WDS 2015

Mössbauer Spectrometry of Magnetic Iron-Oxide–Based Nanoparticles

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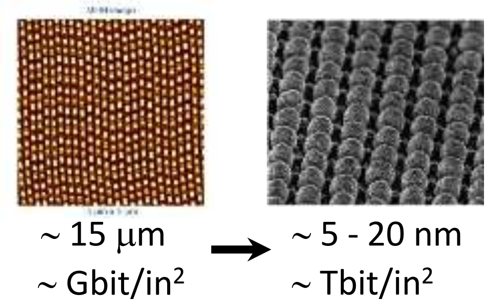
3rd of June 2015 Prague

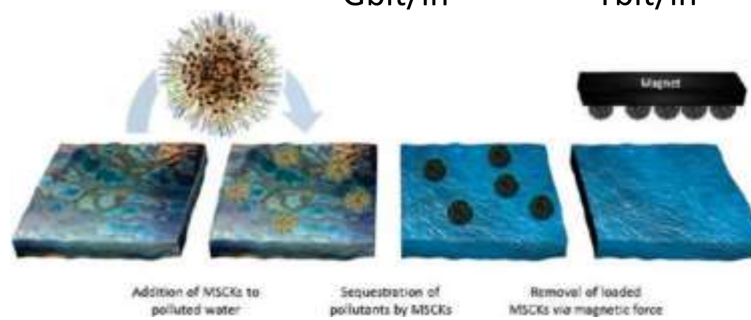
Outline

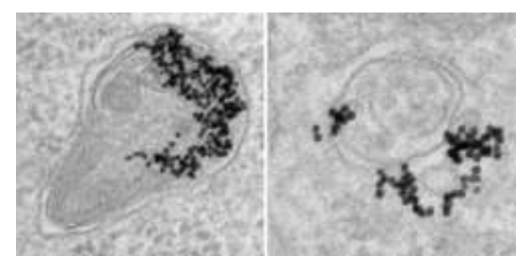
1) Motivation for the study
2) Search for suitable materials
3) Mössbauer spectrometry as a tool to investigate cationic distribution over the crystalographic sites
4) Preparation of ε-phase of ferric oxide Fe_2O_3
5) Substituted ε-$M_xFe_{2-x}O_3$
6) Substituted spinels $M_xFe_{3-x}O_4$
7) Conclusions

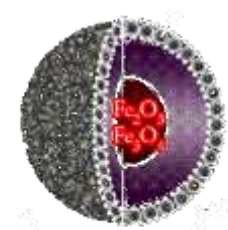
Perspective applications of iron-oxide-based nanoparticles

- Electronics:
  - high-density magnetic data storage
  - mm-wave absorbers for high-speed WiFi
  - production of hydrogen gas
  - photovoltaics
  - gas sensors
- Catalysis
- Cleaning of polluted water (ferrofluids)
- Nanomedicine: *targetting, diagnosis, therapy*
  - contrast increase agents for MRI diagnostic (in vivo)
  - hyperthermia of tumors (in vivo)
  - targeted drug delivery, tracking and release (in vivo)
  - cell labeling and separation (in vitro)
  - every application request a material of specific properties





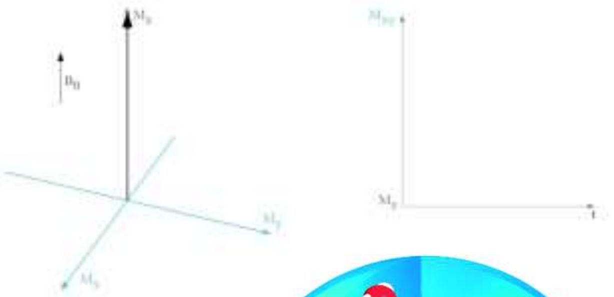


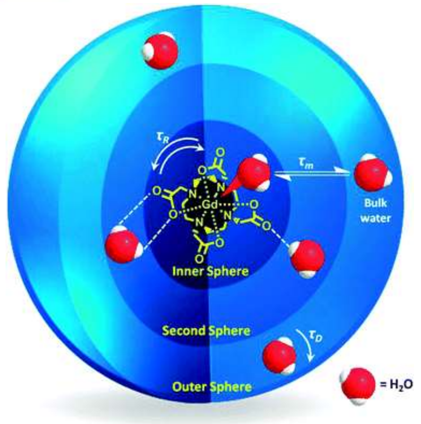


Nanomedical applications – MRI

Basic concept of MRI:

- T_1 spin-lattice relaxation $\quad M_z = M_0 . e^{-\frac{t}{T_1}}$
- T_2 spin-spin relaxation $\quad M_{xy} = M_{xy0} . e^{-\frac{t}{T_2}}$
- τ (pulse of B_{rf})«T_1, T_2 -> NMR signal
- pulse sequences -> T_1, T_2 of ^{1}H of water present in tissues
- various tissues differs in T_1, T_2 -> contrast in MR image
- contrast agents (CA) affect T_1, T_2 by magnetic dipol interaction of ^{1}H spins with magnetization of CA

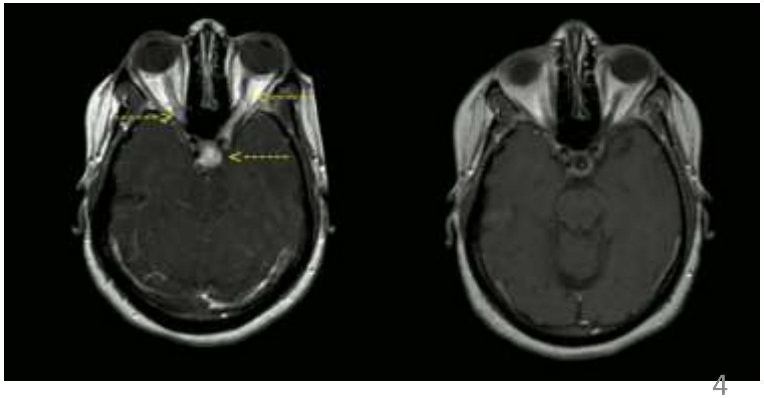




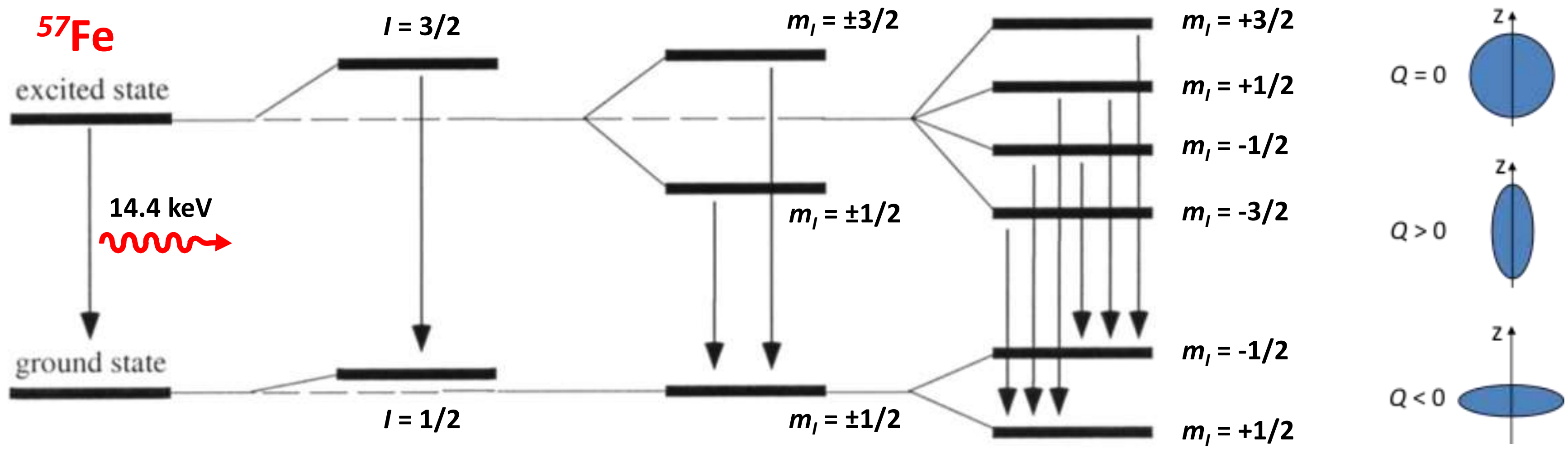
$$r_{2,MAR} = \frac{R_{2,MAR}}{[\mathrm{Fe}]} = \frac{a v_{mat} r^2 \mu_0^2 \gamma^2 M^2}{9D}$$

