Solid State and bio-physics at ISOLDE

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Outline

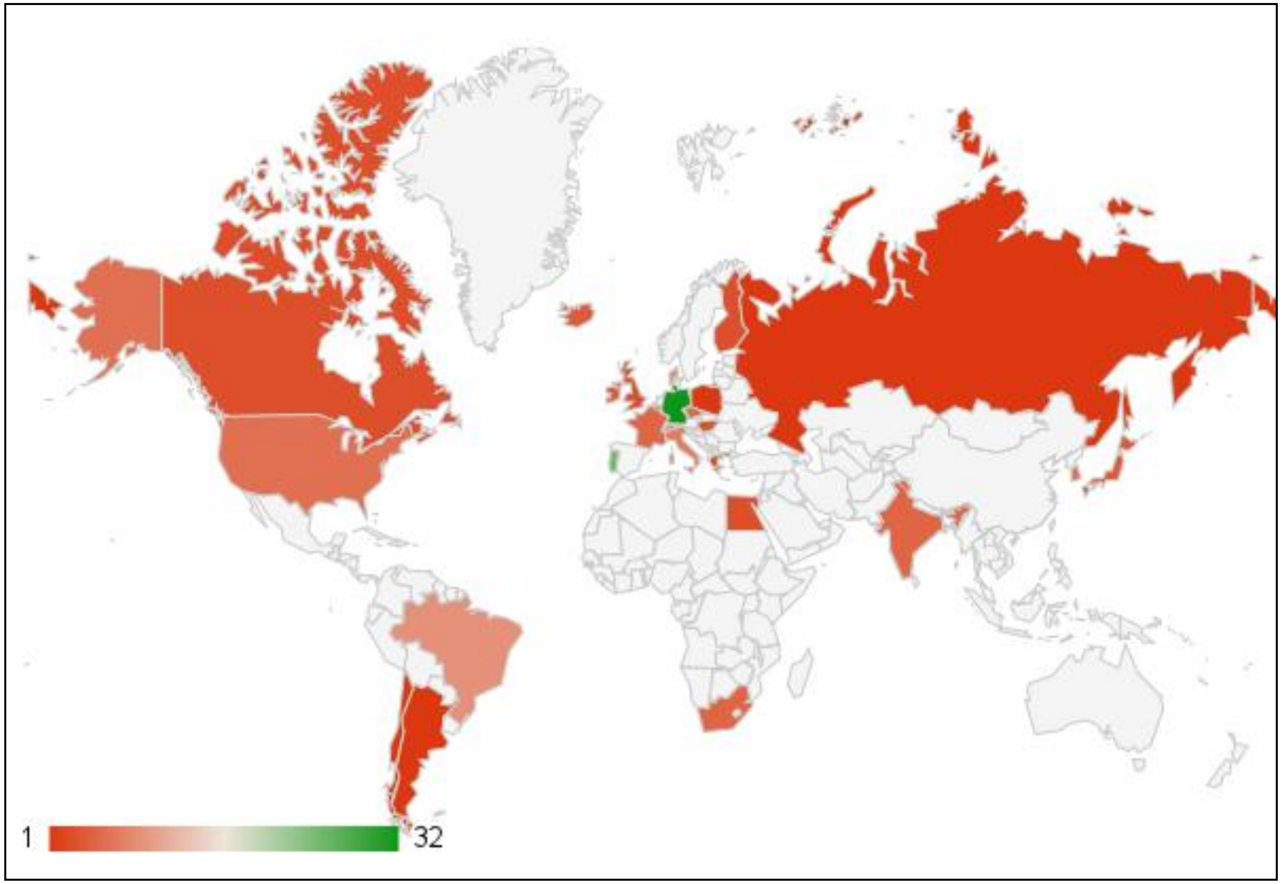
- Overview of the community
- Introduction to techniques used in nuclear solid state physics
- Techniques used at ISOLDE
- Focus on some recent results in solid state and biophysics.

SSP @ ISOLDE: Diverse community

Solid State physics:
Semiconductors,
Metals

Materials scientists:
High Tc
Superconductors,
Multiferroic materials

Biophysics:
structural properties &
role of heavy metals in
proteins, DNA.



SSP collaborations

Running experiments/letters of intent	24
Participating countries	26
Scientists	160

Radioactive isotopes for solid state physics? Why & How??

Nothing is more easy to detect with high sensitivity than nuclear radiation, i.e. very low concentrations of radioactive impurity atoms in a material can be detected.

The radioactive isotopes ("probes") act as "spies" transmitting information with atomic resolution via their decay.

- Crucially: what information do you get?????
- Adds extra dimension to "normal spectroscopies" e.g. optical / electrical characterisation of semiconductors
- Provides extremely local probe which is applied to variety of systems

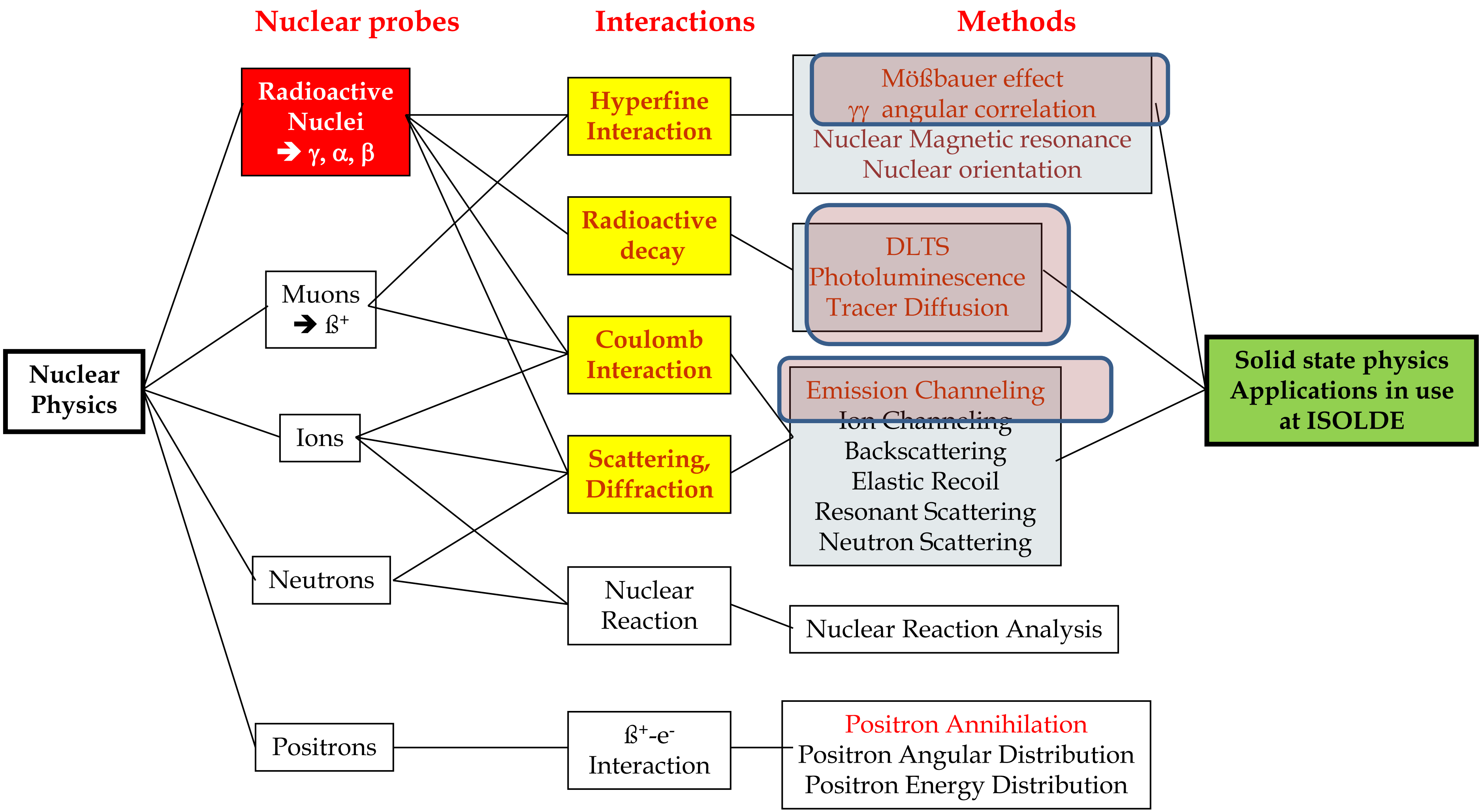
You need

A facility providing a large variety of radioactive isotope (if possible, isotopically clean)

You have to introduce the isotopes into the semiconductor

- ➢by ion implantation
- ➢by diffusion
- ➢during crystal growth
- ➢by nuclear reaction with one of the constituents of the solid

Techniques used at ISOLDE



Techniques & facilities available

Hyperfine Interactions:

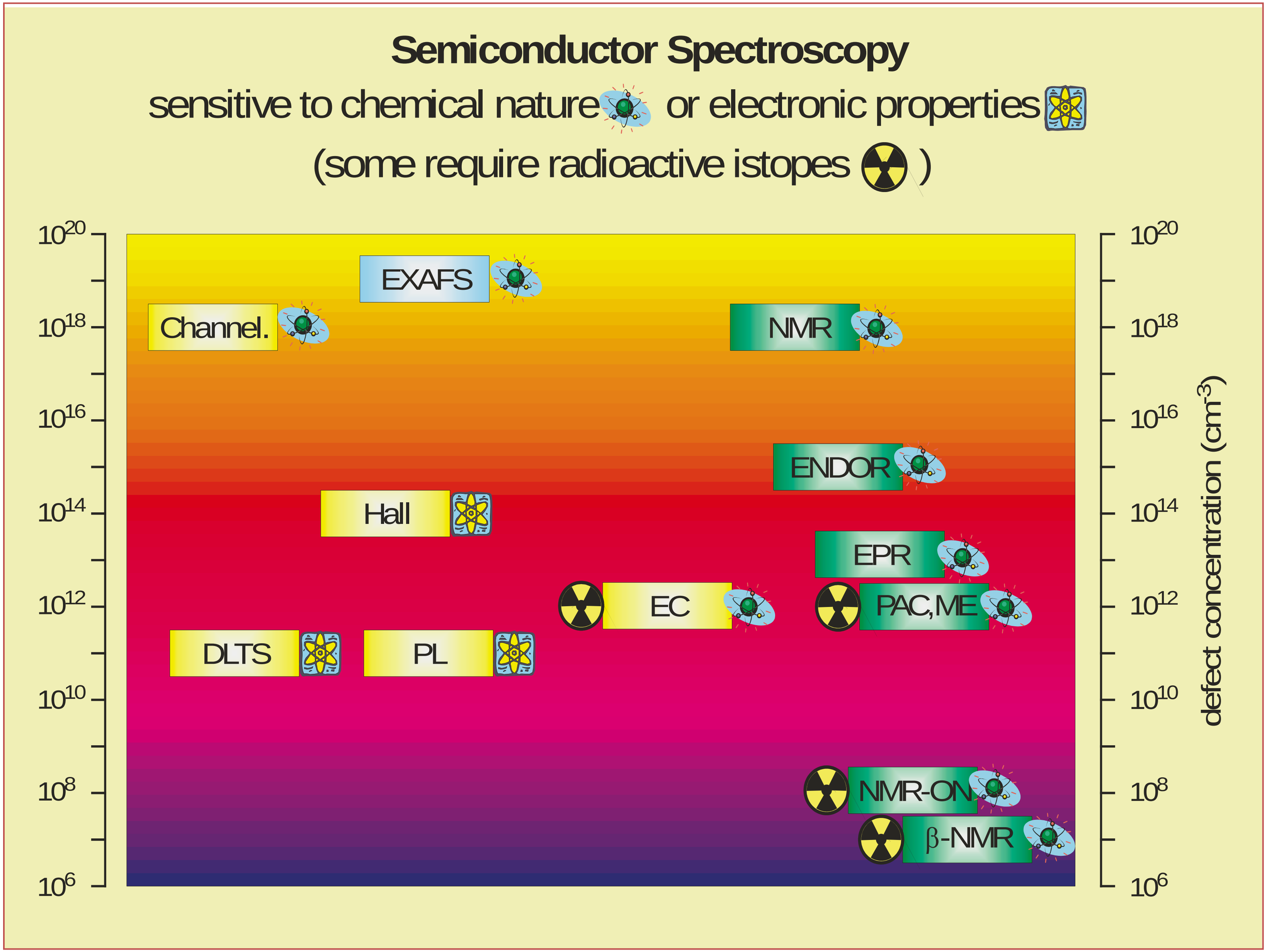
- **PAC** (See Prof Das' talk)
  - 9 γ-γ machines on-site
  - 4 detectors; 6 detectors: analogue and digital.
  - Online UHV beamline for surface physics
- **Mossbauer Effect**: 3 online chambers available.
- **β-NMR** including novel system developed for biophysics.

