# LECTURE 9:
Mössbauer Spectroscopy

- **Gamma rays**

- **Recoil energy & Resonance absorption**

- **Doppler effect**

- **Chemical (valence), structural (coordination) & magnetic properties**

- **Suggested reading:**
  https://www.rsc.org/Membership/Networking/InterestGroups/MossbauerSpect/Intropart1.asp

Our Mössbauer spectrometer
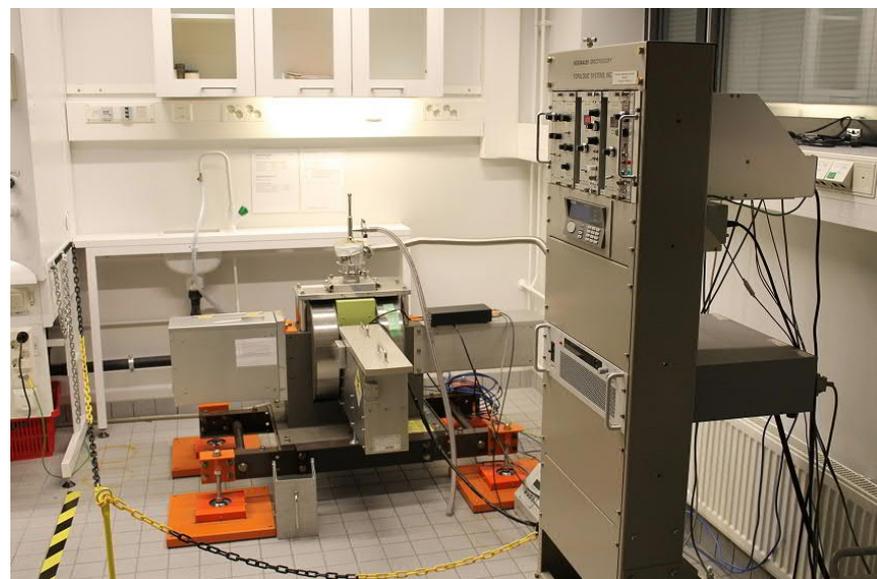
GAMMA RAYS

- Shortest wavelength (highest energy) part of electromagnetic radiation

- Energy in the order of transitions in atomic nucleus

- Atom nucleus has different energy levels:
  (lowest energy) ground state and (higher energy) excited states (life times <1 μs)

- When the nucleus returns from an excited state (E_e) to the ground state (E_g),
  the **energy difference** is emitted as gamma rays ($\boldsymbol{E_0} = E_e - E_g$)

THE ELECTROMAGNETIC SPECTRUM

Wavelength (in meters)	10^3	10^2	10^1	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}

Size of a wavelength: longer ← → shorter

Soccer Field, House, Baseball, This Period, Cell, Bacteria, Virus, Protein, Water Molecule

Common name of wave: RADIO WAVES, MICROWAVES, INFRARED, VISIBLE, ULTRAVIOLET, "SOFT" X RAYS, "HARD" X RAYS, GAMMA RAYS

Sources: AM Radio, rf Cavity, FM Radio, Microwave Oven, Radar, People, Light Bulb, The ALS, X-Ray Machines, Radioactive Elements

Frequency (waves per second)	10^6	10^7	10^8	10^9	10^{10}	10^{11}	10^{12}	10^{13}	10^{14}	10^{15}	10^{16}	10^{17}	10^{18}	10^{19}	10^{20}

Energy of one photon (electron volts): lower ← → higher

Energy of one photon (electron volts)	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1	10^1	10^2	10^3	10^4	10^5	10^6

RECOIL ENERGY

- Based on the *Momentum Conservation Law*, when gamma rays are emitted the nucleus gets a **recoil impulse** (p_r) of the opposite direction (c.f. what happens to the boat when the passanger jumps from it to the dock)

$$p_r = mv_r = -E_0 / c \quad (m, v_r : \text{mass and speed of the emitting species})$$

- Corresponding **recoil energy:** $E_r \approx 10^{-2}$ eV

    e.g. free ^{57}Fe atom: $E_0 = 14.4$ keV, $E_r = 2.0$ meV)

- Note: for less-energetic radiation v_r and E_r are negligble

$$E_r = mv_r^2 / 2 = p_r^2 / 2m = E_0^2 / 2mc^2$$

- Due to the recoil energy (i.e. energy loss) gamma rays lose their capability to be absorbed by similar atom nuclii

    i.e. so-called **RESONANCE ABSORPTION** is **NOT** possible

RECOIL-FREE EMISSION

- <u>Recoil may be avoided if the emitting nucleus is part of crystal lattice</u>: the entire crystal lattice receives the recoil energy, and the recoil becomes meaningless (c.f. the boat is tightly anchored)

- Accordingly the resonance absorption becomes possible

- The recoil-less emission is nowadays known for around 100 nuclii

- Note: different isotopes of the same element behave differently (c.f. ND)

- Probability of recoil emission (f) increases:
    - with decreasing E_0 (lightest elements have too high E_0)
    - with decreasing temperature

MÖSSBAUER PHENOMENON

- Gamma rays emitted in recoil-less manner can be absorbed by similar atoms (nuclii)

  → **RESONANCE ABSORPTION**

- 1957 Rudolf Mössbauer:

  recoil-less resonance absorption for ^{191}Ir (Nobel 1961)

  → **MÖSSBAUER SPECTROSCOPY**

     or **NGR** (Nuclear Gamma Resonance)

- Mössbauer spectroscopy possible only for transitions between the ground state and the lowest excited state

  → gamma energies less than ~100 keV

- By far most commonly utilized Mössbauer nucleus is ^{57}Fe (14.4 keV): $f \approx 1$ at room temperature

^{57}Fe is the most commonly utilized Mössbauer nucleus; here we concentrate on it only.

Mössbauer Spectroscopy

- **Source of gamma rays: containing e.g. radioactive Co^{57}**
- **Sample (absorbing gamma rays): containing e.g. Fe^{57}**
- **REQUIREMENT: Resonance absorption → source is vibrated**
- **Detector: measures the intensity of the gamma-ray beam that is transmitted (typical configuration) through the sample**

radioactive source

detector

vibrator

sample

control electronics

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data acquistion
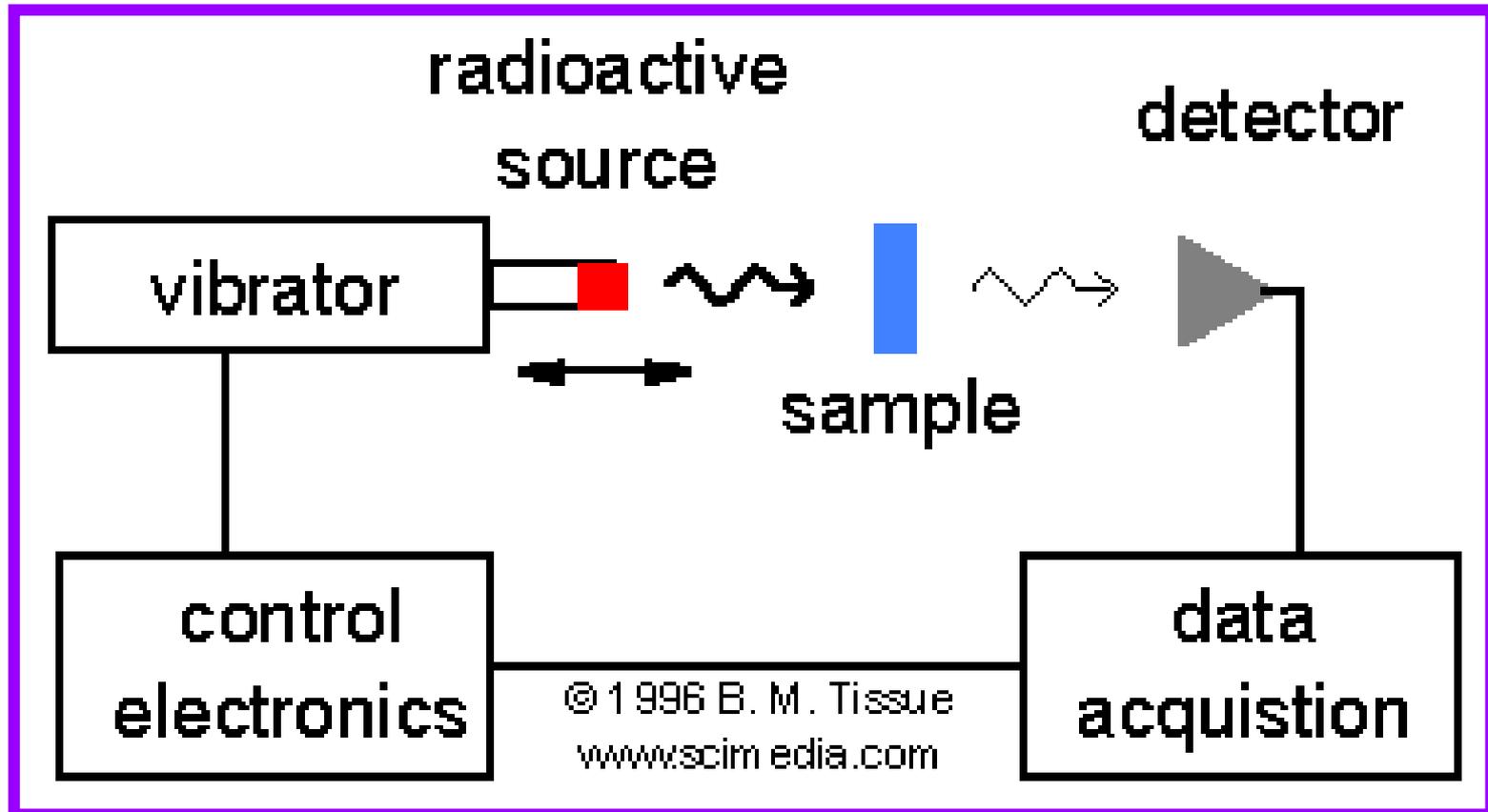
^{57}Co - ^{57}Fe

