

SCHEDULE

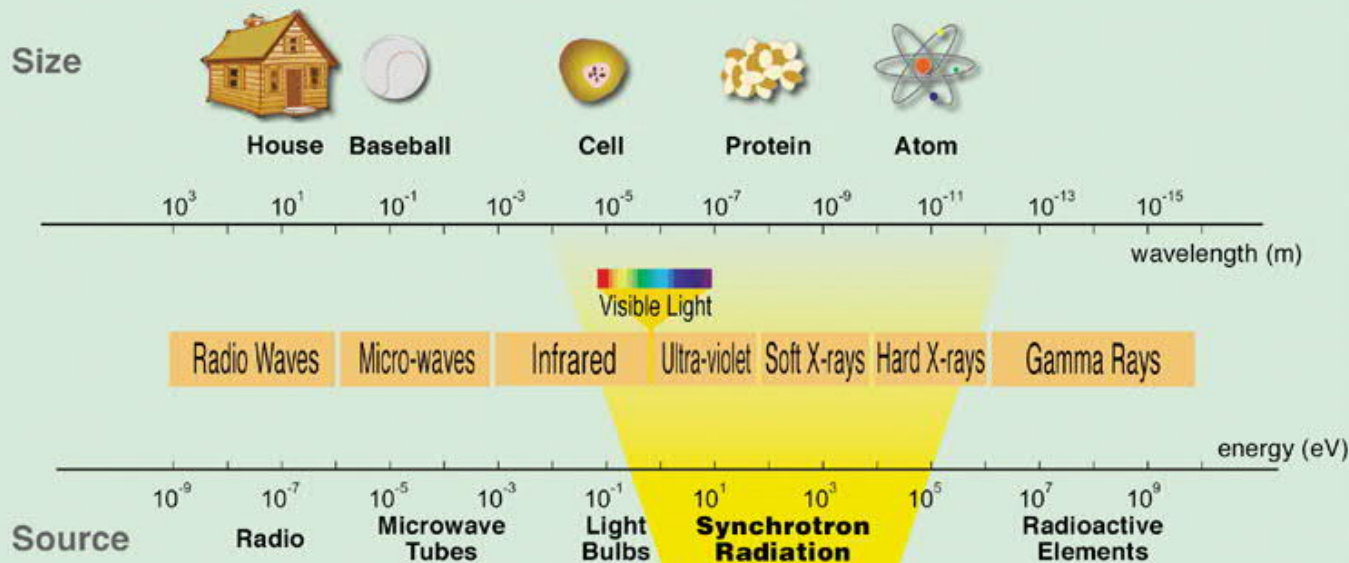
	Date	Topic
1.	Tue 14.09.	Lec-1: Introduction
2.	Fri 17.09.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Fri 17.09.	EXERCISE 1
4.	Tue 21.09.	Lec-3: Crystal chemistry & BVS
5.	Fri 24.09.	Lec-4: Molecular Symmetry & Point Groups
6.	Fri 24.09.	EXERCISE 2
7.	Tue 28.10.	Lec-5: Crystallography & Space Groups
8.	Fri 01.10.	Lec-6: XRD & Reciprocal Lattice
9.	Fri 01.10.	EXERCISE 3
10.	Tue 05.10.	Lec-7: ND
11.	Fri 08.10.	Lec-8: Rietveld
12.	Fri 08.10	EXERCISE 4: Rietveld
13.	Tue 12.10.	Lec-9: Synchrotron rad. & XAS & RIXS
14.	Fri 15.10.	Lec-10: EXAFS & Mössbauer
15.	Fri 15.10.	EXERCISE 5
16.	Tue 19.10.	Seminars: XPS, ED, HRTEM, SEM, AFM
17.	Fri 22.10.	Lec-11: GI-XRD & XRR (10.00-11.30)
18.	Fri 22.10.	EXERCISE 6: XRR (12.00→)

EXAM: Friday, Oct. 29th, 2021

SYNCHROTRON RADIATION

- Continuous band of electromagnetic spectrum including infrared, visible light, ultraviolet and x-rays
- Accidentally discovered in an electron synchrotron of the General Electric Company, USA, in 1947

The Electromagnetic Spectrum

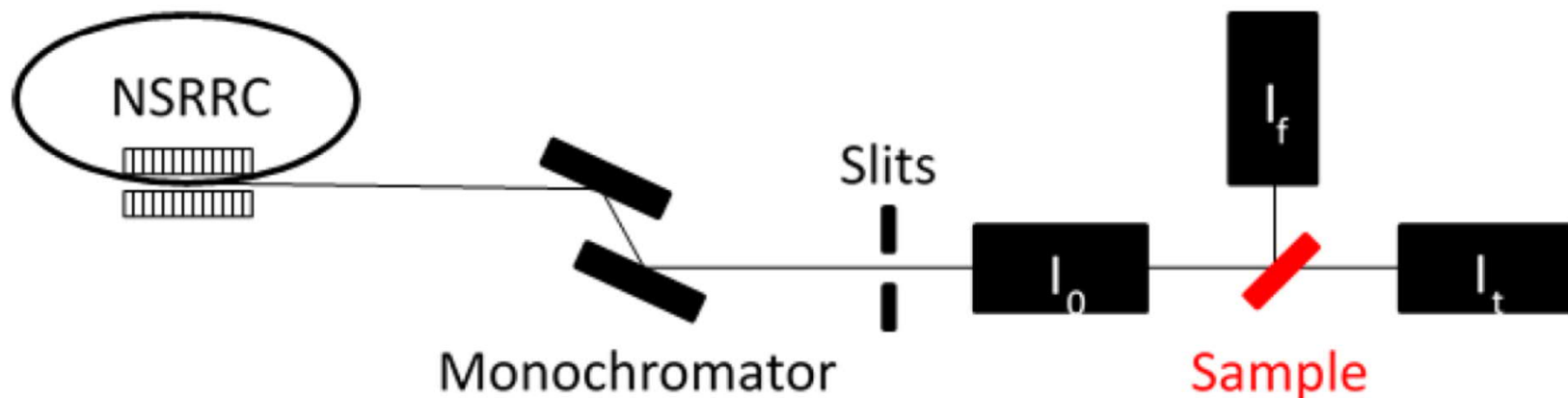


National Synchrotron Radiation Research Center (NSRRC), Hsinchu, TAIWAN



XANES & EXAFS

- Collaboration with Dr. Jin-Ming Chen
→ 38 joint publications since 2001
- Cu-K, Cu-L, Fe-K, Fe-L, Co-L, Ru-L, Nb-L, Ta-L, Mo-L, W-L, Bi-L, Ce-M, Sr-K, Se-K, **O-K**



NSRRC, Taiwan

National Synchrotron Radiation Research Center

- Relatively small synchrotron
- Particularly suitable for light elements, e.g. oxygen → We are frequent users
- Creation of ACCELERATED ELECTRONS
 - electrons are injected from an **Electron Gun**
 - pre-accelerated to 50 MeV in a linear **LINAC**
 - accelerated to 1.5 GeV in a **Booster Ring**

Electron Gun



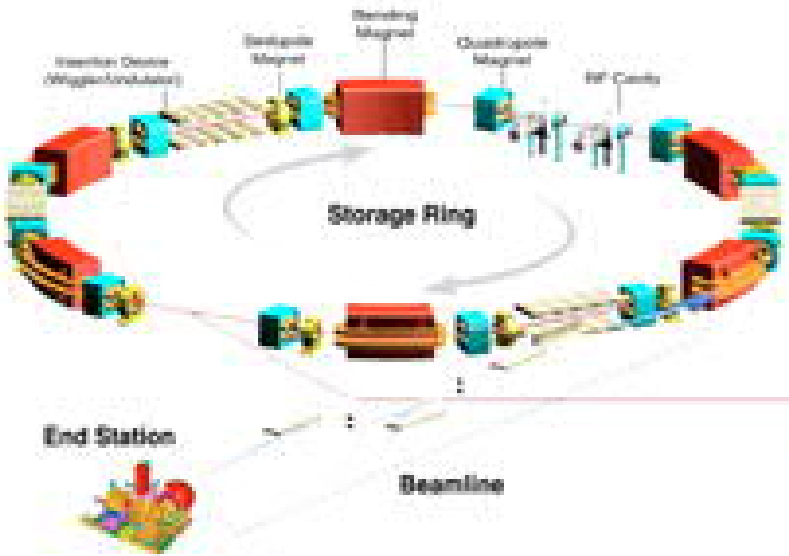
- Booster Ring (72 m in circumference):**
- Electrons with 99.999995 % of light speed

LINAC

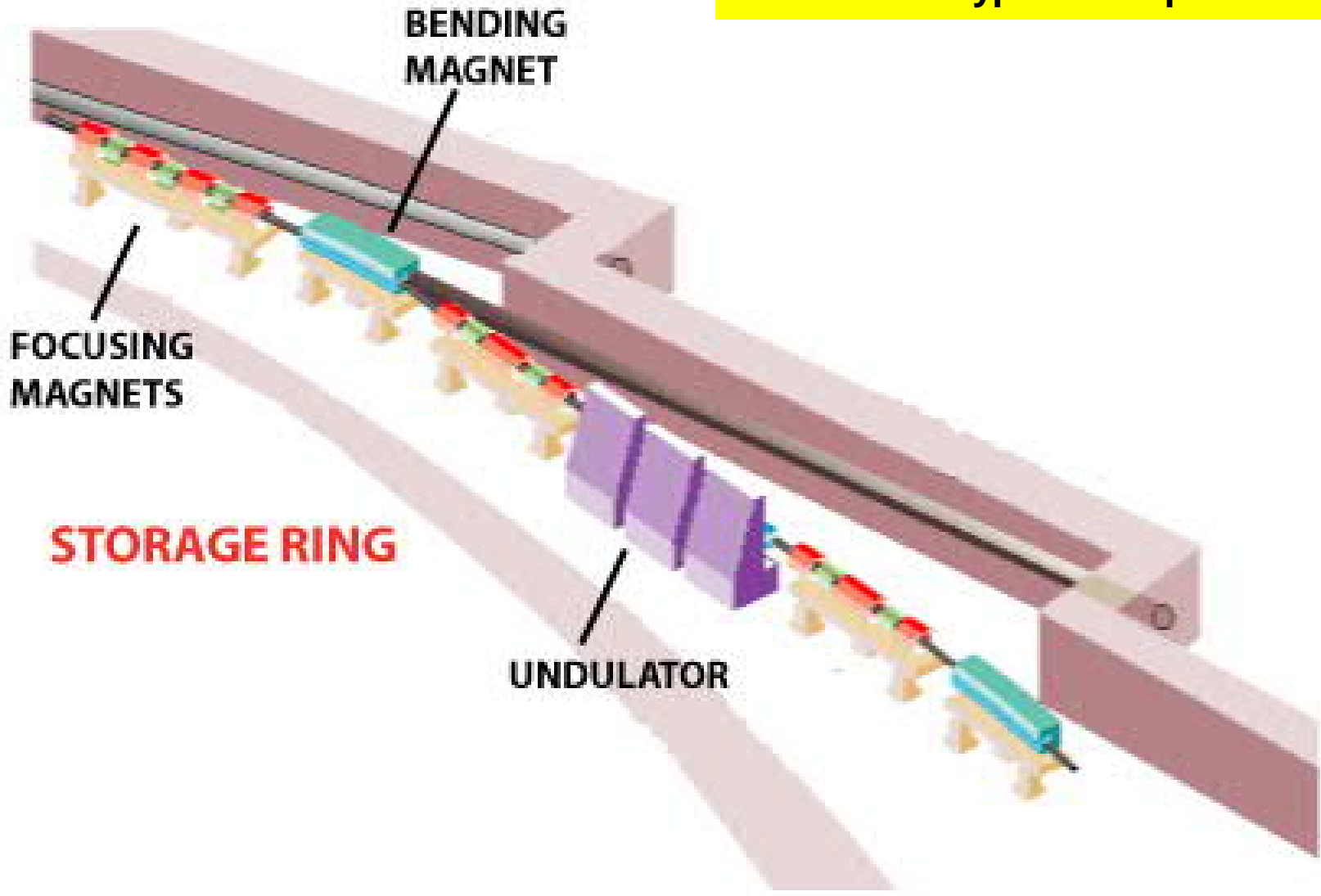


Accelerated electrons are sent through a 70-meter long **Transport Line** into a hexagonal, 120-meter **Storage Ring**, where they circulate with an energy of 1.5 GeV in ultra-high-vacuum pipes for several hours, emitting synchrotron radiation.

