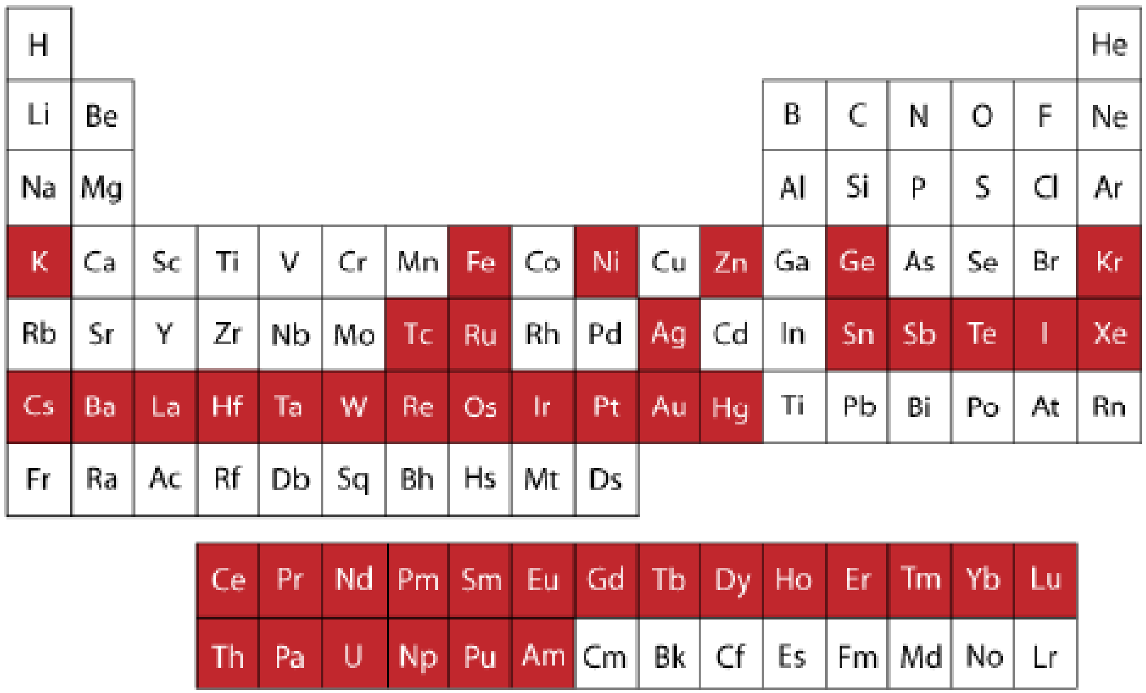
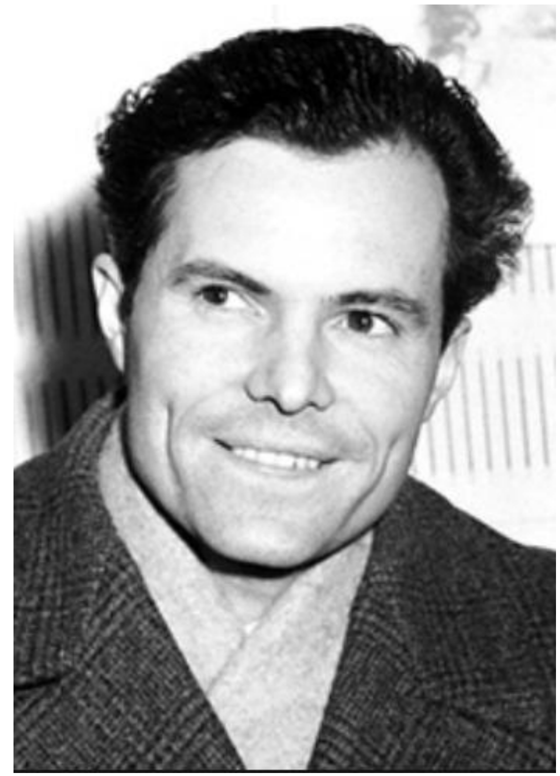
Mössbauer Spectroscopy
Rückstossfreie Kernabsorption/-fluoreszenz





Rudolf Mössbauer
1929-2011
TU München
Discovery 1958
Nobel prize 1961

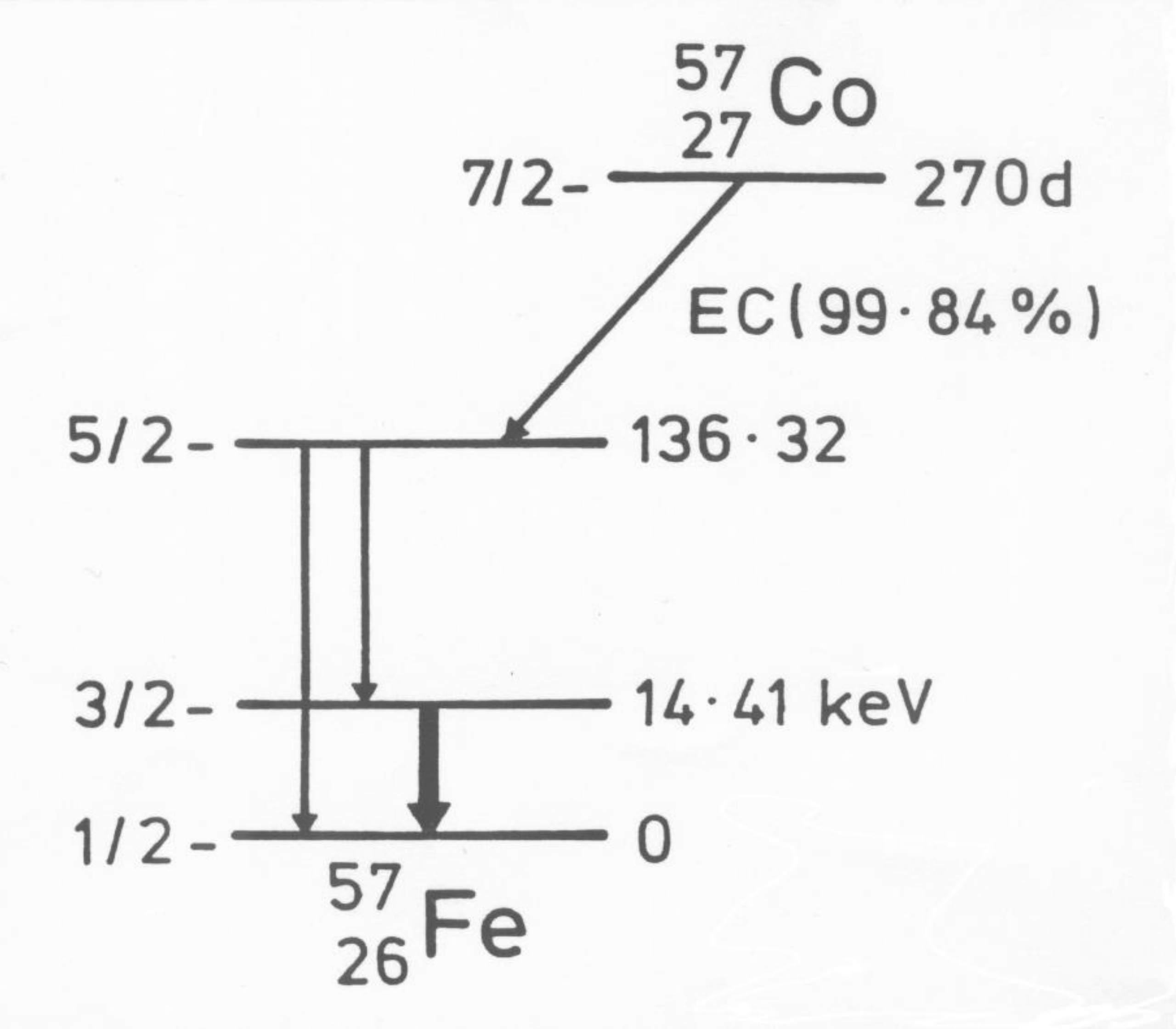
Many potentials, but few truly useful candidates: Fe, Sn, Sb, Eu, Te, I

Spectroscopic features

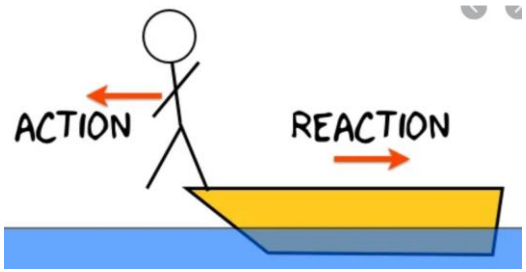
- Transitions between nuclear angular momentum states, I_1 –> I_2
- Wavelength range: 10^{-11} to 10^{-13} m: γ-rays
- Energy range: 10 keV to MeV
- Simple transmission geometry

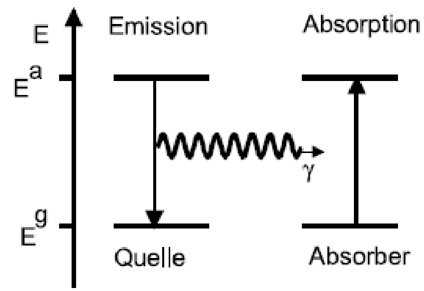
  Source/energy modulation/sample/detector
- monochromatic radiation
- Detectors: Geiger counter, scintillator

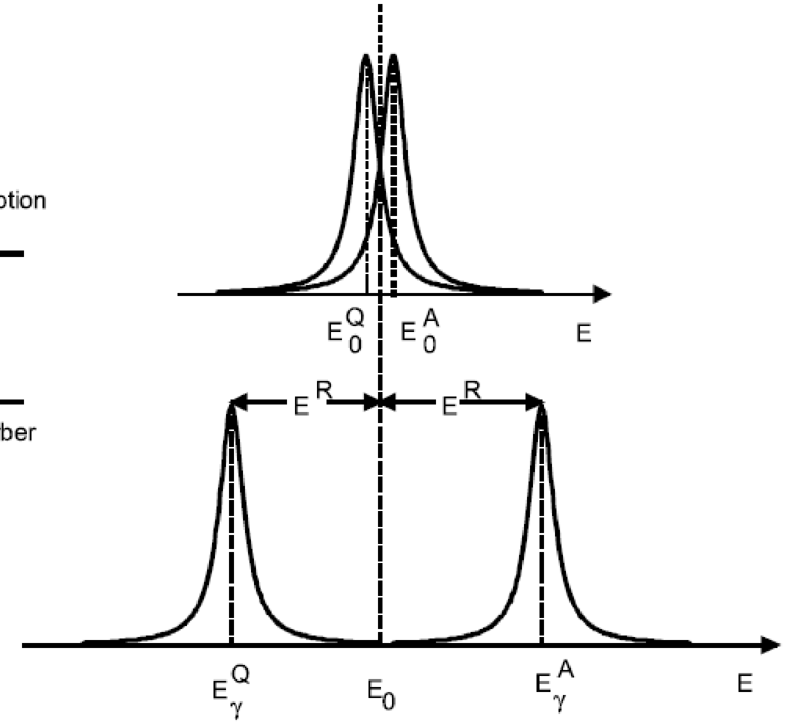
Nuclear decay of ^{57}Co



Recoil effect







Source: $E\gamma^Q = E_0 - E_R$

Absorber: $E\gamma^A = E_0 + E_R$

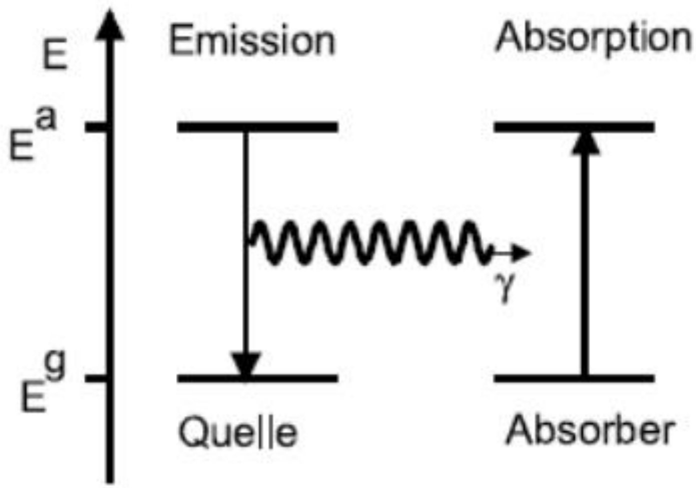
Momentum conservation:

$$p_n = -p_\gamma = -\frac{h}{\lambda} = -\frac{E_\gamma}{c}$$

$$E_R = \frac{1}{2} mv^2 = \frac{p_{Kern}^2}{2m} = \frac{p_\gamma^2}{2m}$$

The recoil effect causes an energy difference of $2E_R$ between the source and the absorber. Mössbauer‘s realization: the whole crystal, not the individual atom Is subject to the recoil effect. Thus m is the mass of the whole crystal, not the mass of the individual nucleus.

