SCHEDULE

	Date		Topic
1.	Wed	28.02.	Lec-1: Introduction
2.	Mon	04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	04.03.	EXERCISE 1
4.	Wed	06.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	08.03.	Lec-4: Symmetry & Point Groups
6.	Mon	11.03.	EXERCISE 2
7.	Wed	20.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	22.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	25.03.	EXERCISE 3 (Linda) Ke4
10.	Thu	04.04.	Lec-7: Rietveld (Linda)
11.	Fri	05.04.	EXERCISE 4: Rietveld (Linda)
	Mon	08.04.	EXERCISE 4: Rietveld (Linda)
12.	Thu	11.04.	Lec-8: ND & GI-XRD 12:15-14, Ke3
13.	Fri	12.04.	Lec-9: XRR & Ellipsometry (Topias) 12:15-14, Ke4
14.	Mon	15.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
	Wed	17.04.	EXERCISE 5: XRR (Topias) 14:15-16 Ke3
15.	Mon	22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Thu	25.04.	Mössbauer 12:15-14, Ke3
17.	Fri	26.04.	EXERCISE 6
18.	Mon	29.04.	Seminars: IR, Raman, XPS, SEM, EELS (14:00→16:30)
19.	Mon	06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY
20.	Mon	13.05.	EXAM (13-17; to be confirmed ?)

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Topics: **IR, Raman, XPS, SEM, EELS**
- Seminar presentation is mandatory
- Presentation slides will be put up in MyCourses afterwards
- **Seminars are part of the course content and it is likely that there will be questions in the exam related to these seminars**
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation: **20+5** minutes
- Rough content of the presentation:

  - principle of the technique
  - type of information gained
  - interpretation of the measured data
  - pros & cons
  - **two to four research examples**
    (you will be given some relevant research papers for an example)

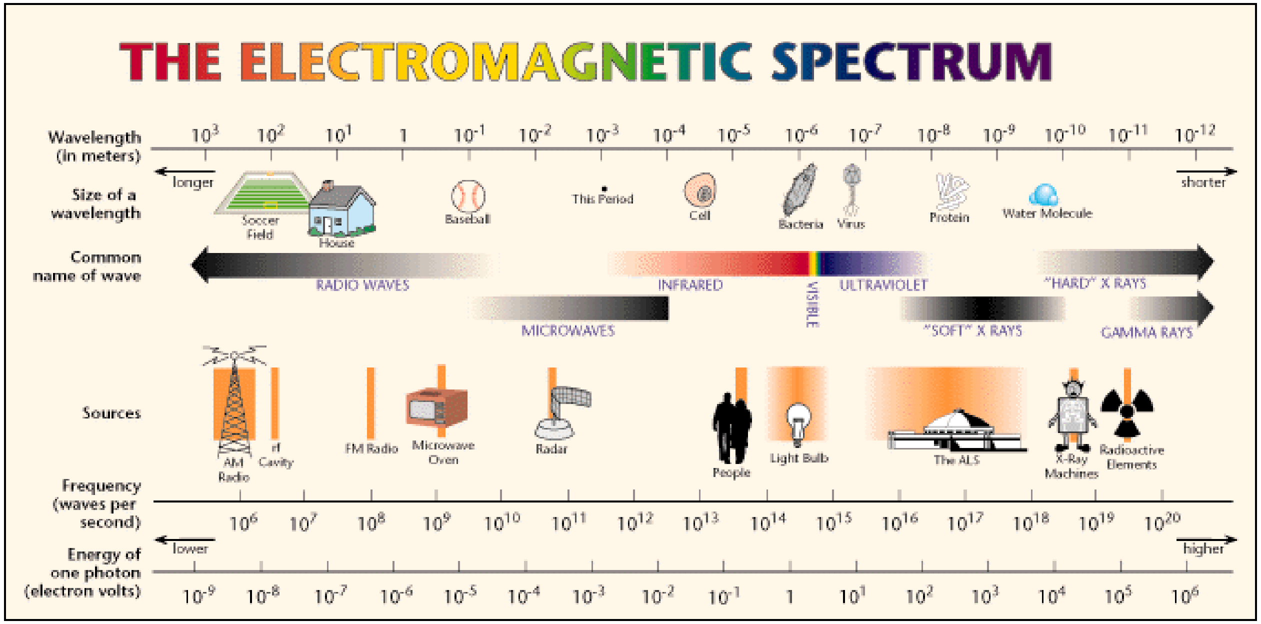
LECTURE 11:
Mössbauer Spectroscopy

- **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 (γ-rays)

- Highest energy part of electromagnetic radiation; Henri Becquerel in 1896
- 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 ($\mathbf{E_0} = E_e - E_g$)
- **Gamma rays can be profuced only with discrete energies**
- Gamma rays penetrate extremely long distances through materials; to stop them, few centimeters of lead or a meter of concrete required



RECOIL ENERGY

- ***Momentum Conservation Law:***

When gamma rays are emitted from the nucleus, the nucleus itself gets **Recoil Impulse (p_{Rec})** of the opposite direction, with **Recoil Energy (E_{Rec})** (think what happens to the boat when the passanger jumps from it to the dock)

$$E_{Rec} = mv_{Rec}^2 / 2 = p_{Rec}^2 / 2m = E_0^2 / 2mc^2$$

- Recoil energies for gamma rays of the order of $E_{Rec} \approx 10^{-2}$ eV

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

- **Note:** for less-energetic radiation, recoils exist in principle, but v_r and E_{Rec} are negligble

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

→ so-called **RESONANCE ABSORPTION** is **NOT** possible

→ radiation emitted by a nucleus can not be anymore absorbed by a similar atom

→ gamma-ray spectroscopy not possible

RECOIL-FREE EMISSION

- Recoil **may** be avoided if the emitting nucleus is part of crystal lattice:

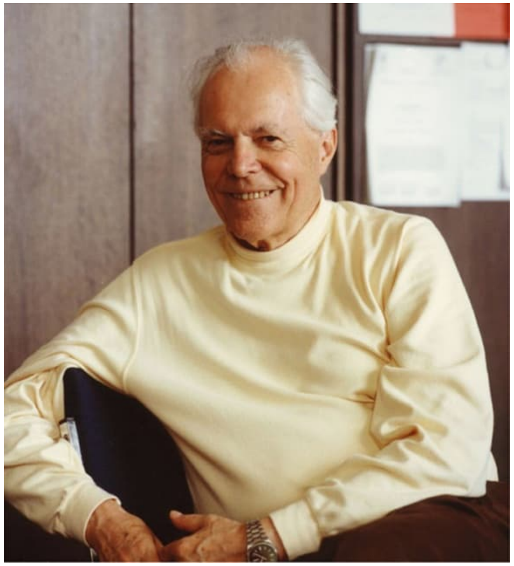
  → Entire crystal lattice receives the recoil energy, and the recoil becomes meaningless (the boat is tightly anchored!)