Transport Line



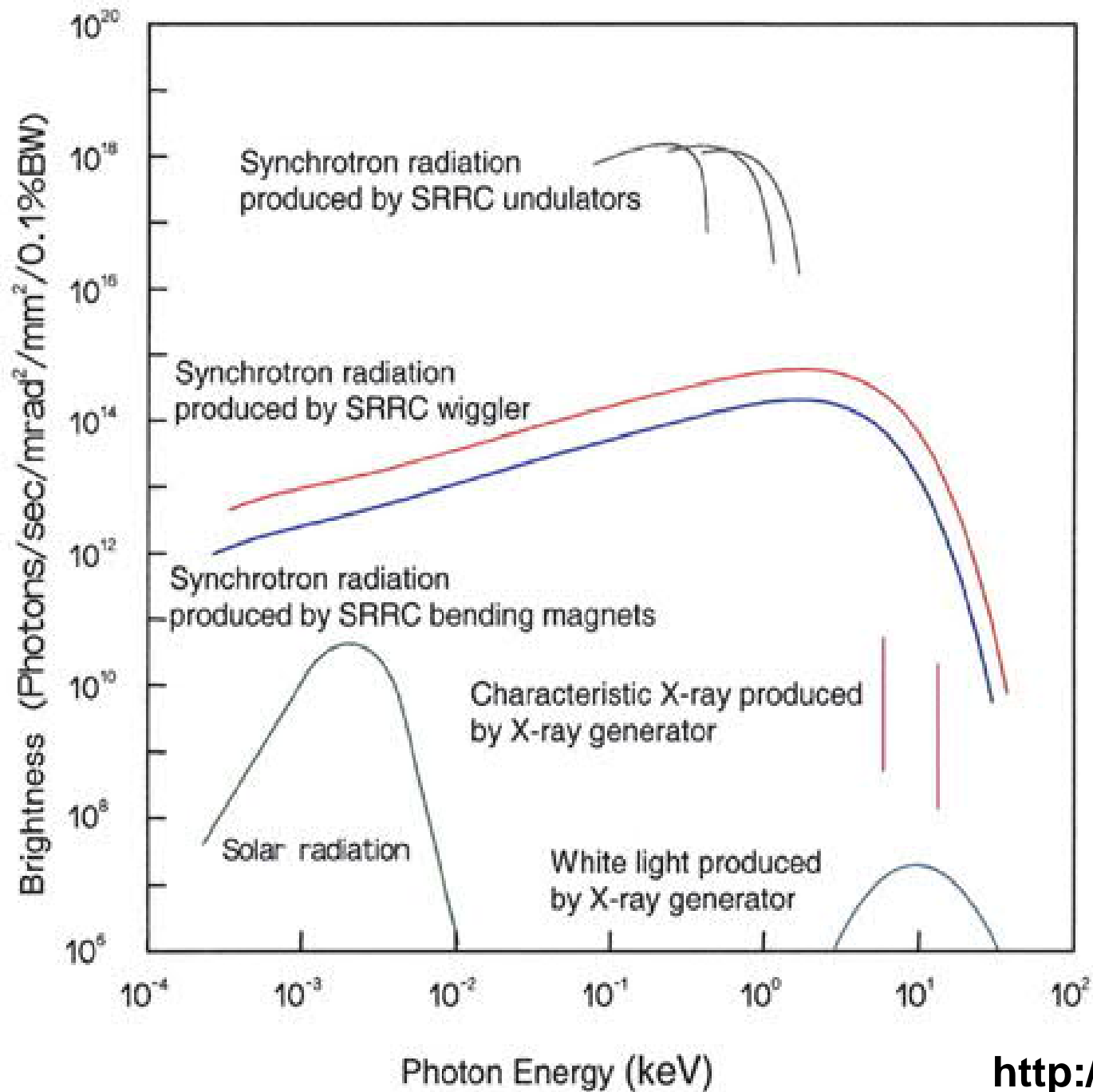
There are different types of **magnets** attached to the storage ring to generate X-ray light with different characteristics for different types of experiments



The emitted light is channeled through **Beamlines** to the **Experimental Stations**, where experiments are conducted.



HFM: Horizontal Focussing Mirror
VFM: Vertical Focussing Mirror
RFM: Refocussing Mirror



XAS: X-ray Absorption Spectroscopy

XAFS: X-ray Absorption Fine-Structure

XANES: X-ray Absorption Near-Edge Structure

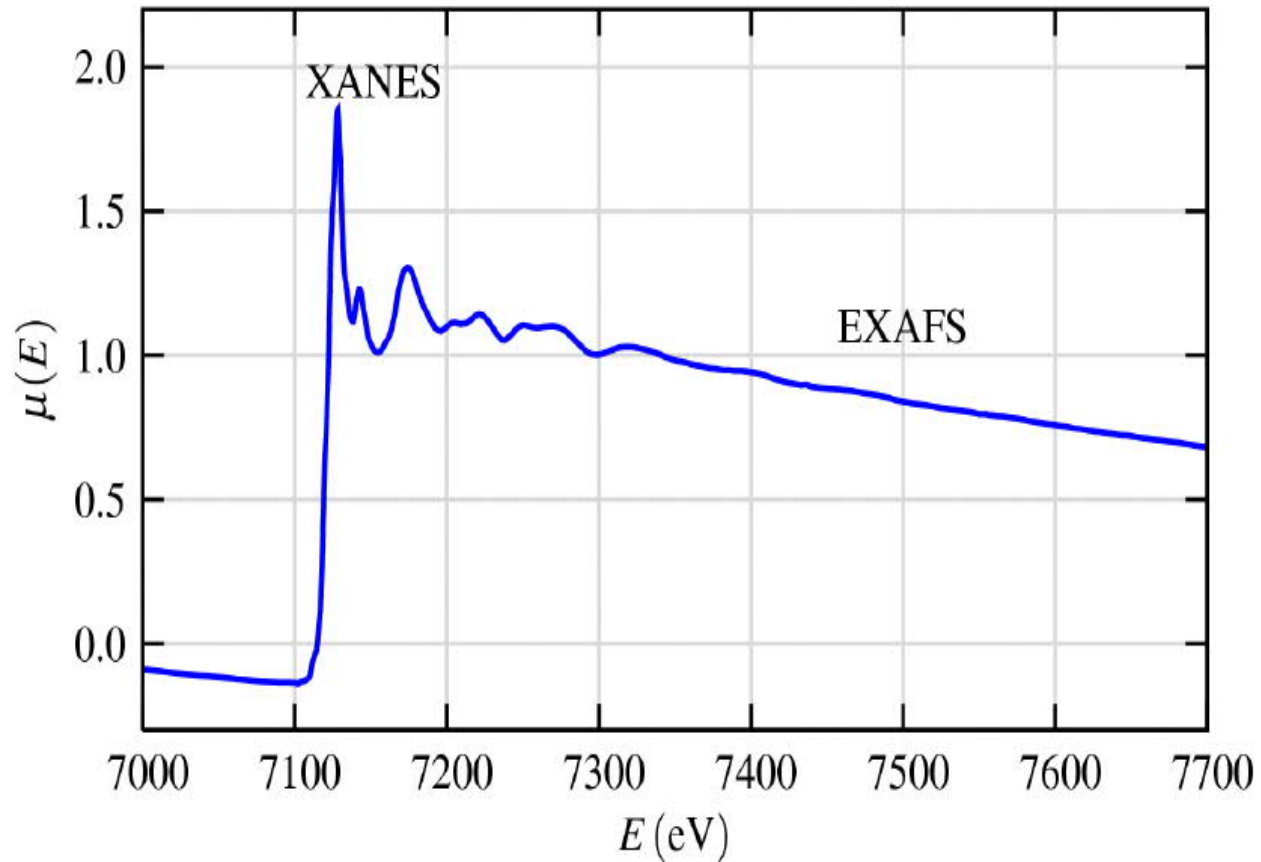
RIXS: Resonant Inelastic X-ray Scattering

EXAFS: Extended X-ray Absorption Fine-Structure

EXAFS

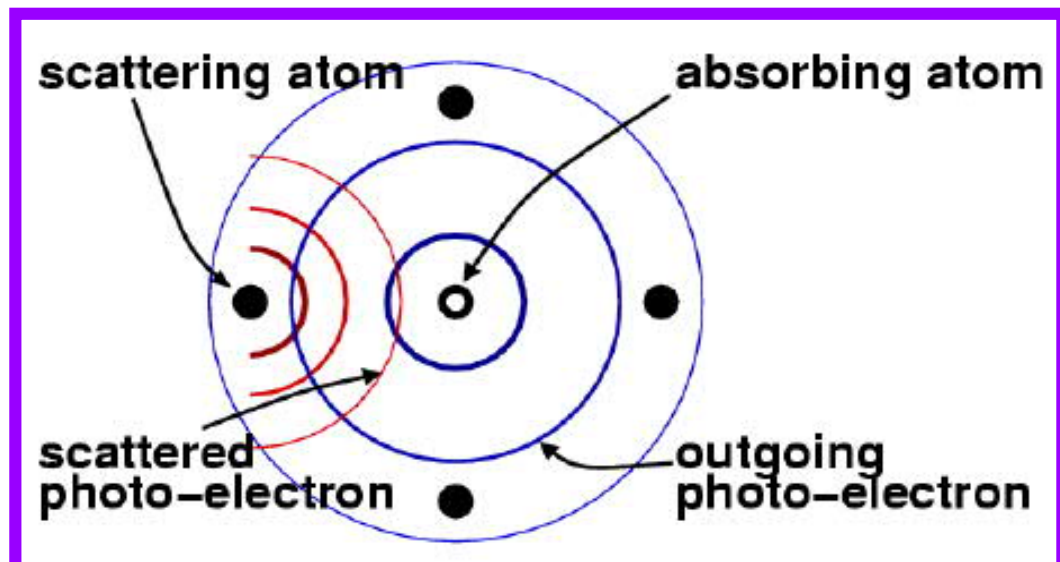
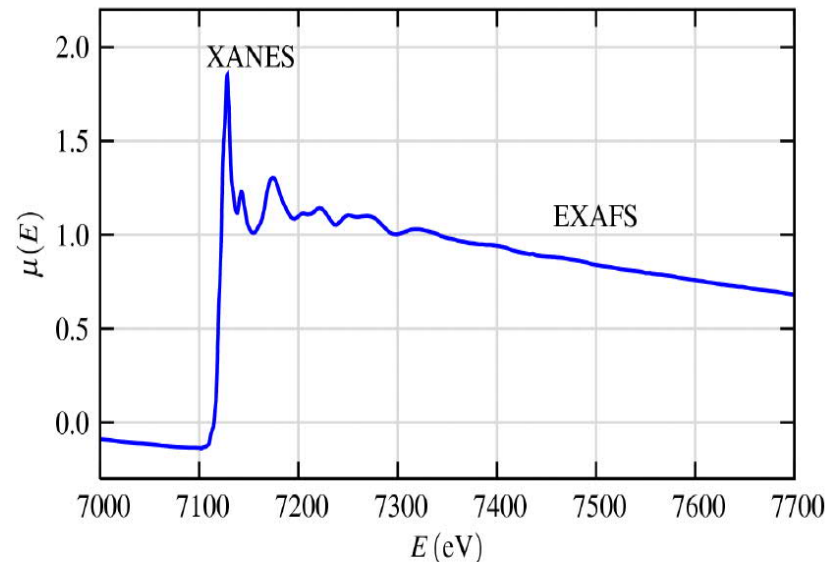
- X-ray absorption is measured in the vicinity of absorption edge
- Synchrotron radiation → **intense** and **continuous** X-ray radiation
- Absorption edge energy is element specific → EXAFS is element specific
- Possible for all elements except for the very lightest elements

μ : absorption coefficient



EXAFS (Extended X-ray Absorption Fine Structure)

- Oscillations in the high-energy side of the absorption edge
- Oscillations explained in the 1970s → EXAFS theory
- Simplified explanation: x-ray energy absorbed → photoelectrons removed from inner shell → sphere waves → scatter from the **neighbouring atoms**
Due to this backscattering → interference effect → **oscillations** → **EXAFS**
- Oscillations depend on **neighbouring atoms (type, number, distance)**