In general, the energy difference between the nuclear ground state and the Nuclear excited state will also depend on the chemical/electronic environment. This is the main motivations for chemists in exploring the Mössbauer effect.



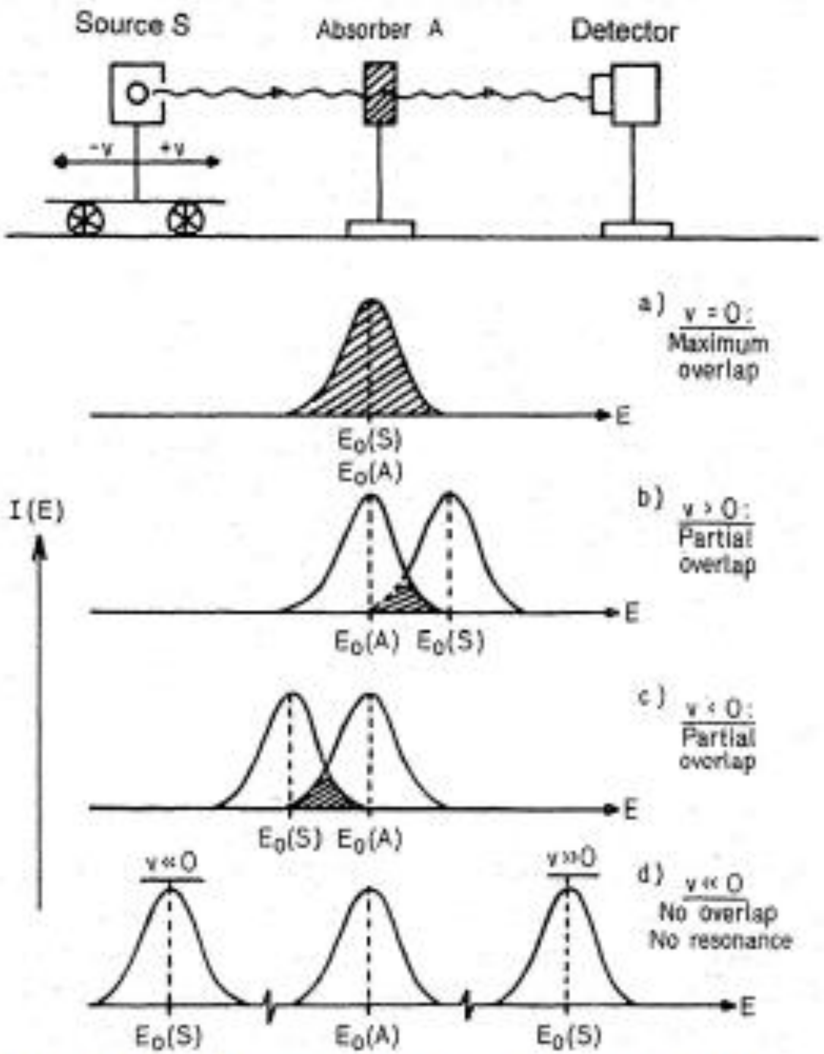
The source emits monochromatic radiation. To achieve resonance with the sample (called the absorber), we need to be able to vary the energy of the source. This is done by moving the source relative to the absorber with a range of relative velocities, leading to energy variations by the Doppler effect

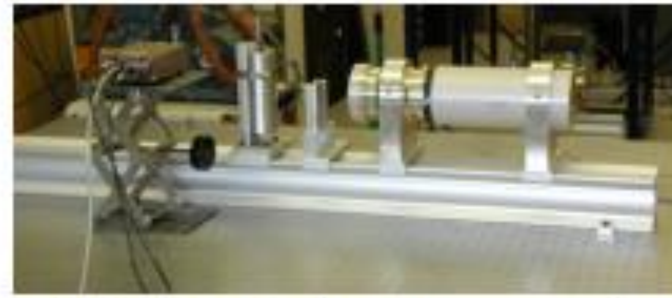
$$\mathbf{E_\gamma = E_0(1 \pm \frac{v}{c})}$$

Principle of Mössbauer Spectroscopy

Doppler Effect

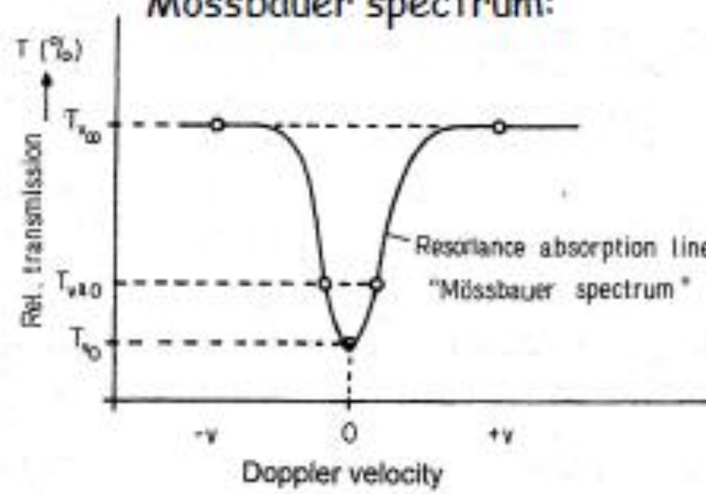
$$E_\gamma = E_0\left(1 \pm \frac{v}{c}\right)$$





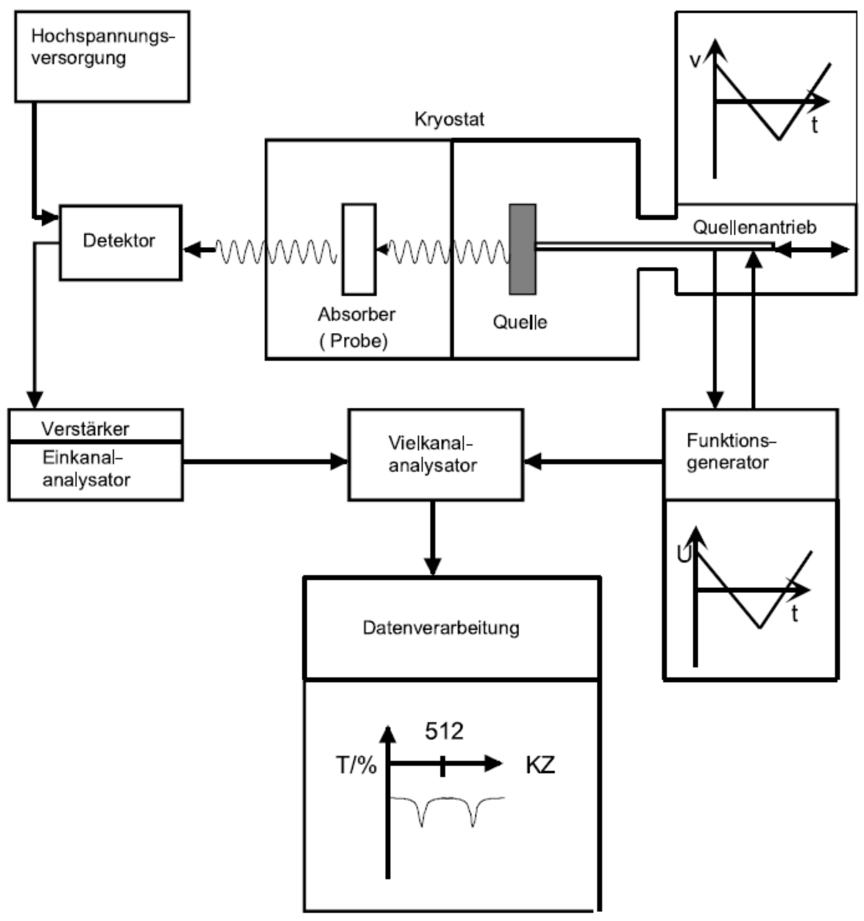
Variation of the source speed causes the change in energy due to the Doppler effect

Mössbauer spectrum:



Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

The Spectrometer

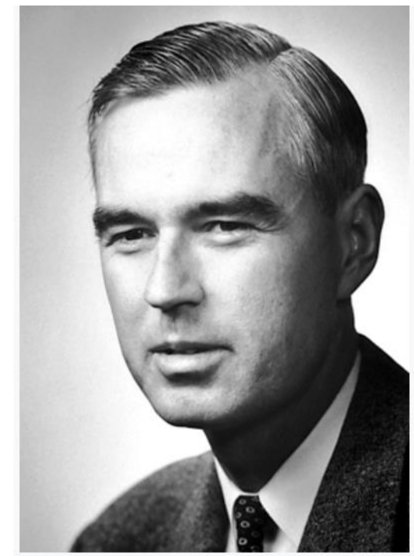


The Lamb Mössbauer factor

Even though translational recoil effects do not occur in the solid state, there are energy mismatch effects arising from phonons created during the nuclear transitions. Resonance can only occur for zero-phonon transitions. The probability of such a zero-phonon transition is called the Lamb Mössbauer factor f. This factor is always $0 \leq f \leq 1$.

f depends on E_γ and the mean squared vibrational amplitude

$$f = \exp - \left(\frac{E_\gamma}{c\hbar}\right)^2 \langle x^2 \rangle$$



Willis Lamb
1913-2008
Stanford, Oxford, Yale, Columbia, U.Arizona
Nobel Prize 1955

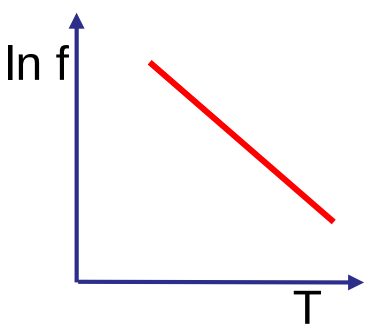
$\langle x^2 \rangle$, in turn, depends on the vibrational density of states and on the temperature. Use of the Debye model leads to the expression:

$$f = \exp\left[- \frac{6E_R}{k_B\Theta_D} \cdot \left(\frac{1}{4} + \left(\frac{T}{\Theta_D}\right)^2 \int_0^{\Theta_D/T} \frac{x\,dx}{e^x - 1}\right)\right] ; \quad x = \frac{h\nu}{Tk_B} \qquad \Theta_D = \frac{h\nu_{max}}{k_B} = \text{Debye temp.}$$

