Nuclear-chemical synthesis of iron compounds and their Mössbauer identification

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

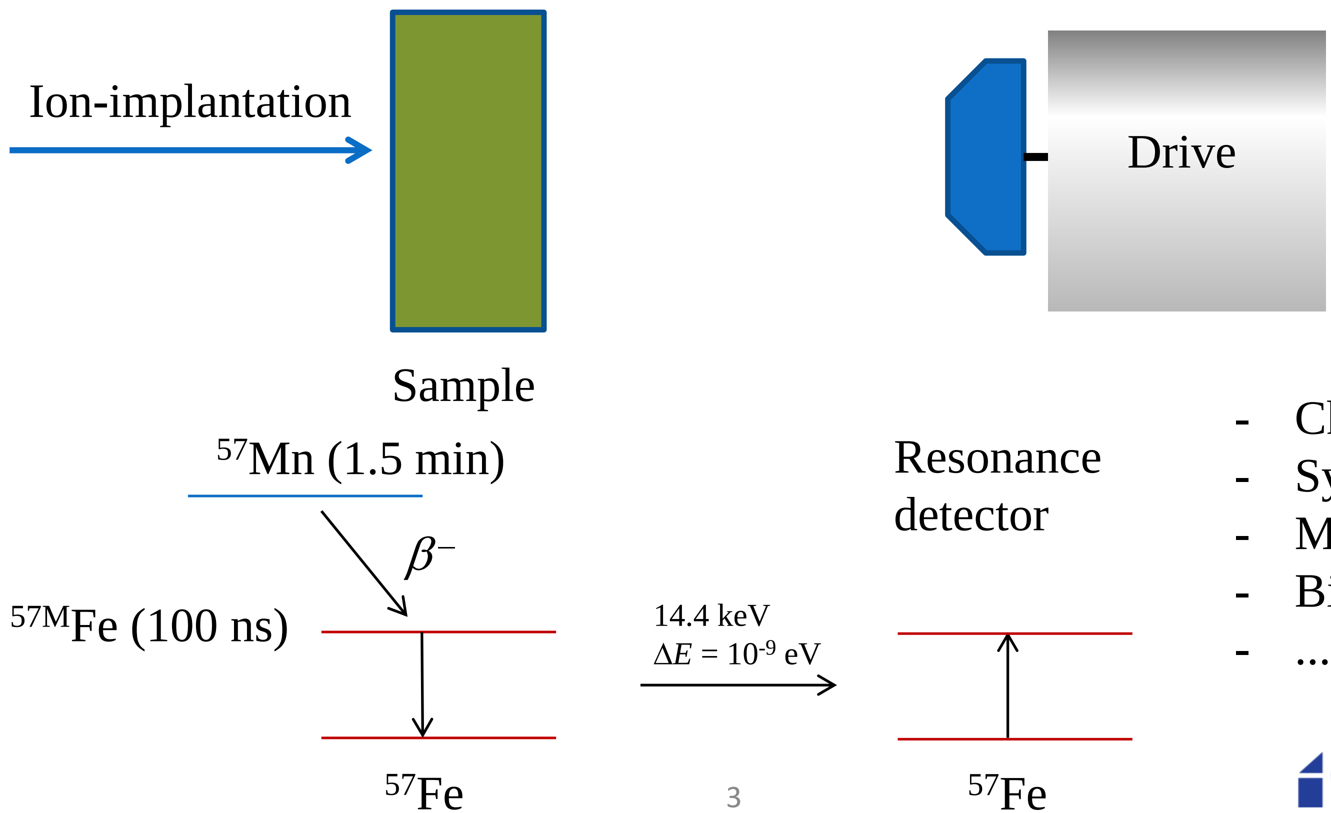
H. P. Gunnlaugsson, S. K. Dedushenko, L. Hemmingsen *et al.*,

Outline

- Introduction about ^{57}Mn ($T_{½}$ = 1.5 min.) → ^{57}Fe
- Chemistry with ^{57}Mn
- Physics/chemistry that can be addressed here
- Mössbauer collaboration at ISOLDE/CERN
- Beam request

