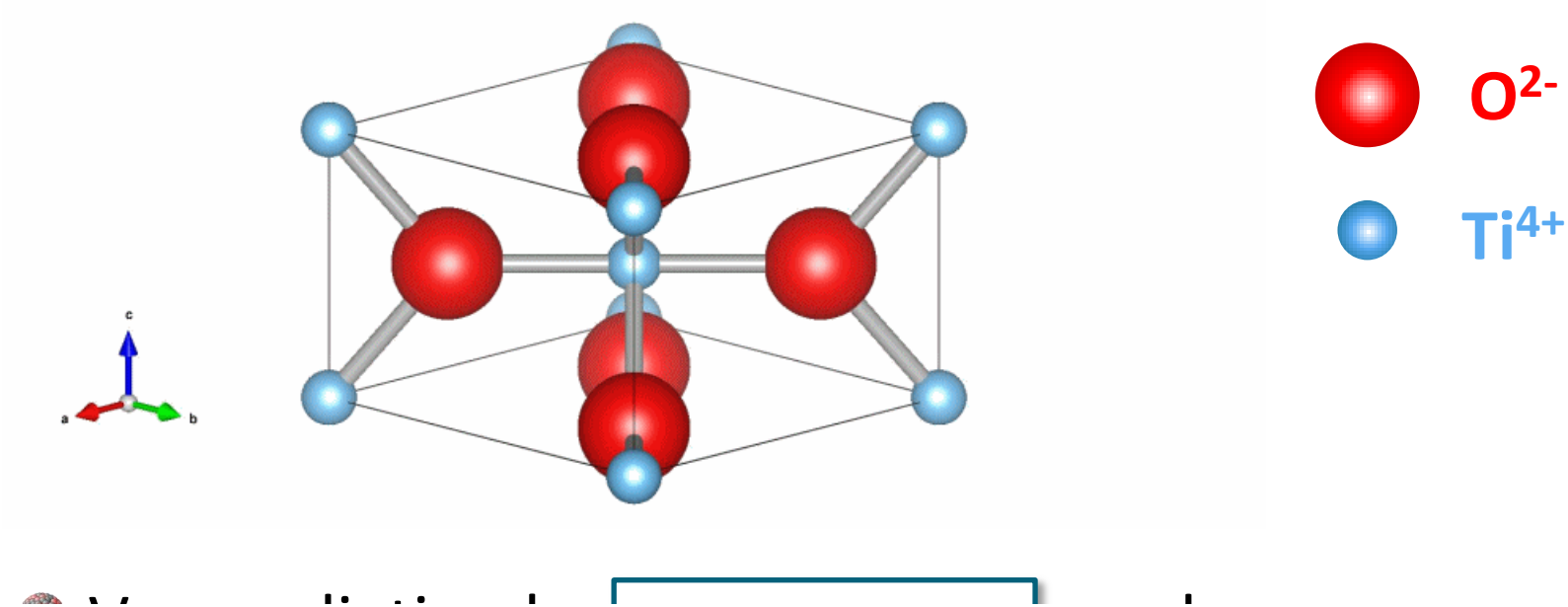
Defect annealing in Mn/Fe implanted TiO_2 (rutile)

H. P. Gunnlaugsson on behalf of the Mössbauer collaboration at ISOLDE/CERN (IS501)

- Motivations
- Experimental
- Results
- Discussion/conclusion

TiO_2 (rutile) motivations



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Charge-transfer ferromagnetism in oxide nanoparticles