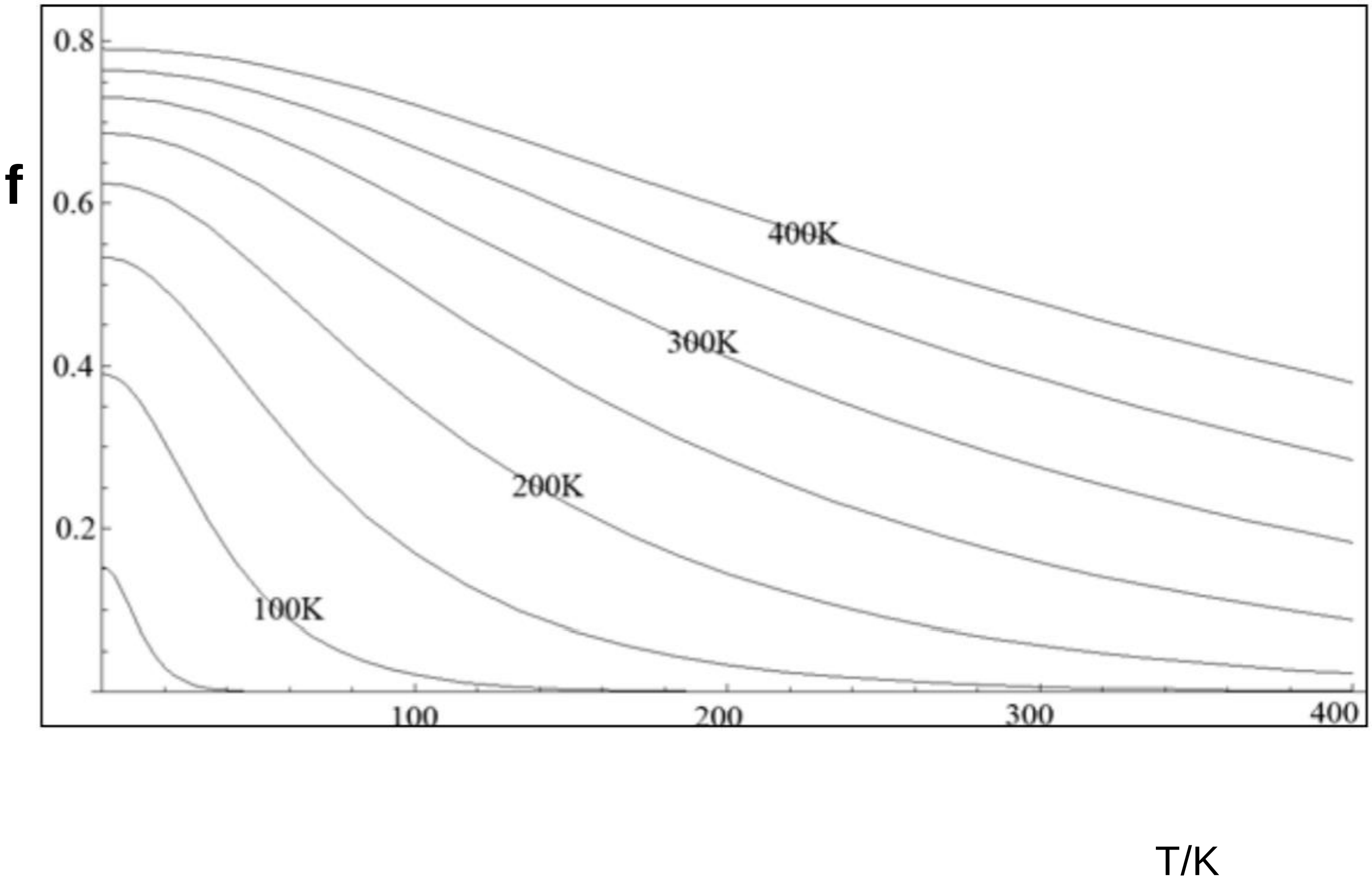
In the high-temperature limit, $\Theta_D \ll T$, we find:

$$f = \exp - \frac{6E_\gamma T}{k_B\Theta_D^2}$$

Thus, by plotting ln f vs T, the Debye temperature can be obtained



Effect of the Debye temperature upon the Mössbauer recoil-free fraction



Hyperfine Interactions

- Electrical interactions:
  - Coulombic interactions: Isomer shift
  - Quadrupolar interactions: Quadrupole splitting
- Magnetic interactions: Zeeman splitting

The electrostatic interaction

$$E_{el} = \int \rho(\vec{r}) V(\vec{r}) d\tau$$

$$V(\vec{r}) = V(0) + \sum_{\alpha} x_{\alpha} \left(\frac{\partial V}{x_{\alpha}} \right)_{r=0} + \frac{1}{2!} \sum_{\alpha,ß} x_{\alpha} x_{ß} \left(\frac{\partial^2 V}{x_{\alpha} x_{\beta}} \right)_{r=o} + \ldots$$

$$E_{el} = V(0) \int \rho d\tau + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho d\tau + \frac{1}{2!} \sum_{\alpha,\beta} V_{\alpha,\beta} \int x_{\alpha} x_{\beta} \rho d\tau + \ldots\ldots\ldots$$

Coulomb term   dipole term   quadrupole term

$$V_{\alpha} \equiv \left(\frac{\partial V}{\partial x_{\alpha}} \right)_{r=0}$$

Cartesian electric field components

$$V_{\alpha,\beta} \equiv \left(\frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \right)_{r=0}$$

Cartesian electric field gradient components

The Electrostatic Interaction

$$E_{el} = \frac{1}{2}\sum_{\alpha=1}^{3}\left(V_{\alpha\alpha}\right)_0 \int \rho_n(r)\, x_\alpha^2\, d\tau = \frac{1}{2}\sum_{\alpha=1}^{3}\left(V_{\alpha\alpha}\right)_0 \int \rho_n(r)\left(x_\alpha^2 - \frac{r^2}{3}\right)d\tau$$

$$+\frac{1}{6}\sum_{\alpha=1}^{3}\left(V_{\alpha\alpha}\right)_0 \int \rho_n(r)\, r^2 d\tau$$

In addition, we have

where $\mathbf{r^2 = \sum x_\alpha{}^2 = x^2 + y^2 + z^2}$

$$-\sum_1^3 \mathbf{V_{\alpha\alpha}} = -|\boldsymbol{\psi_0}|^2 \frac{\mathbf{e}}{\boldsymbol{\varepsilon_o}}$$

Poisson eq.

$$E_{el} = \underbrace{\frac{1}{2}\sum_{\alpha=1}^{3}\left(V_{\alpha\alpha}\right)_0 \int \rho_n(r)\left(x_\alpha^2 - \frac{r^2}{3}\right)d\tau}_{\text{EFG} \times \text{quadrupole moment}} + \frac{1}{6\varepsilon_0} e\left|\psi(0)\right|^2 \int \rho_n(r)\, r^2\, d\tau$$

(1) Quadrupole

(2) Coulombic interaction integrated over nuclear volume

The Mössbauer isomer shift

Part (2) of the above equation is different for the nuclear ground state and the Nuclear excited state because the charge distribution and the nuclear dimensions change upon excitation. This fact causes the nuclear isomer shift

$E^g = \frac{\mathbf{e}}{\mathbf{6\varepsilon_o}}|\boldsymbol{\psi}_\mathbf{0}|^2 \times \int \rho_\mathbf{n}{}^\mathbf{g}(\mathrm{r})\mathbf{r^2 d\tau}$ for the nuclear ground state

$E^a = \frac{\mathbf{e}}{\mathbf{6\varepsilon_o}}|\boldsymbol{\psi}_\mathbf{0}|^2 \times \int \rho_\mathbf{n}{}^\mathbf{a}(\mathrm{r})\mathbf{r^2 d\tau}$ for the nuclear excited state

The corresponding energy difference can now be written for both the source („Quelle“, Q) and the absorber A

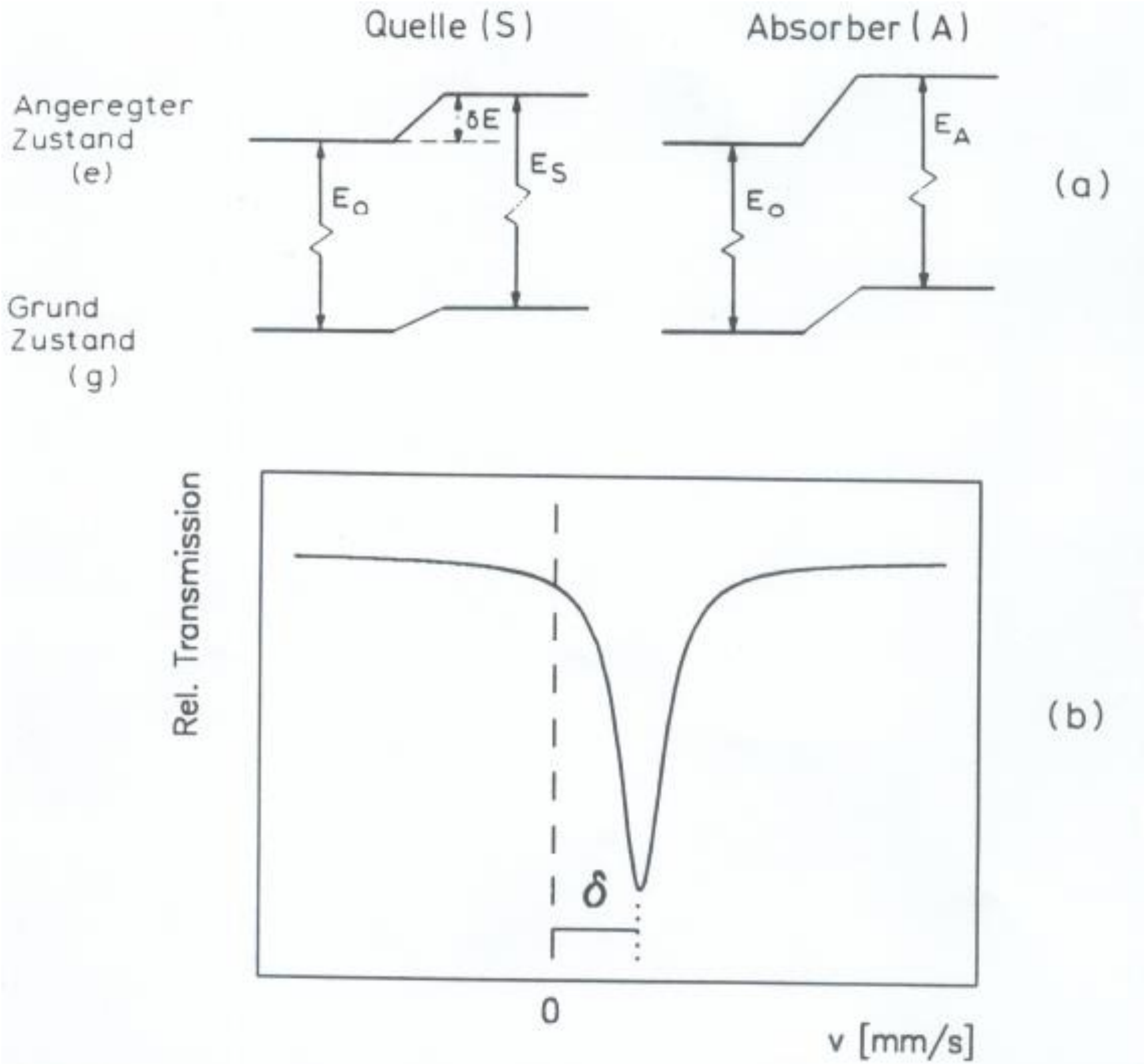
$$\Delta E_Q = E_Q^a - E_Q^g = \frac{1}{6\varepsilon_0} e|\psi(0)|_Q{}^2 \left\{\int \rho_Q^a(r) r^2 d\tau - \int \rho_Q^g(r) r^2 d\tau\right\}$$

$$\Delta E_A = E_A^a - E_A^g = \frac{1}{6\varepsilon_0} e|\psi(0)|_A{}^2 \left\{\int \rho_A^a(r) r^2 d\tau - \int \rho_A^g(r) r^2 d\tau\right\}$$

