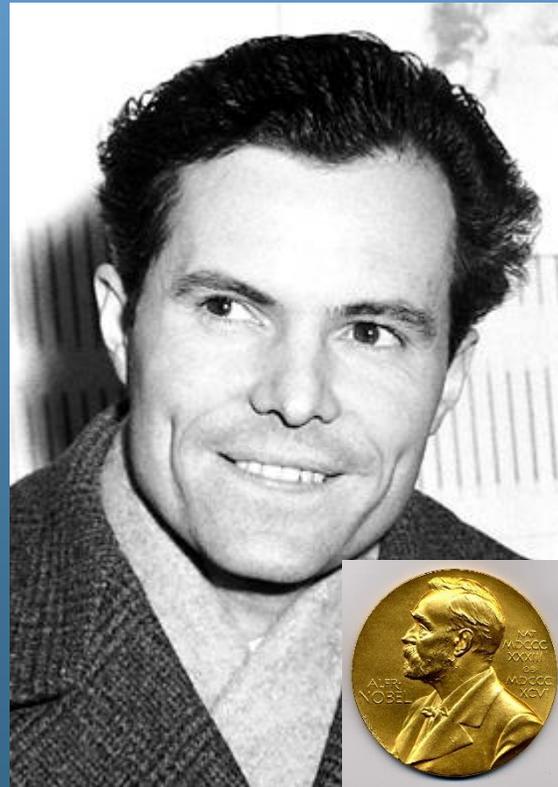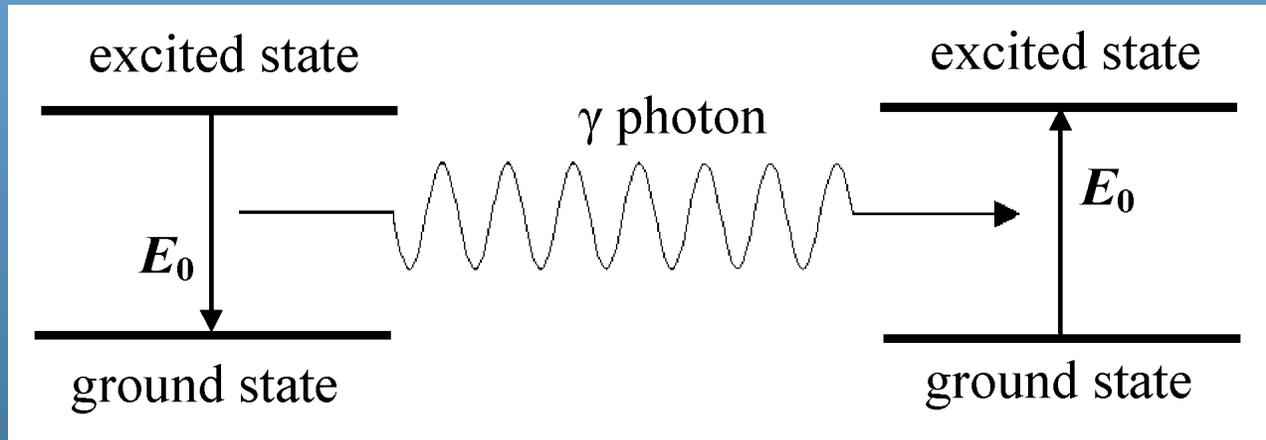# Mössbauer Spectroscopy

The Mössbauer-effect

The **Mössbauer effect** is the nuclear resonance fluorescence of γ rays.

In normal (atomic) spectroscopies such a phenomenon is quite common and taken as absolutely normal….

This is not the case for nuclei, but why is it interesting for anybody at all?

The energy of the excited nuclear levels is characterized by a $C(E_0, \Gamma/2)$ Cauchy distribution function whose (un-normalized) density function is called a **Lorentzian** (or **Breit–Wigner**) **curve** in physics (Breit and Wigner 1936):

$$L(E) = A \frac{\Gamma}{2\pi} \frac{1}{(E - E_0)^2 + \left(\dfrac{\Gamma}{2}\right)^2}$$

E_0 Line position (energy)

Γ Line width at half maximum

For the natural line width the Heisenberg relation holds:

$$\Gamma\tau = \hbar$$

τ Average life time of the excited state of the nucleus

The average lifetime for ^{57}Fe: 9.8×10^{-8} s
Planck's constant: 4.136×10^{-15} eVs

The line width: 6.72×10^{-9} eV (!)

The extremely low line width may allow one to measure energy at a resolution of the nanoelectronvolt!

One has to find a phenomenon in which this linewidth plays a role.

Nuclear resonance fluorescence!

But!

$$E_{recoil} = \frac{E_\gamma^2}{2Mc^2}$$

For the 14.4 keV radiation of [57]Fe: E_{recoil}= **1.92x10^{-3} eV**
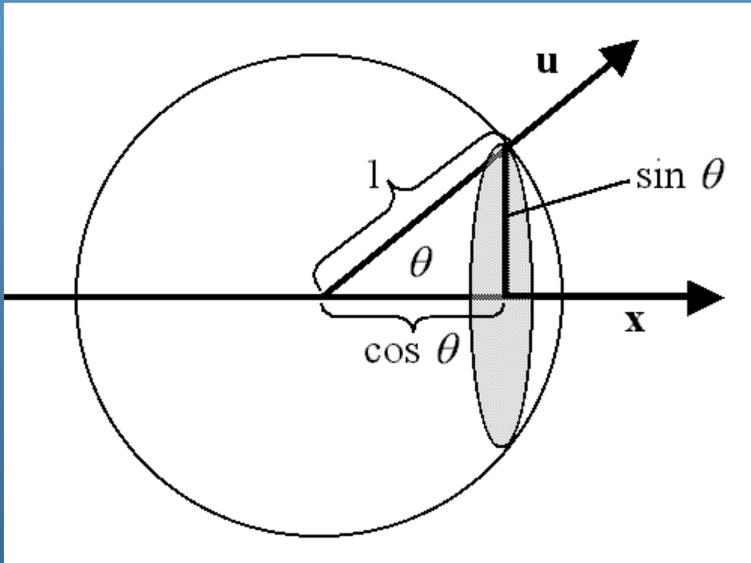
Resonace condition destroyed....

How can one yet accomplish the nuclear resonance fluorescence experiment?

Let us broaden the gamma line, so that the absorption and emission spectra have some overlap!

Method: thermal broadening using the Doppler principle

Thermal broadening in a gas:

$$E_\gamma = (E_0 - E_R)\left(1 + \frac{u}{c}\cos\theta\right)$$

Averaging u and Θ

$$\langle E_\gamma\rangle = (E_0 - E_R)\left(1 + \frac{\langle u\rangle}{c}\langle\cos\theta\rangle\right)$$

The expected value of Eγ is not affected by the Doppler motion, but its variance is:

$$D^2(E_\gamma) = \left\langle (E_\gamma - \langle E_\gamma\rangle)^2\right\rangle = (E_0 - E_R)^2\frac{\langle u^2\rangle}{c^2}\langle\cos^2\theta\rangle = (E_0 - E_R)^2\frac{\langle u^2\rangle}{3c^2}$$

Temperature dependence from Boltzmann:

$$\frac{M\langle u^2\rangle}{2} = \frac{3kT}{2}$$

Now the standard deviation of the energy:

$$D(E_\gamma) = (E_0 - E_R)\sqrt{\frac{kT}{Mc^2}} \approx E_0\sqrt{\frac{kT}{Mc^2}} = \sqrt{2kTE_R}$$
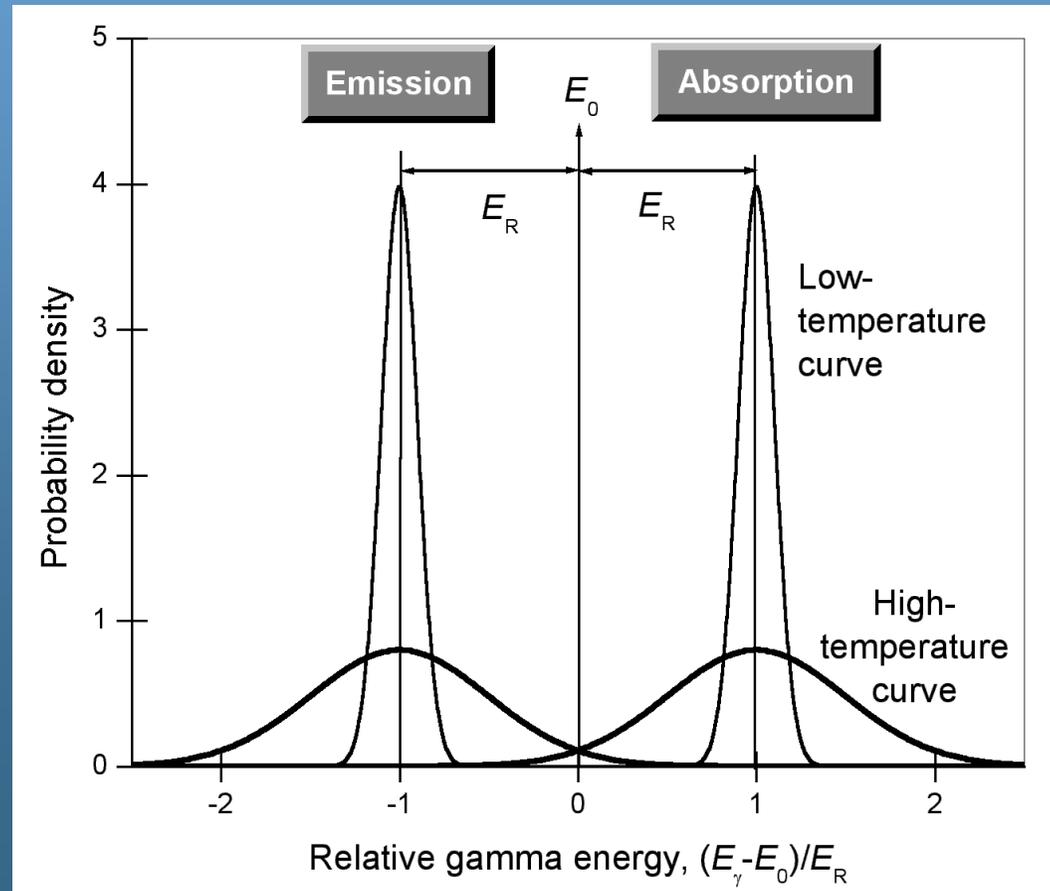
Thus overlap between the emission and absorption lines may be achieved by heating the system. Nuclear resonance fluorescence is re-established.

But does it really make sense???

No!

The nanoelectronvolt resolution is lost....

Emission E_0 Absorption

E_R E_R

Low-temperature curve

High-temperature curve

Probability density

Relative gamma energy, $(E_\gamma - E_0)/E_R$

One has to find a way to „get rid" of the recoil energy so that the original line width and therefore the energy resolution for any spectroscopy built on this phenomenon is preserved.

Quantization of lattice vibrations helps!

The recoil energy may be transferred…

?
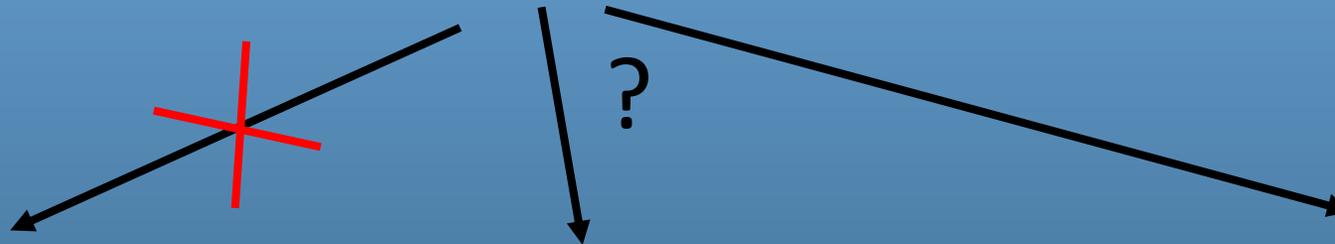
…to the atom ejected from the lattice, in the form of kinetic energy.

…to the lattice, in the form of vibrational energy.

…to the whole crystal grain as a rigid body, in the form of kinetic energy.

If the recoil energy is not enough to generate a phonon (lattice vibration quantum) the third scenario will be realised. In this case, the recoil energy is taken by the whole crystal grain the mass of which is huge as compared to that of a single atom. Thus the recoil energy becomes negligible even relative to the line width.

„Recoilless" nuclear gamma resonance absorption/emission

Description of lattice vibrations:

Einstein:

$$\hbar\omega_{\mathrm{E}} = k\theta_{\mathrm{E}}$$

$$E_{\mathrm{E}} = \hbar\omega_{\mathrm{E}} = \frac{\hbar c_{\mathrm{s}}}{\lambdabar_{\mathrm{s}}} = \frac{\pi\hbar c_{\mathrm{s}}}{a}$$

where a is the lattice constant, c_{s} is the speed of the sound waves in the solid, and $2\pi\lambdabar_{\mathrm{s}}$ is the wavelength of the sound associated with the vibration. The wavelength is supposed to satisfy the condition $\lambdabar_{\mathrm{s}} = 2a$.

Debye:

$$p(\omega) = \begin{cases} 3\dfrac{\omega^2}{\omega_{\mathrm{D}}^3} & \text{for } 0 \leq \omega \leq \omega_{\mathrm{D}} \\[2ex] 0 & \text{elsewhere} \end{cases}$$

$$\hbar\omega_{\mathrm{D}} = k\theta_{\mathrm{D}}$$

Debye-temperature

Debye-frequency

Due to quantization:

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

The mean energy for a given frequency ω at a given temperature T:

$$\bar{\varepsilon}(\omega,T) = \frac{\sum_{n=0}^{\infty} \varepsilon_n \exp\left(-\frac{\varepsilon_n}{kT}\right)}{\sum_{n=0}^{\infty} \exp\left(-\frac{\varepsilon_n}{kT}\right)} = \left(\bar{n}(\omega,T) + \frac{1}{2}\right)\hbar\omega$$

where

$$\bar{n}(\omega,T) = \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}$$

(Bose-Einstein distribution function)

In quantum theory, the time-average of the square displacement (and similarly that of the square speed) of an atom doing harmonic oscillation along the x axis with frequency ω is given as follows:

$$\left\langle x^2 \right\rangle_{\omega,T} = \frac{\left\langle \dot{x}^2 \right\rangle_{\omega,T}}{\omega^2} = \left(\bar{n}(\omega,T) + \frac{1}{2}\right)\frac{\hbar}{M\omega}$$

The **mean square displacement** at a given temperature is obtained by averaging the time-average of the square displacement over all frequencies:

$$\langle x^2 \rangle_T = \int\limits_0^{\omega_D} \langle x^2 \rangle_{\omega,T}\, p(\omega)\, \mathrm{d}\omega = \frac{3\hbar^2}{Mk\theta_D}\left[\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int\limits_0^{\theta_D/T} \frac{x}{e^x - 1}\, \mathrm{d}x\right]$$

→ Mössbauer-Lamb - factor

The **mean square velocity** of the lattice vibration at a given temperature can be derived similarly to that of mean square displacement:

$$\langle u^2 \rangle_T = \int\limits_0^{\omega_D} \langle u^2 \rangle_{\omega,T}\, p(\omega)\, \mathrm{d}\omega = \frac{9k\theta_D}{M}\left[\frac{1}{8} + \left(\frac{T}{\theta_D}\right)^4 \int\limits_0^{\theta_D/T} \frac{x^3}{e^x - 1}\, \mathrm{d}x\right]$$

→ Second order Doppler shift

Why is the mean square displacement interesting for us?

The general formula to describe the time and spatial dependence of the amplitude of the electromagnetic field emitted by a nucleus:

$$\xi = \xi_0 \exp\left[i\left(\omega_0 t - \kappa x\right)\right]$$

amplitude

κ wave number

ω_0 frequency

In case of harmonic oscillation of the atom: $x = a\cos\omega t$, thus:

$$\xi = \xi_0 \exp\left[i\left(\omega_0 t - \kappa a \cos\omega t\right)\right]$$

The new radiation will be a modulated one, the only question is if this vibration does contain the original ω_0 mode?

This will give the contribution of the recoilless events!

Method: Fourier transformation and finding the relative intensity of the ω_0 mode!

Mössbauer-Lamb factor: f

For weak modulation (when $\kappa a/\omega$ is small), the following is valid*:

$$f = J_0^2(\kappa x_0)$$

Maximum displacement of the vibrating atom

$$J_0(\mathrm{z}) = \sum_{k=0}^{\infty} (-1)^k \left(\frac{z^k}{2^k\, k!} \right)^2$$

First order Bessel function

Since there are several different vibration modes:

$$f = \prod_m J_0^2(\kappa x_m)$$

*This always holds in practice

The amplitude of the vibration of the atoms is always small (typically 10^{-5} fraction of the lattice constant), thus the Bessel function becomes very simple by stopping with the summation at k=1:

$$J_0(z) \cong 1 - \frac{1}{4}z^2$$

$$e^x \cong 1 + x$$

$$\ln f \cong -\frac{1}{2}\sum_m \kappa^2 x_m^2$$

Since the definition of the mean square displacement is:

$$\langle x^2 \rangle = \frac{1}{2}\sum_m x_m^2$$

The Mössbauer-Lamb factor:

$$f = \exp(-k^2 \langle x^2 \rangle_T) = \exp\left(-\frac{\langle x^2 \rangle_T}{\lambdabar^2}\right)$$

$$k = \frac{2\pi}{\lambda} = \frac{1}{\lambdabar} = \frac{E_0}{\hbar c}$$

For high Mossbauer-Lamb-factor:
➤ Low mean square displacement
➤ High wavelength (low energy)

...is preferred

The Mössbauer-Lamb factor expressed within the Debye-model (that gave $<x^2>$):

$$f(T) = \exp\left\{-\frac{6E_R}{k\theta_D}\left(\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int\limits_0^{\theta_D/T} \frac{x}{e^x - 1}\,dx\right)\right\}$$

Debye-temperature: where the discrete vibrational spectrum becomes continuous

Please note that the Debye model had been developed for a monatomic cubic lattice, and thus the quantitative results applied to an arbitrary lattice must be taken with some suspicion.

The Mössbauer periodic table. Shaded cells contain elements with no known Mössbauer isotope. Unshaded cells also indicate the mass number(s) of the Mössbauer isotope(s) below the chemical symbol. We have indicated no more than two (of the most important) isotopes for each of the elements. An asterisk '∗' after the last mass number means that there are further Mössbauer isotopes not shown here.

May be measured at room temperature.

12.4-keV Nuclear Resonance of ^{45}Sc
Basic Features

Excitation energy: $E = 12.40 \pm 0.05$ keV, [1,2,3,6]
excited state lifetime: $\tau = 0.47$ s, [1,5,6]
natural energy width: $\Gamma = \hbar/\tau = 1.4$ feV,
resonance quality: $Q = \Gamma/E \simeq 10^{19}$,
internal conversion coefficient: $\alpha \simeq 630$, [4,5,6]
^{45}Sc natural abundance: 100%,

room temperature Lamb-Mössbauer factor: $f_{\text{LM}} \simeq 0.8$,

$3/2^+$ 12.4 keV $\tau_0 \simeq 470$ ms

IC > 99%

e^-, K_α, K_β

$7/2^-$ 0.0

$^{45}_{21}$Sc$_{24}$ stable
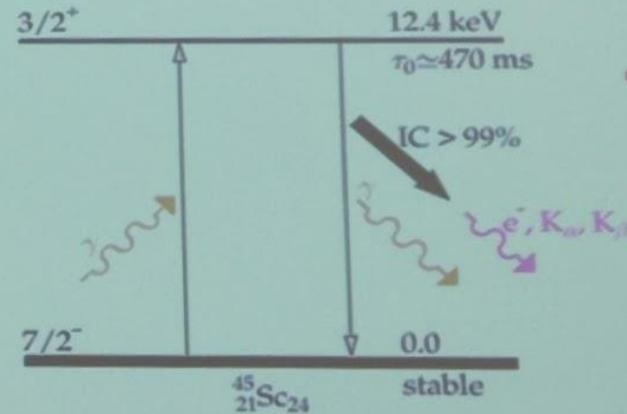
[1] Holland R.E., Lynch F.J., Nystén K.E., PRL 13 (1964) 241-243.
[2] Freedman, M. S., Porter, F. T. & Wagner F.Jr, Phys. Rev. 140, B563-B565 (1965).
[3] Porter, F. T., Freedman, M. S., Wagner F., & Orlandini, K. A., Phys. Rev. 146, 774-780 (1966).
[4] Jones, K. W. and Schwarzschild, Phys. Rev. 148, 11481150 (1966).
[5] Blaugrund, A. E., Holland, R. E. & Lynch, F. J., Phys. Rev. 159, 926930 (1967).

[6] Burrows, T. W., Nuclear Data Sheets 109, 171-296 (2008).

With the help of the Mössbauer effect, hyperfine interactions can be measured because the linewidth of the emitted radiation is preserved. But HOW?

Method: Let us measure the absorption of gamma rays emitted by a particular nucleus by another nucleus of the same kind as a function of energy!

How to tune the energy of the emitted gamma rays on a scale of 10^{-10} eV resolution?

Doppler's principle:

$$\Delta E = \frac{v}{c} E_\gamma$$

source

absorber   detector
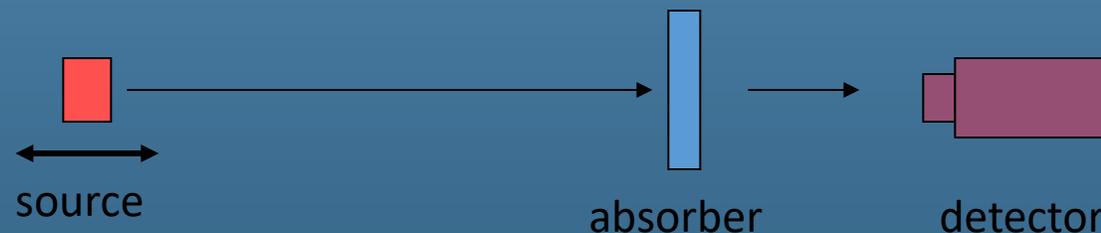
The emitted line is a Lorentzian line.

Let us apply the description of the vibrational amplitude of the emitted radiation for a large ensemble of atoms:

$$\xi = \xi_0 \exp(i\,\omega_0\,t - \Gamma t/2)$$

The spatial variation is omitted because we deal with the non-modulated line only! But the large ensemble of atoms decay according to the genaral decay law with decay constant Γ.

To switch from the time domain to the energy (frequency) domain, one has to calculate the Fourier transform of the above formula:

$$a(\omega) = \frac{1}{2\pi} \int_0^\infty \exp(i\omega_0 t - \Gamma t/2)\exp(-i\,\omega t)\mathrm{d}t$$

This yields the amplitude distribution of the ω_o frequency radiation:

$$a(\omega) = \frac{1}{2\pi} \frac{1}{\omega - \omega_0 + i\Gamma/2}$$

From this, the normalised intensity of this radiation

$$I(\omega) = 2\pi\Gamma|a(\omega)|^2 = \frac{\Gamma}{2\pi} \frac{1}{(\omega - \omega_0)^2 + \Gamma^2/4}$$

A Lorentzian with maximum intensity at ω_o and line width Γ.

This is the shape of the emitted line and also the profile of the absorption.
How can one describe the measured line profile in a Mössbauer spectrum?

Convolution of functions:

$$f_{X+Y}(z) = f_X * f_Y(z) \equiv \int_{-\infty}^{+\infty} f_X(z-u) f_Y(u)\, du$$

When needed, the original function may be calculated from the resultant spectrum by deconvolution, using a special feature of Fourier trasformation (φ) applied for convolution integrals:

$$\varphi(f_{X+Y}) = \varphi(f_X * f_Y) = \varphi(f_X)\varphi(f_Y)$$

source   absorber   detector

u

Absorption line

Emitted line

u_1

u_2

u_3

u_4

Intensity (counts)

u_1 u_2 u_3 u_4

Doppler velocity   (mm s^{-1})
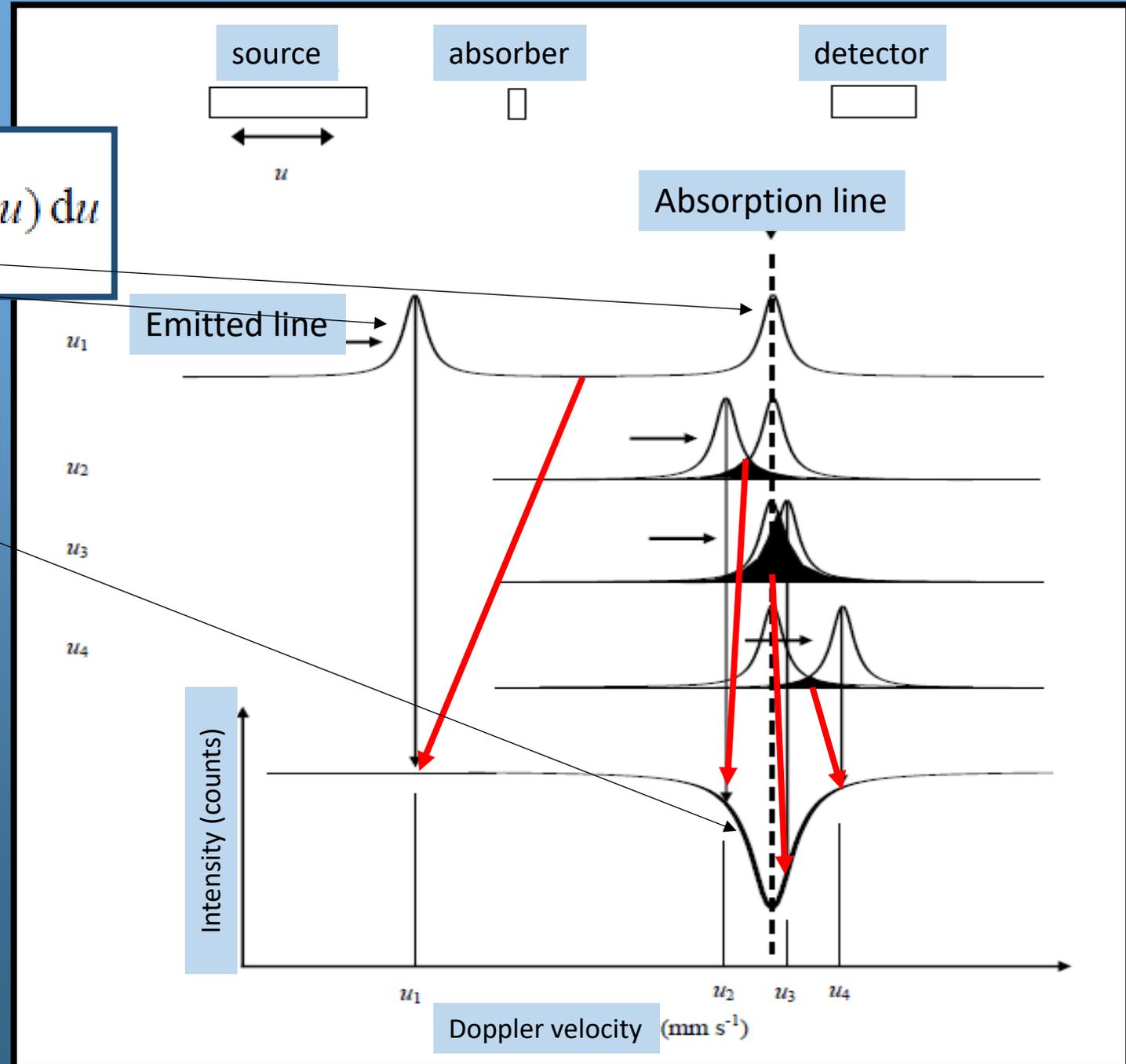
Aside:

Phenomenological description of attenuation (absorption) of radiation:
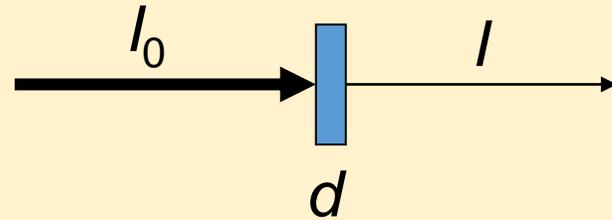
$$I = I_0 \exp(-\mu d) = I_0 \exp(-\frac{\mu}{\rho} d\rho) = I_0 \exp(-\mu_m d_s)$$

Mass absorption coefficient

Surface density

Applying this math for the Lorentzians playing role in a Mössbauer experiment, we end up with the Transmission integral, T(u):

$$T(u) = \left\{ 1 - f_S + \int_{-\infty}^{+\infty} \frac{\frac{\Gamma f_S}{2\pi}}{(E - E_0)^2 + \left(\frac{\Gamma}{2}\right)^2} \exp\left(-\frac{\tau_A \left(\frac{\Gamma}{2}\right)^2}{\left[E - E_0\left(1 - \frac{u}{c}\right)\right]^2 + \left(\frac{\Gamma}{2}\right)^2} \right) dE \right\} e^{-\mu_A d_A}$$

Emitted Lorentzian

Absorbed Lorentzian

f_s = Mössbauer-Lamb factor in the source

$$\tau_A = f_A n_A a_A d_A \sigma$$

g^{-1} g cm^{-2} cm^2

Here the source is considered having zero thickness!

Due to nuclear (Mössbauer) absorption in the absorber with effective thickness τ_A

Due to electronic absorption in the absorber with thickness d_A

Lambert-Beer absorption Law!

If the effective thickness of the absorber is very small (i.e., $\tau_A \to 0$), then the exponential in the integrand can be replaced by the linear terms of its Taylor series. As a result, the peak shape can be expressed by the following integral:

$$\eta(u) = f_S \tau_A \int_{-\infty}^{+\infty} \frac{\frac{\Gamma}{2\pi}}{(E-E_0)^2 + \left(\frac{\Gamma}{2}\right)^2} \times \frac{\left(\frac{\Gamma}{2}\right)^2}{\left[E-E_0\left(1-\frac{u}{c}\right)\right]^2 + \left(\frac{\Gamma}{2}\right)^2} \, dE$$

The resultant spectrum (convolution of two Lorentzians) will be a Lorentzian, too, with doubled line width!