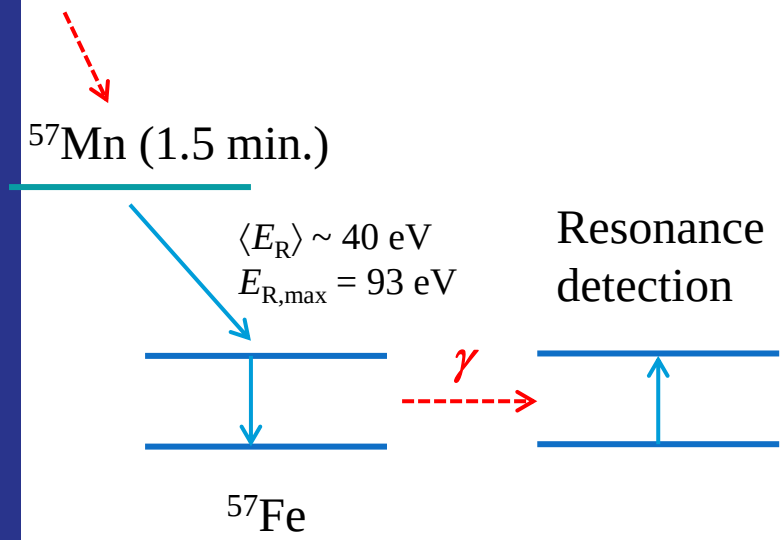
J M D Coey, Kwanruthai Wongsaprom[1], J Alaria and M Venkatesan

Experimental

^{57}Mn for ^{57}Fe Mössbauer spectroscopy

General principle:

Implantation of short lived parent isotopes

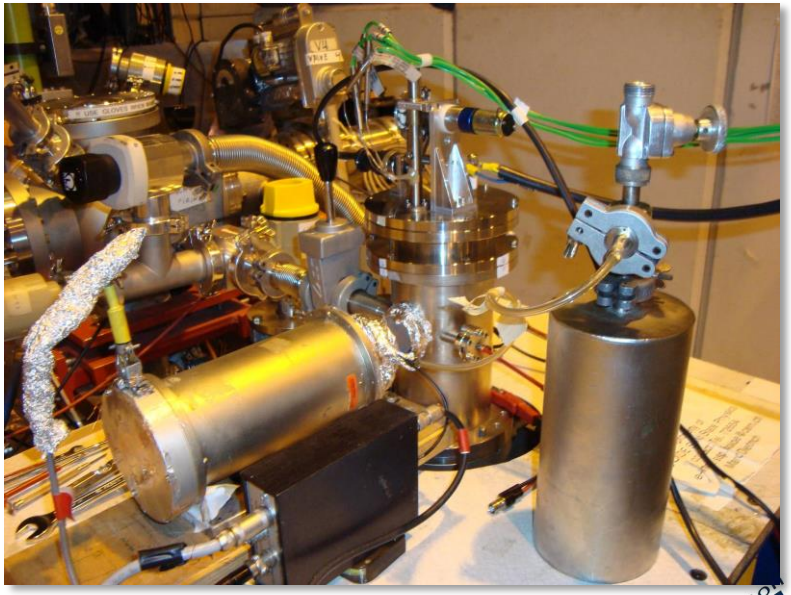


Mössbauer spectroscopy/Hyperfine interactions: Sensitive only to nn – nnn effects

