

SCHEDULE

	Date	Topic
1.	Wed 01.03.	Lec-1: Introduction
2.	Mon 06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon 06.03.	EXERCISE 1
4.	Wed 08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri 10.03.	Lec-4: Symmetry & Point Groups
6.	Mon 13.03.	EXERCISE 2
7.	Wed 15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri 17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon 20.03.	EXERCISE 3 (Linda)
10.	Fri 31.03.	Lec-7: Rietveld (Linda)
11.	Mon 03.04	EXERCISE 4: Rietveld (Linda)
12.	Wed 12.04.	Lec-8: ND & GI-XRD
13.	Fri 14.04.	Lec-9: XRR (Topias)
14.	Mon 17.04.	EXERCISE 5: XRR (Topias)
15.	Wed 19.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Fri 21.04.	Lec-11: Mössbauer
17.	Fri 21.04.	EXERCISE 6
18.	Fri 28.04.	Seminars: EELS, XPS, FTIR, Raman
19.	Wed 03.05.	Seminars: ED, HRTEM, SEM, AFM
20.	Wed 10.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY

EXAM: Wednesday, May 17th

SEMINARS

- EELS Aleksi Rantanen & Jasmin Sonphasit
- XPS Umaid Lone
- IR Fasiha Israr & Lisa Riedlsperger
- Raman Zonghang Song & Xueran Tao
- SEM Trang Pham & Erkka Koskenniemi
- AFM Joakim Kattelus & Matilda Antila
- HRTEM Luiza Souza & Henrik Stenbrink
- ED Christer Söderholm & Shadab Ishtiaq

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Topics: **EELS, IR, Raman, XPS, SEM, AFM, HRTEM, ED**
- 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: 25+5 minutes
- Rough content of the presentation:
 - principle of the technique(s)
 - 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)

GRADING (max 100 points)

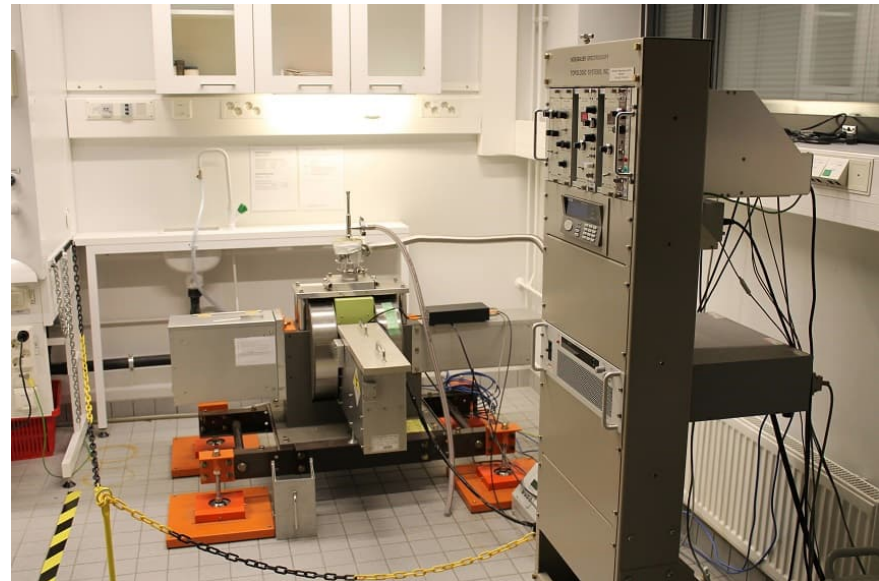
- Exam: 0 – 44 points
- Exercises: = 0 – 36 (= 6 x 6) points
- Seminar (mandatory): 10 – 20 points

LECTURE 11: Mössbauer Spectroscopy

- Gamma rays
- Recoil energy & Resonance absorption
- Doppler effect
- Chemical (valence), structural (coordination) & magnetic properties
- Suggested reading:

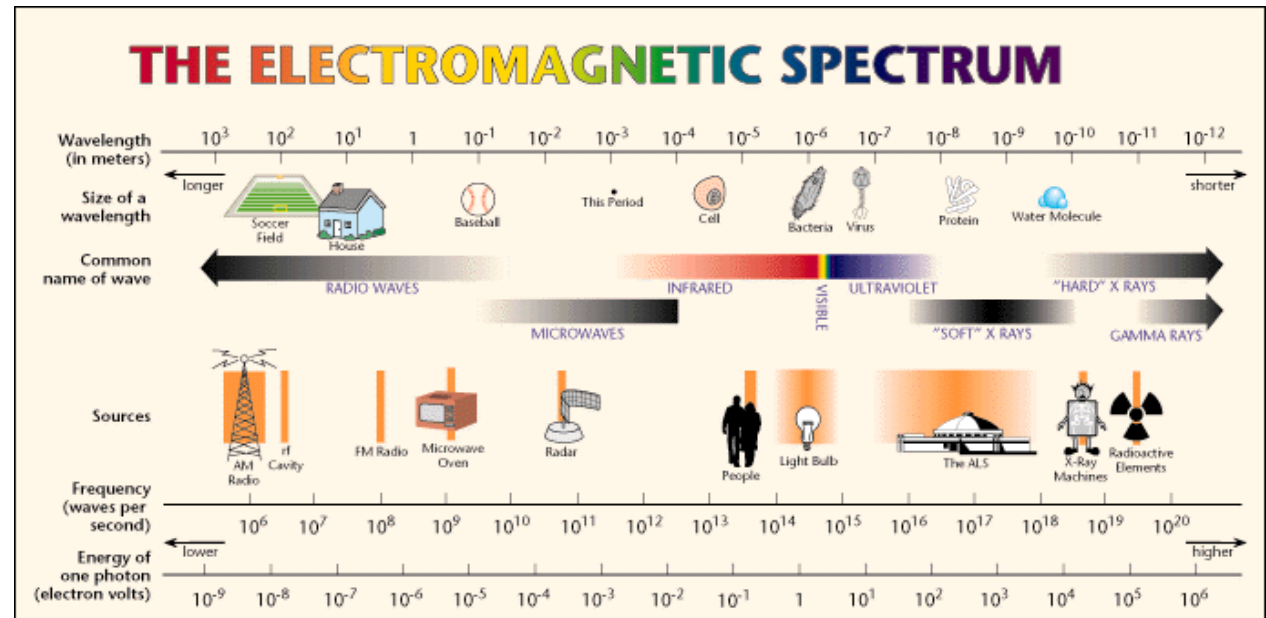
<https://www.rsc.org/Membership/Networking/InterestGroups/MossbauerSpect/Intropart1.asp>

Our Mössbauer spectrometer



GAMMA RAYS

- 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 $< 1 \mu\text{s}$)
- When the nucleus returns from an excited state (E_e) to the ground state (E_g), the **energy difference** is emitted as gamma rays ($E_0 = E_e - E_g$)
- **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_r) of the opposite direction (think what happens to the boat when the passenger 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 negligible

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

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

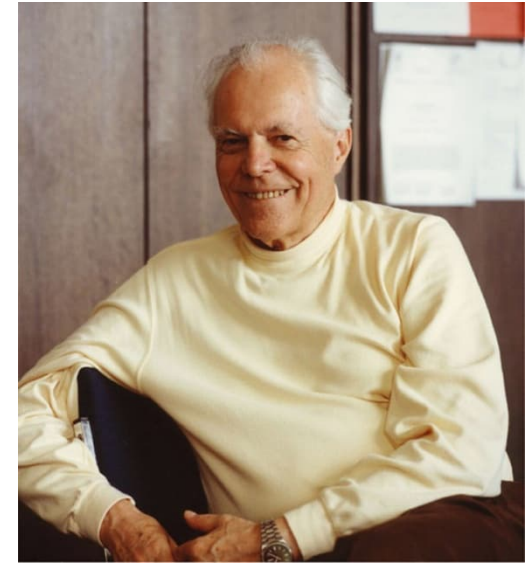
→ so-called **RESONANCE ABSORPTION** (i.e. spectroscopy) is **NOT** possible

RECOIL-FREE EMISSION

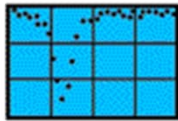
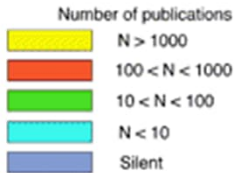
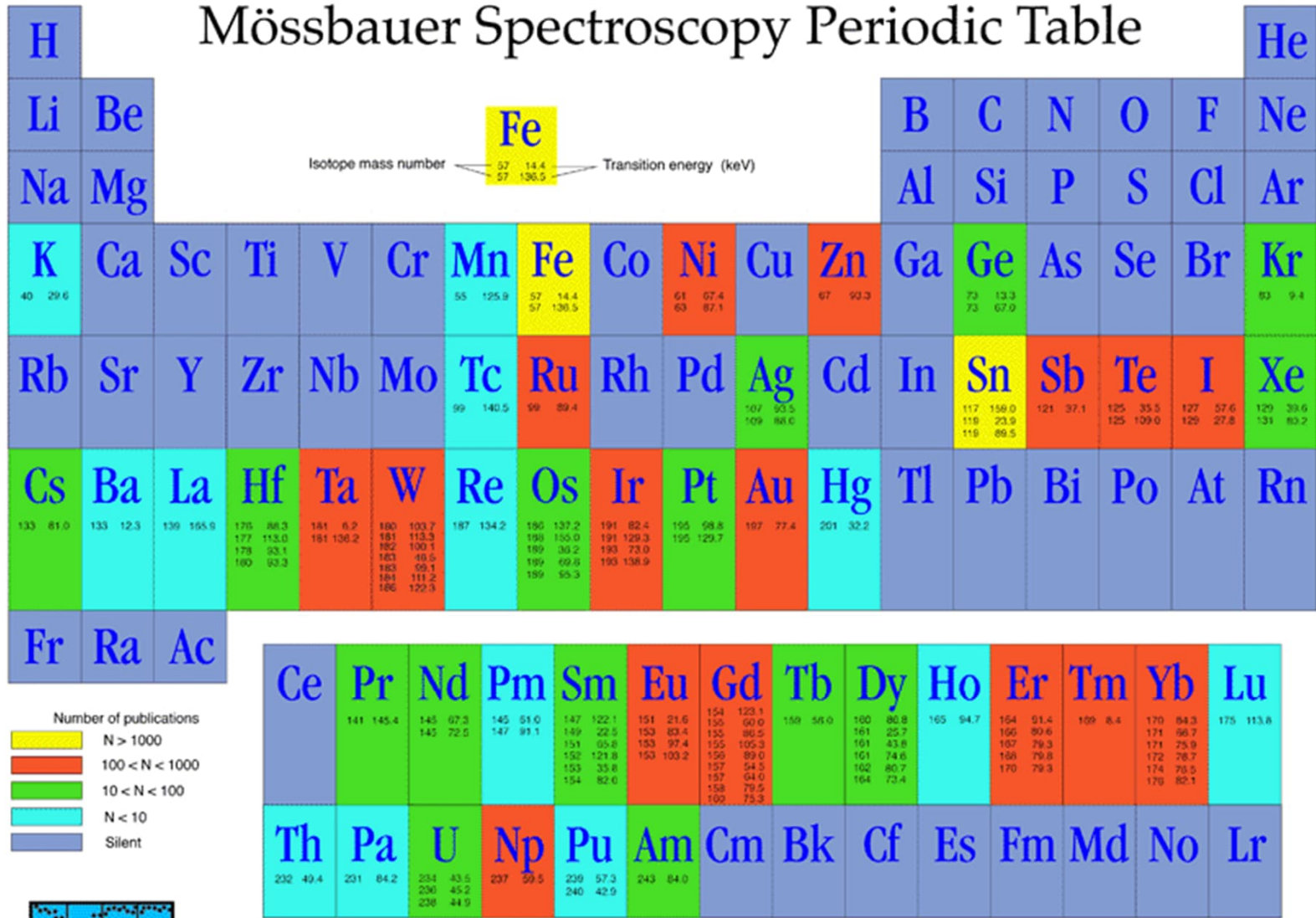
- Recoil may be avoided if the emitting nucleus is part of crystal lattice:
the entire crystal lattice receives the recoil energy, and the recoil becomes meaningless (the boat is tightly anchored!)
- Accordingly the resonance absorption becomes possible
- The recoil-less emission is nowadays known for 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



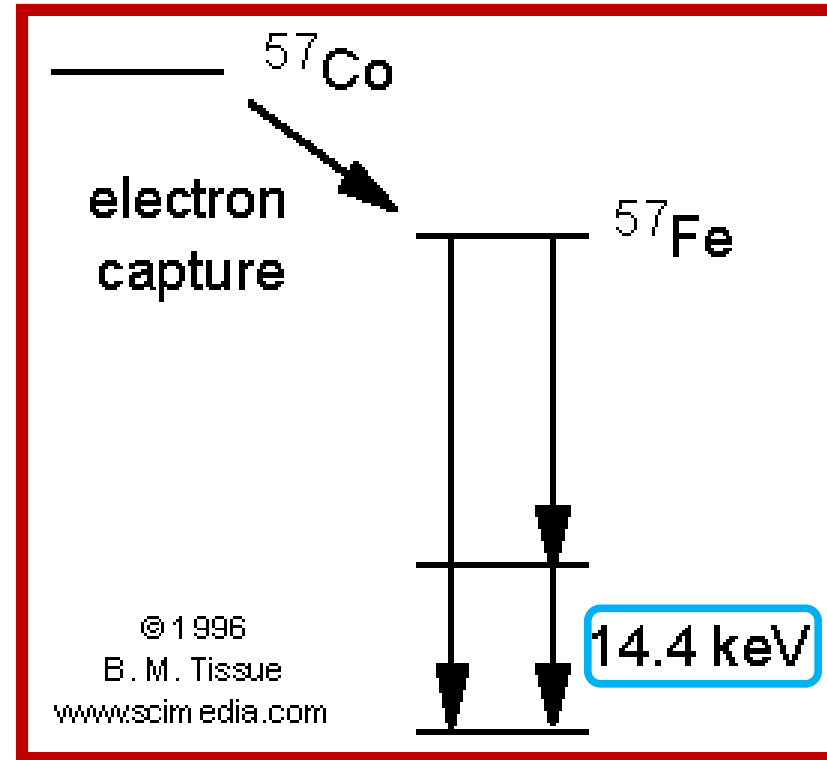
Mössbauer Effect Data Center

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 $^{57}\text{Fe}^*$ nucleus
(^{57}Co can be prepared from iron relatively easily in a cyclotron)
- Part (9 %) of excited $^{57}\text{Fe}^*$ 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 $^{57}\text{Fe}^*$ 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)

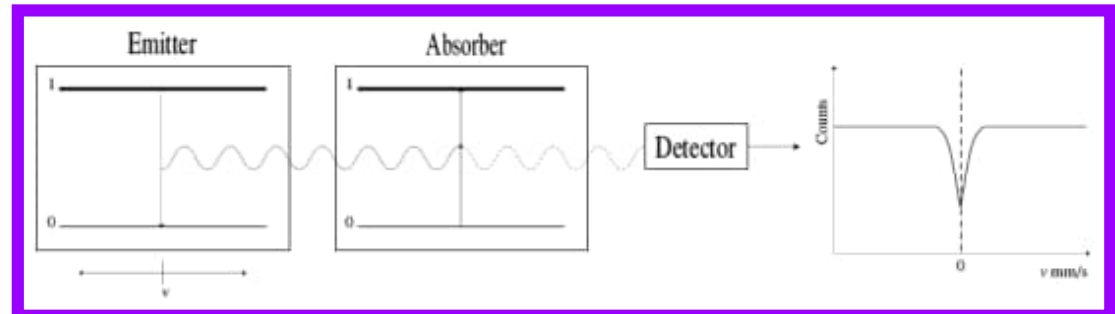
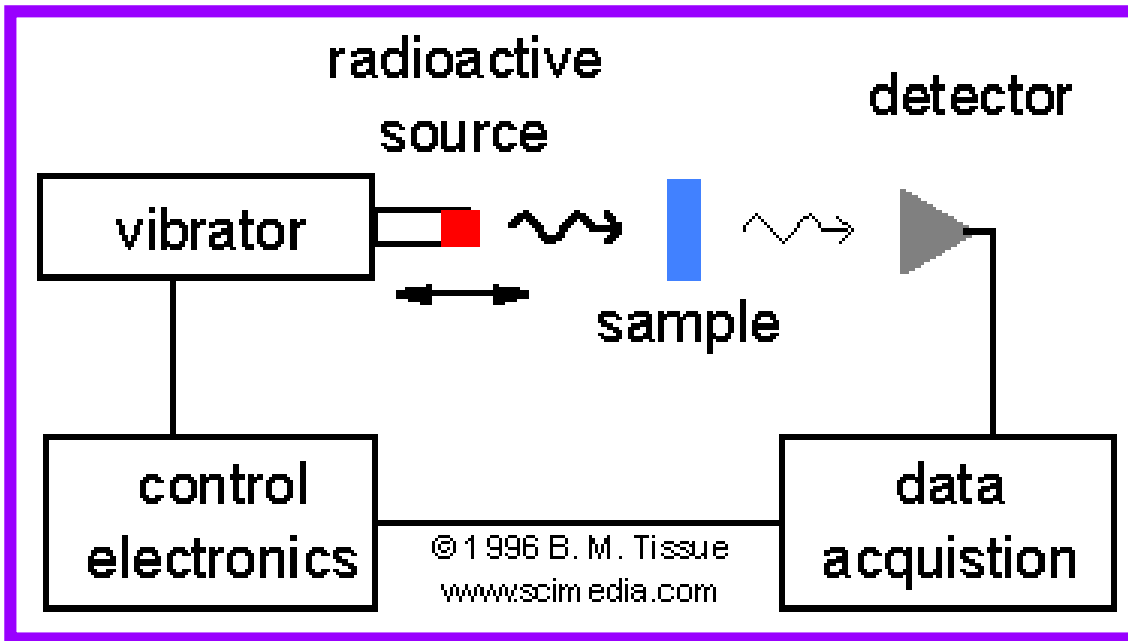


RECORDING of MÖSSBAUER SPECTRUM

- 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

Mössbauer Spectroscopy

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

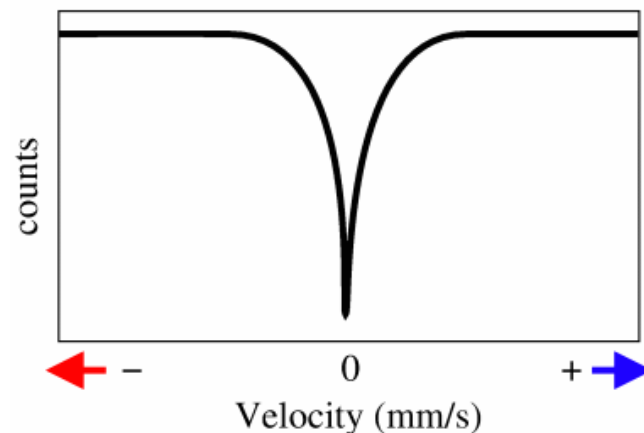
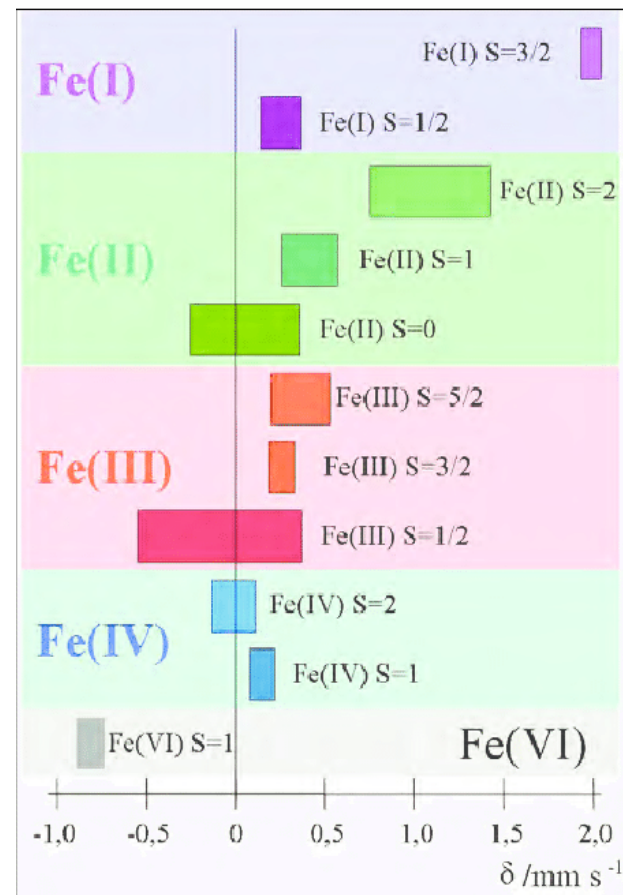


MÖSSBAUER SPECTROSCOPY

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

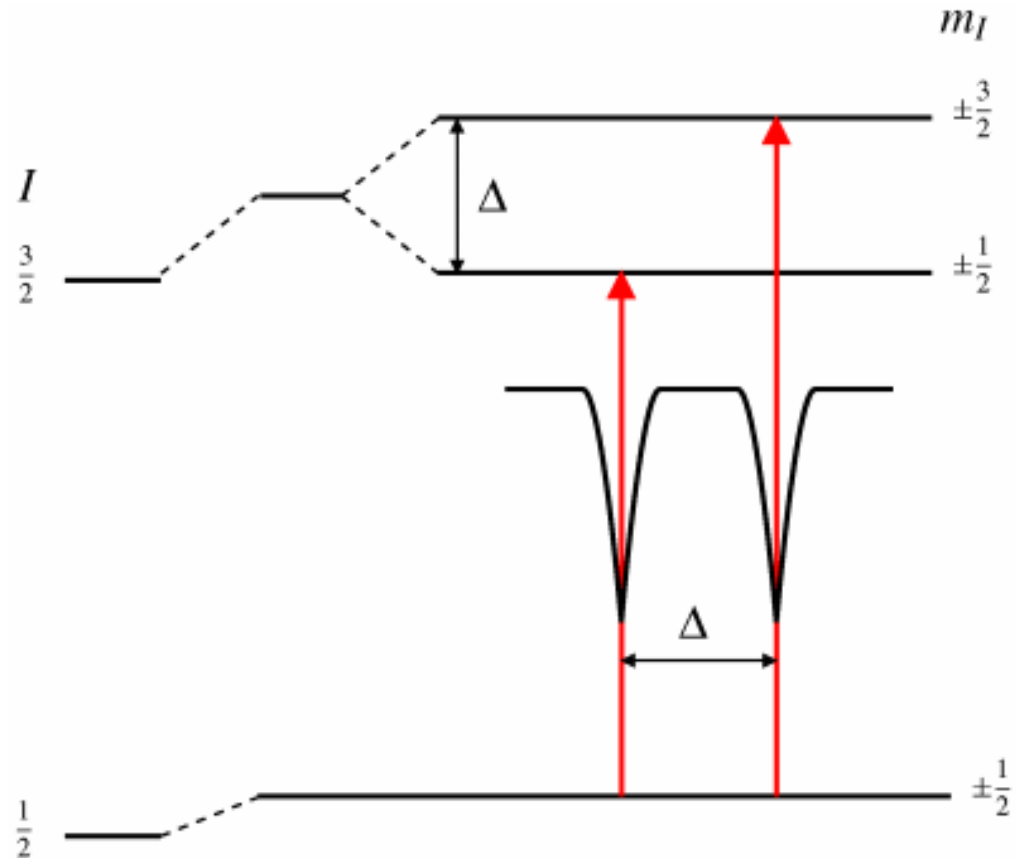
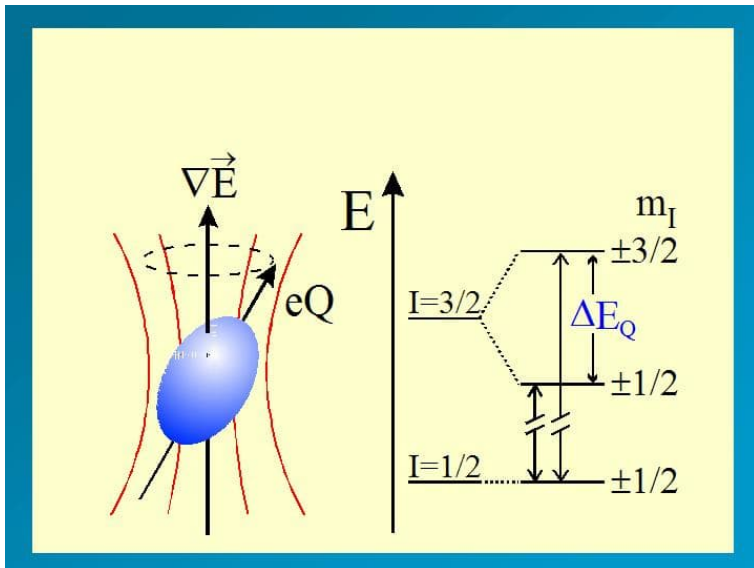
- Isomer shift (IS, δ or ΔE_0) depends:
electron densities about the nucleus
 - directly on s-orbital electron configuration
 - indirectly on p/d/f-orbital electron configuration
- In case of iron (3d transition metal) the different oxidation states/spin states differ in terms of the d-orbital electron configuration (which then slightly affects the s-orbital density)
- Isomer shift is given against a standard
- Typically used standards:
 - ^{119}Sn : SnO_2
 - ^{57}Fe : Fe metal (officially $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$)



ELECTRIC QUADRUPOLE INTERACTION

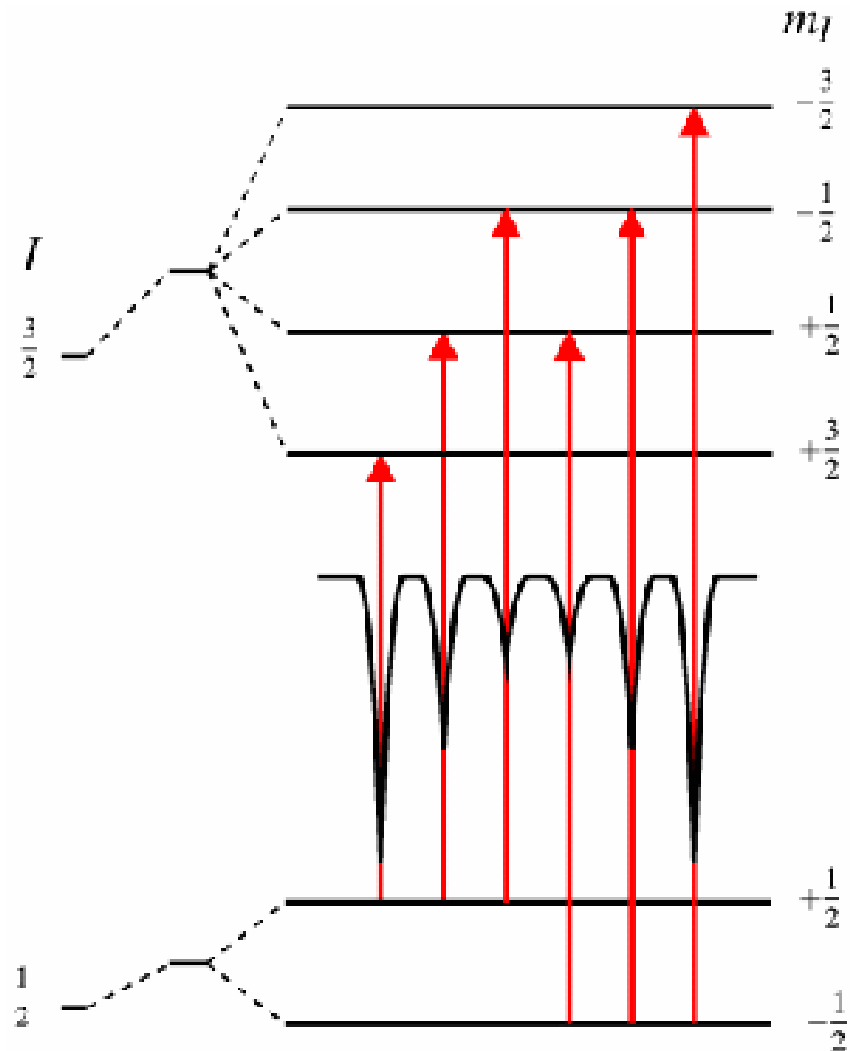
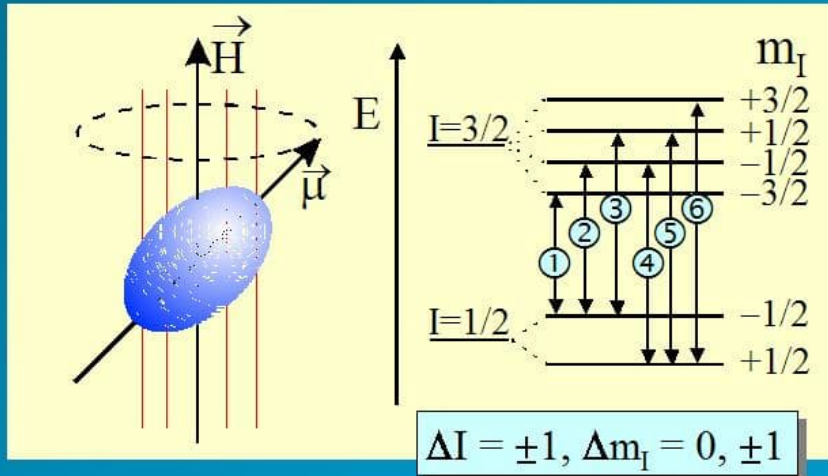
Electric field gradient about the nucleus is created by two factors:

- surrounding ions (major factor):
symmetric \rightarrow no splitting; asymmetric \rightarrow splitting
- valence electrons of the Mössbauer nucleus (minor effect)

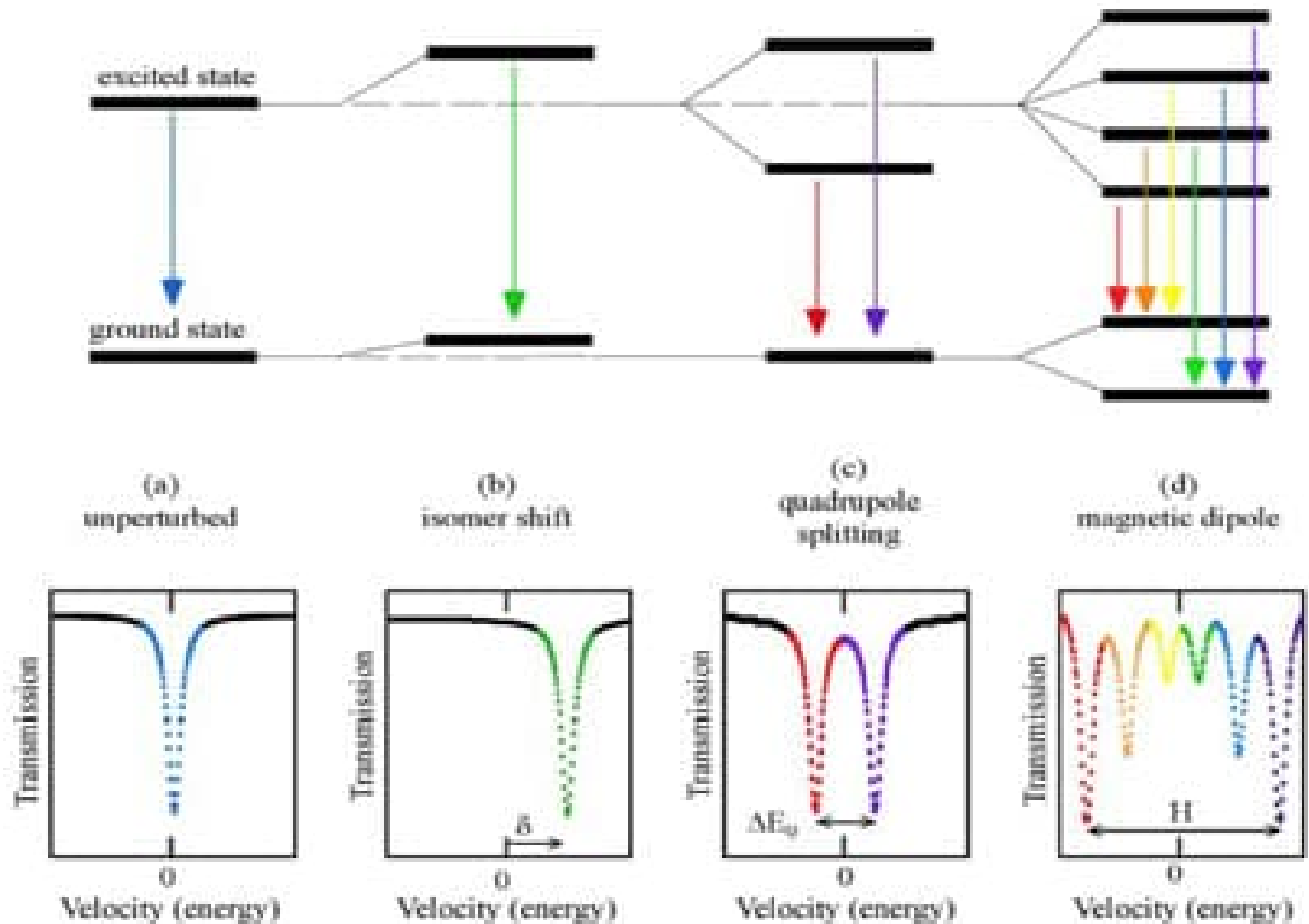


Magnetic Dipole Interaction

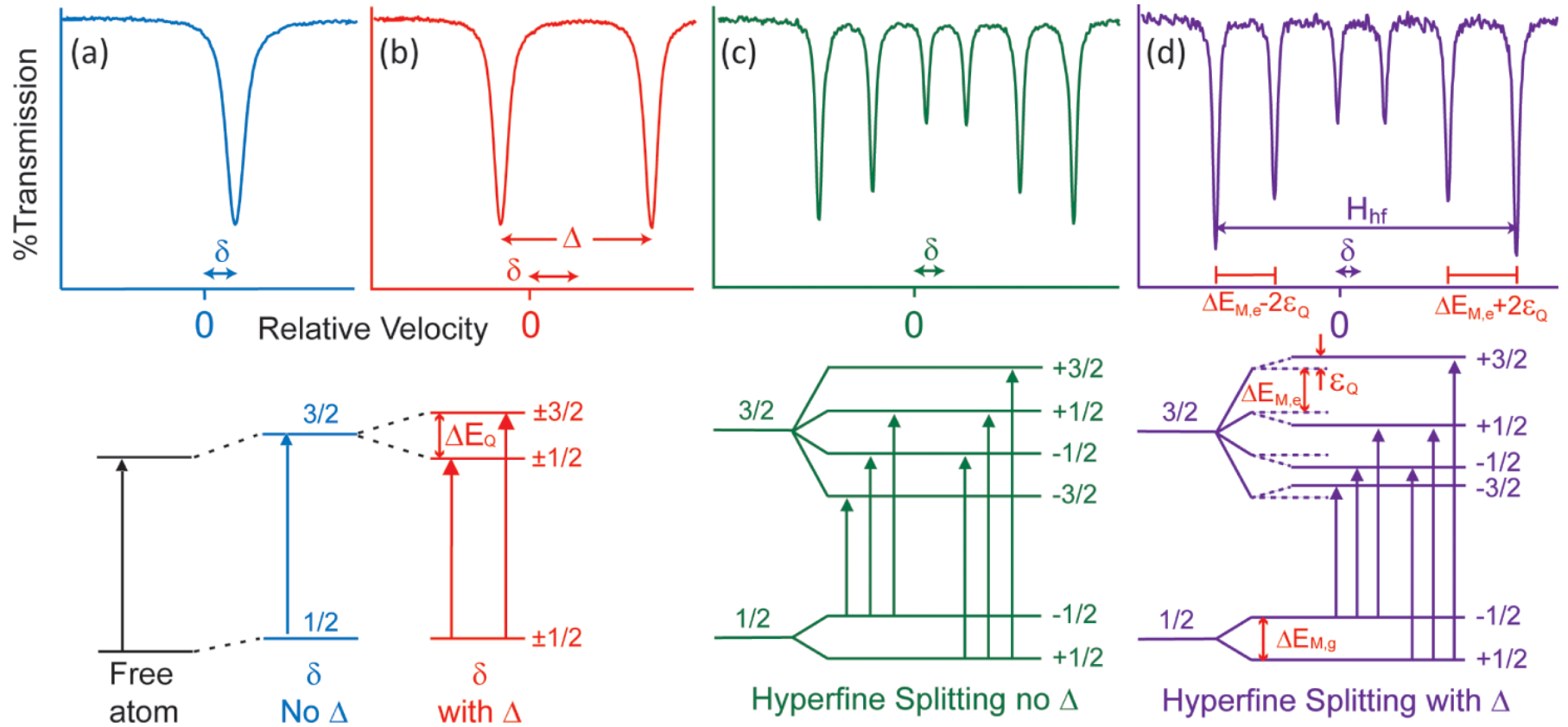
Magnetic Splitting ΔE_M



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

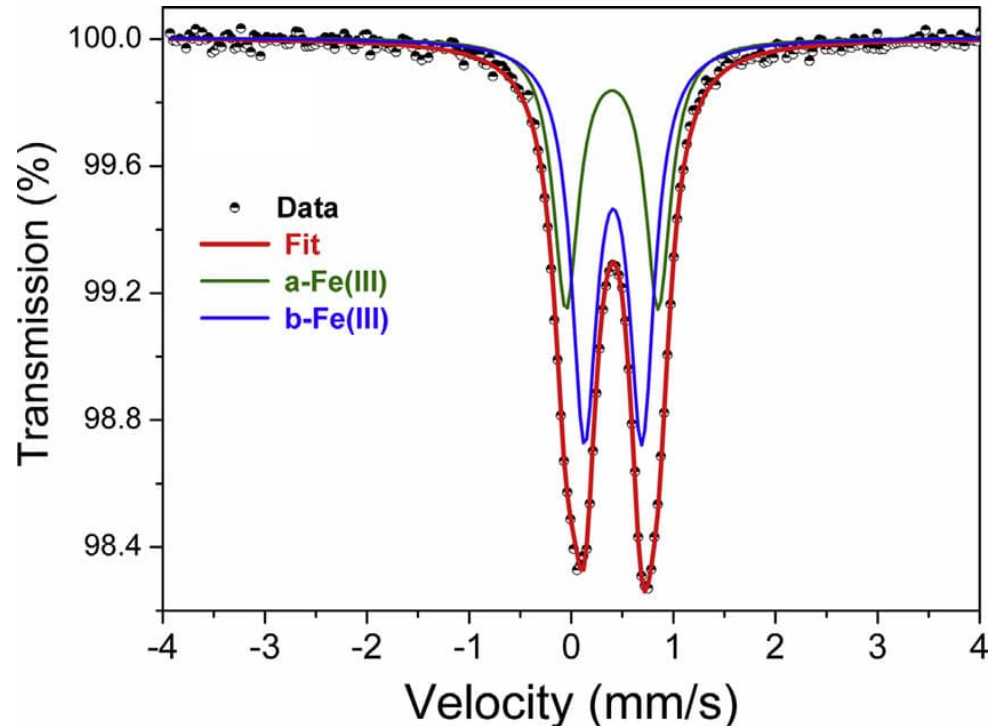
→ intensity ratio of sub-spectra = concentration ratio of corresp. Fe species

EXAMPLE: overall spectrum consists of two sub-spectra

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

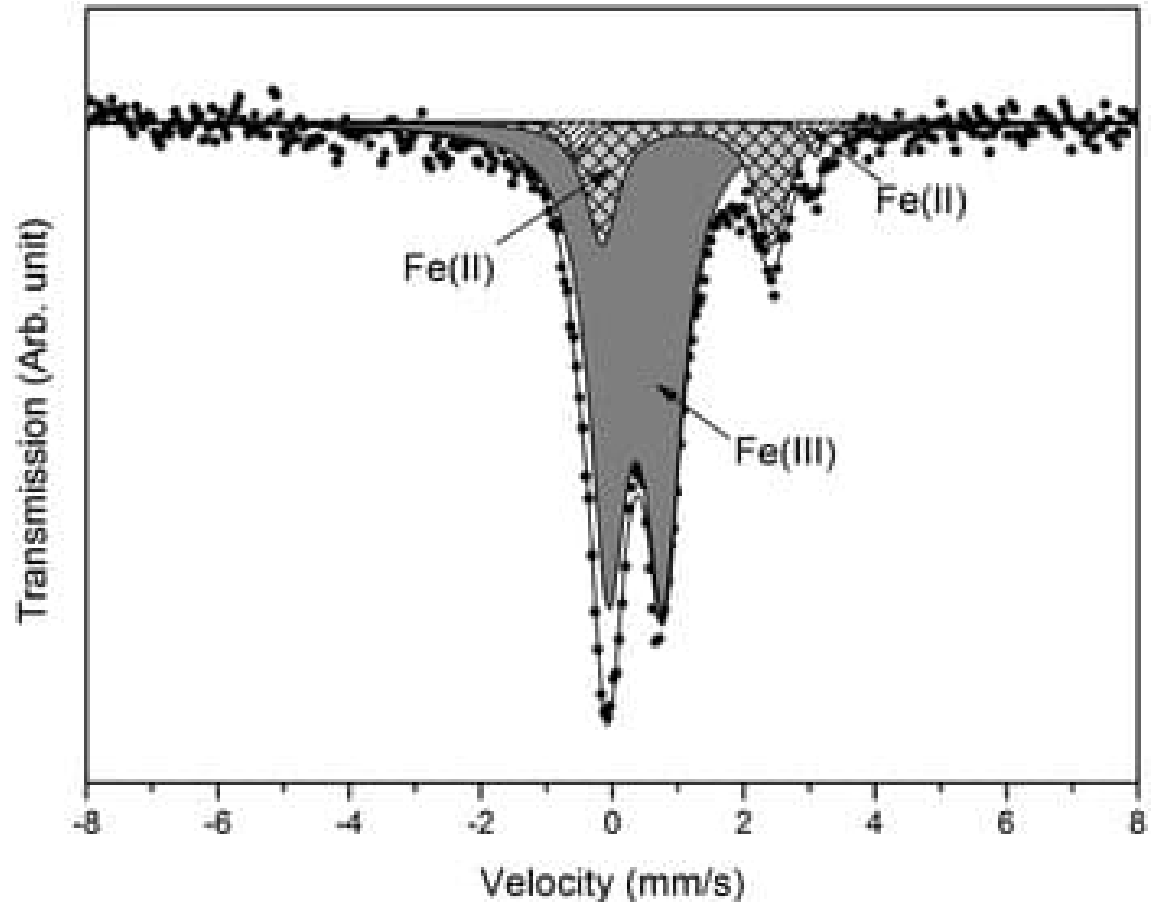
- Same isomer shift → same valence (+III)

- 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) (precise concentrations from spectral areas)
- Both Fe(III) than Fe(II) in asymmetric coordination, but Fe(II) more asymmetric



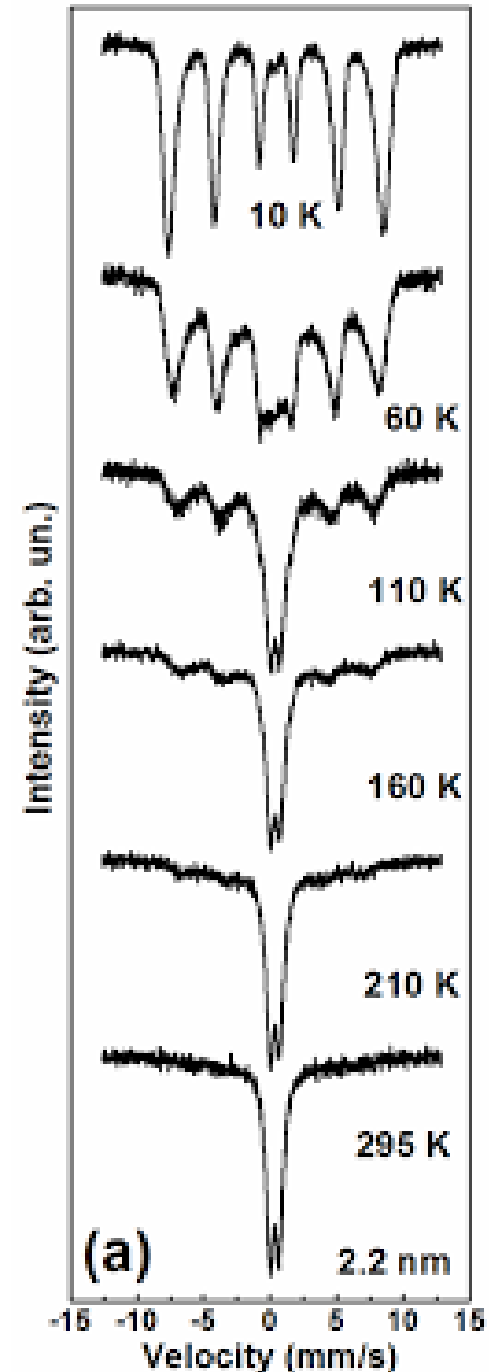
Temperature-dependent measurements

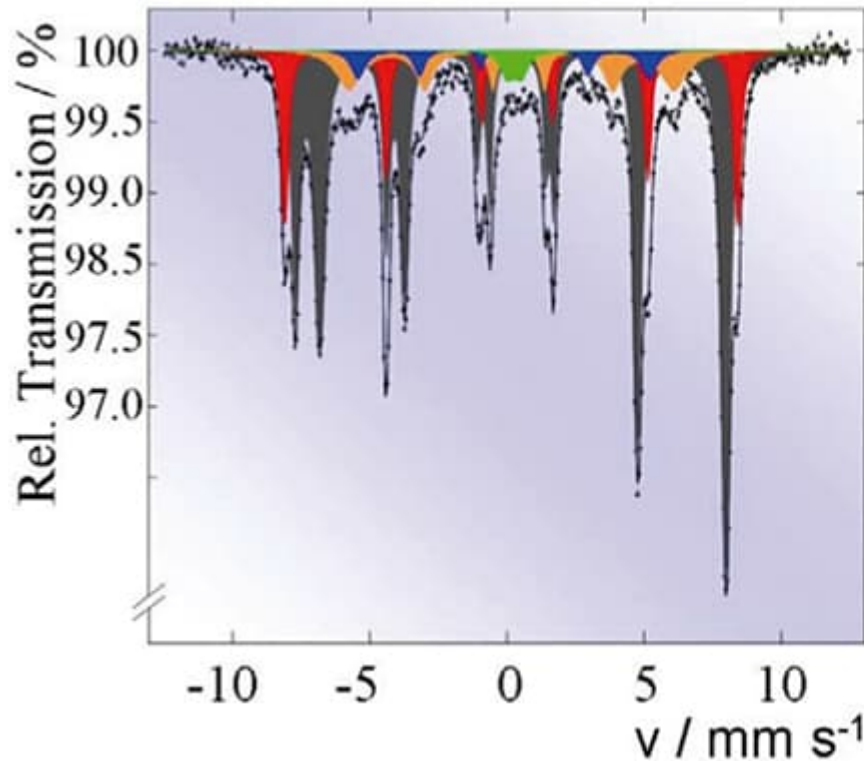
→ employed e.g. to investigate magnetic transitions

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



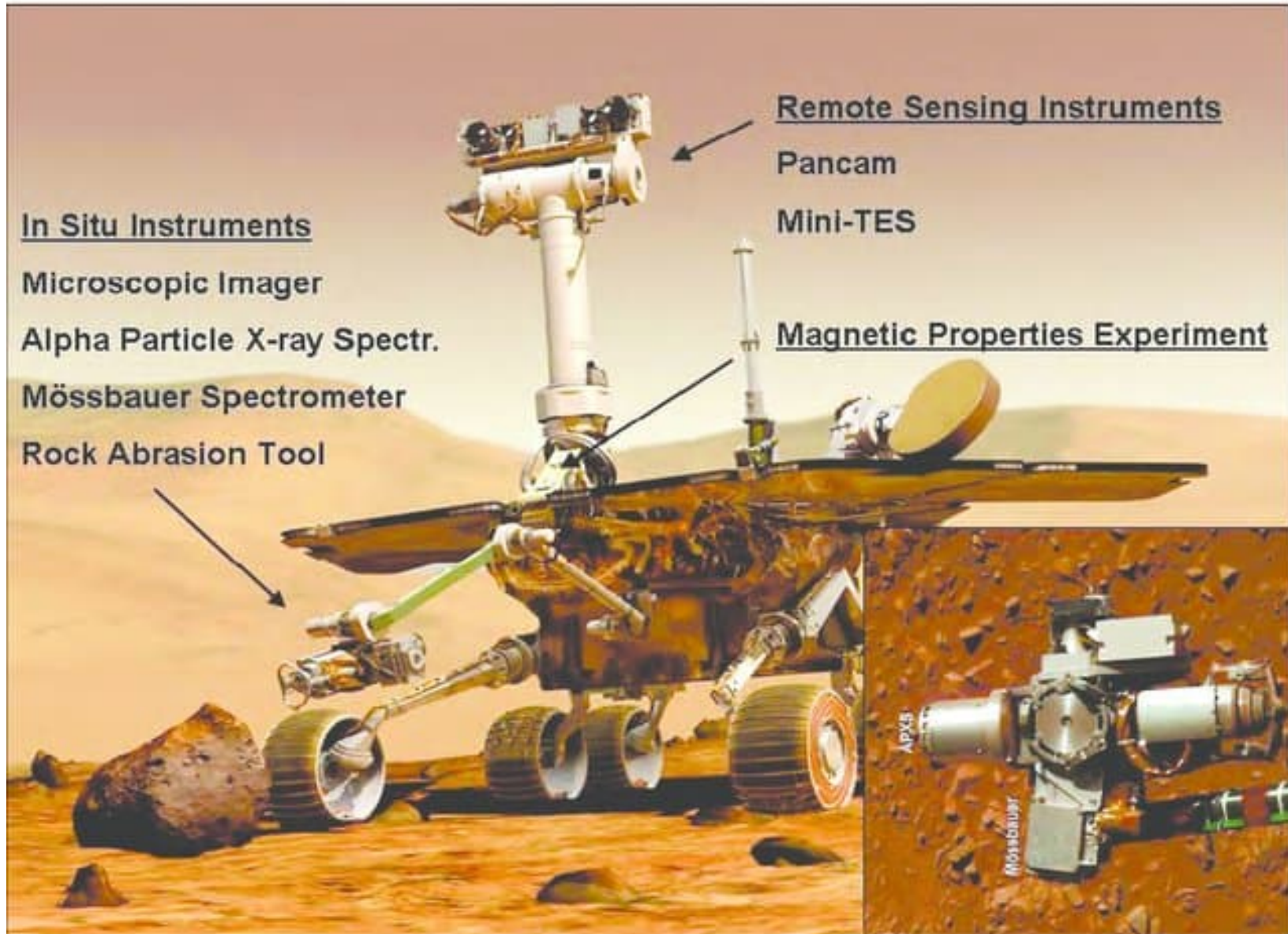


<u>Constituents</u>	<u>A/%</u>
Hematite, $\alpha\text{-Fe}_2\text{O}_3$	16
Magnetite, Fe_3O_4	64
Goethite, $\alpha\text{-FeOOH}$	13
Martensite	5
$\beta/\gamma\text{-FeOOH}$	2

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):

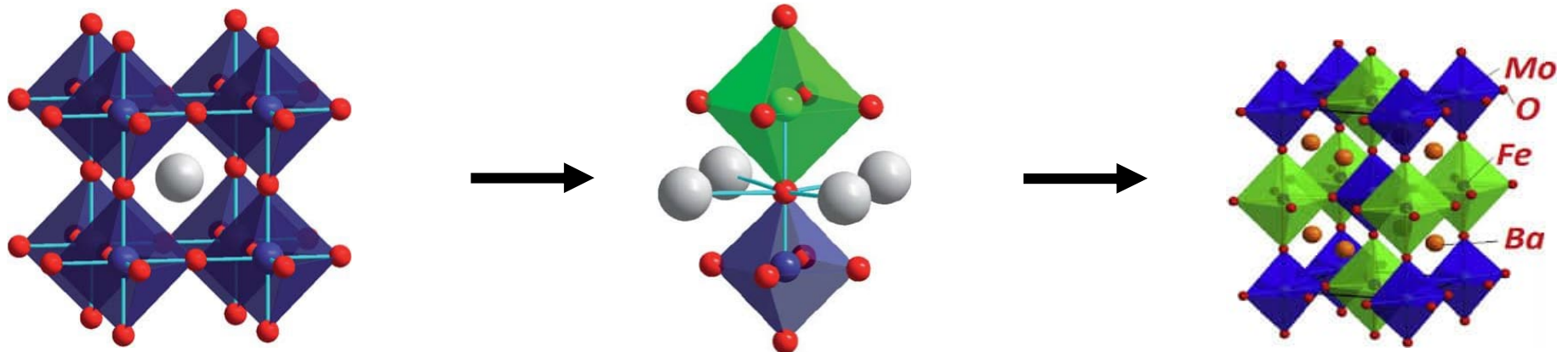
Mössbauer spectrometer is one of the instruments on the robotic arm



Mössbauer examples for DOUBLE PEROVSKITES

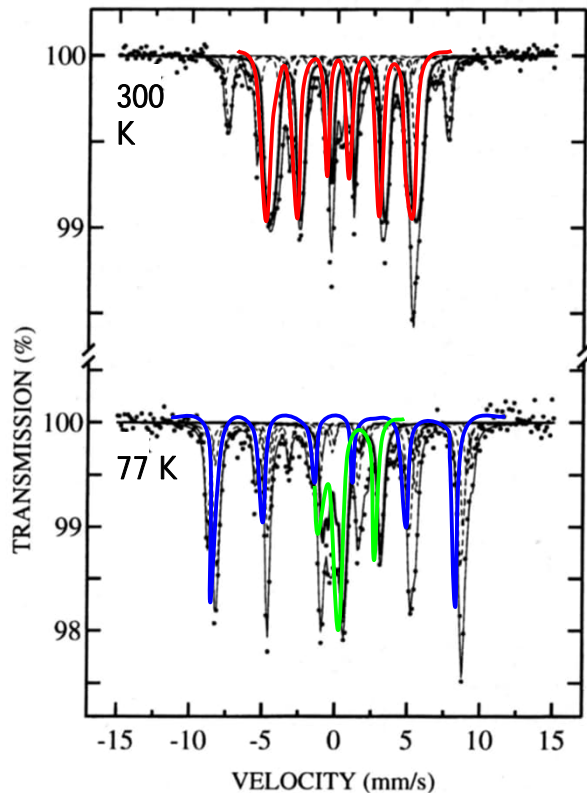
RECALL from the first lecture:

- 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 $\text{Sr}_2\text{FeMoO}_6$: 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 $\text{Sr}_2\text{FeMoO}_6$ (this kind of disorder destroys rapidly the ferrimagnetic/halfmetallic properties)

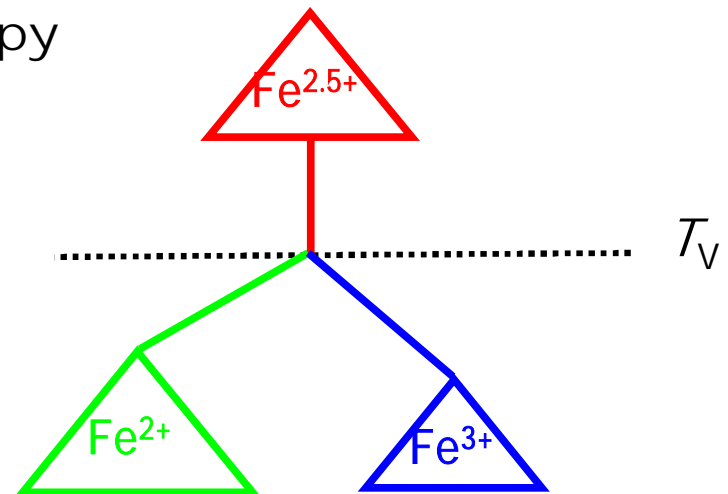


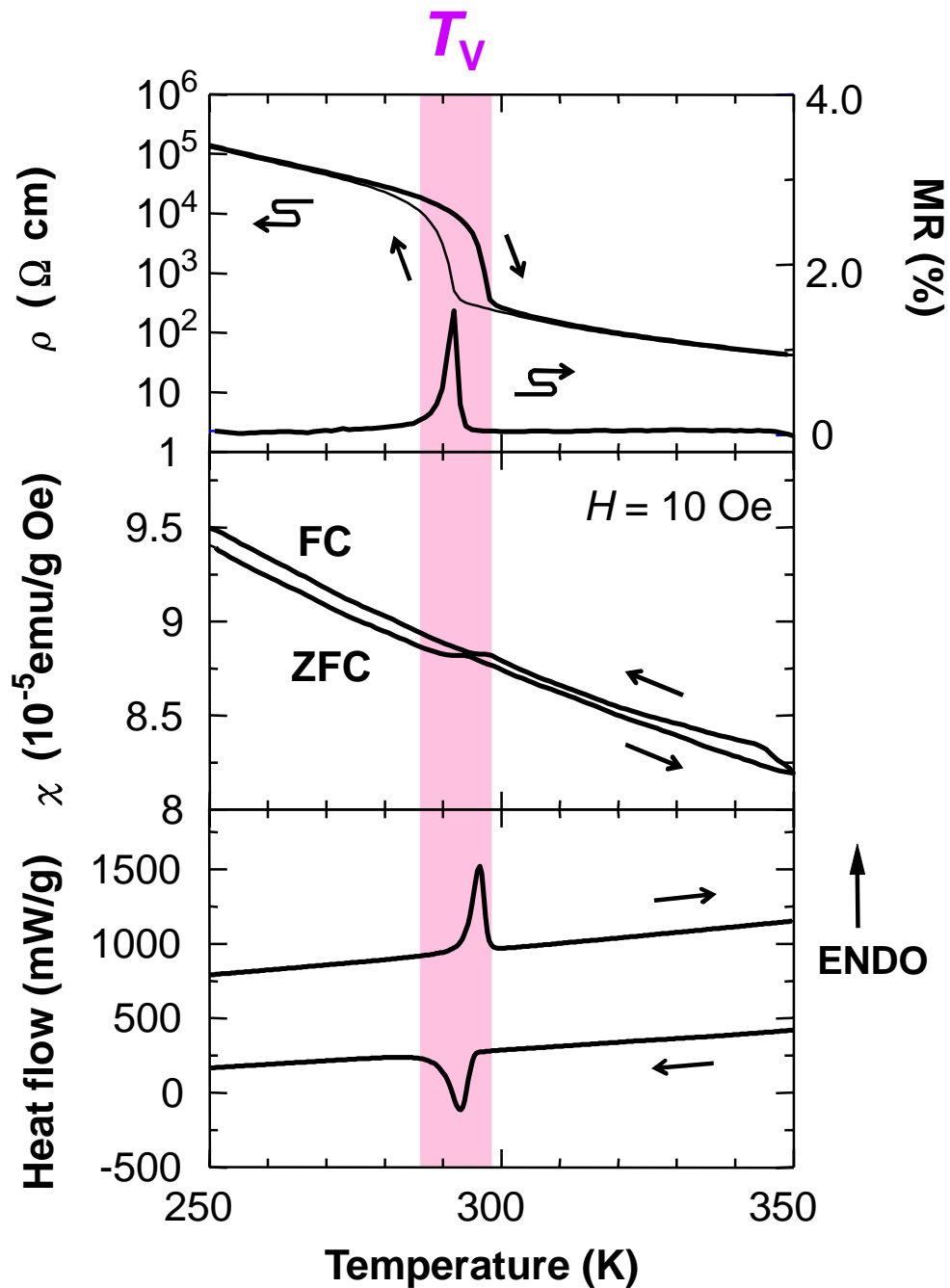
A-site ordered DP with oxygen vacancies $\text{Ba}^{\text{II}}\text{Sm}^{\text{III}}\text{Fe}_2\text{O}_{5.0}$

- Question: $2 \text{Fe}^{2.5}$ or $\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$
- Mössbauer spectra tell us: there is a transition of $2 \text{Fe}^{2.5} \rightarrow \text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}$ at a certain temperature (Verwey temperature T_V)
- Above T_V : only one sextet \rightarrow only one type iron \rightarrow magnetic $\text{Fe}^{2.5}$
- Below T_V : two different sextets $\rightarrow \text{Fe}^{\text{II}} + \text{Fe}^{\text{III}} \rightarrow$ both magnetic but Fe^{III} with larger magnetic field (wider splitting of sextet)



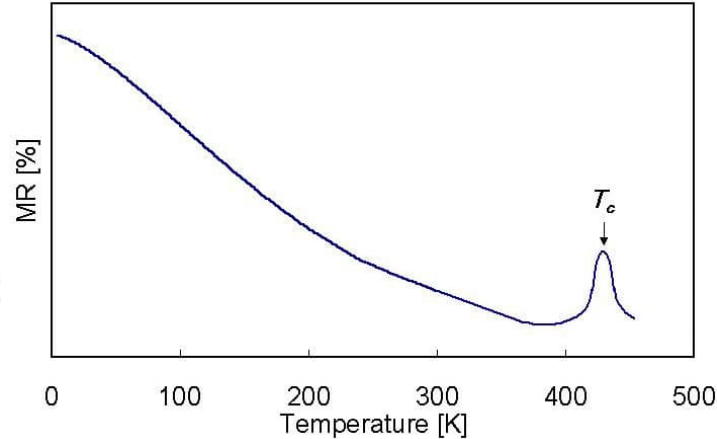
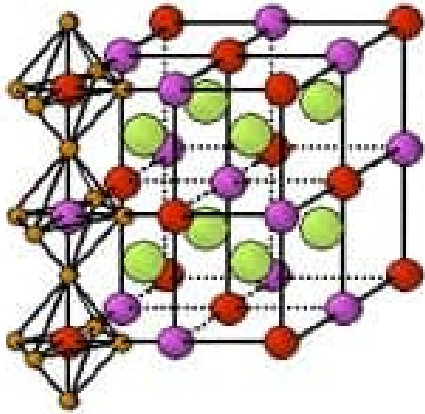
^{57}Fe
Mössbauer
spectroscopy





$\text{BaSmFe}_2\text{O}_{5.0}$

Many physical
properties change at T_V

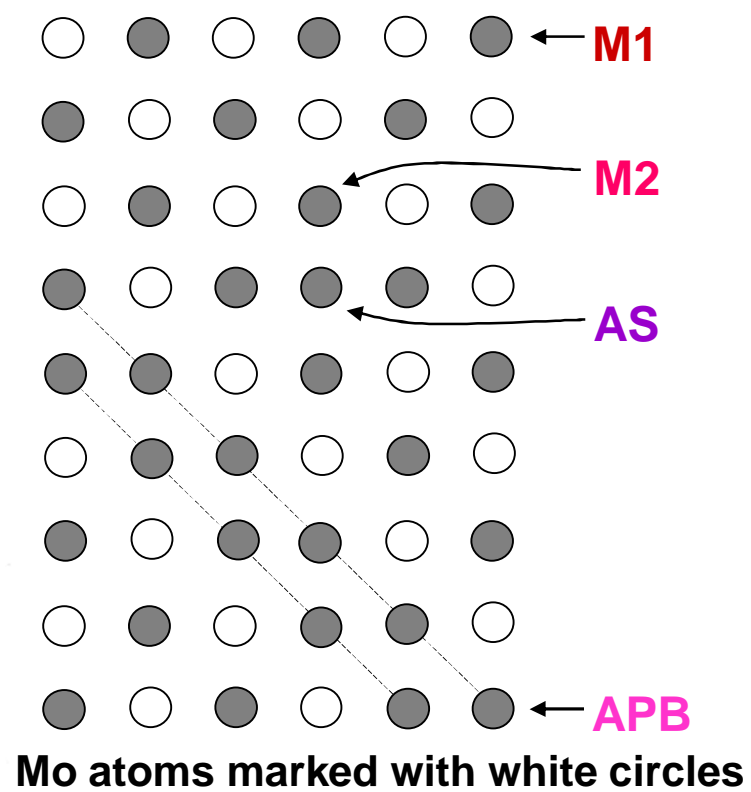
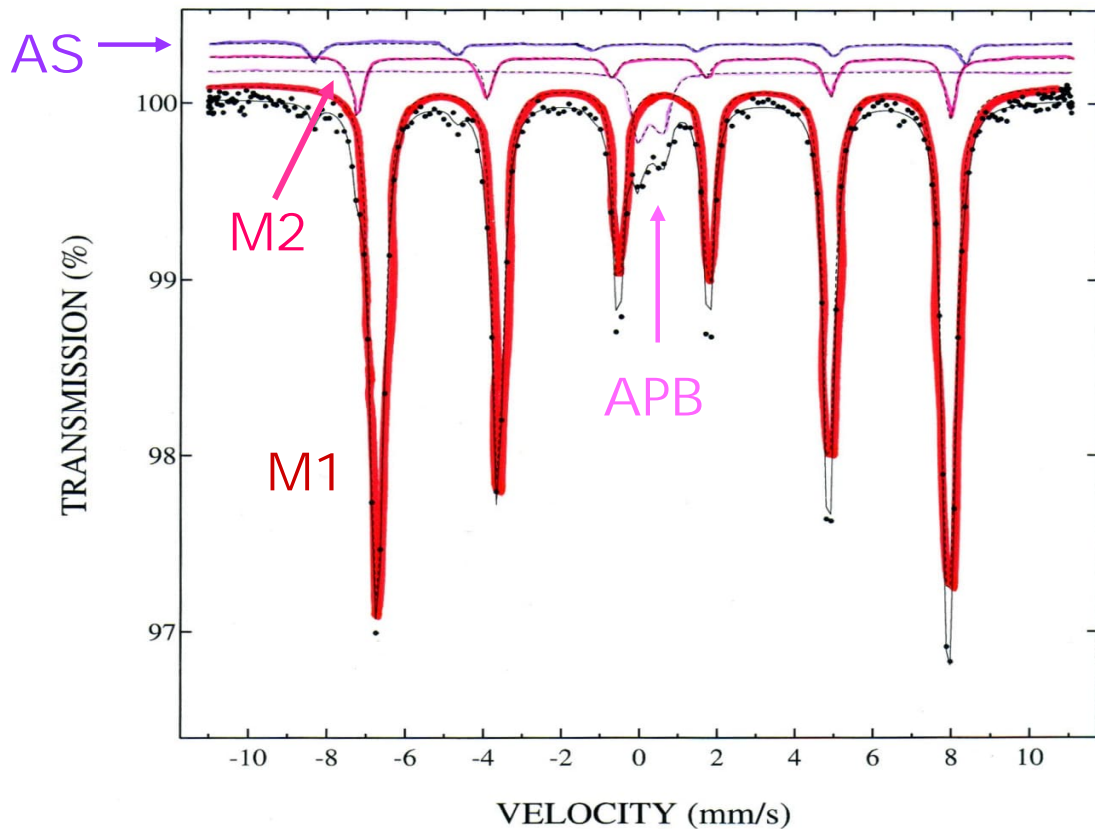


**B-site ordered
double perovskite**

- **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: $\text{Fe}^{\text{III}} d^5$ (*hs*) & $\text{Mo}^{\text{V}} d^1$**
- **Mössbauer: $\text{Fe}^{2.5}$ & $\text{Mo}^{5.5}$**

Mixed-valent iron: $\text{Sr}_2\text{Fe}^{\text{II/III}}\text{Mo}^{\text{V/VI}}\text{O}_6$

“Evidence for **Valence Fluctuation** of Fe in $\text{Sr}_2\text{FeMoO}_{6-w}$ Double Perovskite”,
J. Lindén, T. Yamamoto, M. Karppinen, H. Yamauchi and T. Pietari,
Appl. Phys. Lett. 76, 2925 (2000).



We can see for $\text{Sr}_2\text{FeMoO}_6$ 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 $\text{Fe}^{2.5}$
- 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)