Mössbauer spectrometry as a tool for study of solid state materials

Lab for MS

FACULTAS MATHEMATICA PHYSICAQUE

27th of November 2015 Prague

Outline

1) Theoretical background of Mössbauer effect
2) Application potential – advantages and disadvantages of MS
3) Experimental setups and fields of their application
4) Hyperfine interactions and their connection to physical quantities
5) Mössbauer spectrometry in specific conditions

Energetic scale of electronic and nuclear interactions

chemical bonding, lattice energy	1 - 10 eV
electron transitions	0.5 - 5 eV
thermal oscilations	0.05 - 0.5 eV

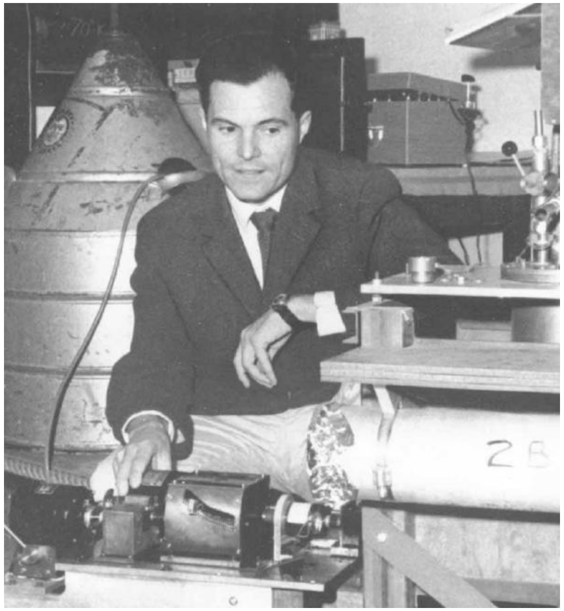
atomic fluorescence
GOOD OBSERVABILITY
resolution ≈ 10^{-8}

lattice oscilations (phonons)	0.005 - 0.05 eV

γ radiation	10^4 - 10^5 eV
nuclear recoil, Doppler shift	10^{-4} - 10^{-2} eV
nuclear quadrupole splitting	≈ 10^{-5} eV
nuclear Zeeman splitting	≈ 10^{-5} eV
Heisenberg linewidth (uncertainity principle)	10^{-9} - 10^{-6} eV

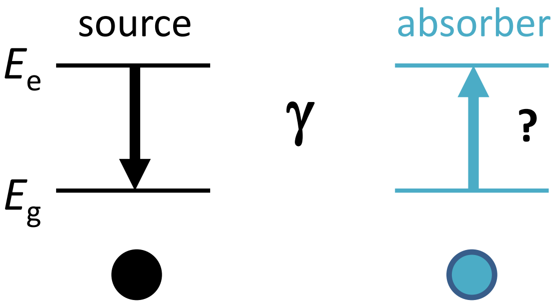
nuclear fluorescence
VERY DIFFICULT
resolution ≈ 10^{-13}

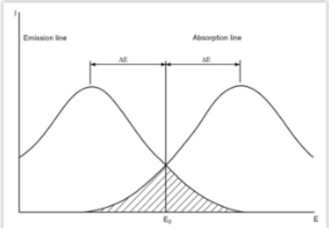
Basic concepts of the method I



Rudolf Ludwig Mössbauer
The Nobel Prize in Physics 1961 *"for his researches concerning the resonance absorption of gamma radiation and his discovery in this connection of the effect which bears his name„* **...** ***^{191}Ir crystal***

- recoiless nuclear resonant absorption of γ-ray





- Will the absorption occure?
- **free atoms** case:

recoil energy :(

$$E_0 = E_e - E_g \qquad E_\gamma = E_0 + \hbar\left(\vec{k}.\vec{v}\right) - \frac{E_\gamma^2}{2mc^2}$$

$$\Gamma = \frac{\hbar}{\tau_{ex}} \approx 10^{-9}\,eV$$

v-dependent Doppler shift $\approx 10^{-2}\,eV$

mass of atom

$E_R \approx 2\times10^{-3}\,eV$

- γ emitted is lower in E than E needed for absorption to occure – **no resonant absorption**
- How to get rid of these contributions?

Basic concepts of the method II

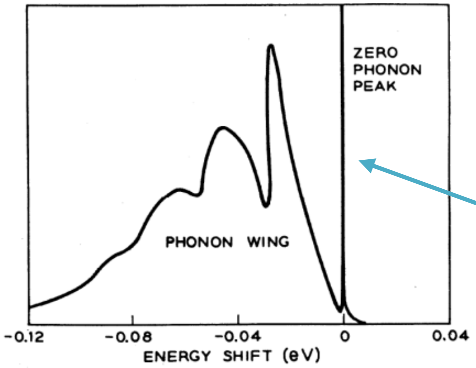
- **nucleus in crystal lattice** case:

$$E_R = E_{trans} + E_{vib}$$

- effective mass of crystal M >> m

$$E_{trans} = \frac{E_\gamma^2}{2Mc^2} \ll \Gamma$$

- E_{vib} is converted into crystal lattice vibrations - „phonon-free“ mode



Theroretical spectrum of the 129 keV γ-ray of ^{191}Ir

recoil-free line

- **What we can measure?**
- tiny changes in the energy levels of an atomic nucleus in response to its environment (hyperfine interactions)
- one of the most sensitive technique - high energy resolution given by relative energy uncertainity up to 10^{-16}