Lattice location using emission channelling: 3 offiline and 1 online setup

Radiotracer diffusion: online and offline systems

Semiconductor spectroscopy: full PL and DLTS characterisation labs

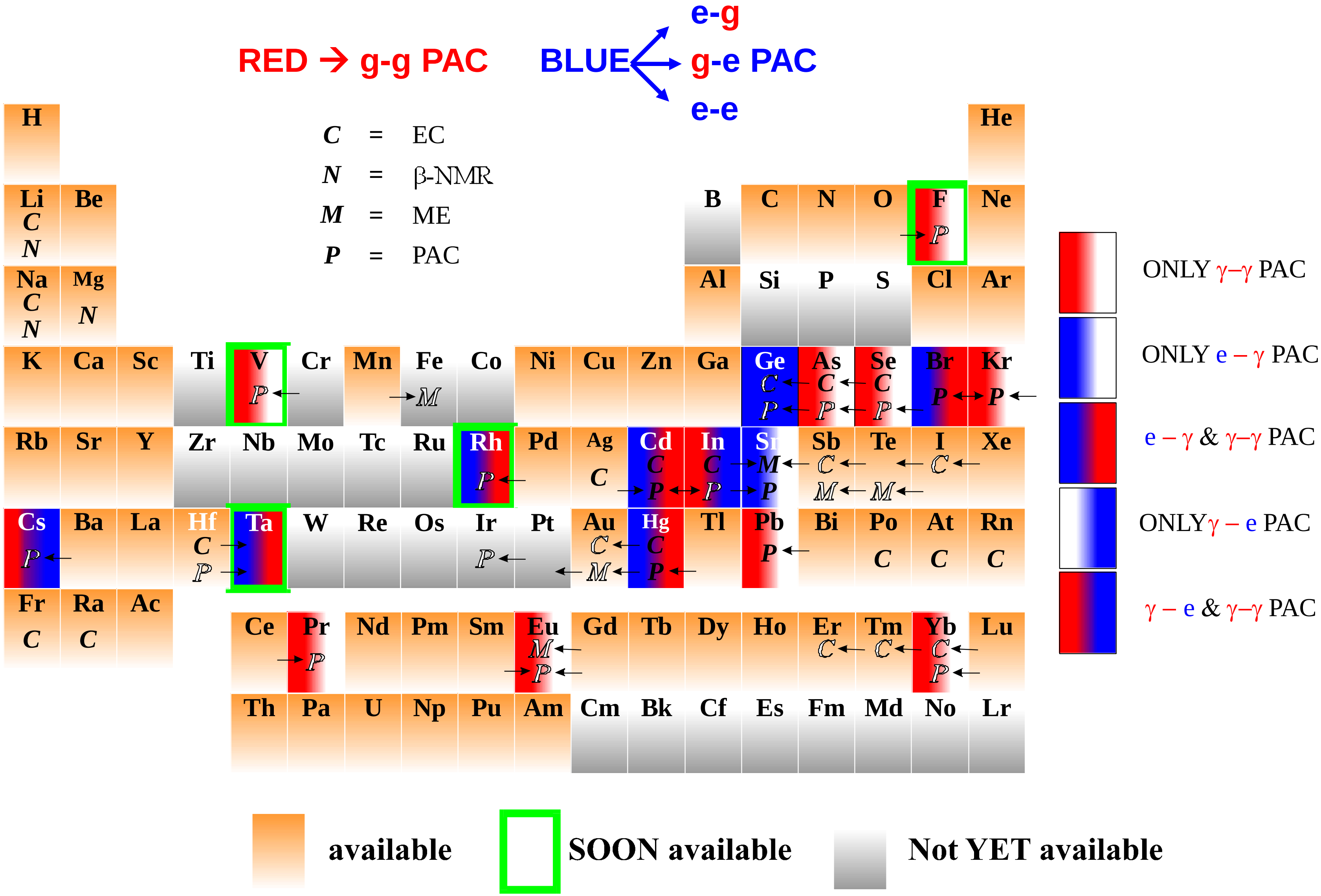
Dedicated suite of offline labs for sample preparation, treatment and measurement.



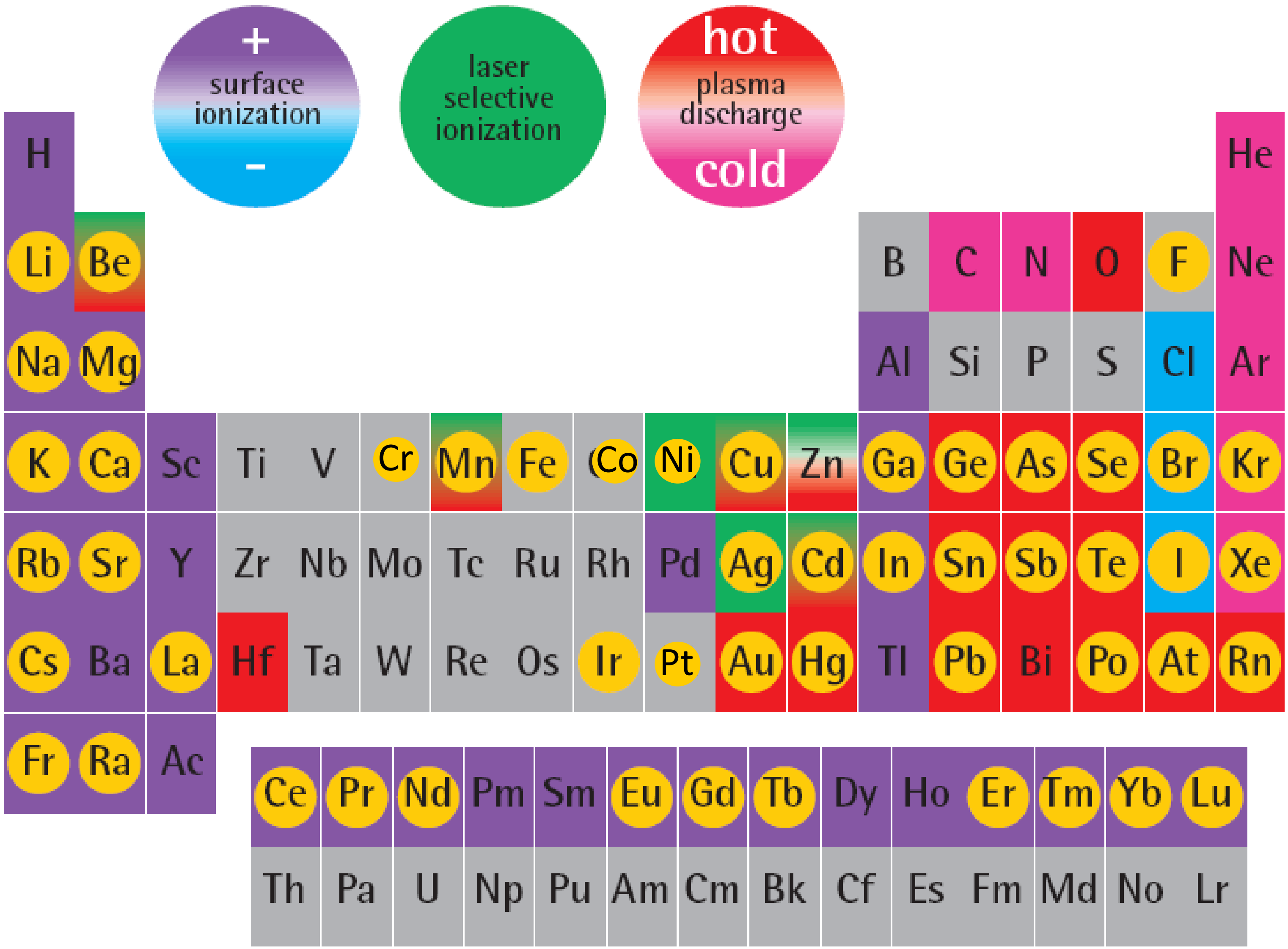
Experimental techniques used with radioactive isotopes at ISOLDE

Nuclear SSP Elements produced at ISOLDE

low energies & high multipolarities → highly converted cascades → e-g PAC

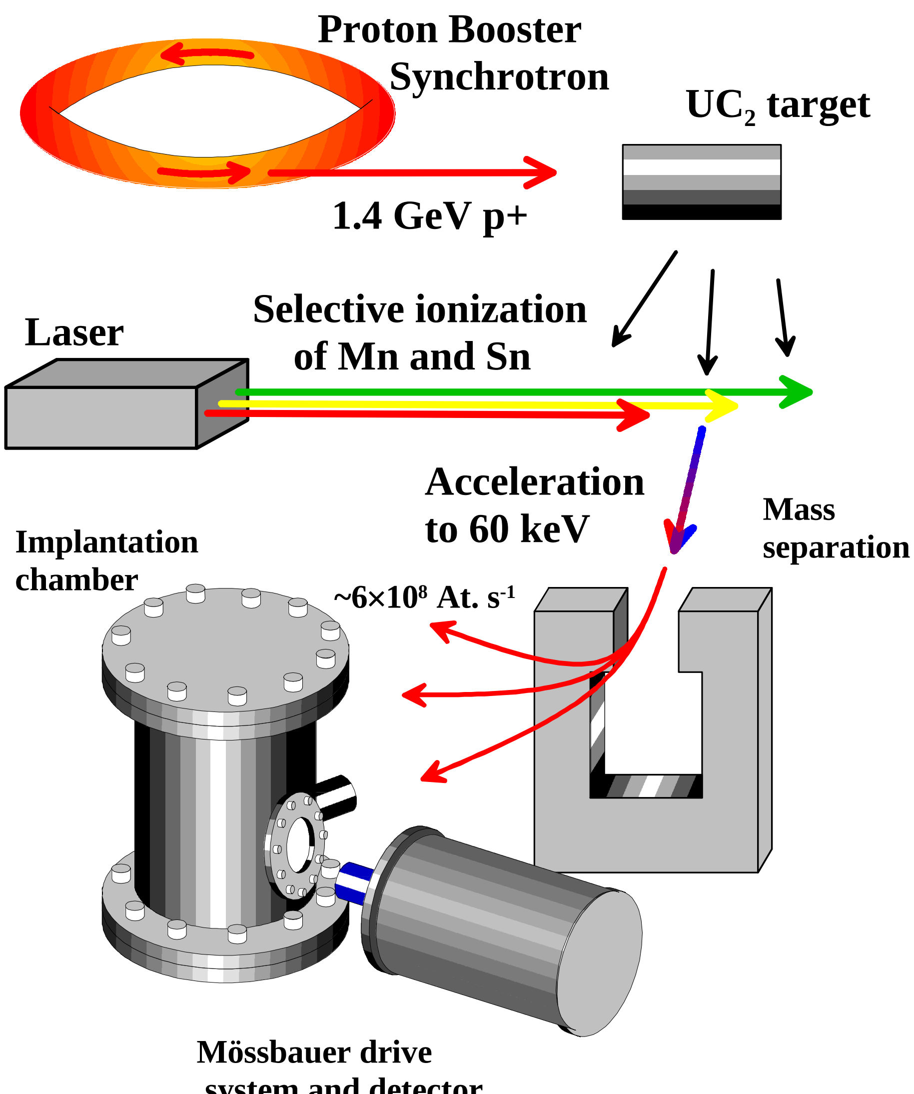


ISOLDE table of elements



Isotopes of this element [yellow circle] used for solid state physics or life science