General requirements for nanoparticles:

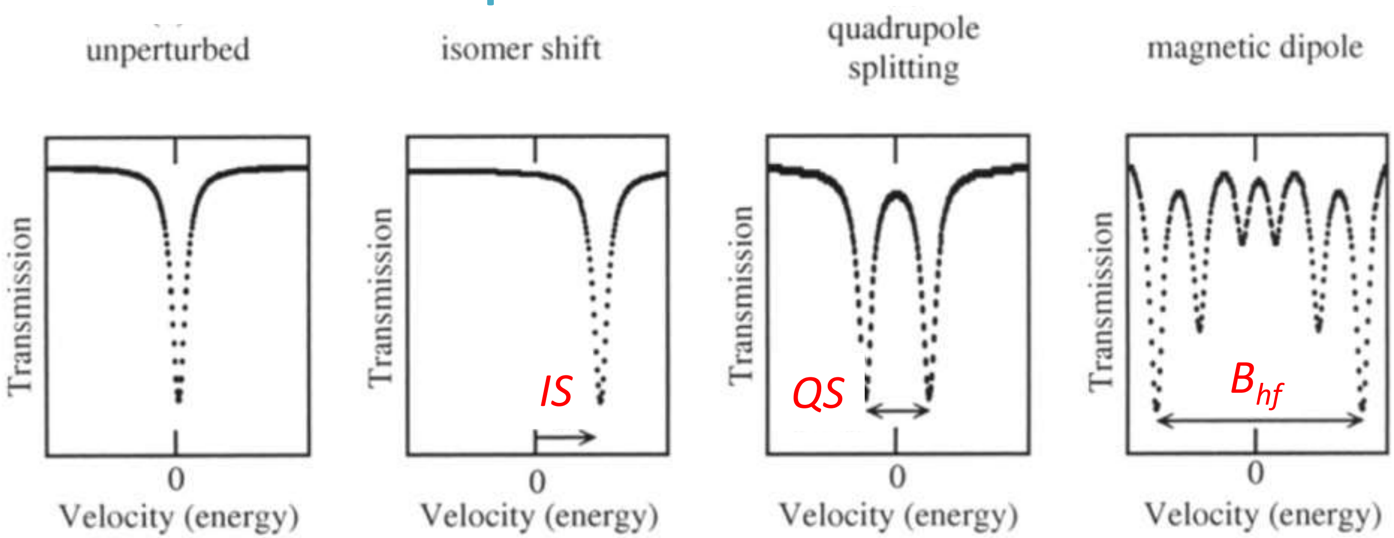
- particle size (20-60 nm)
- narrow distribution
- reduced tendency to clustering
- stability in aqueous solution
- low toxicity, optimized biodegrability

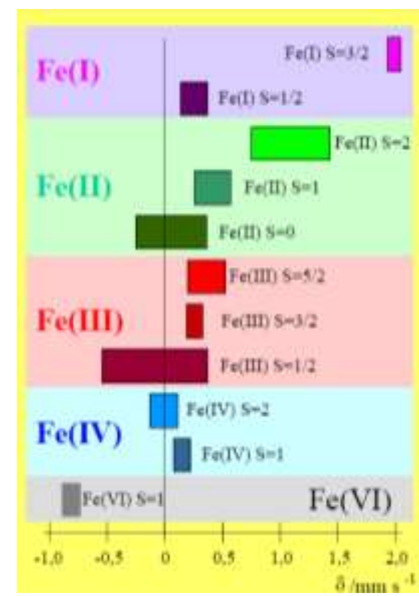


Mössbauer spectroscopy (MS)



MS parameters:





Nanoparticles of ε-phase Fe_2O_3

Methods of preparation:

- hydrothermal method
- microemulsion method
- sol-gel synthesis followed by heat treatment (HT)
- impregnation of mesoporous amorphous silica matrix (pores 5-7 nm) by nitrates $Fe(NO_3)_3$ + HT

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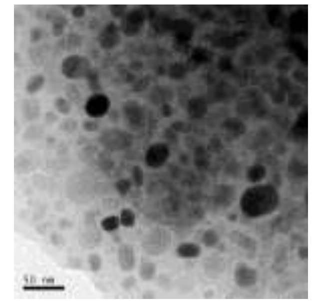
sol-gel



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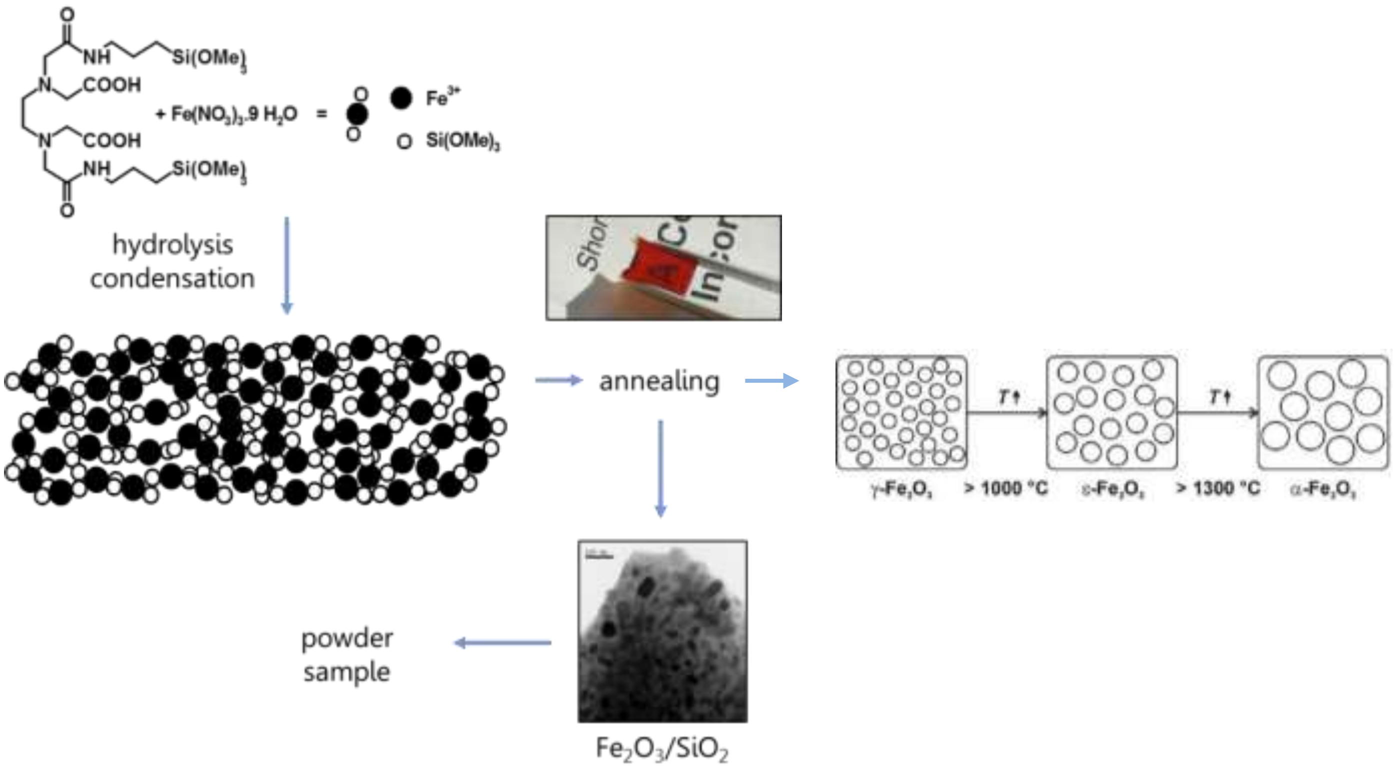
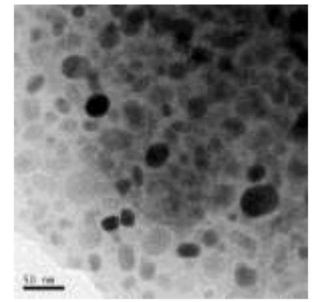