The difference ΔE_A-ΔE_Q is then known as the isomer shift

$$\delta = \Delta E_A - \Delta E_Q = \frac{1}{6\varepsilon_0} e \underbrace{\left\{|\psi(0)|_A^2 - |\psi(0)|_Q^2\right\}}_{\text{Difference in s-electron densities}} \underbrace{\left\{\int \rho^a(r) r^2 d\tau - \int \rho^g(r) r^2 d\tau\right\}}_{\text{Change in nuclear dimensions upon excitation}}$$

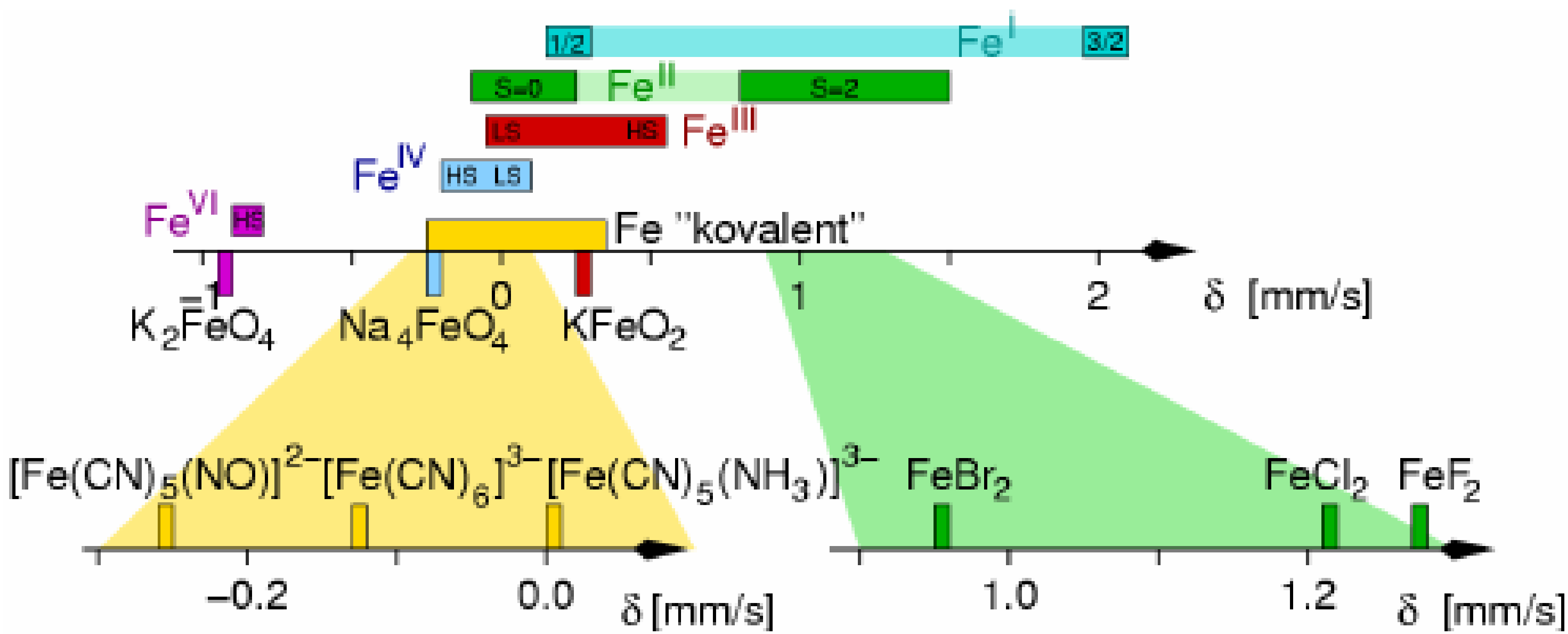
The Mössbauer Isomer shift



Isomer shift and oxidation number of Fe Compounds

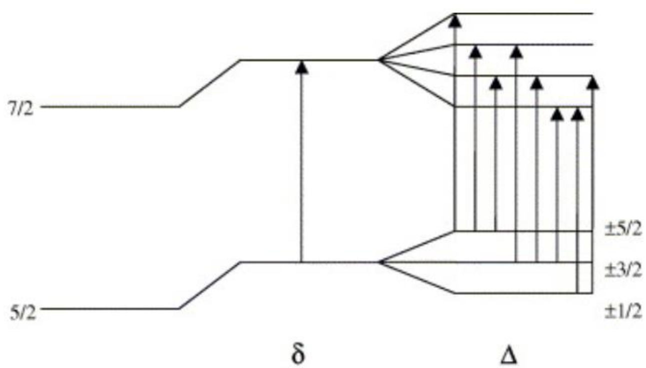
^{57}Fe: nucleus shrinks upon excitation:
s-electron density controlled via screening effect of the d-electrons in the valence shell

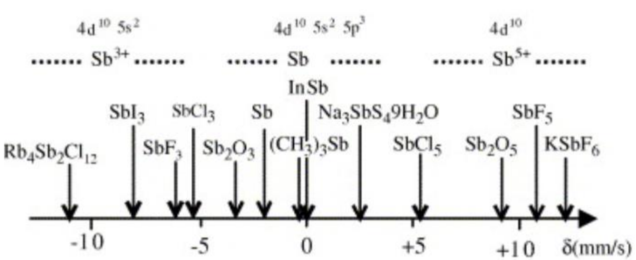
$$\delta = \Delta E_A - \Delta E_Q = \frac{1}{6\varepsilon_0} e\left\{\underbrace{\left|\psi(0)\right|_A^2}_{\text{rises with increasing Oxidation number}} - \left|\psi(0)\right|_Q^2\right\}\underbrace{\left\{\int \rho^a(r)\, r^2 d\tau - \int \rho^g(r)\, r^2 d\tau\right\}}_{< 0}$$

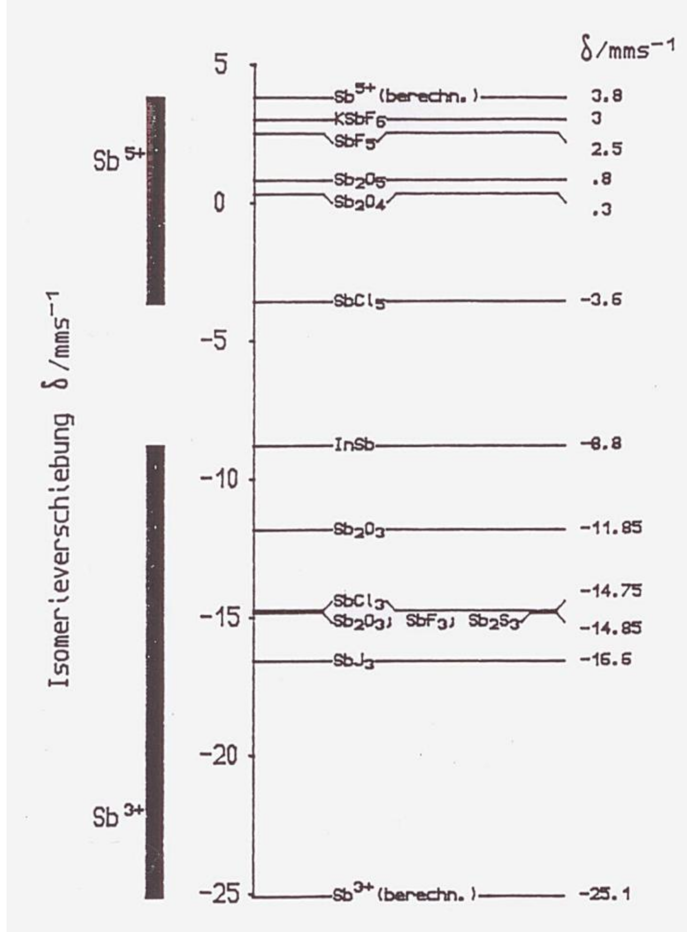


^{121}Sb Mössbauer in Antimony Compounds

$$\delta = \Delta E_A - \Delta E_Q = \frac{1}{6\varepsilon_0} e \underbrace{\left\{|\psi(0)|_A^2 - |\psi(0)|_Q^2\right\}}_{\text{rises with increasing Oxidation number}} \underbrace{\left\{\int \rho^a(r) r^2 d\tau - \int \rho^g(r) r^2 d\tau\right\}}_{<0}$$