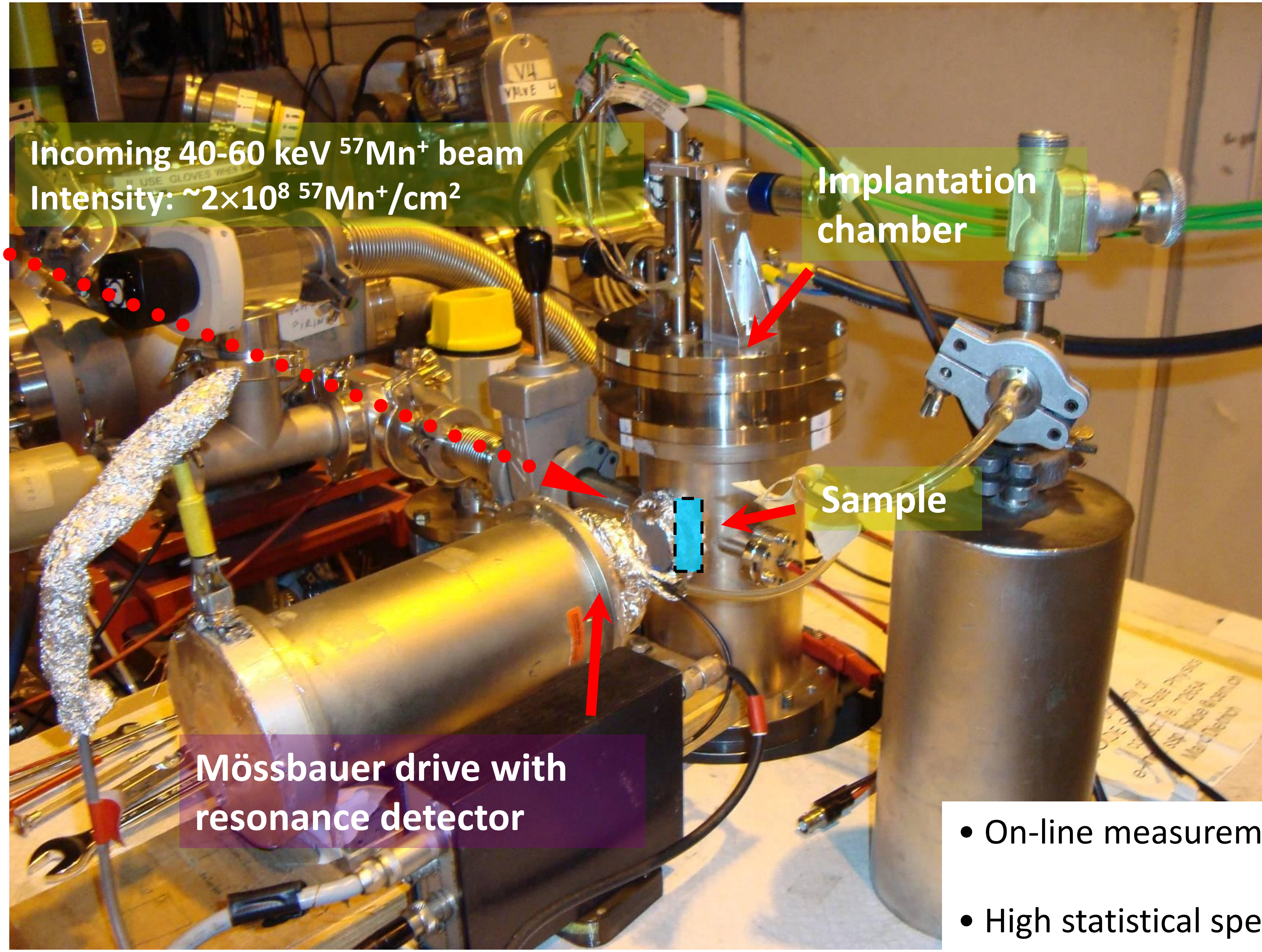
Magnetic semiconductors studied using Mossbauer spectroscopy



Development of 57Mn beam in late 1990s (with laser ionisation) brought about a new era in Mossbauer experiments at ISOLDE.

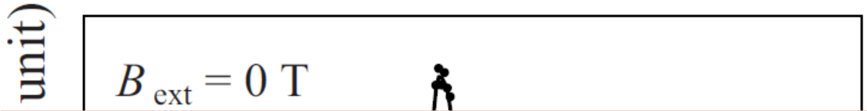
- Very clean, intense beam of ^{57}Mn (>3e8 ions sec^{-1})
- Allows collection of single Mossbauer spectrum in ~ 3 mins.
- Able to collect many hundreds over course of a 3 day run.
- Allows low concentrations of probe atoms to be used (~10^{-4}At%)

Experimental setup



- On-line measurements
- High statistical spectrum

ZnO: a ferromagnetic semiconductor?



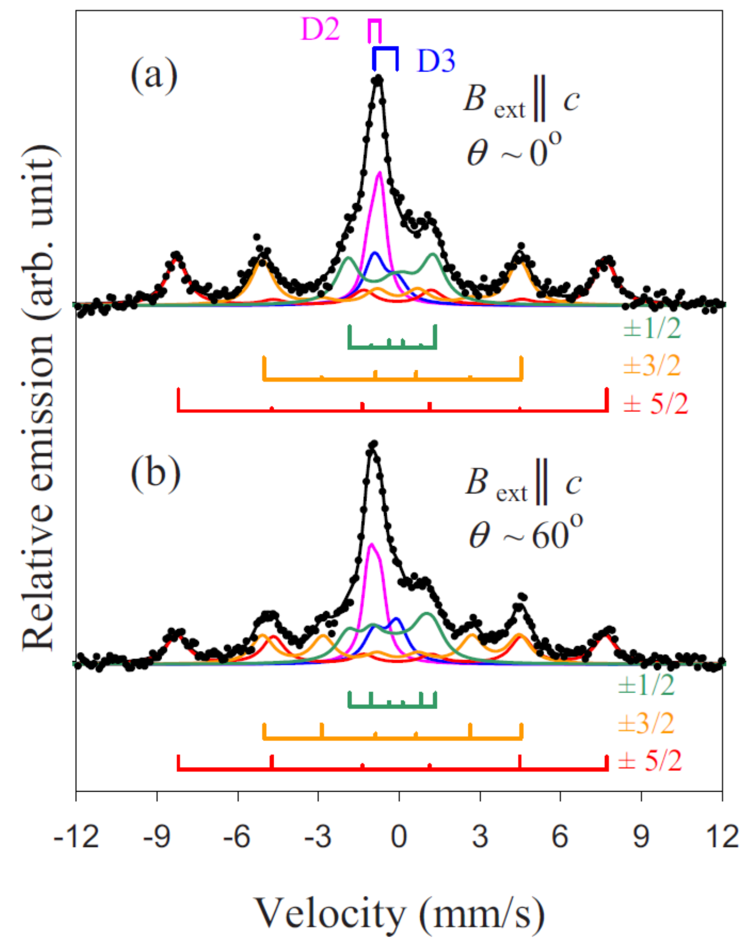
Not quite.

Further reults in an external magnetic field show that the spectrum shown to be a slowly relaxing paramagnetic system .

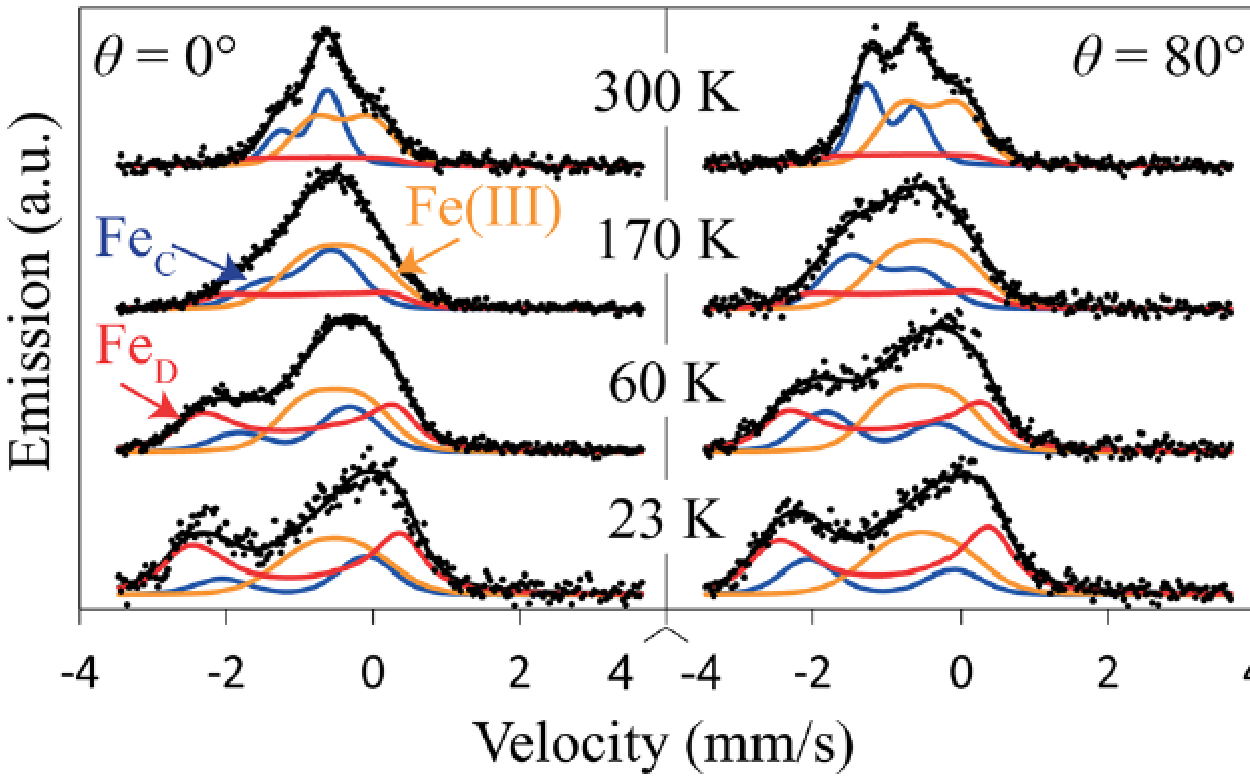
Gunnlaugsson *et al* (APL **97** 142501 2010)

room temperature!!!).

- Time to celebrate?