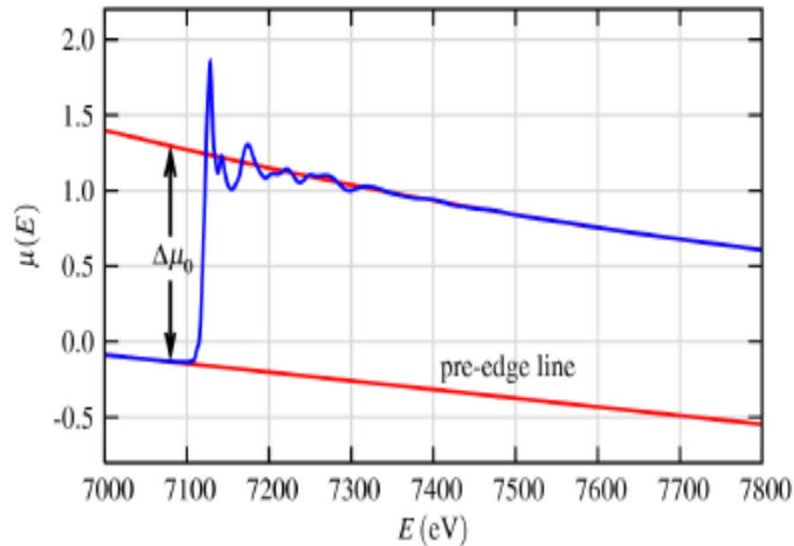


STEPS in EXAFS DATA ANALYSIS

- Conversion of measured intensities to $\mu(E)$
- Pre-edge background subtraction (instrumental errors etc)
- $\mu(E)$ normalized to vary from 0 to 1
- Post-edge background removal (smooth curve)
- Conversion from energy to (photoelectron) wave number: $E \rightarrow k$
- Weighting k values (to give more impact for higher k values)
- Fourier transform from k to R (= distance) space
- Isolation of appropriate "shells" by Fourier filtering
- Modelling to EXAFS equation to get: R and N (= coordination number)

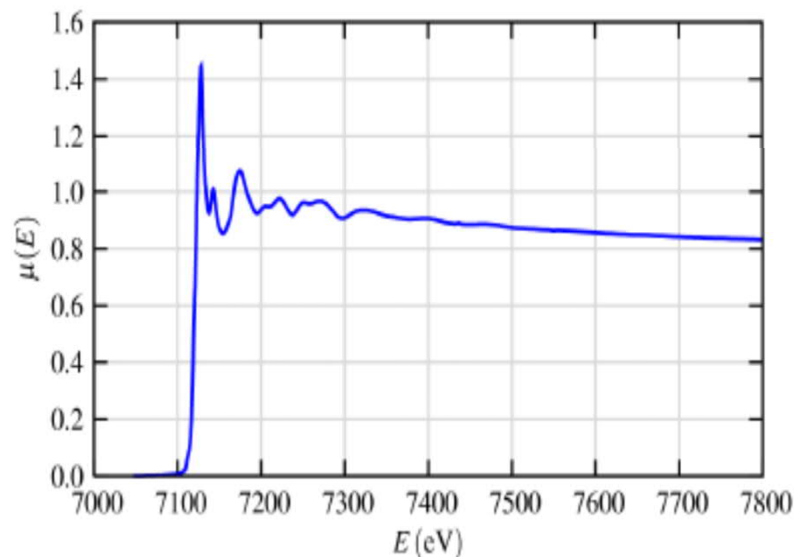
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

- Absorption coefficient (μ) versus X-ray energy
- Pre-edge background subtraction
- Normalization



Pre-Edge Subtraction

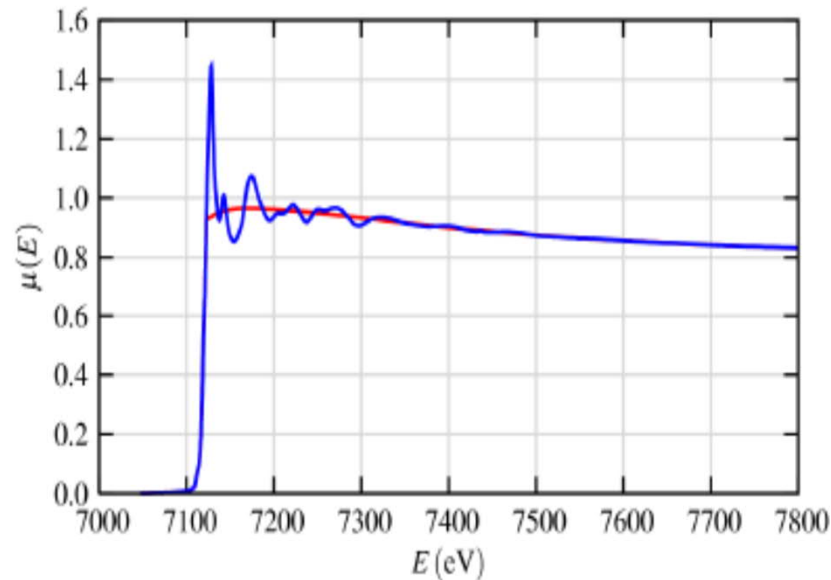
We subtract away the background that fits the *pre-edge* region. This gets rid of the absorption due to other edges (say, the Fe L_{III} edge).



Normalization

We estimate the *edge step*, $\Delta\mu_0(E_0)$ by extrapolating a simple fit to the above $\mu(E)$ to the edge. We normalize by this value to get the absorption from 1 x-ray.

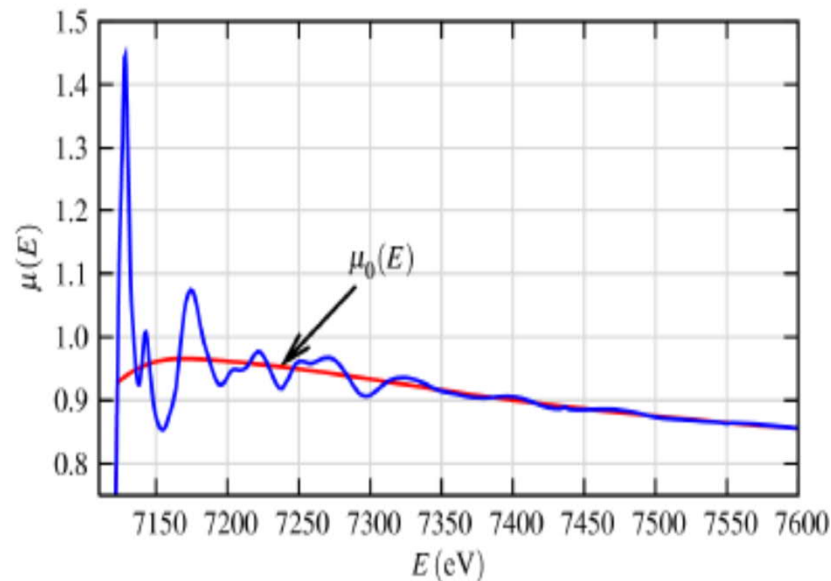
- **Post-edge background subtraction**



Post-Edge Background

We don't have a measurement of $\mu_0(E)$ (the absorption coefficient without neighboring atoms).

We approximate $\mu_0(E)$ by an adjustable, smooth function: a *spline*.

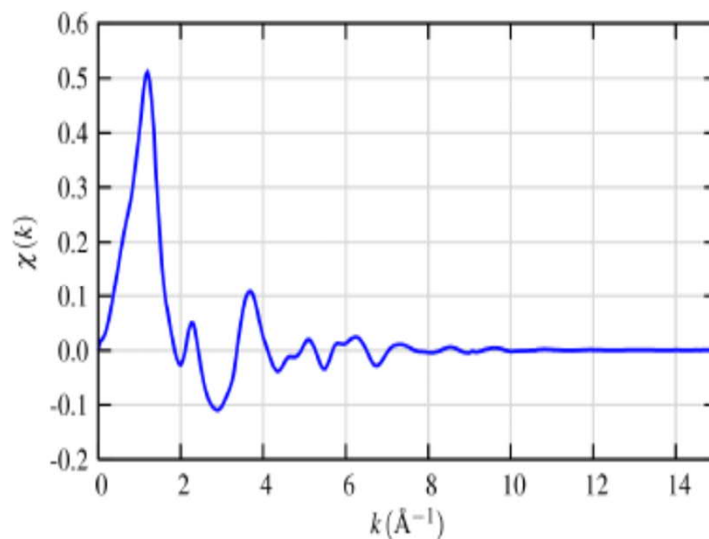


This can be somewhat dangerous – a flexible enough spline could match the $\mu(E)$ and remove all the EXAFS!

We want a spline that will match the *low frequency* components of $\mu_0(E)$.

- Conversion from energy to (photoelectron) wave number: $E \rightarrow k$
- Weighting k values (to give more impact for higher k values)

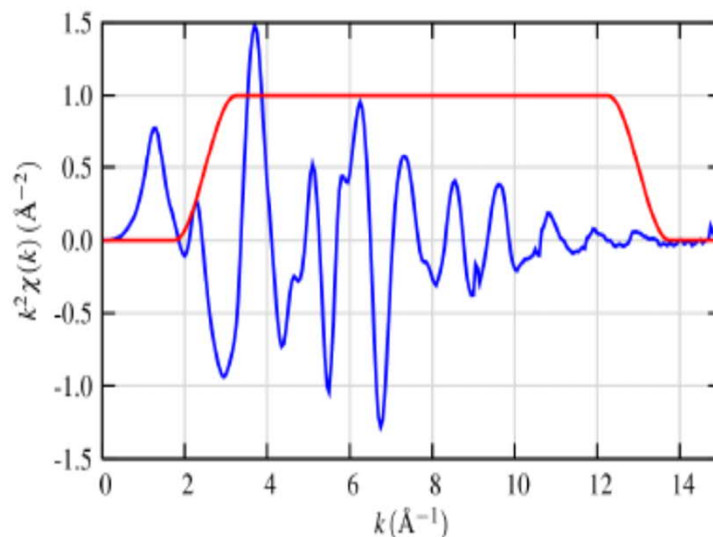
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$



$\chi(k)$

The raw EXAFS $\chi(k)$ usually decays quickly with k , and difficult to assess or interpret by itself.

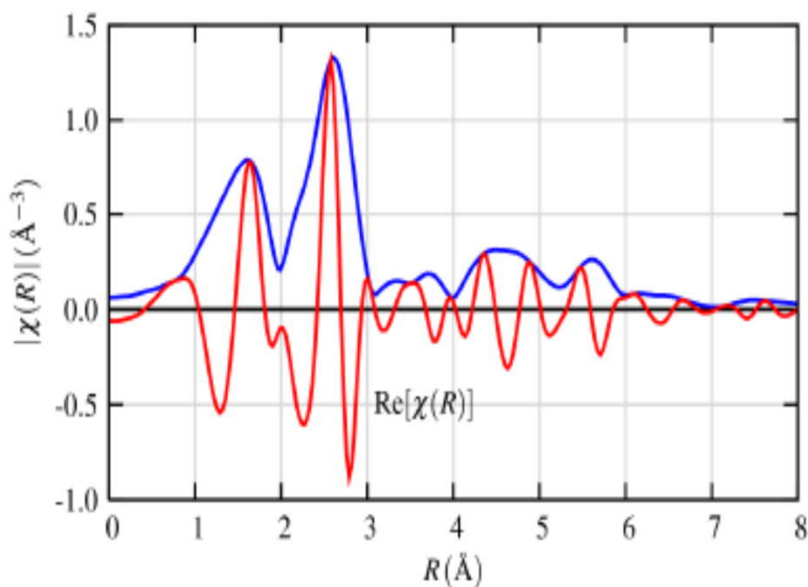
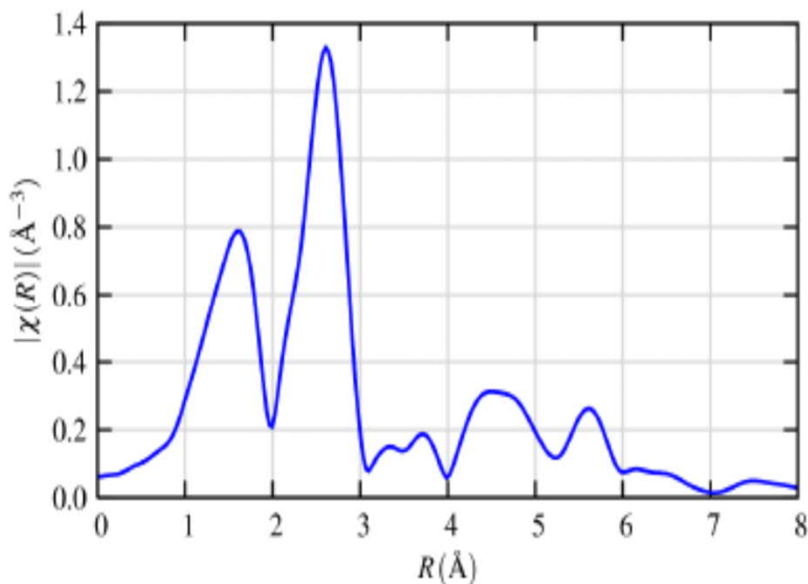
It is customary to weight the higher- k portion of the spectra by multiplying by k^2 or k^3 .



k -weighted $\chi(k)$: $k^2\chi(k)$

$\chi(k)$ is composed of sine waves, so we'll Fourier Transform from k to R -space. To avoid "ringing", we'll multiply by a *window function*.

- Fourier transform from k to R (= distance) space
- Isolation of appropriate "shells" by Fourier filtering



$\chi(R)$

The Fourier Transform of $k^2\chi(k)$ has 2 main peaks, for the first 2 coordination shells: Fe-O and Fe-Fe.

