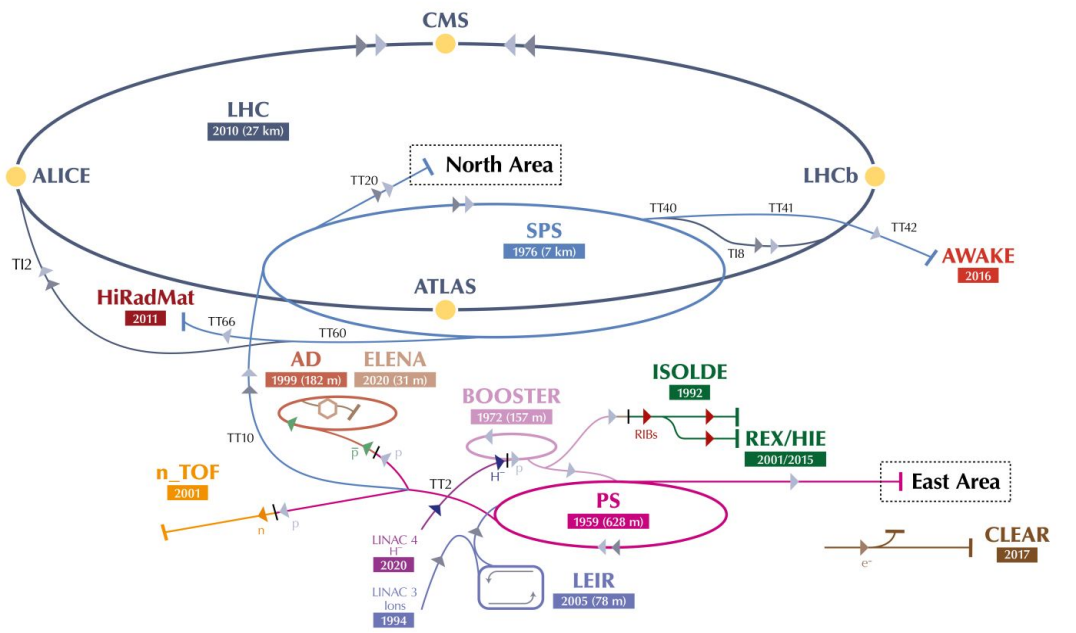
Structural properties of semiconductors doped with radioactive ions