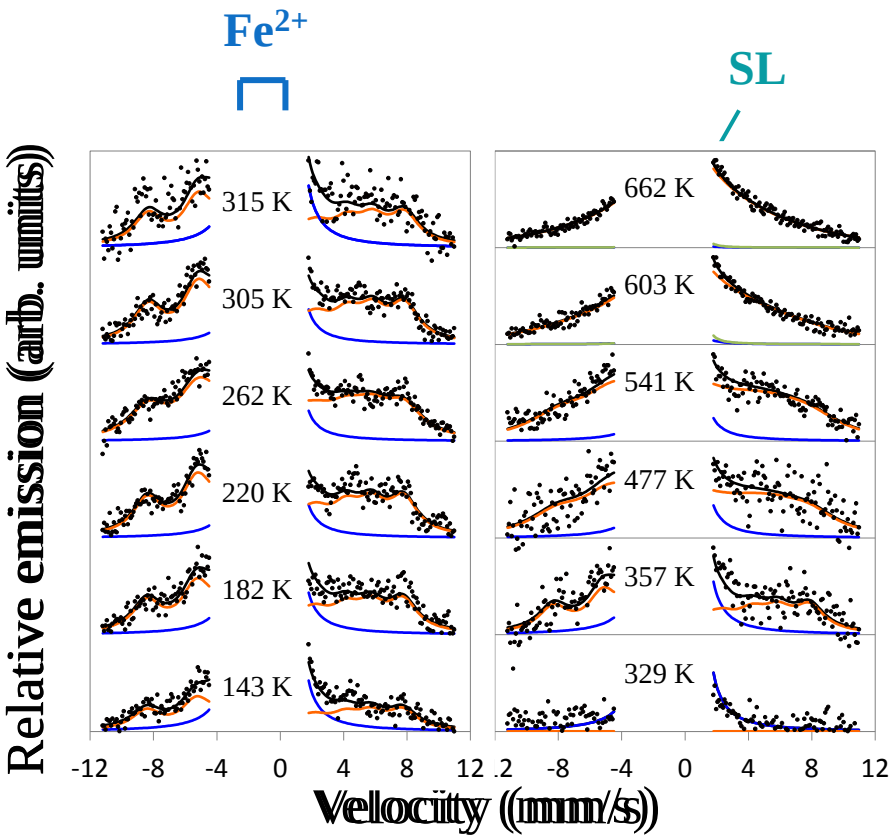
Major benefits

- Fe charge state (Fe^{3+}/Fe^{2+})
- Fe site symmetry
- Fe^{3+} spin relaxation

- High dilution ~10^{-4} at.%
- Creation of defects

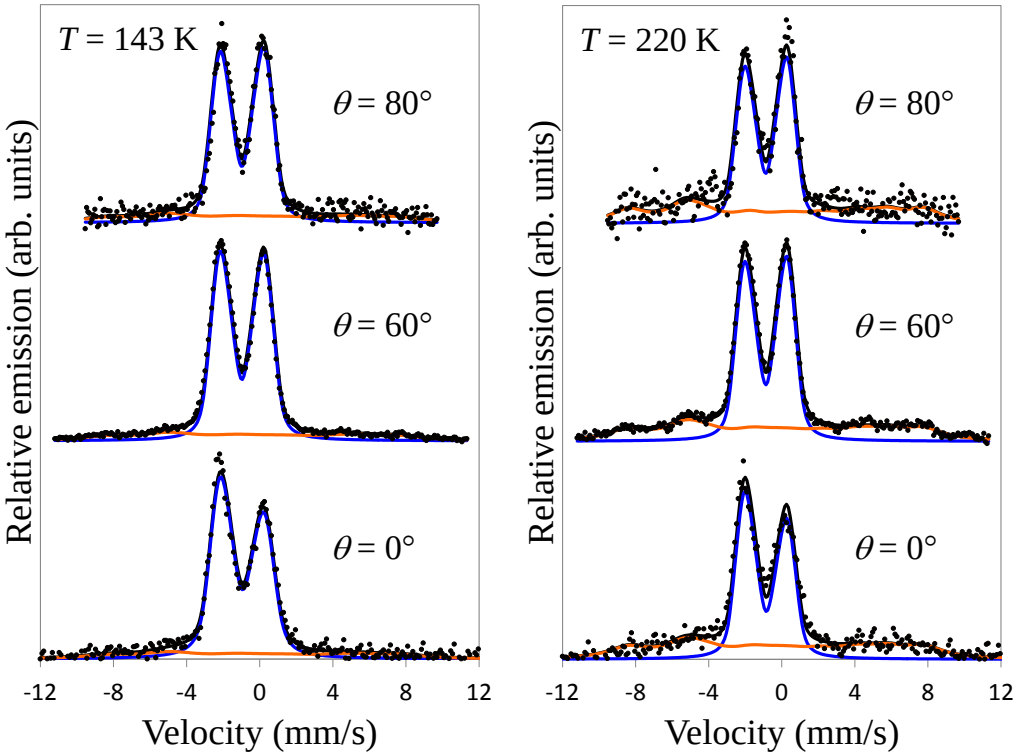


Results: Temperature series



- Dominated by Fe^{2+} species
- Single line (SL) component at highest *T*'s
- Something on the wings
- … consistent with slow relaxing paramagnetic Fe^{3+} ⇒ SL due to Fe^{3+}

