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

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Synopsis

Small particles and transition to superparamagnetism

Magnetic measurements and superparamagnetism - blocking temperatures T_B

Nanoparticles of Fe_2O_3 oxide

Synthesis and characterization

Mössbauer spectroscopy and magnetic properties

Mössbauer spectra at various temperatures

Analysis of ZFC/FC magnetic moments

Distribution of blocking temperatures

Comparison with Mössbauer spectra

Conclusions

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(s) broaden(s) and finally collapse 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 (~10^{-7}s for ^{57}Fe)

and

D.C. magnetic measurements (seconds)

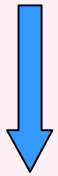
Magnetic measurements and superparamagnetism

D.C. magnetization curves — hysteresis — yes / no — rather crude discrimination

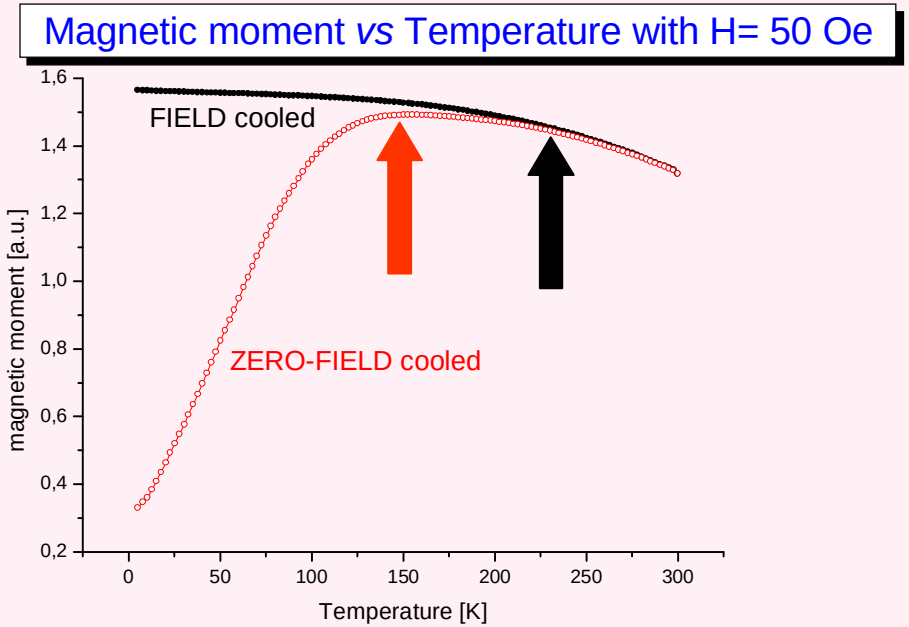
Temperature dependence of magnetization (susceptibility) — with increasing T

after
- cooling in zero field (ZFC) — curve M(T) displaying maximum ≠ T_B ?
- cooling in (non-zero) field (FC) — decreasing and merging with ZFC (at T_B?)

For distribution of particle sizes



Distribution of blocking temperatures



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 of T_B 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