- Radioactive ^{57}Co precursor decays to excited ^{57}Fe* nucleus

  (^{57}Co can be prepared from iron relatively easily in a syclotron)

- Part (9 %) of excited ^{57}Fe* decays back to ground state but part (91 %) of it decays via a lower-energy excited state (life time 99 ns)

- Part (10 %) of the lower-energy excited ^{57}Fe* decays further to ground state emitting 14.4 keV gamma rays

- ^{57}Fe is one of the stable isotopes of iron; its portion in natural iron is 2 % (isotope enrichment possible but expensive)
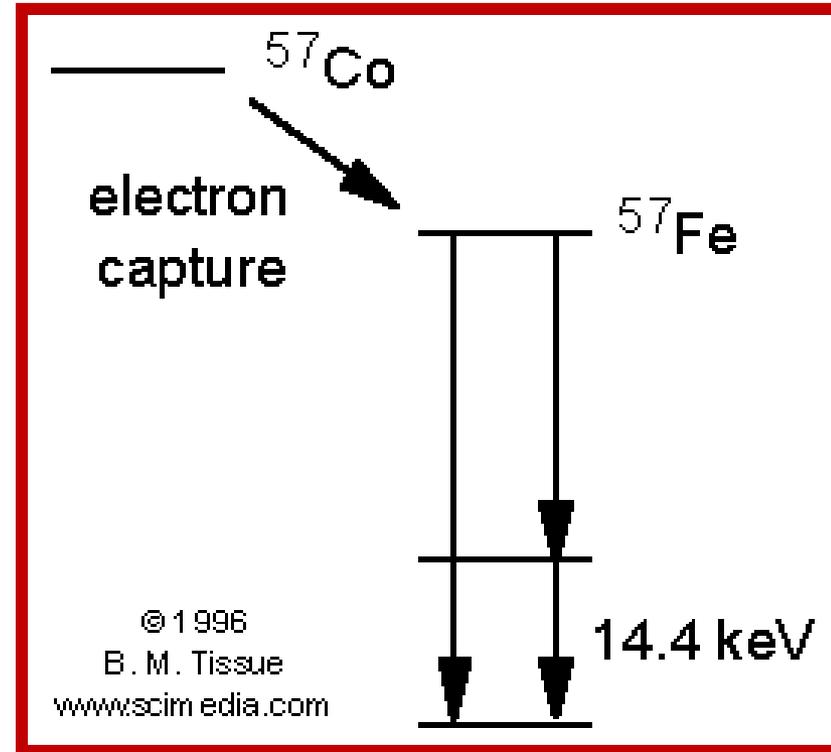
RECORDING of MÖSSBAUER SPECTRUM

- E_0 slightly depends on the environment of the Mössbauer nucleus

  (e.g. E_0 of ^{57}Fe is different in Fe metal and in $FeSO_4$)

  → ΔE_0 is a parameter that reflects the difference of the two environments

- In Mössbauer measurement it is possible to experimentally observe the resonance absorption (i.e. absorption when $\Delta E_0 = 0$) → ΔE_0 needs to be made zero by slightly changing the E_0 value of either the emitting or absorbing nucleus

- Control of E_0 is possible only through **Doppler effect**, i.e. by moving either the source (emitting nucleus) or the sample (absorbing nucleus)

  → in Mössbauer spectroscopy the energy axis is given in the unit of mm/s

  → the required velocities vary between 1 ~ 1000 mm/s

- Measurement geometry: transmission (most common) or reflection

  ➤ Gamma rays get weaker quite fast → relatively thin sample in transmission measurement → amount of Mössbauer isotope typically 0.1~10 mg

  ➤ In reflection measurement information from surface (0.2~20 μm) → thin films
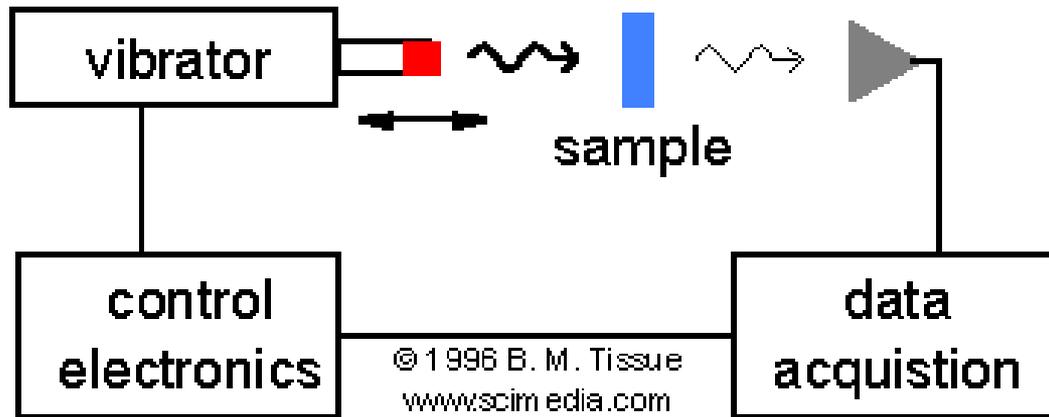
- A solid sample is exposed to gamma-ray beam, and a detector measures the beam intensity transmitted through the sample.

- The gamma-ray energy is varied by vibrating the gamma-ray source. The velocity of the source results in a small energy shift due to the Doppler effect.

- In Mössbauer spectrum, gamma-ray intensity is plotted as a function of the source velocity.

- At velocities corresponding to the resonant energy levels of the sample, some of the gamma-rays are absorbed, seen as negative peaks in the spectrum.

- The number, positions and intensities of the peaks provide information about the chemical environment of the absorbing nuclei in the sample.
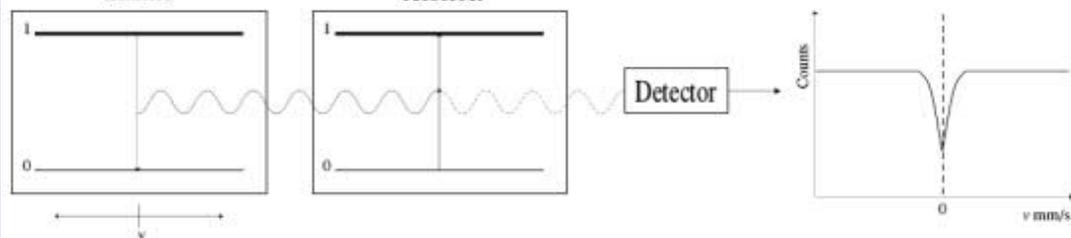
MÖSSBAUER SPECTROSCOPY

- E_0 depends (weakly) on the environment of the Mössbauer nucleus
  - → **local environment** of the Mössbauer-active nucleus
  - → called **HYPERFINE INTERCATIONS**

  - (*i*) **chemical** (oxidation state, spin state): **Isomer shift**
  - (*ii*) **electric** (coordination sphere): **Quadrupole splitting**
  - (*iii*) **magnetic** (magnetic ordering): **Magnetic splitting**