Nuclear data of some Mössbauer nuclides:

Nuclide	E_γ (keV)	$\tau_{1/2}$ (ns)	α_{IC}	A (%)	I	Q	μ (μ_N)	g	σ_0 (10^{-24} m²)	W_0 (mm/s)	$\Delta R/R$ (x10^{-4})
^{57}Fe	0			2.14	1/2-	0.0	0.090604	0.118821			
	14.4130	97.81	8.21		3/2-	0.21	-0.15532	-0.067897	256	0.1940	-14
^{119}Sn	0			8.58	1/2+	0.0	-1.0461	-0.8283			
	23.871	17.75	5.12		3/2+	-0.06	0.633	0.167	140	0.647	+1.2
^{141}Pr	0			100	5/2+	-0.059	4.162	0.10820			
	145.4	1.85	0.46		7/2+	-	2.87	0.0533	10.6	1.017	-
^{151}Eu	0			47.82	5/2+	1.14	3.465	0.6083			
	21.532	9.7	28.60		7/2+	1.50	2.587	0.3244	23.77	1.31	+3.0

Gamma-energy · Half life · Internal conversion coefficient · Natural abundance · Nuclear spin, parity · Quadrupole moment · Magnetic moment · Giromagnetic factor · Gamma-absorption cross section · Natural line width · Change of nuclear radius

2020 sept 30

The decay scheme of ^{57}Co:
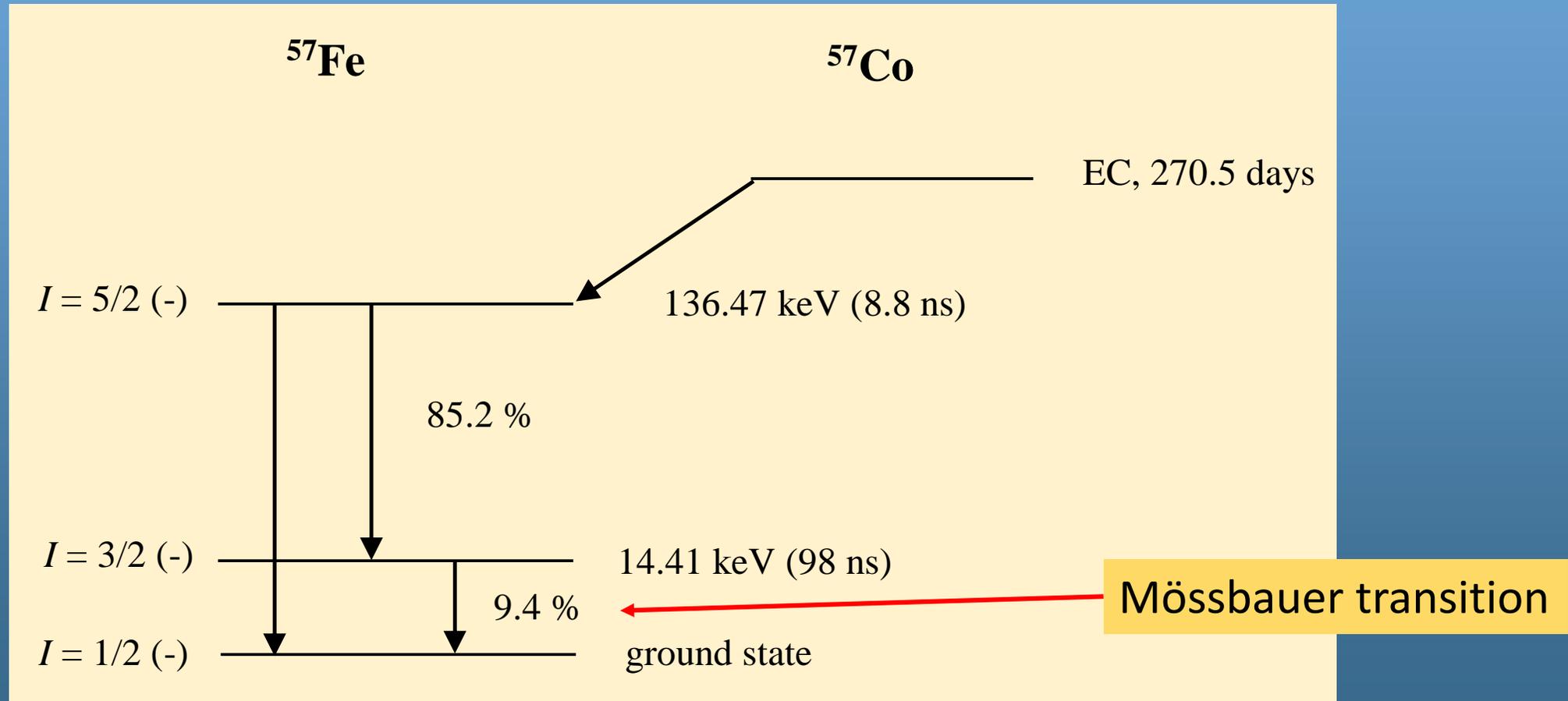
What kind of information may be read from a Mössbauer spectrum?

Fe-CDTA complex

2022 okt 6
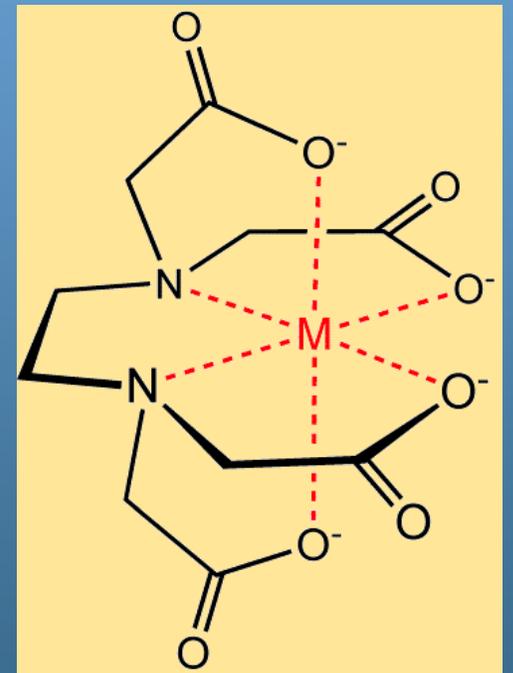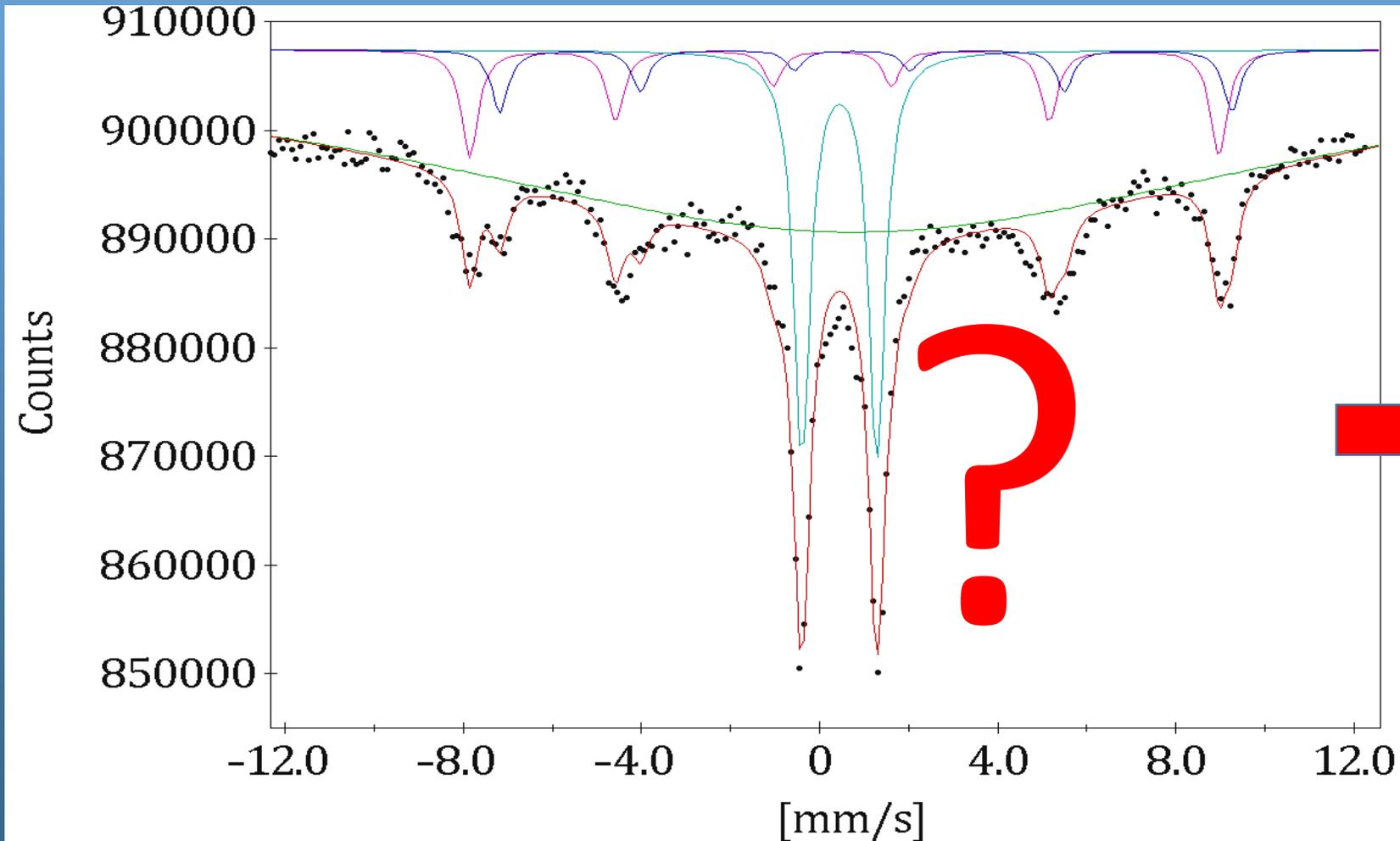
Vibrational properties of the lattice

Debye temperature from temperature dependence of the area of the Mössbauer (sub)spectrum:

$$f(T) = \exp\left\{-\frac{6E_R}{k\theta_D}\left(\frac{1}{4} + \left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1}\,dx\right)\right\}$$
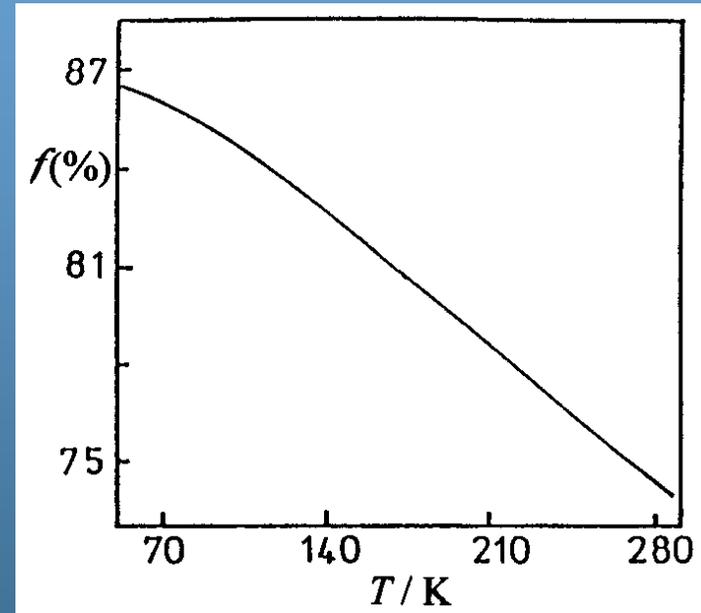
Note! The physical meaning of the Debye temperature for complicated (non-cubic, non- monoatomic) lattices is badly defined. One may learn from tendencies.

Debye temperature from the second order Doppler shift of the Mössbauer (sub)spectrum

Important: An alternative definition of the Mössbauer effect is that the gamma emission or absorption of the nucleus does not cause change in the vibrational state of the lattice, i.e., no phonon generation takes place.

But! Since the mass equivalent of the gamma photon is not negligible, the energy of the given phonon level will be altered:

$$\delta E = \left.\frac{\partial E}{\partial M}\right|_{Mv=const.} \delta M = \left.\frac{\partial \frac{(Mv)^2}{2M}}{\partial M}\right|_{Mv=const.} \delta M = -\frac{v^2}{2}\left(-\frac{E_\gamma}{c^2}\right) = \frac{1}{2}E_\gamma\left(\frac{v}{c}\right)^2$$

The derivation is made at the condition when the momentum of the nucleus is constant ("recoilless").

The second order Doppler shift contains the mean square velocity of the atom which has already been calculated from the Debye model:

$$\langle u^2 \rangle_T = \int_0^{\omega_D} \langle u^2 \rangle_{\omega,T}\, p(\omega)\, \mathrm{d}\omega = \frac{9k\theta_D}{M}\left[\frac{1}{8} + \left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}\, \mathrm{d}x\right]$$

$$\delta E = \frac{9k\Theta_D E_\gamma}{Mc^2}\left\{\frac{1}{4} + 2\left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} \frac{z^3}{\exp(z) - 1}\, \mathrm{d}z\right\}$$
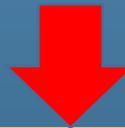
Significant shift may occur in the line positions if the temperature of the source and the absorber is not the same.

Keep in mind that if the Debye temperature is determined from the f-factors and also from the temperature shift, the results should not be expected to be the same!

Hyperfine Interactions

Interaction between the nucleus and the electrons
(nuclear charge in the electric potential of the electrons)

$$E_{\text{C}} = \int \rho_{\text{nucl.}}(\mathbf{r}) V_{\text{el.}}(\mathbf{r}) d\tau$$

Applying the Taylor series for the potential of the electrons:

$$E_C \approx V_0 \int \rho(\mathbf{r}) d\tau + \sum_{i=1}^{3} \left(\frac{\partial V}{\partial x_i} \right)_0 \int \rho(\mathbf{r}) x_i d\tau + \frac{1}{2} \sum_{i,j=1}^{3} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \int \rho(\mathbf{r}) x_i x_j d\tau$$

Nuclear charge   **Dipole moment**   **Quadrupole interaction**

This is zero because nuclei have no dipole moment

The electric field gradient tensor V can be diagonalised by proper orientation of the coordinate system. Then the third part of E_c is:

$$E_3 = \frac{1}{2}\sum_{i=1}^{3}\left(\frac{\partial^2 V}{\partial x_i^2}\right)_0 \int \rho(\mathbf{r})x_i^2 d\tau \equiv \frac{1}{2}\sum_{i=1}^{3}V_{ii}\int \rho(\mathbf{r})x_i^2 d\tau$$

In this formula, the three Descartes coordinates vary independently. Let us separate a spherically symmetrical part where the three coordinates are constrained to be the same. Then:

$$r^2 = \sum_{i=1}^{3}x_i^2 = 3x^2$$

Therefore:

$$E_3 = \frac{1}{2}\sum_{i=1}^{3}V_{ii}\int \rho(\mathbf{r})\frac{r^2}{3}d\tau + \frac{1}{6}\sum_{i=1}^{3}V_{ii}\int \rho(\mathbf{r})\left(3x_i^2 - r^2\right)d\tau$$

Spherically symmetric contribution

Nuclear quadrupole moment

Isomer shift

Quadrupole splitting

$$E_{spherical} = \frac{1}{2}\sum_{i=1}^{3} V_{ii} \int \varrho(r)\frac{r^2}{3}d\tau = \frac{1}{6}(\Delta V)_0 Ze\langle r^2\rangle \overset{!}{=} -\frac{1}{6}\frac{\varrho_e}{\varepsilon_0}Ze\langle r^2\rangle = -\frac{1}{10}\frac{\varrho_e}{\varepsilon_0}ZeR^2$$

Charge equivalent radius

$$E_{spherical} = \frac{1}{10\varepsilon_0}Ze^2R^2|\psi(0)|^2$$

Only the s-state, considered uniform within the nucleus

The hyperfine interaction depends on the nuclear radius and the electron density within the nucleus.

Note: $E_{spherical}$ is energy shift (ΔE) that is solely due to the fact that the nucleus has a finite size.
One can calculate this for the ground state and for the excited state. If the nuclear radius is different (not necessarily!), the difference of the two ΔE values will yield the shift in the gamma energy:

$$\Delta E_\gamma = \frac{2\pi}{5}Ze^2(R_{excited}^2 - R_{ground}^2)\left[\left|\Psi(0)_{given\ chemical\ environment}\right|^2\right]$$

Now calculating the gamma energy difference for two different chemical environments (one in the source and one in the absorber) will yield the **Isomer Shift**:

$$\delta = \frac{2\pi}{5} Ze^2 (R_{excited}^2 - R_{ground}^2)[|\Psi(0)_{absorber}|^2 - |\Psi(0)_{source}|^2]$$
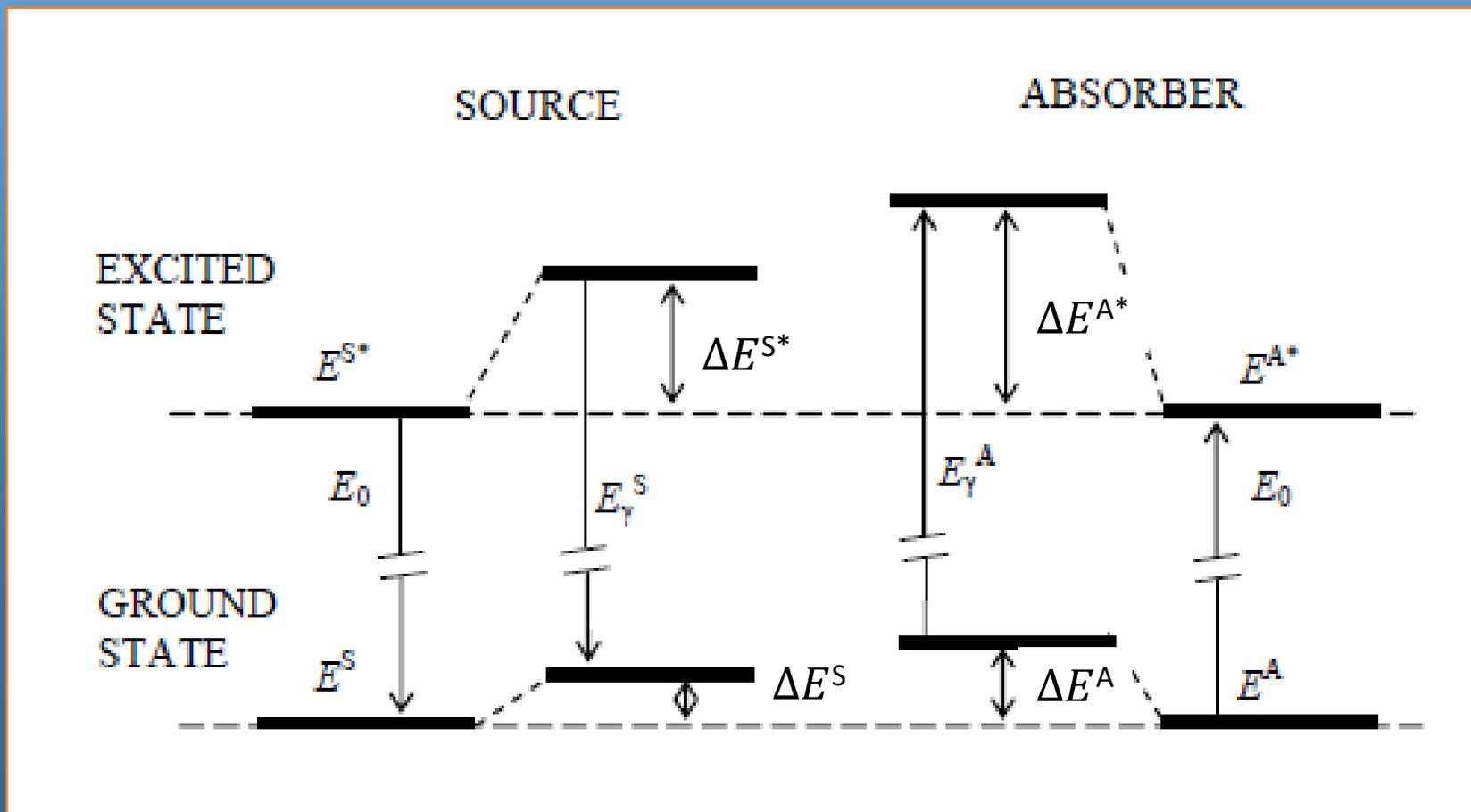
How to measure the isomer shift?

Mössbauer apparatus:

Gamma spectrum of ^{57}Co

Escape peak
1.8 keV

Characteristic X-ray of ^{57}Fe
6.4 keV

Mössbauer line
14.4 keV

Kr-filled proportional counter

drive

feedback amplifier

reference

Velocity function generator
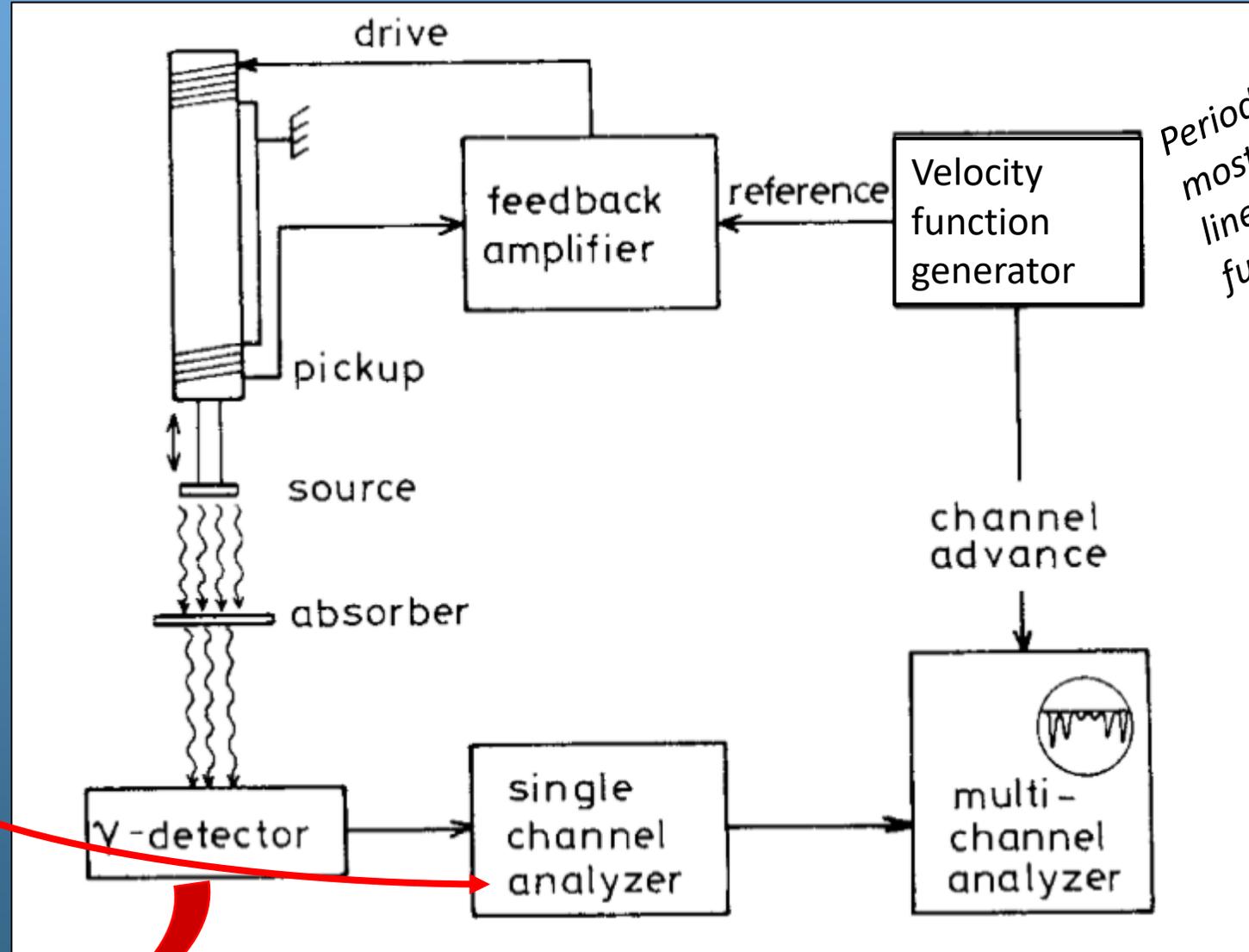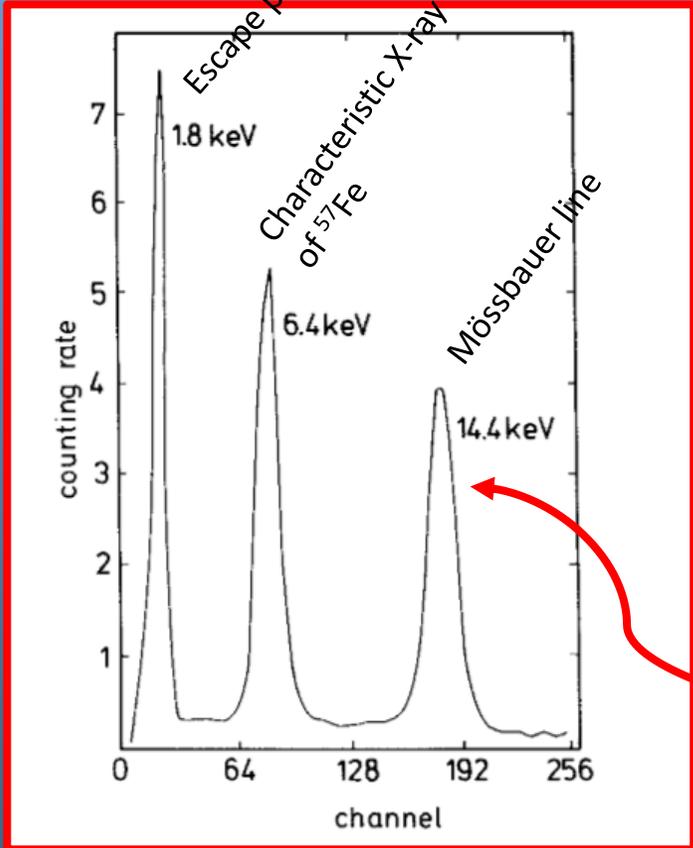
Periodic, in most cases linear v(t) function

pickup

source

absorber

channel advance

γ-detector

single channel analyzer

multi-channel analyzer

Information from the isomer shift: oxidation state and spin state

Typical ranges of isomer ^{57}Fe shifts

relative to metallic iron

Fe^{2+}

Fe^{3+}

Fe^{4+}
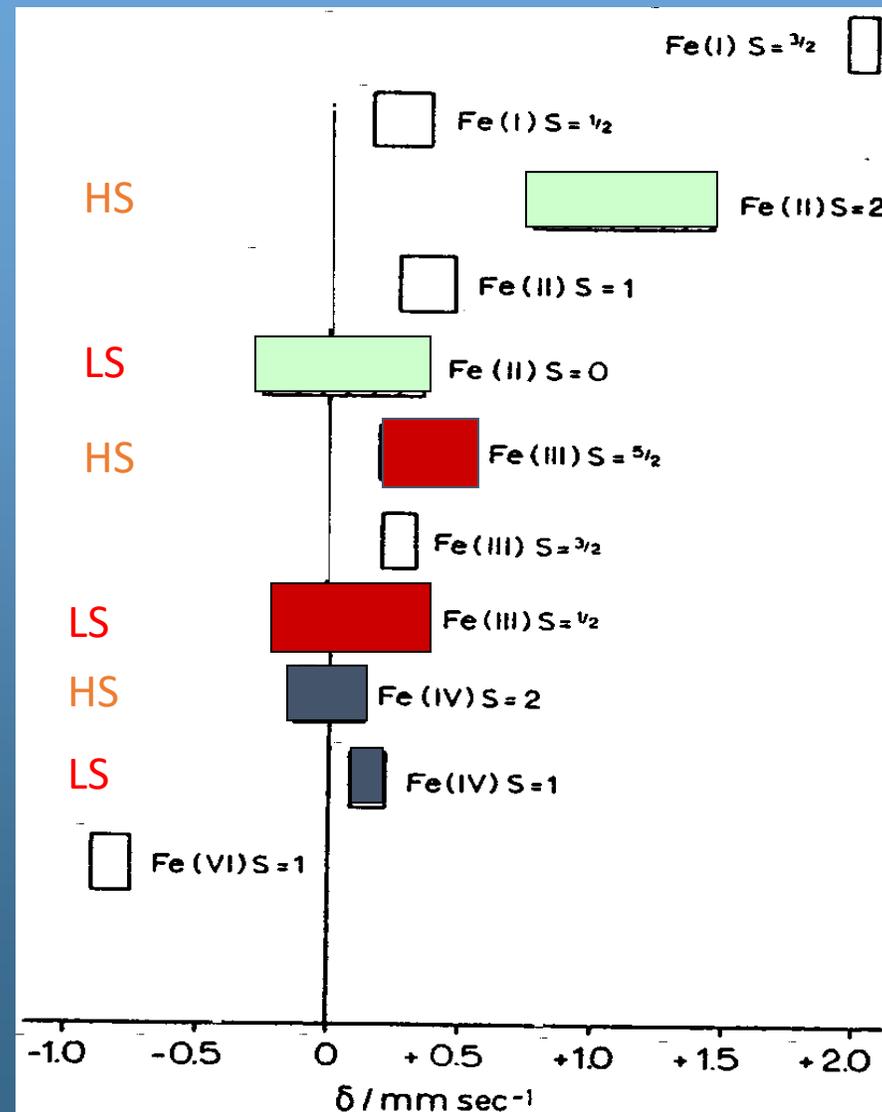
For ^{57}Fe, the isomer shift decreases with the electron density in the nucleus.

Question: Why does the isomer shift increase with the 3d electron density?

Gütlich. P., Link. R., and Trautwein. A., 1978, *Mössbauer Spectroscopy and Transition Metal Chemistry* (Berlin: Springer Verlag).

$$\delta = \frac{2\pi}{5} Ze^2 (R_{excited}^2 - R_{ground}^2)[|\Psi(0)_{absorber}|^2 - |\Psi(0)_{source}|^2]$$

Electron density in atomic hydrogen w(r) = r² [R$_{n\ell}$(r)]²

3s

3p

3d

2s

2p

1s

r / 10⁻¹⁰ m
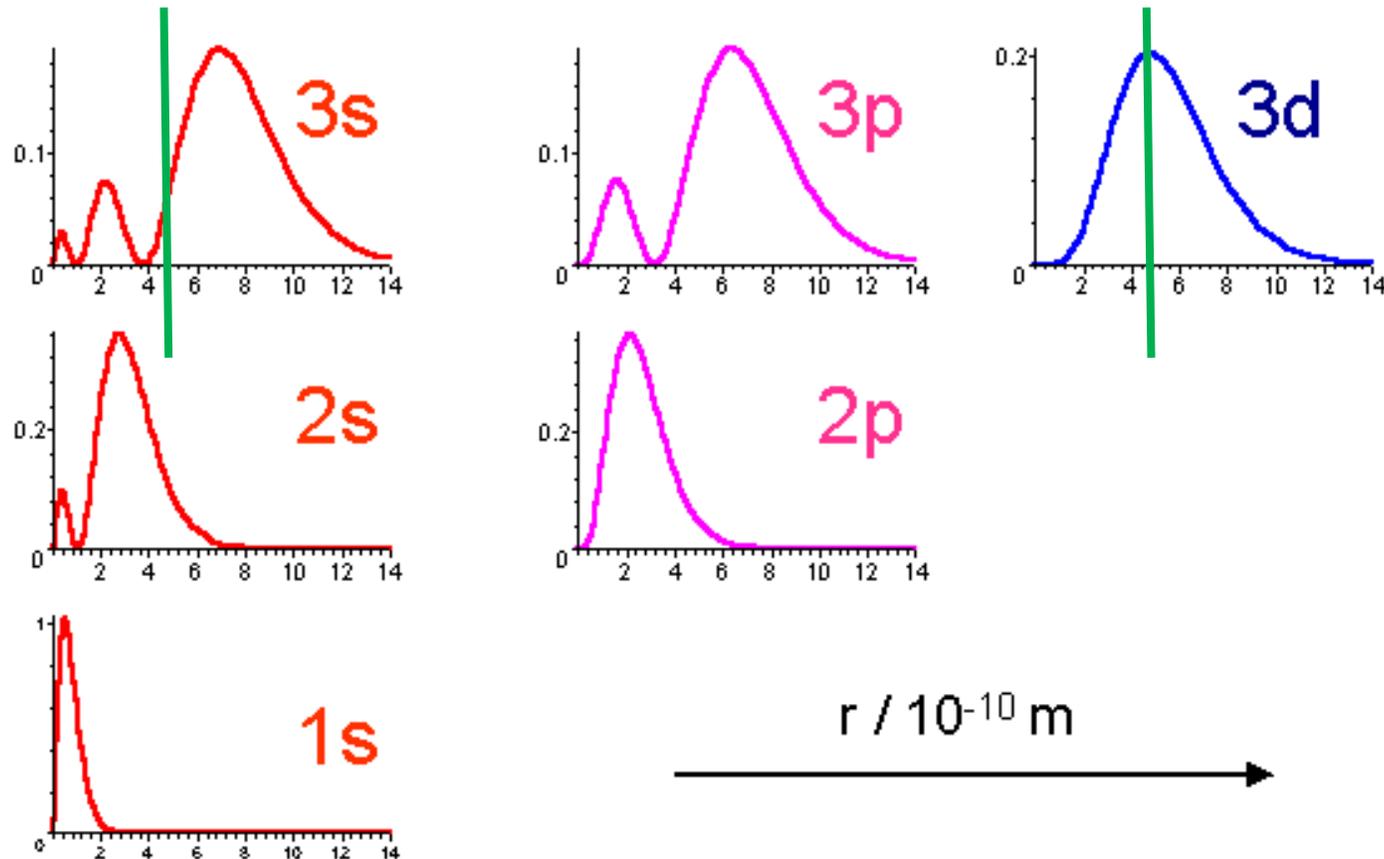
Repulsion between the 3d orbital and the main peak of the 3s orbital dominates, resulting in reduction of the 3s electron density in the nucleus.