Experimental

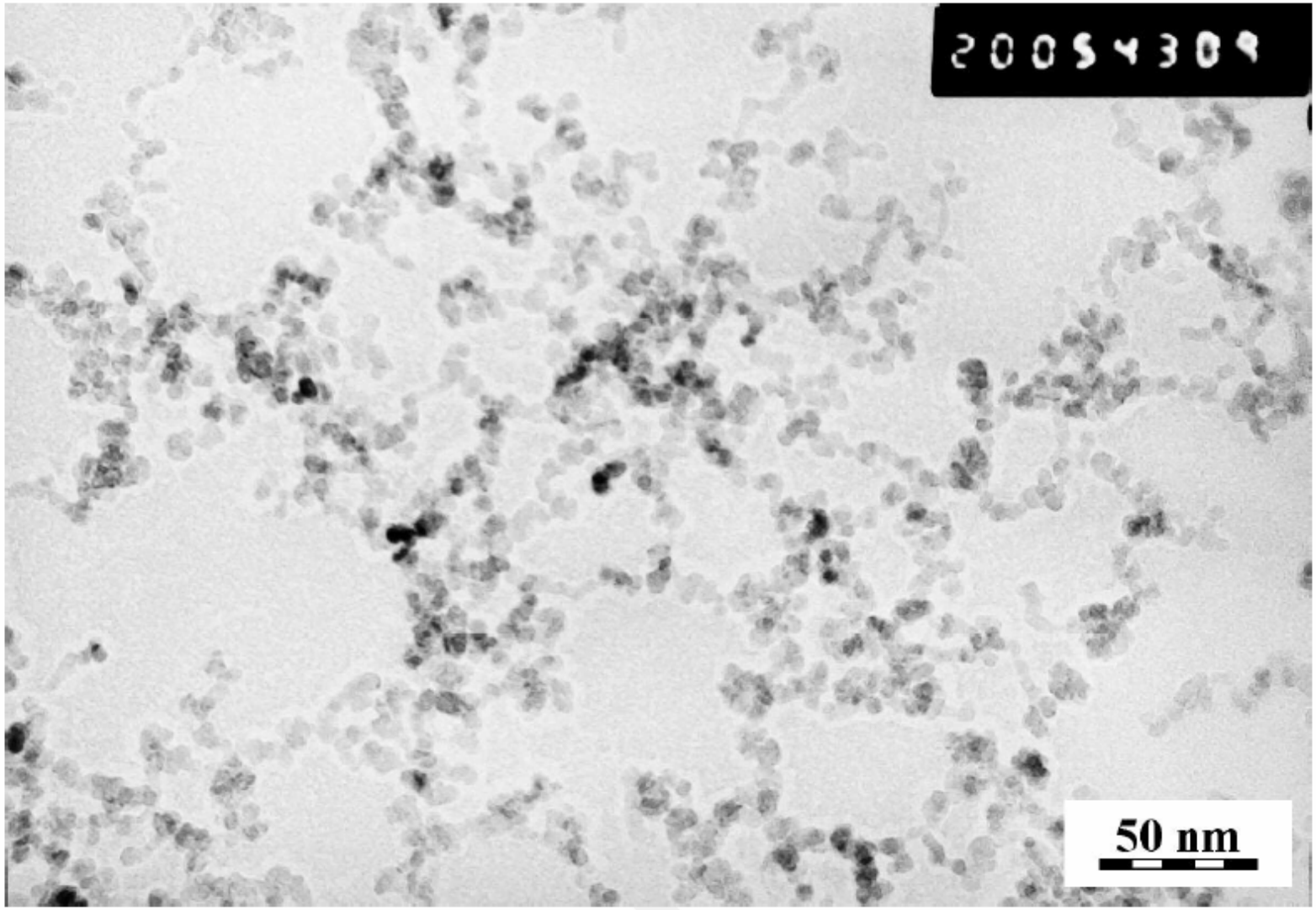
Synthesis of dextran-stabilized γ-Fe_2O_3 (maghemite?) nanoparticles

Magnetic **iron oxide colloid** was prepared by **chemical coprecipitation** of Fe(II) and Fe(III) salts with ammonium hydroxide in (Carboxymethyl)-dextran solution and subsequent **oxidation** with sodium **hypochlorite** to **avoid uncontrolled oxidation** of primarily formed magnetite **by air oxygen**.

Precipitation method produces very fine **nanoparticles**, with **CM-dextran** providing **sterical stabilization** of magnetic nanoparticles:
COOH group possesses affinity to Fe3+ ions, the dextran part allows the dispersion in water and **prevents aggregation** of the particles forming a **stable colloid**.

Colloidal **magnetic phase** precipitated in the presence of (carboxymethyl)dextran **formed "chains"** of fine **particles about 5 nm** in **diameter** and with **narrow** size **distribution** (PDI = 1.06). (Fig. 1)

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



Experimental cntnd

Phase compositions of the magnetic iron oxide particles (and PGMA composite microspheres) and

size of the magnetic crystallites determined by **X-ray powder diffraction** (Bruker D8 diffractometer equipped with CuK, Sol-X energy dispersive detector). XRD patterns analyzed with the Rietveld method using the FULLPROF program.