Nanoparticles of *ε*-phase Fe_2O_3

sol-gel



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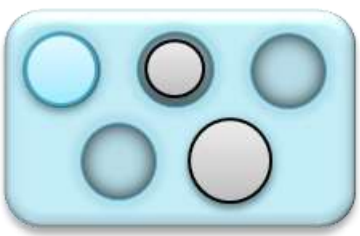

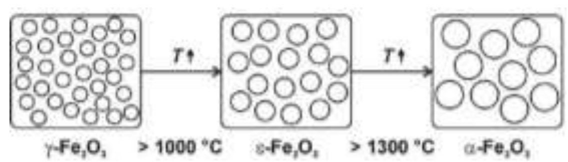

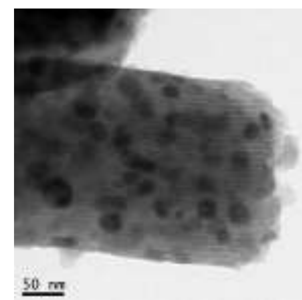

impregnation

Nanoparticles of ε-phase Fe_2O_3

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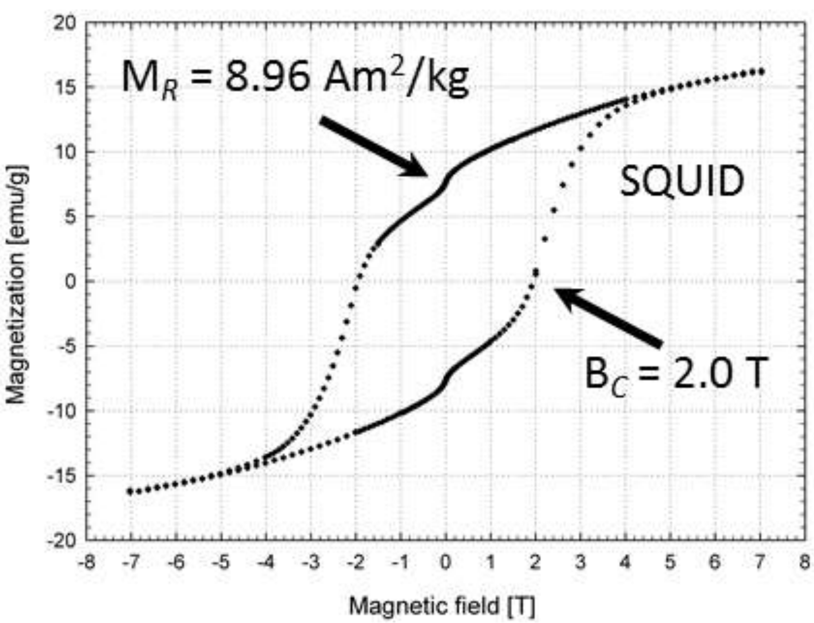
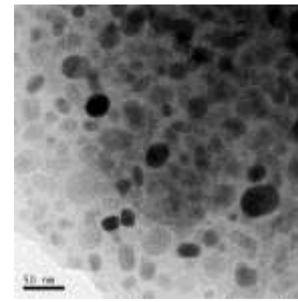
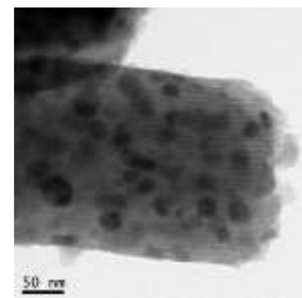
- sol-gel synthesis followed by heat treatment (HT)
- impregnation of mesoporous amorphous silica matrix (pores 5-7 nm) by nitrates $Fe(NO_3)_3$ + HT



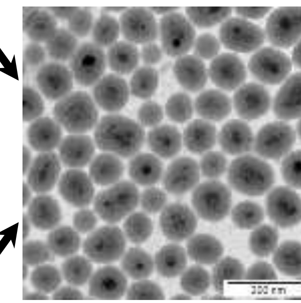
Increase of magnetization by substitutions of Fe by diamagnetic iont.

sol-gel





impregnation



ε-Fe_2O_3 coated in SiO_2

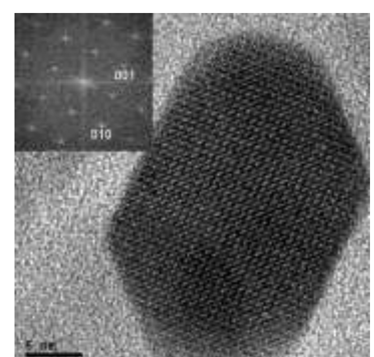
Separation of NP:

Optimal thickness?

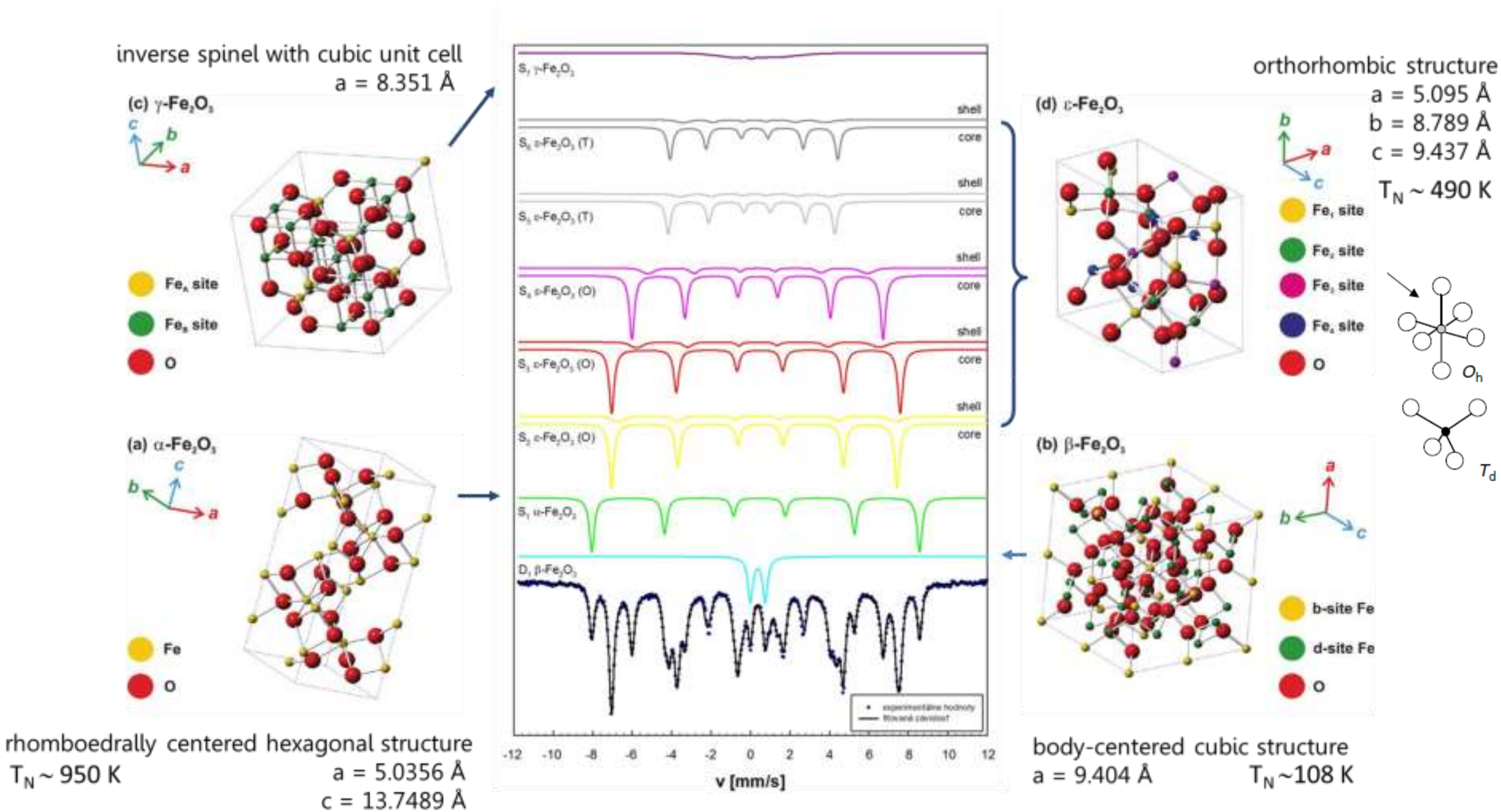
Restriction of agglomeration?

