Magnetic Properties of Hematite (α-Fe_2O_3) Nanoparticles by View of Mössbauer spectroscopy

Jiří Tuček

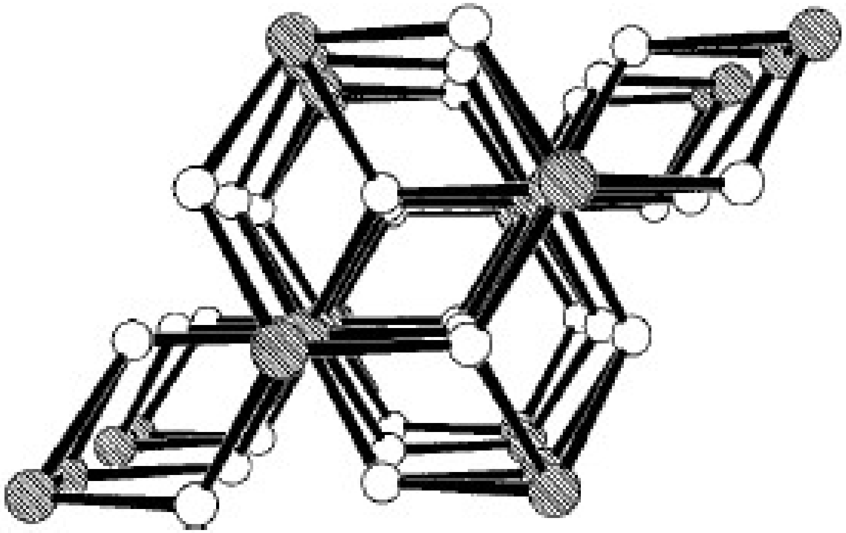
1. Structure of hematite

Fe_2O_3

α-Fe_2O_3 β-Fe_2O_3 γ-Fe_2O_3 ε-Fe_2O_3

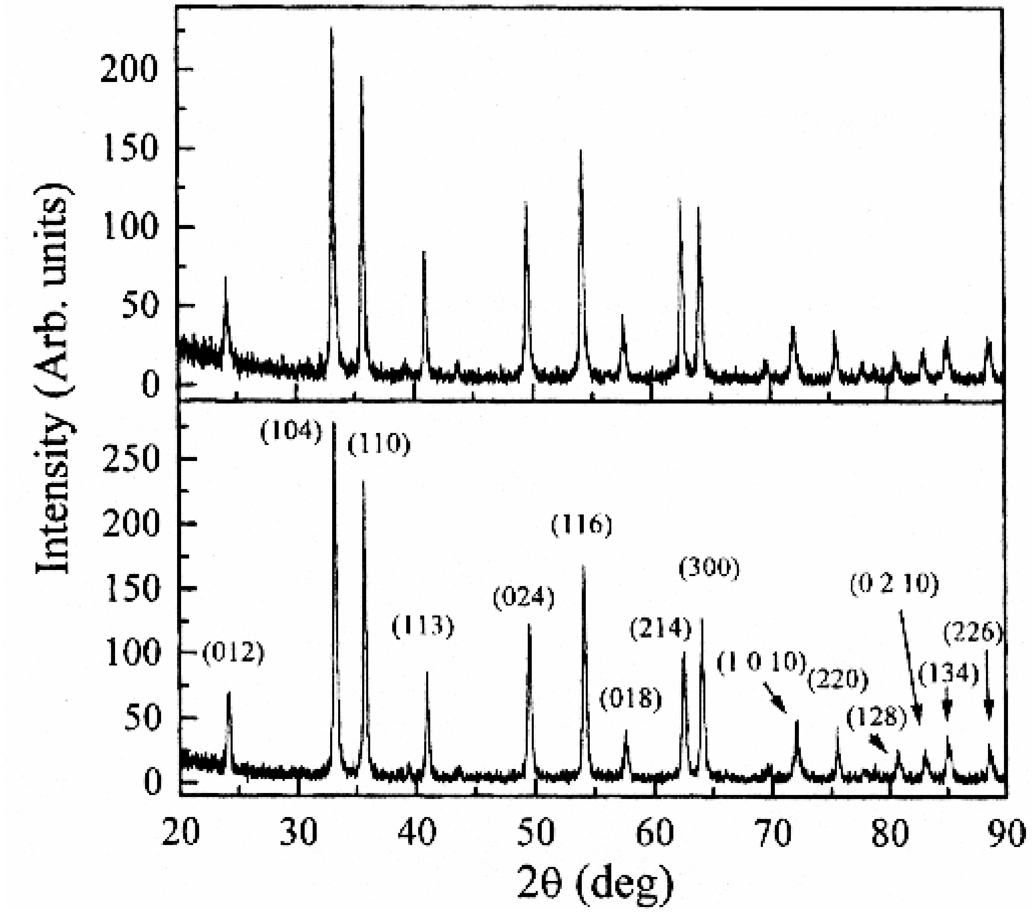
- **Crystal structure of corrundum, it is refined either in rhombohedral (R3c) or hexagonal (D^6_{3d}) space group**