More on ZnO

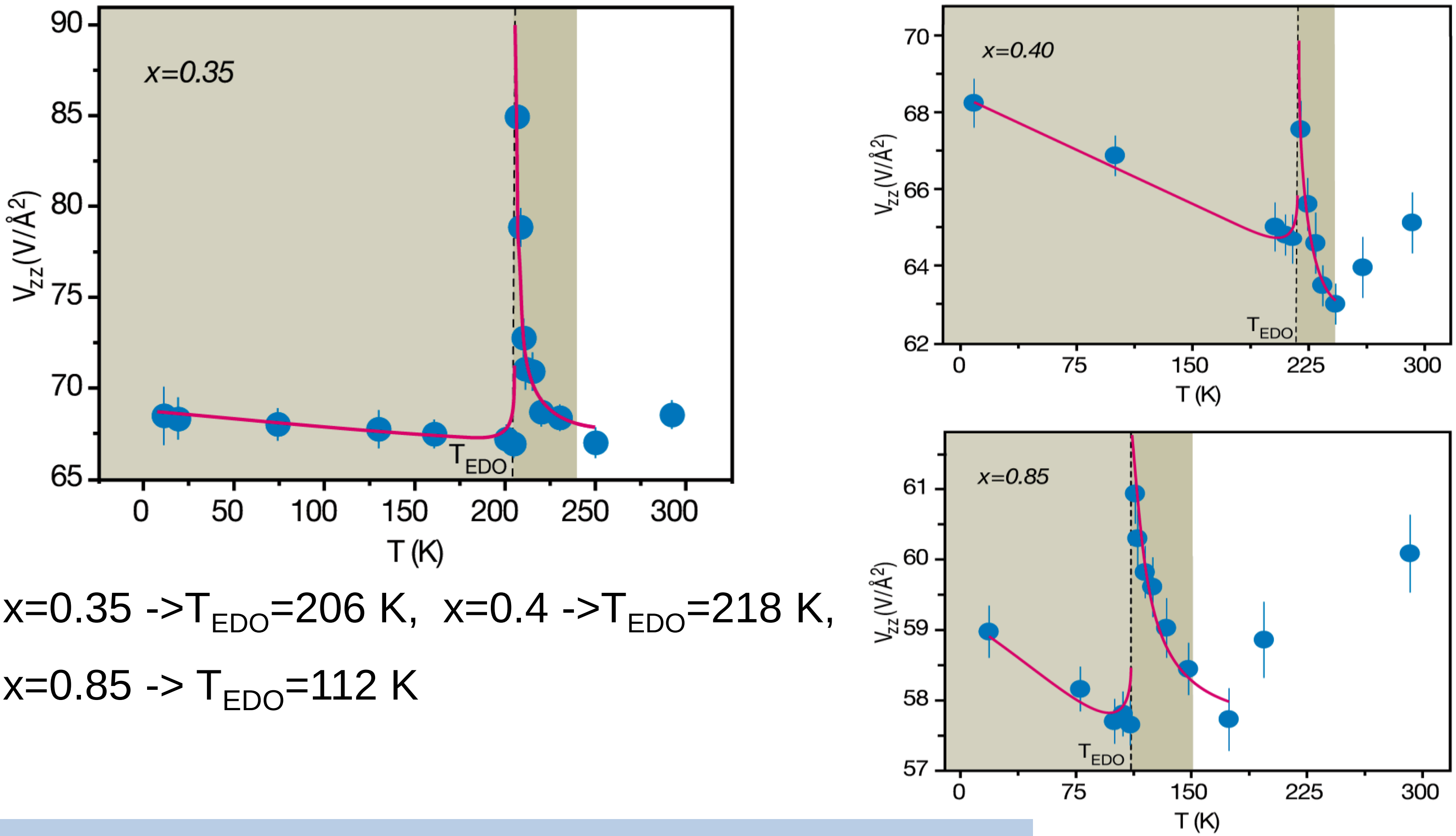


After high-dose implantations, precipitates of Fe-III are formed. These form clusters yielding misleading information about the nature of magnetism in ZnO (as reported by many groups over the last number of years).

Gunnlaugsson *et al* (APL **100 042109** 2012)

PAC results: Local Probe Studies / $Pr_{1-x}Ca_xMnO_3$ system

Results: Electric susceptibility / spontaneous polarization below T_C



x=0.35 -> T_{EDO}=206 K, x=0.4 -> T_{EDO}=218 K,

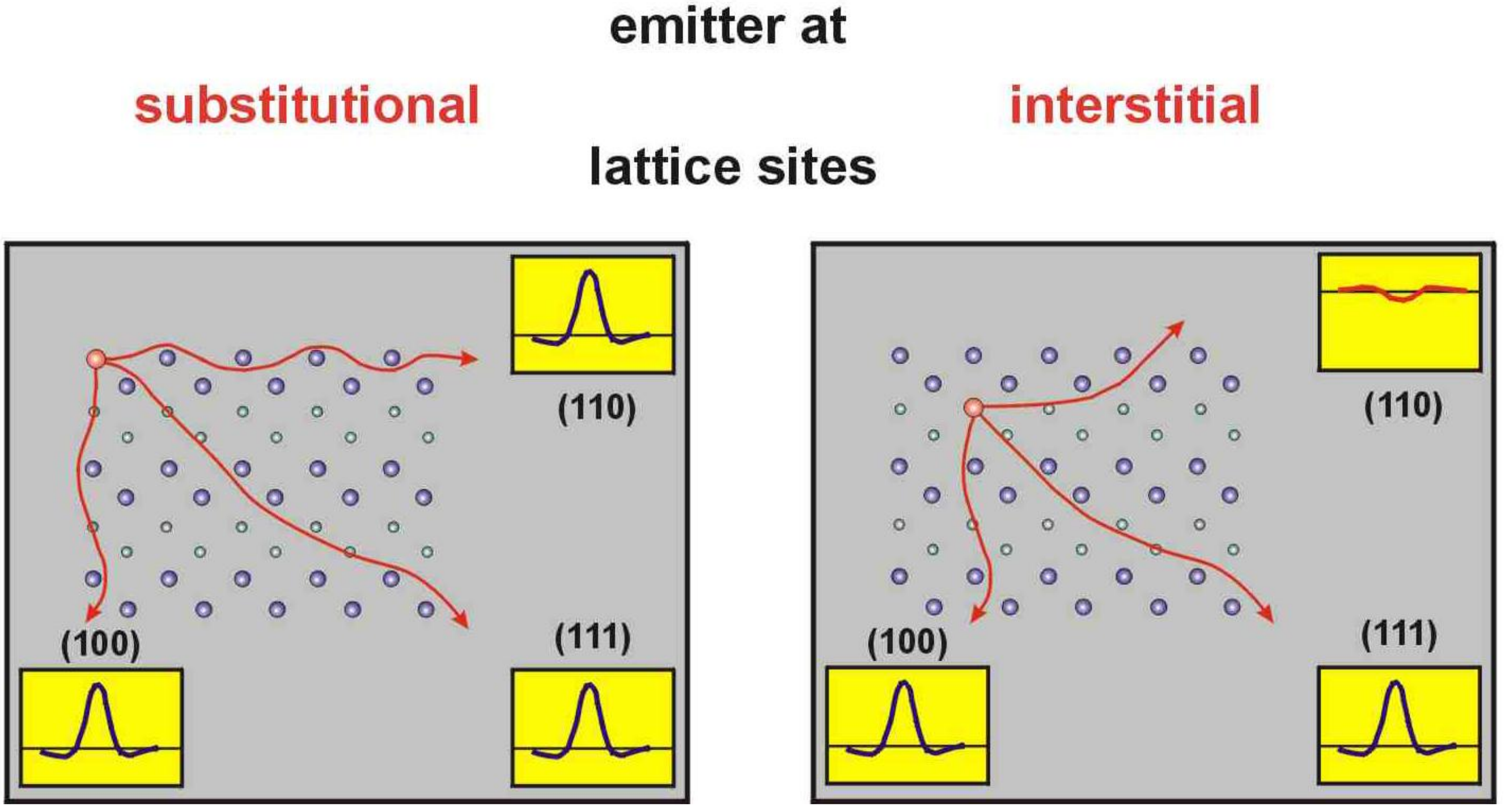
x=0.85 -> T_{EDO}=112 K

Described as first-order dielectric phase transition below T_{co}

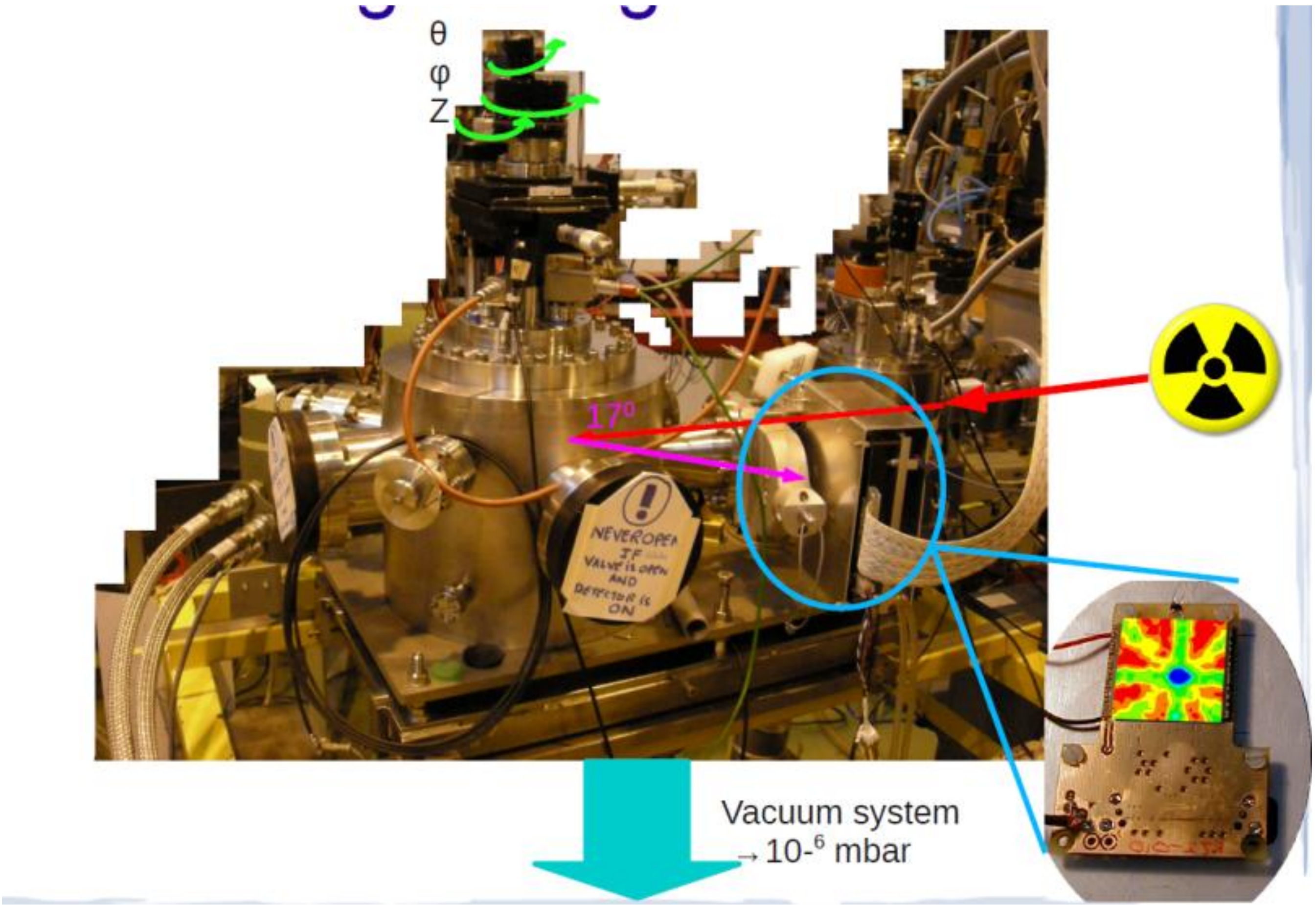
A.M.L. Lopes et al., Phys. Rev. Lett. 100, 155702 (2008)

Emission channelling: locating impurity atoms in the lattice

Channelling of charged particle in crystal, channels along high symmetry directions.



Emission channelling: locating impurity atoms in the lattice



Since 2009, online system available, able to measure isotopes with half-lives of ~1min.

Position sensitive detectors produced at CERN (Medipix project).

Spintronics: Location of Mn in $Ga_{1-x}Mn_xAs$

- GaAs: a dilute magnetic semiconductor, not yet at room temperature.
- Emission channelling results showed that Mn is surprisingly stable at interstitial sites in GaAs (400C).
- Results that have consequences for "defect engineering" of this material.