Factors affecting the achievable effect

- Debye-Waller factor/ Mössbauer-Lamb factor
  - probability of recoil-free absorption/emission of γ-quanta

$$f_D(T)=\exp\left\{-\frac{\hbar^2k^2}{2M}\frac{3}{2k_B\Theta}\left[1+\frac{2\pi^2}{3}\left(\frac{T}{\Theta}\right)^2\right]\right\} \qquad T \,\square\, \Theta$$

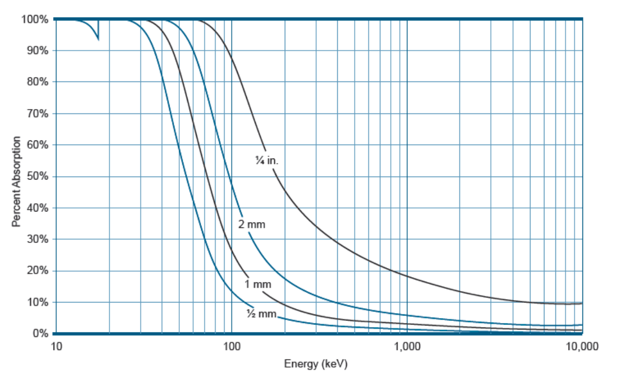
recoil energy ≈ E_γ^2 Debye temperature

- source of radiation
  - existence of suitable source
  - observed γ transition must lead to ground state
  - sufficiently large *f* (low T, low E_γ 5-180 KeV, high Θ, large M)
  - sufficiently long lifetime of Mössbauer level ≈10^{-6}-10^{-11} s (narrow linewidth, better energy resolution)
  - properties of parent isotope – lifetime, preparation, cost, handling and use in laboratory
- detection of radiation
  - absorption efficiency
  - YAP scintillator ($YAlO_3$: Ce crystal) (40 % of NaI(Tl) light output), fast scintillation-decay time (25 ns)

isotope	**E_γ [keV]**	**f**
^{57}Fe	14,4	0,91
^{191}Ir	129	0,06

Perfect nucleus for MS

YAP Absorption Efficiency



Some isotopes used in MS

IZOTOP	n[%]	E_0[keV]	$\tau_{1/2}$[s]	Γ/E_0	R[10^{-2}eV]	MATERSKÉ JADRO
Fe^{57}	2,17	14,4	10^{-7}	$3{,}2.10^{-13}$	0,19	Co^{57}
		136,4	$8{,}7.10^{-9}$	$3{,}8.10^{-13}$	17,5	
Ni^{61}	1,25	67,4	$5{,}3.10^{-9}$	$1{,}2.10^{-12}$	4	Cu^{61}
Zn^{67}	4,11	93	$9{,}4.10^{-6}$	$5{,}3.10^{-16}$	6,9	Ga^{67}
Ge^{73}	7,76	67	$1{,}6.10^{-9}$	$4{,}3.10^{-12}$	3,3	As^{73}
Ag^{107}	51,35	93	44,3	$1{,}1.10^{-22}$	4,3	Ag^{107}*
Sn^{119}	8,58	23,8	$1{,}9.10^{-8}$	10^{-12}	0,26	Sn^{119}*
Dy^{161}	18,88	25,7	$2{,}8.10^{-8}$	$6{,}2.10^{-13}$	0,22	Tb^{161}
		74,5	3.10^{-9}	2.10^{-12}	1,8	
W^{182}	26,4	100	$1{,}3.10^{-9}$	$3{,}5.10^{-12}$	2,9	Ta^{182}
Ir^{191}	38,5	129,4	$1{,}3.10^{-10}$	$2{,}7.10^{-11}$	4,7	Os^{191},Pt^{191}
Ir^{193}	61,5	73	$5{,}7.10^{-9}$	$1{,}1.10^{-12}$	1,5	Pt^{193}, Os^{193}
Au^{197}	100	77,3	$1{,}9.10^{-9}$	$3{,}1.10^{-12}$	1,6	Pt^{197}, Hg^{197}
U^{238}	0	45	$2{,}3.10^{-10}$	$4{,}3.10^{-11}$	0,45	Pu^{240}

mostly studied

mostly theoretical studies (80s)