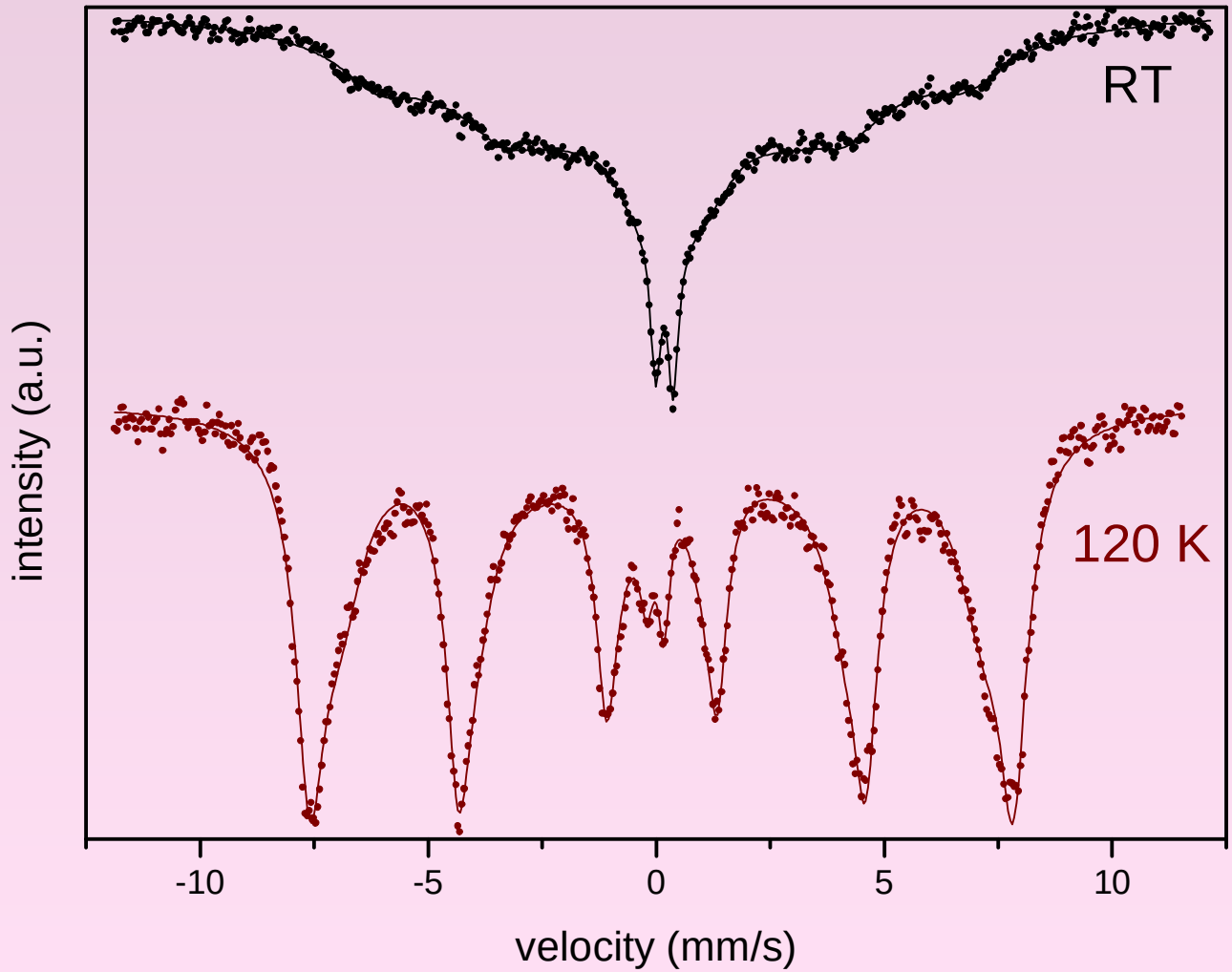
Instrumental, strain and size **contributions** to peak **broadening** resolved using Thompson-Cox-Hastings pseudo-Voigt profile. Instrumental resolution was **checked** by measuring **tungsten powder** with grain size of **9.4 μm**.

Magnetic properties were measured by **SQUID** magnetometer (MPMS5 by Quantum Design, USA) in the temperature range 5-295 K in the fields up to **5 T**.

The **Mössbauer spectra** acquired in the transmission mode with 57Co/Rh source moving with constant acceleration. Calibration by a standard α–Fe foil and I.S. expressed with respect to this standard at 293 K.

Samples were measured in a Janis cryosystem at temperatures **120 – 300K** . The spectra were fitted with the help of the NORMOS program.

