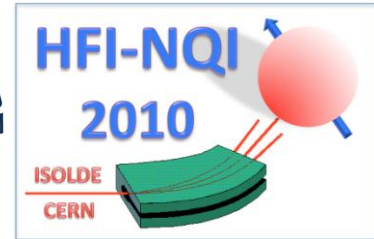
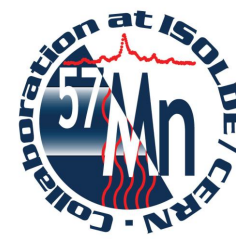


Magnetism in Iron Implanted Oxides: A Status Report



H. P. Gunnlaugsson/R. Sielemann,

^{57}Mn Mössbauer collaboration at
ISOLDE/CERN

^{57}Mn Mössbauer collaboration at ISOLDE/CERN

Århus: H. P. Gunnlaugsson,
G. Weyer

CERN: K. Johnston

Milan: R. Mantovan, M. Fanciulli

Reykjavík: T. E. Mølholt,
S. Ólafsson, H. P. Gíslason

South Africa: D. Naidoo,
K. Baruth-Ram, H. Masenda,
W. Dlamini, W. N. Sibanda

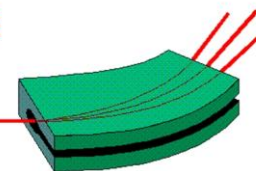
Leuven: G. Langouche

Berlin: R. Sielemann

Japan: Y. Yutaka, Y. Kobahashi



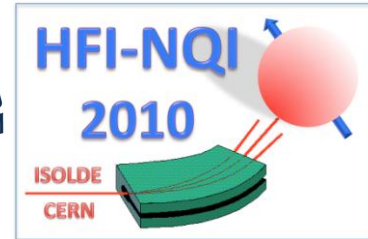
ISOLDE
CERN



HZB Helmholtz
Zentrum Berlin



Magnetism in Iron Implanted Oxides: A Status Report



Motivation (Magnetism in TM doped oxides)

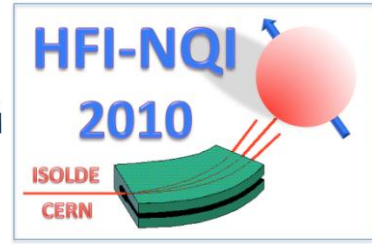
Physical/technical introduction (CERN Mössbauer)

Experimental spectra Mn/Fe in ZnO and others

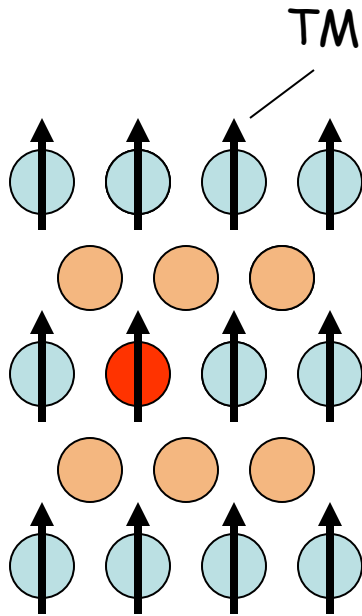
Ordered Magnetism versus Paramagnetism

Conclusion

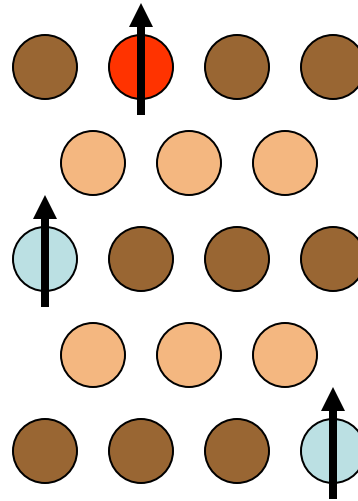
Magnetic inventory



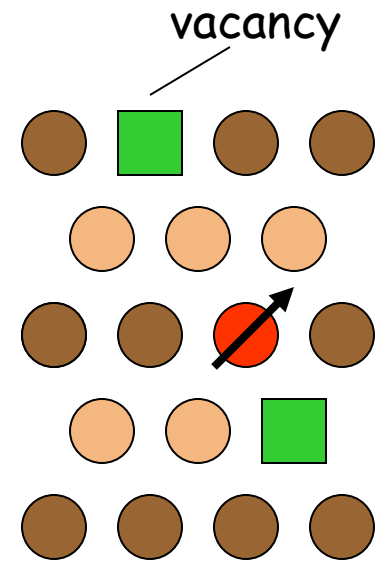
Transition
metal
probe



Metals
alloys
componds

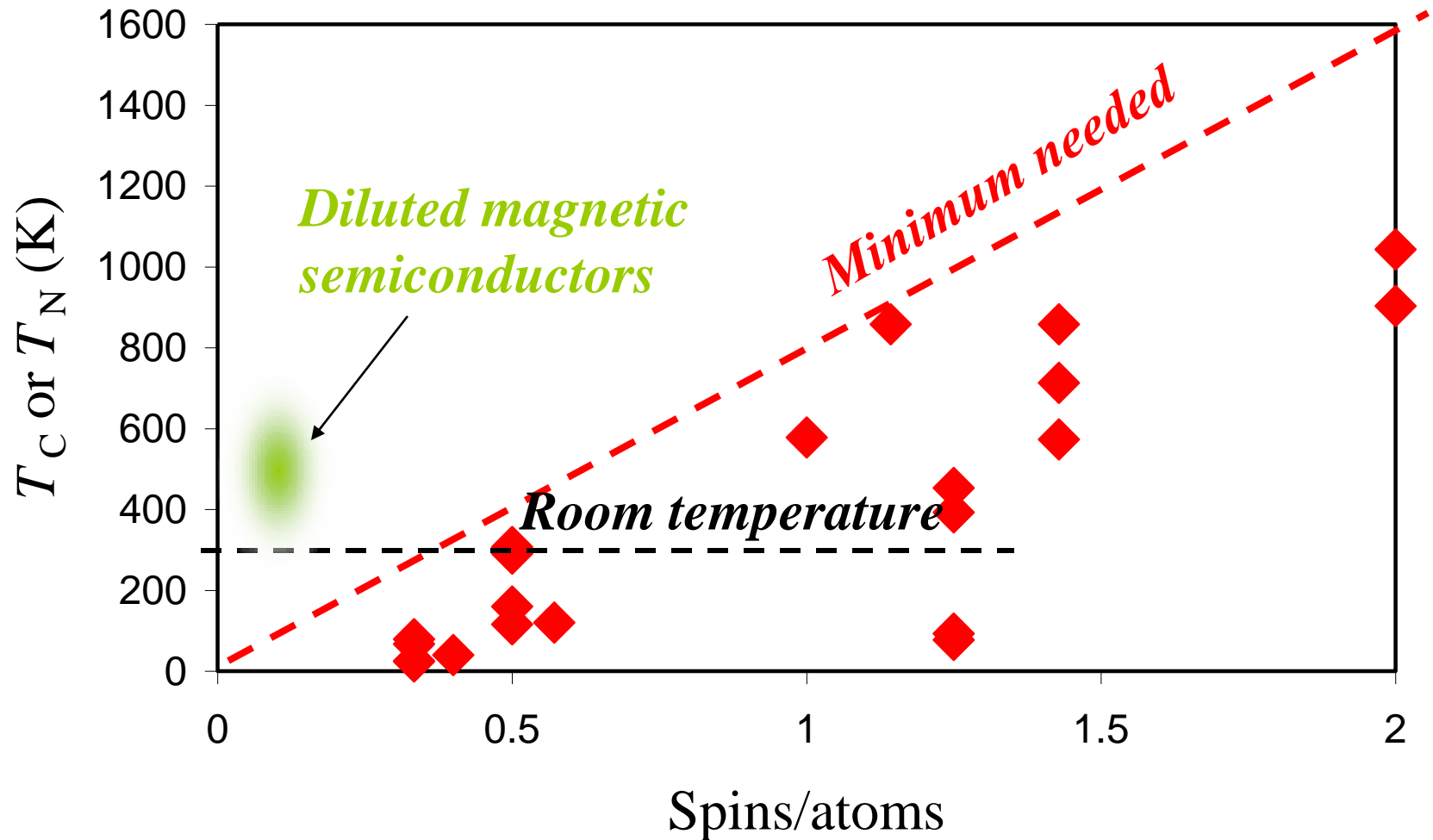
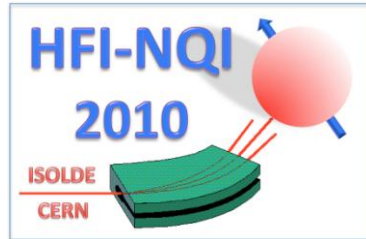


Dilute
magnets

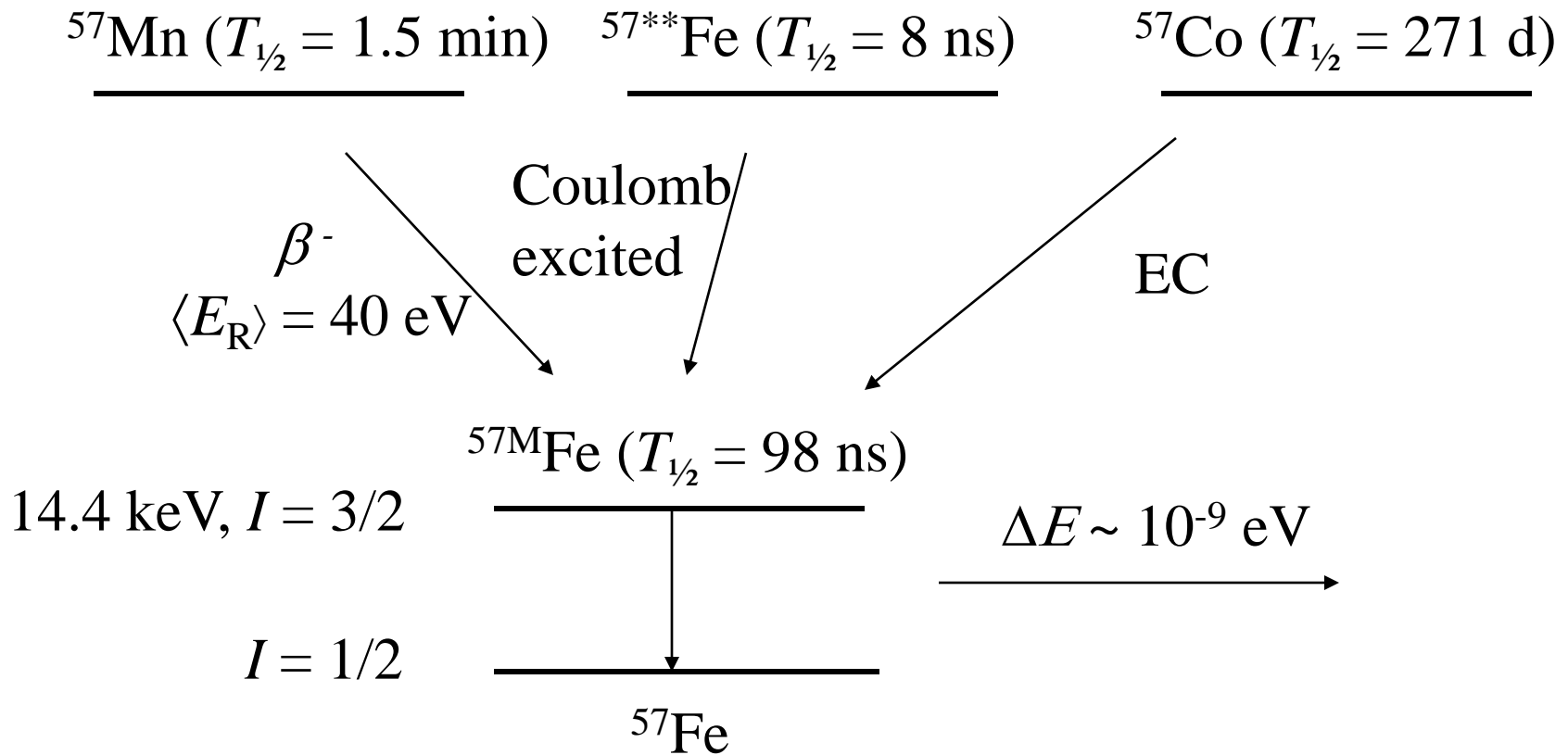
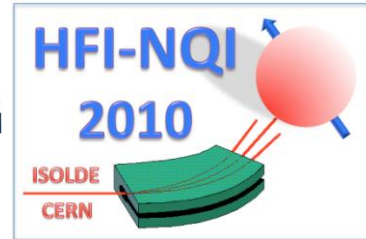


Defect
magnetism

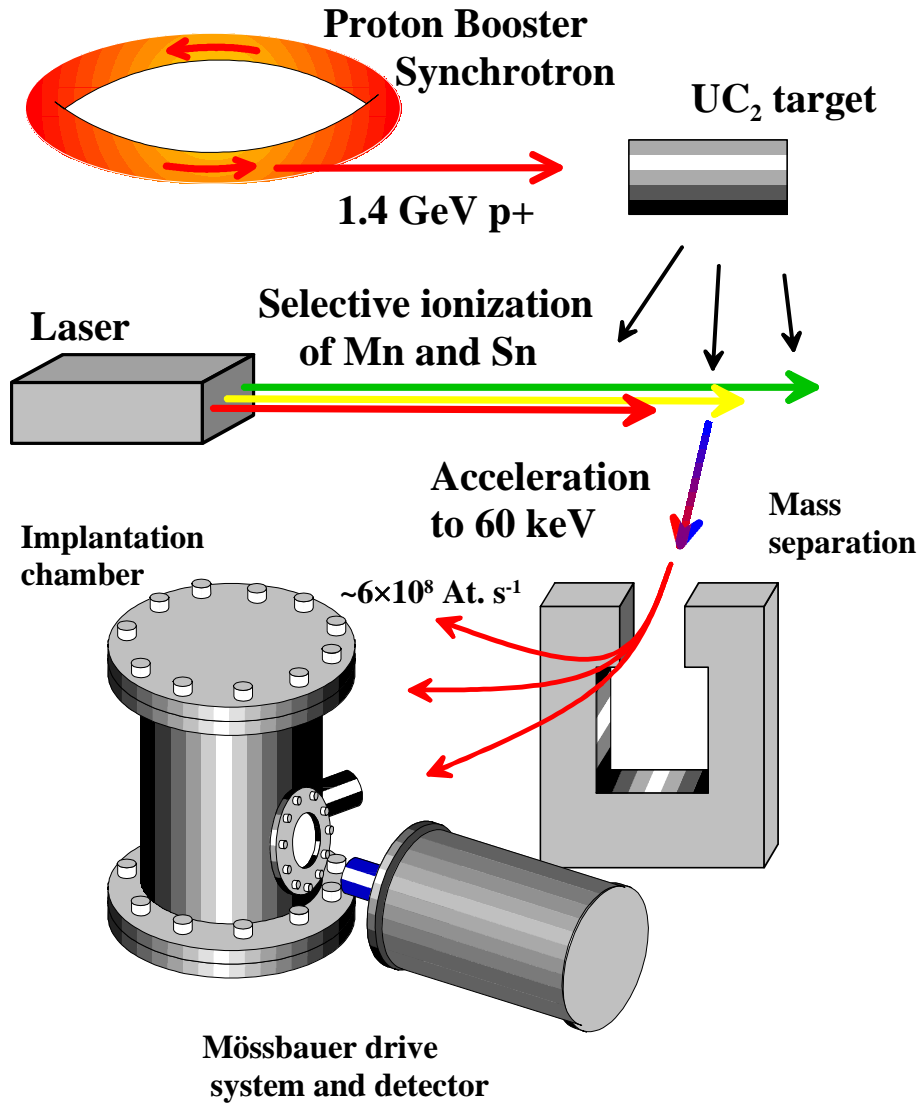
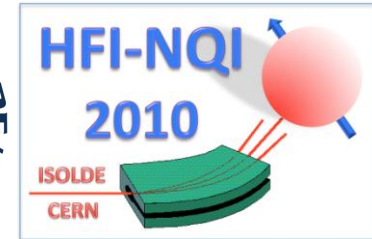
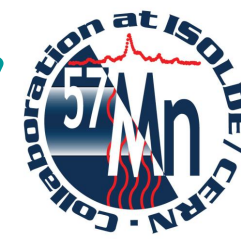
Ferromagnetism



^{57}Fe emission Mössbauer spectroscopy



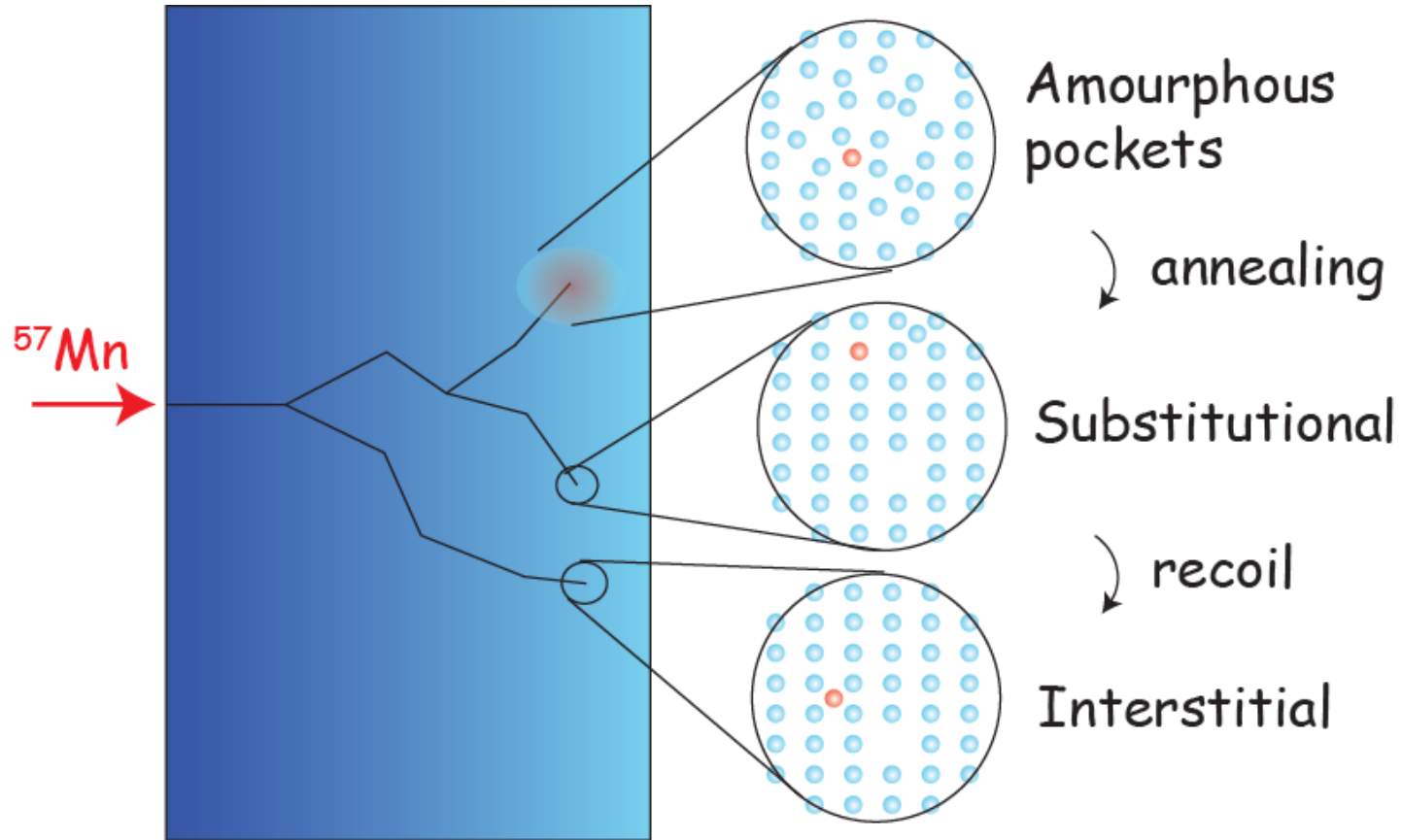
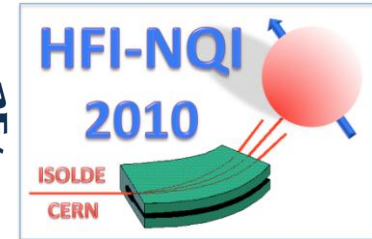
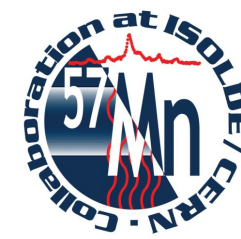
Mössbauer spectroscopy at ISOLDE/CERN



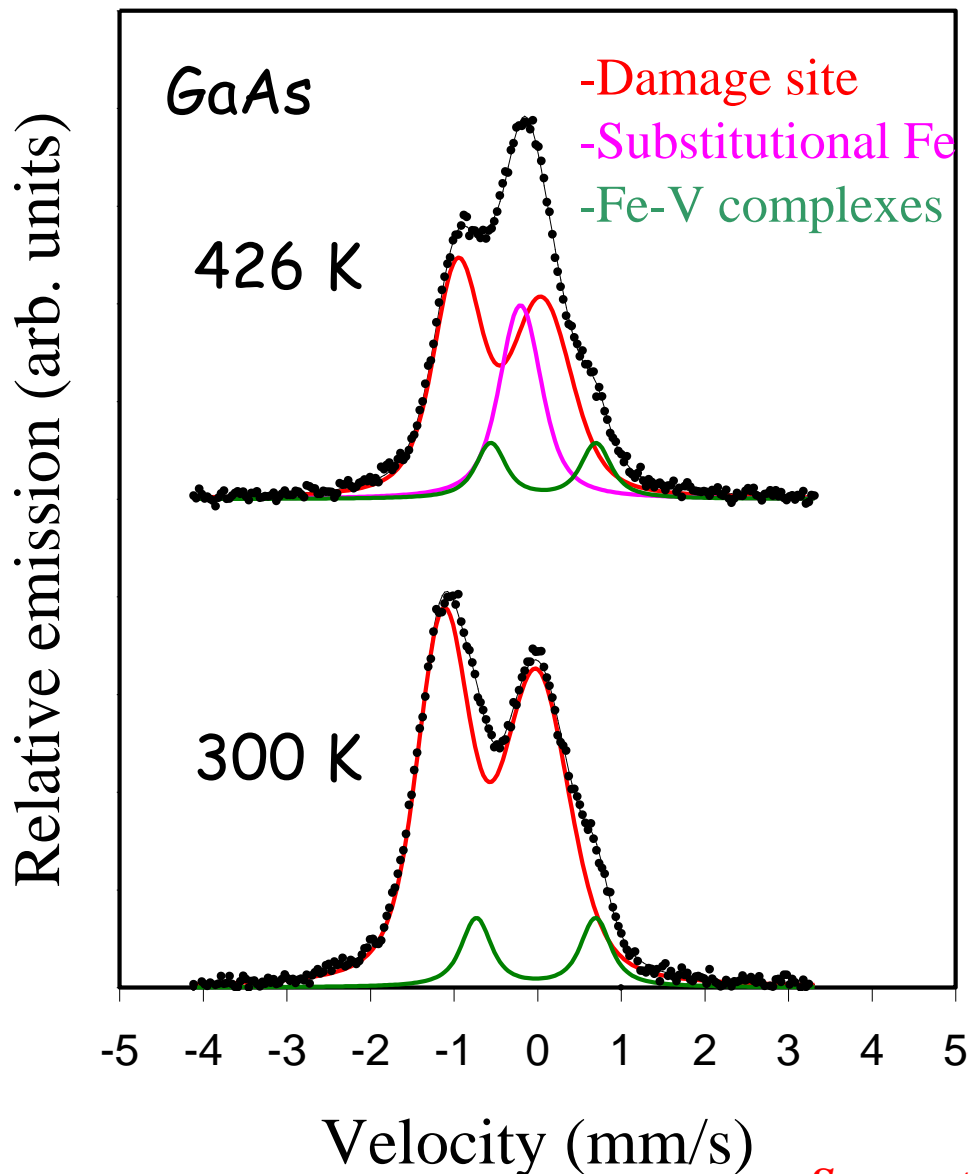
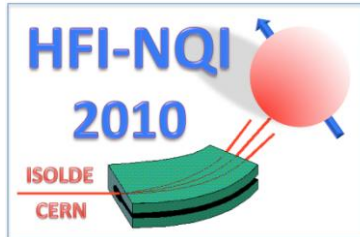
Highlights:

- Low concentrations of probe atoms ($\sim 10^{-4}$ At.%)
- Valence state of Fe
- Site symmetry
- Magnetic interactions

Implantation of ^{57}Mn



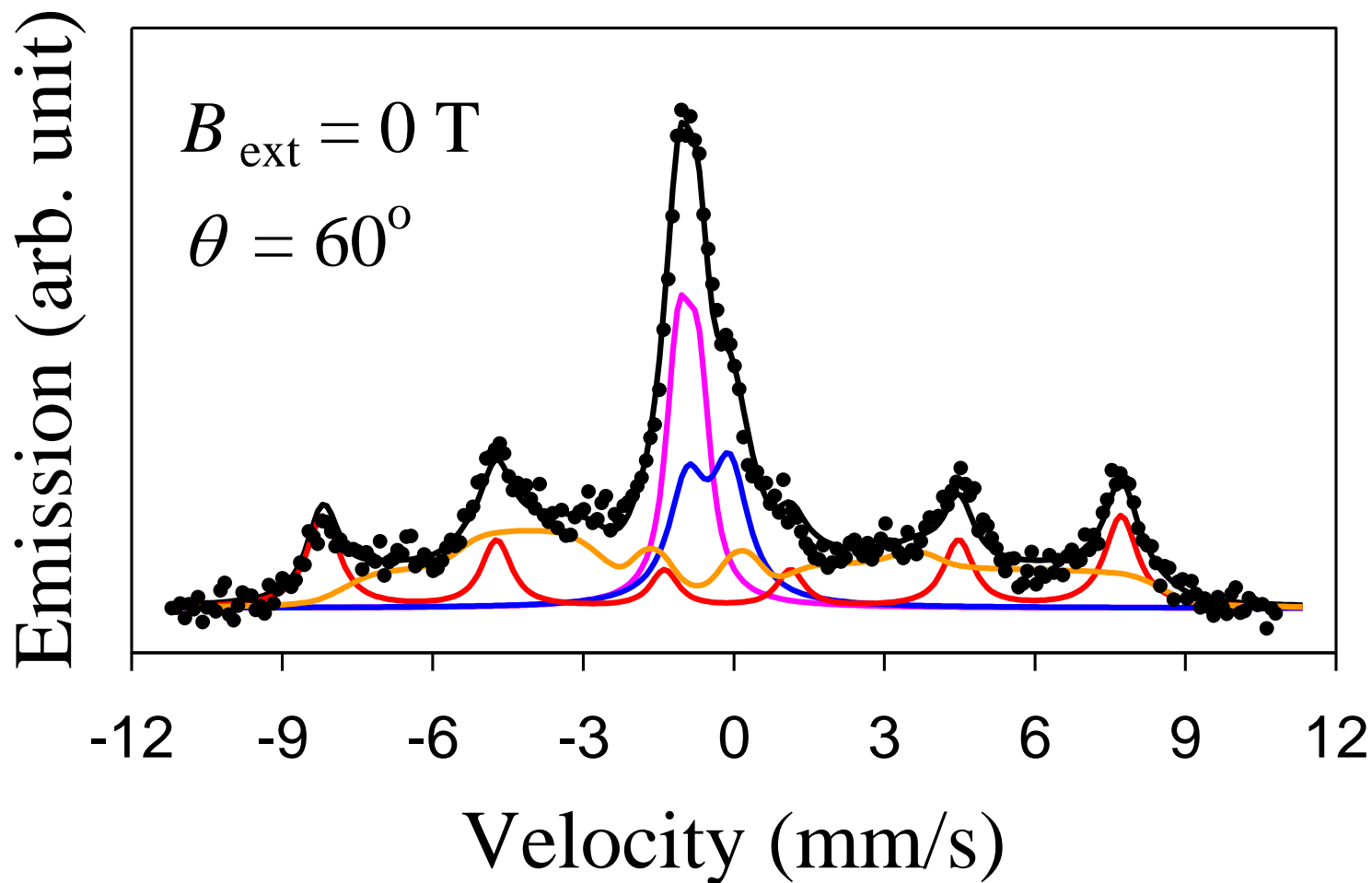
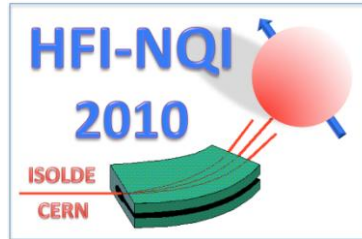
III-V semiconductors



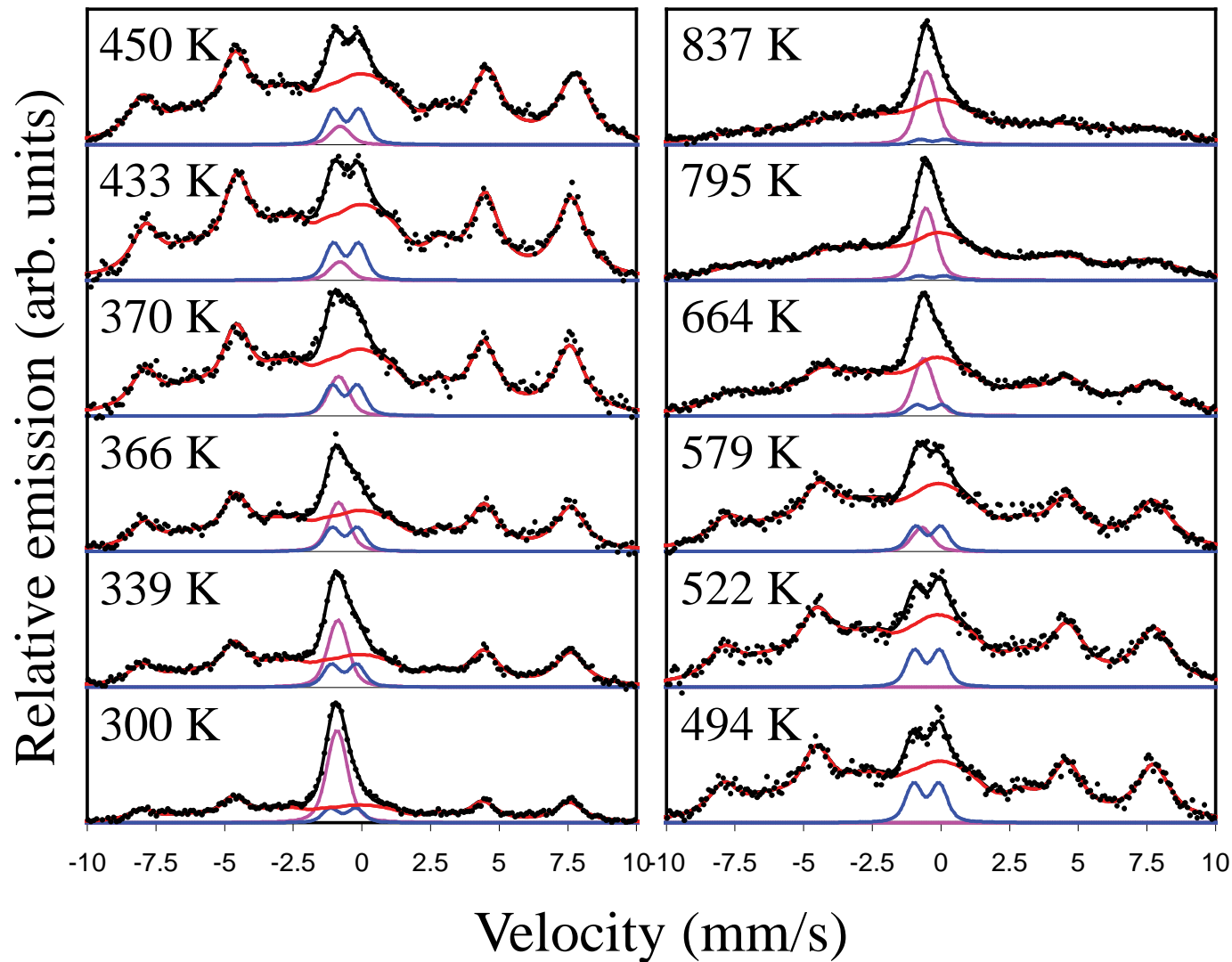
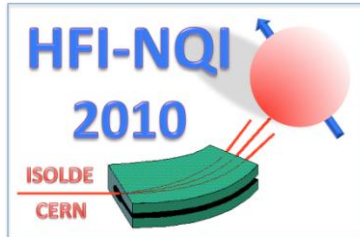
No 6-line magnetic pattern!

See poster presented by Hilary Masenda (PS3-24)

ZnO without external magnetic field

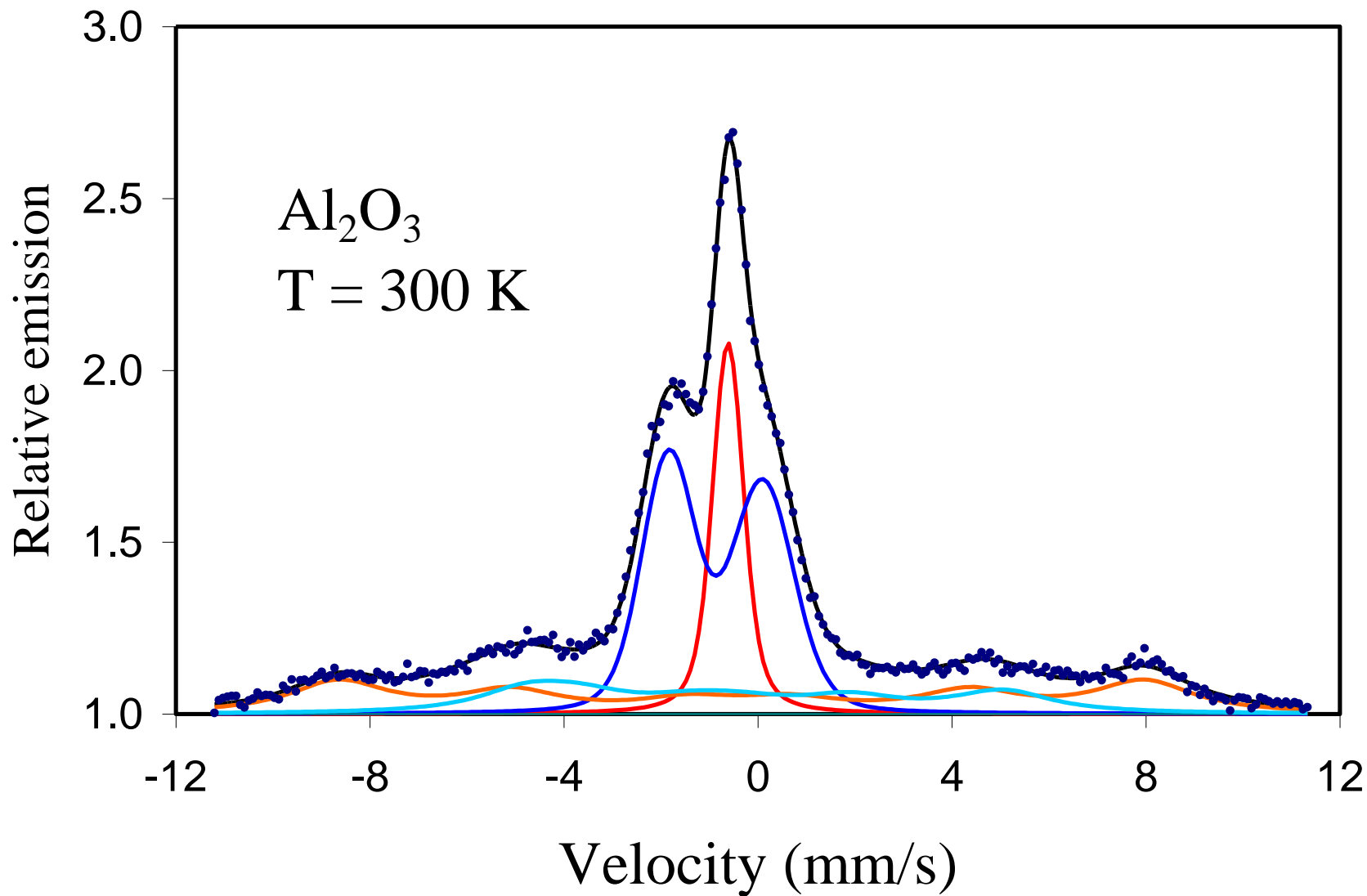
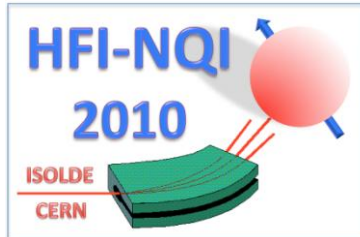


ZnO temperature series



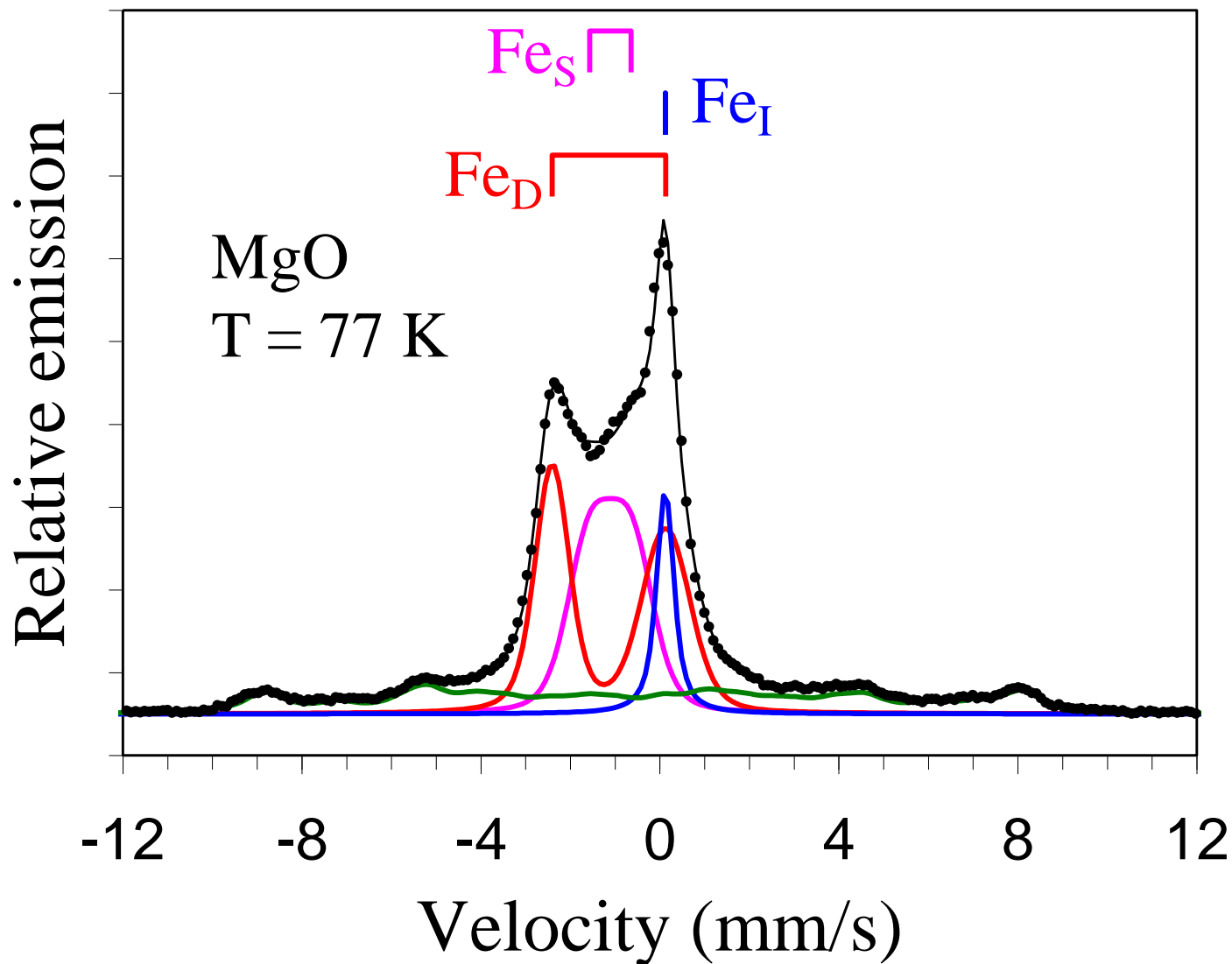
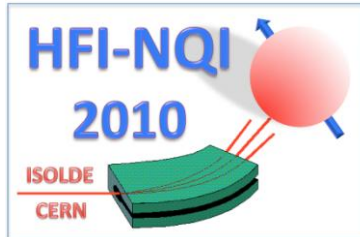
See talk given by T. Mølholt after this talk

Other oxides:



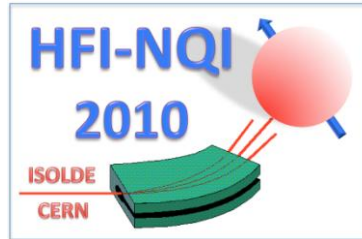
See poster presented by H. P. Gunnalugsson (PS3-23)

Other oxides:



See talk given by T. Mølholt after this talk and (PS3-22)

Mössbauer spectroscopy of magnetic materials



$$\hat{H} = -\boldsymbol{\mu}\mathbf{B} = -g_N\beta_N\hat{I} \cdot \mathbf{B}$$

^{57}Mn ($T_{1/2} = 1.5$ min)

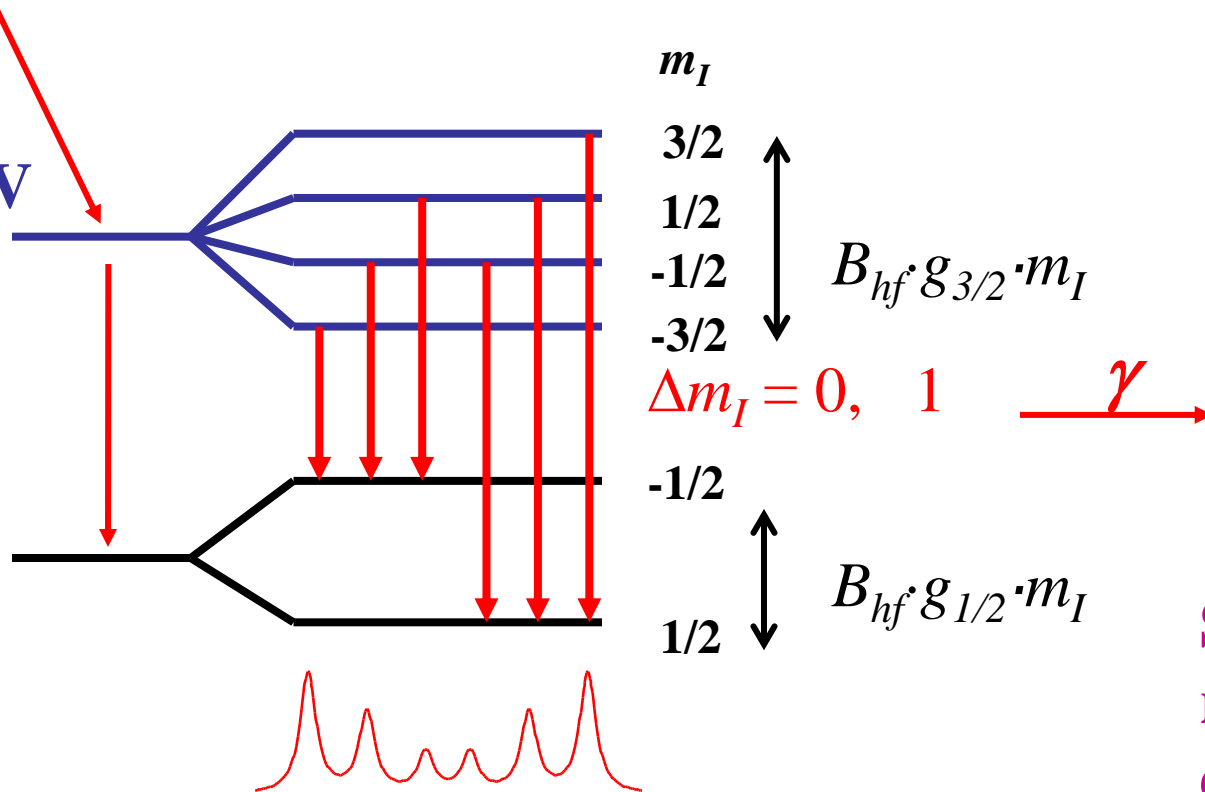
$^{57*}\text{Fe}$ 14.4 keV

$T_{1/2} = 98$ ns

$I = 3/2$

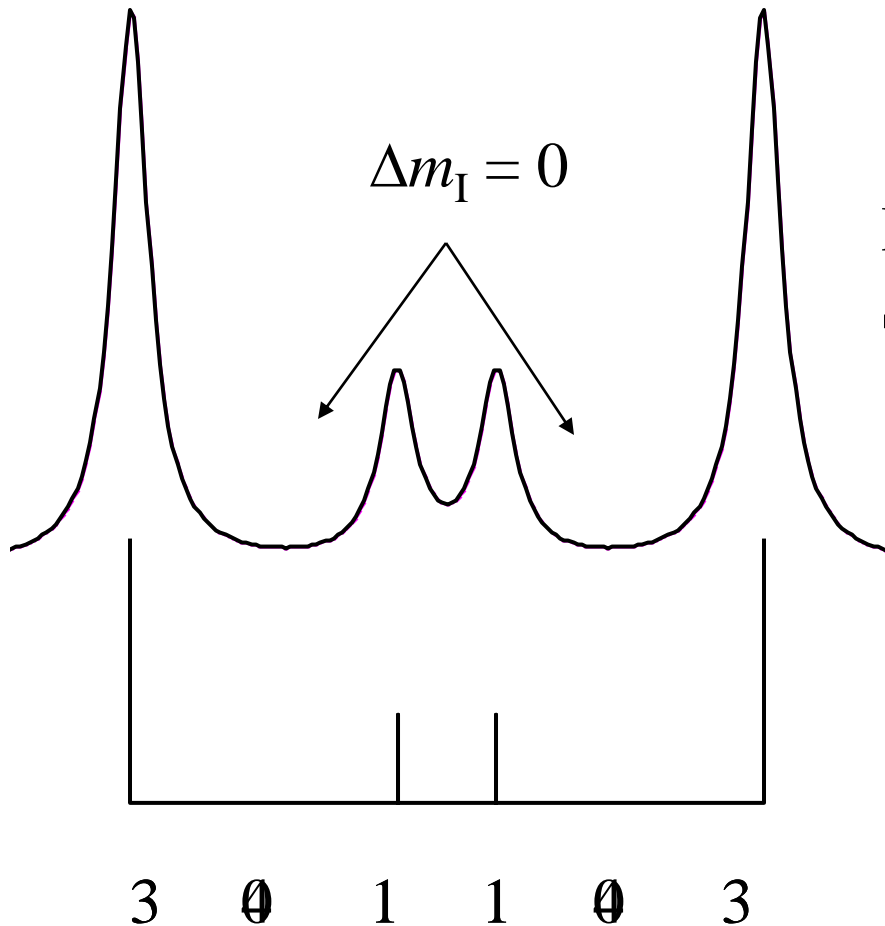
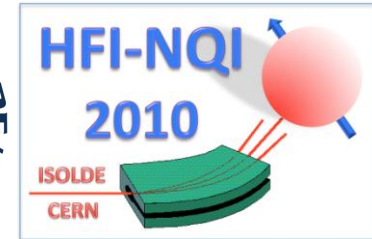
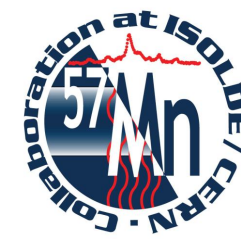
^{57}Fe

$I = 1/2$



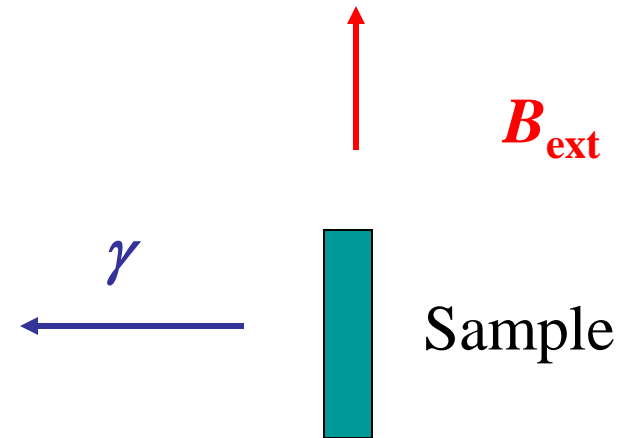
Single line resonance detector

Ferromagnetism ($S = 5/2$ good quantum number)



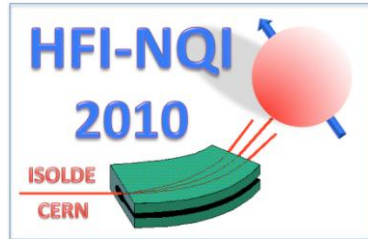
Mössbauer
Spectrum

Relative
line
ratios



Individual line ratios
depend on the angle
between B_{ext} and γ

Temperature dependent magnetic order

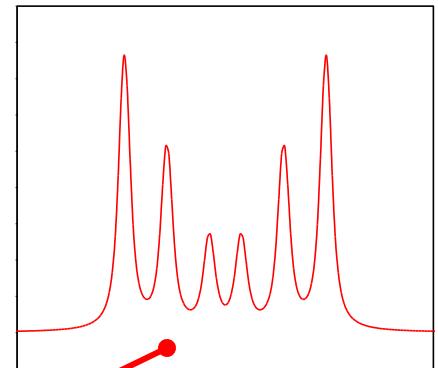
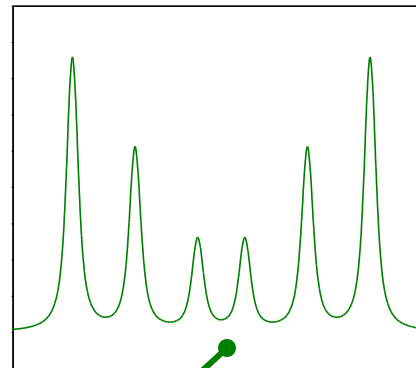
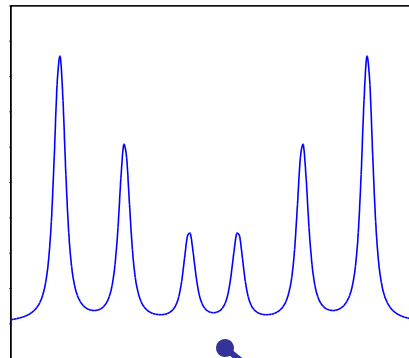


Cold  Hot

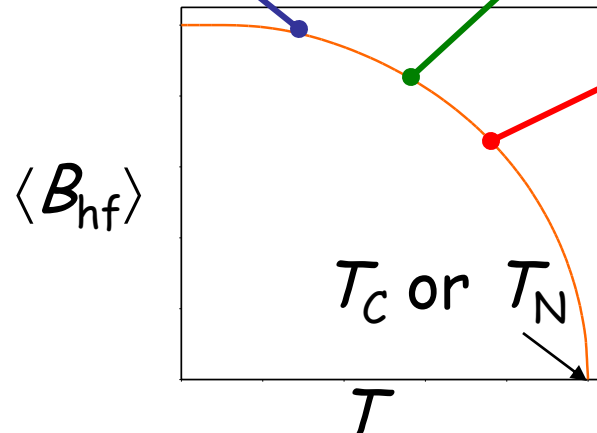
Spins



Mössbauer spectra



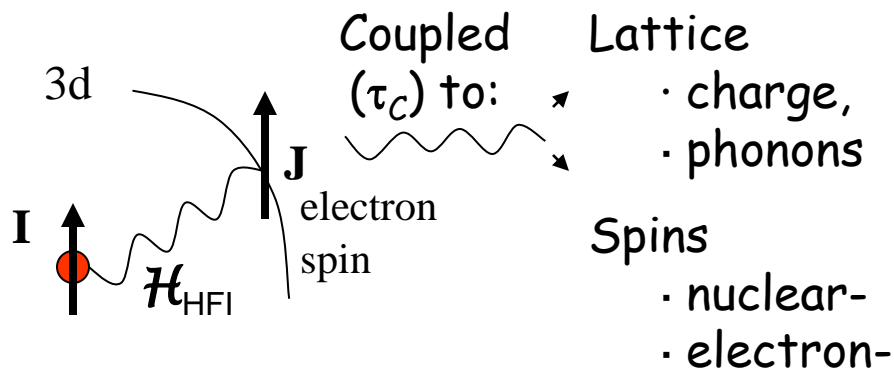
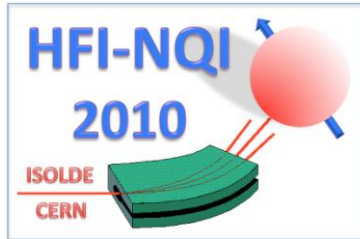
Magnetic hyperfine field



$$- T \uparrow \Rightarrow \langle B_{hf} \rangle \downarrow$$

- No line broadening

Slow paramagnetic relaxations



Conditions for static B_{hf}

$$\tau_c \geq \tau_L \quad (\text{Nucl. Larmor time})$$

$$\tau_c \geq \tau_N \quad (\text{lifetime of Mössbauer state})$$

$\Rightarrow B_{hf}$ not T dependent

\Rightarrow Otherwise broadened

Spin lattice relaxations

	m_l		m_l
$\text{Fe}^{3+} (3d^5)$	-2 ↑	$\text{Fe}^{2+} (3d^6)$	-2 ↑
	-1 ↑		-1 ↑
${}^6S_{5/2}$	0 ↑	5D_4	0 ↑
	1 ↑		1 ↑
	2 ↑		2 ↑↓



Lattice vibrations

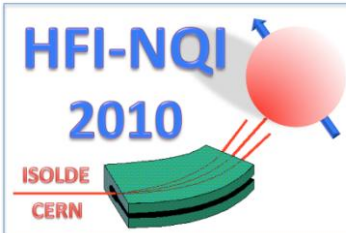
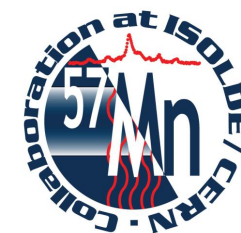
Spin-spin relaxations

$$\Omega_{ss} \propto \langle 2 | H_{dd} + H_{ex} | 1 \rangle$$

$$\times \exp(-|E_2 - E_1|)$$

Broadening in MS
if $> \sim 0.1$ at. %

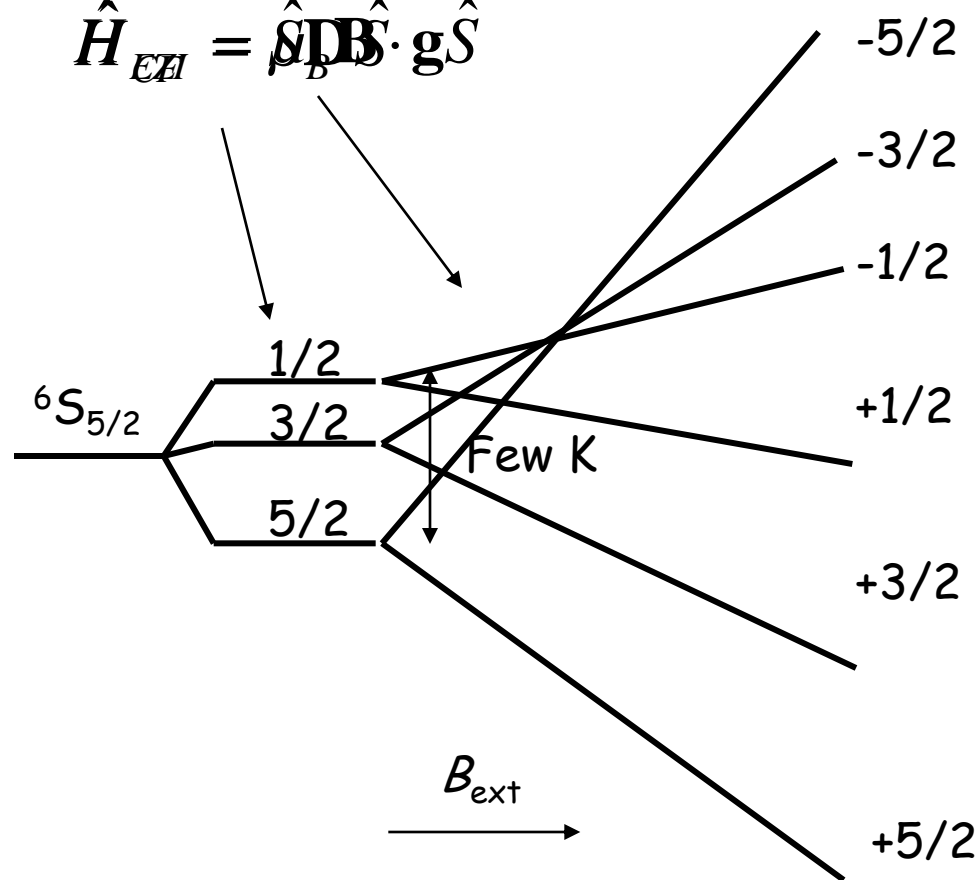
Mössbauer spectra of paramagnetic Fe^{3+}



Needs electron spin operators!

$$\hat{H} = \hat{H}_{CF} + \hat{H}_{EZI} + \hat{H}_{HFI} + \hat{H}_{NQI} + \dots$$

$$\hat{H}_{EZI} = \hat{S} \hat{D} \hat{B} \cdot g \hat{S}$$

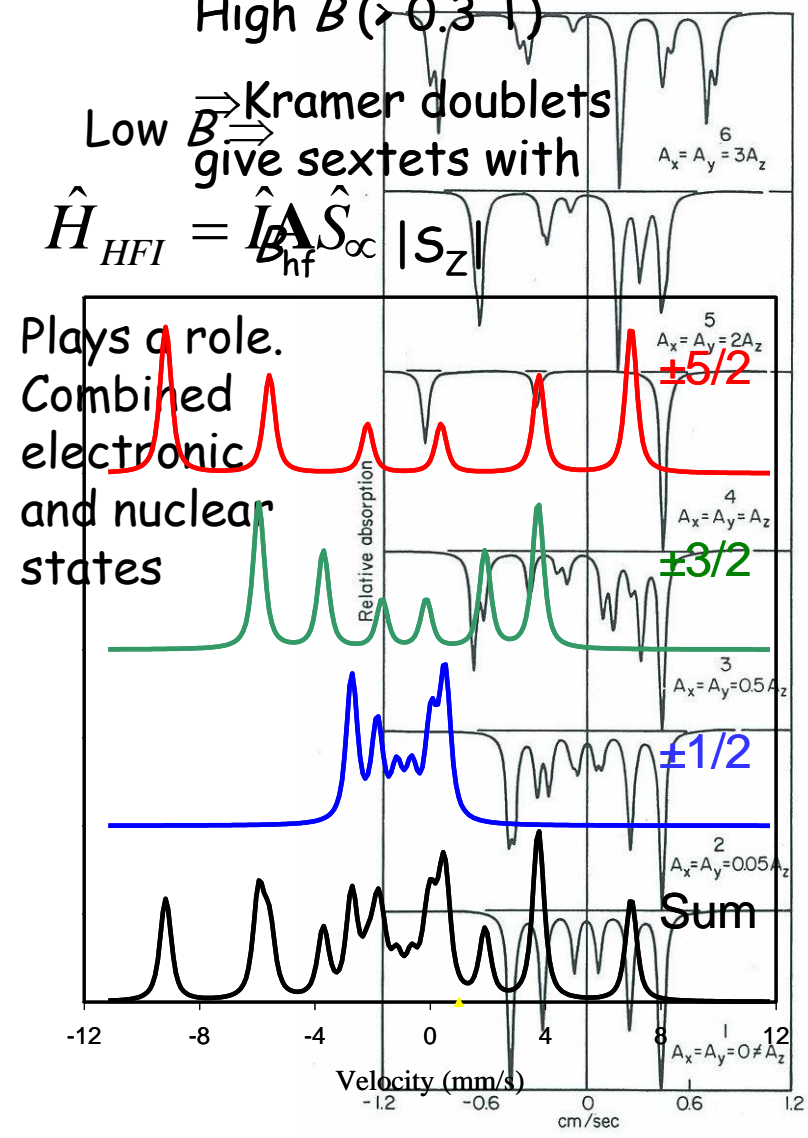


High $B (> 0.3 \text{ T})$

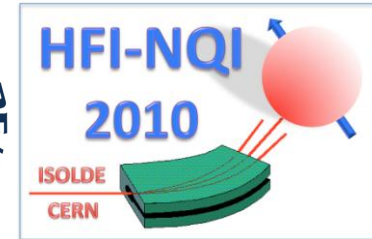
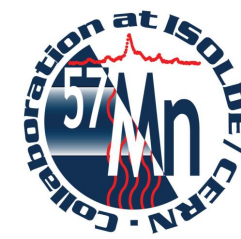
Low $B \Rightarrow$ Kramer doublets give sextets with

$$\hat{H}_{HFI} = \hat{I} \hat{A}_{hf} \hat{S}_{\infty} |S_z|$$

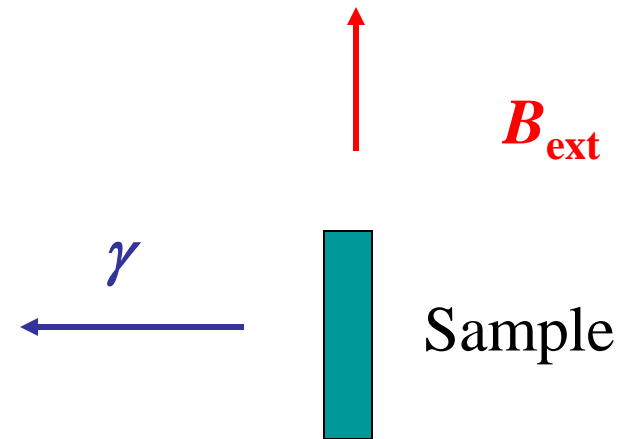
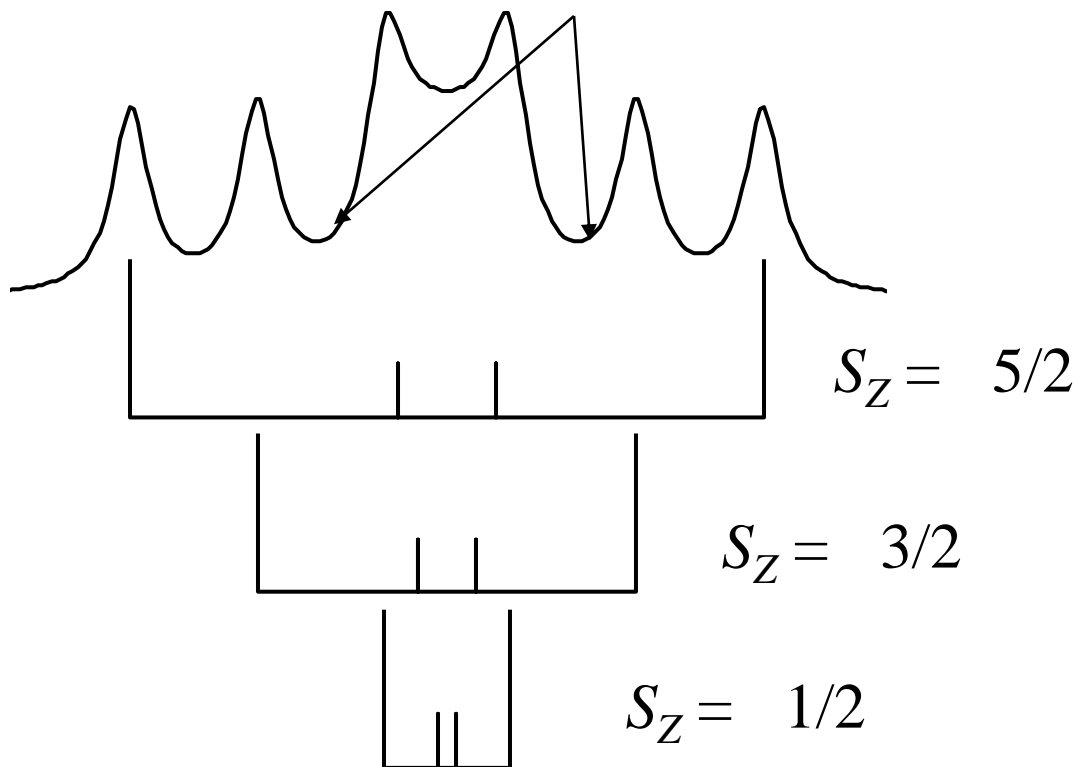
Plays a role. Combined electronic and nuclear states



Paramagnetism (slow relaxation)

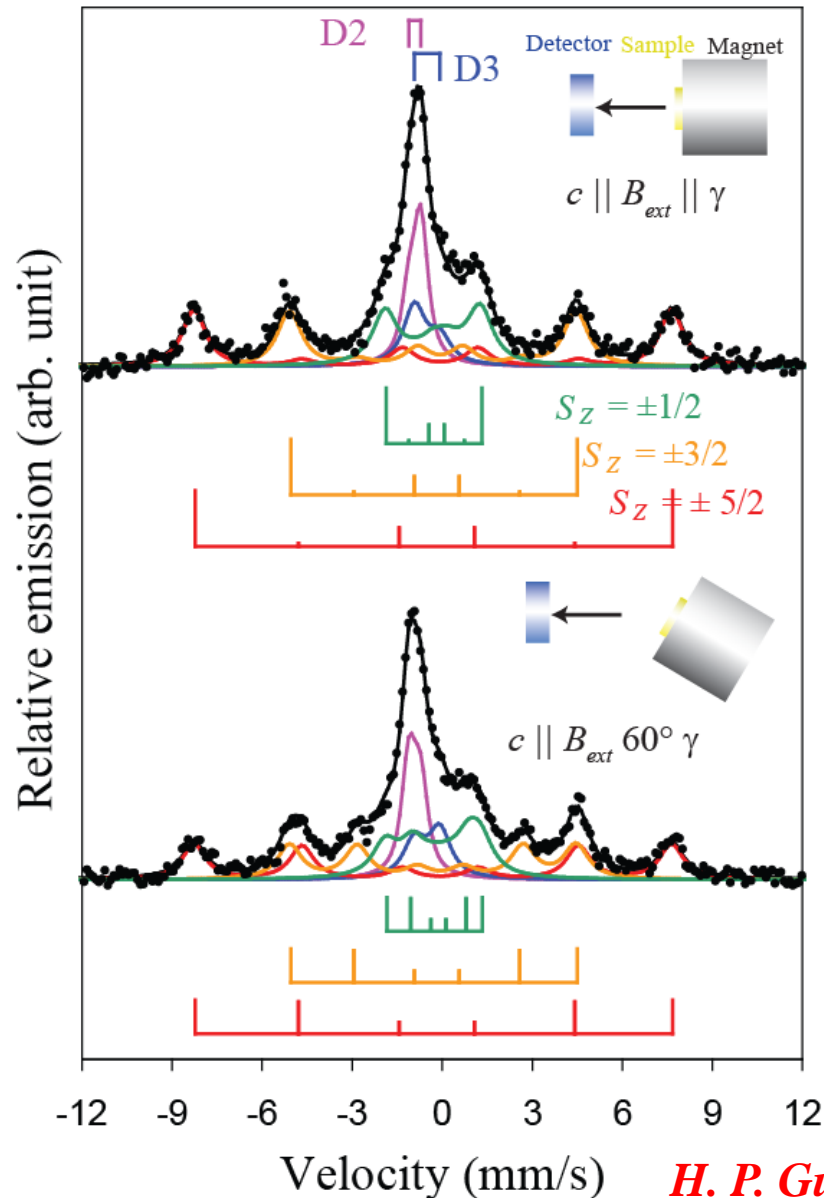
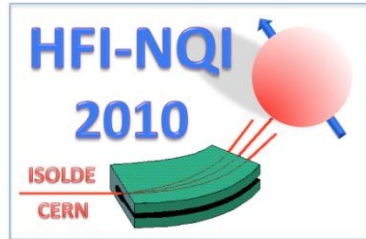


$$\Delta m_I = 0 \text{ from } S_Z = \pm 3/2$$



Individual line ratios depend on the angle between B_{ext} and γ

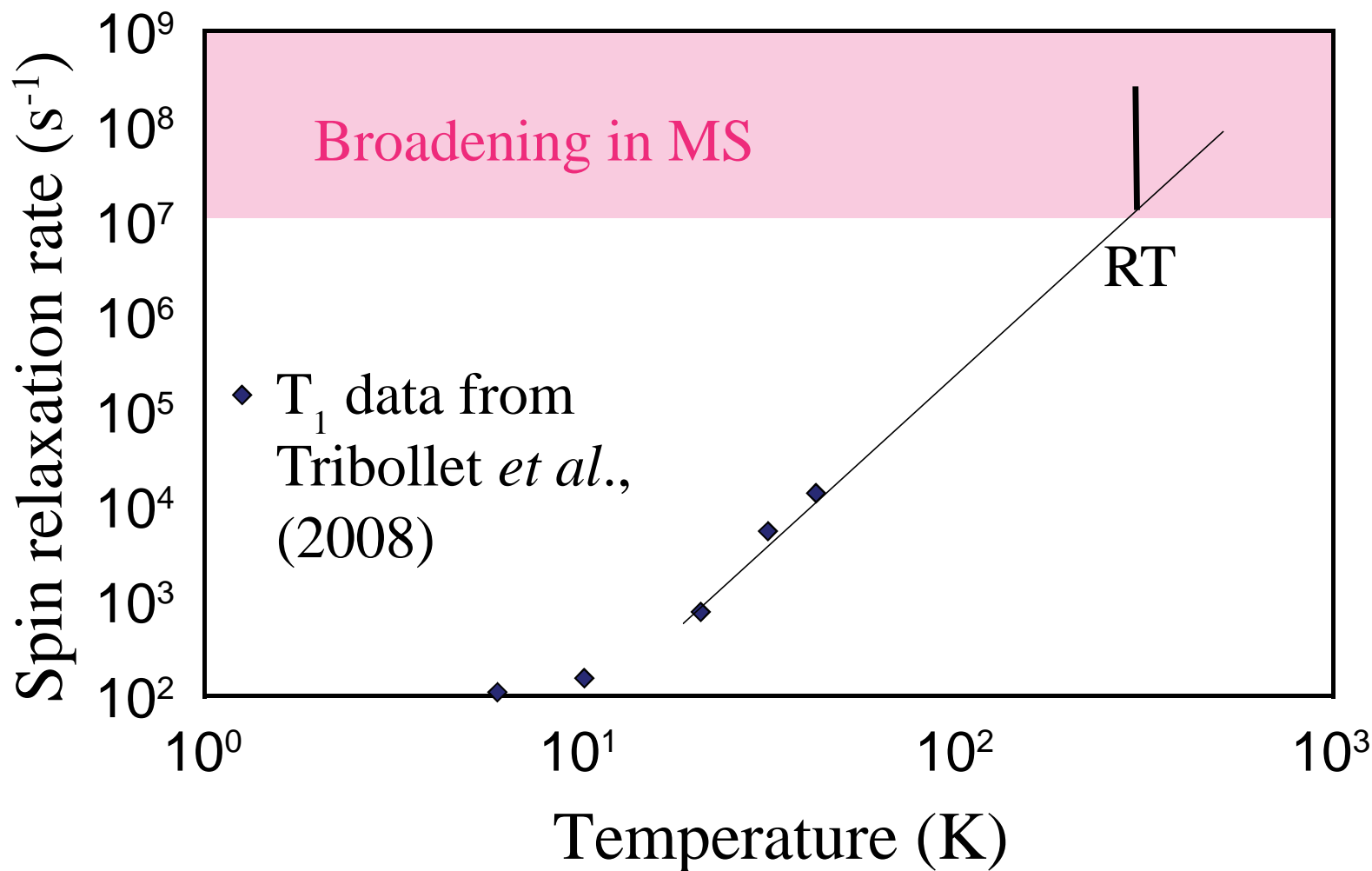
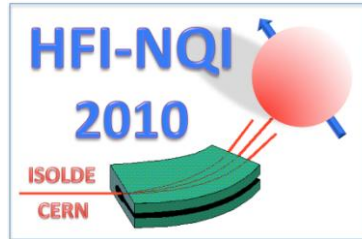
ZnO at RT in $B_{ext} = 0.6 \text{ T}$



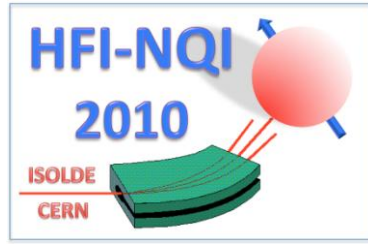
Sextet originating from Kramer doublets clearly observed

No relaxation at RT?

Slow paramagnetic relaxations at RT plausible?



Does defect magnetism exist?



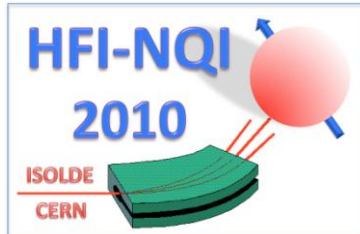
In ZnO, implanted Mn/Fe Fe^{3+} shows slow paramagnetic relaxations

-> No spin-spin relaxations with defects

<- Theory overestimates range of magnetism from isolated defects (Zunger et al., 2010), data misinterpreted and precipitation not documented (Pötzger et al., 2008+)

Is defect or dilute magnetism myth?

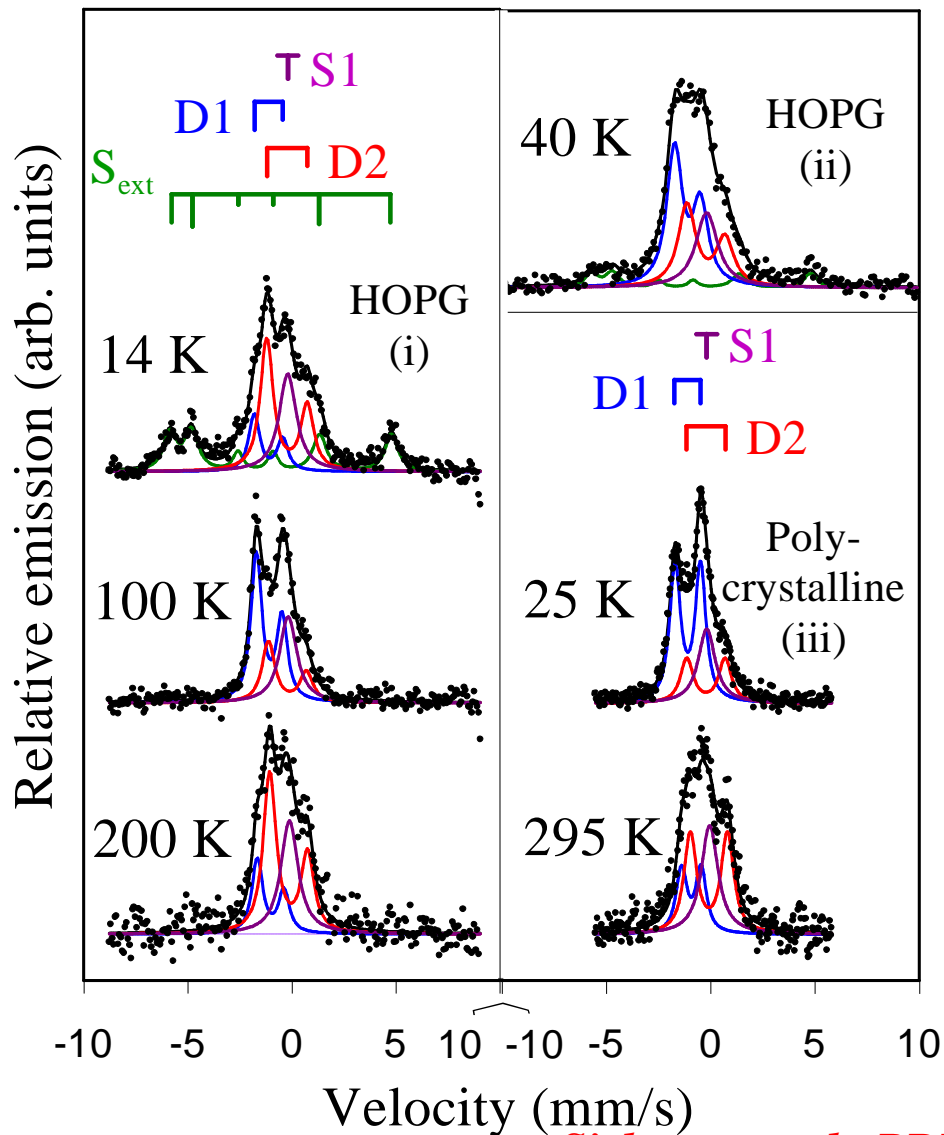
Defect magnetism exists!



-Implantation of $^{57}\text{Fe}^{2+}$ into Graphite

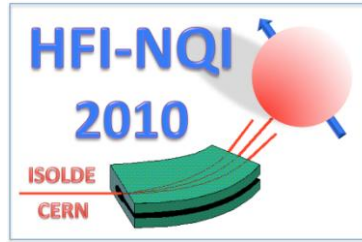
-Sextet (Fe^{2+}) observed at 14 K

-Reduced B_{hf} at 40 K (not a static B_{hf})



Sieleman et al., PRL, 2007

Conclusions/summary



- Implanted Mn/Fe ions in oxides lead to TM in various charge states and lattice sites
- Fe as 3+ state has extremely long relaxation time and displays static (para)-magnetic spectra. Most extreme case Fe in ZnO.
- Application of external magnetic field decouples perturbing fields and yields spectrum looking like an effective magnetic field.
- Identification of defect related magnetism by Mössbauer spectroscopy has been observed at very low temperatures in graphite.

Thank you



IS443 summer 2009

missing K. Johnston, M. Fanciulli,
K. Baruth-Ram, Y. Kobahashi