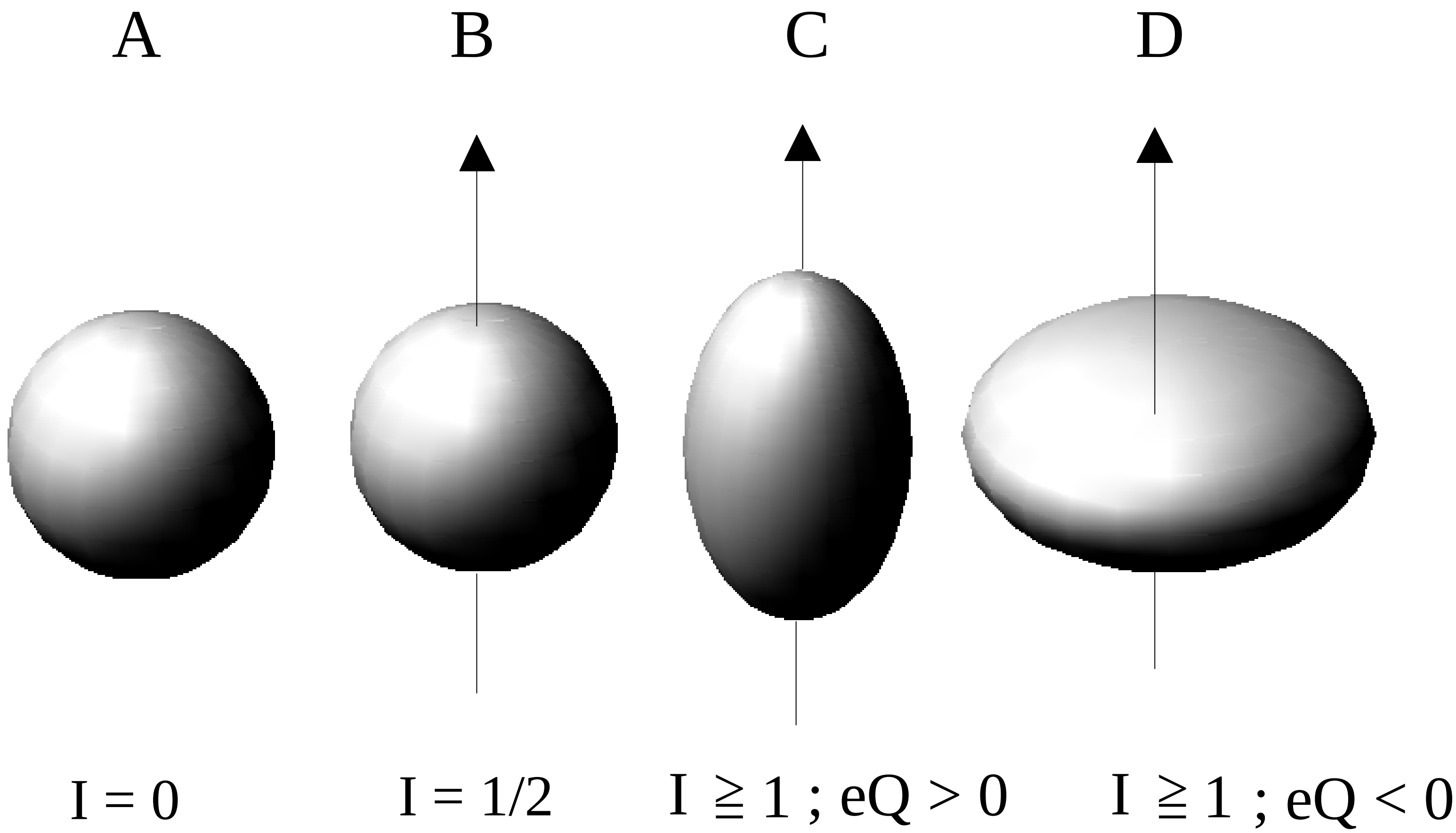




s- electron density affected by ligand electronegativity

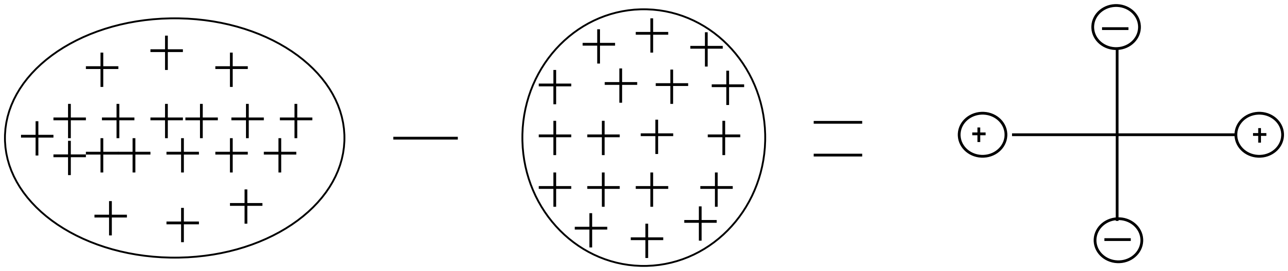
Nuclear electric quadrupole moment:

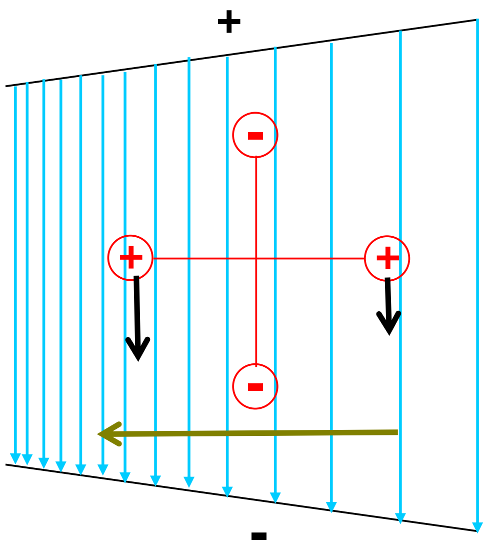
non-spherical distribution of nuclear charge



$eQ \sim 10^{-25}$ to 10^{-30} m^2

The physical picture





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This quadrupole moment interacts with local electric field gradients created by the bonding environment of the nuclei.

-> probe of local symmetry

The Quadrupolar Hamiltonian

$$E_{el} = V(0)\int \rho\, d\tau + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho\, d\tau + \boxed{\frac{1}{2!}\sum_{\alpha,\beta} V_{\alpha,\beta} \int x_{\alpha} x_{\beta} \rho\, d\tau} + \ldots\ldots..$$

Coulomb term dipole term quadrupole term

$$Q_{\alpha\beta} = \int \left(3x_{\alpha}x_{\beta} - \delta_{\alpha\beta} r^2\right)\rho\, d\tau$$

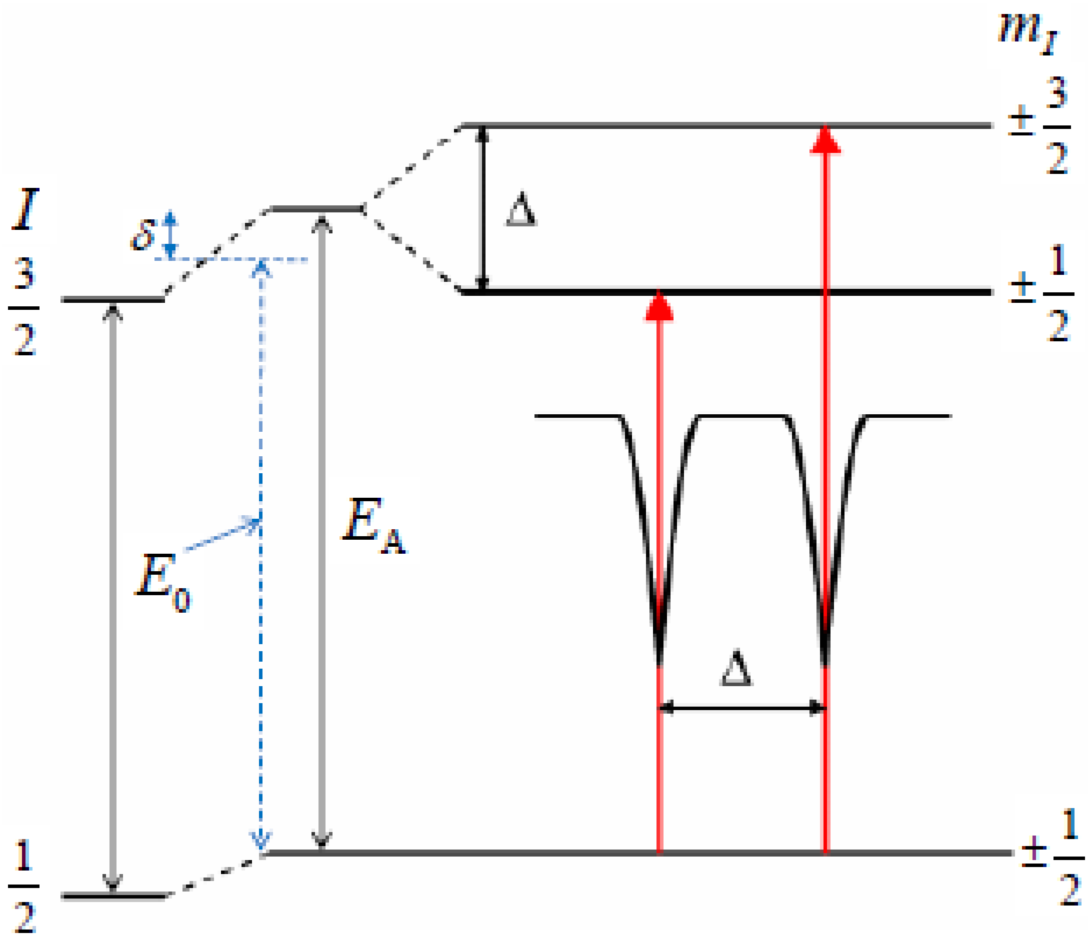
$$E_Q = \frac{1}{6}\sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta}$$

$$\hat{Q}_{\alpha\beta} = \left[\frac{3(\hat{I}_{\alpha}\hat{I}_{\beta} + \hat{I}_{\beta}\hat{I}_{\alpha})}{2} - \delta_{\alpha\beta}\hat{I}^2\right] \cdot \frac{eQ}{I(2I-1)}$$

Expressed in spin coordinates
Wigner-Eckart-Theorem

$$\hat{H}_Q = \frac{e^2 qQ}{4I(2I-1)}\left[\left(3\hat{I}_{z'}^2 - \hat{I}^2\right) + \eta\left(\hat{I}_{y'}^2 - \hat{I}_{x'}^2\right)\right]$$

Quadrupole Splitting (I=3/2, ^{57}Fe)



- The quadrupole splitting arises from asymmetric distribution (gradient) of electron density around the absorbing nucleus

$$E^a_{\pm 3/2} - E^g = E_0 + IS + e^2qQ/4$$
$$E^a_{\pm 1/2} - E^g = E_0 + IS - e^2qQ/4$$

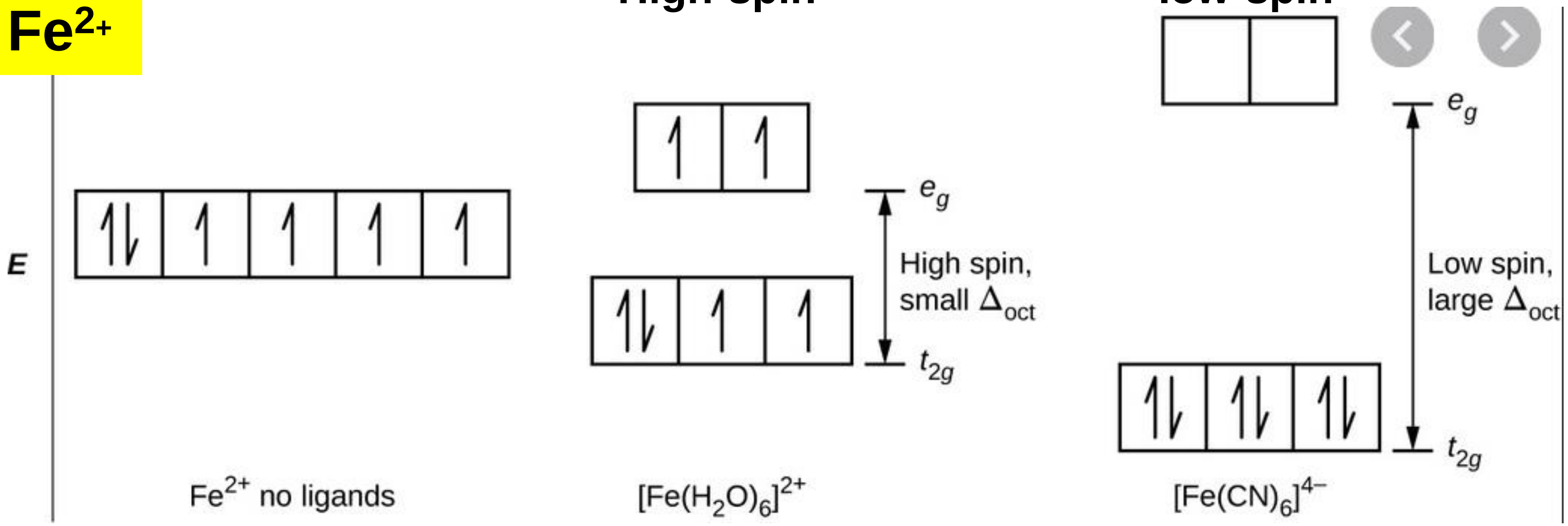
Quadrupole splitting
$QS = e^2qQ/2$
for axial symmetry

Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Differentiation of Fe oxidation states and spin configurations

