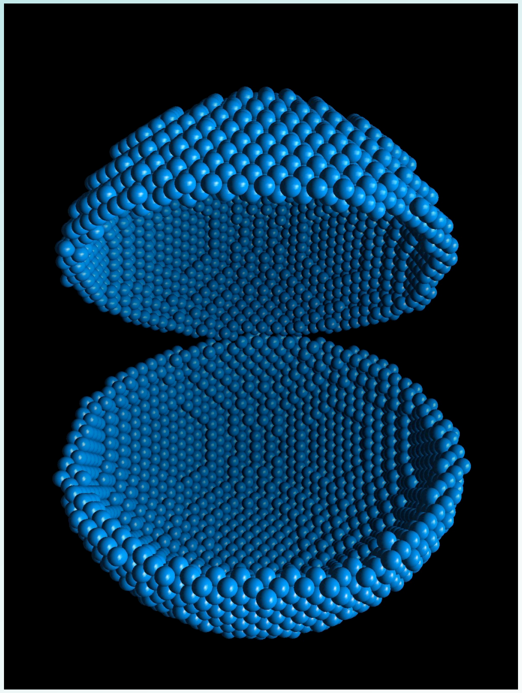


(a) Fe_xPt_{1-x} (Hexane) (b) Fe_xPt_{1-x} (Water)

V. Salgueiriño-Maceira, L. M. Liz-Marzán, M.F. , LANGMUIR **20** (2004) 6946

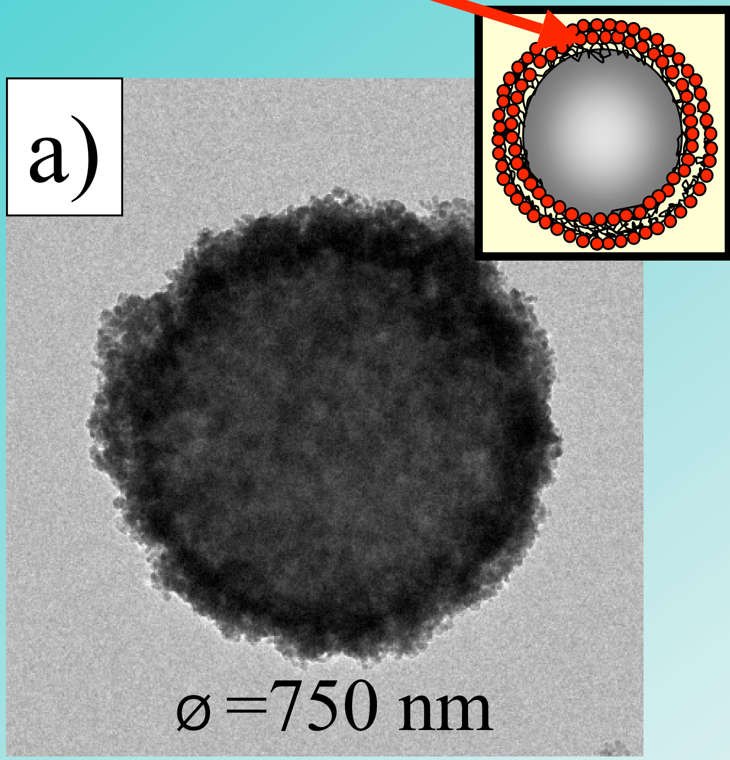
Surface Functionalization
some possibilities

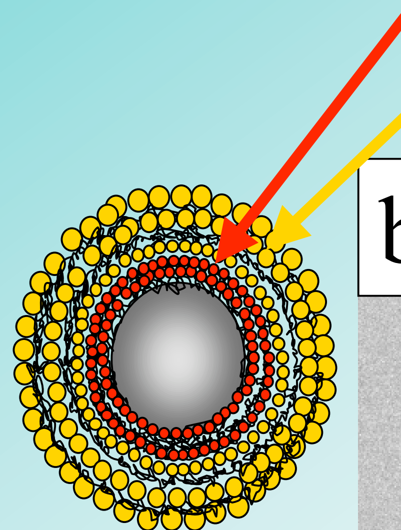
- Plasma cleaning
- Silica coating
- Exchange of ligands
  _ water based Fe_xPt_{1-x}
- Magnetic capsules

