Superparamagnetic properties of □-Fe_2O_3 particles: Mössbauer spectroscopy and DC magnetic measurements

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Synopsis

Mössbauer spectroscopy with ^{57}Fe

Transmission (absorption) and Conversion Electron MS

Hyperfine interactions

Zeeman splitting and relative intensities of lines

Hyperfine field and short range order

(Small particles and transition to superparamagnetism)

Example: Nanoparticles of Fe_2O_3 oxide

Mössbauer spectroscopy and magnetic properties

Collaborators: A. Lančok, E. Pollert, M. Maryško

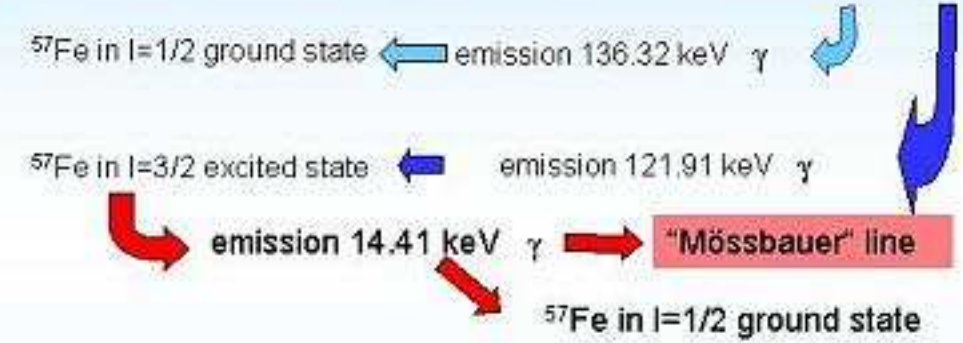
Mössbauer spectra at various temperatures

ZFC/FC magnetic moments, distribution of blocking temperatures

Mössbauer spectroscopy with ^{57}Fe

Magnetic materials containing Fe - "Mössbauer" isotope ^{57}Fe (natural abundance 2.19%)

Radioactive source ^{57}Co (electron capture with half time 270 d) ⇒ ^{57}Fe in excited I=7/2 state



Absorption process

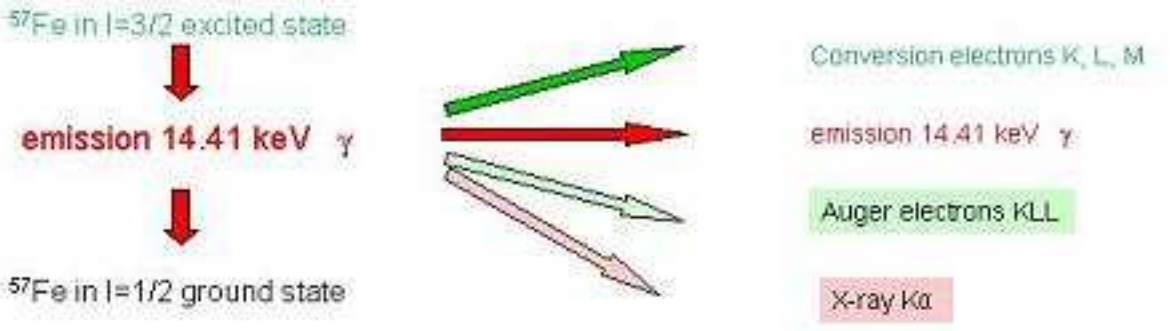


Table 1. Transition from excited to ground state of the ^{57}Fe nucleus

Energies and probabilities of processes during de-excitation

type	energy	[keV]	probability	
γ emmision	E_0	14.4	$1 / 1+\alpha$	0.09
e conv K	$E_0 - B_K$	7.3	$\alpha_K / 1+\alpha$	0.81
e conv L	$E_0 - B_L$	13.6	$\alpha_L / 1+\alpha$	0.09
e conv M	$E_0 - B_M$	14.3	$\alpha_M / 1+\alpha$	0.01
e Auger KLL	$B_K - 2B_L$	5.4..5.7	$\alpha_K (1-(FY)_K) / 1+\alpha$	0.57
$X_{K\alpha}$	$B_K - B_L$	6.3	$\alpha_K (FY)_K / 1+\alpha$	0.24

