Mössbauer-Spektroskopie

Methodenseminar

V. Ksenofontov

Referenzen und Zitaten:

Prof. P. Gütlich
Lecture Notes „Mössbauer Spectroscopy“

Mössbauer-Spektroskopie

1. Prinzip
2. Hyperfeinwechselwirkungen
3. Anwendungen

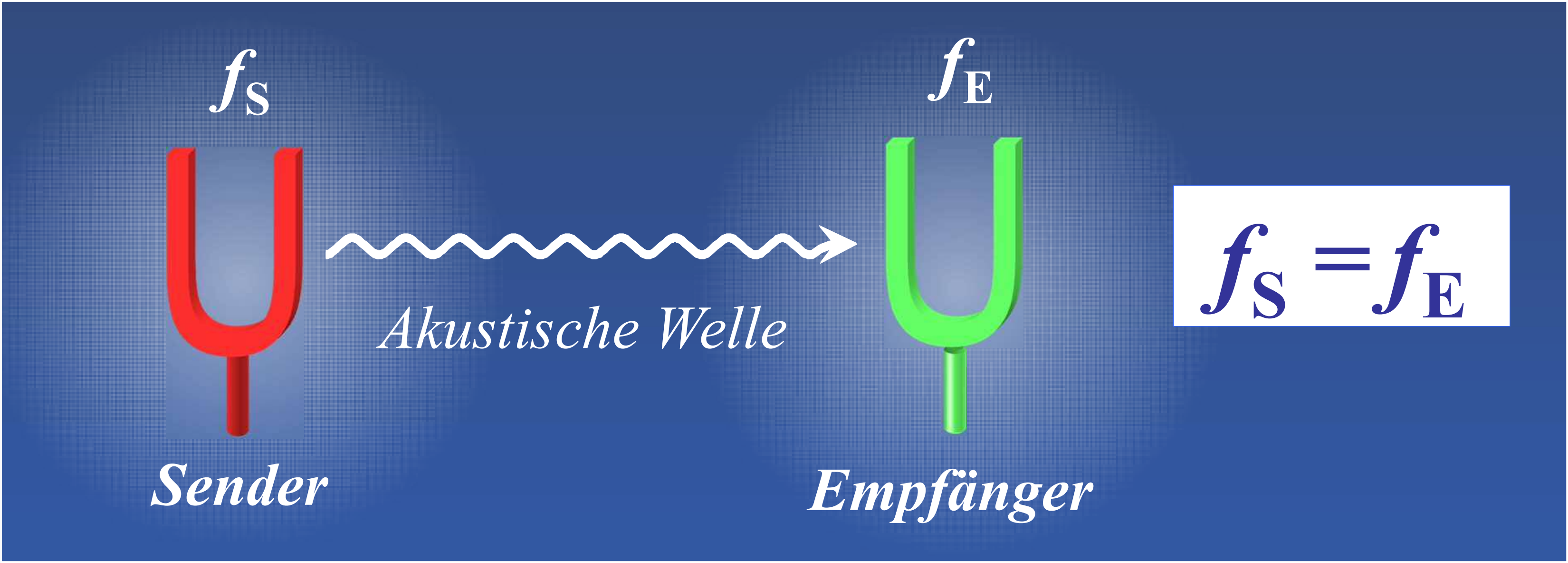
Mössbauereffekt

Resonante Absorption von elektromagnetische Strahlung (γ-Photonen) aus dem Zerfall Angeregte Atomkerne – Mössbauereffekt.

- in Festkörper

- Energieschärfe ($10^{-13} – 10^{-15}$)!!!!

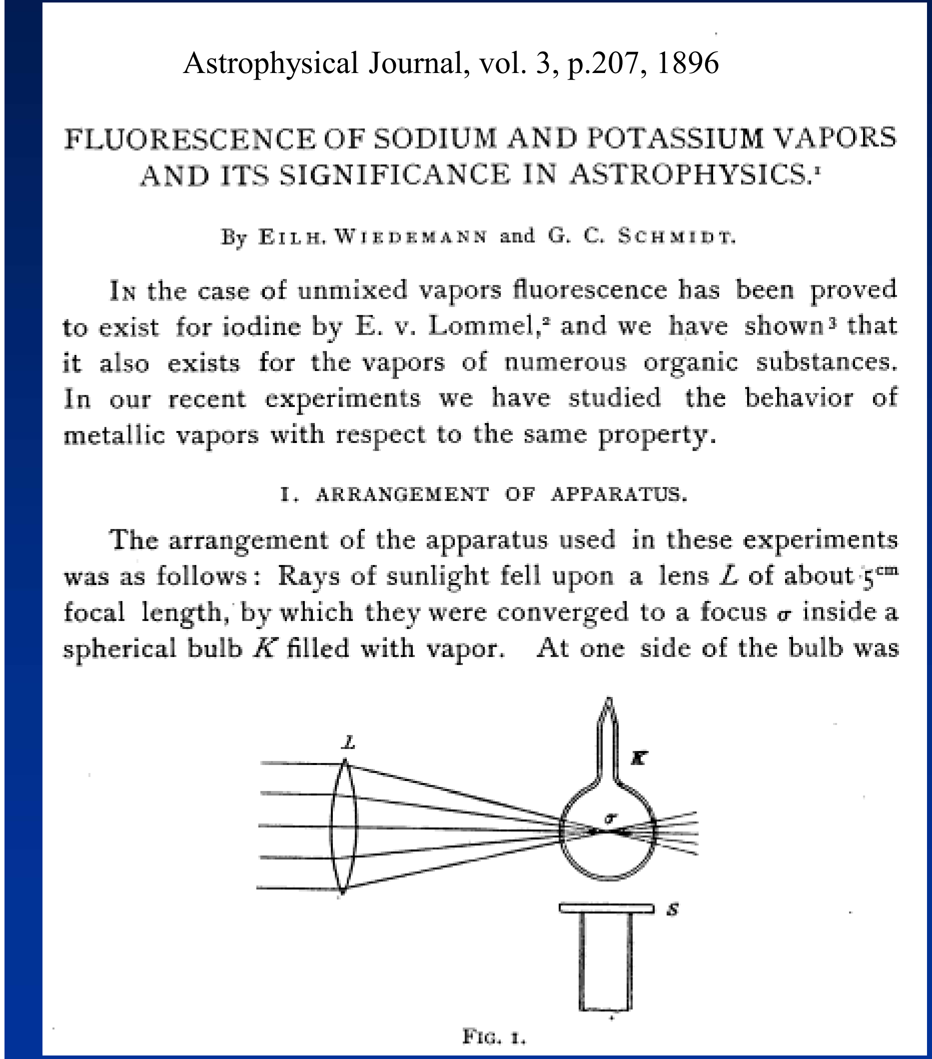
Zwei Stimmgabeln in Resonanz



Statt Stimmgabeln: Atome

Werner Kuhn (1929): die Resonanzabsorption von γ-Strahlung

Natrium-Resonanzfluoreszenz



Astrophysical Journal, vol. 3, p.207, 1896

FLUORESCENCE OF SODIUM AND POTASSIUM VAPORS AND ITS SIGNIFICANCE IN ASTROPHYSICS.[1]

By EILH. WIEDEMANN and G. C. SCHMIDT.

IN the case of unmixed vapors fluorescence has been proved to exist for iodine by E. v. Lommel,[2] and we have shown[3] that it also exists for the vapors of numerous organic substances. In our recent experiments we have studied the behavior of metallic vapors with respect to the same property.

I. ARRANGEMENT OF APPARATUS.

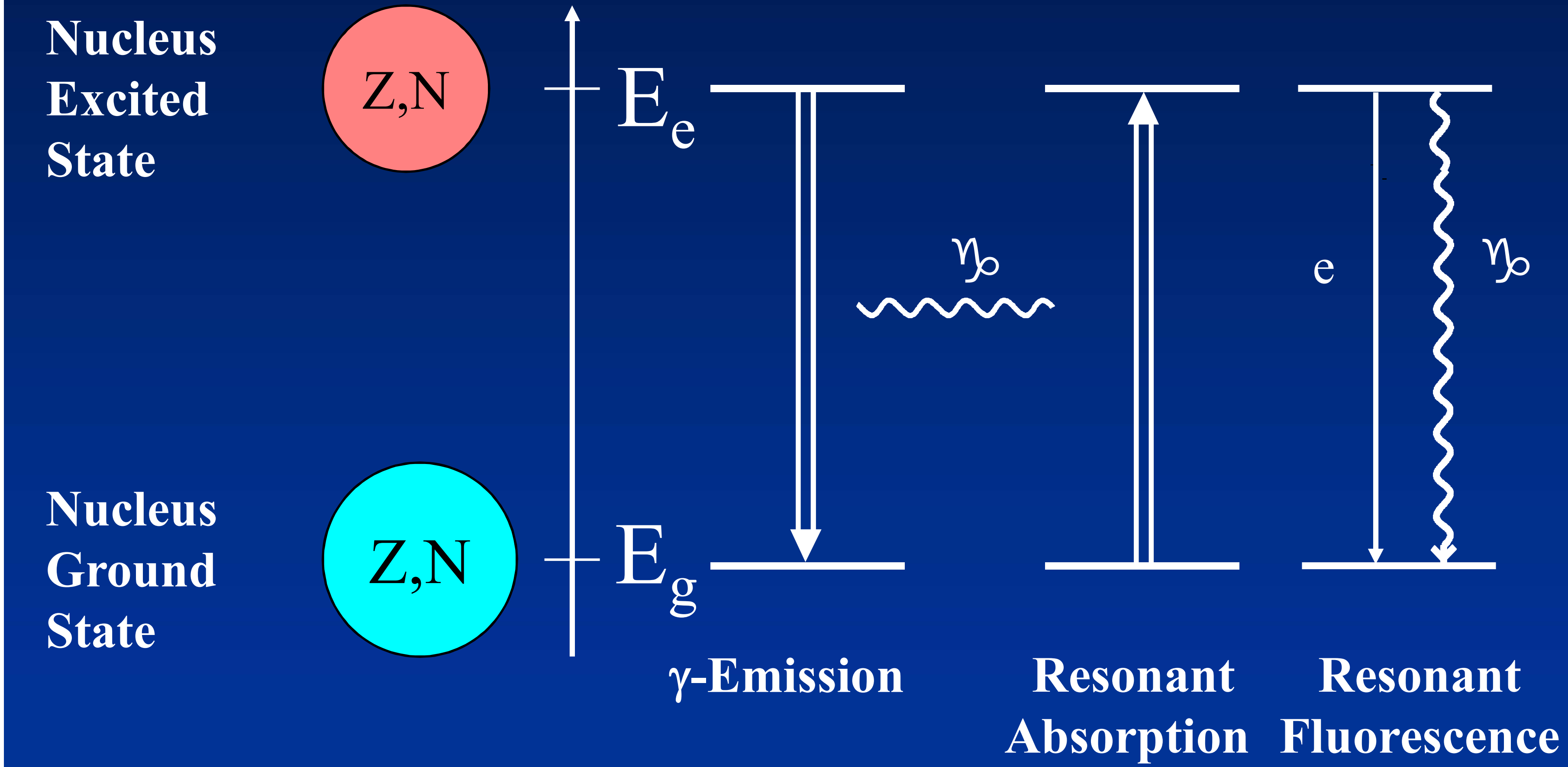
The arrangement of the apparatus used in these experiments was as follows: Rays of sunlight fell upon a lens L of about 5^{cm} focal length, by which they were converged to a focus σ inside a spherical bulb K filled with vapor. At one side of the bulb was

FIG. 1.

Die gesamte Röhre leuchtet unter Emission der gelben Na-D-Linie auf, wenn sie im geheizten Zustand mit Na-Spektrallicht durchstrahlt wird.

Ref.: http://ocw.mit.edu/

Rückstoßfreie Kernresonanz- absorption von γ-Strahlung



Übergangsenergie: $E_\gamma = E_a - E_g$

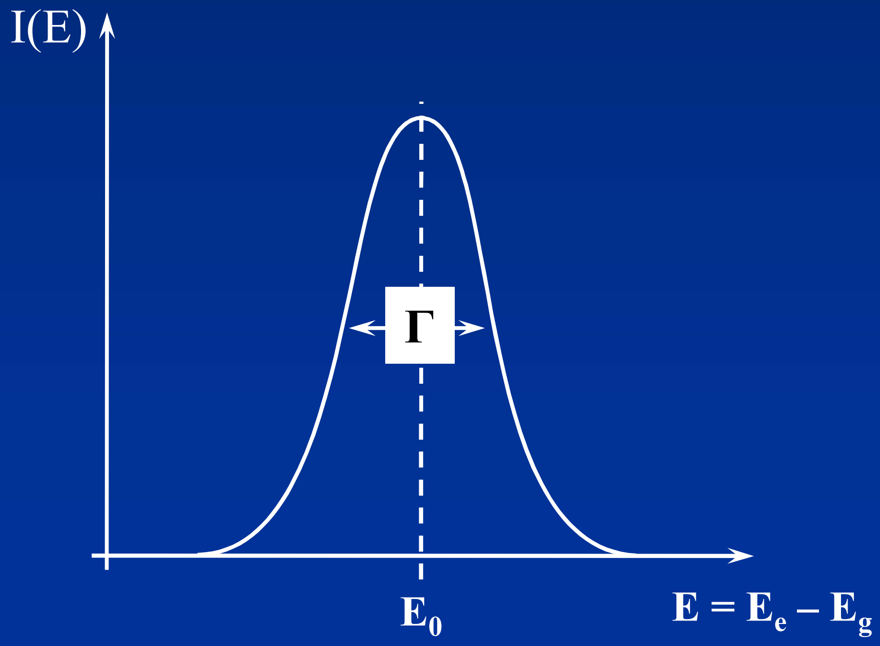
Ursachen für den späten Nachweis

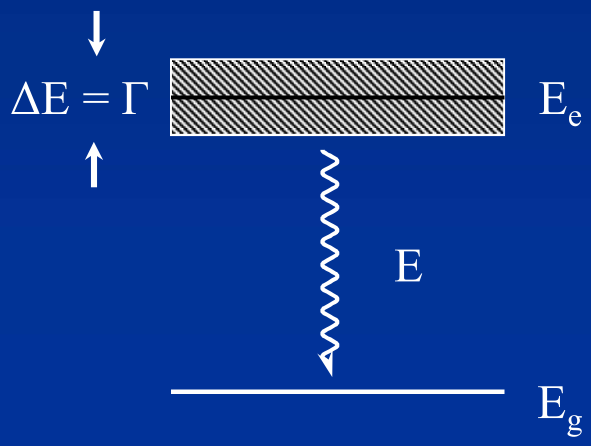
Mittlere Lebensdauer des angeregten Kernzustands:

Geeignet: $10^{-6}\,\mathrm{s} \geq \tau_N \geq 10^{-11}\,\mathrm{s}$

Die mittlere Lebensdauer τ_N bestimmt die Resonanzlinienbreite gemäß der **Heisenbergschen Unschärfe-Relation**: $\boldsymbol{\Gamma \cdot \tau_N = \hbar}$.

(Die mittlere Lebensdauer τ_N ist mit der Halbwertzeit $t_{1/2}$ korreliert: $\tau_N = \ln 2 \cdot t_{1/2}$).

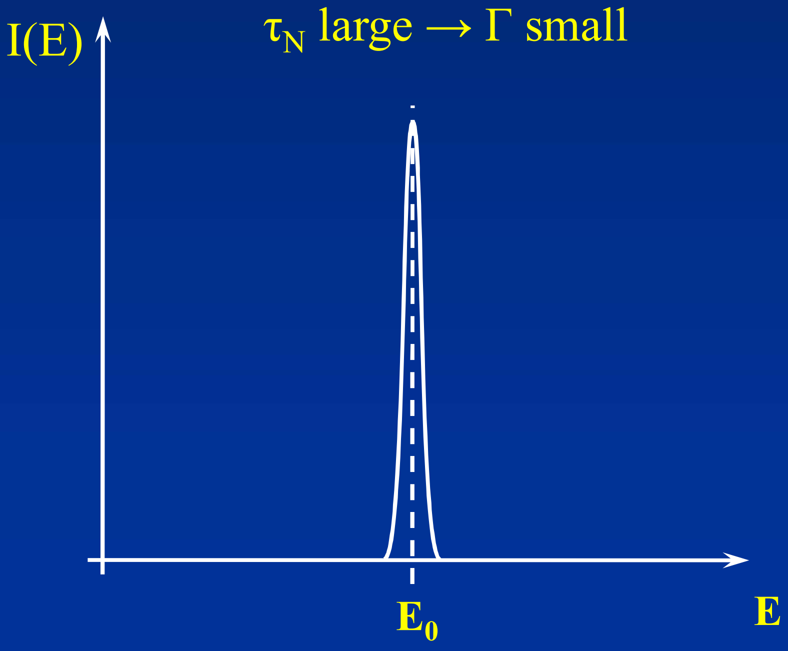


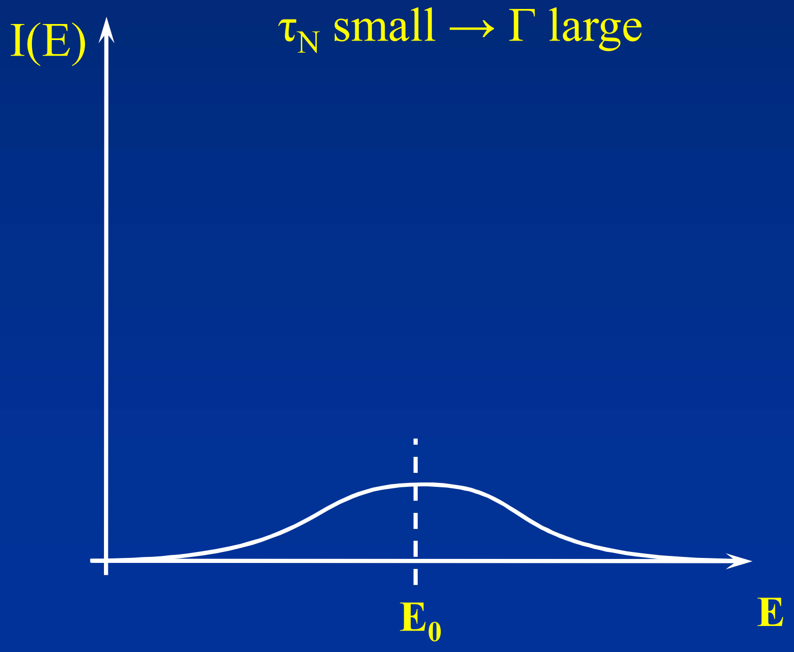


According to Weisskopf and Wigner the distribution of energies about the energy E_0 (= transition probability as function of transition energy E) is given by the **Breit-Wigner (or Lorentzian) formula**:

$$\boxed{I(E) = \frac{(\Gamma/2)^2}{(E-E_0)^2 + (\Gamma/2)^2}}$$

The mean lifetime τ determines the width of the resonance lines ($\Gamma \cdot \tau = \hbar$).
The mean lifetime τ is related to the halflife $t_{1/2}$ by the relation $\tau = \ln 2 \cdot t_{1/2}$.





Resonanzschärfe Γ/E_γ

beim Mössbauer-Effekt mit der Übergangsenergie E_γ

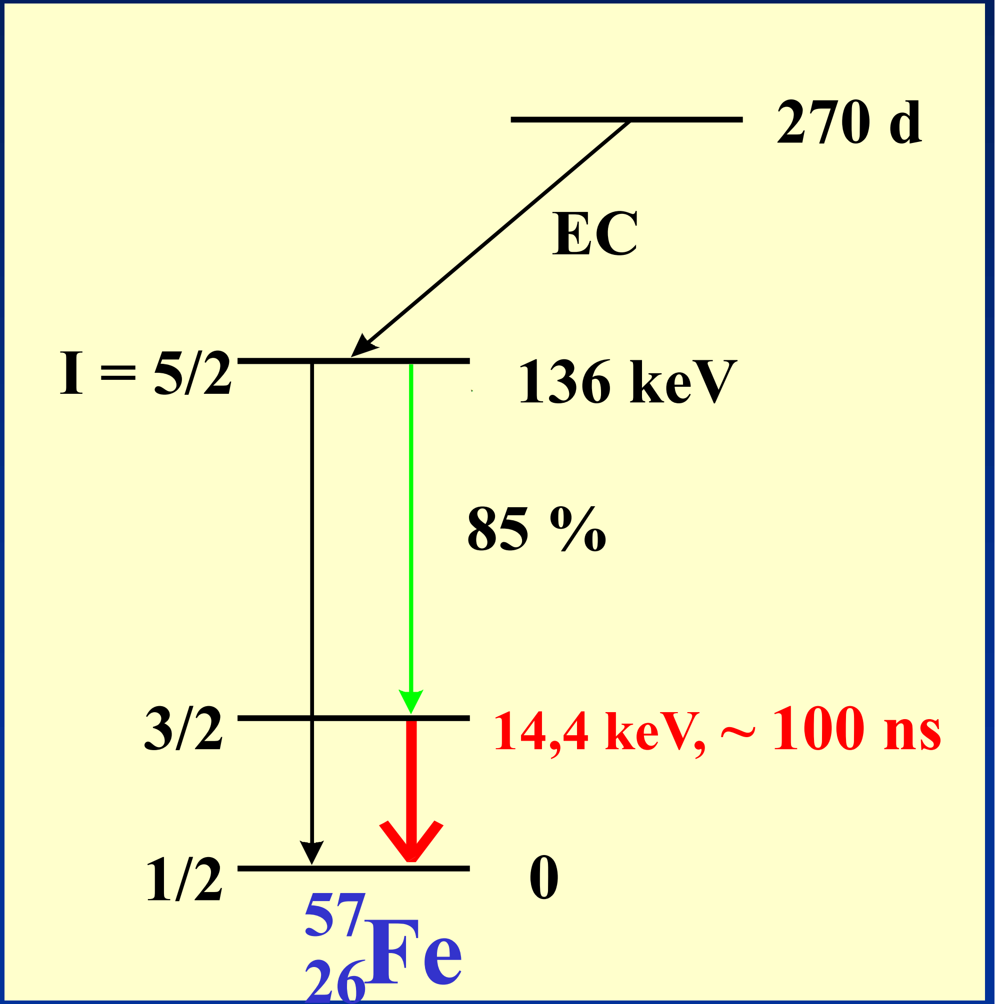
^{57}Fe mit $E_\gamma = 14\,400$ eV

$\tau_N = 1.4 \cdot 10^{-7}$ s →
$\Gamma = \hbar/\tau_N = 4.6 \cdot 10^{-9}$ eV

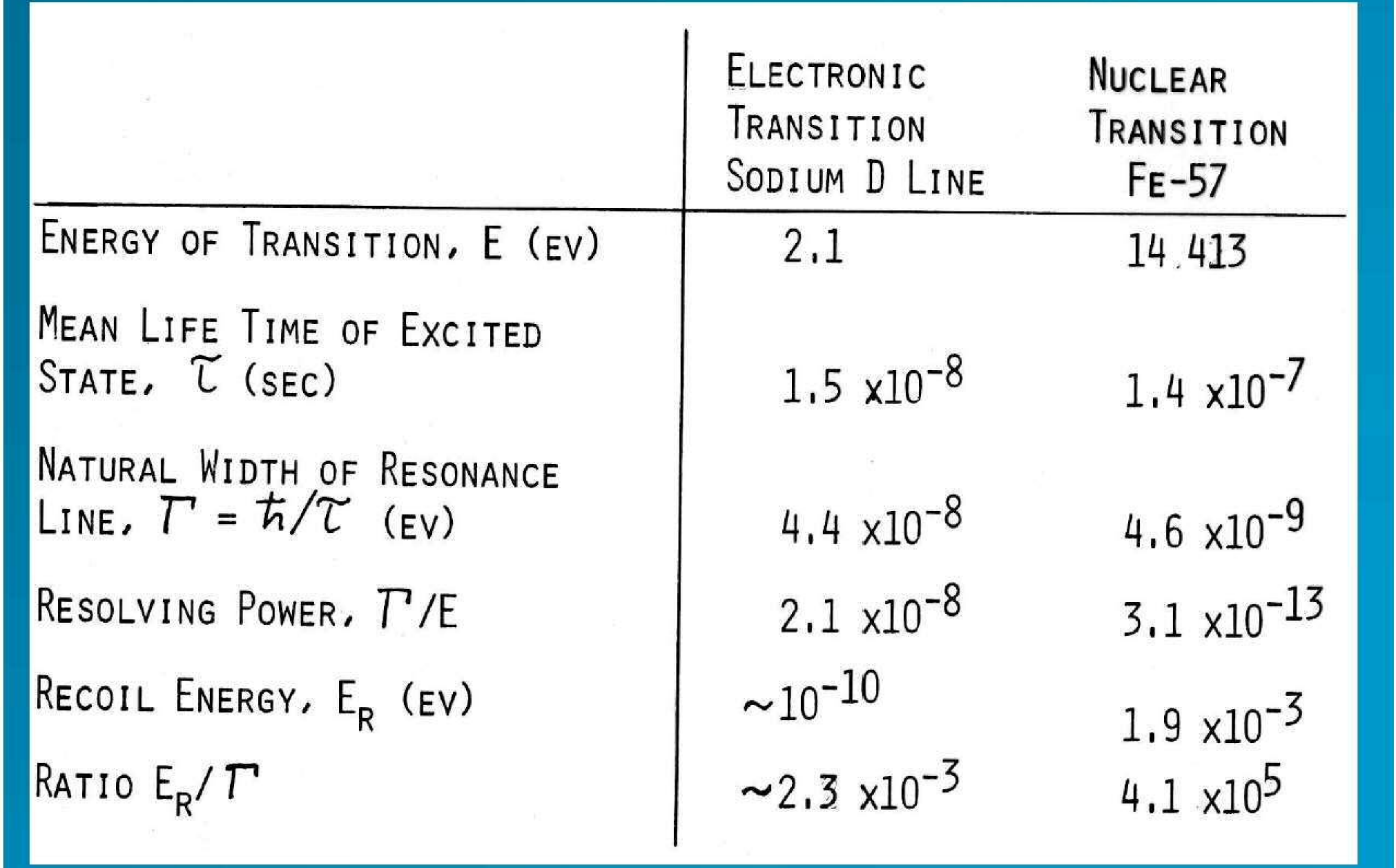
$\Gamma/E_\gamma = \mathbf{3.3 \cdot 10^{-13}}$

(Optische Übergänge: $\Gamma/E \sim 10^{-8}$)

Kernzerfall von ^{57}Co
für ^{57}Fe Mössbauer-Resonanz)



Comparison Between Electronic and Nuclear Transitions



	Electronic Transition Sodium D Line	Nuclear Transition Fe-57
Energy of Transition, E (eV)	2.1	14.413
Mean Life Time of Excited State, τ (sec)	1.5×10^{-8}	1.4×10^{-7}
Natural Width of Resonance Line, $\Gamma = \hbar/\tau$ (eV)	4.4×10^{-8}	4.6×10^{-9}
Resolving Power, Γ/E	2.1×10^{-8}	3.1×10^{-13}
Recoil Energy, E_R (eV)	$\sim 10^{-10}$	1.9×10^{-3}
Ratio E_R/Γ	$\sim 2.3 \times 10^{-3}$	4.1×10^{5}

Rückstoß-Effekt!!!!!

Bei Emission und Absorption von γ -Quanten mit der Energie E_γ erleidet ein **freies atom oder Molekül** (Gas, Flüssigkeit) mit der Masse **m** einen Rückstoß mit der Energie E_R:

$$\mathbf{E_R = E_\gamma{}^2/2mc^2}$$

der um 5-6 Größenordnungen größer ist als die natürliche Linienbreite Γ
→ Keine Resonanz möglich.

Frei emittierendes Atom

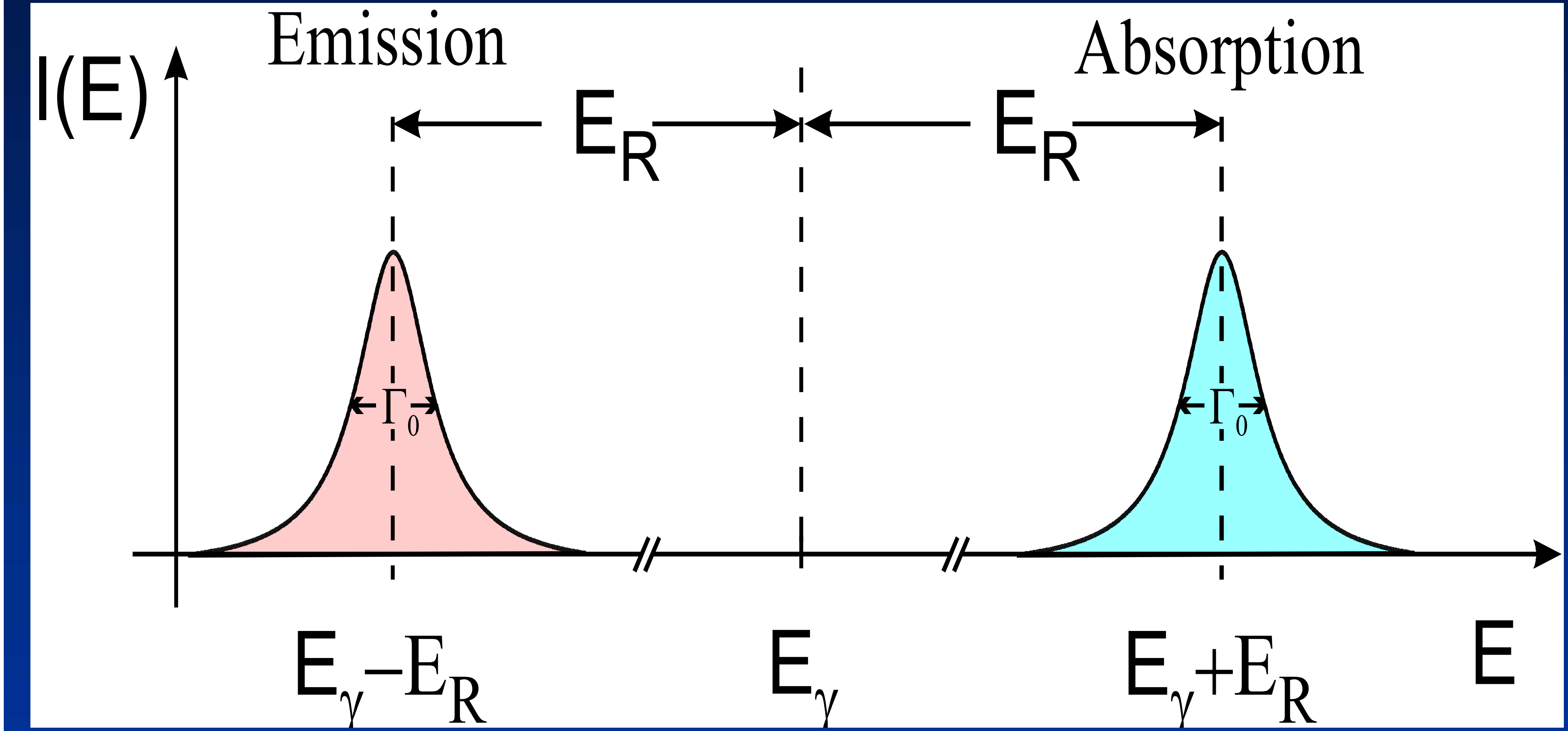
Rückstoß

$E_R = E_\gamma{}^2/2mc^2$

γ-Quantum

$E_\gamma = E_0 - E_R$

Rückstoß-Effekt

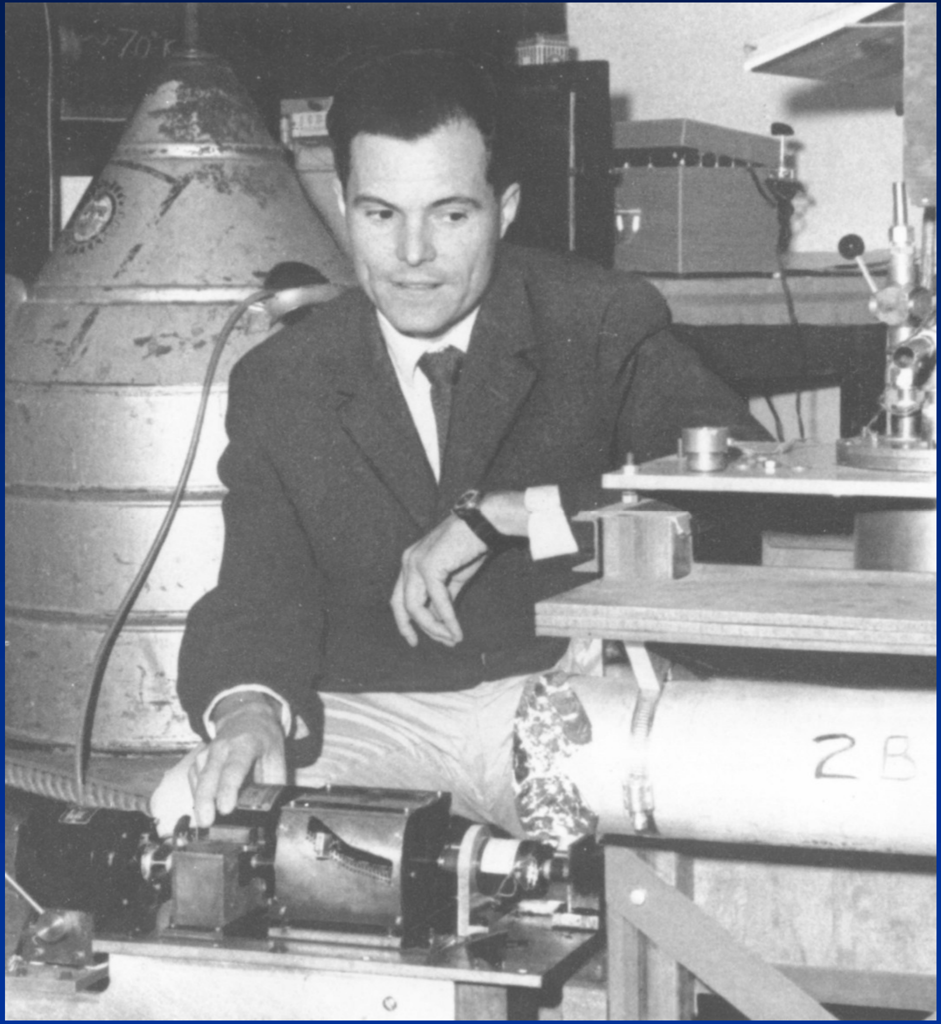


$$E_R = \frac{E_\gamma^2}{2mc^2}$$

$$^{57}\mathrm{Fe}: E_R = 2 \cdot 10^{-3}\,\mathrm{eV}$$

$$\Gamma_0 = 4.6 \cdot 10^{-9}\,\mathrm{eV}$$

Rudolf L. Mössbauer (1929-2011)
Nobel-Preis 1961



R.L. Mössbauer made his first observation of recoilless nuclear resonant absorption in ^{191}Ir.

R.L. Mössbauer,
Z. Physik, 1958, 151, 124.
R.L. Mössbauer,
Naturwissenschaften, 1958, 45, 538

Rückstoßfreie Kernresonanzabsorption von γ-Strahlen

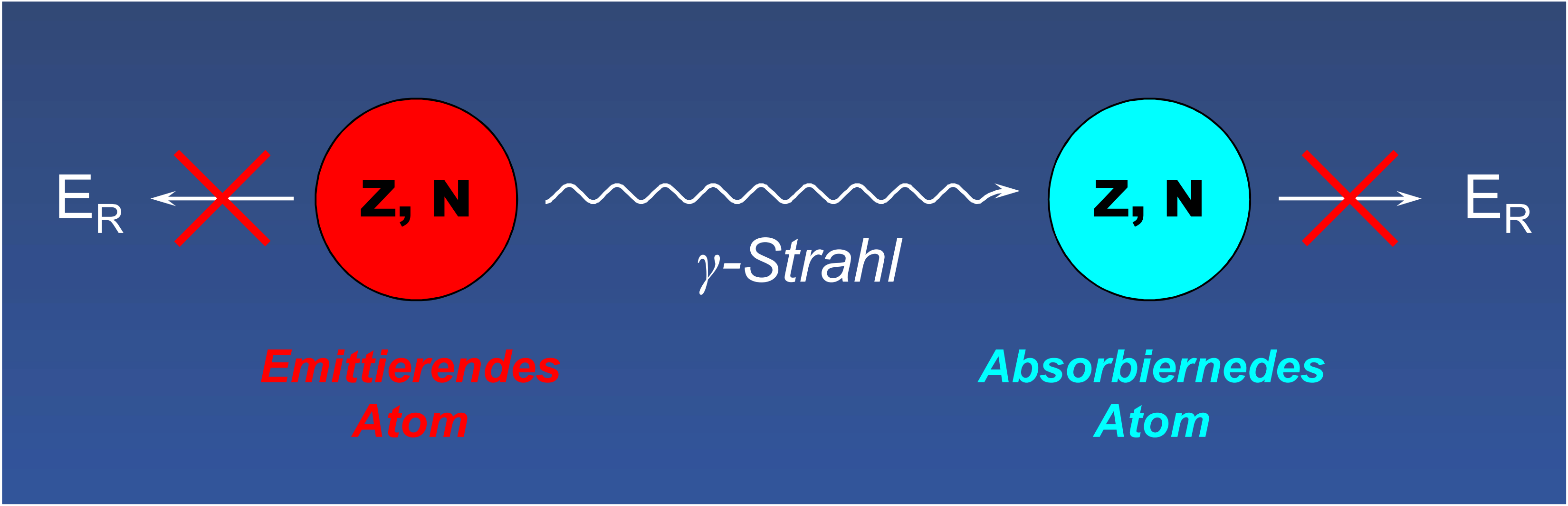
Professor Dr. Rudolf L. Mössbauer

1948	Abitur an der Oberrealschule München-Pasing
1955	Diplom in Physik an der TU München
1955-57	Max-Planck-Institut für medizinische Forschung in Heidelberg
1958	Promotion an der TU München bei Prof. Dr. Heinz Maier-Leibnitz: im selben Jahr gelingt ihm der direkte experimentelle Nachweis des Mößbauer-Effekts
1960-64	forscht Mößbauer am California Institute of Technology
1961	Nobelpreis für Physik zusammen mit Robert Hofstadter „für seine Untersuchungen zur Resonanzabsorption von Gammastrahlung und die in diesem Zusammenhang gemachte Entdeckung des nach ihm benannten Effektes“
1965	Ordinarius für Experimentalphysik an der TU München
1972-77	Direktor am Institut Laue-Langevin in Grenoble
1977	Bis zum Emeritierung in 1997 wieder Ordinarius an der TU München

Lösung des Problems

Die Atome der Quelle und des Absorbers in das Gitter eines Festkörpers eingebaut sind!

Eliminierung des Rückstoß-Efffekts Bei Emission und Absorption von γ-Strahlung

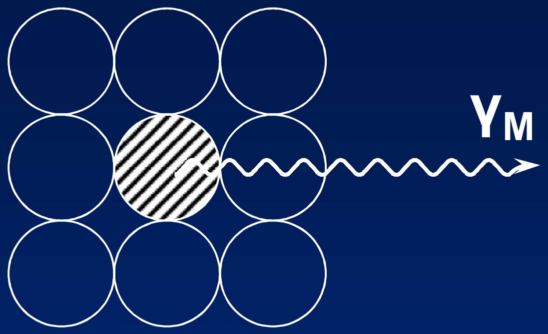


Im Kristall der Masse M: $E_R = E_{transl} + E_{vib}$

m ⟶ M: $\boxed{E_R = E_\gamma{}^2/2Mc^2 << \Gamma_0}$

E_{vib} ist quantisiert (Einstein-Modell, Debye-Modell)

Im Festkörper (z.B. Kristall)



Verteilt sich die Rückstoßenergie gemäß

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

E_{transl} : Auf den ganzen Kristall der Masse M
übertragener linearer Impuls .
E_{transl} $<< \Gamma$, since M >>m.

E_{vib} : wird in Anregung von Gitterschwingungen umgesetzt.
E_{vib} ist quantisiert. ⇨ Einstein-Modell, Debye-Modell:

Mit der Wahrscheinlichkeit ***f***, Lamb-Mössbauer-Faktor (Debye-Waller-Faktor) genannt, bleibt das quantenmechanische Phononensystem bei Emission und Absorption von γ-Quanten unverändert (*zero phonon processes*) .
Nur dieser Anteil ***f*** ist für die Kernresoanzabsorption nutzbar.
→ **Mössbauer-Effekt.**

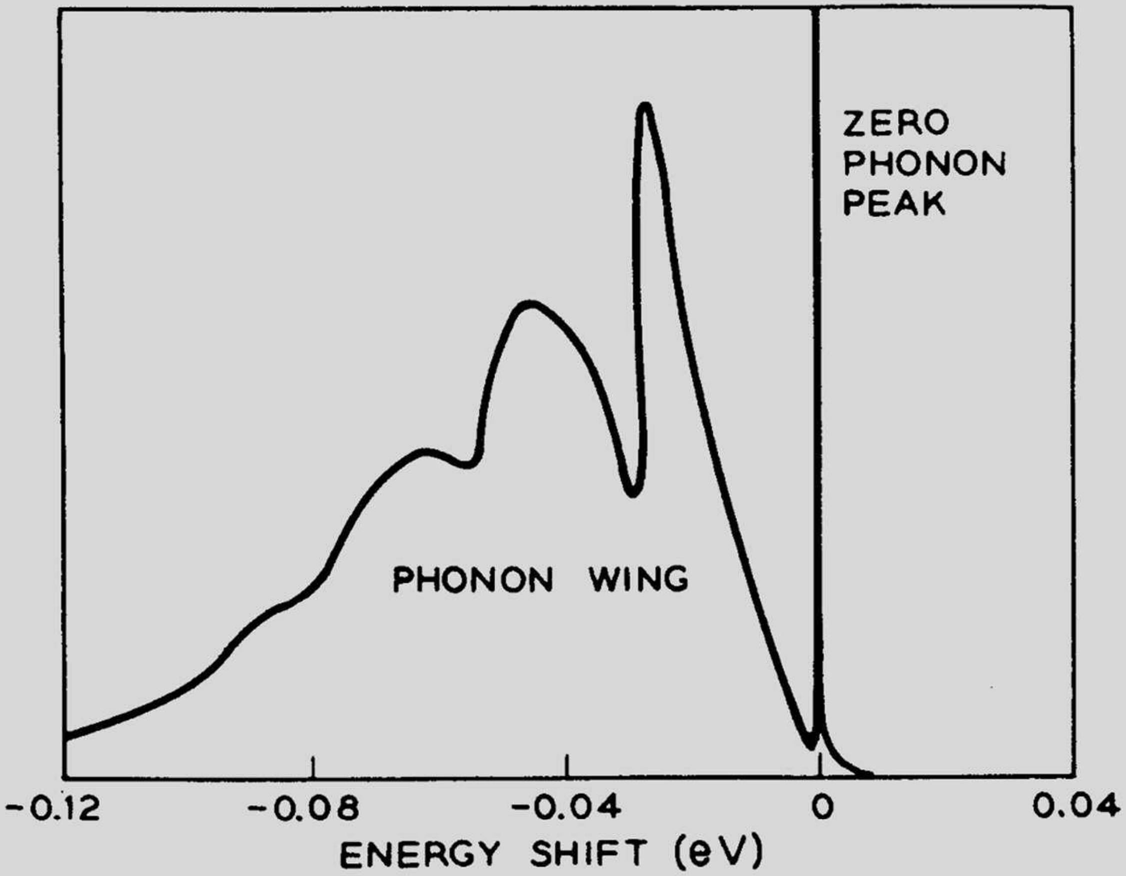
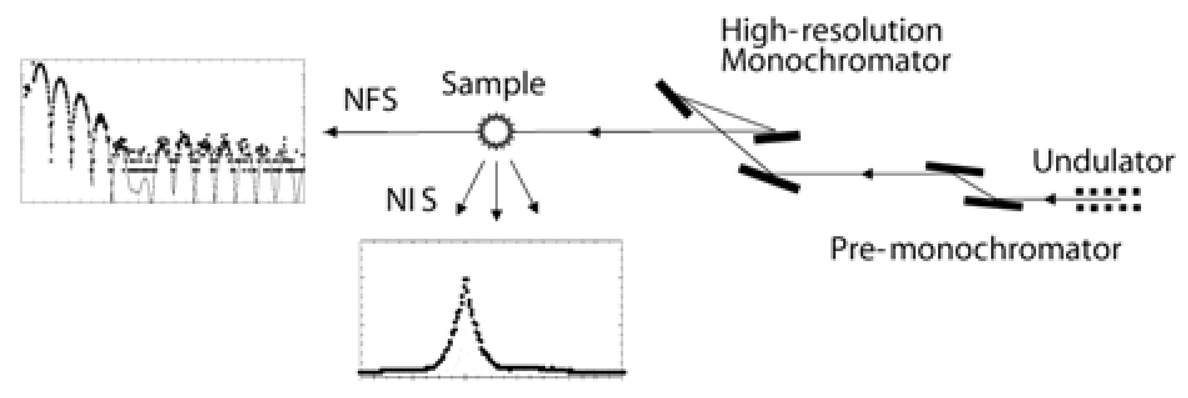


FIG. 1. The theoretical spectrum of the 129 keV gamma ray of Ir^{191} emitted by an atom in iridium metal at low temperature [2]. The Mössbauer spectrometer is sensitive only to the narrow, recoil-free line at zero energy shift, which contains 5.7% of the total area under the curve.