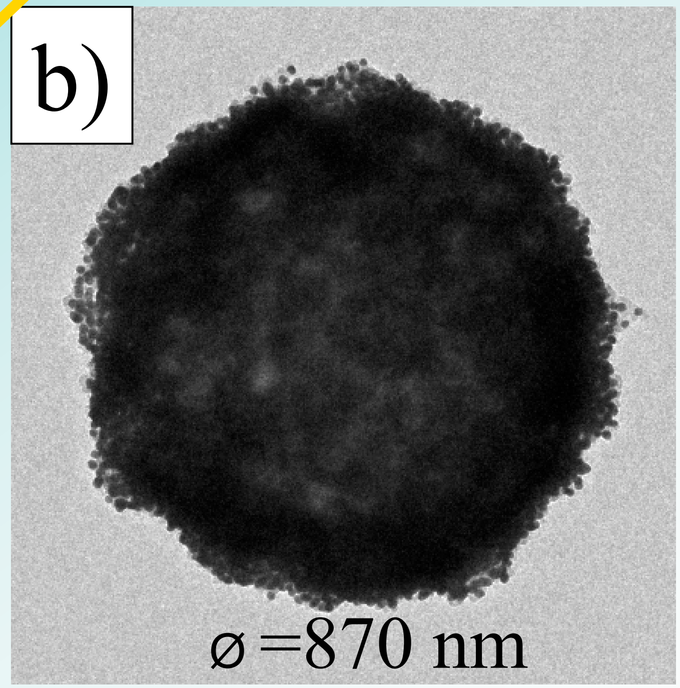


Multilayer-Composite Core-Shell Colloids

nanoparticles around a Latex core







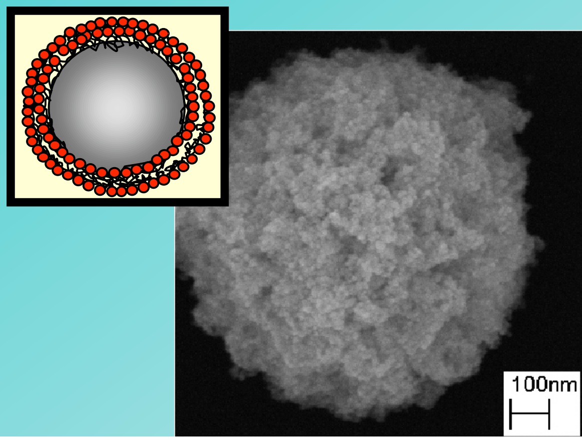
Au nanoparticles are encapsulated in a thin layer of silica.

J. Vac. Sci. Technol. A**21** (2003) 1515

J. Mater. Chem. **15** (2005) 2095

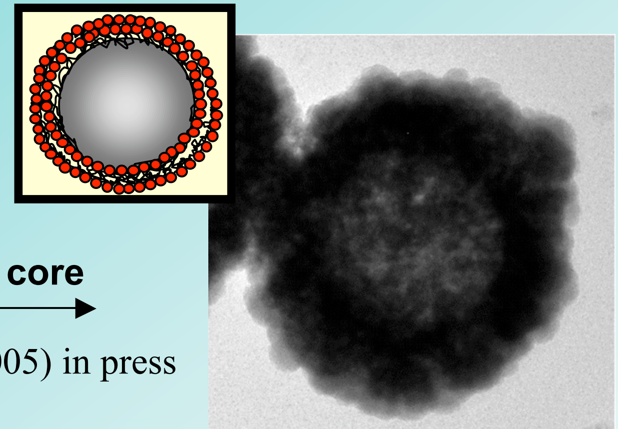
Magnetic Capsules (app. 900 nm)

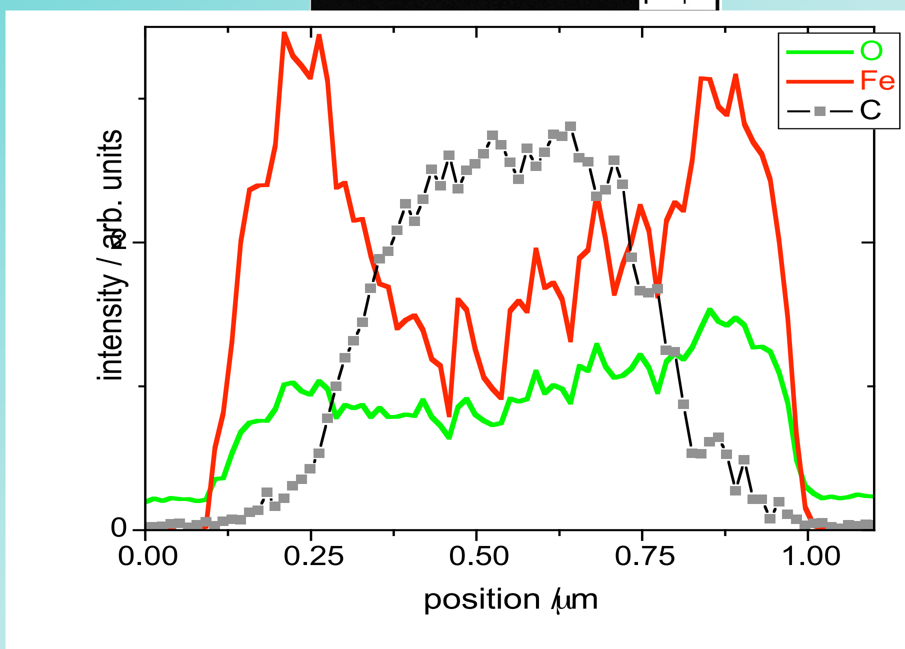
Latex sphere coated by Magnetite nanoparticles