Hyperfine interactions

Restriction to ^{57}Fe

nucleus

electron shell

volume charge density

wave function inside the nucleus

electrostatic

isomer (chemical) shift

quadrupole moment

gradient of electric field

quadrupole splitting (shift)

dipole moment

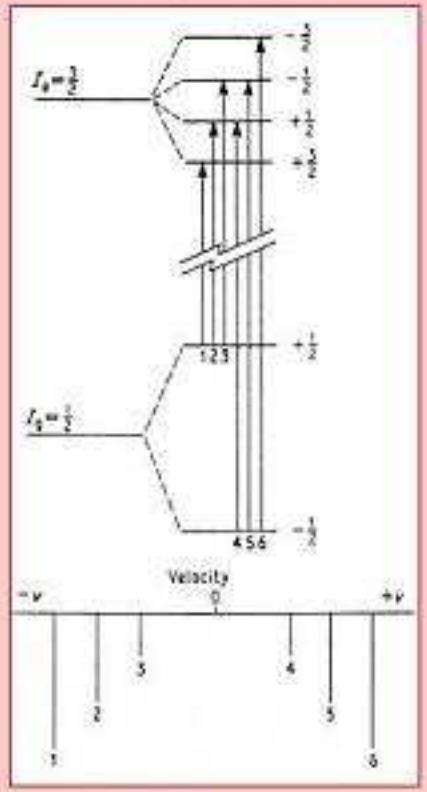
(effective) magnetic field inside the nucleus (s-electrons)

magnetic

nuclear Zeeman effect (splitting)

Zeeman splitting and relative intensities of lines

If the ^{57}Fe nucleus is exposed to an effective magnetic field B, its ground (I_g = 1/2) and excited (I_e = 3/2) states are split



$$E_m = - g_N \mu_N B m_z$$

g_N - nuclear Landé factor

μ_N - nuclear magneton

m_z - magnetic quantum number equal: I, I-1,...-I

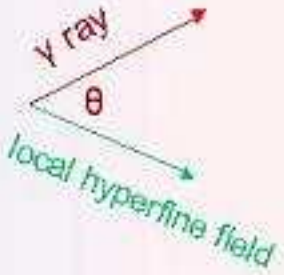
and 4 levels

into 2

Transitions with Δm equal to 0 and ±1 only allowed

spectrum consists of 6 lines

The relative intensities depend on θ



given by the Clepsch-Gordan coefficients:

$$I_1 = I_6 = 3/8\ (1 + \cos^2\theta)$$

$$I_2 = I_5 = 1/2\ (1 - \cos^2\theta)$$

$$I_3 = I_4 = 1/8\ (1 + \cos^2\theta)$$

with the ratio of 2nd (5th) and 3rd (4th) lines

$$I_{2,5} / I_{3,4} = 4 \sin^2\theta / (1 + \cos^2\theta)$$

= 0 for parallel

= 4 for perpendicular

orientations

= 2 for (homogeneously) random distribution of the local moments (fields)

formally corresponding to an effective angle of 54.7°

The ratio $I_{1,6} / I_{3,4}$ = 3 independently of the orientation (additional constraint for fitting).

Hyperfine field and short range order

Hyperfine field vs electronic magnetic moment:

directly

densities of the spin-up and spin-down s-electrons, $\varphi^2(r) \neq 0$ in the volume of the nucleus,

indirectly

screening of s-electrons by d-electrons sensitive to the moments of d-electrons

But generally B = f(electronic magnetic moment)
more complicated than B = K μ_e

B sensitive to the type and number of nearest (**n.n.**) and also next nearest (n.n.n.) neighbours

change of $\varphi^2(r)$ caused by bonding - similar to the above case

interactions with the neighbouring magnetic moments

B depends in a discrete way on the number of magnetic n.n.