Effect on relaxivity?

HRTEM of ε-Fe_2O_3 nanoparticle



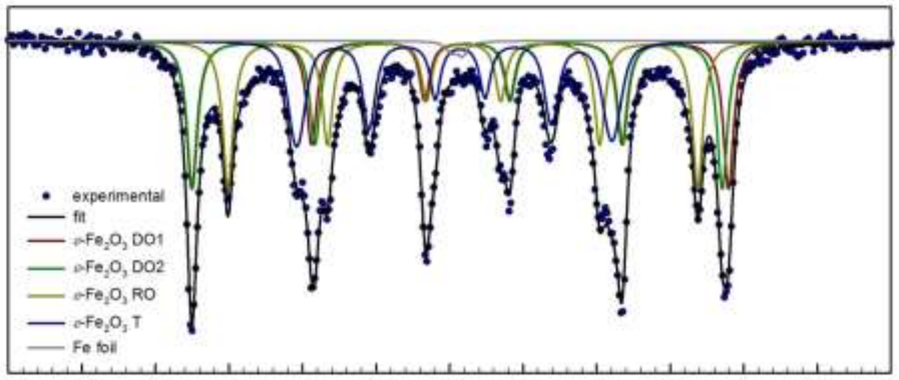
MS of ε-Fe_2O_3 prepared by sol-gel method



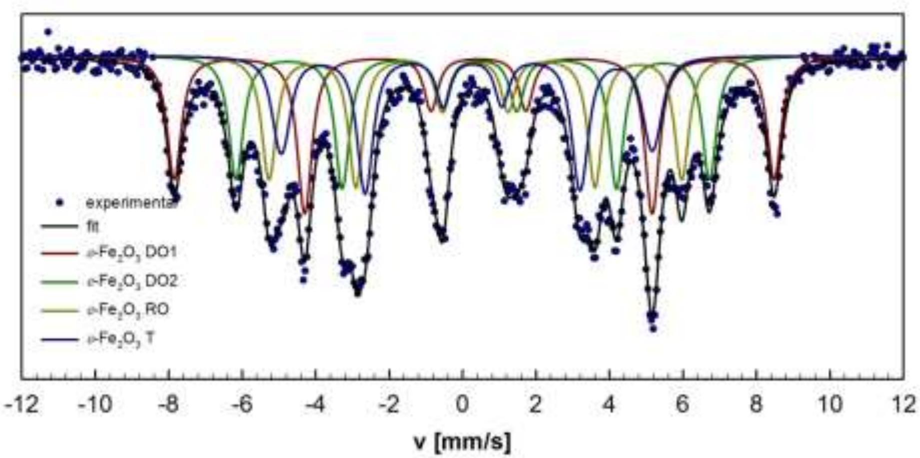
- using amorphous silica matrix was obtained max **92 % ε-Fe_2O_3**
- restraint of spacial growth, prevention of agglomeration and formation of hematite
- other factors - iron concentration and content of organics in precursor, annealing temperature

MS of pure ε-Fe_2O_3 prepared by impregnation

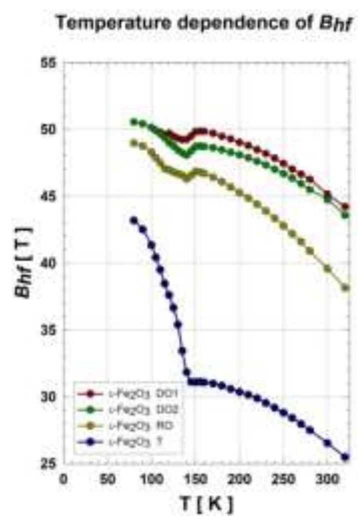
ε-Fe_2O_3 nanoparticles (T=300 K, B=0 T)

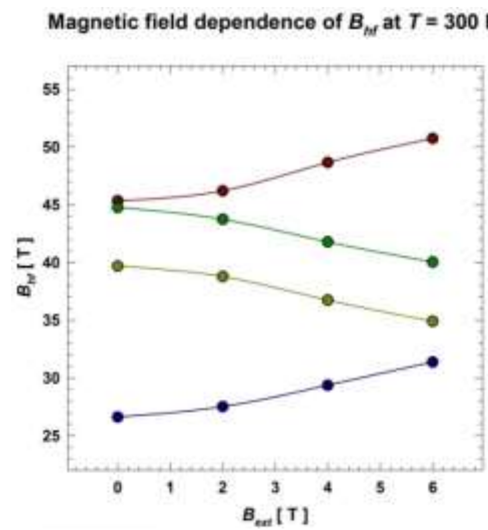


ε-Fe_2O_3 nanoparticles (T=300 K, B=6 T)



- separation of spectral components in Mössbauer spectra under the influence of an external field



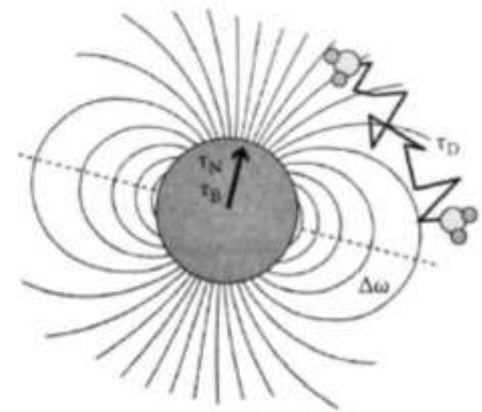


- using silica matrix with tube-like pores was obtained **99 % ε-Fe_2O_3**
- restraint of spacial growth to one direction crucial for formation of ε-Fe_2O_3, no β-Fe_2O_3 and minimal content of α-Fe_2O_3

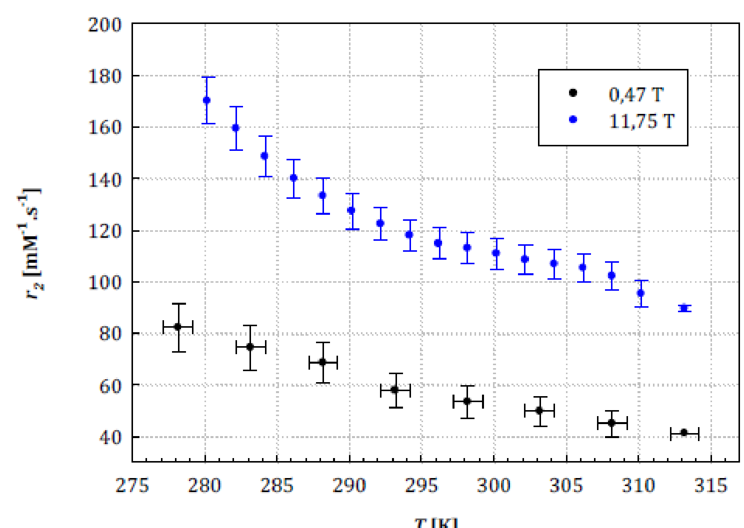
MS of pure ε-Fe_2O_3 prepared by impregnation

- ferrimagnetic nanoparticle in blocked state... static M
- Motional Averaging Regime (MAR), also outer-sphere regime