2022 10 13

Source: https://chemistry.stackexchange.com/questions/47893/what-are-the-height-and-width-of-the-large-and-small-nodes-of-the-sp3-hybridized

Fe²⁺ and Fe³⁺ states in an amphibole sample:

jaeger.earthsci.unimelb.edu.au
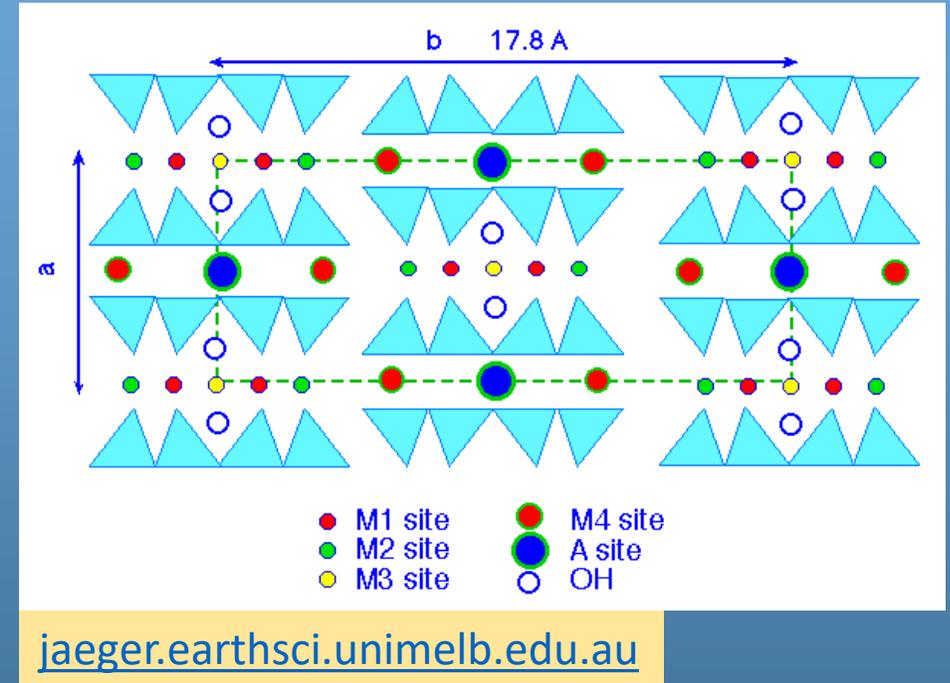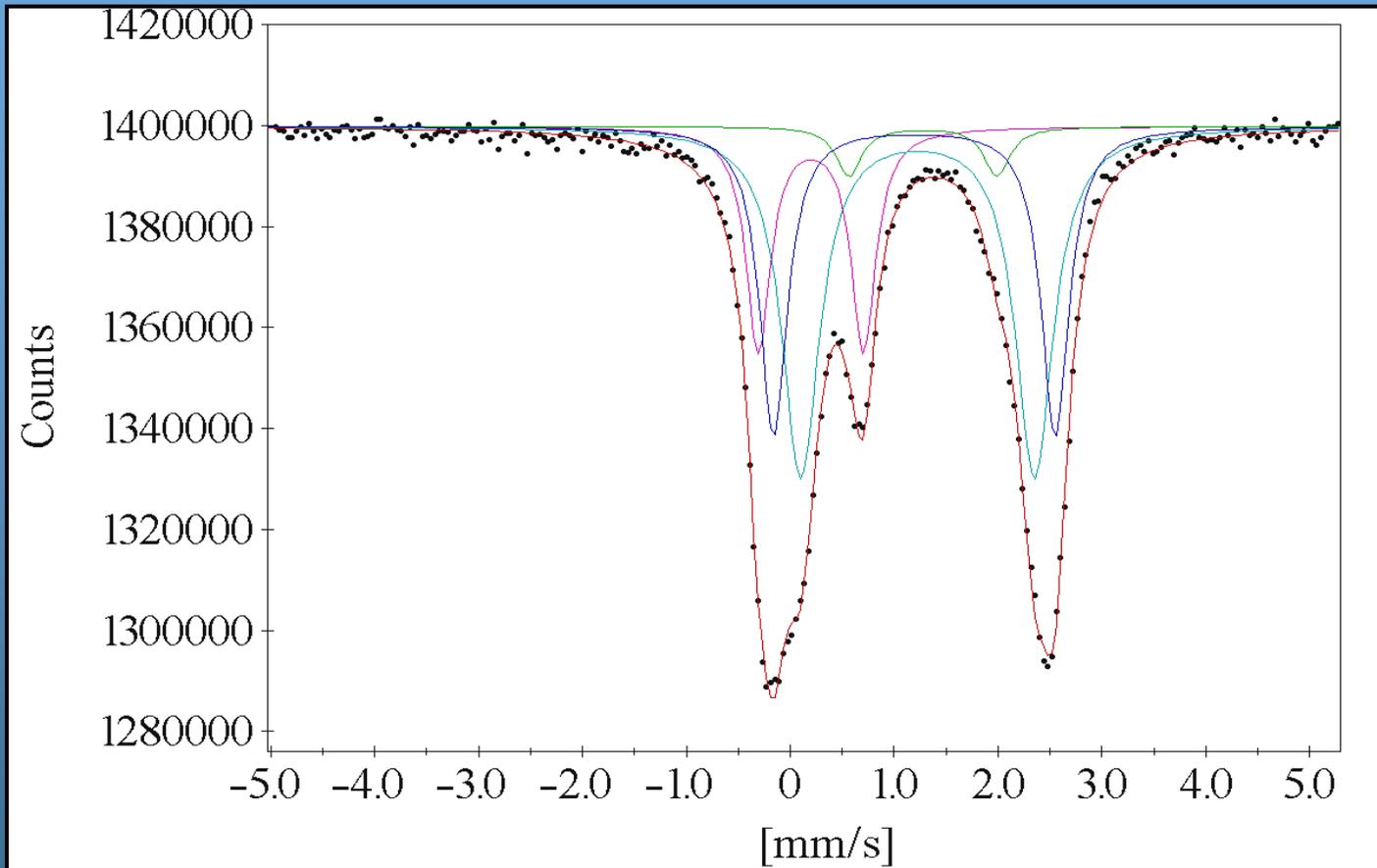
119mSn isomer shifts
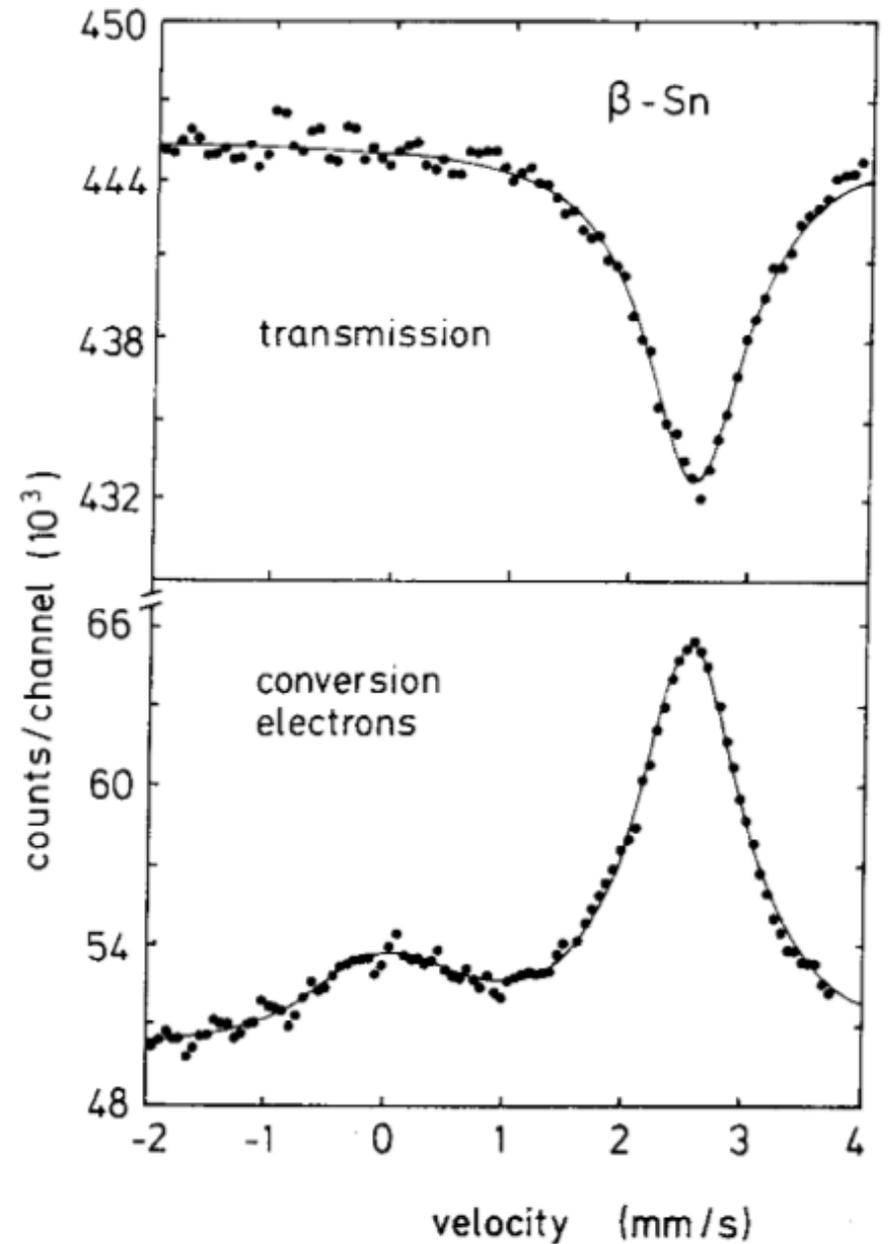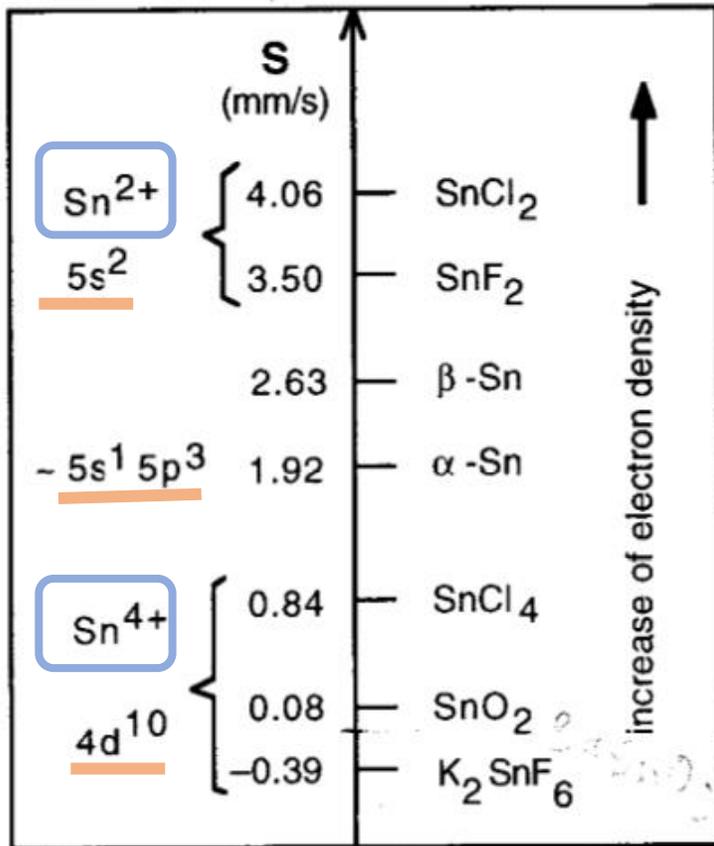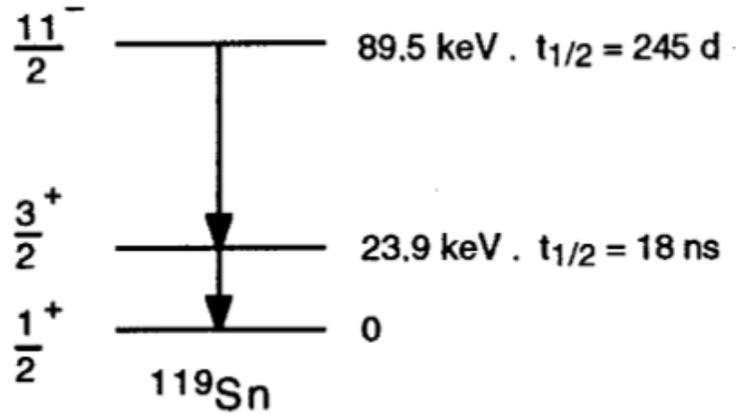
The electric quadrupole interaction

Electric field gradient tensor:

$$V_{ij} = -\frac{\partial^2 V}{\partial x_i \partial x_j} \qquad (x_i, x_j = x, y, z)$$

After diagonalization the matrix can be given by components V_{xx}, V_{yy} and V_{zz}.

According to the Laplace equation $\nabla^2 V = V_{xx} + V_{yy} + V_{zz} = 0$

(outside the sources of the electric field)

$V_{i,j}$ is given by: $\qquad V_{zz} \qquad$ and $\qquad \eta = \dfrac{V_{xx} - V_{yy}}{V_{zz}}$

such that $|V_{xx}| \leq |V_{vv}| \leq |V_{zz}|$ is satisfied

the nuclear quadrupole moment operator:

$$\mathbf{Q}_{ik} = \frac{3Q}{2I(2I-1)}\left[\mathbf{I}_i\mathbf{I}_k + \mathbf{I}_k\mathbf{I}_i - \frac{2}{3}\mathbf{I}^2\delta_{ik}\right]$$

where $\mathbf{I}$ is the nuclear spin operator and δ_{ik} is the *Kronecker delta*

The energy term for the quadrupole interaction:

$$\frac{e}{6}\sum_{i,k}V_{ik}Q_{ik}$$

The Hamiltonian for the quadrupole interaction:

$$\mathbf{H}_Q = \frac{e}{6}\sum_i V_{ii}\mathbf{Q}_{ii} = \frac{eQ}{2I(2I-1)}\left[V_{xx}\mathbf{I}_x^2 + V_{yy}\mathbf{I}_y^2 + V_{zz}\mathbf{I}_z^2\right] =$$

$$= \frac{eQV_{zz}}{4I(2I-1)}\left[3\mathbf{I}_z^2 - \mathbf{I}^2 + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)\right] =$$

$$= \frac{eQV_{zz}}{4I(2I-1)}\left[3m_I^2 - I(I+1) + \frac{\eta}{2}(\mathbf{I}_+^2 + \mathbf{I}_-^2)\right]$$

where $\mathbf{I}$, $\mathbf{I}_x$, $\mathbf{I}_y$, $\mathbf{I}_z$, $\mathbf{I}_+ = \mathbf{I}_x + i\mathbf{I}_y$ and $\mathbf{I}_- = \mathbf{I}_x - i\mathbf{I}_y$ are the nuclear spin operators, I is the nuclear spin and m_I is its z component (**magnetic quantum number**)

The eigenvalues can be given as follows:

$$E_Q = \frac{eQV_{zz}}{4I(2I-1)}[3I_z^2 - I(I+1)]\left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

An important case is $I=3/2$, having two energy levels at $+eQV_{zz}/4$ for $I_z=\pm3/2$ and $-e^2QV_{zz}/4$ for $I_z=\pm1/2$ in case of axial symmetry ($\eta=0$)

This scheme is valid for ^{57}Fe and ^{119m}Sn
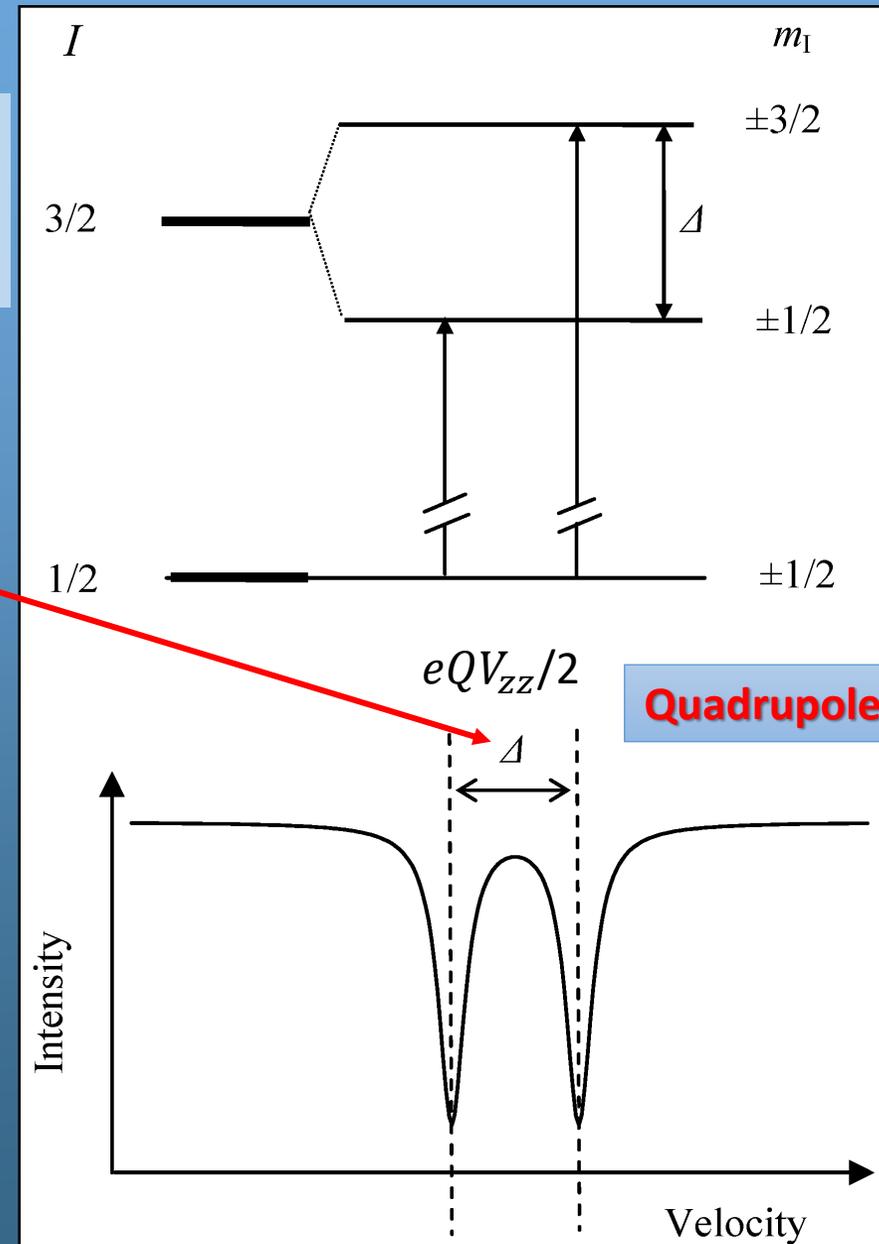
Contribution of the different atomic orbitals to $(q=V_{zz}/e)$ may be calculated:

Orbital	q	η
p_z	$-\frac{4}{5}\langle r^{-3}\rangle$	0
p_x	$+\frac{2}{5}\langle r^{-3}\rangle$	-3
p_y	$+\frac{2}{5}\langle r^{-3}\rangle$	$+3$
$d_{x^2-y^2}$	$+\frac{4}{7}\langle r^{-3}\rangle$	0
d_{z^2}	$-\frac{4}{7}\langle r^{-3}\rangle$	0
d_{xy}	$+\frac{4}{7}\langle r^{-3}\rangle$	0
d_{xz}	$-\frac{2}{7}\langle r^{-3}\rangle$	$+3$
d_{yz}	$-\frac{2}{7}\langle r^{-3}\rangle$	-3
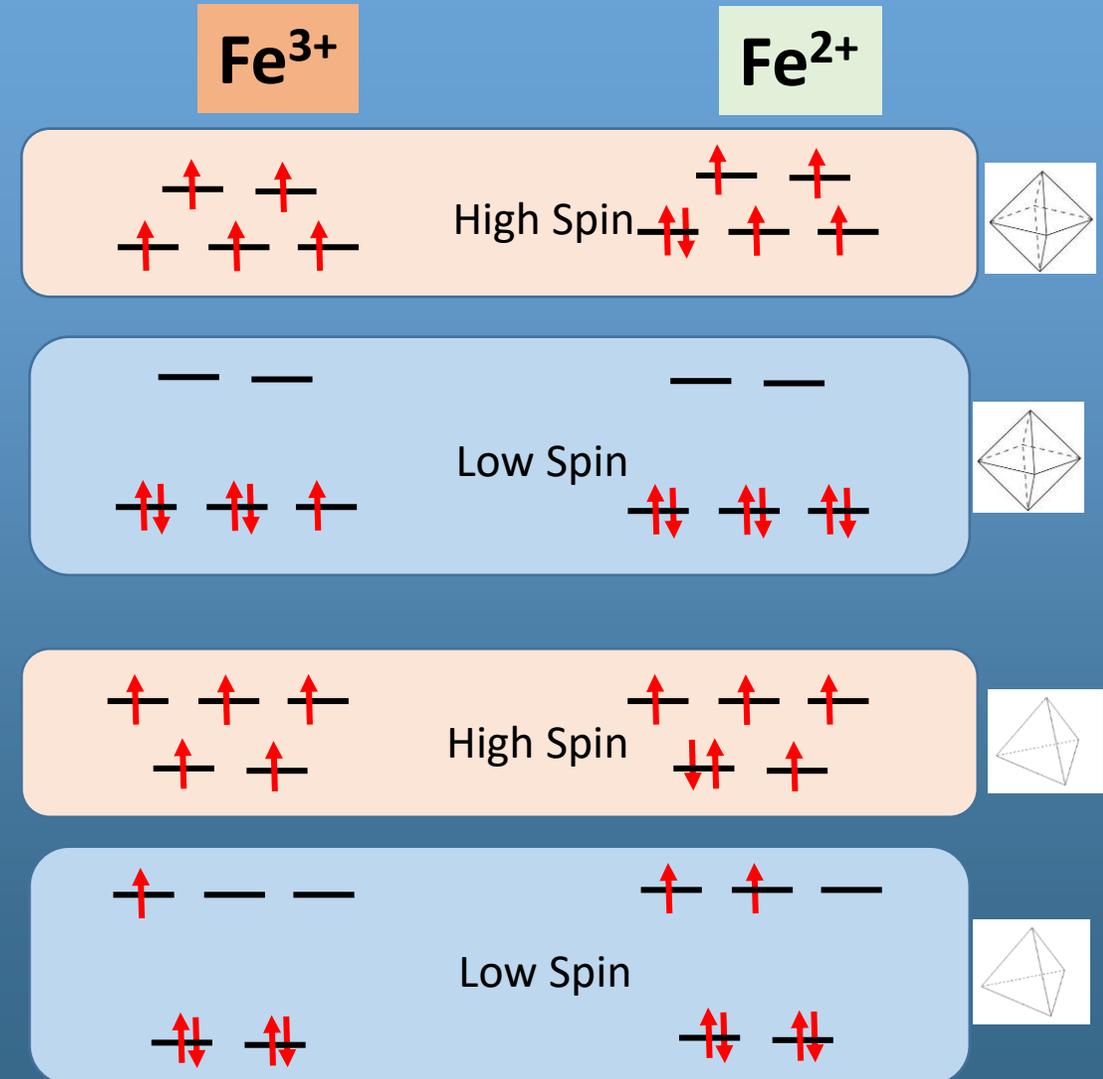
Magnetic dipole interaction

„nuclear Zeeman effect"

The Hamiltonian of the interaction:

$$\hat{\mathbf{H}} = -\hat{\boldsymbol{\mu}}\,\mathbf{B} = -g\mu_N I\mathbf{B}$$

Eigenvalues:

$$E_m = \mu\,\mathbf{B}\frac{m_I}{I} = -g_I\mu_N\mathbf{B}m_I$$

Manifestation:
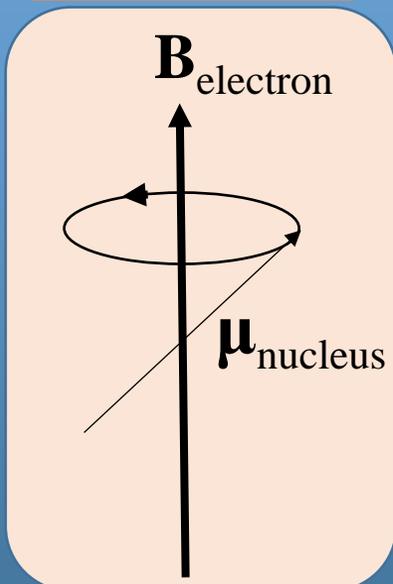
$\mathbf{B}_{electron}$

$\boldsymbol{\mu}_{nucleus}$

Larmor precession of the nuclear magnetic moment around the magnetic field of the atomic electrons.

Magnetic Splitting
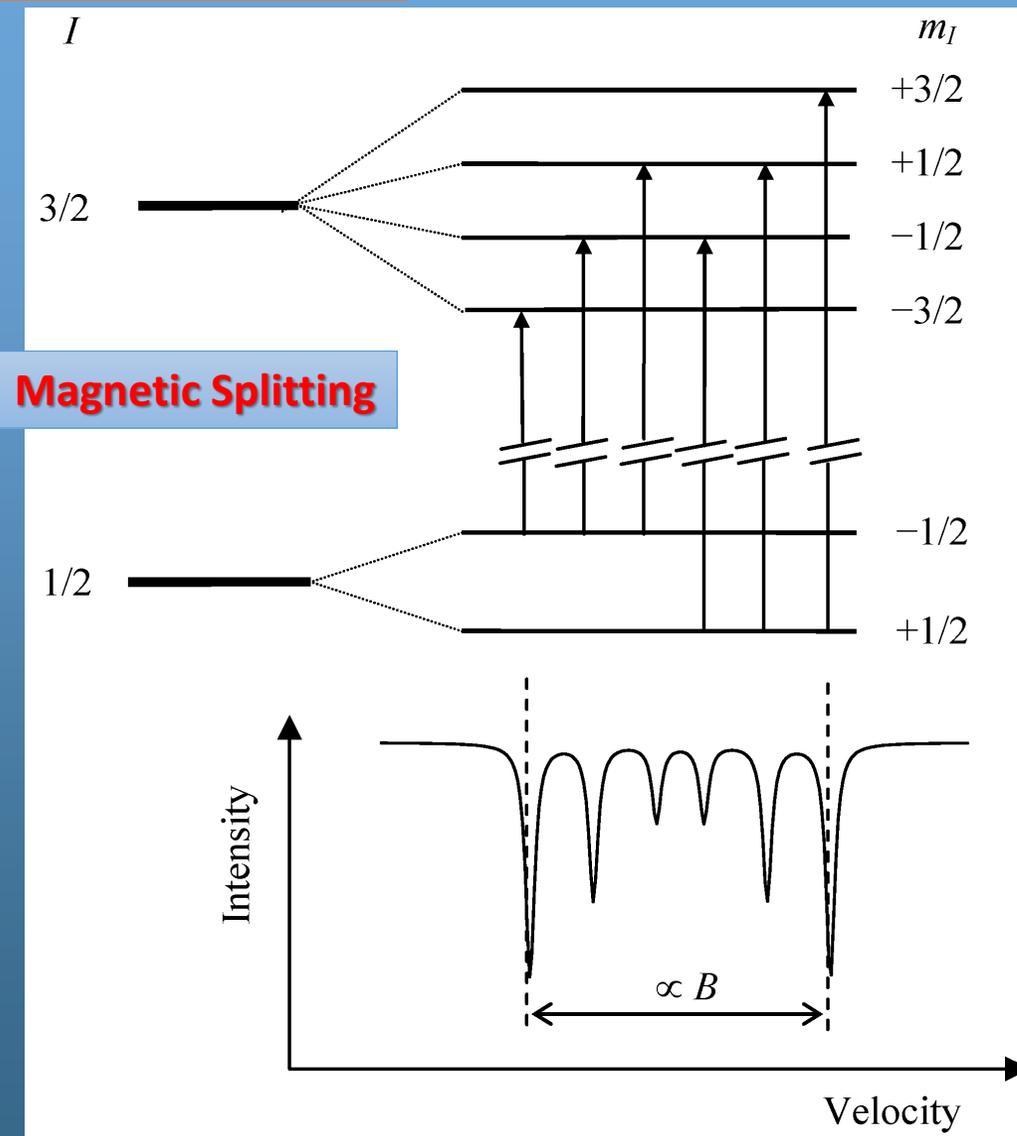
Selection rules: $\Delta m_I = 0, \pm 1$

In case of ^{57}Fe, one may expect magnetic splitting of the spectra in every case since the nucleus has magnetic moment, and the electron configuration of (high spin) Fe^{2+} and Fe^{3+} both have very strong magnetic fields (S=5/2 and S=2, respectively).

Why is the magnetic splitting not observed in most cases?

In order to observe magnetic interaction between the nucleus and the electrons, there has to be enough time for the Larmor precession.

The life time of the excited state of the nucleus (Mössbauer lifeteime) should be longer than the Larmor precession cycle time:

$$t_{Larmor} < t_{Mössbauer}$$

and

The electronic paramagnetic relaxation time should be longer than the Larmor precession cycle time:

$$t_{Larmor} < t_{relaxation}$$

This typically holds

This typically does not hold for solid paramagnetic materials

Combined quadrupole and magnetic interaction

$$E_{MQ} = -g\mu_n B m_I + (-1)^{|m_I|+1/2} \frac{eQV_{zz}}{4} \frac{3\cos^2\vartheta - 1}{2}$$

This is valid if $\left|eQV_{zz}\right| << \left|\mu B\right|$ holds.

(small quadrupole perurbation of the magnetic interaction)
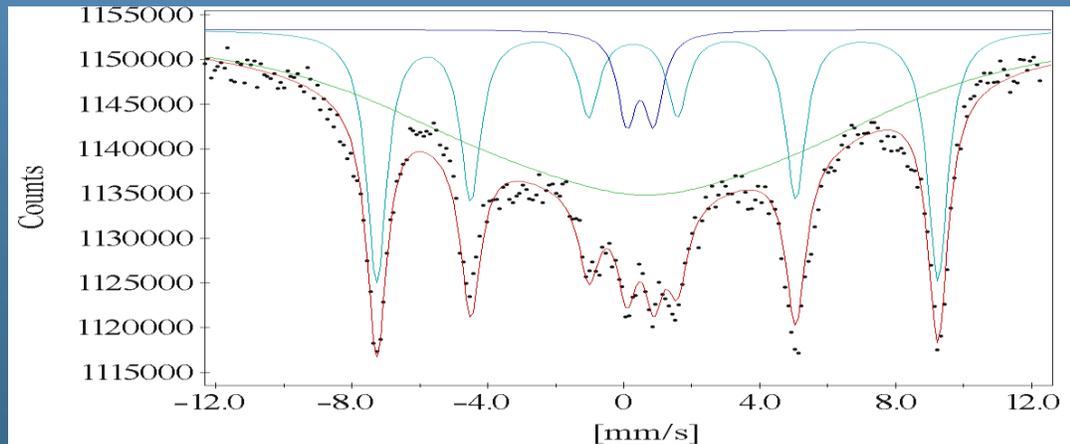
Dihapto-peroxo-cyclohexane-diamine-Fe^{III}

example
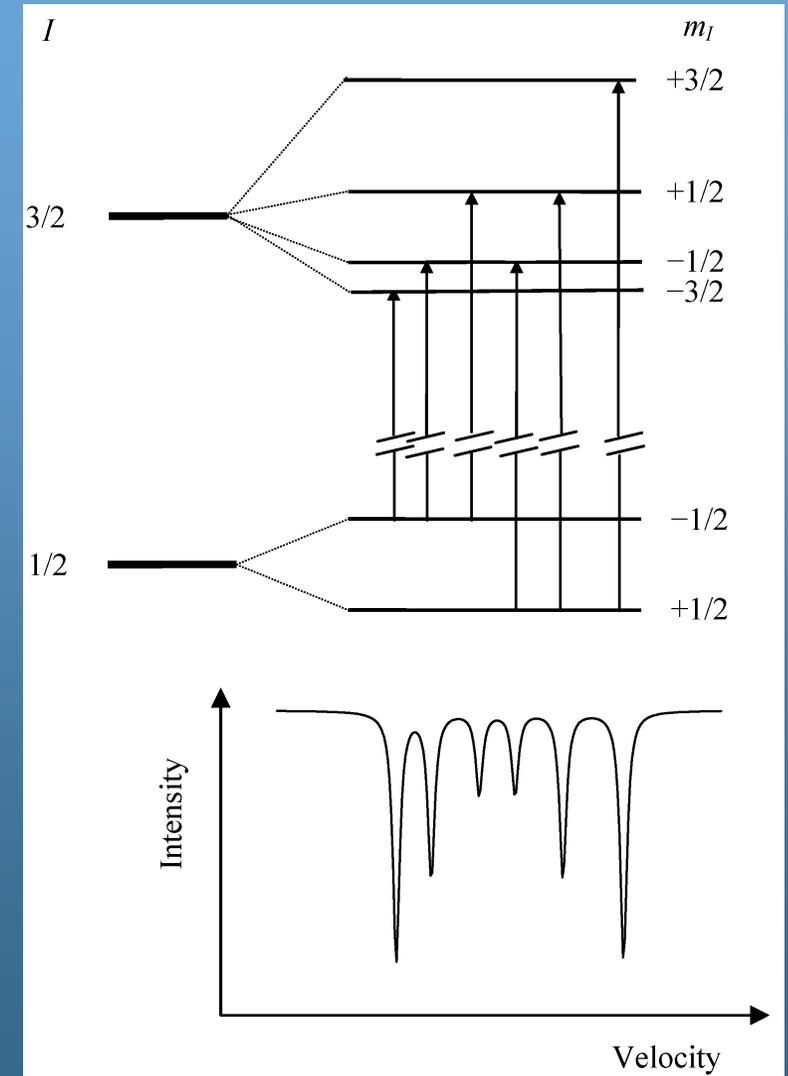
Line intensities in Mössbauer spectra

the relative intensity of the line belonging to the transition $|I_e, m_e\rangle \rightarrow |I_g, m_g\rangle$:

(Wigner-Eckart theory)

$$I(I_e, m_e, I_g, m_g, \sigma lm) \propto \begin{pmatrix} I_g & l & I_e \\ -m_g & m & m_e \end{pmatrix}^2 F_{lm}(\theta)$$

3j symbol   Angular dependence

e: excited state
g: ground state
σlm: refers to the multipolarity

polar angle enclosed by direction of observation and the *z* axis of the principal axis system (e.g., V_{zz}, *B*)

Note that while the 3j symbol is connected with the quantummechanical probabilities of being the nucleus in a certain state (and therefore transitions between these states) the angular dependence is due to the transfer of angular momentum (a vector quantity) between the nucleus and the photon.