also studied

$R = \Gamma_{res}$ [mm/s] $= 2\Gamma_{nat}$

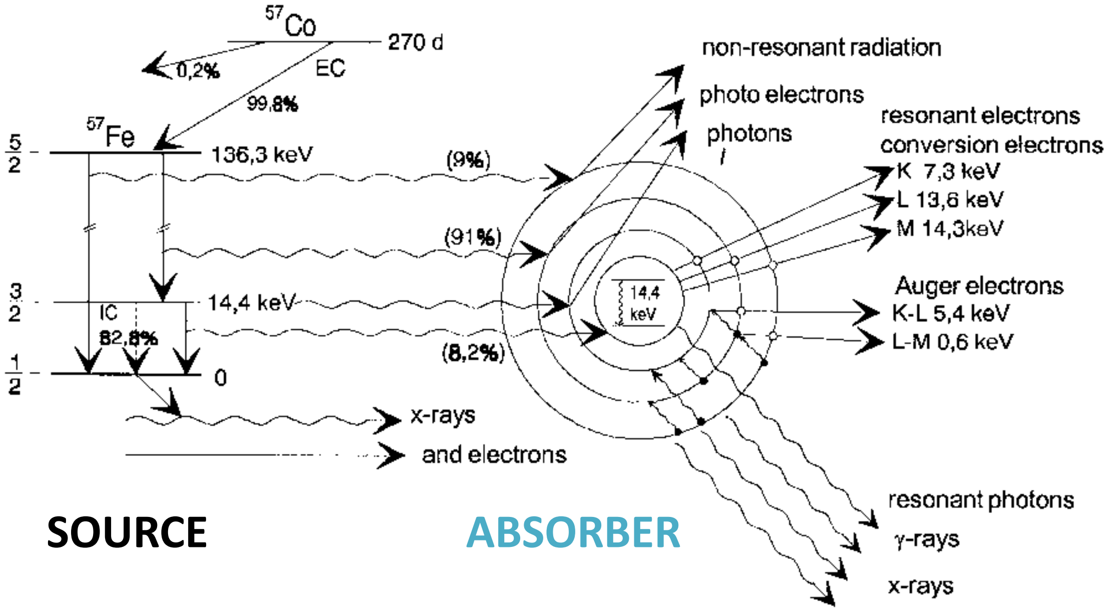
totally 44 active elements

Emission probabilities for ^{57}Fe

- only small portion of detected radiation contains the information about the state of nucleus

Mössbauer level →

Ground state →



SOURCE **ABSORBER**

Transition from excited to ground state of ^{57}Fe nucleus

	ENERGY	[keV]	PROBABILITY	-
γ emmision	**E_0**	**14.4**	**1 / 1+α**	**0.09**
Conv e^- K	$E_0 - B_K$	7.3	α_K / 1+α	0.81
Conv e^- L	$E_0 - B_L$	13.6	α_L / 1+α	0.09
Conv e^- M	$E_0 - B_M$	14.3	α_M / 1+α	0.01
Auger e^- KLL	$B_K - 2B_L$	5.4..5.7	α_K (1-(FY)$_K$) / 1+α	0.57
$X_{K\alpha}$	$B_K - B_L$	6.3	α_K (FY)$_K$) / 1+α	0.24

Experimental setup for ^{57}Fe MS

1) transmission geometry (**MS**)

    - absorption spectrum

2) backscatter geometry

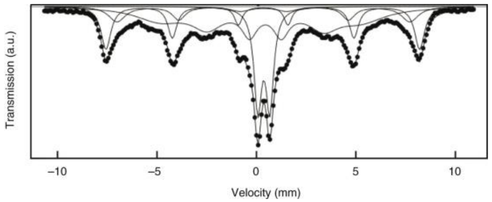
    - conversion electron MS (**CEMS**)
    - emission spectrum

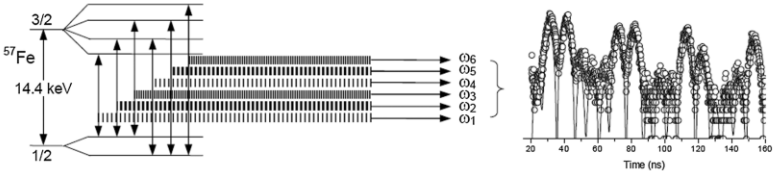
1) synchrotron radiation sources

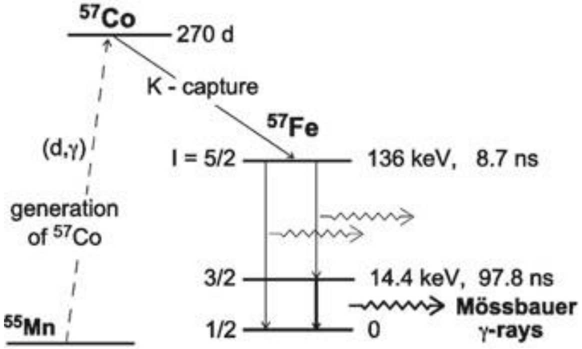
    - nuclear forward scattering (**NFS**)
    - time domain – quantum beats

2) new possibilities (ELI beamlines)

    - pulse-probe methods







Experimental results:

- microscopic information
    - valence state
    - spin state
    - nearest neighbours
- macroscopic information
    - content of given phase
    - cationic distribution
    - magnetic properties (superparamagnetism)

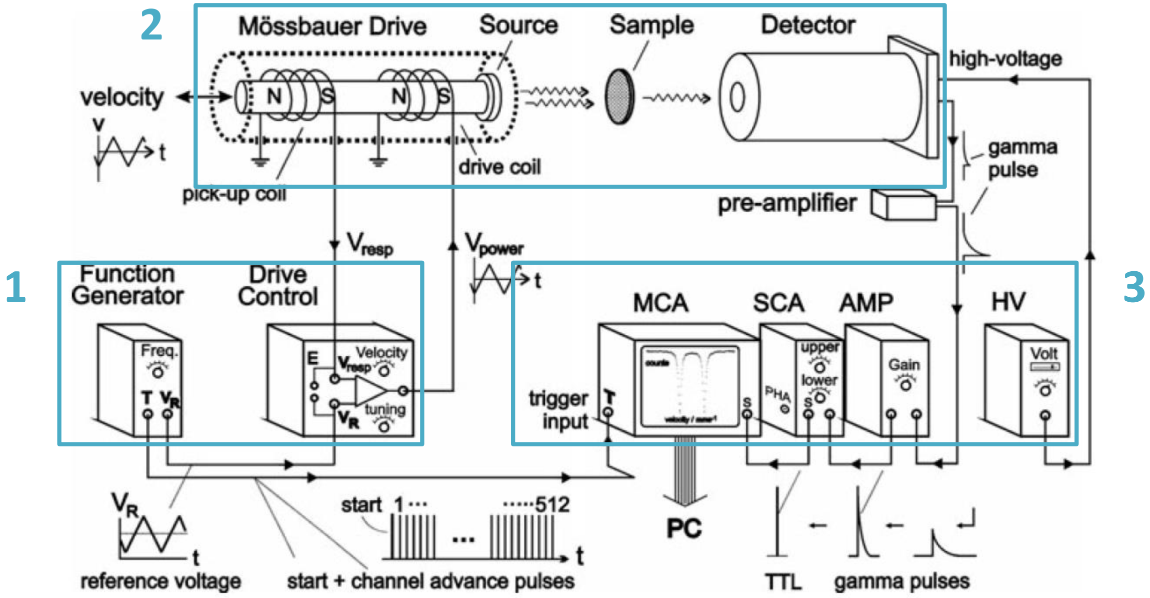
Experimental arrangement – Transmission MS