Results: Angular dependence

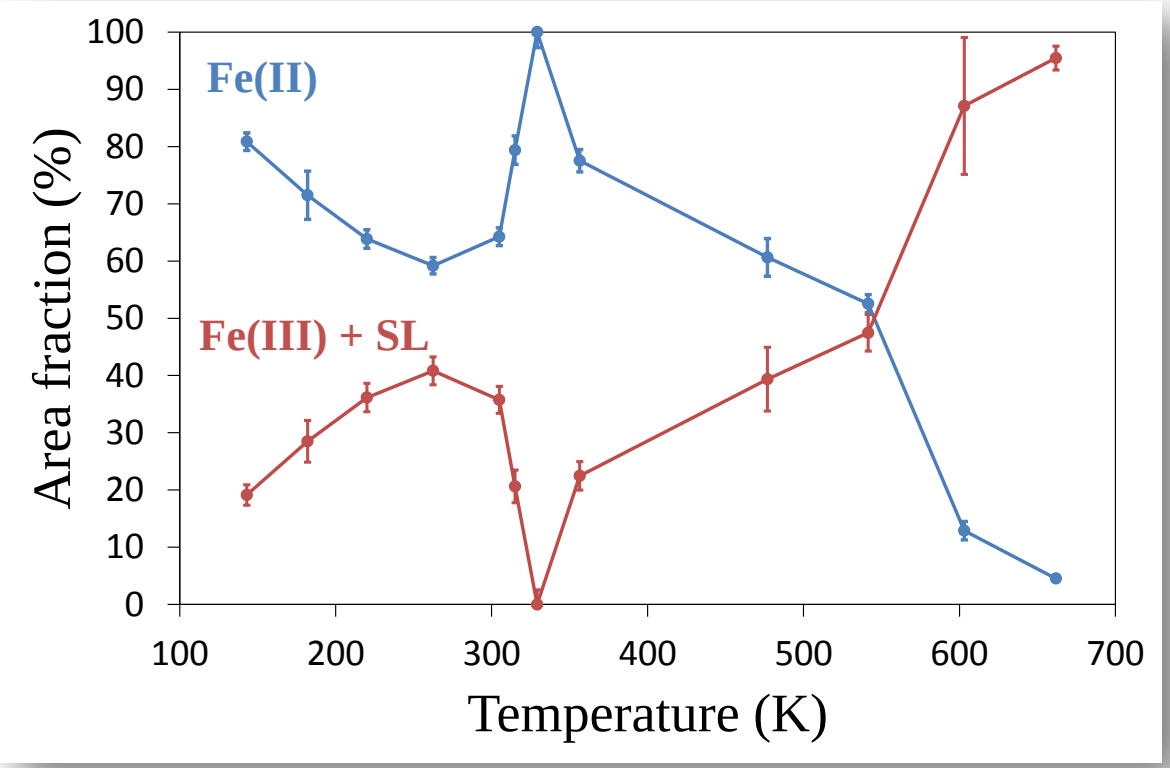


- Clear angular dependence
- **Fe^{2+}** can probe the lattice structure through the quadrupole interaction

Results: Spectral area

V_O V_{Ti} V_O V_{Ti} V_O

$Fe^{2+/3+}$ $Fe^{2+/3+}$ Fe^{3+}



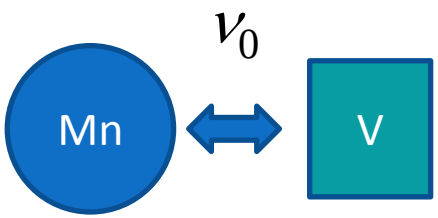
- Pure TiO_2: Fe as Fe^{3+}
- + Oxygen vacancies (V_O) $\Rightarrow$ Fe^{2+}
- + Titanium vacancies (V_{Ti}) $\Rightarrow$ $Fe^{3+(/4+)}$

Pair disociation

- Probability of dissociation:

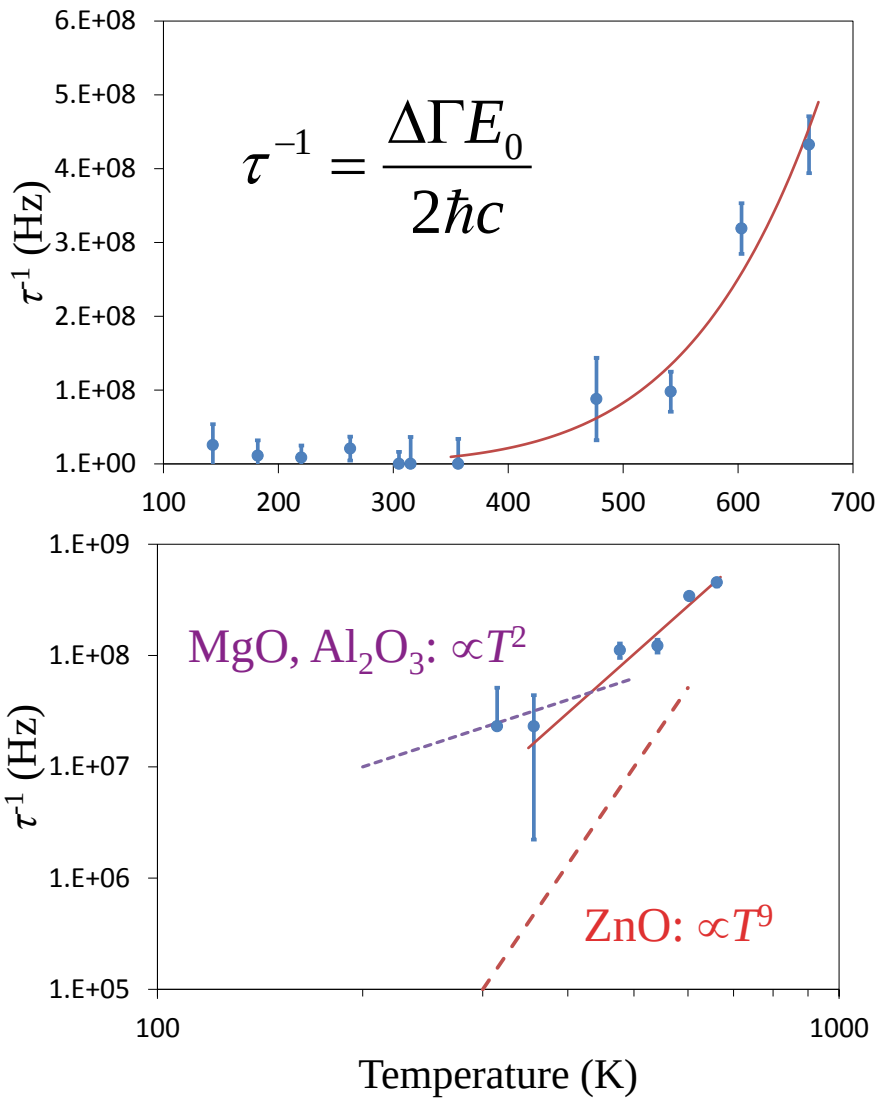
$$p(T) = \frac{\nu_0 \cdot \tau \cdot e^{-\Delta E / kT}}{\nu_0 \cdot \tau \cdot e^{-\Delta E / kT} + 1}$$

$$p(T_A) = ½ \Rightarrow \Delta E = T_A k \ln(\nu_0 \cdot \tau)$$



Complex:	**Diss. Energy**	**Binding energy**
		[Navarro et al., 2011] (theory)
Mn – V_O:	1.60(15) eV	~1.6 eV
	:	

Fe^{3+} relaxation rates



- We find $\tau^{-1} \propto T^{4(1)}$
- Theory suggests T^2
- Similar inconsistency in ZnO [Mølholt et al., Phys. Scripta, 2011]
- Reason for this is unknown

Discussion/summary

- ^{57}Mn implantations into TiO_2 single crystals and Mössbauer measurements on the daughter ^{57}Fe
- A model of the annealing:
  - V_O stabilize Fe^{2+} state at $T < 550$ K
  - V_{Ti} promote Fe^{3+} state at $T < 330$ K
- V_O-Mn(/Fe) dissociation energy
  - Experimental (here) 1.60(15) eV
  - Theory [Navarro11] ~1.6 eV
- No defect related magnetism is found, but paramagnetism with "abnormal" temperature dependence
- No interstitial Fe $\Rightarrow$ displacement energy > 93 eV, consistent with theory (~130 eV [Thomas et al., 2005])