- All information (*i*) ~ (*iii*) with one measurement

- Perfectly **specific** for the investigated nucleus

- If the Mössbauer-active nucleus exists in the sample in different environments the overall spectrum consists of the sub-spectra with the relative abundancies of the corresponding different species of the Mössbauer-active nucleus **(sum of sub-spectra)**

ISOMER SHIFT

- Isomer shift (IS, δ or ΔE_0) depends:

  electron densities about the nucleus

  $\rightarrow$ directly on s-orbital electron configuration
  $\rightarrow$ indirectly on p/d/f-orbital electron configuration

- In case of iron (3d transition metal) the different oxidation states/spin states differ in terms of the d-orbital electron configuration (which then slightly affects the s-orbital density)

- Isomer shift is given against a standard

- Typically used standards:

  ^{119}Sn: SnO_2
  ^{57}Fe: Fe metal (officially $Na_2[Fe(CN)_5NO]$)

Fe(I) S=3/2
Fe(I) S=1/2
Fe(I)
Fe(II) S=2
Fe(II) S=1
Fe(II)
Fe(II) S=0
Fe(III) S=5/2
Fe(III) S=3/2
Fe(III)
Fe(III) S=1/2
Fe(IV) S=2
Fe(IV)
Fe(IV) S=1
Fe(VI) S=1
Fe(VI)

-1,0   -0,5   0   0,5   1,0   1,5   2,0
δ /mm s^{-1}

counts

$-$ 0 $+$
Velocity (mm/s)
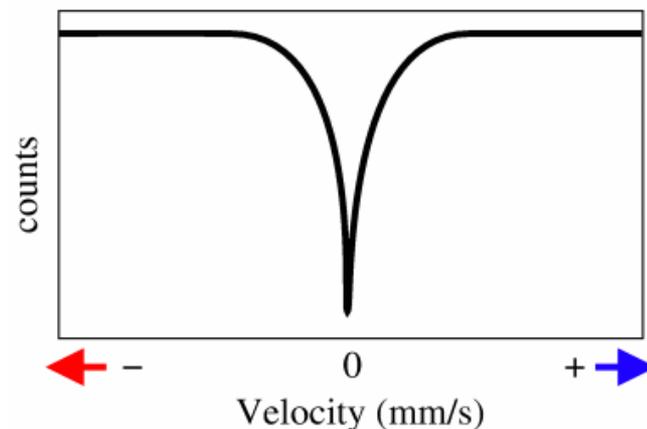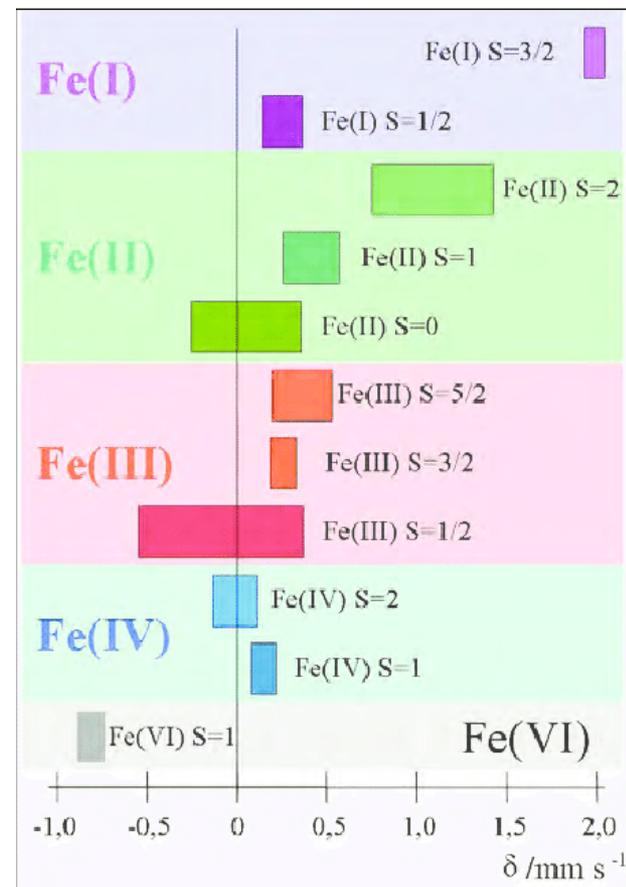
ELECTRIC QUADRUPOLE INTERACTION

Electric field gradient about the nucleus is created by two factors:

- surrounding ions (major factor):
  symmetric → no splitting, asymmetric → splitting

- valence electrons of the Mössbauer nucleus (minor effect)
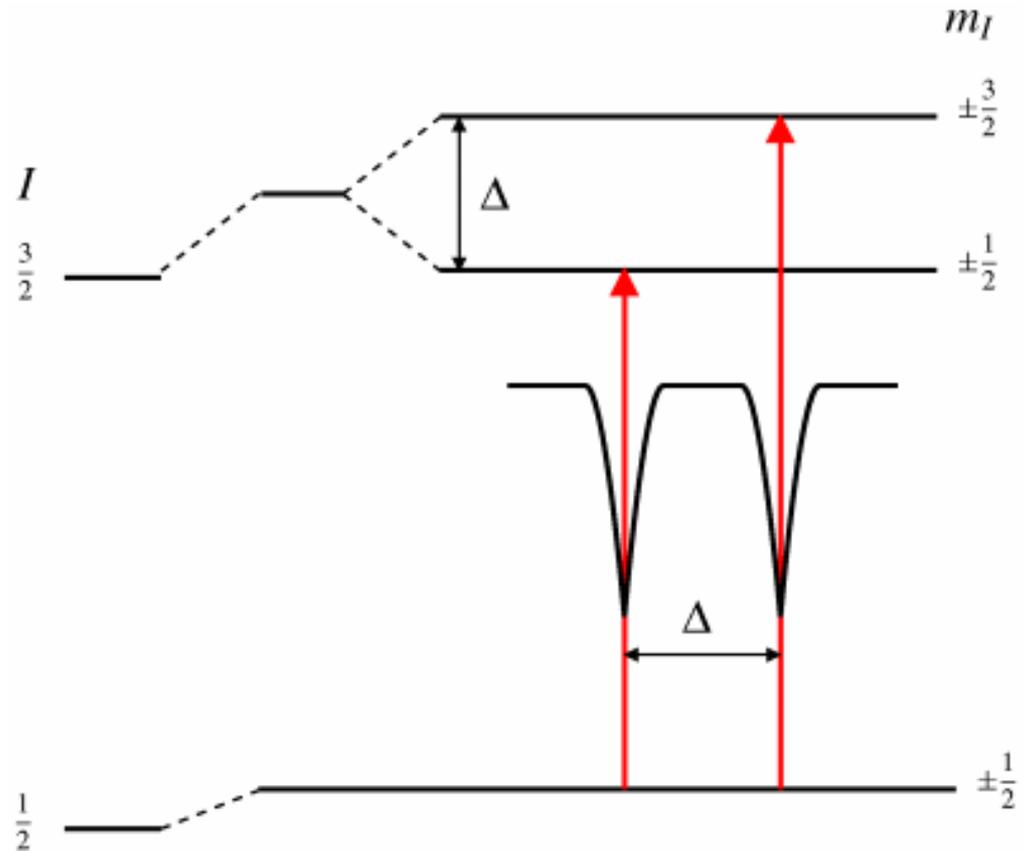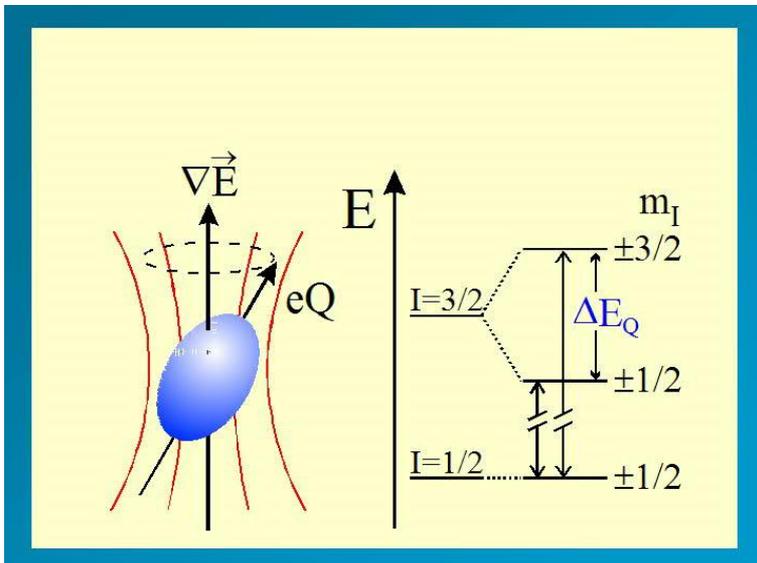
Magnetic Dipole Interaction
Magnetic Splitting ΔE_M

$\Delta I = \pm 1, \ \Delta m_I = 0, \pm 1$
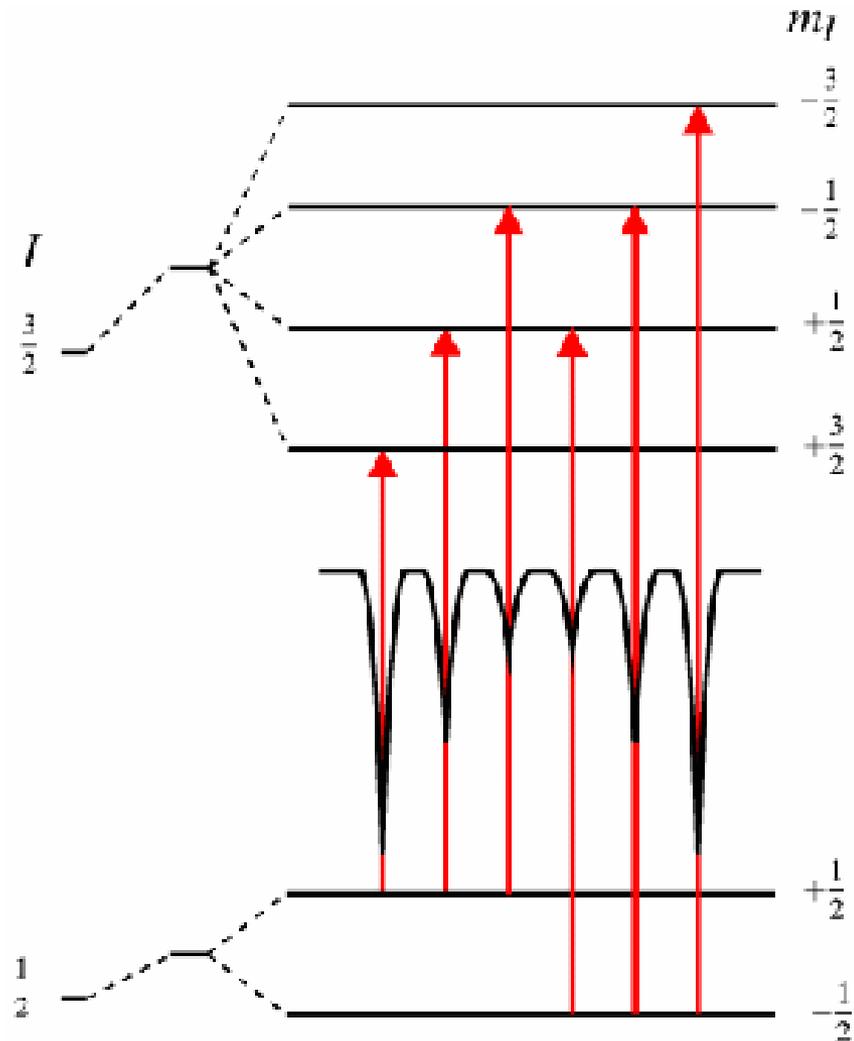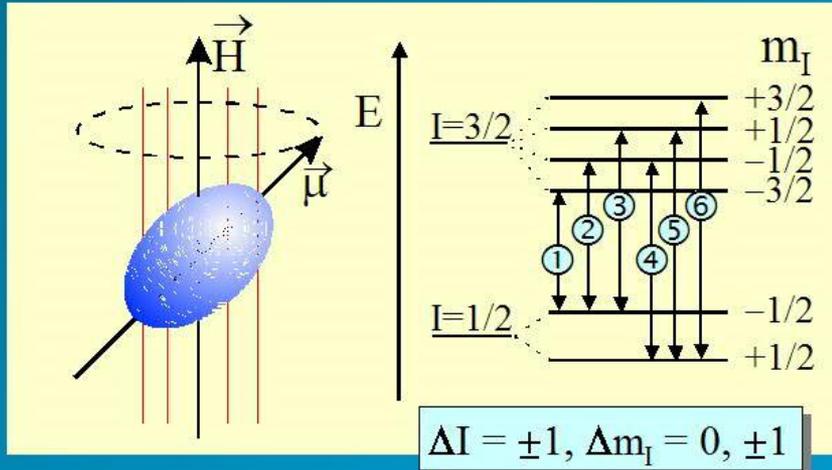
Summary of HYPERFINE INTERACTIONS affecting Mössbauer spectra

(a) unperturbed

(b) isomer shift

(c) quadrupole splitting

(d) magnetic dipole
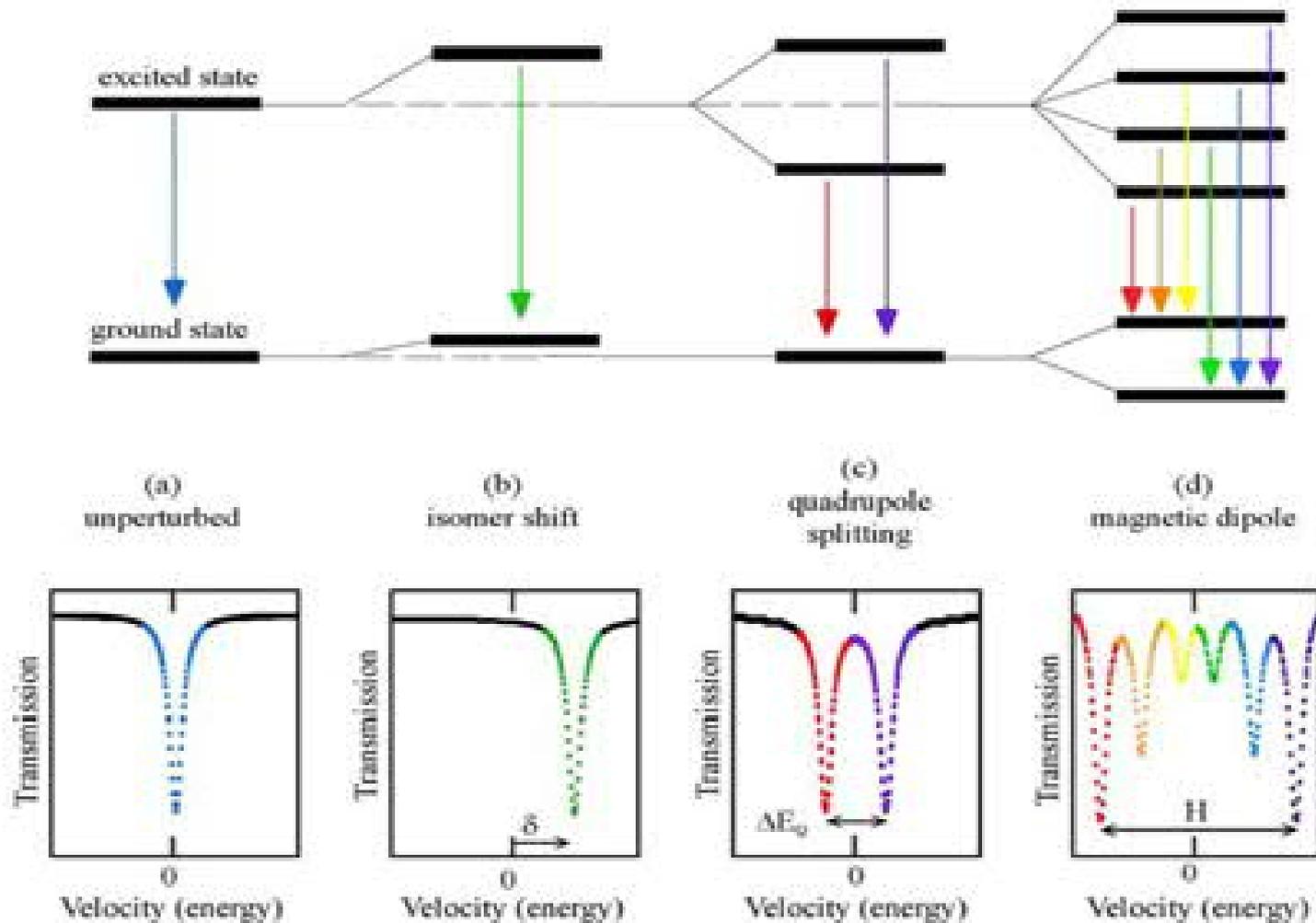
Isomer shift (IS or δ), Quadrupole splitting (Δ) & Magnetic splitting (H_{hf})

Different iron species in the sample

→ **spectrum consists of sub-spectra of each different Fe species**

→ **intensity ratio of sub-spectra = concentration ratio of corresp. Fe species**

EXAMPLE: overall spectrum consists of two sub-spectra

- **Intensity/concentration ratio: b-Fe / a-Fe = 2 : 1**

- **Same isomer shift → same valence (+III)**

- **Slightly larger quadrupole splitting for a-Fe → more asymmetric coordination**
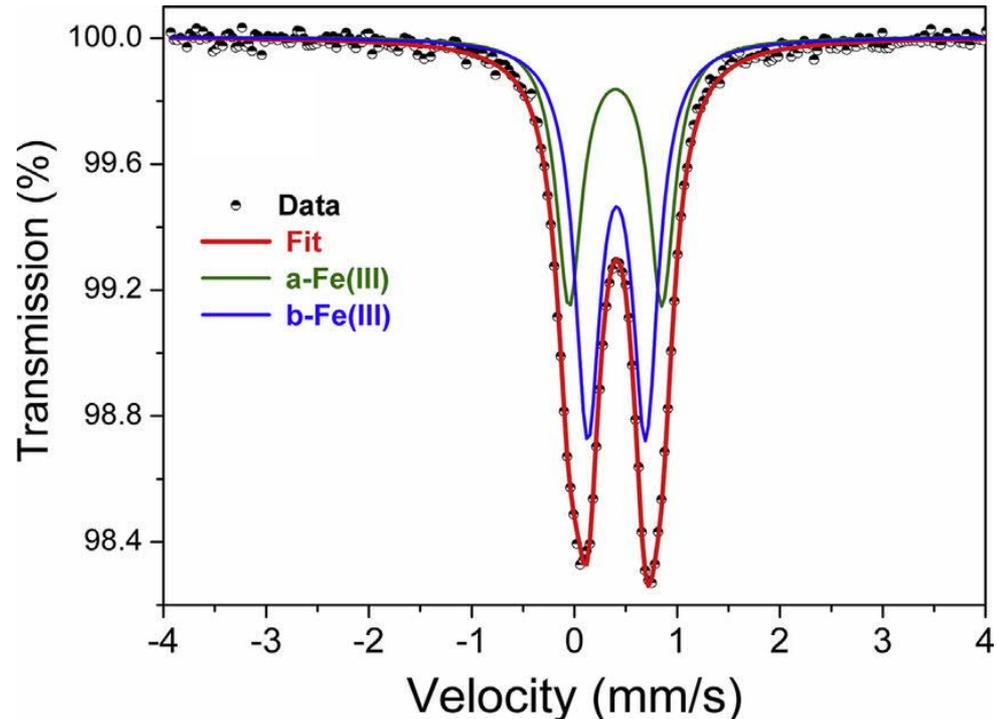
Another EXAMPLE

- Overall spectrum consists of two sub-spectra

- Both di- and trivalent iron

- Much more Fe(III) than Fe(II) (presice concentrations from spectral areas)

- Both Fe(III) than Fe(II) in asymmetric coordination, but Fe(II) more asymmetric
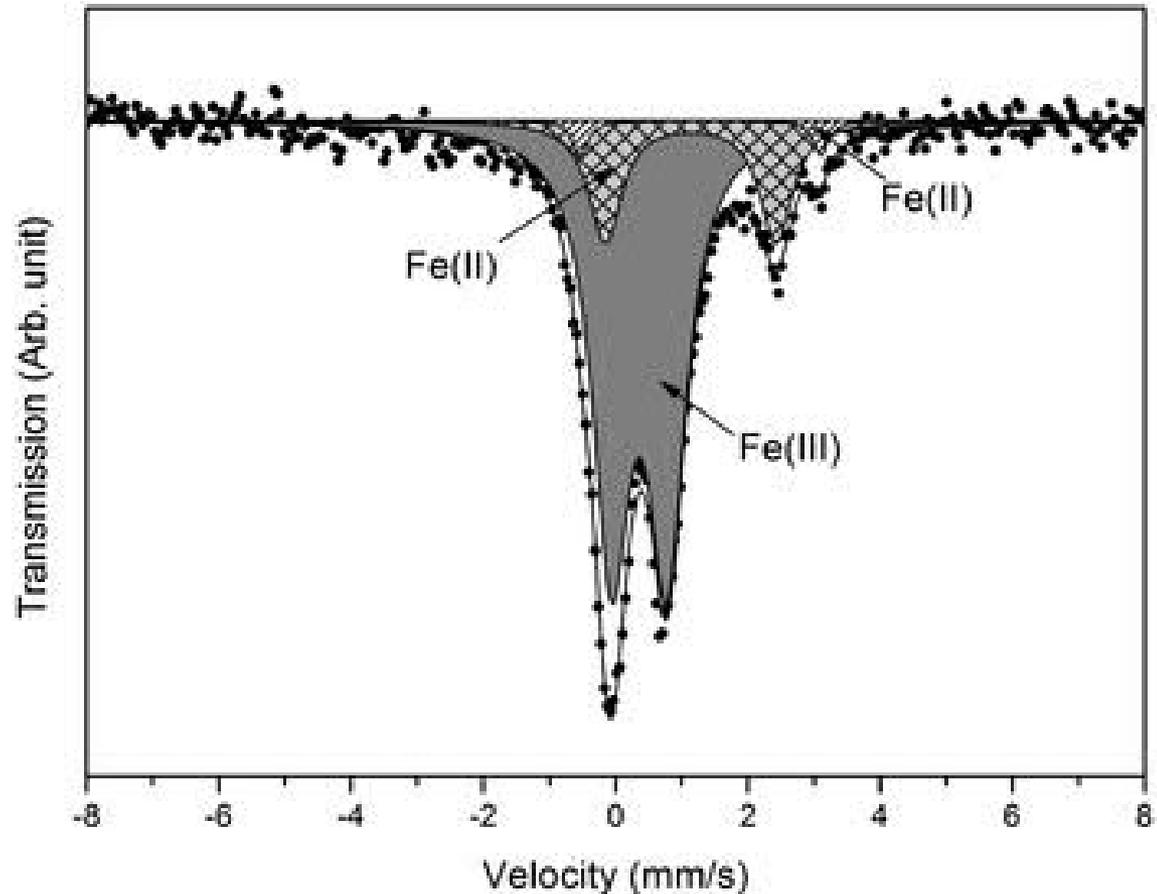
Temperature-dependent measurements

→ **employed e.g. to investigate magnetic transitions**

EXAMPLE:

- completely ferro/ferri/antiferro-magnetic at 10 K

- completely paramagnetic at 295 K

NOTE: Can not straightforwardly distinguish the type or magnetic ordering, i.e. ferro, ferri or antiferro
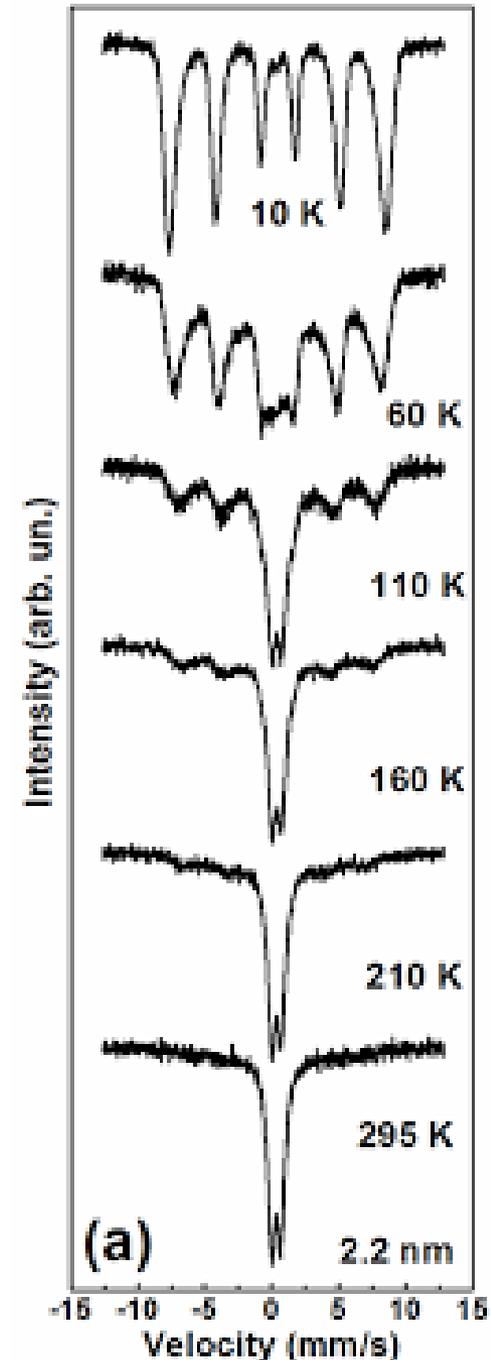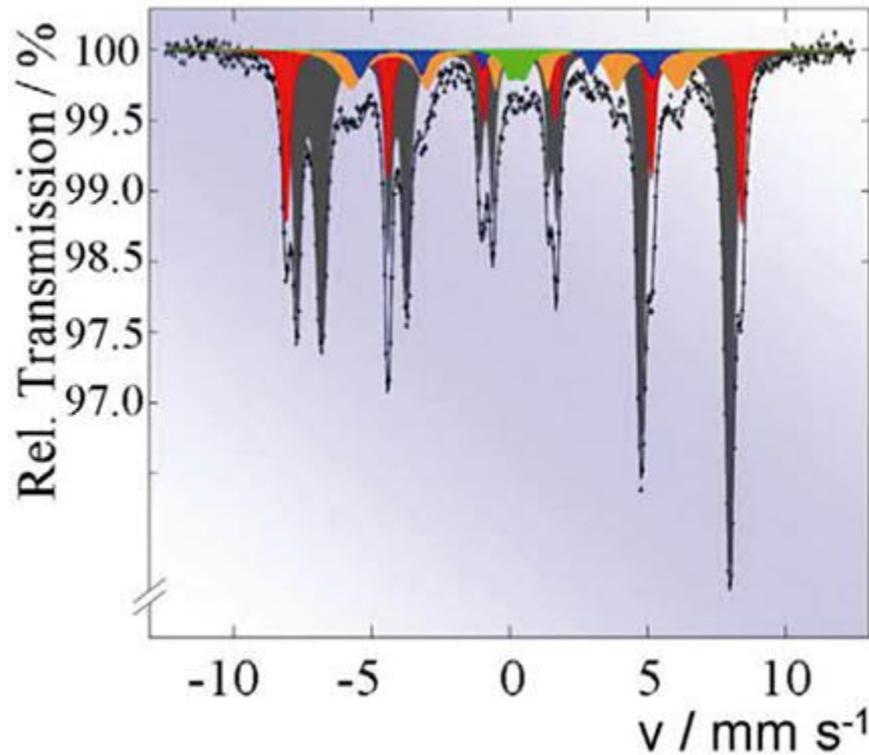
Routine Mössbauer analysis of finely dispersed corrosion particles formed in the cooling system of a power plant

# NASA Mars Exploration Rovers: Spirit & Opportunity (launched in 2003):

Mössbauer spectrometer is one of the instruments on the robotic arm
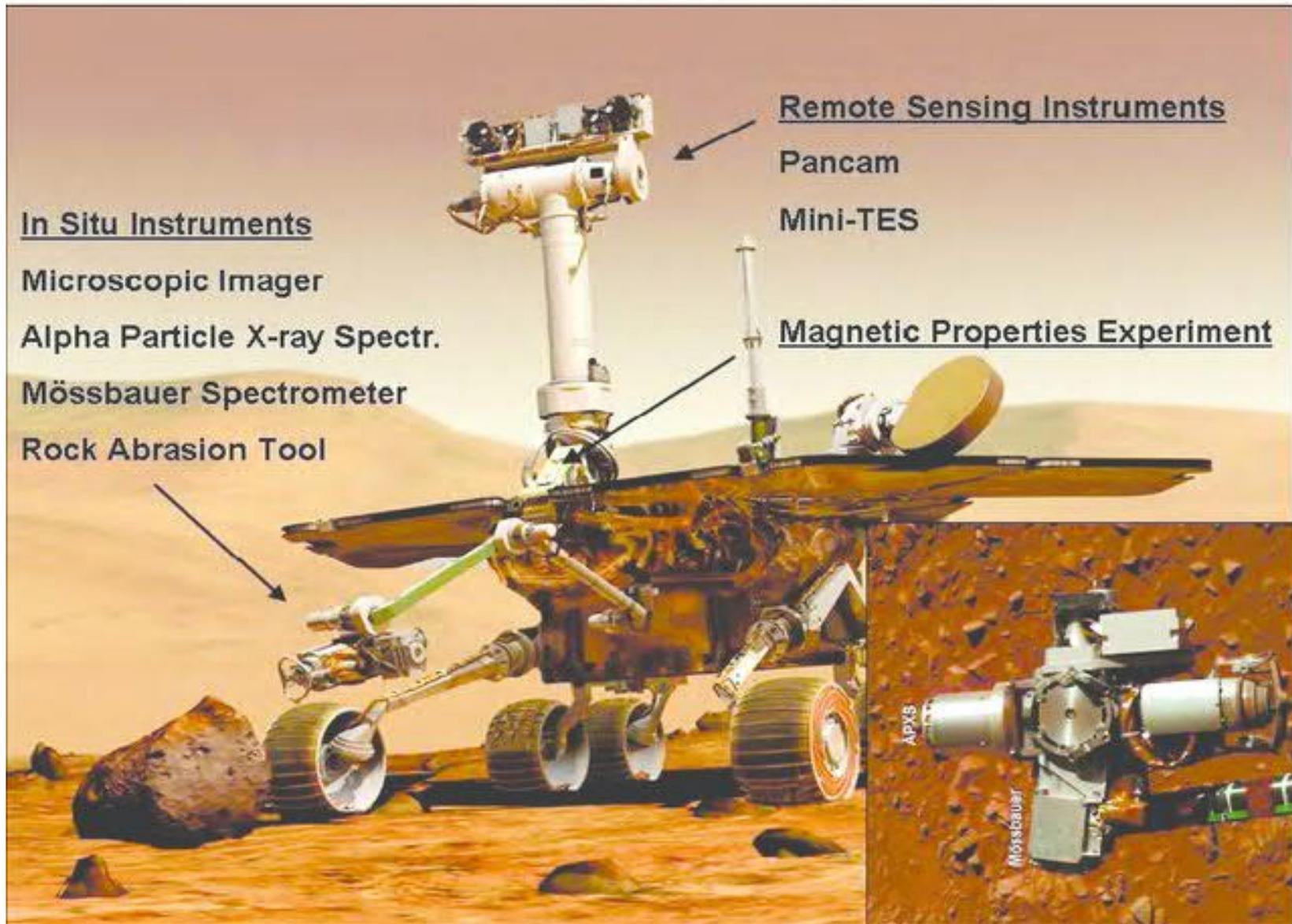
# Mössbauer examples for DOUBLE PEROVSKITES

RECALL from the first lecture:

- Two different cations (**B'** and **B"**) occupy the B-site with 50%/50% ratio and in an ordered manner → B-site ordered double perovskite

- Two different cations (**A'** and **A"**) occupy the A-site with the 50%/50% ratio and in an ordered manner → A-site ordered double perovskite

- Example: B-site ordered halfmetallic Sr_2FeMoO_6: simultaneously ferrimagnetic and electrically conducting → magnetic-field control of conductivity → spintronics