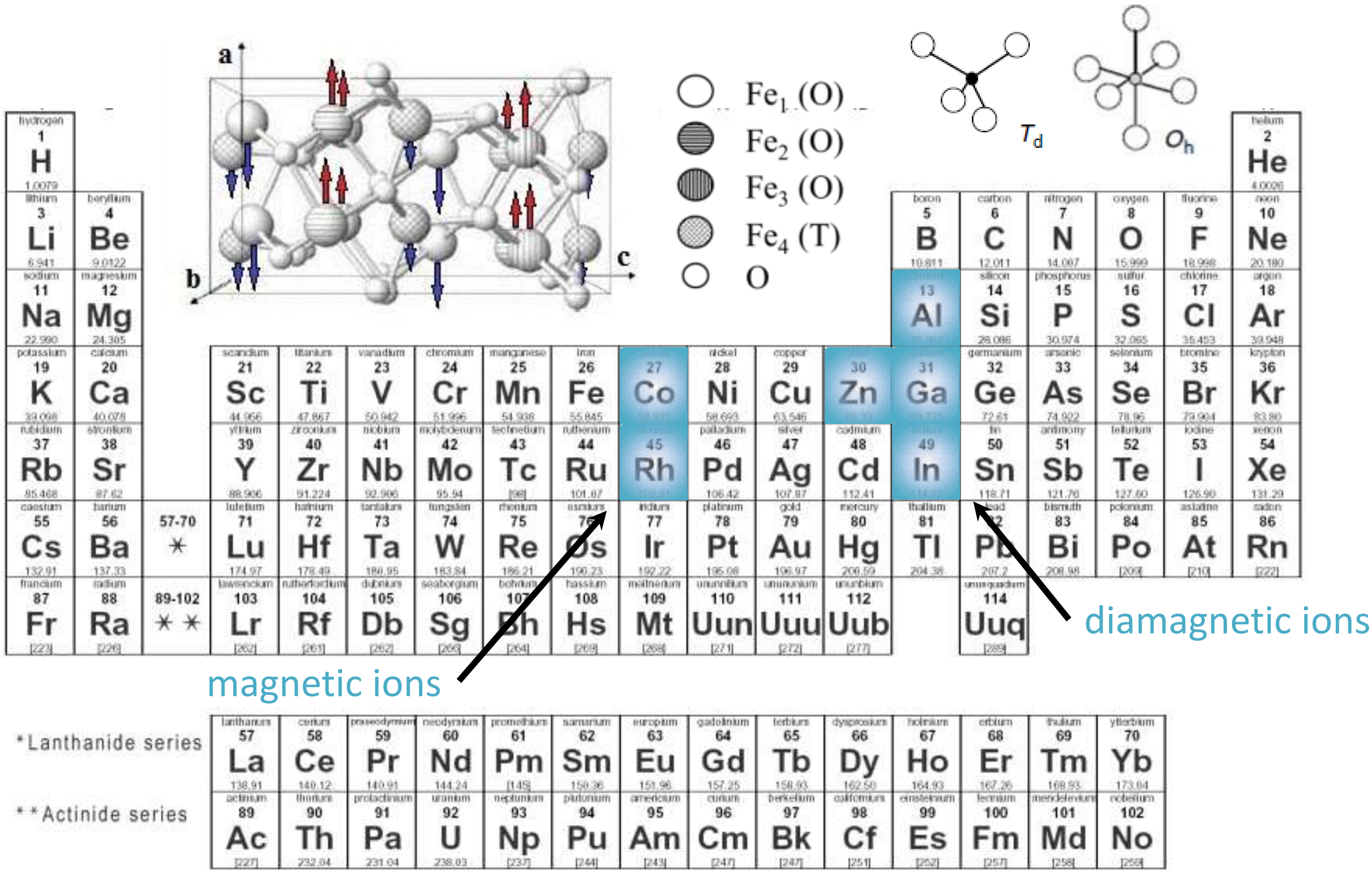
$$r_{2,MAR} = \frac{R_{2,MAR}}{[\mathrm{Fe}]} = \frac{a v_{mat} r^2 \mu_0^2 \gamma^2 M^2}{9D}$$



- coated ε-Fe_2O_3 for T_2-weighted MRI
- $r_2(\varepsilon$-$Fe_2O_3)$ – 2 to 5 times smaller than r_2 of commercial superparamagnetic γ-Fe_2O_3 or Fe_3O_4 due to lower magnetization in external fields
- can be improved by substitutions

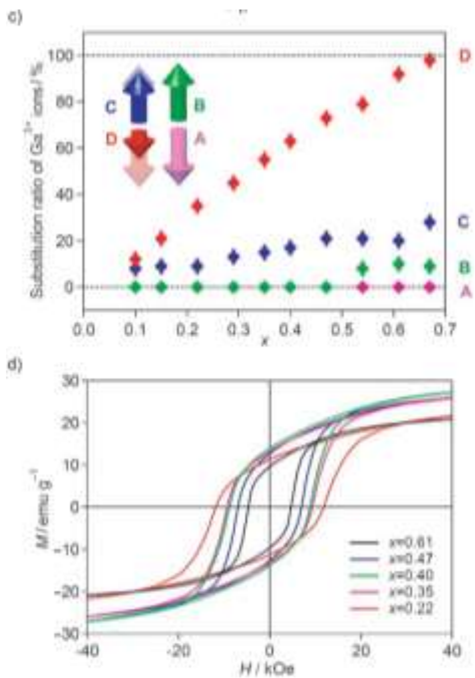


Substituted ε-$M_xFe_{2-x}O_3$ for MRI



Substituted ε-$M_xFe_{2-x}O_3$ for MRI

- Ga, Al substitutions –> magnetization increased 2 to 4 times, modification of T_C in the range from 0 to 495 K
- Ga, Al, In substitutions –> increase of H_C
- distribution of ions over the crystallographic positions differs from that for bulk samples
- studies only for nanoparticles prepared by sol-gel method (ε-phase stabilized by Ba^{2+} and Ca^{2+} ions)



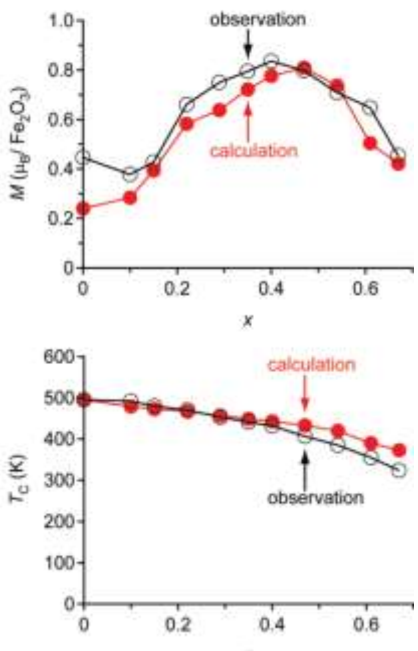
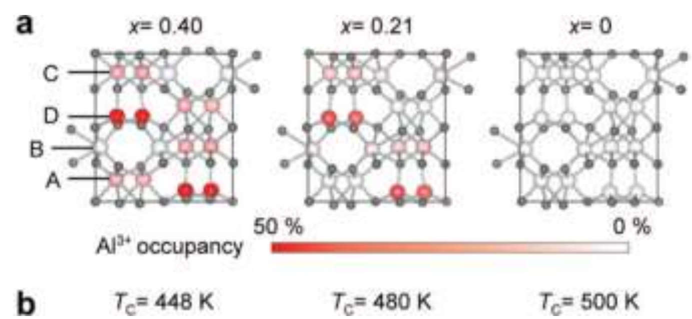


Table 2. Magnetic Properties of ε-$Al_xFe_{2-x}O_3$

x	T_C/K	H_c/kOe[a]	M_s/emu g^{-1}[a]
0	500	22.5	14.9
0.06	496	19.1	15.1
0.09	490	17.5	14.6
0.21	480	14.9	17.0
0.30	466	13.8	20.3
0.40	448	10.2	19.7

[a] Values measured at 300 K.