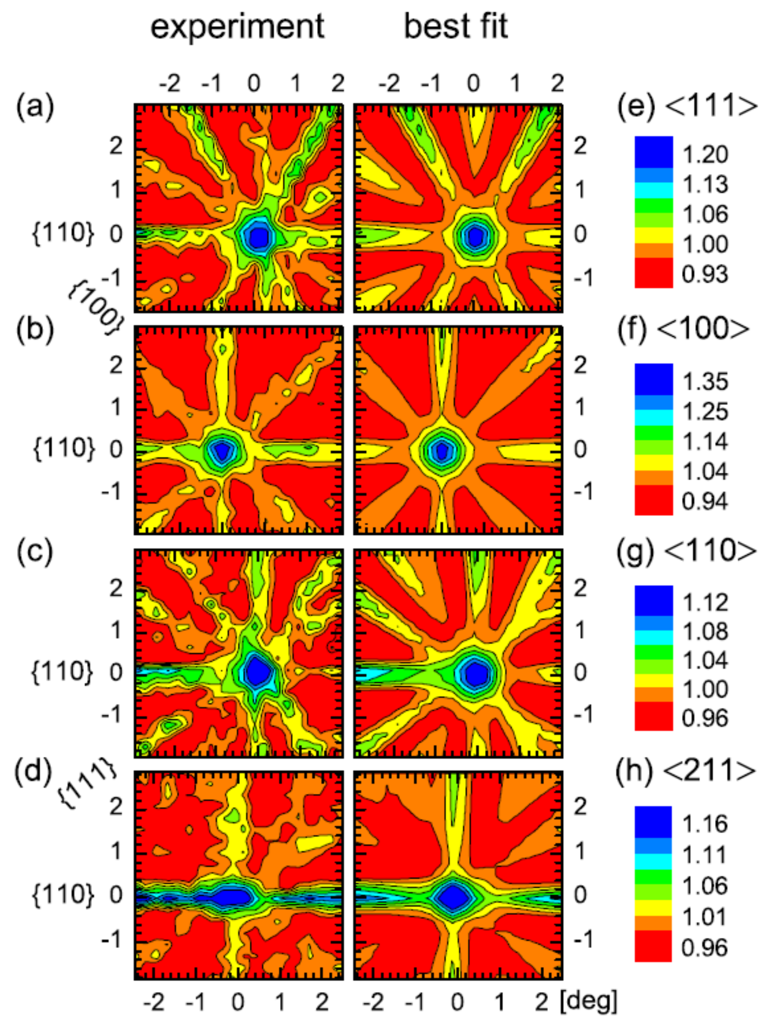


FIG. 1. (Color online) [(a)–(d)] Normalized experimental β^- emission channeling patterns in the vicinity of the ⟨111⟩, ⟨100⟩, ⟨110⟩, and ⟨211⟩ directions following annealing at 300 °C. [(e)–(h)] Corresponding best fits yielding 71% and 29% of the Mn atoms on S_{Ga} and T_{As} sites, respectively.

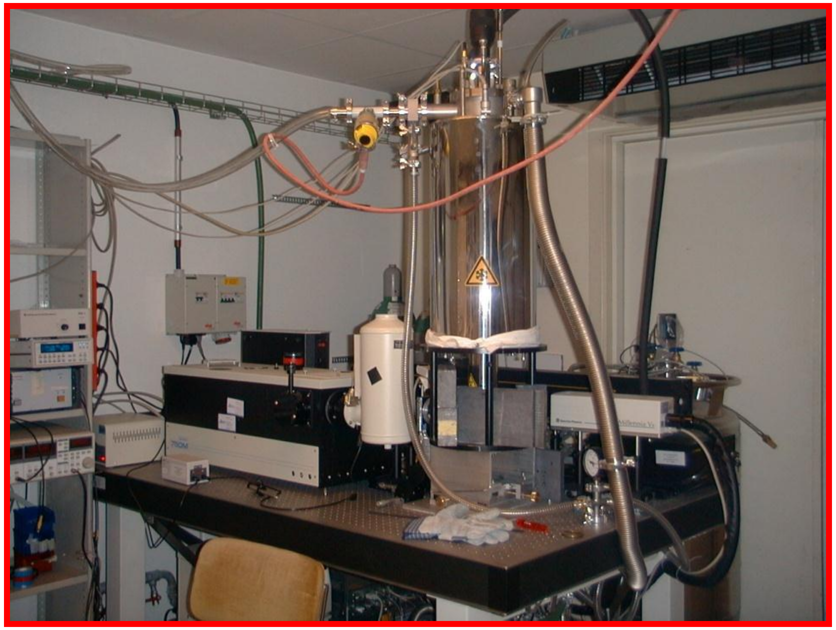
Pereira *et al* APL **98** 201905 (2011)

PL Characterisation of Semiconductors

- ✓ One of the principal techniques in semiconductor research.
- ✓ High Spectral resolution
- ✓ Non-destructive
- ✓ No need for contacts
- ✓ Very sensitive (can probe ppb)
- ✓ Relatively flexible and straightforward
- ✓ Can be extended to include external perturbations.

X Not quantitative
X Low concentrations may be more optically efficient
X Lack of chemical information (except for some rare cases where isotope shifts are observed)

PL + L-DLTS apparatus at ISOLDE



LASER

- HeCd (3,8 eV)
- Nd:YAG (2,3 nm)
- Diode (1,9 nm)

Cryostat

He-Bathcryostat (1,5 – 300 K)

Closed cycle

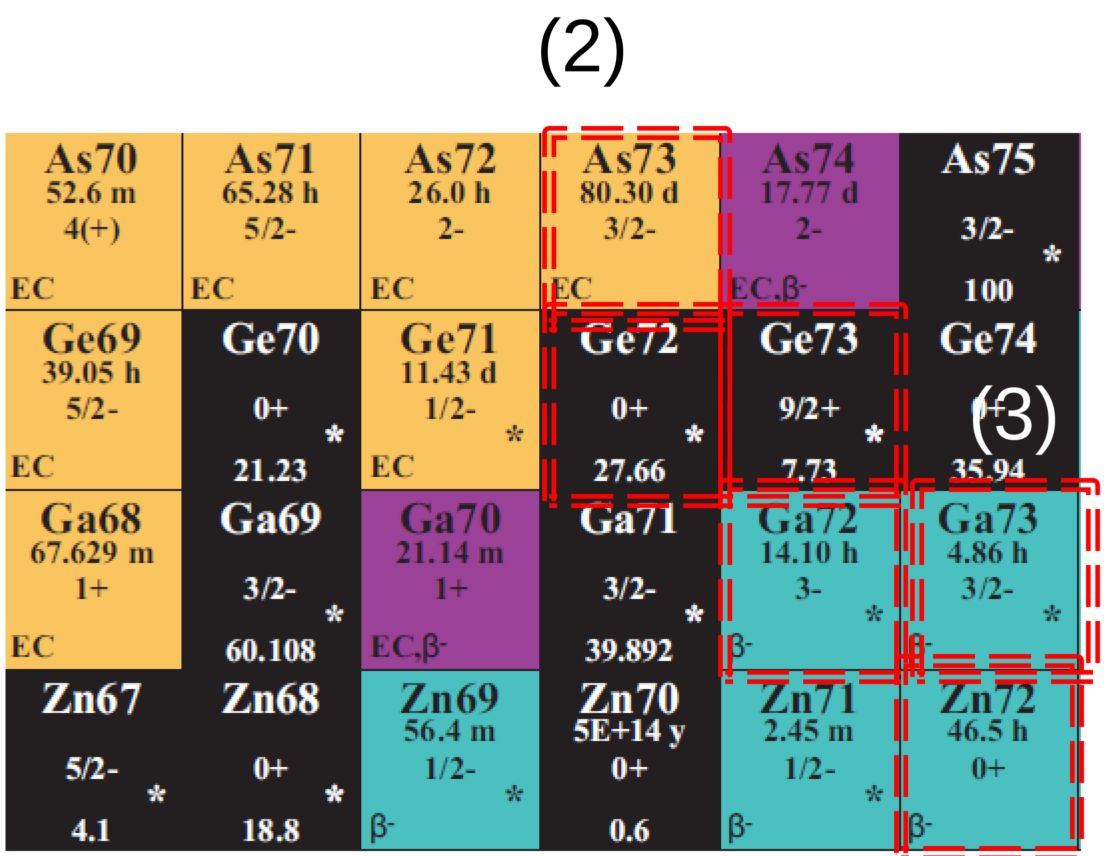
Monochromator

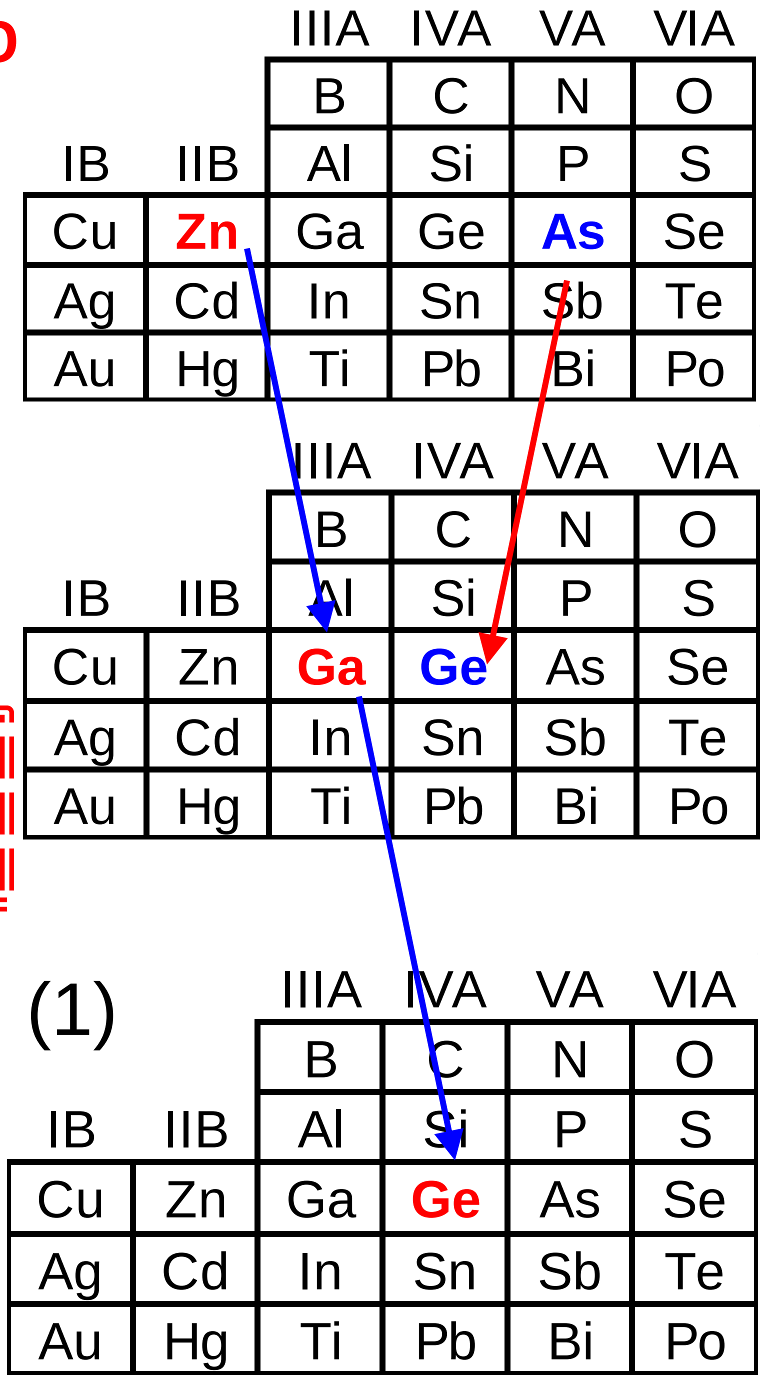
- Focus: 0,75 m
- Gratings: 150 – 1800 l/mm