- We also discussed about so-called antisite defects if the ordering is not perfect; for example some Fe atoms occupying the Mo site in Sr_2FeMoO_6 (this kind of disorder distroyes rapidly the ferrimagnetic/halfmetallic properties)
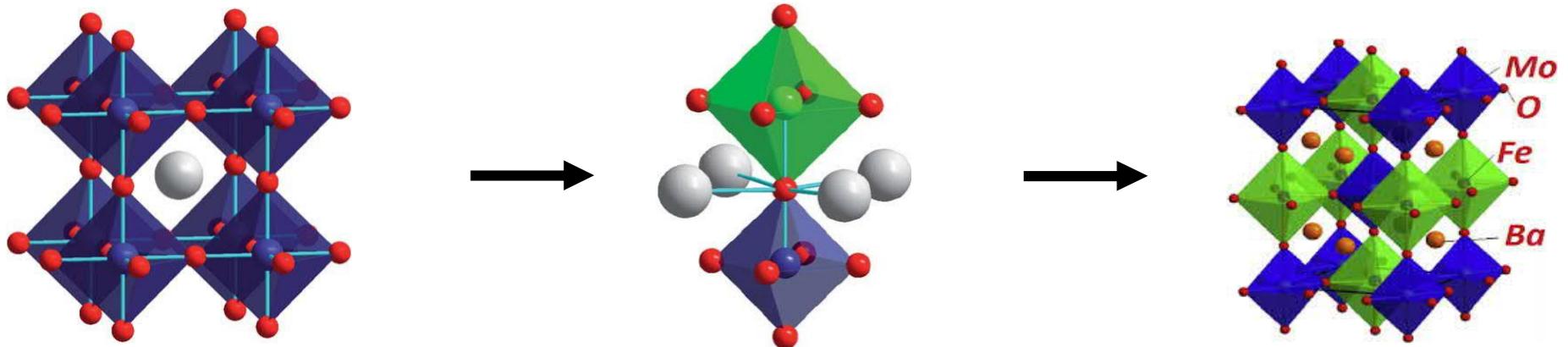
A-site ordered DP with oxygen vacancies $Ba^{II}Sm^{III}Fe_2O_{5.0}$

- **Question: 2 $Fe^{2.5}$ or Fe^{II} + Fe^{III}**

- **Mössbauer spectra tell us: there is a transition of 2 $Fe^{2.5}$ → Fe^{II} + Fe^{III} at a certain temperature (Verwey temperature T_V)**

- **Above TV: only one sextet → only one type iron → magnetic $Fe^{2.5}$**

- **Below TV: two different sextets → Fe^{II} + Fe^{III} → both magnetic but Fe^{III} with larger magnetic field (wider splitting of sectet)**

T_V

ρ (Ω cm)

10^6
10^5
10^4
10^3
10^2
10
1

MR (%)

4.0

2.0

0

χ (10^{-5}emu/g Oe)

9.5

9

8.5

8

FC

ZFC

H = 10 Oe

Heat flow (mW/g)

1500

1000

500

0

-500

ENDO

Temperature (K)

250

300

350
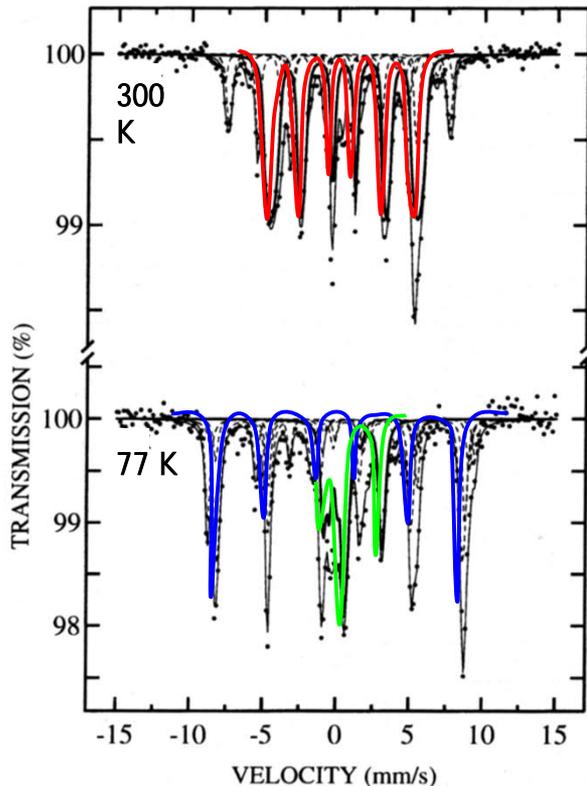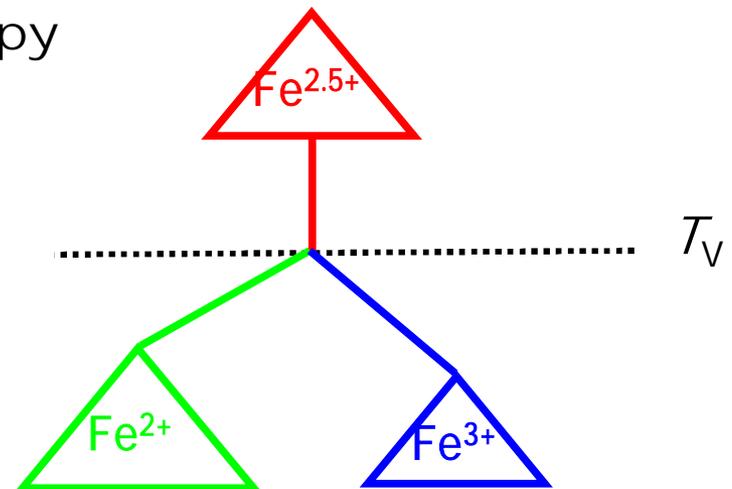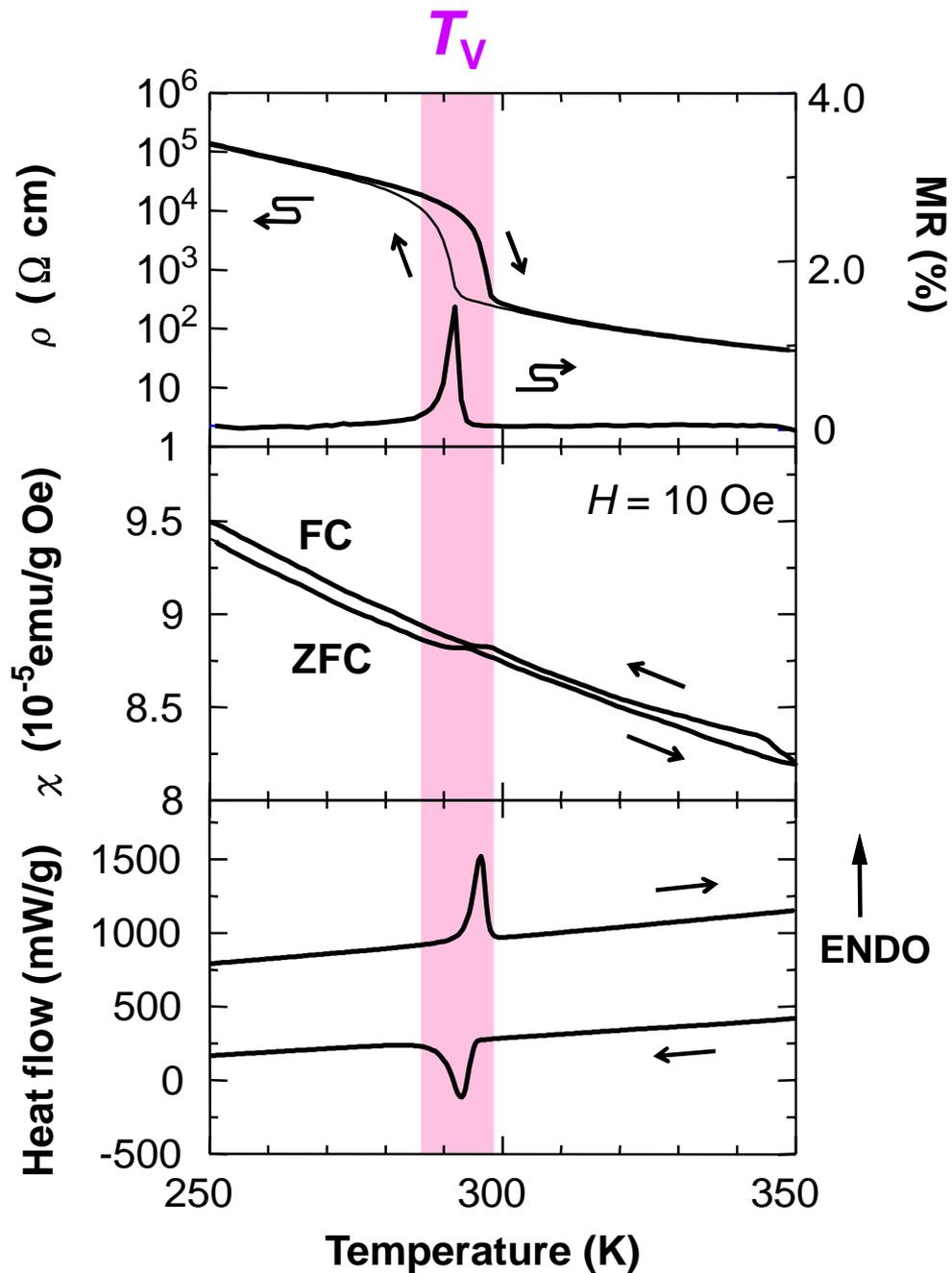
BaSmFe$_2$O$_{5.0}$