Moessbauer spectra at room temperature and 120 K



Parameters of the Mössbauer spectra

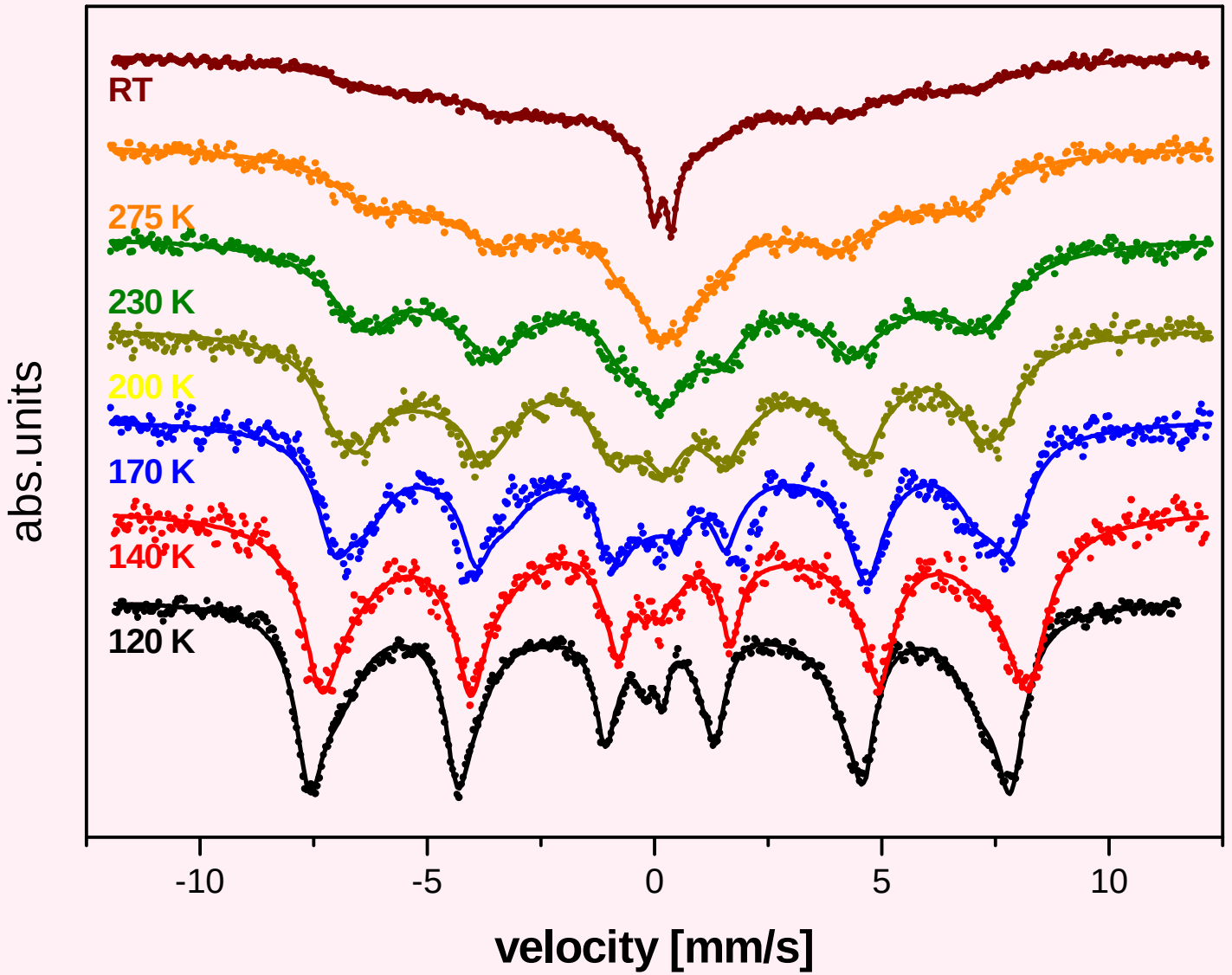
	RT			120 K		
	B_{hf}	ISO	r. a. %	B_{hf}	ISO	r.a. %
Sextet 1	40.3	0.38	14.4	47.9	0.13	38.3
Sextet 2				44.0	0.10	41.8
Broad sextet	25.9	0.29	76.0	26.4	0.34	16.7
Doublet 1		0.37	5.0		~0.0	3.2
Doublet 2		0.18	4.6			