^{57}Mn ($T_{½}$ = 1.5 min.) and ^{57}Fe eMS

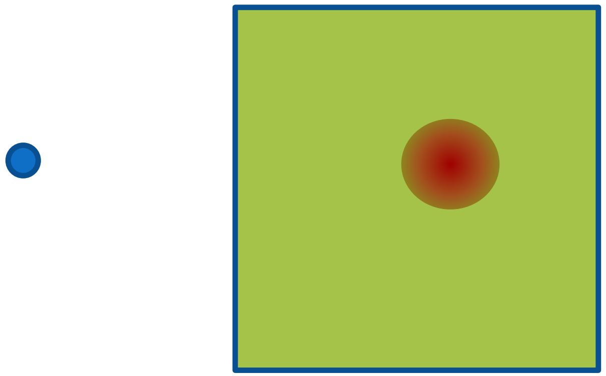
- Beam developed in 1996-1997: ~$3 \cdot 10^{8}$ s^{-1}
- Used for eMS in many experiments: *IS-359*, *IS-426*, *IS-443*, IS-501, **IS-576**, **IS-578**, **I-161**, **IS-611**, **IS-612** & IS-630

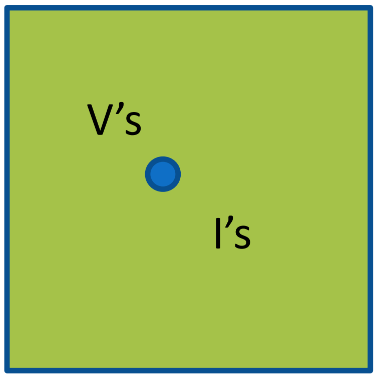


- Charge state
- Symmetry
- Magnetism
- Binding prop.
- ....

Ion-implantation

- Creates amorphous zones/regions
  - Anneal (sometimes) at low temperatures
  - Cases which cannot (easily) be studied with ion-implantation
- Point defects
  - Study of interactions of Fe/Mn atoms with point defects



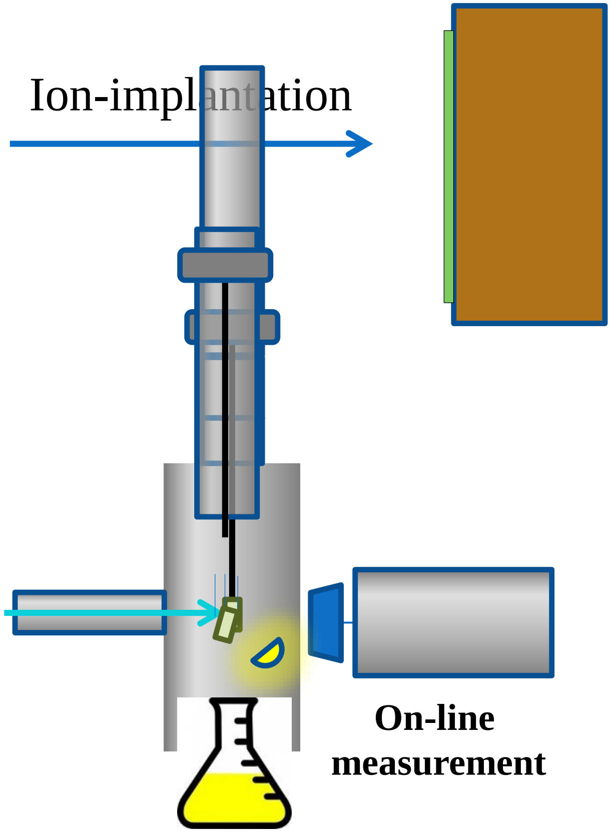


Make materials with the probe

- Surface physics
  - Used successfully in ASPIC/VITO
  - Implantation into catcher $\Rightarrow$ transfer $\Rightarrow$ MBE growth
  - Measurements with Perturbed Angular Correlation (PAC) spectroscopy
  - Dictated by the life-time of the radioactive probe
  - Many fundamental papers on surface physics in the 1990's
- Biophysics
  - Used successfully for different isotopes (^{111m}Cd, ^{199}Hg, ...) all with $T_{1/2} > 30$ minutes
  - Implantation into ice $\Rightarrow$ thawing $\Rightarrow$ reactions
  - Measurements with PAC

Chemistry and eMS with ^{57}Mn (1.5 min)