Many physical properties change at T$_V$

Sr_2FeMoO_6
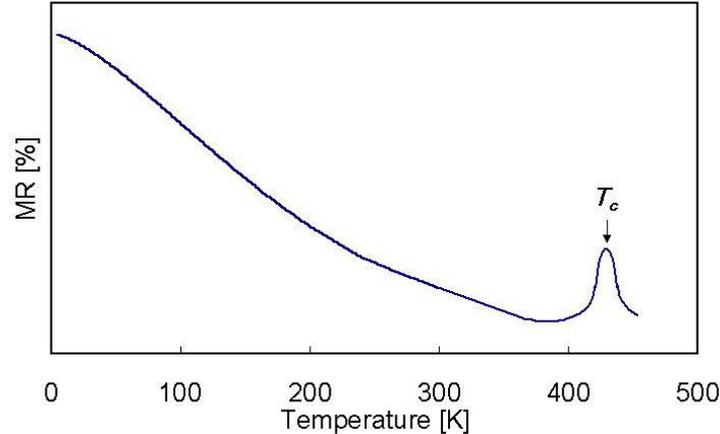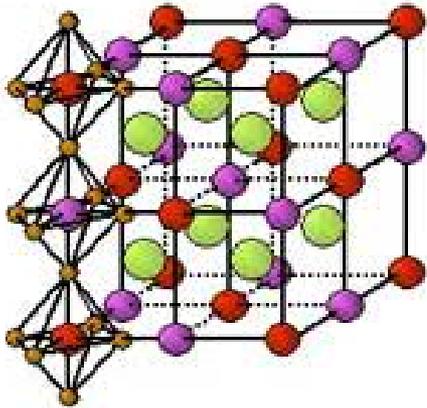
B-site ordered
double perovskite

- **Ferrimagnetic conductor (T_C = 420 K)**

- **Halfmetallic: spin polarization of conduction electrons
  →Tunneling-type magnetoresistance below T_C**
  K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, *Nature* **395**, 677 (1998).

- **First assumption: Fe^{III} d^5 (*hs*) & Mo^V d^1**

- **Mössbauer: $Fe^{2.5}$ & $Mo^{5.5}$**

Mixed-valent iron: $Sr_2Fe^{II/III}Mo^{V/VI}O_6$

"Evidence for **Valence Fluctuation** of Fe in Sr_2FeMoO_{6-w} Double Perovskite",
J. Lindén, T. Yamamoto, M. Karppinen, H. Yamauchi and T. Pietari,
Appl. Phys. Lett. 76, 2925 (2000).

AS
100
TRANSMISSION (%)
M2
99
APB
98
M1
97

VELOCITY (mm/s)
-10 -8 -6 -4 -2 0 2 4 6 8 10

← M1
→ M2
← AS
← APB

Mo atoms marked with white circles
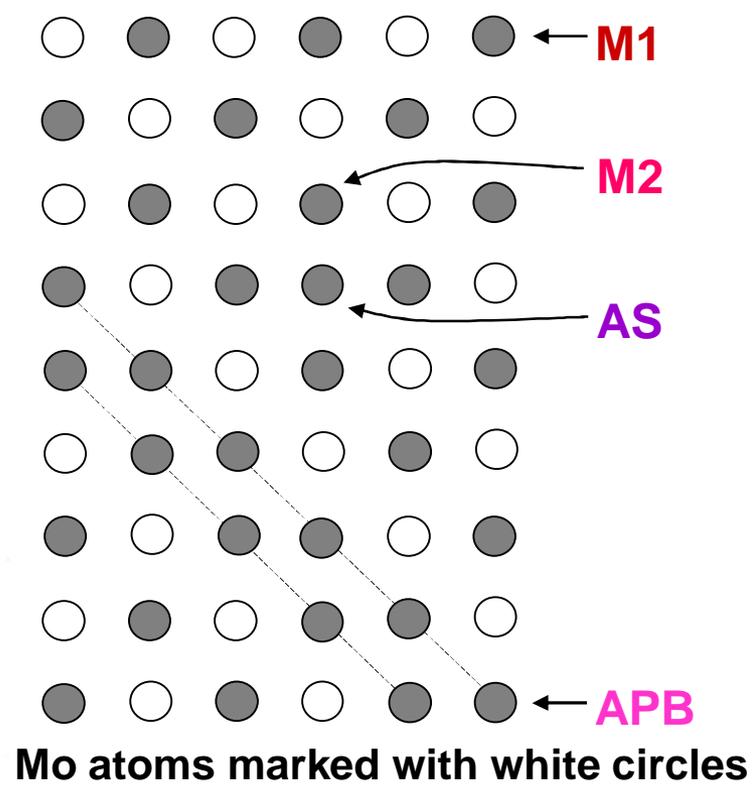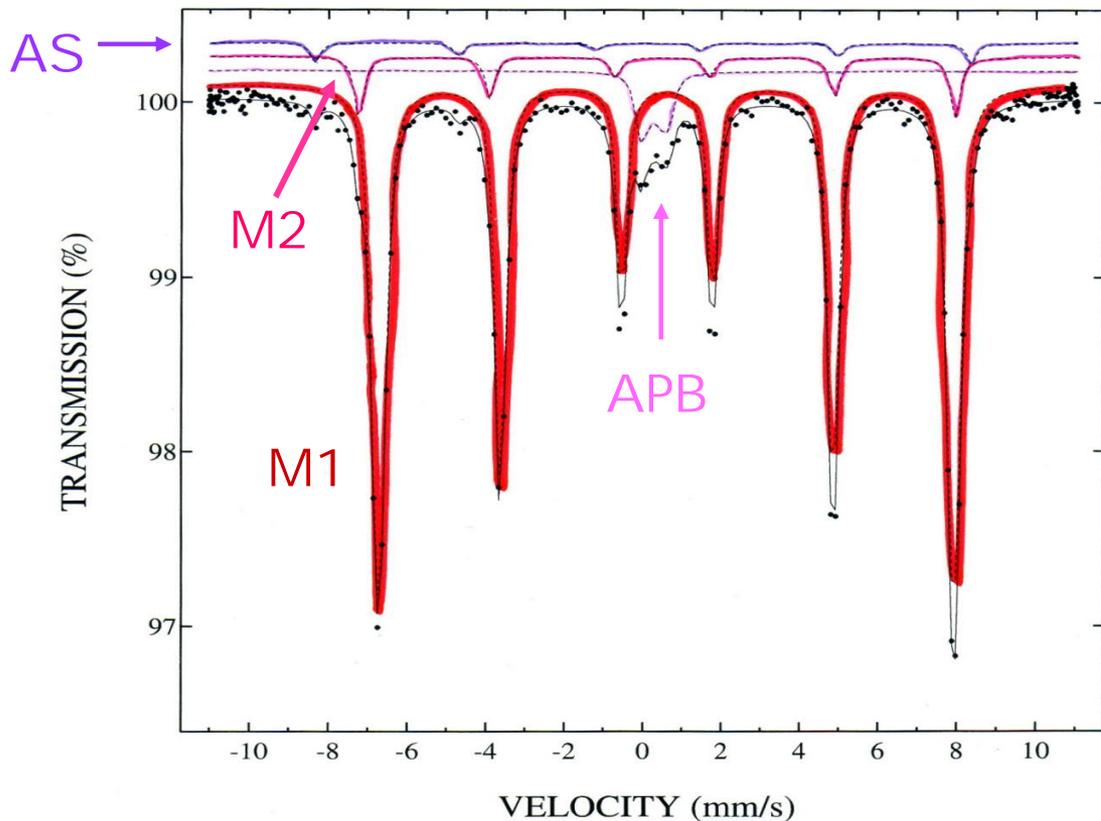
We can see for Sr_2FeMoO_6 sample by ^{57}Fe Mössbauer Spectroscopy:

- **Iron is magnetically ordered (sextets)**

- **There are many sextets → different types of iron atoms (ideally only one type)**

- **For the main (M1) sextet isomer shift (IS) corresponds to mixed-valent $Fe^{2.5}$**

- **There is also sextet with trivalent Fe^{3+}: it is due to antisite (AS) iron atoms**

- **Iron atoms next to AS-Fe atoms (M2) have valence between 2.5 and 3**

- **We can also see iron atoms with very low "frustrated" magnetic field; these are trivalent iron atoms at so-called antiphase boundaries (APB)**