For a sextet when random directional averaging applies:

$$A_1 : A_2 : A_3 : A_4 : A_5 : A_6 = 3 : 2 : 1 : 1 : 2 : 3,$$

In an oriented sample, only the 2nd and 5th line intensity may vary as compared to the others:

$$\frac{A_{2,5}}{A_{1,6}} = \frac{4\sin^2\theta}{3(1+\cos^2\theta)}$$

Iron metal measured in external magnetic field:

γ and B random

γ and B parallel

γ and B perpendicular
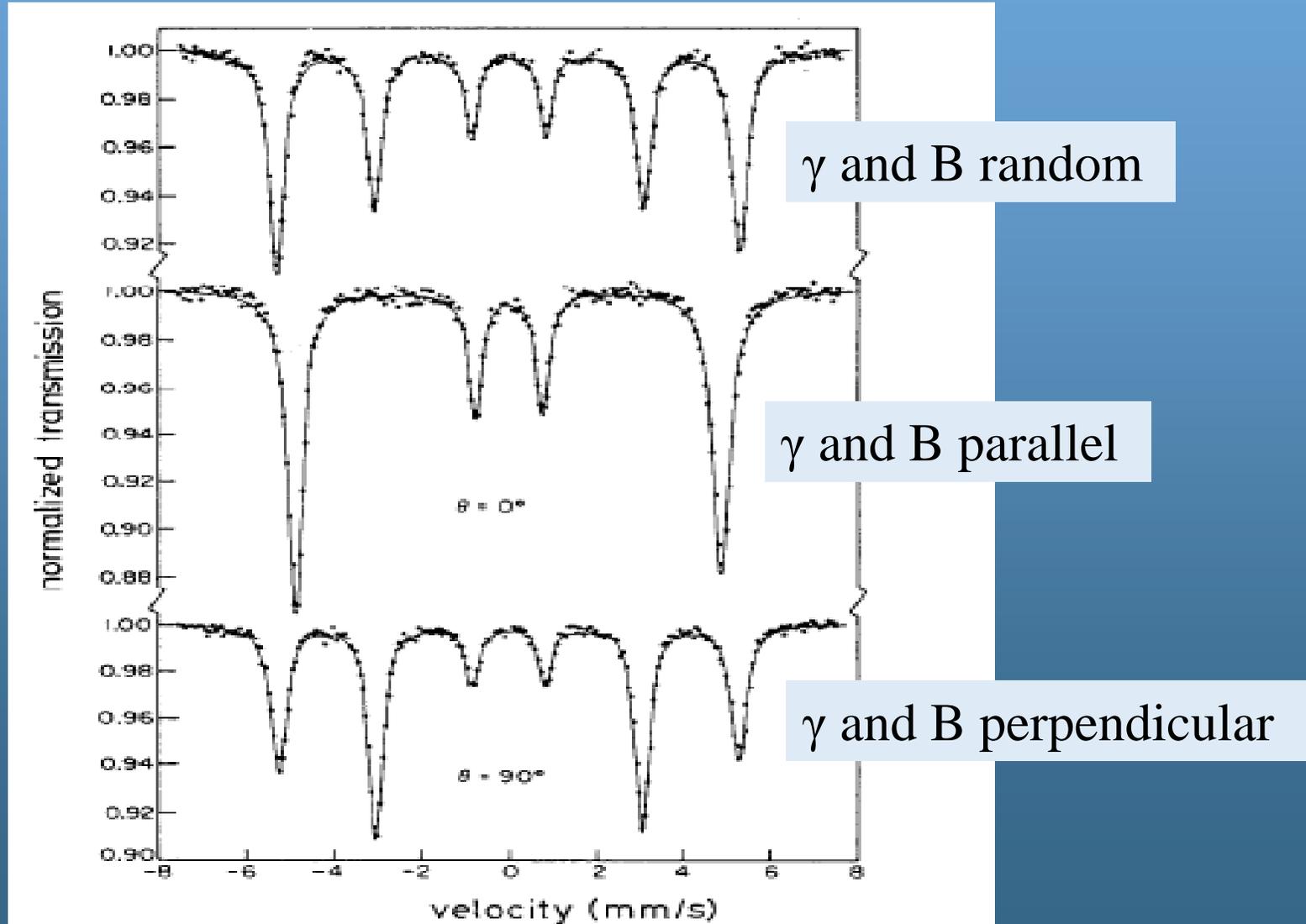
Spectrum analysis

Task:
Fitting a series of counts assigned to velocities with combinations of Lorentzians (or much more complicated line shapes…)

Method: Least squares

Control: chi square

$$\chi^2(\underline{v}) = \sum_{i=1}^{h} \frac{(W_i - f_i(\underline{v}))^2}{W_i}$$

This checks the goodness of the model.

Tool:
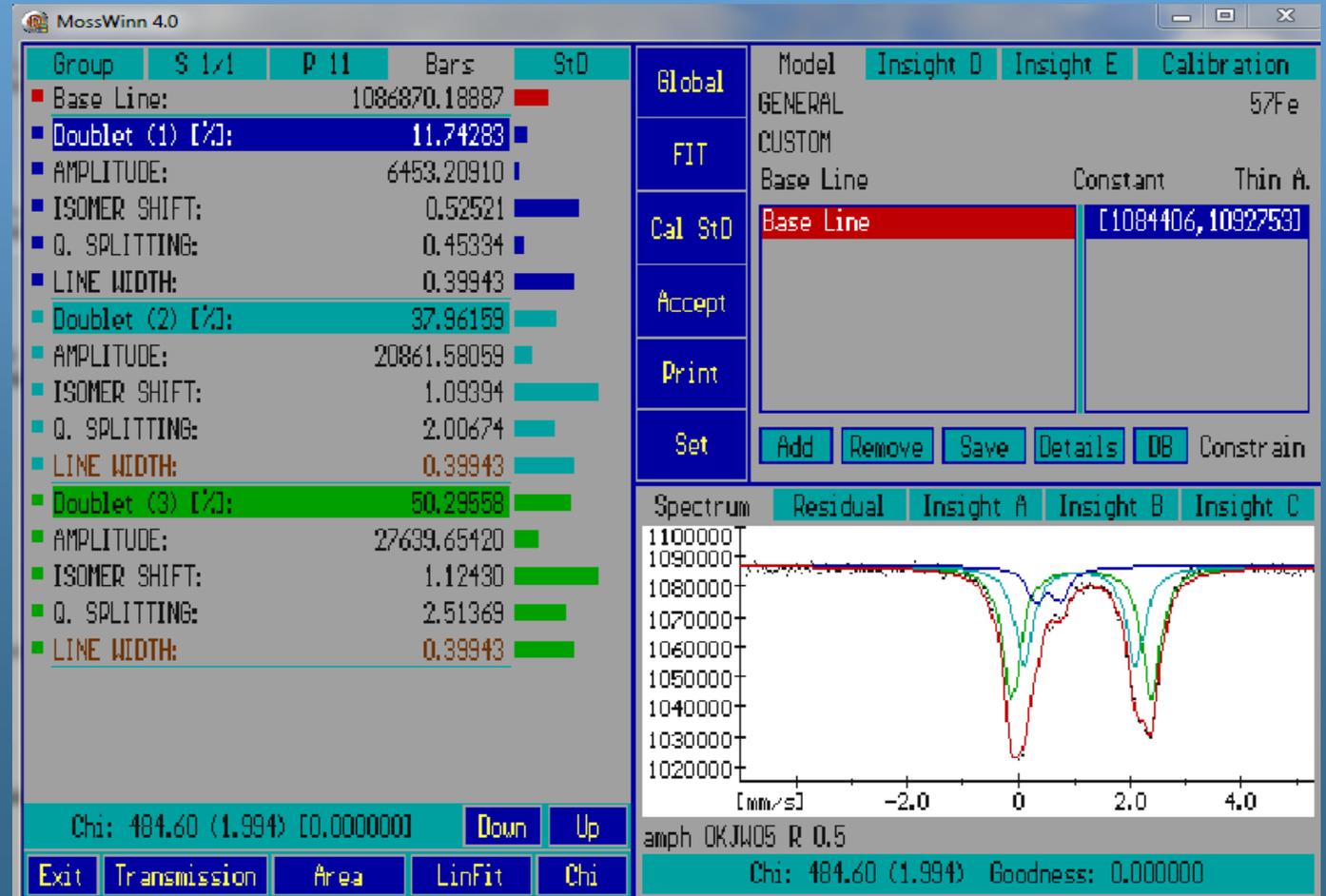
$$Fe_3O_4 = (Fe^{3+}_{tet})_A(Fe^{3+}_{oct}Fe^{2+}_{oct})_BO_4$$

(inverse spinel!)

The unit cell (spinel):

Oxygen

Fe at Site A

→ **Fe^{3+} state**

Fe at Site B

↘ **Mixed Fe^{3+}/Fe^{2+} state**
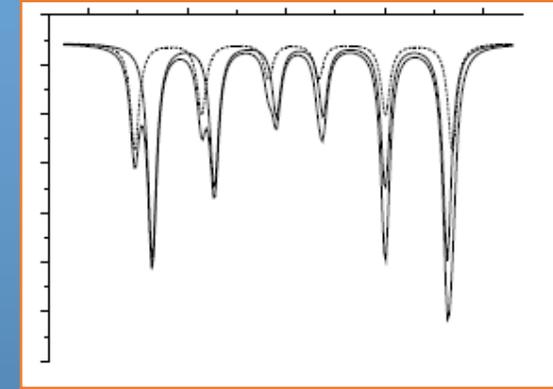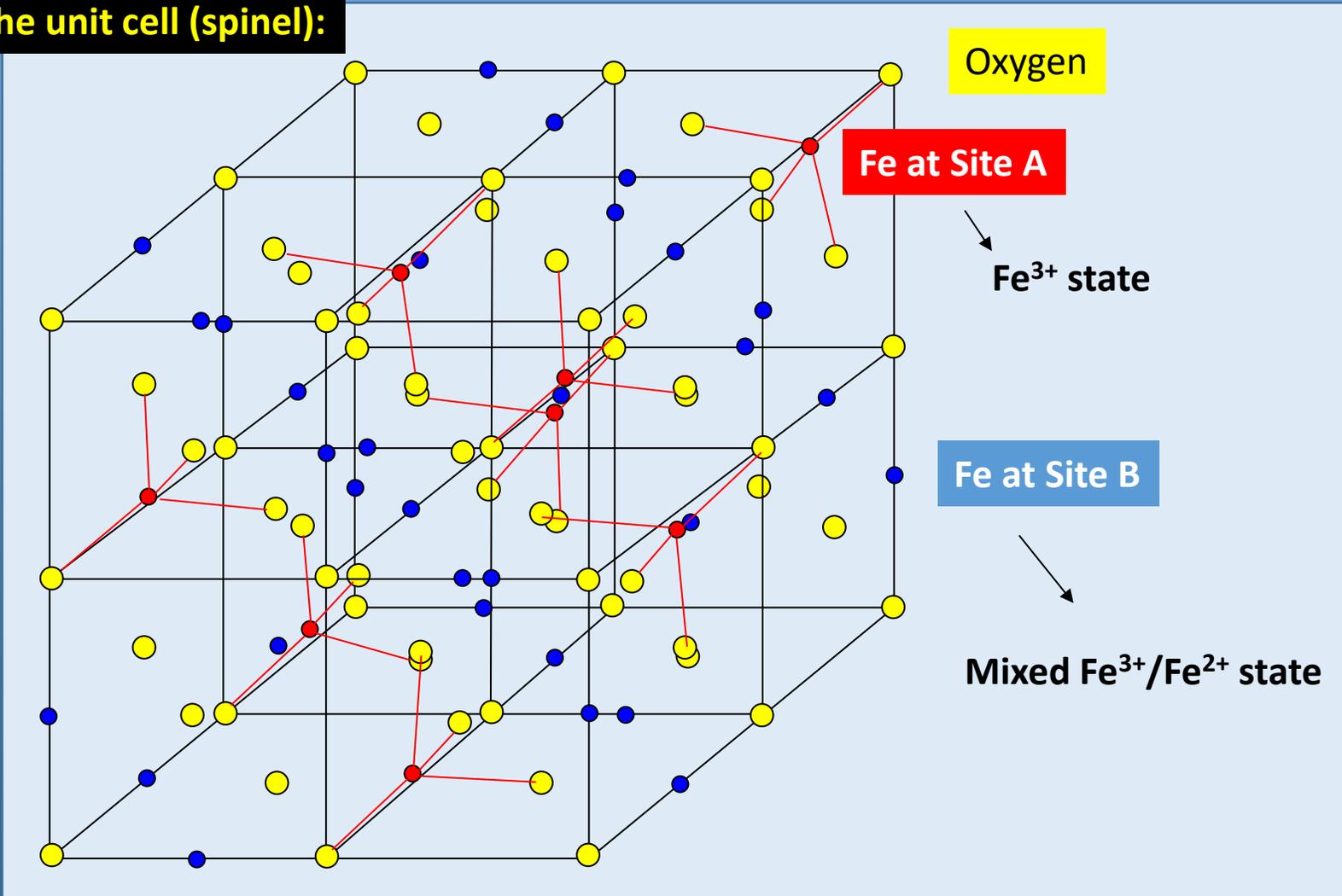
Mössbauer parameters:

Tetrahedral Fe^{3+}
δ = 0.38 mm/s
B = 49.9 T

Octahedral Fe$^{2.5+}$
δ = 0.69 mm/s
B = 46.4 T

The Mössbauer spectrum of hematite recorded at the Morin temperature (260 K):
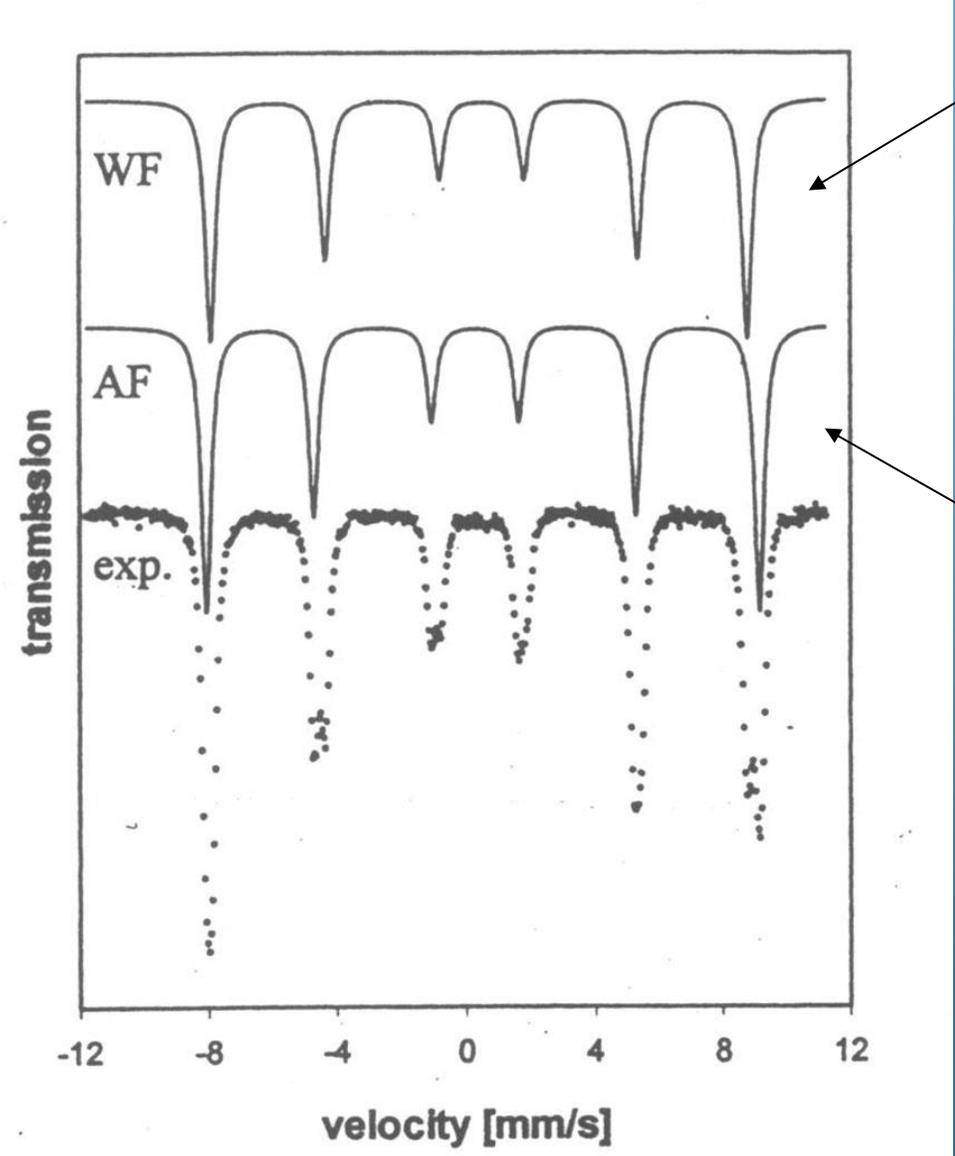
Exists above T_M, weakly ferromagnetic (spin canting)

(EFG ⊥ μ)

spins turn by about 90°

	δ (mm/s)	ε (mm/s)	B (T)
295 K	0.37	-0.197	51.75
4.2 K	0.49	+0.41	54.17

Exists below T_M, antiferromagnetic

(EFG ∥ μ)
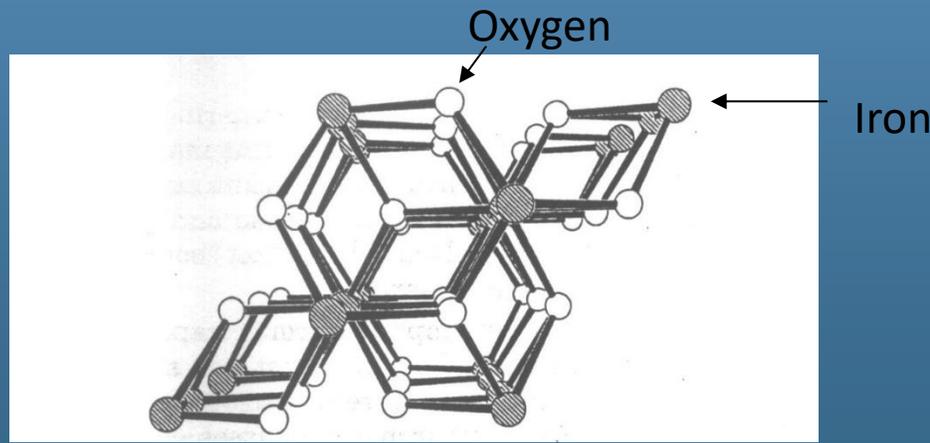
Source: R. Zboril et al., Chem. Mater. 14 (2002) p.972

Oxygen

Iron

Mössbauer Study of the Thermal Degradation of Iron loaded Ion Exchange Resins

Carbon nanostructures

Graphene

Nanotubes

Bucky balls
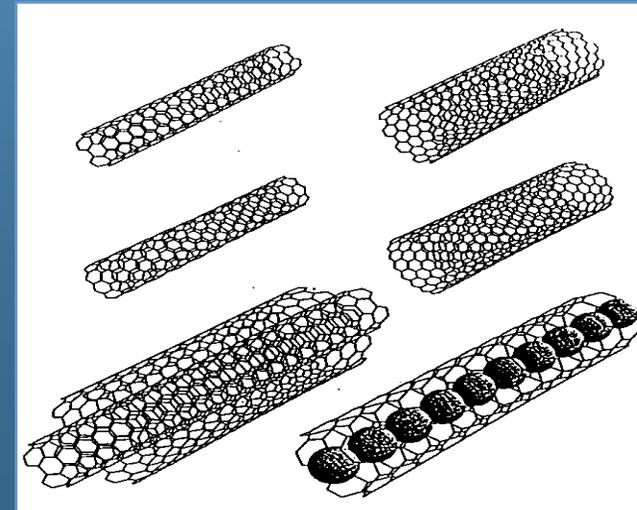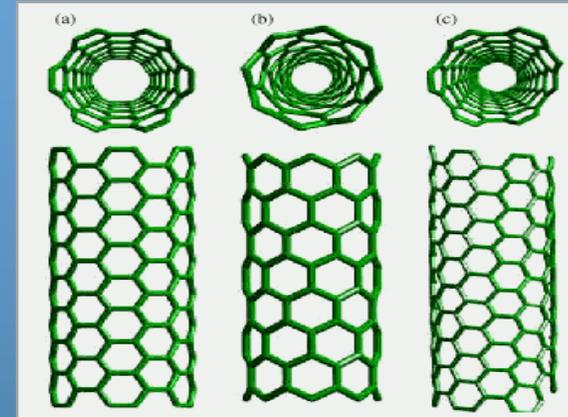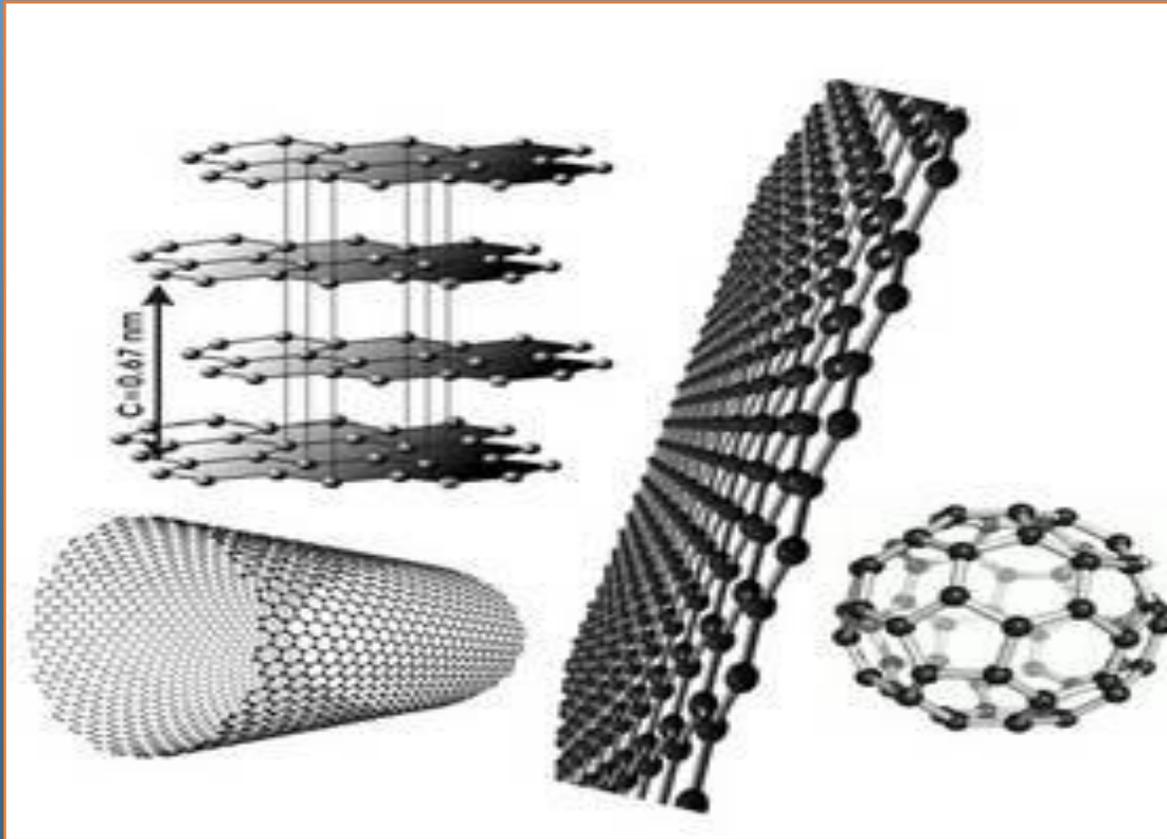
To produce nanostructures….

Source of carbon: organic substance (ion exchanger resin)

Source of iron: adsorbed iron salts

Preparation: thermal degradation

Primary methods for characterization:
- **Mössbauer Spectroscopy**
- XRD
- SEM

1000 ^{o}C

900 ^{o}C

800 ^{o}C

700 ^{o}C

600 ^{o}C

500 ^{o}C

400 ^{o}C

Phase analysis of iron containing phases...

Expected main phases:
metallic iron, iron-carbon alloys, oxides that form under relatively reductive conditions

Special phenomena may be expected because:

•Finely dispersed iron can help formation of nano-structures
(non-equilibrium phases can form)

•Extreme excess of carbon is present as compared to iron production by reduction of iron oxides with coal, from where iron-carbon phases became known.
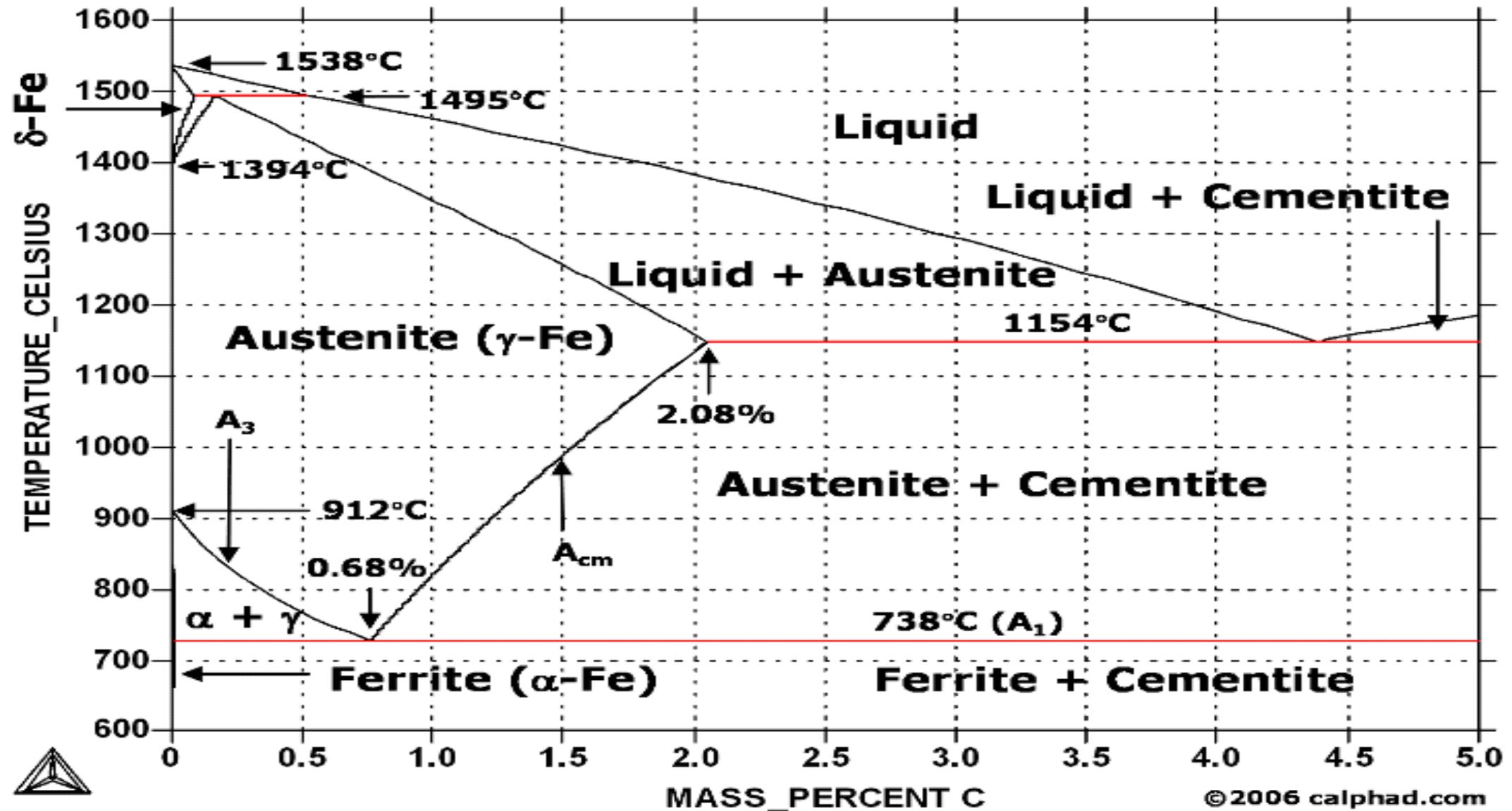
Iron-carbon equilibrium phase diagram

γ–FCC
austenite

Bain model

Non-eq. phase!

α'–BCT
martensite

α–BCC
ferrite

● Fe   ○ C
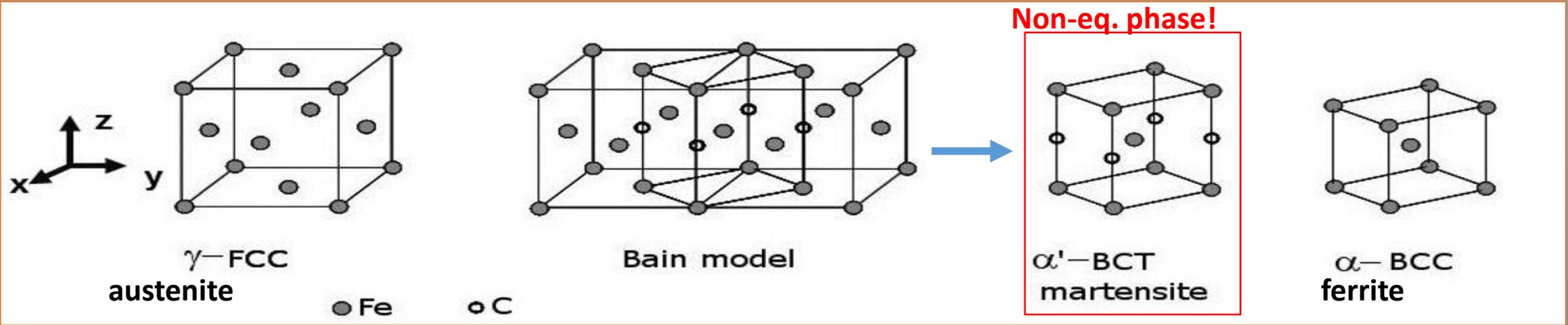
The "Bain model" is FCC austenite with carbon interstitial atoms in it, which then transforms to BCT martensite on cooling.