Fe^{2+}

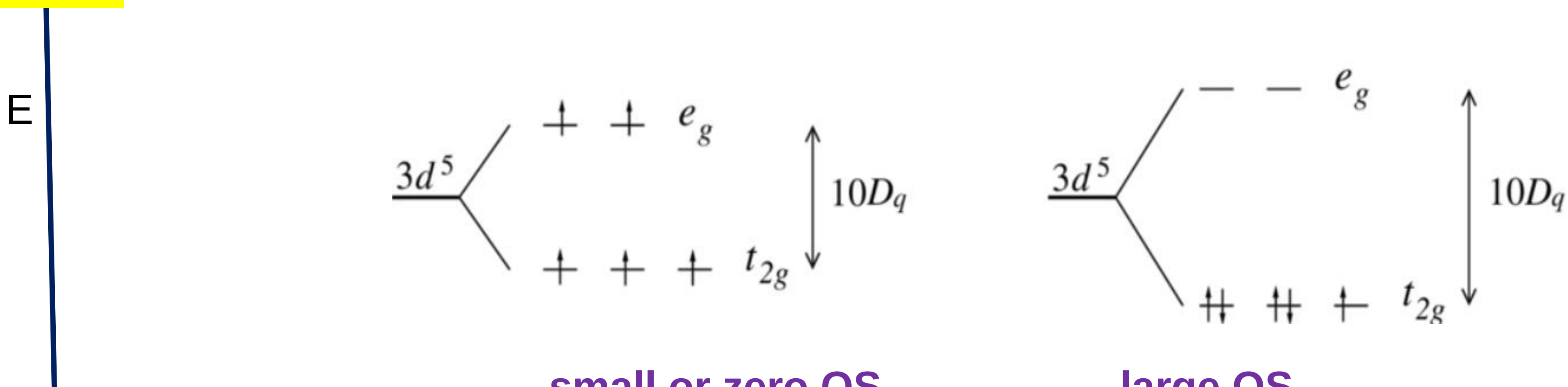
High-spin **low-spin**



large QS

small or zero QS

Fe^{3+}

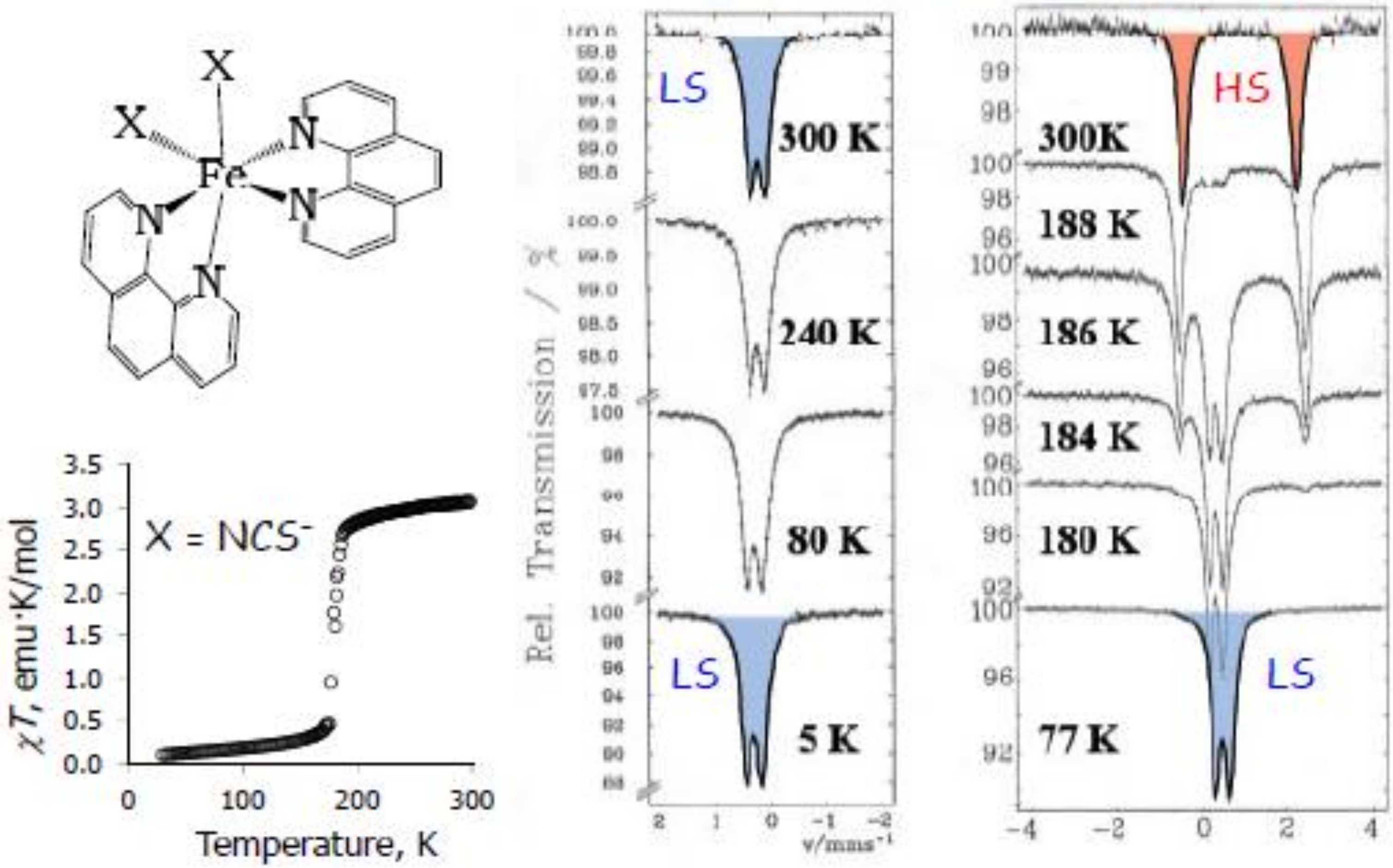


small or zero QS

large QS

Mössbauer Spectrum of a Spin-Crossover Compound

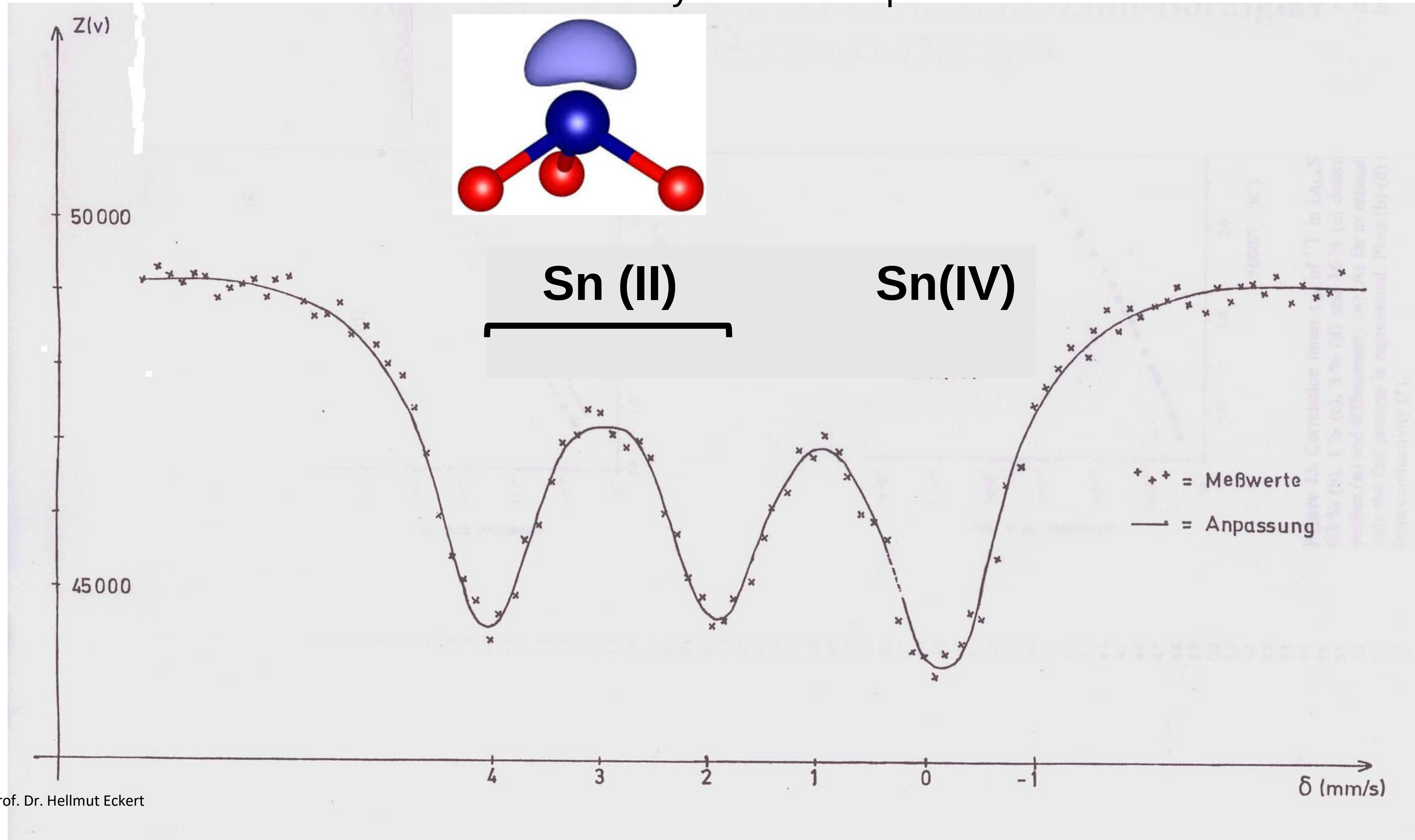
Example: $[Fe(phen)_3]Cl_2$ vs. $Fe(phen)_2(NCS)_2$



Gütlich, P. *Lectures Notes on Mössbauer Spectroscopy*. University of Mainz.

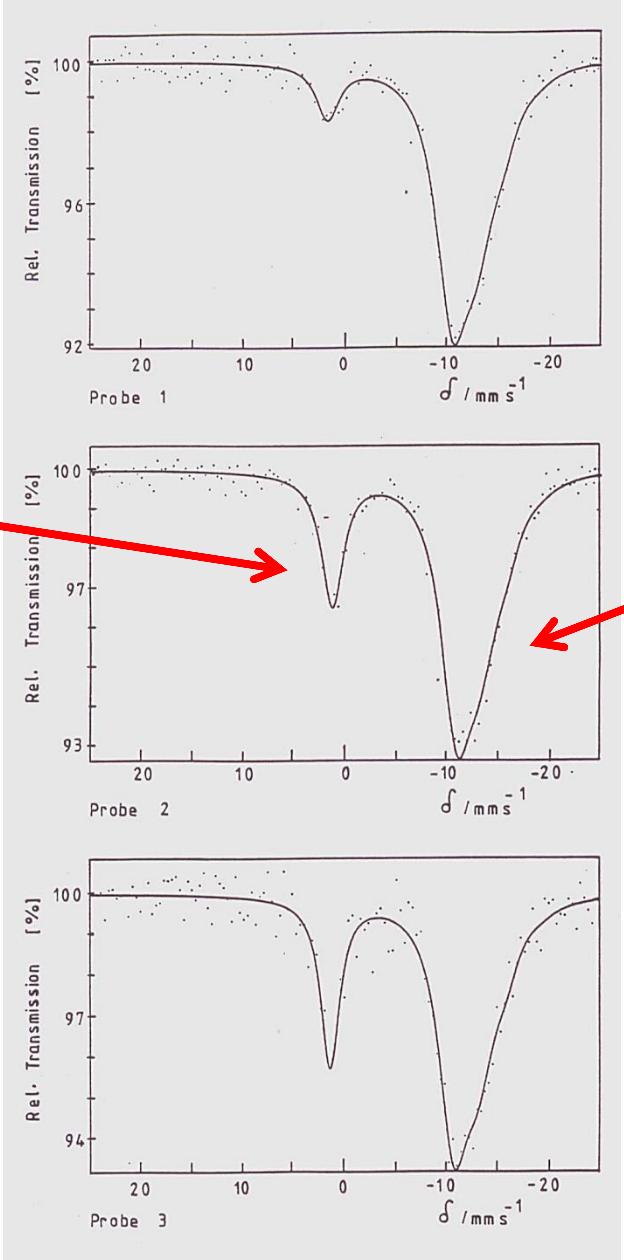
^{119}Sn Mössbauer spectrum of a borate glass 53.3 B_2O_3-25.5 Na2O-17.2 SnO