[1] W.M. Visscher, Ann. Phys. *9*, 194, 1960

NIS with synchrotron radiation

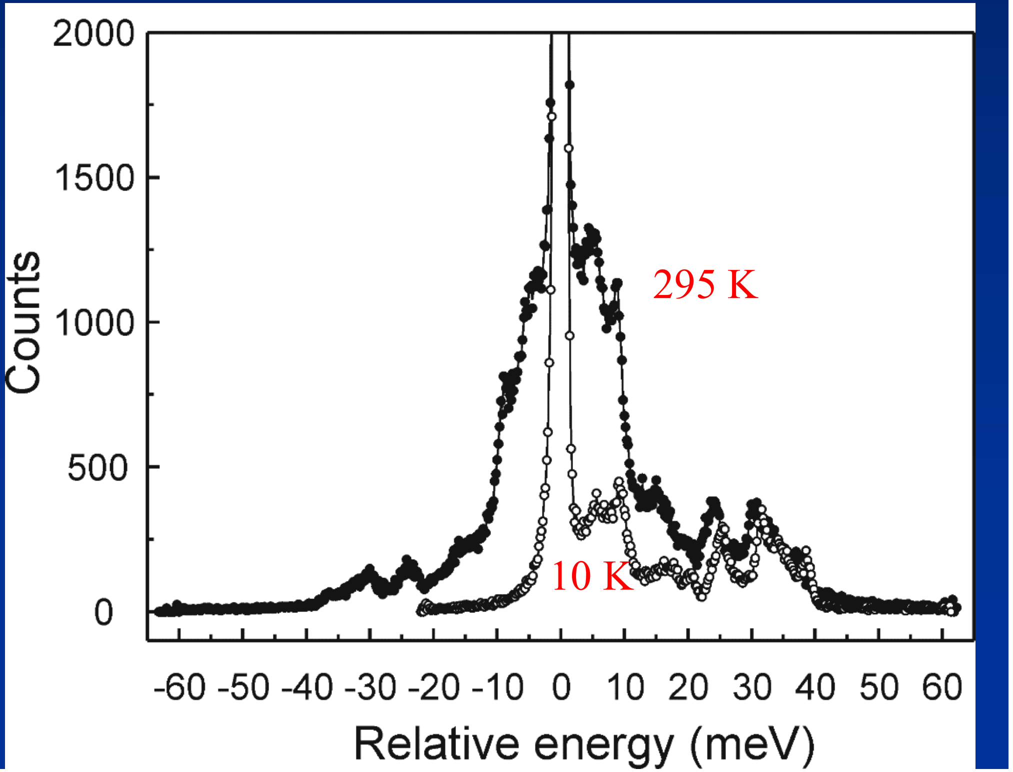
NIS: determination of the local phonon DOS at the Mössbauer atom



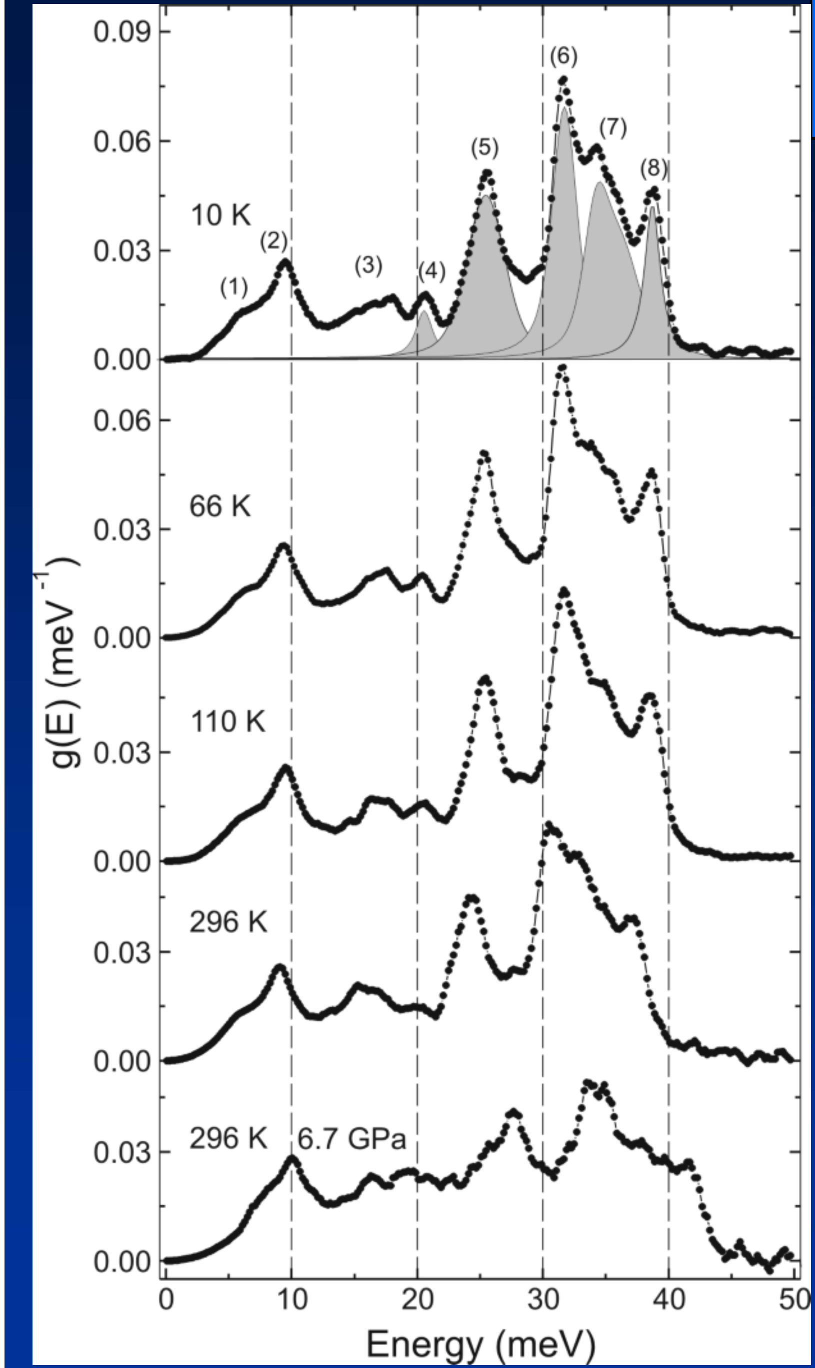
^{57}Fe-NIS studies performed with a resolution of 0.75 – 0.95 meV at 14.4 keV at beamline ID18 of ESRF

^{57}Fe-NIS spectra of $Fe_{1.01}Se$ at 295 K (full circles) and at 10 K (open circles)

V.Ksenofontov, G.Wortmann, A.I.Chumakov et al., PRB **81**, 184510 (2010)



^{57}Fe phonon-DOS in sc $Fe_{1.01}Se$ as function of T and p



- Fe-partial phonon-DOS *g(E)* for $Fe_{1.01}Se$ at different temperatures (above) and at a pressure of 6.7 GPa at 296 K (below). At 10 K, resolved optical modes are indicated, e.g. the B_{1g} Raman mode at 25.5 meV (labeled 5).

- Lowering of temperature results in a sharpening of the spectral features and an increase of the mode energies by ~4%.

- No significant changes between the spectra at 110 K (tetr. phase) and 66 K (orthorh. phase).

- Application of 6.7 GPa ($\Delta V \sim -14\%$) at 296 K leads to strong increases of the energies of the optical modes by ~12%, and larger shifts of the acoustic modes by ~30% for mode (1) and ~14% for mode (2).

V. Ksenofontov, et al., PRB 81, 184510 (2010).

Lamb-Mössbauer-Faktor
(Debye-Waller-Faktor)

Mit ***f*** bezeichnet man den Anteil an γ-Quanten, der ***rückstoßfrei*** emittiert und absorbiert wird.

Der Parameter ***f*** ist mit Schwingungseigenschaften des Kristallgitters korreliert:

$$f = \exp\{-(\langle x^2\rangle/\lambda^2)(2\pi)^2\} = \exp\{-(2\pi)^2\, E_\gamma^2 \langle x^2\rangle/(hc)^2\}$$

$\langle x^2\rangle$: mittleres Quadrat der Schwingungsaplitude in x-Richtung

λ: Wellenlänge der γ-Strahlung, wobei $E_\gamma = h\nu = h\cdot c/\lambda$.

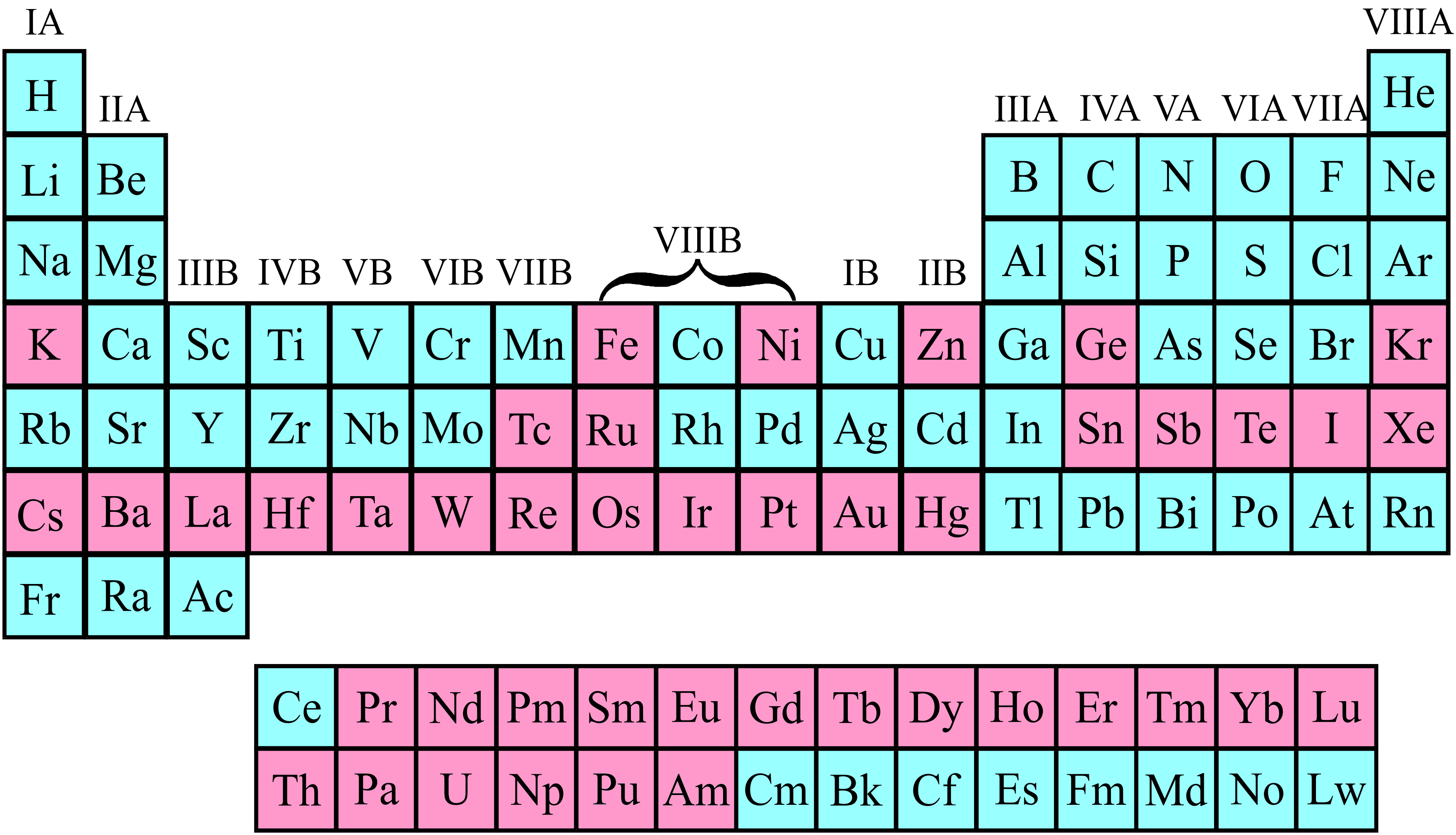
Rückstoßfrei Emission und Absorption von γ-Strahlung

Bedingung für die Wahrscheinlichkeit einer rückstoßfreien Emission und Absorption von γ-Quanten :

$$\mathbf{E_R = E_\gamma^2/2m < k_B\Theta_D}$$

k_B = Boltzmann–Konstante, Θ_D = Debye–Temperatur

Mössbauer-aktive Elemente



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
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
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Experimentelle Resonanzbedingungen

Übergangsenergie: $E_\gamma = E_a - E_g$

Geeignet: $5 \text{ keV} \leq E_\gamma \leq 180 \text{ keV}$

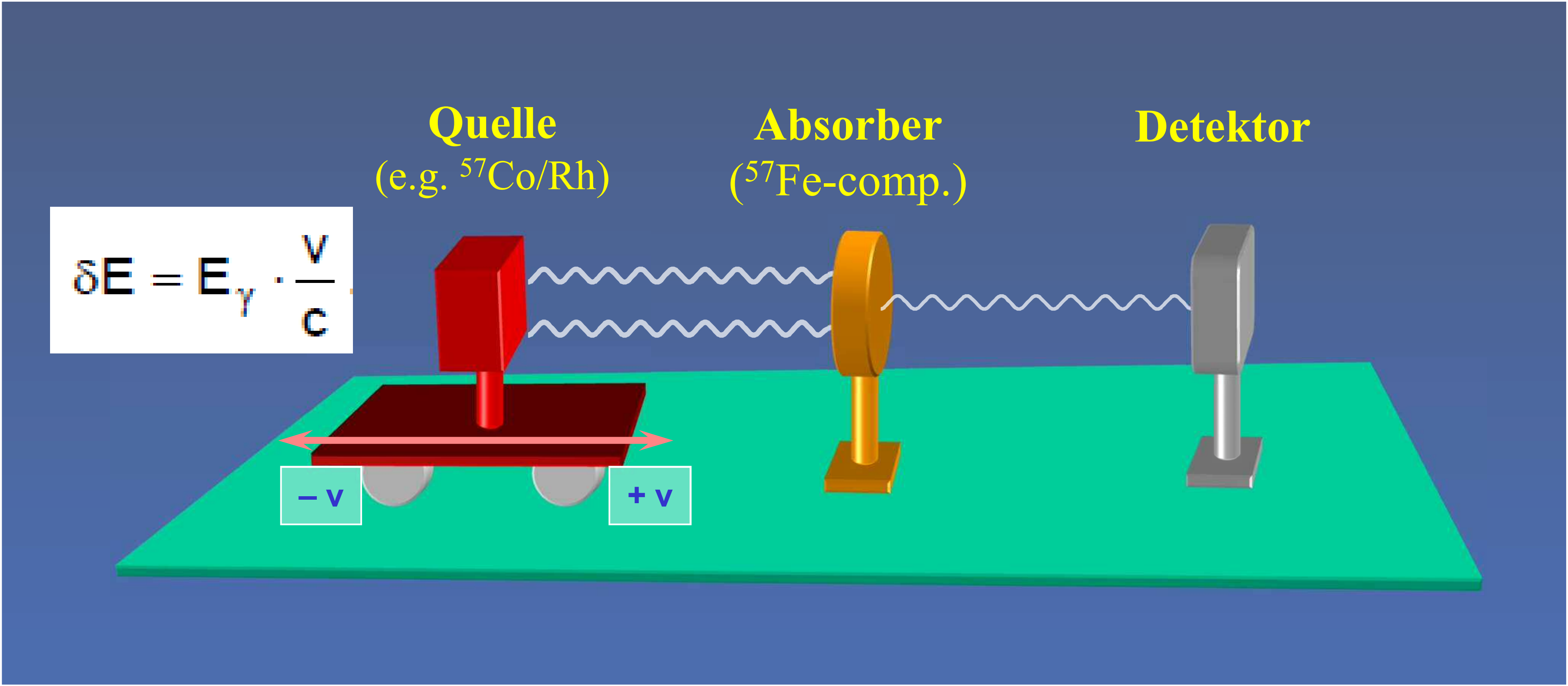
Wenn $E_\gamma \leq 5$ keV:	Totale nicht-resonante Absorption der γ-Strahlen in Quelle bzw. Absorber
Wenn $E_\gamma \geq 180$ keV:	Rückstoß-Energie $\mathbf{E_R = E_\gamma^2/2mc^2}$ wird zu groß und zerstört die Resonanz.

Nuclear parameters for selected Mössbauer isotopes

Isotope	E_γ/keV	Γ_r/(mm s^{-1}) = 2 Γ_{nat}	I_g	I_e	α	Natural abundance %	Nuclear decay*
^{57}Fe	14.41	0.192	1/2–	3/2–	8.17	2.17	^{57}Co(EC 270 d)
^{61}Ni	67.40	0.78	3/2–	5/2–	0.12	1.25	^{61}Co(β^-99 m)
^{119}Sn	23.87	0.626	1/2+	3/2+	5.12	8.58	^{119m}Sn(IT 50 d)
^{121}Sb	37.15	2.1	5/2+	7/2+	~10	57.25	^{121m}Sn(β^-76 y)
^{125}Te	35.48	5.02	1/2+	3/2+	12.7	6.99	^{125}I(EC 60d)
^{127}I	57.60	2.54	5/2+	7/2+	3.70	100	^{127m}Te (β^-109 d)
^{129}I	27.72	0.59	7/2+	5/2+	5.3	nil	^{129m}Te (β^-33 d)
^{149}Sm	22.5	1.60	7/2–	5/2–	~12	13.9	^{149}Eu(EC 106 d)
^{151}Eu	21.6	1.44	5/2+	7/2+	29	47.8	^{151}Gd(EC 120 d)
^{161}Dy	25.65	0.37	5/2+	5/2–	~2.5	18.88	^{161}Tb(β^-6.9 d)
^{193}Ir	73.0	0.60	3/2+	1/2+	~6	61.5	^{193}Os(β^-31 h)
^{197}Au	77.34	1.87	3/2+	1/2+	4.0	100	^{197}Pt(β^-18 h)
^{237}Np	59.54	0.067	5/2+	5/2–	1.06	nil	^{241}Am(α458 y)

*EC = electron capture, β^- = beta-decay, IT = isomeric transition, α – alpha-decay

Mössbauer Experiment



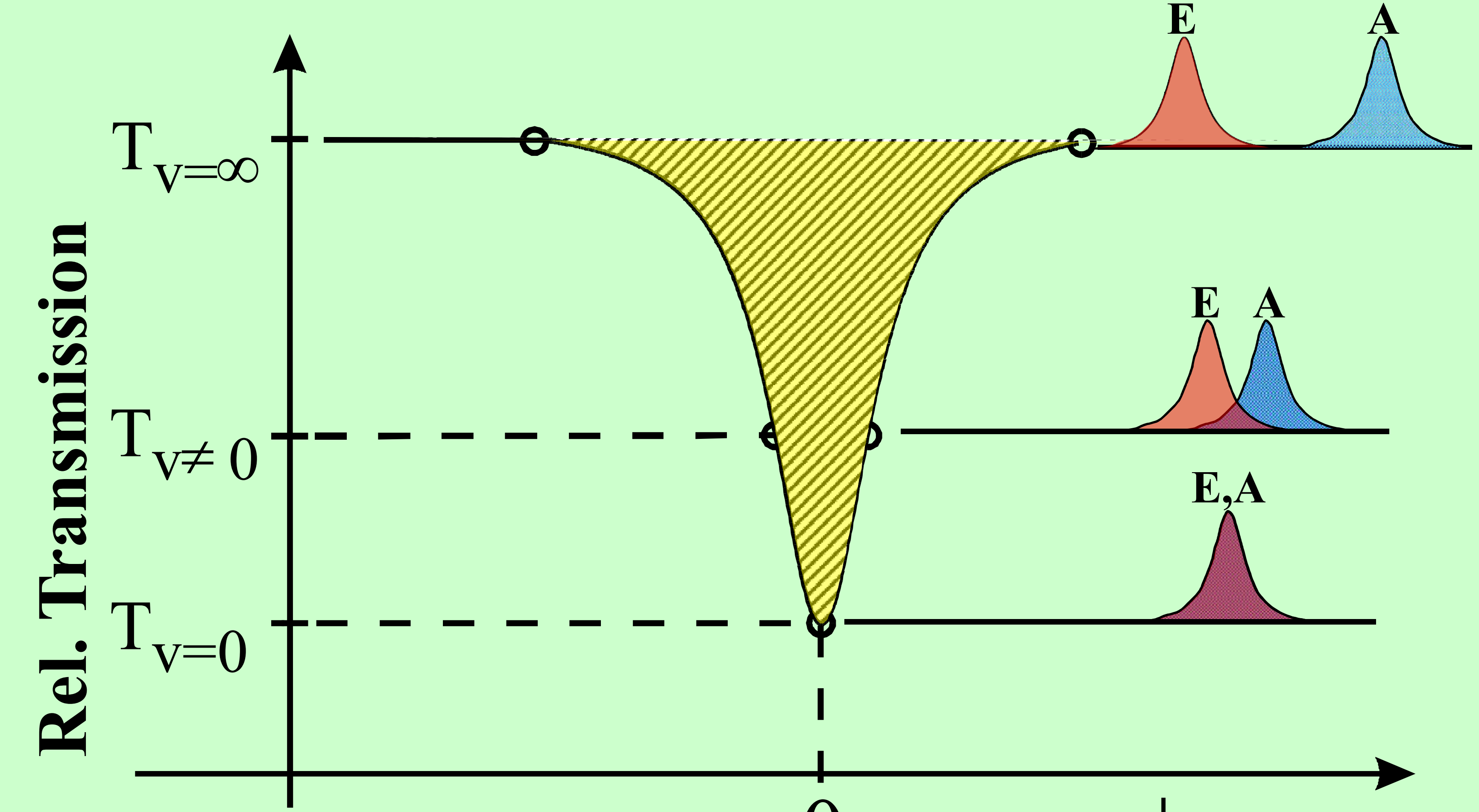
Quelle und Absorber werden relativ zu einander bewegt mit der

Doppler-Geschwindigkeit v:

$$\delta E = E_\gamma \cdot \frac{v}{c}$$

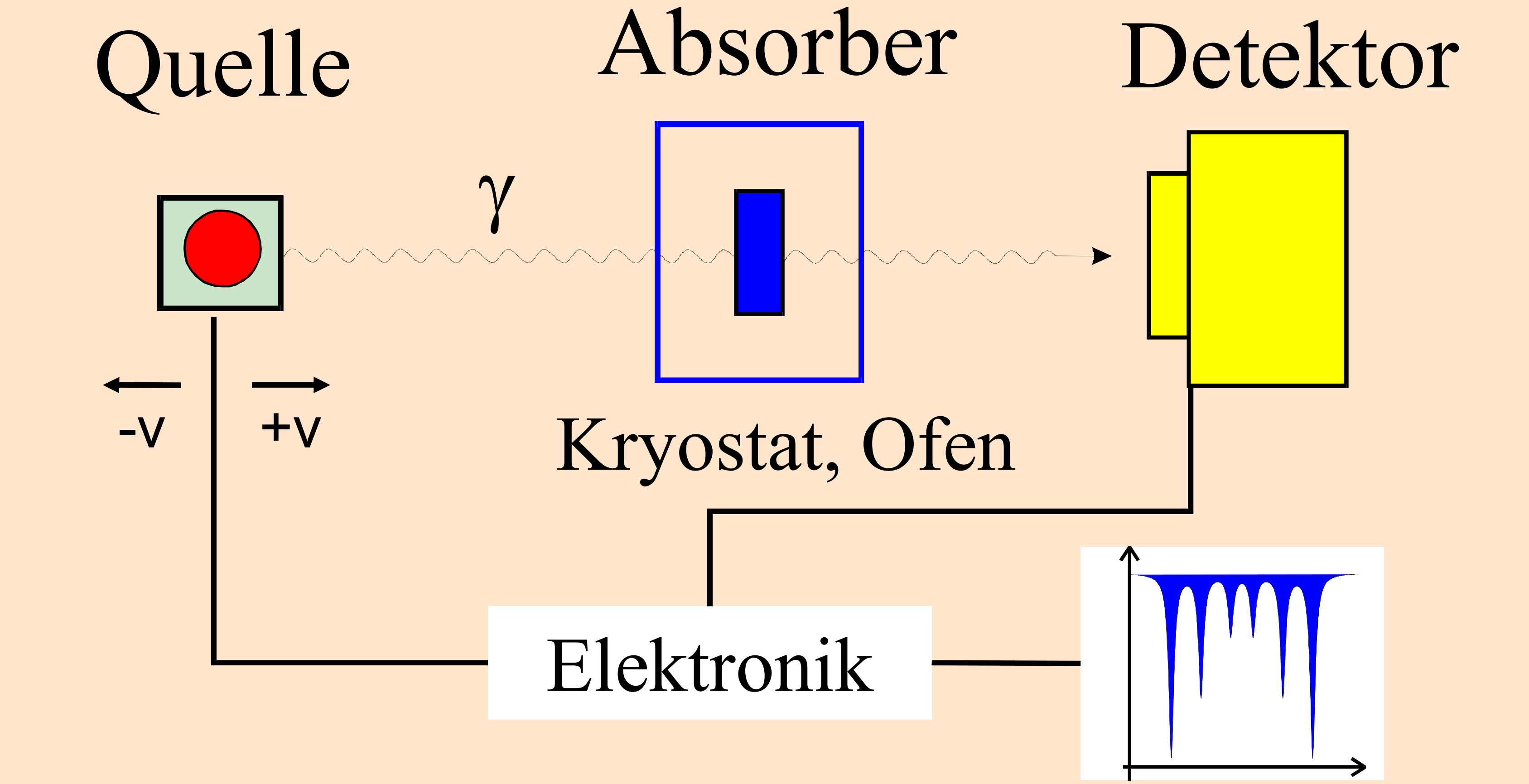
^{57}Fe : $\Gamma_0 = 4.7 \cdot 10^{-9}$ eV, $E_\gamma = 14400$ eV, $v = 0.096$ mm s^{-1}

Mössbauer-Spektrum



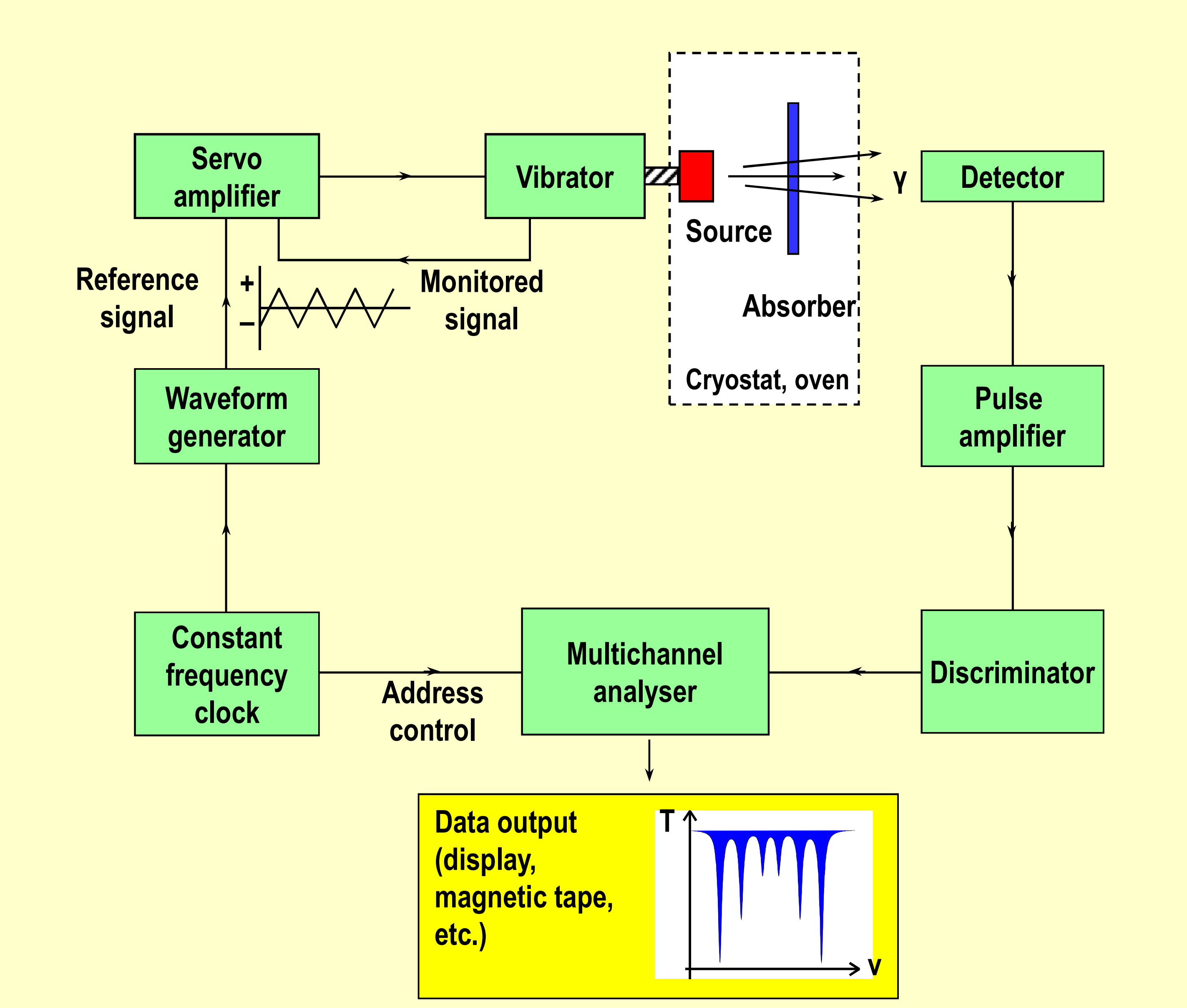
$$\delta E = E_\gamma \cdot \frac{v}{c}$$

Mössbauer Experiment



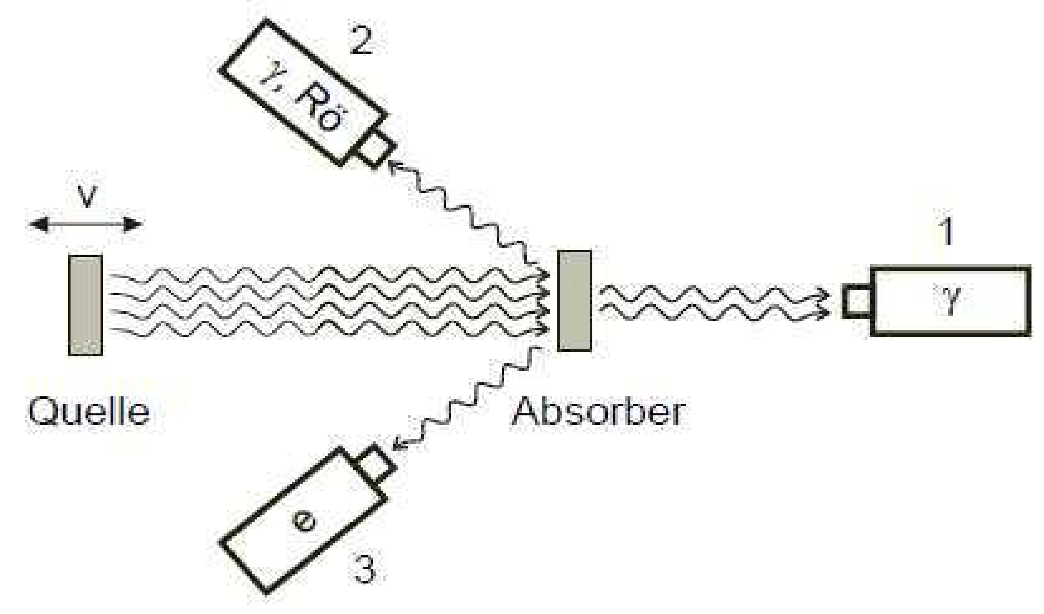
Atomkerne des gleichen Nuklids im angeregten (Quelle) und im Grundzustand (Absorber).

Schematischer Aufbau eines Mössbauer-Spektrometers



Mössbauer Experiment

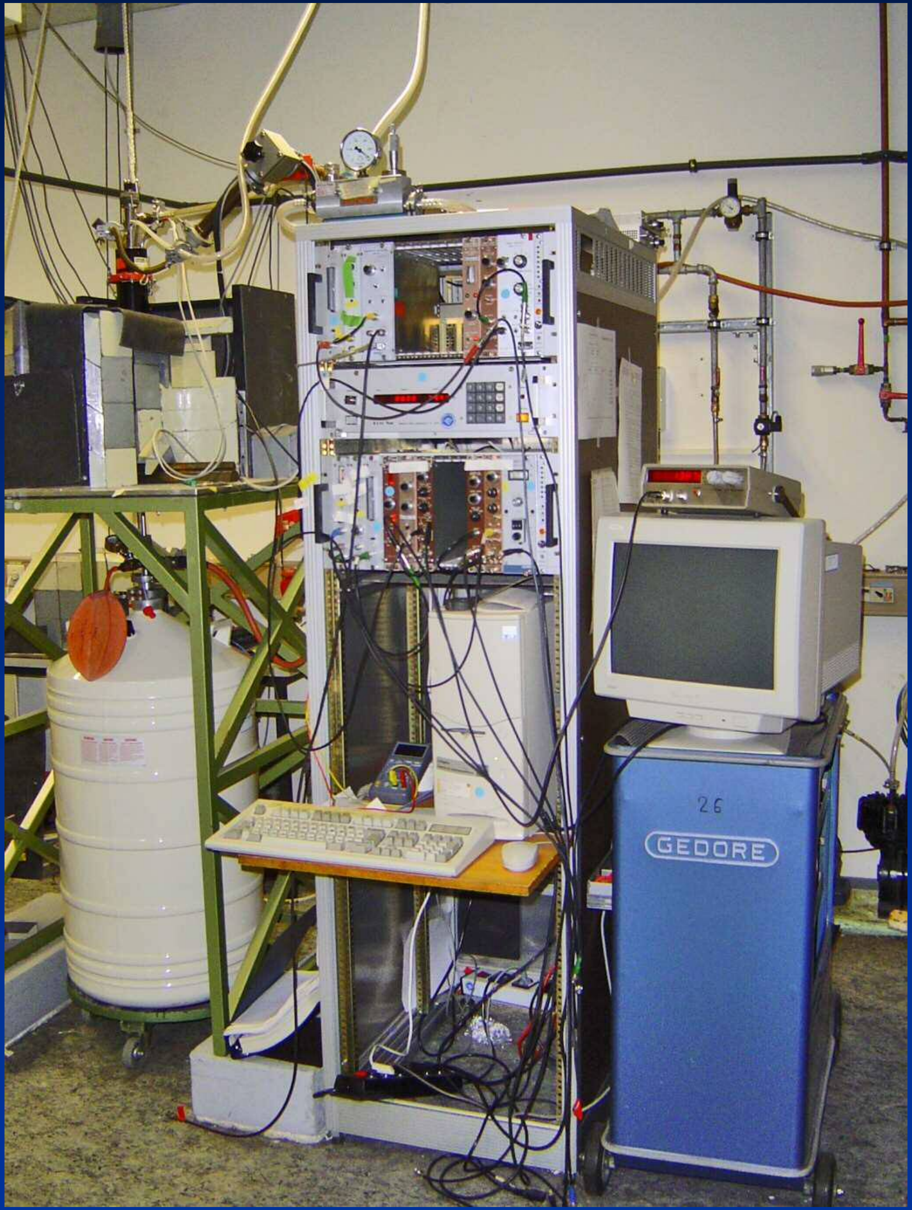
<u>Rückstreugeometrie</u>
Reemittierte γ-Quanten
Tiefe: ca. 1000 nm



<u>Transmissionsgeometrie</u>
Durchdringende γ-Quanten
Tiefe: Bulk

<u>Konversionselektronen</u>
CEMS – Conversion Electron Mössbauer Spectroscopy
Tiefe: ca. 100 nm

Mössbauer-Spektrometer



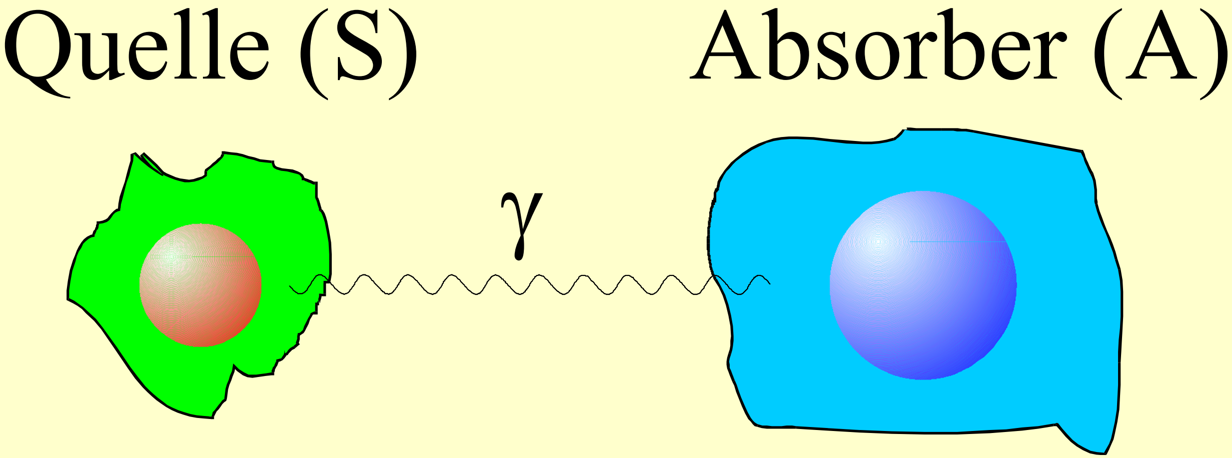
Hyperfein-Wechselwirkungen zwischen Atomkern und Elektronen und Mössbauer-Parameter

- **Elektrische Monopol-Wechselwirkung**
  ⇒ „Isomerie-Verschiebung“ δ
- **Elektrische Quadrupol-Wechselwirkung**

  ⇒ „Quadrupol-Aufspaltung“ΔE_Q
- **Magnetische Dipol-Wechselwirkung**
  ⇒ „Magnetische Aufspaltung“ ΔE_M

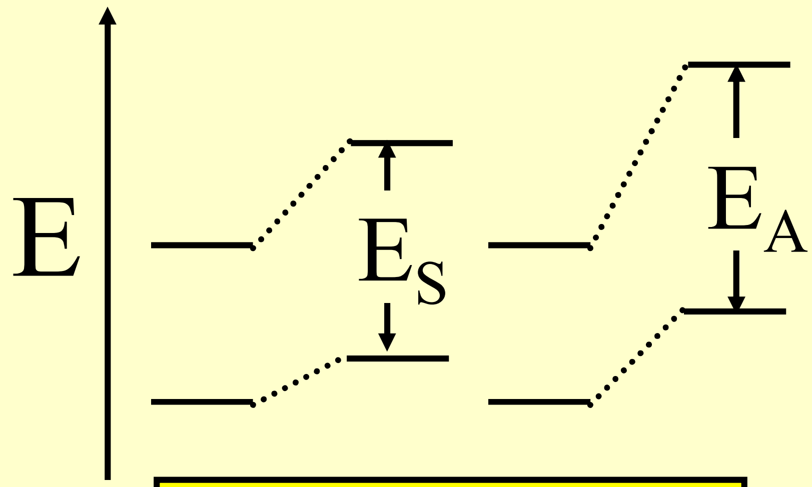
Elektrische Monopol-Wechselwirkung

Isomerie-Verschiebung δ

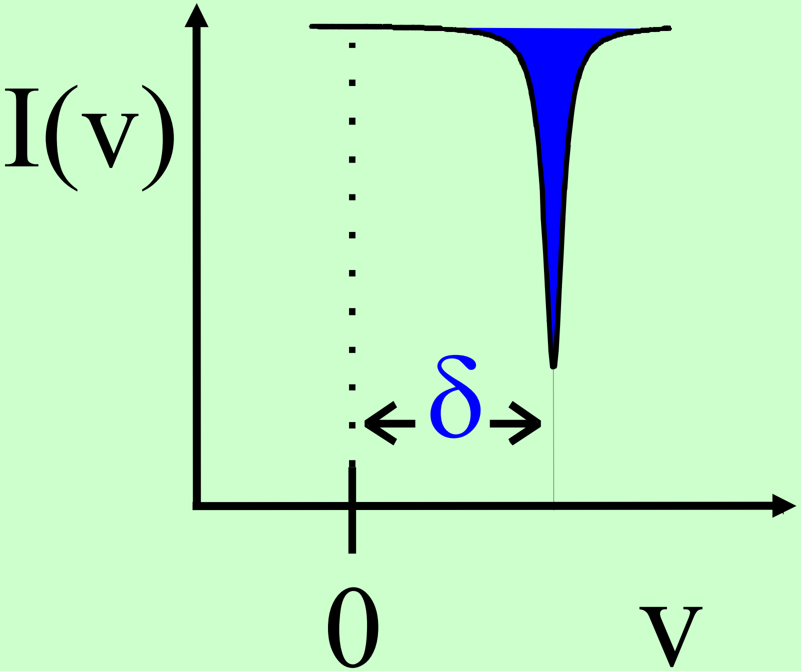


Kernradius $R_e \neq R_g$

Elektronendichte $\rho_S \neq \rho_A$



$$E_A - E_S = \delta$$



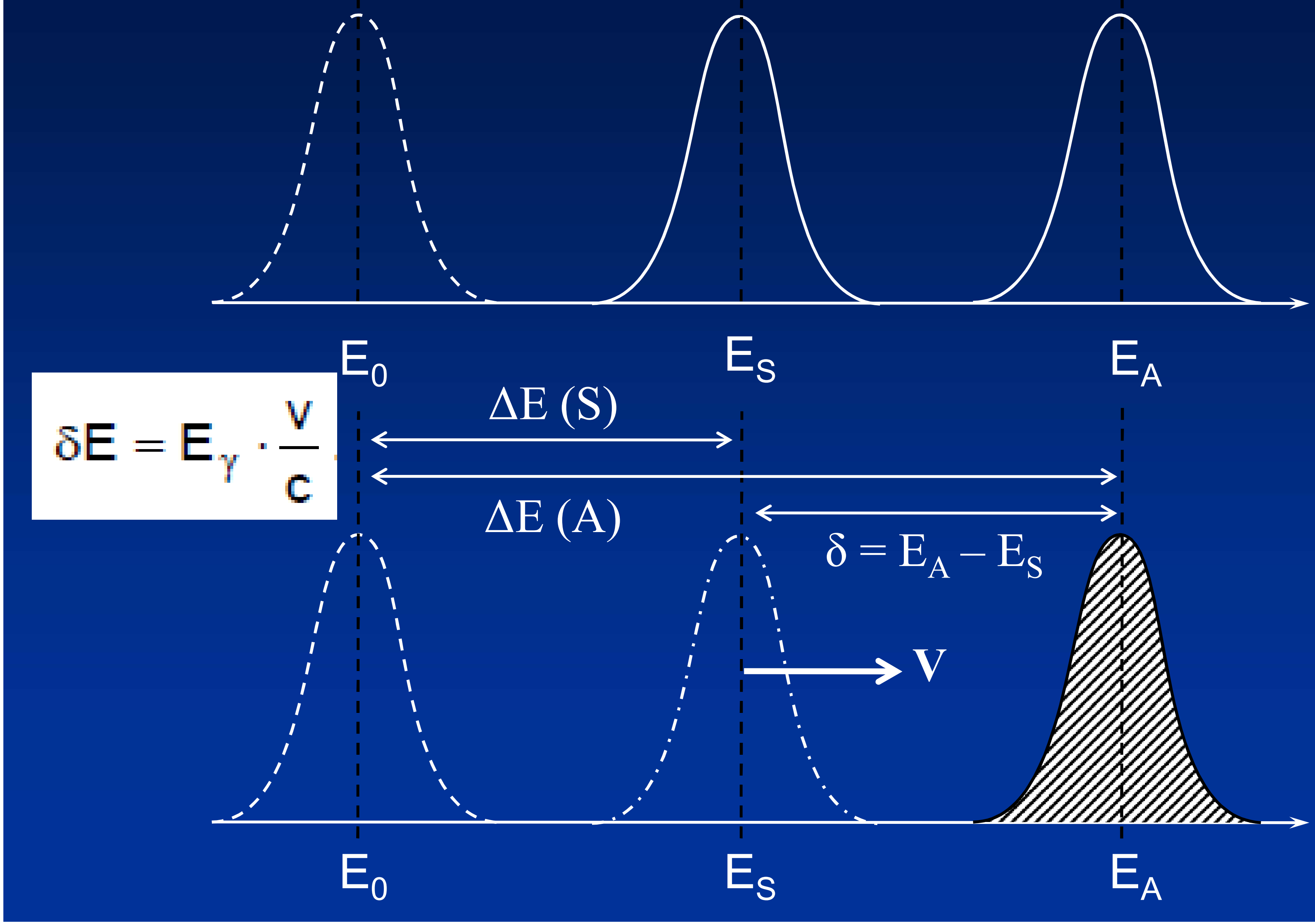
Oxidationszustand

Spinzustand

Bindungseigenschaften

Elektronegativität

Messung der Isomerieverschiebung durch Ausnutzung des Doppler-Effekts.