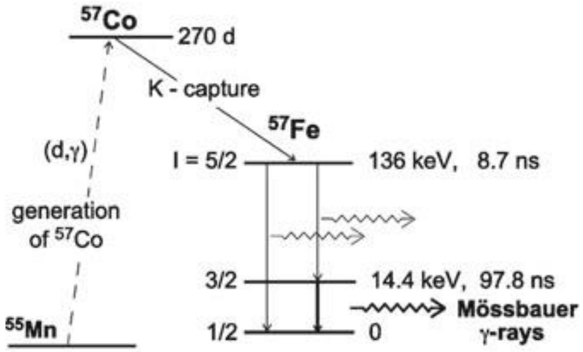
Doppler shift

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

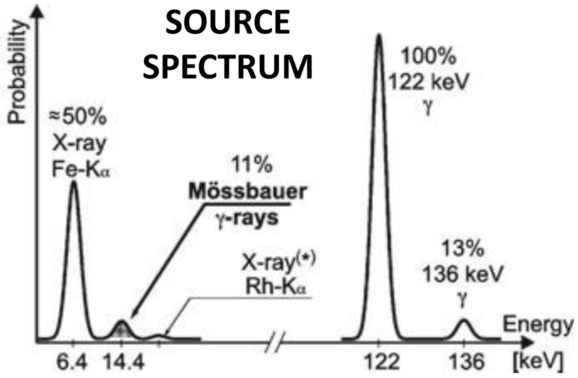
1 mm/s =

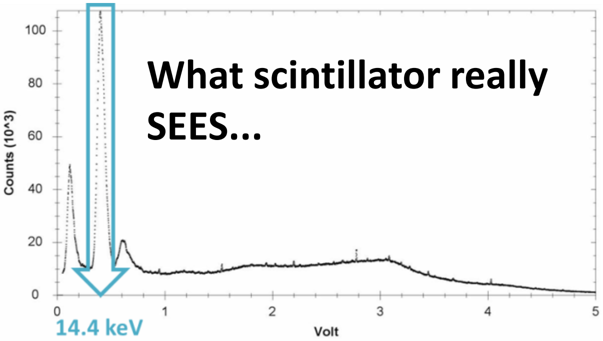
48.0766 neV



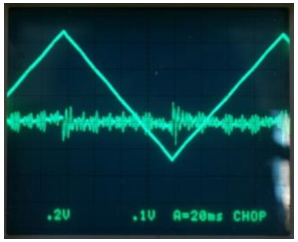


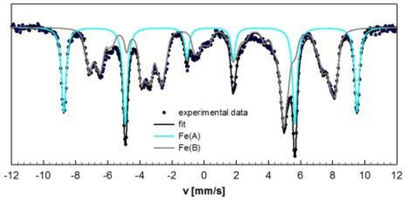
SOURCE SPECTRUM

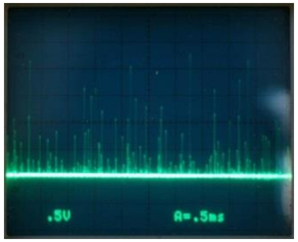




What scintillator really SEES...