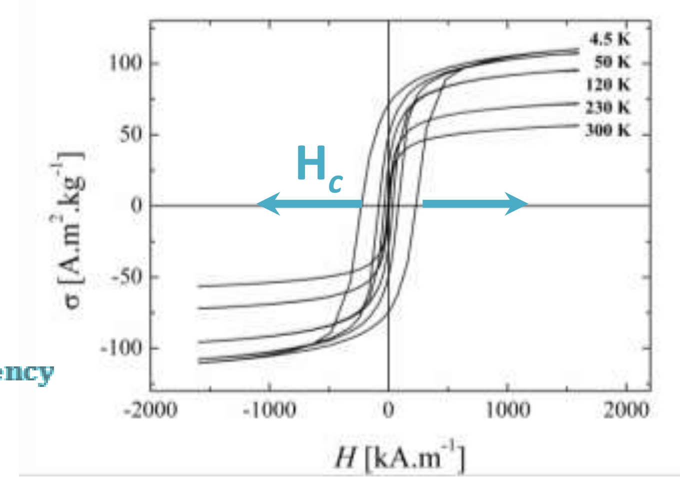
- Rh, In substitutions –> destabilization of ε-Fe_2O_3 structure, tranformation to corund structure

Nanomedical applications - Hyperthermia

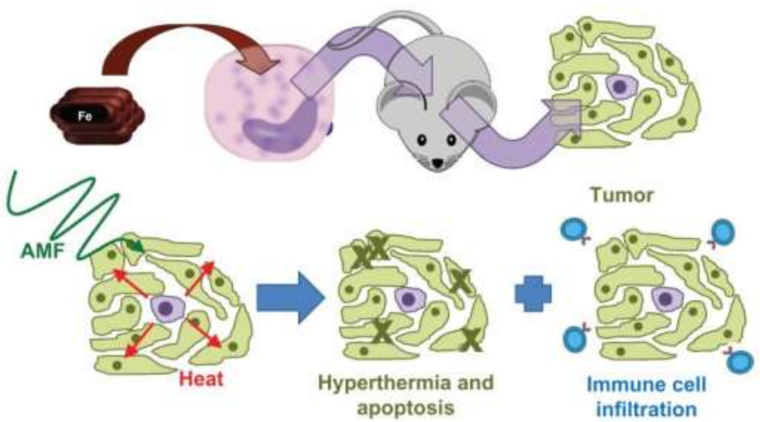
- complementary cancer treatment
- local heating-up of tumor cells up to 41-46 °C
- SAR ≈ hysteresis losses during repeated cycles (100-400 kHz)

$$\mathrm{SAR} = 4{,}1868\frac{P}{m_e} = C_e\frac{\Delta T}{\Delta t}$$

$$\text{Power Dissipated} = \text{Area of B} - \text{H Curve} \times \text{Volume of Material} \times \text{Frequency}$$

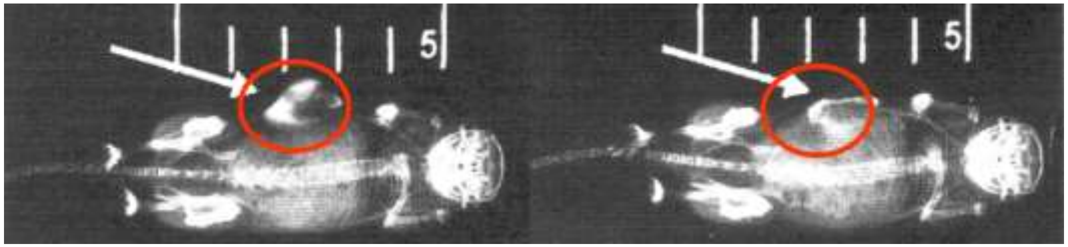


DC hysteresis loop of $Co_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles



Specific requirements:

- enhanced SAR – increase of H_c
- autoregulation by T_C adjustment (40-60 °C)

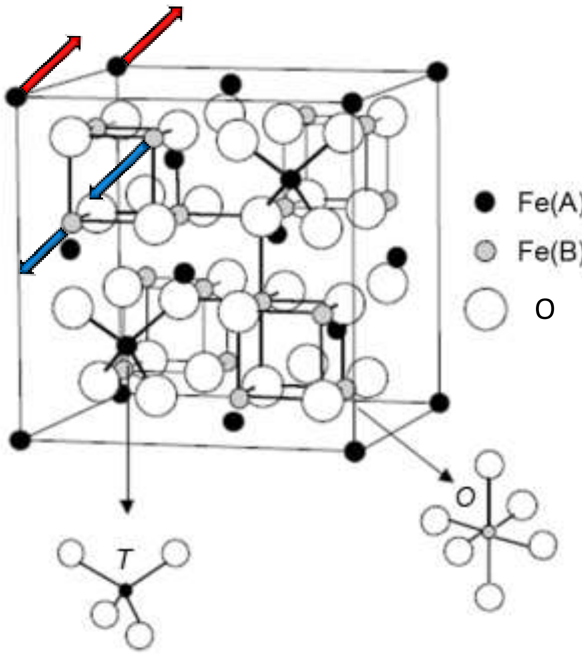


Magnetite Fe_3O_4

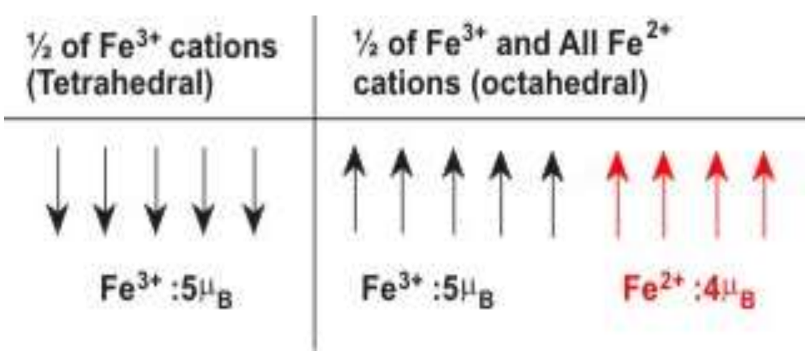
cubic inverse spinel structure
a = 8.394 Å
$T_C \sim 847$ K

$(Fe^{3+})_A[Fe^{2+}Fe^{3+}]_BO_4$

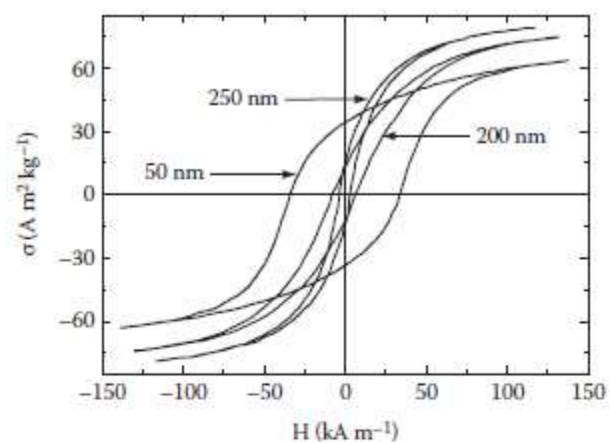
monoclinic structure below $T_V \sim 125$ K
a = 5.912 Å
b = 5.945 Å
c = 8.388 Å



- 8 formulas in elementary cell
- 8 tetrahedral A sites, 16 octahedral B sites
- ferrimagnetic ordering
- phase structural transition and spin reorientation at T_V <111> -> <100>



→ **4 μ_B**

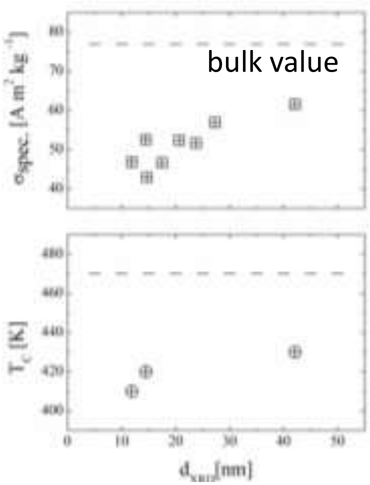


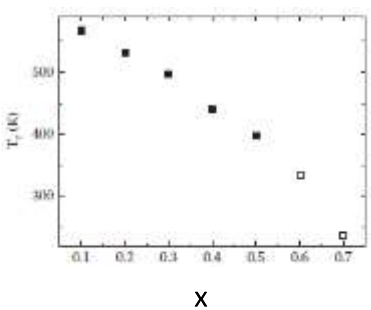
Substituted $M_xFe_{3-x}O_4$-based nanoparticles

Parameters' dependence:

- substituent and its properties
- distribution over the crystalographic sites
- particle size