Adeleh Mokhles Gerami

The CERN accelerator complex
Complexe des accélérateurs du CERN

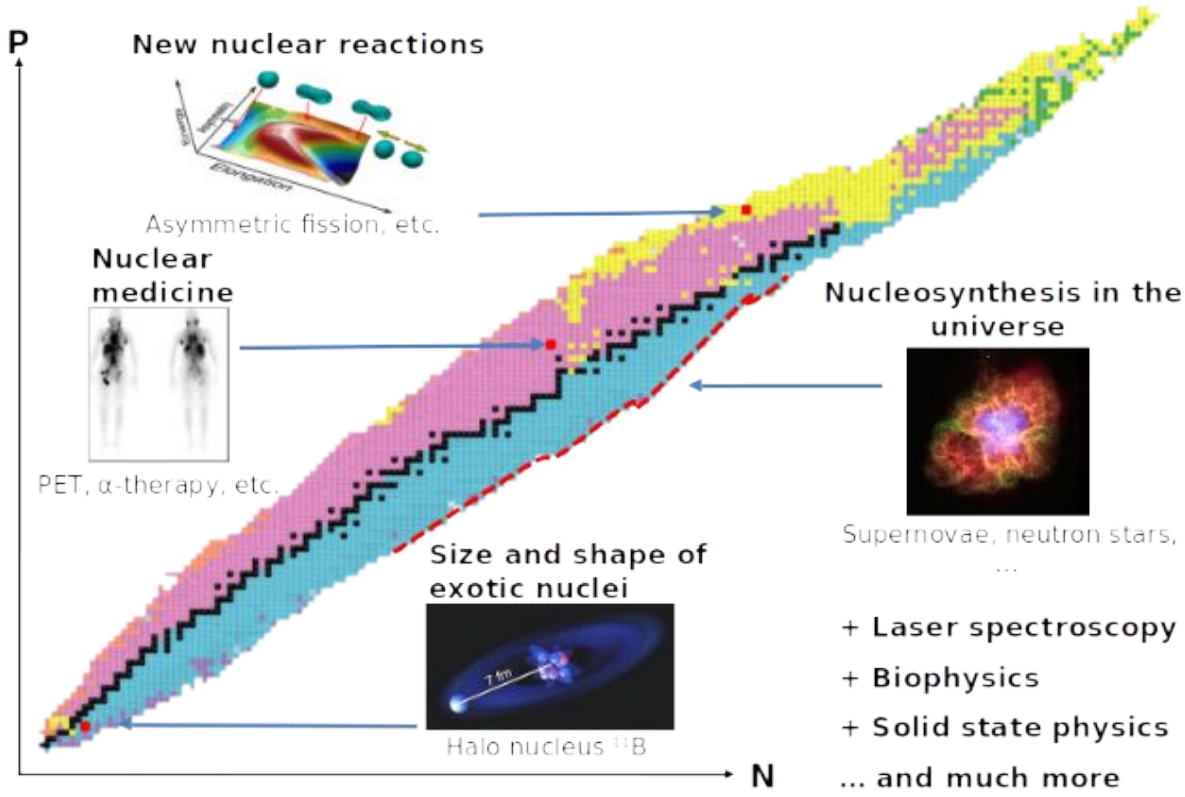


H⁻ (hydrogen anions) p (protons) ions RIBs (Radioactive Ion Beams) n (neutrons) $\bar{p}$ (antiprotons) e^- (electrons)

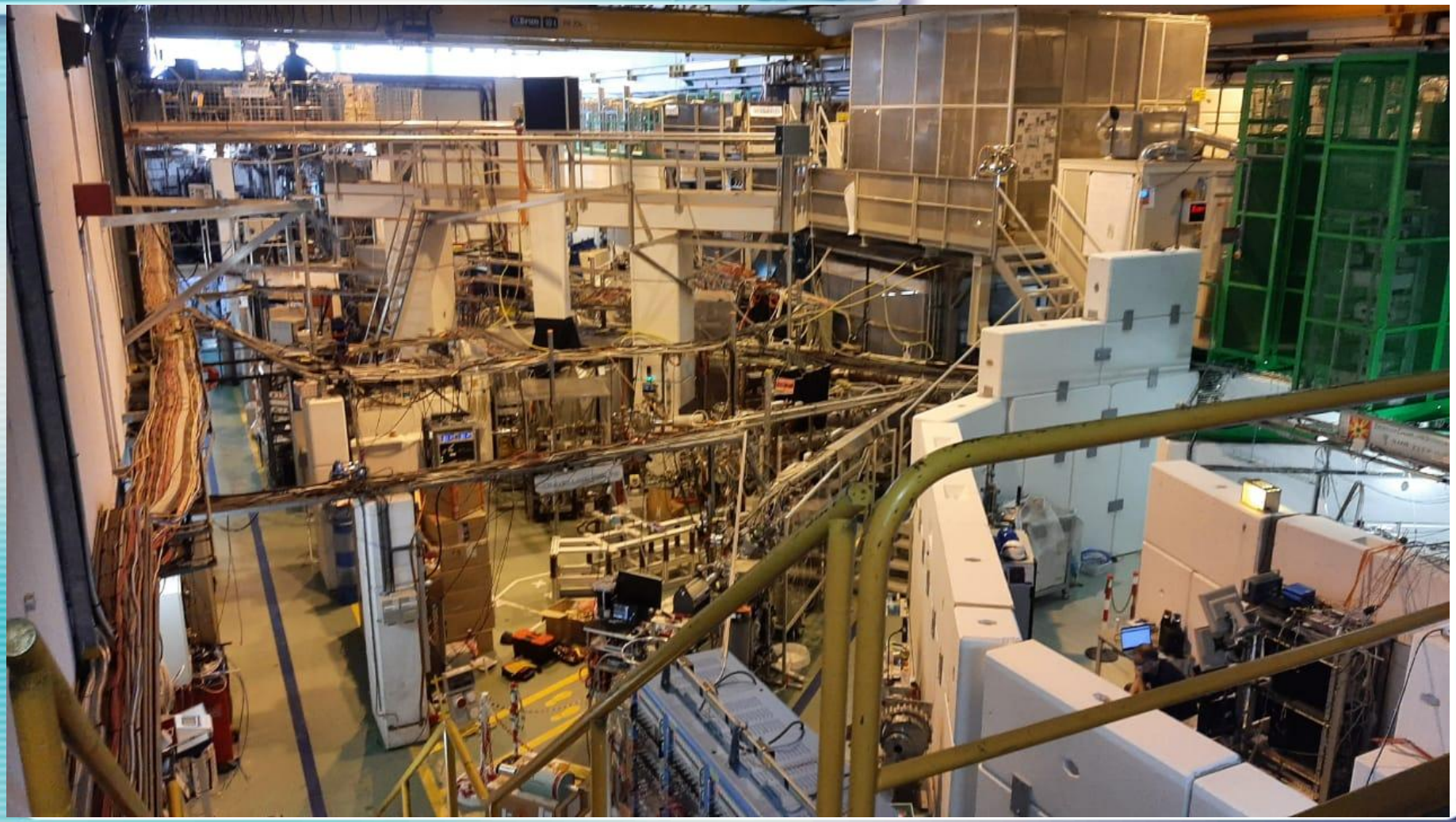
LHC - Large Hadron Collider // SPS - Super Proton Synchrotron // PS - Proton Synchrotron // AD - Antiproton Decelerator // CLEAR - CERN Linear Electron Accelerator for Research // AWAKE - Advanced WAKefield Experiment // ISOLDE - Isotope Separator OnLine // REX/HIE - Radioactive EXperiment/High Intensity and Energy ISOLDE // LEIR - Low Energy Ion Ring // LINAC - LINear ACcelerator // n_TOF - Neutrons Time Of Flight // HiRadMat - High-Radiation to Materials