Experimental spectrum may be decomposed to well-defined sextets

Small particles and transition to superparamagnetism

Mössbauer Spectroscopy

Each ^{57}Fe atom with given SRO

Time average of **B** over 10^{-7}s = 0

Sextet collapses to doublet/singlet

Diffraction Methods (XR, E, N)

Coherent volume with translational symmetry

Broadening of diffraction line for small particle size

Spontaneous change of direction of

atomic moments : **paramagnetism**

particle moments : **superparamagnetism**

For **superparamagnetism** decisive K . V

Anisotropy constant K
and particle volume V

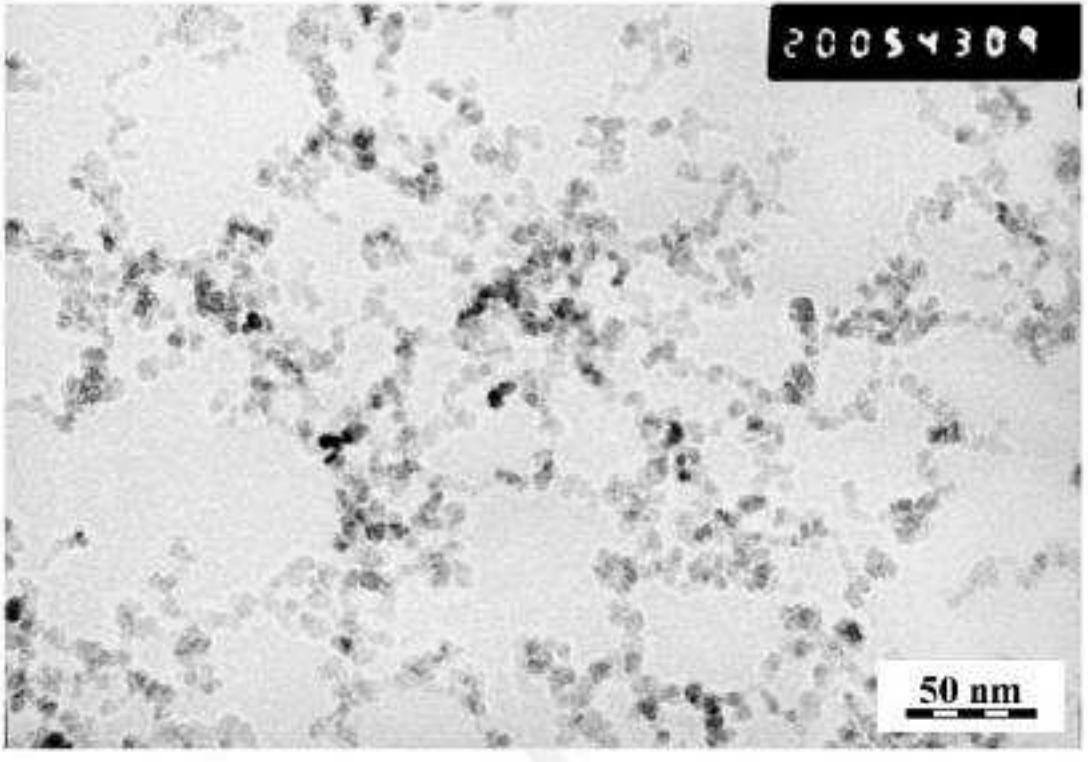
vs $\mathbf{k_B . T}$ (Boltzmann constant x Temperature)

Note different characteristic time in Mössbauer Spectroscopy

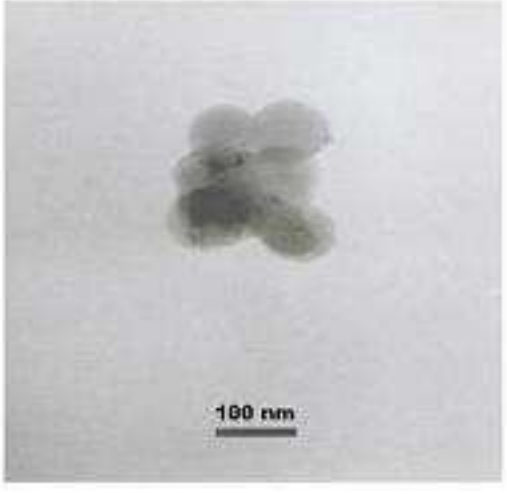
and

D.C. magnetic measuremnts

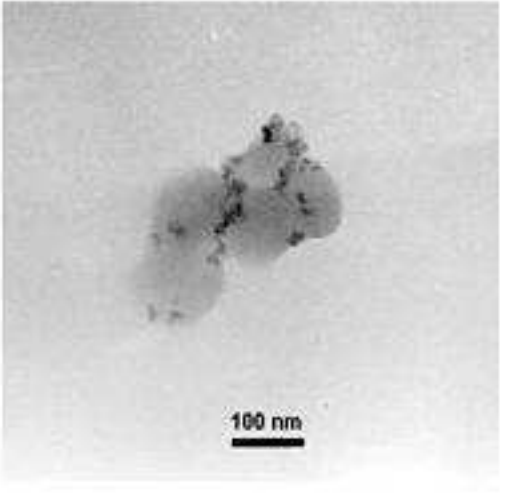
Magnetic poly(glycidyl methacrylate)microspheres containing maghemite prepared by emulsion polymerization