Structure of most common iron-carbon equilibrium phases
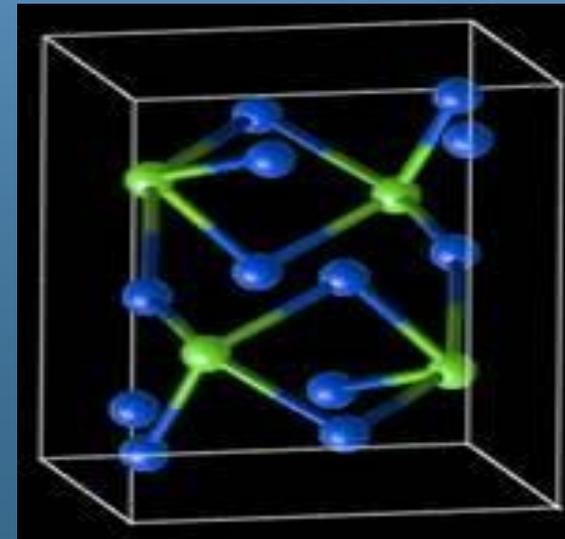
Cementite Fe$_3$C

Structure of most common oxides…
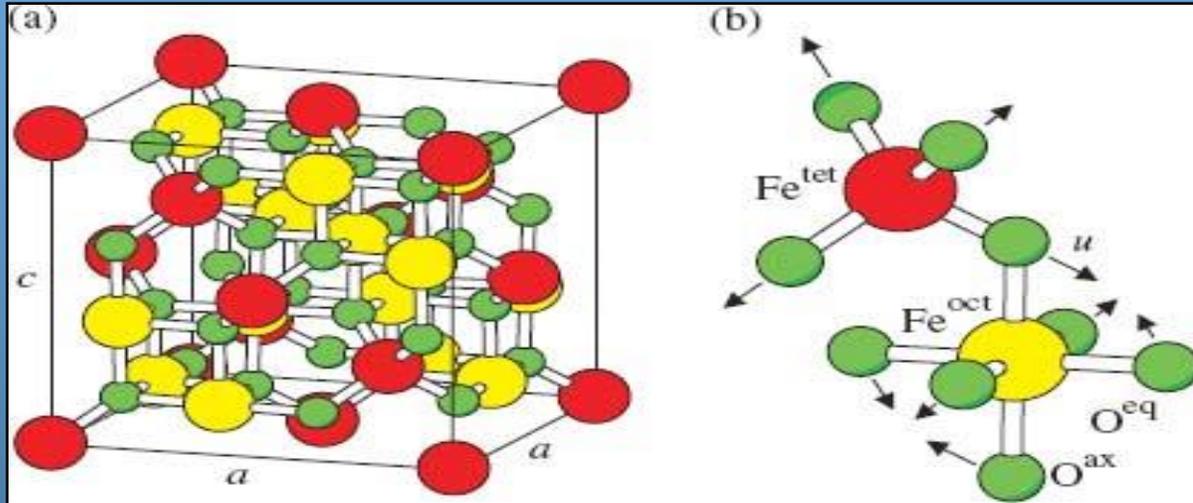
Magnetite, Fe_3O_4

Wustite, $FeO_{1-\delta}$

Fe₃N

Fe₄N

Fe

N

N on
● 2c site   ○ 2b site   ○ 2d site
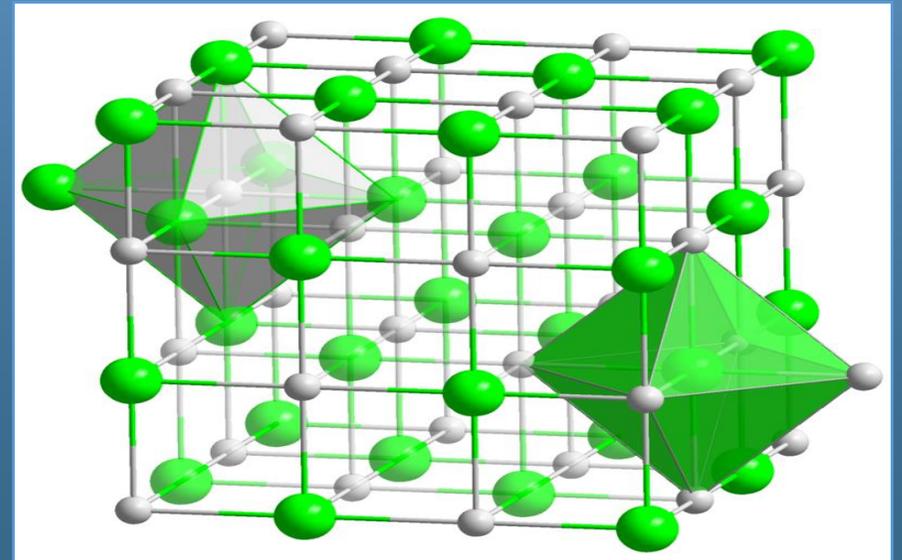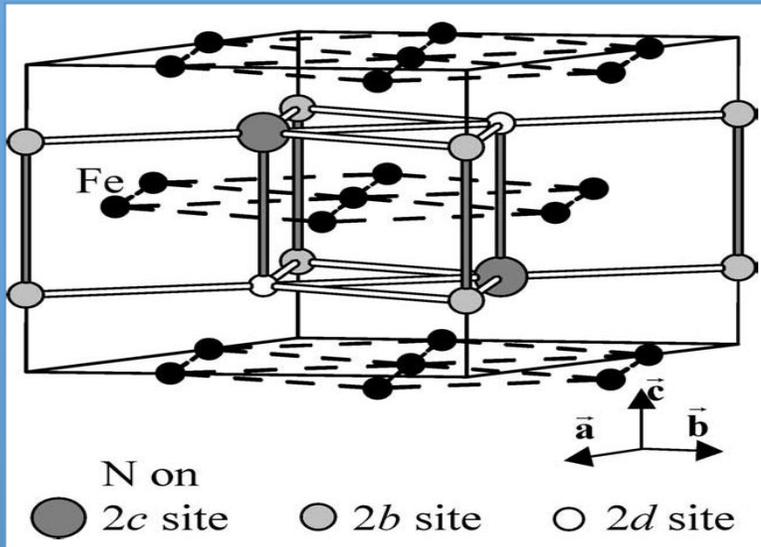
T. Liapina et al. / Acta Materialia 52 (2004) 173–180
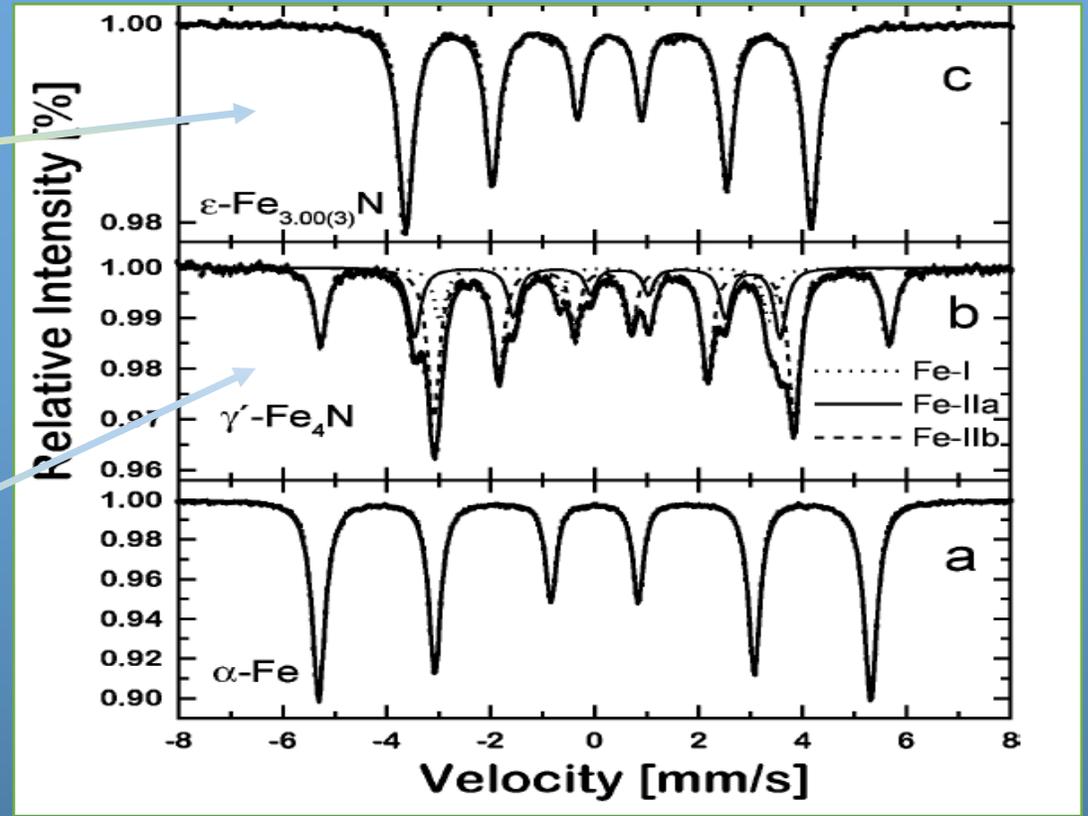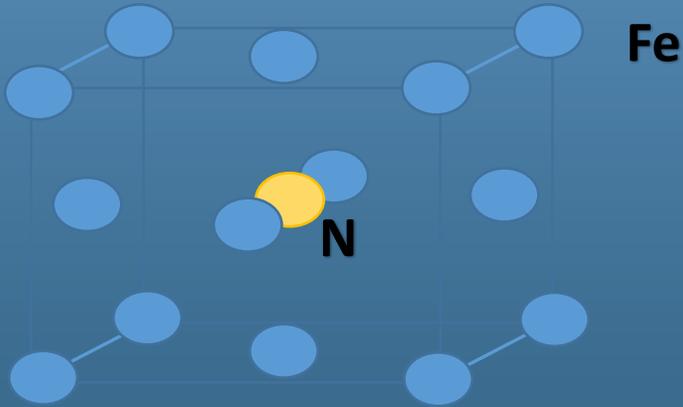
Phase	Site	IS [mm/s]	QS [mm/s]	H [T]	LW [mm/s]	Fraction [RA%]
α-Fe	Fe	0.00(1)	0.00(1)	33.0(1)	0.28(1)	100.0(5)
γ'-Fe$_4$N	Fe-I	0.20(2)	0.01(1)	34.0(2)	0.27(1)	25.7(14)
	Fe-IIa	0.27(2)	−0.21(2)	21.9(2)	0.27(1)	23.8(15)
	Fe-IIb	0.27(2)	0.10(2)	21.6(2)	0.27(1)	50.5(5)
ε-Fe$_{3.00(2)}$N	Fe-II	0.28(2)	−0.01(1)	24.6(2)	0.37(1)	100.0(10)
Cementite:		0.21	0	20.5		

Loading with iron(III) nitrate

Mössbauer spectroscopy:

50 % α-Fe
13 % γ-Fe
37 % ? superparamagnetic phase

XRD

Average grain size: 10 nm
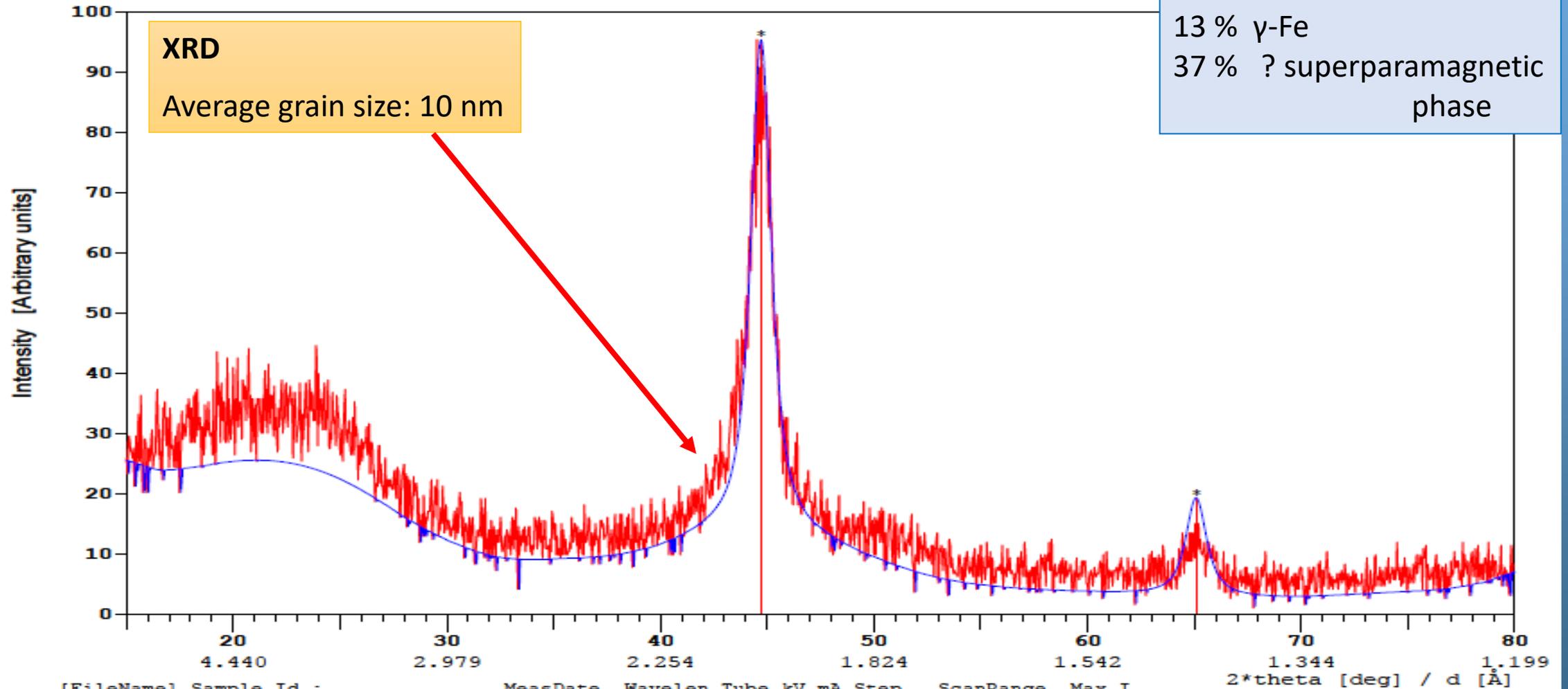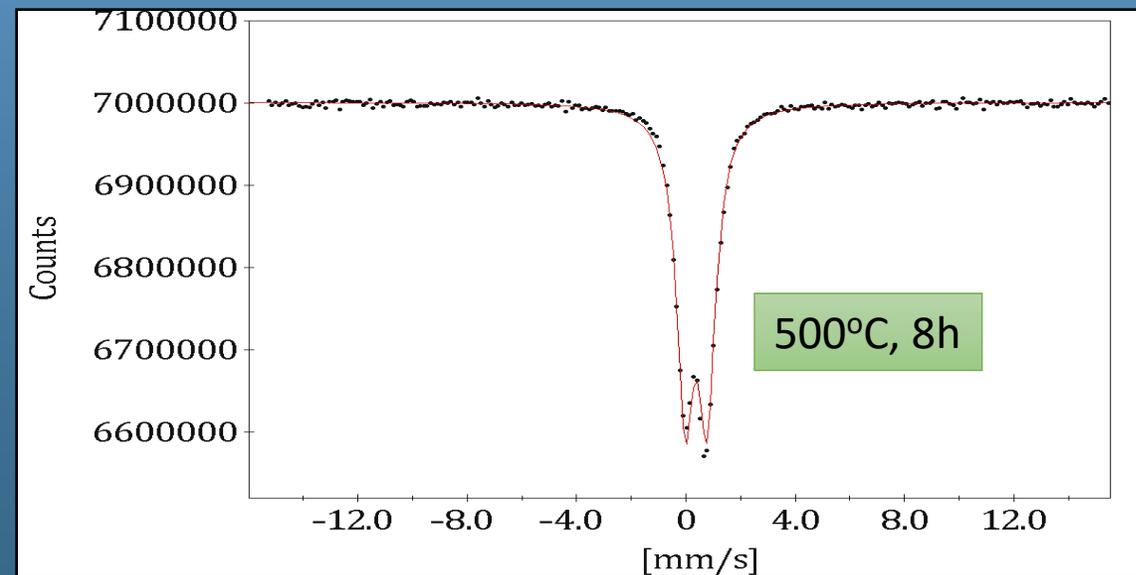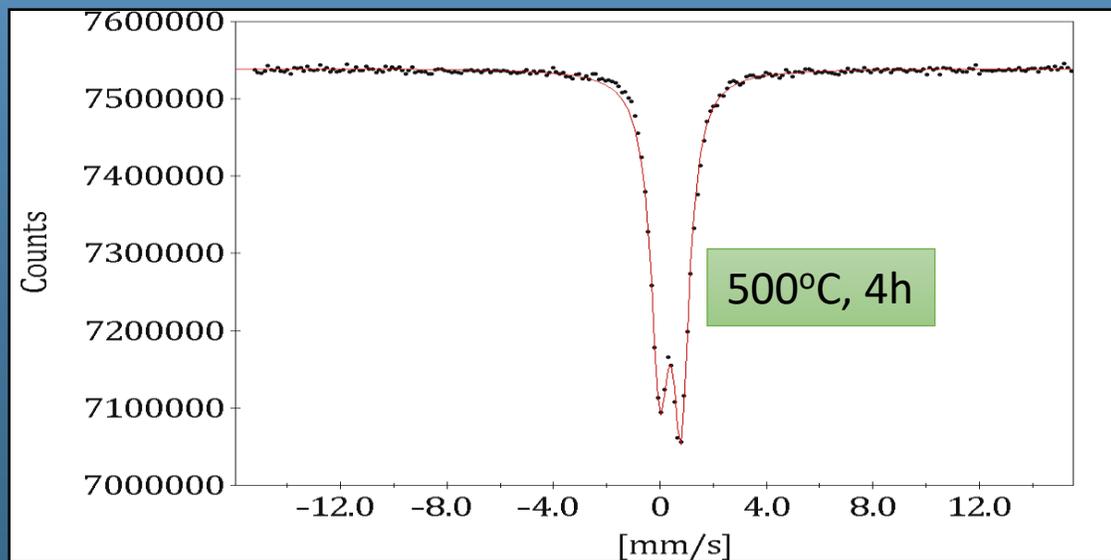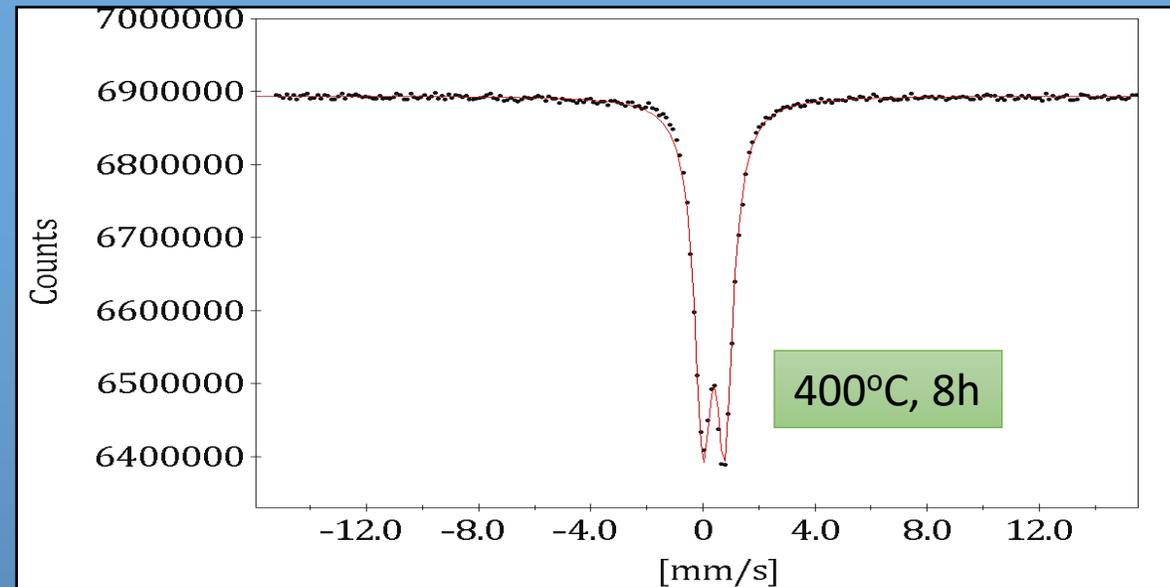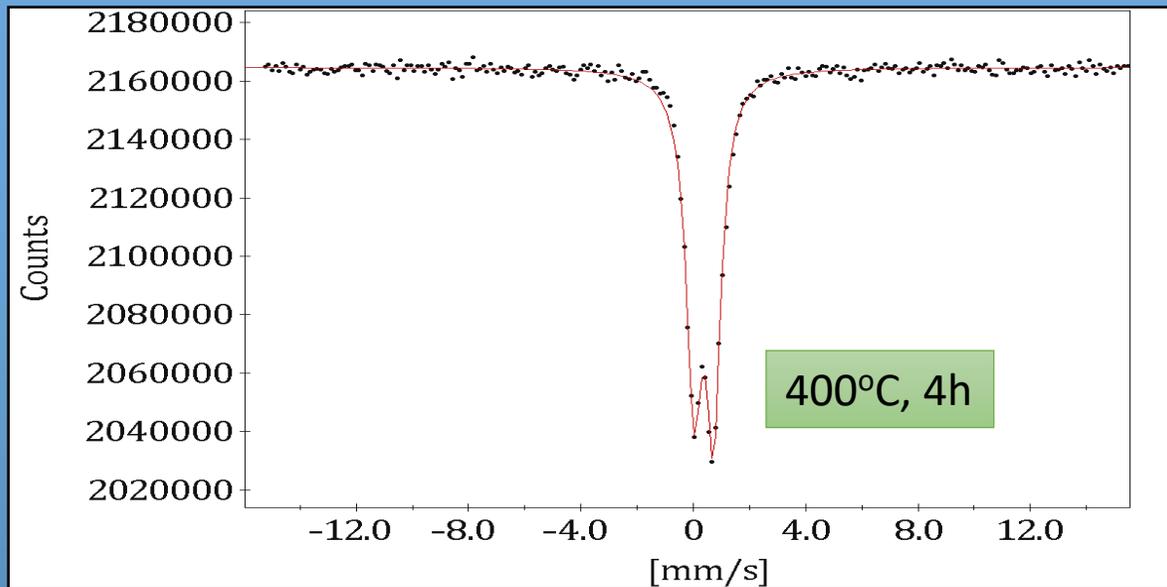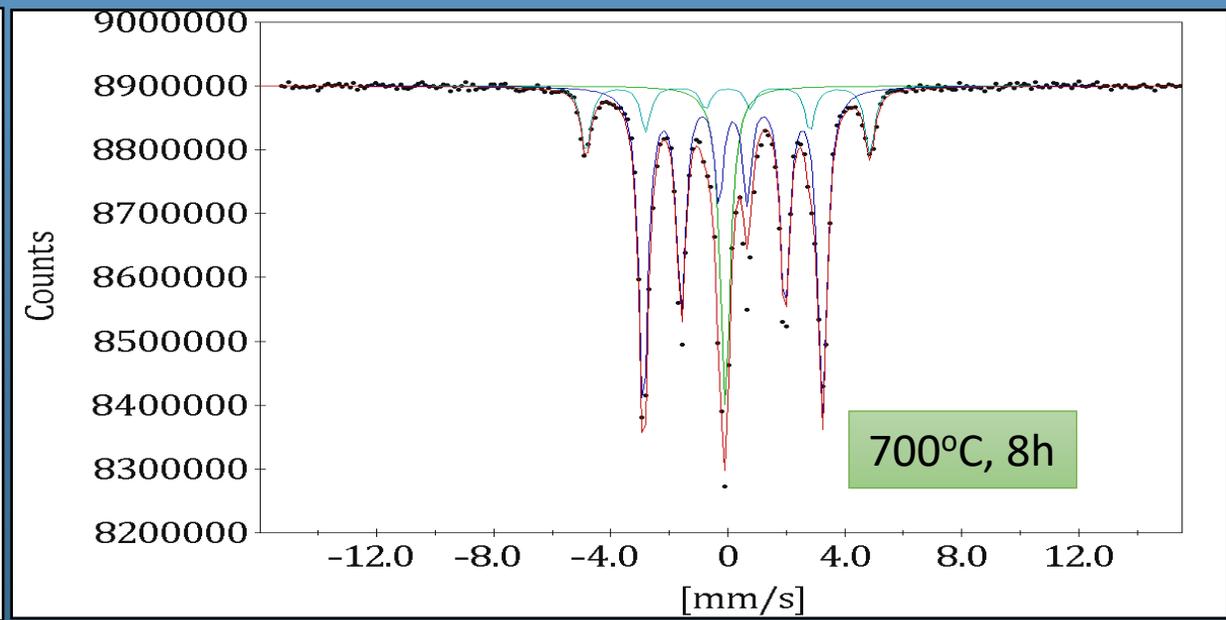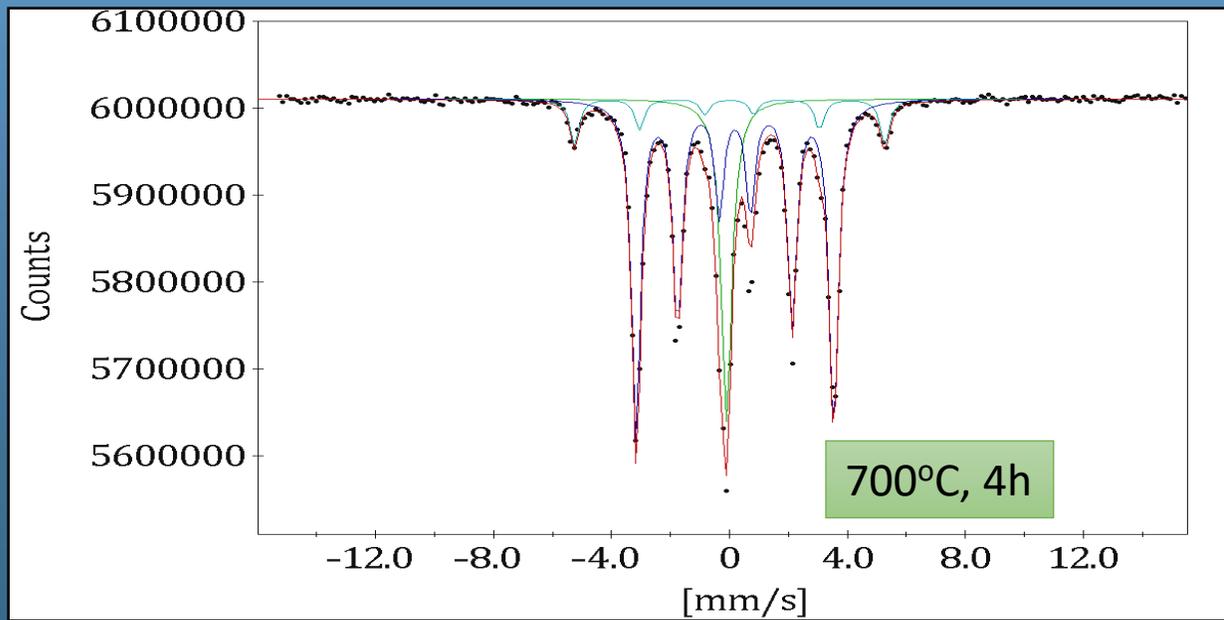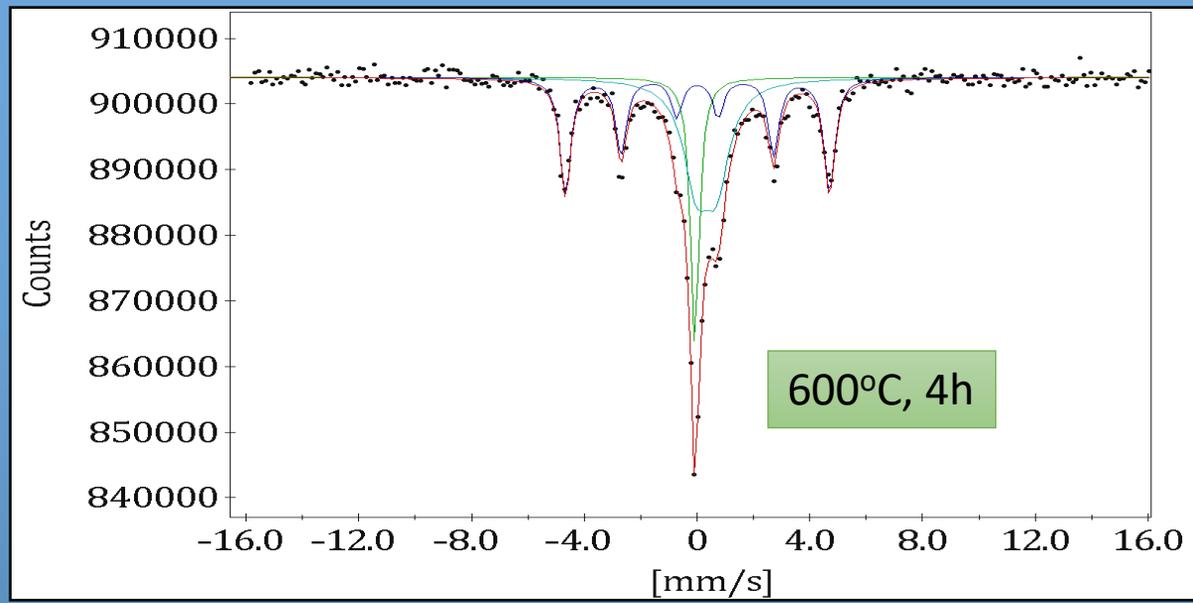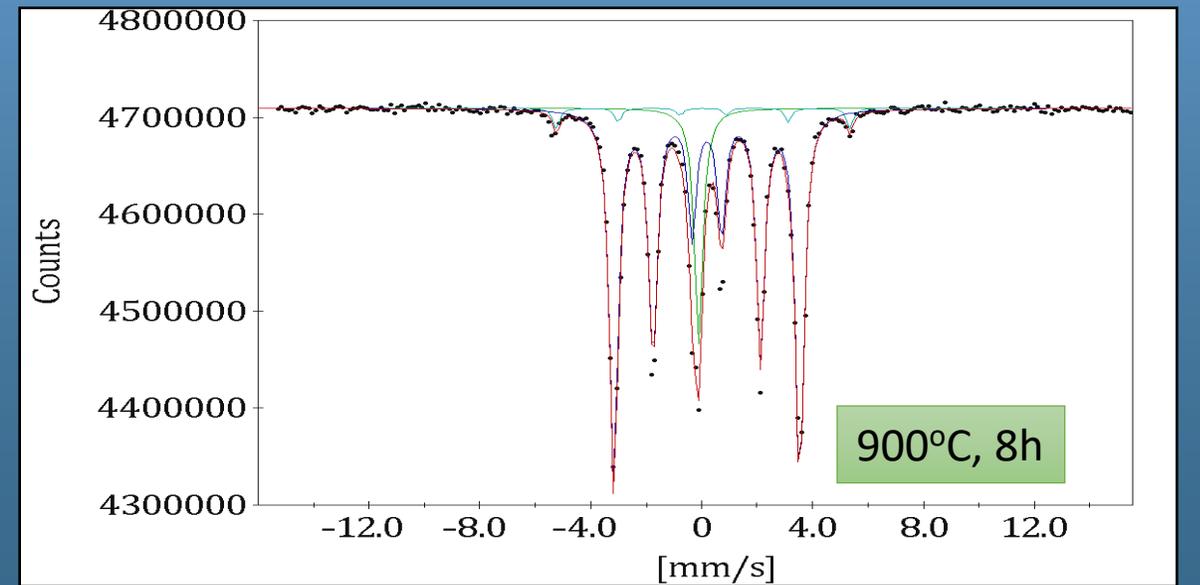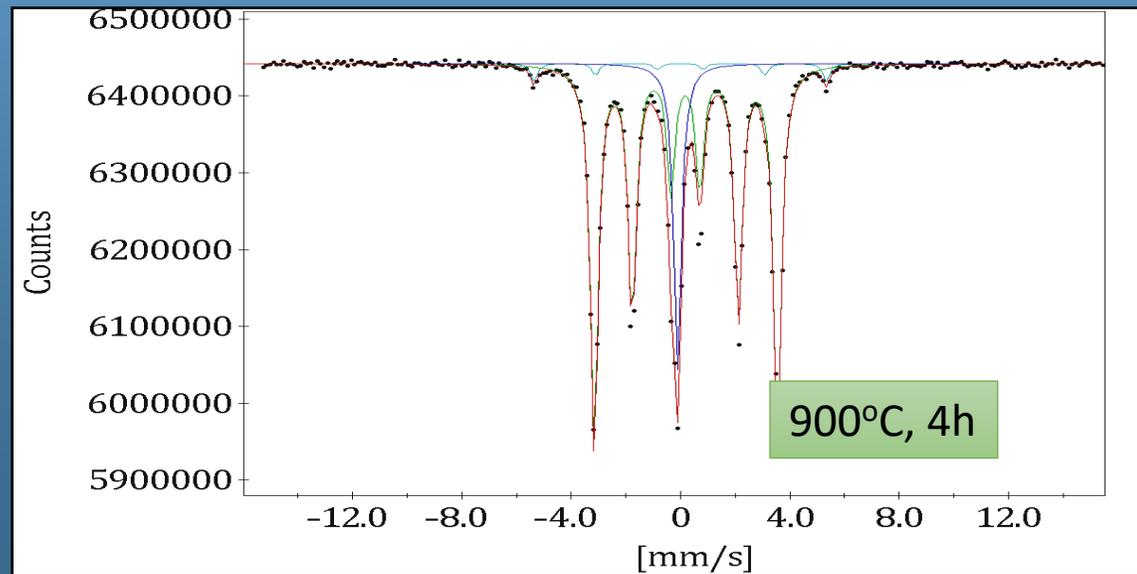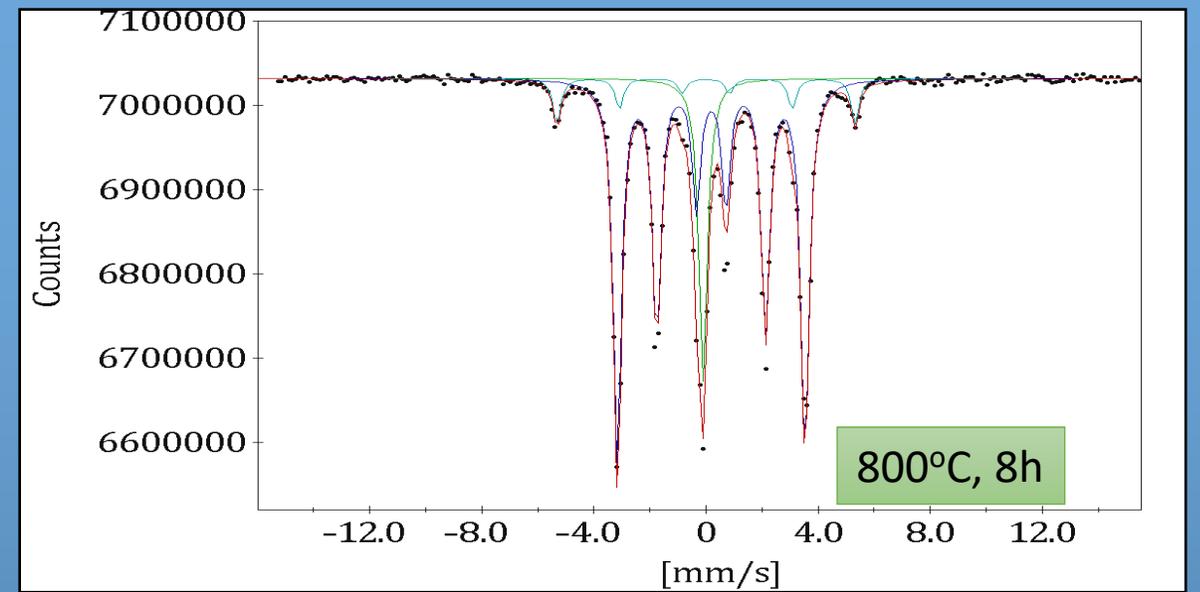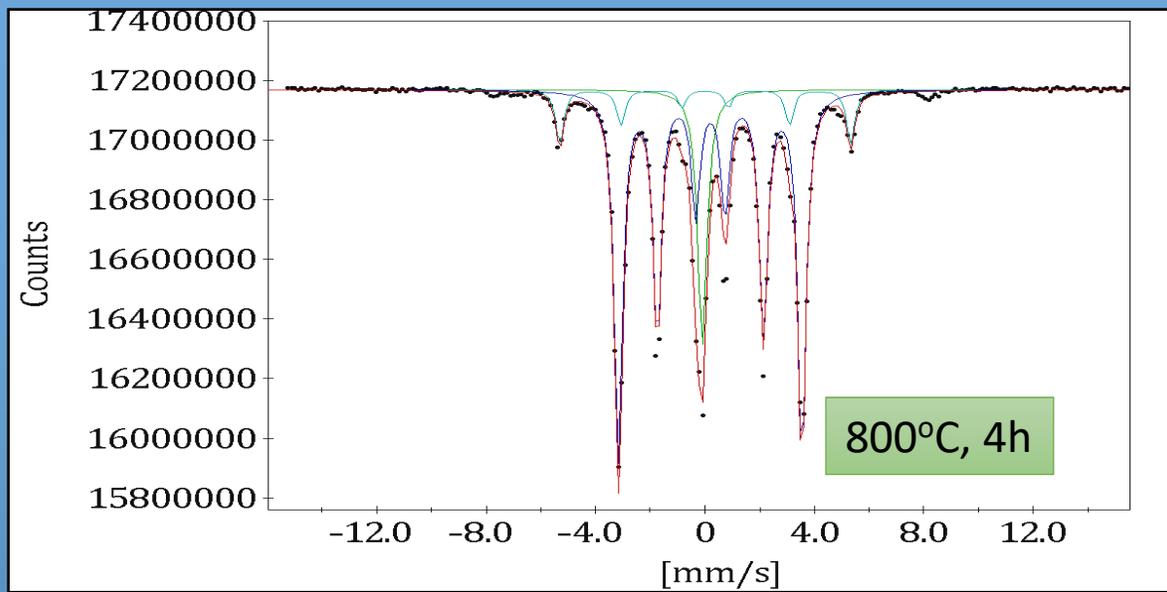
Thermal evolution of iron containing phases in nitrate loaded resin