$Co_{0.5}Zn_{0.5}Fe_2O_4$





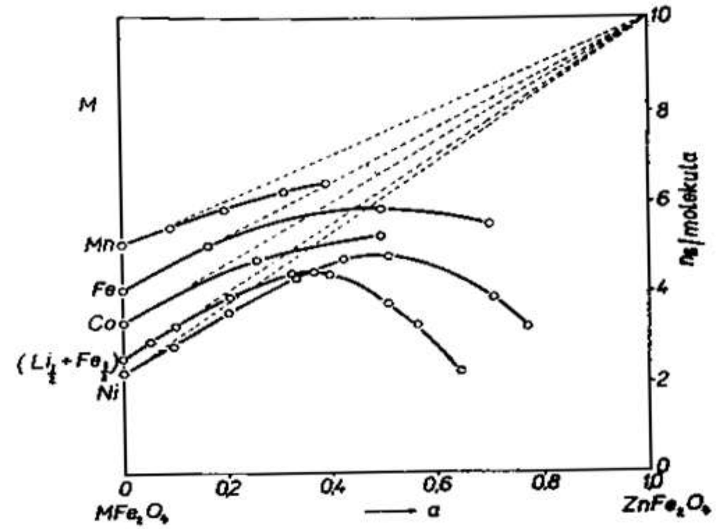
$T_c(Fe_3O_4$ bulk) 847 K 4 μ_B
$T_c(CoFe_2O_4$ bulk) 769 K 3 μ_B

Bulk... what about nano?
Zn^{2+} -> A sites
Co^{2+} -> B sites

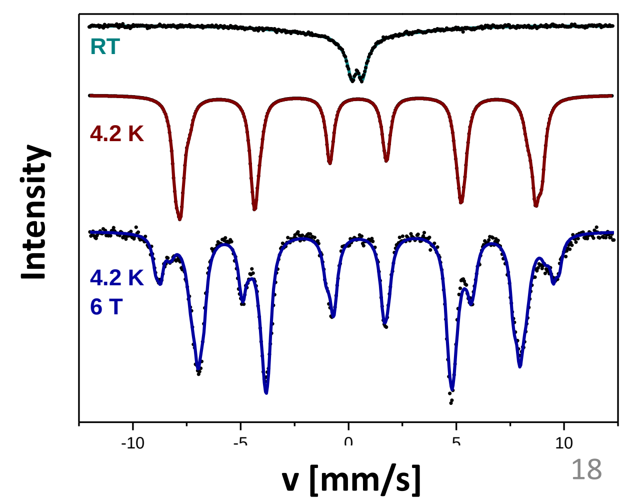
MS@RT:
1 sextet for Fe in A sites
4 sextets for Fe in B sites

MS@LHT:
splitting
IS ... valency
B_{hf} ... cation distribution

$M_{1-x}Zn_xFe_2O_4$ (bulk)



$Co_{1-x}Zn_xFe_2O_4/SiO_2$ (10 nm)



To sum up... ...perspectives.

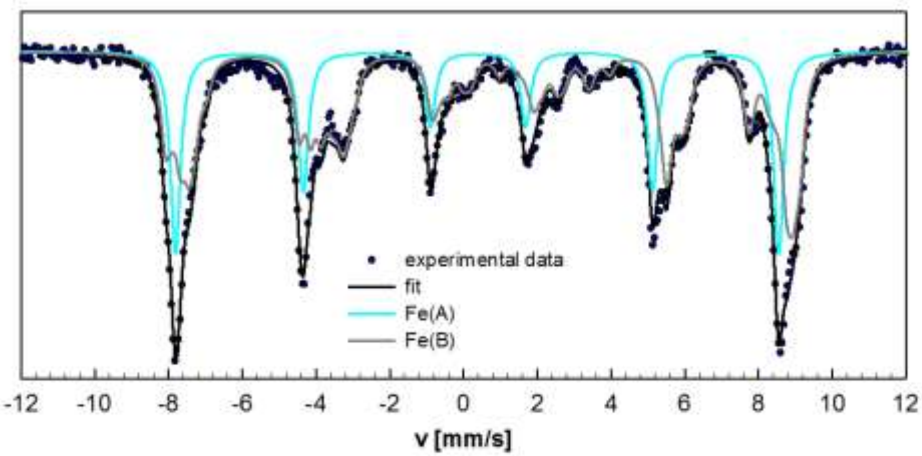
1) Optimal method to synthetize the pure ε-Fe_2O_3 nanoparticles
2) First measurements at ε-Fe_2O_3 and $Co_{1-x}Zn_xFe_2O_4$ nanoparticles
3) Substitutions of Fe in ε-$M_xFe_{2-x}O_3$ and spinel $M_xFe_{3-x}O_4$ nanoparticles by diamagnetic ions to to increase net magnetization and relaxivity parameter for MR imaging
4) Substitutions of Fe by diamagnetic ions of two species into the same material

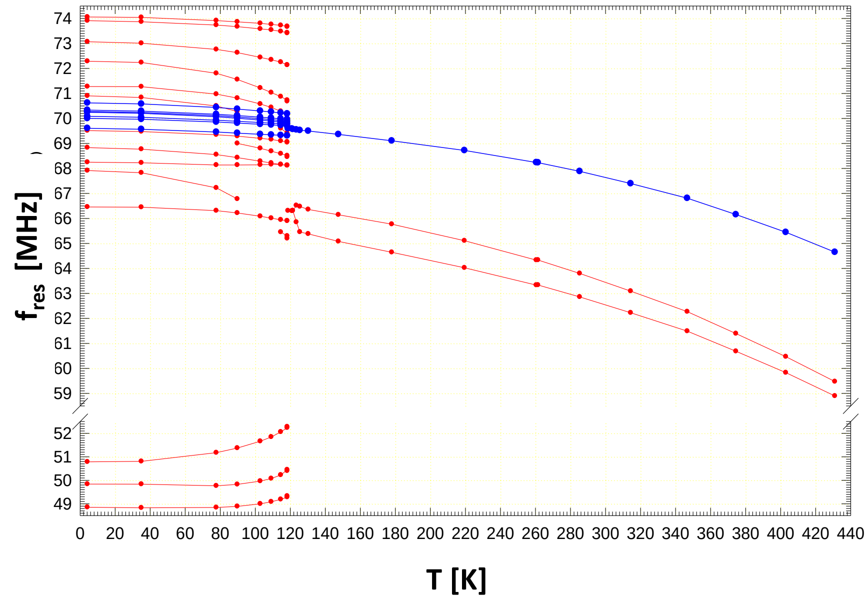
Thank you for your attention!

...waiting for your questions/comments.

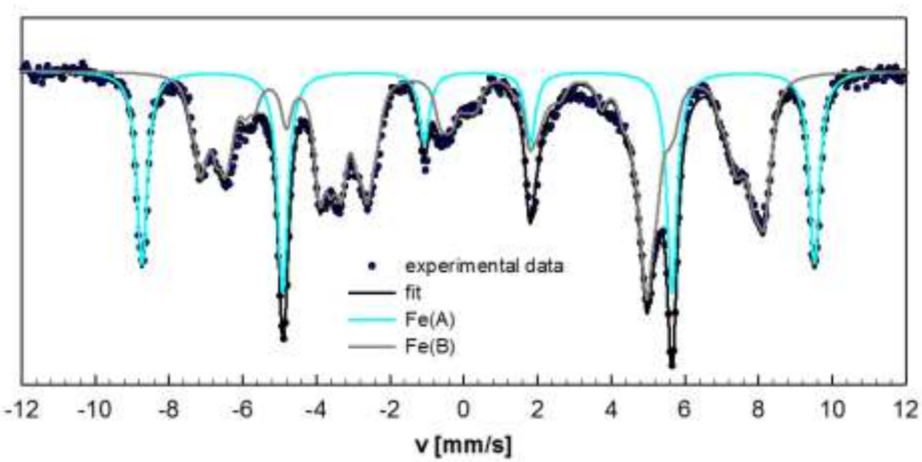
Mössbauer study of magnetite Fe_3O_4

Pure powder sample of Fe_3O_4 (T=4,2 K, B=0 T)





Pure powder sample of Fe_3O_4 (T=4,2 K, B=6 T)