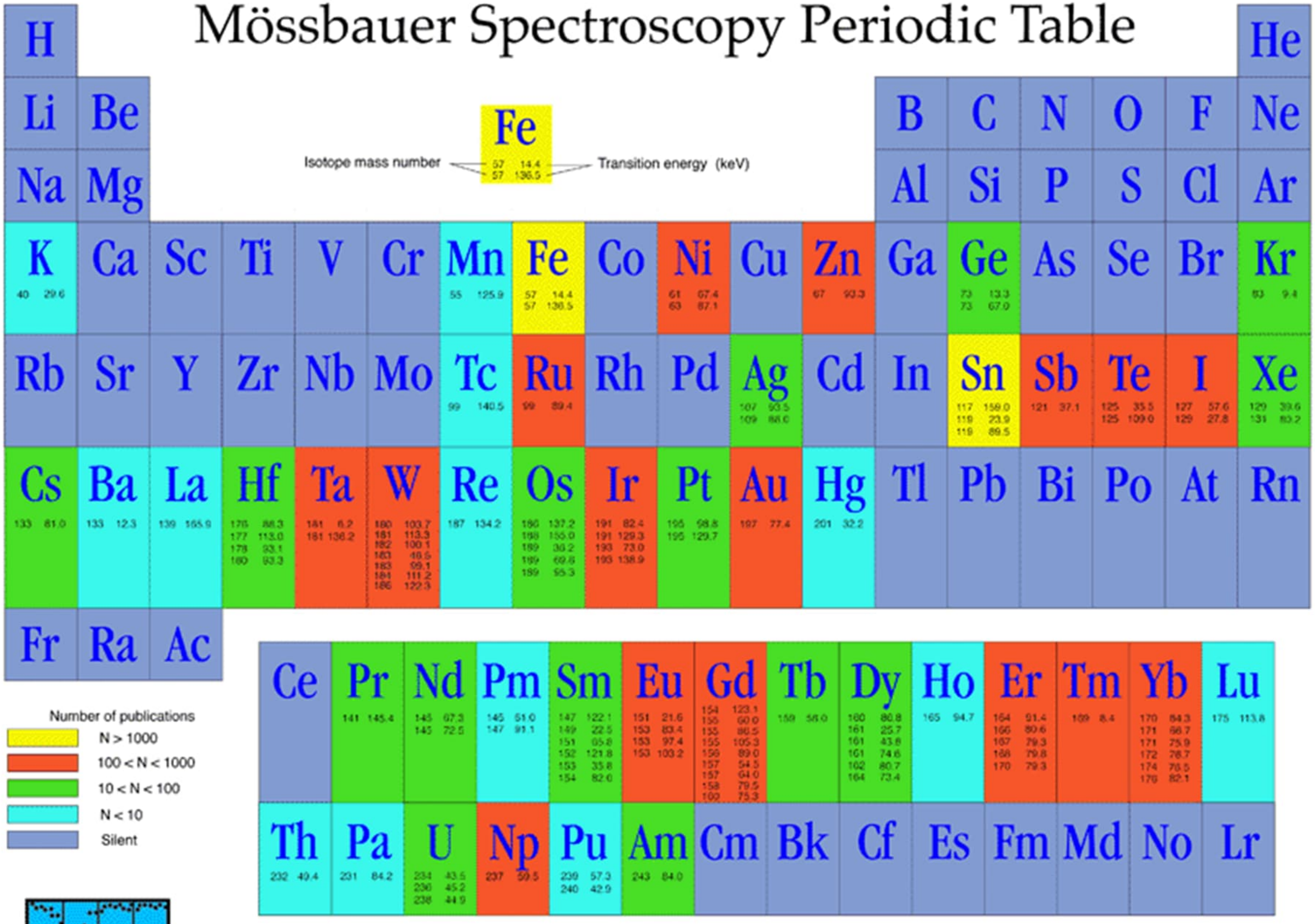
- Accordingly the resonance absorption becomes possible
- The recoil-less emission is nowadays known for around 100 nuclii
- Note: different isotopes of the same element behave differently (c.f. ND)
- Probability of recoil emission (*f*) increases:

  - 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





Mössbauer Spectroscopy Periodic Table

Fe
57 14.4
57 136.5

Isotope mass number — Transition energy (keV)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K 40 29.6	Ca	Sc	Ti	V	Cr	Mn 55 125.9	Fe 57 14.4 57 136.5	Co	Ni 61 67.4 63 87.1	Cu	Zn 67 93.3	Ga	Ge 73 13.3 73 67.0	As	Se	Br	Kr 83 9.4
Rb	Sr	Y	Zr	Nb	Mo	Tc 99 140.5	Ru 99 89.4	Rh	Pd	Ag 107 93.5 109 88.0	Cd	In	Sn 117 158.0 119 23.9 119 89.5	Sb 121 37.1	Te 125 35.5 125 109.0	I 127 57.6 129 27.8	Xe 129 39.6 131 80.2
Cs 133 81.0	Ba 133 12.3	La 139 165.9	Hf 176 88.3 177 113.0 178 93.1 180 93.3	Ta 181 6.2 181 136.2	W 180 103.7 181 113.3 182 100.1 183 46.5 183 99.1 184 111.2 186 122.3	Re 187 134.2	Os 186 137.2 188 155.0 189 36.2 189 69.6 189 95.3	Ir 191 82.4 191 129.3 193 73.0 193 138.9	Pt 195 98.8 195 129.7	Au 197 77.4	Hg 201 32.2	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr 141 145.4	Nd 145 67.3 145 72.5	Pm 145 61.0 147 91.1	Sm 147 122.1 149 22.5 151 65.8 152 121.8 153 35.8 154 82.0	Eu 151 21.6 153 83.4 153 97.4 153 103.2	Gd 154 123.1 155 60.0 155 86.5 155 105.3 156 89.0 157 54.5 157 64.0 158 79.5 160 75.3	Tb 159 58.0	Dy 160 86.8 161 25.7 161 43.8 161 74.6 162 80.7 164 73.4	Ho 165 94.7	Er 164 91.4 166 80.6 167 79.3 168 79.8 170 79.3	Tm 169 8.4	Yb 170 84.3 171 66.7 171 75.9 172 78.7 174 76.5 176 82.1	Lu 175 113.8
Th 232 49.4	Pa 231 84.2	U 234 43.5 236 45.2 238 44.9	Np 237 59.5	Pu 239 57.3 240 42.9	Am 243 84.0	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Number of publications

- 🟨 N > 1000
- 🟥 100 < N < 1000
- 🟩 10 < N < 100
- 🟦 N < 10
- ⬛ Silent

Mössbauer Effect Data Center Tel: (828) 251-6617 Fax: (828) 232-5179 Email: medc@unca.edu Web: www.unca.edu/medc

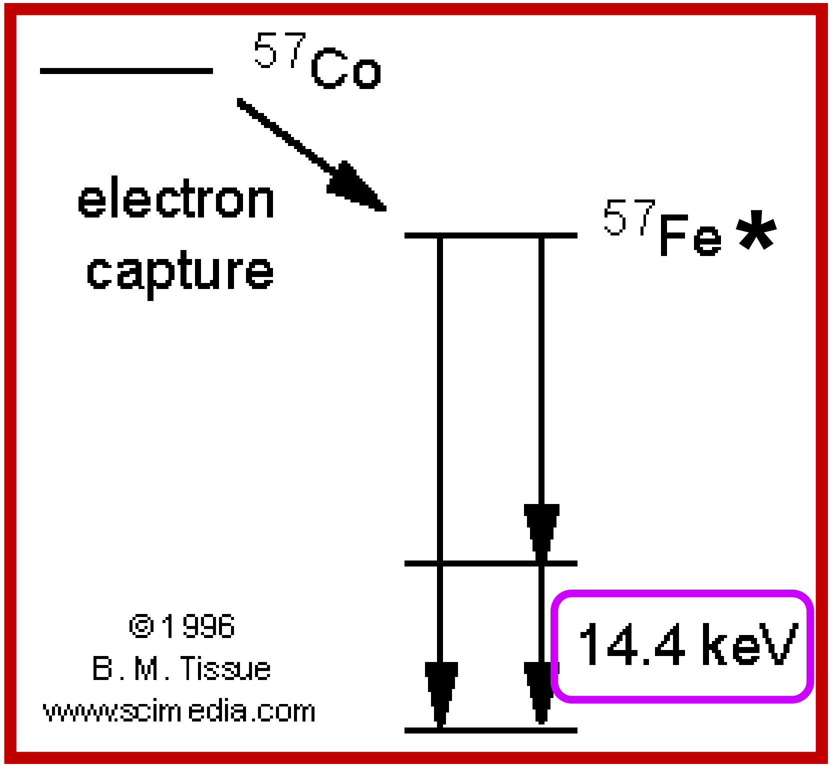
^{57}Fe is the most commonly utilized Mössbauer nucleus; here we concentrate on it only.

^{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 a larger part (91%) decays via a lower-energy excited state (life time 99 ns)
- Further, part (10%) of this lower-energy ^{57}Fe* decays 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)

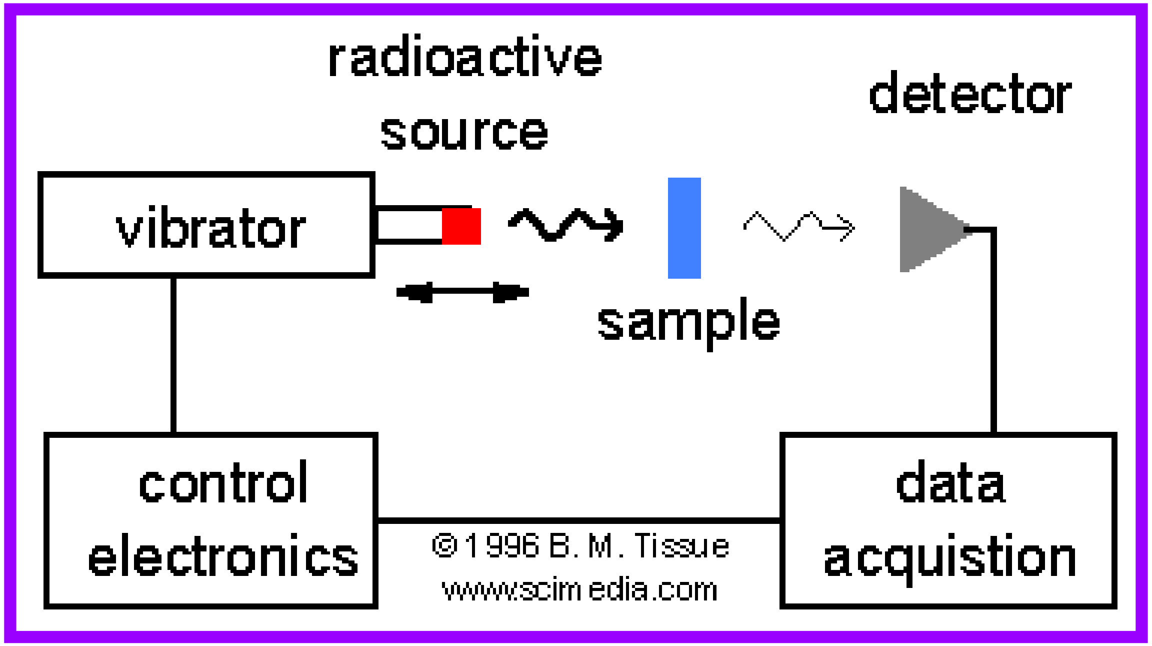
  → in Mössbauer spectroscopy the energy axis is given in the unit of mm/s