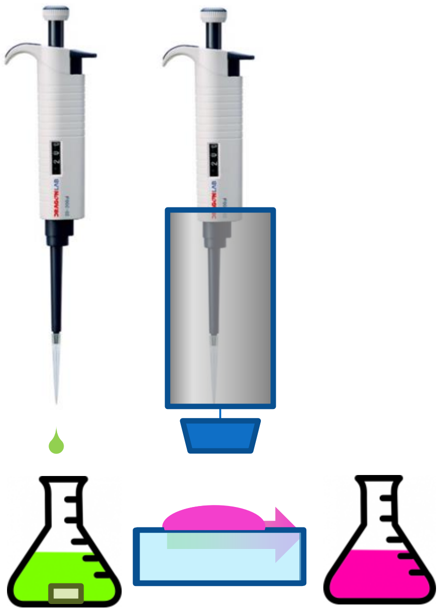
- Implantation into thin foils on suitable (inert targets). 100 Å Mn or Zn on Cu or glass seem promising
- Removal from vacuum (~5 sec)
  - Addition to on-line eMS chamber available
- Dissolution ($Mn_{metal} \rightarrow Mn_{aq}^{2+}$)
  - ~1 M acid: instantaneous
  - 0.2 M acid: few seconds



Chemistry with ^{57}Mn (cont)

- Chemical reactions
  - ➢ 1-300 seconds
- Transfer to a cold finger
- Off-line measurements (77 K – 273 K)

- Variables:
  - ➢ Acid strength
  - ➢ Reaction time/temperature
  - ➢ Measurement temperature
  - ➢ ...



Chemical reaction (1-300 s)

Risk involved

- Radioactivity
  - ~27 μSv/h at 30 cm distance
  - ~50 μSv (total dose during ~5 day experiments)
  - Transfer of (radiactive) acids in confined spaces
- Protocols have to be made that ensure the safety at all levels of measurements
  - Practice-practice-practice, ...
- Risk assessment
  - ~25 min wait time in case of spills (radioactive)
  - Water to thin out chemical spills?
- No long lived impurities (MR-TOF)
  - No radioactive waste (only chemical)

Physics & eMS

- Mössbauer spectrum:

- $\delta \propto |\psi(0)|^2$
  - $\propto$ charge/spin state of the atom

- $\Delta E_Q \propto V_{ZZ}$
  - ~ coordination

- Area $\propto f(T, \theta_D)$
  - ~ binding properties

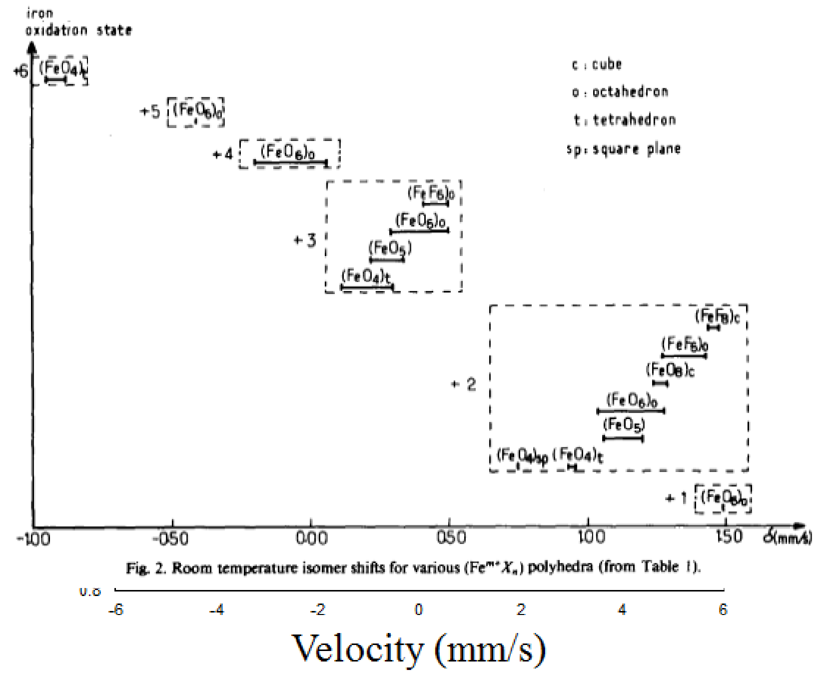


Fig. 2. Room temperature isomer shifts for various ($Fe^{m+}X_n$) polyhedra (from Table 1).