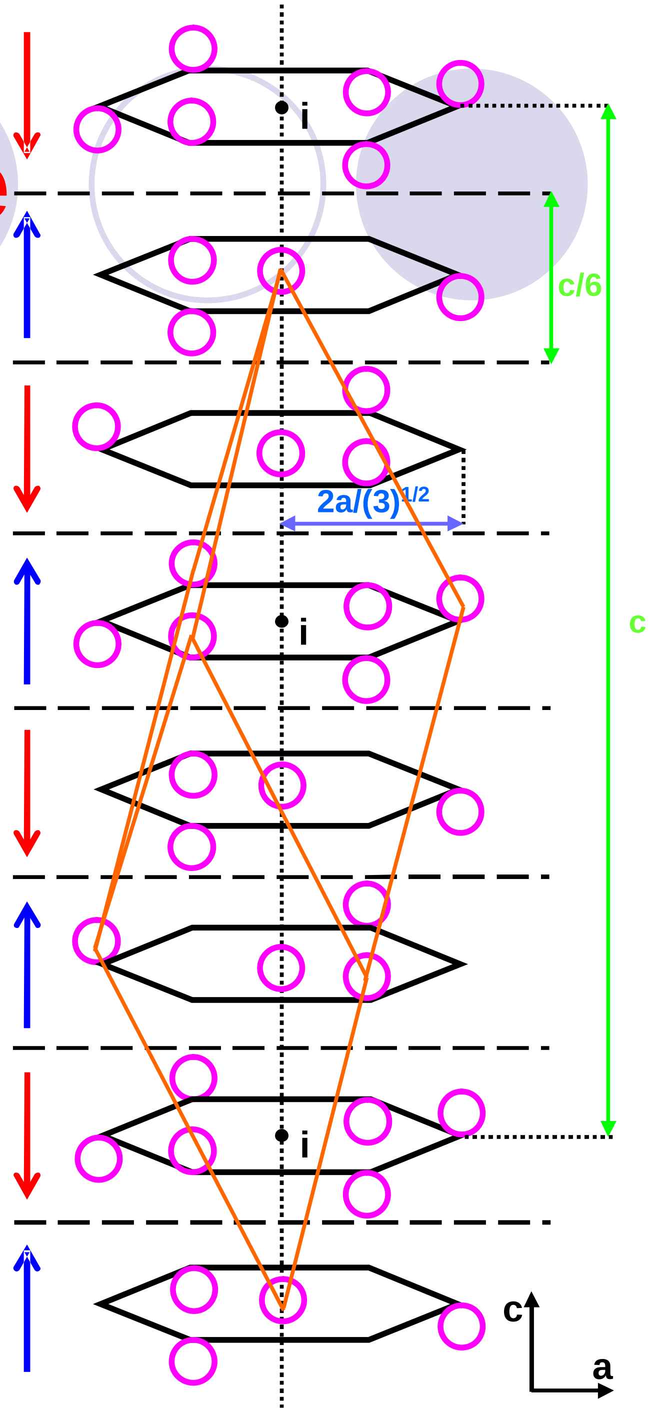
Hexagonal space group		Rhombohedral space group	
a (Å)	5.038 ± 0.002	a (Å)	5.4279
c (Å)	13.722 ± 0.012	α	55° 16´
Fe	0, 0, z, …	Fe	z, z, z, …
O	x, 0, ¼,…	O	x, ½ - x, ¼, …



- **With pressure, the crystal structure changes to orthorhombic space group with a = 4.58 Å, b = 4.95 Å a c = 6.72 Å**

1. Structure of hematite

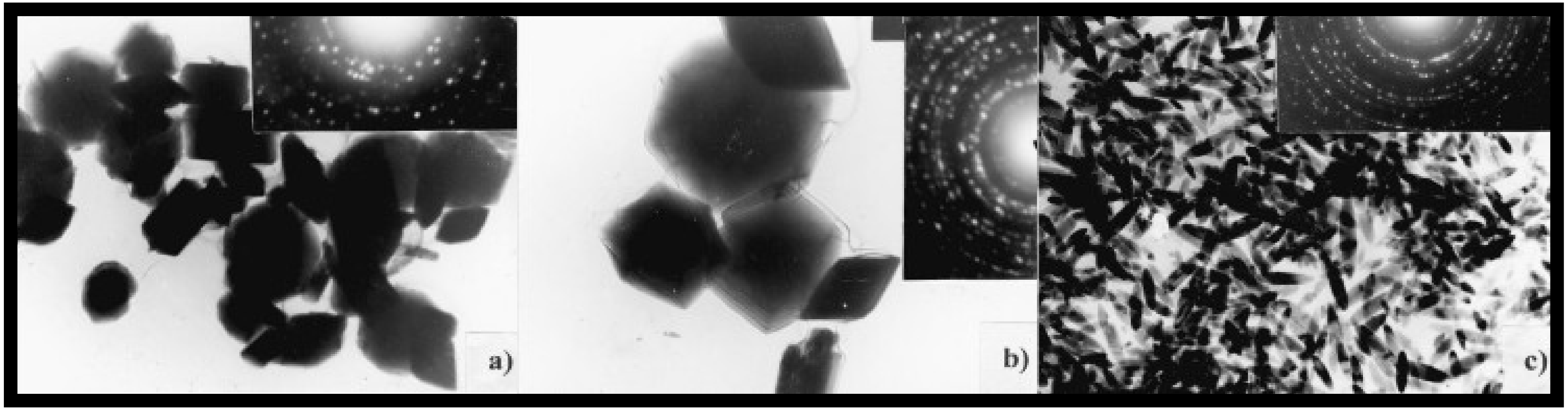




- ➢ **Decrease of lattice parameters occurs with Al-for-Fe substitution**

2. Usage and synthesis of nanoparticles

- **Usage**: limited due to small magnetic moment, hematite is employed in various branches such as catalysis, **mineralogy and biology**, its high activity and selectivity is used in Fisher-Tropsch catalytic synthesis of hydrocarbon from CO and H_2, nanoparticles of hematite are now utilized as a part of humidity sensors
- **Synthesis of hematite nanoparticles**: final product of thermal conversion of series of compounds with **Fe(II) a Fe(III)** and final form of thermally-induced transformations of other iron oxides, **hydrolysis of ferric salts in strong acidic environments**, **sol-gel method**, **hydrothermal reaction method**, γ-FeOOH → γ-Fe_2O_3 → α-Fe_2O_3,…

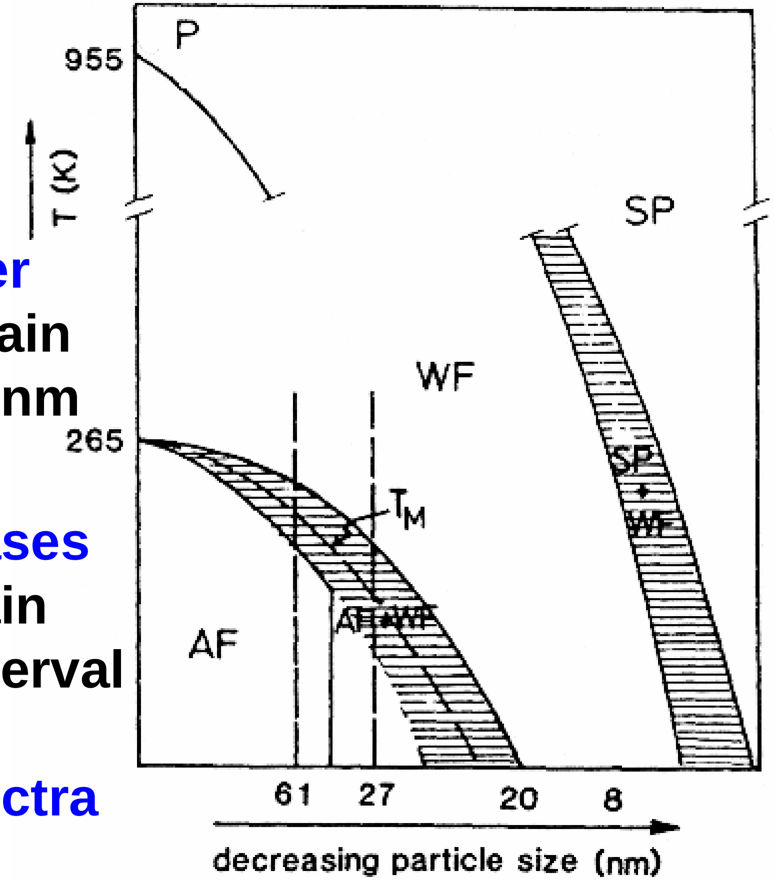


3. Magnetism of hematite

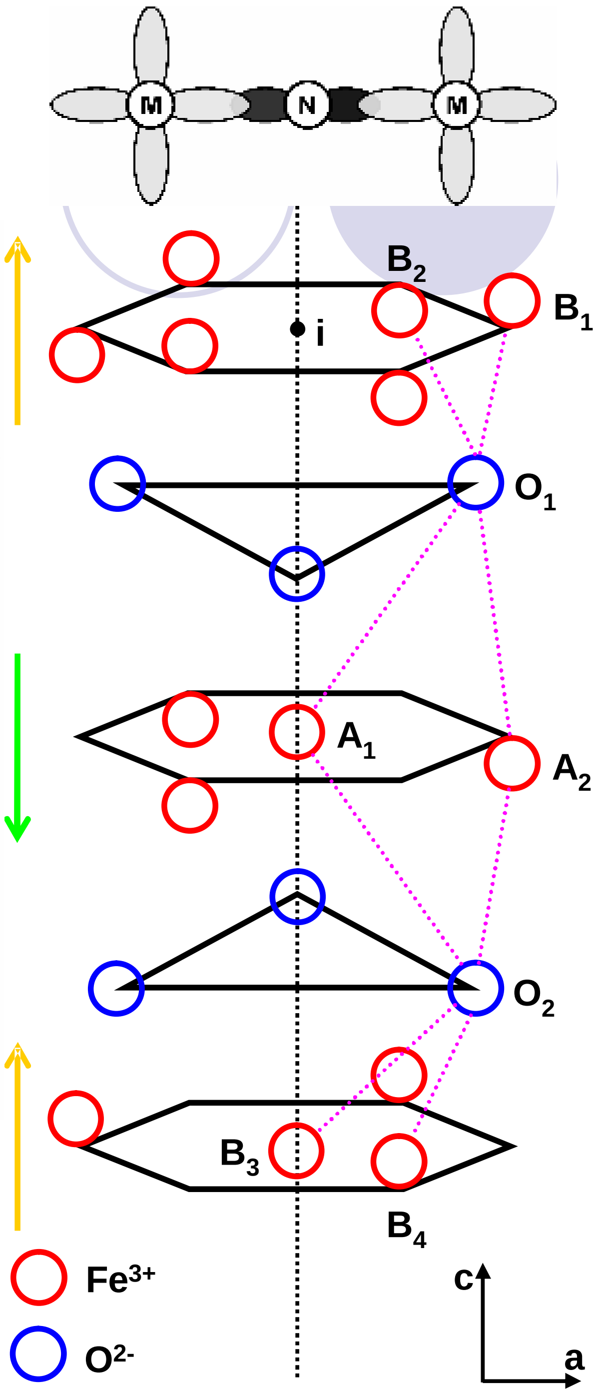
- Magnetic material with dvou different magnetic orderings under the Neél temperature ($T_N = 960$ K), hematite is paramagnetic above T_N
- The magnetic state of hematite is dominantly determined by strong magnetic interaction among magnetic moments of Fe^{3+} ions, mediated by antiferromagnetic indirect exchange interaction via d-orbitals of O^{2-} ionts
- Important phenomenon → Morin transition (MT), characterized by temperature T_M, at which the alignement of magnetic moments into mutually perpendicular directions takes place, $T_M = 263 – 267$ K.
- Below T_M → AF phase → hematite is purely antiferromagnetic, when the magnetitude of magnetization of both sublattices is the same, but they have opposite direction → collinear antiferromagnetic ordering, spins lie in rhombohedral, i.e. [111], direction
- Above T_M → WF phase → hematite is weakly ferromagnetic due to noncollinearity of sublattice magnetizations, which are inclined to each other by the angle different from 180° → spins lie in basal plane (111) → small canting angle and small ferromagnetic moment due to Dzyaloshinsky antisymmetric interaction
- MT is first-order thermodynamic transition, when 90° spin-flop occurs; it results from ceaseless competition between strong magnetic dipolar anisotropy (MDA → favours the orientation of spins in basal plane) and local iont anisotropy (LIA, spin-orbitální interaction → favours the orientation of spins in [111] plane) with different thermal dependencies, at MT → MDA = LIA → the sign of total magnetocrystalline anisotropy (MCA) changes

3. Magnetism of hematite

- Critical diameter for single–domain structure → 30 nm
- AF and WF phases coexist in certain temperature interval → overlap in Mössbauer spectra

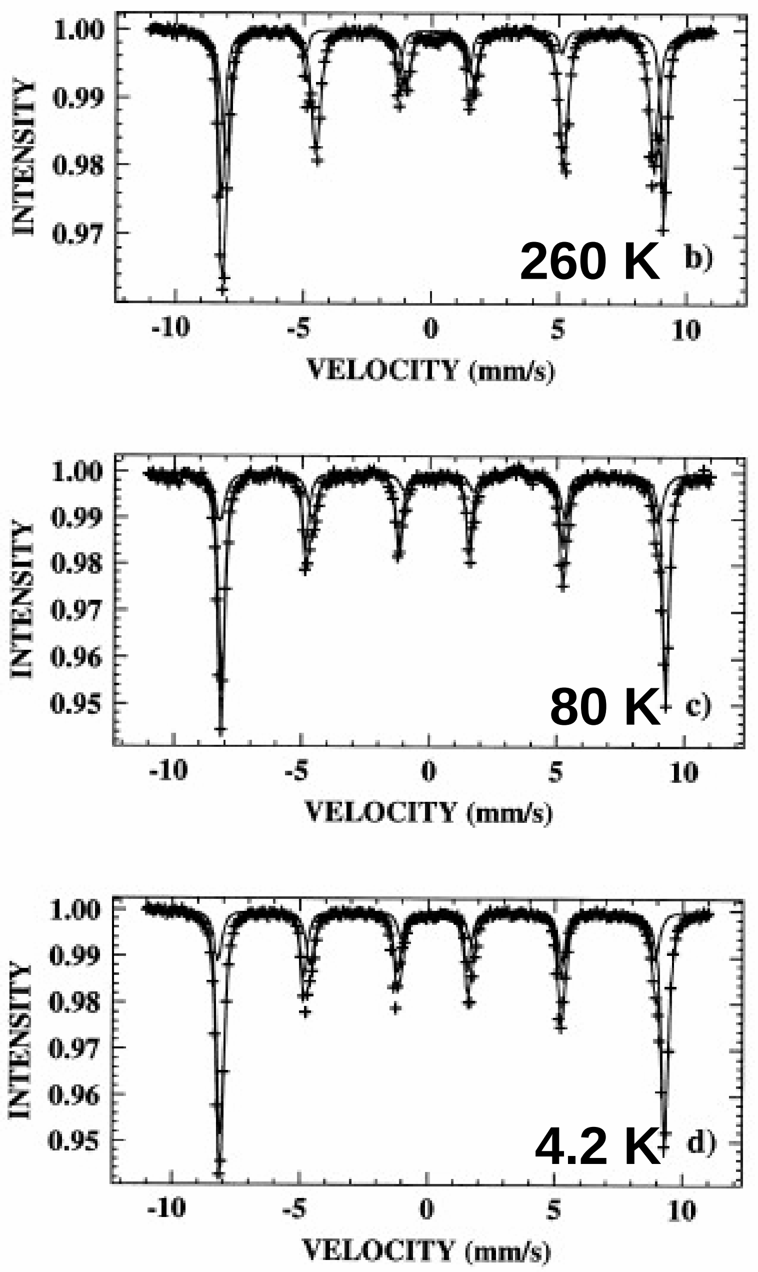


- T_M depends on the size of the particles (below 20 nm → only WF phase), lattice defects (low crystallinity, vacancies), substitution (Al with 8mol% → only WF phase), deviations from stechiometry, surface effects and morphology



4. ZF-MS of hematite

- Temperature evolution of Mössbauer spectra of crystalline hematite reflects MT by existence of two sextets
- T_M (Mössbauer) → temperrature, when the portion of AF sextet is reduced to 50 % of its intensity at low temperature
- When fitting → IS, Γ a $\Delta\Gamma$ are the same for WF and AF phase, the intensity ratio of lines (ideally ≈ 3:2:1) is T independent
- Coexistence of AF and WF sextets → asymmetry in spectrum → 1st and 5th lines are deeper than 6th and 2nd lines
- IS (RT) → 0.37 mm/s (Fe^{3+} with $S = 5/2$), $T\downarrow$ - $\delta\uparrow$, at MT $\Delta\delta = 0.03$ mm/s
- QS → $2\varepsilon_Q = 0.40$ mm/s (WF phase), for AF phase $2\varepsilon_Q = -0.20$ mm/s
- H_{hf} (RT) → 51.7 T, at MT discontinuity of H_{hf}, i.e. $\Delta H_{hf} = 0.9$ T



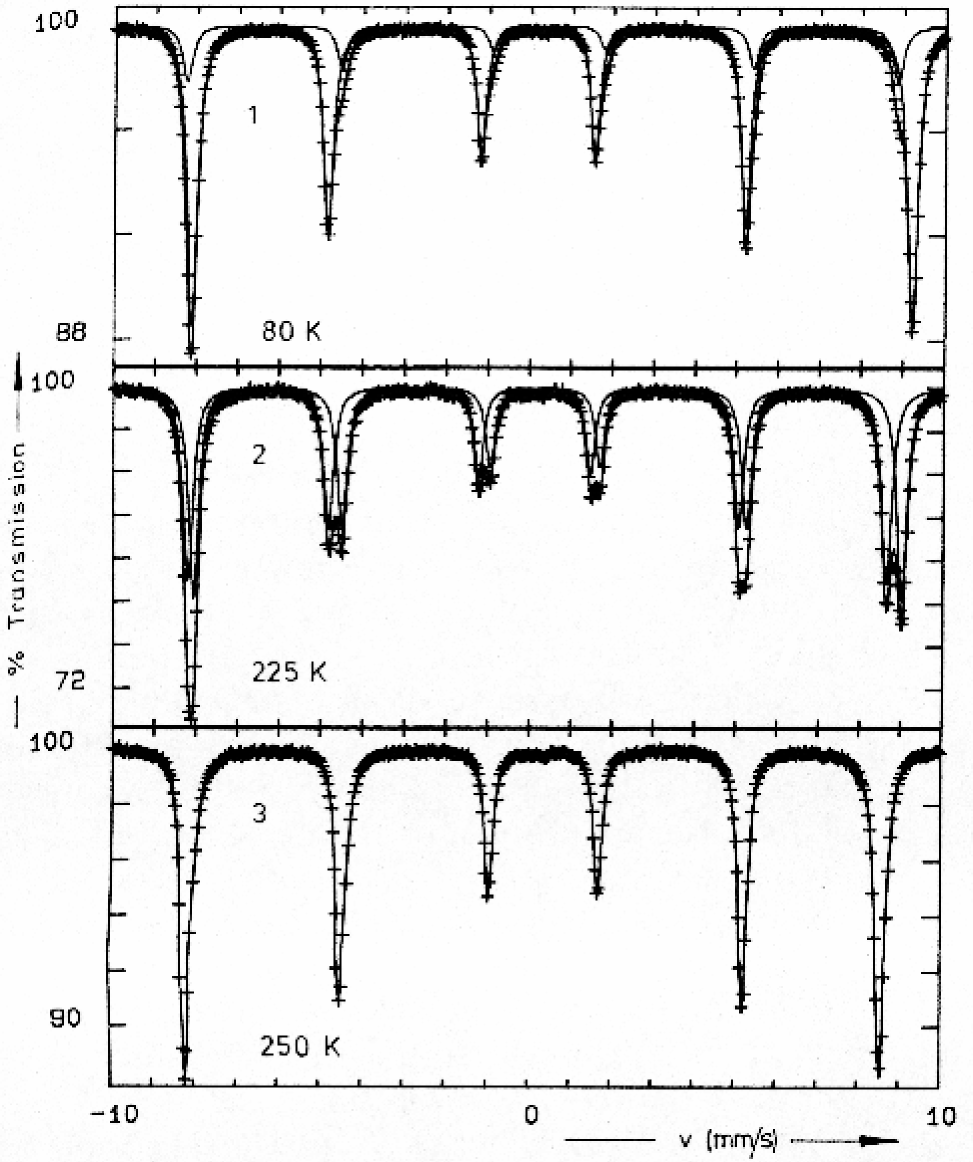
4. ZF-MS of hematite

Shift of MT

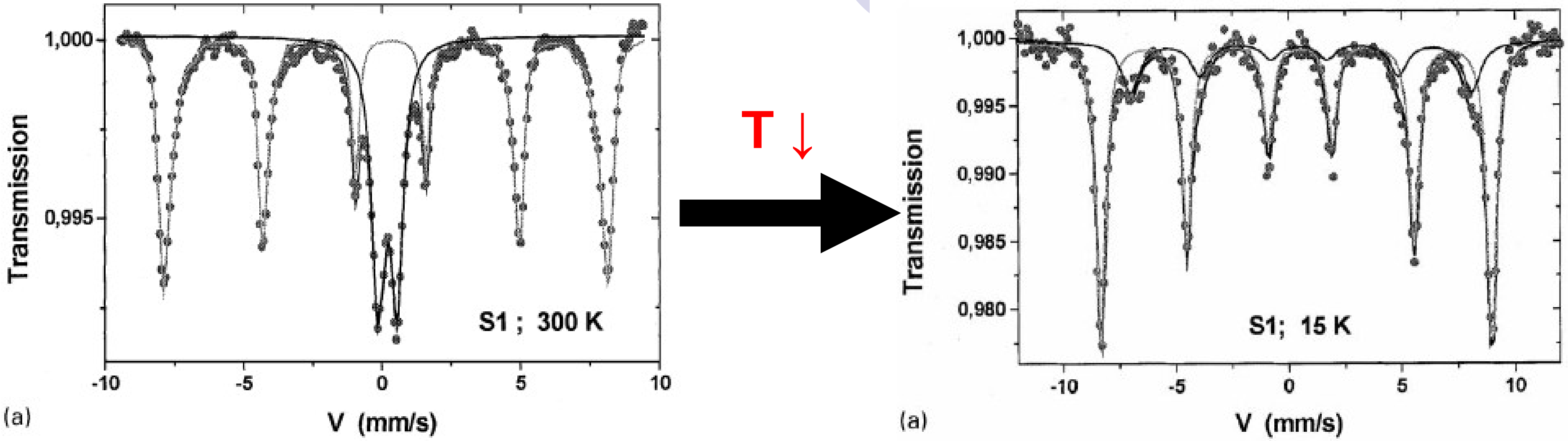
Dominant AF phase at the expanse of WF phase

Coexistence of WF and AF phase

Only WF phase



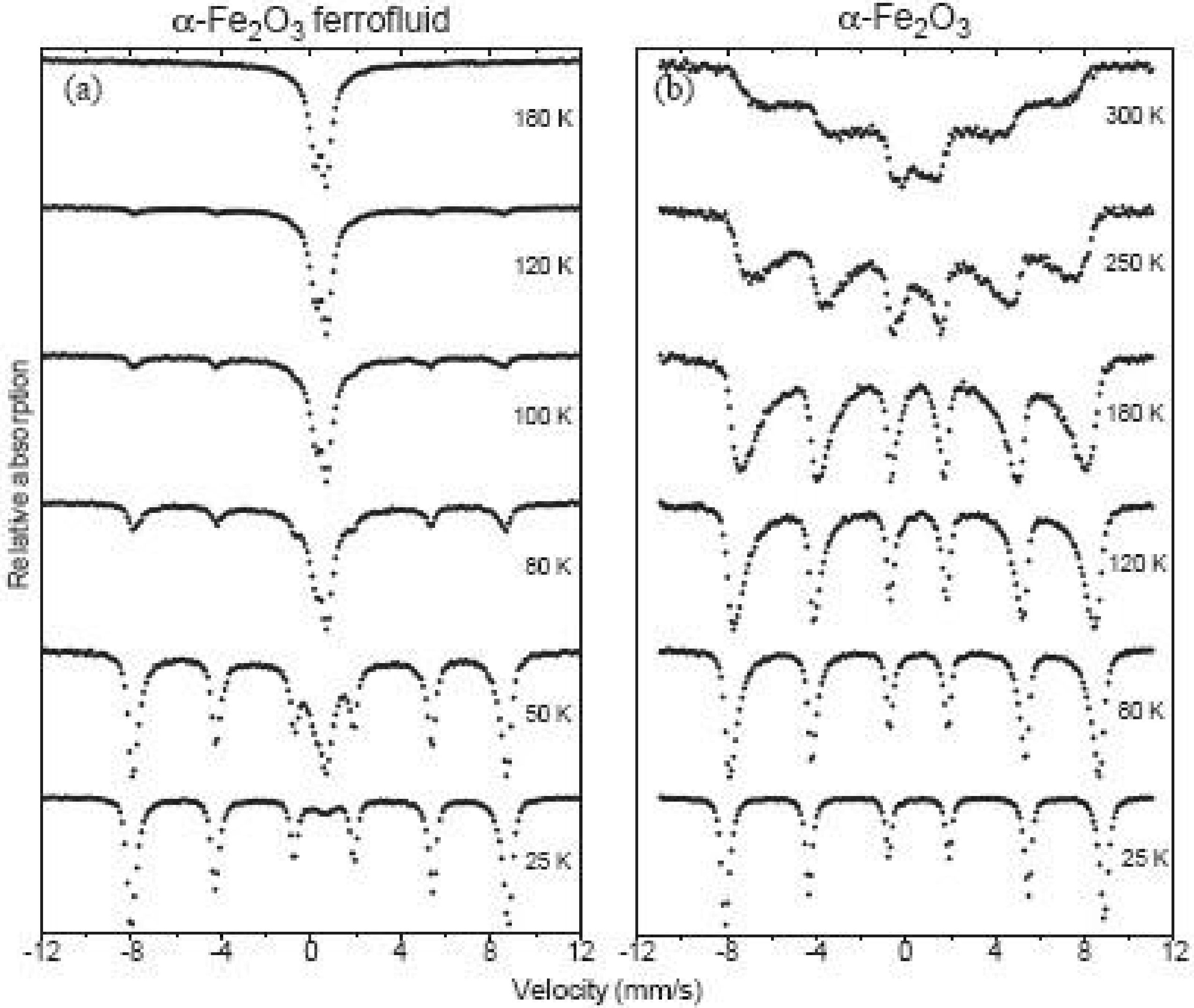
4. ZF-MS of hematite



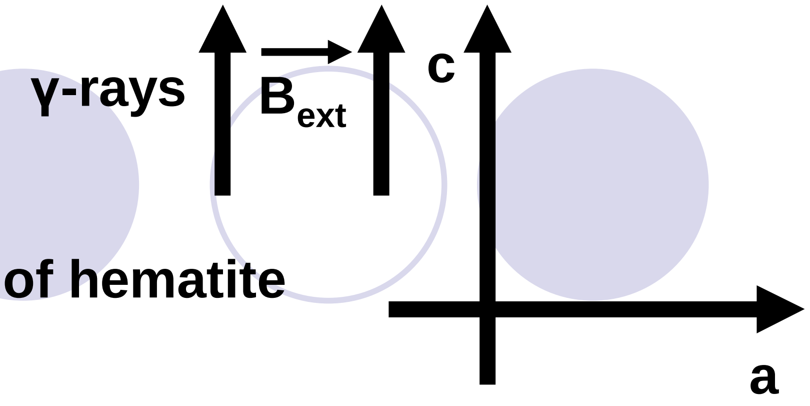
- Superparamagnetism → dominant phenomenon for particles of ≈ 20 nm
- Very fast relaxation, $\tau_0 = 10^{-11}$ s → sharp sextet-dublet transition, broadening of lines, influence of collective magnetic excitations below T_B
- The core of the nanoparticle exhibits a higher TM than the surface, WF phase advances tovards the core due to different MCA at the surface
- Ultrafine particles → decrease in TM, influence of surface anisotropy and change of orientations of easy axes of magnetizations
- Influence of interparticle interactions → increase of T_B → in accordance with Dorman-Bessais-Fiorani (DBF) model

4. ZF-MS of hematite

Influence of interparticle interactions → spin-glass-like behaviour



5. AF-MS of hematite

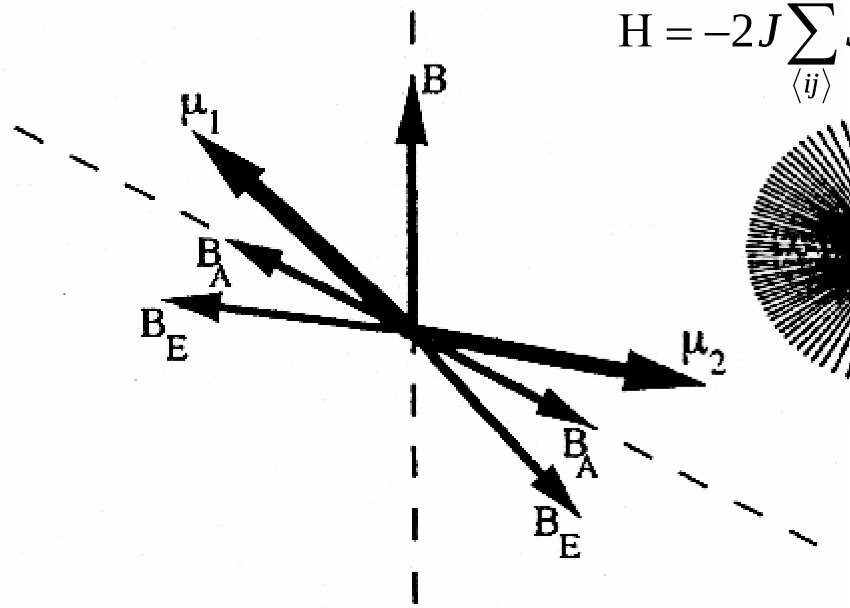


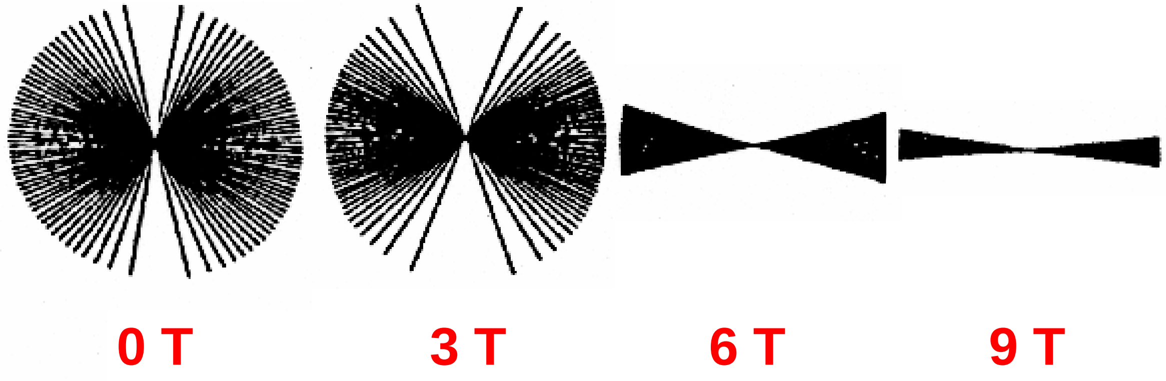
Description of AF-MS of hematite

↓

1. **Atomic spin Hamiltonian (Two-sublattice model)**
2. **Probability distributions of hyperfine fields**
3. **Superoperator method (EQ interaction as perturbation to MD interaction)**
4. **LD model**
5. **Wivel-Mørup model (Model-Independent Approach)**

$$H = -2J\sum_{\langle ij\rangle}\vec{S}_i.\vec{S}'_j - K\sum_i (S_{zi})^2 - K'\sum_i (S'_{zj})^2 - g\mu_B\vec{B}.\left(\sum_i \vec{S}_i + \sum_j \vec{S}'_j\right)$$



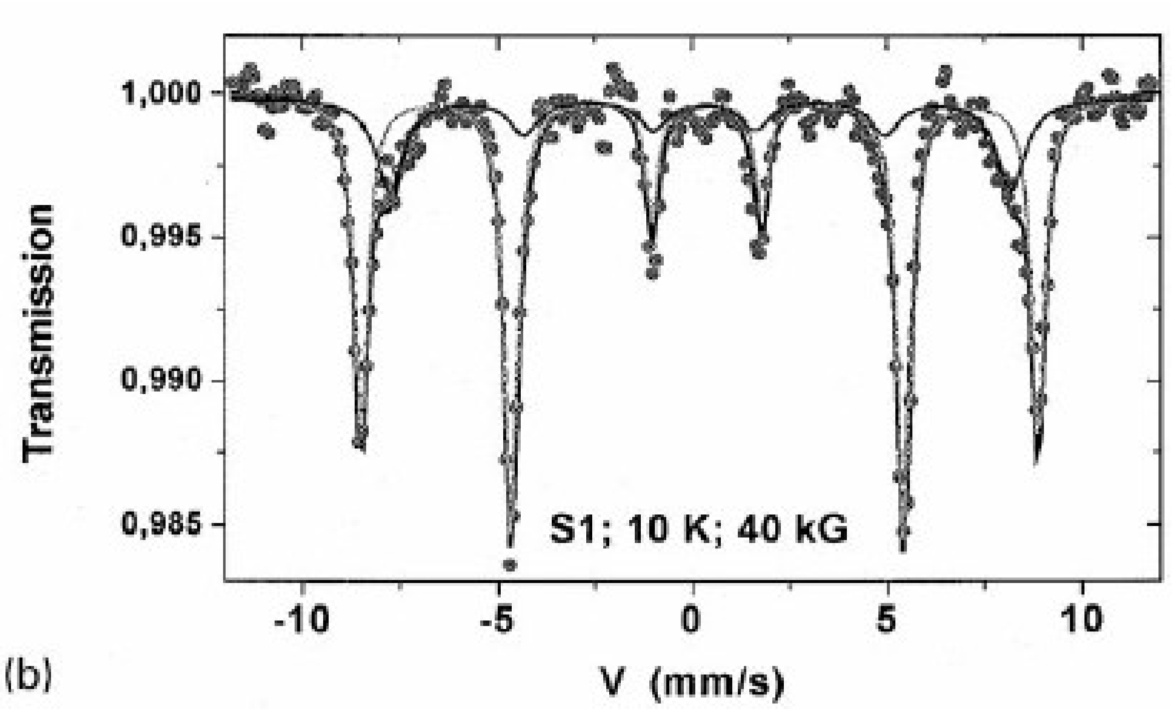


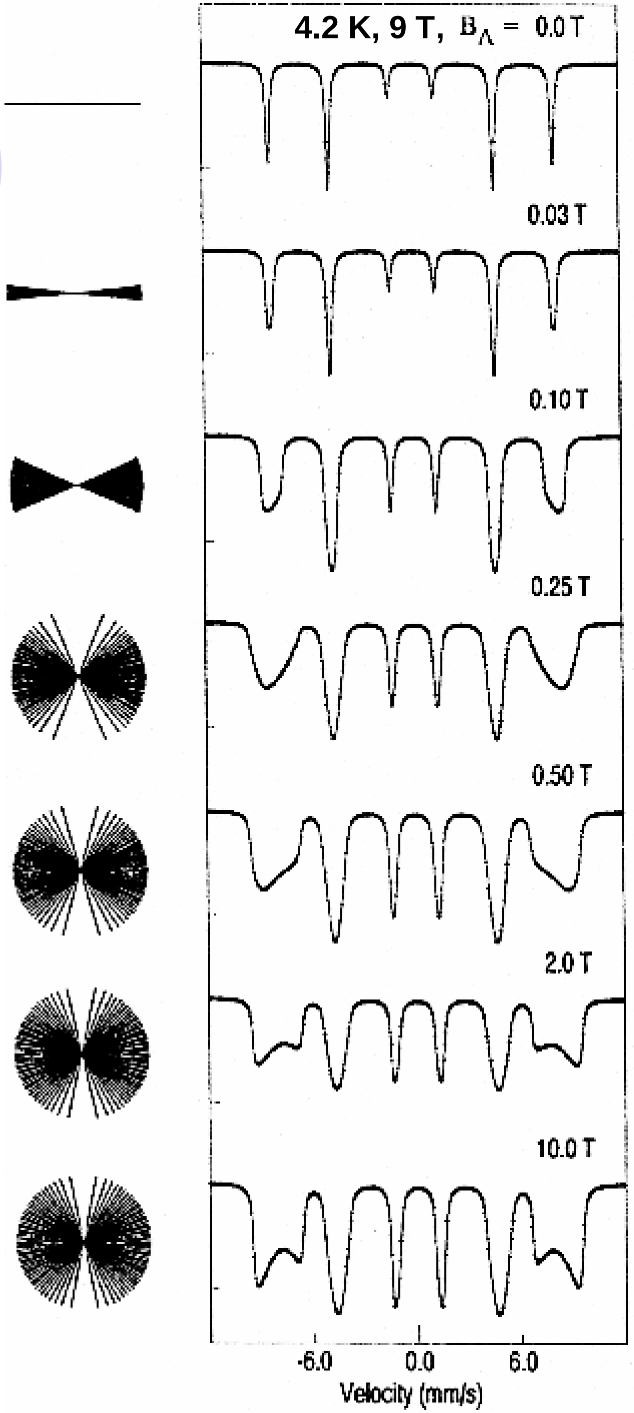
5. AF-MS of hematite

Effective canting angle θ_c from intensities of the 2nd and 5th lines

$$\sin^2(\theta_c) = \frac{\frac{1}{2}\frac{A_{2,5}}{A_{3,4}}}{1+\frac{1}{4}\frac{A_{2,5}}{A_{3,4}}}$$

$A_{2,3}/A_{3,4} = 4$ indicates the alignement of spins in direction perpendicular to an external magnetic field





5. AF-MS of hematite

Critical field H_{sf}, which is necassary to flop the spins spinů into perpendicular direction

$$H_{sf} = \sqrt{\frac{2K}{\chi_{\perp} - \chi_{\parallel}}} \qquad H_{sf} = \sqrt{2H_E H_A - H_A^2}, \quad T = 0\,\mathrm{K}$$

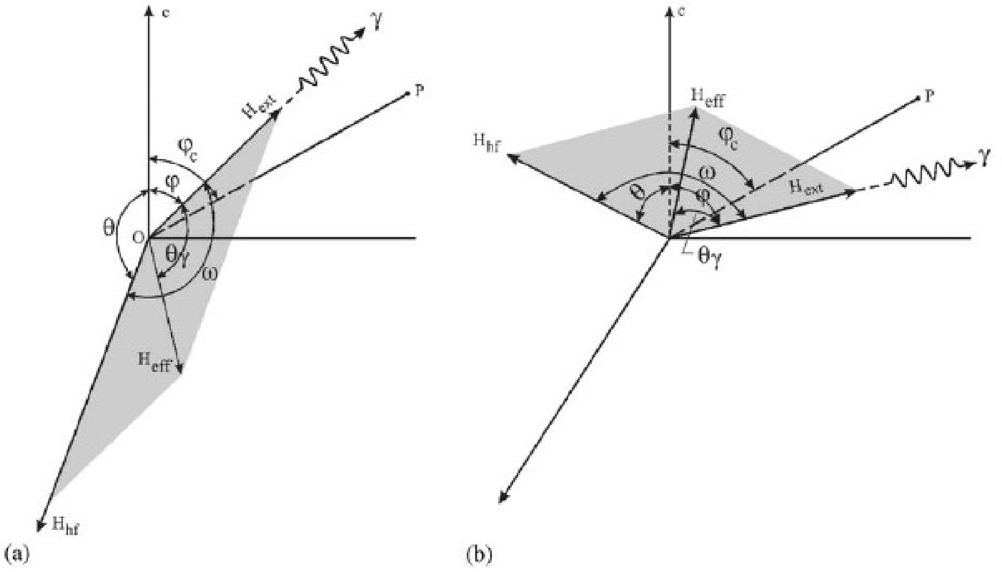
Parallel-field spin-flop transition

[external field in the direction of c-axis (rhombohedral [111]) of hematite]

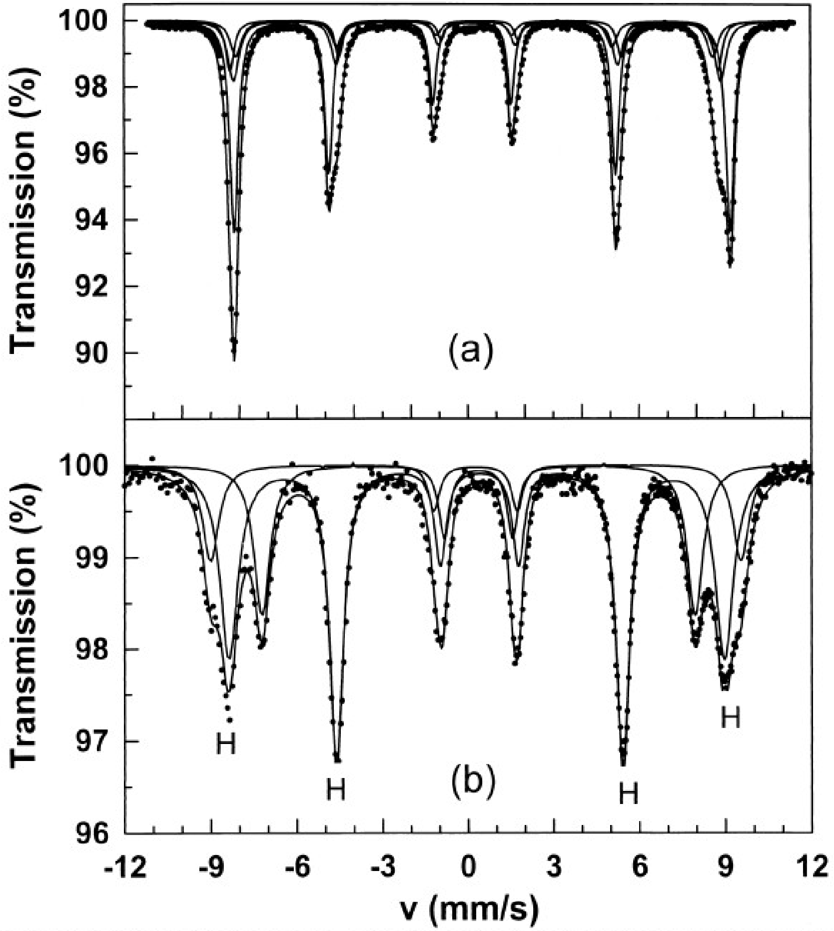
X

Transverse-field spin-flop transition - screw rotation

[external field in perpendicular direction to c-axis of hematite]



5. AF-MS of hematite



4.2 K, 0 T

4.2 K, 9 T

Mössbauer Parameters of the α- and γ-Fe_2O_3 Phases Present in Sample Gp275.

	α-Fe_2O_3				γ-Fe_2O_3			
	δ (mm/s)	$2\epsilon_Q$ (mm/s)	H^* (kOe)	RA	δ (mm/s)	$2\epsilon_Q$ (mm/s)	H^* (kOe)	RA
H_{ext} = 60 kOe	0.46	−0.10	538	0.63	0.38	0.0	575	0.14
					0.47	0.0	470	0.23
H_{ext} = 0	0.45	0.34	538	0.54	0.38	0.0	515	0.12
	0.45	−0.20	530	0.13	0.47	0.0	530	0.21

6. AF-MS of hematite – Models

1. **Atomic spin Hamiltonian (Two-sublattice model)**

↓

simple model for materials with two sublattices, constant J is the same for all interactions, for small particles the devations from the suitable fits occurs, it models well the influence of exchange anisotropy

2. **Probability distributions of hyperfine fields**

↓

suitable for determination of probability distributions of spins alignement in space

3. **Superoperator method** (EQ interaction as pertubation to MD interaction)

↓

solving secular equations, suitable for monitoring the influence of surface anisotropy, to much sextets, some of them do not have physical or chemical meanings

4. **LD model**

↓

introduces several interaction constants (9), hematite is considered as simple two sublattice antiferomagnet, it does not take into an account the influence of the size of the particles

5. **Wivel-Mørup model (Model-Independent Approach)**

↓

influence of the size of the particles and collective magnetic excitations are taken into account

7. Summary and outlook

- **Mössbauer spectroscopy is a powerful tool for investigation of magnetic properties of hematite**
- **There are several areas, that needs further clarification → for synthetic nanoparticle, the appearance of the third sextet in transition interval of WF and AF phase (its origin is not clear yet → WF-like phase & AF-like phase); in AF-MS several models for description, no one is universal, the description becomes difficult for ultrafine particles with high anisotropy and significant surface effects; the influence of morphology has not been studied yet (orientation of easy axes of magnetization → it is possible to monitor it by AF-MS); the influence of synthesis conditions on magnetic properties of prepared nanoparticles etc.**
- **We aim at studying the magnetic moments within the particles with induced spin orientation due to morphology etc.**