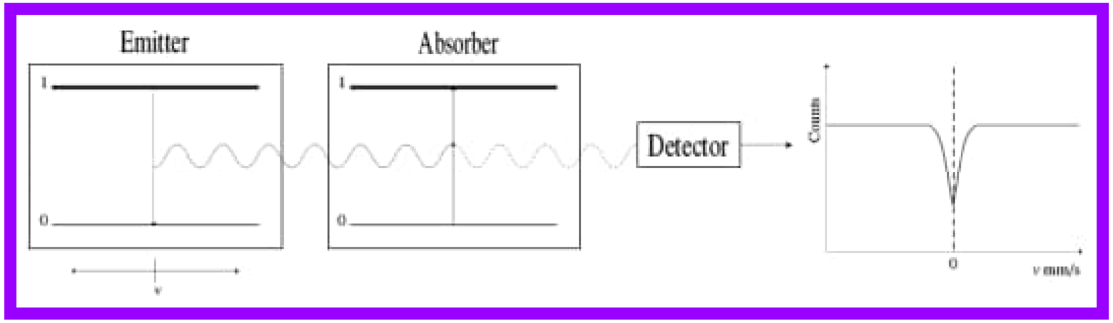
  → the required velocities vary between 1 ~ 1000 mm/s

- 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

^{57}Fe Mössbauer Spectroscopy

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

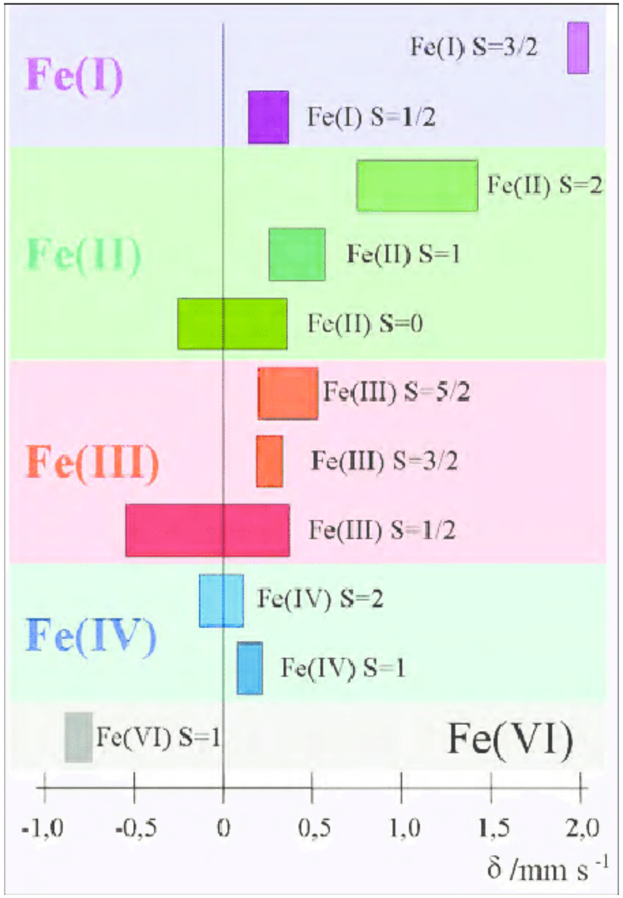
  → directly on s-orbital electron configuration
  → indirectly on p/d/f-orbital electron configuration

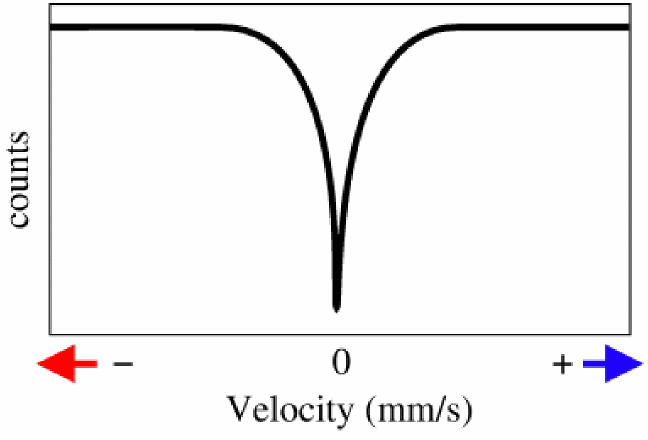
- In case of iron (3d transition metal) the different oxidation states/spin states differ in terms of the d-orbital electron configuration
  (which then slightly affects the s-orbital density)

- Isomer shift is given against a standard

- Typically used standards:

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

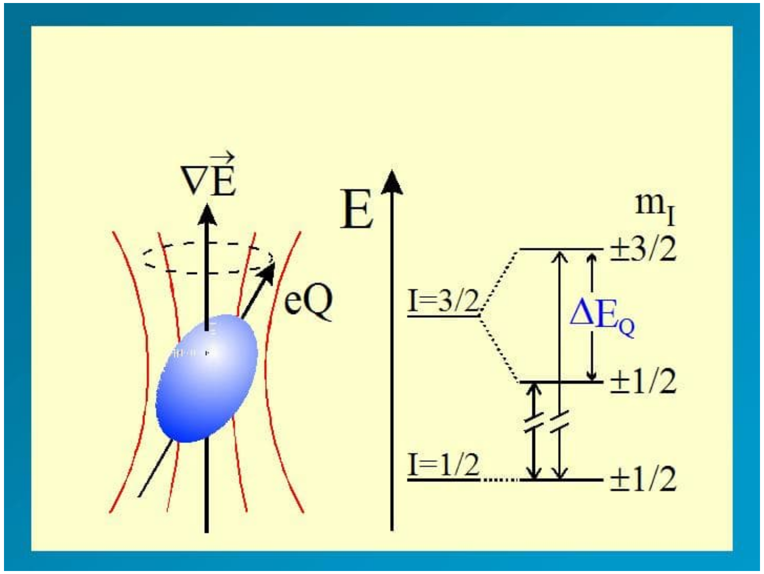


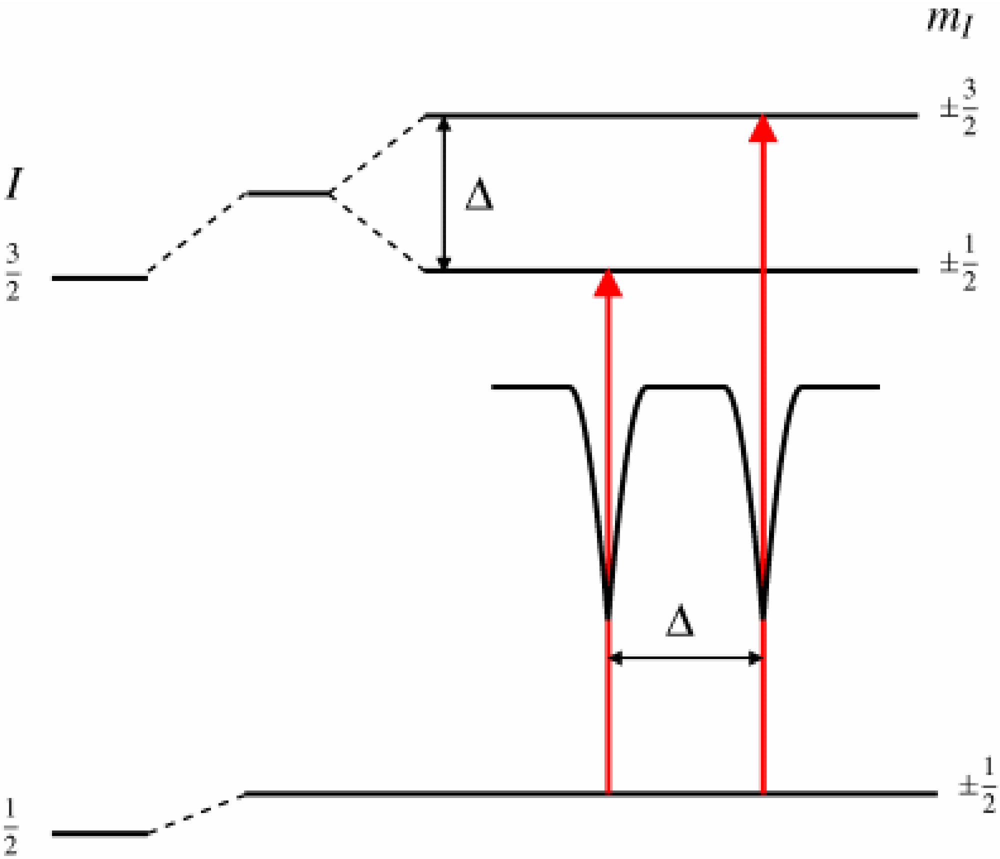


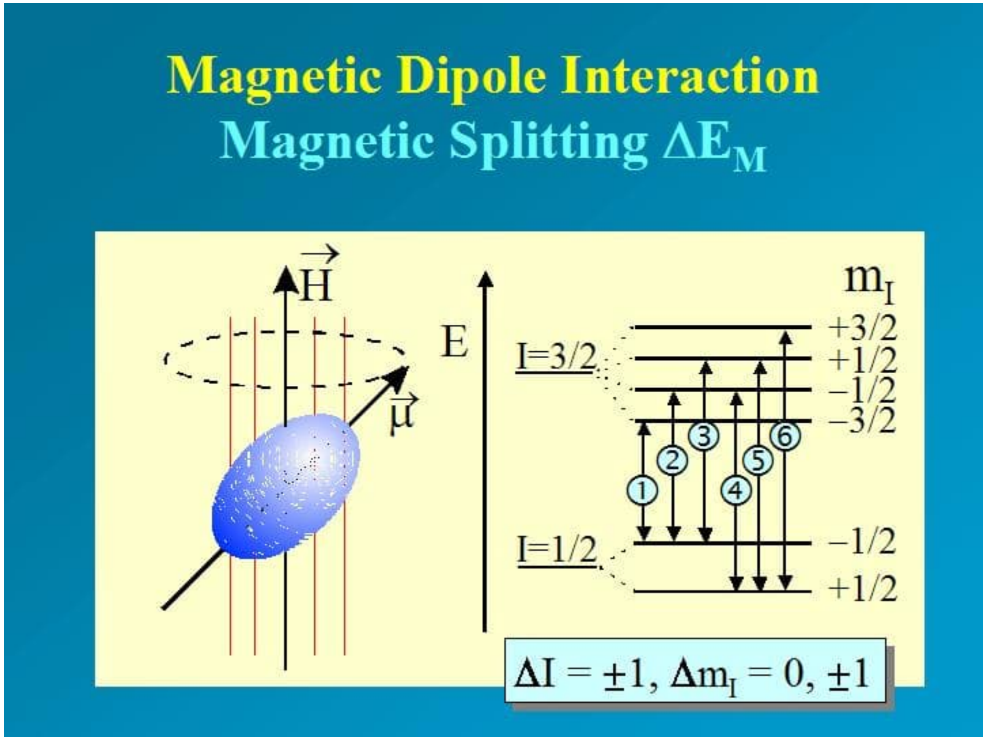
ELECTRIC QUADRUPOLE INTERACTION

Surrounding ions create electric field gradient about the nucleus:

- Symmetric → no splitting
- Asymmetric → splitting



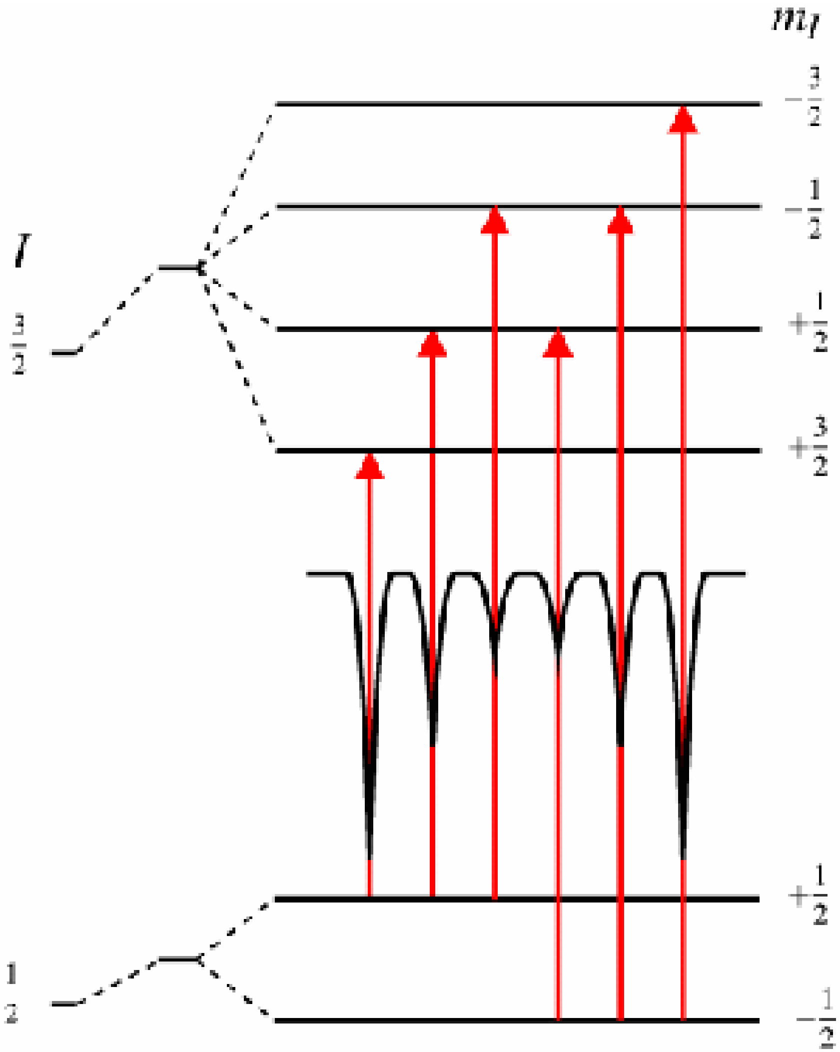




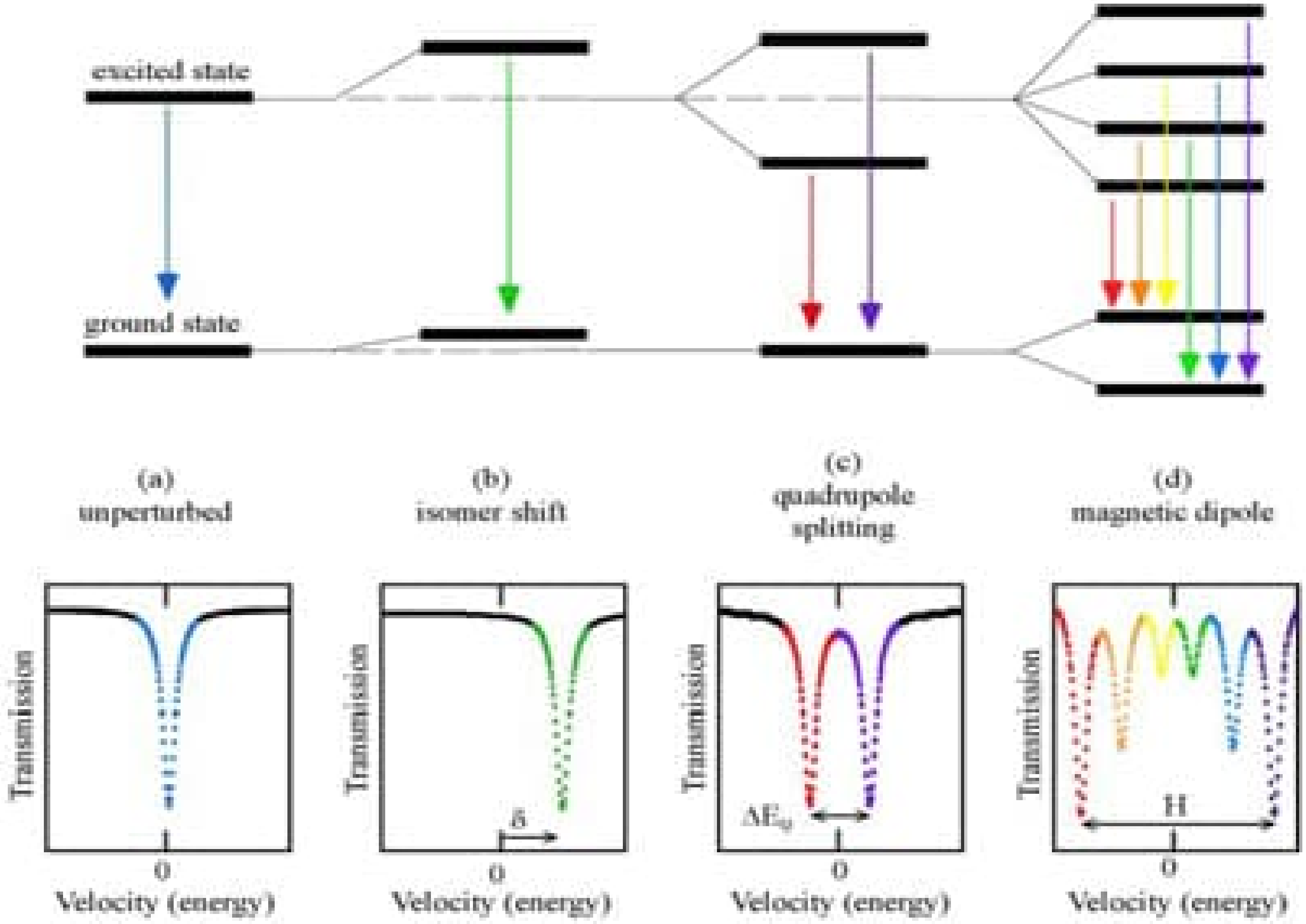
Magnetic Dipole Interaction

Magnetic Splitting ΔE_M

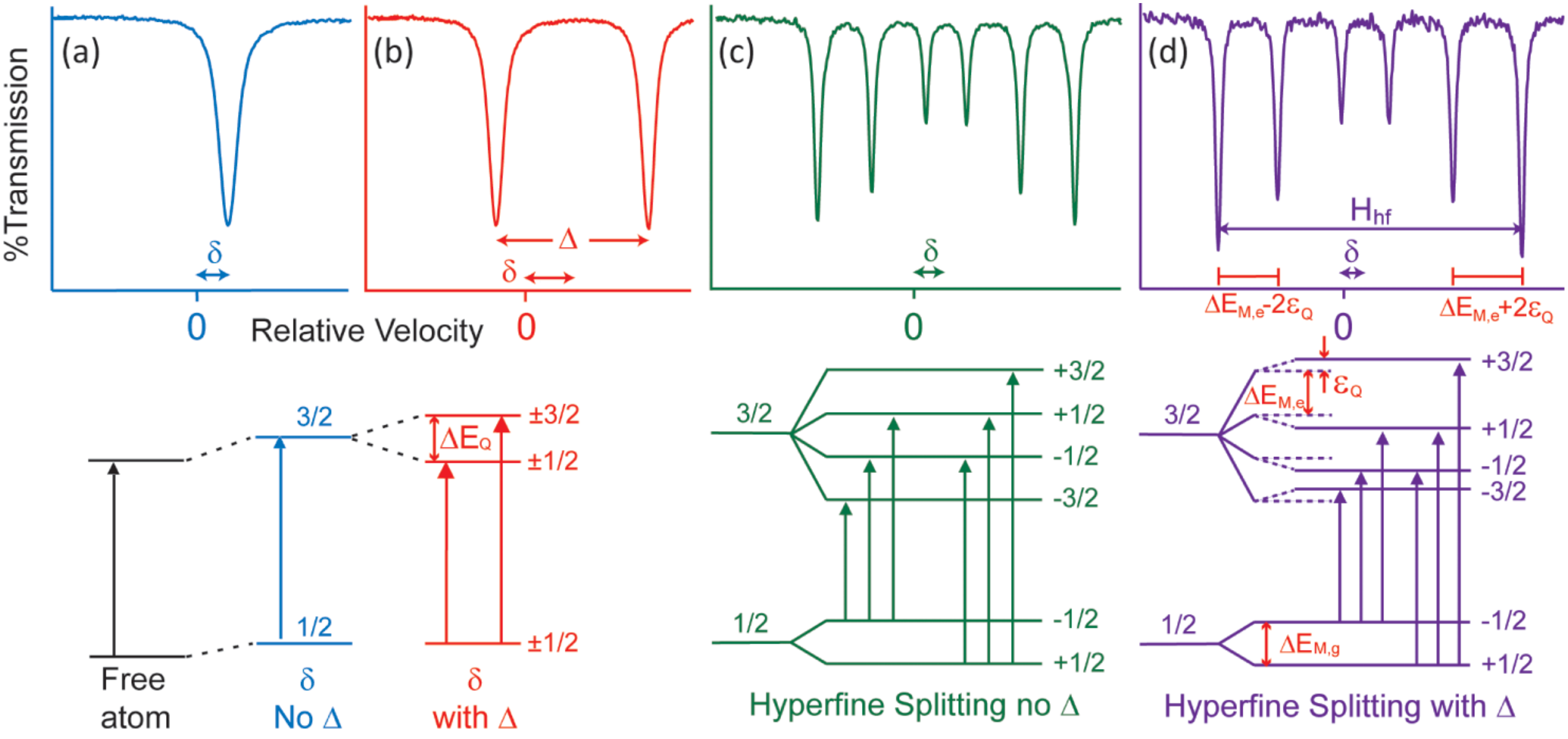
$\Delta I = \pm 1, \Delta m_I = 0, \pm 1$



Summary of HYPERFINE INTERACTIONS affecting Mössbauer spectra



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



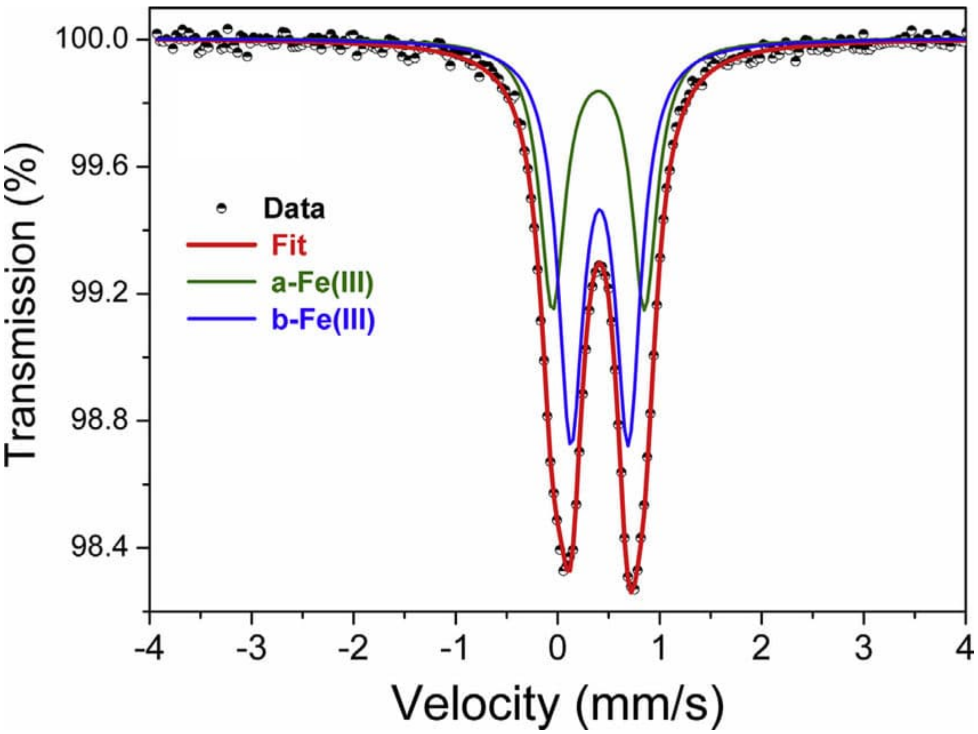
Different iron species in the sample

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

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

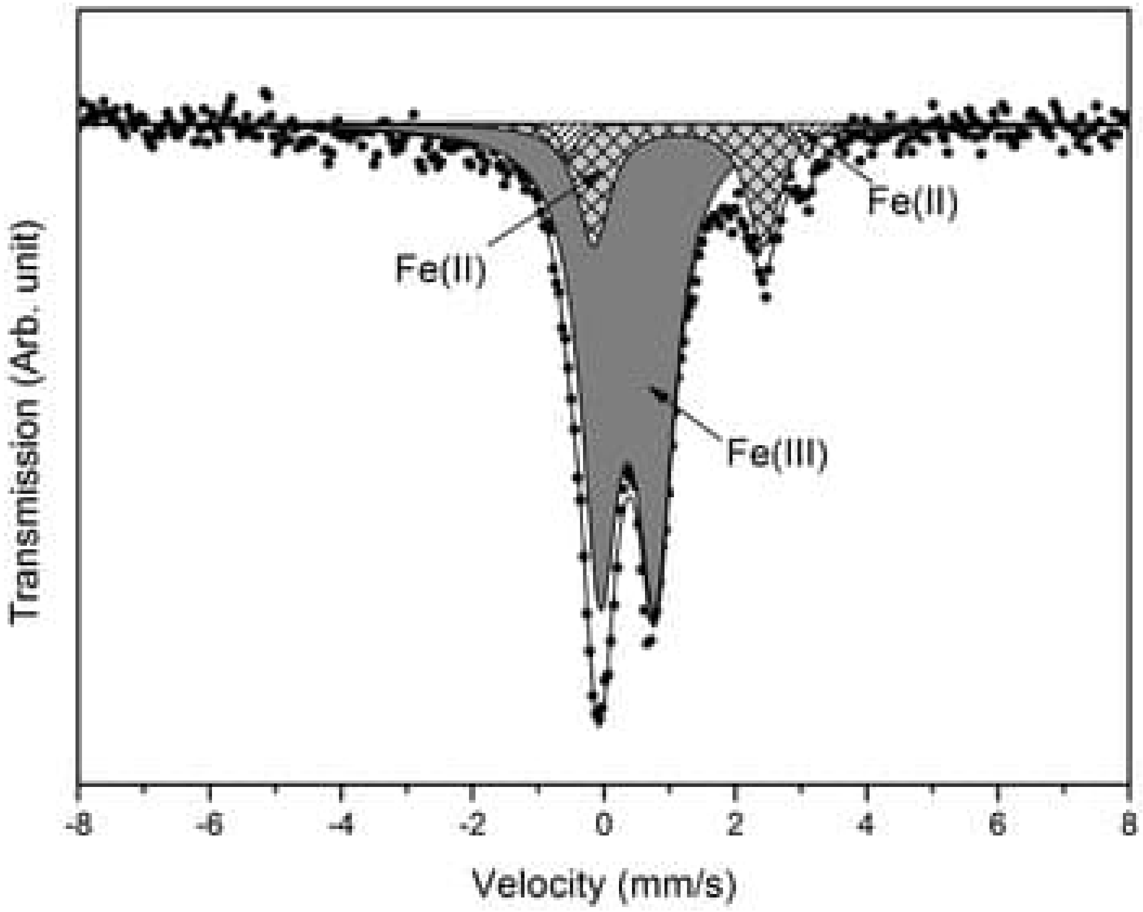
EXAMPLE: overall spectrum consists of two sub-spectra

- **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

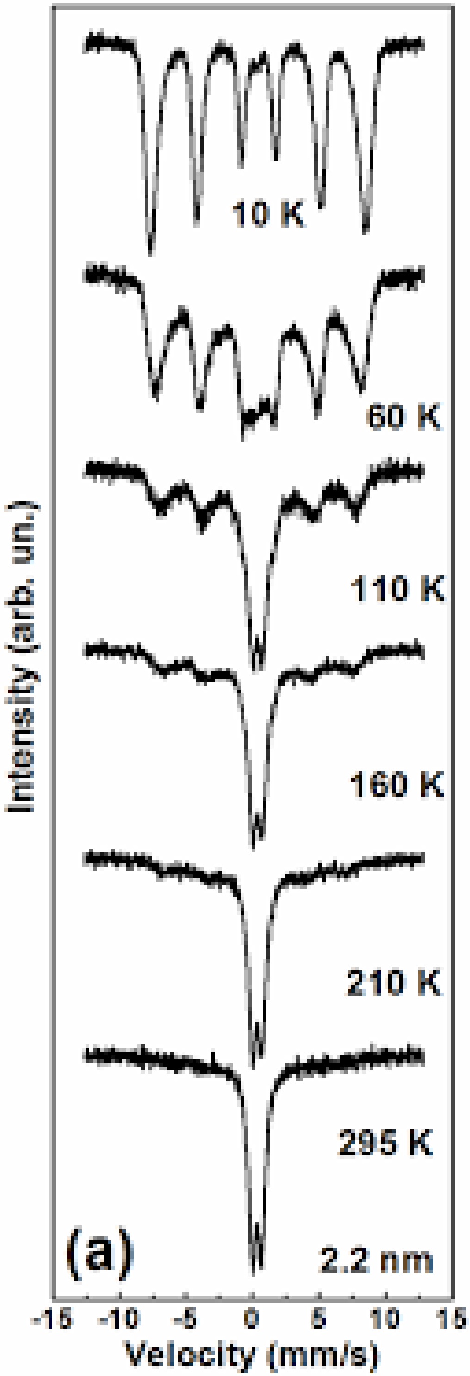
→ **employed e.g. to investigate magnetic transitions**

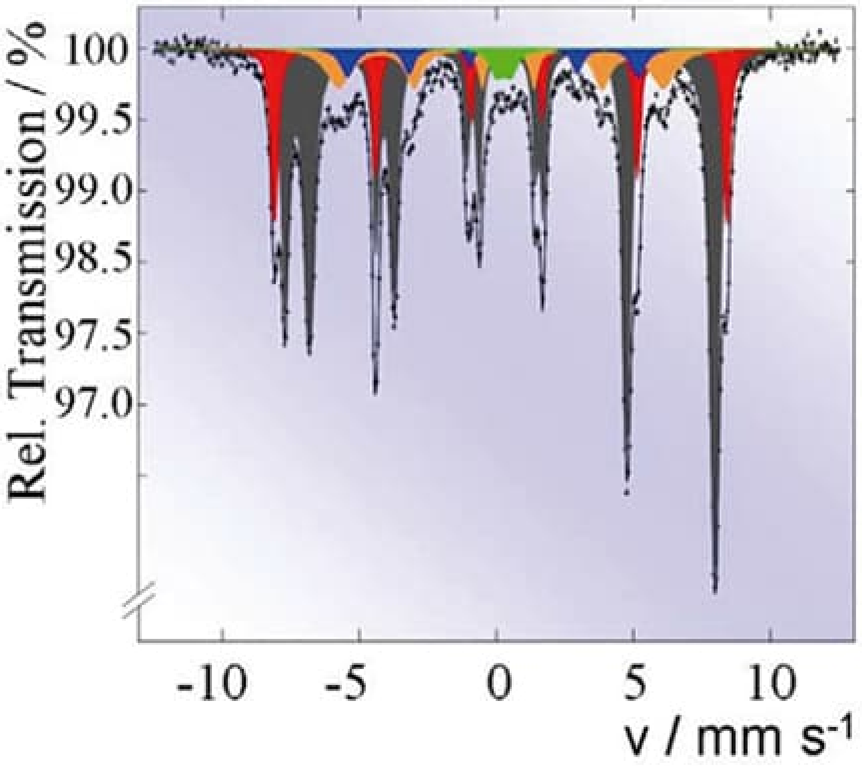
EXAMPLE:

- 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



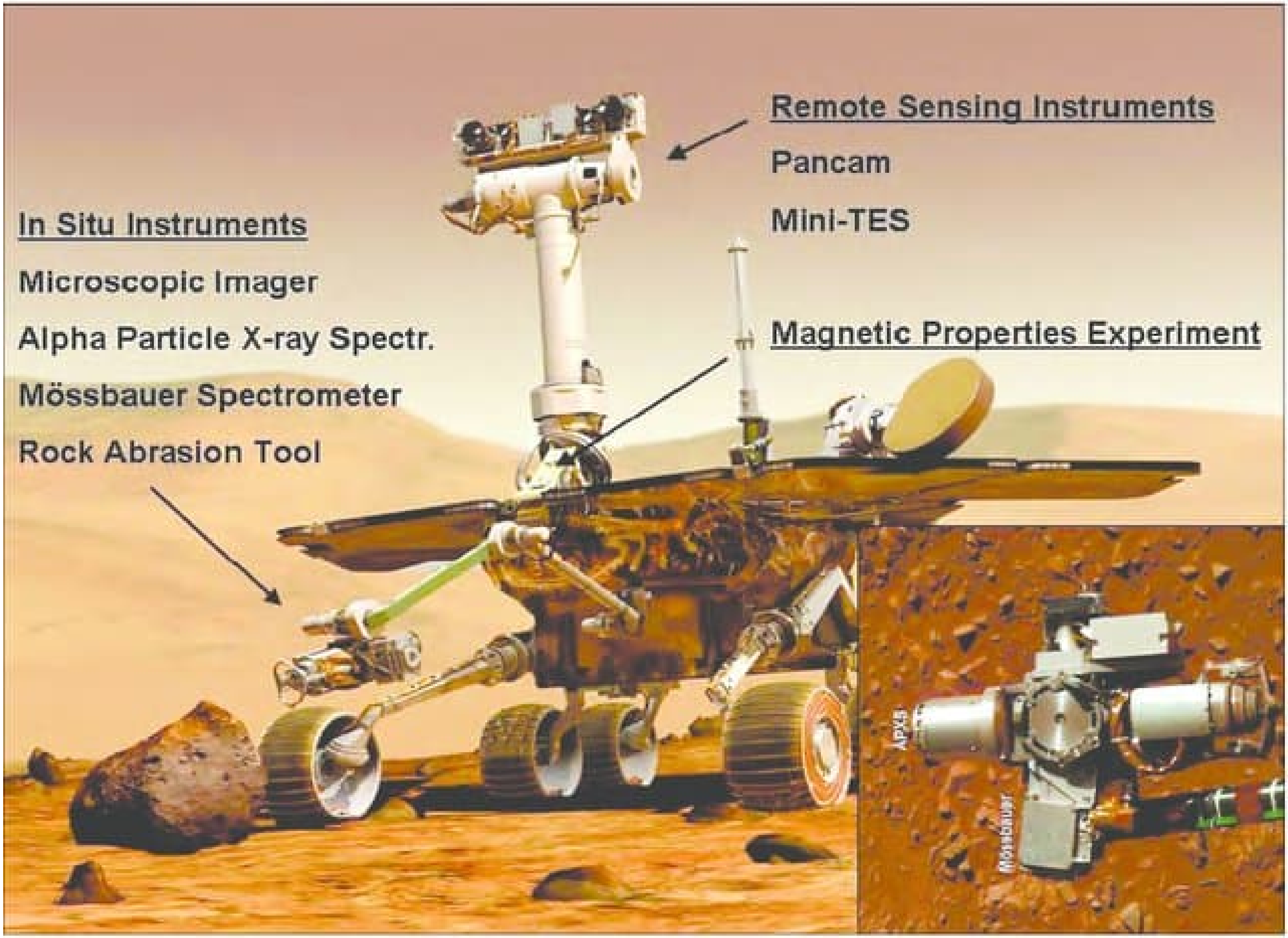


Constituents	A/%
Hematite, α-Fe_2O_3	16
Magnetite, Fe_3O_4	64
Goethite, α-FeOOH	13
Martensite	5
β/γ - FeOOH	2

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):

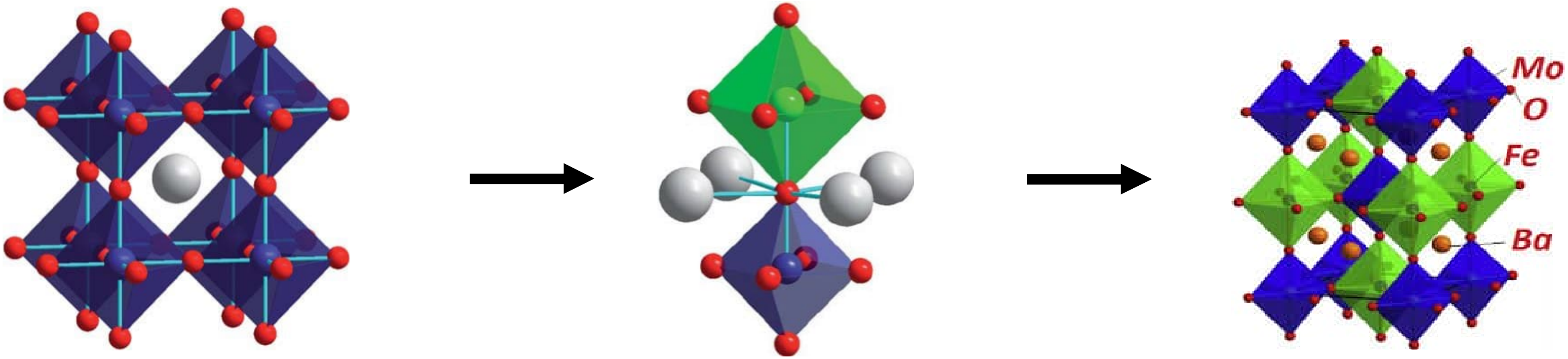
Mössbauer spectrometer is one of the instruments on the robotic arm



Mössbauer examples for DOUBLE PEROVSKITES

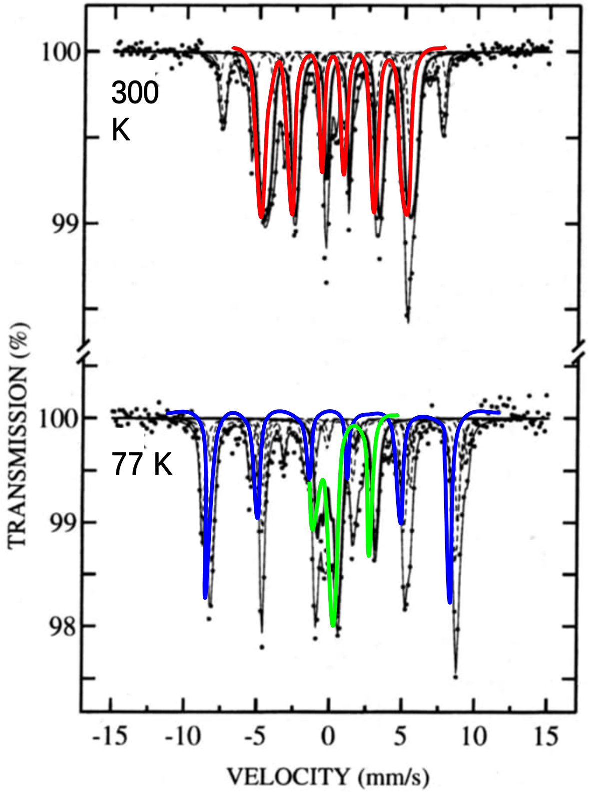
RECALL from the first lecture:

- 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 $Sr_2\mathbf{FeMo}O_6$: 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)

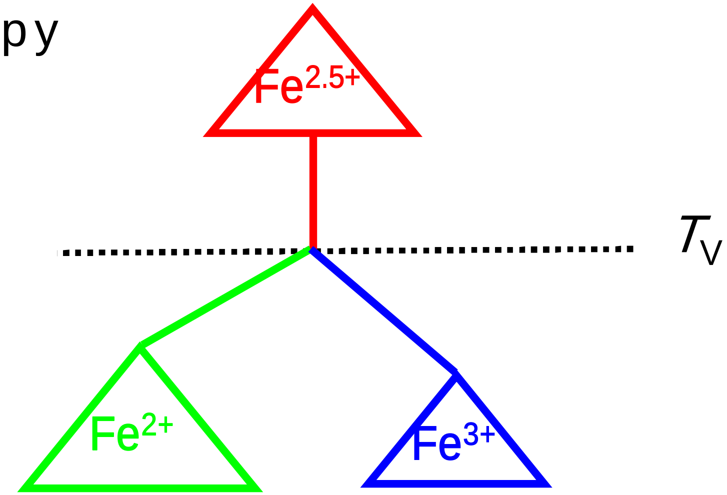


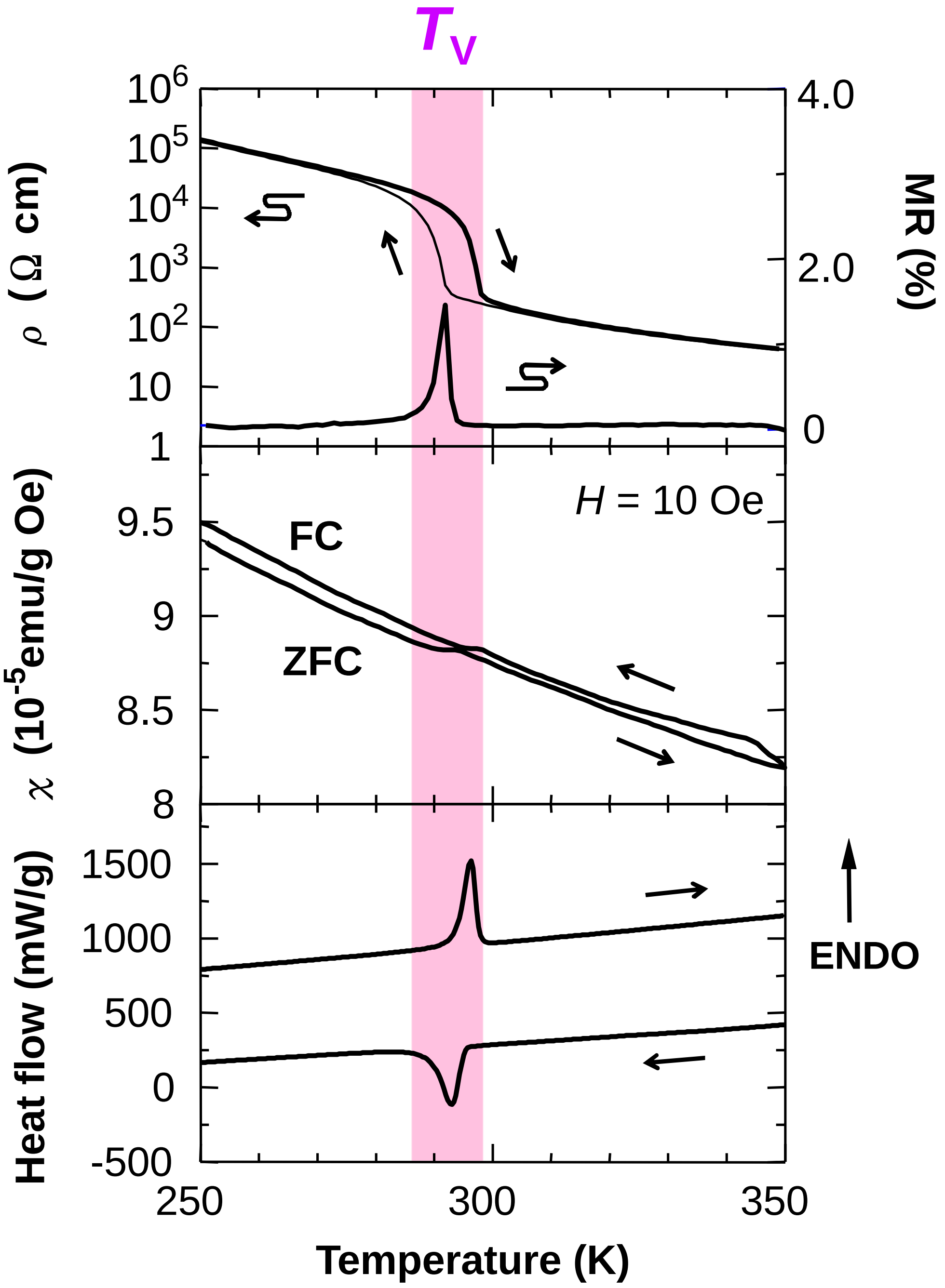
A-site ordered DP with oxygen vacancies $Ba^{II}Sm^{III}Fe_2O_{5.0}$

- **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)**



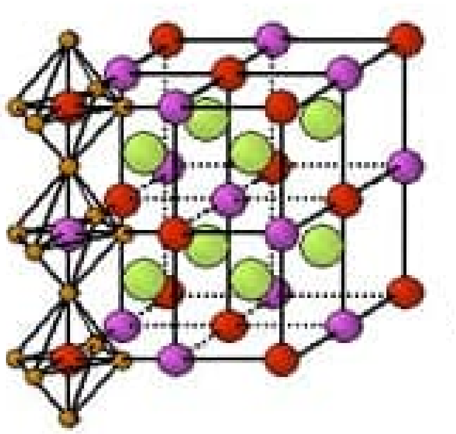
^{57}Fe Mössbauer spectroscopy

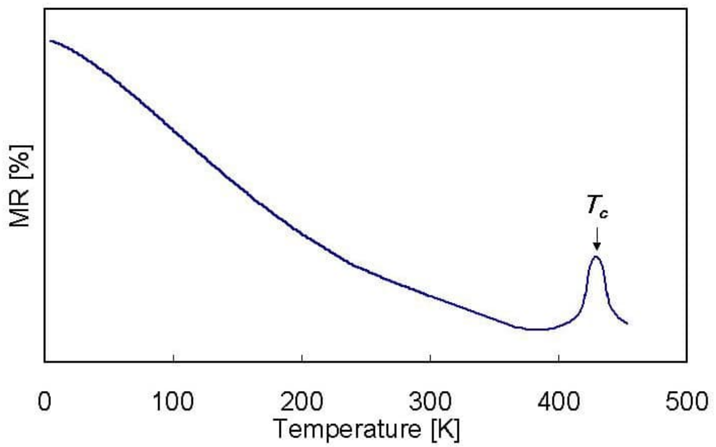




$BaSmFe_2O_{5.0}$

Many physical properties change at T_V





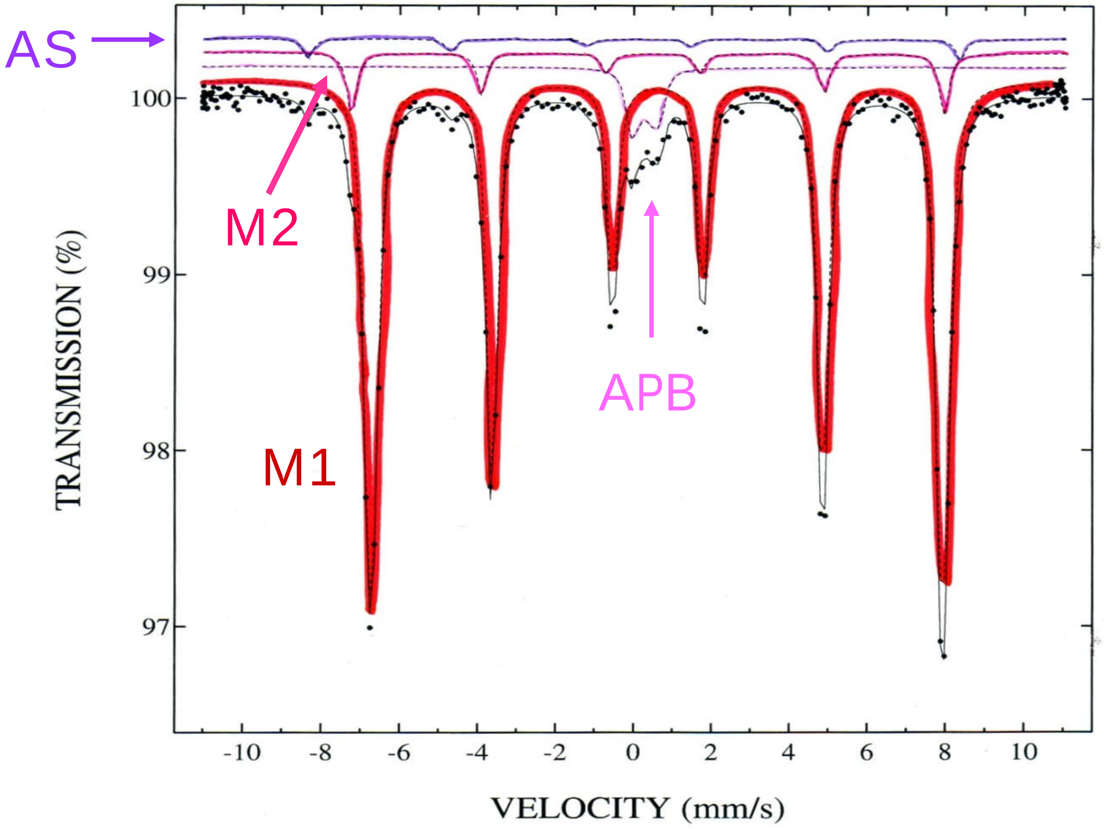
Sr_2FeMoO_6

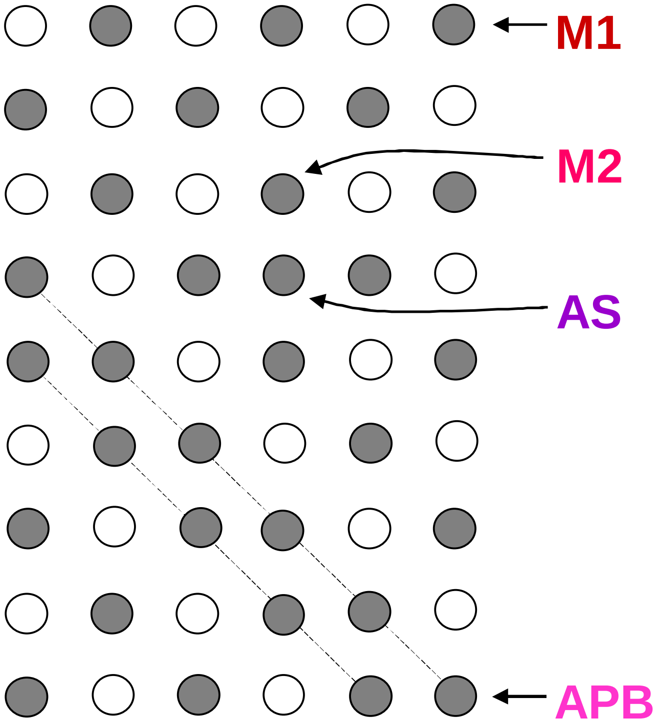
***B*-site ordered double perovskite**

- **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).





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)