Really superparamagnetic?
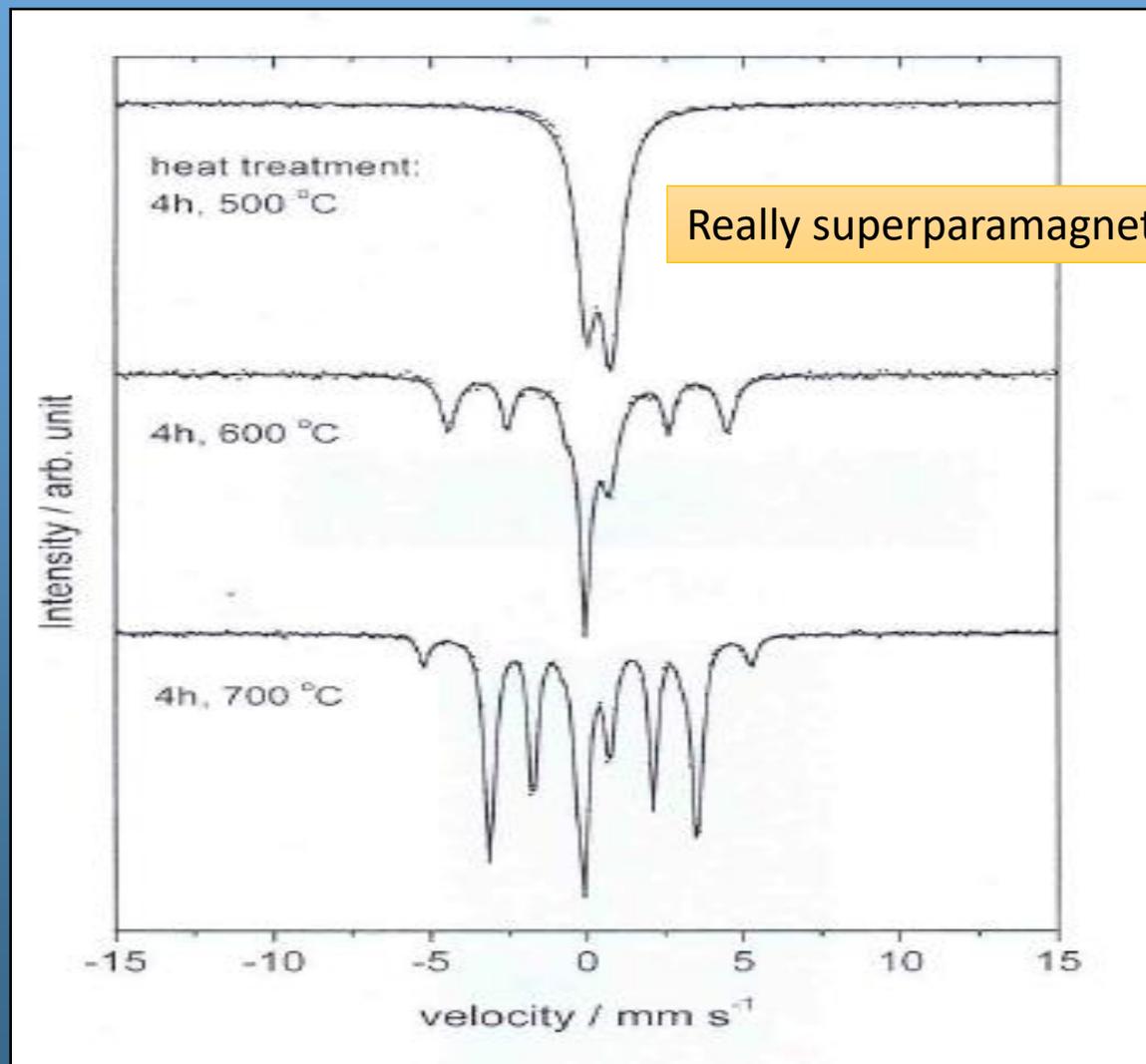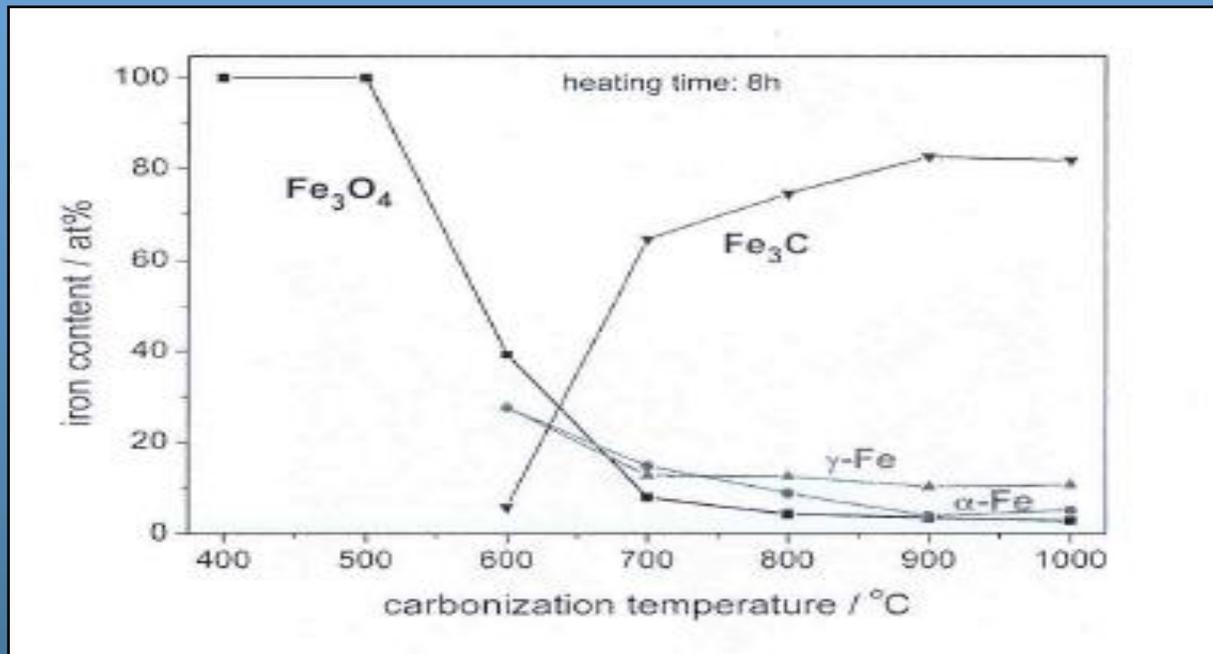
Superparamagnetic magnetite in nitrate loaded resin (400°C, 4h)

8 h
900 ºC
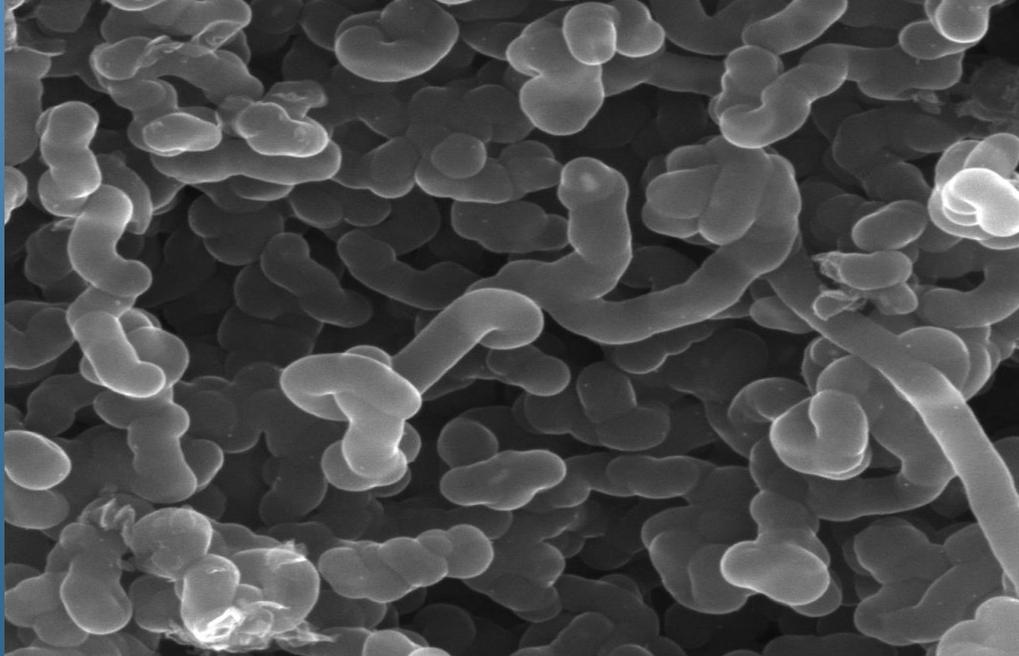
The colossal magnetoresistant (CMR) $La_{0.8}Sr_{0.2}CoO_{3-\delta}$

The CMR effect: Substantial decrease of resisitivity upon ferromagnetic ordering.

Suggested common feature of every CMR material: superparamagnetic-like behavior around T_c

Emission Mössbauer measurement....

1. Different doping site pereferences of Fe and Co.

2. „Nucleogenic" and „normal" ^{57}Fe probe.

Electron Capture decay of ^{57}Co:

^{57}Fe ^{57}Co

I

5/2   136.3 keV $\tau_{1/2}$ = 89 ns

85.9 %

3/2   14.4 keV $\tau_{1/2}$ =99.3 ns

9.4 %   (Mössbauer transition)

1/2
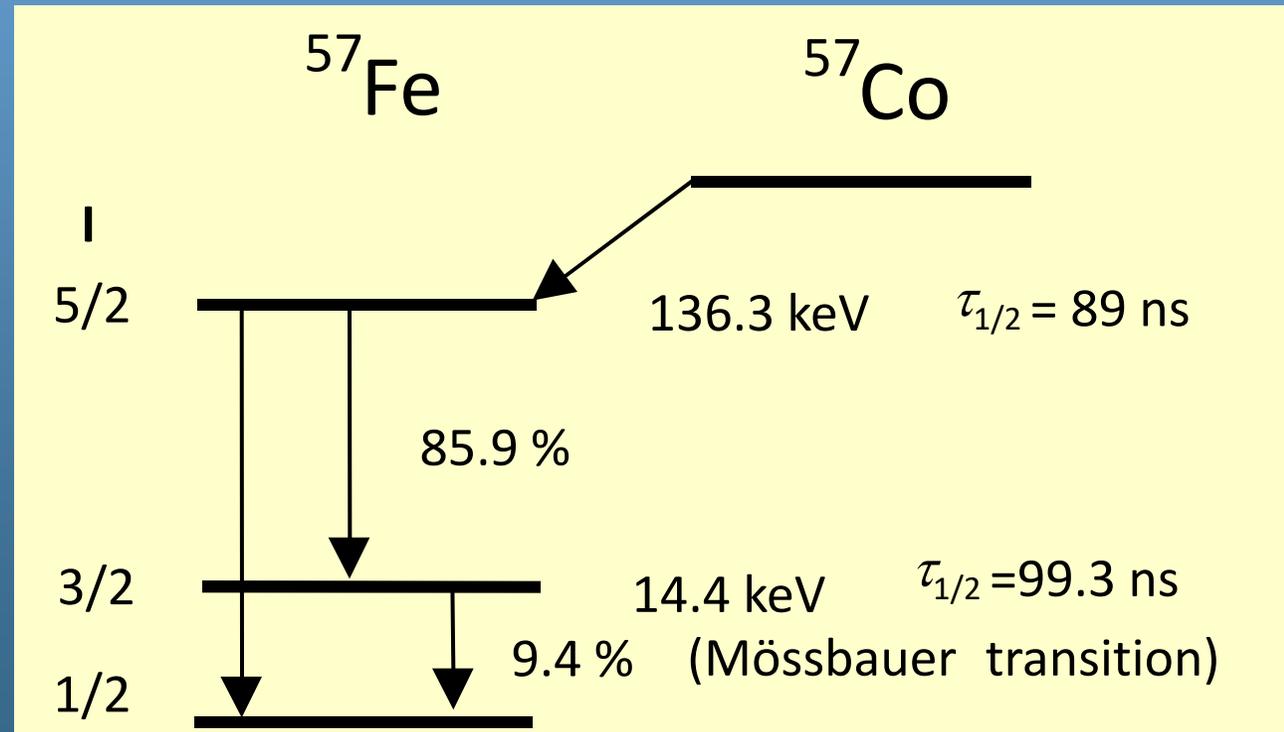
3. After-effects - never observed in perovskites.

The unit cell of perovskite:
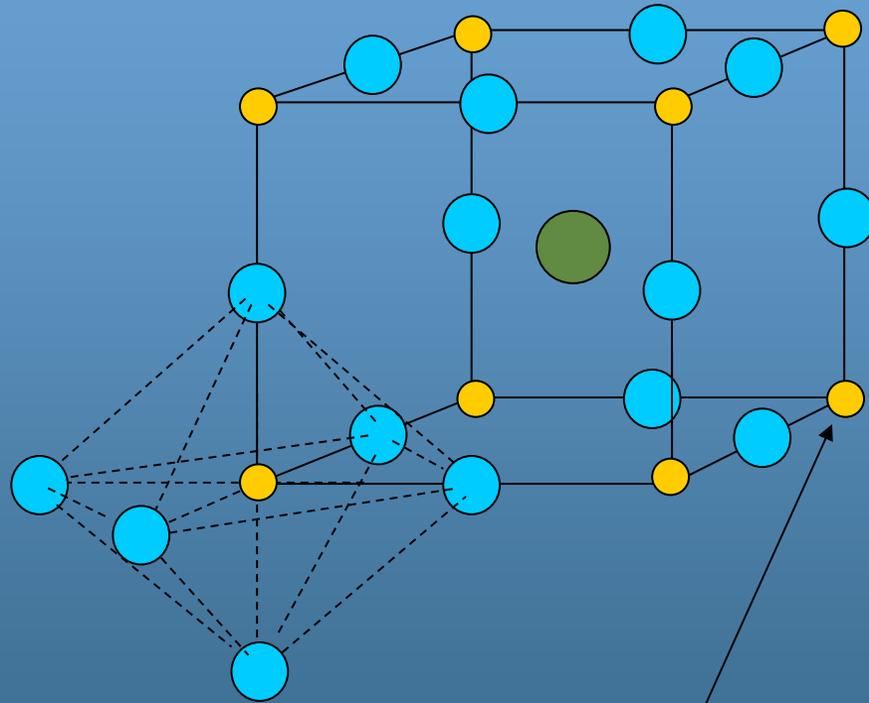
O

Co (Site B)

La,Sr (Site A)

ABO$_3$ structure

^{57}Co-substitution

Temperature dependence of the emission Mössbauer spectrum of $(La_{0.8}Sr_{0.2})CoO_{3-d}$ I.
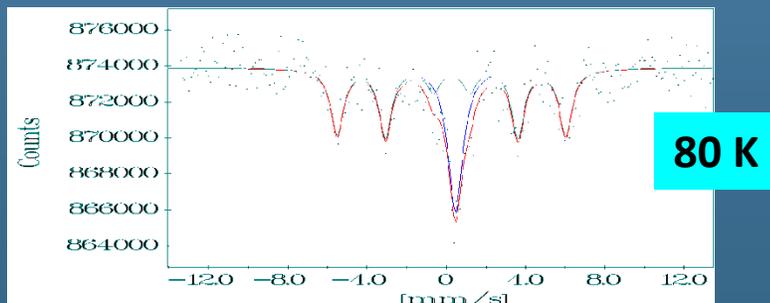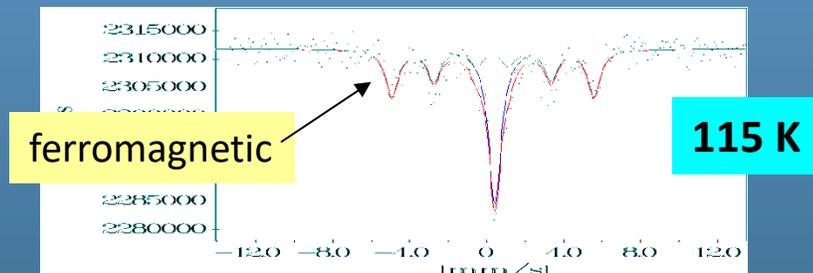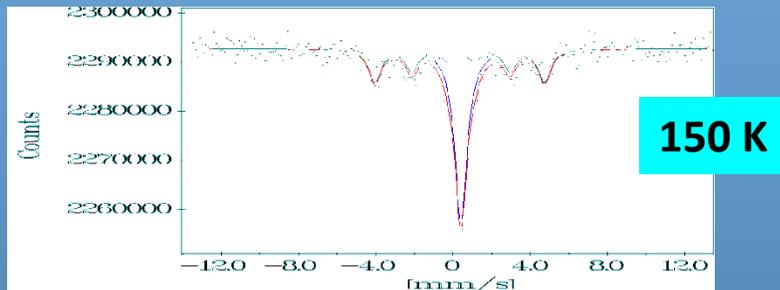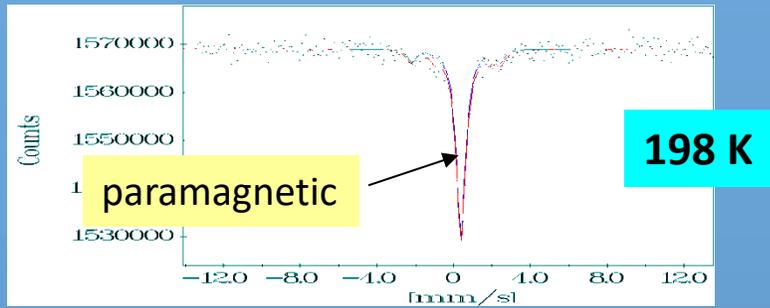
Main observations:

- Co-existence of the paramagnetic and the ferromagnetic phase in a wide temperature range.

- Different isomer shifts for the sextet and for the singlet.

Relaxation phenomena:

Larmor precession:

slow relaxation

$$\tau_{Larmor} < \tau_{relax}$$
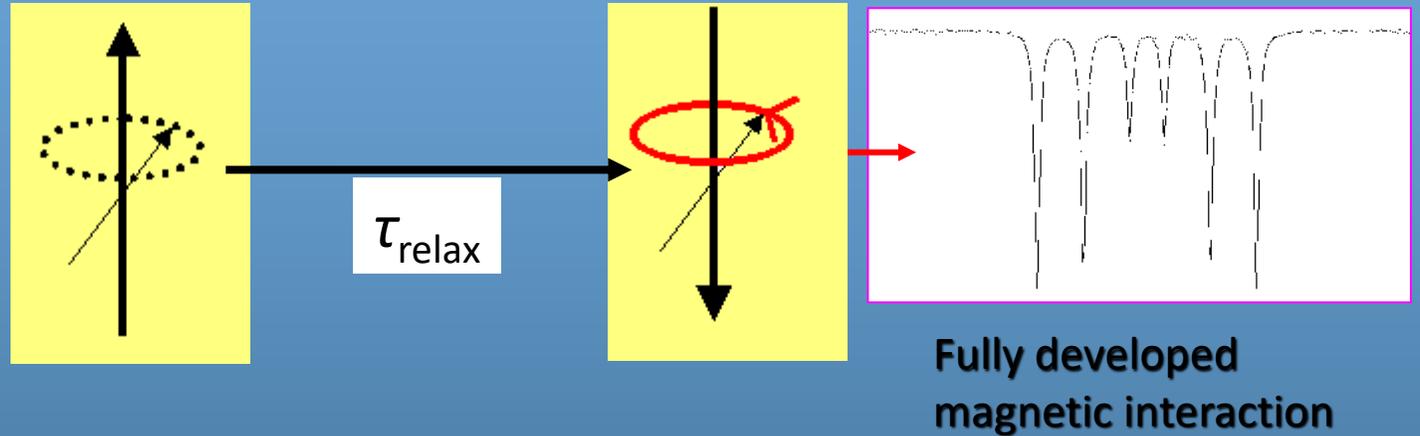
τ_{relax}

Fully developed magnetic interaction

fast relaxation

$$\tau_{Larmor} > \tau_{relax}$$

τ_{relax}
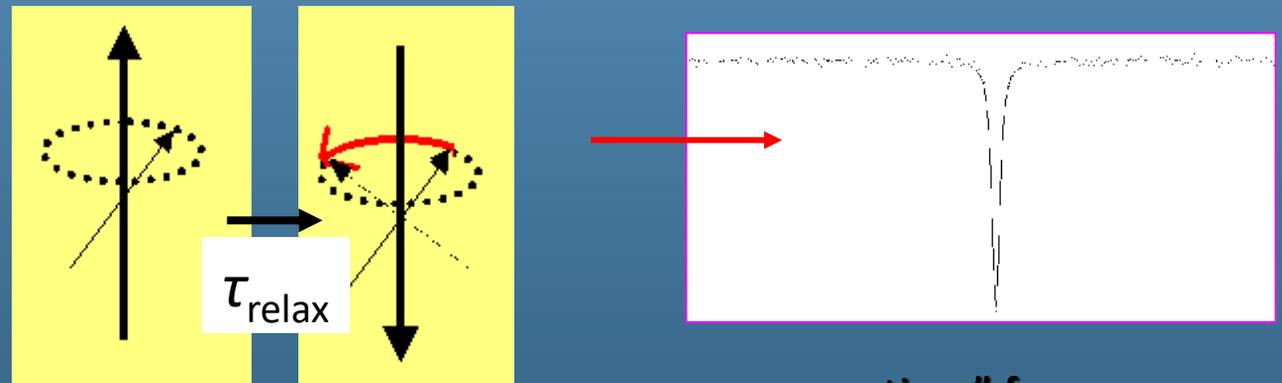
„no time" for magnetic interaction

= magnetic moment of the electronic system

= magnetic moment of the nucleus

72

Superparamagnetic clusters?