$$\delta E = E_\gamma \cdot \frac{v}{c}$$

$$\Delta E(S) = E_S - E_0 = C\,|\Psi(0)|_S^2\,(R_e^2 - R_g^2), \qquad C = \tfrac{2}{3}\pi Z e^2$$

$$\Delta E(A) = E_A - E_0 = C\,|\Psi(0)|_A^2\,(R_e^2 - R_g^2)$$

$$\delta = \Delta E(A) - \Delta E(S) = E_A - E_S$$

$$\boxed{\boldsymbol{\delta = C\,\{|\Psi(0)|_A^2 - |\Psi(0)|_S^2\}(R_e^2 - R_g^2)}}$$

Für unveränderte Quelle: $|\Psi(0)|_S^2 = \text{const}$

⇨ $\boldsymbol{\delta = C\,\{|\Psi(0)|_A^2\}(R_e^2 - R_g^2)}$

Merke:

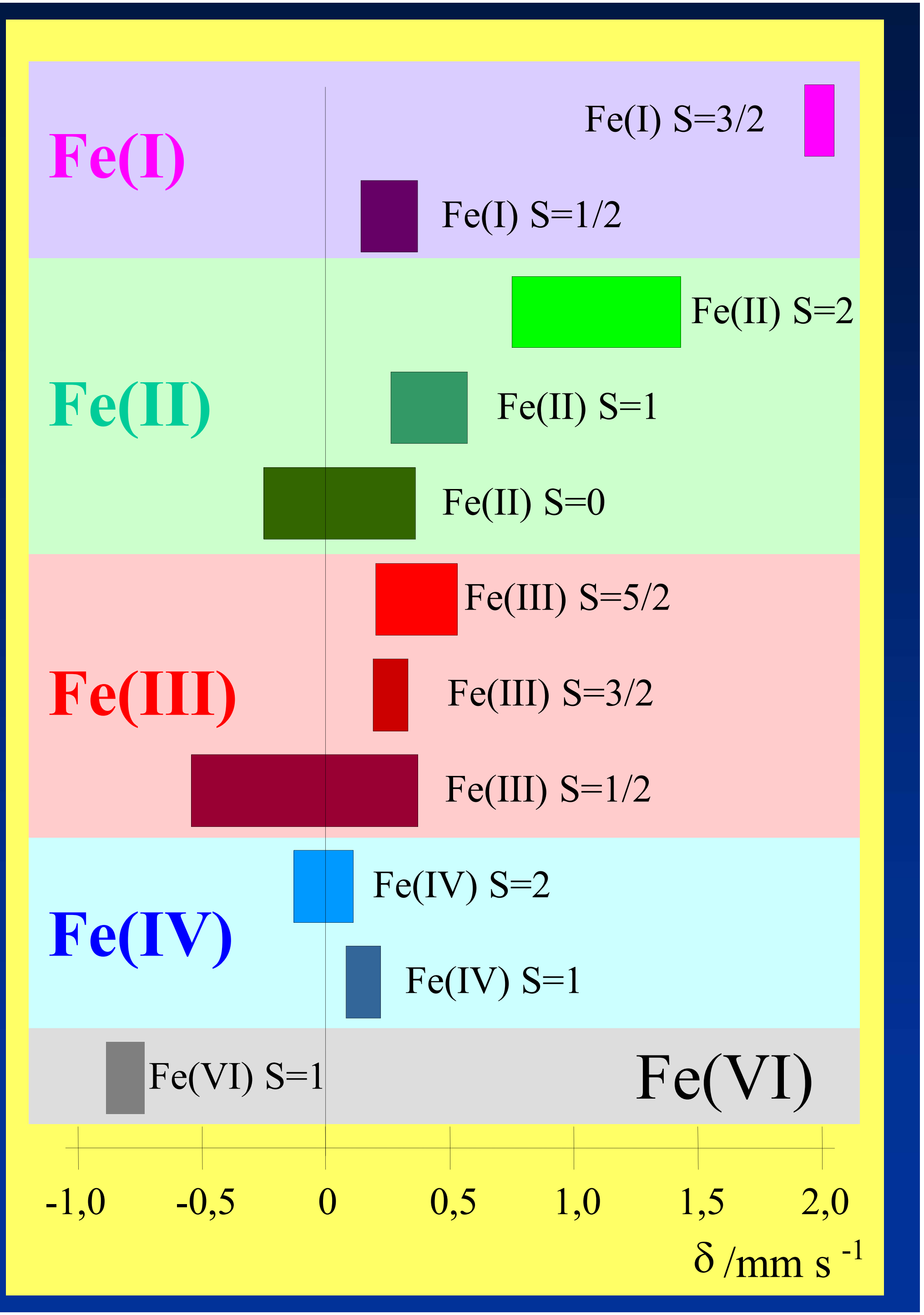
Für ^{57}Fe : $(R_e^2 - R_g^2) < 0$

Isomerieverschiebung δ von Eisenverbindungen

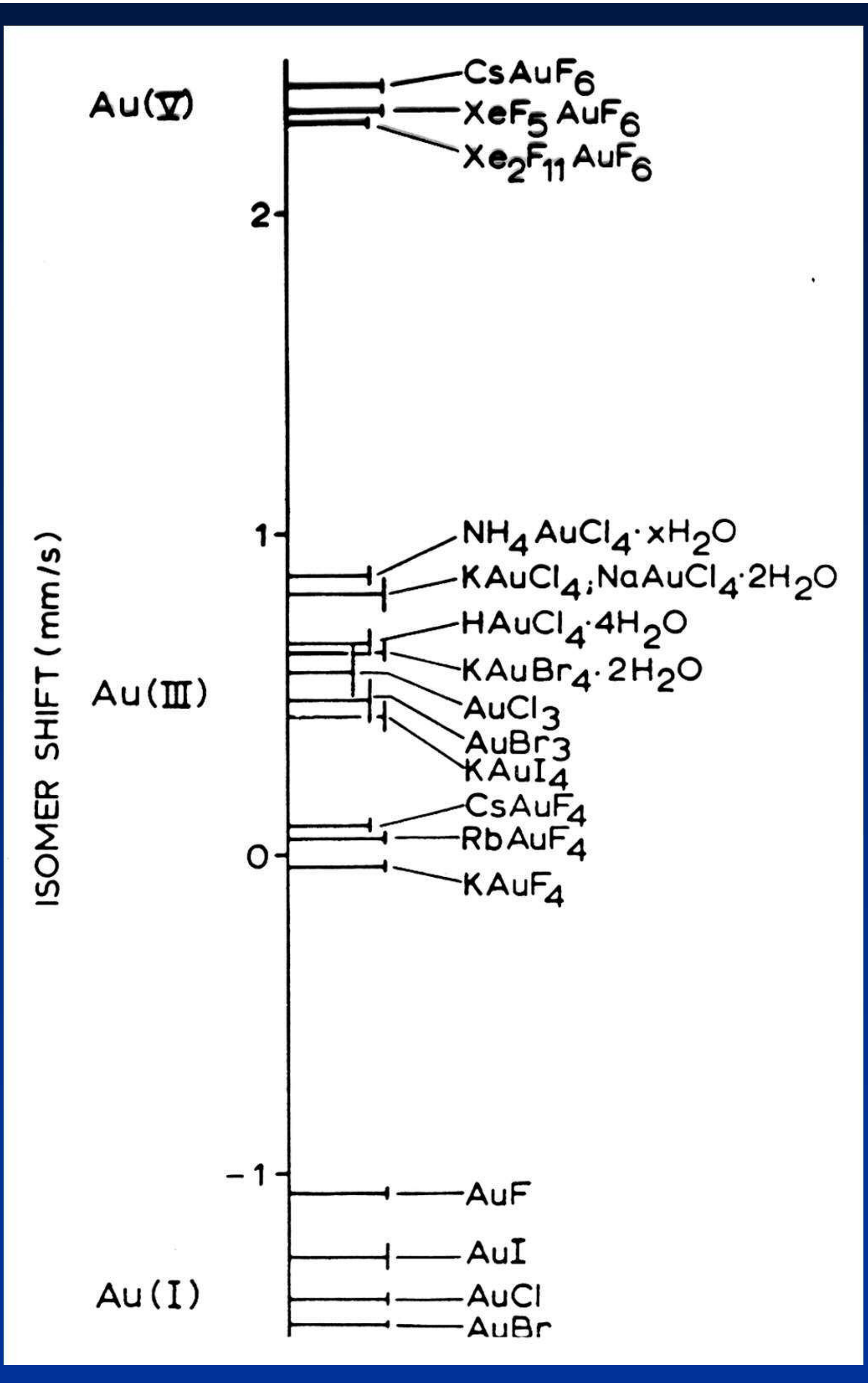
$$\delta = C\,\{|\Psi(0)|_A^{\,2} - |\Psi(0)|_S^{\,2}\}(R_e^{\,2} - R_g^{\,2})$$

Für ^{57}Fe :

$(R_e^{\,2} - R_g^{\,2}) < 0$



Isomerieverschiebung von Goldverbindungen: ^{197}Au-Mössbauer-Spektroskopie

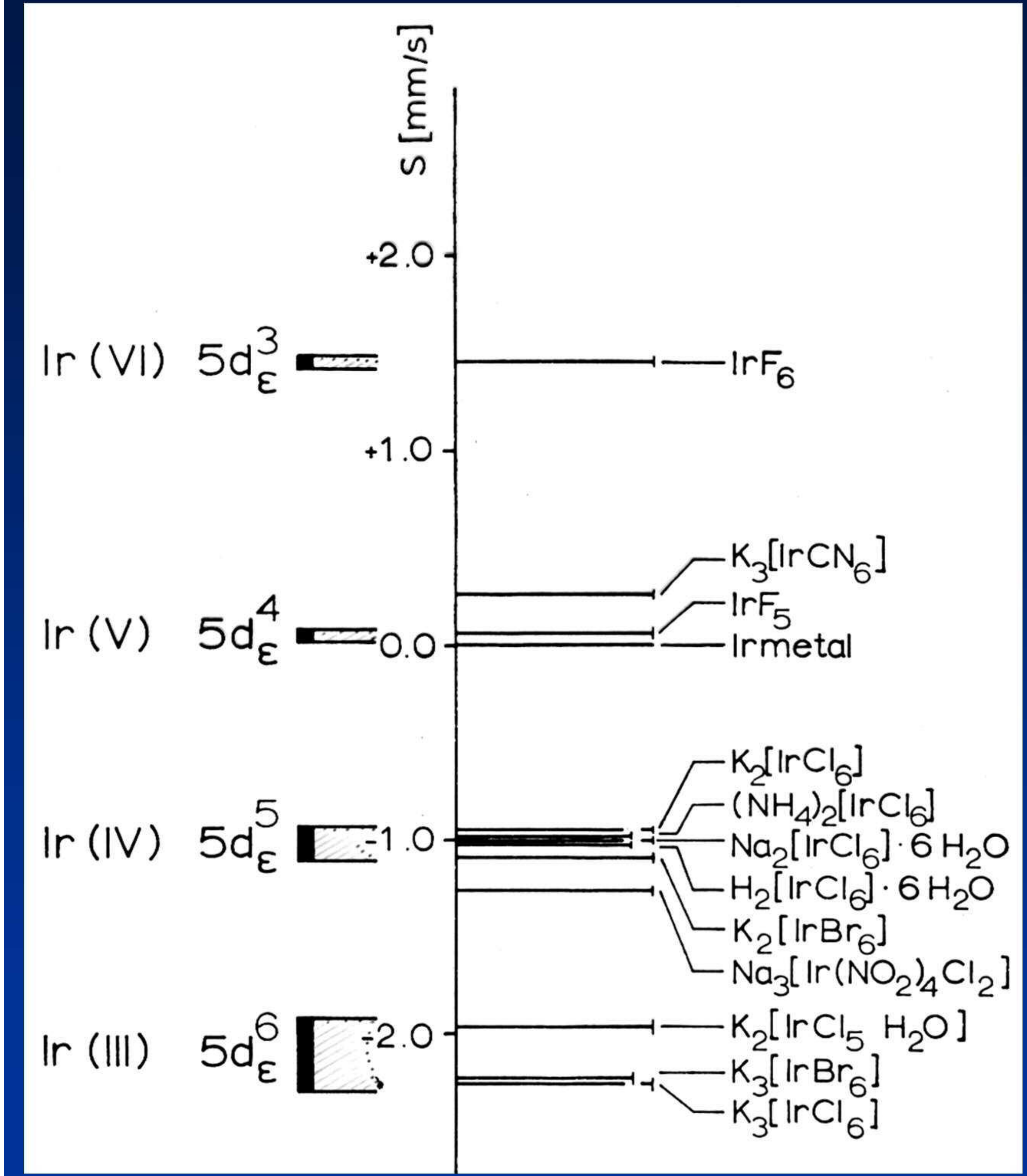


Au: [Xe]$4f^{14}5d^{10}6s^1$

Au(I): $5d^{10}$
Au(III): $5d^8$
Au(V): $5d^6$

^{197}Au : $(R_e^2 - R_g^2) > 0$

Isomerieverschiebung von Iridiumverbindungen: ^{193}Ir-Mössbauer Spectroskopie



^{193}Ir :

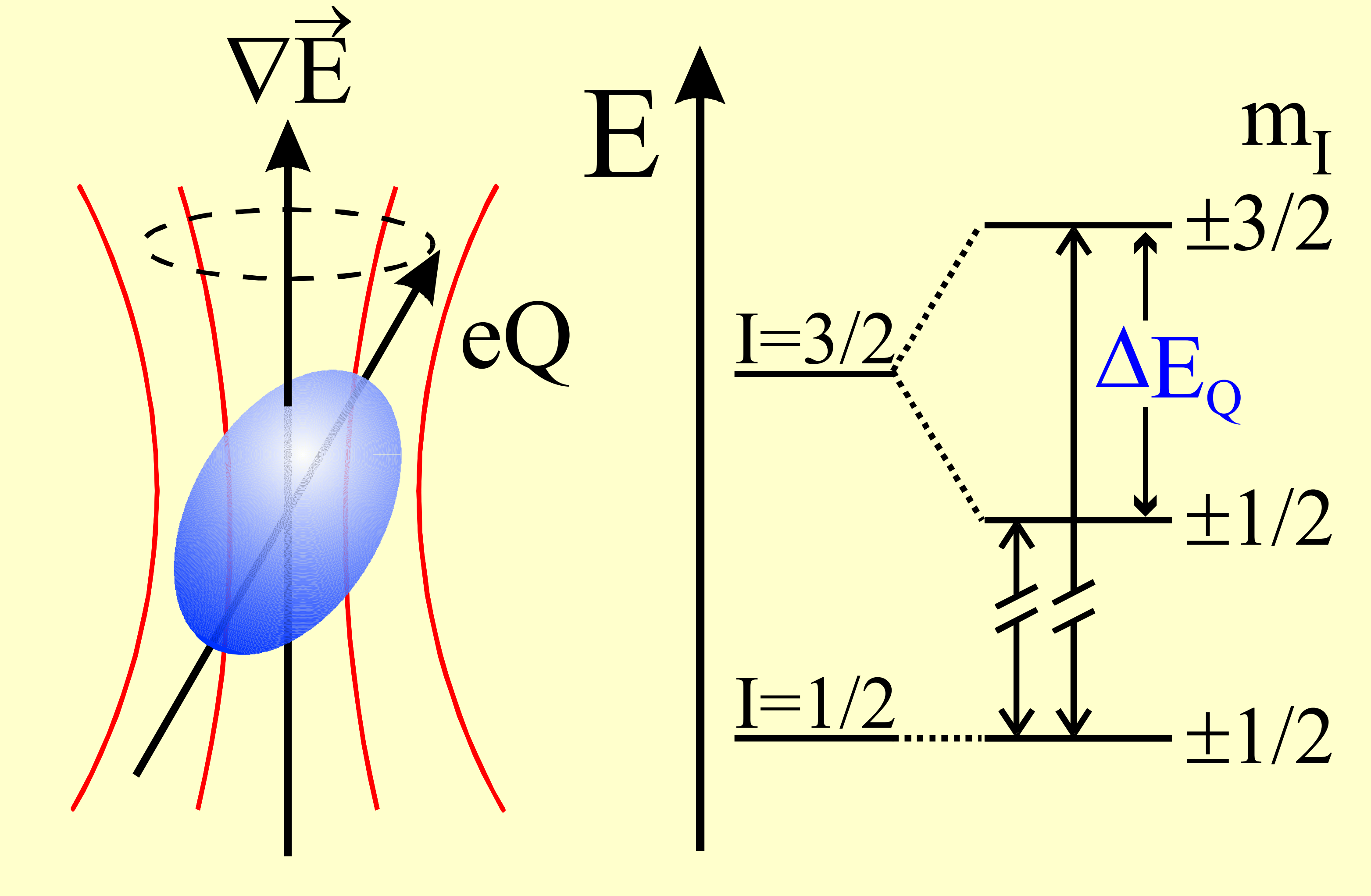
$(R_e^2 - R_g^2) > 0$

(F. Wagner et al.)

Elektrische Quadrupol-Wechselwirkung

Quadrupol-Aufspaltung ΔE_Q

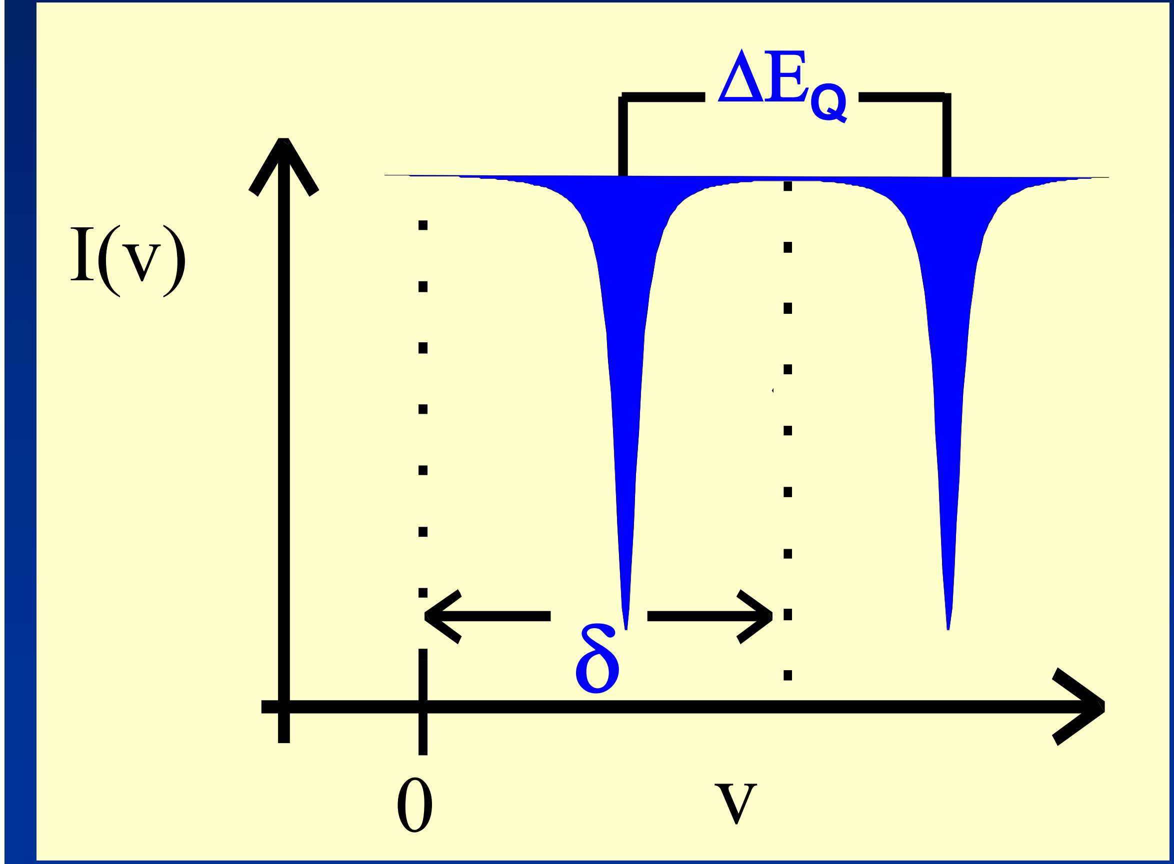
Kernspin I: (I + ½) Zustände

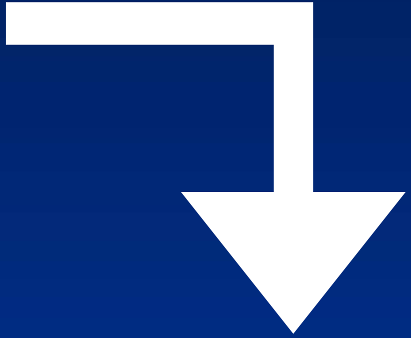


$\Delta E_Q \sim eQ \cdot V_{zz}$

Q – Kernquadrupolmoment, V_{zz} – z-Komponente des EFG

^{57}Fe: Q = 0,082 b, ΔE_Q = 1 mm/s → $V_{zz} = 2{,}34 \cdot 10^{18}$ V/m^2





Oxidations-, Spinzustand, Symmetrie

Two kinds of contributions to the EFG:

$$\mathbf{(EFG)^{total} = (EFG)^{val} + (EFG)^{lat}}$$

or in the principal axes system and $\eta = 0$:

$$\mathbf{(V_{zz})^{total} = (V_{zz})^{val} + (V_{zz})^{lat}}$$

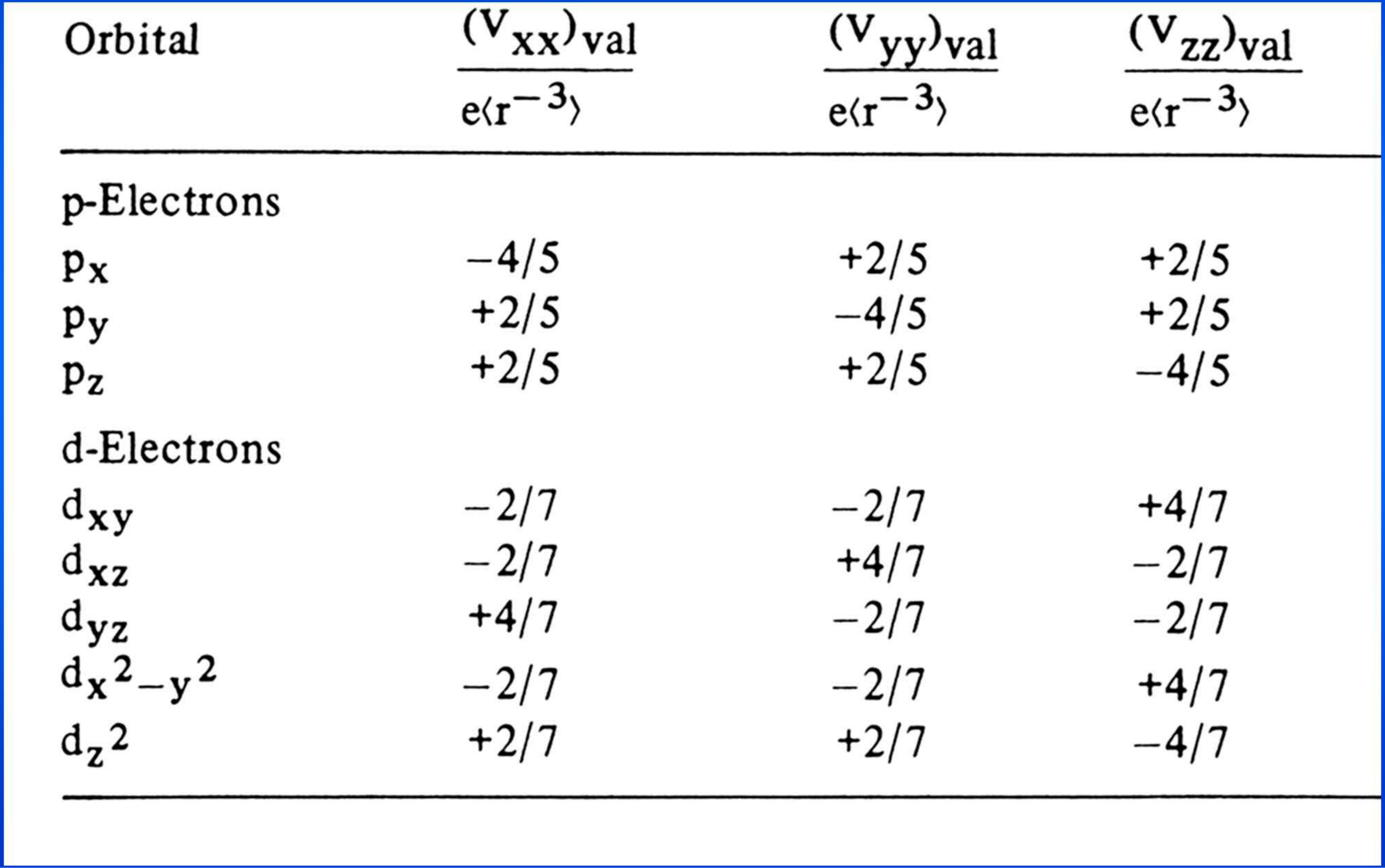
The **lattice contribution $(V_{zz})^{lat}$** arises from non-cubic arrangement of the next nearest neighbours

$$(V_{zz})^{lat} = \sum_{i=1}^{n} q_i r_i^{-3} (3\cos^2 \vartheta_i - 1)$$

q_i: charge on ligand *i*

r_i: distance of ligand *i* from Mössbauer central atom

Diagonal $(\mathrm{EFG})^{\mathrm{val}}$ tensor elements for p- and d-electrons (per electron)

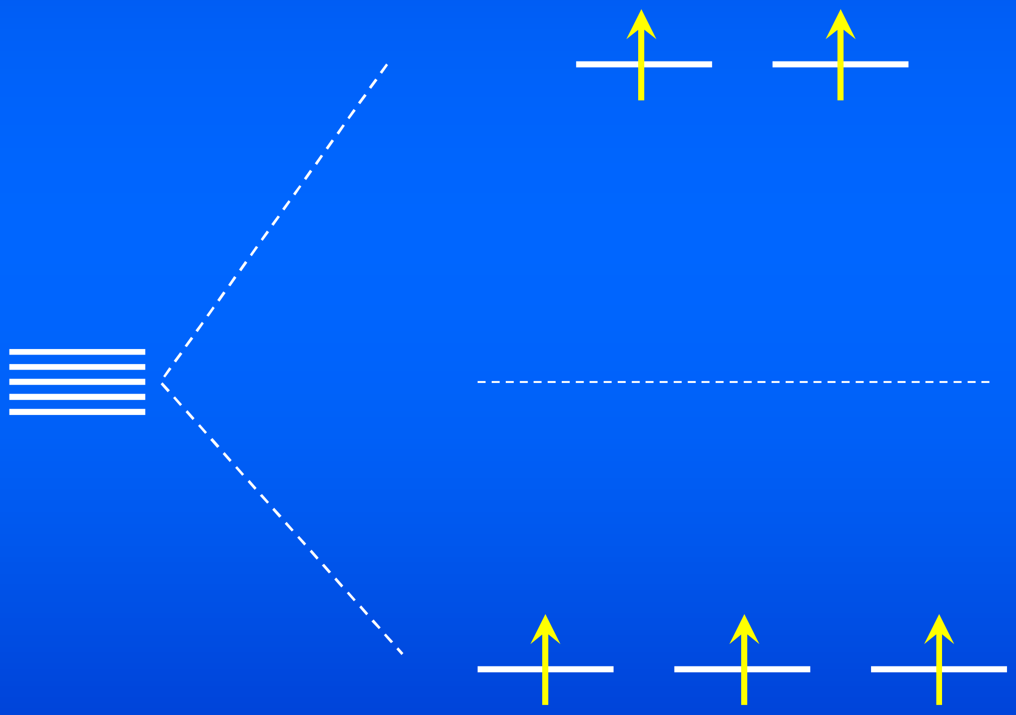


Orbital	$\frac{(V_{xx})_{val}}{e\langle r^{-3}\rangle}$	$\frac{(V_{yy})_{val}}{e\langle r^{-3}\rangle}$	$\frac{(V_{zz})_{val}}{e\langle r^{-3}\rangle}$
p-Electrons			
p_x	$-4/5$	$+2/5$	$+2/5$
p_y	$+2/5$	$-4/5$	$+2/5$
p_z	$+2/5$	$+2/5$	$-4/5$
d-Electrons			
d_{xy}	$-2/7$	$-2/7$	$+4/7$
d_{xz}	$-2/7$	$+4/7$	$-2/7$
d_{yz}	$+4/7$	$-2/7$	$-2/7$
$d_{x^2-y^2}$	$-2/7$	$-2/7$	$+4/7$
d_{z^2}	$+2/7$	$+2/7$	$-4/7$

Example: $[Fe(H_2O)_6]^{3+}$, $^6A_1$

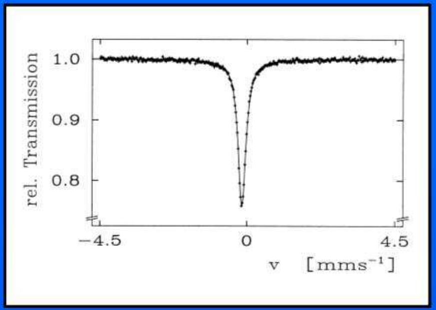
Free Ion

$[ML_6]$ (O_h)



$|z^2\rangle$

$|x^2-y^2\rangle$



$|xz\rangle$

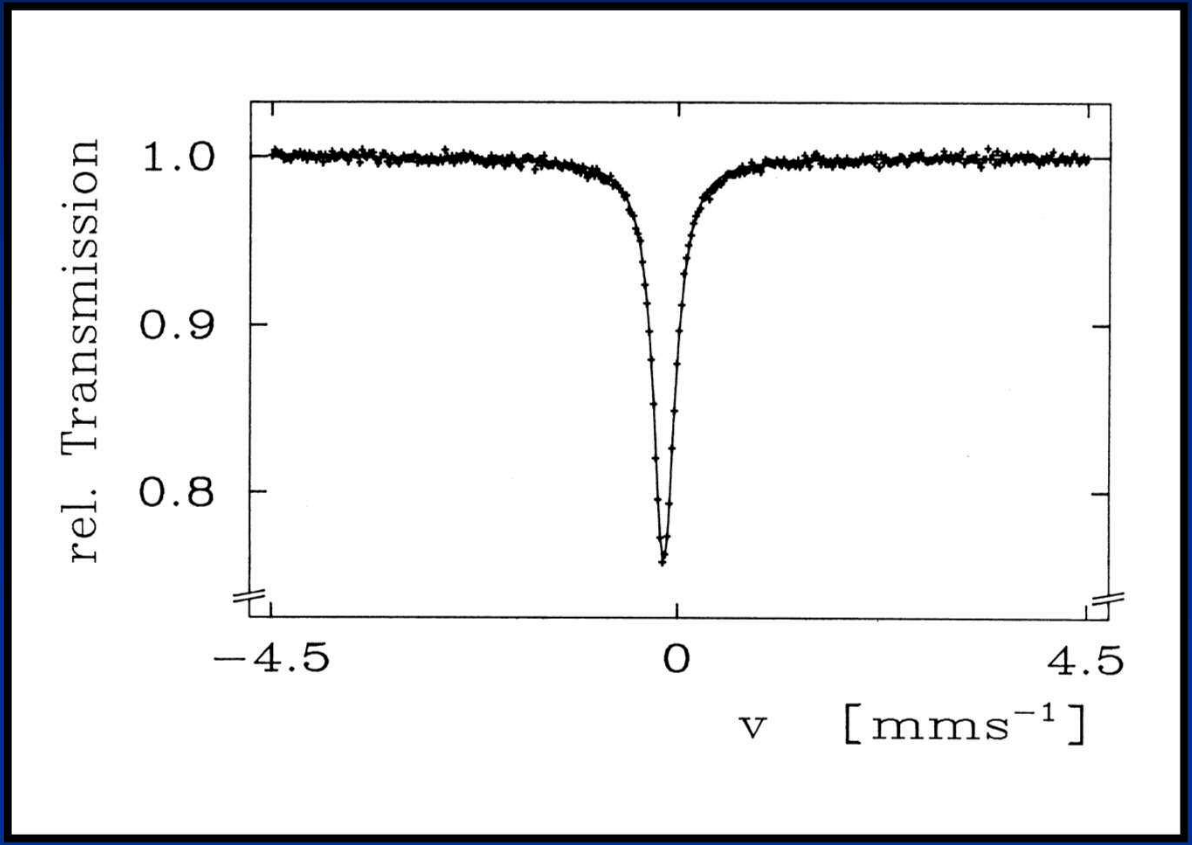
$|yz\rangle$

$|xy\rangle$

$EFG^{lat} = 0$

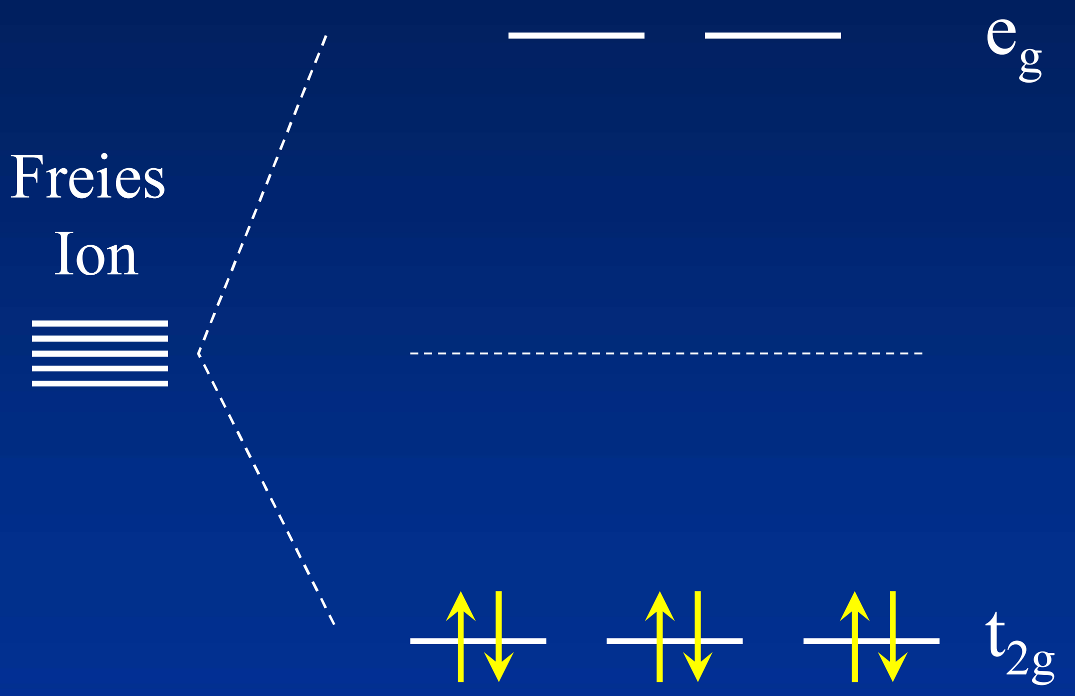
$EFG^{val} = 0$

$K_4[Fe(CN)_6]$
Fe(II)-LS, S=0
cubic



$K_4[Fe(CN)_6]$

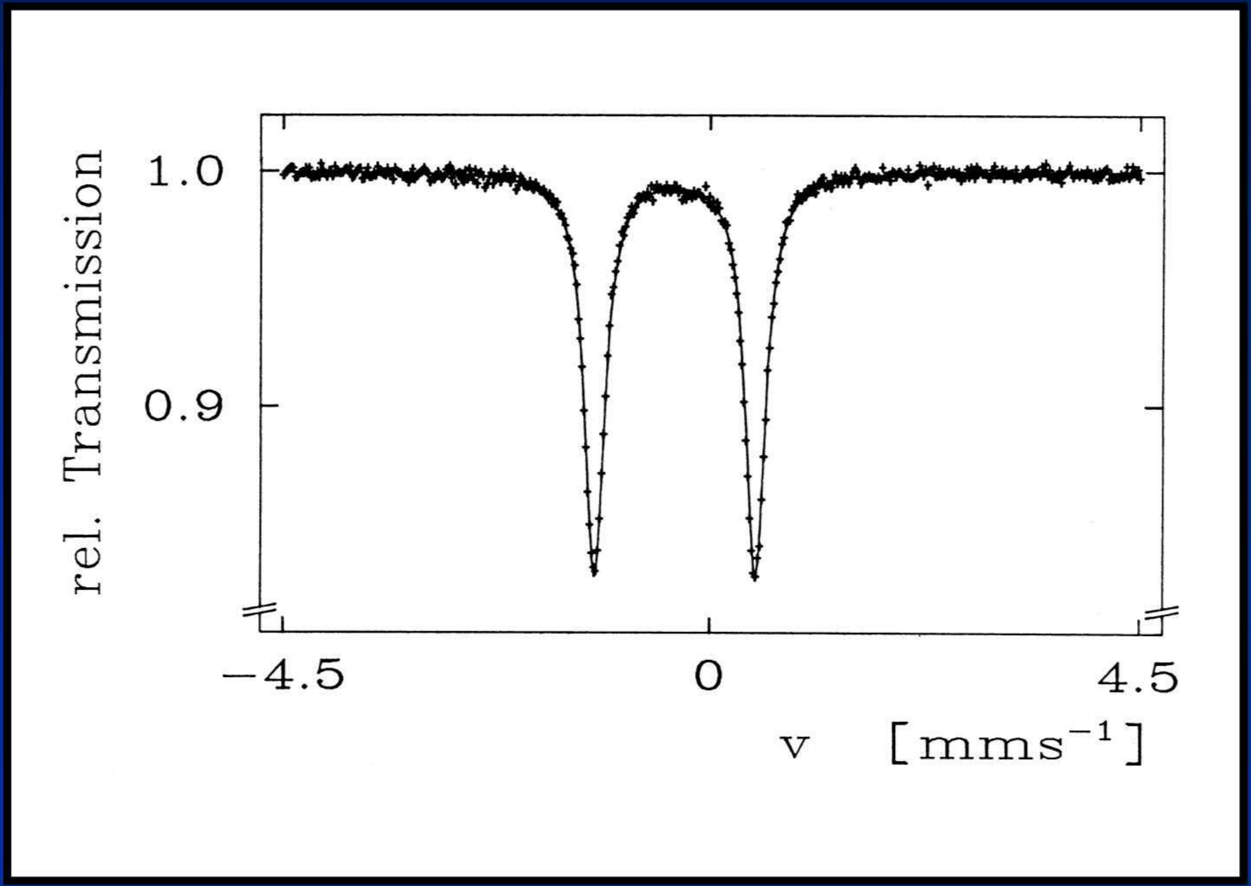
O_h



$$EFG^{lat} = 0$$

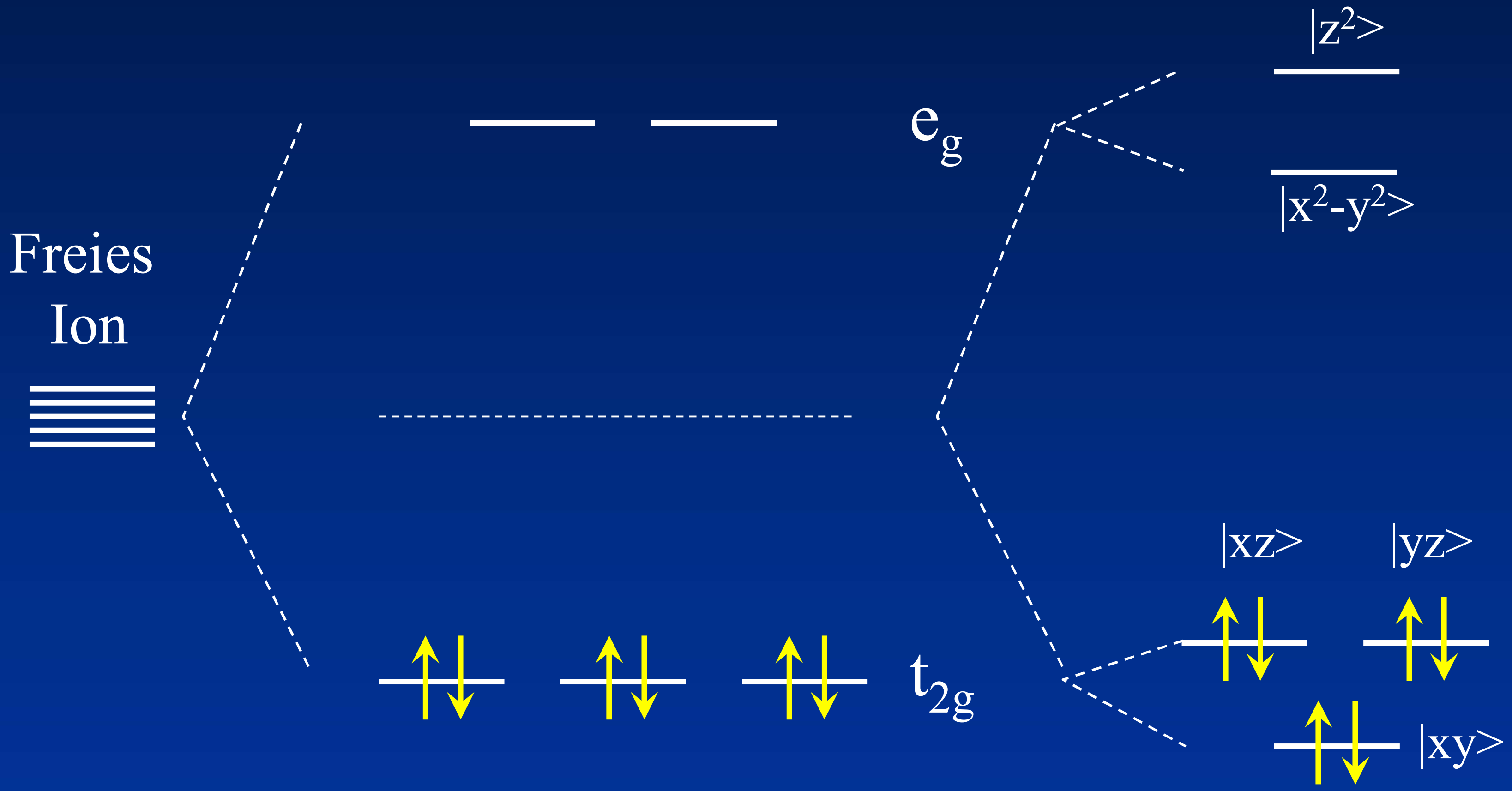
$$EFG^{val} = 0$$

$Na_2[Fe(CN)_5NO]$
Fe(II)-LS, S=0
tetragonal



$K_4[Fe(CN)_6]$ **$Na_2[Fe(CN)_5(NO)]$**

O_h **C_{4v}**



Freies Ion

e_g

t_{2g}

$|z^2\rangle$

$|x^2-y^2\rangle$

$|xz\rangle$ $|yz\rangle$

$|xy\rangle$

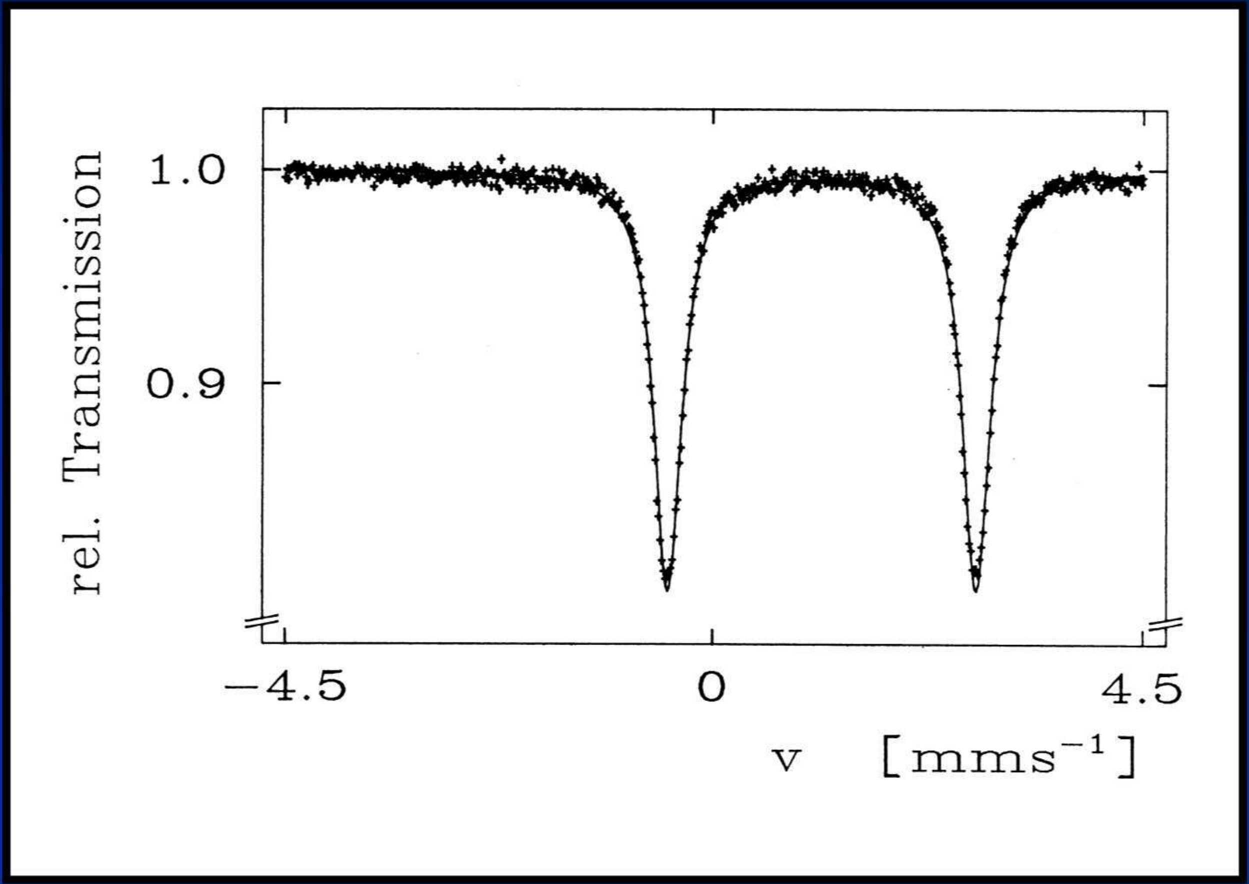
$EFG^{lat} = 0$ $\ldots \neq 0$

$EFG^{val} = 0$ $\ldots = 0$

$FeSO_4 \cdot 7H_2O$

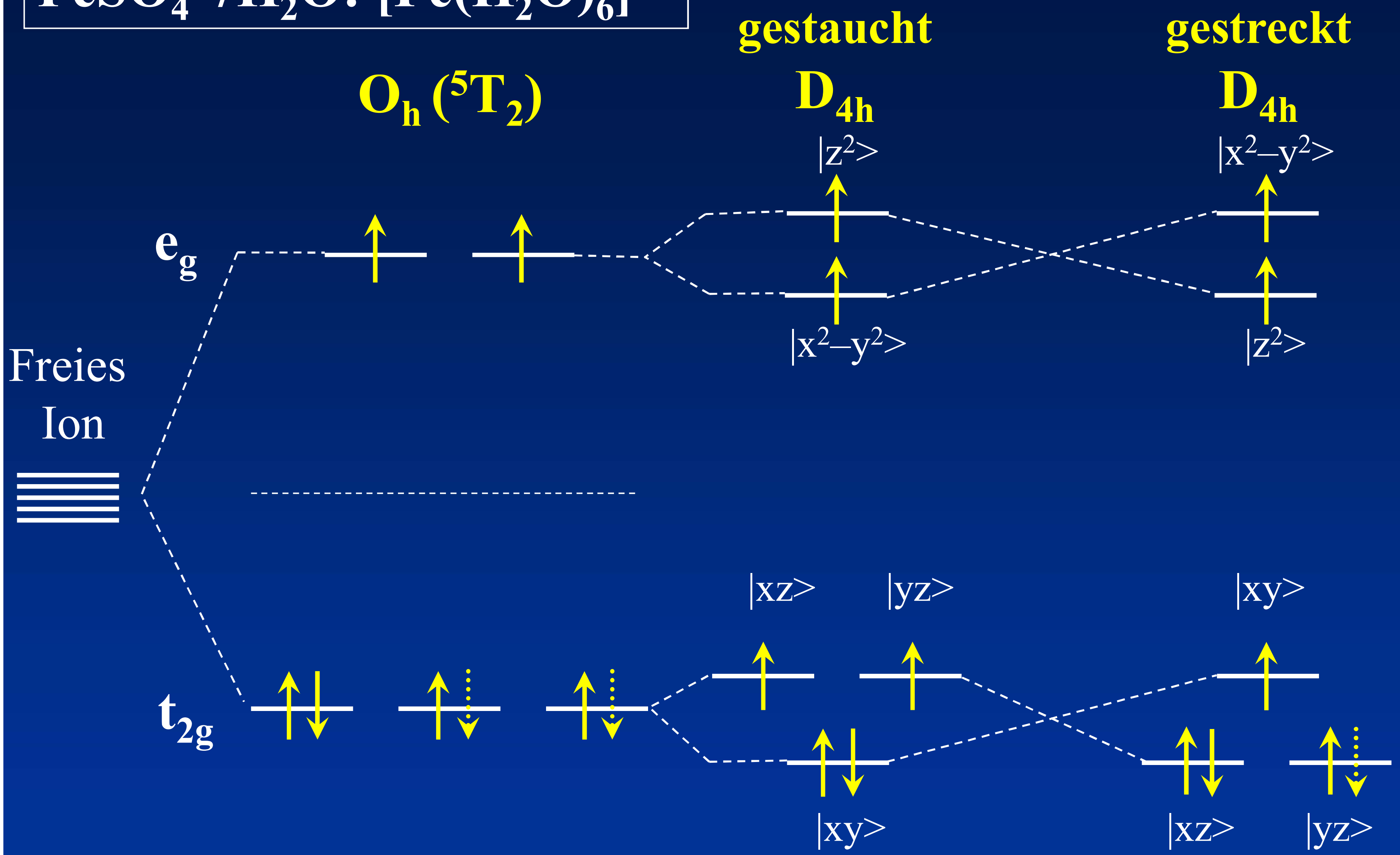
$[Fe(H_2O)_6]^{2+}$

Fe(II)-HS, S=2



$FeSO_4 \cdot 7H_2O$: $[Fe(H_2O)_6]^{2+}$

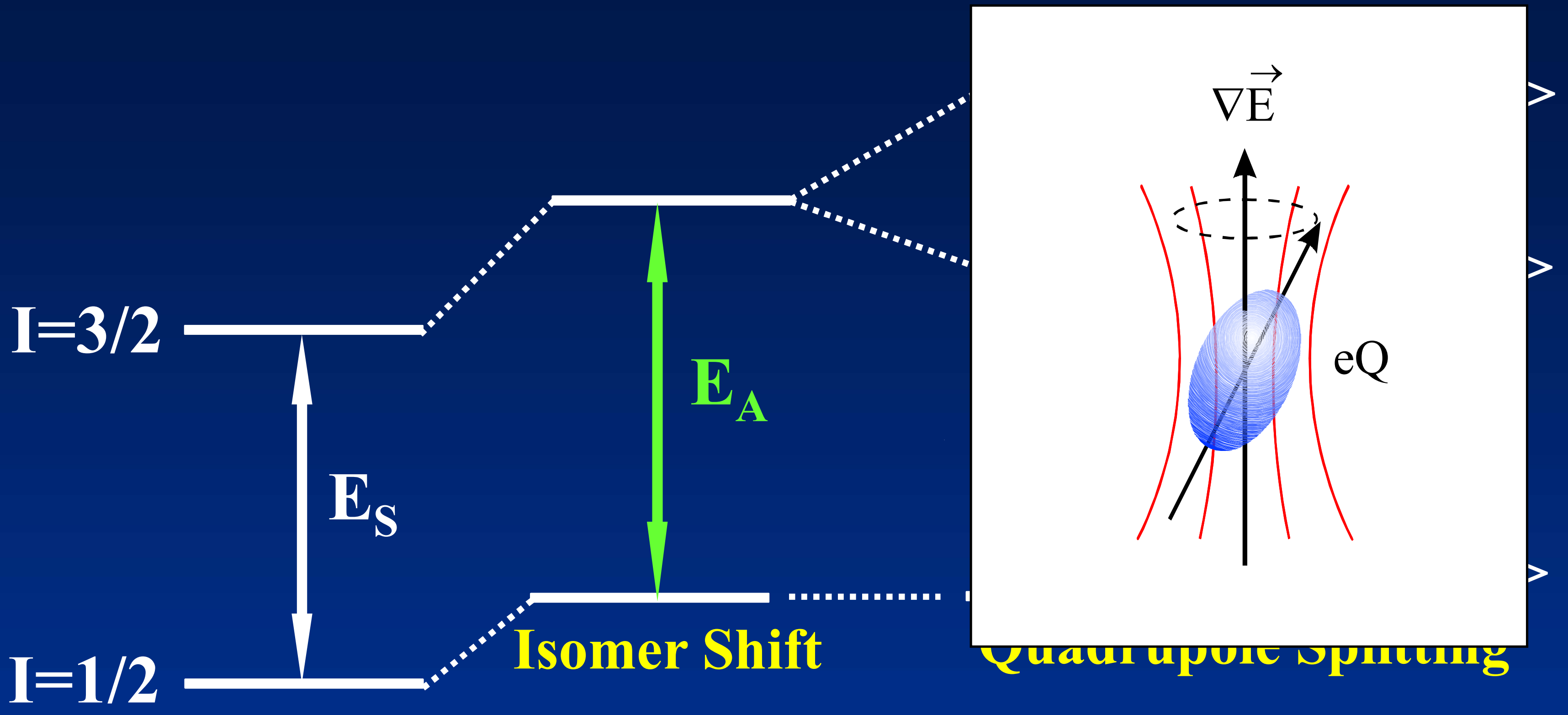
Jahn-Teller-Verzerrung



EFG^{lat} …	= 0	≠ 0, klein	≠ 0, klein
EFG^{val} …	= 0	≠ 0, groß	≠ 0, klein

Electric Monopole Int.

Electric Quadrupole Int.



$I=3/2$

$I=1/2$

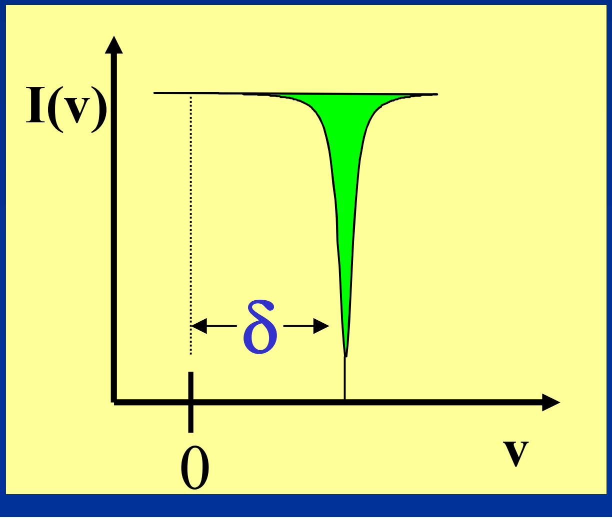
E_S

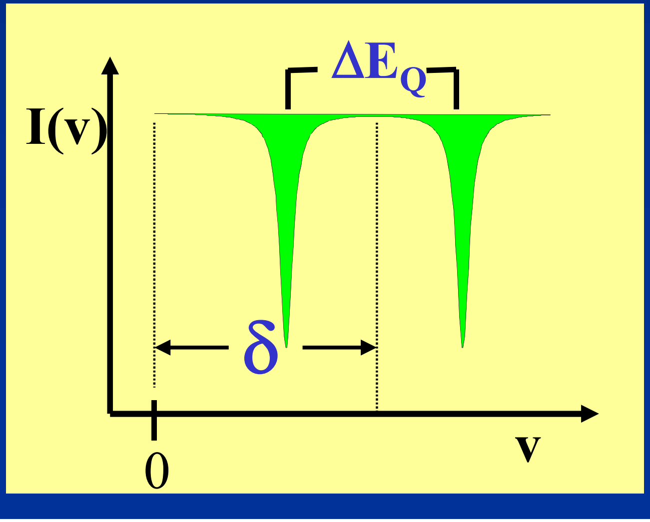
E_A

Isomer Shift

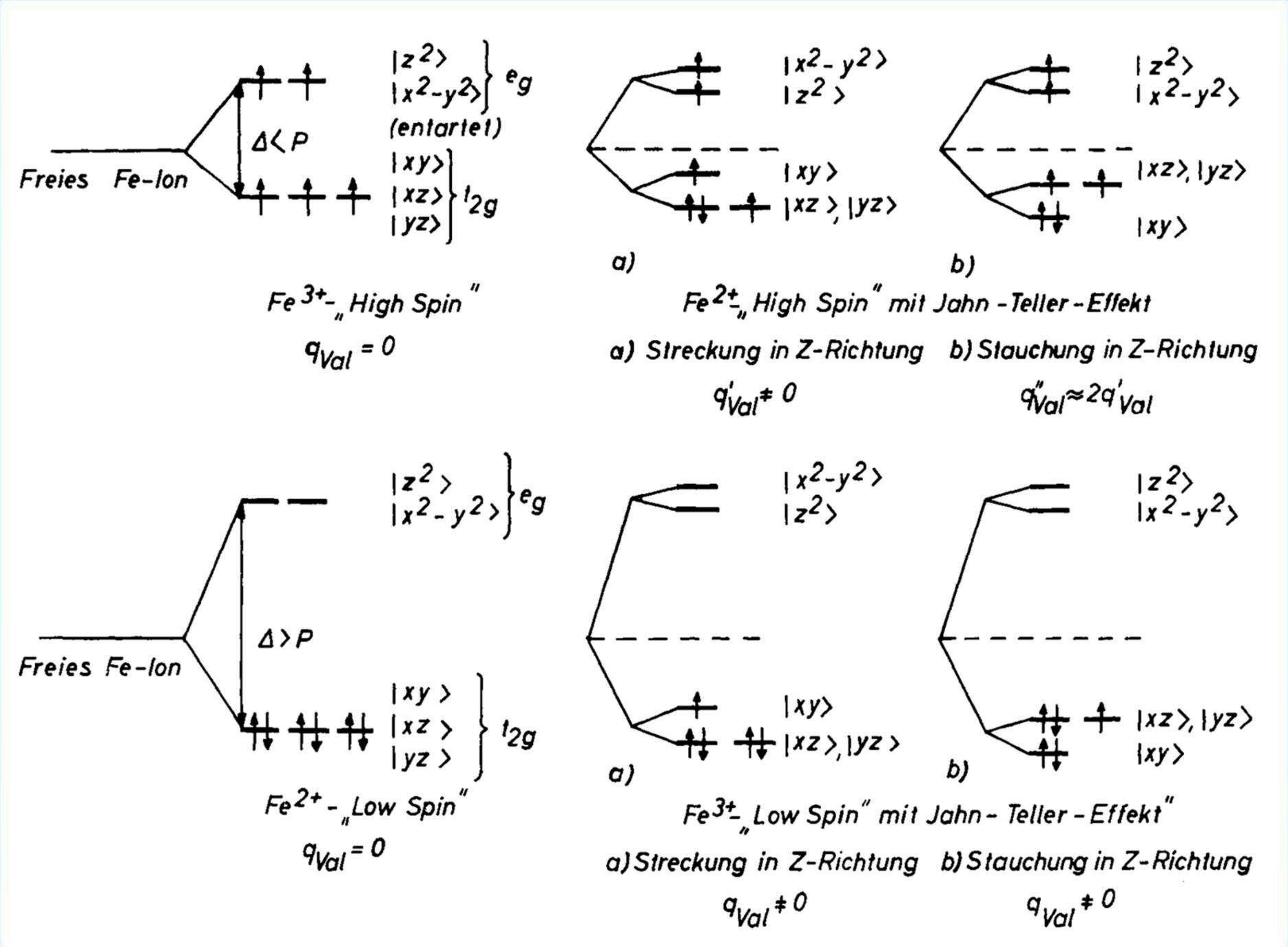
Quadrupole Splitting

$\delta = E_S - E_A$





Valence electron contribution (EFG)^{val} to Electric Field Gradient of Iron Compounds



Fe^{3+}-„High Spin"

$q_{Val} = 0$

Fe^{2+}-„High Spin" mit Jahn-Teller-Effekt

a) Streckung in Z-Richtung b) Stauchung in Z-Richtung

$q'_{Val} \neq 0$ $q''_{Val} \approx 2q'_{Val}$

Fe^{2+}-„Low Spin"

$q_{Val} = 0$

Fe^{3+}-„Low Spin" mit Jahn-Teller-Effekt"

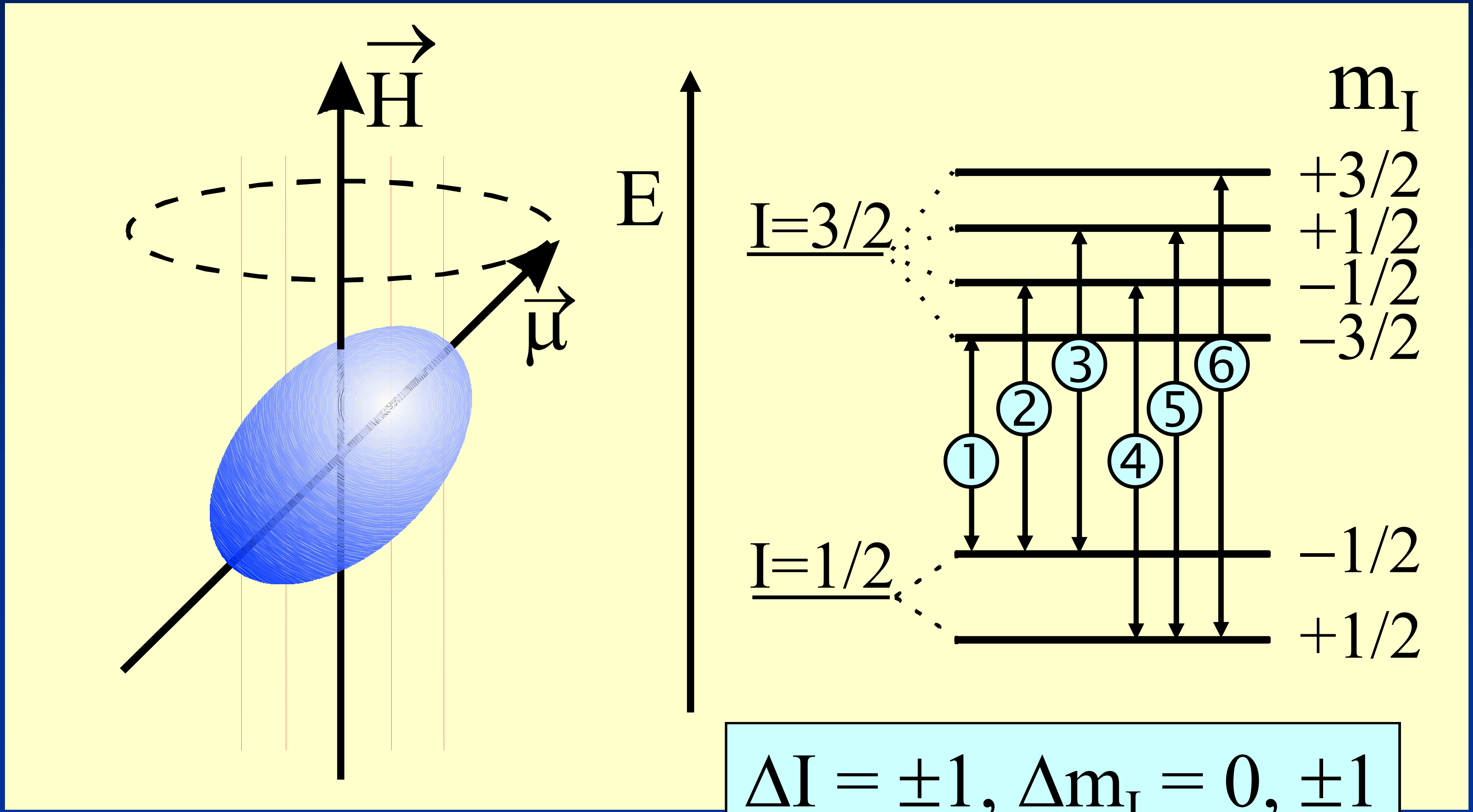
a) Streckung in Z-Richtung b) Stauchung in Z-Richtung

$q_{Val} \neq 0$ $q_{Val} \neq 0$

Magnetische Dipol-Wechselwirkung

Magnetische Aufspaltung ΔE_M

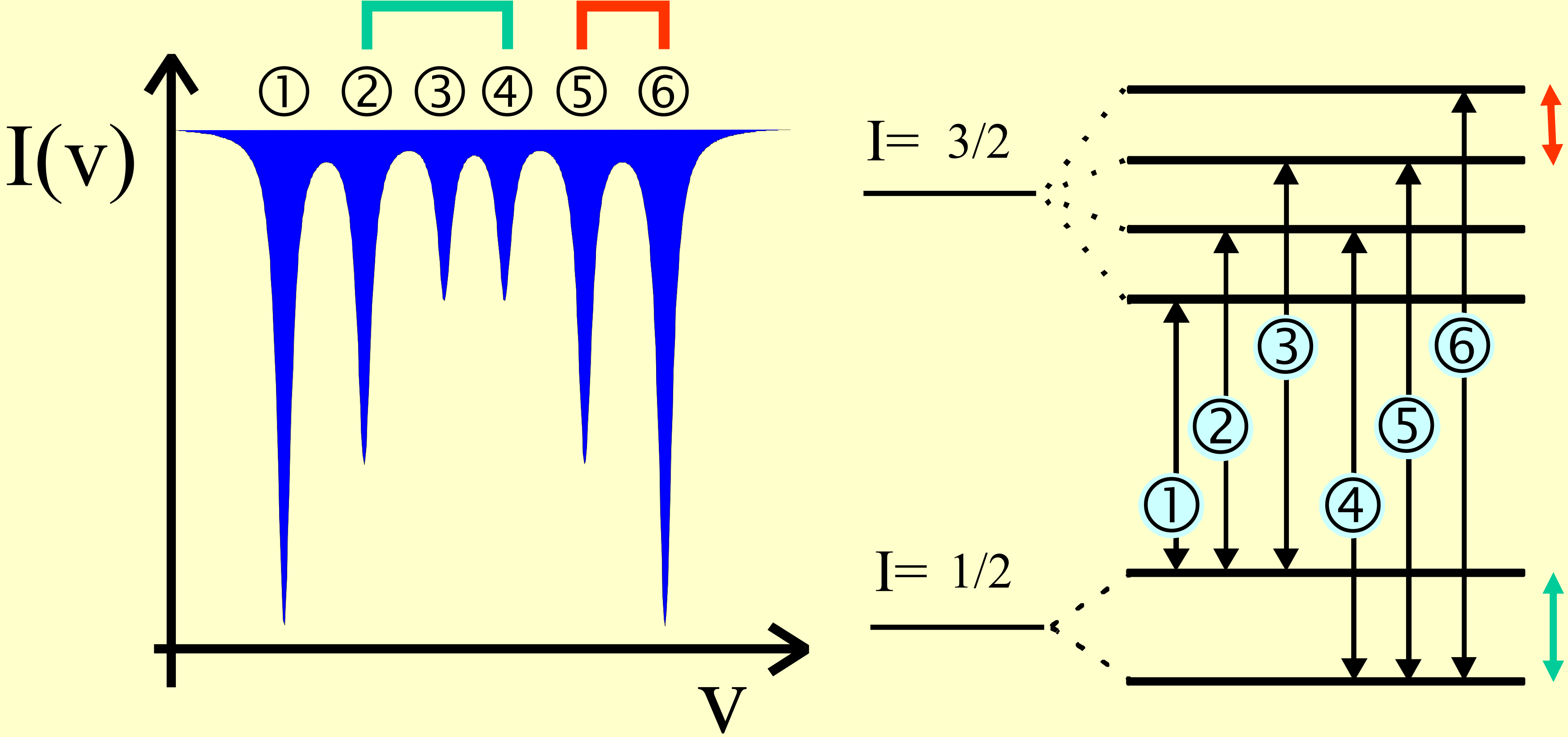
I -Kernspin, m_I –magnetische Spinquantenzahl



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

$$E_M(m_I) = -\mu H_{hf} m_I / I$$

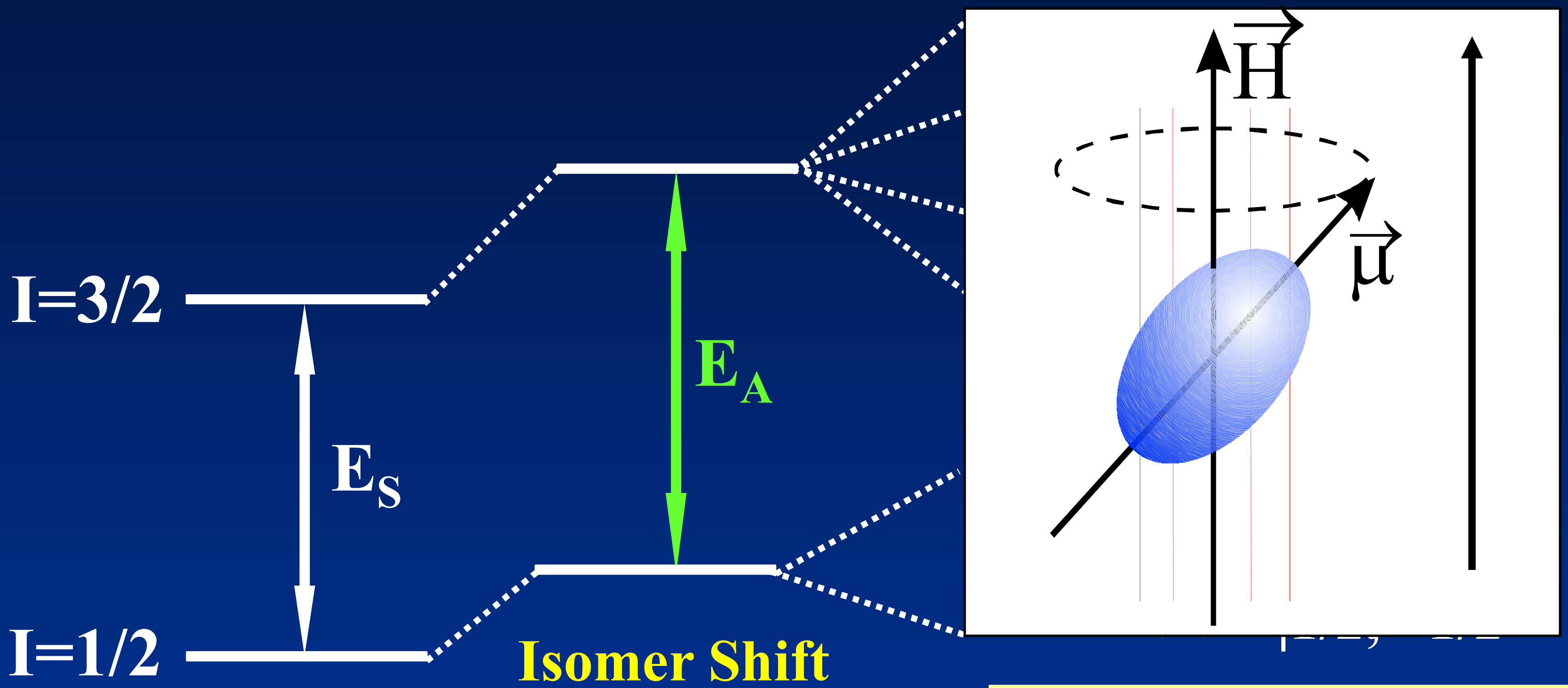
I -Kernspin, m_I –magnetische Spinquantenzahl



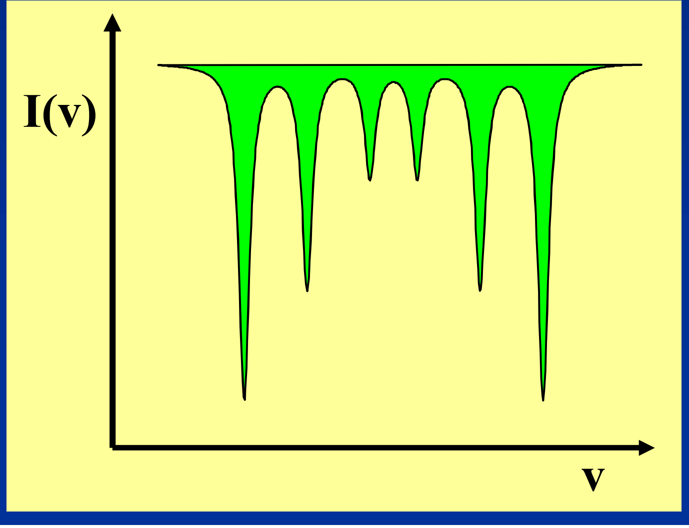
Ferro-, Antiferro-,
Ferri -Magnetismus

Electric Monopole Int.

Magnetic Dipole Int.



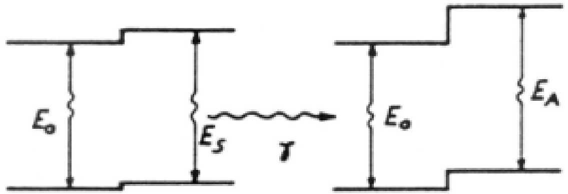
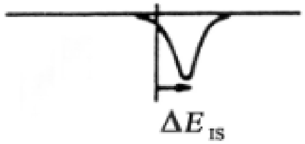
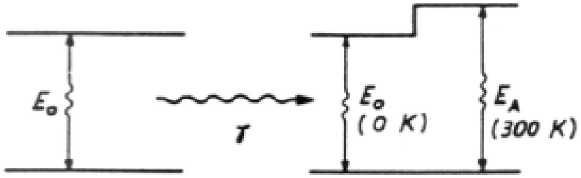
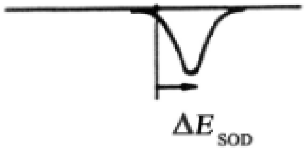
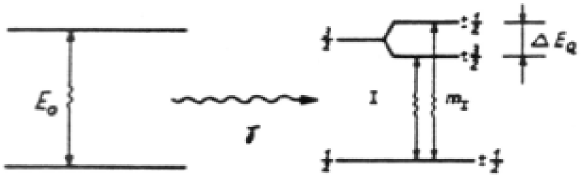
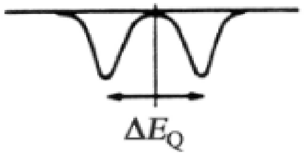
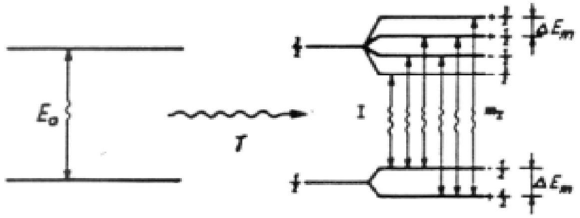
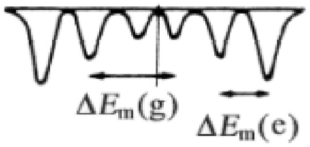
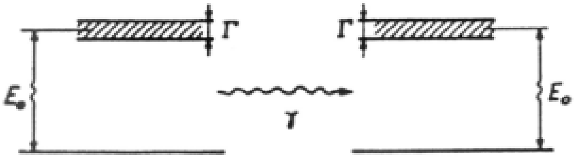
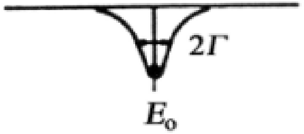
Magnetic Dipole Splitting



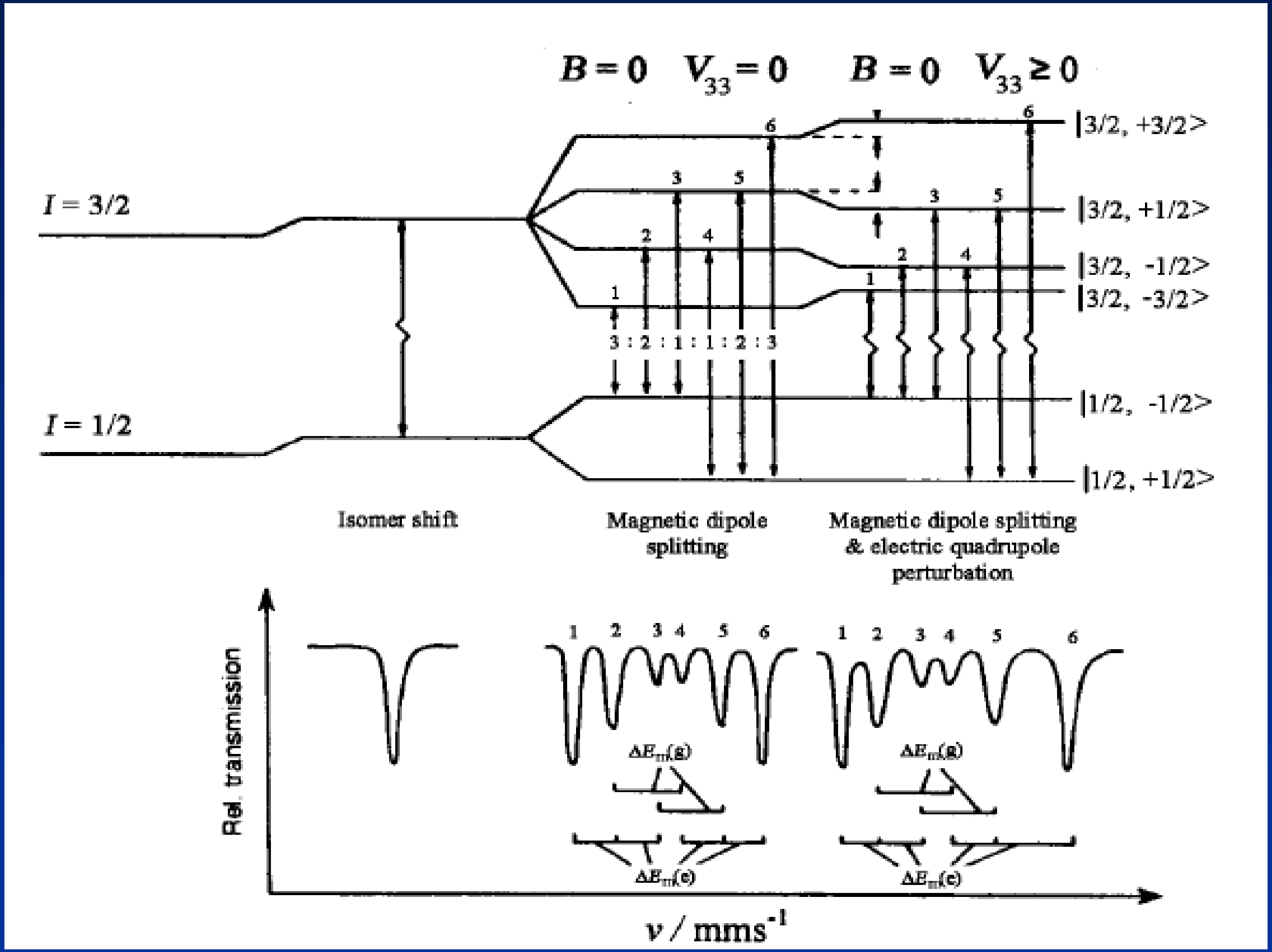
Bedingungen für Hyperfeinwechselwirkungen

Art der Wechselwirkung	**Kern-Bedingung**	**Elektronische Bedingung**	**Konsequenz**
Elektr. Monopol-Wechselw.	$R_a^2 \neq R_g^2$	$\lvert\Psi(0)\rvert_A^2 \neq \lvert\Psi(0)\rvert_S^2$	Unterschiedliche Verschiebg. der Kernenergienivieaus ⇨ **Isomer shift δ**
Elektr. Quadrupol-Wechselw.	Elektr. Quadrupolmoment $eQ \neq 0$ $(I > ½)$	EFG ≠ 0	Kernenergieniveaus spalten auf in I + ½ Subniveaus $\lvert I, \pm m_I >$ (zweifach entartet) ⇨ **Quadrupol-Aufspaltung ΔE_Q**
Magnetische Dipol-Wechselw.	Magn. Dipolmoment $\mu \neq 0$ $(I > 0)$	H ≠ 0	Kernniveaus $\lvert I >$ spalten auf in 2I+1 Niveaus $\lvert I, m_I >$ mit $m_I = +I, +I-1, \ldots, -I$ ⇨ **Magnet. Dipol-Aufspaltung ΔE_M**

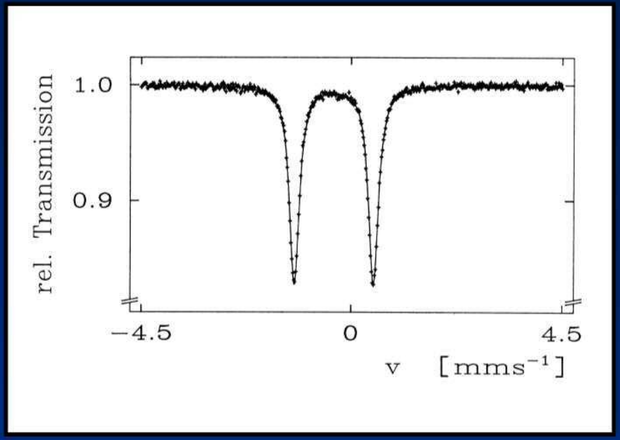
Mössbauer-Parameters

Parameter Formula	^{57}Fe energy level diagram with allowed transition Source (S) Absorber (A)	Schematic representation of absorption vs. relative speed of source and absorber
Chemical isomer shift $\delta_C \propto \Delta E_{IS} = \beta\,\Delta\left\|\Psi(0)\right\|^2$		
Second order Doppler shift $\delta_{SOD} \propto \Delta E_{SOD} = -\frac{\langle u^2\rangle}{2c^2}E_0$		
Quadrupole splitting $\Delta \propto \Delta E_Q = \frac{1}{2}eQV_{33}\sqrt{1+\frac{\eta^2}{3}}$		
Magnetic splitting $\Delta_m \propto \Delta E_m = -g_I\mu_N B$		
Peak width $W \ge W_0 \propto 2\Gamma = 2\frac{\hbar\ln 2}{T_{1/2}}$		

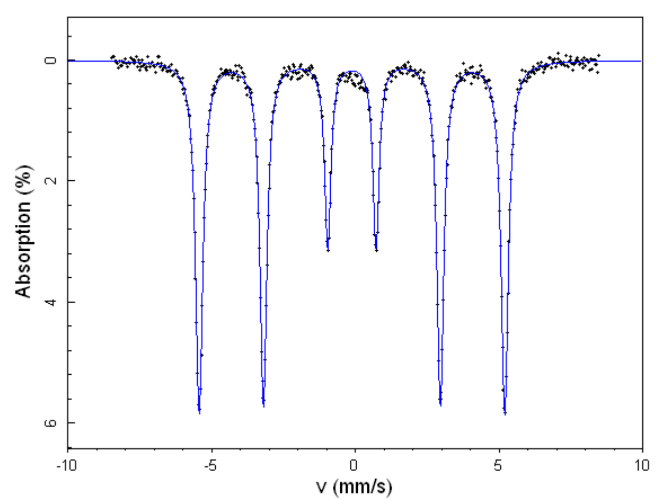
Elektrische Quadrupol- und Magnetische Dipol-Wechselwirkung (Kombinierte)



Auswertungsbeispiele



$Na_2[Fe(CN)_5NO]$
Fe(II)-LS, S=0
tetragonal



Alfa-Fe, cubic

Anwendungen der Mössbauer-Spektroskopie in Chemie und Materialforschung

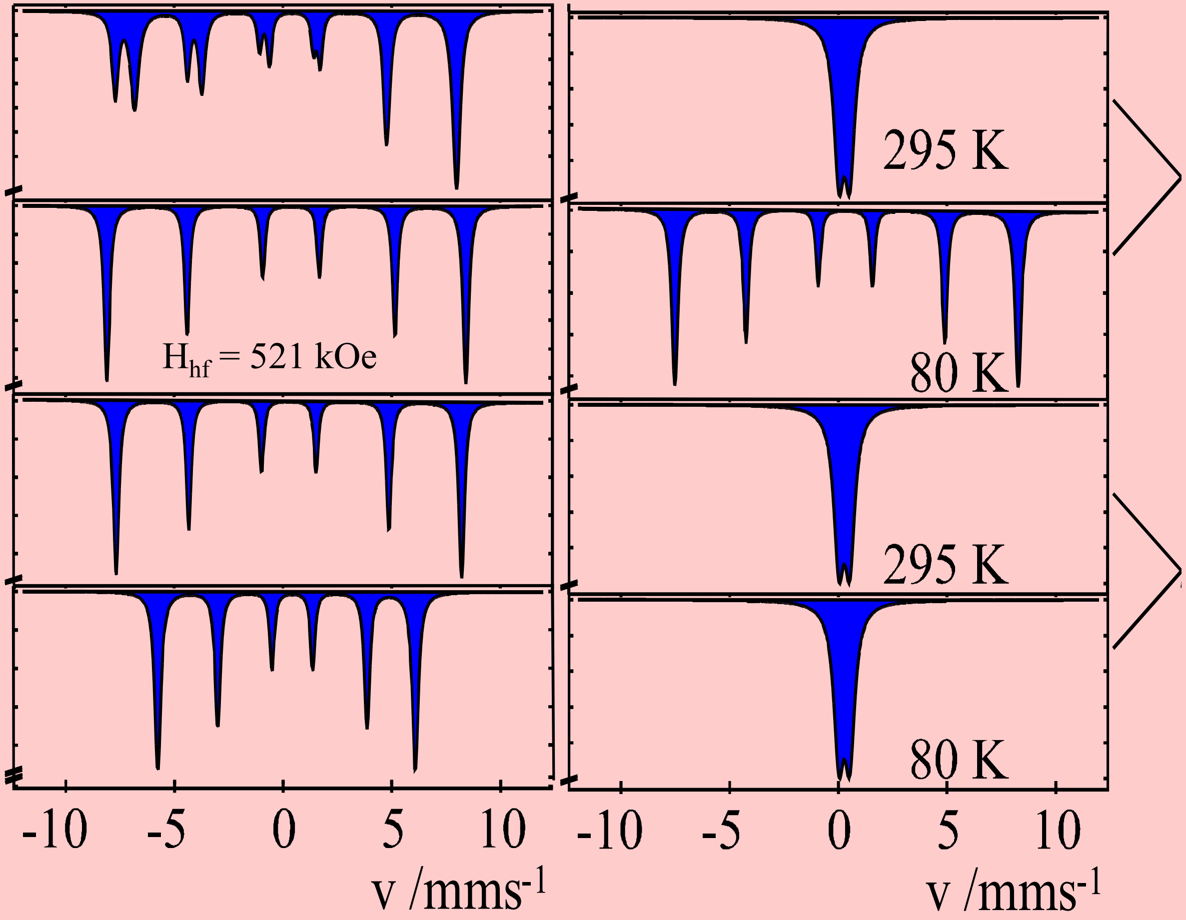
^{57}Fe-Mössbauer-Spektren von Korrosions-Produkten

Magnetite
Fe_3O_4

Hämatite
α-Fe_2O_3

Maghemite
γ-Fe_2O_3

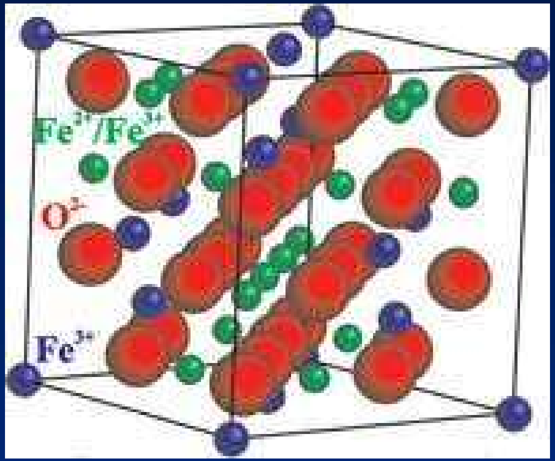
Goethite
α-FeOOH
AF at RT
Δ(para) =0.60 mms-1
H(RT) = 384 kOe
δ(RT)= 0.35 mms-1
ε(RT) = -0.15 mms-1
H(0 K) =504 kOe



Akagadite
β-FeOOH
Δ(T>RT) =0.70 mms-1
δ = 0.30 mms-1
AF below 295 K
H(0 K) = 475 kOe
ε(0 K) = -0.1 mms-1

Lepidochrocite
γ-FeOOH
Δ(RT) = 0.55 mms-1
δ = 0.30 mms-1
AF below 77 K
H(0 K) = 460 kOe
ε(0 K) < 0.1 mms-1

Verwey transition in magnetite Fe_3O_4



Vervey-Mott concept of CO within the *B*-sites

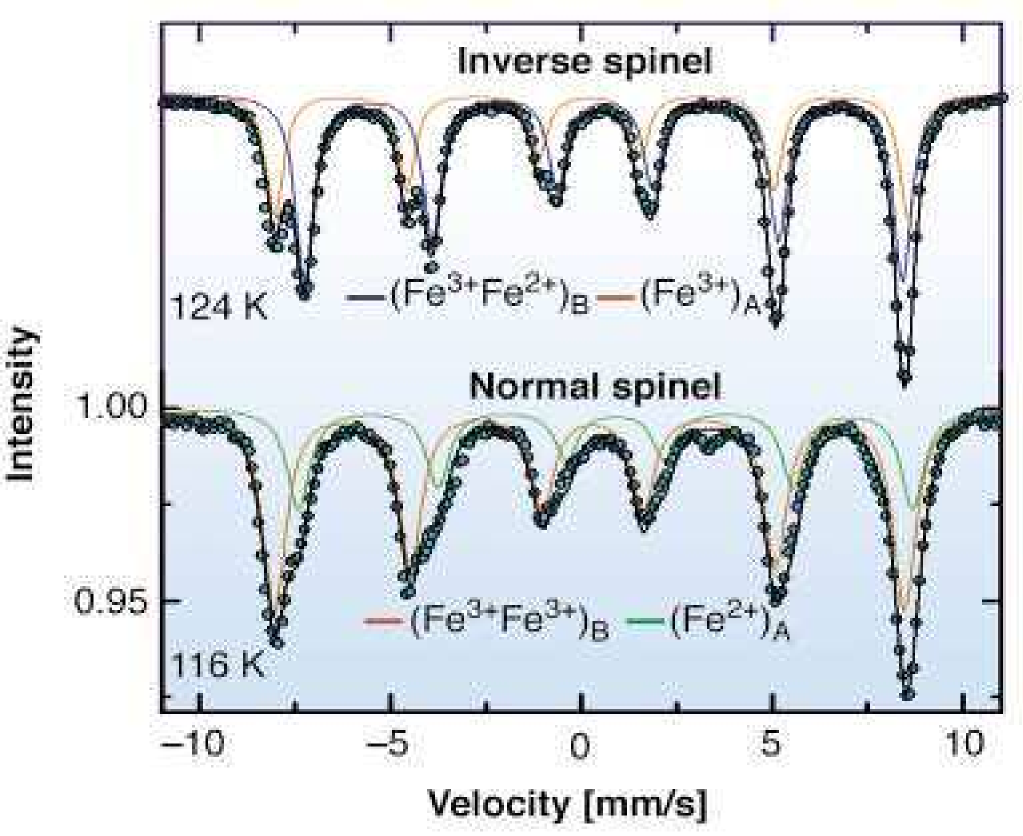
metallic $\qquad\qquad\qquad$ insulator

$$[Fe^{3+}]_A[2\,Fe^{3+} + e^-]_B \xrightarrow{T \le T_V} [Fe^{3+}]_A[Fe^{2+}Fe^{3+}]_B$$

Structural transformation: cubic - cubic-distorted

inverse spinel $\qquad\qquad\qquad$ normal spinel

$$[Fe^{3+}]_A[Fe^{3+}Fe^{2+}]_B \underset{T > T_V}{\overset{T < T_V}{\rightleftarrows}} [Fe^{2+}]_A[Fe^{3+}Fe^{3+}]_B$$



M. P. Pasternak, W. M. Xu, G. Kh. Rozenberg, R. D. Taylor, and R. Jeanloz, *J. Magn. Magn. Mater.*, **265**, L107 (2003).

Quadrupolaufspaltung und magnetisches Hyperfeinfeld bei 4,2 K für einige Eisenoxide und Hydroxide

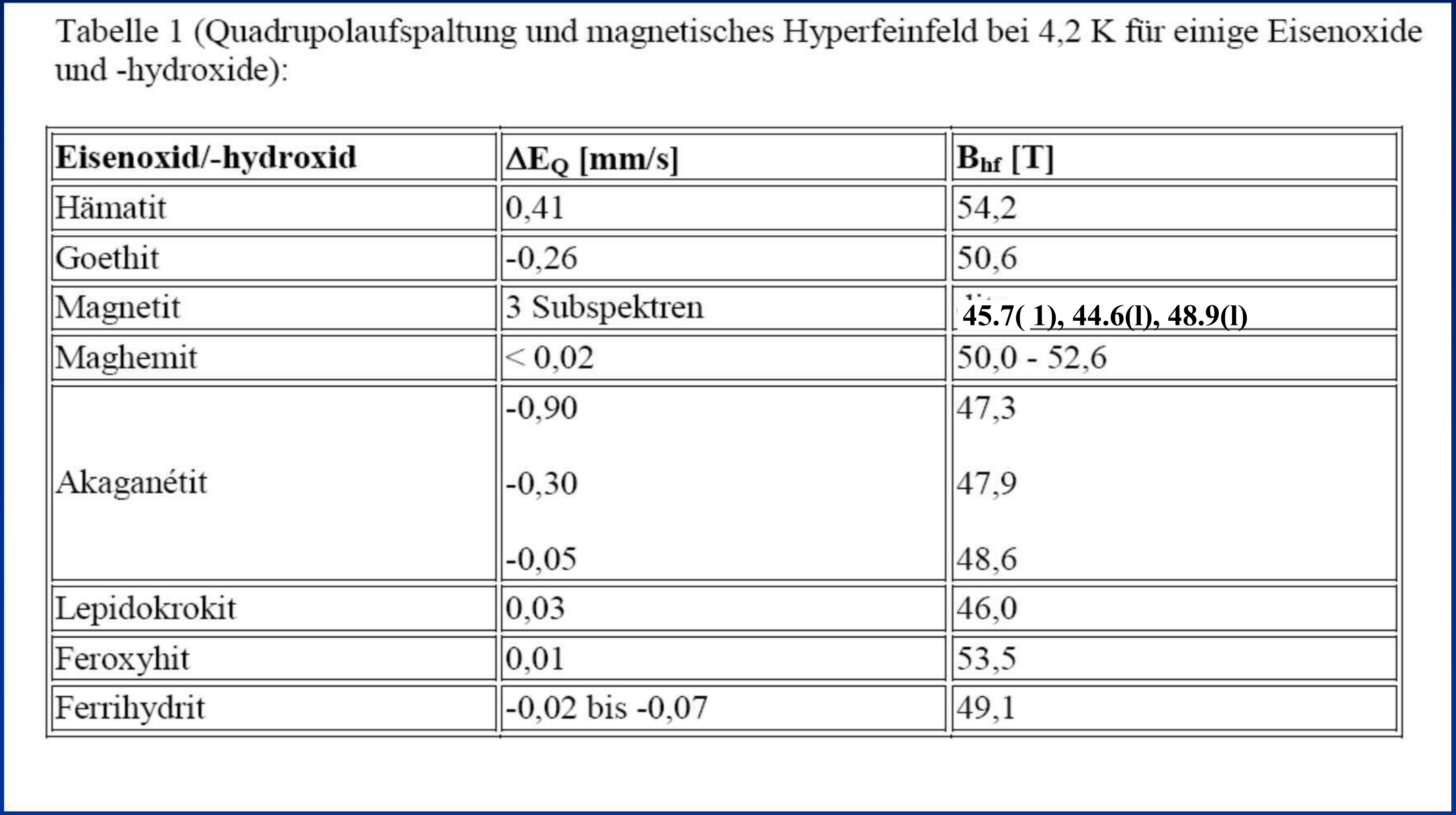
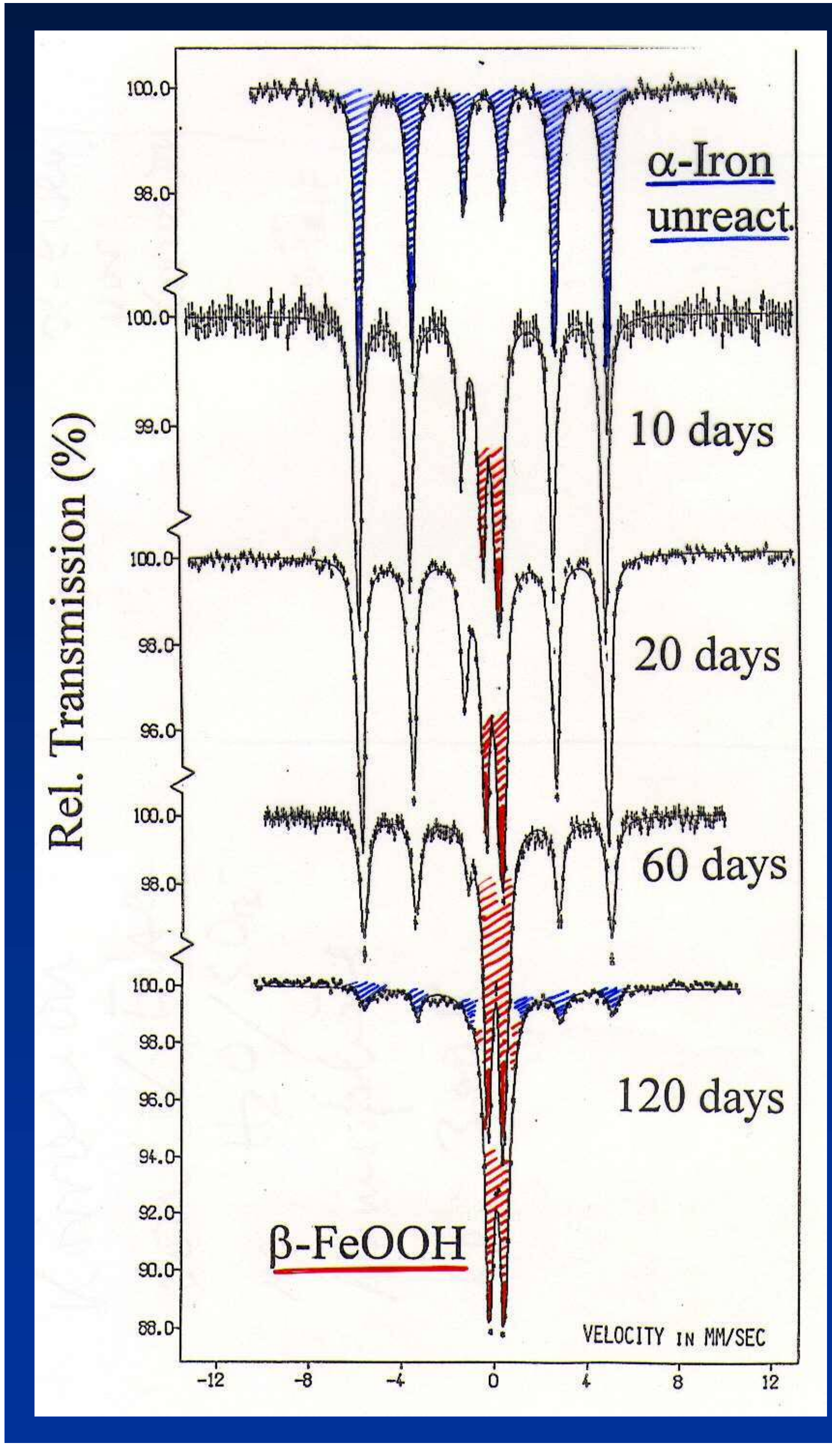


Tabelle 1 (Quadrupolaufspaltung und magnetisches Hyperfeinfeld bei 4,2 K für einige Eisenoxide und -hydroxide):

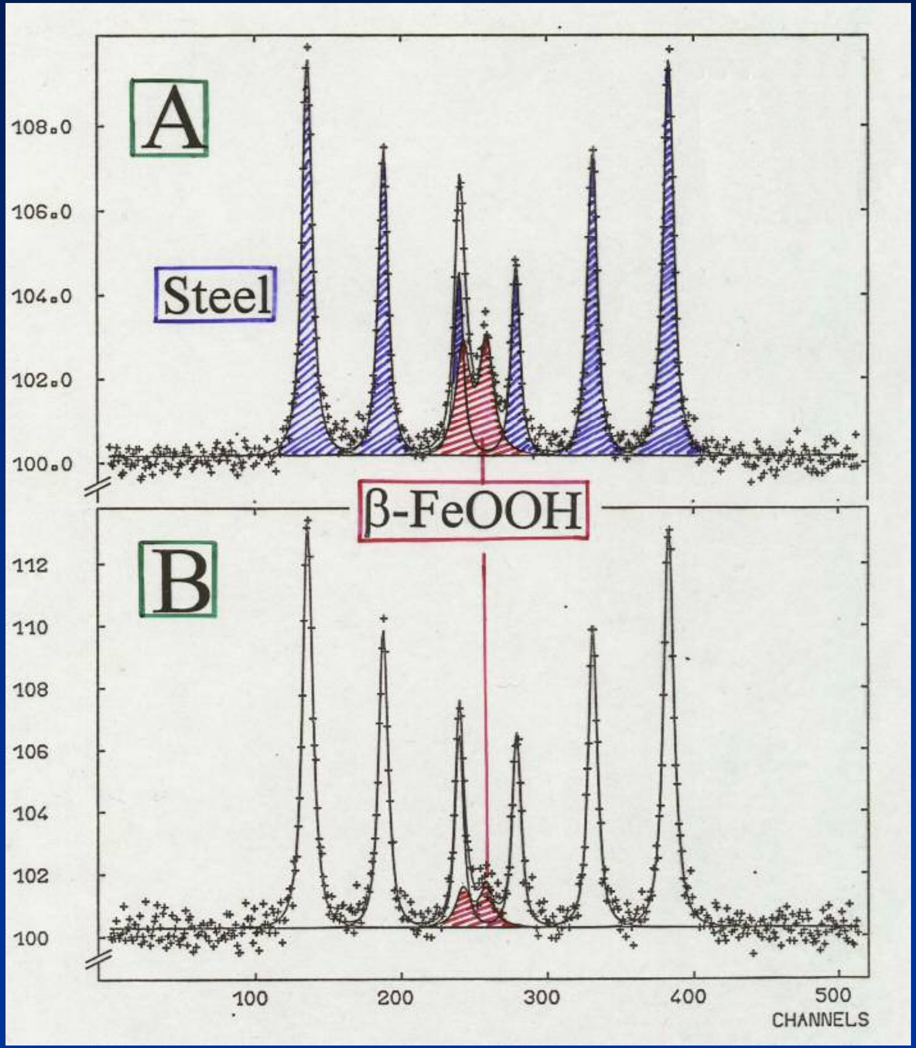
Eisenoxid/-hydroxid	**ΔE_Q [mm/s]**	**B_{hf} [T]**
Hämatit	0,41	54,2
Goethit	-0,26	50,6
Magnetit	3 Subspektren	**45.7(1), 44.6(l), 48.9(l)**
Maghemit	< 0,02	50,0 - 52,6
Akaganétit	-0,90 -0,30 -0,05	47,3 47,9 48,6
Lepidokrokit	0,03	46,0
Feroxyhit	0,01	53,5
Ferrihydrit	-0,02 bis -0,07	49,1

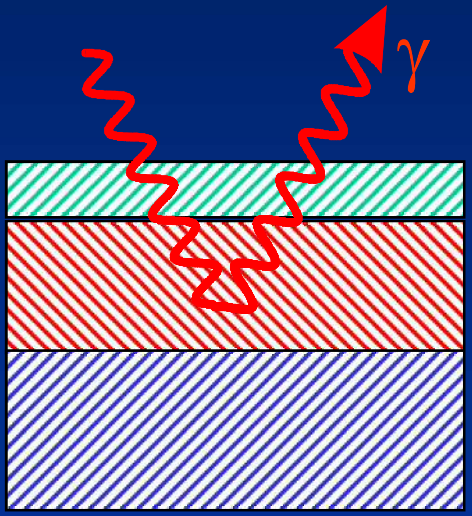


Corrosion of α-Iron in H_2O/SO_2 atmosphere at 300 K

Corrosion product is β-FeOOH

Lacquer Coating
Against Corrosion of Steel




γ

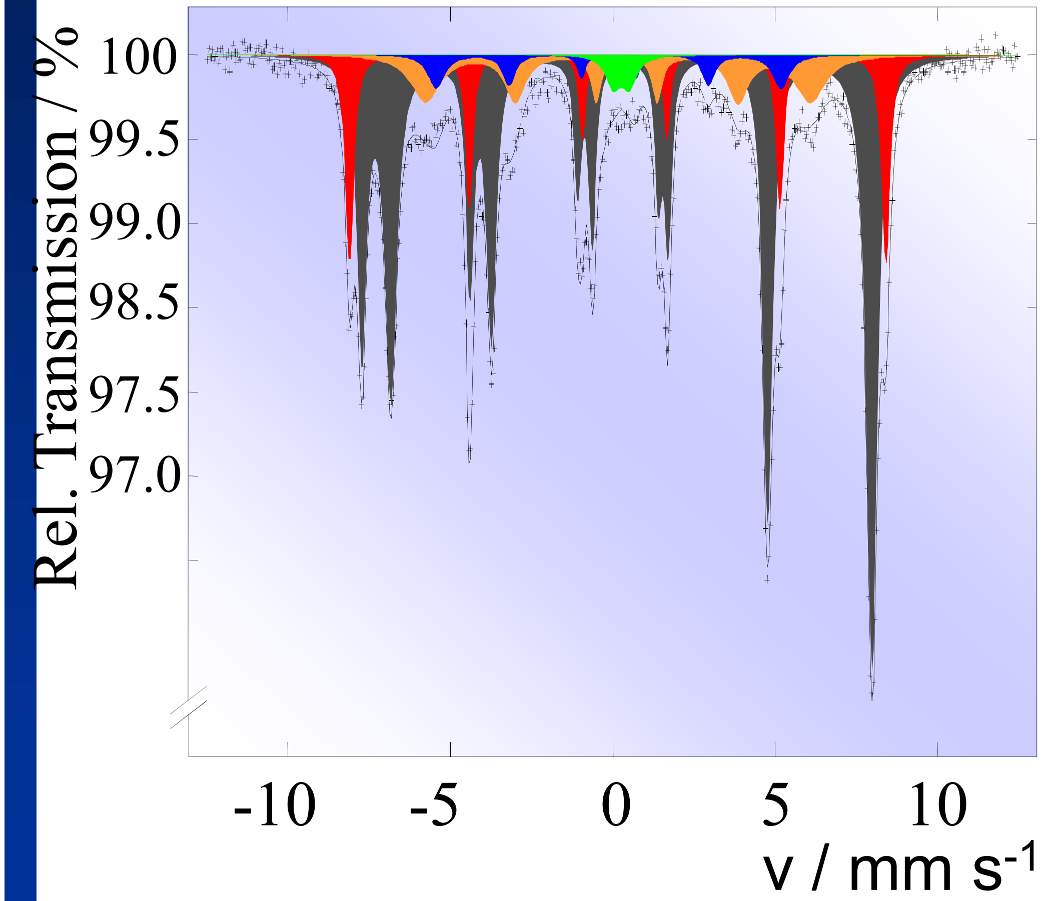
Lacquer

Rust

Steel

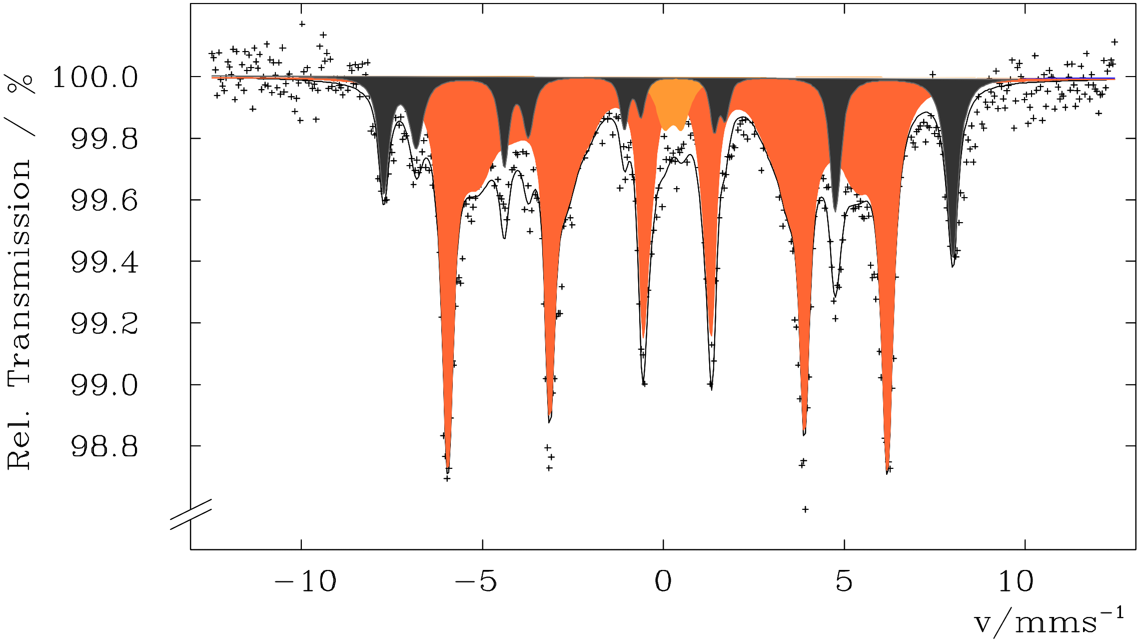
A, B : Different lacquers,
Same corrosion conditions

Corrosion Products in Cooling Systems of Power Plants



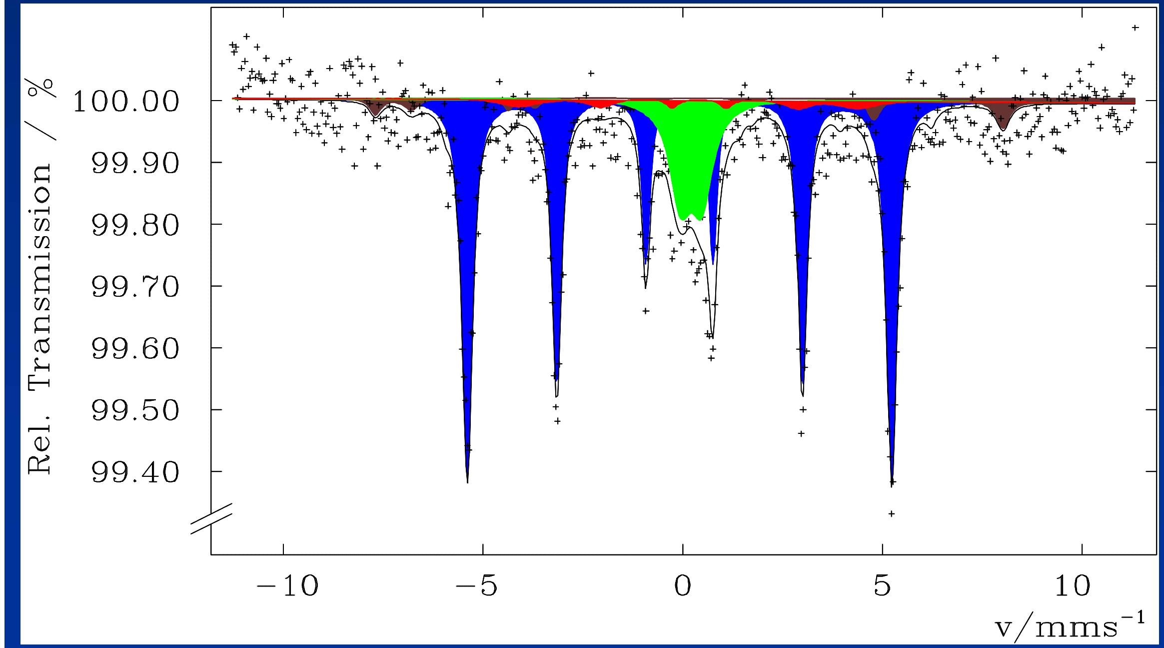
Constituents	A/%
Hematite, α-Fe_2O_3	16
Magnetite, Fe_3O_4	64
Goethite, α-FeOOH	13
Martensite	5
β/γ - FeOOH	2

^{57}Fe-Mössbauer-Spektrum einer 1 US Dollar-Note



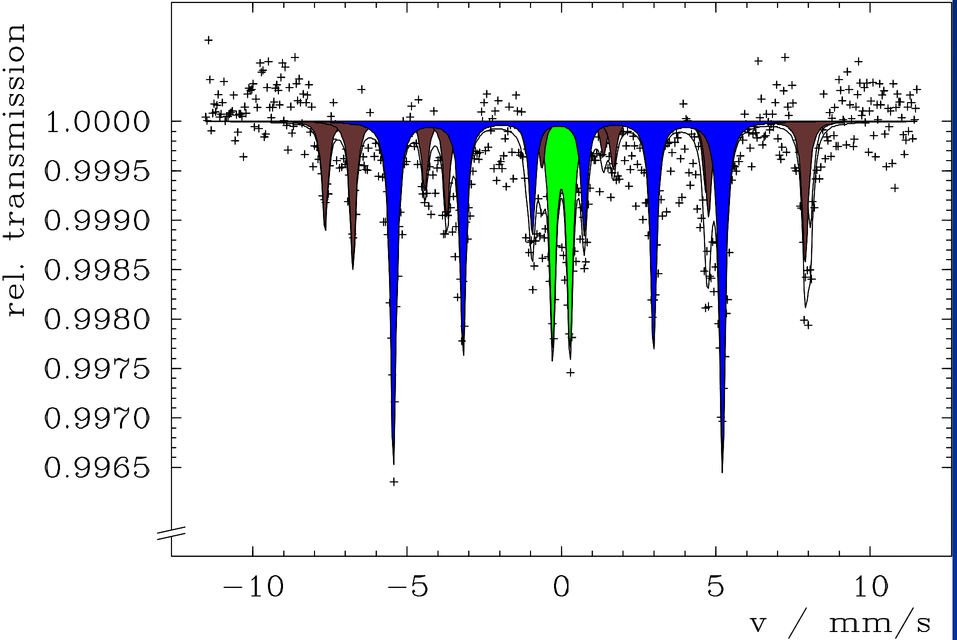
Bestandteile	**Anteil-%**
Magnetit, Fe_3O_4	**20**
Goethit, α-FeOOH	**80**

^{57}Fe-Mössbauer-Spektrum vom 100 DM-Schein

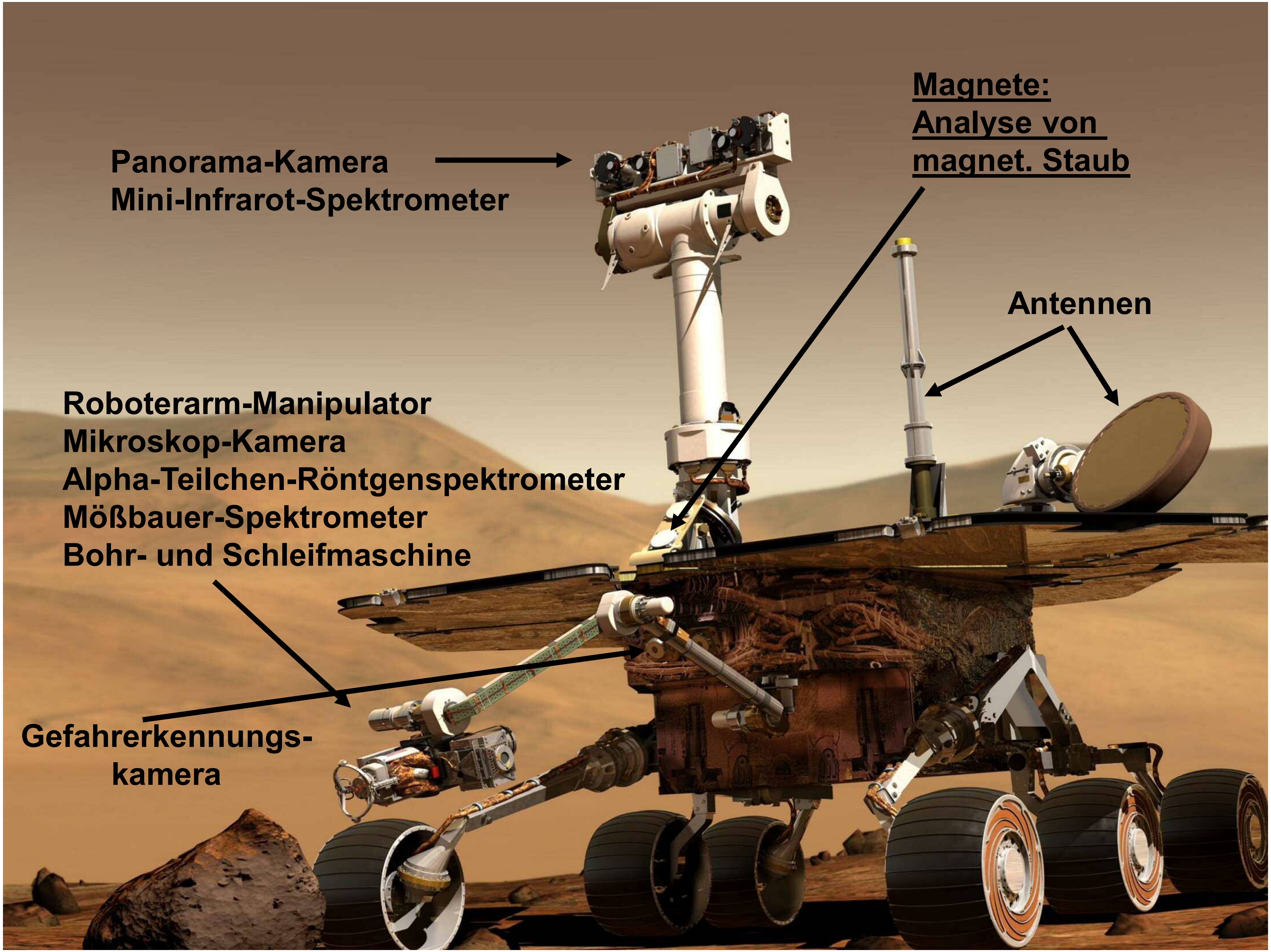


Bestandteile	Anteil-/%
Metallisches Eisen	70
Superpara. Eisen(III)	18
Magnetit	6
Hämatit	6

^{57}Fe-Mössbauer-Spektrum eines 50 Euro-Scheins



Constituents	**area-/%**
α Iron	**48**
Magnetite	**36**
doublet	**16**



Panorama-Kamera
Mini-Infrarot-Spektrometer

Magnete:
Analyse von
magnet. Staub

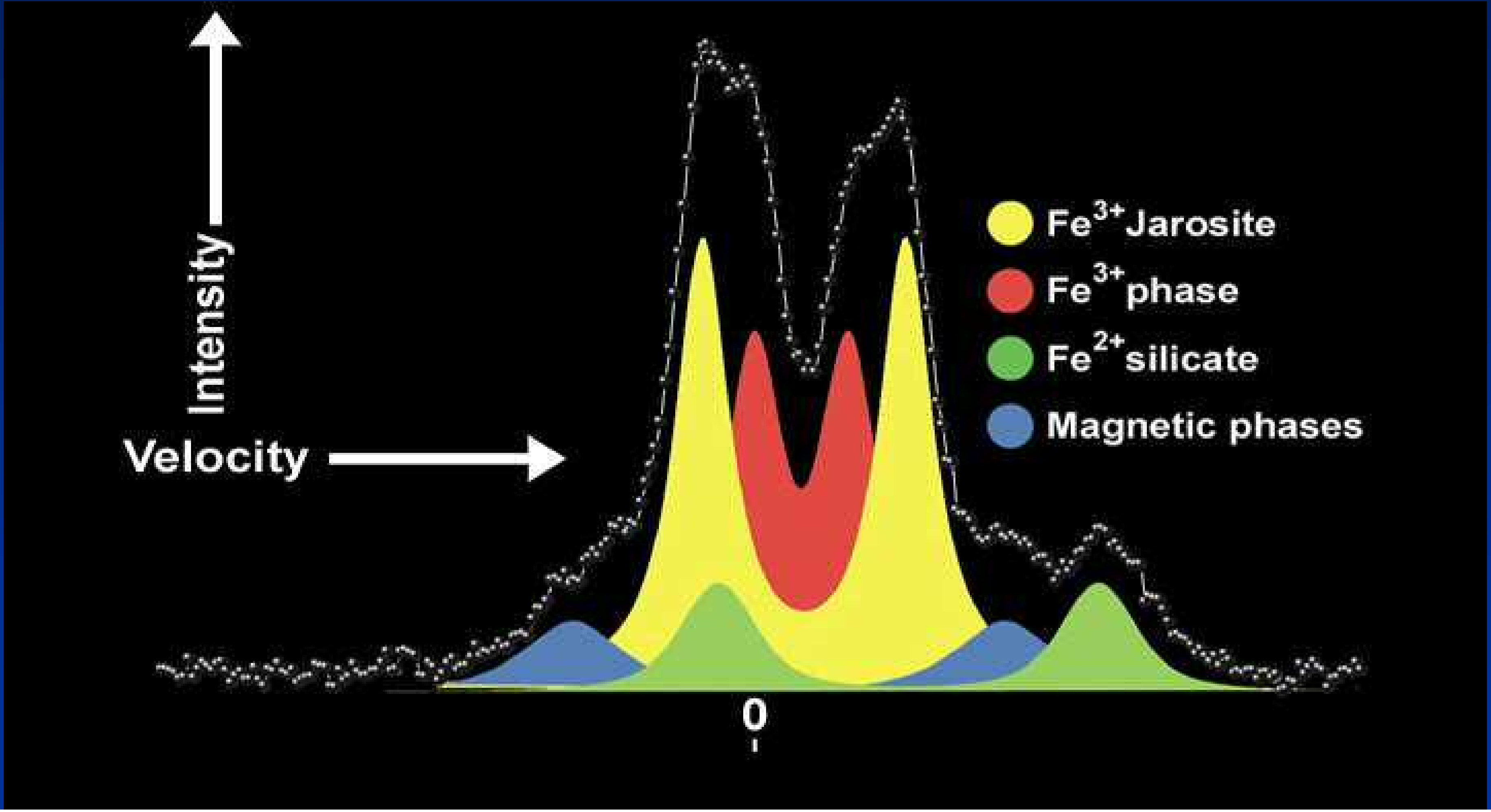
Antennen

Roboterarm-Manipulator
Mikroskop-Kamera
Alpha-Teilchen-Röntgenspektrometer
Mößbauer-Spektrometer
Bohr- und Schleifmaschine

Gefahrerkennungs-
kamera

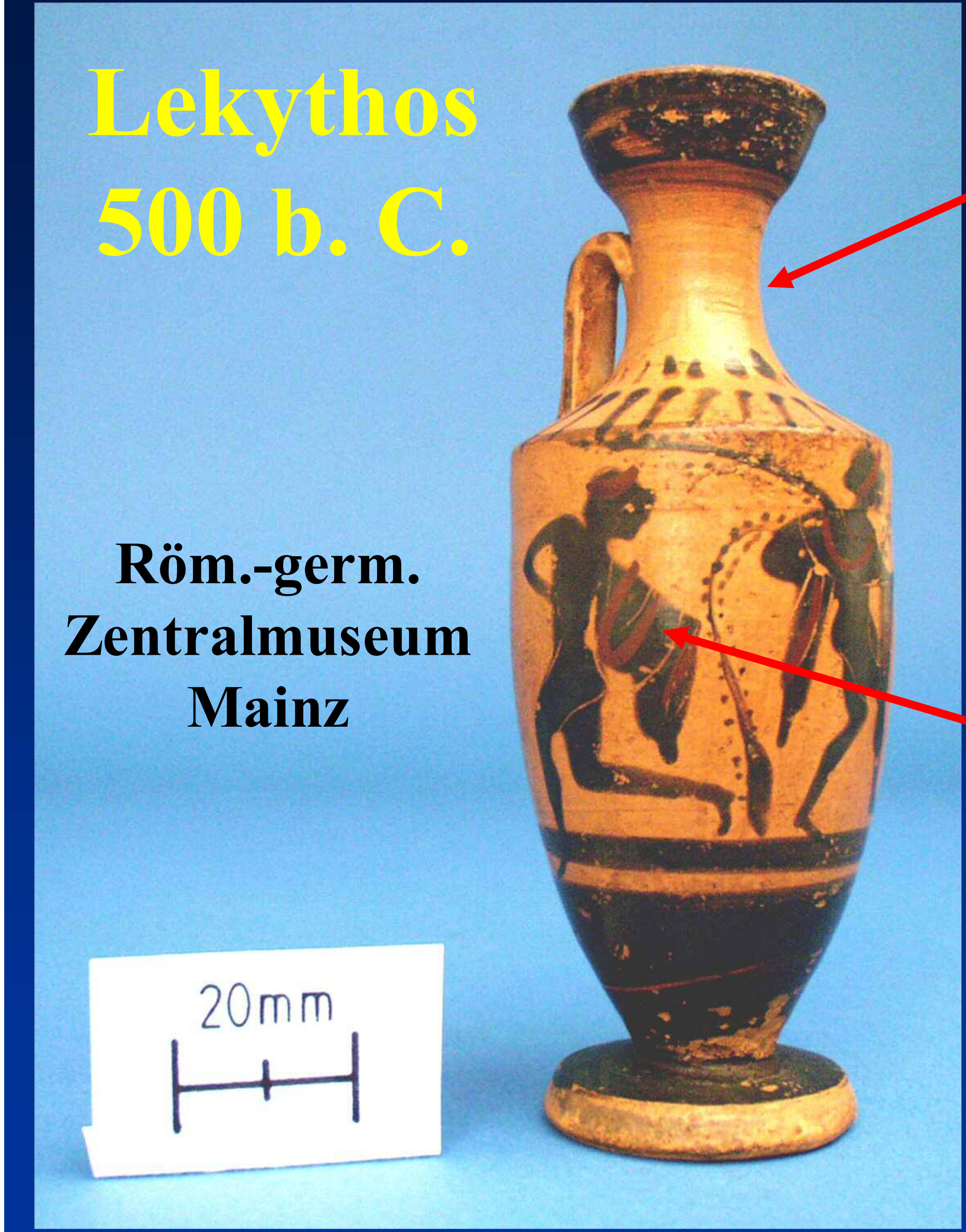
Mössbauer-Spektrum von *El Capitan* in *Meridiani Planum*

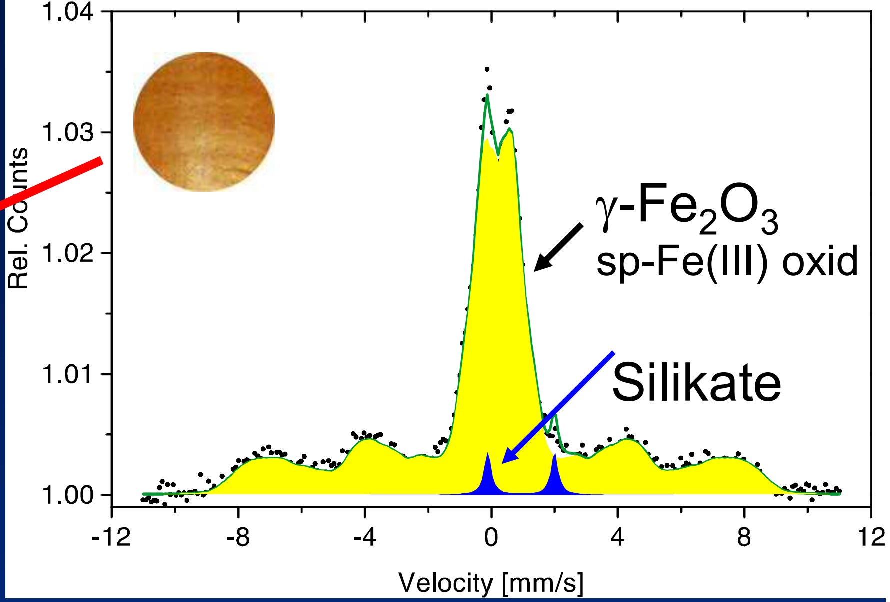
Jarosit: (K, Na, X^+)$Fe_3(SO_4)_2(OH)_6$

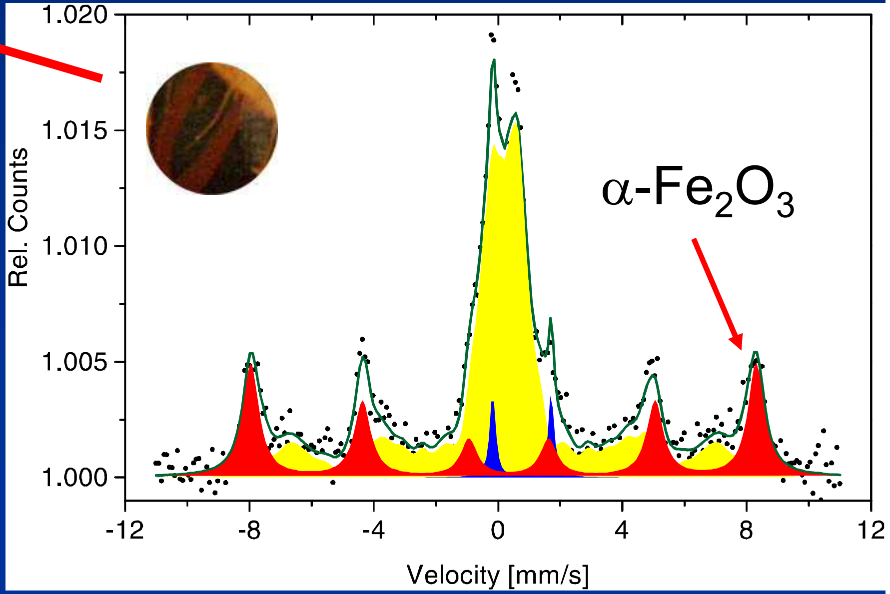


Lekythos 500 b. C.

Röm.-germ. Zentralmuseum Mainz

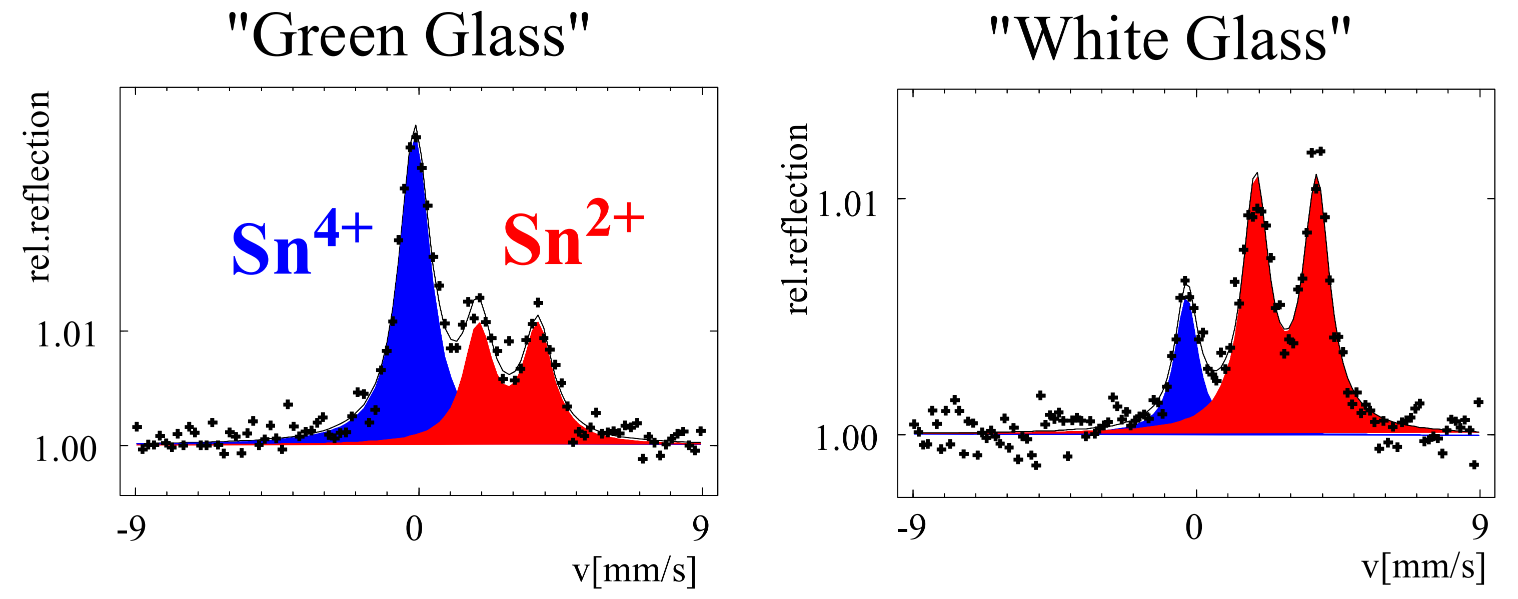






Tin in Surface of Floatglass

Problem:
Surface properties depends on oxidation state of tin.



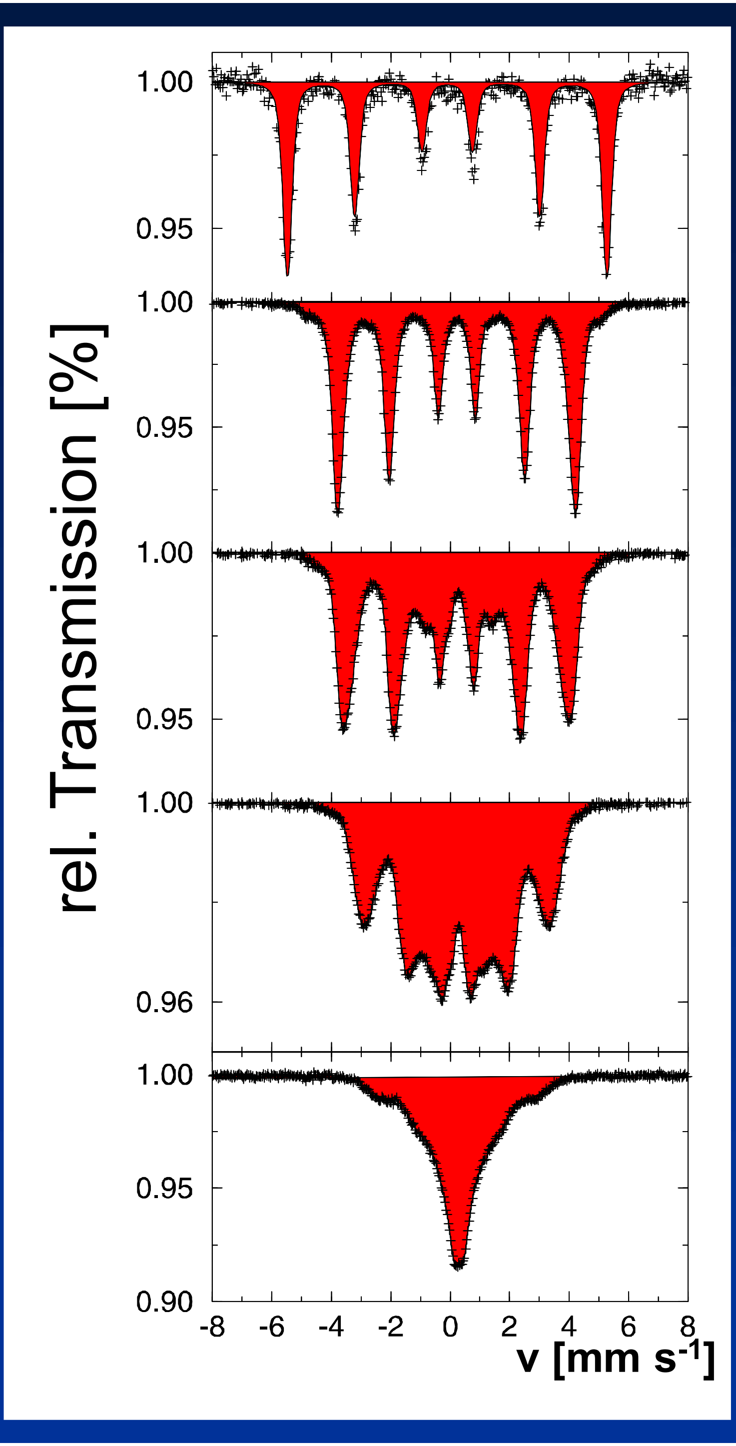
Quantative determination of Sn^{2+} / Sn^{4+}
by CEMS in dependence of

a) Glass composition
b) Production conditions

Metallurgy

High-Temperature Nitrification of Steel

Fe_3N_x at 293 K



x = 0

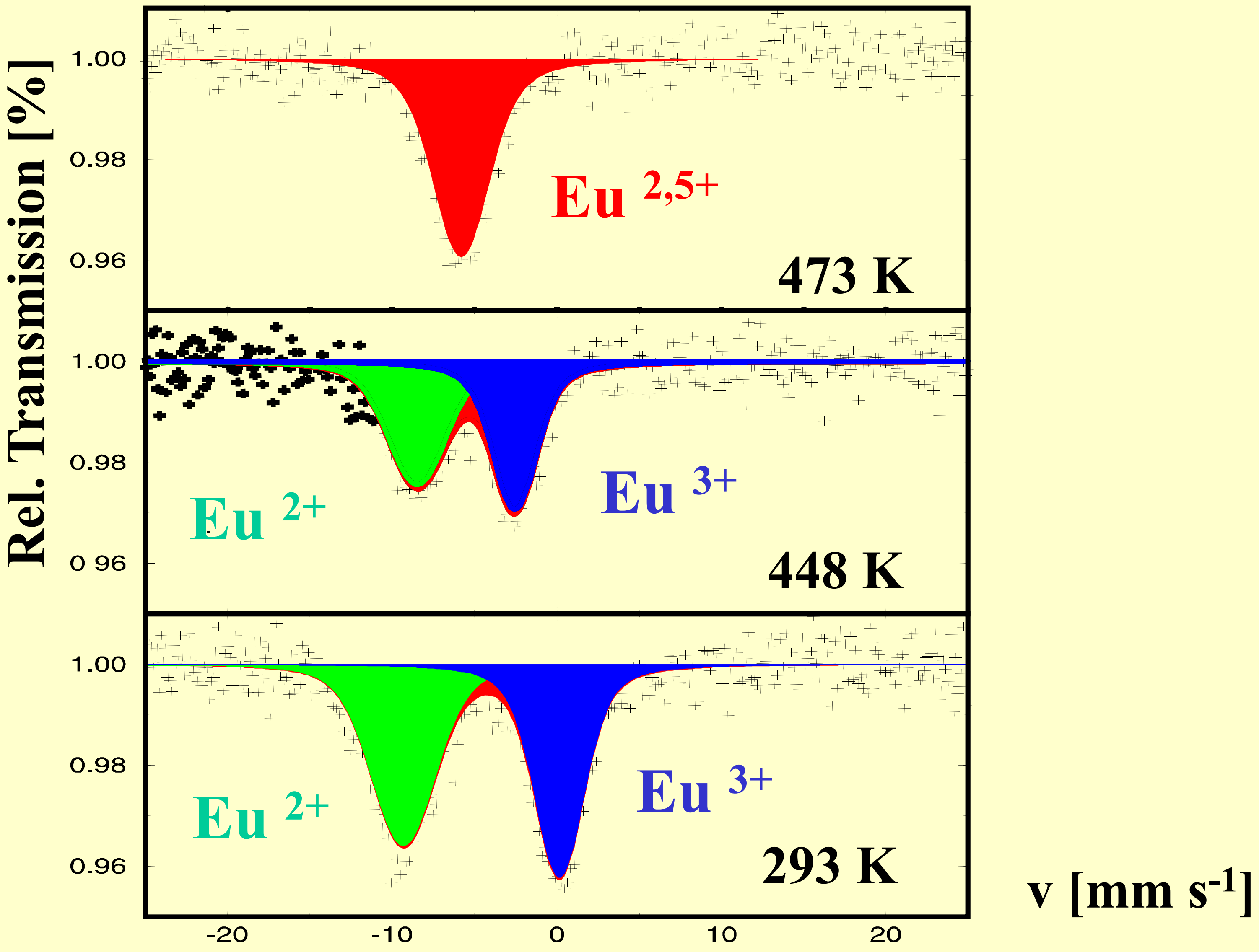
x = 1

x = 1,1

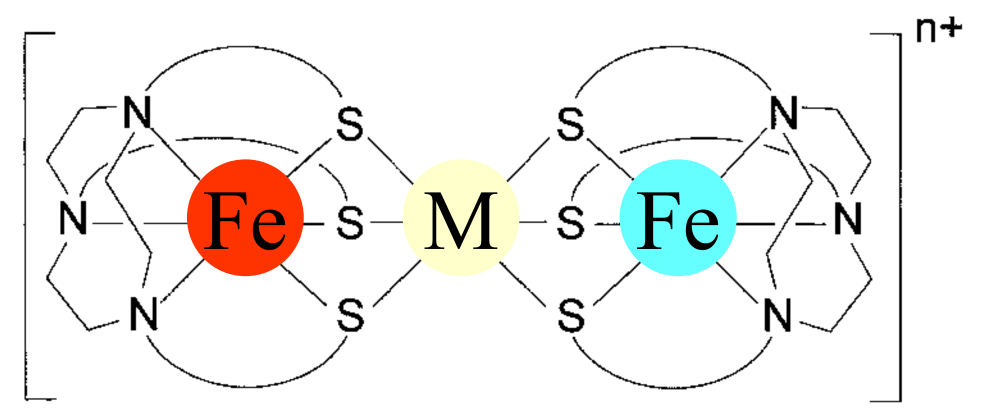
x = 1,22

x = 1,3

^{151}Eu Mössbauer Spectra of EuNiP



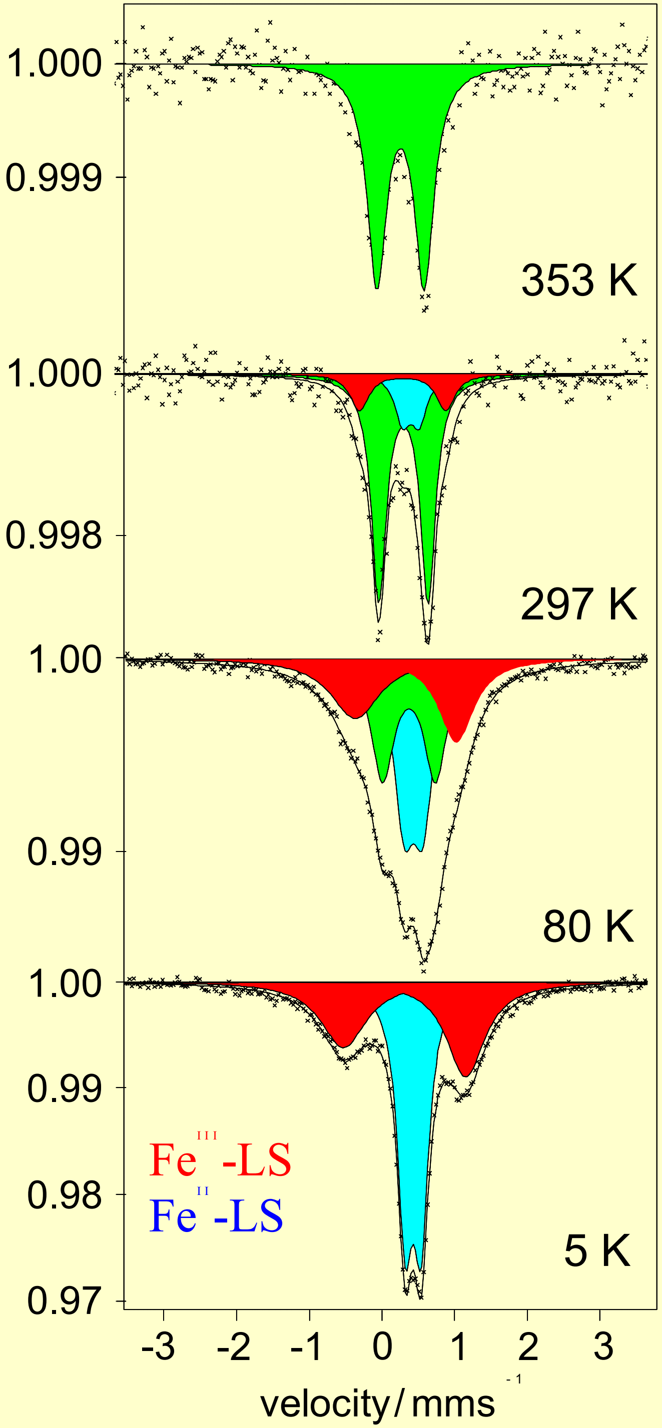
Valence Fluctuation in



$[L\,Fe^{III}Co^{III}Fe^{II}L]^{2+}$

$k \sim 10^{7}\ s^{-1}$

Bill, Trautwein, Wieghardt;
JACS 1999

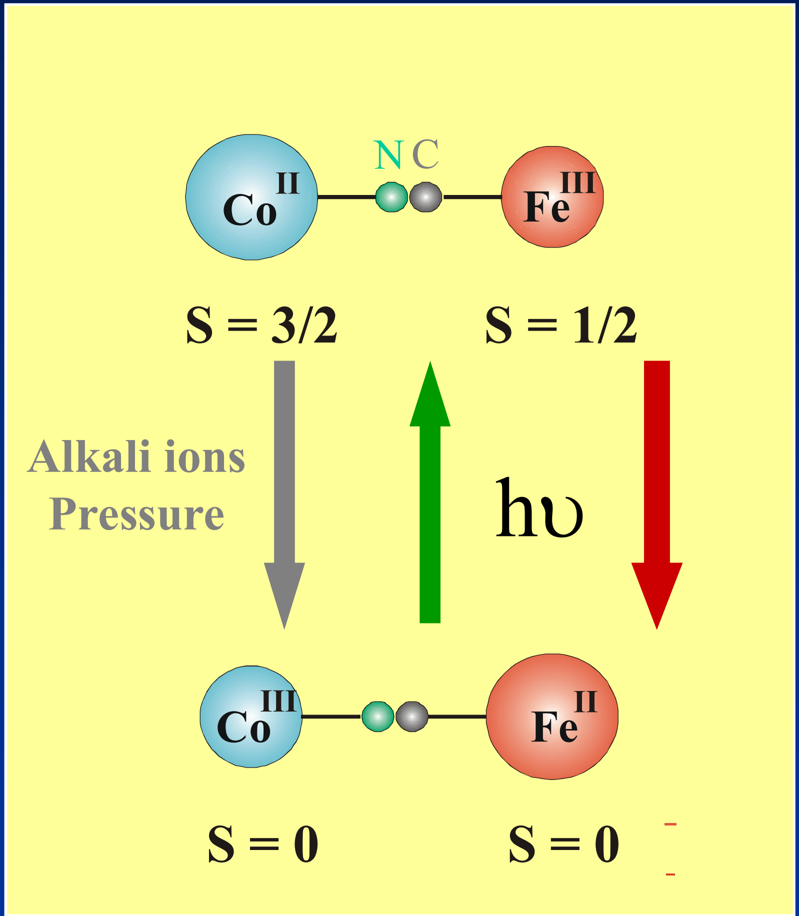


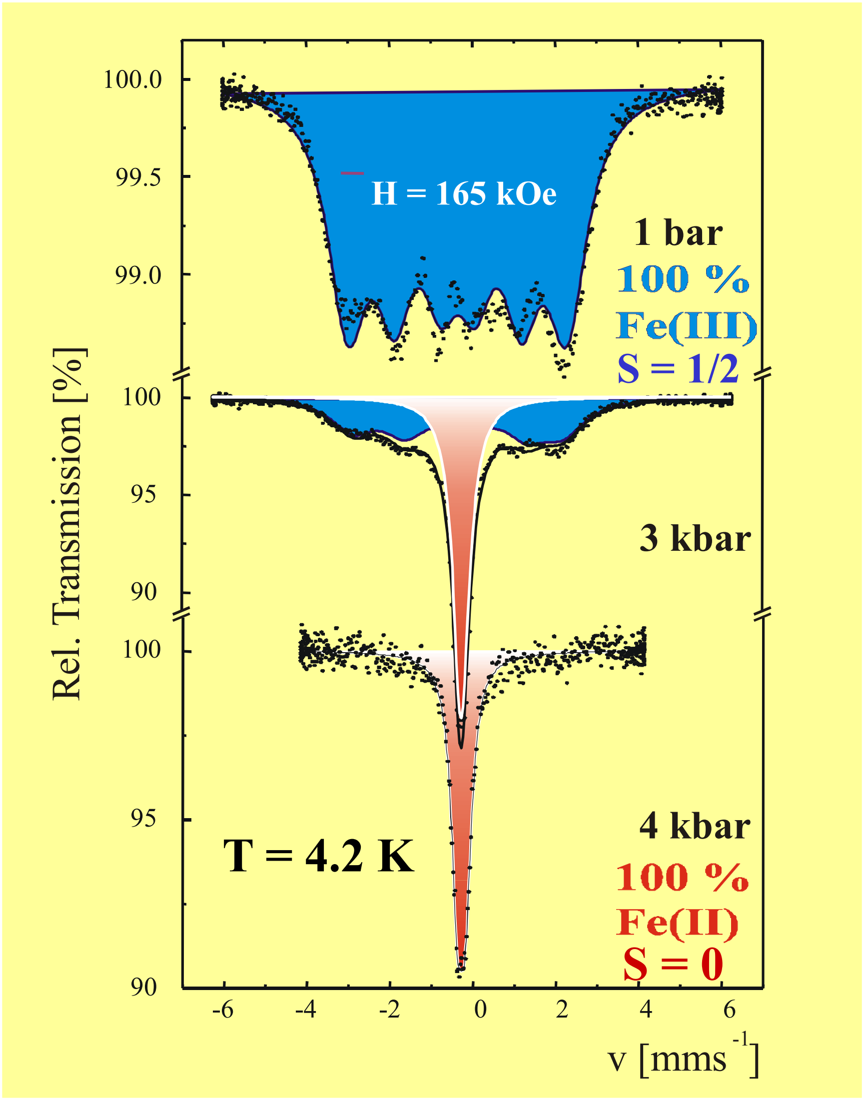
Hydrostatic High Pressure Cells for Magnetic and Mössbauer Studies

2 K < T < 400 K
p < 14 Kbar

Pressure-induced electron transfer in ferrimagnetic Prussian blue analogs

$K_{0.1}Co_4[Fe(CN)_6]_{2.7}\cdot 18\ H_2O$

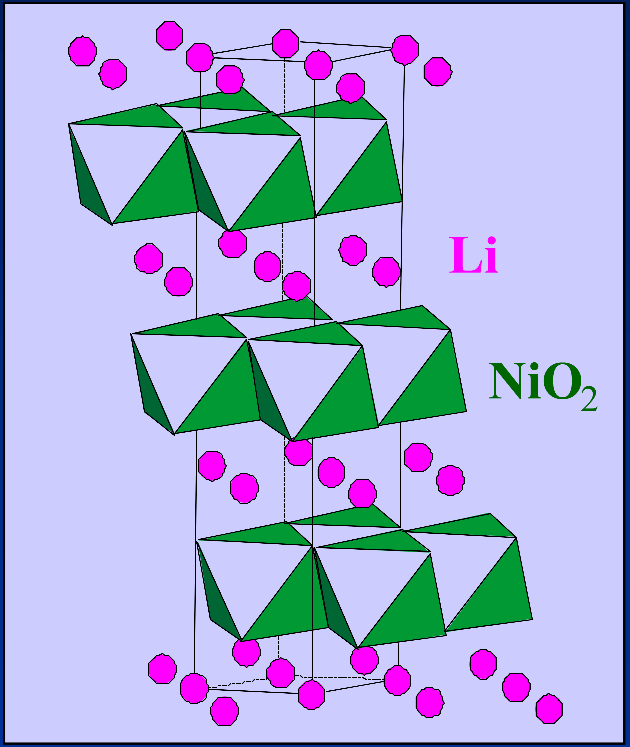




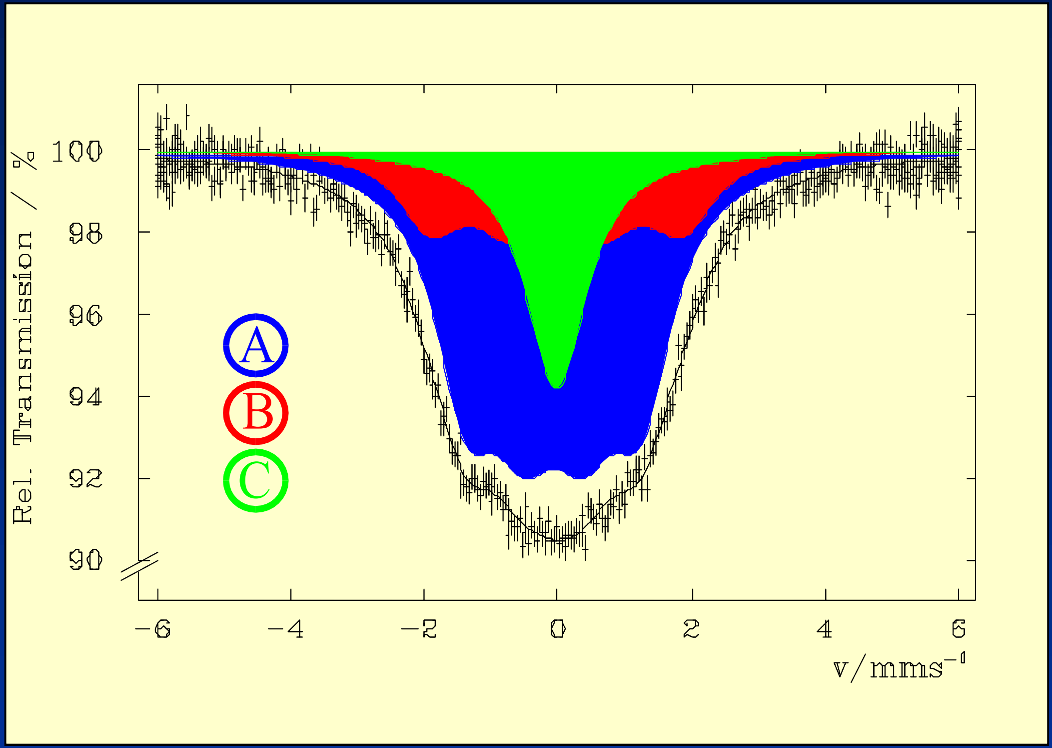
Ksenofontov, Verdaguer, Gütlich et al. (Phys. Rev. B, 2003)

STOICHIOMETRY OF $Li_{1-x}Ni_{1+x}O_2$ STUDIED BY ^{61}Ni MÖSSBAUER SPECTROSCOPY

$Li^{1+}_{1-x}Ni(C)^{2+}_{x}$



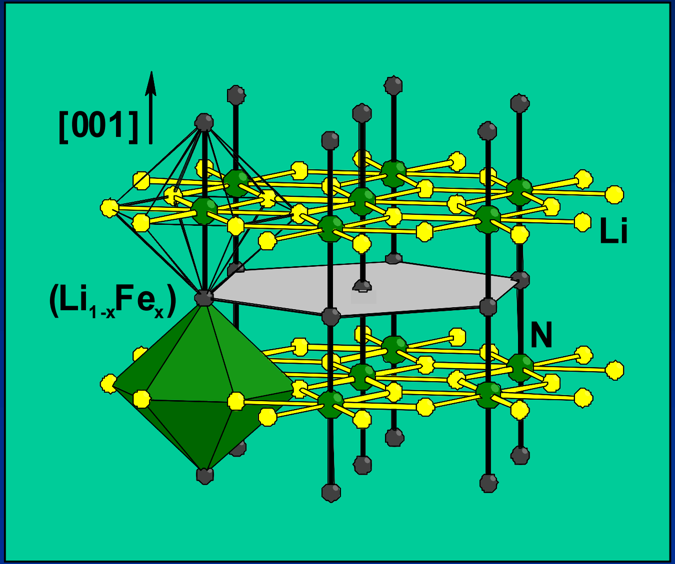
$Ni(A)^{3+}_{1-x}Ni(B)^{2+}_{x}O_2$

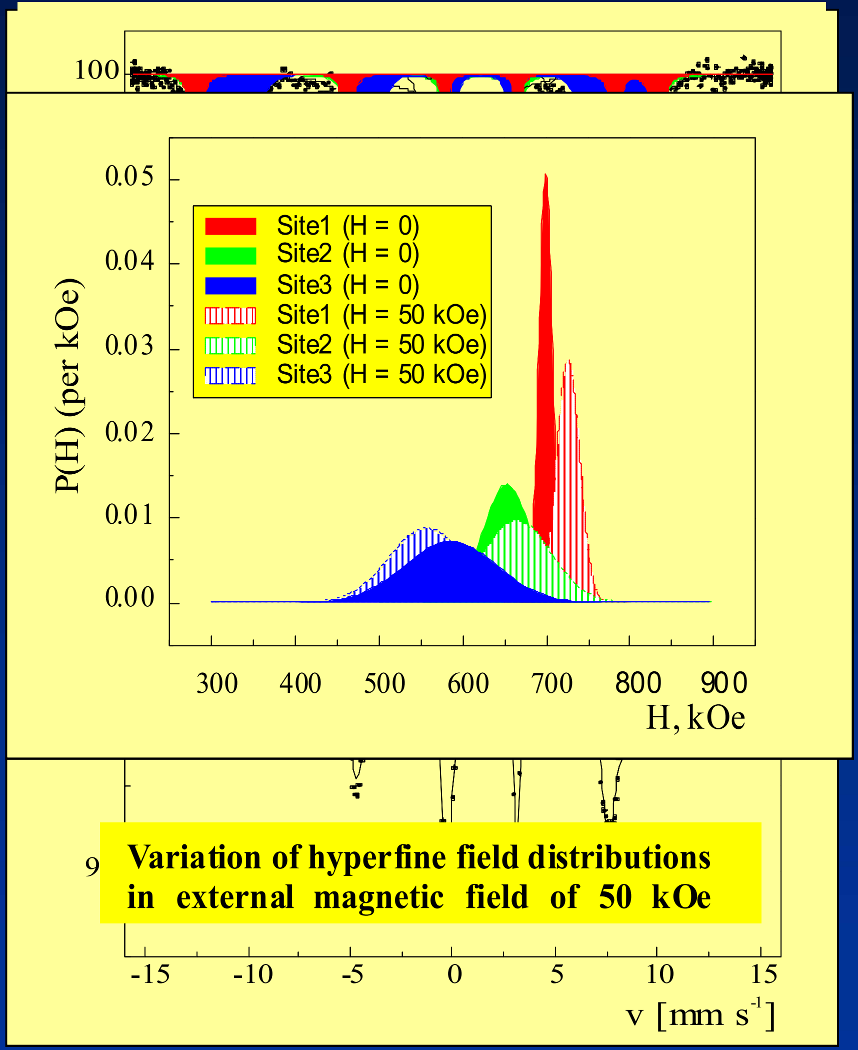


V. Ksenofontov, S.Reiman, D. Walcher, Y. Garcia, N . Doroshenko and P. Gütlich
Hyperfine Interact. **139/140,** 107 (2002)

Largest magnetic fields ever observed in an iron compound: a Lithium-Nitridoferrate(I)

$Li_2[(Li_{1-x}Fe^{I}_{x})N]$ ($x = 0.16$)





Variation of hyperfine field distributions in external magnetic field of 50 kOe

J. Klatyk, W. Schnelle, F. R. Wagner, R. Niewa, P. Novák, R. Kniep, M. Waldeck, V. Ksenofontov and P. Gütlich, Phys. Rev. Lett. **88**, 207202 (2002)

in-situ-Mössbauer Spectroscopy of the Reaction of Synthesis of $Li_2[(Li_{1-x}Fe_x)N]$

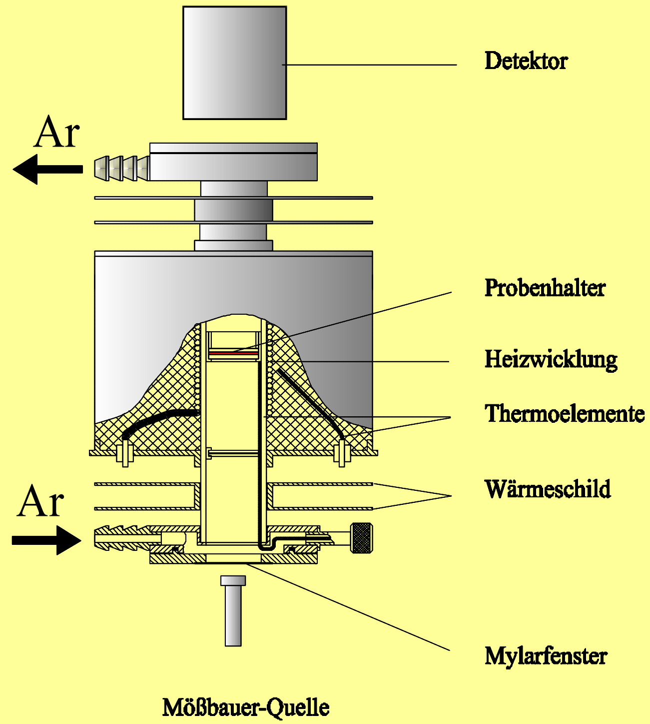
Preparation of $Li_2[(Li_{1-x}Fe^{I}_{x})N]$:

$$3Li_3[Fe^{III}N_2] \underset{N_2}{\overset{Ar\ \ 600^{o}C\text{-}800^{o}C}{\rightleftarrows}} Li_2[Li_{0.25}Fe^{I}_{0.75}] + N_2$$

Suggestion:

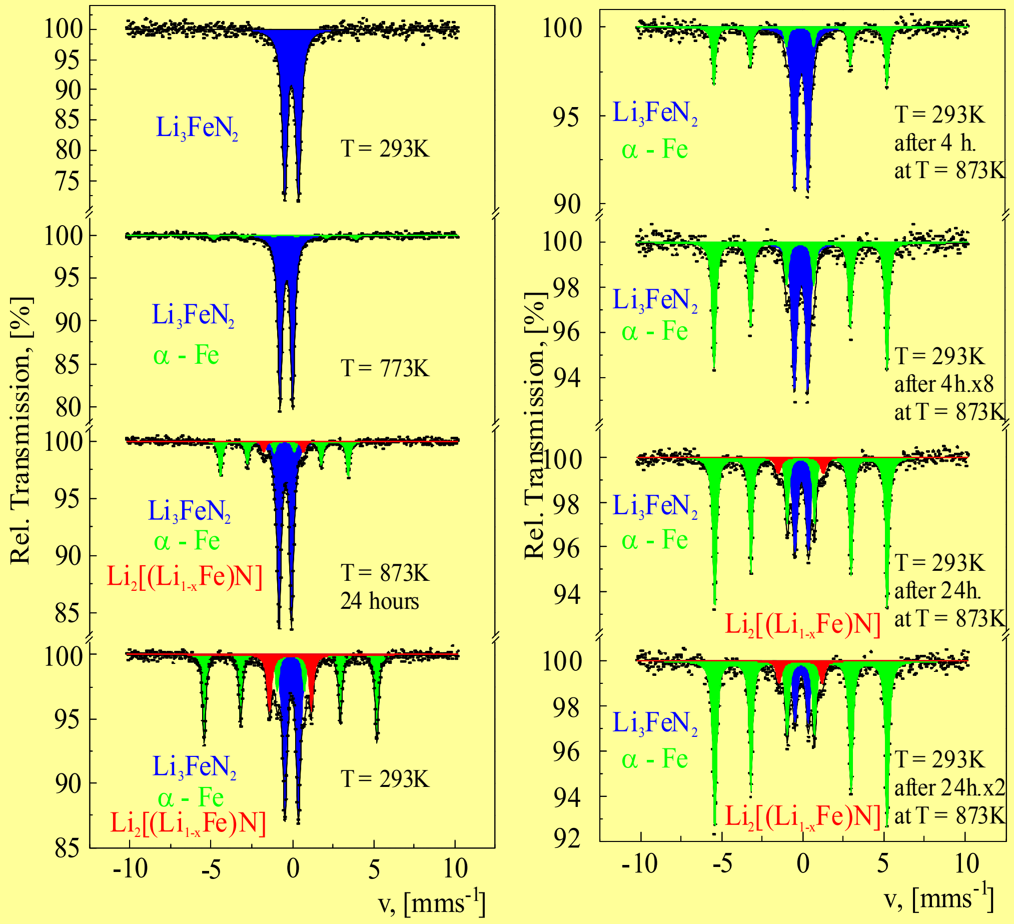
$$Li_3[Fe^{III}N_2] \longrightarrow Li_4[Fe^{II}N_2]^{10} \longrightarrow Li_2[(Li_{1x}Fe^{I}_{x})N]$$

Ofen für *in-situ* -
Mößbauer-Messungen bis 1130 K



V. Ksenofontov, S. Reiman, M. Waldeck, R. Niewa, R. Kniep, P. Gütlich. *Z. Anorg. Allg. Chem.* **2003**, *629*, 17871794

Mößbauer study of the decomposition kinetics of $Li_3[Fe^{III}N_2]$



$Li_3[Fe^{III}N_2]$

$\downarrow$

$Li_2[(Li_{1-x}Fe^{I}_{x})N]$

+

$(1-x)Fe$

+

$x/3\ Li_3N$

+

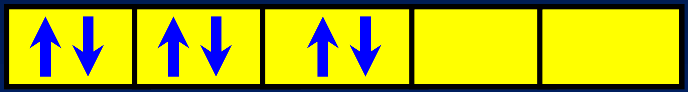
$(3-x)/6\ N_2$

V. Ksenofontov, S. Reiman, M. Waldeck, R. Niewa, R. Kniep, P. Gütlich. *Z. Anorg. Allg. Chem.* **2003**, *629*, 17871794

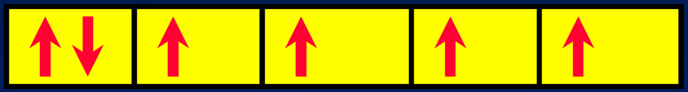
Thermisch und optisch schaltbare Komplexverbindungen von Eisen(II)

Eisen(II), $3d^6$

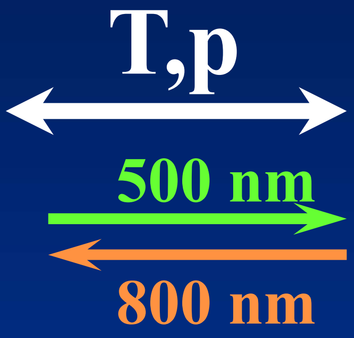
3d-Orbitale



3d-Orbitale



S = 0
“Low Spin”
diamagn.



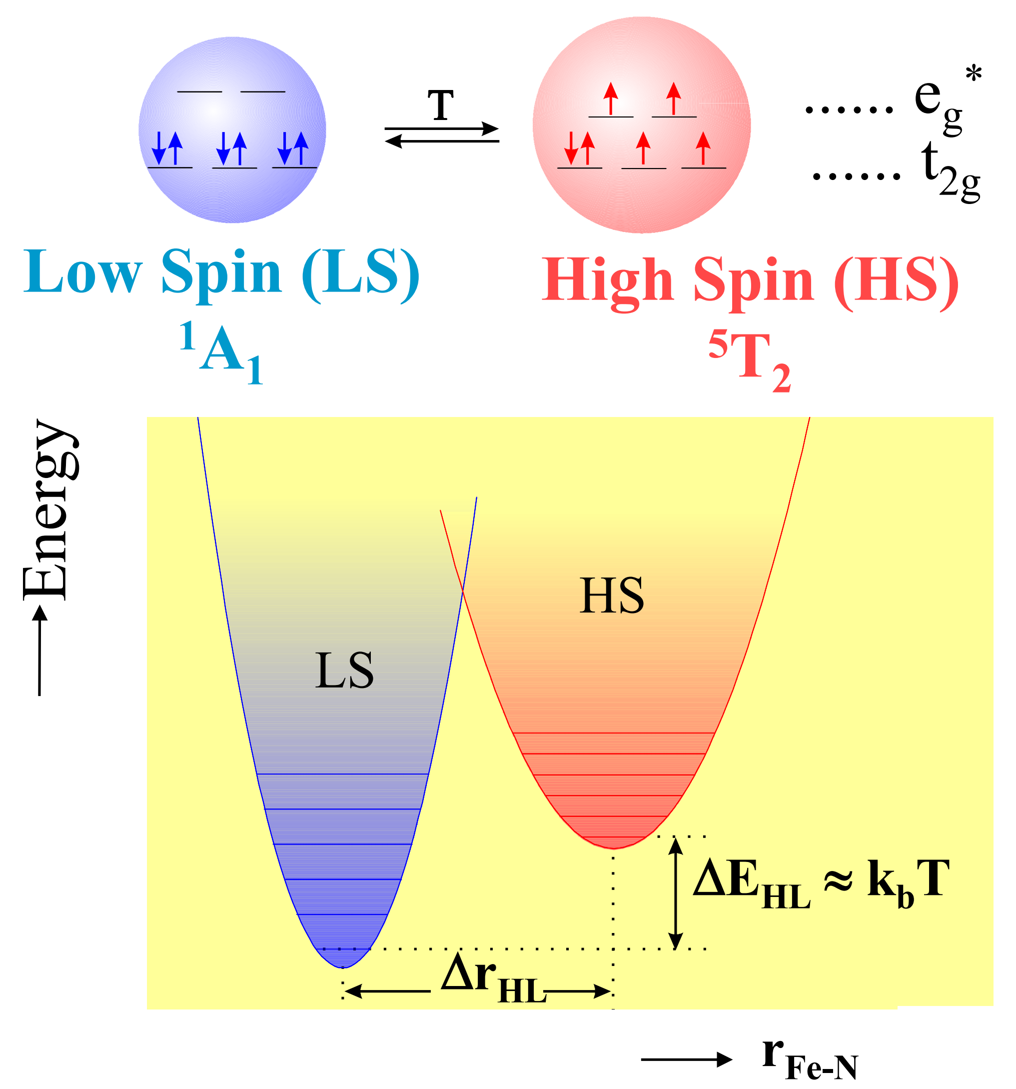
S = 2
“High Spin”
paramagn.

Spinübergang
(Spin Crossover)

LS ↔ HS
In Übergangsmetall-Komplexen mit $3d^4$...$3d^7$

häufig in	**seltener in**
$3d^5$: Eisen(III)	$3d^4$: Mangan(III)
$3d^6$: Eisen(II)	$3d^6$: Kobalt(III)
$3d^7$: Kobalt(II)	

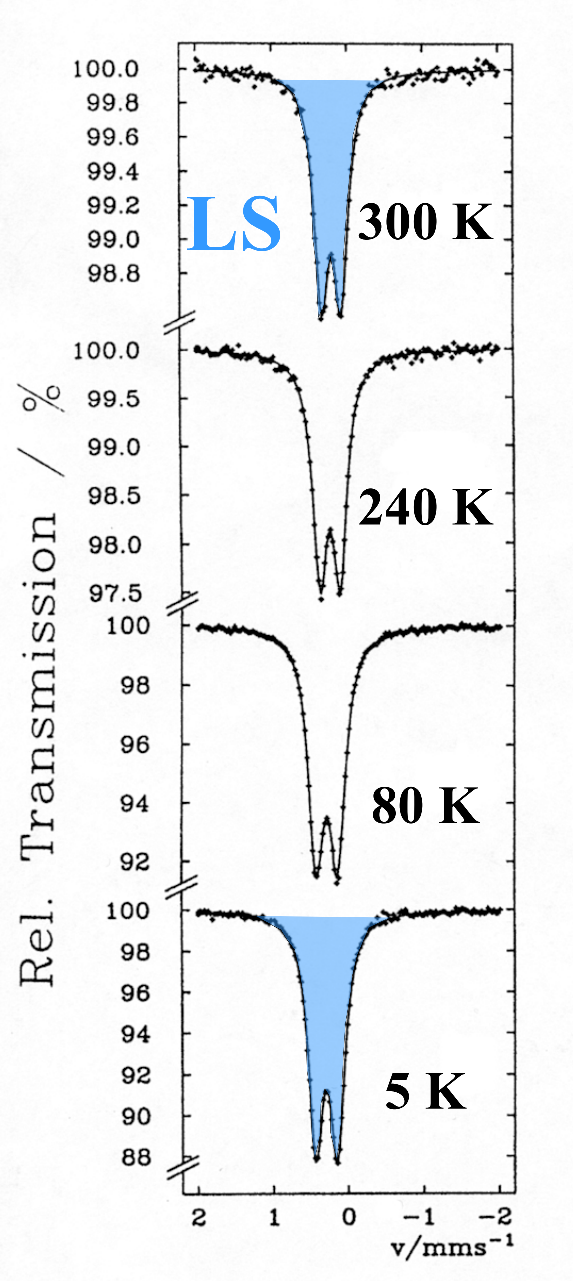
Thermal Spin Crossover in Iron(II) Compounds

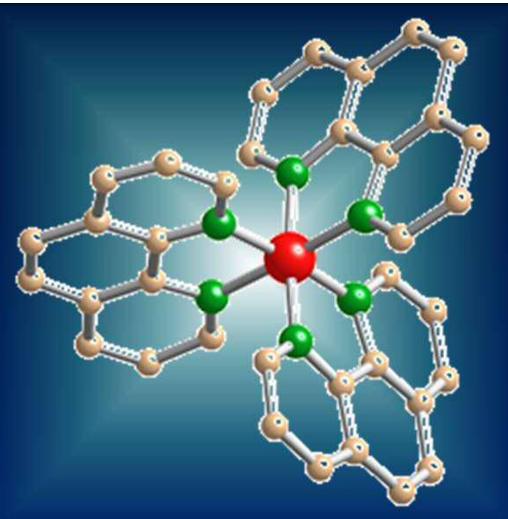


Low Spin (LS)
$^1A_1$

High Spin (HS)
$^5T_2$

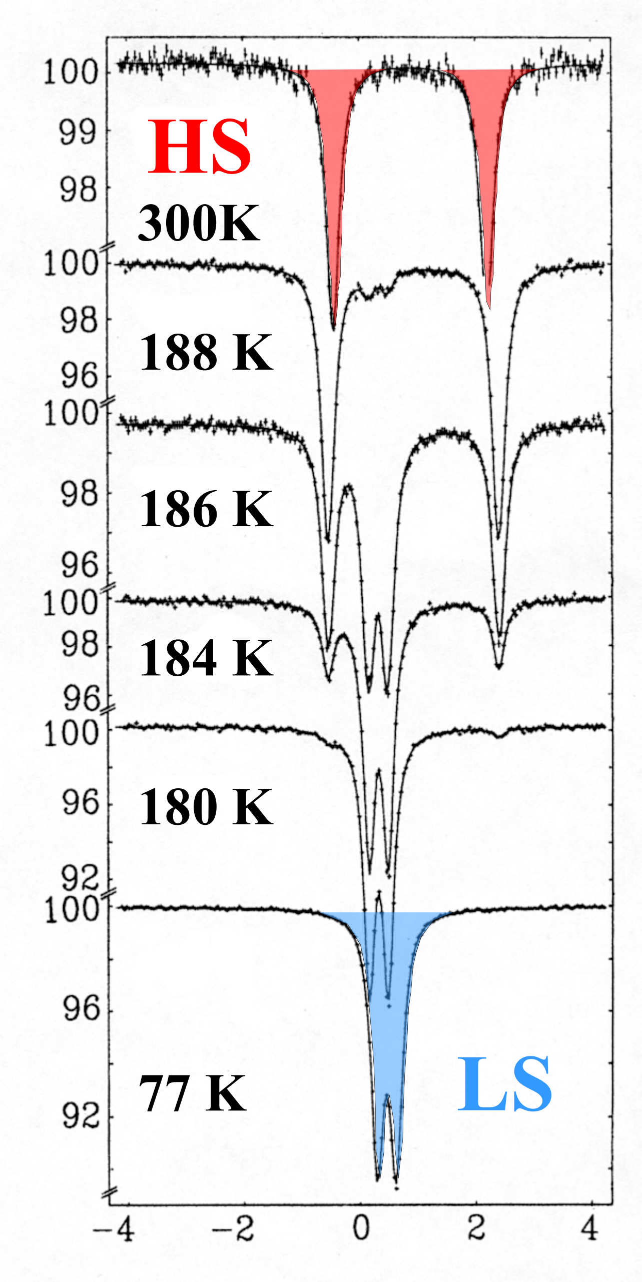
$[Fe^{II}(phen)_3]X_2$



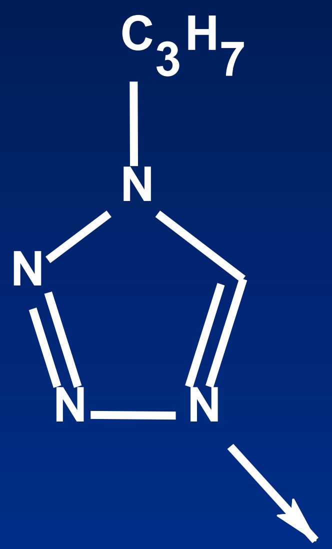


„Tuning“ the Ligand Field by Ligand Replacement

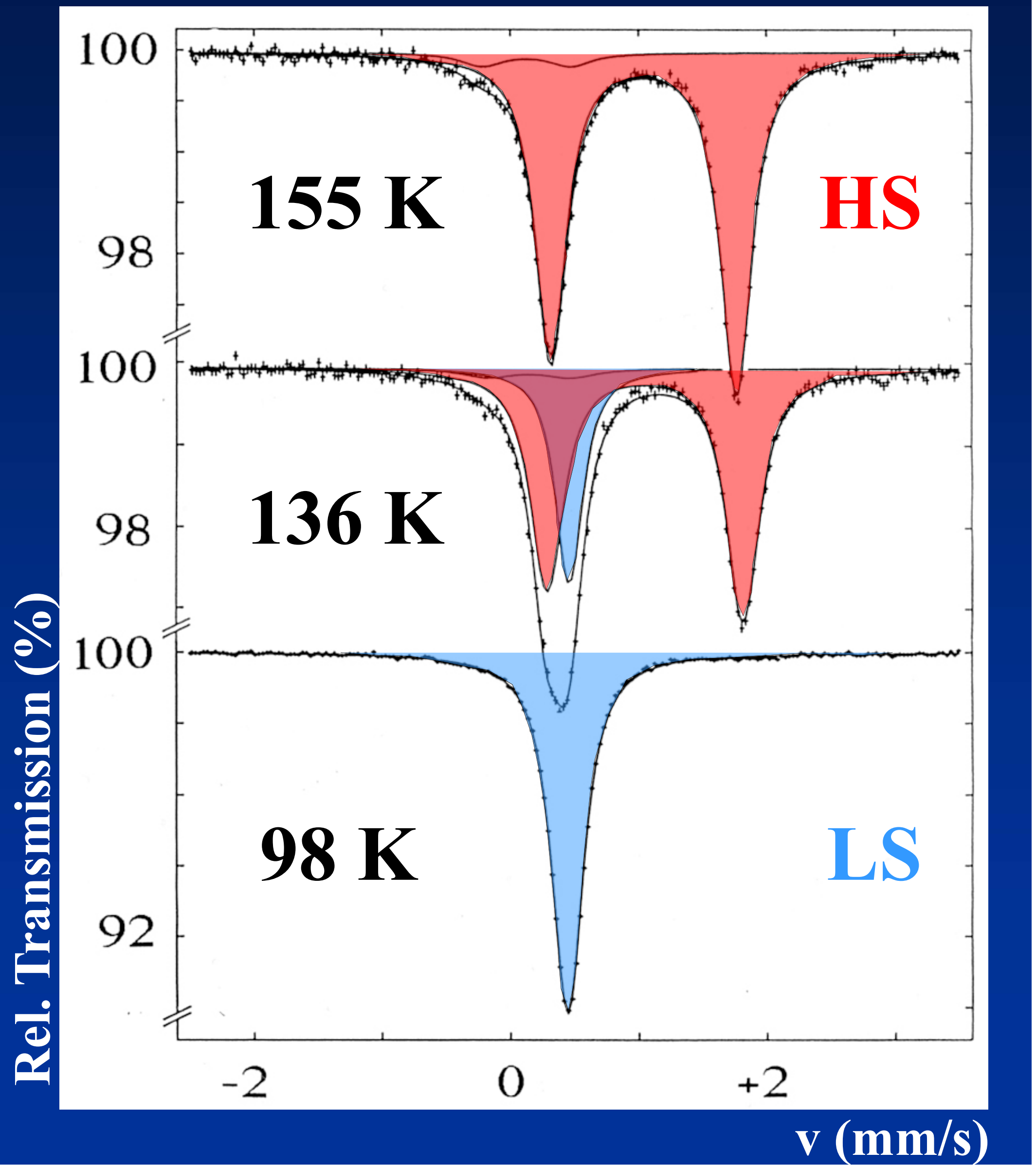
$[Fe^{II}(phen)_2(NCS)_2]$



$[Fe(ptz)_6](BF_4)_2$



ptz

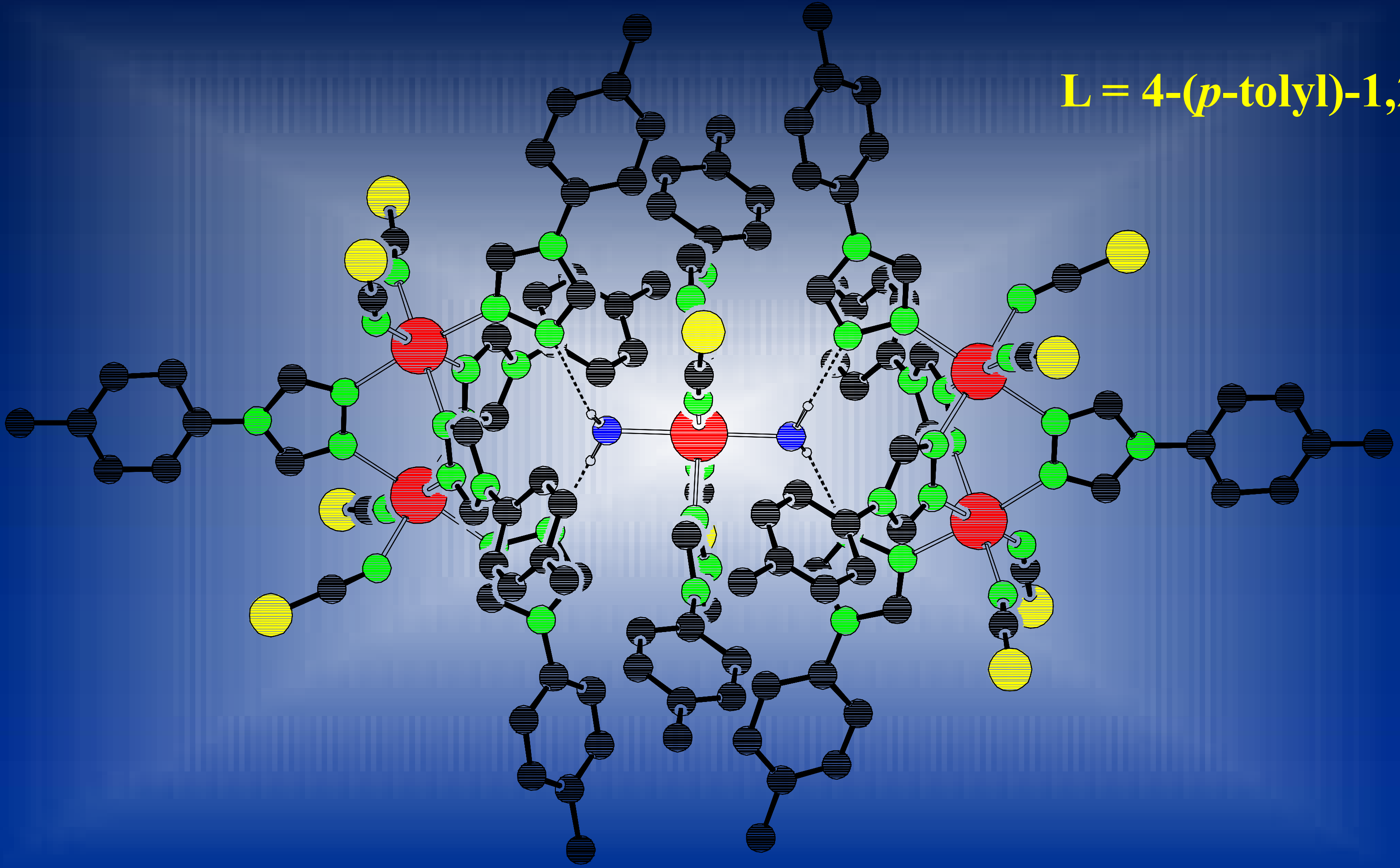


Thermal Spin Crossover

Pentanuclear Iron(II) Triazole Complex

$[Fe_2(L)_5(NCS)_4]_2[Fe(L)_2(NCS)_2H_2O)_2]\cdot H_2O$

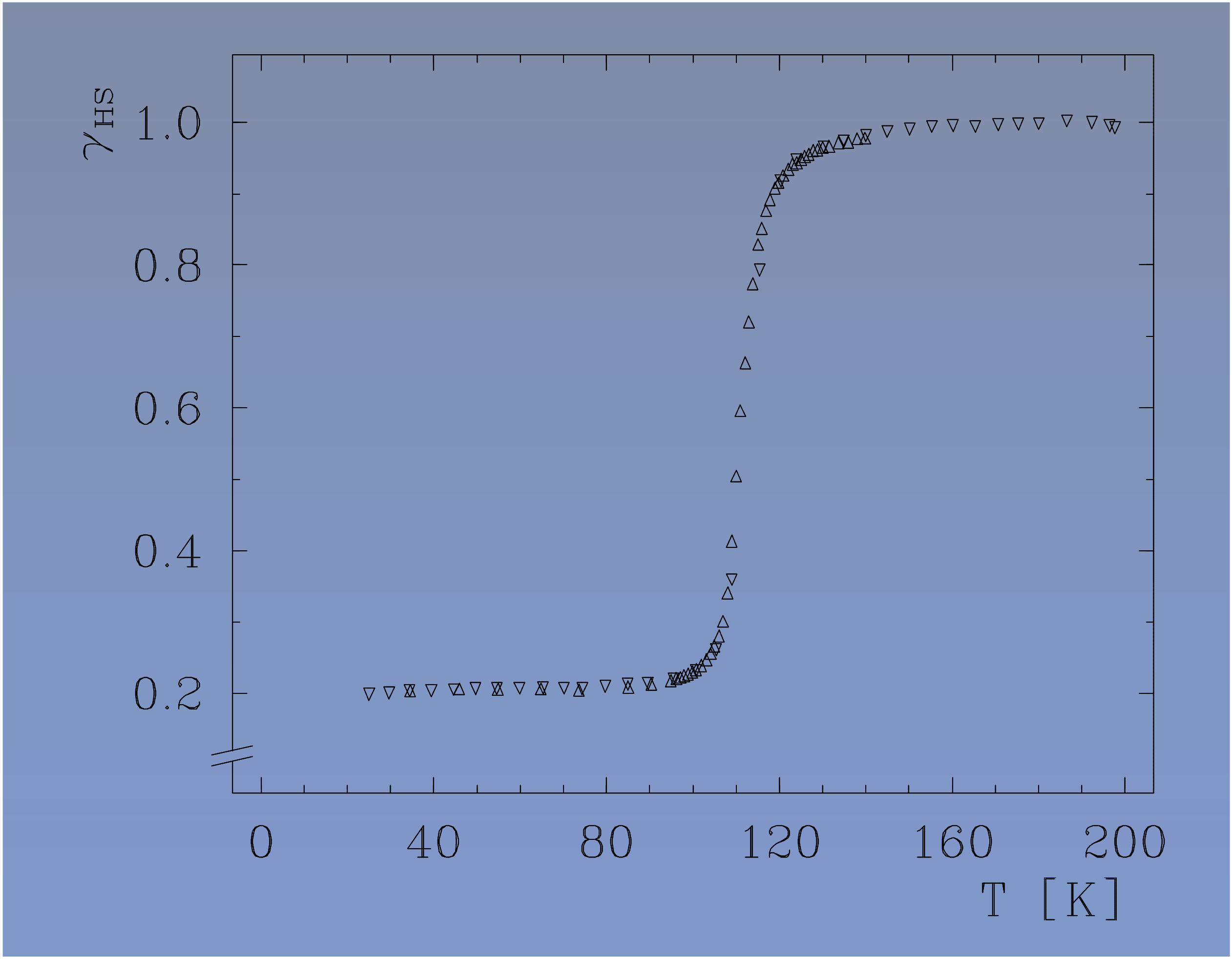
L = 4-(*p*-tolyl)-1,2,4-triazole



J.J.A. Kolnaar, J. Haasnoot, J. Reedijk, G. Schmitt, V. Ksenofontov, P. Gütlich, et al.,
Eur. J. Inorg. Chem. *5* (1999) 881

$[Fe_2[TolTrz)_5(NCS)_4]_2[Fe(TolTrz)_2(NCS)_2H_2O)_2]\cdot H_2O$

Molar fraction $\gamma_{HS}(T)$ from magn. susceptibility measurements

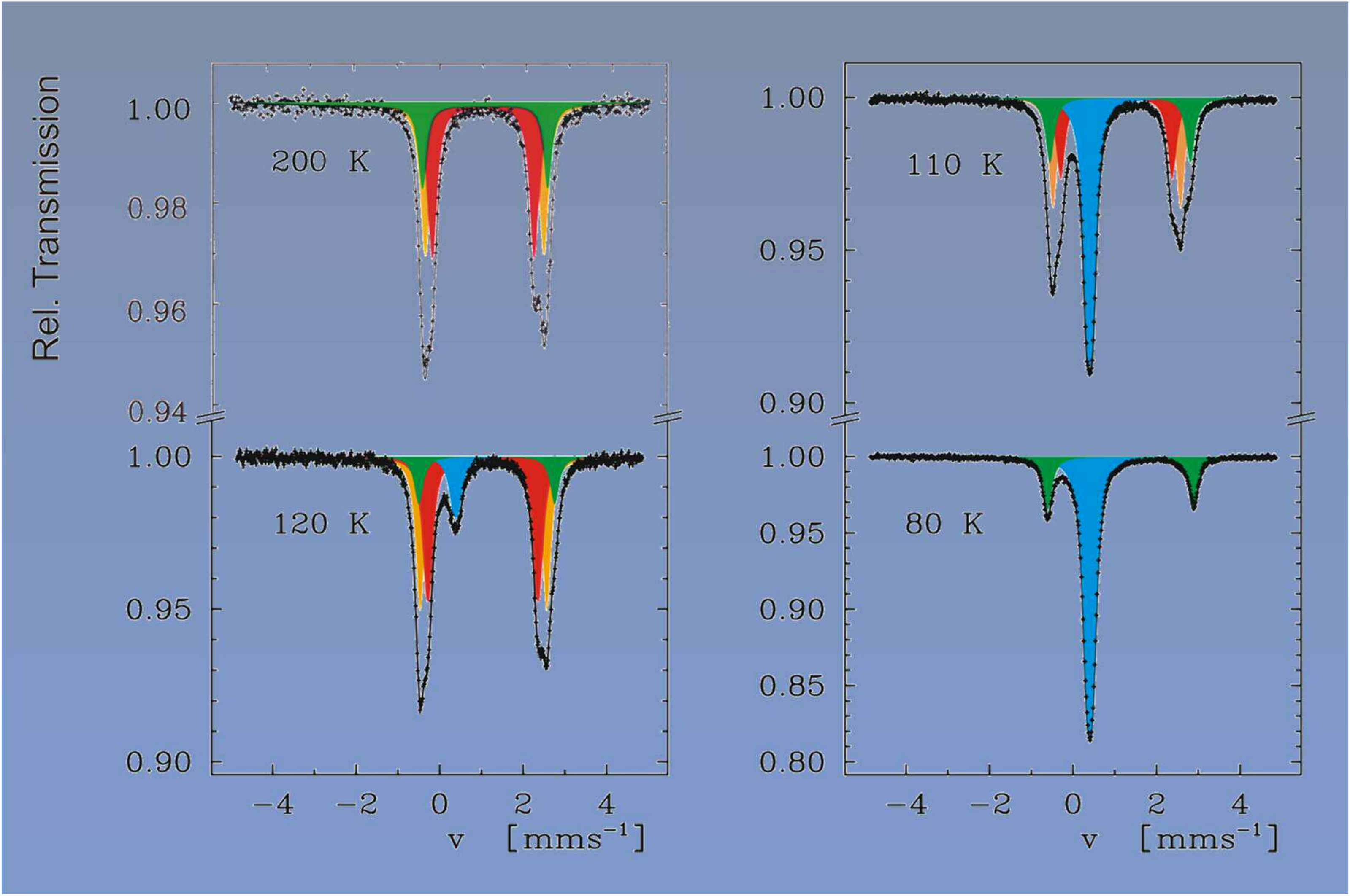


Four Fe(II) sites, with FeN_6 core, undergo thermal spin transition. One Fe(II) site, with FeN_4O_2 core, remains in HS state.

J.J.A. Kolnaar, J. Haasnoot, J. Reedijk, G. Schmitt, V. Ksenofontov, P. Gütlich, et al., Eur. J. Inorg. Chem. 5 (1999) 881

$[Fe_2[TolTrz)_5(NCS)_4]_2[Fe(TolTrz)_2(NCS)_2H_2O)_2]\cdot H_2O$

Mössbauer spectra as function of temperature



J.J.A. Kolnaar, J. Haasnoot, J. Reedijk, G. Schmitt, V. Ksenofontov, P. Gütlich, et al.,
Eur. J. Inorg. Chem. *5* (1999) 881

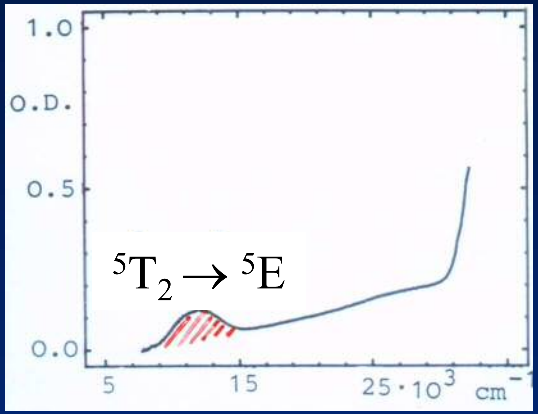
Auswertungsbeispiel

Pentanuclear Iron(II) Triazole Complex

$[Fe(ptz)_6](BF_4)_2$

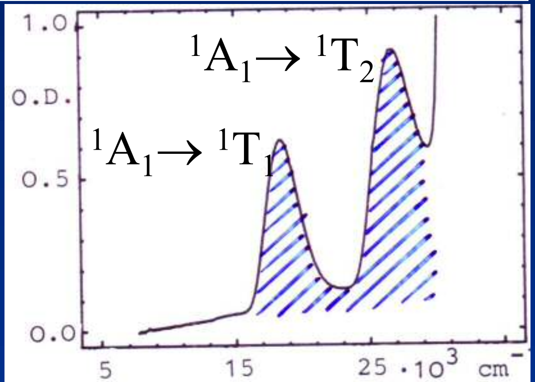
Decurtins
Gütlich
Hauser
Spiering
(1984)

HS



300 K

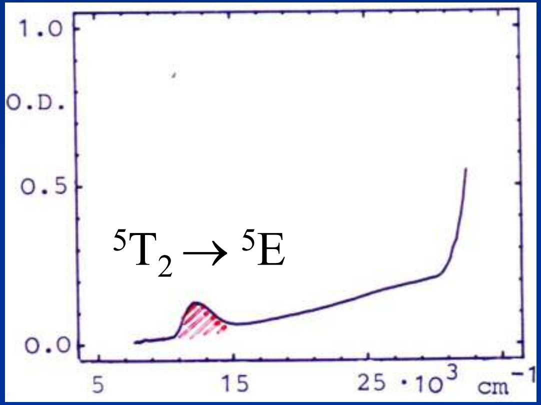
LS



80 K

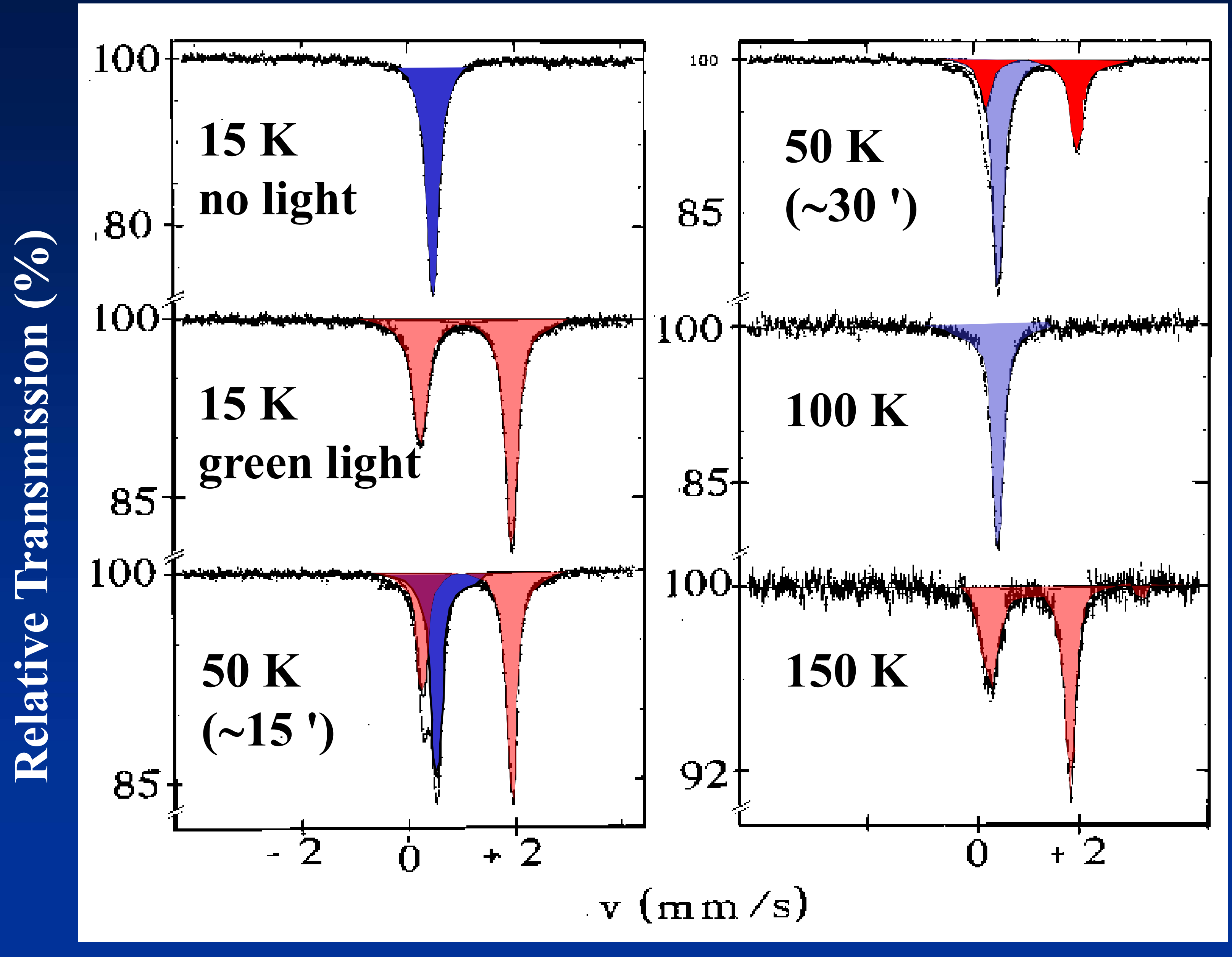
HS

LS



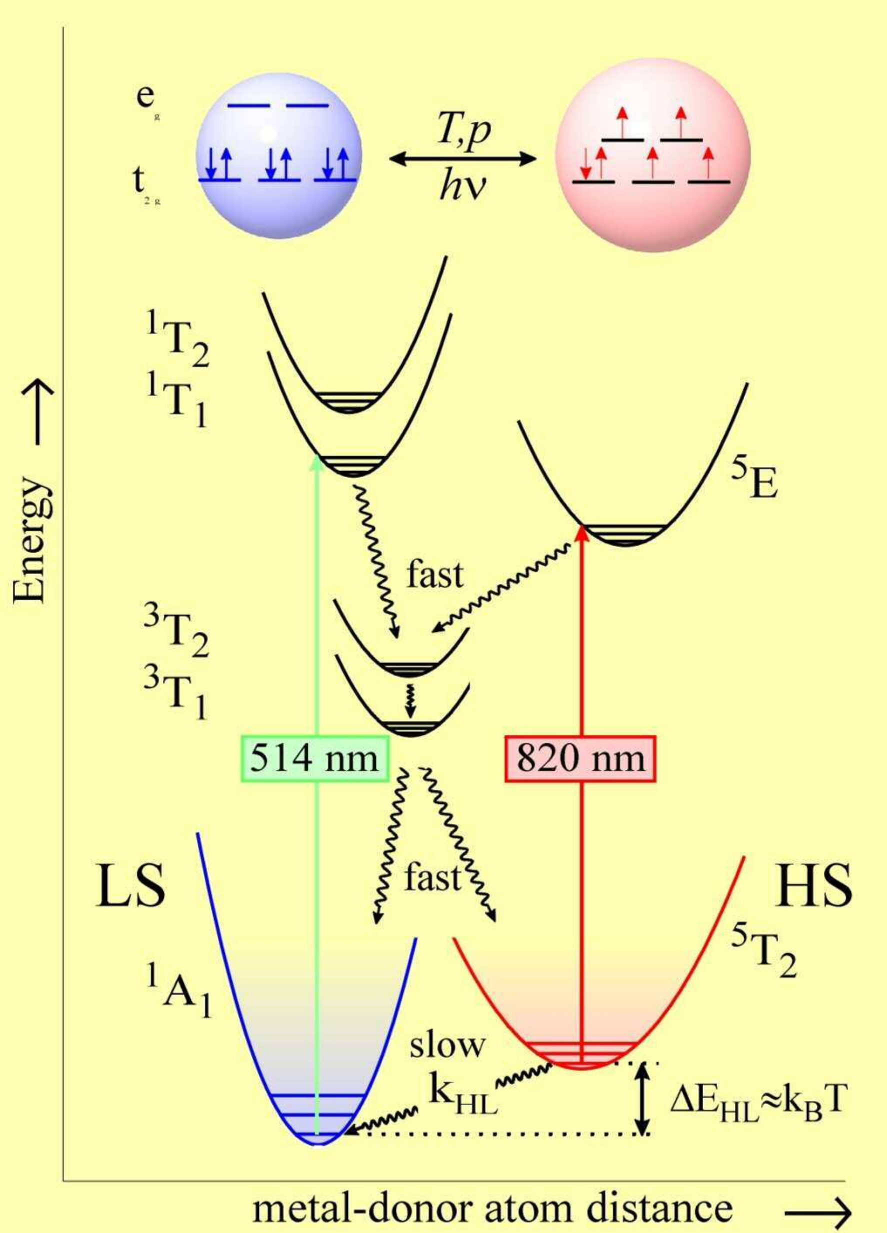
10 K
green light

[Fe(ptz)$_6$](BF$_4$)$_2$: Light-Induced SCO



Light-Induced Excited Spin State Trapping

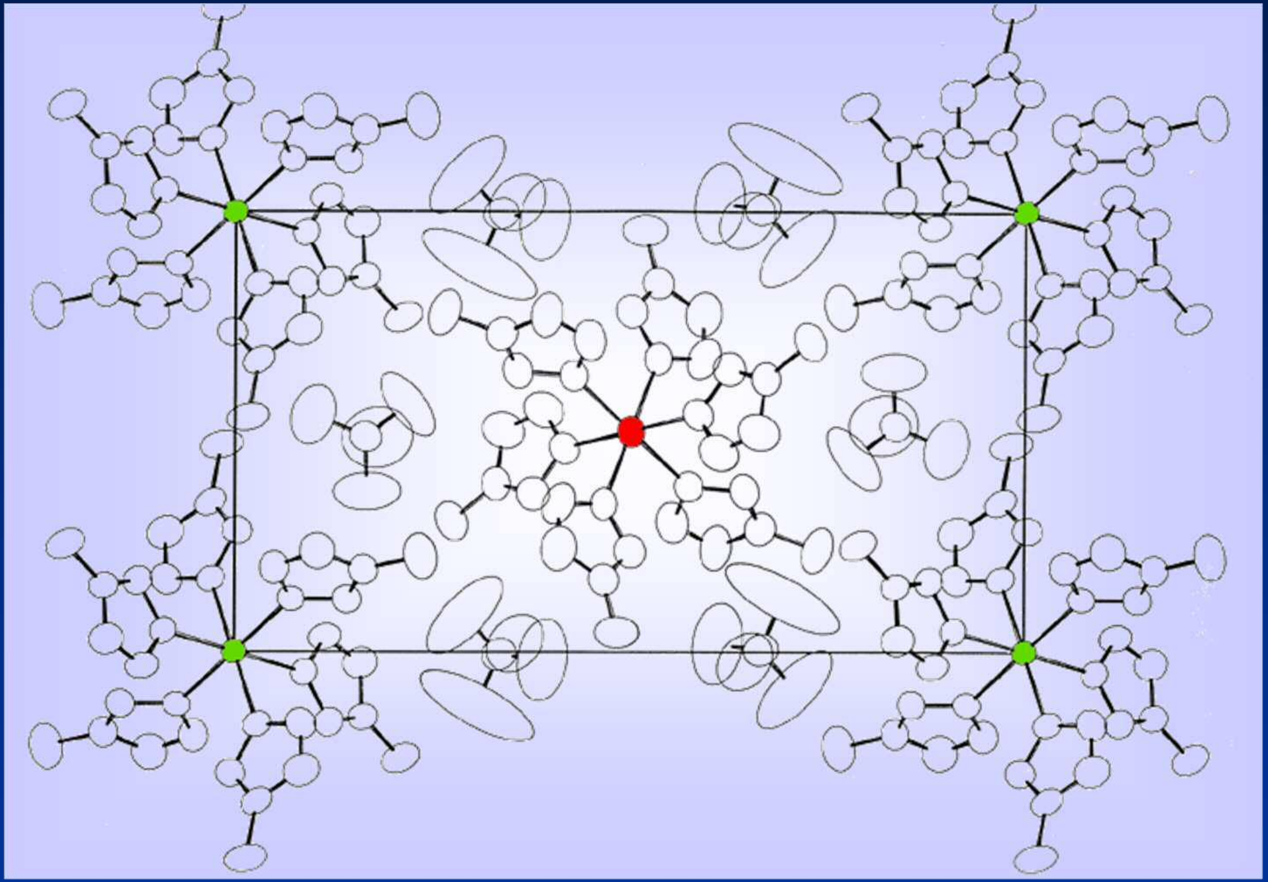
“LIESST“



Decurtins, Gütlich,
Hasselbach, Hauser,
Spiering,
Inorg. Chem. *24* **(1985)**
2174

$[Fe(mtz)_6](BF_4)_2$

mtz = 1-methyl-1H-tetrazole



Fe(II) (B)
2.161 (5) Å
2.197 (5) Å
2.207 (4) Å

Fe(II) (A)
2.181 (5) Å
2.181 (5) Å
2.181 (7) Å

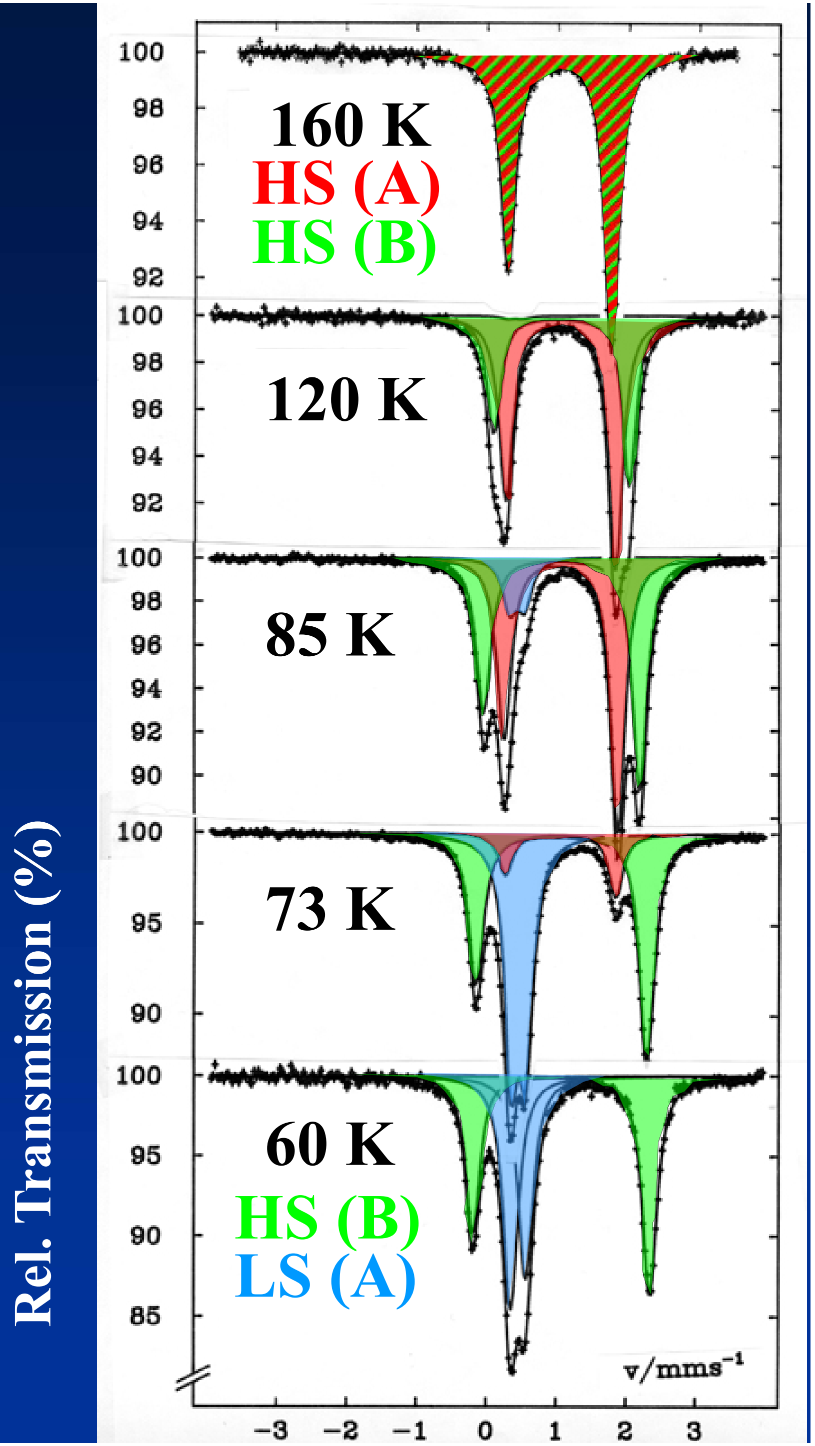
The crystal structure of $[Fe(mtz)_6](BF_4)_2$ shows that iron(II) ions occupy two slightly different lattice positions, denoted as A and B sites, at a ratio of 1:1. At room temperature the two kinds of Fe(II) ions are in the HS state as confirmed by Mössbauer spectroscopy.

$[Fe(mtz)_6](BF_4)_2$

T-dependent
^{57}Fe Mössbauer spectra

**Thermal Spin
Crossover
at A-sites**

Poganiuch, Decurtins, Gütlich

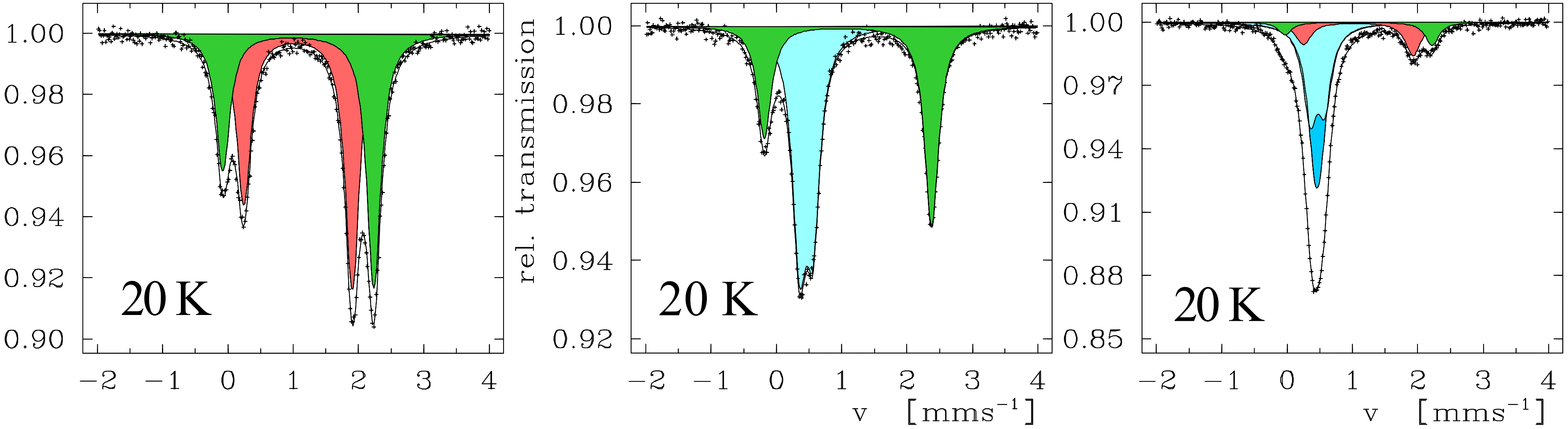


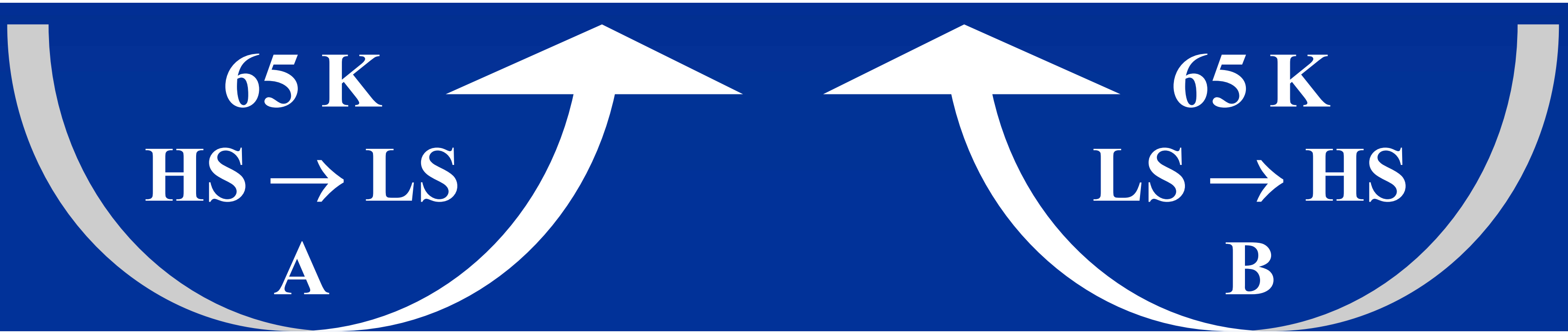
$[Fe(mtz)_6](BF_4)_2$

LIESST in Sites A and B

λ = 514 nm

λ = 820 nm





65 K
HS → LS
A

65 K
LS → HS
B

$[Fe(mtz)_6](BF_4)_2$

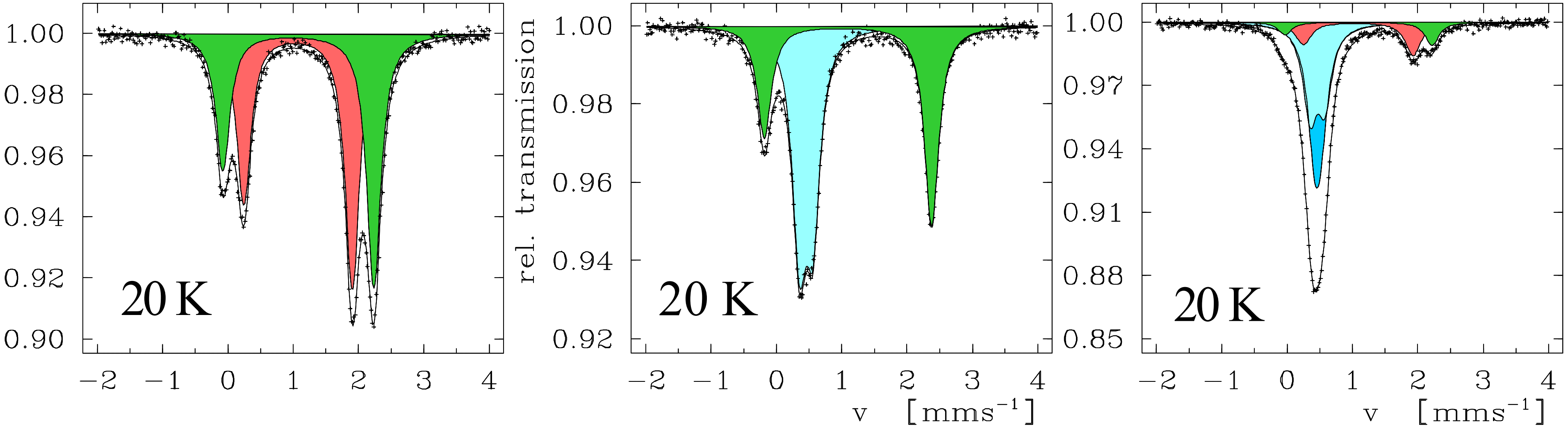
LIESST and Reverse-LIESST in Sites A and B