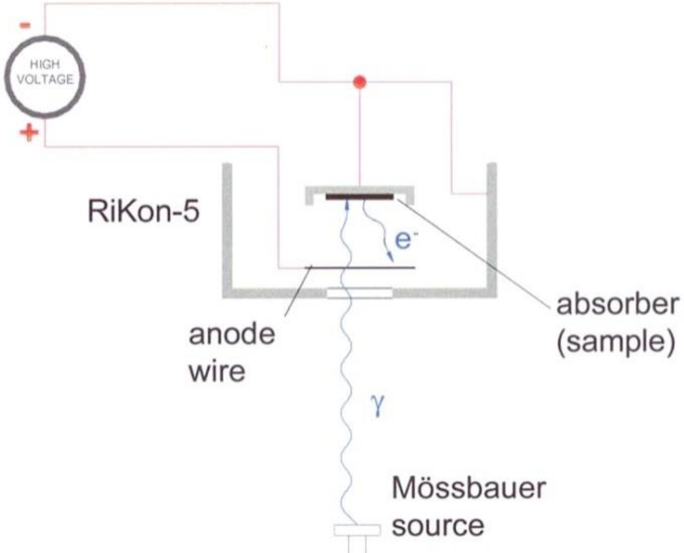


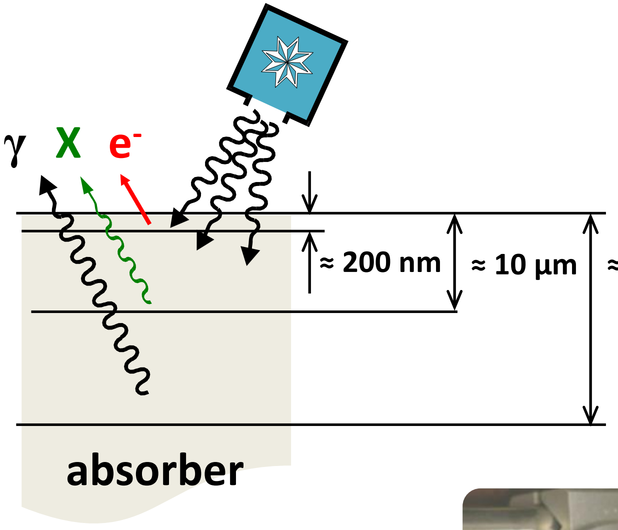




Conversion electron Mössbauer spectroscopy

- depth information up to 200 nm
- applications :
  - magnetic properties of layers
  - surface layer composition
  - defects, aging





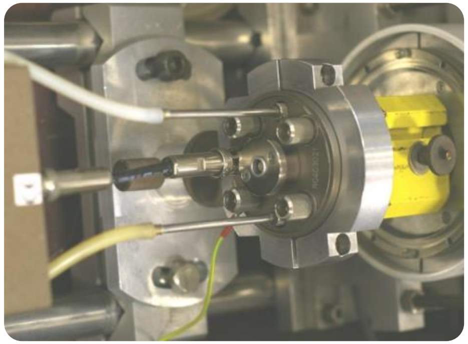
Working gas:

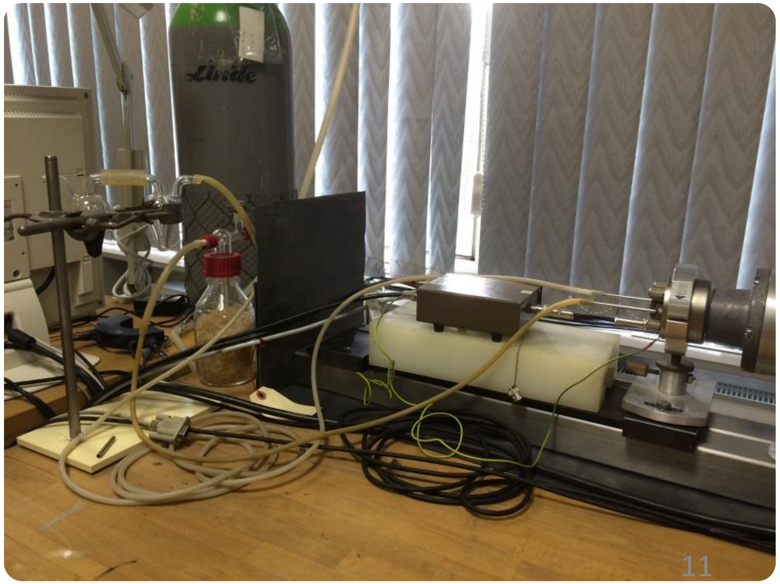
96% He + 4% CH_4

95% He + 5% N_2

Sample:

Ø = 16 mm, d_{max} ~ 1 mm





Hyperfine interactions and Mössbauer parametres

- interactions between a nucleus and elec. and mag. fields created by electrons and other nuclei in the solid
- affect the properties of the '**local probe**' – nucleus
- total energy: $\left\langle \psi \middle| \hat{H} \middle| \psi \right\rangle = E_{hf} = E_{el} + E_{mag} = \int \rho(\vec{r})\phi(\vec{r})d^3r - \vec{\mu}.\vec{B}$

Taylor expansion of the potential

Zeeman effect

$$E_{el} = E_{el}^{(0)} + E_{el}^{(1)} + E_{el}^{(2)} + \dots$$

0

$$E_{el}^{(2)} = E_C + E_Q$$

- E_C – monopole term, isomer shift (***IS*,*δ***)
- E_Q – quadrupole term, quadrupole shift/splitting (***QS*,*ΔE*$_{\mathbf{Q}}$**)
- E_{mag} – hyperfine field (***B*$_{\mathbf{hf}}$**)

Electric monopole interaction

- Coulomb interaction of nuclear charge distribution with electron distribution at site of nucleus (both source and absorber)
- only s-electrons have non-zero probability