TEM pictures of PGMA microspheres with various concentrations of Fe_2O_3

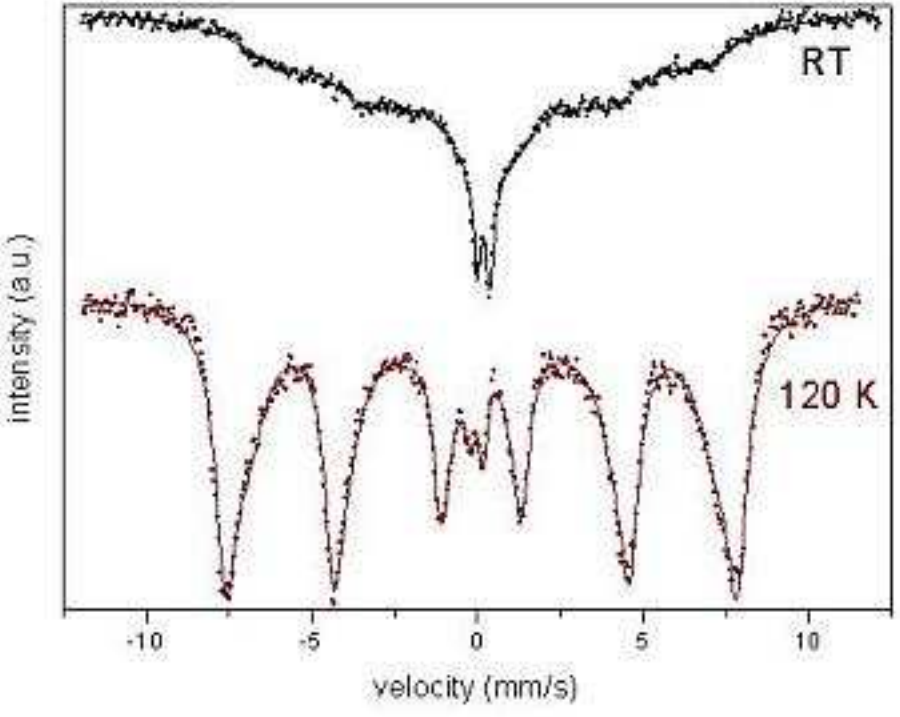


0.8 wt % of Fe_2O_3



6.2 wt % of Fe_2O_3

Moessbauer spectra at room temperature and 120 K



Parameters of the Mössbauer spectra

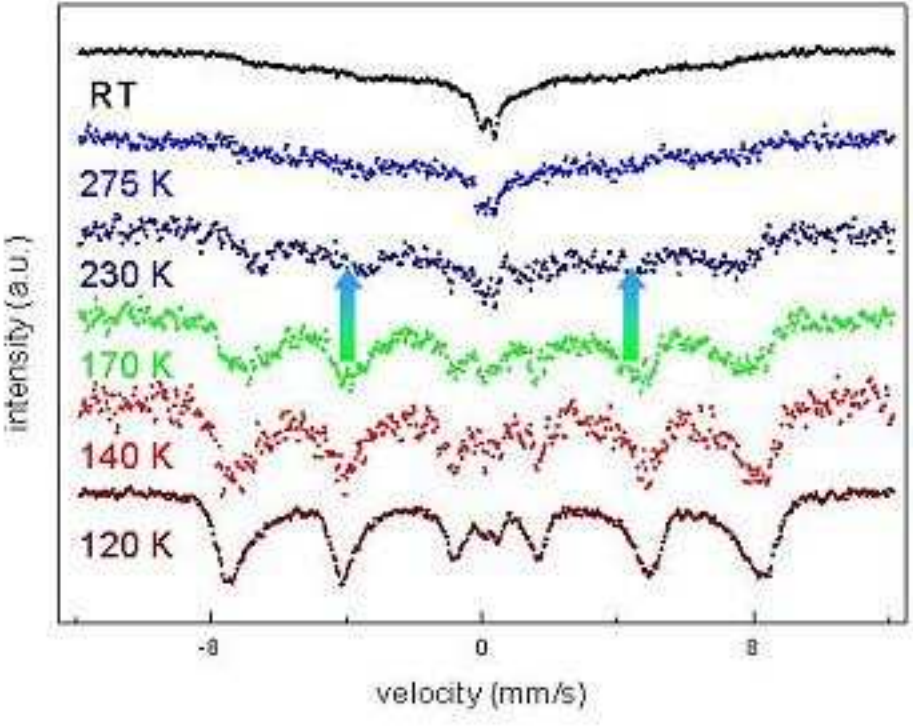
	RT			120 K		
	B_{hf}	ISO	r. a. %	B_{hf}	ISO	r.a. %
Sextet 1	40.3	0.38	14.4	47.9	0.13	38.3
Sextet 2				44.0	0.10	41.8
Broad sextet	25.9	0.29	76.0	26.4	0.34	16.7
Doublet 1		0.37	5.0		~0.0	3.2
Doublet 2		0.18	4.6			