Chart of radioactive ions at ISOLDE

Nuclear chart for ISOLDE



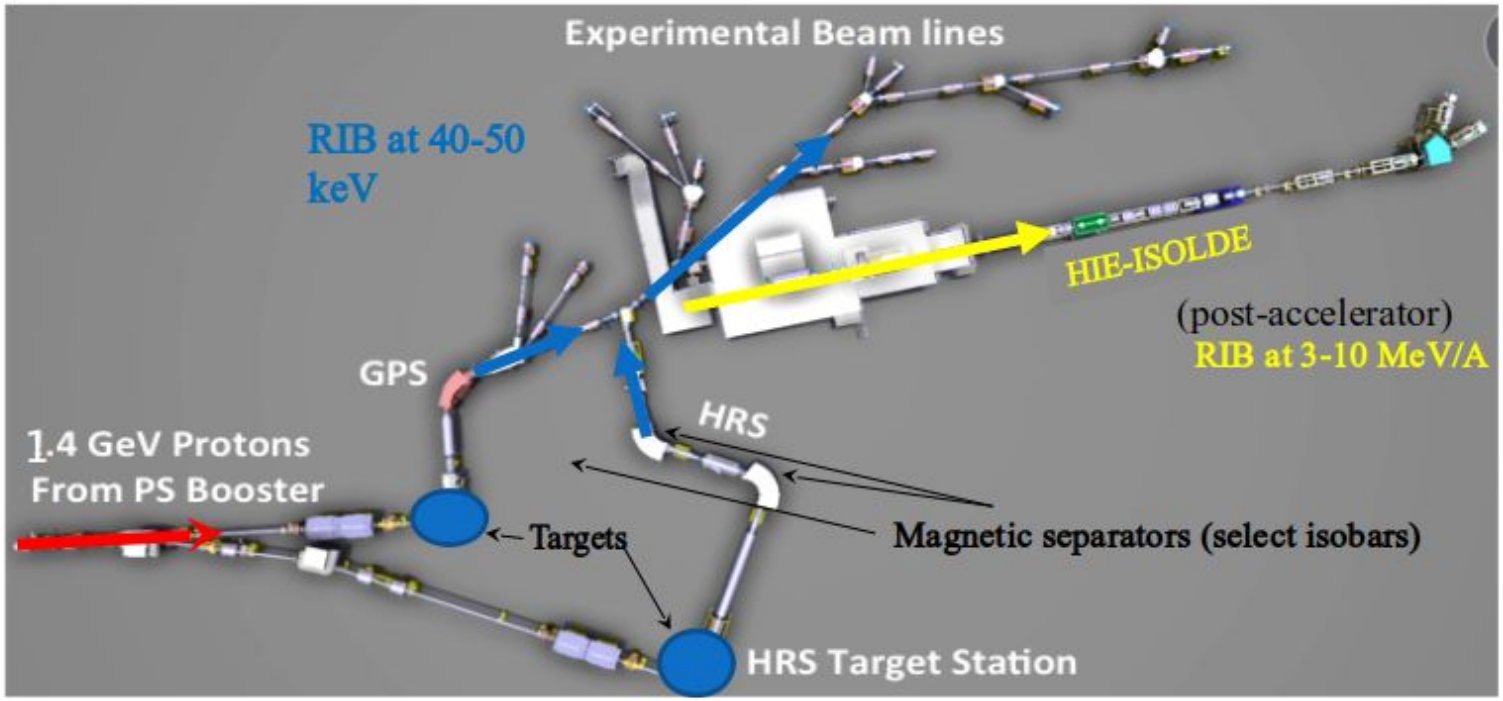
ISOLDE



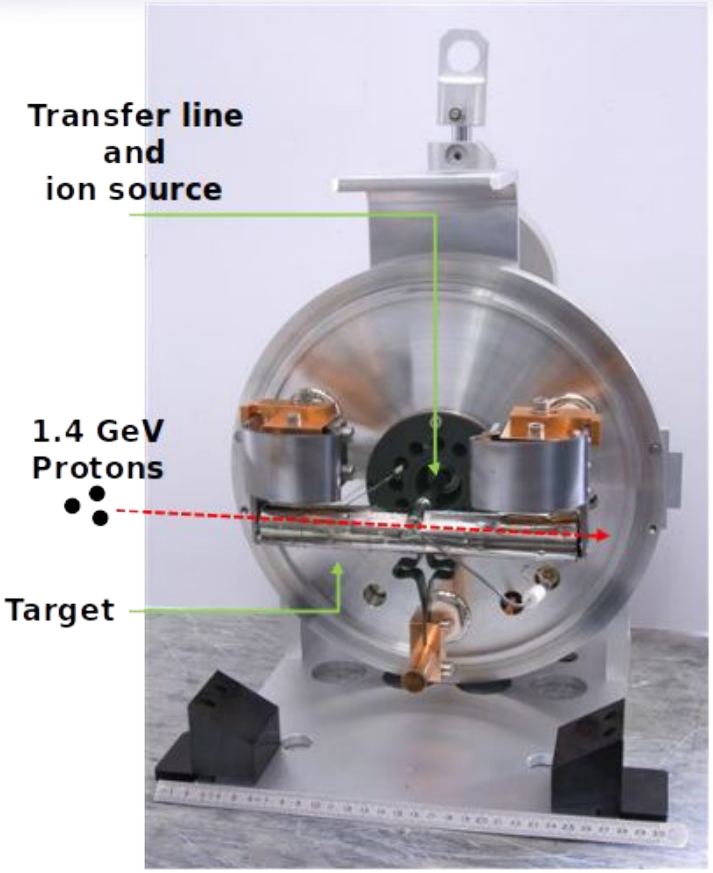