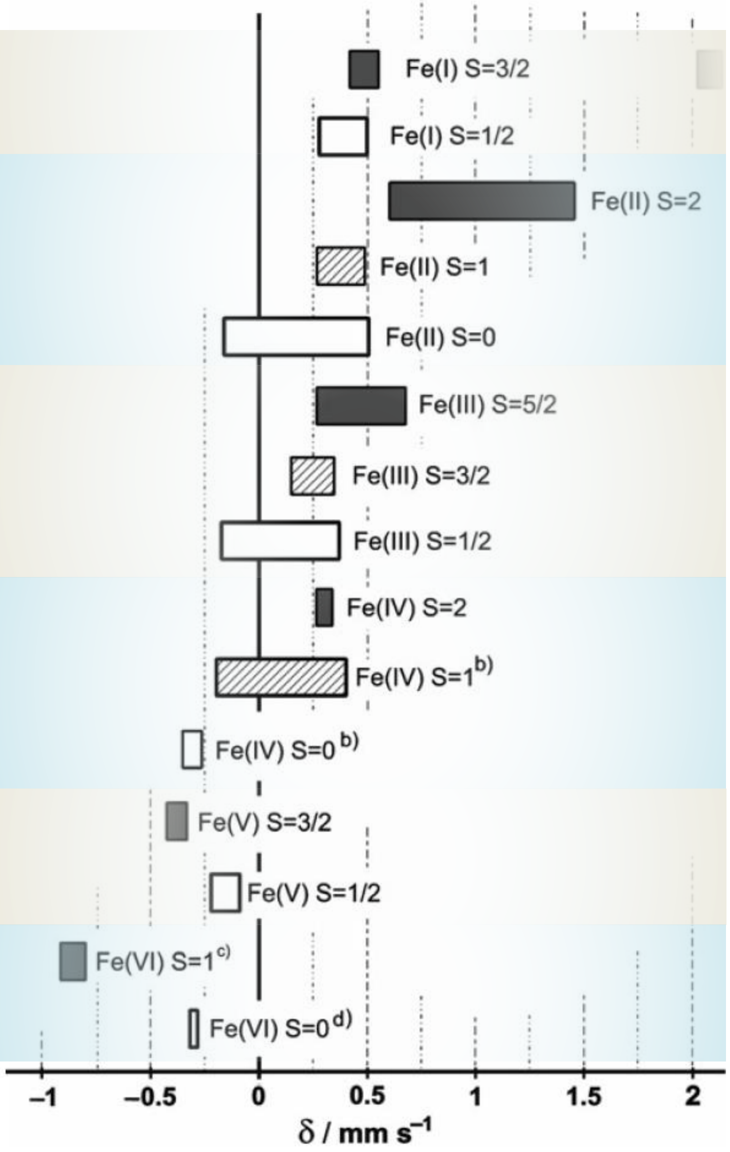
- **Isomer shift:**

$$\delta = \frac{2\pi}{5} Z e^2 \left[\langle r_e^2 \rangle - \langle r_g^2 \rangle \right] \cdot \left\{ \left| \psi_A(0) \right|^2 - \left| \psi_S(0) \right|^2 \right\}$$

nuclear radius, negative for ^{57}Fe

electron density at site

- calibration to 13µm-foil of cubic α-Fe
- provides information about:
  - oxidation state
  - spin state (HS, LS)
  - bonding properties (covalency, electronegativity)



Electric quadrupole interaction

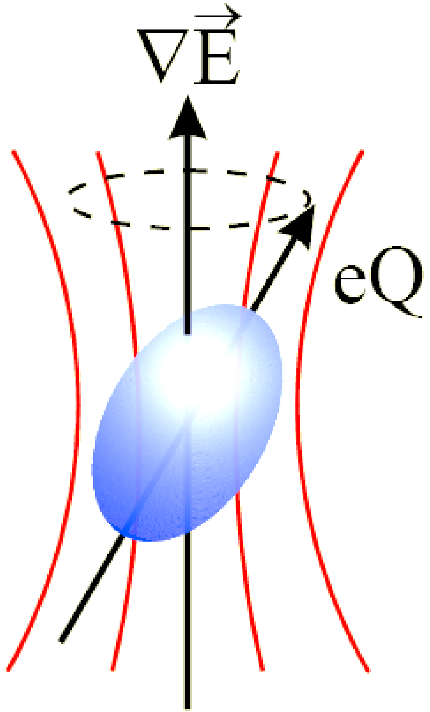
- interaction between the quadrupole moment of the nucleus Q and electric field gradient (EFG tensor)

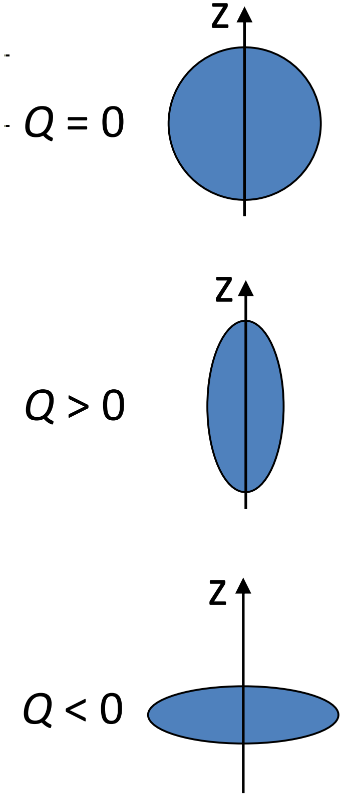
$$\mathrm{EFG} = \left[-\vec{\nabla}\vec{E}\right] = \left[\vec{\nabla}\vec{\nabla}V\right] = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix}$$

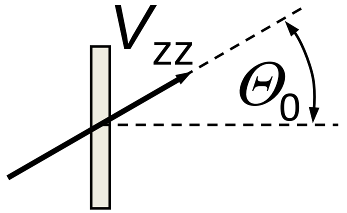
- only excited state (I > 1/2) has non-zero Q
- **Quadrupole splitting:**

$$\Delta E_{\mathrm{Q}} = \frac{1}{2} eQV_{zz}\left(1 + \frac{1}{3}\eta^2\right)^{½} \qquad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

- asymmetry parameter : $0 \leq \eta \leq 1$
- provides information about:
  - oxidation state
  - spin state (HS, LS)
  - local crystal symmetry (zero vs non-zero EFG)
  - bonding properties