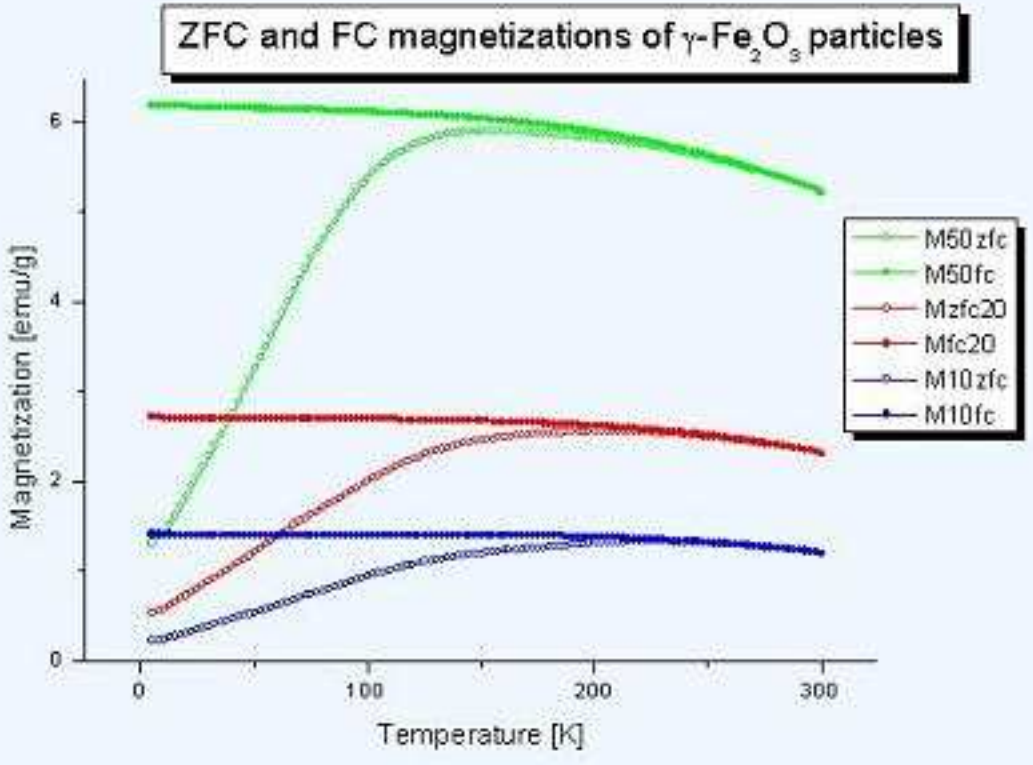
mostly ordered

mostly superparamagnetic phase? Fe^{3+} !

maghemite

Changes of Mössbauer spectra with rising temperature




ZFC and FC magnetizations of γ-Fe2O3 particles
Magnetization [emu/g]
Temperature [K]
0
2
4
6
0
100
200
300
M50zfc
M50fc
Mzfc20
Mfc20
M10zfc
M10fc

Blocking temperatures and their distribution

Even for 1 particle T_B is rather an interval – better: time of relaxation to equilibrium

time of measurement

Néel-Brown (Arhenius-type expression) $\tau = \tau_0 \exp(\Delta E / kT)$ with $\Delta E = K.V$

non-interacting, uniaxial

System of particles, way of averaging, change of ΔE by interactions

increase or decrease of T_B ?