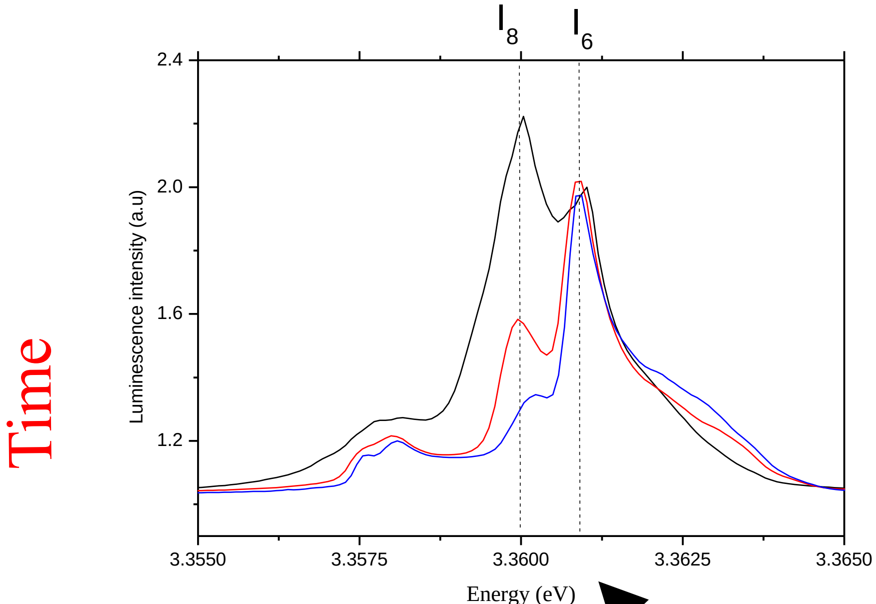
Detectors

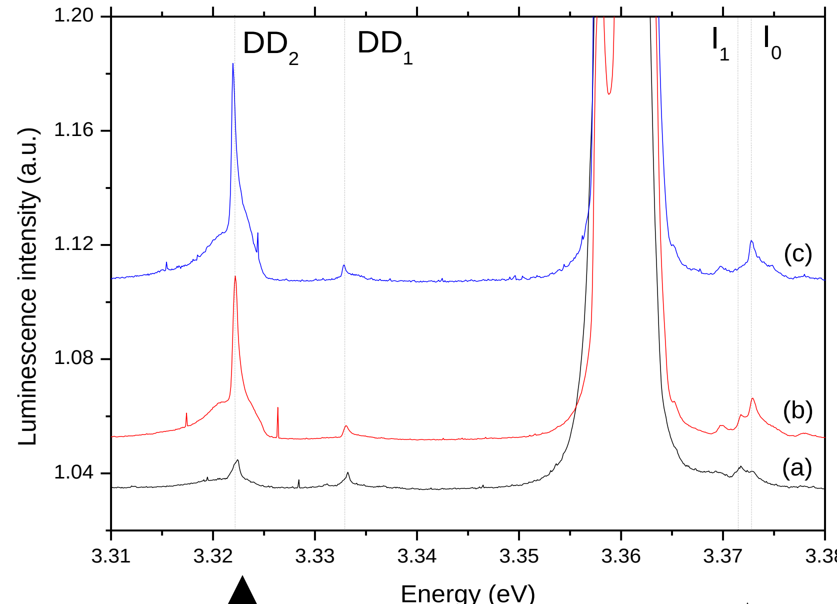
- CCD-camera (1,1 - 6,2 eV)
- Ge-Diode (0,7 - 1,5 eV)

Fundamental properties of donors in ZnO





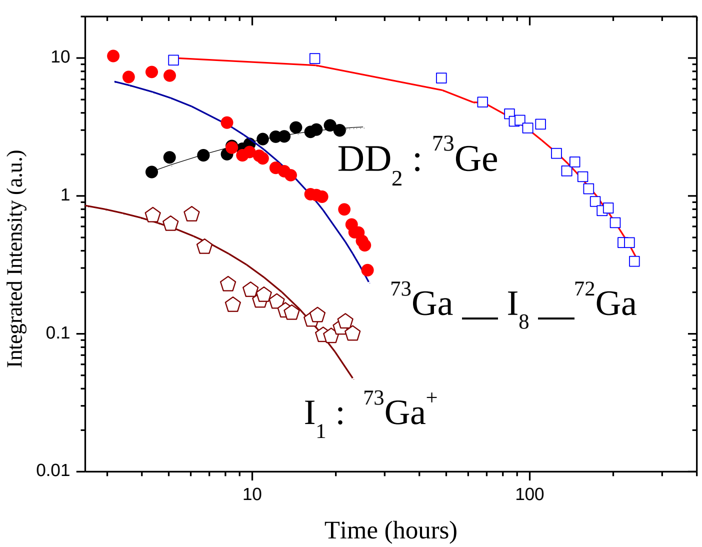




I_8

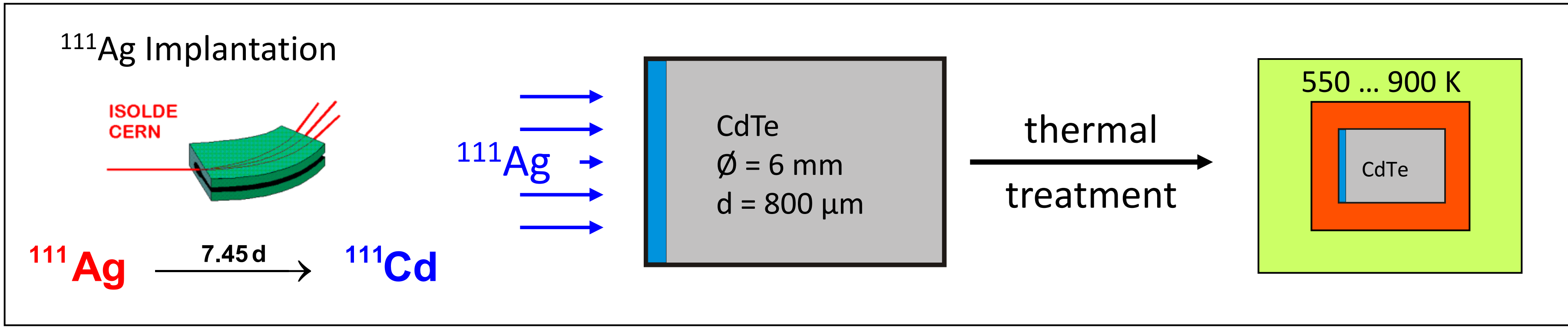
DD_2

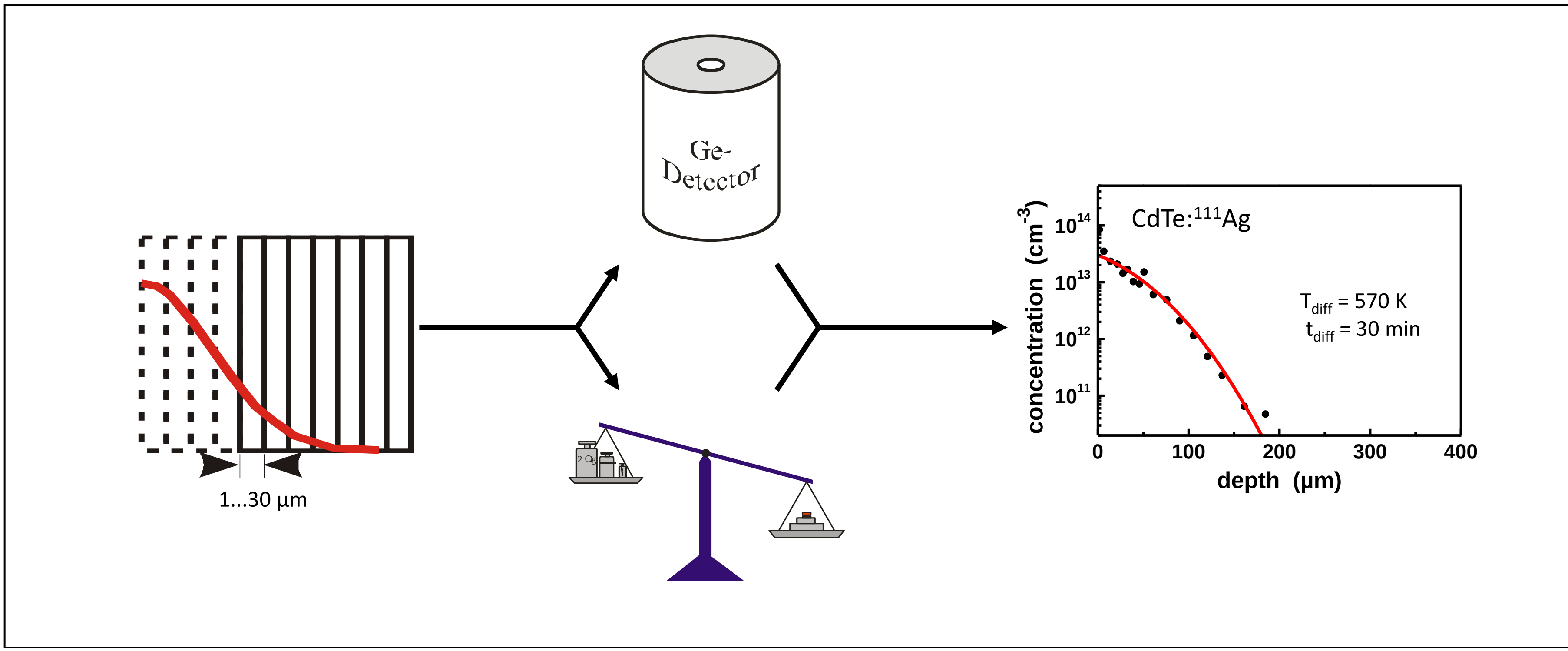
I_1



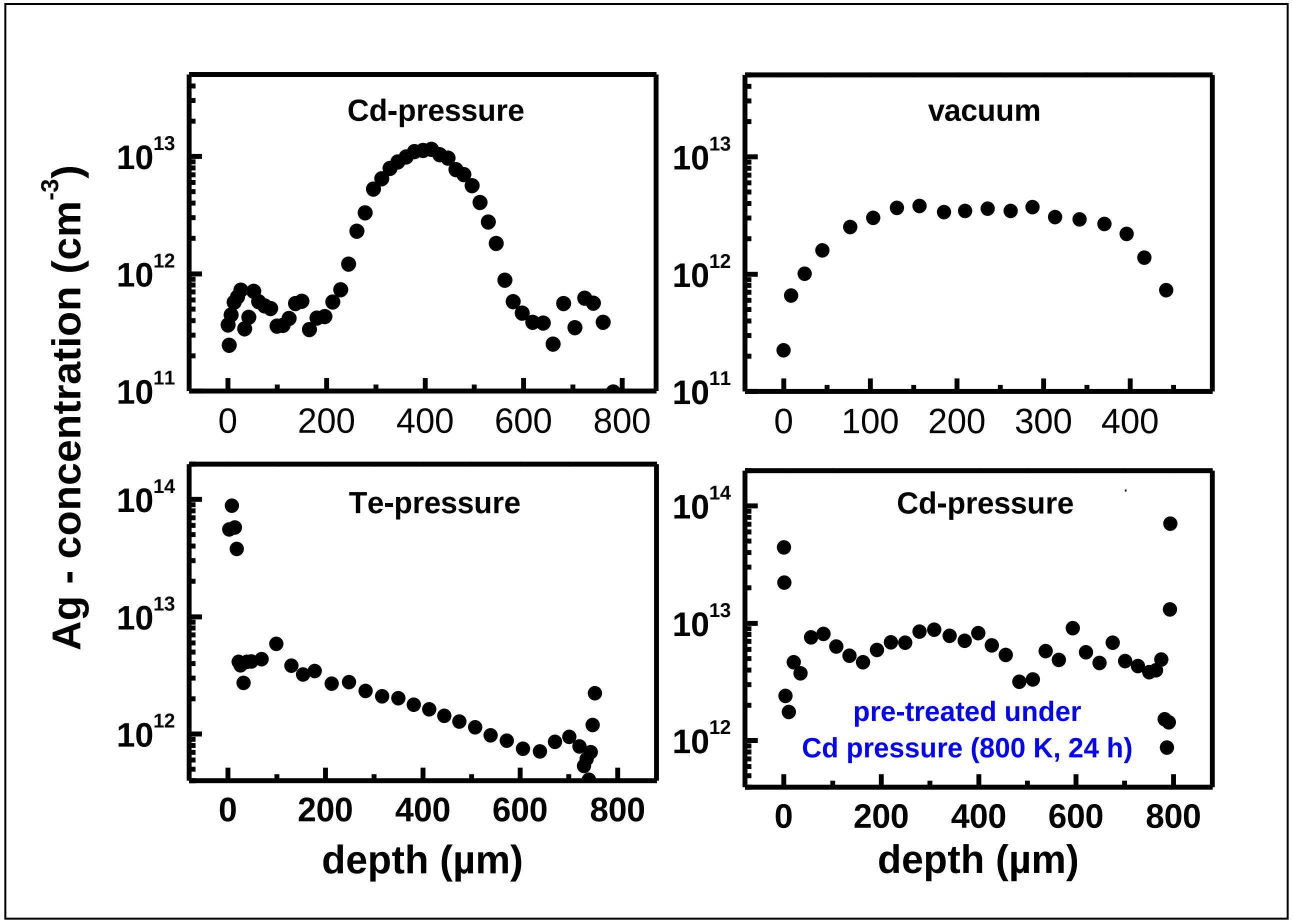
I_8 feature decays as Ga decays; So does the weak I_1 line; DD_2 grows as Ge is produced. First chemical identification of Ga and Ge in ZnO, (**PRB 73, 165212 (2006)**) and **PRB 83 125205 (2011)**)