Low *T*

fast relaxation

slow relaxation

sextet

singlet

High *T*

fast relaxation

slow relaxation
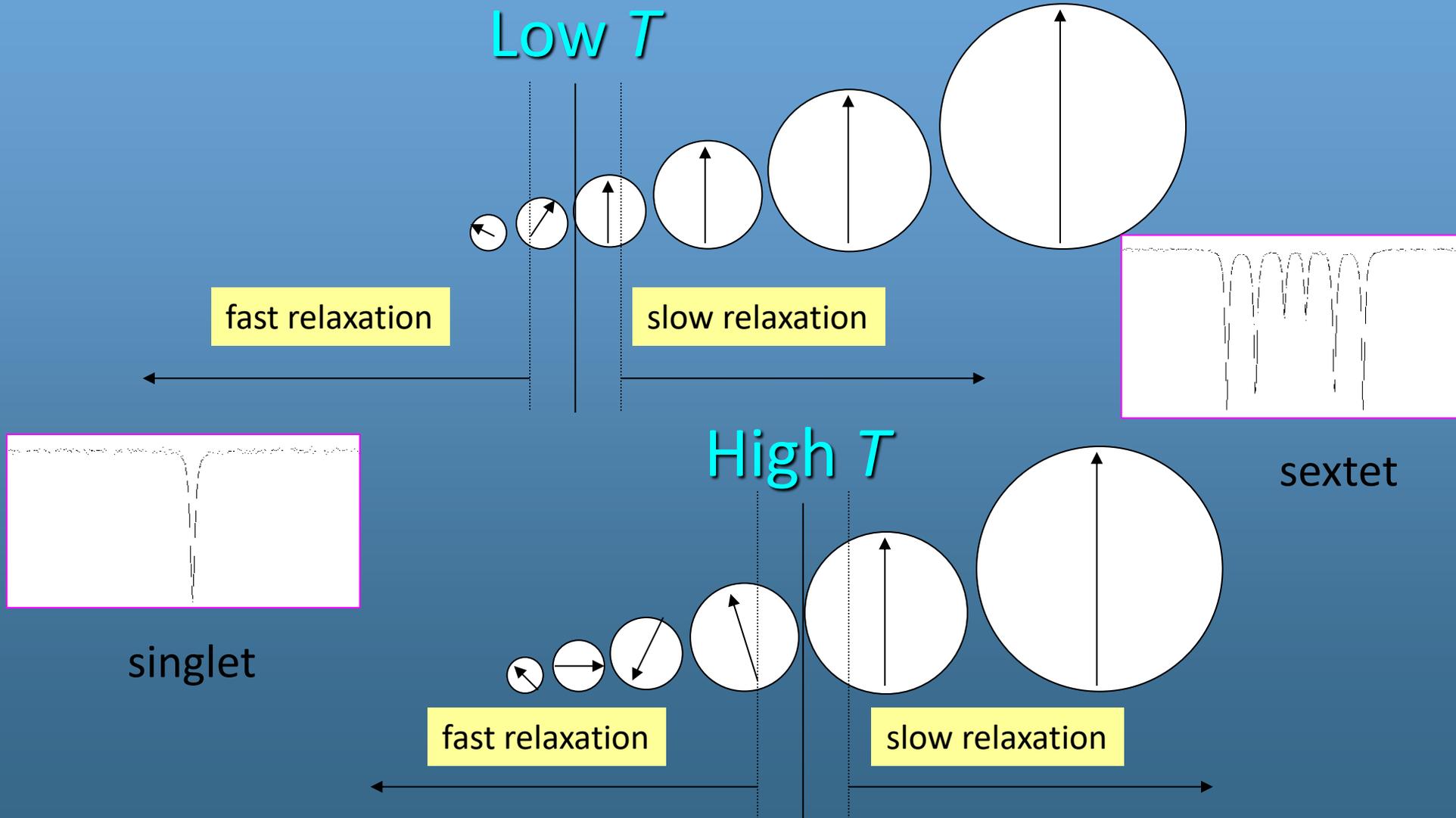
Temperature dependence of the emission Mössbauer spectrum of $(La_{0.8}Sr_{0.2})CoO_{3-d}$ II.
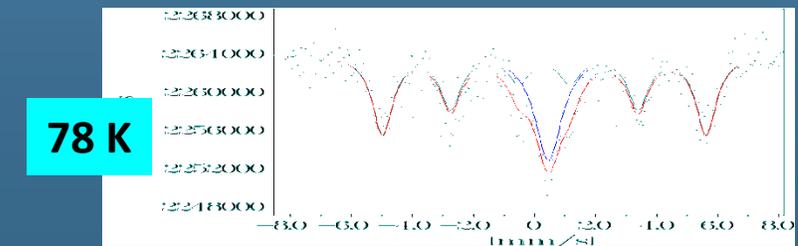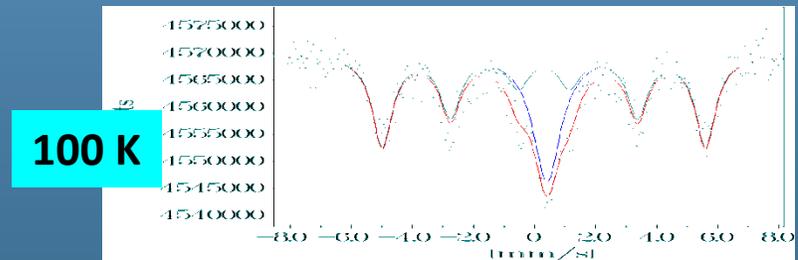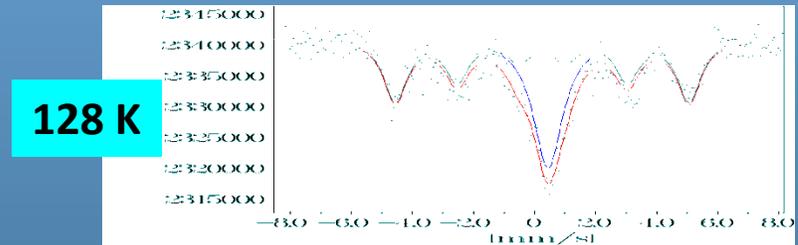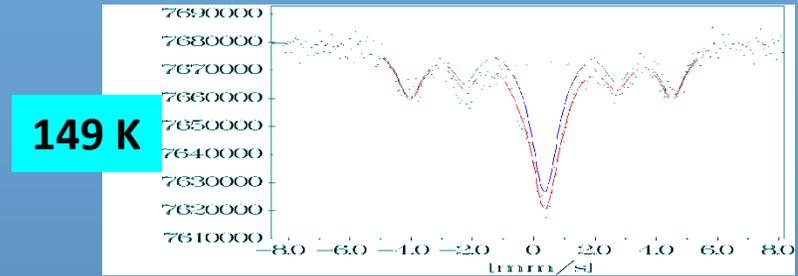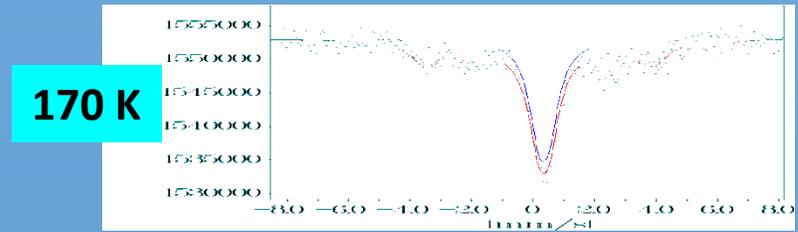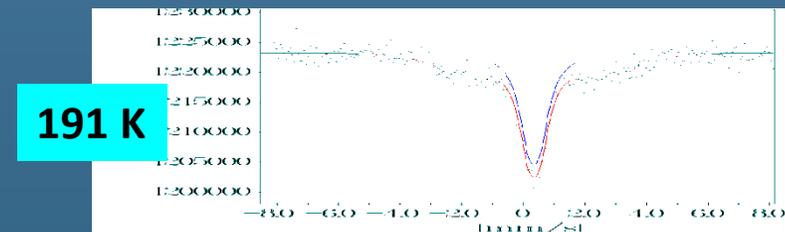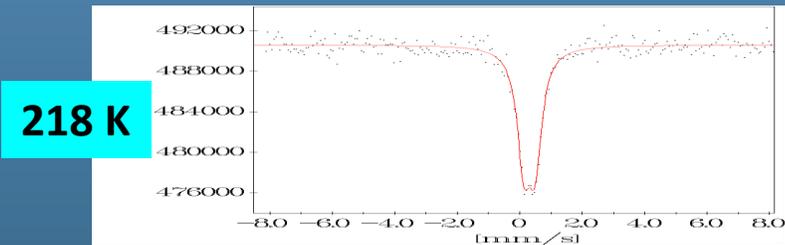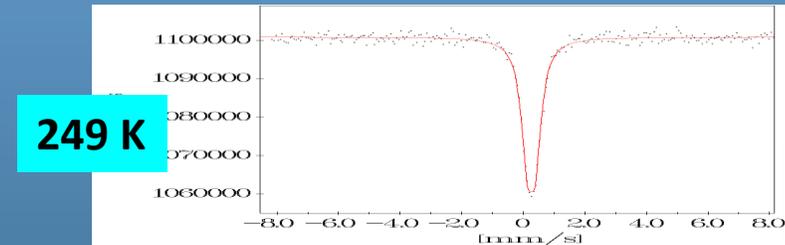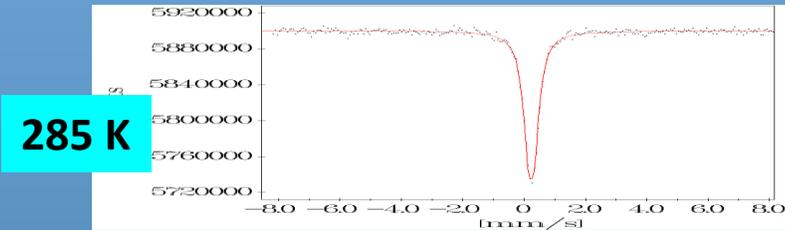
Relative spectral areas of the paramagnetic and the ferromagnetic fraction

paramagnetic fraction

Experiment I

Experiment II

Experiment III (reduced)

ferromagnetic fraction

relative area / %

T / K
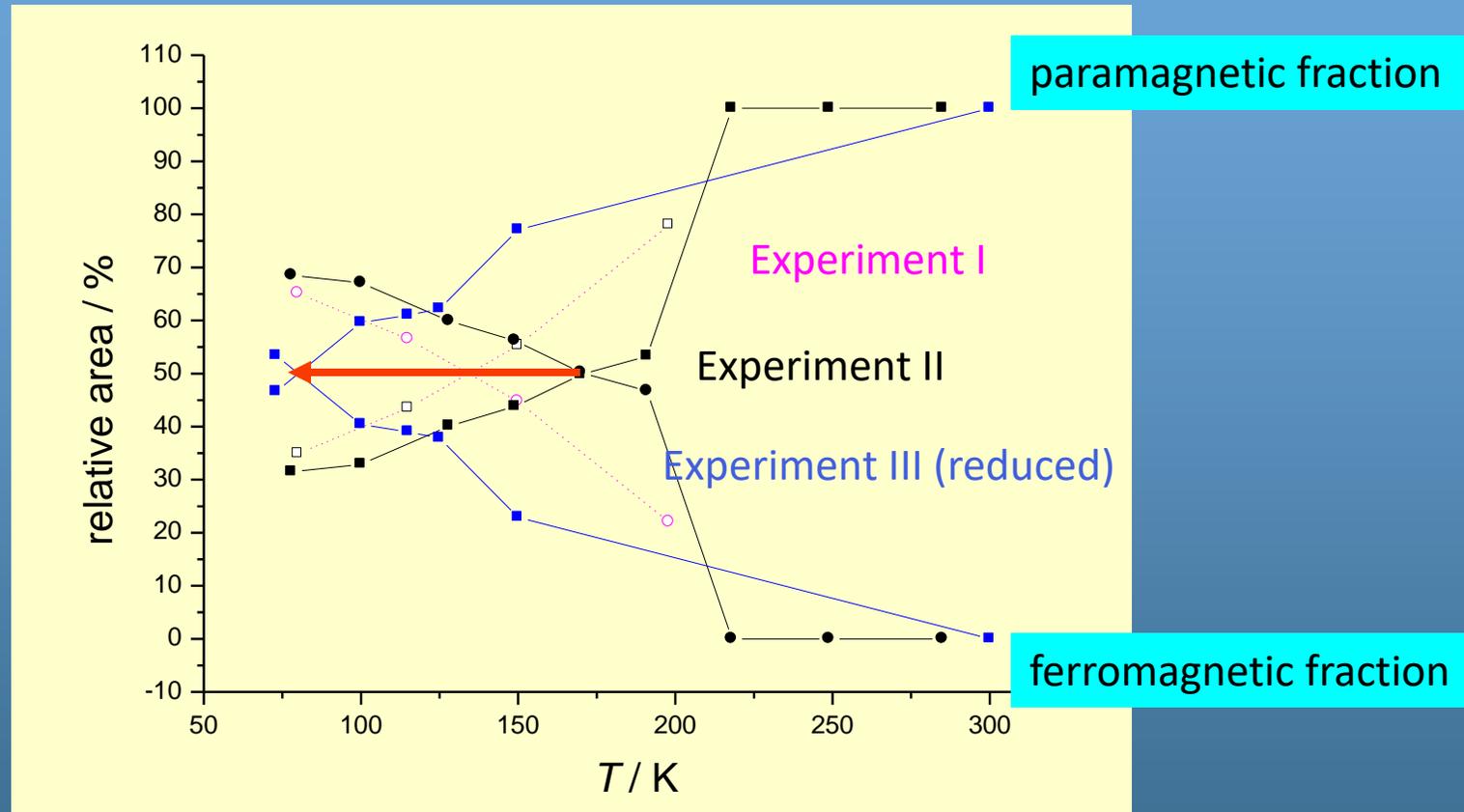
The superparamagnetic transition temperature is shifted downward upon oxygen removal.

magnetic cluster size reduced!

Hyperfine magnetic field in the ferromagnetic fraction
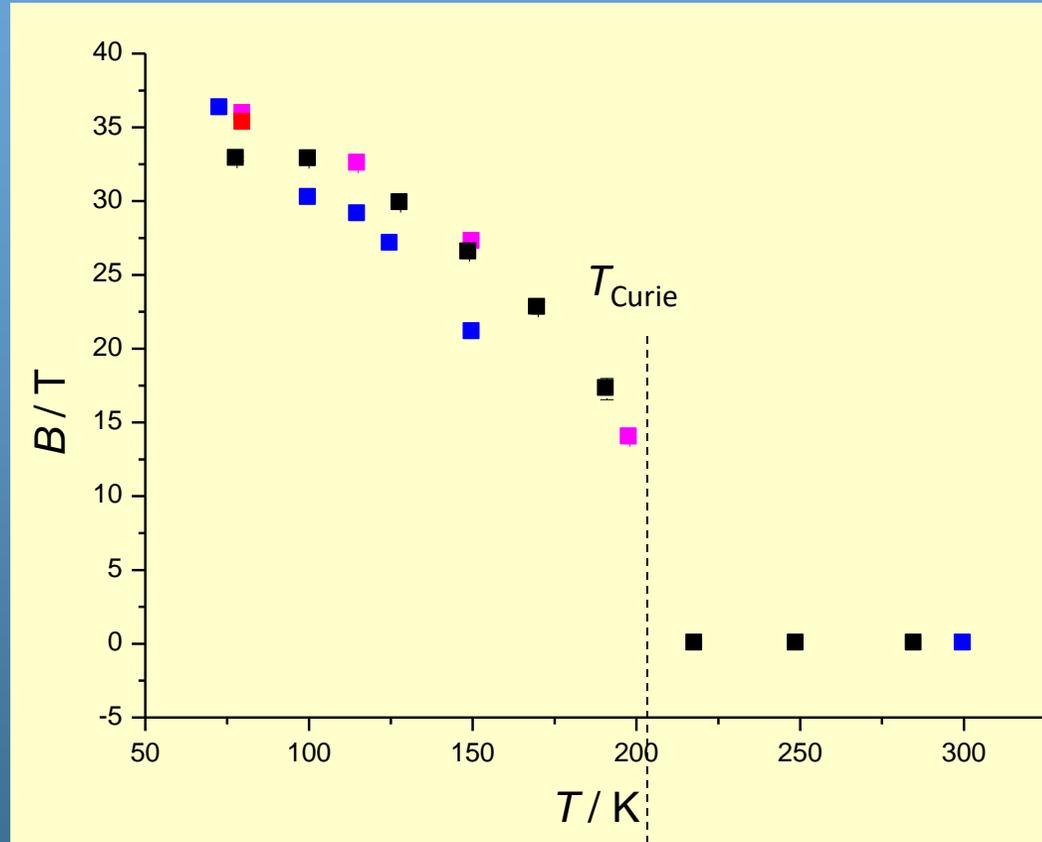
Experiment I

Experiment II

Experiment III (red.)

Experiment IV

Slight decrease of the field upon dexygenation.
The Curie temperature does not seem to change.

Isomer shifts in the paramagnetic and ferromagnetic fractions
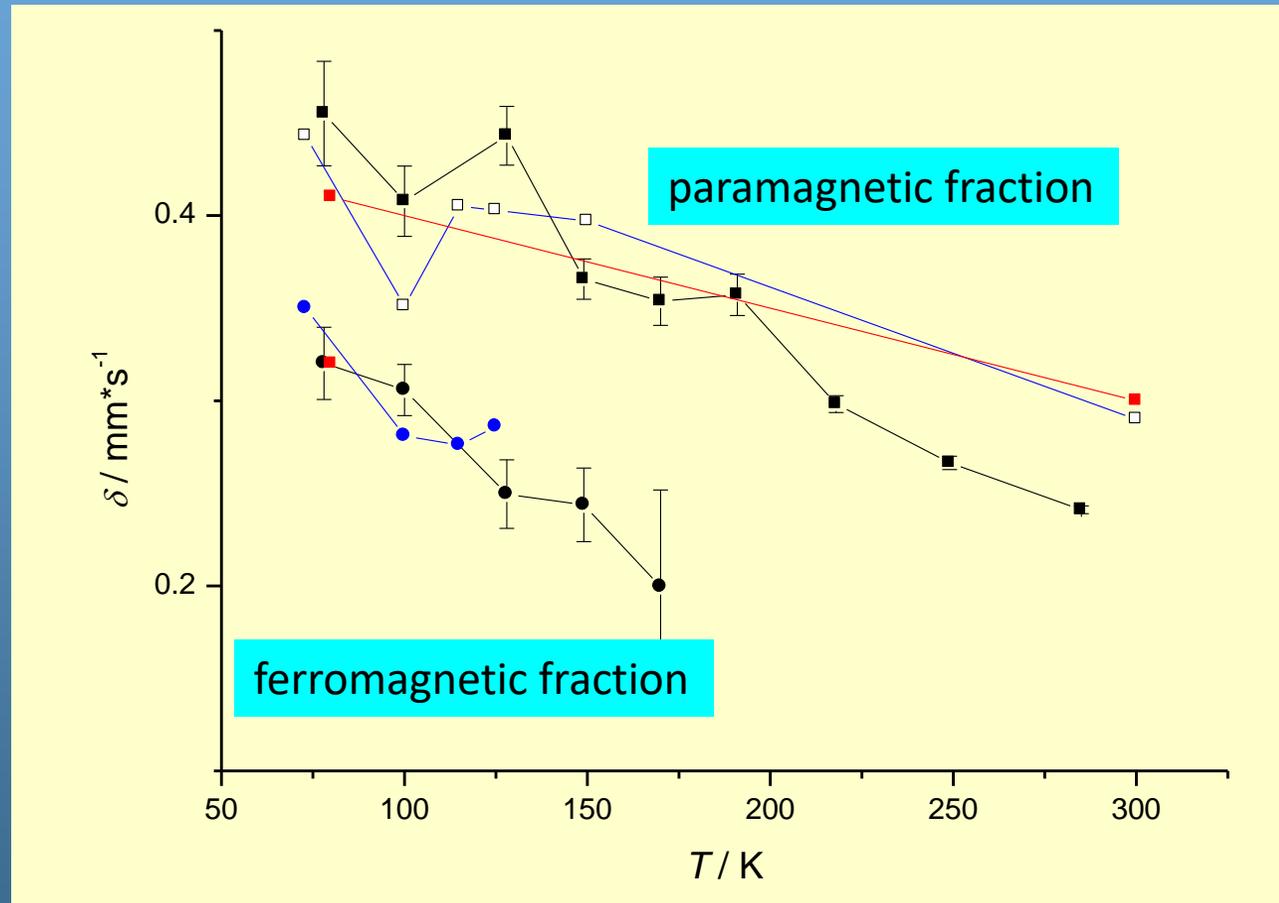
Considerable difference between the isomer shifts
in the ferromagnetic and in the paramagnetic fraction.
(insensitive to oxygen removal)

Why is the isomer shift lower in the ferromagnetic phase?
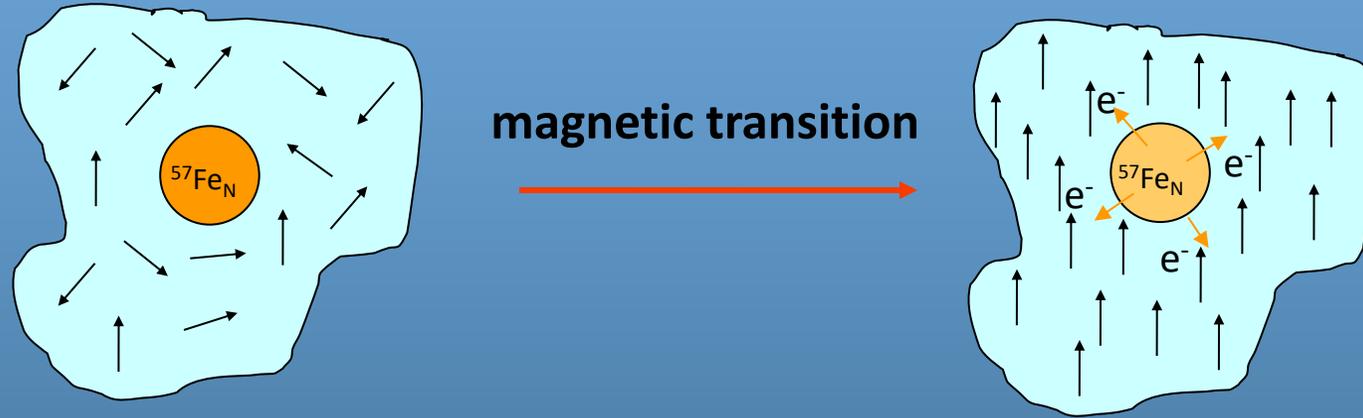
Nucleogenic ^{57}Fe
in paramagnetic host

magnetic transition

Nucleogenic ^{57}Fe
in ferromagnetic host

**The ferromagnetic host lattice has
an electron withdrawing effect on the Fe3d level.**

Requires itinerant electrons (metallicity).

FROZEN SOLUTION STUDIES IN COORDINATION CHEMISTRY

• Characterization of iron(III) complexes with various X ligands (EDTA, CDTA)

• Tracking reactions with hydrogen peroxide in solution phase, identifying intermediary species.

Ethylenediaminetetraacetic acid (EDTA)
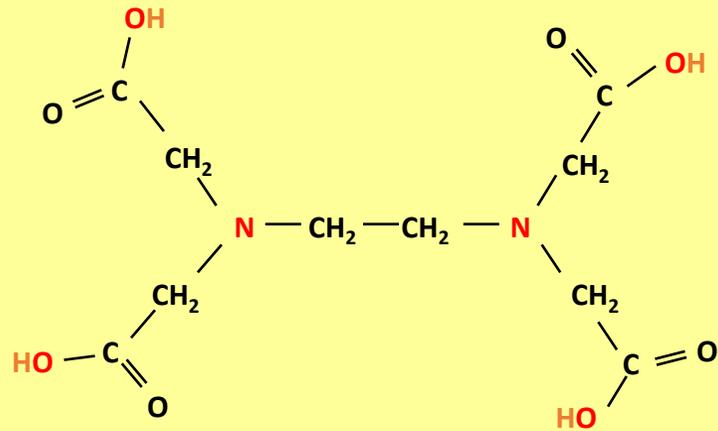
Cyclohexanediaminetetraacetic acid (CDTA)
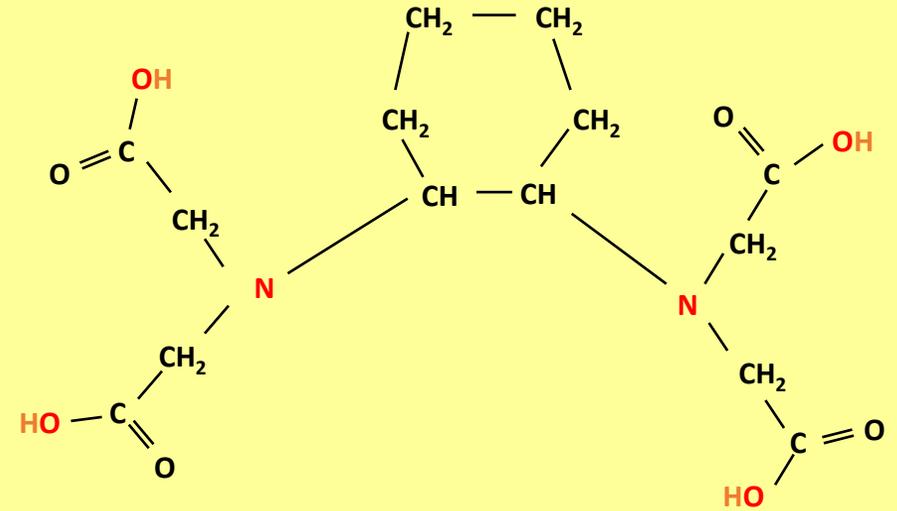
- Hexadentate chelate
- Quaternary acid

Characterization of „Fe^{III}(EDTA)"

Species [Fe(EDTA)(H$_2$O)]$^-$

(observed in solid Na[Fe(EDTA)(H$_2$O)]·2 H$_2$O)
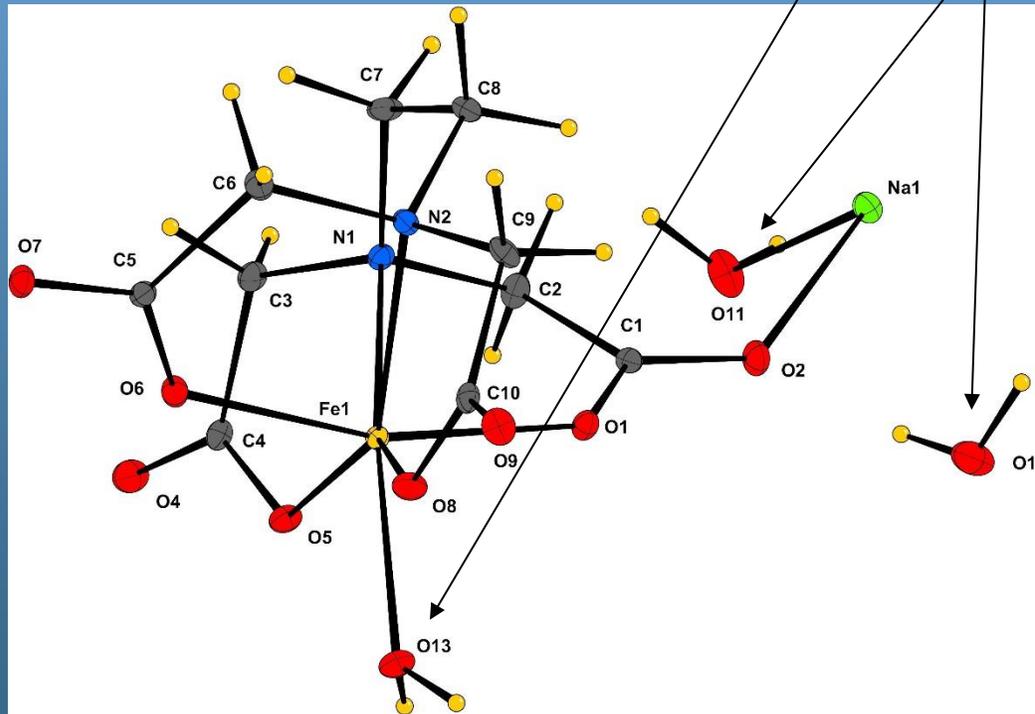
Single crystal XRD

T = 80 K
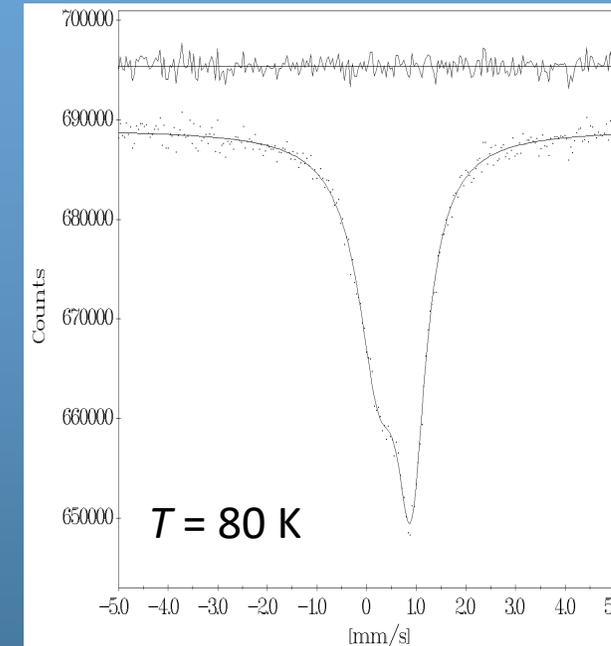
δ = 0.57 mm/s
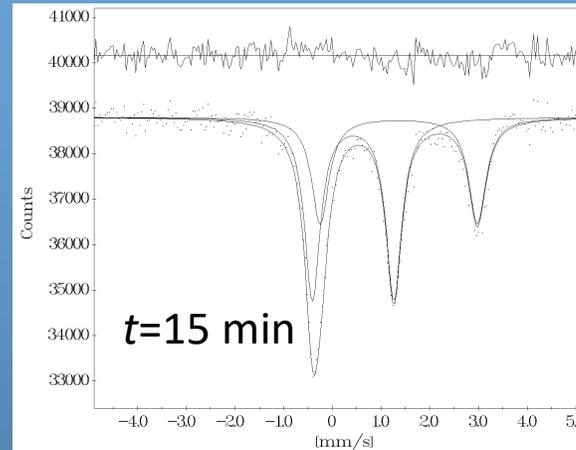
(single component relaxation fit with Blume-Tjon model)

„Fe^{III}(EDTA)" in aqueous solution
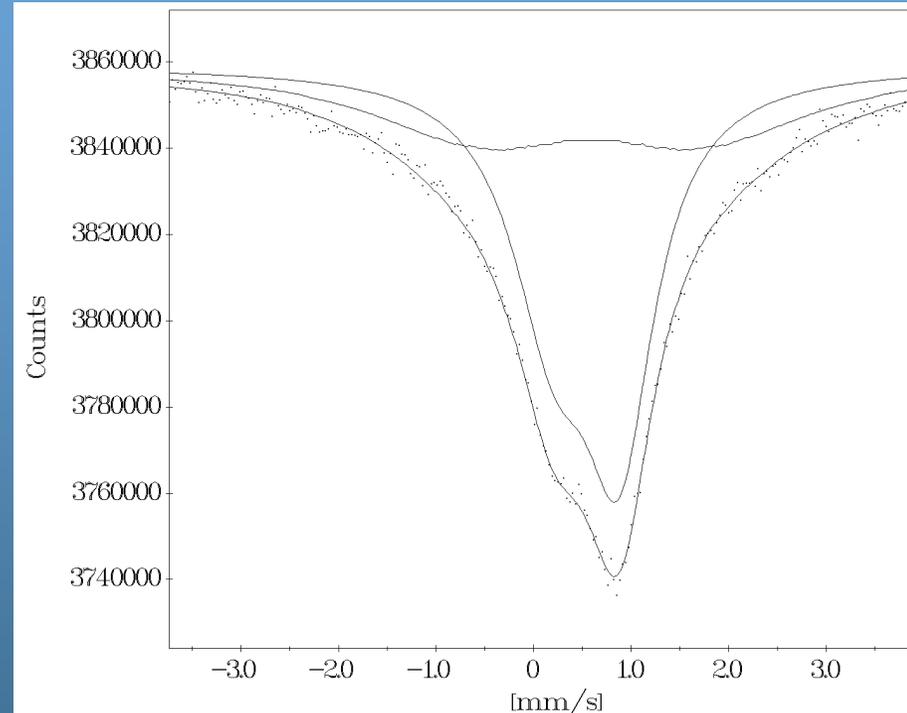
Frozen saturated solution of Na[Fe(EDTA)(H$_2$O)]·2 H$_2$O

Interesting concentration intervals are much lower.