Sterochemically active lone pair on Sn^{2+}

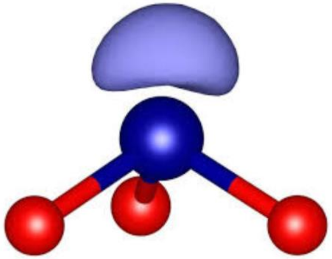


Distinction of Sb(III) and Sb(V) in some borate glasses

Sb (V)



Sb (III)



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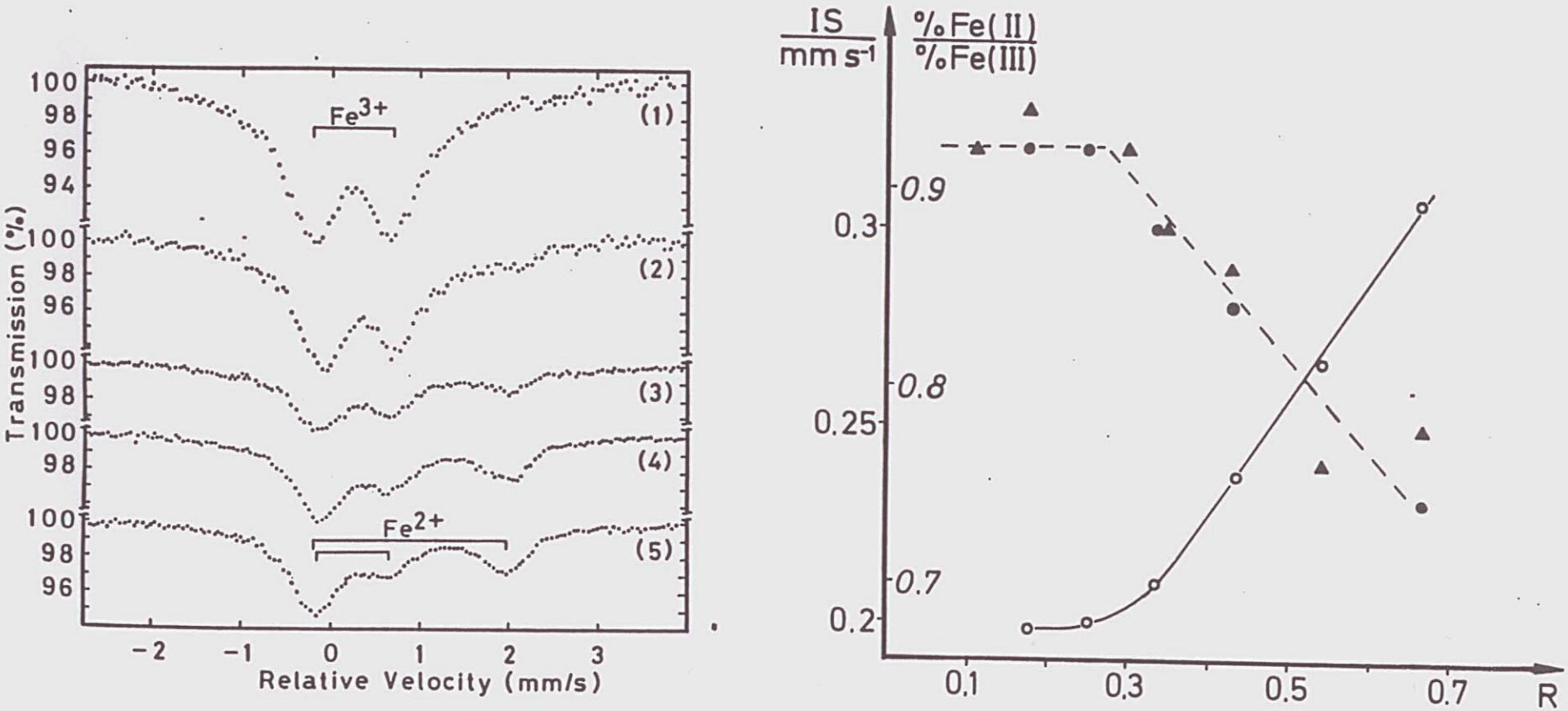
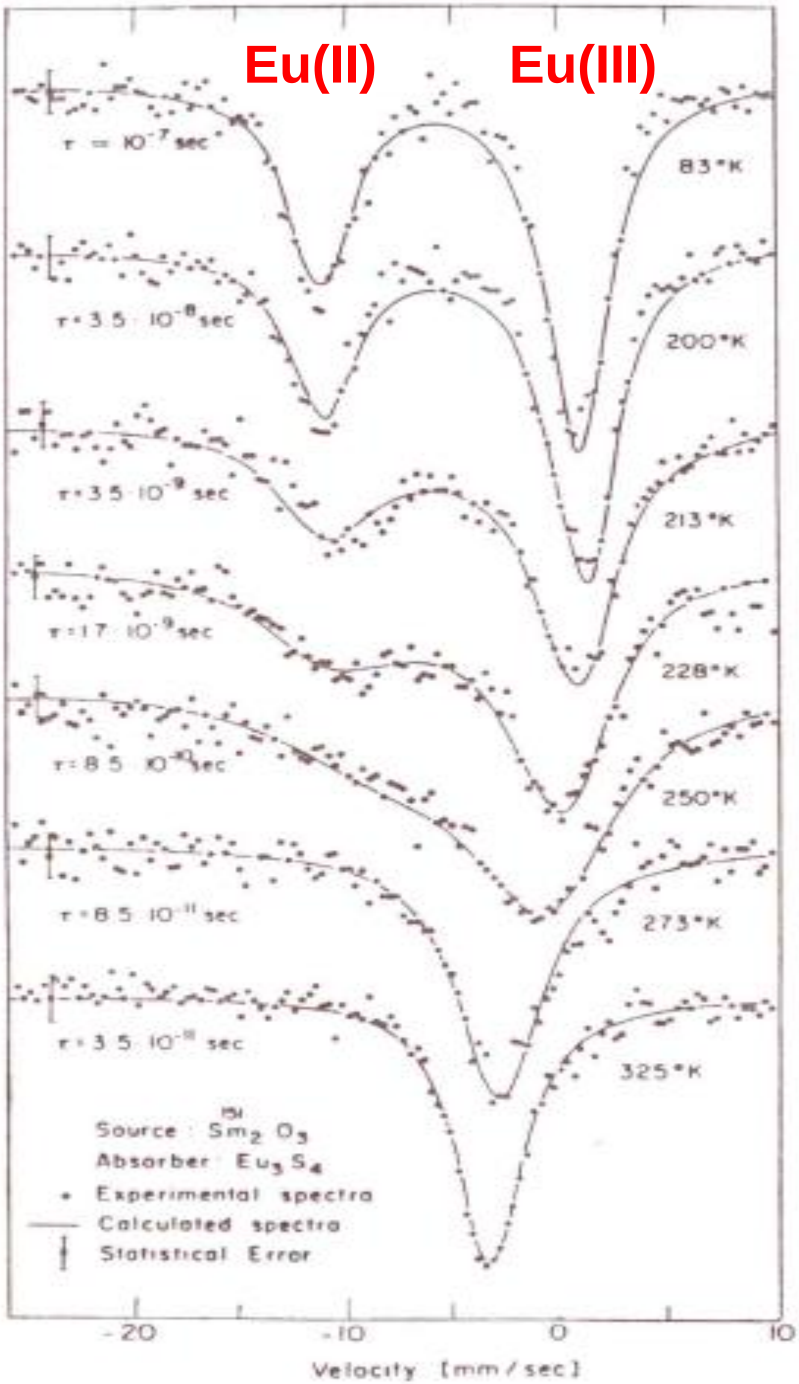
Mössbauer Spectra of γ-irradiated borate glasses



^{151}Eu Mössbauer of Eu_3S_4:

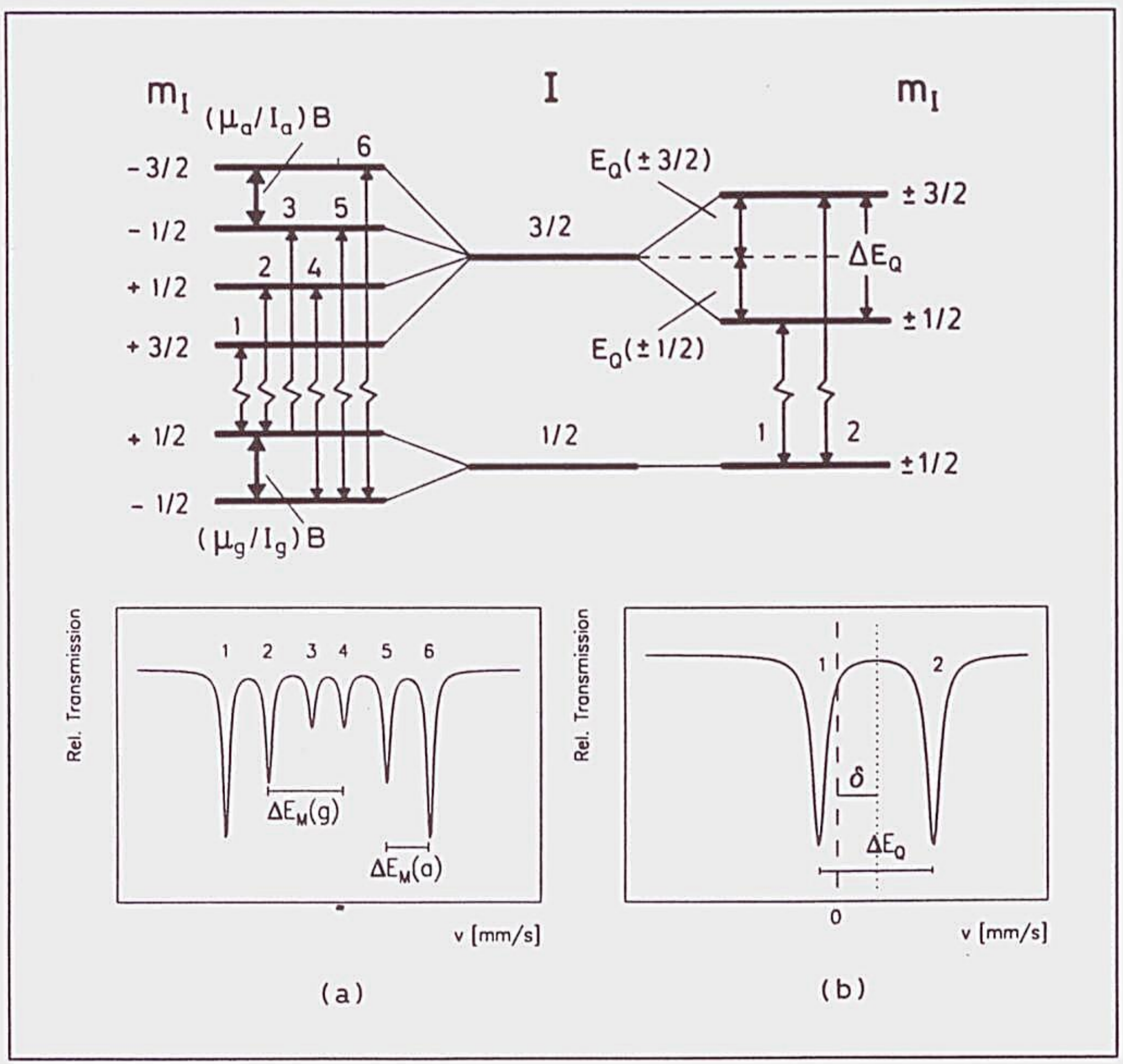
T- dependent electron hopping



Intermediate Chemical exchange region

Fast averaging regime

Magnetic Hyperfine Interaction



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$E^a_{m'} = E_0 + m'_I\gamma'\hbar B$
$E^g_m = m_I\gamma\hbar B$