The Fe-O distance in FeO is 2.14Å, but the first peak is at 1.6Å. This shift in the first peak is due to the **phase-shift**, $\delta(k)$: $\sin[2kR + \delta(k)]$.

A shift of -0.5Å is typical.

$\chi(R)$ is complex:

The FT makes $\chi(R)$ complex. Usually only the amplitude is shown, but there are really oscillations in $\chi(R)$.

Both real and imaginary components are used in modeling.

Modelling to EXAFS equation: R (distance) and N (coordination number)

To model the EXAFS, we use the *EXAFS Equation*:

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$

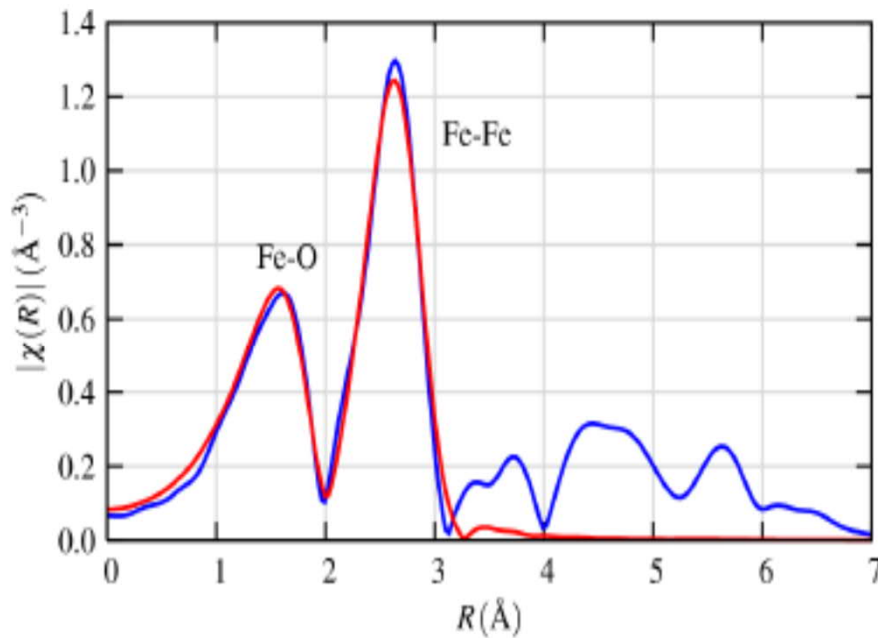
where $f(k)$ and $\delta(k)$ are *photo-electron scattering properties* of the neighboring atom. (The sum is over “shells” of similar neighboring atoms).

If we know these properties, we can determine:

- R distance to neighboring atom.
- N coordination number of neighboring atom.
- σ^2 mean-square disorder of neighbor distance.

The scattering amplitude $f(k)$ and phase-shift $\delta(k)$ depend on atomic number Z of the scattering atom, so we can also determine the species of the neighboring atom.

REMEMBER: phase-shift of ca. 0.5 Å possible



$|\chi(R)|$ data for FeO (blue), and fit of 1st and 2nd shells (red).

The results are fairly consistent with the known values for crystalline FeO:

6 O at 2.13Å, 12 Fe at 3.02Å.

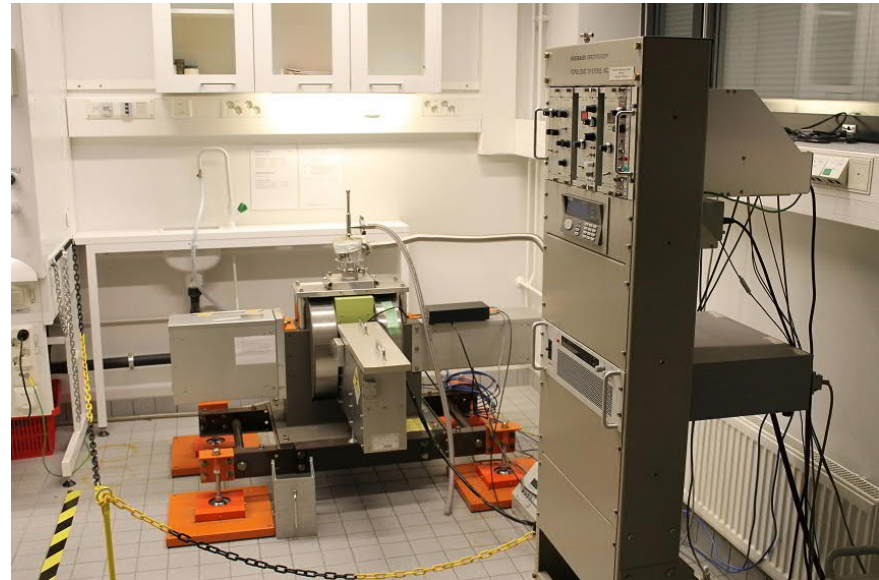
Fit results (uncertainties in parentheses):

Shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
Fe-O	6.0(1.0)	2.10(.02)	0.015(.003)	-2.1(0.8)
Fe-Fe	11.7(1.3)	3.05(.02)	0.014(.002)	-2.1(0.8)

Mössbauer Spectroscopy

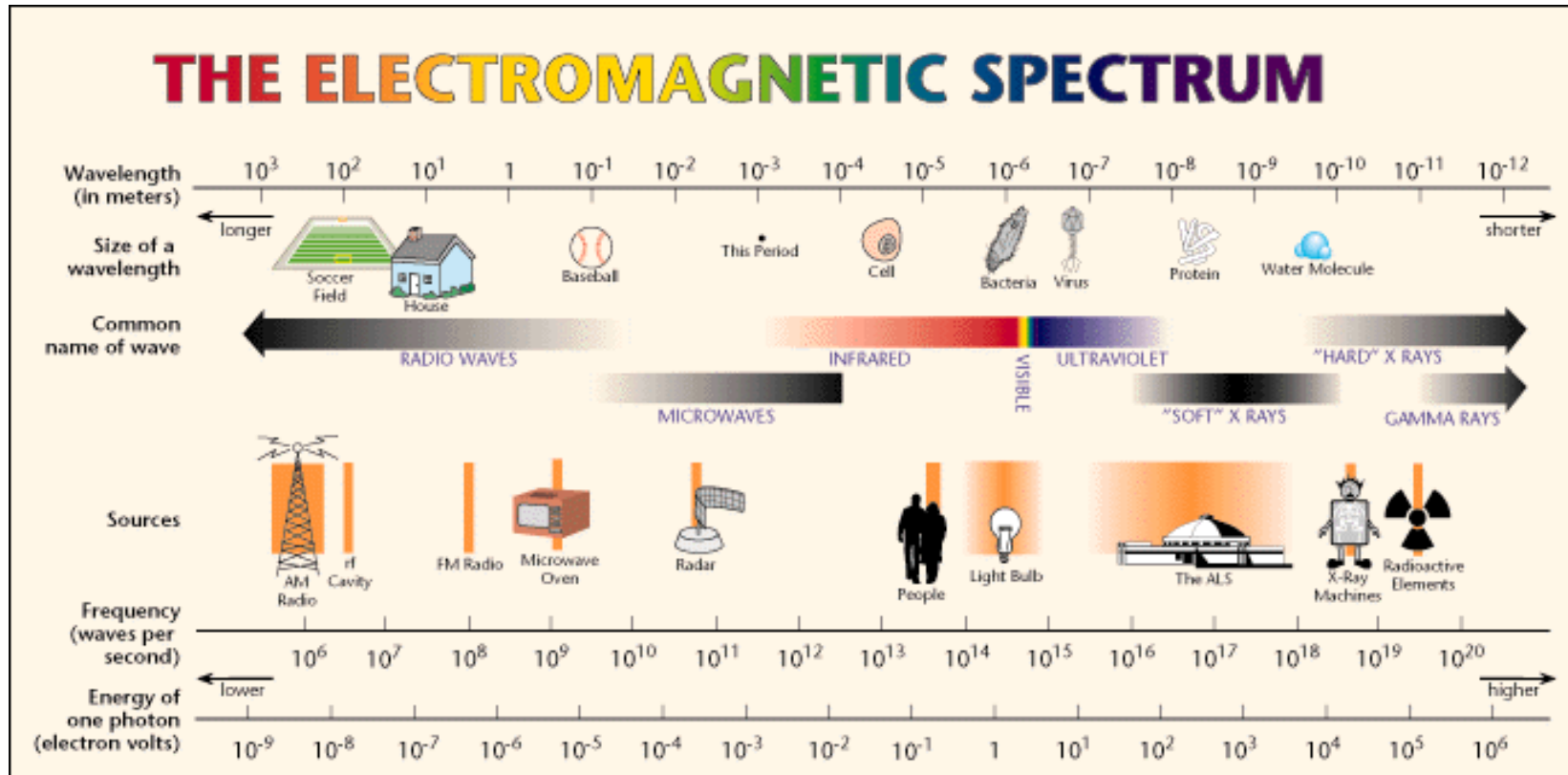
- Gamma rays
- Concepts: Recoil energy & Resonance absorption & Doppler effect
- Mössbauer Phenomenon
- Information obtained:
Chemical (valence), structural (coordination) & magnetic properties
- Suggested reading:
<https://www.rsc.org/Membership/Networking/InterestGroups/MossbauerSpect/Intropart1.asp>

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 $< 1 \mu\text{s}$)
- When the nucleus returns from an excited state (E_e) to the ground state (E_g), the **energy difference** is emitted as gamma rays ($E_0 = E_e - E_g$)



RECOIL ENERGY

- **Momentum Conservation Law:** when gamma rays are emitted the nucleus gets a **recoil impulse** of the opposite direction (imagine what happens to the boat when the passenger jumps from it to the dock)

- Corresponding **recoil energy (= energy loss):** $E_{\text{recoil}} \approx 10^{-2} \text{ eV}$

$$E_{\text{recoil}} = E_0^2 / 2mc^2$$

- For less-energetic radiation E_{recoil} is negligible
- Due to the recoil energy, gamma rays lose their capability to be absorbed by similar atom nuclei

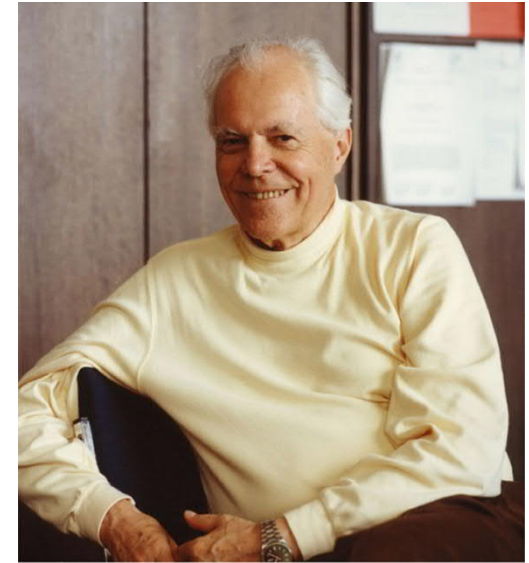
i.e. so-called **RESONANCE ABSORPTION** is **NOT** possible

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 (with increasing atomic number)
 - with decreasing temperature

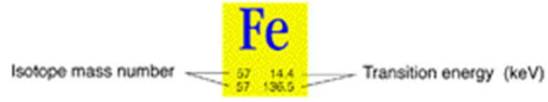
MÖSSBAUER PHENOMENON

- 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 ca. 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

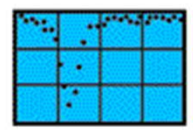
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
40 29.6						55 195.9	57 14.4 57 136.5		61 67.4 60 87.1		67 90.3		73 13.3 73 67.9				83 9.4
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
						99 140.5	99 89.4			107 53.5 109 86.6			117 159.0 118 23.9 118 86.5	121 37.1	125 35.5 125 109.0	127 57.6 129 27.8	129 39.6 131 83.2
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
133 81.0	133 12.3	139 165.9	175 86.3 177 113.0 178 33.1 180 93.3	181 6.2 181 136.2	180 103.7 181 113.3 182 100.1 183 48.9 183 99.1 184 111.2 186 122.3	187 134.2	186 137.2 189 150.0 189 30.2 190 138.9	191 82.4 191 129.3 193 73.0	195 98.8 195 120.7	197 77.4	201 32.2		207 83.8 208 2.0 208 83.8				
Fr	Ra	Ac															