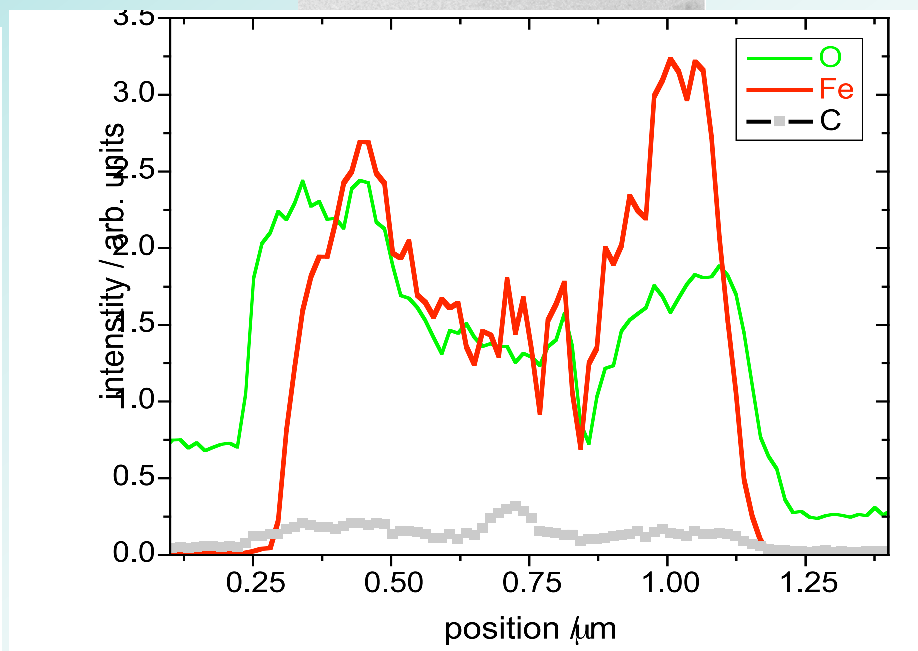


Removal of core

Phase Trans.(2005) in press





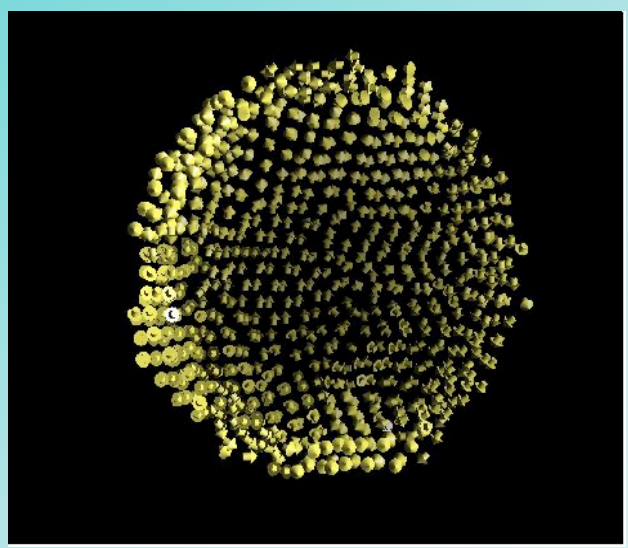


Dynamics of nanostructured magnetic hollow microspheres

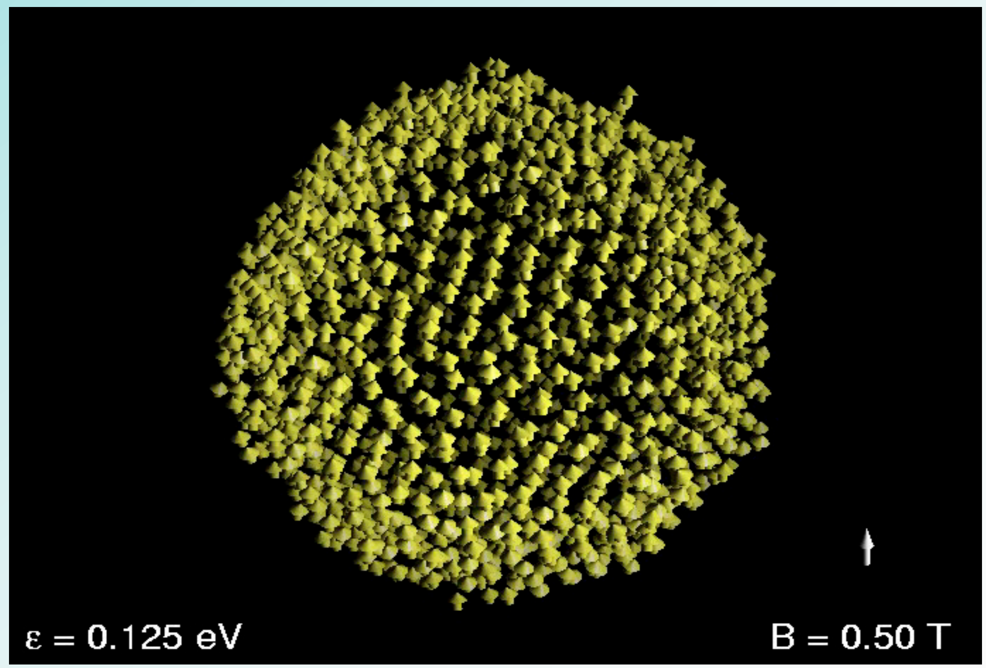
Simulation by M. E. Gruner and P.Entel

Fachbereich Physik, Universität Duisburg-Essen, Campus Duisburg

Rotating magnetic field B



Simulation:
M. E. Gruner and P. Entel



Experiment:
A. Schlacher, M. Spasova and M. Farle

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U. Wiedwald
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J. Lindner
M. Spasova
Z. Frait (Prague)

HRTEM, TEM, SEM, EDX

M. Spasova C. Kisielowski (NCEM)
H. Zähres
O. Dmitrieva
S. Stappert -> *(Sachtleben Chemie)*
B. Stahlmecke

XAS , XMCD

C. Antoniak, U. Wiedwald
J. Lindner, M. Acet
K. Fauth (Würzburg)
H.-G. Boyen (Ulm)
A. Rogalev , F. Wilhelm (ESRF)

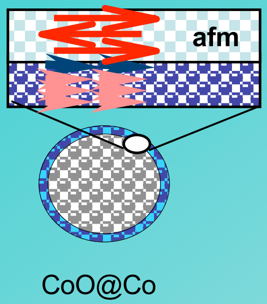