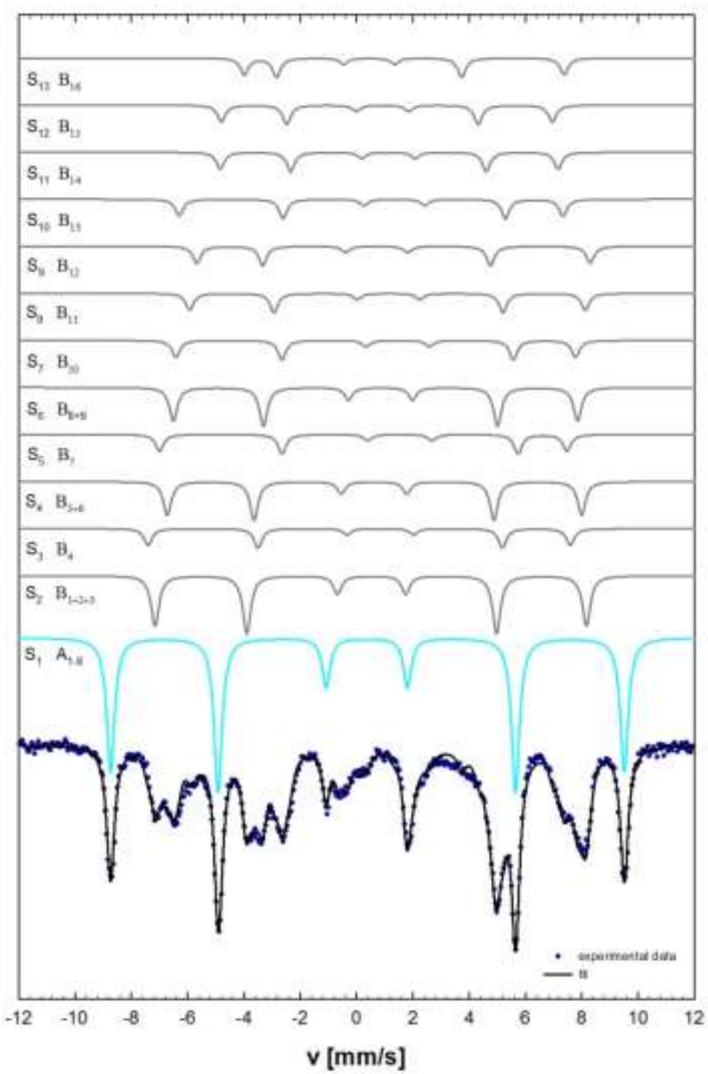


A B

$$(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$$

Mössbauer study of magnetite Fe_3O_4

Powder sample of Fe_3O_4 of 99,99 % purity
(T=4,2 K, B=6 T)



komponenta	Fe pozícia	IS [mm/s]	B = 0 T Δ_Q [mm/s]	B = 0 T B_{hf} [T]	B = 6 T Δ_Q [mm/s]	B = 6 T B_{eff} [T]	intenzita [y:1]
S_1	A_{1-8}	0,38	-0,02	50,8	0,02	56,7	8
S_2	B_{1+2+3}	0,52	0,00	53,5	-0,03	47,6	3
S_3	B_4	0,47	0,12	52,4	-0,75	46,6	1
S_4	B_{5+6}	0,63	-0,06	51,6	0,02	45,7	2
S_5	B_7	0,89	-0,71	50,8	-1,30	45,0	1
S_6	B_{8+9}	0,76	-0,22	50,5	-0,18	44,6	2
S_7	B_{10}	1,07	-0,69	49,9	-0,78	44,1	1
S_8	B_{11}	1,12	-0,25	49,5	-0,04	43,7	1
S_9	B_{12}	1,02	-0,99	49,3	0,60	43,4	1
S_{10}	B_{13}	0,93	-0,86	48,2	-0,83	42,4	1
S_{11}	B_{14}	1,15	1,24	36,8	0,03	37,3	1
S_{12}	B_{15}	1,00	1,83	36,2	0,16	36,5	1
S_{13}	B_{16}	1,07	2,06	35,4	1,25	35,3	1

Nanoparticles of ε-phase Fe_2O_3

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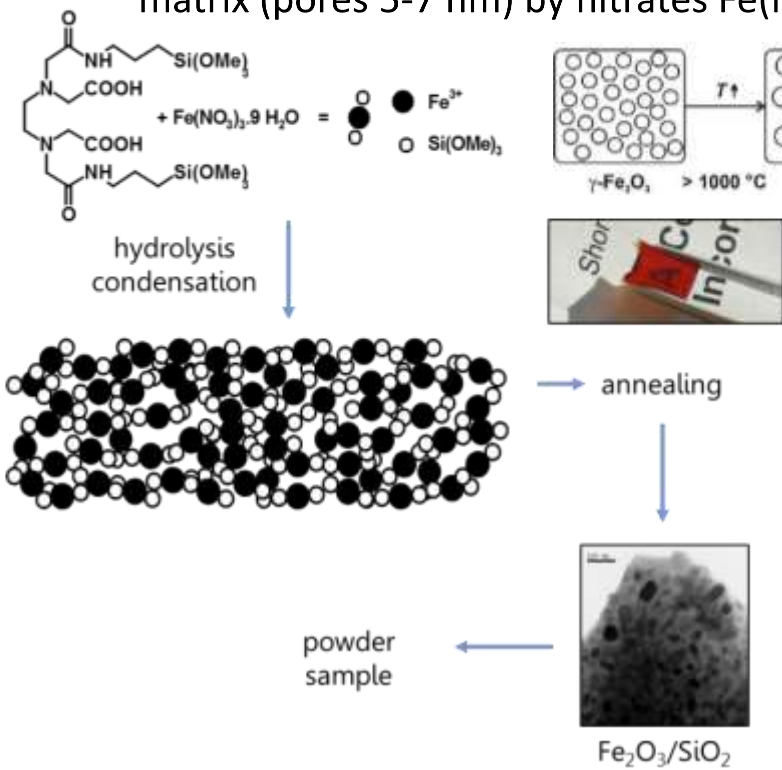
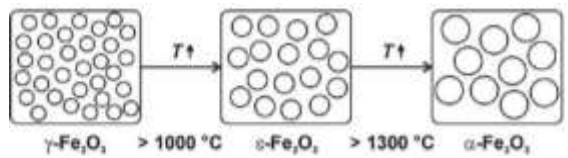
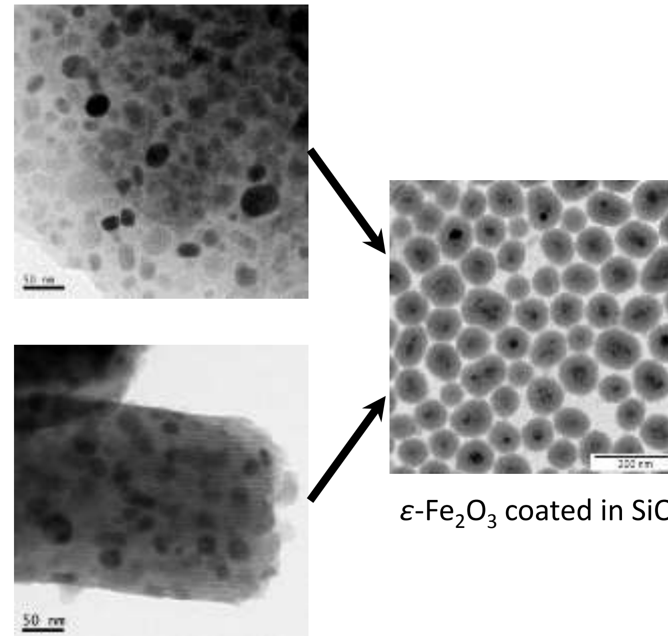
- sol-gel synthesis followed by heat treatment (HT)
- impregnation of mesoporous amorphous silica matrix (pores 5-7 nm) by nitrates $Fe(NO_3)_3$ + HT



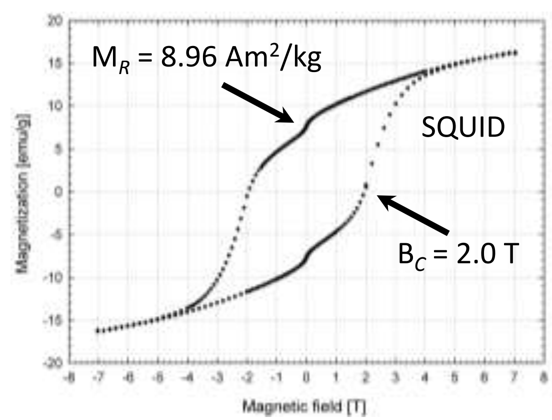


sol-gel



impregnation

ε-Fe_2O_3 coated in SiO_2



HRTEM of ε-Fe_2O_3 nanoparticle