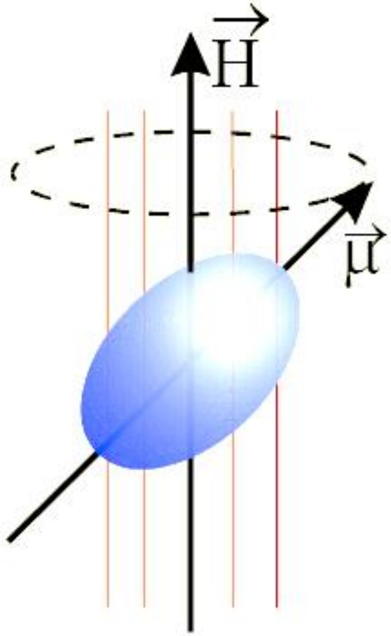






$$I_2/I_1 = \frac{3(1+\cos^2\theta_0)}{5 - 3\cos^2\theta_0}$$

Magnetic dipole interaction



- interaction between nuclear magnetic dipole moment m_I and magnetic field B at the site of nucleus:

$$E_{m_I} = -g_N \mu_N B_{eff} m_I = -\gamma \hbar B_{eff} m_I$$

- leads to Zeeman splitting of both levels into (2I+1) sublevels
- selection rules: $\Delta I = \pm 1$, $\Delta m_I = 0, \pm 1$
- **Origin of hyperfine fiels at nuclei:**

$$B_{eff} = B_{hf} + B_{ext}$$

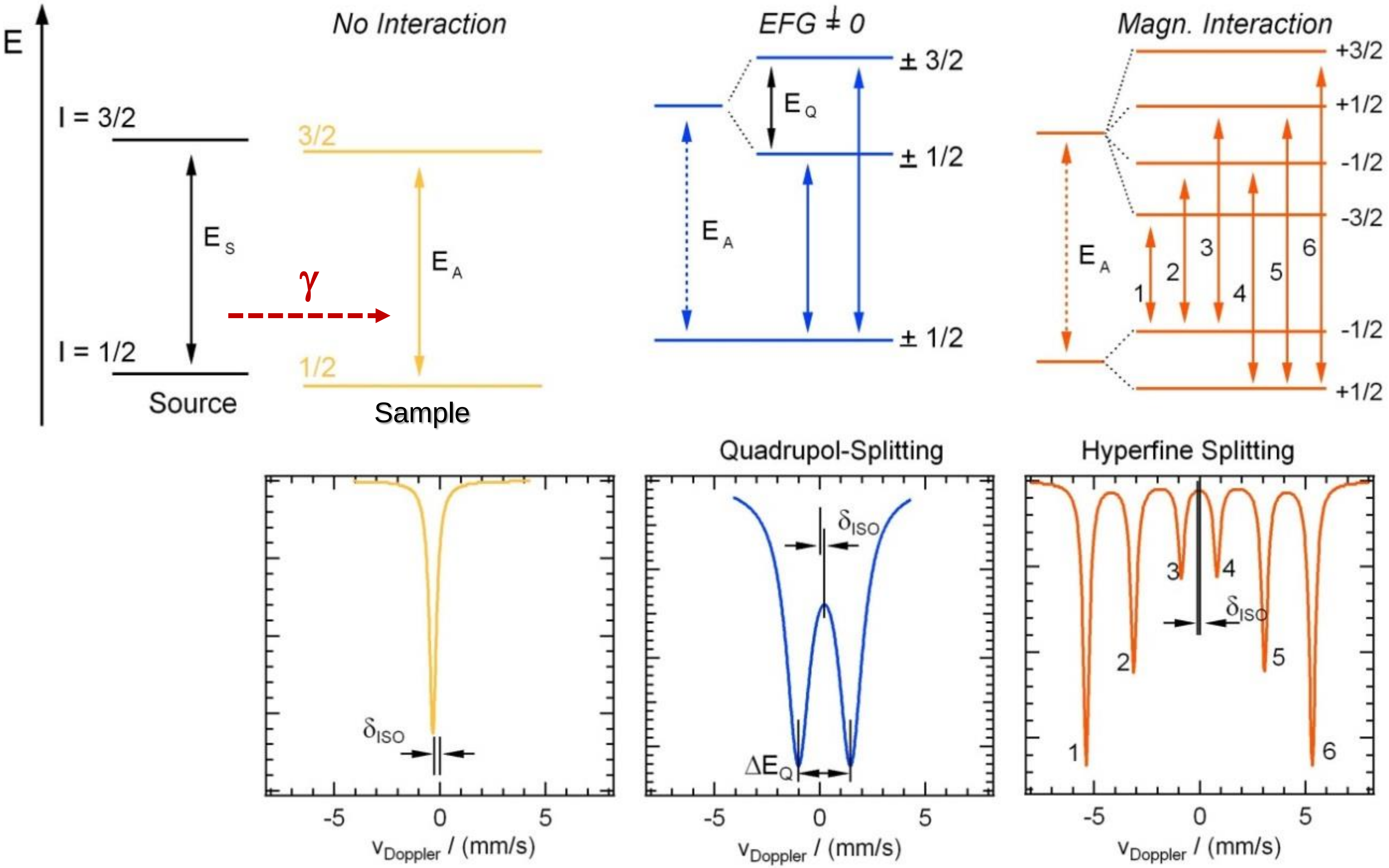
$$B_{hf} = B_{orb} + B_{dip} + B_{Fermi}$$

  - orbital contribution – open shell valence electrons
  - dipolar contribution – elctron spins, magnetic moments of surrounding ions
  - Fermi contact interaction – s-electrons polarized by magnetic moments of open shell d-electrons

- provides information about magnetic structure, mag. and struc. transitions

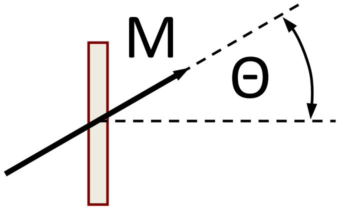
Combined mag. dipole and elec. quadrupole interaction

$$E_{\mathrm{Q}}(m_I,\theta,\phi)^{(1)} = -1^{|m_I|+1/2}(eQV_{zz}/8)\cdot(3\cos^2\theta - 1 + \eta\cdot\sin^2\theta\cos 2\phi)$$