J.J. Lu et al., JMMM 209(2000)37

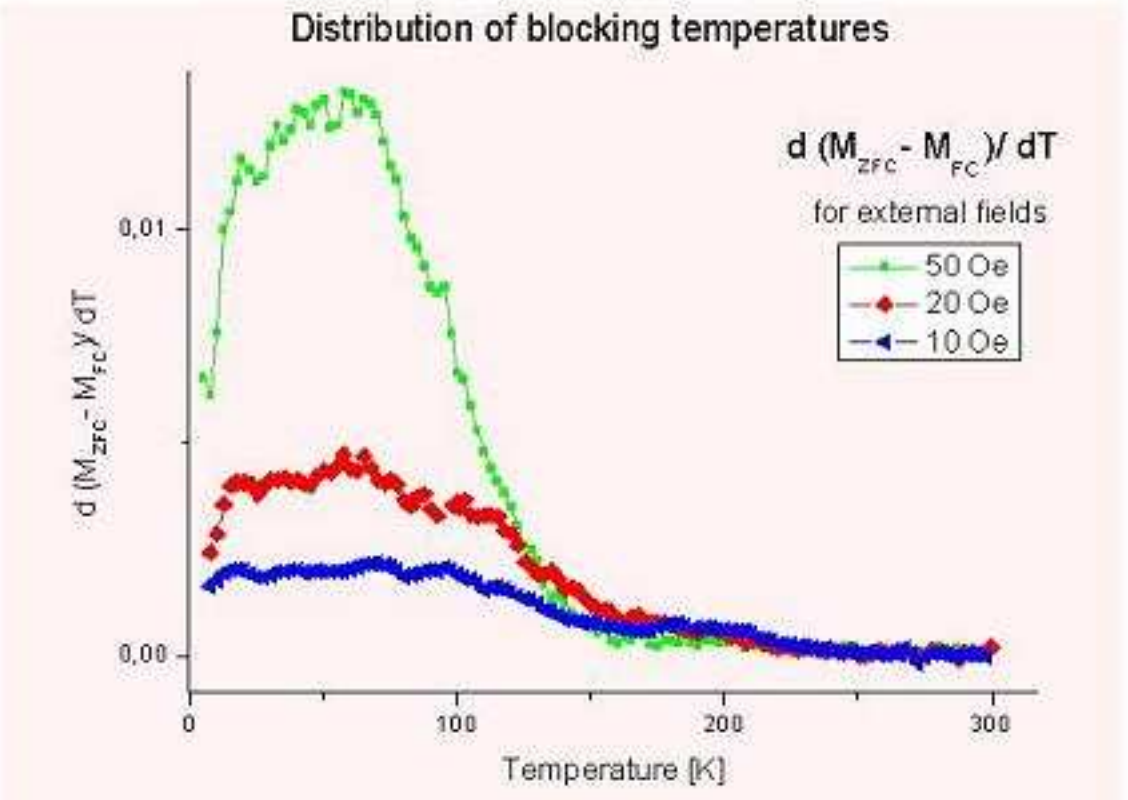
claimed: distribution proportional to $d\,(M_{ZFC} - M_{FC}) / dT$

M.C. simulation for continuous distribution of particle sizes

with increasing probe field

maximum of $M_{ZFC}(T)$ shifted up

maximum of $d(\Delta M)/dT$ shifted down


Distribution of blocking temperatures
d (M_ZFC - M_FC)/ dT
for external fields
50 Oe
20 Oe
10 Oe
d (M_ZFC - M_FC)/ dT
0,01
0,00
0
100
200
300
Temperature [K]

Conclusions for the Iron-oxide particles

Phase composition → not clear from XRD nor r.t. Möss. spectra

→ Mössbauer spectra at 120 K indicated maghemite as main phase

Transition between ordered and superparamagnetic state → From Mössbauer spectra (170 – 230 K) and 10^{-7}s

From analysis of ZFC/FC magnetizations distribution of blocking temperatures → Maxima depending on the magnetic field intensity at (13 – 60 K) for DC magnetizations ≈ s

Moral: When speaking about superparamagnetic particles, always state the relevant time window and temperature!

T h a n k

Y O U !