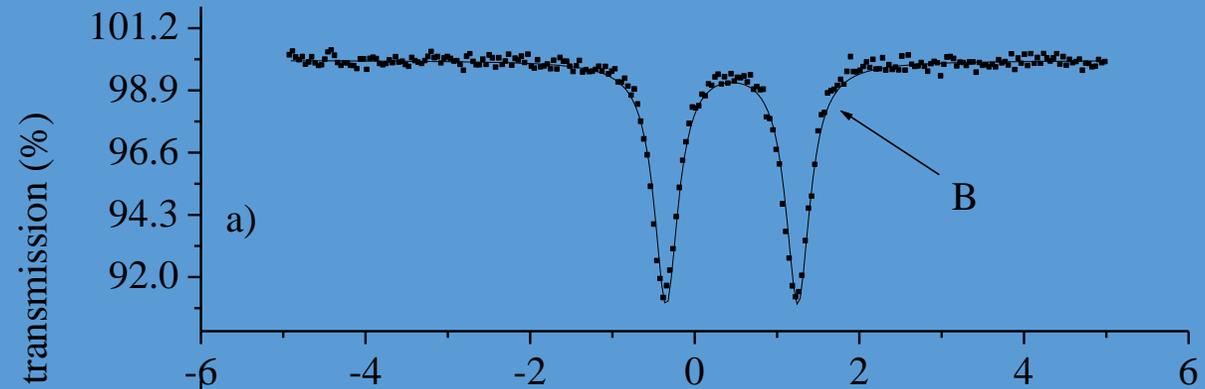„Fe^{III}(EDTA)" in aqueous solution, pH dependence at c=0.1 M
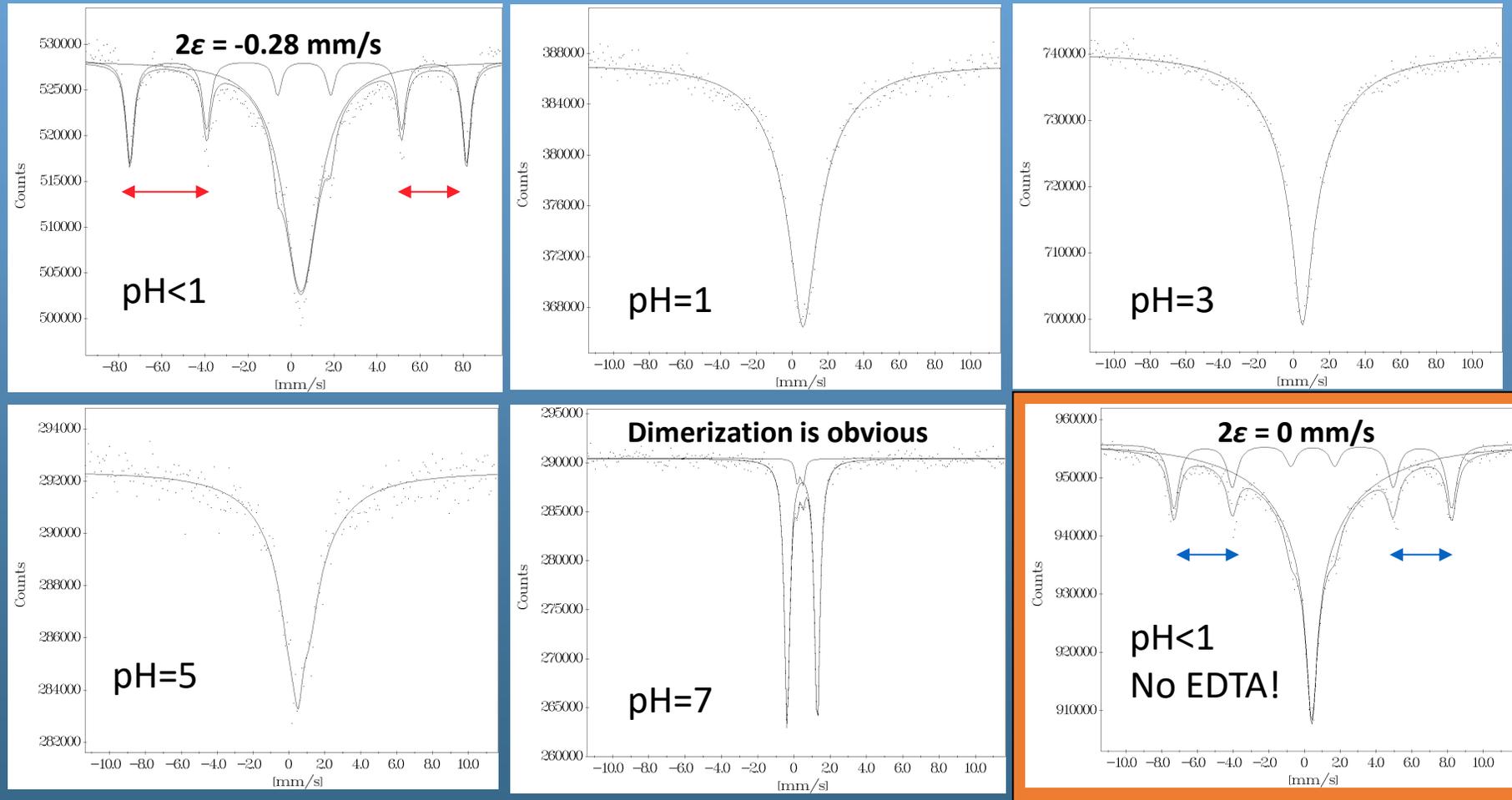
Formation of Fe^{III}EDTA from Fe^{II} salt at pH=7.06 and *c*=0.025 M

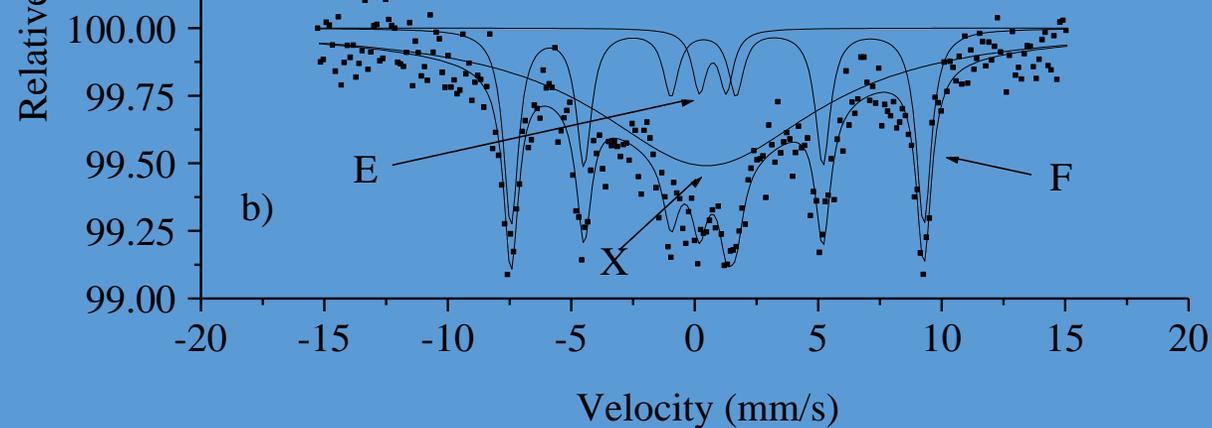$[Fe(H_2O)_6]^{2+}$

$[(EDTA)Fe-O-Fe(EDTA)]^{4-}$
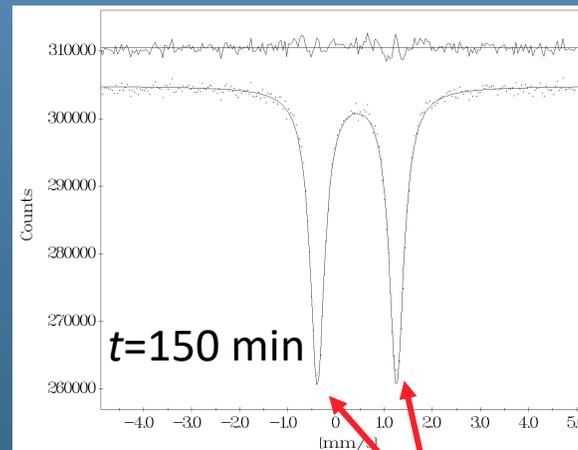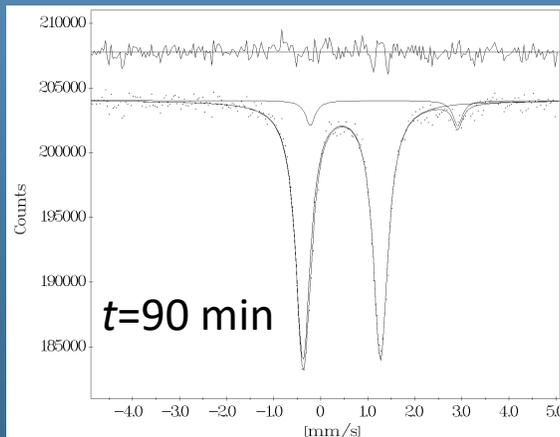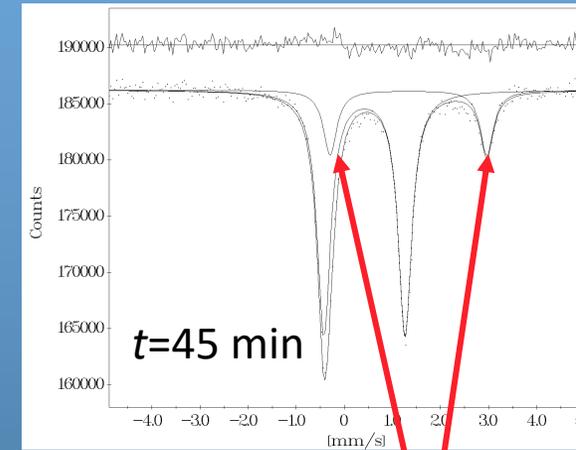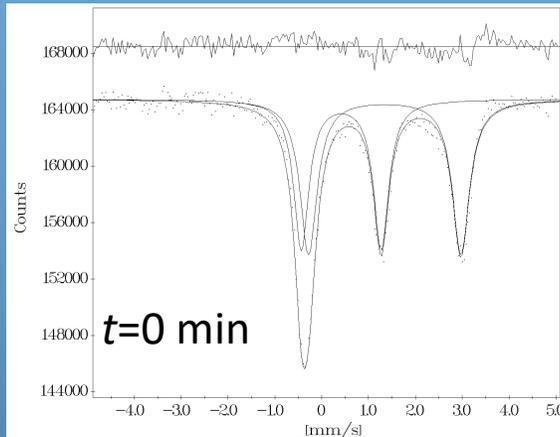
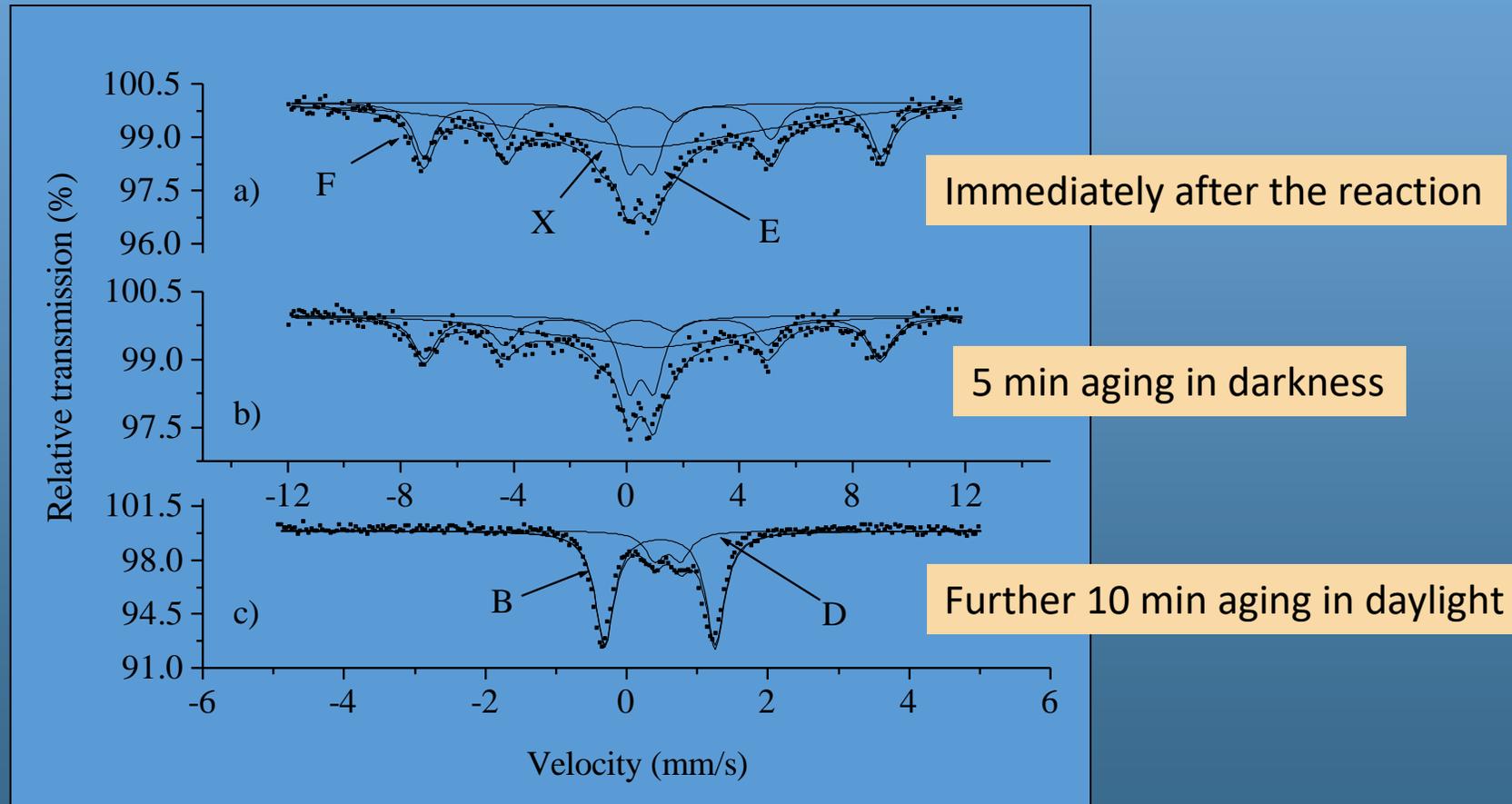„Fe^{III}(EDTA)" at high pH, reaction with H$_2$O$_2$ - I.

Before reaction:

After reaction:

pH = 10.4

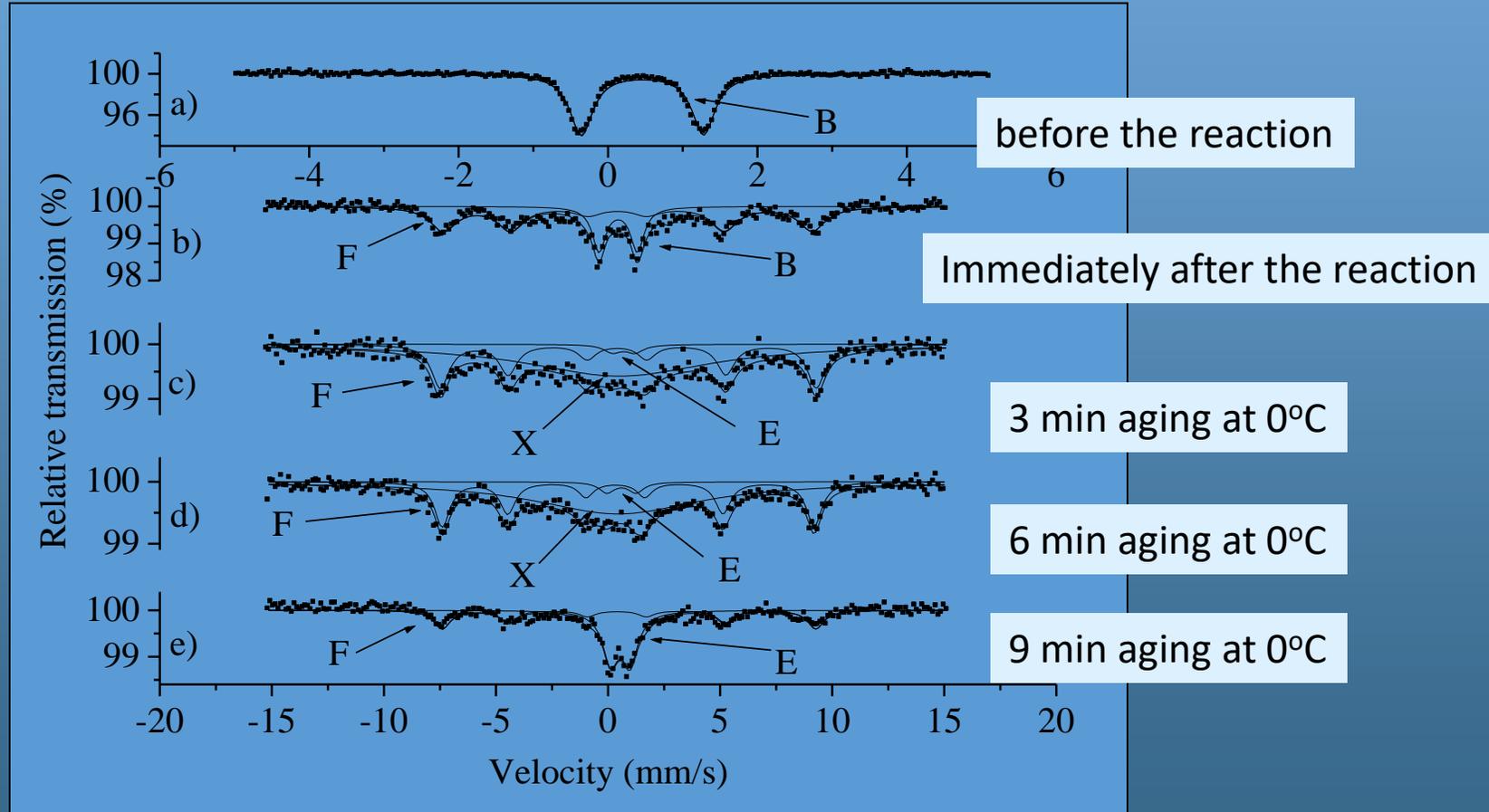„Fe^{III}(EDTA)" at high pH, reaction with H$_2$O$_2$ - II.

pH = 10.4

„Fe^{III}(EDTA)" at high pH, reaction with H$_2$O$_2$ - III.

Immediately after the reaction

4 min aging

10 min aging
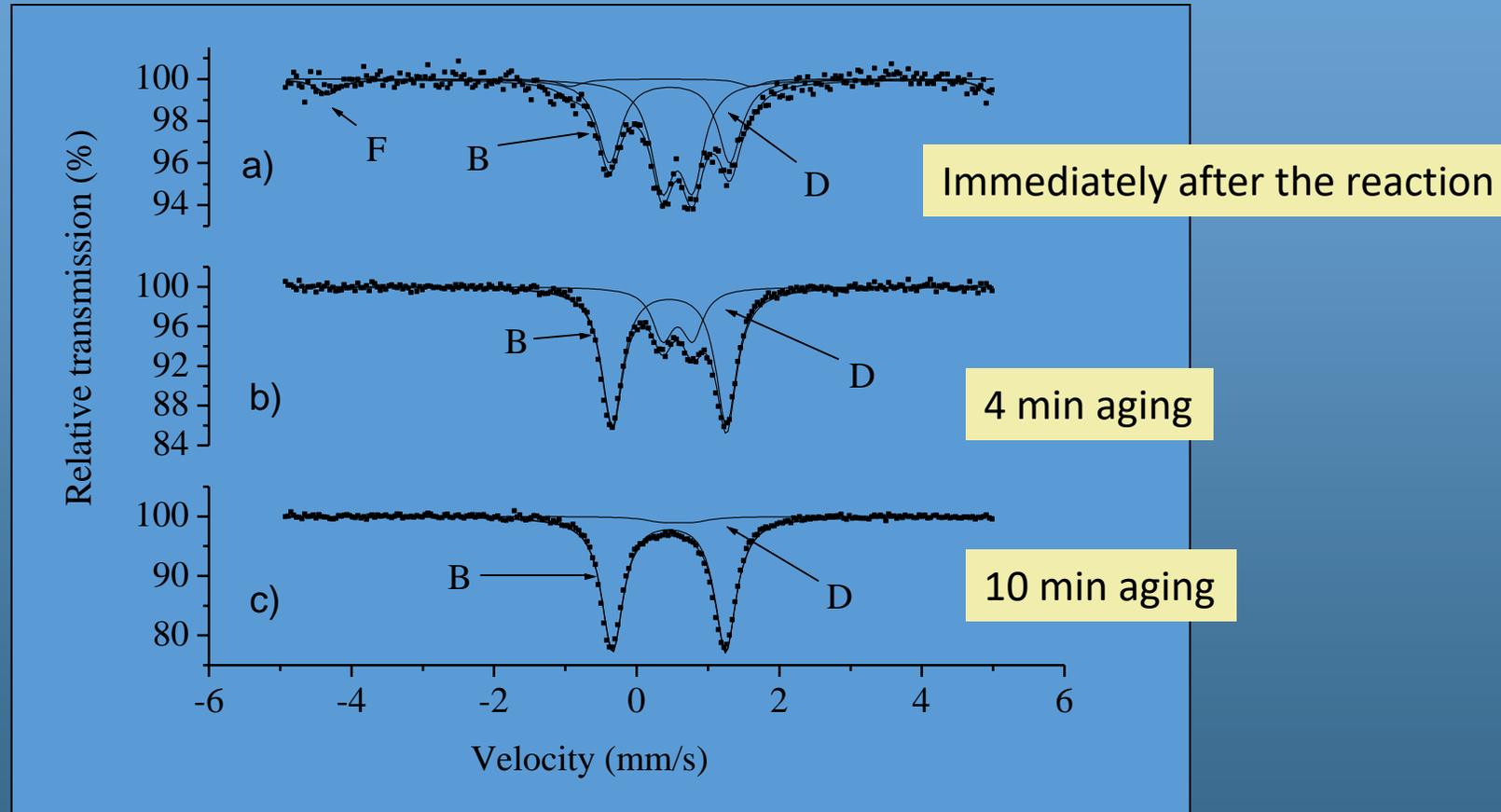
pH = 10.4

„Fe^{III}(EDTA)" at high pH, reaction with H$_2$O$_2$ - IV.

pH = 10.4, $T_{reaction}$ = 0°C

„Fe^{III}(EDTA)" at high pH, reaction with H$_2$O$_2$ - summary of observed species

| Species	Description	pH	Coord. number	δ (mm/s)	Δ or $2\varepsilon^*$ (mm/s)	B(T)
S	**[Fe(EDTA)(H$_2$O)]$^-$** in solid Na[Fe(EDTA)(H$_2$O)]·2H$_2$O		7	0.57(1)	0.66(1)	~0
A1	**[Fe(EDTA–H)(H$_2$O)]**	~1.0	6	0.48(11)	+0.16(45)	30(6)
A2	**[Fe(EDTA)]$^-$**	~1.0	6	0.43(2)	–0.44(5)	41.2(2)
B	**[(EDTA)Fe–O–Fe(EDTA)]$^{4-}$**	~10.4	6	0.455(5)	1.60(5)	0
F	**[(EDTA)Fe(η^2-O$_2$)]$^{3-}$**	~10.4	7	0.62(4)	+0.53(5)	51.1(5)
D	**[(EDTA)Fe–(OO)(OH)–Fe(EDTA)]$^{5-}$**	~10.4	7	0.57(1)	0.40(3)	0
E	**[(EDTA)Fe–(OO)–Fe(EDTA)]$^{4-}$**	~10.4	6	0.47(3)	0.85(4)	0

Reaction scheme for the formation of dihapto-peroxo-Fe^{III}EDTA:
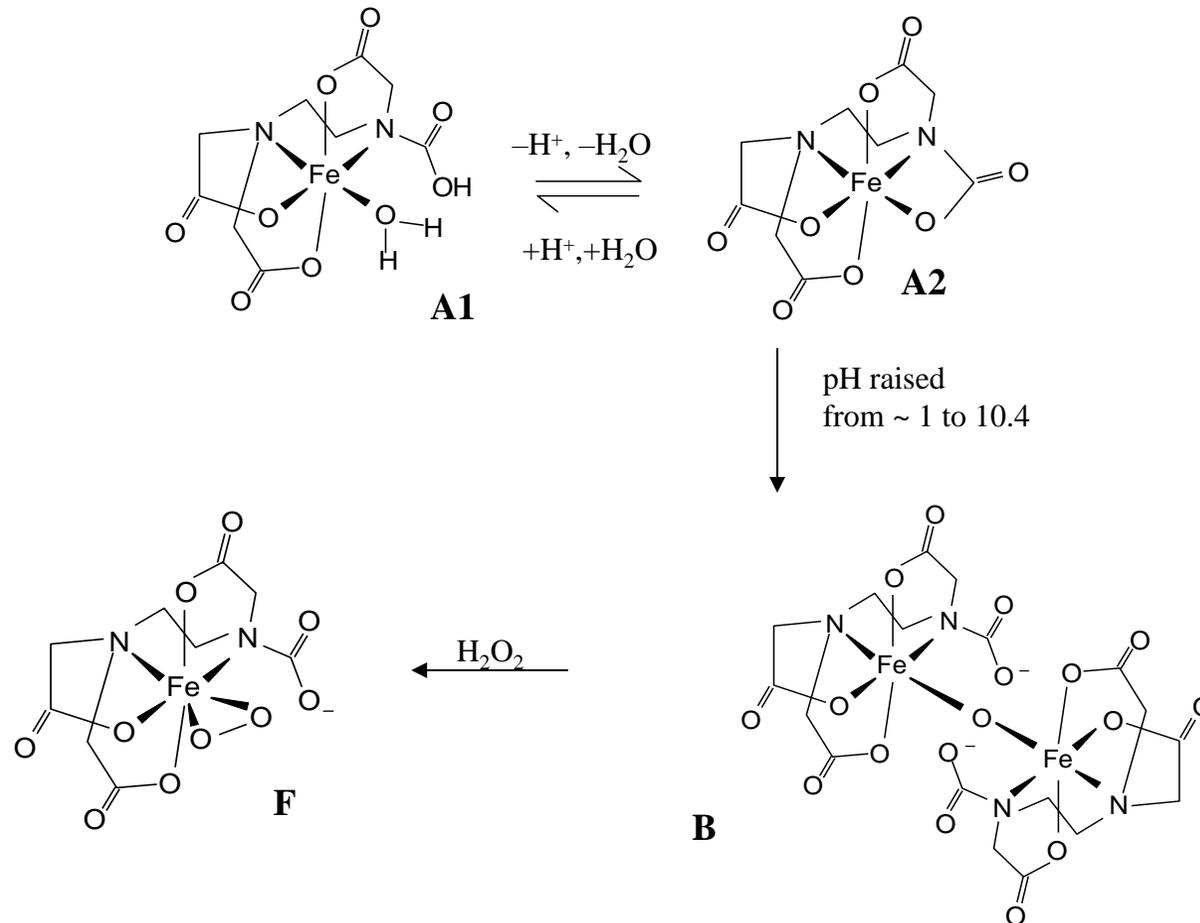
Reaction scheme for the decomposition of dihapto-peroxo-Fe^{III}EDTA:
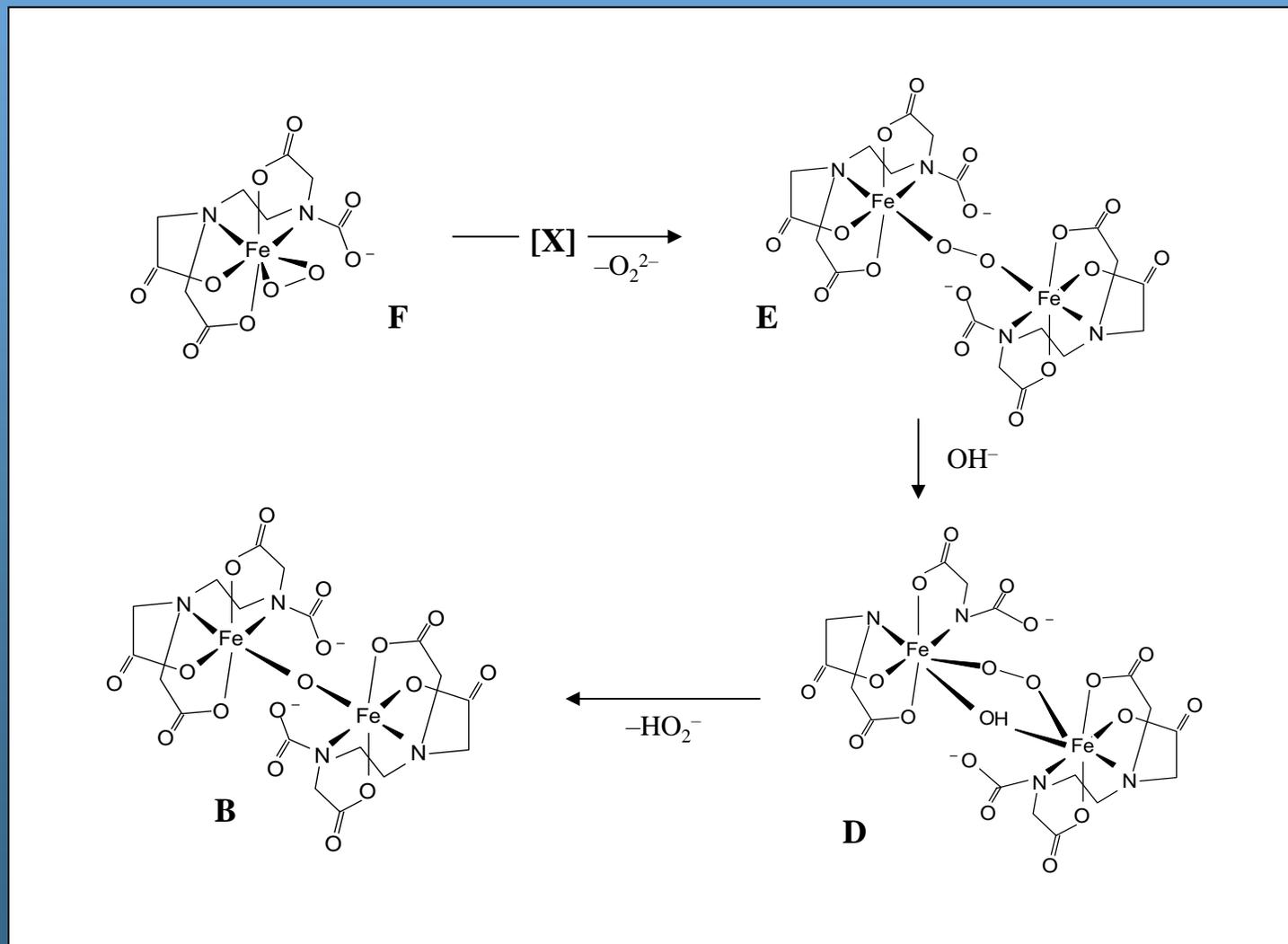
Fe^{III}CDTA measured – preliminary*

sextet I

pH = 8.1

sextet II

pH = 10.4

sextet II+III

pH = 11.3
H$_2$O$_2$ added

sextet III
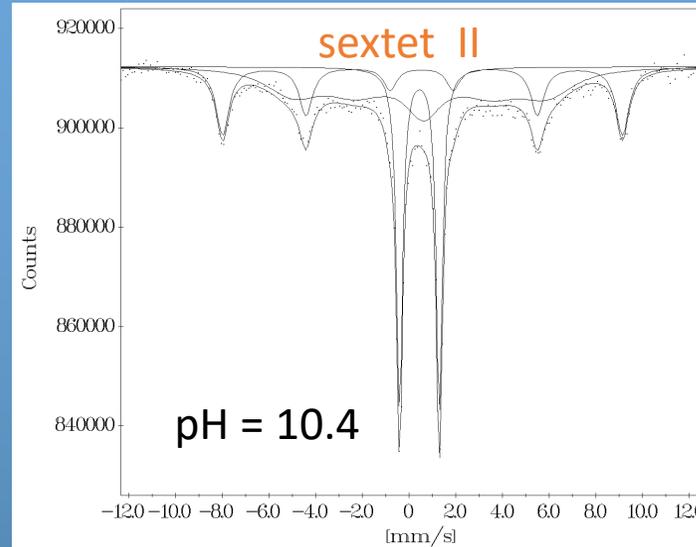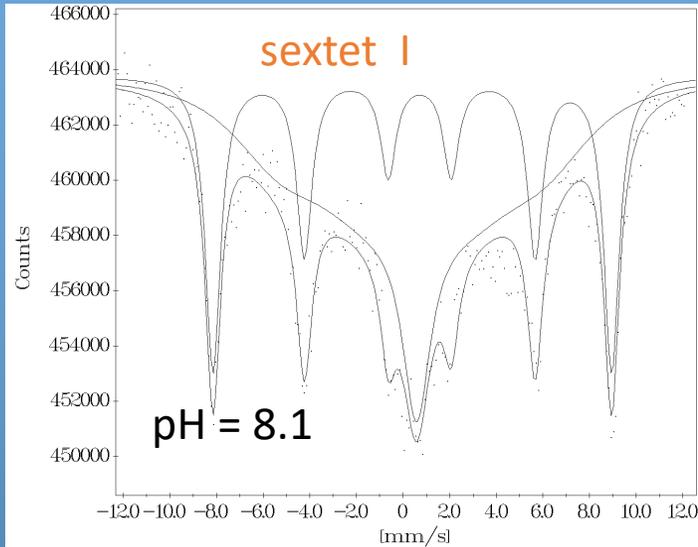
c = 0.02 M
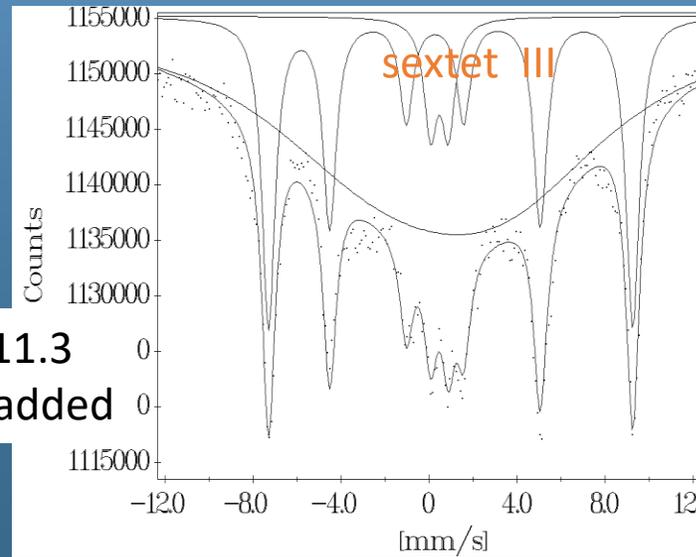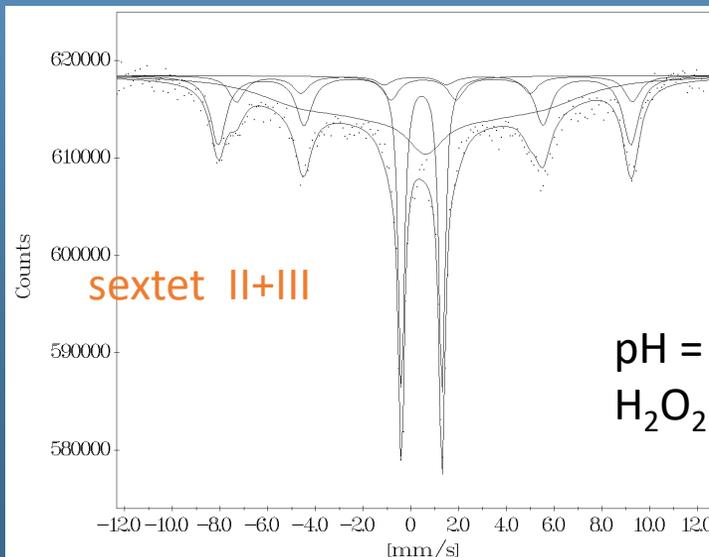
quadrupole shifts:

I.: -0.32
II.: +0.05
III.: +0.71

*With contribution of Rudi van Eldik and Ariane Brausam