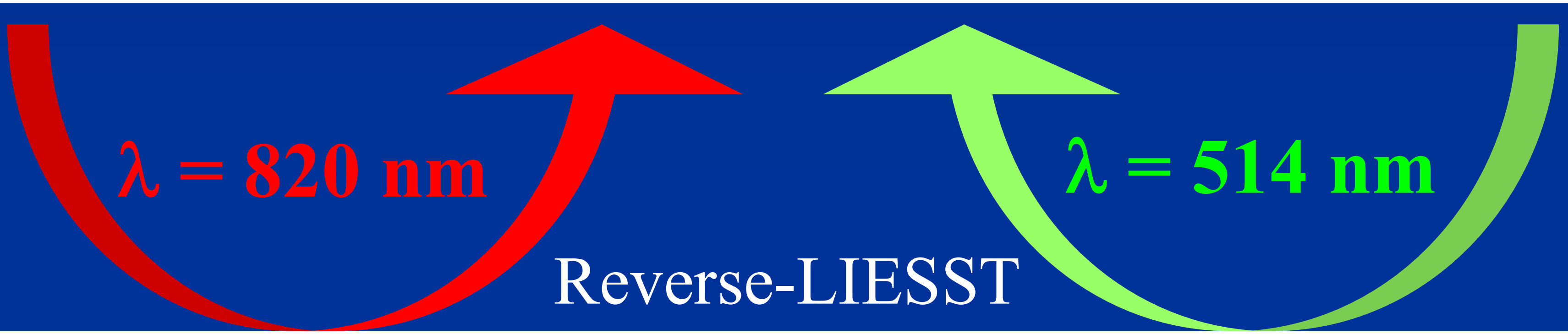
A

λ = 514 nm

B

λ = 820 nm



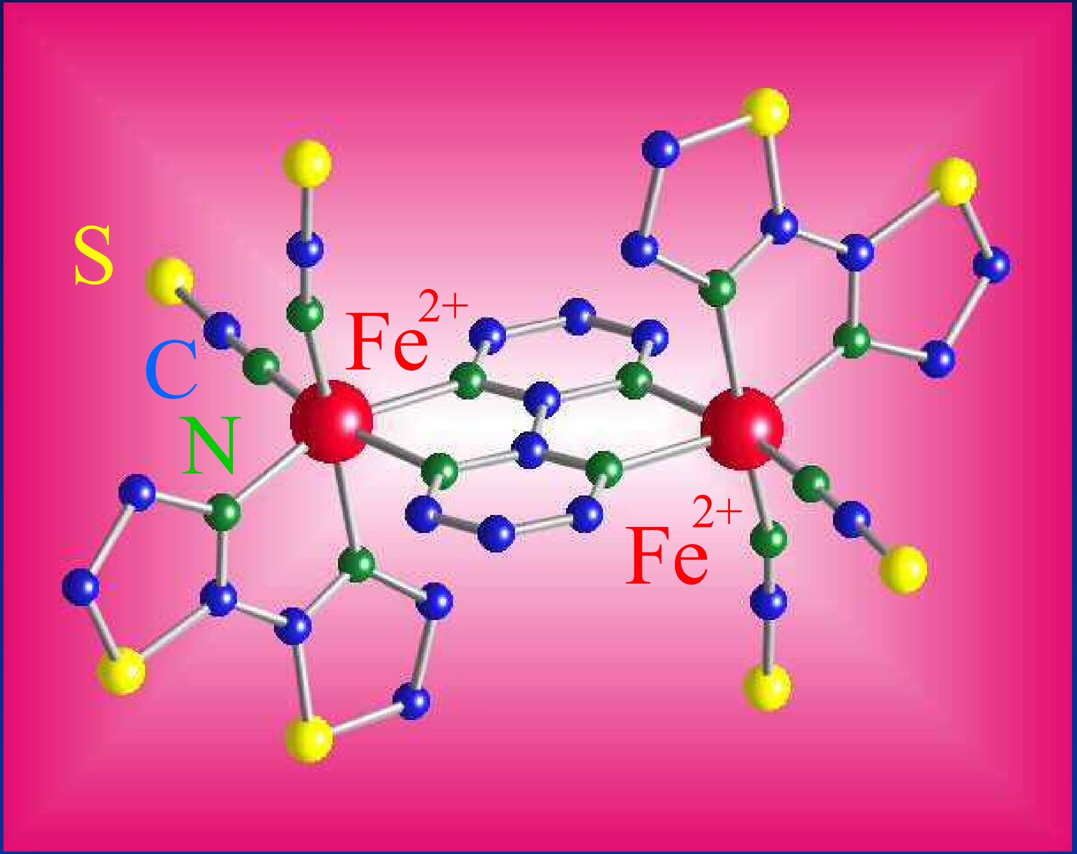


λ = 820 nm

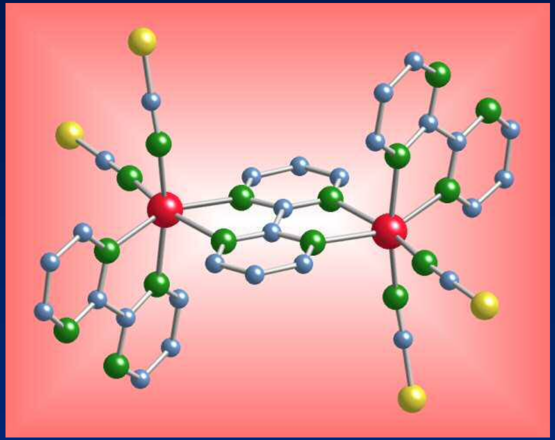
λ = 514 nm

Reverse-LIESST

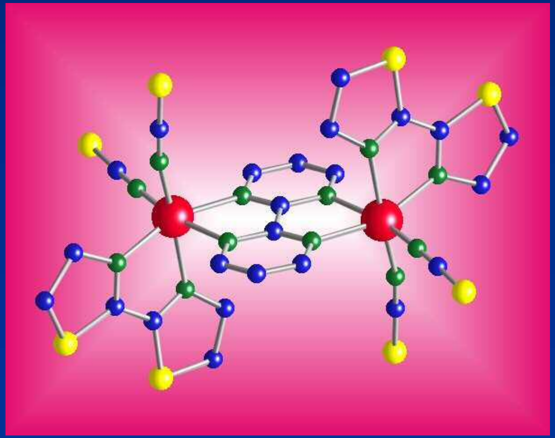
Dinuclear Iron(II) Compounds



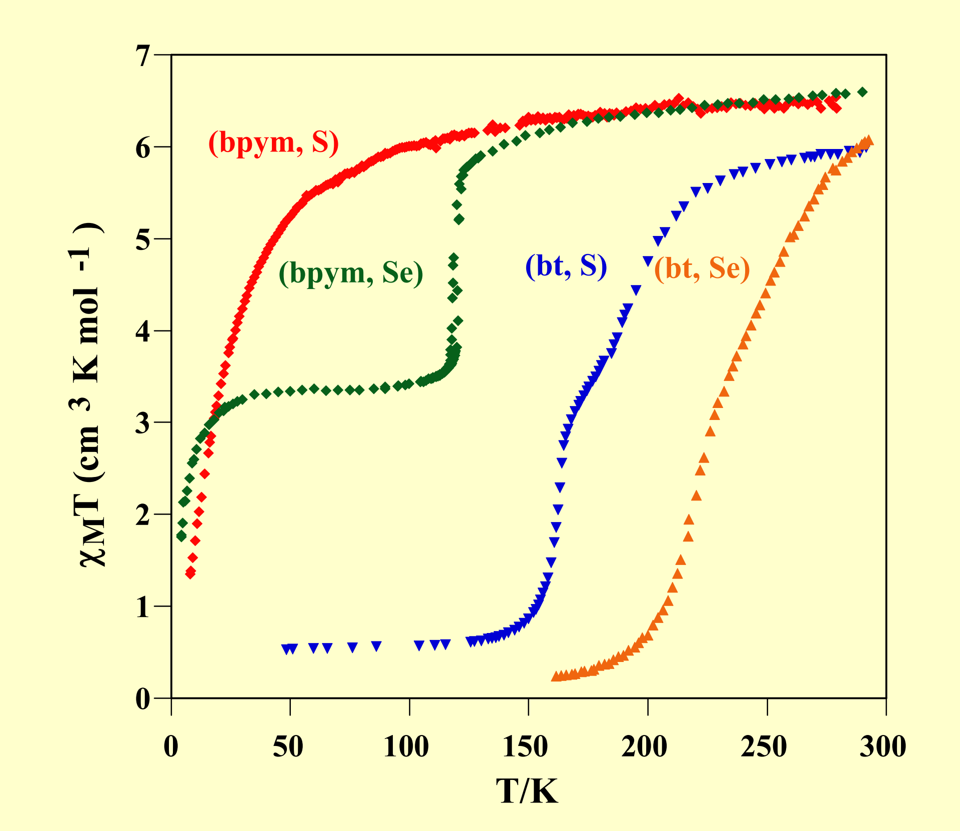
Spin Crossover and AF Coupling in Dinuclear Iron(II) Compounds



{[Fe(bpym)(NCS)$_2$]$_2$bpym}



{[Fe(bt)(NCS)$_2$]$_2$bpym}



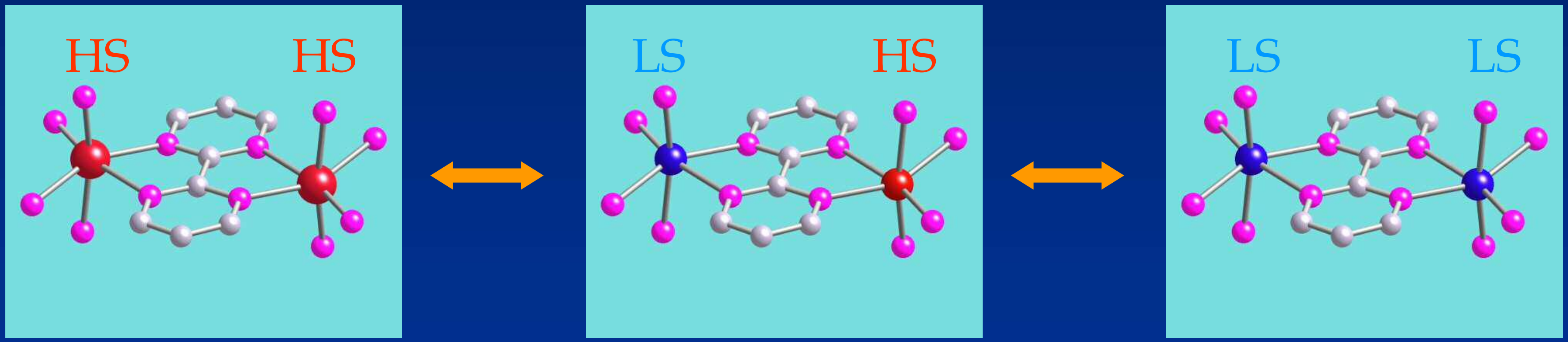
Magnetic Coupling
Two-step Spin Transition

J. A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret , J. Zarembowitch. ***J. Am. Chem. Soc***.114 (**1992**) 4650.
A. B. Gaspar, V. Ksenofontov, M. C. Muñoz, J. A.Real, P.Gütlich, manuscript in preparation.

The nature of the plateau in the two-step *spin transition*

The two step character of the spin transition is a macroscopic response of what happens on molecular level:

existence of different spin pairs



$S_a = S_b = 2$

Antiferromagnetically Coupled State

$S_a = 0 \quad S_b = 2$

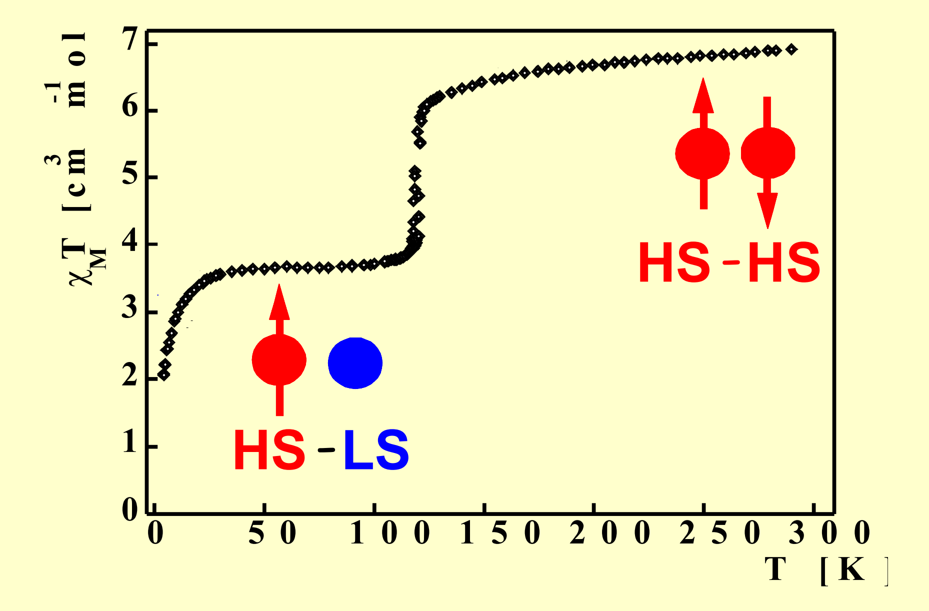
Uncoupled State

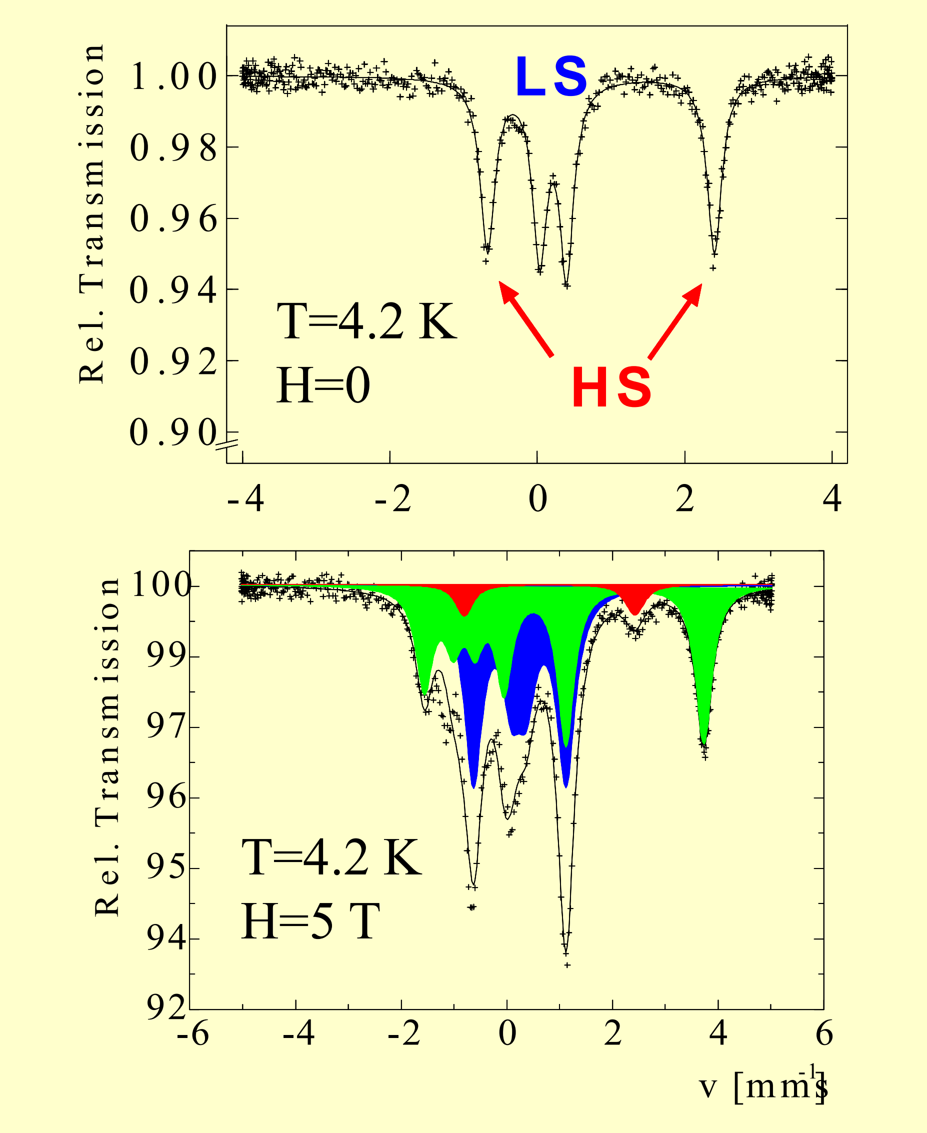
$S_a = S_b = 0$

Diamagnetic State

Mössbauer Spectroscopy of

$[\mathrm{Fe\ bpym\ (NCSe)_2}]_2\mathrm{bpym}$ in External Magnetic Field





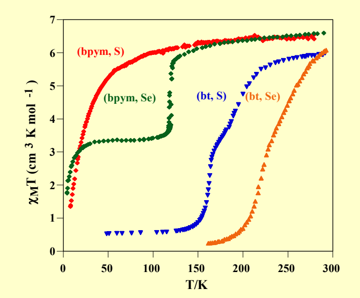
🟦 **LS in LS–LS and in HS–LS**

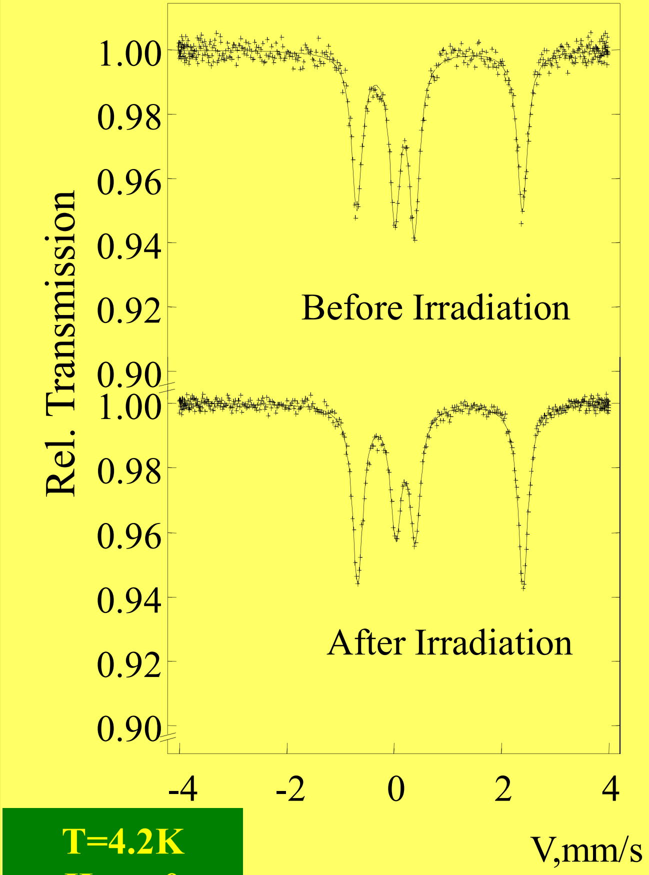
🟩 **HS in HS–LS**

🟥 **HS–HS**

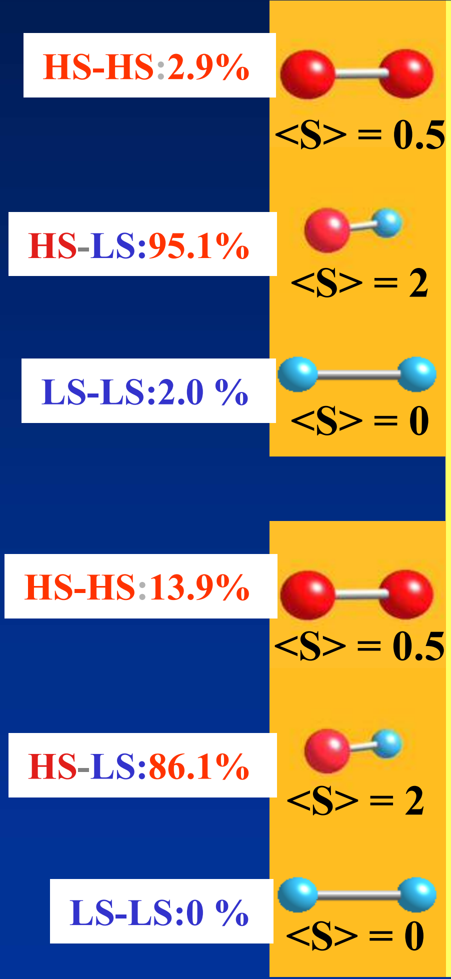
Ksenofontov, Spiering, Reiman, Garcia,
Gaspar, Moliner, Real, Gütlich
Chem. Phys. Lett. *348* **(2001)** 381

LIESST Effect in {[Fe(bpym)(NCSe)$_2$]$_2$bpym}





T=4.2K
Hext=0



HS-HS:2.9%

<S> = 0.5

HS-LS:95.1%

<S> = 2

LS-LS:2.0 %

<S> = 0

HS-HS:13.9%

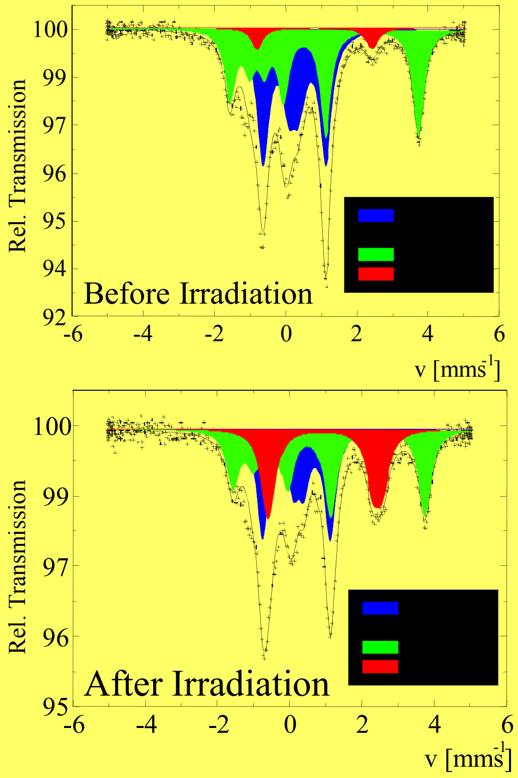
<S> = 0.5

HS-LS:86.1%

<S> = 2

LS-LS:0 %

<S> = 0

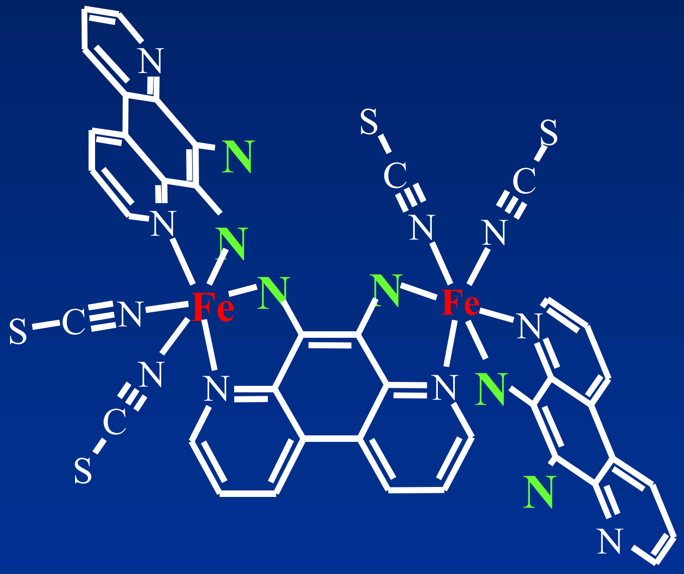


T=4.2K
Hext=5T

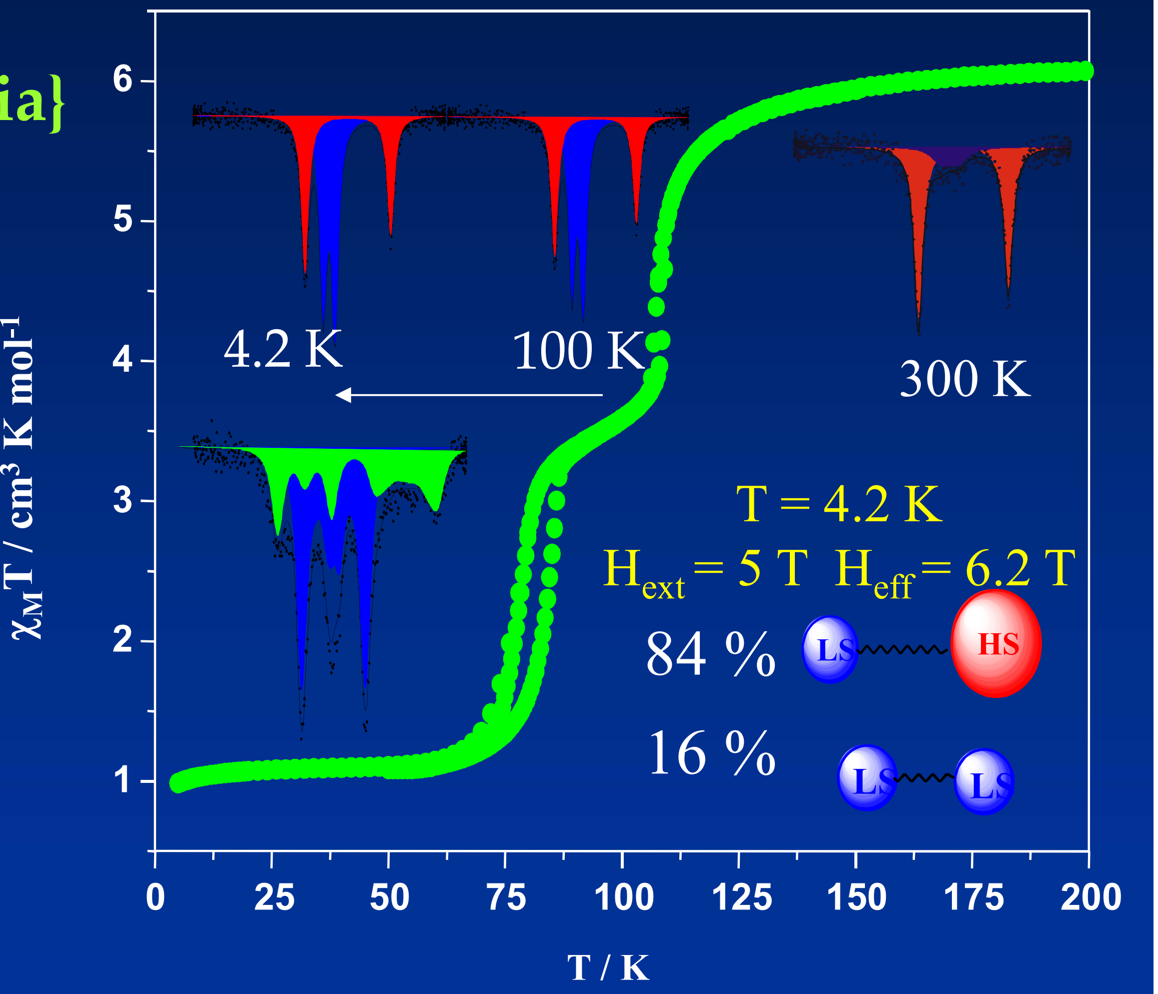
V. Ksenofontov, H. Spiering, S. Reiman, Y. Garcia, A. B. Gaspar, N. Moliner, J. A. Real, P. Gütlich.
Chem. Phys. Lett. 348 (**2001**) 381 ; ***Hyperfine Interactions***. 141/142, 47-52 (**2002**)

The nature of the plateau in the spin transition curve of dinuclear compounds

$\{[\mathrm{Fe(phdia)(NCS)_2}]_2\mathrm{phdia}\}$

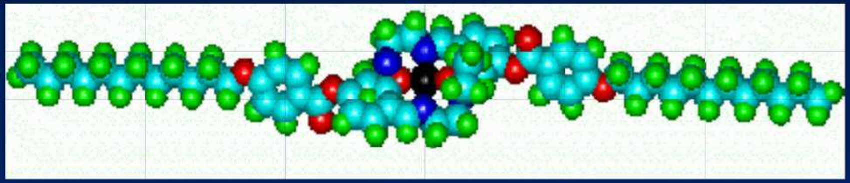


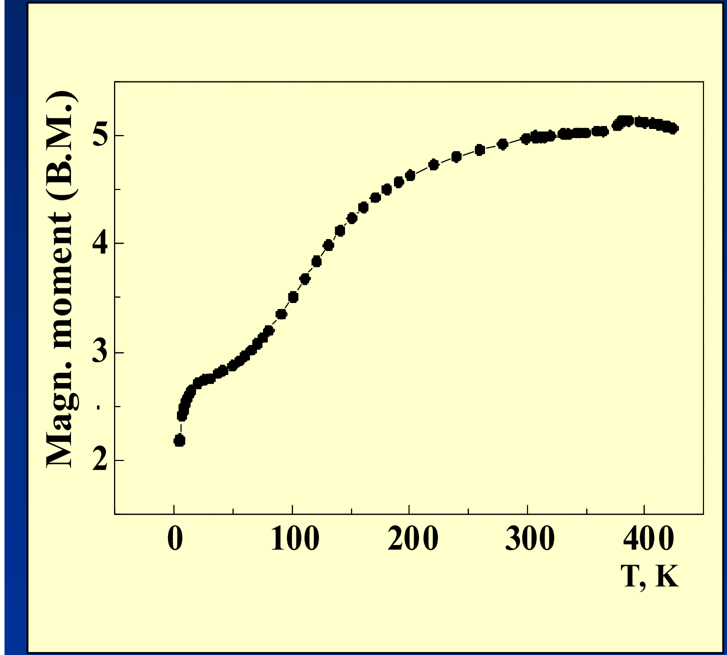
N = NH_2

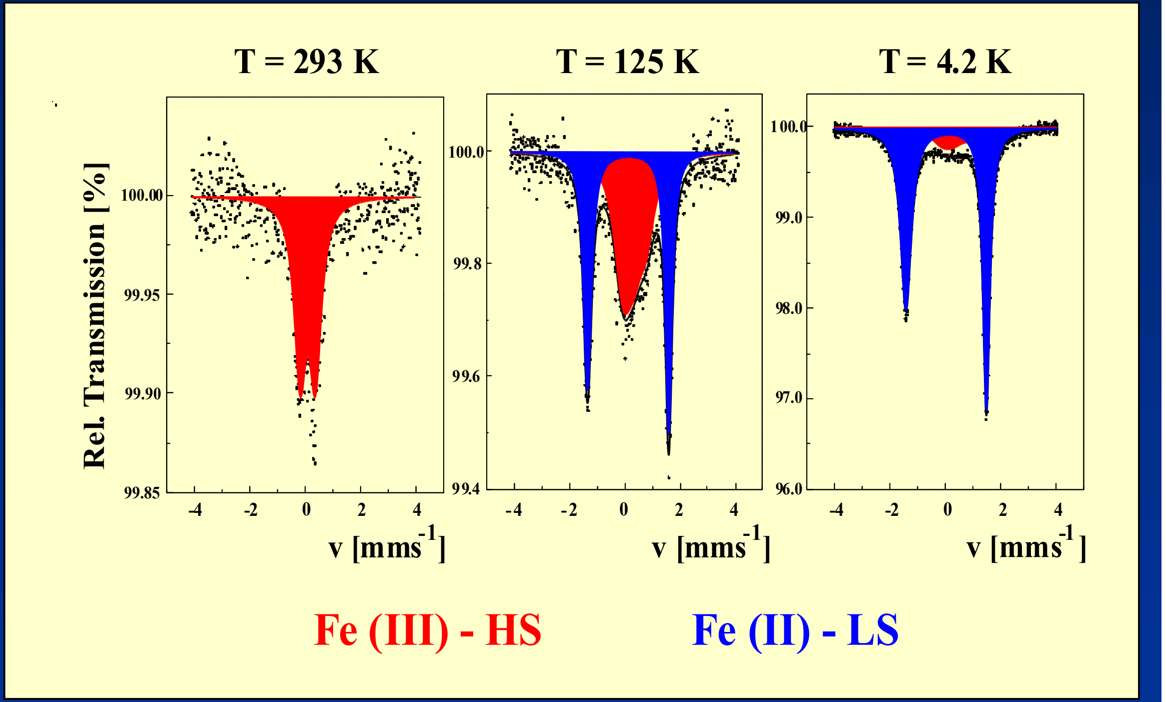


Ksenofontov, Gaspar, Gütlich, Real. *Chem. Eur. J,* 2004, *in press.*

Coexistence of Thermal Spin Transition and Liquid Crystal Properties





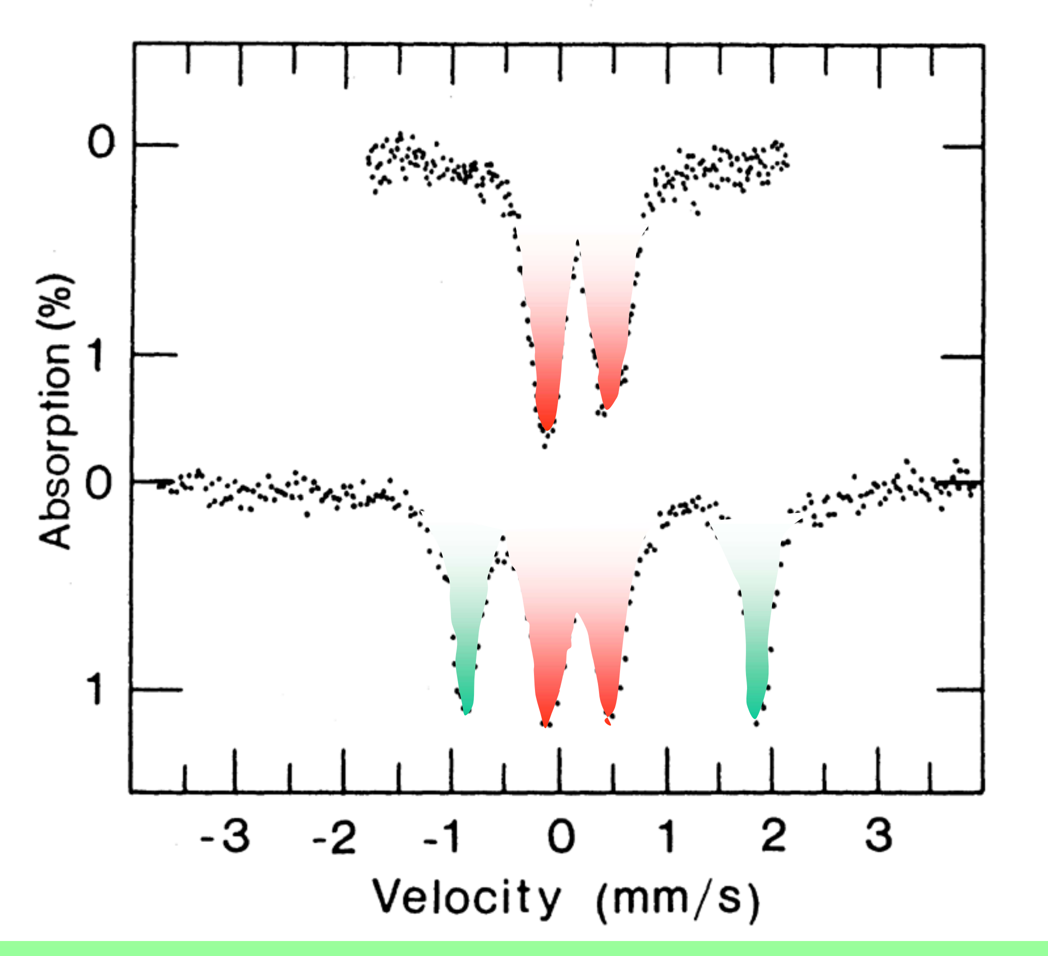


Yu. Galyametdinov, V. Ksenofontov, W. Haase and P. Gütlich
Angew. Chem. **113**, 4399 (2001)

Bioinorganic Compounds

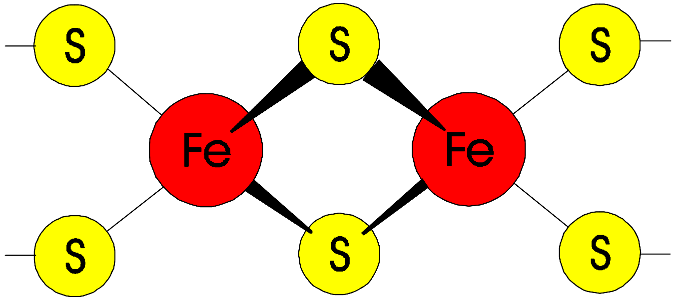
Ferredoxin (green alga)

Two-Iron Center Protein



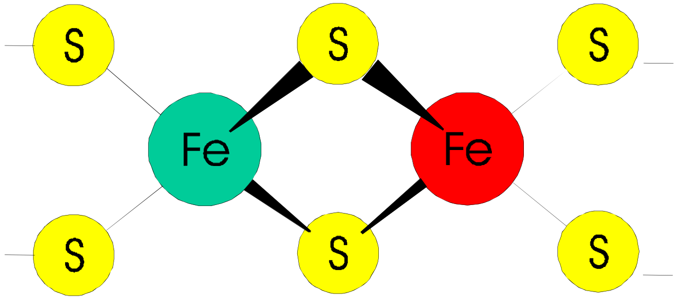
C. E. Johnson et al. (1971)

Oxidized



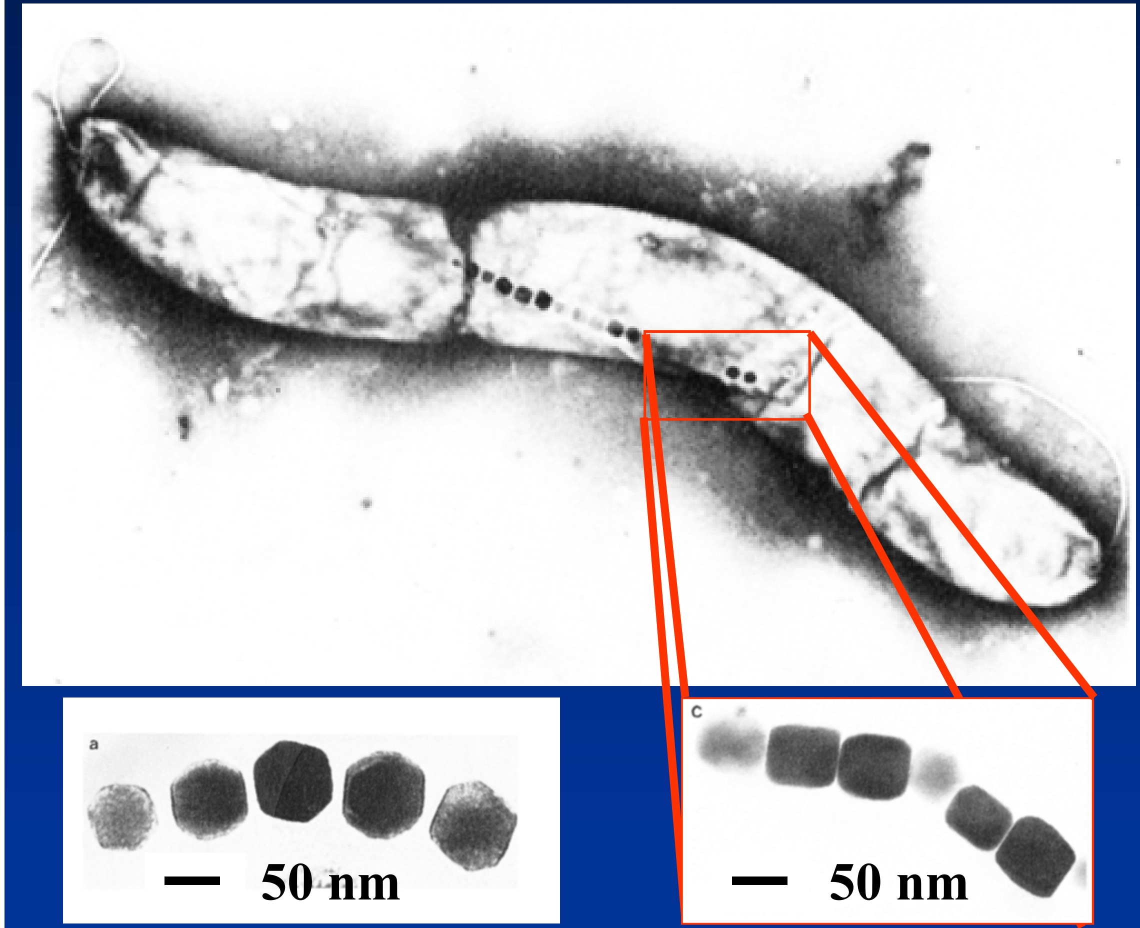
S=5/2 ↑ S=5/2 ↓

Reduced



S=2 ↑ S=5/2 ↓

Fe_3O_4 in Magnetotactic Bacteria
Aquaspirillum Magnetotacticum

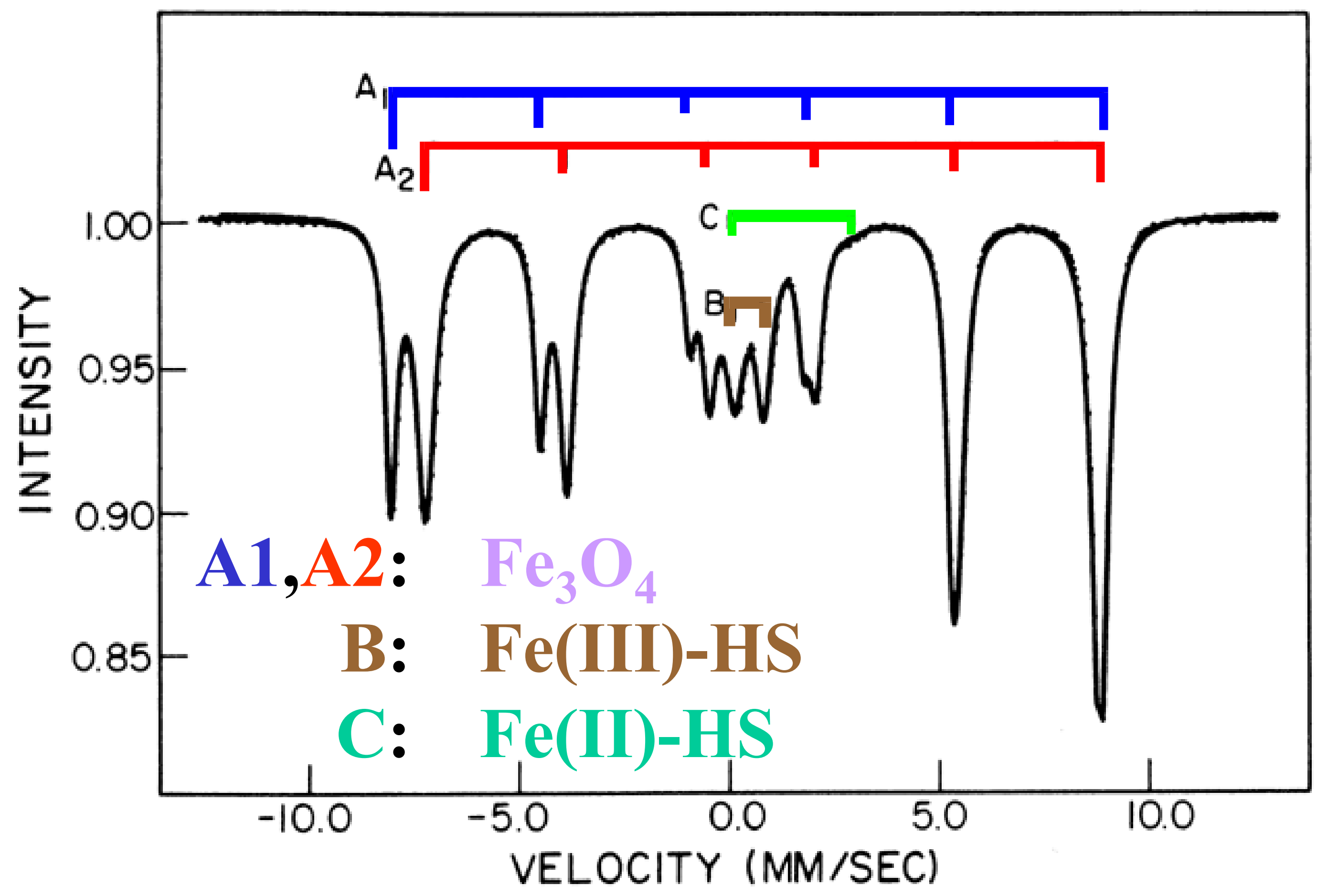


Hexagonal Cubic

Biomagnetic compass: Microorganisms follow geomagnetic field due to magnetic particles (40 – 120 nm)

^{57}Fe Mössbauer Spectrum of Magnetic Particles in Magnetotactic Bacteria

Frankel, Papaefthymiou, 1983:



A1,A2: Fe_3O_4

B: Fe(III)-HS

C: Fe(II)-HS

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