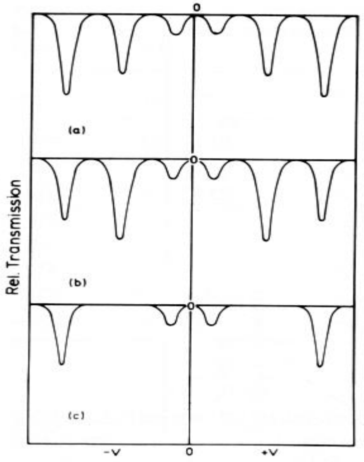
Relative intensities of absorption lines

- given by Clebsh-Gordan coeficients



θ - angle between the direction of the mag. field at the nucleus and the beam of γ-radiation

TRANSITION	Δm_I	ANGULAR DEPENDENCE
$\pm 3/2 \rightarrow \pm 1/2$	± 1	$I_1 = I_6 = 3/8\ (1 + \cos^2\theta)$
$\pm 1/2 \rightarrow \pm 1/2$	0	$I_2 = I_5 = 1/2\ (1 - \cos^2\theta)$
$\mp 1/2 \rightarrow \pm 1/2$	± 1	$I_3 = I_4 = 1/8\ (1 + \cos^2\theta)$



powder

Θ = 90°

Θ = 0°

$I_{2,5} / I_{3,4} = 4 \sin^2\theta / (1 + \cos^2\theta)$

→ = 2 for random orientation of local moments (fields) 3:2:1:1:2:3

→ = 4 for θ = 90° 3:4:1:1:4:3

→ = 0 for θ = 0° 3:0:1:1:0:3

$I_{1,6} / I_{3,4} = 3$ → doesn't depend on the orientation

MS in low temperatures and high fields

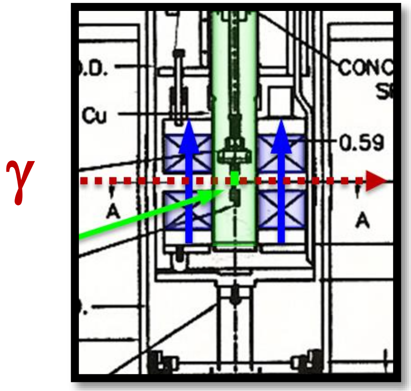
Low temperatures:

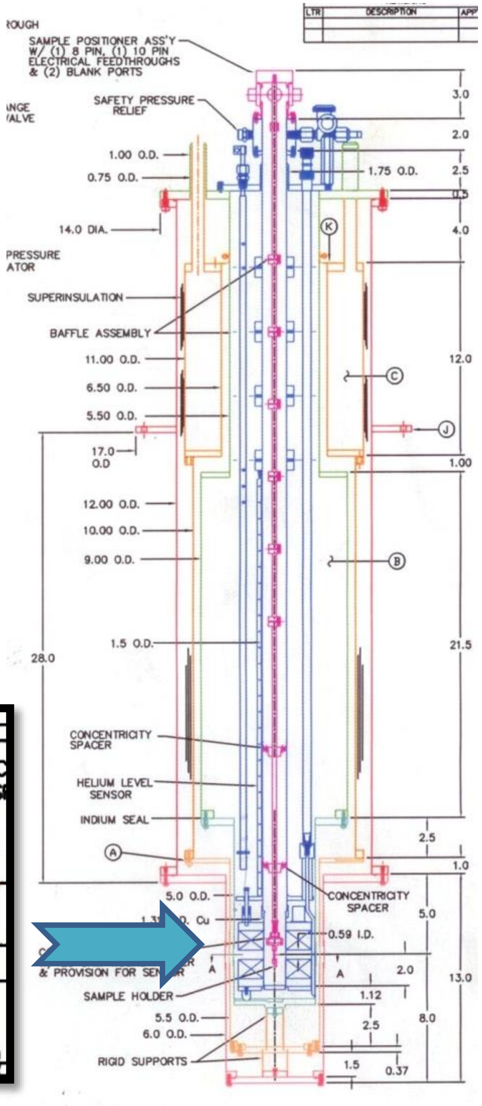
- 4.2 - 320 K
- narrow spectral lines
- temperature induced changes of magnetic state
- study of relaxation phenomena

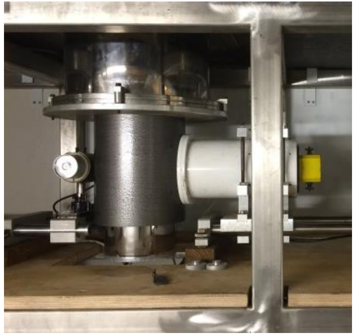
External mag. field:

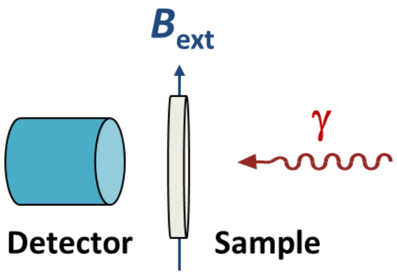
- 0 - 6 T
- separation of nonequivalent iron positions
- magnetic state

- sample:
  - Ø = 16 mm
  - d ≈ 30 µm









MS in extreme conditions

- High temperatures:

- High pressures: