Mössbauer studies of dilute magnetic semiconductors (IS-443)

R. Mantovan[1], M. Fanciulli[1], H.P. Gunnlaugsson[2], G.Weyer[2],
R. Sielemann[3], D. Naidoo[4], K. Bharuth-Ram[5], S. Olafsson[6], G. Langouche[7],
K. Johnston[8]

[1]Laboratorio Nazionale MDM CNR-INFM, Agrate Brianza (MI) 20041, Italy

[2]Department of Physics and Astronomy,University of Aarhus, DK-8000 Århus C, Denmark

[3]Hahn-Meitner Institute, 14109 Berlin, Germany

[4]School of Physics, University of the Witwatersrand, WITS 2050, South Africa

[5]School of Physics, University of KwaZulu-Natal, Durban 4041, South Africa

[6]Physics Department, Science Institute University of Iceland, Iceland

[7]Department of Physics, Katholieke Universiteit, Leuven, Belgium

[8]EP Division, CERN, CH-1211 Geneva 23, Switzerland

*(CERN-INTC-2006-005; INTC-**P-203**.)*

Outline

- Motivation
- ^{57}Fe Mössbauer spectroscopy at ISOLDE-CERN
- Mössbauer results on ^{57}Mn (→^{57}Fe) -implanted ZnO
- Dose dependence effects
- An explanation for the observed magnetism in terms of defects
- Conclusions

Magnetism in ZnO

*[T. Dietl, H. Ohno, F. Matsukura, J. Cibert., and D. Ferrand, Science **287**, 1019 (**2000**)]*

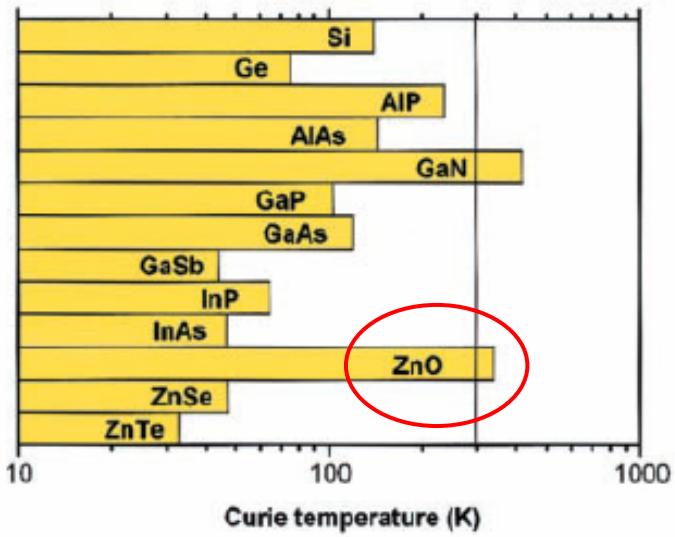


Fig. 3. Computed values of the Curie temperature T_C for various p-type semiconductors containing 5% of Mn and 3.5×10^{20} holes per cm^3.

2005

Is it possible to create magnetic semiconductors that work at room temperature?
Such devices have been demonstrated at low temperatures but not yet in a range warm enough for spintronics applications.

- Magnetic oxides/semiconductors: multifuncional materials for spintronics
- Curie temperature >>300 K is needed

Magnetism in ZnO: contradictory experimental findings

*[S. J. Pearton et al., Semicond. Sci. Technol. **19** (2004) R59–R74.]*

Compound	TM content	Substrate	Fabrication method	Growth temperature (°C)	Oxygen pressure (Torr)	Post-annealing	T_c (K)	Notes
ZnO:Mn	<0.35	*c*-Sapphire	PLD	600	5×10^{-5}		N/A	
ZnO:Mn	0.36	*c*-Sapphire	PLD	600	5×10^{-5}		N/A	Spin-glass
$Zn_{1-x}TM_xO$		*c*-Sapphire	PLD	500–600	1×10^{-9} to 10^{-6}		N/A	
ZnO:Co	0.02–0.5	*c*-Sapphire	PLD	300–700	1×10^{-6} to 10^{-1}			Spin-glass
ZnO:Mn	0.01–0.36	*c*-Sapphire	PLD	610	5×10^{-5}			Paramagnetic
ZnO:(Co, Mn, Cr, or Ni)	0.05–0.25	*r*-Sapphire	PLD	350–600	$2–4 \times 10^{-5}$		280–300	2 μ_B/Co
ZnO:Ni	0.01–0.25	*c*-Sapphire	PLD	300–700	1×10^{-5}			Superparamagnetic or ferromagnetic
ZnO:V	0.05–0.15	*r*-Sapphire	PLD	300	10^{-5} to 10^{-3}		>350	0.5 μ_B V^{-1}
ZnO:(Co, Fe)	<0.15	SiO_2/Si	Magnetron sputtering	600	2×10^{-3}	600 °C, 10 min, 1.0×10^{-5} Ton	>300	12–15 emu cm^{-3}
ZnO:Co	0.03–0.05	Bulk ZnO	Ion implantation			700 °C, 5 min under O_2	>300	Oriented Co precipitates
ZnO:Co	0–0.25	*c*-Sapphire	Sol–gel	<350		700 °C, 1 min	>350	0.56 μ_B/Co
ZnO:Mn	0–0.3	*c*-Sapphire	PLD				>30–45	0.15–0.17 μ_B/Mn
ZnO:Mn	<0.04		Sintered pellets	500–700	Air, atmospheric pressure		>425	0.006 emu gm^{-1}, single phase
ZnO:Mn	0.02	Fused quartz	PLD	400			>425	0.05 emu gm^{-1}, single phase
ZnO:(Fe, Cu)	0–0.1	Solid state reaction	897				550	0.75 μ_B/Fe
ZnO:Co	0.015		PLD	650	5×10^{-5}		>300	Ferromagnetic
ZnO:(Co, Al)	0.04–0.12	Glass	RF sputtering		1×10^{-2} in Ar		>350	0.21 μ_B/Co
ZnO:Mn	0.04–0.09	*c*-Sapphire	Reactive sputtering	200–380			>400	3 μ_B/Co
ZnO:(Mn, Sn)	0–0.3		Implantation			5 min, 700 °C	250	Ferromagnetic

- The (3d-) doped and pure ZnO has been reported to be ferromagnetic, paramagnetic, and in the spin glass state

- The origin of the magnetism in ZnO is still a matter of debate in the scientific community

Mössbauer spectroscopy at ISOLDE-CERN (IS-443)

- Implantation of ZnO with radioactive $^{57}Mn^{+}$ ($T_{½}$ = 1.5 min.), decaying to the ^{57m}Fe Mössbauer level ($T_{½}$ = 100 ns)

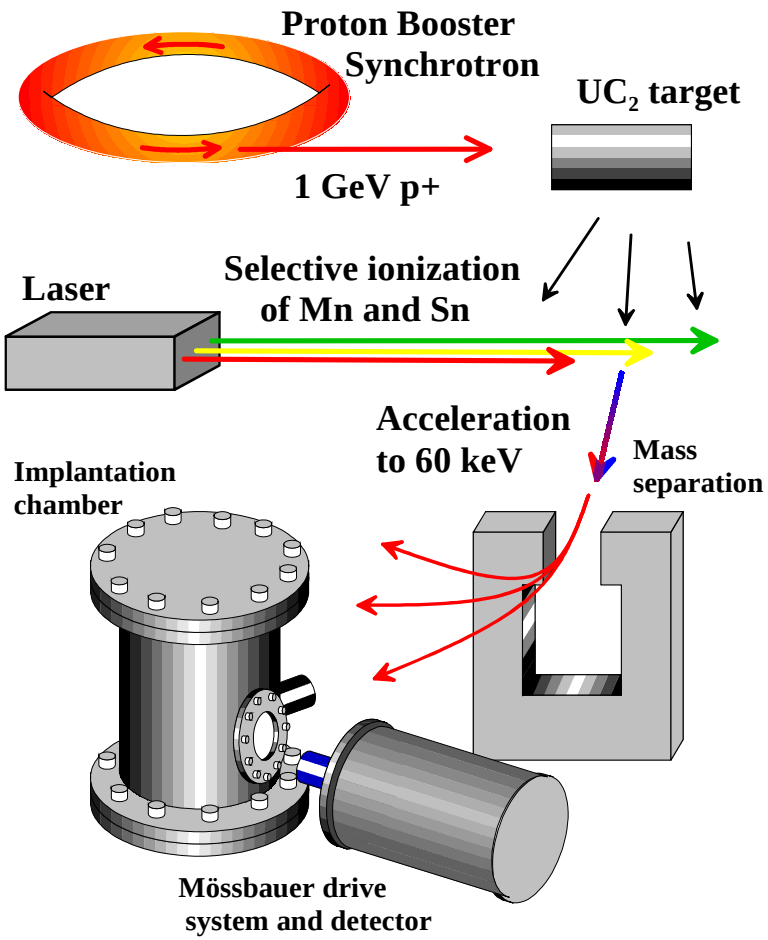
- 100% element selective→structural and magnetic information at the Fe sites

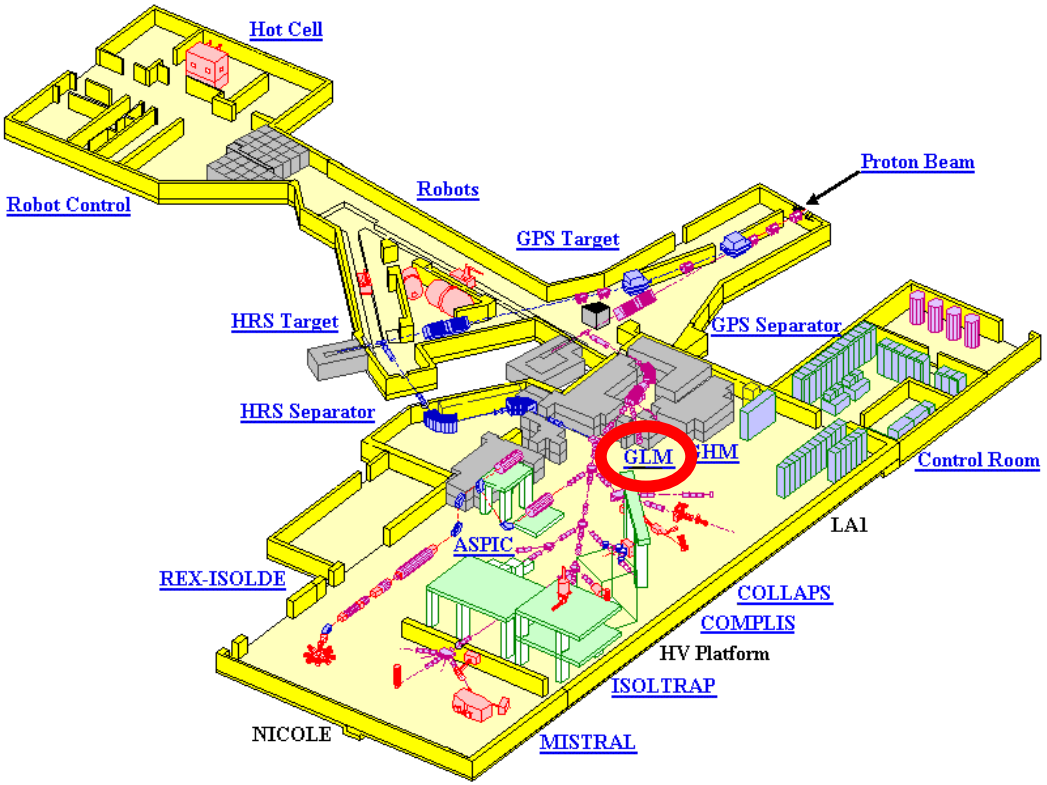
- The implantation process induces a large amount of defects (~10^3/ion)
  → their interaction with the implanted Mn/Fe probe can be studied

- Fluences ~10^{10}-10^{13} $^{57}Mn^{+}/cm^2$ to record a Mössbauer spectrum (local concentration ~10^{16} cm^{-3})→single isolated Fe impurities (~10^{-5} Fe at.%) →truly dilute semiconductors are produced

study of the magnetism at the atomic scale and role of defects

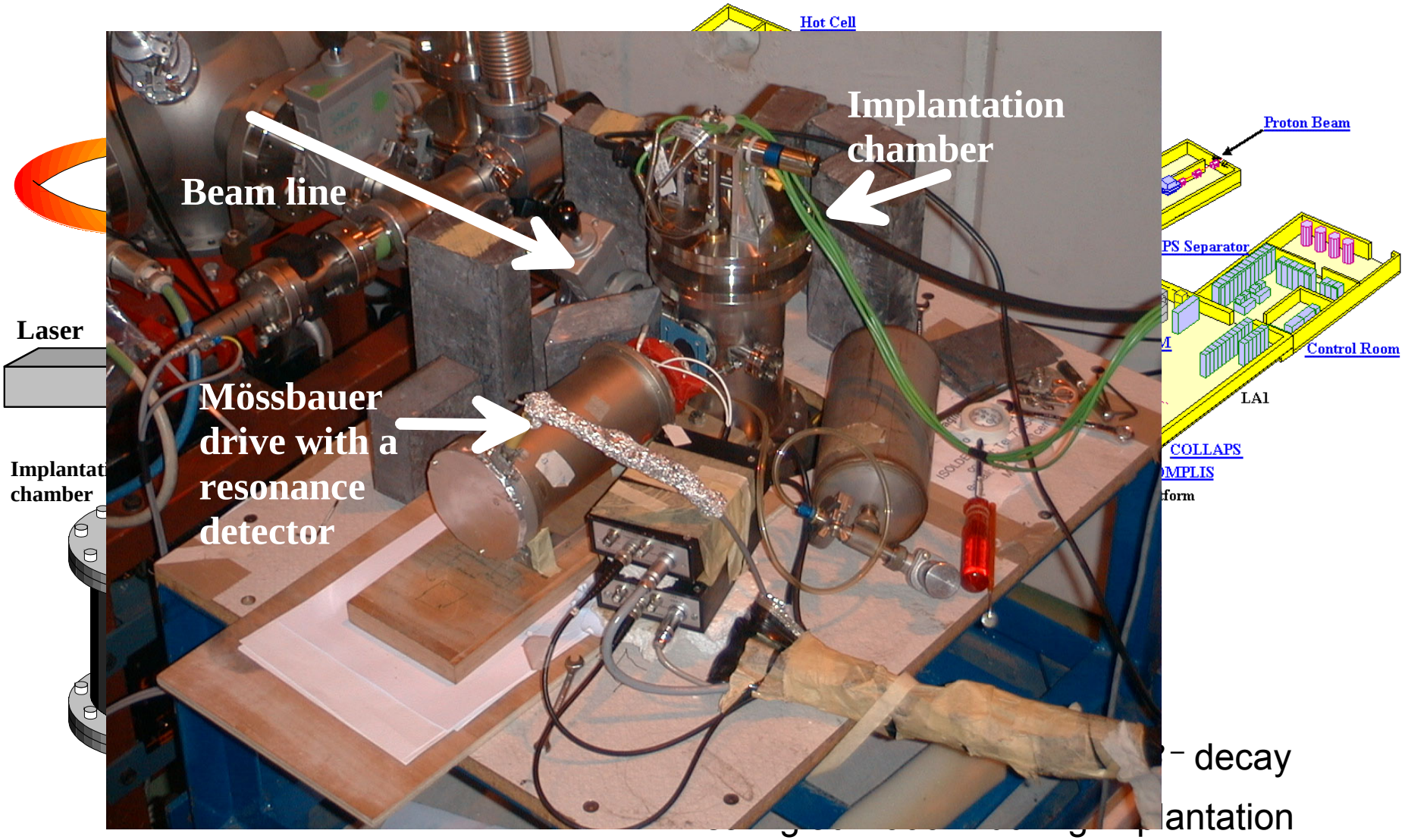
Mössbauer spectroscopy at ISOLDE-CERN (IS-443)





- ^{57}Mn → ^{57m}Fe ($T_{½}$ = 1.5 min.)
- $\langle E_R \rangle$~40 eV during the Mn→Fe β^- decay
- Annealing at<1000 K during implantation
- Typically ~5 min to record one spectrum

Mössbauer spectroscopy at ISOLDE-CERN (IS-443)

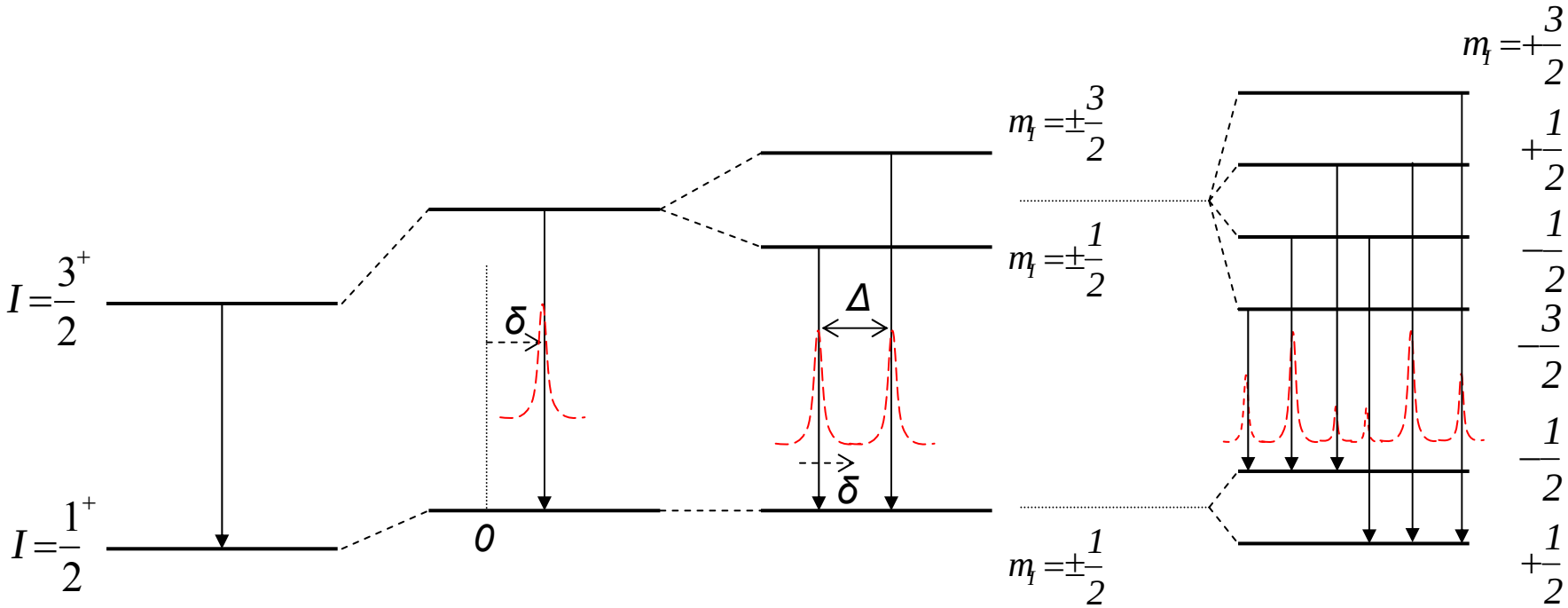


^{2} ⁻ decay

antation

•Typically ~5 min to record one spectrum

Hyperfine interactions at the ^{57}Fe nuclear sites



$$IS = \alpha\left(\left|\psi(0)\right|_A^2 - \left|\psi(0)\right|_S^2\right)$$

chemical bond
oxidation state

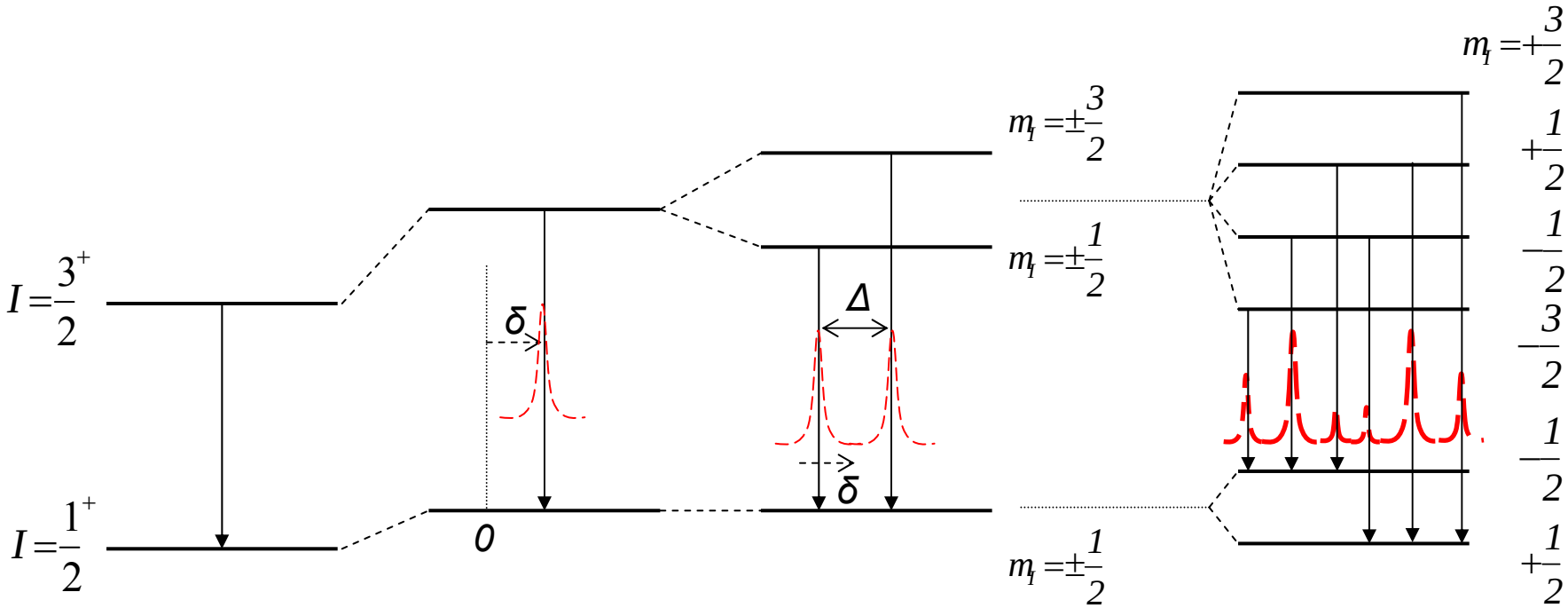
$$QS = \frac{1}{2} eQV_{zz}\left(1 + \frac{\eta^3}{3}\right)^{\frac{1}{2}}$$

local symmetry
(valence electrons, lattice)

$$E_m = -g\mu_N H m_I$$

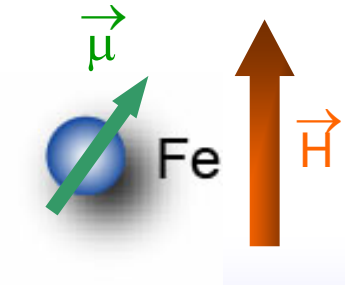
local magnetic field

Hyperfine interactions at the ^{57}Fe nuclear sites



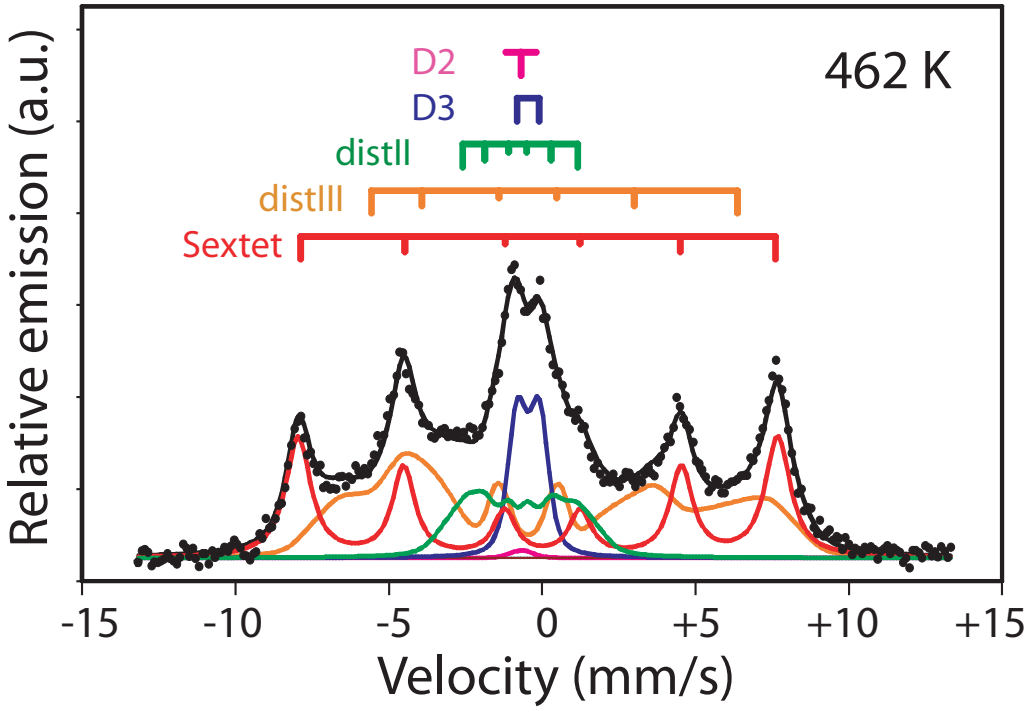
$$E_m = -g\mu_N H m_I$$

$$\mu = -g\mu_N m_I$$



Mössbauer sextet means magnetism at the Fe site

Mössbauer results: strong magnetic contribution >300 K

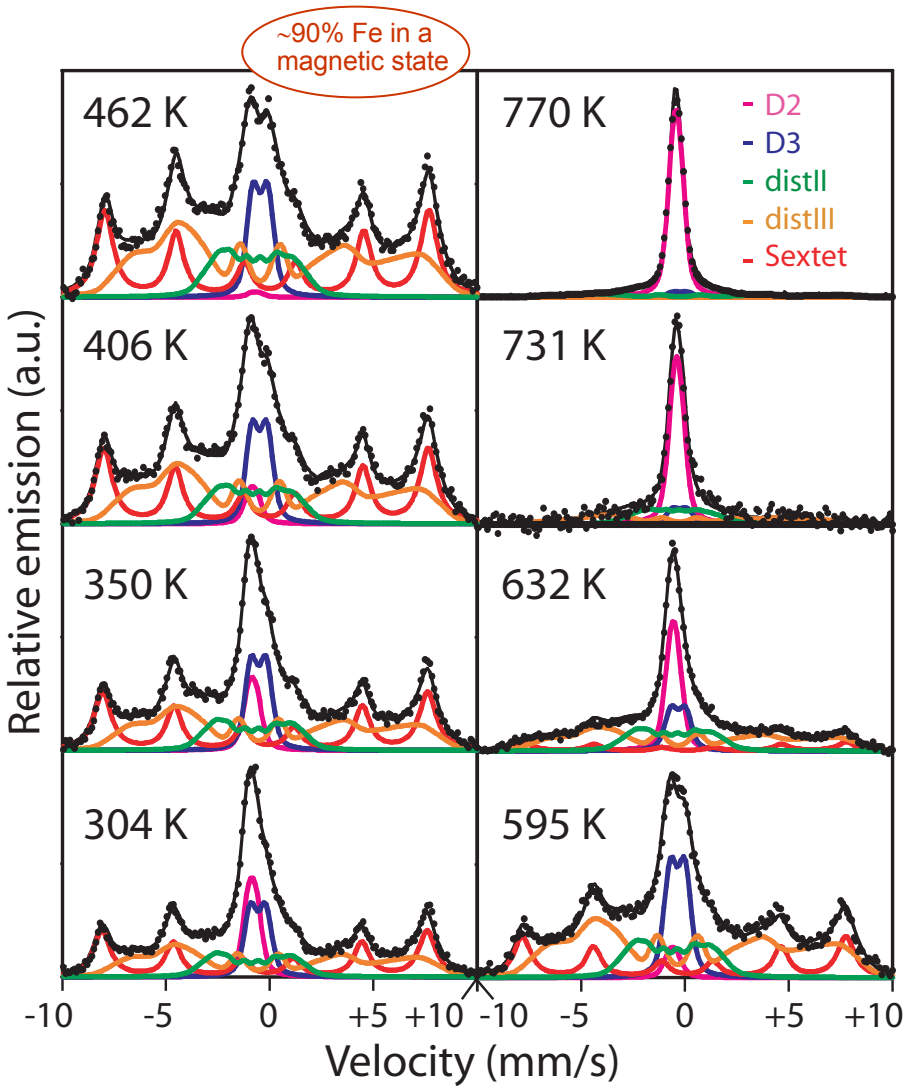


Mössbauer component	B_{hf} (T)	Isomer shift, IS (mm/s)	Quadrupole splitting, QS (mm/s)
D2	-	0.80(1)	0.3(2)
D3	-	0.55(2)	0.73(3)
Sextet	48.3(2)	0.20(2)	0.13(3)
DistIII	37(2)	0.13(4)	-0.83(5)
DistII	12(3)	0.82(5)	-0.11(8)

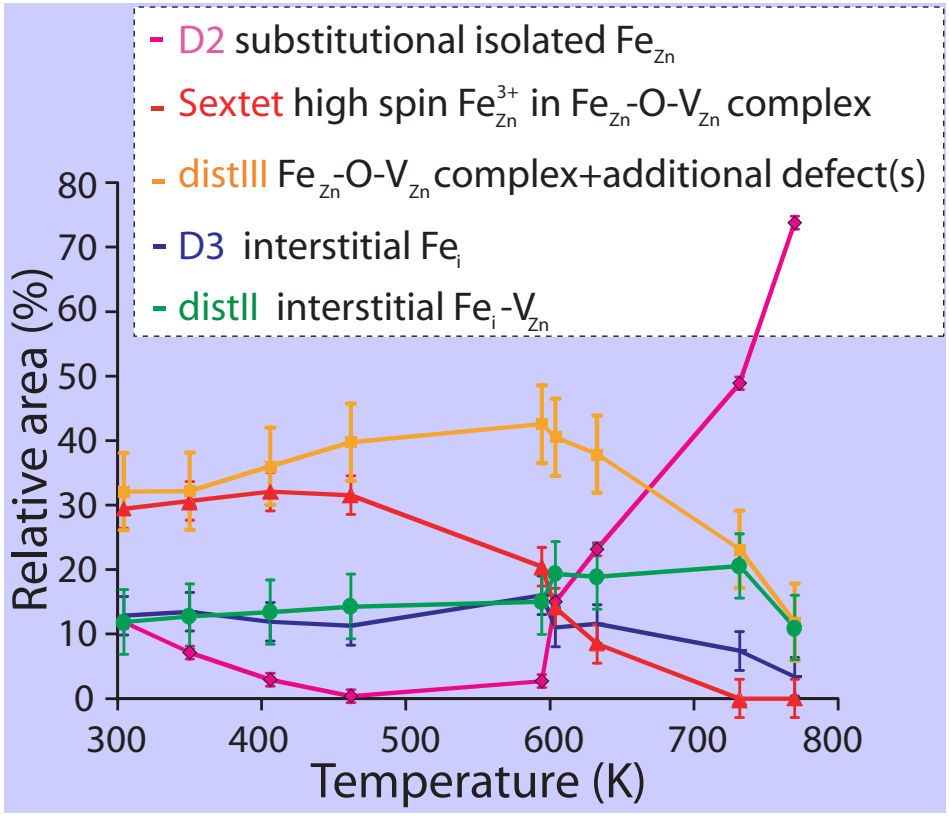
[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

- no secondary phases
- the observed magnetism must be due to the interaction of Mn/Fe with the dense damage cascades created during implantation

Mössbauer results: annealing behavior



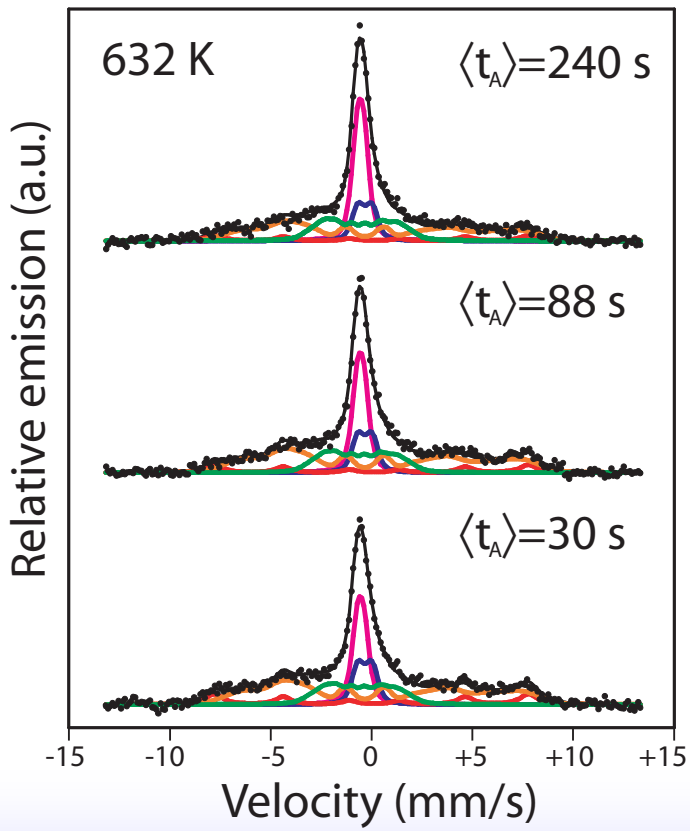
- Low fluence data (≤10^{12} Mn/cm^2)
- Simultaneous fitting procedure
- The linewidths of D2,D3,Sextet are fixed

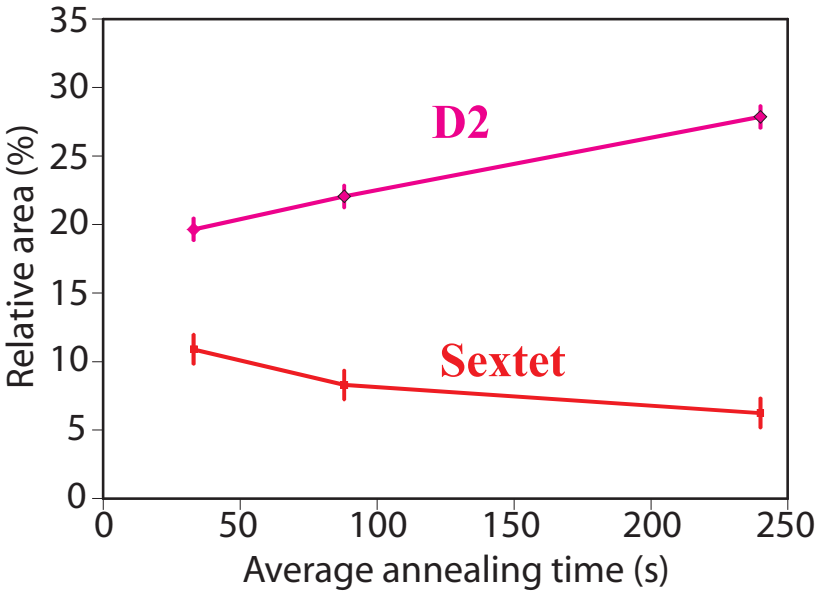


Mössbauer results: time delayed measurements

•Time-dependence of the thermally activated annealing. Principles:

1. Implant (t = 0)
2. Start measurement
3. Measure (0 < t < T½)
4. Measure (T½ < t < 5T½)



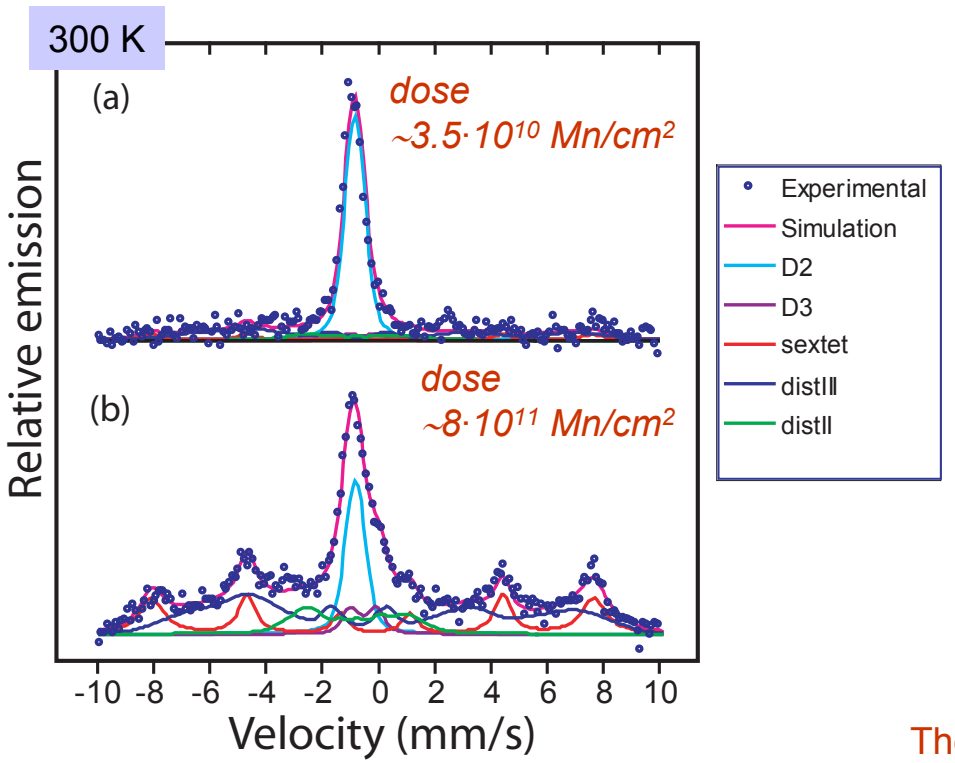


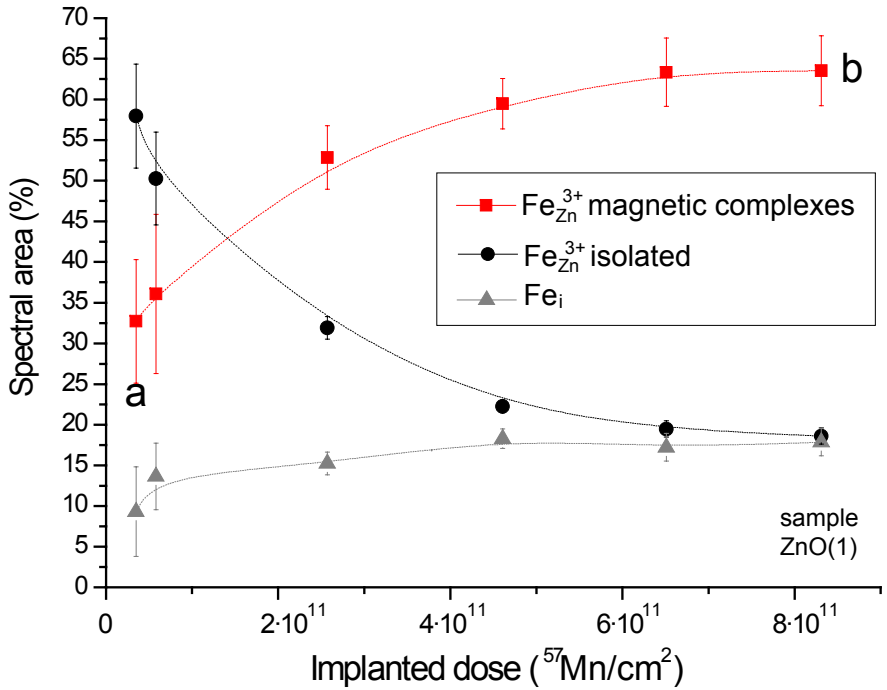
•The conversion of the sextet→D2 occurs on a minute time scale

•The time and temperature dependence of spectral fractions suggest a scenario in which the association of Fe_{Zn} with defect complexes takes place in the 300/462 K and the dissociation of the complex is at ≥600 K

Dose dependence in Mn/Fe-implanted ZnO

- At the early stage of implantation there is a low magnetic contribution
- The sextet+distIII fractions increases with increasing the implanted dose

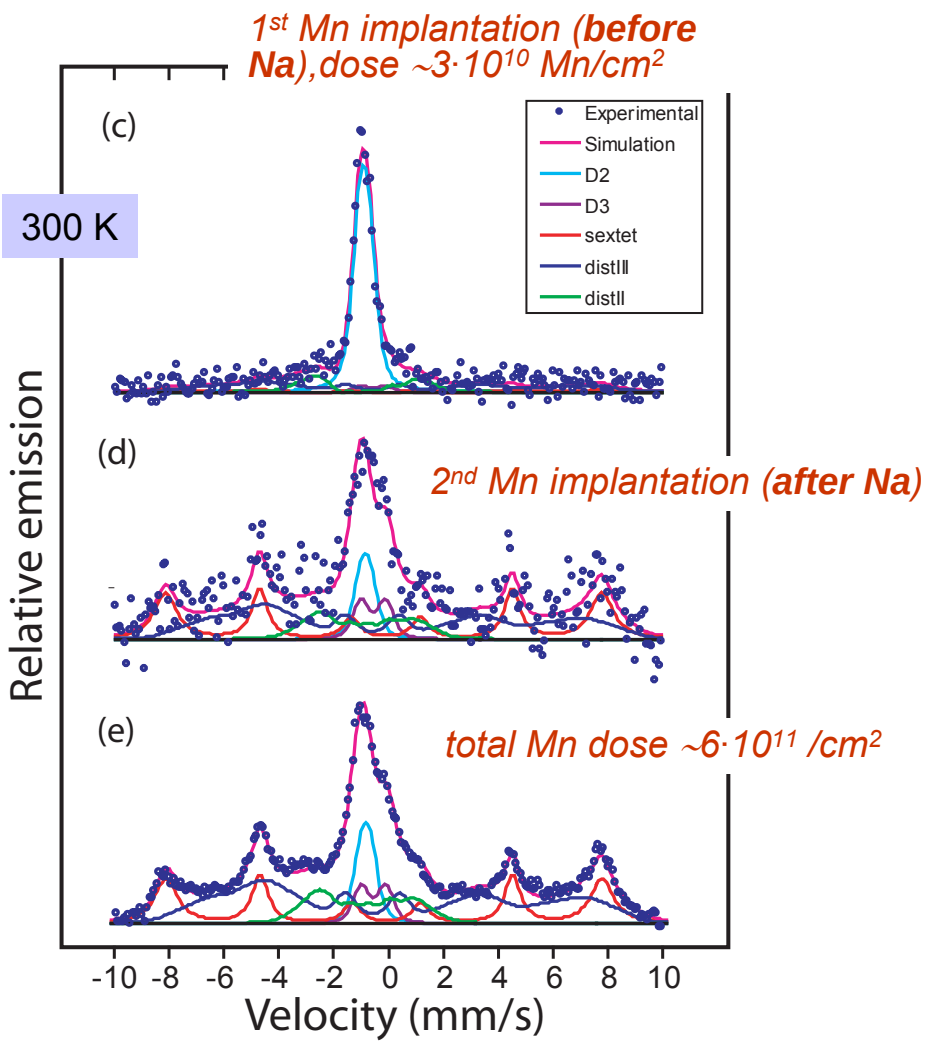


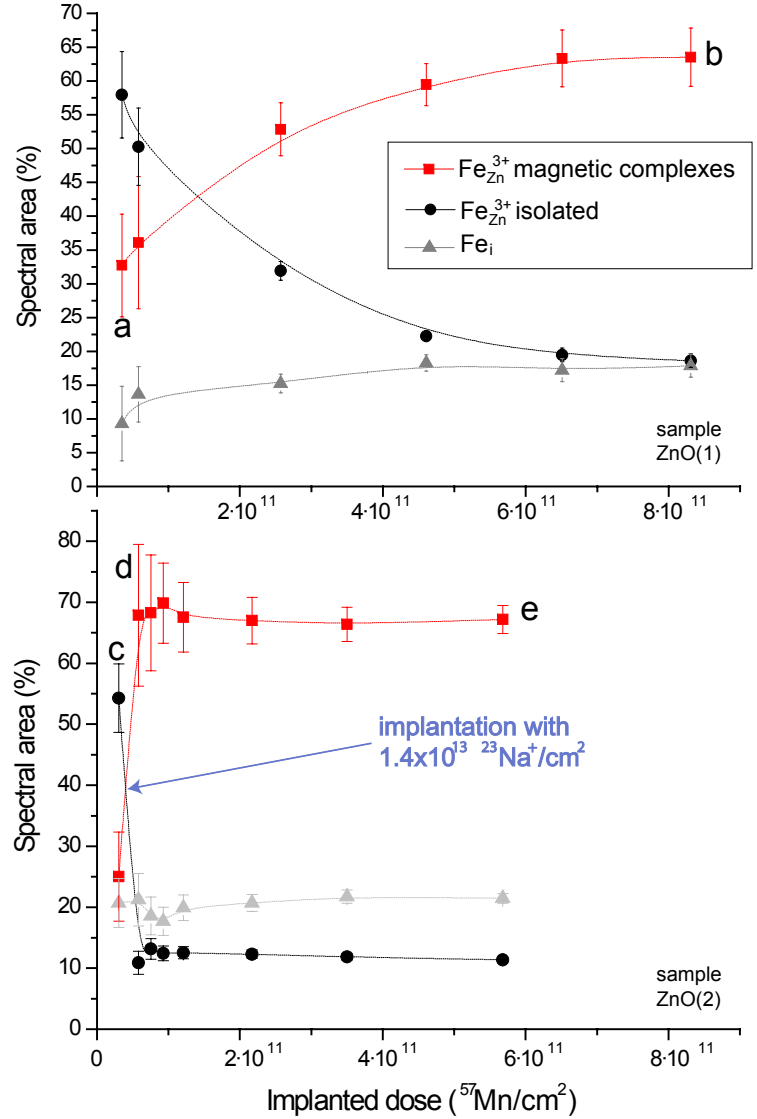


The implanted dose is estimated by considering the background Mössbauer counts and a constant fluence

The dose dependence can be understood by assuming that the implantation-induced defects are responsible for the observed magnetism

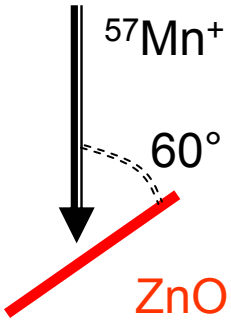
ZnO implanted with stable $^{23}Na^{+}$ (dose: ~$1.4 \cdot 10^{13}$ $^{23}Na^{+}/cm^{2}$)

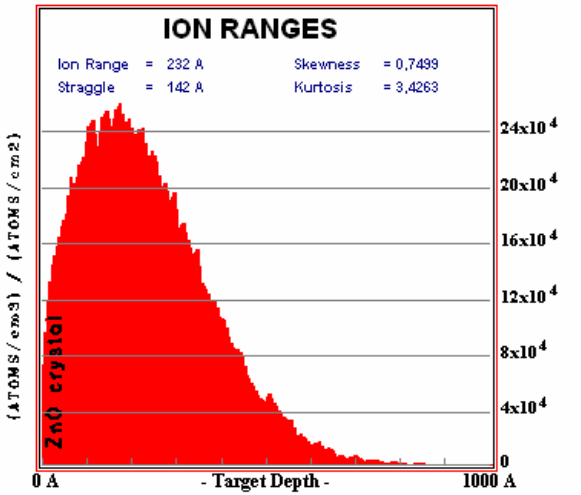


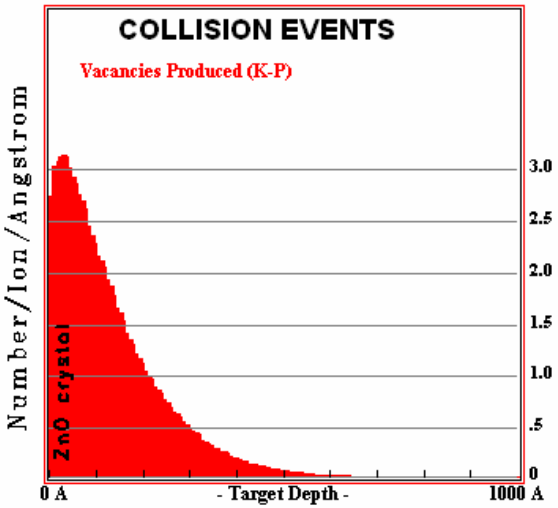


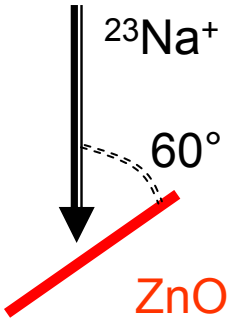
Implantation of 3d elements is possibly not needed to observe magnetism in ZnO, but the implantation-induced defects are necessary

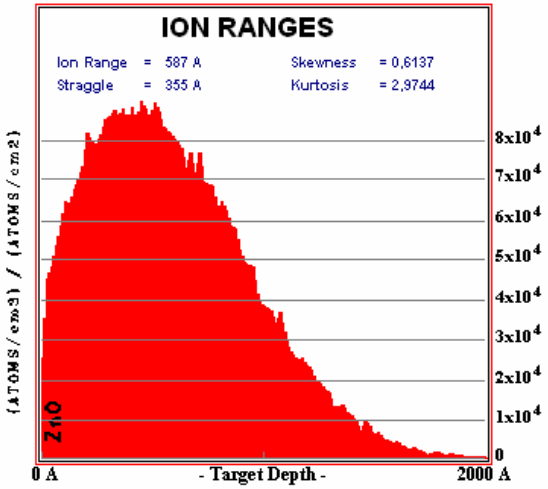
TRIM for the ^{57}Mn and ^{23}Na implantations in ZnO

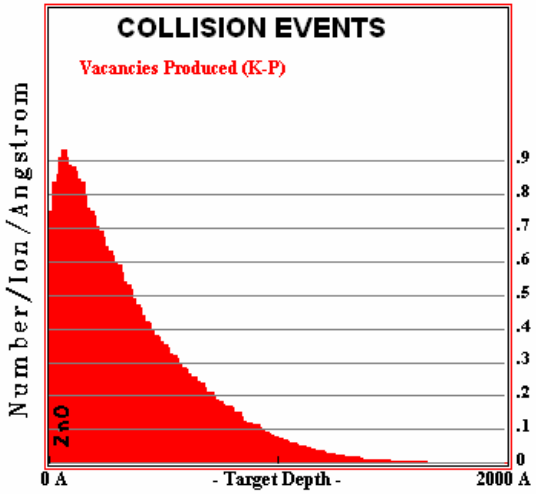






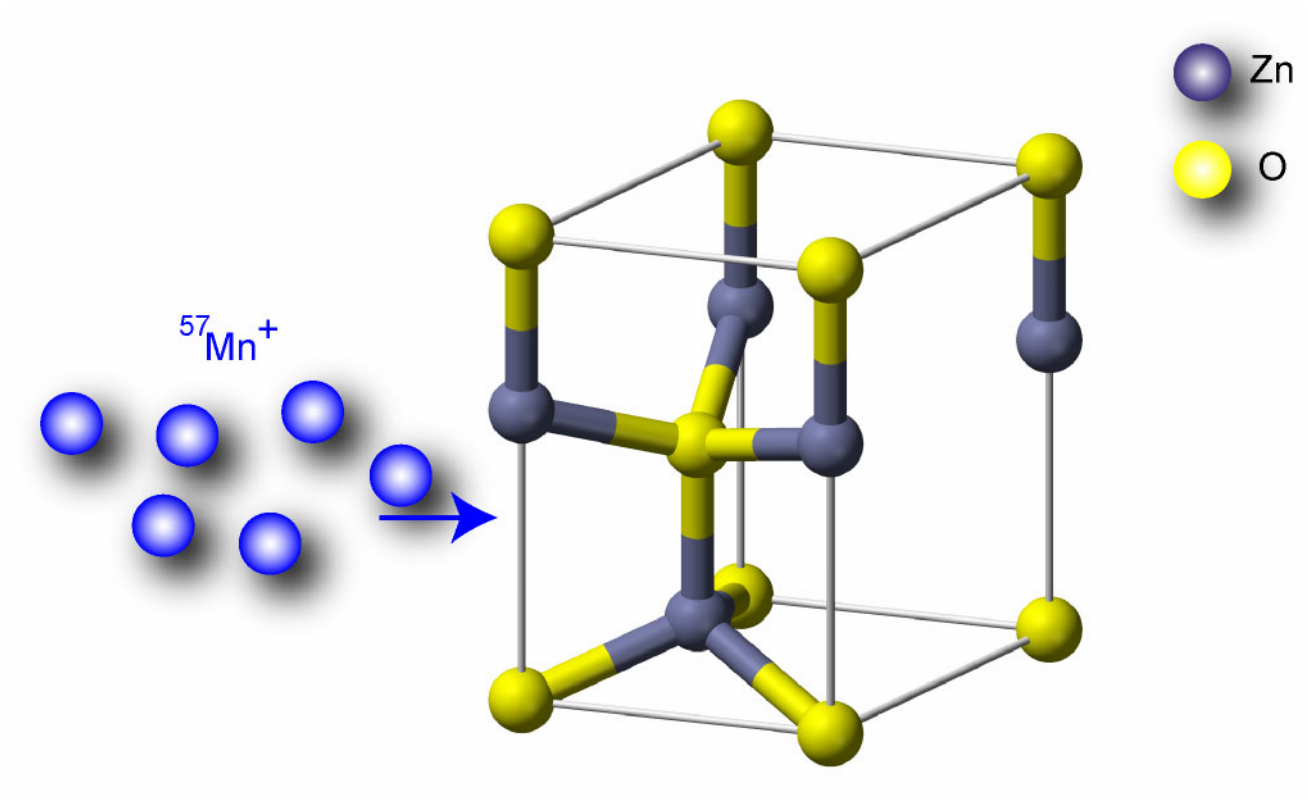






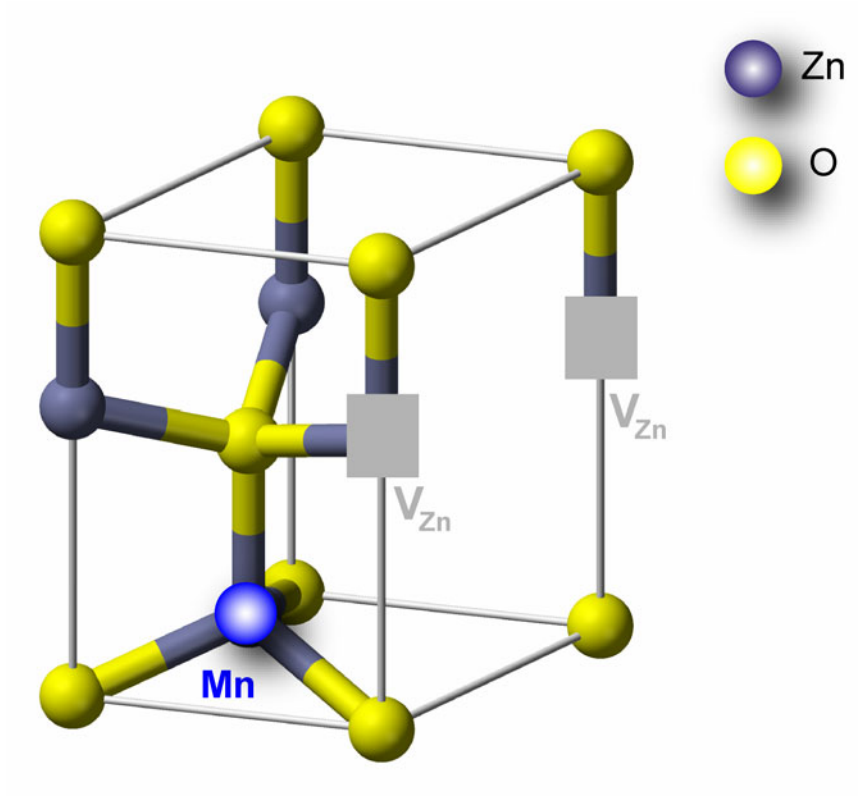
The damage cascades after the ^{57}Mn and ^{23}Na implantation (E=60 keV) overlap

Model for the Fe_{Zn}-O-V_{Zn} formation



[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

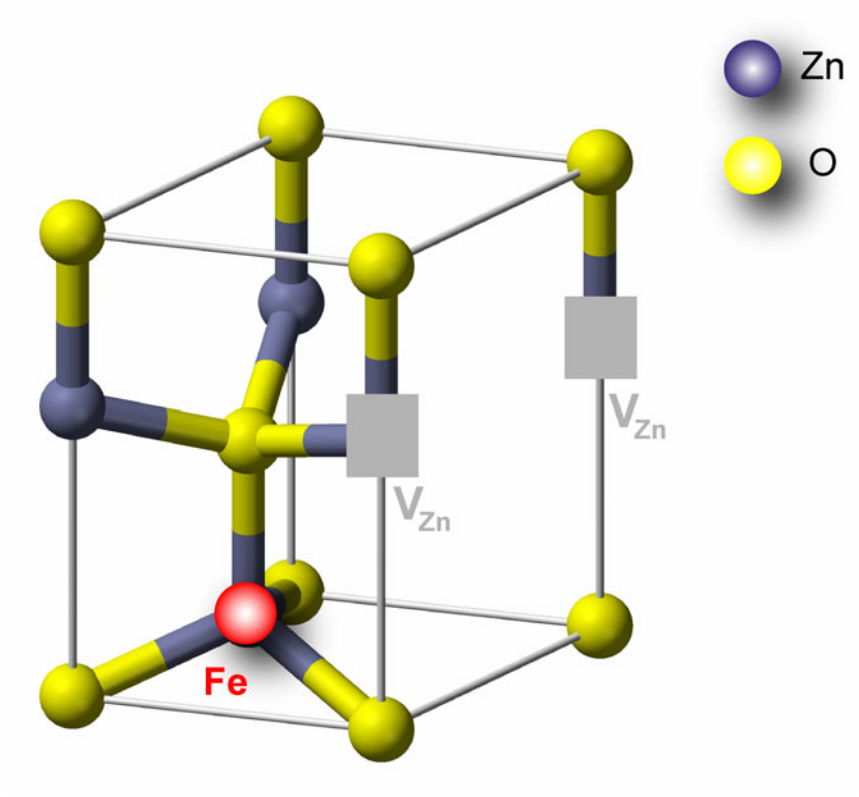
Model for the Fe_{Zn}-O-V_{Zn} formation



Defects induced by ion implantation

[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

Model for the Fe_{Zn}-O-V_{Zn} formation



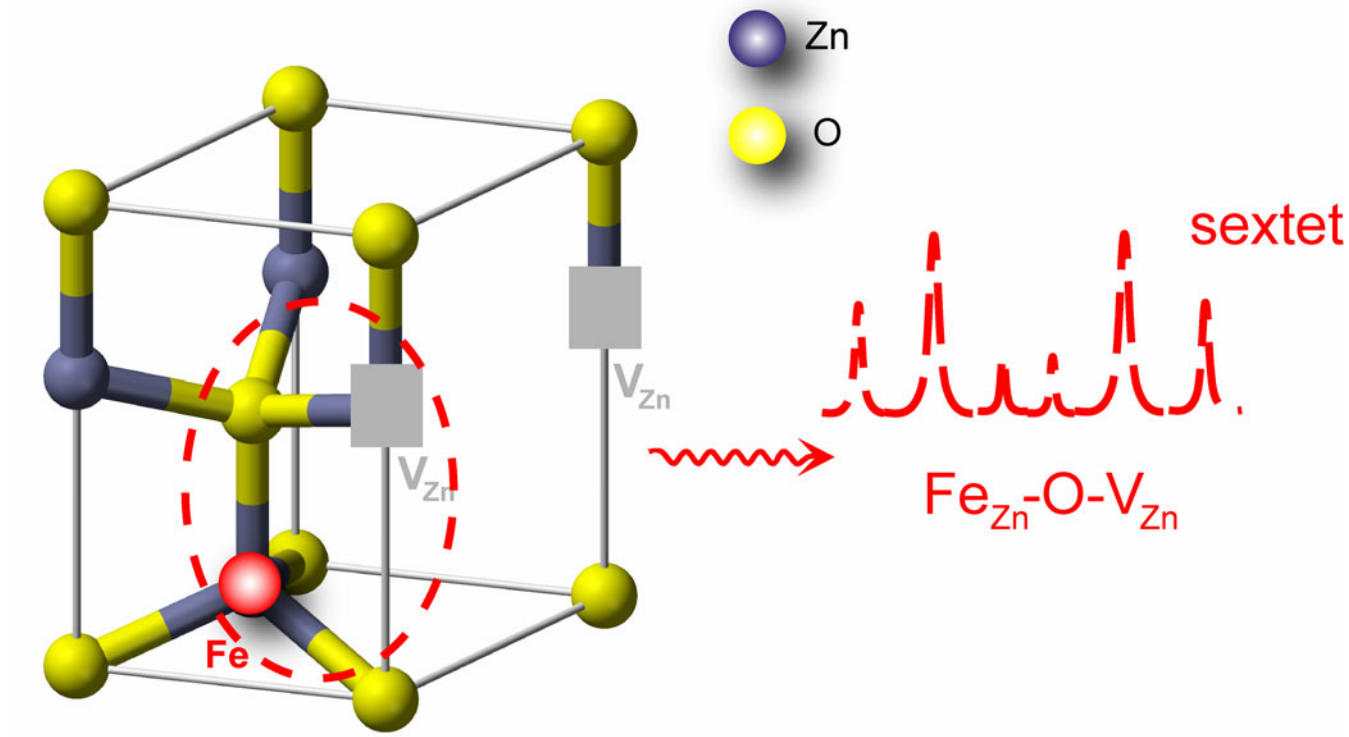
$^{57}Mn \rightarrow {}^{57m}Fe$

($T_{½}$=1.5 min.)

[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

Model for the Fe_{Zn}-O-V_{Zn} formation

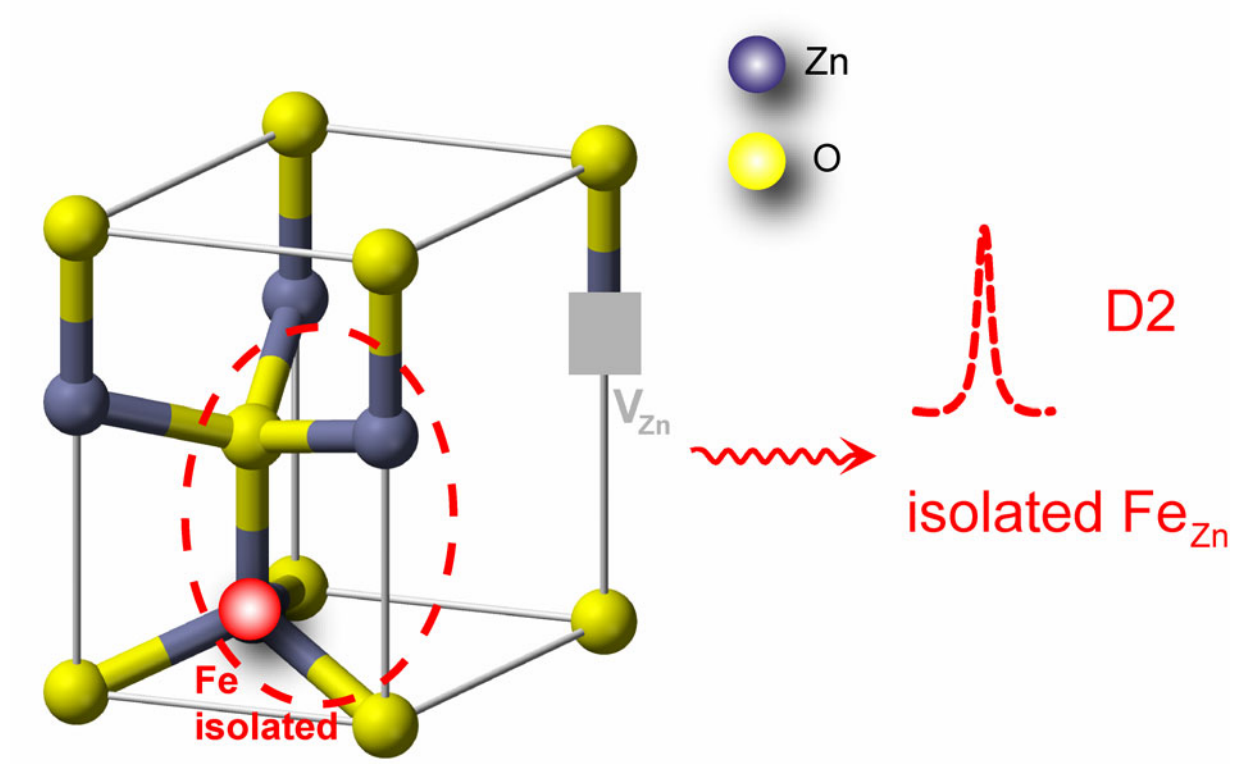
Assumption: V_{Zn} are mobile at $\geq$ 300 K



[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

Model for the Fe_{Zn}-O-V_{Zn} formation

Assumption: V_{Zn} are mobile at $\geq$ 300 K



[G. Weyer, H.P. Gunnlaugsson, R. Mantovan, M. Fanciulli, D. Naidoo, K. Bharuth-Ram, T. Agne, J. Appl. Phys. **102**, 113915 (2007)]

Conclusions

- The majority of the Fe atoms are located on Zn sites in a high-spin Fe^{3+} state at ≤600 K.
- The sextet is due to Fe_{Zn}-O-V_{Zn} complexes (V_{Zn} mobile at T>RT on a minute time scale) that are stable up to ~600 K.
- The formation/annealing of the magnetism in ZnO is interpreted as occurring/disappearing upon the association/dissociation of Mn/Fe complexes with the lattice defects created during the implantation process.

Conclusions

- The majority of the Fe atoms are located on Zn sites in a high-spin Fe^{3+} state at ≤600 K.
- The sextet is due to Fe_{Zn}-O-V_{Zn} complexes (V_{Zn} mobile at T>RT on a minute time scale) that are stable up to ~600 K.
- The formation/annealing of the magnetism in ZnO is interpreted as occurring/disappearing upon the association/dissociation of Mn/Fe complexes with the lattice defects created during the implantation process.

!! Understand the link between the magnetism observed by Mössbauer spectroscopy and the macroscopic magnetism (if any) !!