$E^a_{m'} - E^g_m = E_0 + IS + m'_I\gamma'\hbar B - m_I\gamma\hbar B$

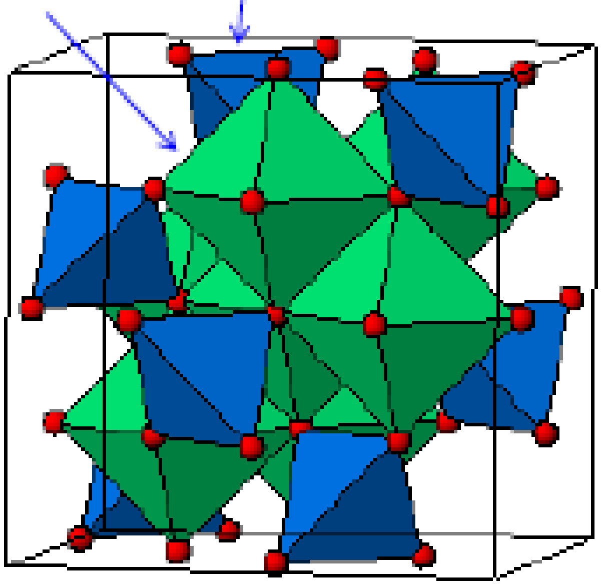
Allowed transitions:
$m_I' - m_I = 0, 1, -1$

Magnetic field can be internal (in ferro- or anti-ferromagnets) or external

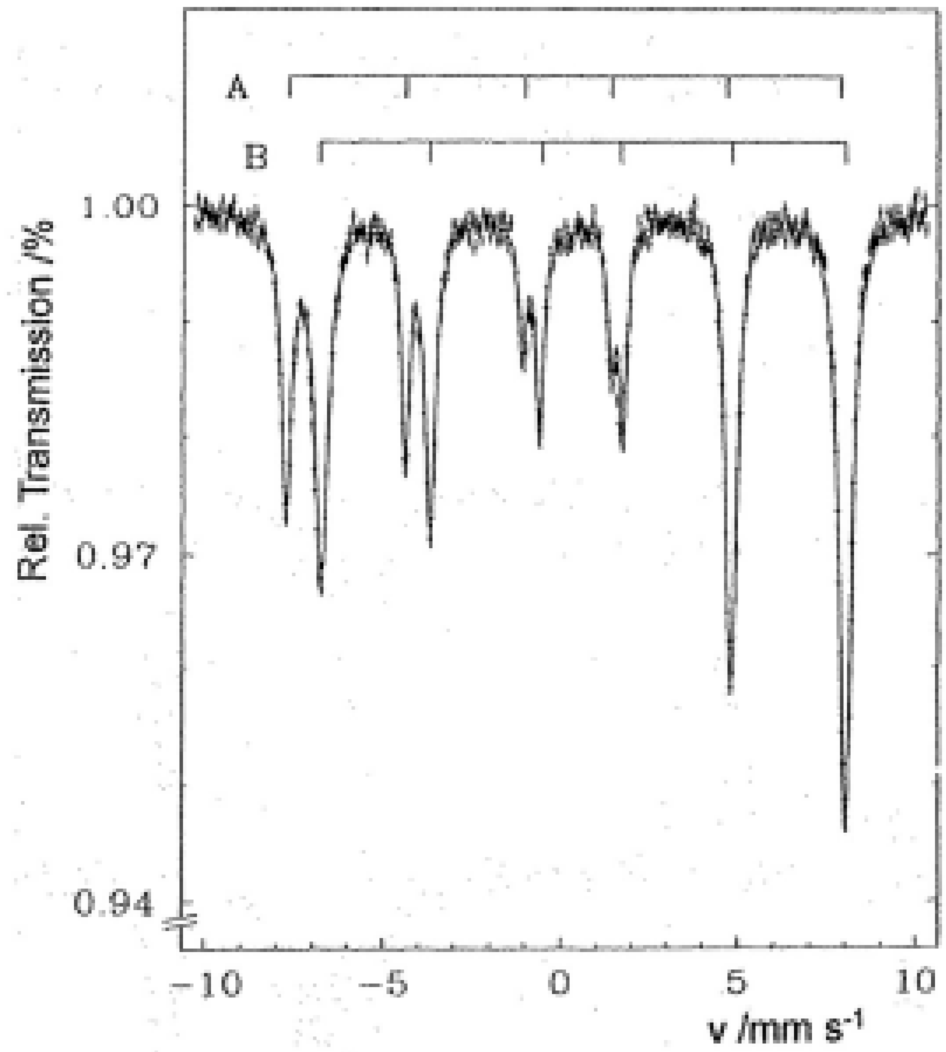
Example: Magnetite, Fe_3O_4

Site A: Fe^{3+}

Site B: Fe^{2+}/Fe^{3+}



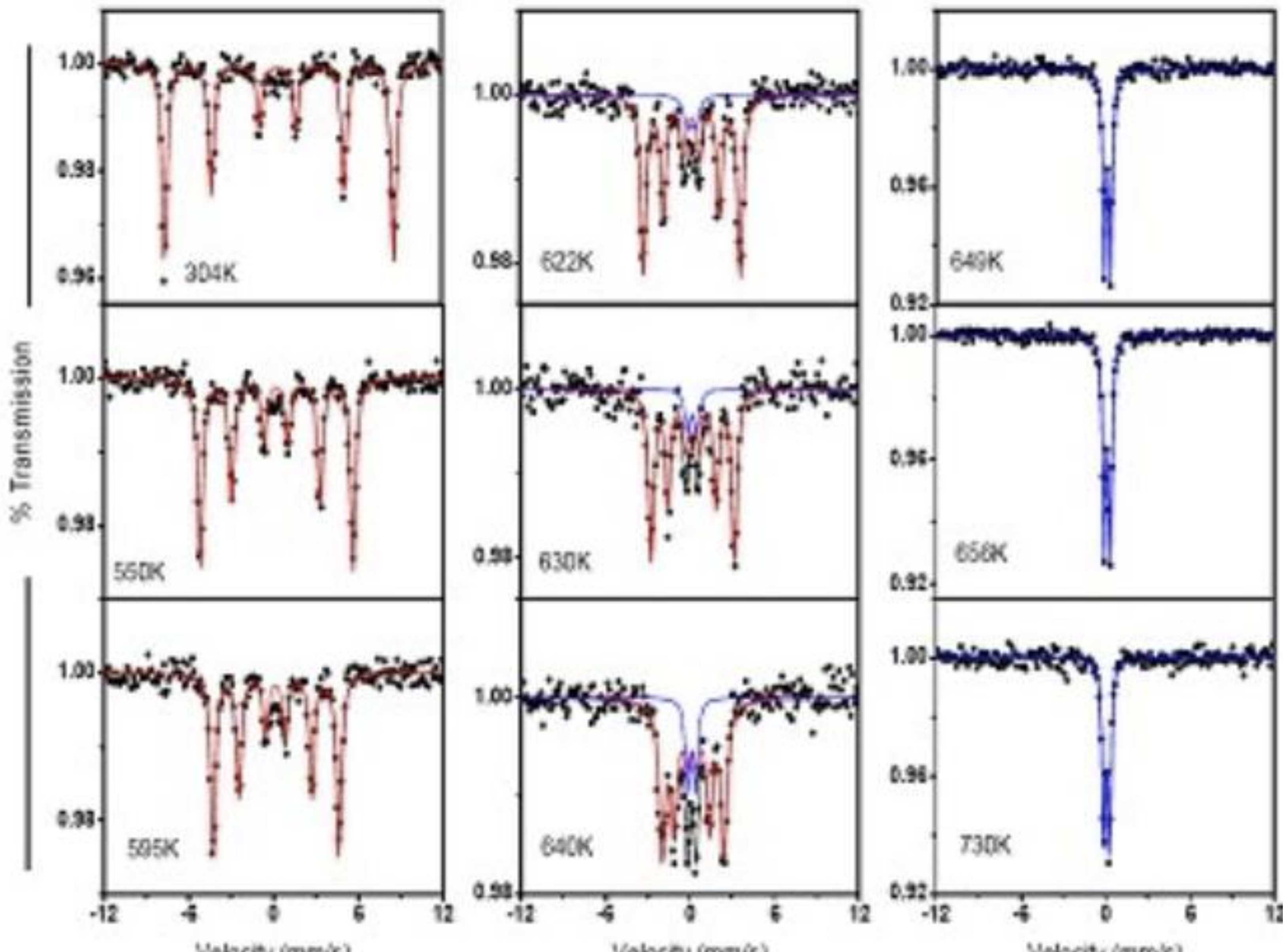
Site B: Class III mixed-valent system



Gütlich, P.; Trautwein, A. X.; Link, R. F. *Mössbauer Spectroscopy and Transition Metal Chemistry*, 1978.

Temperature Dependence

above T_c



Nanocrystalline Fe_3O_4

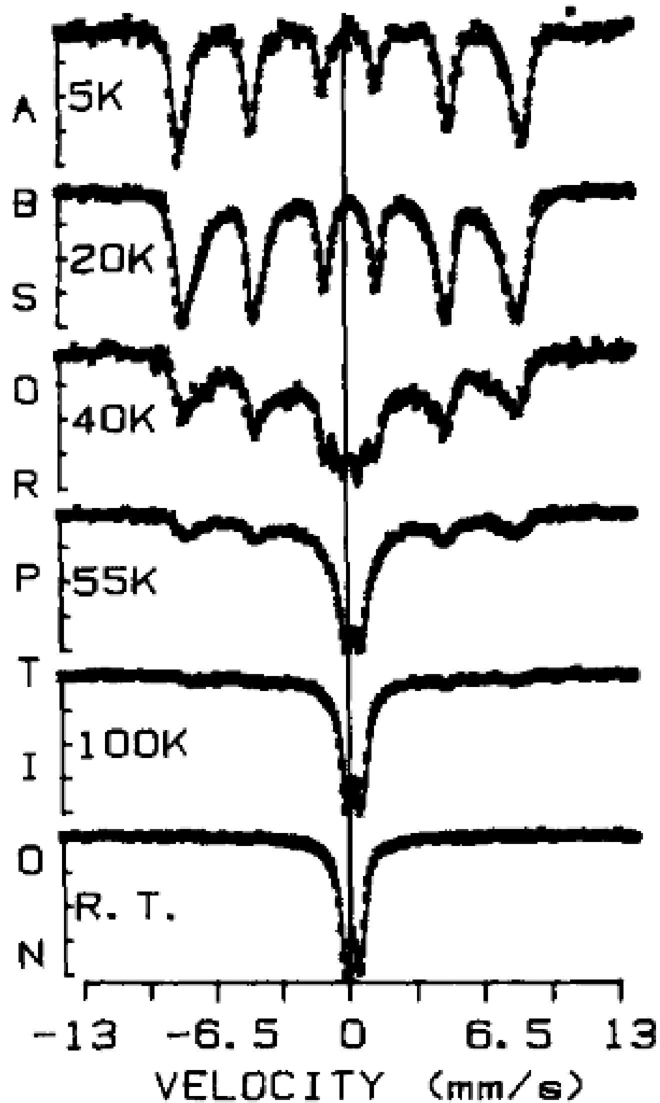


Fig. 1. Mössbauer spectra for the 30 Å Fe_3O_4 ultrafine particle system at various temperatures.

Ordered state

Blocking temperature

Superparamagnetic state

Lehlooh and Mahmood, Journal of Magnetism and Magnetic Materials 151 (1995) 163-166