Number of publications

- N > 1000
- 100 < N < 1000
- 10 < N < 100
- N < 10
- Silent

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	141 145.4	145 67.3 145 72.0	145 51.0 147 91.1	147 122.1 149 22.5 151 95.6 152 121.8 153 35.8 154 82.0	151 21.6 153 83.1 153 97.4 153 103.2	154 123.1 155 60.0 155 86.5 155 105.3 156 89.0 157 54.5 157 64.0 158 79.5 159 73.3	159 58.0	160 80.8 161 25.7 161 43.6 161 74.6 162 80.7 164 72.4	165 94.7	164 91.4 166 80.6 167 79.3 168 79.8 170 79.3	169 8.4	170 84.3 171 58.7 171 75.9 172 78.7 174 79.5 176 82.1	175 113.8
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232 49.4	231 84.2	234 43.5 236 45.2 238 44.0	237 59.5	239 57.3 240 42.9	243 84.0								



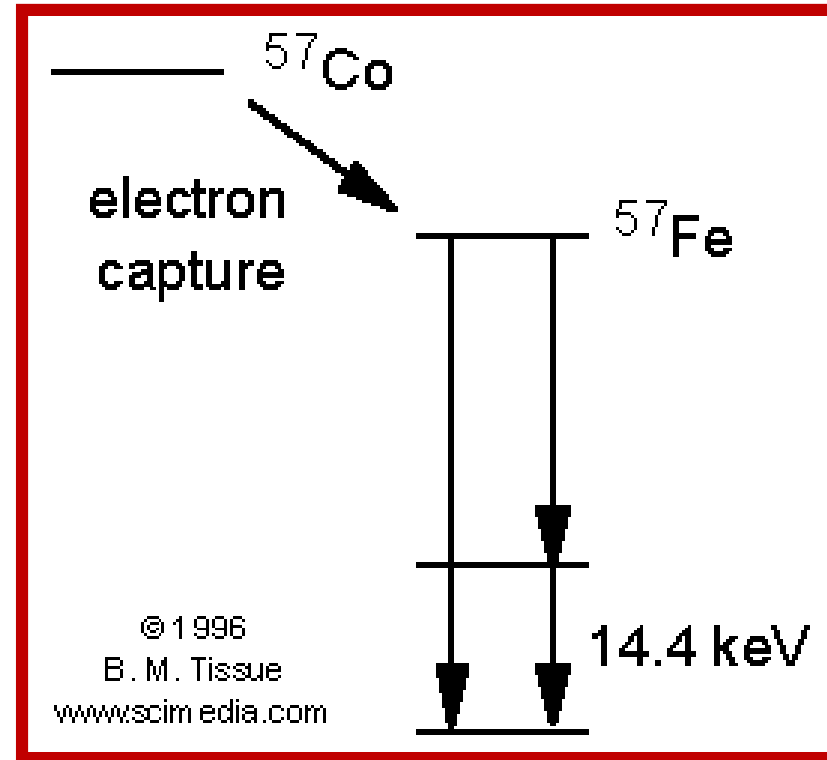
Mössbauer Effect Data Center

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

⁵⁷Fe 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)

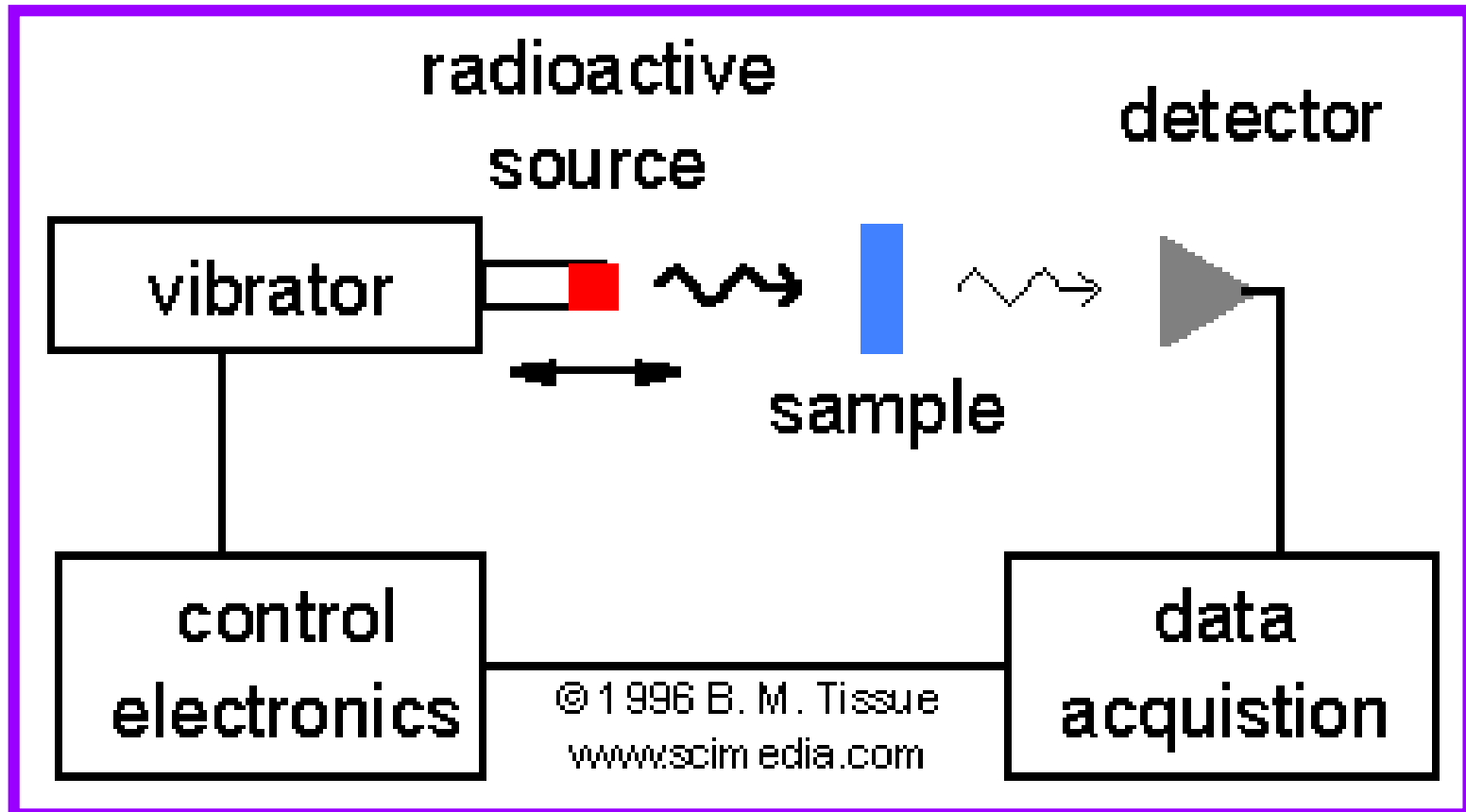


RECORDING of MÖSSBAUER SPECTRUM

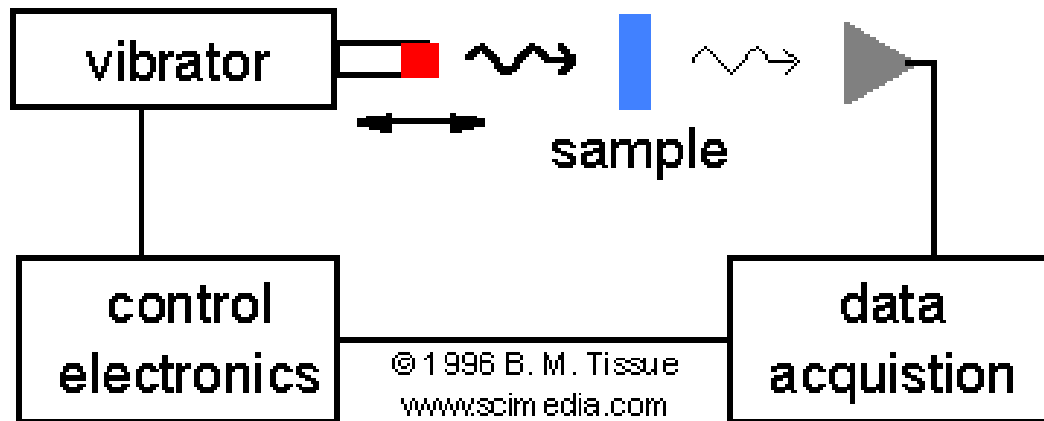
- E_0 slightly depends on the environment of the Mössbauer nucleus (e.g. E_0 of ^{57}Fe is different in Fe metal and in FeSO_4)
 - ΔE_0 is a parameter that reflects the difference of the two environments
- In Mössbauer measurement it is possible to experimentally observe the resonance absorption (i.e. 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: e.g. iron bulk containing 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



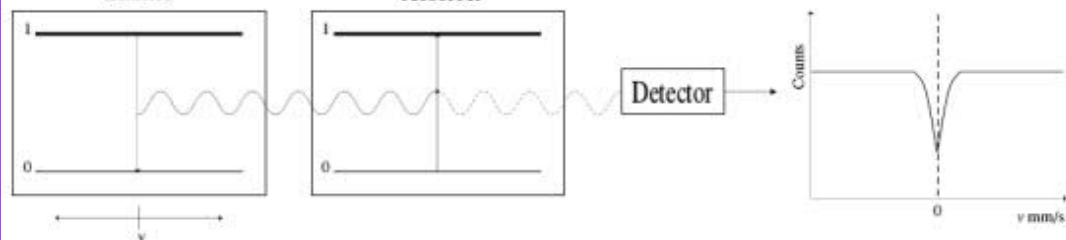
radioactive
source



- 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.

Emitter

Absorber

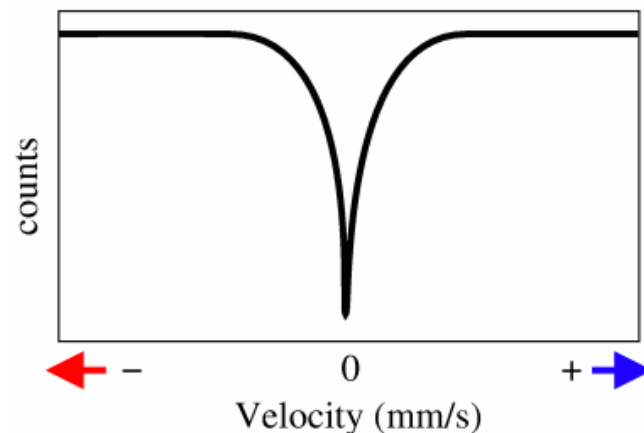
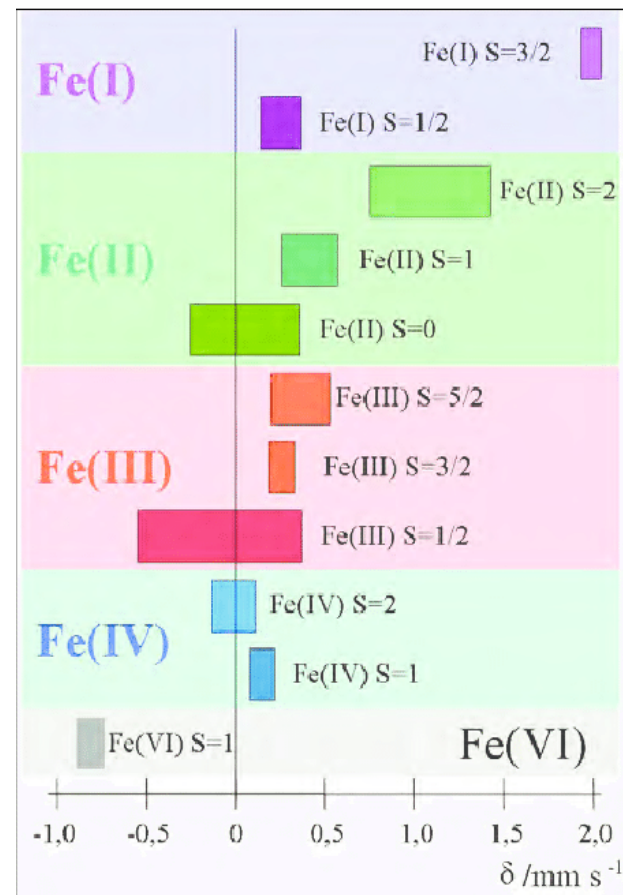


MÖSSBAUER SPECTROSCOPY

- 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**)