Nuclear chemical synthesis

- FeO_2 does not exist (Fe as Fe^{4+})
- However, MnO_2 exists
- $\Rightarrow$
  - Make $^{57}MnO_2$
  - Wait for $^{57}FeO_2$

High charge states of Fe

- "Natural" charge states:
  - Fe: **2+**, **3+**, 4+, *5*+, 6+
  - Mn: **2+**, 3+, **4+**, 5+, **6+,** 7+, 8+
- Oxidation involving Mn^{7+}
  - $2Mn^{2+} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Na^+ + 5Bi^{3+} + 7H_2O$
- Freezing and wait for the decay... (β^-)
- The 100 ns lifetime of $^{57*}Fe$, should not change the local configuration i.e. Fe^{7+} should be measured
- All supported by theoretical calculations

Future ...

- Isotopic exchange
  - $^{57}Mn^{2+} + {}^{55}MnO_4^- = {}^{55}Mn^{2+} + {}^{57}MnO_4^-$
- Precipitation of MnO_2
  - + comparison to direct implantation into MO_2 substrates

- Biological role: Mn^{2+} function as cofactors for a large variety of enzymes and are essential in detoxification of superoxide free radicals in organisms. This project may provide a new analytical method within this field of study

The eMS collaboration

The Mössbauer collaboration at ISOLDE/CERN, >30 active members

Involved in 6 experiments at CERN

Organize the WEMS conference series

Year	Rev. publications
2017	(2)
2016	5
2015	2
2014	4
2013	2
2012	10

Key people:

H. P. Gunnlaugsson, Copenhagen: eMS

S. K. Dedushenko, Moscow : Chemistry & MS

L. Hemmingsen, Copenhagen: Biophysics & PAC

S. P. A. Sauer, Copenhagen: Chemistry, simulations

J. Bendix, Copenhagen, Calculations

Beam request

- For each reaction (See tables), one needs to:
  - vary reaction time/temperature
  - strength (acid)
  - possibly repeat to get sufficient statistics
  - Measurement temperature
  - ....
- Each measurement: ~10 min.
  - +20% calibration
  - +20% contingency
- 14 shifts requested for the next 3 operation years

	Carrier, pH etc.	Reaction
1a 1b 1c	no carrier (-) $MnSO_4$, 10^{-5}M $MnSO_4$, 0.01M	$Mn + 2H^+ \rightarrow Mn^{2+} + H_2\uparrow$ (with 1M H_2SO_4)
2	-	$Mn + HNO_3 \rightarrow Mn^{2+} + \ldots$ (with 1M HNO_3)
3a 3b 3c	- $MnSO_4$, 10^{-5}M $MnSO_4$, 0.01M	$2Mn^{2+} + 5NaBiO_3 + 14H^+ = 2MnO_4^- + 5Na^+ + 5Bi^{3+} + 7H_2O$
4a 4b	$MnSO_4$, 0.01M $MnSO_4$, 2M	$MnO_4^- + C_2O_4^{2-} + OH^- \rightarrow MnO_4^{2-} + CO_3^{2-} + H_2O$ (with NaOH) $MnO_4^- + C_2O_4^{2-} \rightarrow MnO_2\downarrow + CO_2\uparrow$ (in neutral solution)
5a 5b 5c	- $MnSO_4$, 10^{-5}M $MnSO_4$, 0.01M	$MnO_4^- + SO_3^{2-} + OH^- \rightarrow MnO_4^{2-} + SO_4^{2-} + H_2O$ (with NaOH)
6a 6b	- $MnSO_4$, 0.01M	$MnO_4^- + SO_3^{2-} + OH^- \rightarrow MnO_4^{3-} + O_2 + H_2O$ (with strong NaOH)
7a 7b 7c 7d 7e 7f	-, pH=7 -, pH=9 -, pH=14 $MnSO_4$, 0.01M, pH=7 $MnSO_4$, 0.01M, pH=9 $MnSO_4$, 0.01M, pH=14	$Mn^{2+} + H_2O_2$ (30-50%) + NaOH $\rightarrow Mn^{3+}$ / Mn^{4+} (e.g. MnO_2)
8	$MnSO_4$, 0.01M, pH=0 $MnSO_4$, 0.01M, pH=1 $MnSO_4$, 0.01M, pH=3 $MnSO_4$, 0.01M, pH=7 $MnSO_4$, 0.01M, pH=9	${}^{57}Mn^{2+} + {}^{55}MnO_4^- = {}^{55}Mn^{2+} + {}^{57}MnO_4^-$ (isotopic exchange in different media) in acidic should be observed.

Thanks for your attention