Diffusion: experimental procedure





Diffusion: Ag in CdTe



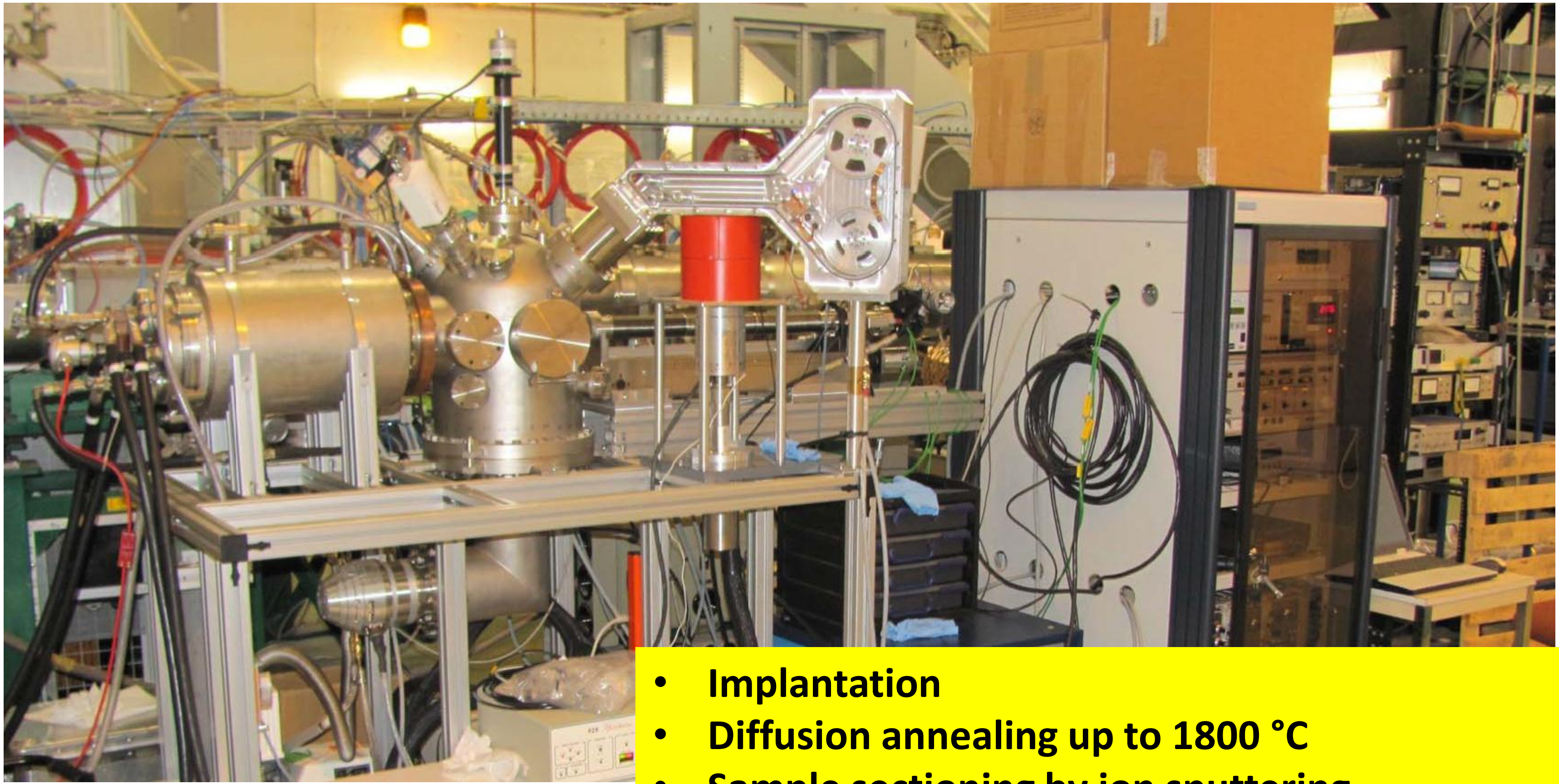
T_{diff} = 825 K

t_{diff} = 60 min

Shapes of diffusion profiles strongly depend on external vapor pressure

H. Wolf, F. Wagner, Th. Wichert, and ISOLDE Collaboration, *Phys. Rev. Lett.* **94,** 125901, 2005

Online Diffusion



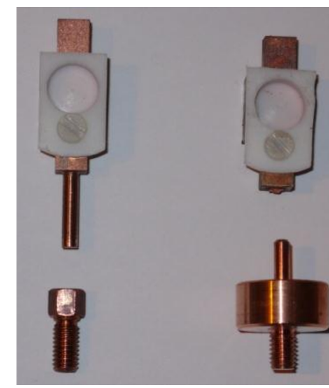
- **Implantation**
- **Diffusion annealing up to 1800 °C**
- **Sample sectioning by ion sputtering**
- **Catching the sputtered ions by a tape system**
- **In situ activity measurement**
- **Remote control**

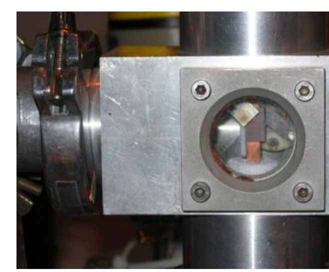
Biophysics at ISOLDE: Radioisotopes for Probing Biomolecular Functionality in Living Matter

PAC isotopes used for biophysics at ISOLDE:

parent	half-life	decay	isomer	half-life (ns)
^{62}Zn	9.186(13) h	EC/β^+	^{62}Cu	4.57(18)
^{99}Mo	65.94(1) h	β^-	^{99}Tc	3.61(7)
^{111m}Cd	48.54(5) min	IT	^{111}Cd	85.0(7)
^{111}In	2.8049(1) days	EC	^{111}Cd	85.0(7)
^{111}Ag	7.45(1) days	β^-	^{111}Cd	85.0(7)
^{133}Ba	10.52(13) years	EC	^{133}Cs	6.27(2)
^{160}Tb	72.3(2) days	β^-	^{160}Dy	2.02(1)
^{181}Hf	42.39(6) days	β^-	^{181}Ta	10.8(1)
^{199m}Hg	42.6(2) min	IT	^{199}Hg	2.45(2)
^{204m}Pb	67.2(3) min	IT	^{204}Pb	265(10)
		isotopes that have only been used for the sum-p		
^{147}Nd	10.98(1) days	β^-	^{147}Pm	2.50(5)
^{152}Eu	13.542(10) years	EC	^{152}Sm	1.428(7)

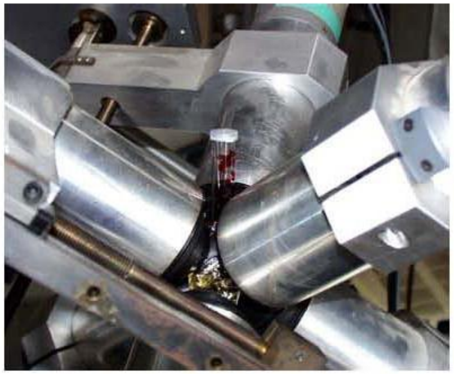
Hemmingsen et al. *Chem. Rev.*, **2004**, 104: 4027



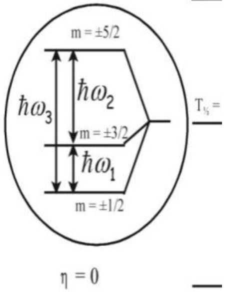


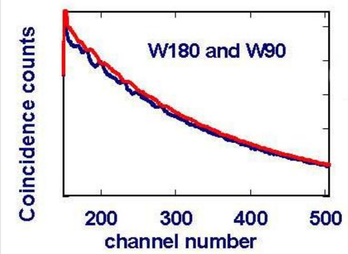
No implantations: collect ativity in ice → chemistry

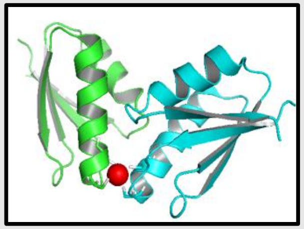
In practice….



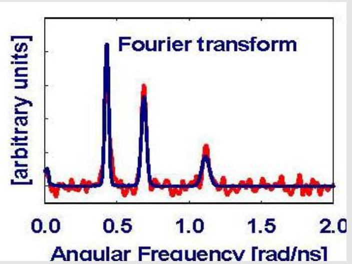
6·180° spectra and 24·90° spectra



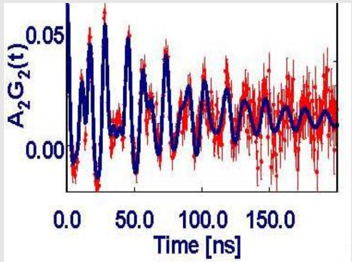




Least χ^2 analysis



Fourier transform



ω_Q and η

BASIL model

QM calculations

compare experiment to model

Metal Ion Binding Site Structure: Fast inter-conversion between species

B

^{111m}Cd-PAC

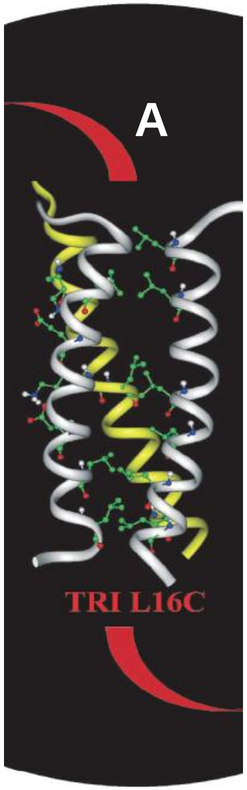
C

^{113}Cd-NMR

B

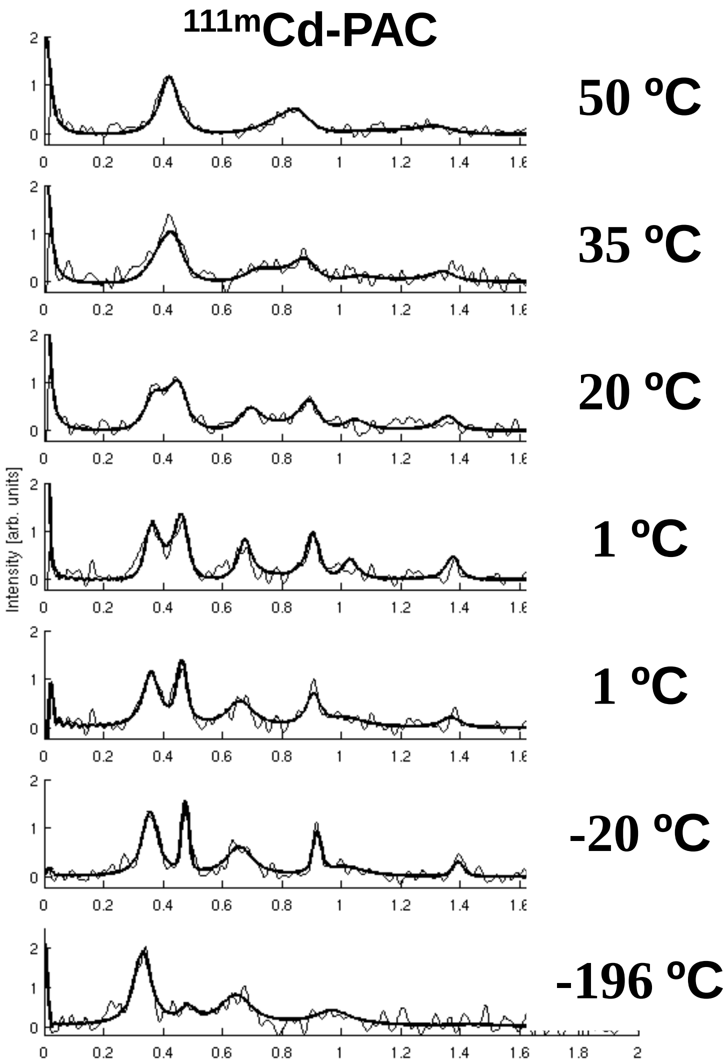
C

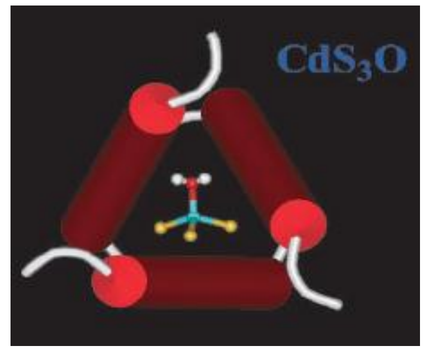
Chemical shift / ppm

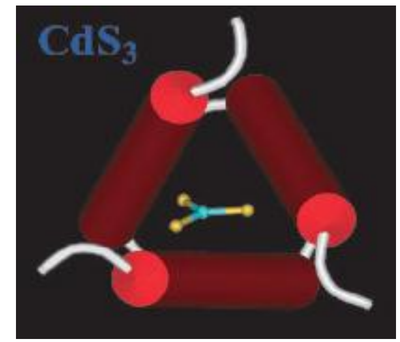


Matzapetakis *et al*. J. Am. Chem. Soc. **2002**, 124: 8042; Lee *et al*. Angew. Chem., **2006**, 45: 2864; Peacock *et al.* Proc. Nat. Acad. Sci. **2008**, 105: 16566

De novo designed heavy metal Ion binding proteins: ns dynamics



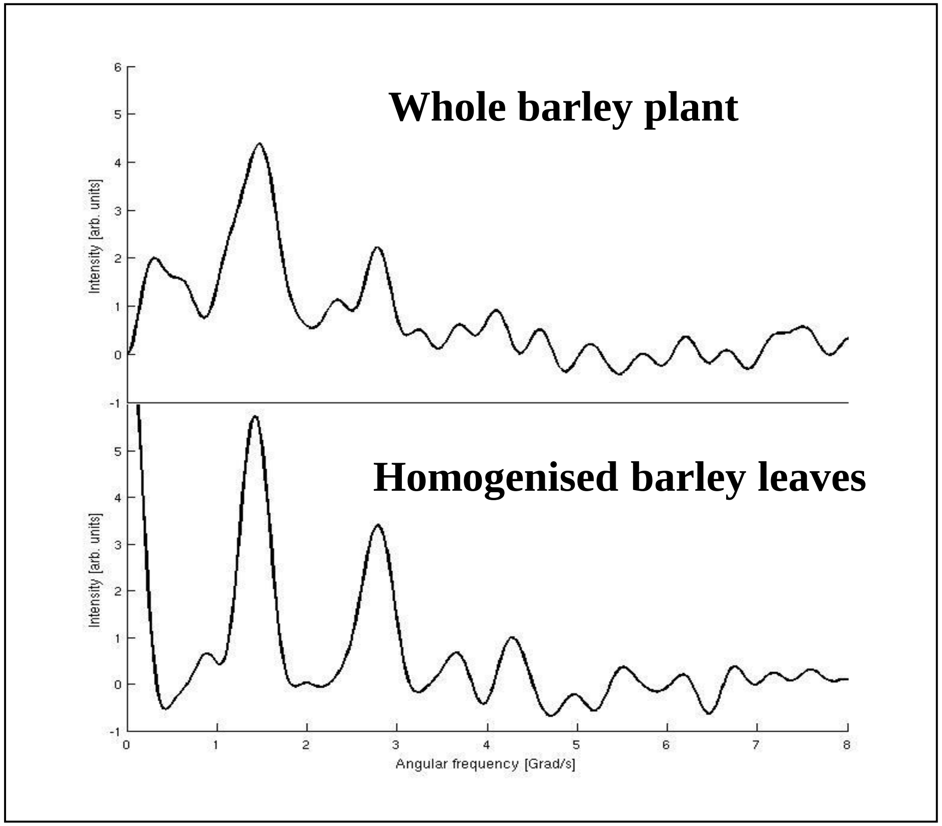




Temp [ºC]	τ_1 [ns]	τ_{-1} [ns]
1	52	48
20	42	36
35	28	20
50	19	12

Stachura et al. Manuscript in preparation

In vivo experiments
Hg(II) binding to barley



- 5-7 days-old plants
- Plant inserted into test tube.
- Fast uptake of Hg(II) (<1h)
- Bound to large molecules, similarities to HgS_2 compounds

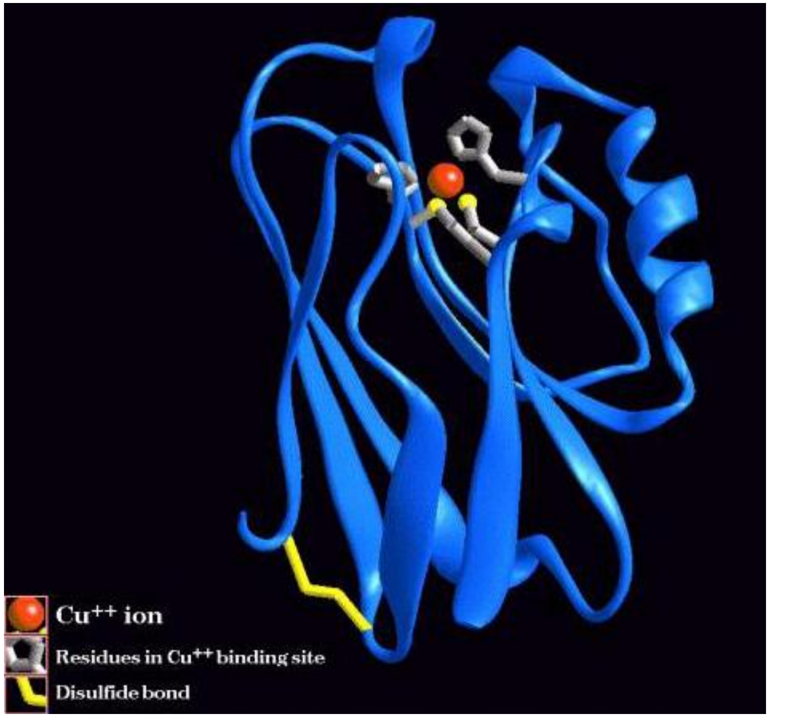
Adolph et al. *Chem. Eur. J.*, **2009**, 15, 7350 – 7358

Beta-NMR applied to biophysics

Beta-NMR

➔ Cu, Zn, Mg, Mn, Fe, Ni

➔ Measurement of electric field gradient



➔ Cu(I) is “invisible” in most (except X-ray and nuclear) spectroscopic techniques because it is a closed shell ion

➔ Cu(I)/Cu(II) are essential in many redox processes and electron transport in biology

Advantages and Limitations of PAC Spectroscopy for biophysics

Advantages:

- Characterisation of structure and dynamics at the PAC probe site (including rotational correlation times)
- High sensitivity to **structural changes**
- Small amount of PAC probe needed (in principle about **1 pmol**)
- **Different physical states** (crystals, surfaces, solutions, *in vivo*...)
- Mechanically stable, allowing for stirring, flow, ...

Limitations:

- Suitable PAC isotopes do not exist for all elements
- PAC isotope **must bind strongly** to the molecule of interest
- Spectral parameters do not uniquely determine structure
- After effects can cause problems (in particular for EC). **(^{111}In)**
- Production of PAC-isotopes

Hemmingsen et al. *Chem. Rev.*, **2004**, 104: 4027; Hemmingsen and Butz, in "Application of Physical Methods to Inorganic and Bioinorganic Chemistry" **2007**, Ed. R.A. Scott, Wiley

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- Torben Molholt, University of Iceland, Iceland
- Monika Stachura, University of Copenhagen, Denmark
- Krish Bharuth-Ram, iThemba Labs, South Africa

Summary

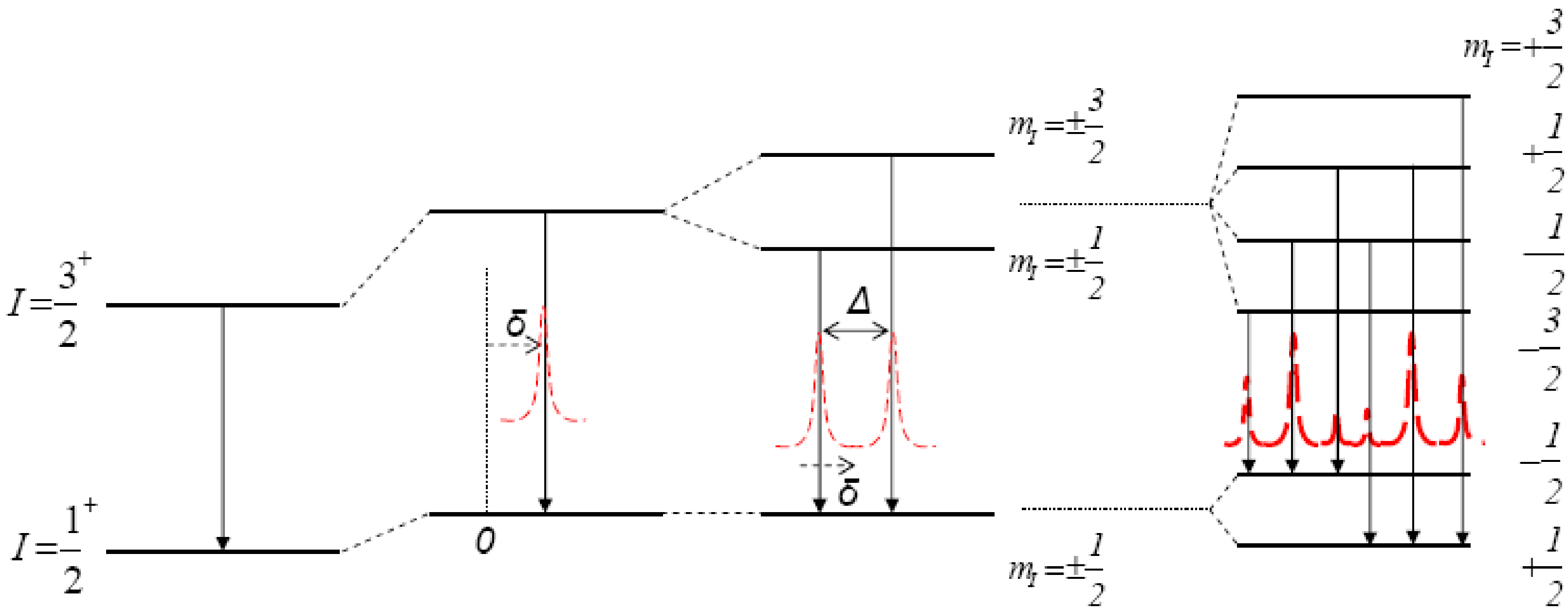
Solid state physics/biophysics: a very active experimental programme at ISOLDE

- Radioactive measurements complement work at home laboratories
- Unique information – be it chemical or local – which is only achievable using radioactive implantations/probes.
- Synergy between groups e.g. extension of biophysics methods for studying graphene and fullerenes (Prof Das).
- Ability to profit from the huge range of beams available at ISOLDE (especially now with online *and* offline setups).
- Many new developments under preparation e.g. β-NMR for biophysics

Much more info at:

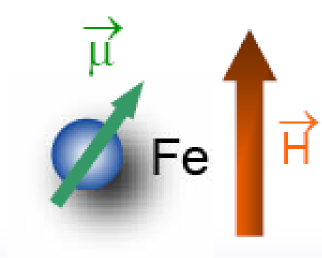
Cern.ch/ssp or follow us on

Splitting of features



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

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



Mossbauer sextet indicates magnetism at the Fe site