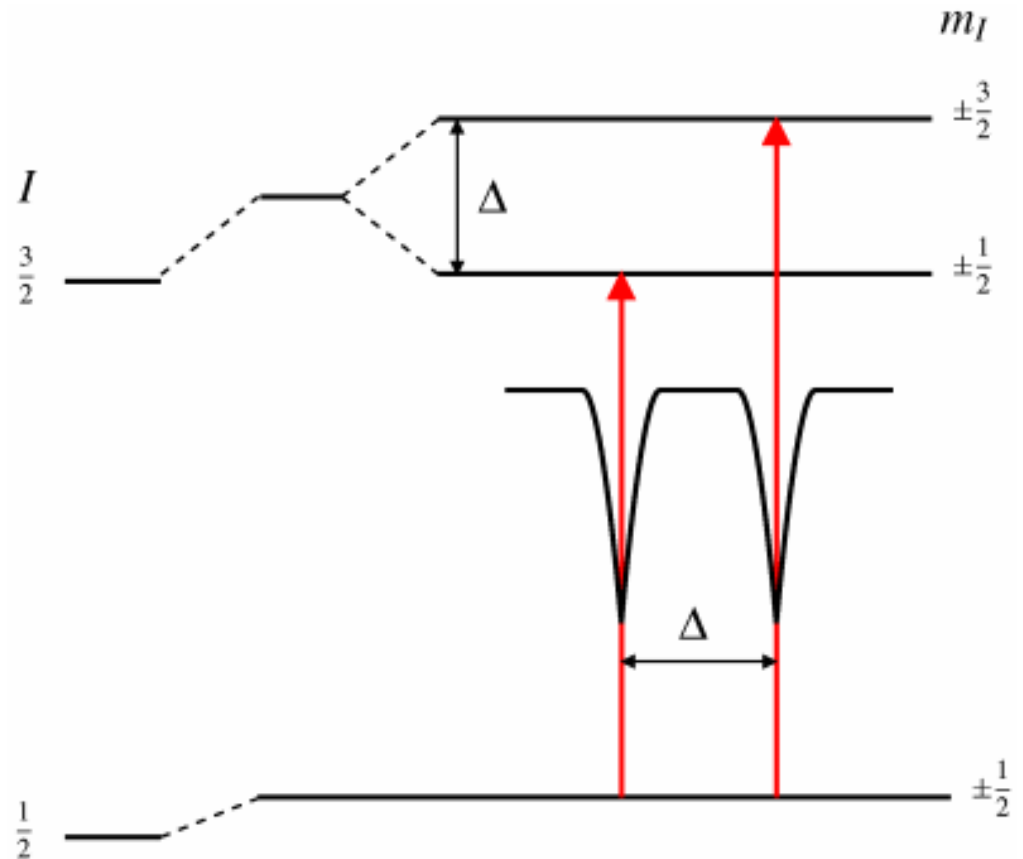
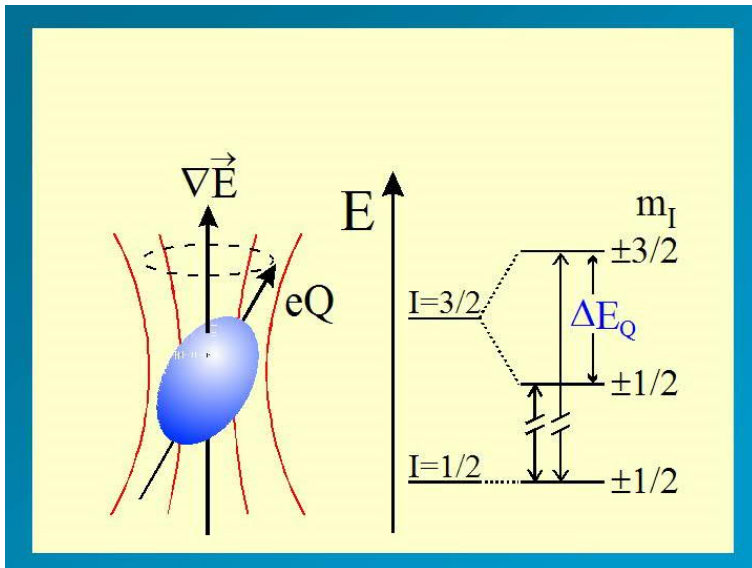
ISOMER SHIFT

- Isomer shift (IS or δ) 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 $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$)



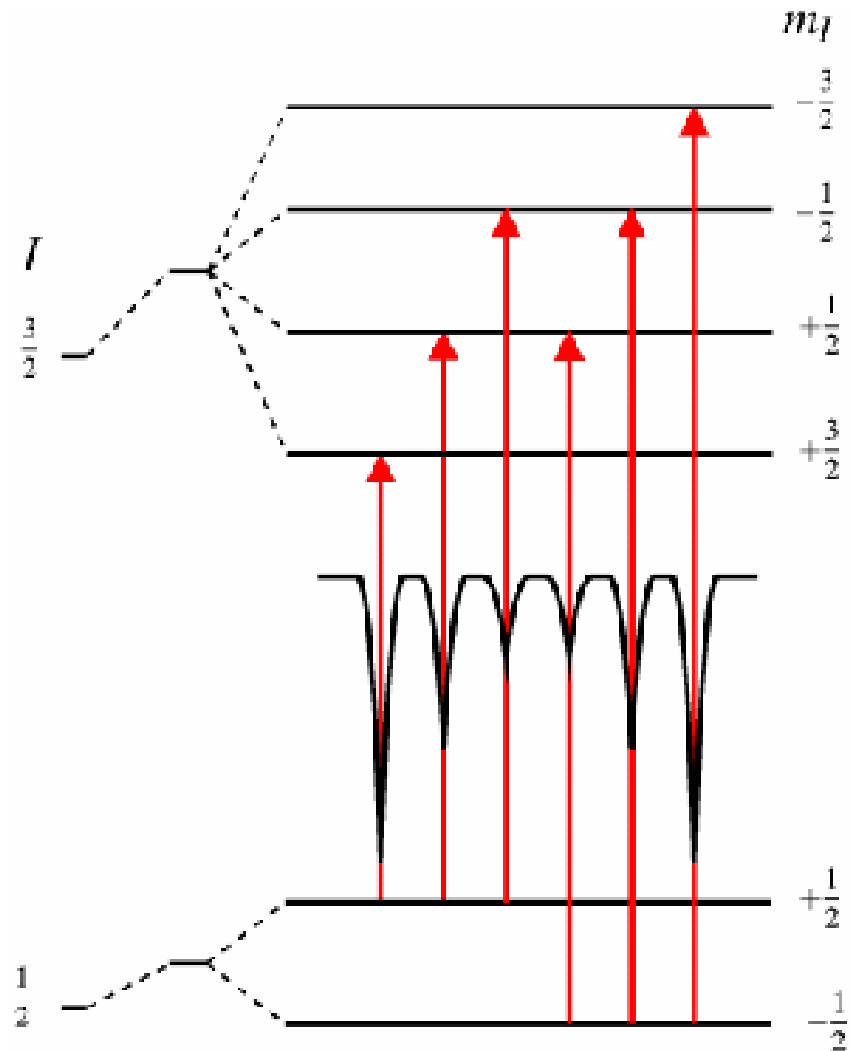
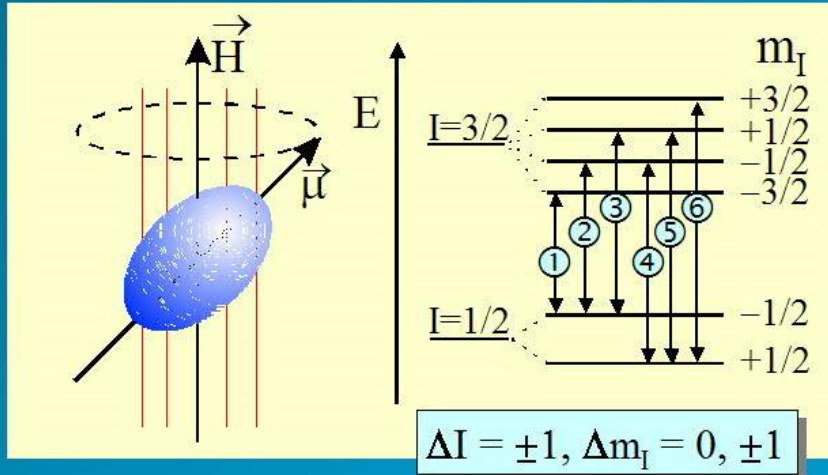
ELECTRIC QUADRUPOLE INTERACTION

- Nucleus feels electric field gradient due to asymmetry of surrounding ions
- symmetric \rightarrow no splitting; asymmetric surrounding \rightarrow splitting

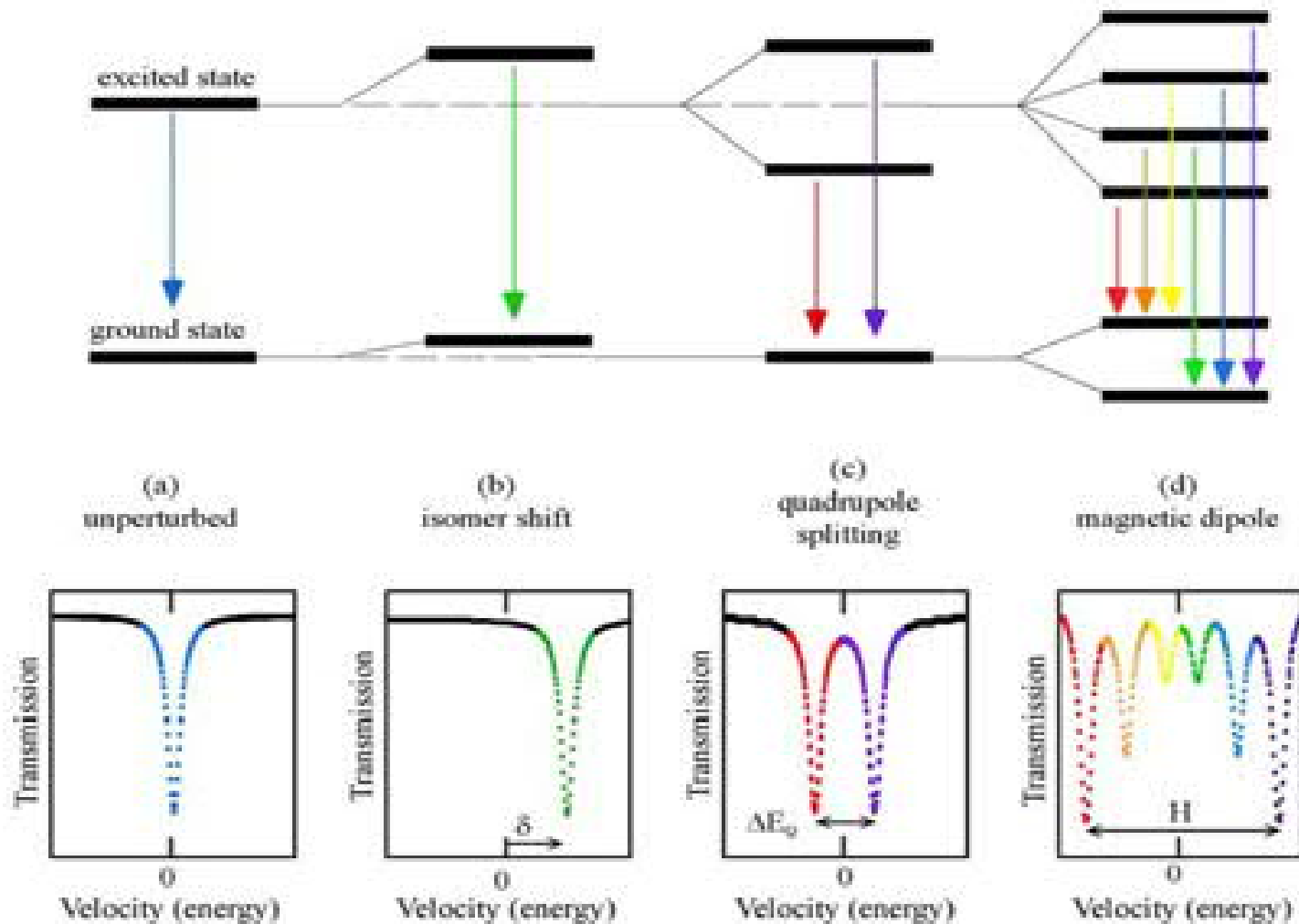


Magnetic Dipole Interaction

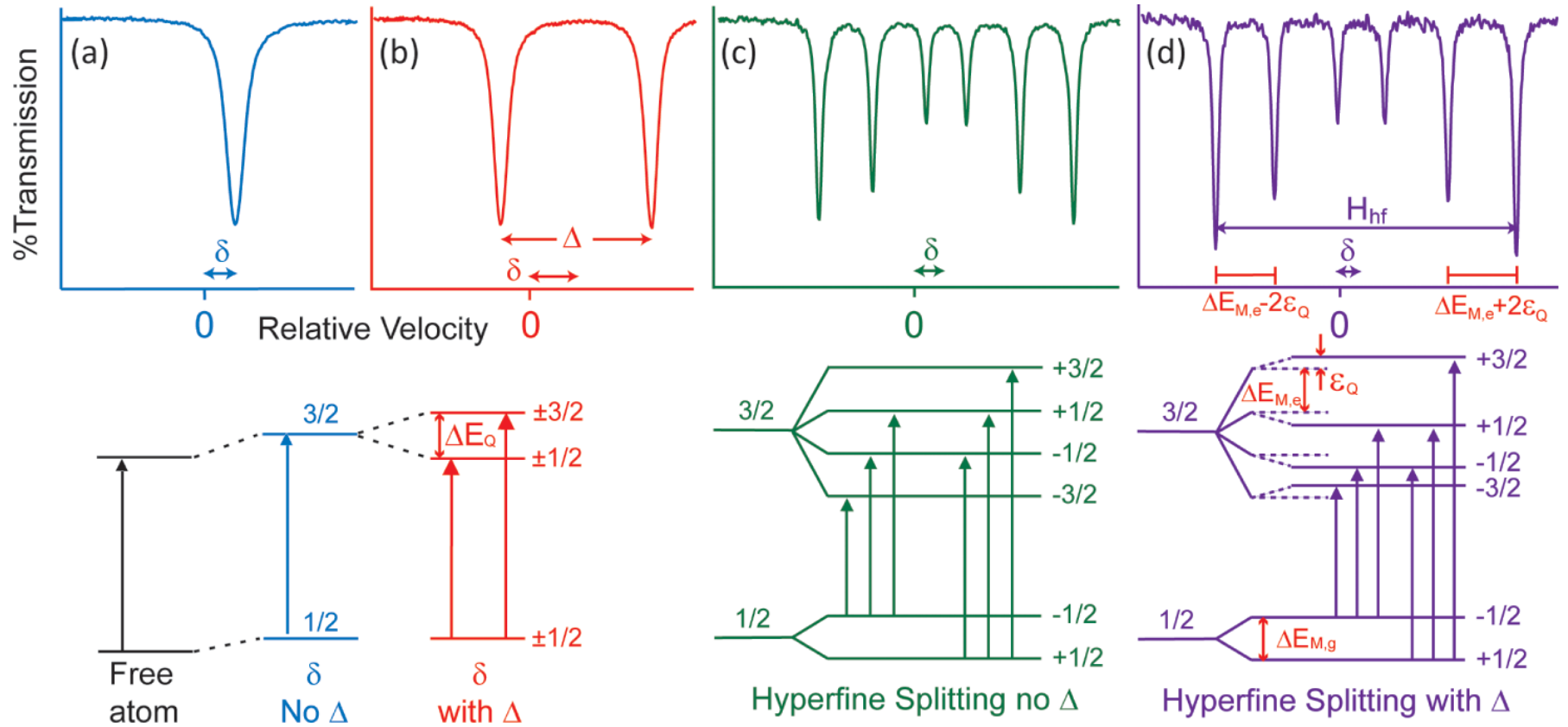
Magnetic Splitting ΔE_M



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

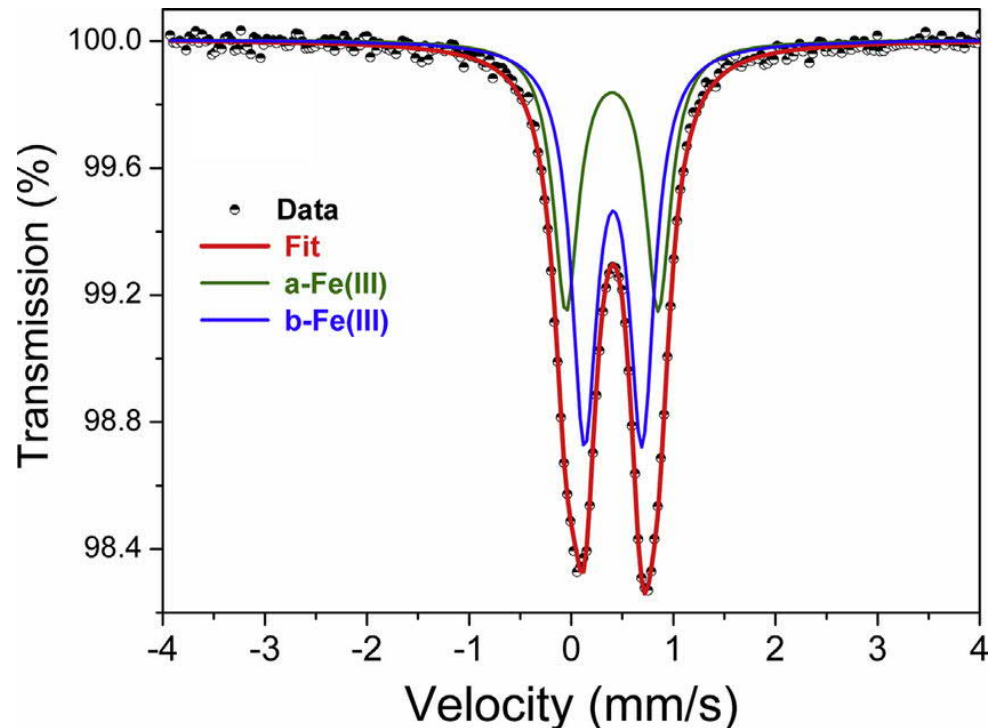
→ intensity ratio of sub-spectra = concentration ratio of corresp. Fe species

EXAMPLE: overall spectrum consists of two sub-spectra

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

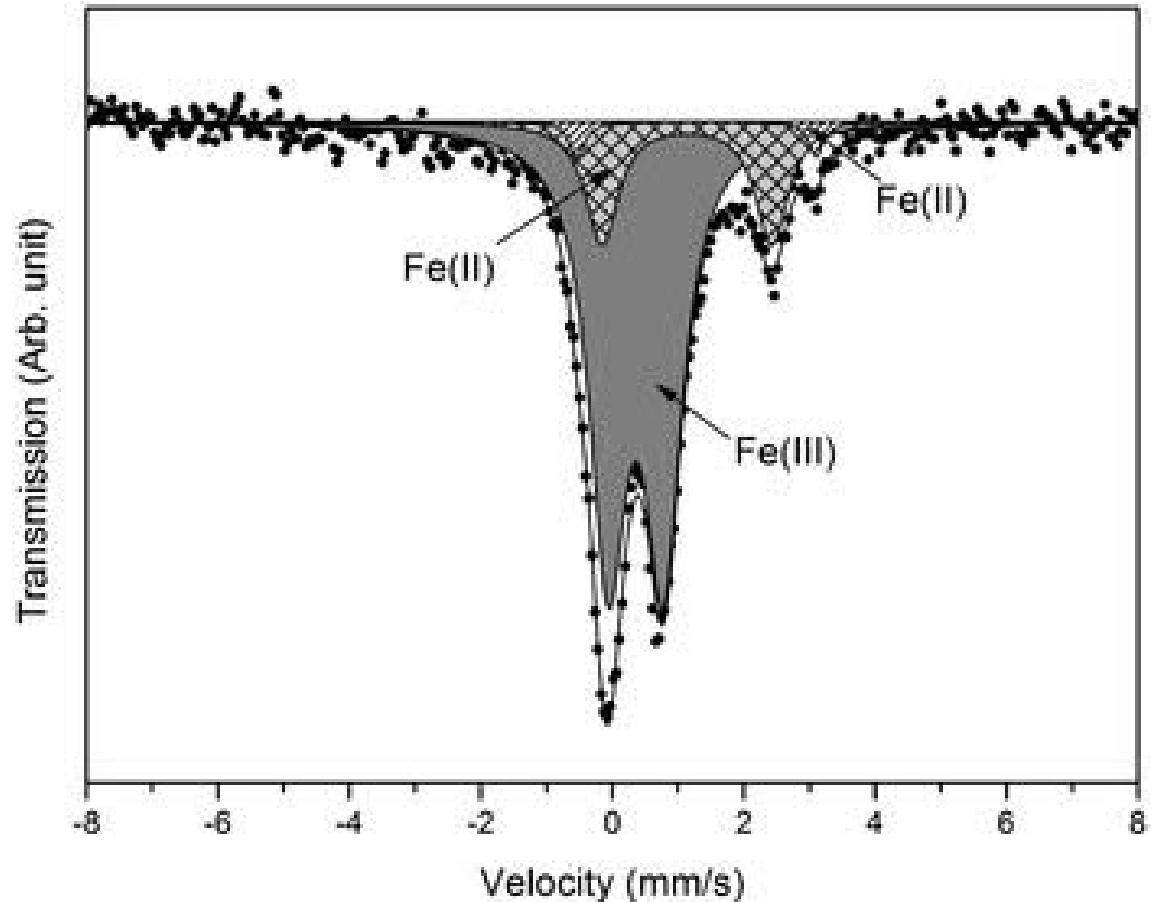
- Same isomer shift → same valence (+III)

- 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



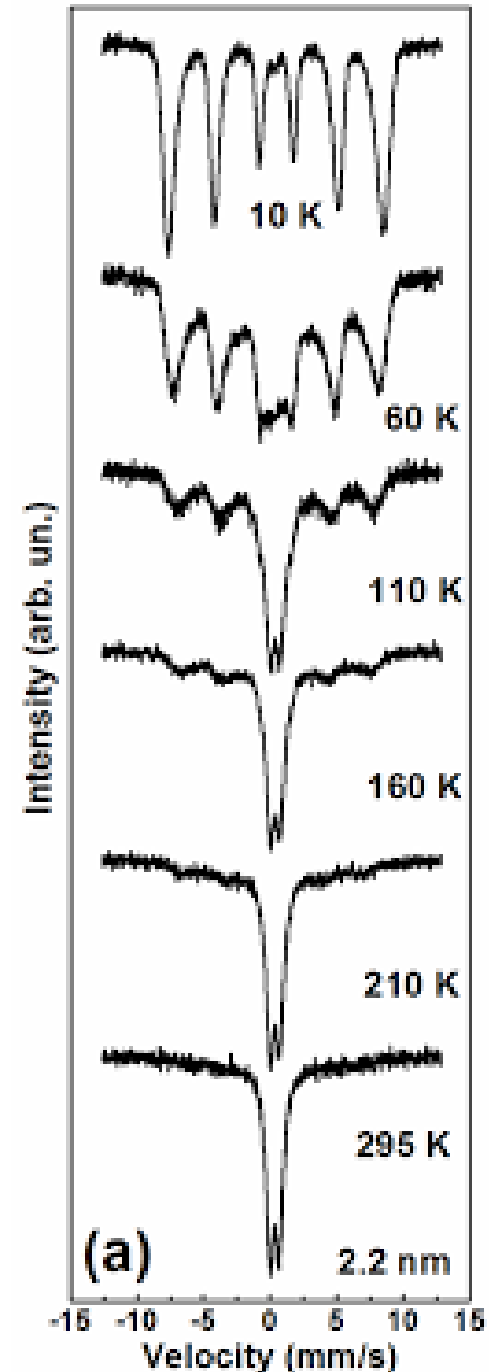
Temperature-dependent measurements

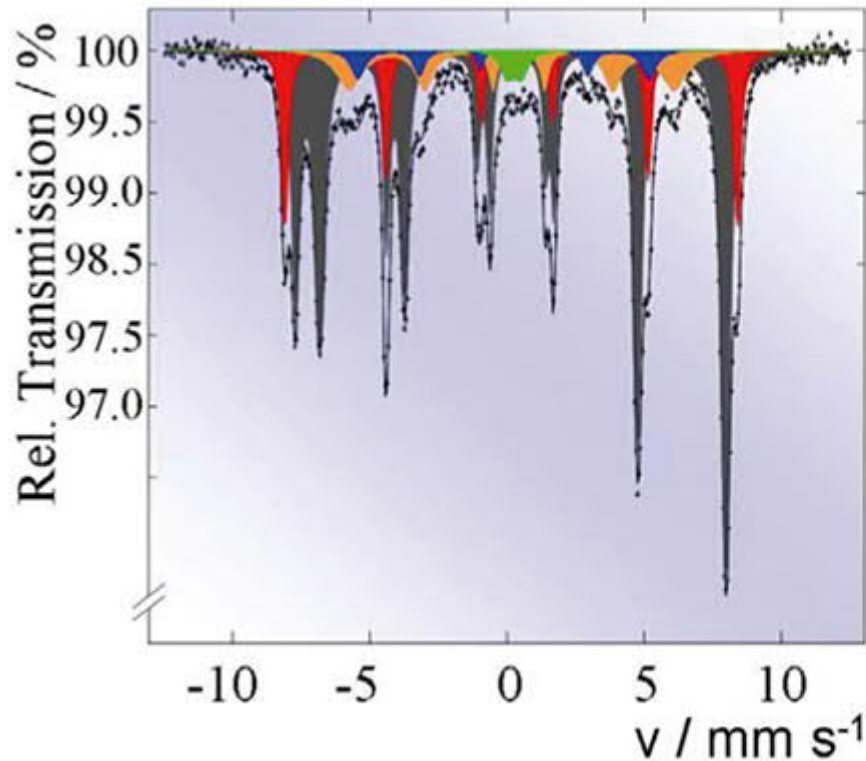
→ employed e.g. to investigate magnetic transitions

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



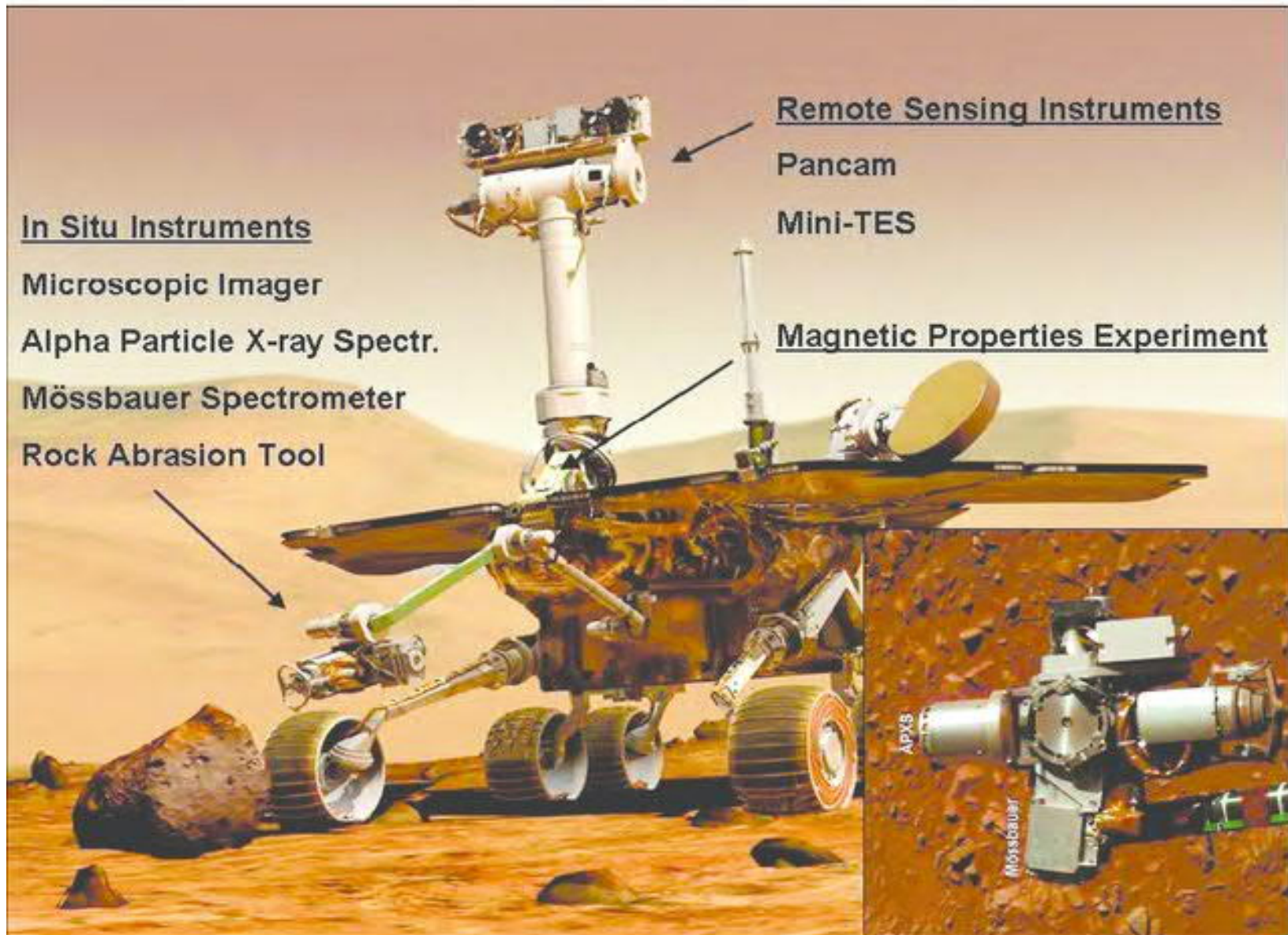


<u>Constituents</u>	<u>A/%</u>
Hematite, $\alpha\text{-Fe}_2\text{O}_3$	16
Magnetite, Fe_3O_4	64
Goethite, $\alpha\text{-FeOOH}$	13
Martensite	5
$\beta/\gamma\text{-FeOOH}$	2

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):

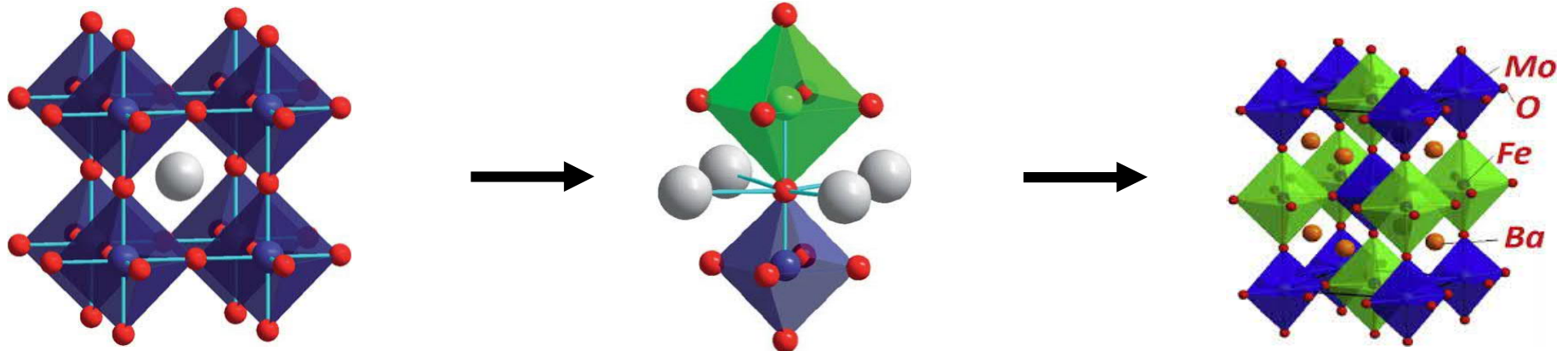
Mössbauer spectrometer is one of the instruments on the robotic arm

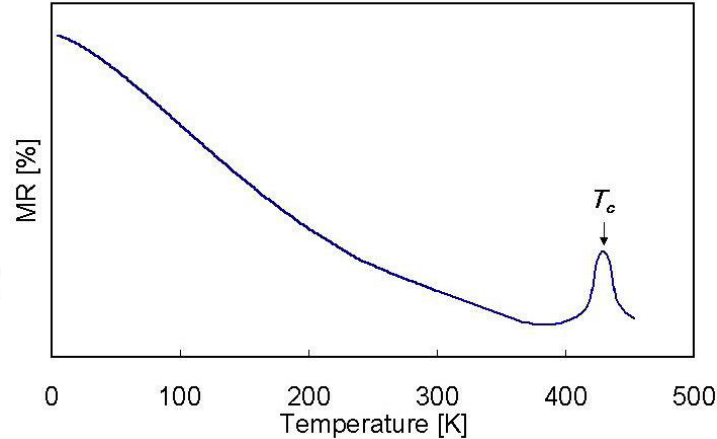
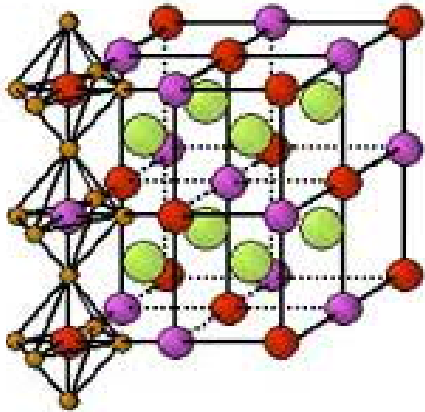


Mössbauer example for B-site ordered DOUBLE PEROVSKITE

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
- 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)



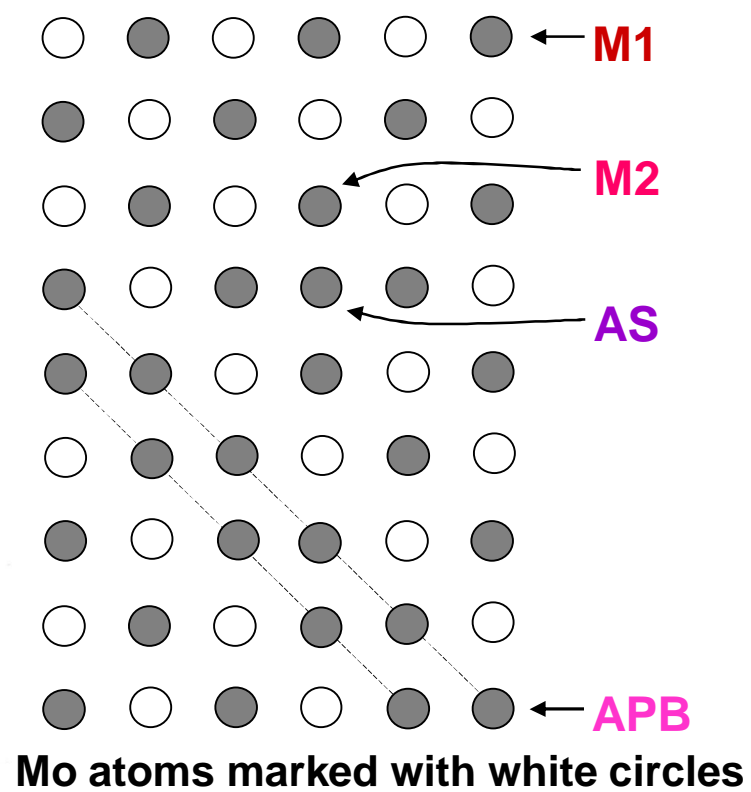
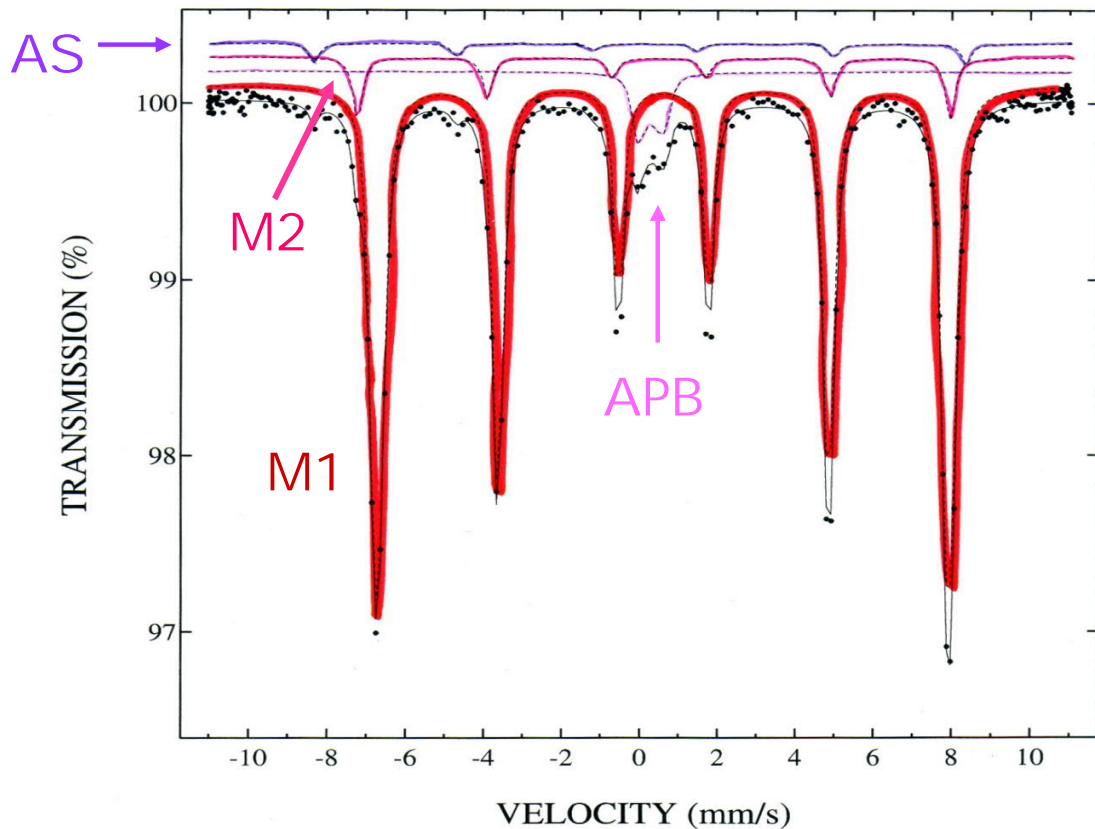


**B-site ordered
double perovskite**

- **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)