mostly ordered

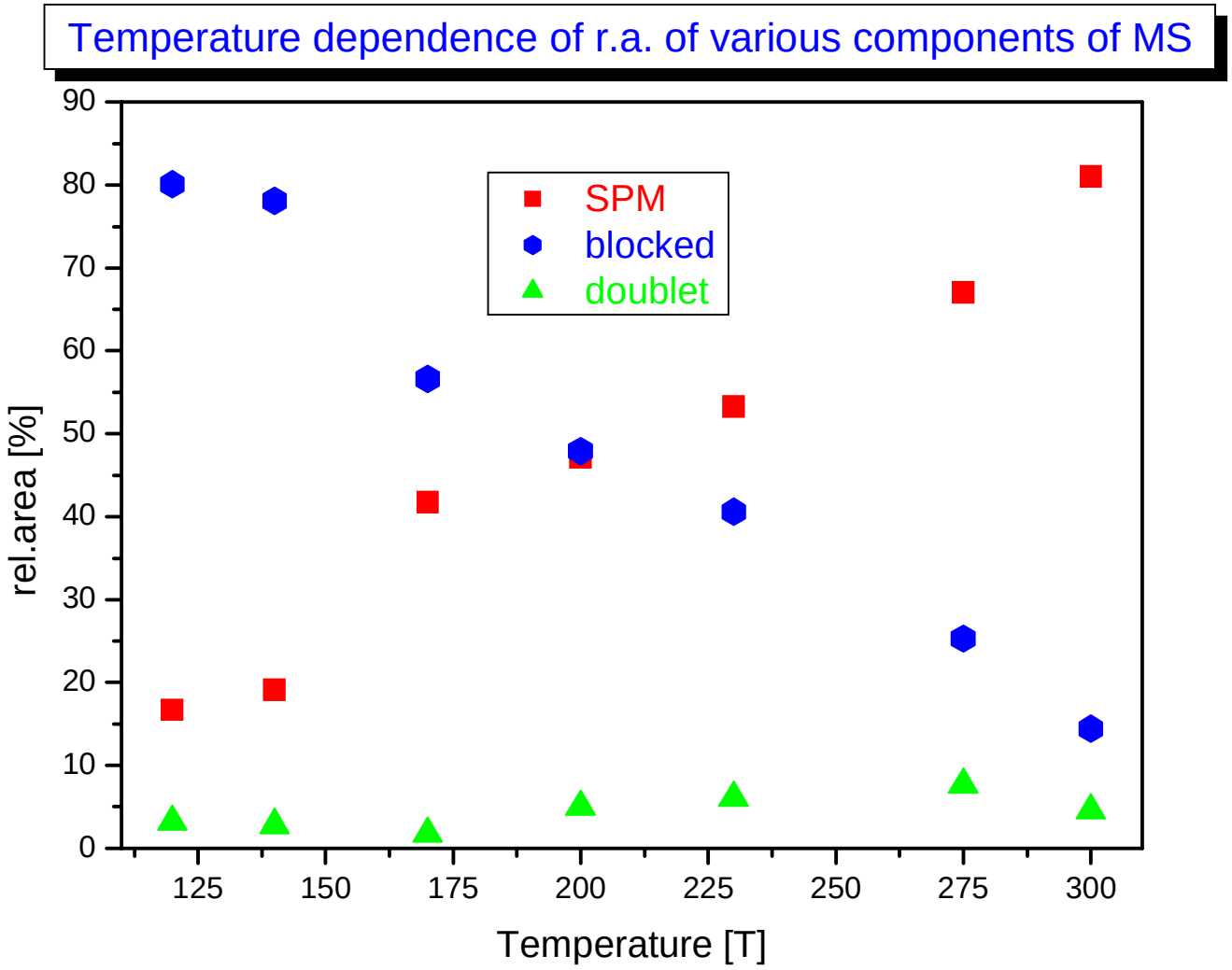
mostly superparamagnetic phase? Fe^{3+} !

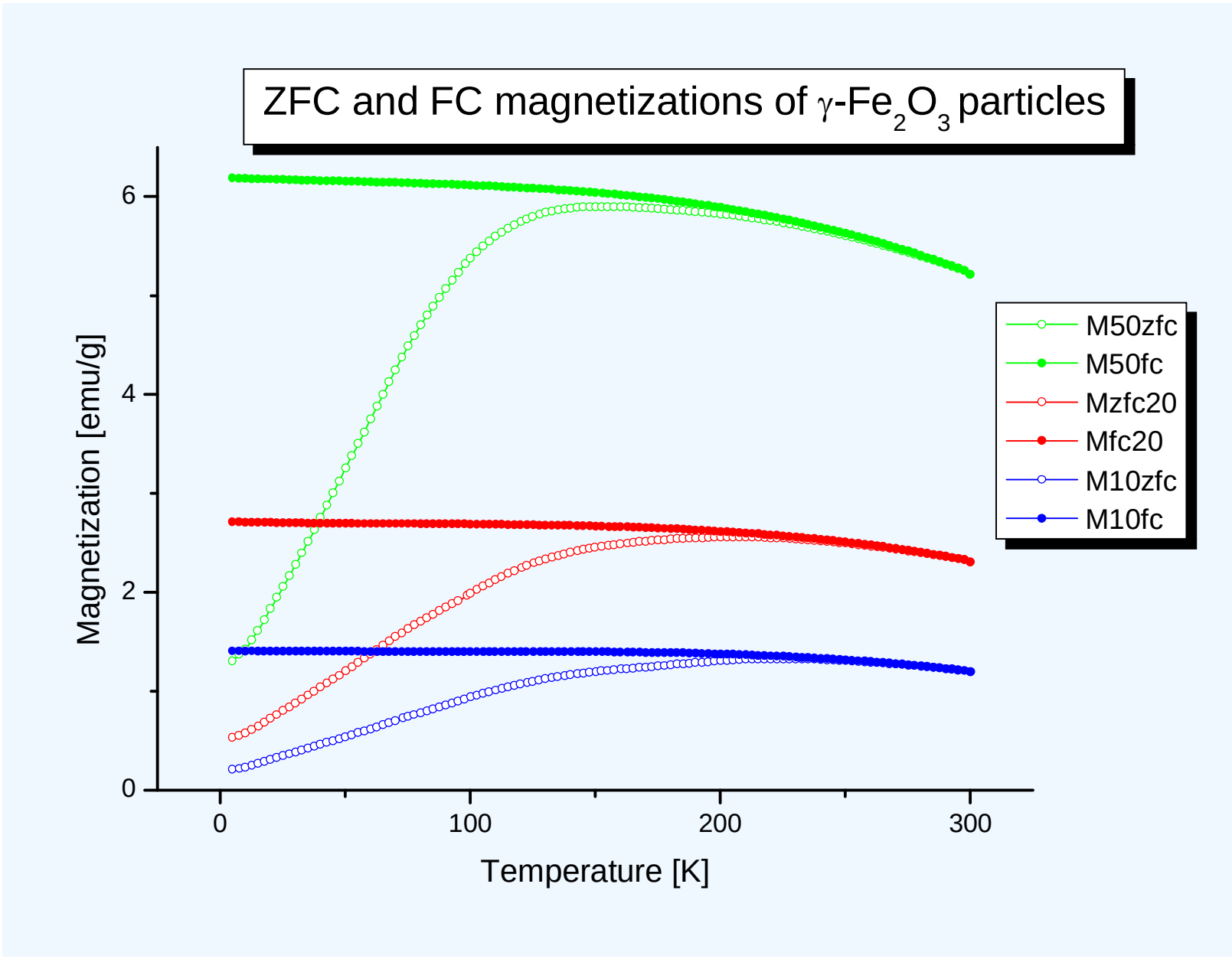
maghemite

Temperature dependence of Mössbauer spectra

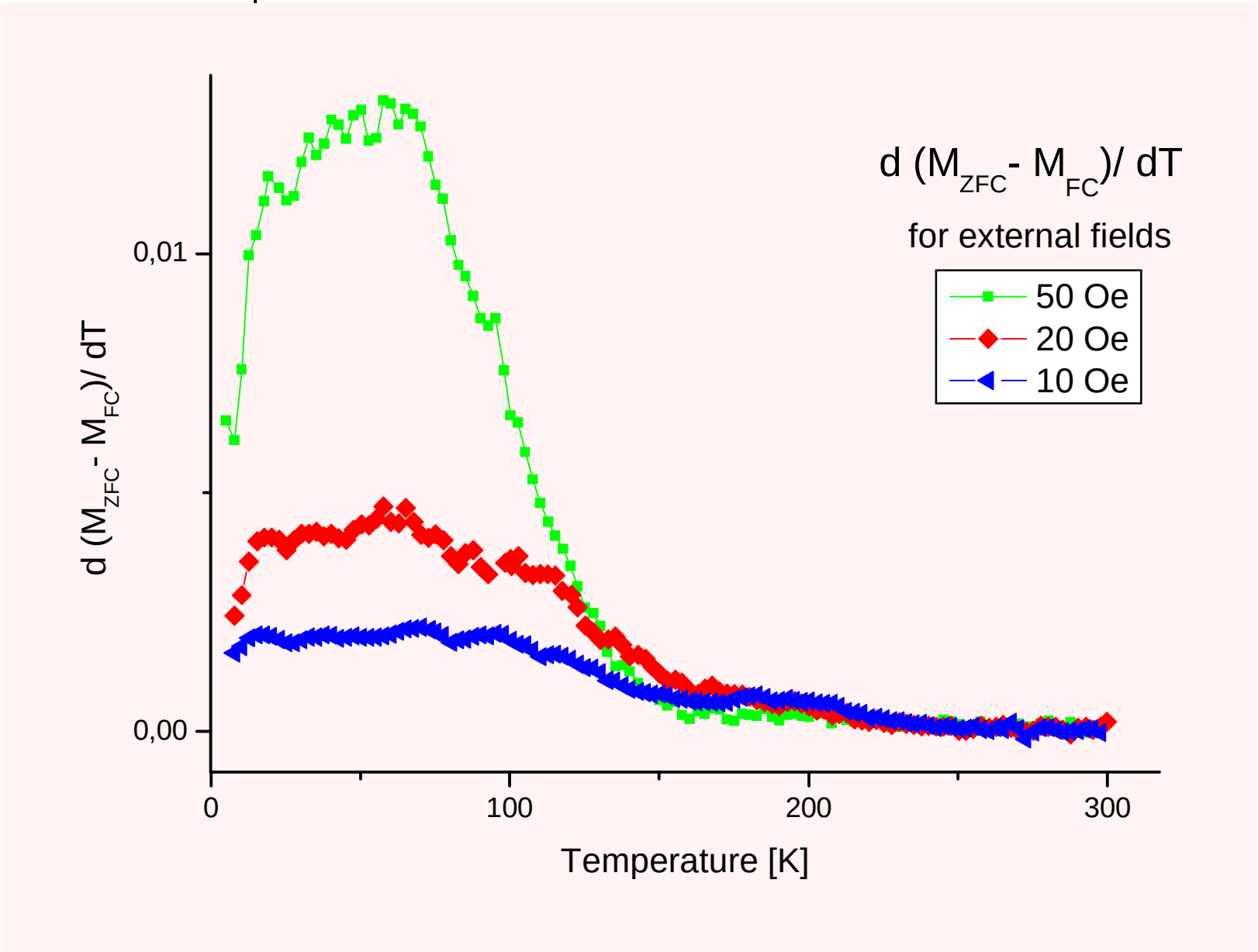


		Sextet 1	Sextet 2	Broad Sextet	Doublet 1	Doublet 2
Room Temp.	B_{hf} [T]		40.3	25.9		
	ISO [mm/s]		0.38	0.29	0.37	0.18
	r.a. [%]		14.4	76.0	5.0	4.6
275 K	B_{hf} [T]		40.4	28.9		
	ISO [mm/s]		0.31	0.29	0.41	0.26
	r.a. [%]		25.3	44.9	22.1	7.7
230 K	B_{hf} [T]		42.4	30.3		
	ISO [mm/s]		0.39	0.46	0.51	0.19
	r.a. [%]		40.6	38.1	15.2	6.1
200 K	B_{hf} [T]	46.3	43.1	30.2		
	ISO [mm/s]	0.34	0.37	-0.41	0.75	-0.4
	r.a. [%]	3.2	44.7	36.7	10.4	5.0
170 K	B_{hf} [T]	46.2	42.0	29.7		
	ISO [mm/s]	0.39	0.51	0.2	0.11	0.31
	r.a. [%]	26.7	29.9	31.2	10.5	1.7
140 K	B_{hf} [T]	48.3	44.7	30.5		
	ISO [mm/s]	0.45	0.4	0.06		-0.03
	r.a. [%]	37.7	40.4	19.1		2.8
120 K	B_{hf} [T]	47.9	44.0	26.4		
	ISO [mm/s]	0.13	0.1	0.34		-0.03
	r.a. [%]	38.3	41.8	16.7		3.2


Temperature dependence of r.a. of various components of MS
SPM
blocked
doublet
rel.area [%]
Temperature [T]
0
10
20
30
40
50
60
70
80
90
125
150
175
200
225
250
275
300


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

Distribution of blocking temperatures



Relaxation time and Energy barrier

$\tau = \tau_0 \exp(\Delta E / kT)$ with $\Delta E = K.V$ for uniaxial magnetocrystalline (spherical particles) anisotropy

Input data:

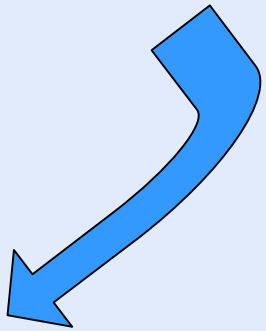
MS: $\tau \approx 10^{-7}$s , T □ (200, 250 K)

ZFC/FC curves: $\tau \approx 1$s T □ (13, 70 K)

V: d ≈ 5 nm cube: 1.25×10^{-25} m^3

sphere: 6.5×10^{-26} m^3

Assumption: **K** independent of temperature



gives $\tau_0 \approx 4.2 \times 10^{-8}$s - 1.7×10^{-11} s

and K ≈ 2.4×10^4 – 3.6×10^5 J/m^3 (=) 2.4×10^5 – 3.6×10^6 erg/cm^3

which plausibly compares in absolute value with LB data

$K_1 = -2.5 \times 10^5$ erg/cm^3 (for cubic crystal)

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 – 80 K) for DC magnetizations ≈ s

Using the MS and DC magnetization data in the Arhenius relation

reasonable values for magnetocrystalline anisotropy and τ_0 were derived

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

Acknowledgment

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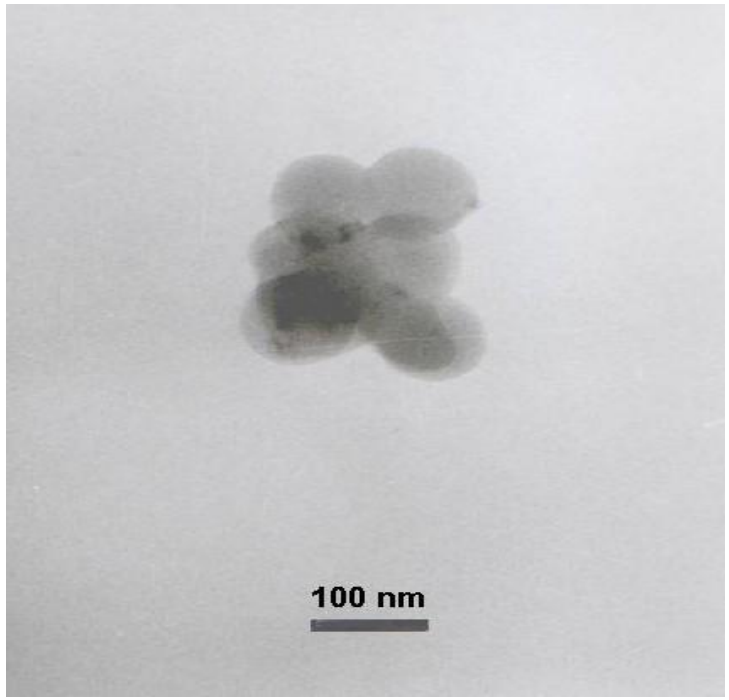
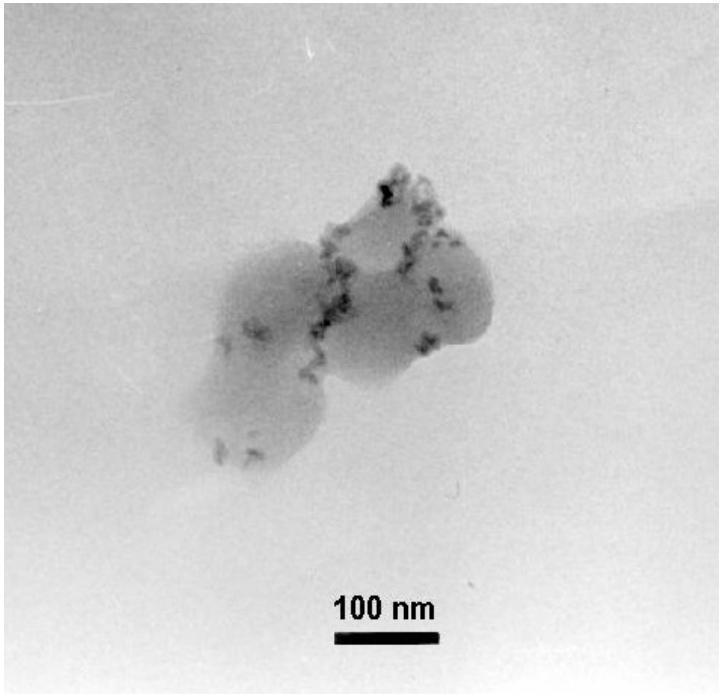
T h a n k

Y O U !

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