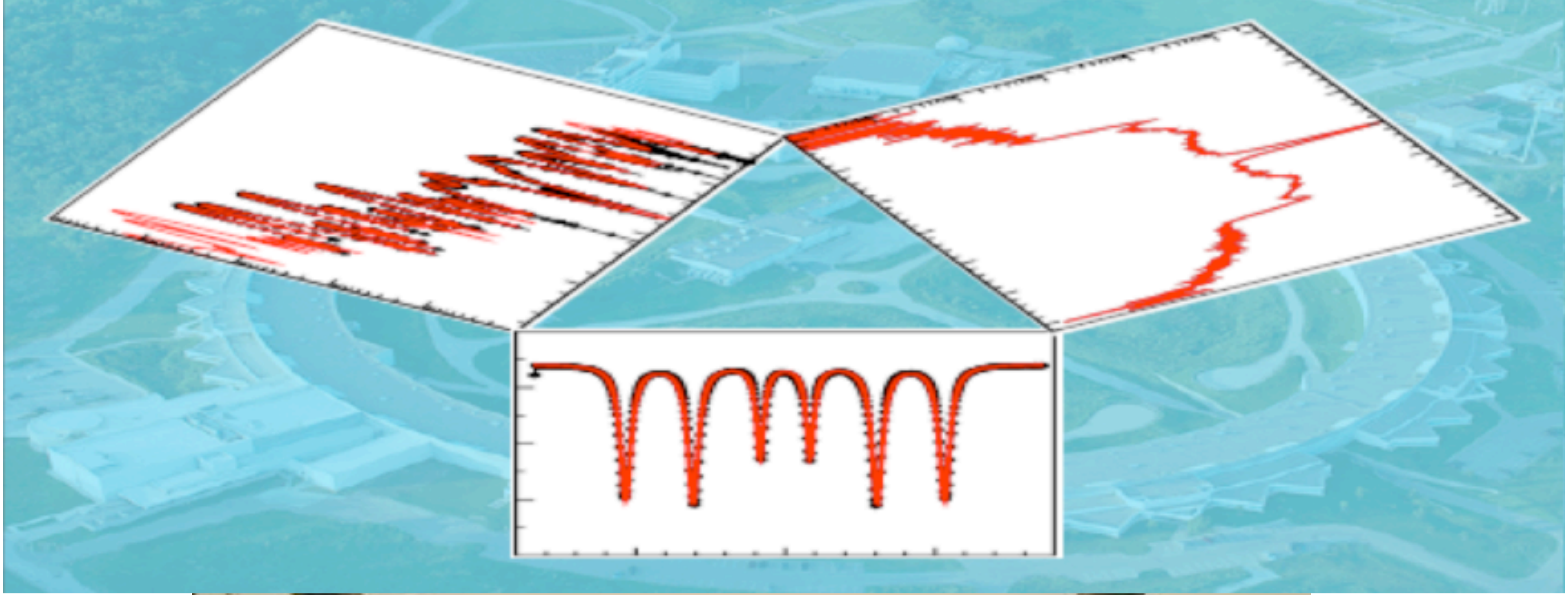
Workshop on Nulcear Resonant Scattering and Data Analysis

Nov. 11-13, 2016

Advanced Photon Source, Argonne National Laboratory



Mössbauer Spectrometry

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Department of Applied Physics and Materials Science <AP|$\hat{h}$|MS>

History
Recoil-Free Fraction
Technique, Samples
Hyperfine Interactions: IS, EFG, HMF
WIEN2k
Mössbauer Community

MÖSSBAUER SPECTROMETRY

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INTRODUCTION

Mössbauer spectrometry is based on the quantum mechanical “Mössbauer effect,” which provides a nonintuitive link between nuclear and solid-state physics. Mössbauer spectrometery measures the spectrum of energies at which specific nuclei absorb γ rays. Curiously, for one nucleus to emit a γ ray and a second nucleus to absorb it with efficiency, the atoms containing the two nuclei must be bonded chemically in solids. A young Rudolf Mössbauer observed this efficient γ-ray emission and absorption process in ^{191}Ir, and explained why the nuclei must be embedded in solids. Mössbauer spectrometry is now performed primarily with the nuclei ^{57}Fe, ^{119}Sn, ^{151}Eu, ^{121}Sb, and ^{161}Dy. Mössbauer spectra can be obtained with other nuclei, but only if the experimenter can accept short radioisotope half-lives, cryogenic temperatures, and the preparation of radiation sources in hot cells.

Most applications of Mössbauer spectrometry in materials science utilize “hyperfine interactions,” in which the electrons around a nucleus perturb the energies of nuclear states. Hyperfine interactions cause very small perturbations of 10^{-9} to 10^{-7} eV in the energies of Mössbauer γ rays. For comparison, the γ rays themselves have energies of 10^4 to 10^5 eV. Surprisingly, these small

Mössbauer atom itself, such as its valence, spin state, or magnetic moment. The Mössbauer effect is sensitive to the arrangements of surrounding atoms, however, because the local crystal structure alters the electronic or magnetic structure at the resonant nucleus. Different chemical and structural environments around the nucleus can often be assigned to specific hyperfine interactions. In such cases, measuring the fractions of nuclei with different hyperfine interactions is equivalent to measuring the fractions of the various chemical and structural environments in a material. Phase fractions and solute distributions, for example, can be determined in this way. The viewpoint from the nucleus is sometimes too small to address problems in the microstructure of materials, however.

Other applications of the Mössbauer effect utilize its sensitivity to vibrations in solids, its timescale for scattering, or its coherence. To date these phenomena have seen little use outside the international community of a few hundred Mössbauer spectroscopists. Nevertheless, some new applications for them have recently become possible with the advent of synchrotron sources for Mössbauer spectrometry.

This article is not a review of the Mössbauer spectrometry, but an instructional reference that gives the working materials scientist a basis for evaluating whether or not Mössbauer spectrometry may be useful for a research problem. There have been a number of books written about the Mössbauer effect and its spectroscopies (see Section “Key References”). Most include reviews of materials research. These reviews typically demonstrate applications of the measurable quantities in Mössbauer spectrometry, and provide copious references.

Mössbauer's Early Work

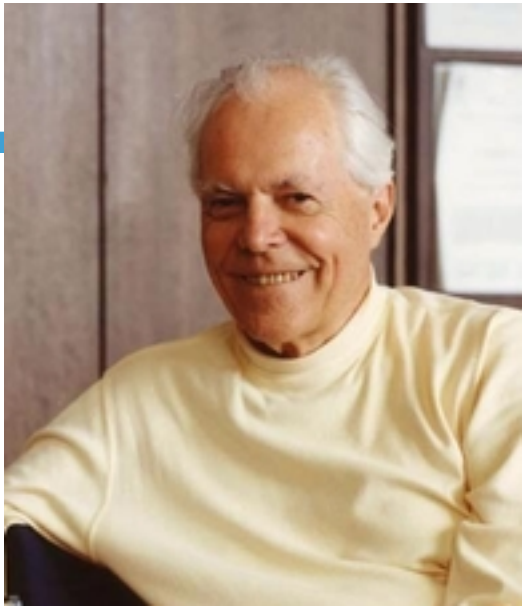
Ph.D. thesis under Heinz Maier-Leibnitz.

Looked for nuclear resonance scattering at high temperatures.

Found best effect at low temperatures in ^{191}Ir.

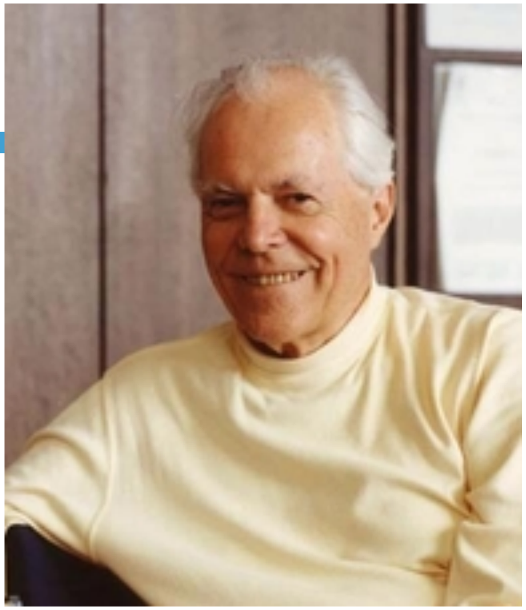
Had read neutron resonance scattering paper by Lamb.

Got the theory right, essentially by adapting Lamb's approach.



Rudolf Mössbauer 1929-2011

Mössbauer's Early Work



Rudolf Mössbauer 1929-2011

Felix Böhm met Rudolf Mössbauer when visiting Germany, and suggested to Feynman that he might come to Caltech.

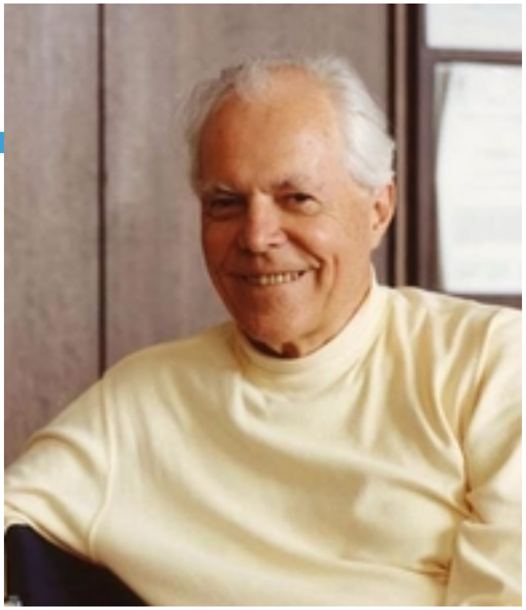
Feynman: "Get the guy."

Came to Caltech, worked with Felix Böhm (co-advised John Poindexter as Ph.D. student).

Explosion of interest in Mössbauer effect after discovery in ^{57}Fe (Argonne, Harvard).

Nobel prize in 1961.

Days of Excitement


Rudolf Mössbauer 1929-2011

Nobel prize in 1961.

Heinz Maier-Leibnitz did not share Nobel Prize.

Emergency meeting of Caltech faculty.

Promoted to Full Professor of Physics in 24 h (fastest promotion process in history of Caltech).

Moved back to TUM ("air pollution in Pasadena", I doubt it).

Coherent nuclear resonant scattering.

Neutrino oscillations 1977 with Böhm.

Proud that he did not publish false results on neutrino oscillations, but not much came of it.

Did not like the "noise" of Mössbauer spectrometry community.

Features of Mössbauer Spectrometry

Mössbauer spectrometry looks outwards from the nucleus.

Energy levels of a nucleus are altered by hyperfine interactions with the atomic electrons.

Hyperfine interactions depend on

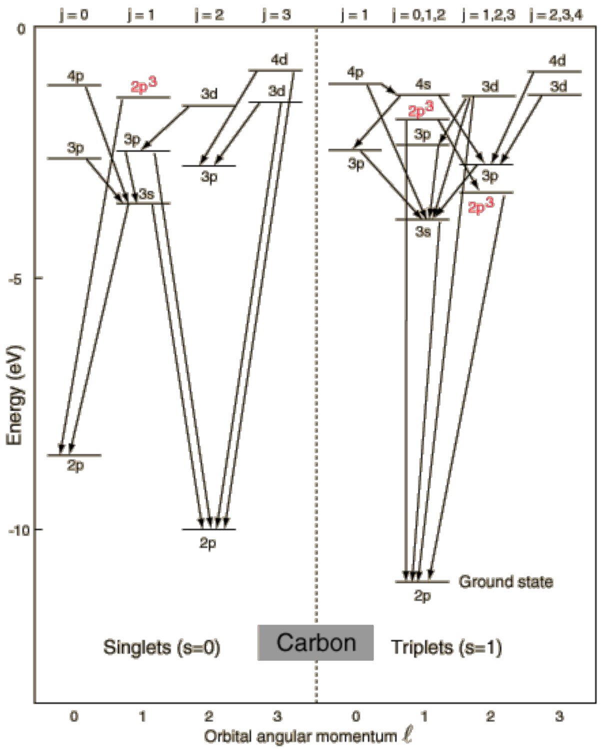
- valence (IS)
- chemical environment (EFG)
- magnetic environment (HMF)

Mössbauer spectrometry can study local atomic arrangements, but there may be better ways to do this in 2016.

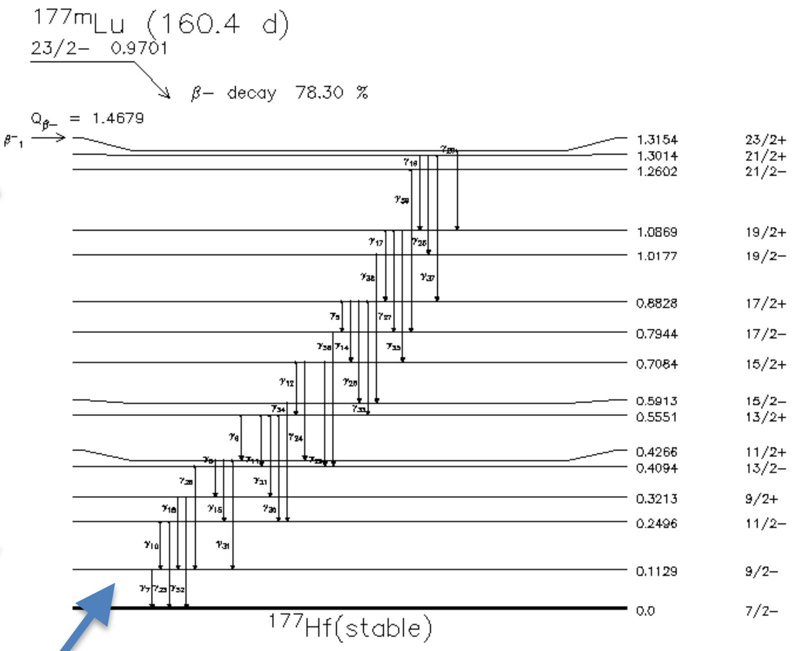
Atomic Energy Levels

Nuclear Energy Levels

1 eV



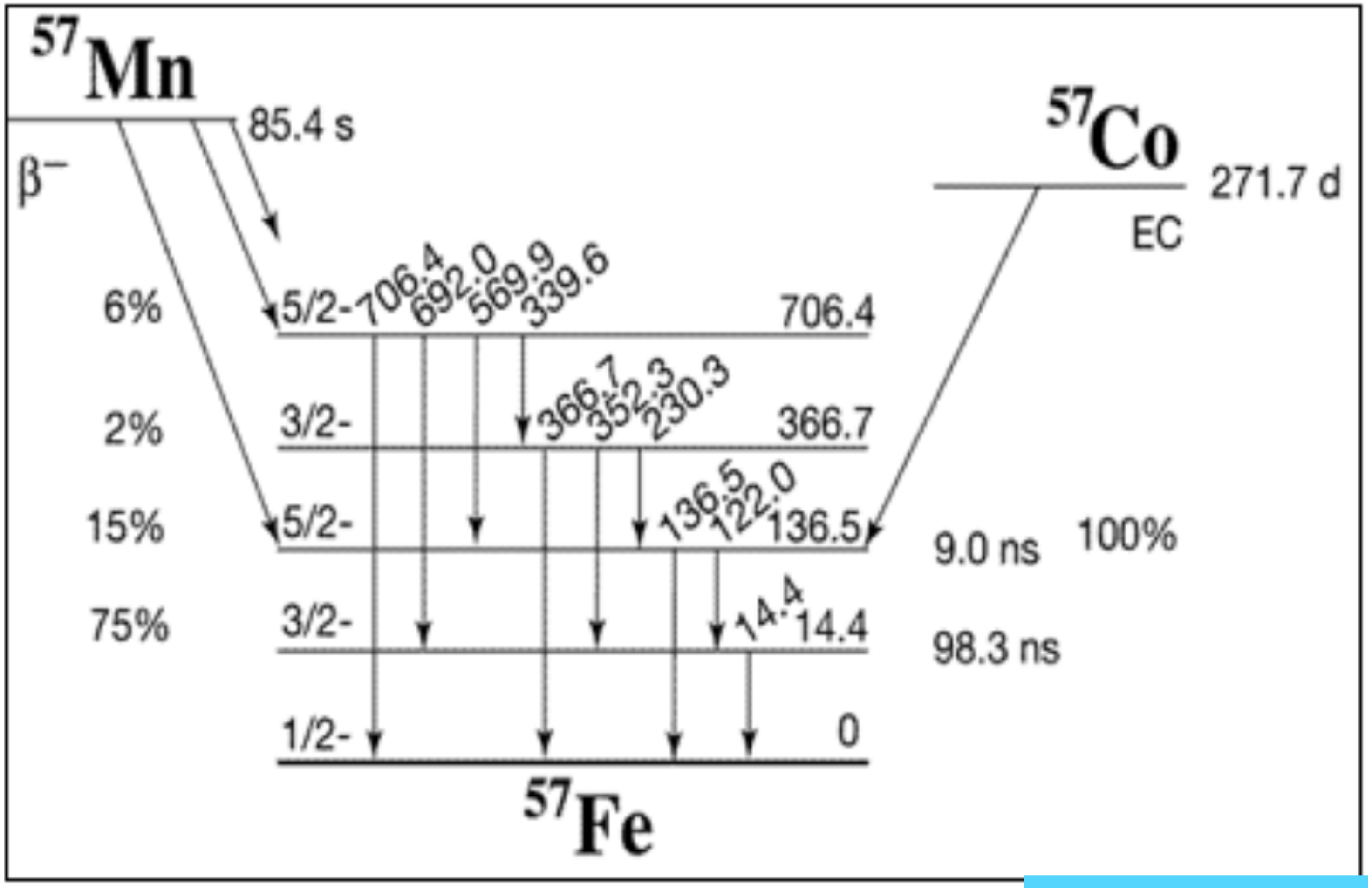
10^6 eV



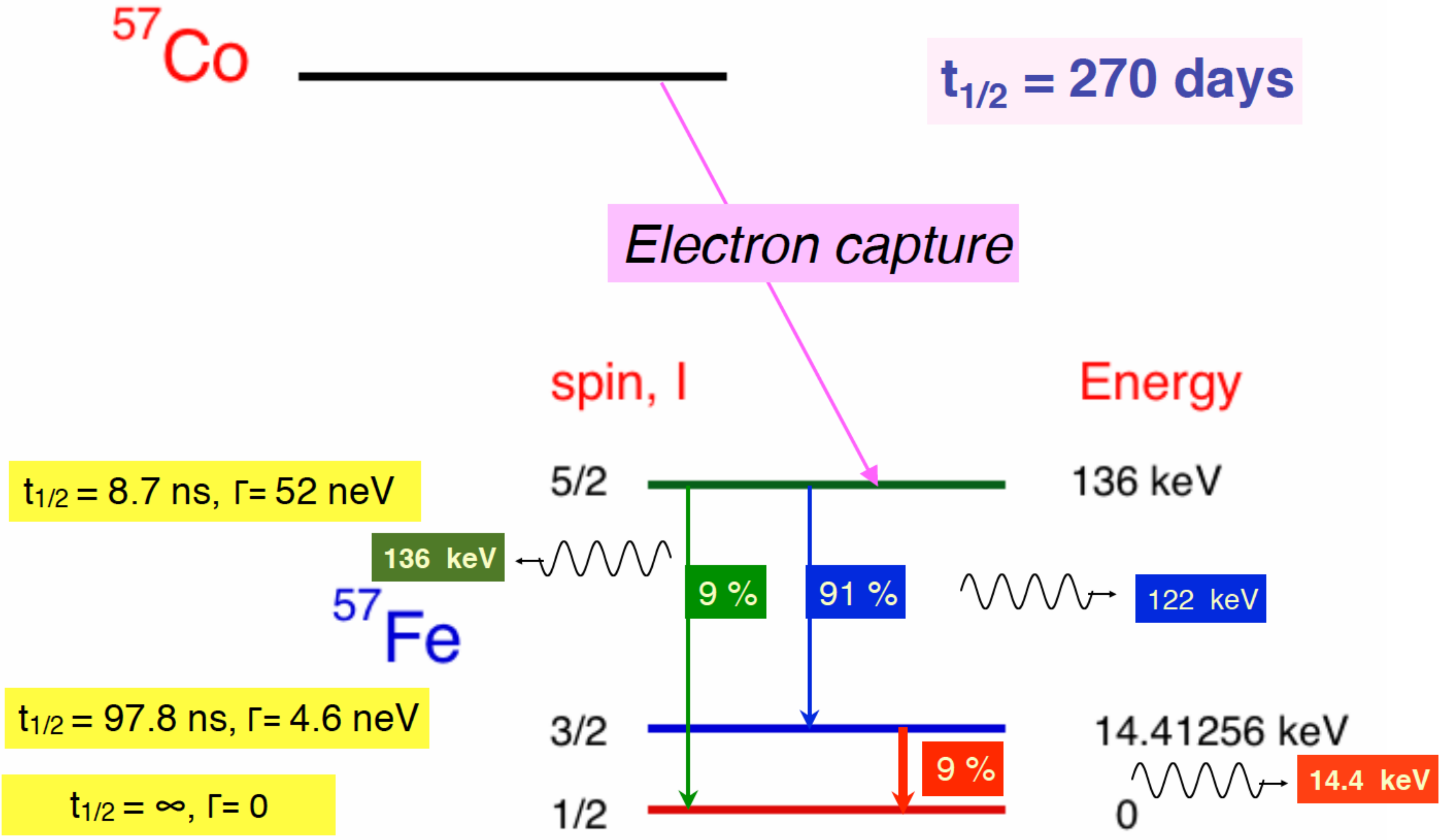
Low nuclear transitions ~10^4 eV

Nuclear energy ~ 10^6 chemical energy

Preparation of Nuclear Excited State



Characteristics of a Mössbauer source



^{57}Co

$t_{1/2}$ = 270 days

Electron capture

spin, I

Energy

$t_{1/2}$ = 8.7 ns, Γ= 52 neV

5/2 — 136 keV

136 keV

9 %

91 %

122 keV

^{57}Fe

$t_{1/2}$ = 97.8 ns, Γ= 4.6 neV

3/2 — 14.41256 keV

9 %

14.4 keV

$t_{1/2}$ = ∞, Γ= 0

1/2 — 0

Given a Low-Energy Nuclear Transition of 14.4 keV…

Photon momentum is: $p = E/c$

Nuclear recoil $p^2/2m = 1.9\text{x}10^{-3}$ eV

Nuclear lifetime $\tau = 1\text{x}10^{-7}\ s$
Nuclear energy width $\varepsilon = h/\tau = 10^{-9}$ eV

With recoil of free nucleus, by a factor of a million to hit the energy precision of a nuclear excitation.

Suppose the Entire Crystal Recoils, Not One Nucleus

Crystal contains 10^7 atoms.

Nuclear recoil $p^2/(2m\ 10^7) = 1.9\text{x}10^{-10}$ eV

Nuclear lifetime $\tau = 1\text{x}10^{-7}\ s$

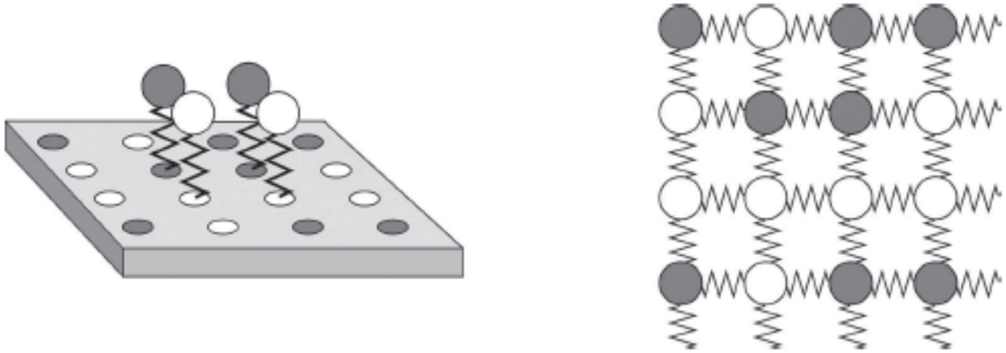
Nuclear energy width $\varepsilon = h/\tau = 10^{-9}$ eV

Now can hit the energy precision of a nuclear excitation and observe nuclear fluorescence.

But how do we get the entire crystal to take up the recoil momentum?

Phonons – Quanta of lattice vibrations

Einstein (1907) quantized energy of normal modes of the lattice.
Simplest approach: put individual atoms on springs.



Einstein model:

$$h\nu = 10^{-2}\,\text{eV}$$

Phonons – Quanta of lattice vibrations

Einstein model:

$h\nu = 10^{-2}\,\text{eV}$

Recoil energy of individual nucleus = $10^{-3}\,\text{eV}$

Not enough to excite a phonon most of the time.

If no phonon excitation, γ-ray energy loss is only $1.9\text{x}10^{-10}\,\text{eV}$.

Nuclear resonance can occur with probility

$p \sim \exp(-E_{\text{rec}}/h\nu) = \exp(-0.1) \sim 0.9$ (beware, no T here)

Phonons – Quanta of lattice vibrations

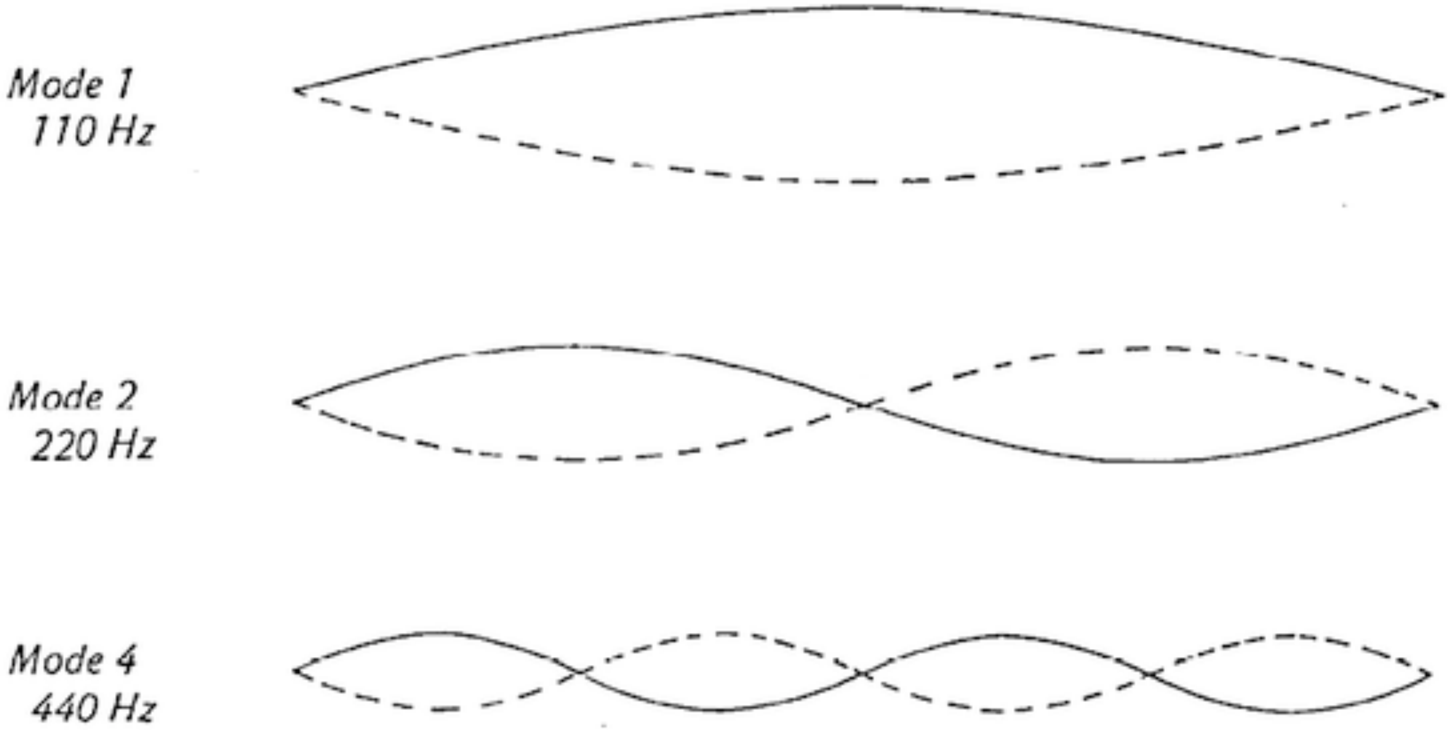
Recoil-free fraction (RFF) or Lamb-Mössbauer factor

Fraction of nuclear gamma emissions (or absorptions) that occur without phonon excitation, and can be nuclear resonant scattering.

Recognizing the quantum origin of this is what led to the Nobel Prize.

Vibrations in Crystals — Normal Modes

- Normal modes are independent and live forever
- Highest frequencies have adjacent atoms out of phase
- Quantize normal modes to get phonons $\varepsilon = \hbar\omega$



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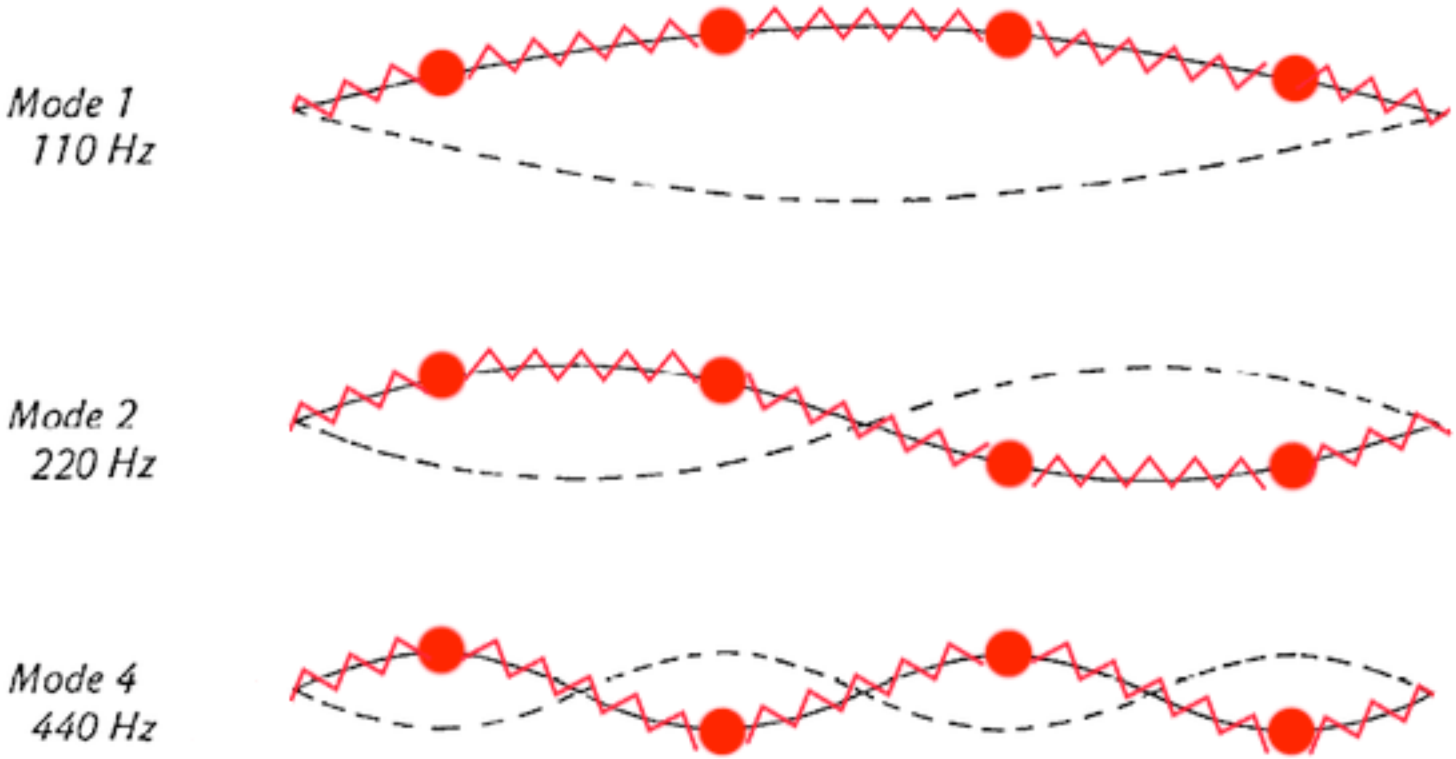


More Rigor for Recoil-Free Fraction

$$\psi_i(\vec{X}) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \mathrm{e}^{+((\mathrm{i}\vec{p}\cdot\vec{X})/\hbar)}\, \phi_i(\vec{p})\, d\vec{p} \qquad (6)$$

The momentum space representation can handily accommodate the impulse of the γ-ray emission, giving the final state of the nuclear center of mass, $\psi_f(X)$.

$$\phi_i(p) \rightarrow \phi_i(p - p_\gamma)$$

This is a translation in momentum space

$$\psi_f\left(\vec{X}\right) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} \mathrm{e}^{+((\mathrm{i}(\vec{p}+\vec{p}_\gamma)\cdot\vec{X})/\hbar)}\, \phi_i(\vec{p})\, d\vec{p} \qquad (7)$$

$$\psi_f\left(\vec{X}\right) = \mathrm{e}^{+((\mathrm{i}\vec{p}_\gamma\cdot\vec{X})/\hbar)}\, \psi_i\left(\vec{X}\right) \qquad (11)$$

More Rigor for Recoil-Free Fraction, f

$$\psi_f\left(\vec{X}\right) = \mathrm{e}^{+((\mathrm{i}\vec{p}_\gamma \cdot \vec{X})/\hbar)}\, \psi_i\left(\vec{X}\right) \tag{11}$$

Recoil-free fraction is projection of initial state on final state

$$\langle i|f\rangle \equiv \int_{-\infty}^{+\infty} \psi_i^*(\vec{X})\psi_f(\vec{X})d\vec{X}$$

$$\langle i|f\rangle \equiv \left\langle i|\mathrm{e}^{+((\mathrm{i}\vec{p}_\gamma \cdot \vec{X})/\hbar)}|i\right\rangle$$

More Rigor for Recoil-Free Fraction, *f*

$$\langle i|f\rangle \equiv \left\langle i\middle|\mathrm{e}^{+((\mathrm{i}\vec{p}_\gamma\cdot\vec{X})/\hbar)}\middle|i\right\rangle$$

RFF, *f*, is:

$$f = \frac{\left|\left\langle i\middle|\mathrm{e}^{+\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|i\right\rangle\right|^2}{\sum_j \left|\left\langle j\middle|\mathrm{e}^{+\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|i\right\rangle\right|^2} \tag{15}$$

$$f = \frac{\left|\left\langle i\middle|\mathrm{e}^{+\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|i\right\rangle\right|^2}{\sum_j \left\langle i\middle|\mathrm{e}^{-\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|j\right\rangle\left\langle j\middle|\mathrm{e}^{+\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|i\right\rangle} \tag{16}$$

Using the closure relation $\Sigma_j |j\rangle\langle j| = 1$, and the normalization $\langle i|\, i\rangle = 1$, Equation 16 becomes

$$f = \left|\left\langle i\middle|\mathrm{e}^{+\mathrm{i}\vec{k}_\gamma\cdot\vec{X}}\middle|i\right\rangle\right|^2 \tag{17}$$

Suppose a Low-Energy Nuclear Transition of 14.4 keV

$E = p/c = h/\lambda c \qquad 2\pi/\lambda = k$

$\lambda = 0.86$ Å

Compare to X-ray Debye-Waller Factor

$$D = \exp[- (\Delta k)^2 <\Delta x^2>]$$

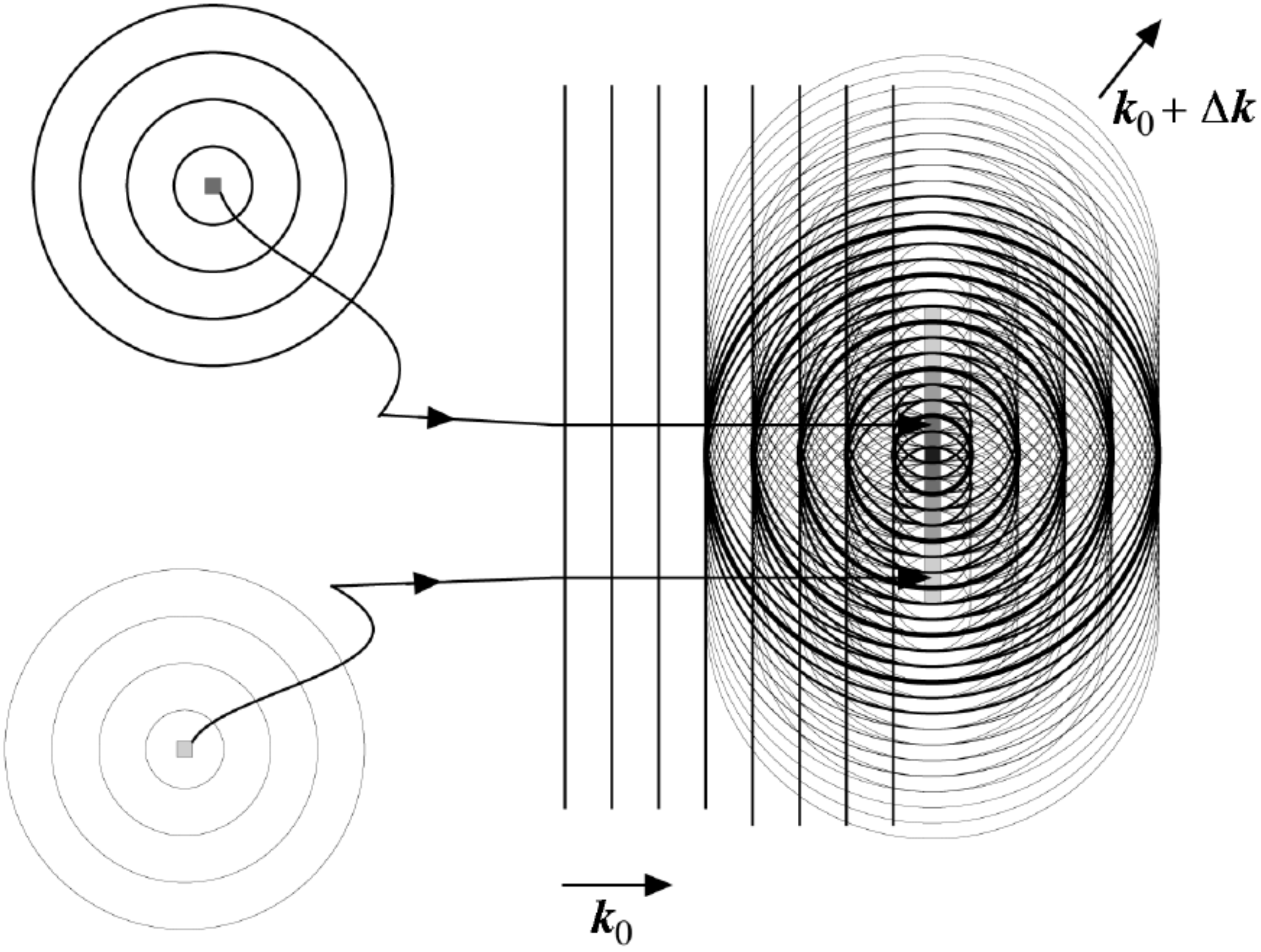
Low T, $\Delta x = 0.01$ Å

$D = 0.99$

High T, $\Delta x = 0.1$ Å

$D = 0.56$

Suppose a Low-Energy Nuclear Transition of 14.4 keV



Elastic Scattering is

$$\Psi_{\rm sc}^{\rm el}(\boldsymbol{Q},\boldsymbol{r}) = \frac{{\rm e}^{-W}}{r}\sum_{\kappa} b_\kappa\,{\rm e}^{{\rm i}\boldsymbol{Q}\cdot\boldsymbol{r}_\kappa}\sum_{l}{\rm e}^{{\rm i}\boldsymbol{Q}\cdot\boldsymbol{r}_l} \equiv \frac{{\rm e}^{-W}}{r}\mathcal{F}(\boldsymbol{Q})\,\mathcal{S}(\boldsymbol{Q})$$

$$I^{\rm el}(\boldsymbol{Q}) = \Psi^{\rm el*}\Psi^{\rm el} = {\rm e}^{-2W}$$

The total scattering cross-section does not depend on temperature. There must be compensation of loss of elastic scattering by inelastic scattering. That is

$$I^{\rm tot}(\boldsymbol{Q}) = \Psi^{\rm tot*}\Psi^{\rm tot} = {\rm e}^{-2W}\,{\rm e}^{+2W}$$

$$\Psi^{\rm tot*}\Psi^{\rm tot} = \frac{1}{\mathcal{R}}\sum_{\kappa}^{\mathcal{R}}{\rm e}^{-\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle} \times\left(1+\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle+\frac{1}{2}(\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle)^2+\ldots\right) \qquad (

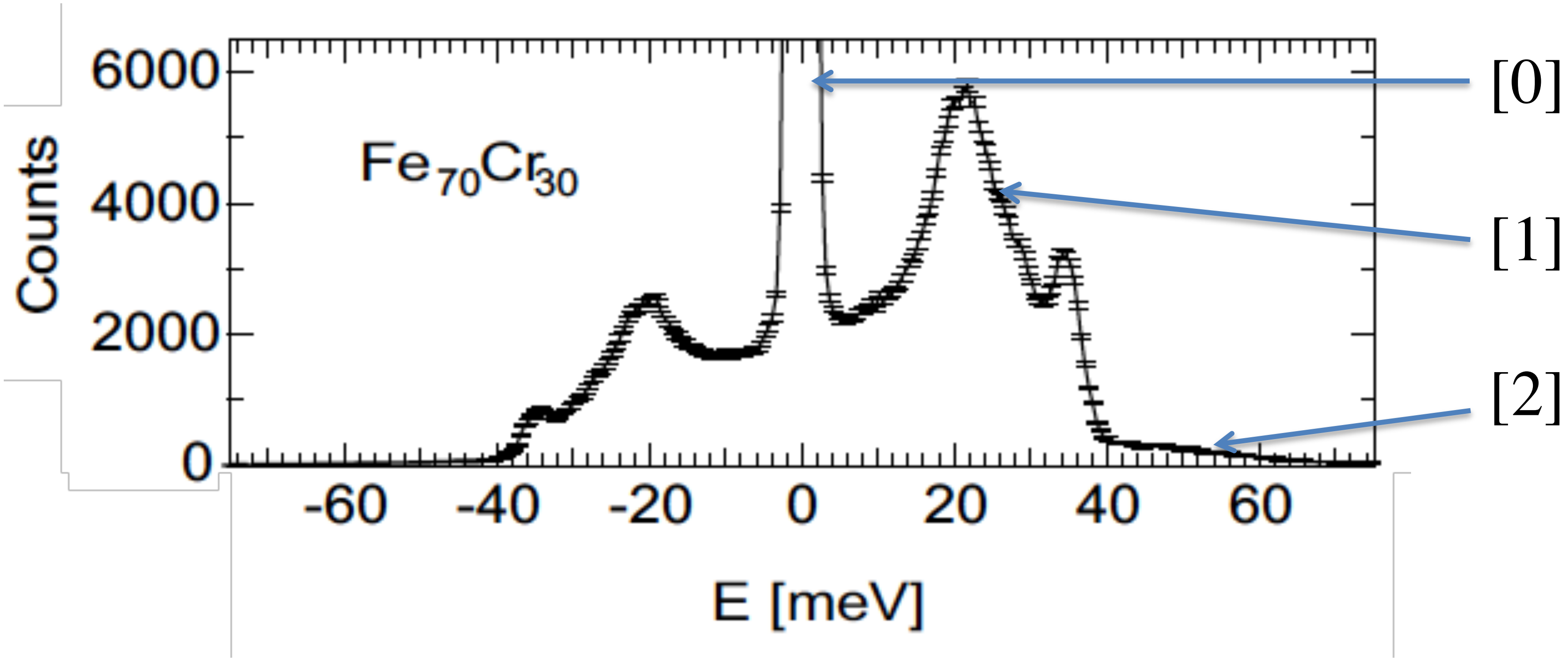
$$I^{\text{tot}}(\boldsymbol{Q}) = \Psi^{\text{tot}*}\Psi^{\text{tot}} = \mathrm{e}^{-2W}\,\mathrm{e}^{+2W}$$

$$\begin{aligned}\Psi^{\text{tot}*}\Psi^{\text{tot}} &= \frac{1}{\mathcal{R}} \sum_{\kappa}^{\mathcal{R}} \mathrm{e}^{-\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle} \\ &\times \left(\underset{[0]}{1} + \underset{[1]}{\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle} + \frac{1}{2}\underset{[2]}{(\langle(\boldsymbol{Q}\cdot\boldsymbol{u}_\kappa)^2\rangle)^2} + \ldots\right) \qquad (2.7\end{aligned}$$

$$Q^2\langle u^2\rangle = \frac{E_{\mathrm{R}}}{\hbar\omega}\,\frac{k_{\mathrm{B}}T}{\hbar\omega}$$

Elastic, 1-Phonon, 2 Phonon Scattering

Elastic, 1-Phonon, 2 Phonon Scattering

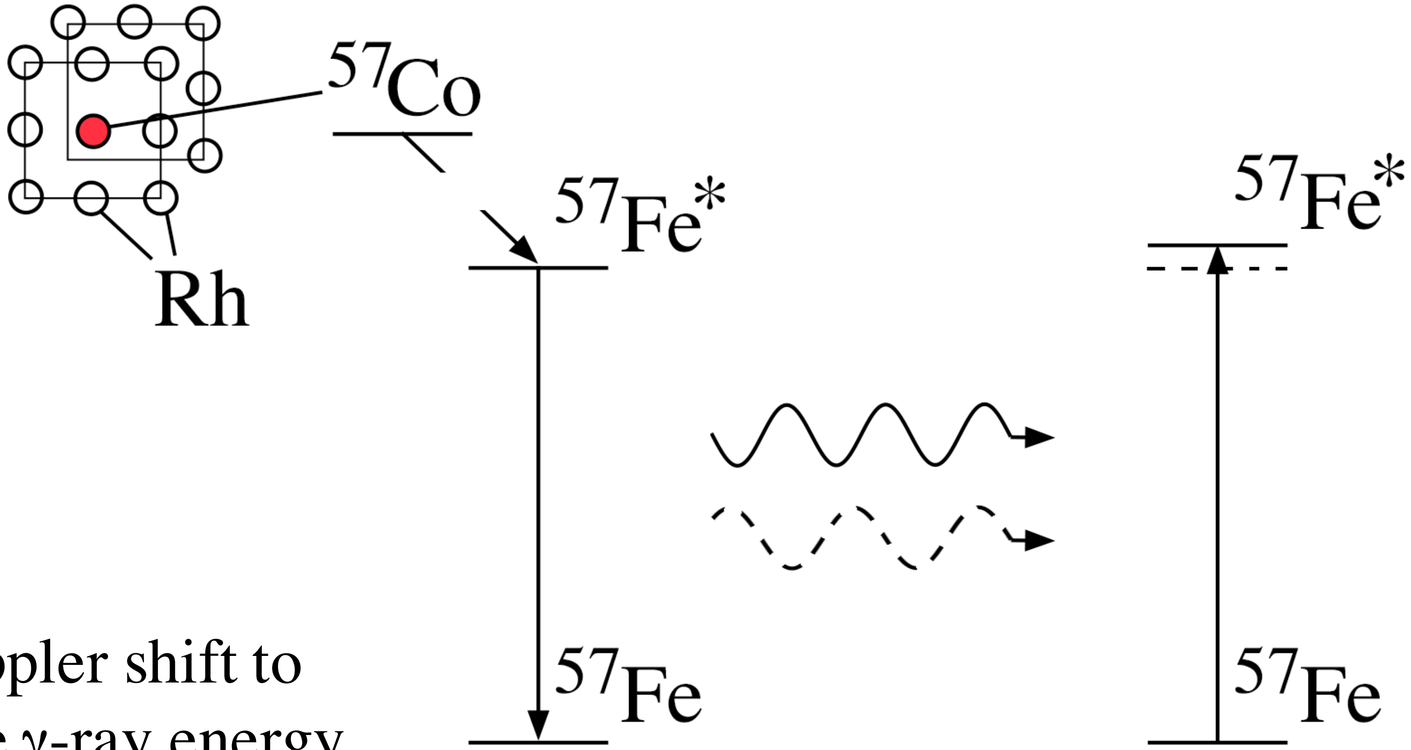


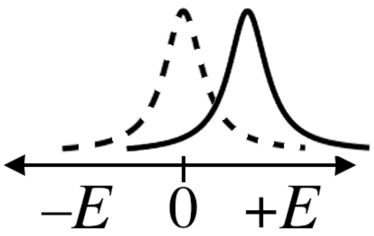
[0]

[1]

[2]

Mössbauer Spectrometry (14.41 keV γ-ray)

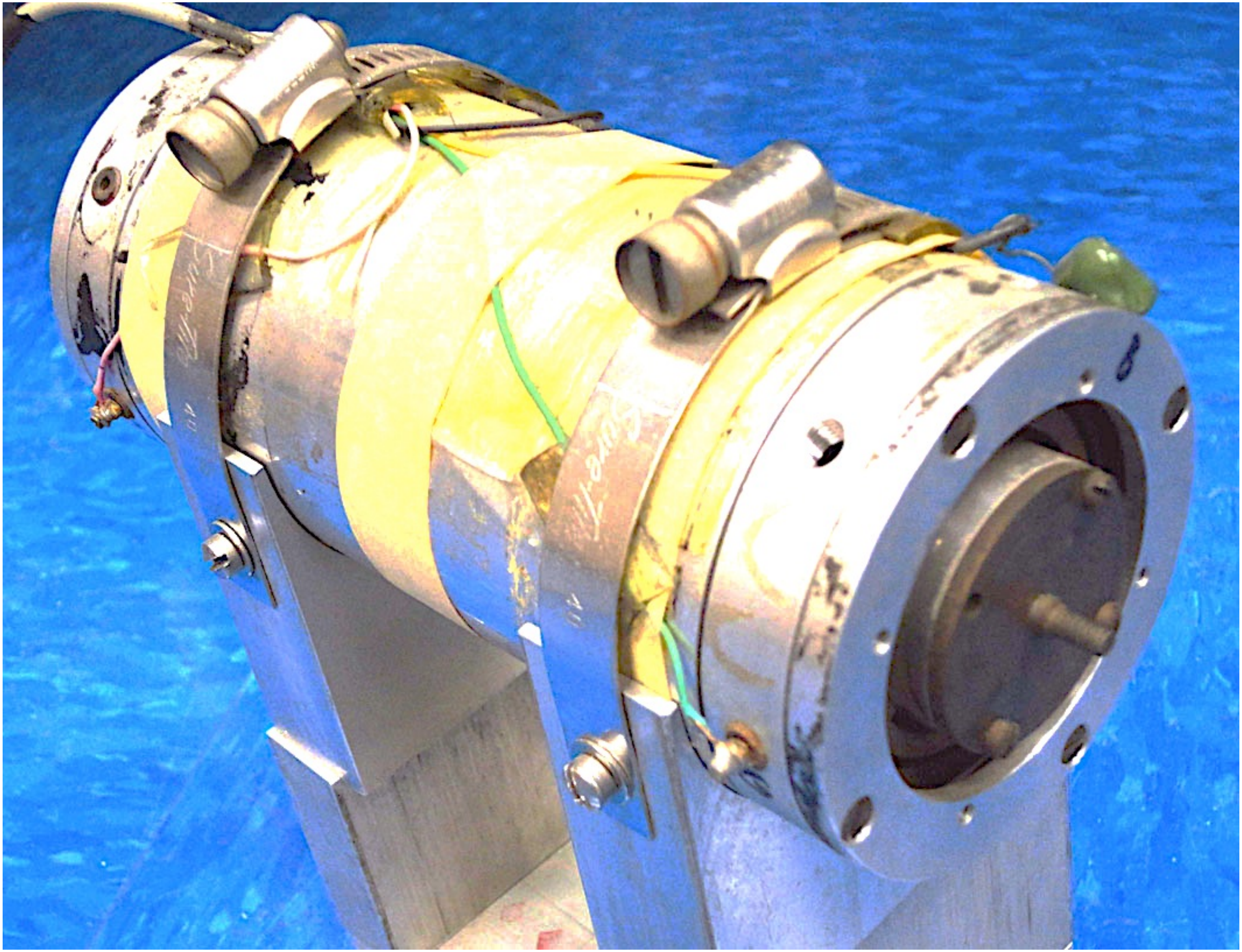




Doppler shift to
tune γ-ray energy

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

$\Delta E \sim 10^{-12}\ 10^{4} = 10^{-8}$ eV

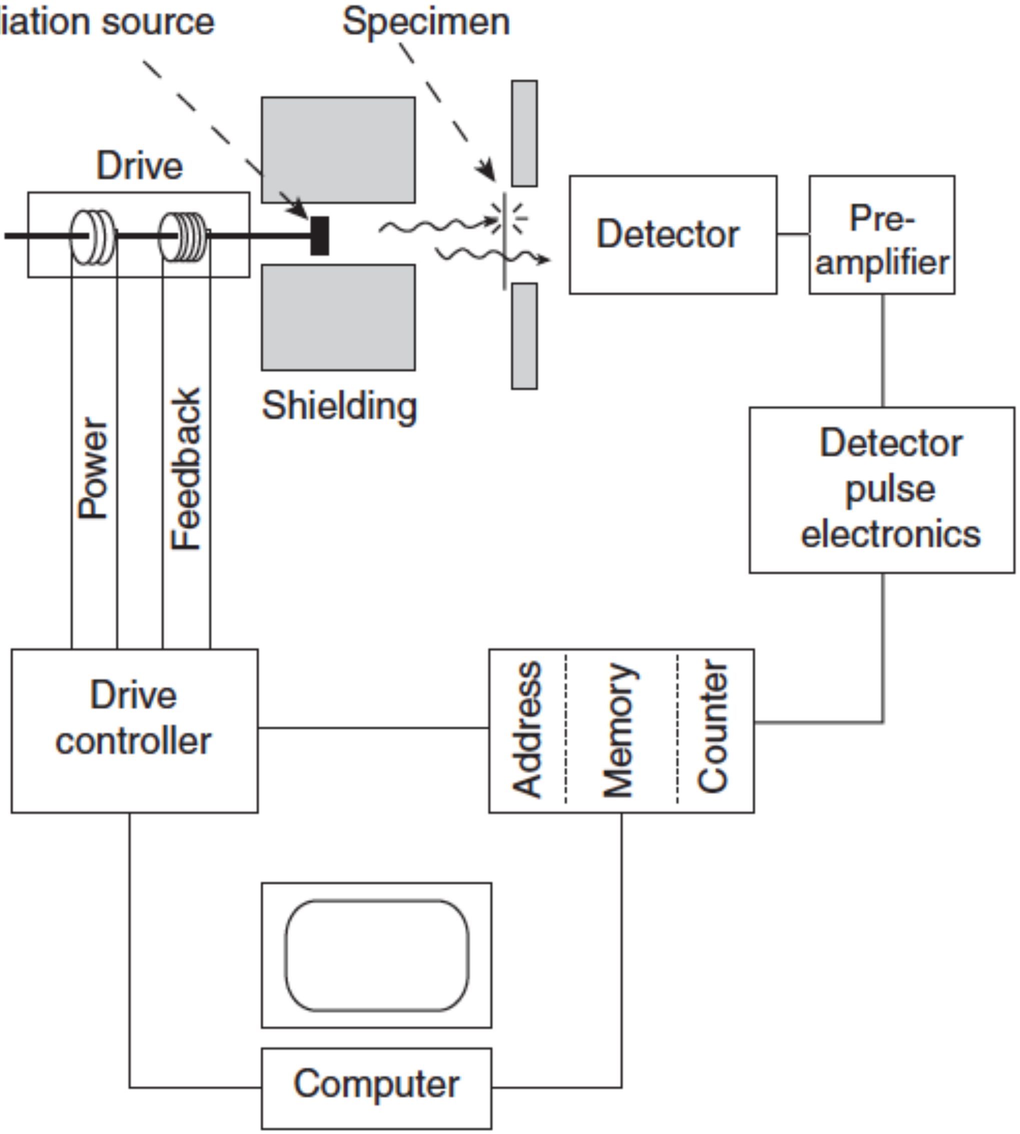


Mössbauer Spectrometer

Doppler shift to tune γ-ray energy

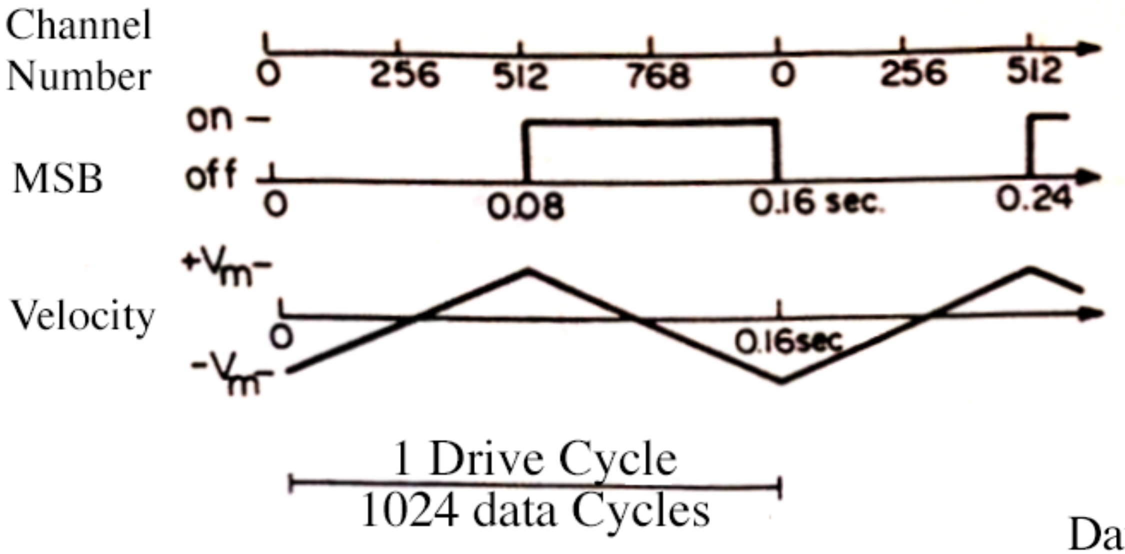
$$\Delta E = \frac{v}{c} E_\gamma$$

$\Delta E \sim 10^{-12}\ 10^{4} = 10^{-8}$ eV

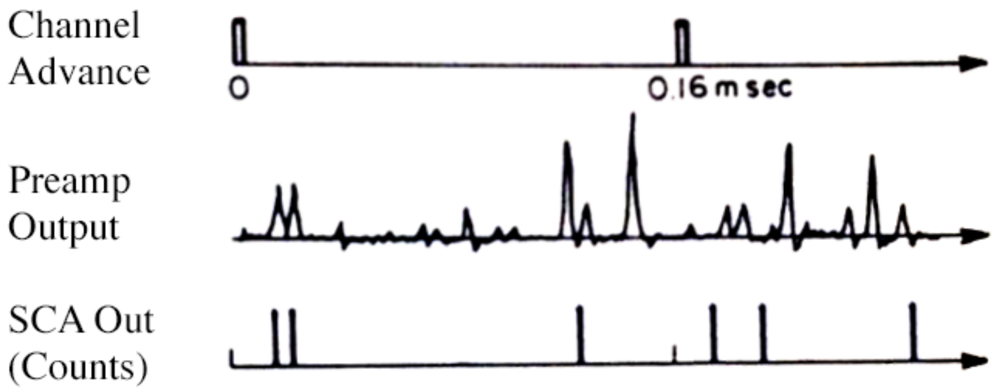


Mössbauer Spectrometer – Timing and Sync

Doppler Drive Cycle (sec)



Data Service (msec)



SAMPLE PREPARATION

The natural thickness of a specimen is t:

$$t \equiv (f_a n_a \sigma_a)^{-1}$$

where f_a is the recoil-free fraction of the Mössbauer isotope in the specimen, n_a is the number of Mössbauer nuclei/cm^3, and σ_a is the cross-section in units of cm^2.

For ^{57}Fe:

$$\sigma_a = 2.6 \text{ x } 10^{-18} \text{ cm}^2$$

SAMPLE PREPARATION

The natural thickness of a specimen is t:

$$t \equiv (f_a n_a \sigma_a)^{-1}$$

$$t = \left(0.80 \times 0.022 \times 7.86\,\mathrm{g/cm^3} \times \frac{1\,\mathrm{mol}}{55.85\,\mathrm{g}} \times 6.023 \times 10^{23}\,\mathrm{atoms/mol} \times 25 \times 10^{-19}\,\mathrm{cm^2} \times \frac{1}{4}\right)^{-1} \quad (30)$$

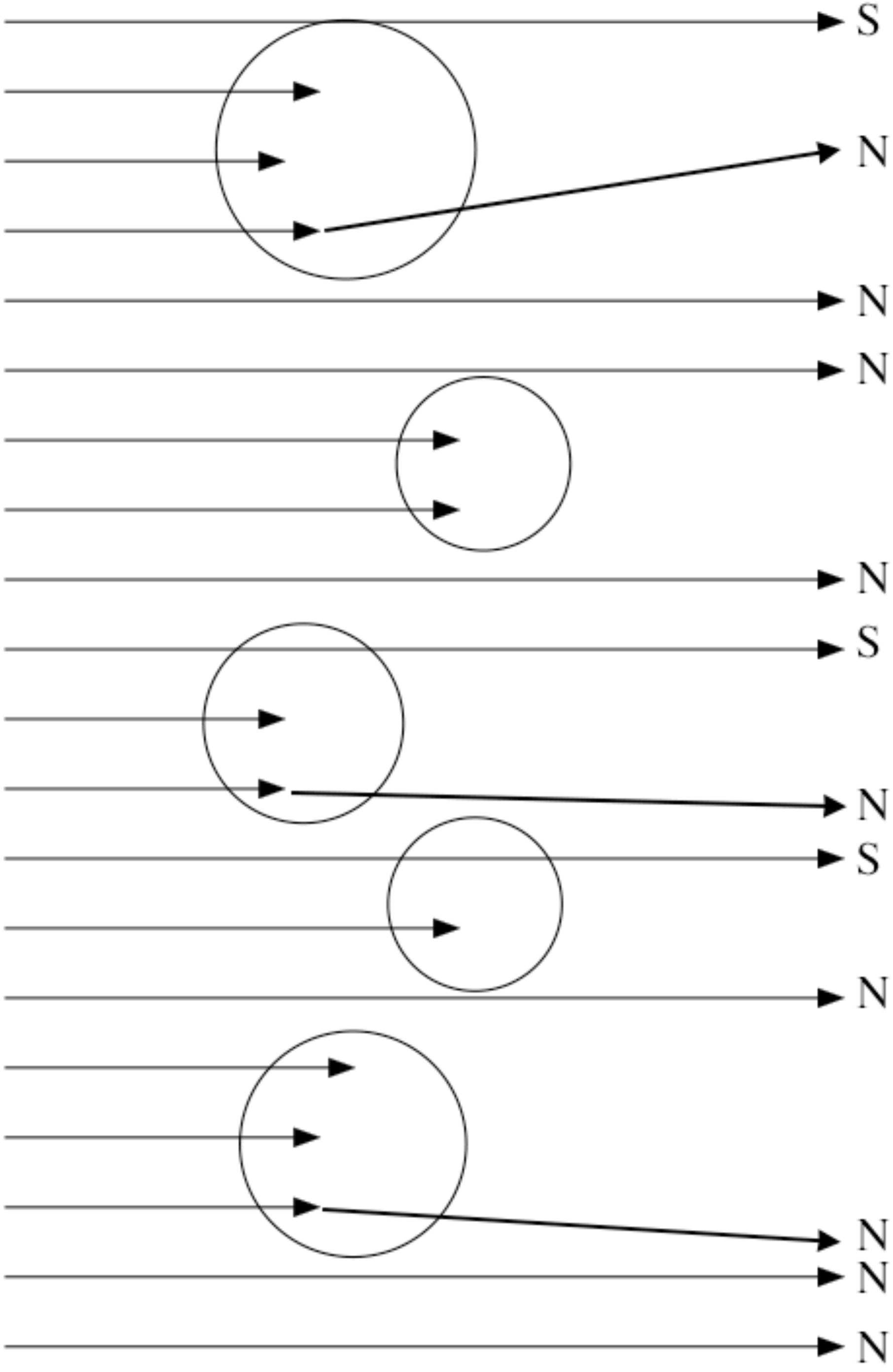
$$t = 11 \times 10^{-4}\,\mathrm{cm} = 11\,\mu\mathrm{m}$$

For single-line absorber, $t = 2.75\ \mu\mathrm{m}$

SAMPLE PREPARATION

For Fe in a light element matrix, just make the sample thicker.

For Fe in Pb, which is highly absorbing, it is not trivial to optimize the sample thickness for best singnal/noise ratio.
Usually, calculate the absorption length of 14.4 keV photons in Pb, and assume this is the best thickness.



Famous Mistake:
Lumpy Sample

High Absorption
High Noise
Low Signal

Hyperfine Interactions

The *s*-electron wavefunctions go inside the nucleus.

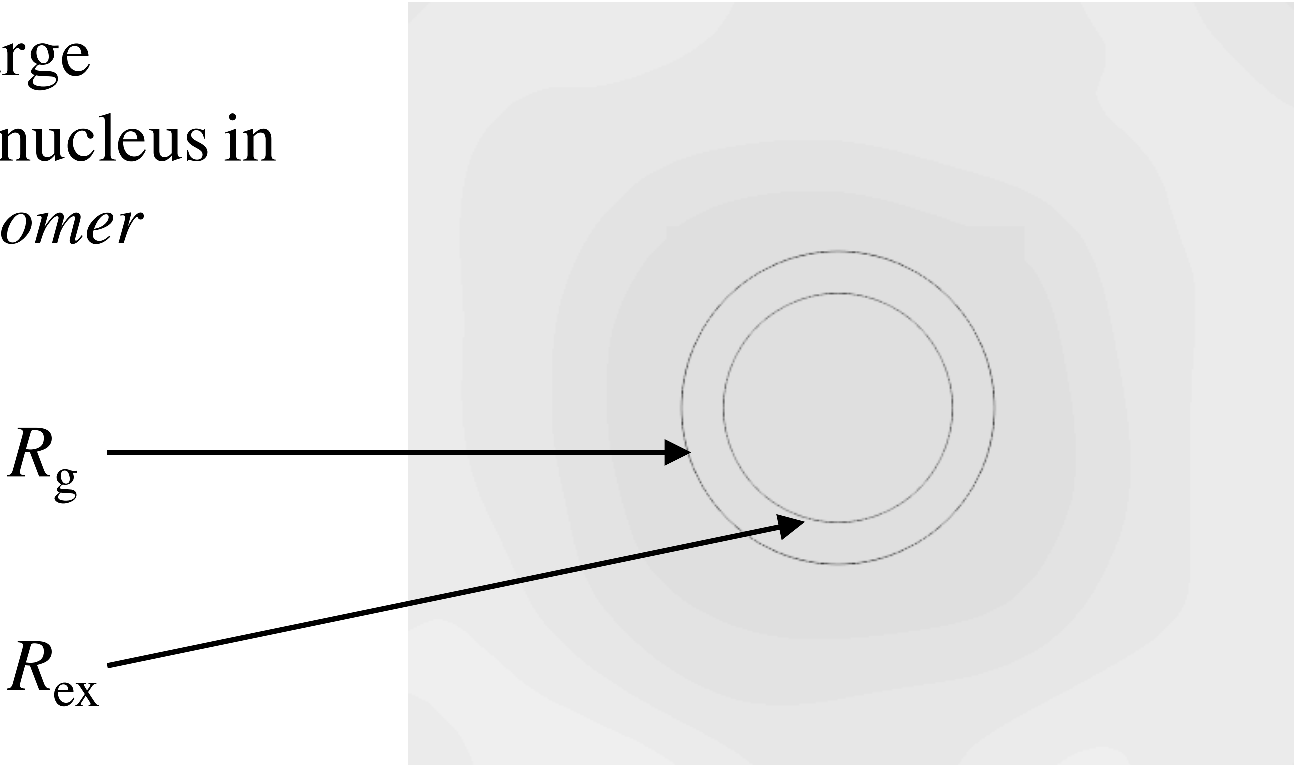
(Really! The electron kinetic energy would be too big if the electron were to swerve to avoid the nucleus.)
We see that ordinary *s*-electrons are at *r*=0 (without normalization):

$$\psi_{1s}(r) = \mathrm{e}^{-\frac{Zr}{a_0}} \,,$$

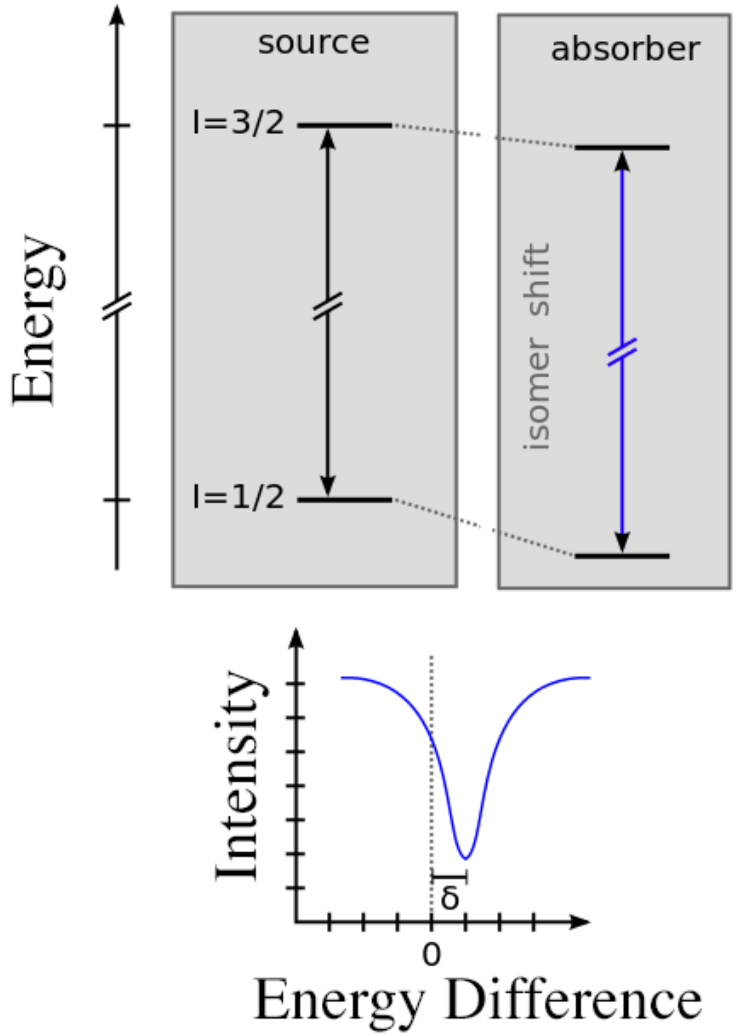
$$\psi_{2s}(r) = \left(2 - \frac{Zr}{a_0}\right) \mathrm{e}^{-\frac{Zr}{2a_0}}$$

Isomer Shift

Overlapping charge densities, larger nucleus in ground state "*Isomer Shift*"



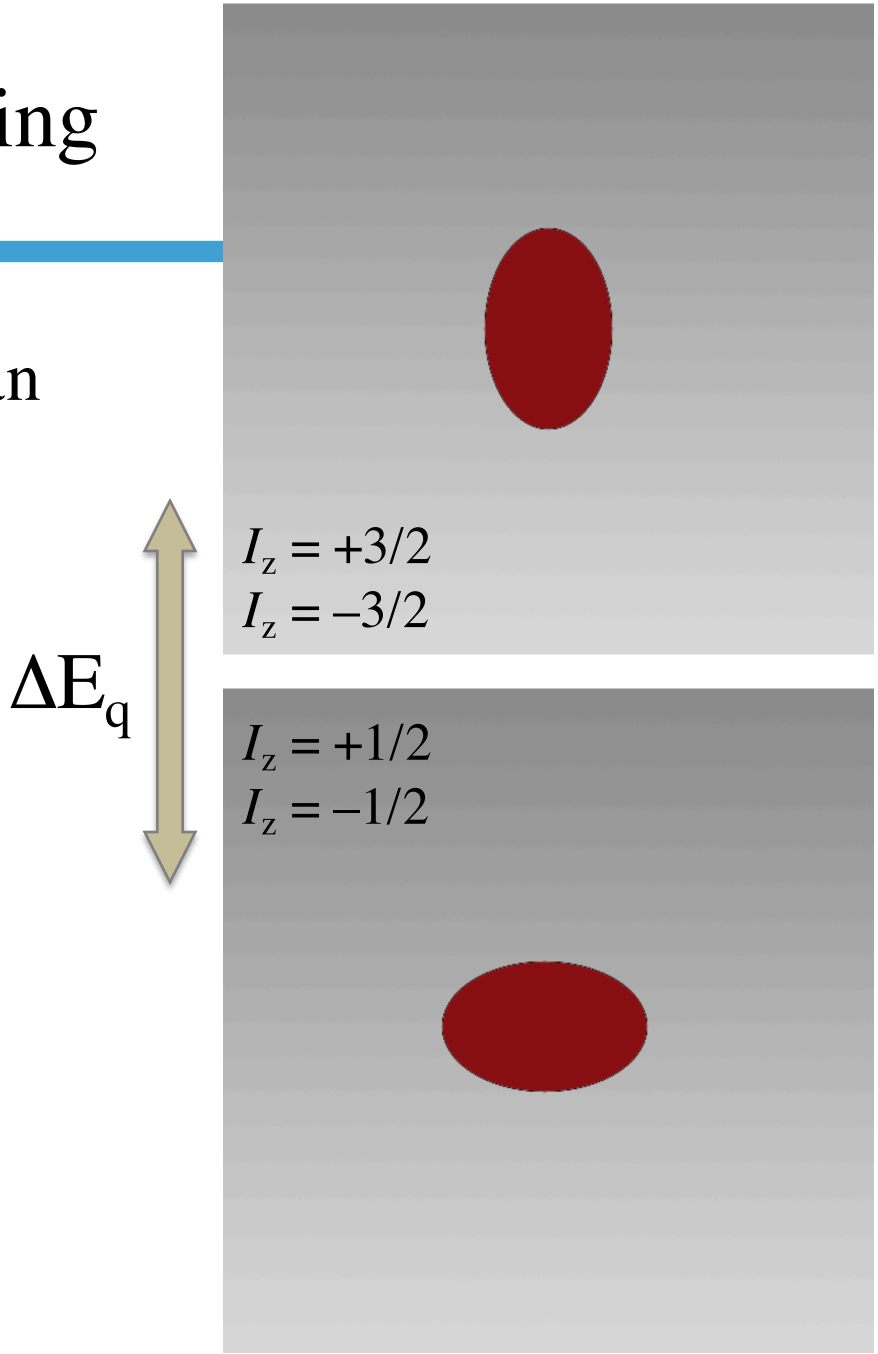
Isomer Shift



Electric Quadrupole Splitting

Nuclear quadrupole moment in an electric field gradient
"*Quadrupole Splitting*"

Excited state has angular momentum *I*=3/2, so it has a nonspherical shape.
Ground state is spherical.

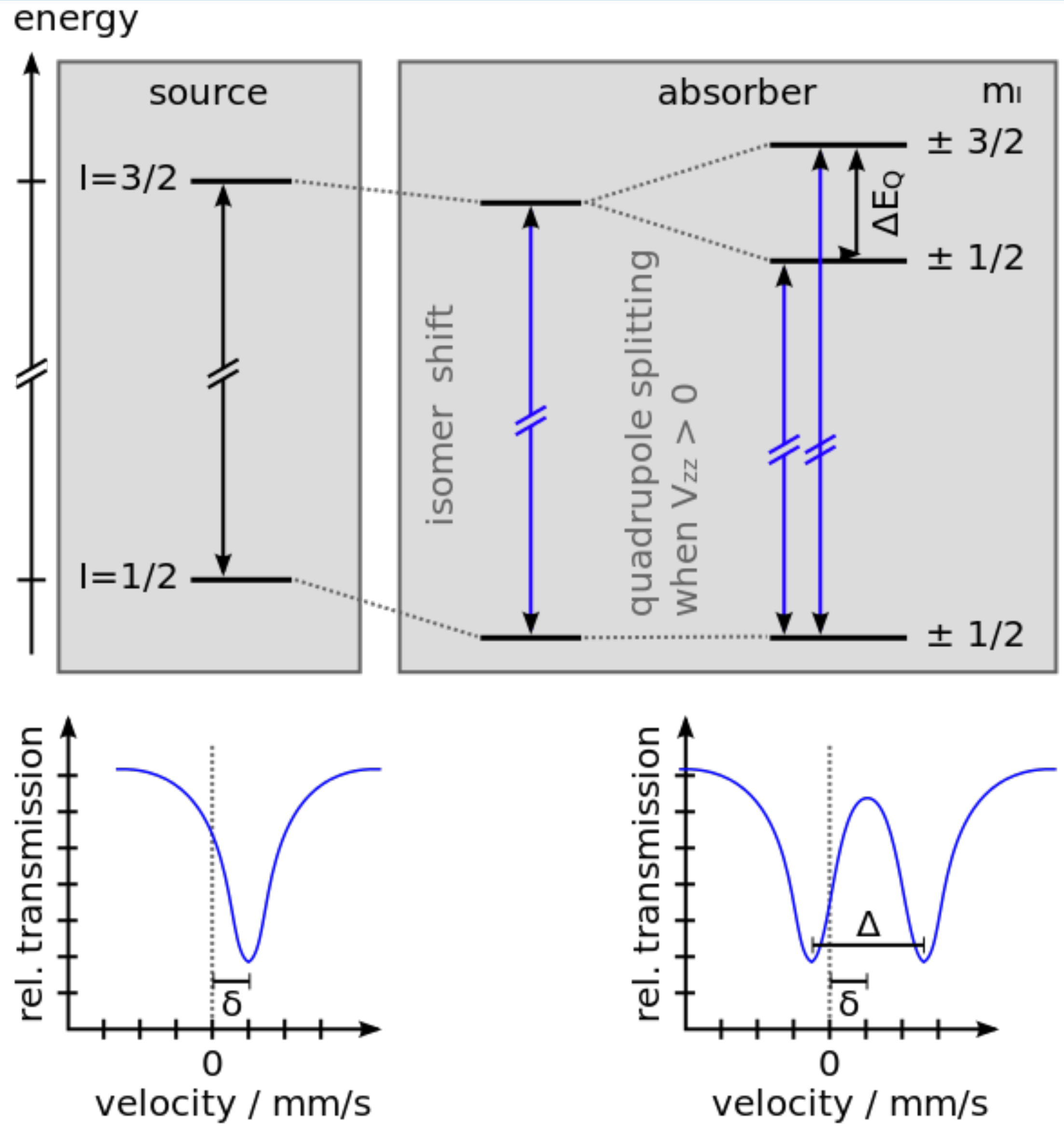


$I_z = +3/2$
$I_z = -3/2$

ΔE_q

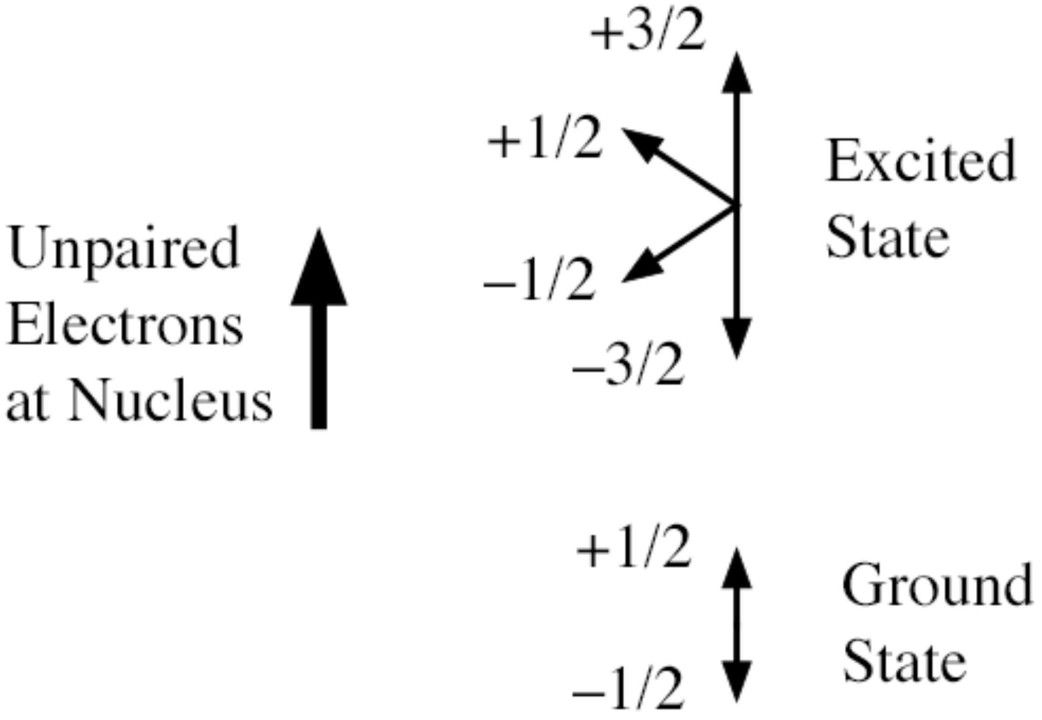
$I_z = +1/2$
$I_z = -1/2$

Electric Quadrupole Splitting Plus Isomer Shift

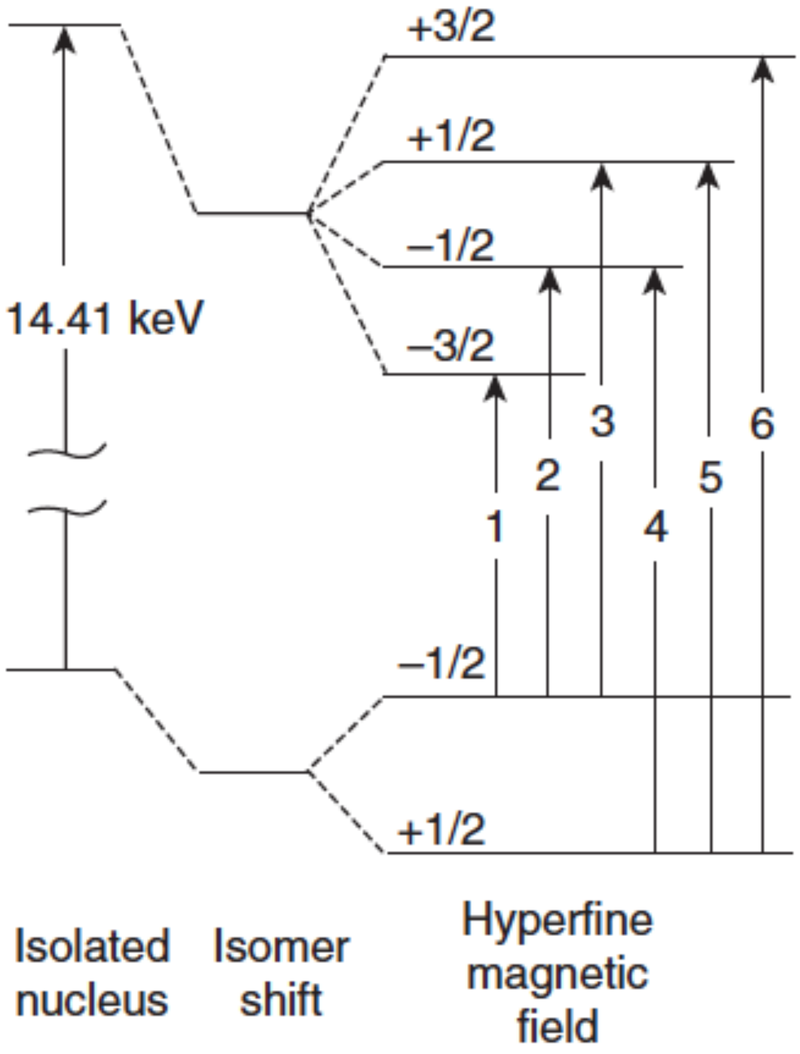


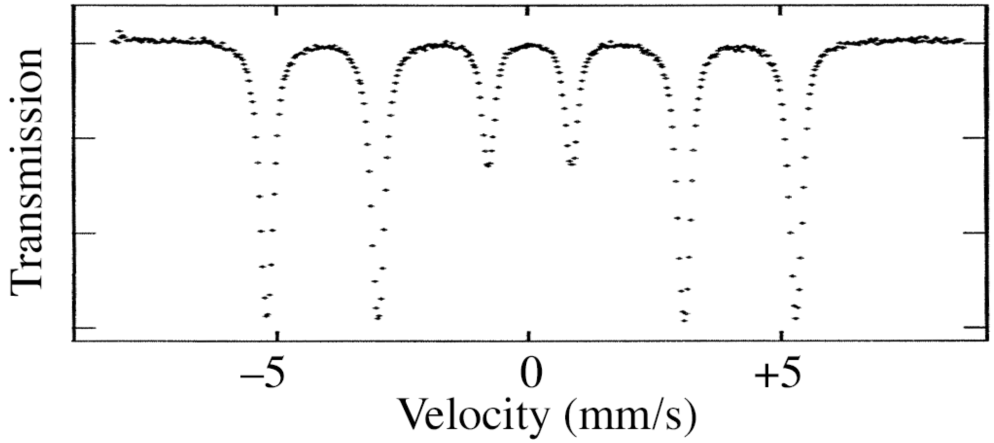
Hyperfine Magnetic Field

Nuclear spin and electron spin “*Hyperfine Magnetic Field*”



Hyperfine Energy Levels





Hyperfine Interactions

1) Overlapping charge densities "*Isomer Shift*"

$$\Delta E_{\mathrm{IS}} = CZe^2\left(R_{\mathrm{ex}}^2 - R_{\mathrm{g}}^2\right)|\psi_{\mathrm{sample}}(0) - \psi_{\mathrm{source}}(0)|^2 \qquad (21)$$

2) Nuclear quadrupole moment in an electric field gradient "*Quadrupole Splitting*"

$$\Delta E_{\mathrm{q}} = \frac{\pm 1}{4} eQV_{zz}\left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

3) Nuclear spin and electron spin "*Hyperfine Magnetic Field*"

$$H_{\mathrm{FC}} = -\frac{8\pi}{3} g_{\mathrm{e}} g_{\mathrm{N}} \mu_{\mathrm{e}} \mu_{\mathrm{N}} \mathbf{I} \cdot \mathbf{S} \delta(\mathbf{r}) \qquad (23)$$

$$H_{\mathrm{eff}} = \frac{8\pi}{3} g_{\mathrm{e}} \mu_{\mathrm{e}} S|\psi(0)|^2$$

4) Note: all have the form (nuclear factor)x(electronic factor)

Fingerprinting Method for Identifying Compounds

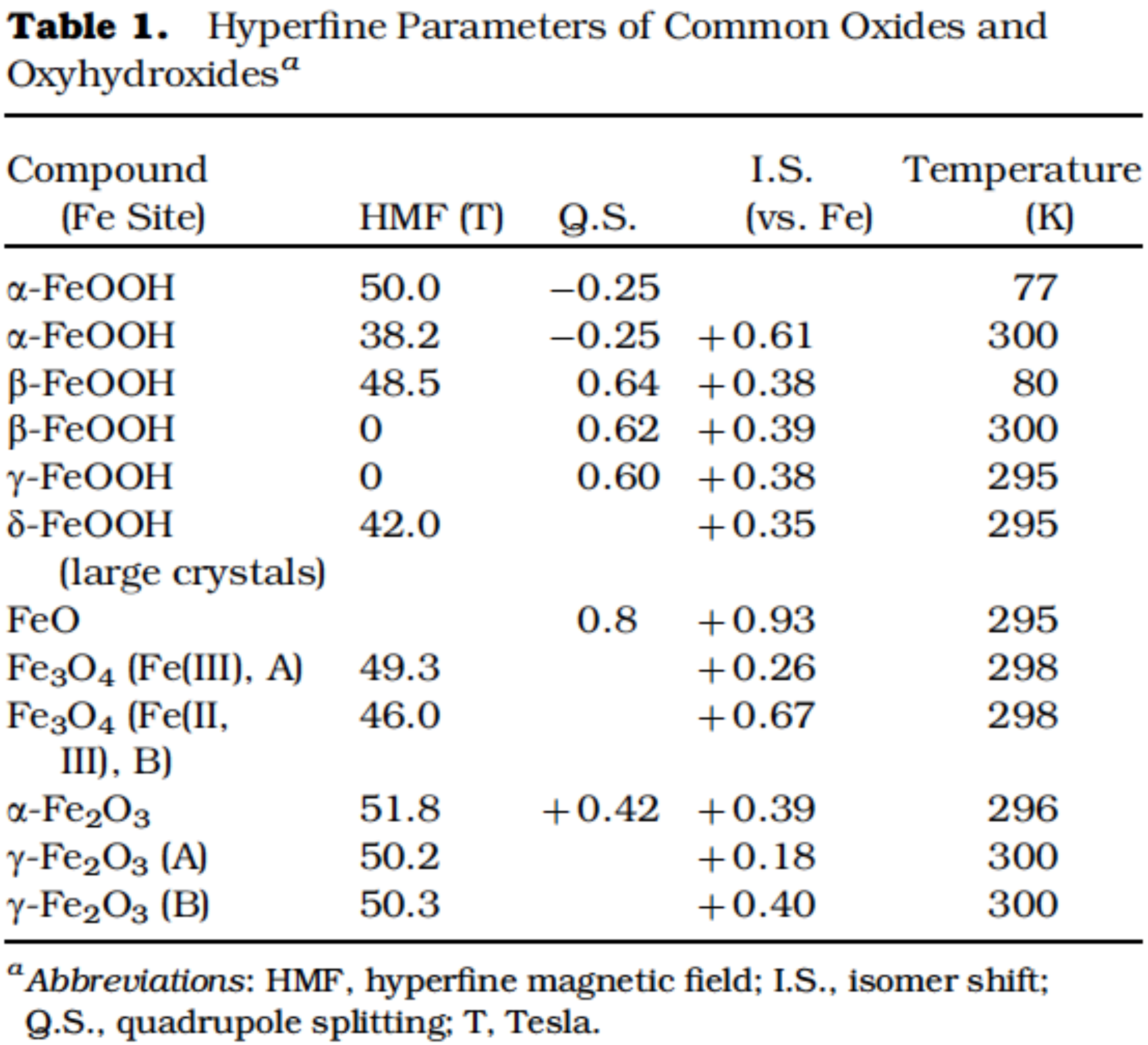


Table 1. Hyperfine Parameters of Common Oxides and Oxyhydroxides[a]

Compound (Fe Site)	HMF (T)	Q.S.	I.S. (vs. Fe)	Temperature (K)
α-FeOOH	50.0	−0.25		77
α-FeOOH	38.2	−0.25	+0.61	300
β-FeOOH	48.5	0.64	+0.38	80
β-FeOOH	0	0.62	+0.39	300
γ-FeOOH	0	0.60	+0.38	295
δ-FeOOH (large crystals)	42.0		+0.35	295
FeO		0.8	+0.93	295
Fe_3O_4 (Fe(III), A)	49.3		+0.26	298
Fe_3O_4 (Fe(II, III), B)	46.0		+0.67	298
α-Fe_2O_3	51.8	+0.42	+0.39	296
γ-Fe_2O_3 (A)	50.2		+0.18	300
γ-Fe_2O_3 (B)	50.3		+0.40	300

[a] *Abbreviations*: HMF, hyperfine magnetic field; I.S., isomer shift; Q.S., quadrupole splitting; T, Tesla.

Isomer Shifts for Fe ions

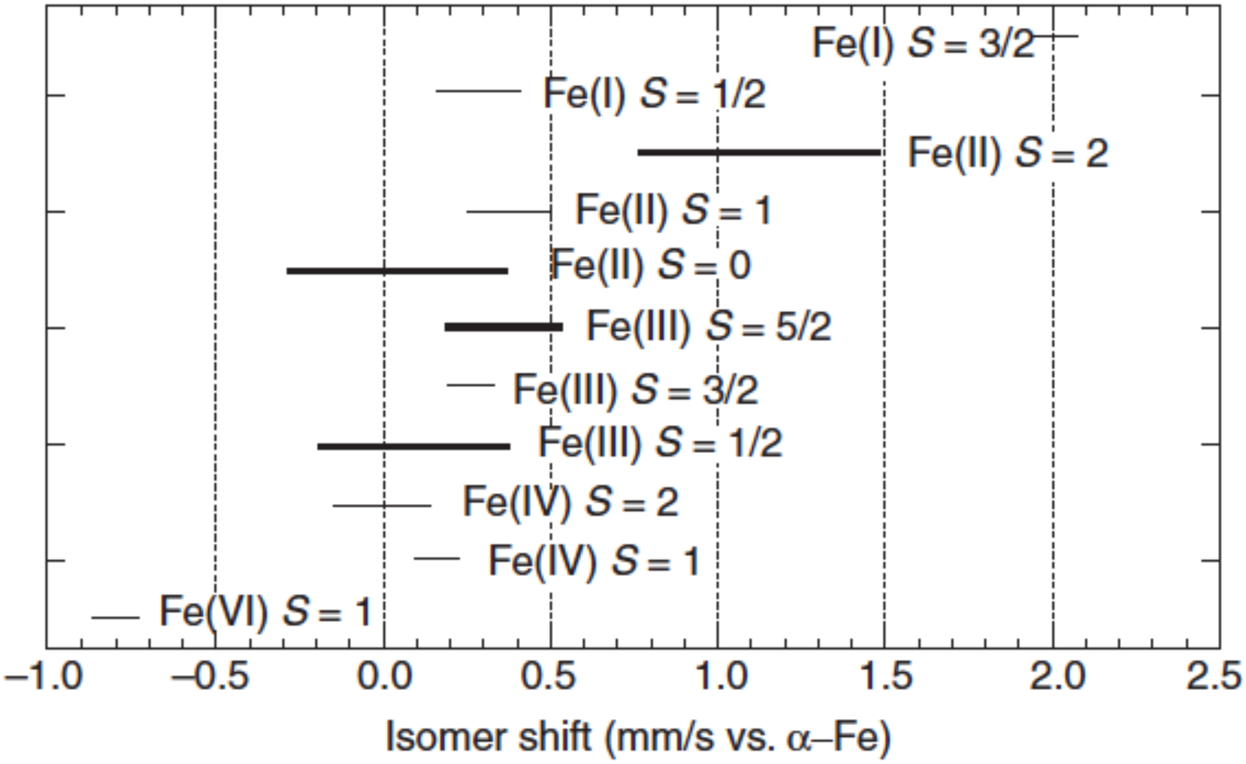
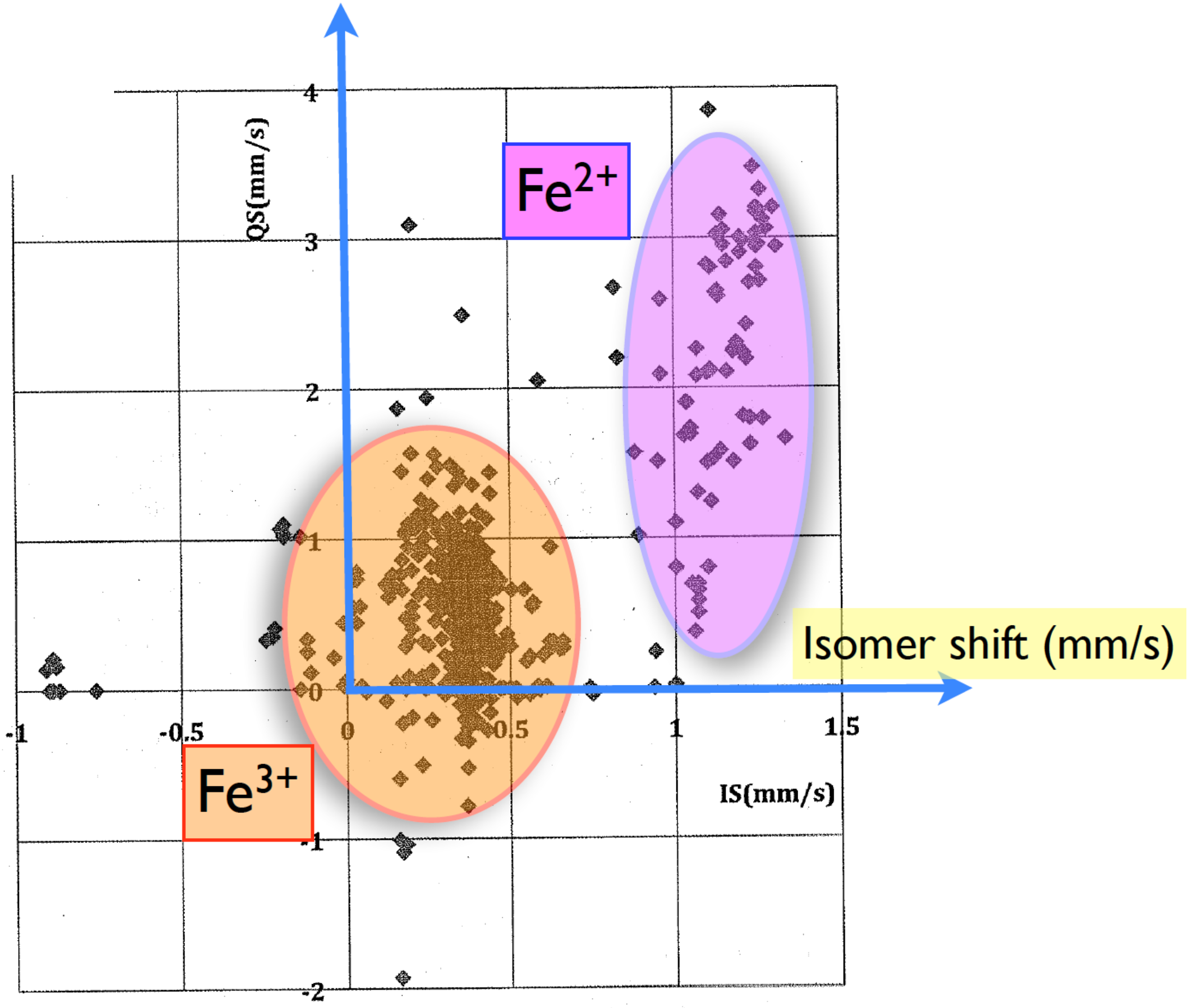
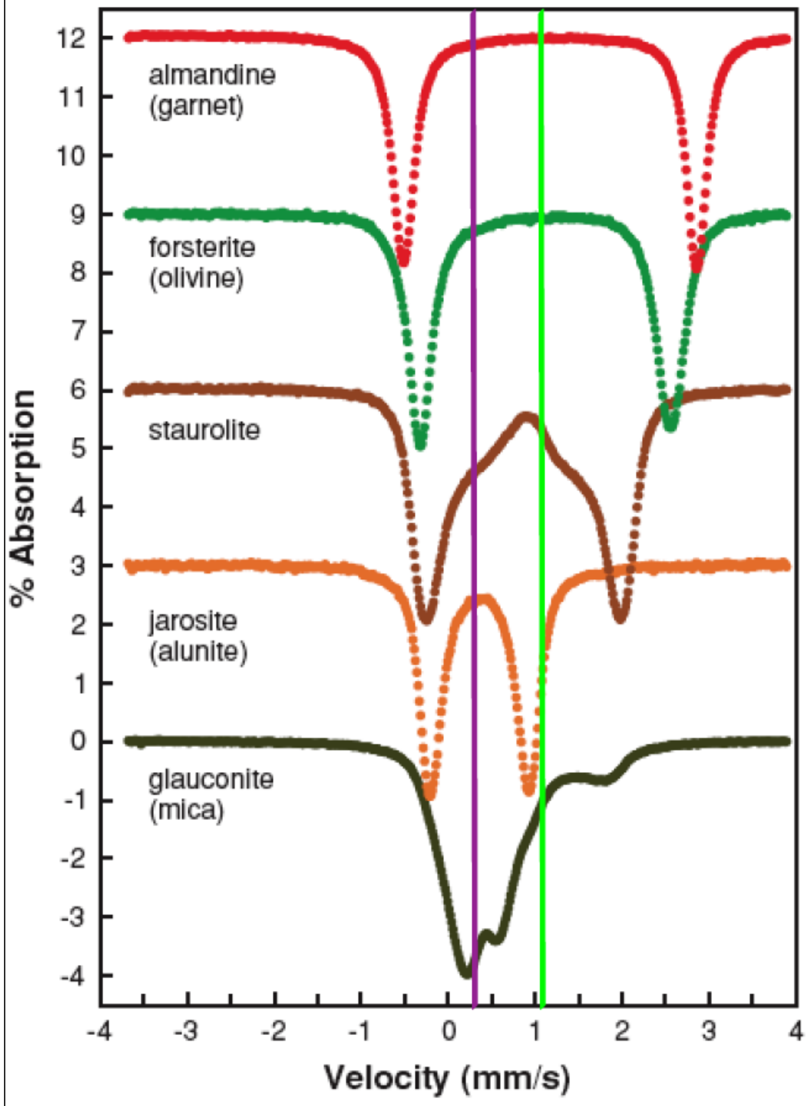
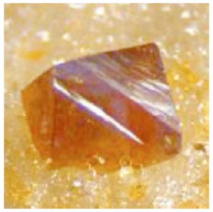
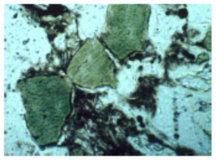


Figure 4. Ranges of isomer shifts in Fe compounds with various valences and spin states, with reference to bcc Fe at 300 K. Thicker lines are more common configurations (Greenwood and Gibb, 1971; Gütlich, 1975).

Combined Isomer Shift and Quadrupole Splitting



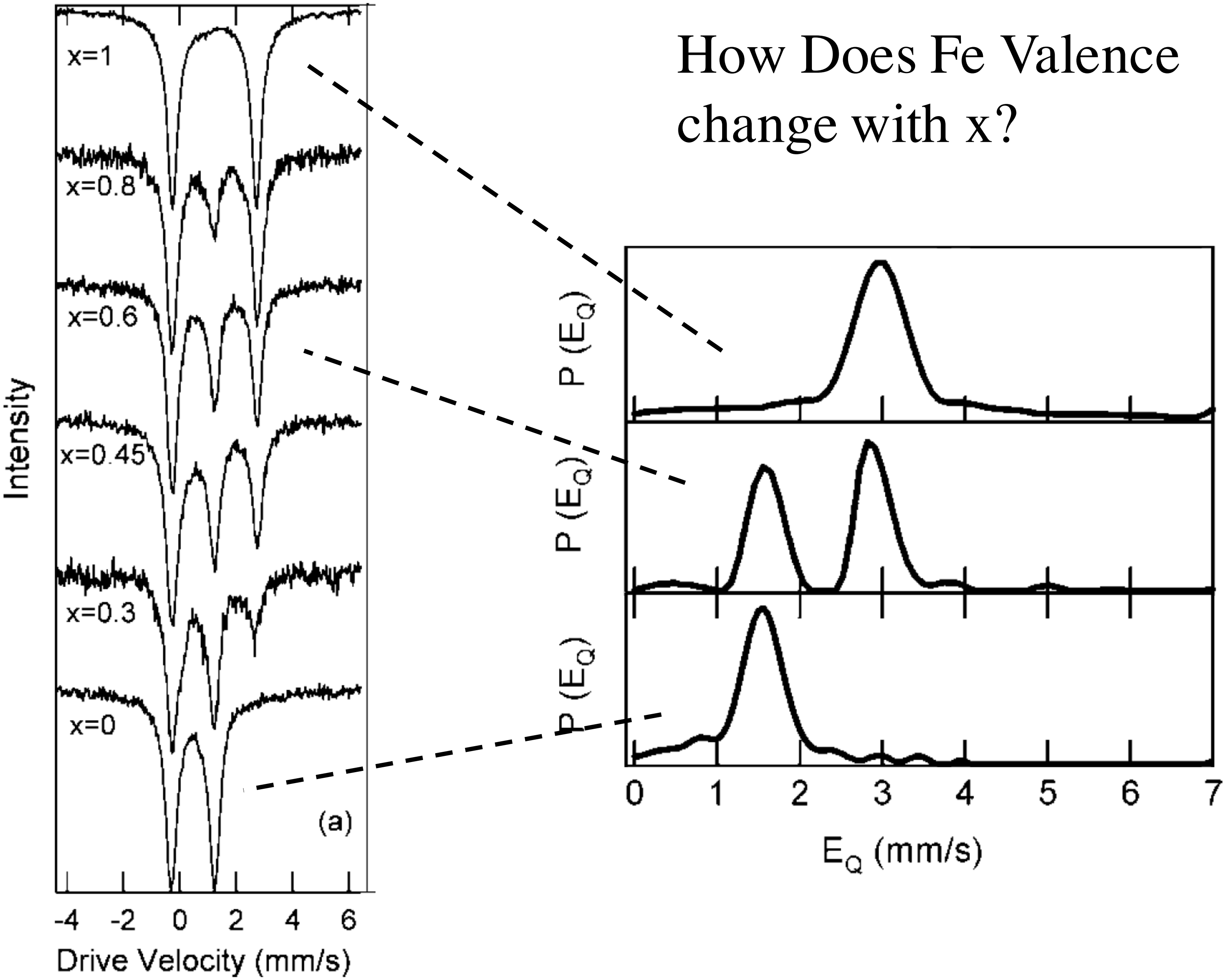


Fe^{2+}, cubic	$Fe^{2+}Al_2Si_3O_{12}$	
Fe^{2+}, octahedral	$(Mg,Fe)_2SiO_4$	
Fe^{2+}, tetrahedral	$Fe_2Al_9(SiO_4)_4(O,OH)_2$	
Fe^{3+}, octahedral	$KFe^{3+}{}_3(OH)_6(SO_4)_2$	
Fe^{3+}, tetrahedral	$(K,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	

M. Darby Dyar, et al, Ann. Rev. Earth. Planet. Sci, 34 (2006) 83

Isomer-Shifted Quadrupole Doublets of Li_xFePO_4

How Does Fe Valence change with x?



Usually the Fe Valence is Stable, But Exceptions…

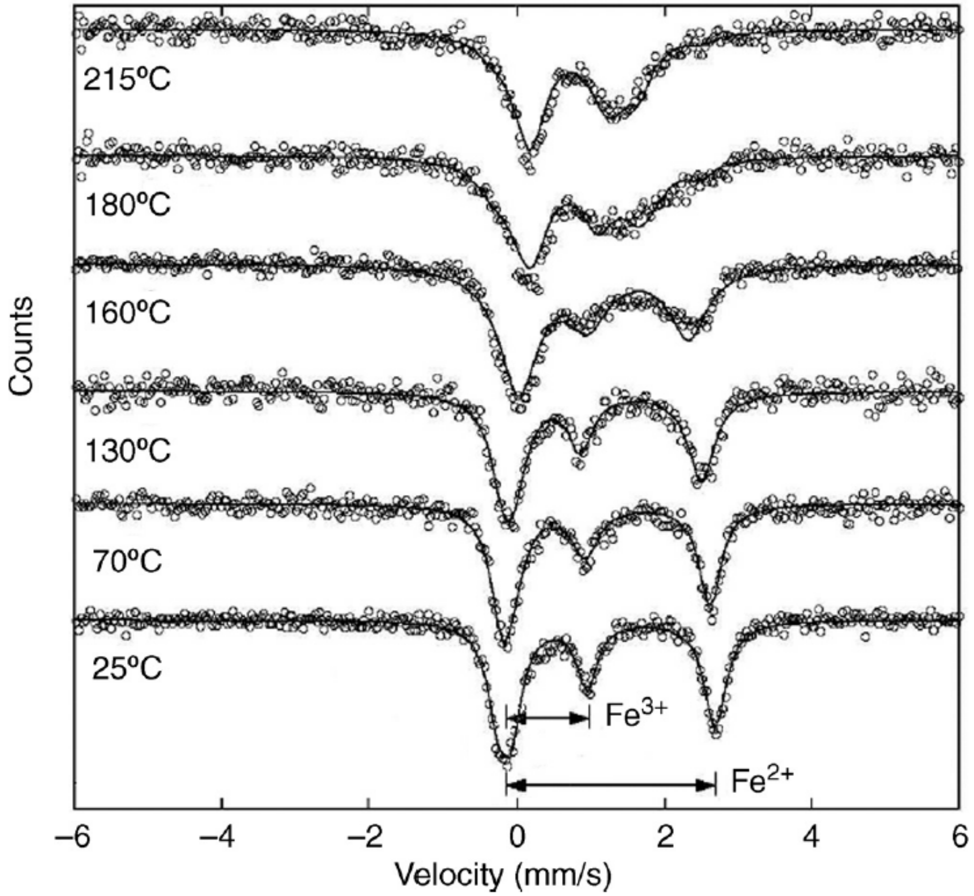


Figure 5. Mössbauer spectra of disordered solid solution of $Li_{0.6}FePO_4$ with the olivine structure, acquired *in situ* at elevated temperatures (Dodd et al., 2007). The merger of the two doublets occurs when the charge hopping frequency is of order of 10^8 Hz or faster.

Temperature dependence of IS and QS

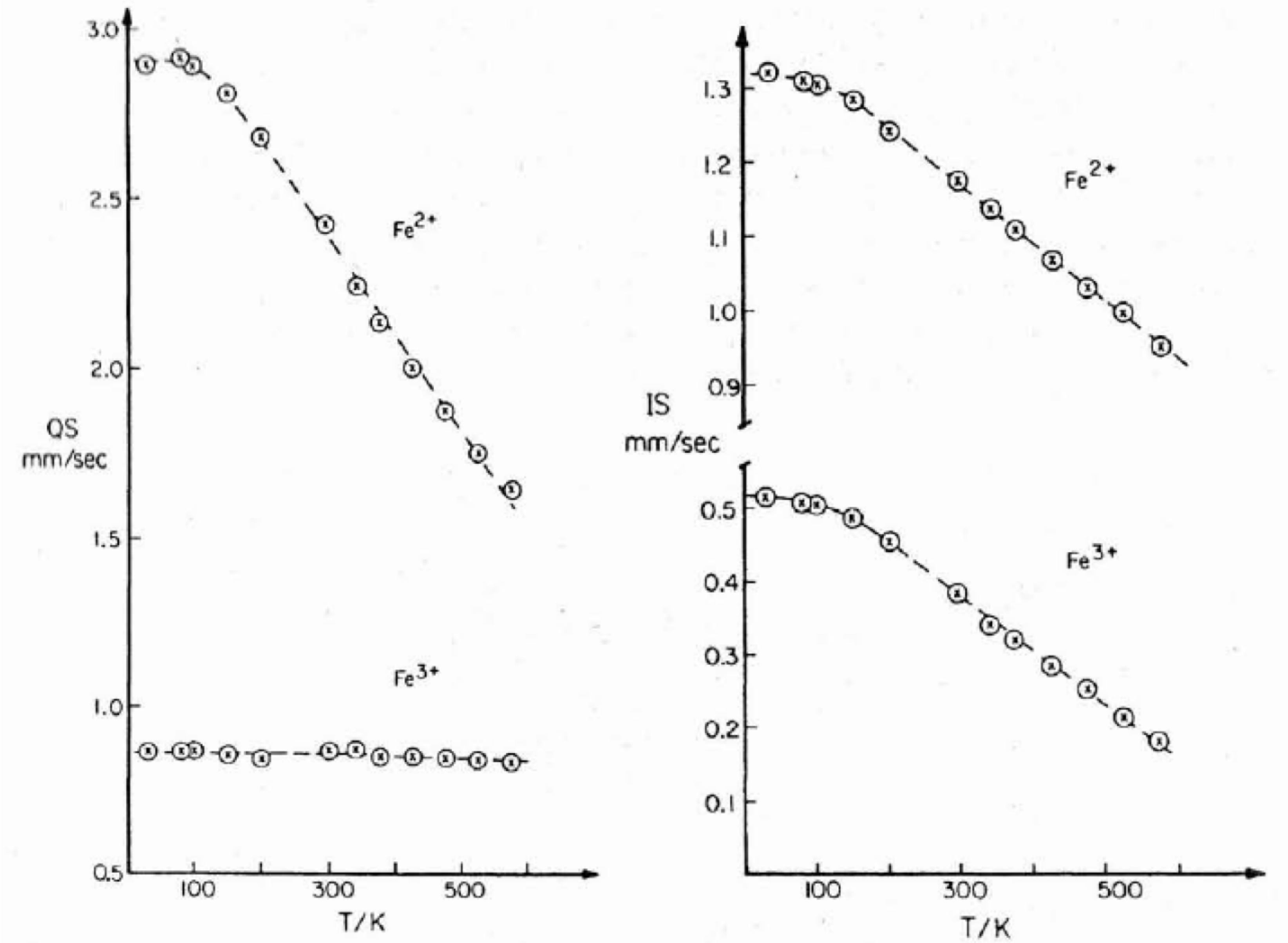
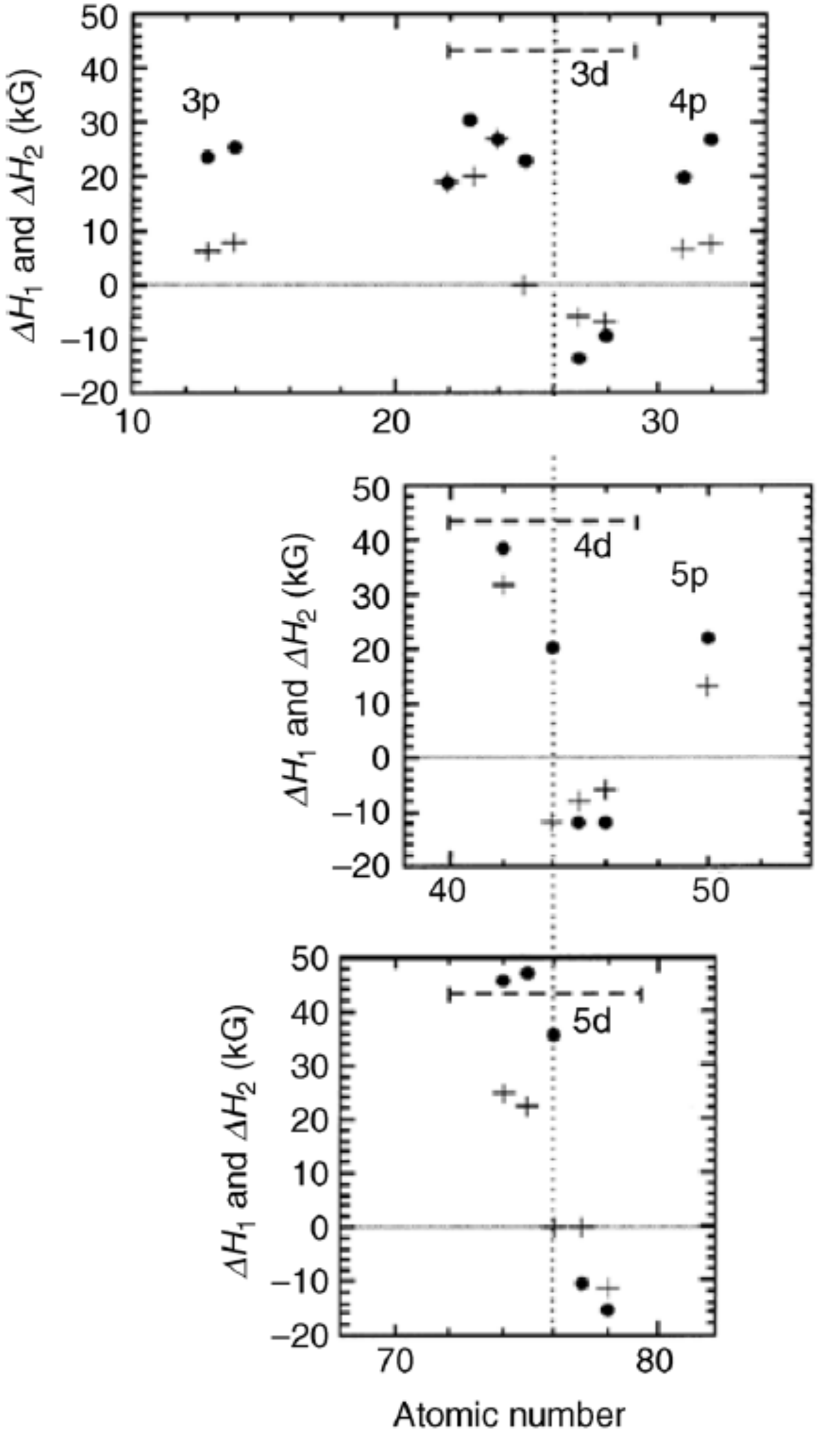


Fig. 8. ***(a)*** Quadrupole splitting QS (ΔE_Q) and ***(b)*** isomer shift IS (δ) of Fe^{2+} and Fe^{3+} in babingtonite, $Ca_2Fe^{2+}Fe^{3+}Si_5O_{14}OH$, plotted as function of the temperature (Amthauer, 1980).

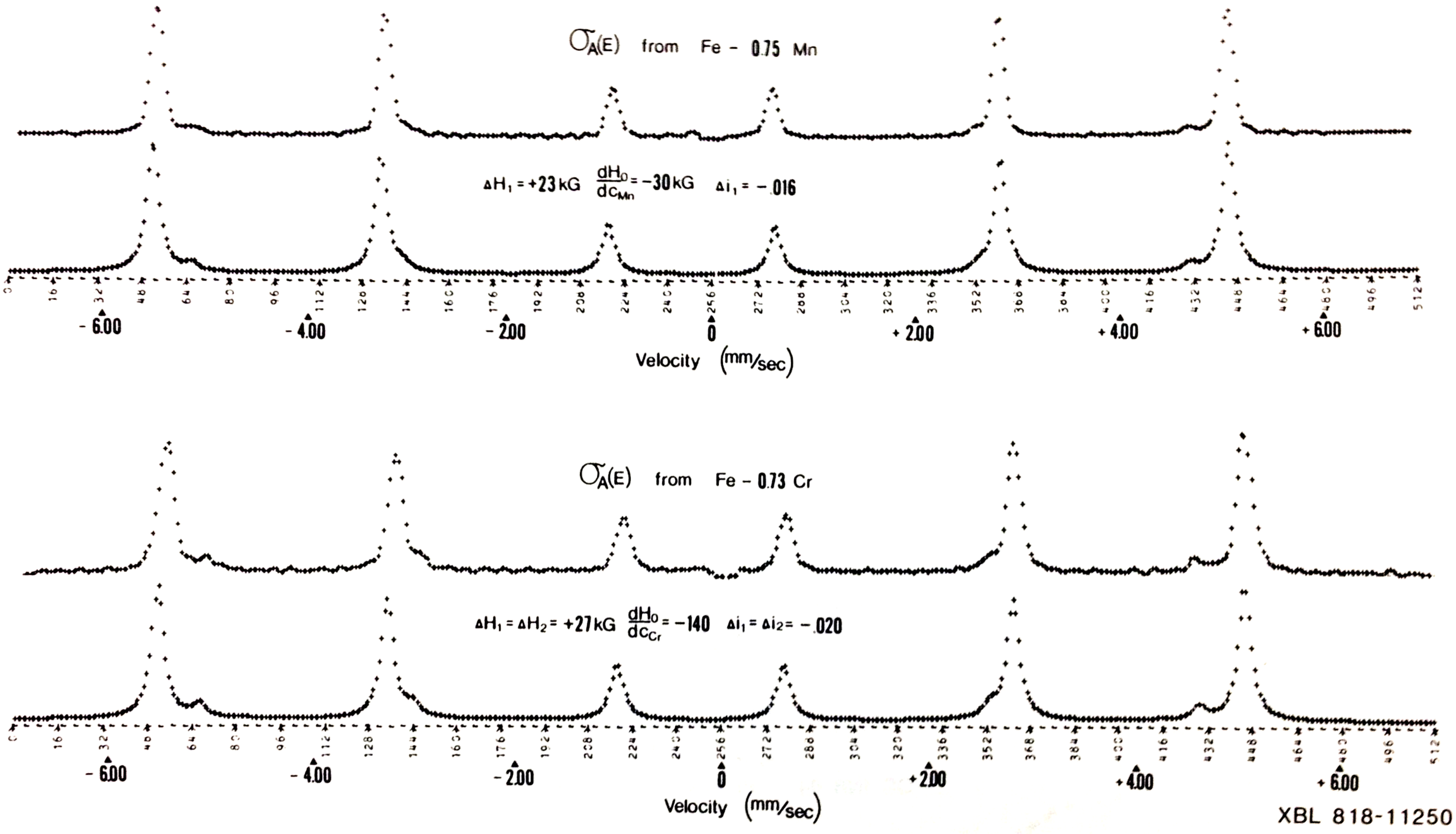
First Nearest Neighbors of ^{57}Fe Alter Its HMF

Phenomenological relation for dilute bcc Fe-X alloys

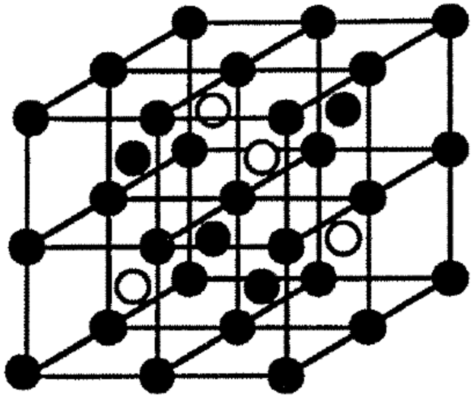
$$\Delta H = n_1\,\Delta H_1 + n_2\,\Delta H_2$$

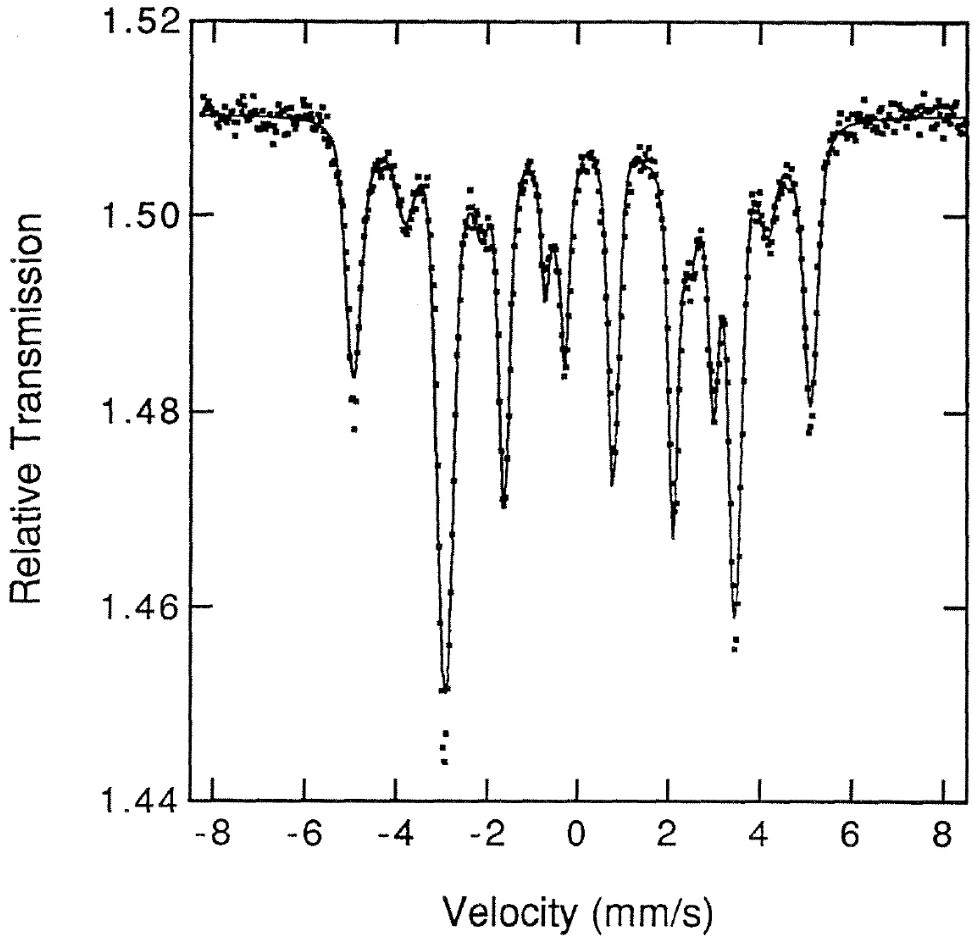


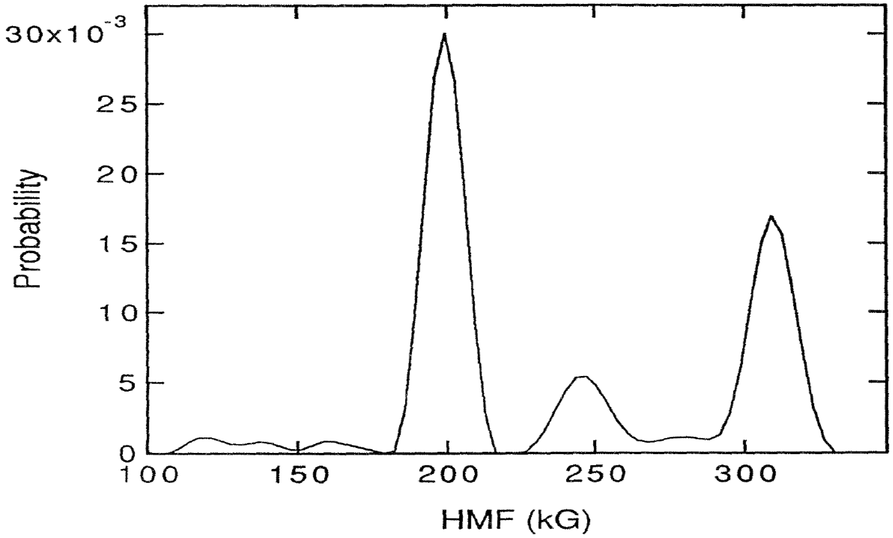
First Nearest Neighbors of ^{57}Fe Alter Its HMF



Fe_3Si Ordered Structure







Transmission Mössbauer spectrum from a well-ordered Fe_3Si sample. The dotted one is the experimental spectrum, and the fitted spectrum is shown as a solid line.

Chemical Ordering in bcc Fe_3Al Solid Solution

Sample prepared as disordered solid solution of Fe-25%Al.

Random numbers of 1nn Al neighbors.

Heated to develop the equilibrium structure that has 1/3 Fe atoms with 0 Al neighbors and 2/3 Fe atoms with 4 Al neighbors.

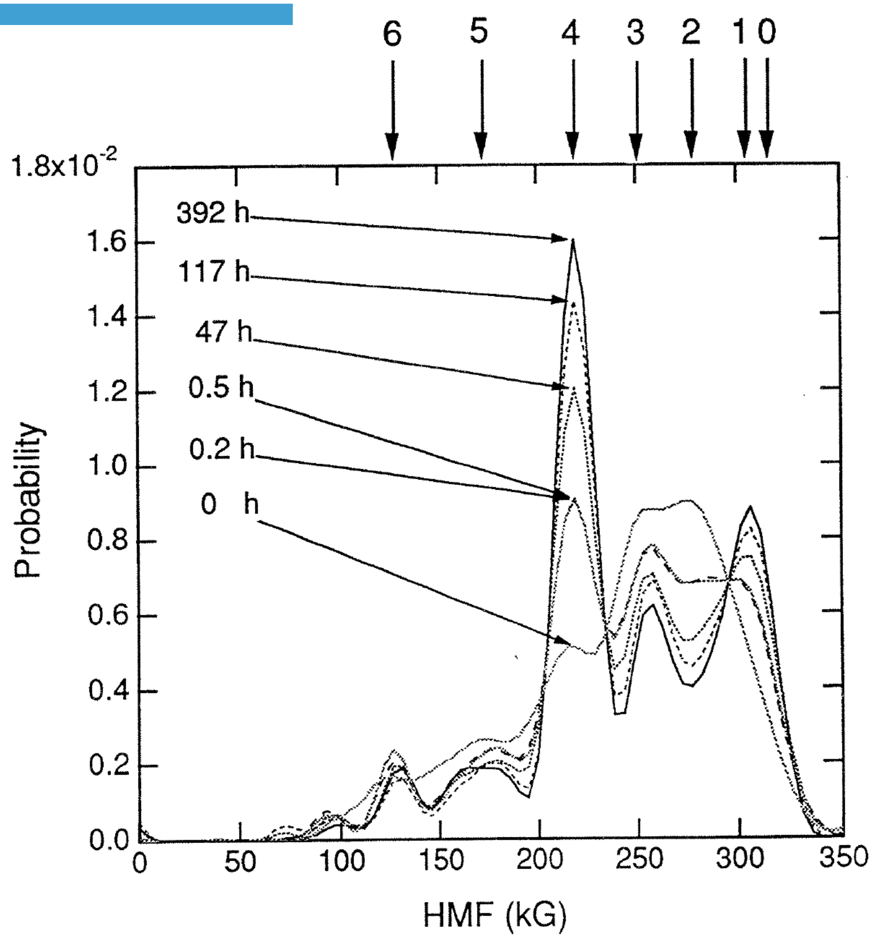
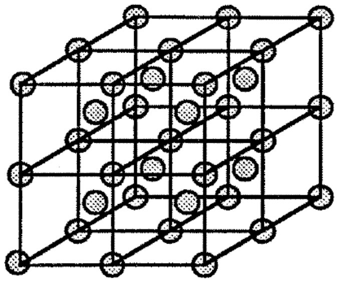
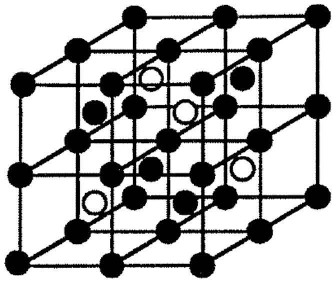


Figure 4.4 Hyperfine magnetic field distributions for the as-quenched Fe_3Al sample and Fe_3Al samples after annealing at 300 °C for various times. Number on top of the figure identify the resonances from ^{57}Fe atoms with different numbers of 1nn Al atoms.

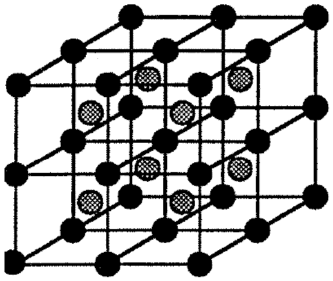
Kinetic Paths Through Independent Order Parameters



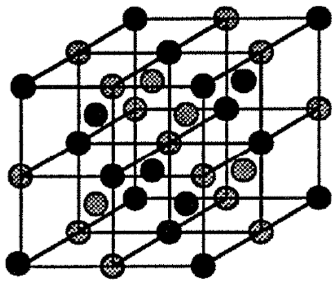
A2 or bcc disorder



$D0_3$ order



B2 order



B32 order

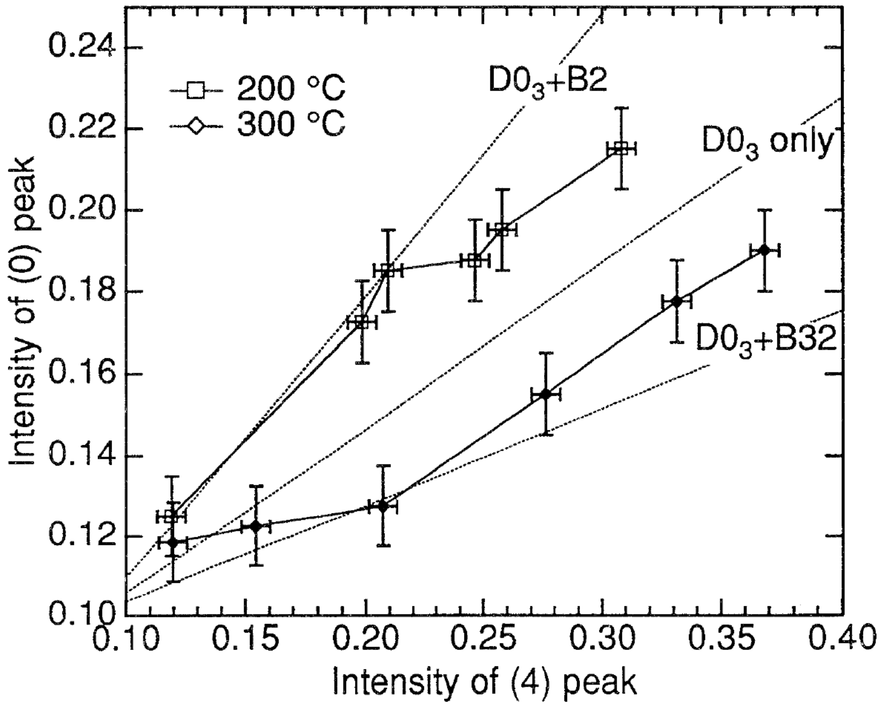


Figure 4.5 Experimentally derived kinetic paths of short range ordering (SRO) for Fe_3Al. The nearly-disordered initial state is on the lower left . The dotted lines were calculated by assuming the growth of $D0_3$ order only (center), 50% $D0_3$ order with 50% B2 order (top), and 25% $D0_3$ order with 75% B32 order (bottom).

WIEN2k

P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz
Inst. f. Materials Chemistry, TU Vienna

- Performs electronic structure calculations of solids using density functional theory (DFT).
- Uses the full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method.
- WIEN2k is an all-electron scheme including relativistic effects.

WIEN2k

- Electric field gradients, isomer shifts, hyperfine fields
- Spin-polarization (ferro- or antiferromagnetic structures), spin-orbit coupling
- X-ray emission and absorption spectra, electron energy loss spectra
- Phonons, with an interface to K.Parlinski's PHONON program

Is ε-Fe Magnetic?

Old Facts:

ε-Fe forms at 12 GPa pressure.
Requires diamond anvil cells, so small volumes.
Mössbauer spectrometry has shown it non-magnetic, even at 4 K.

New DFT Calculations:

Showed ε-Fe is antiferromagnetic, which would not be detected in bulk properties.
Calculations also show a cancellation of core and conduction electron contributions, so HMF~0.
Maybe Mössbauer spectrometry is insensitive to antiferromagnetism in pure ε-Fe?

How to Calculate HMF?

Need polarized electron density very close to nucleus, available from WIEN2k.

$$\mathbf{H}_{eff} = \frac{8\pi}{3}\mu_B \int_0^\infty \left[\rho_\uparrow(r) - \rho_\downarrow(r)\right] \delta_T(r) dr$$

$$\delta_T(r) = \frac{1}{4\pi r^2} \frac{r_T/2}{(r + r_T/2)^2}$$

$$\text{Thomson radius } r_T = \frac{Ze^2}{mc^2}$$

Antiferromagnetic ε-Fe with some Ni in it

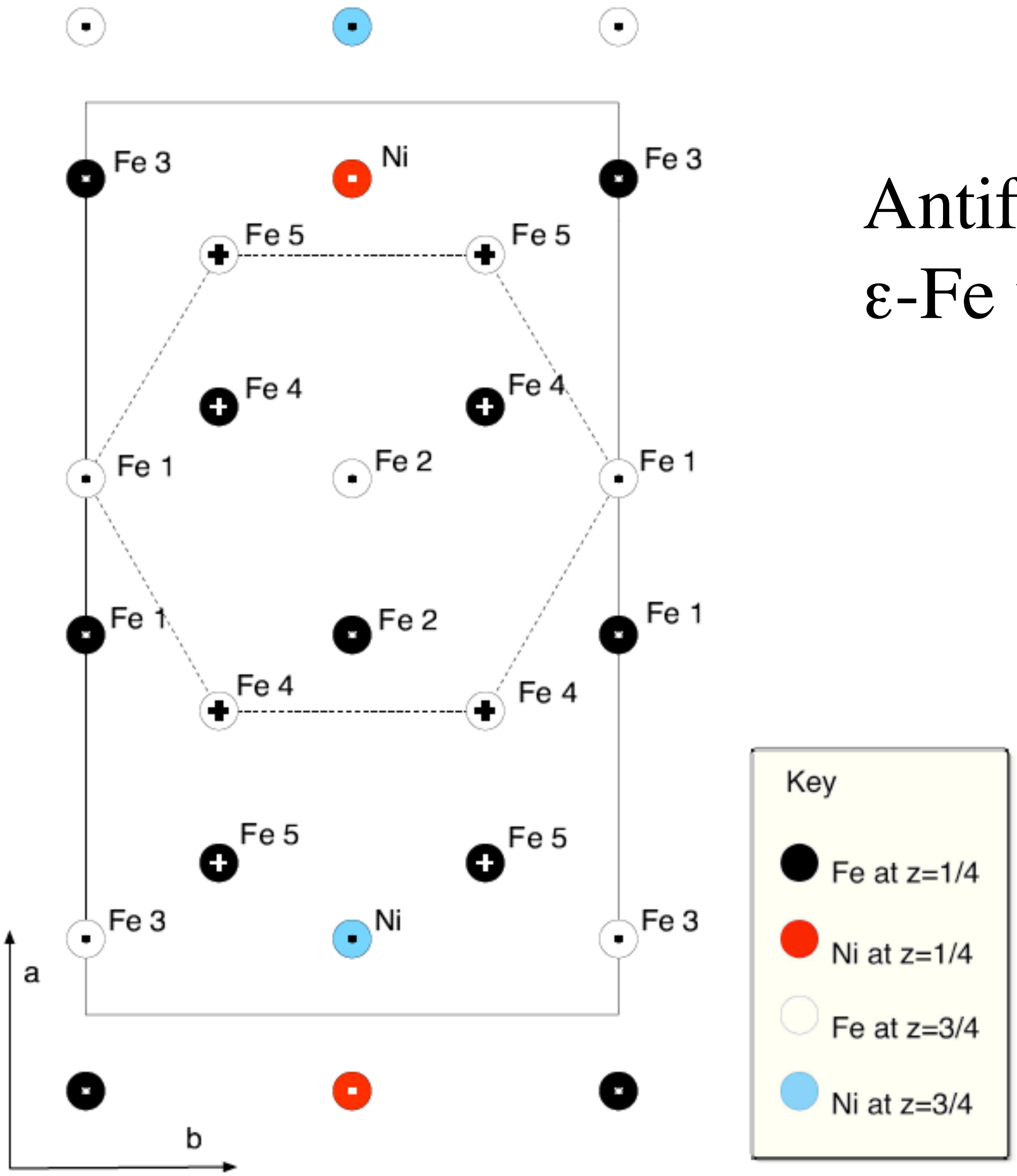


Figure 6.2: The Fe_7Ni_1 supercell with the *afmII* spin structure. Crosses denote a spin orientation pointing into the page, while circles indicate spin pointing out of the page.

Table 6.2: HMF at ^{57}Fe in ϵ-phase *afmII* Fe_7Ni_1[a] and ϵ-phase *afmII* Fe[b]

Atom	B_{val} [kG]	B_{core} [kG]	B_{tot} [kG]
pure Fe	89	-85	4
Fe 1 in Fe_7Ni_1	133	-108	25
Fe 2 in Fe_7Ni_1	117	-107	10
Fe 3 in Fe_7Ni_1	130	-91	39
Fe 4 in Fe_7Ni_1	-85	109	24
Fe 5 in Fe_7Ni_1	-102	168	66

---

[a] ϵ-phase *afmII* Fe_7Ni_1 at primitive cell volume 66.06 au^3

[b] ϵ-phase *afmII* Fe at primitive cell volume 65 au^3

Experiment showed non-magnetic ε-FeNi

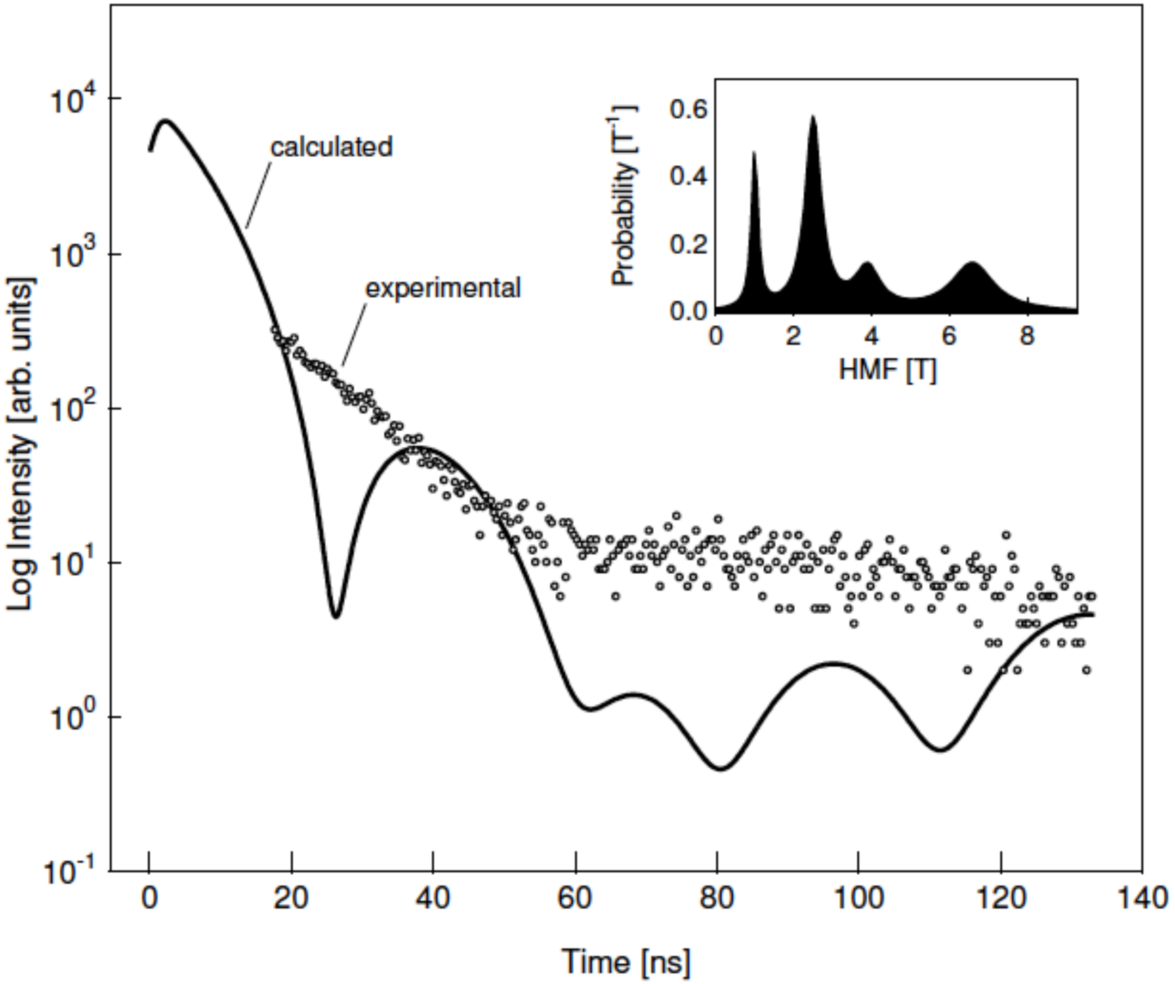
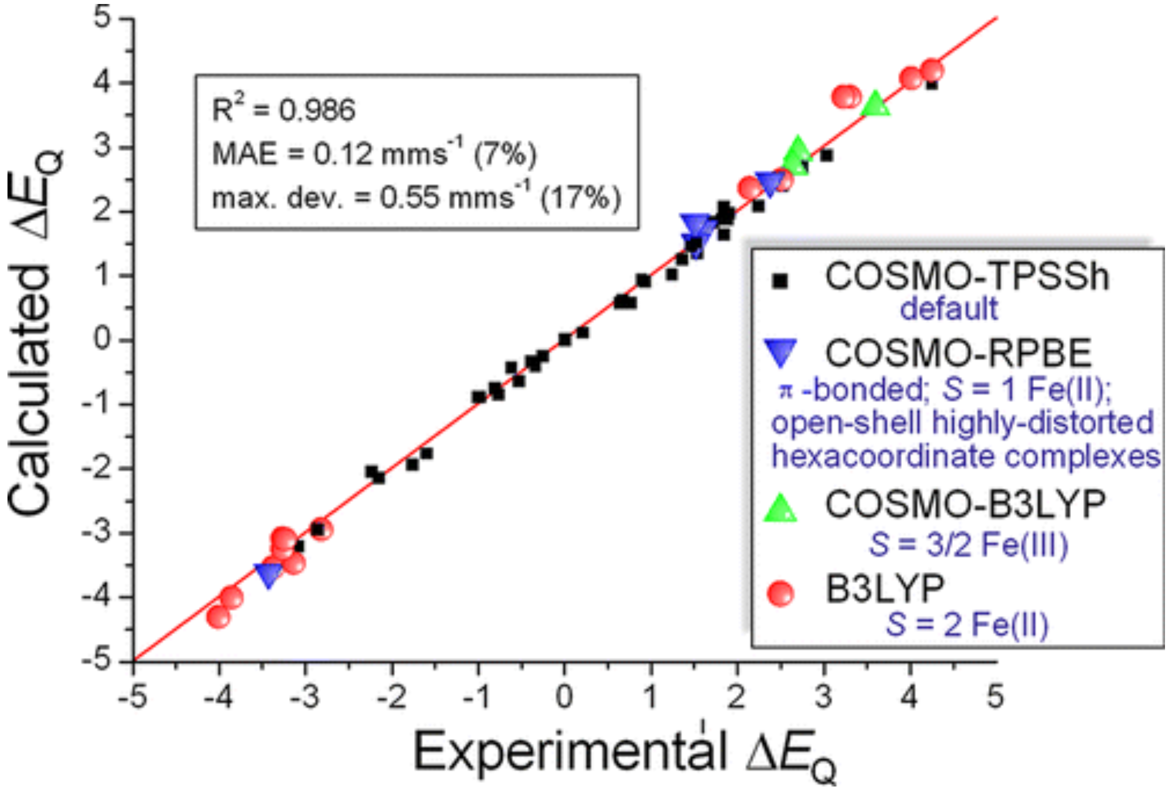


Figure 6.6: Experimental data from hcp $Fe_{92}Ni_8$ at 11 K and a simulated SMS spectrum generated with CONUSS based on DFT calculations of HMF in Fe_7Ni_1. The HMF distribution for the simulated spectrum is inset.

EFGs and ISs



On Predicting Mössbauer Parameters of Iron-Containing Molecules with Density-Functional Theory
Mátyás Pápai and György Vankó from Budapest, Hungary
J. Chem. Theory Comput., 2013, 9 (11), pp 5004–5020

Predicted IS and EFG for a diverse set of Fe complexes.
Sign of EFG is practical to calculate to augment experiment.

Mössbauer Community

Connection between nuclear physics and solids.

Elegance of the method has broad appeal.

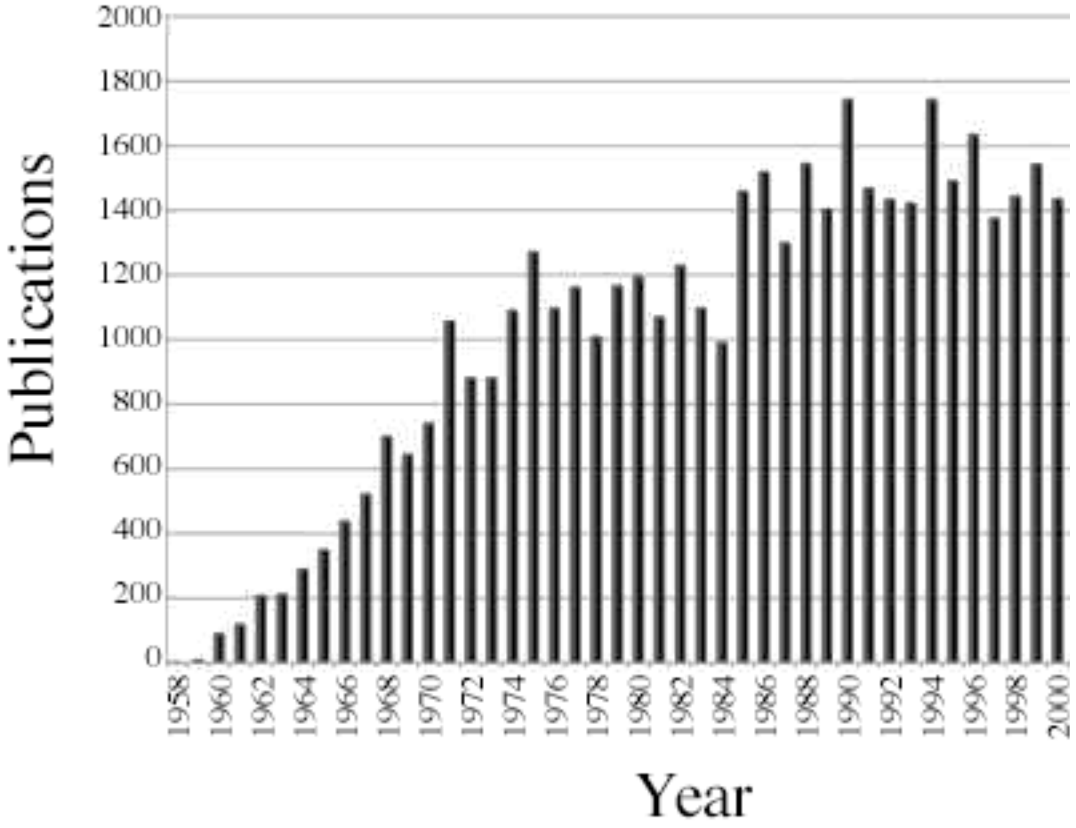
~500 attendees at ICAME, but no parallel sessions.

Effect named after a real person and his Ph.D. thesis work.

Nice words like hyperfine, resonance, excited, harmonic.

International family flavor of Mössbauer community.

Mössbauer Community



So What Happened?

Big drops of activity in USA, UK, Germany, France, Japan, India, China

Growing activity in Latin America, Africa, Oman

Rich get synchrotrons, but fewer of them.
Poor get Doppler drives.

So What Happened? (Opinion)

Anybody can do Mössbauer spectrometry.
Not everybody can interpret the spectra properly.
Even fewer can find cases where Mössbauer spectra give critical insight.
Rudolf Mössbauer described the community as “noisy.”

What Next? (Opinion)

Mössbauer spectrometry still offers a unique viewpoint of materials from the inside out.

Good work in relating the hyperfine structure to the local electronic or atomic structure can still be done with calibrations.
Today, though, we can do some calibrations with density functional theory and all-electron codes.

New opportunities are possible with a Doppler drive and DFT.

End of Presentation