Organometallic Synthesis

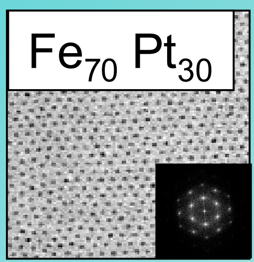
V. Salguerino-Maceira
Shouheng Sun (IBM, Brown Univ.)
M. Hilgendorff, M. Giersig (CAESAR)
L. Liz-Marzan (Vigo,Spain)

Magnetic Capsules

A. Schlachter
M. Spasova

supported by European Union RTN-networks and Deutsche Forschungsgemeinschaft, SFB445

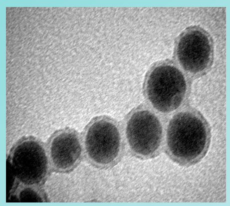


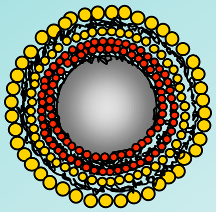


Summary:
Magnetsim of Colloidal particles

- **control removal of organic ligands and oxides**
- **structure dependent enhancement μ_L / μ_S in FePt ($L1_0$)**
- **orbital magnetic moment at the interface Co/CoO**

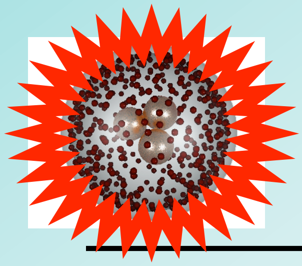
  ⇔ *uncompensated magnetic moments*





⇒ ***No unusual, large magnetic effects***

> 3 nm (≈ 1400 atoms)



Hybrid, luminescent Nanoparticles

http:// agfarle.uni-duisburg.de

All Nanoparticles are magnetic !

Nijmegen High Field Magnet Laboratory