Isotope production

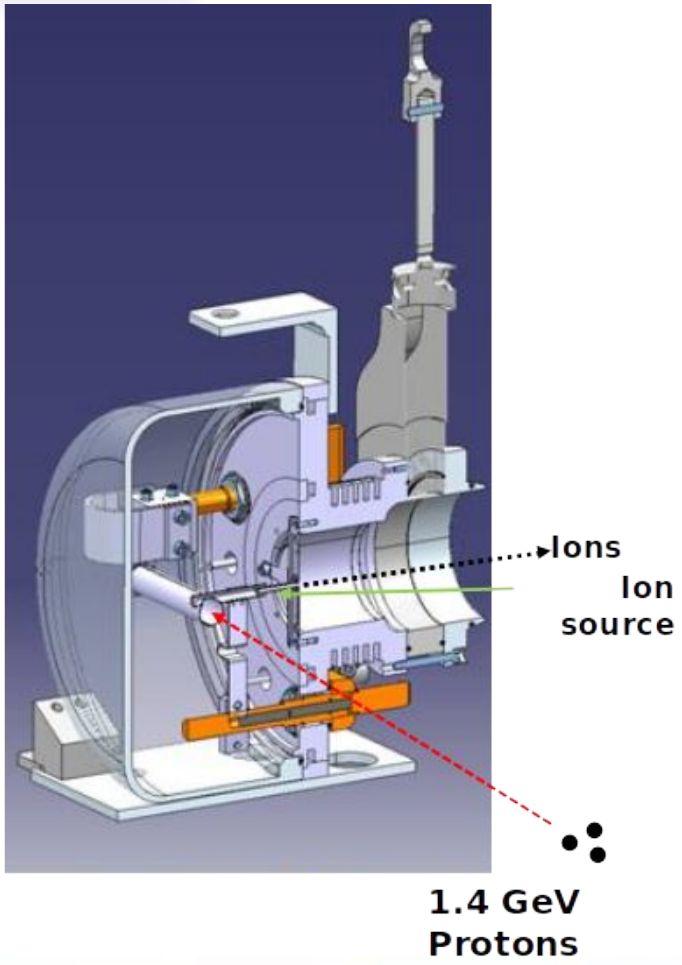
ISOLDE beam facilities

Isotope production via reactions of light beam with thick and heavy target

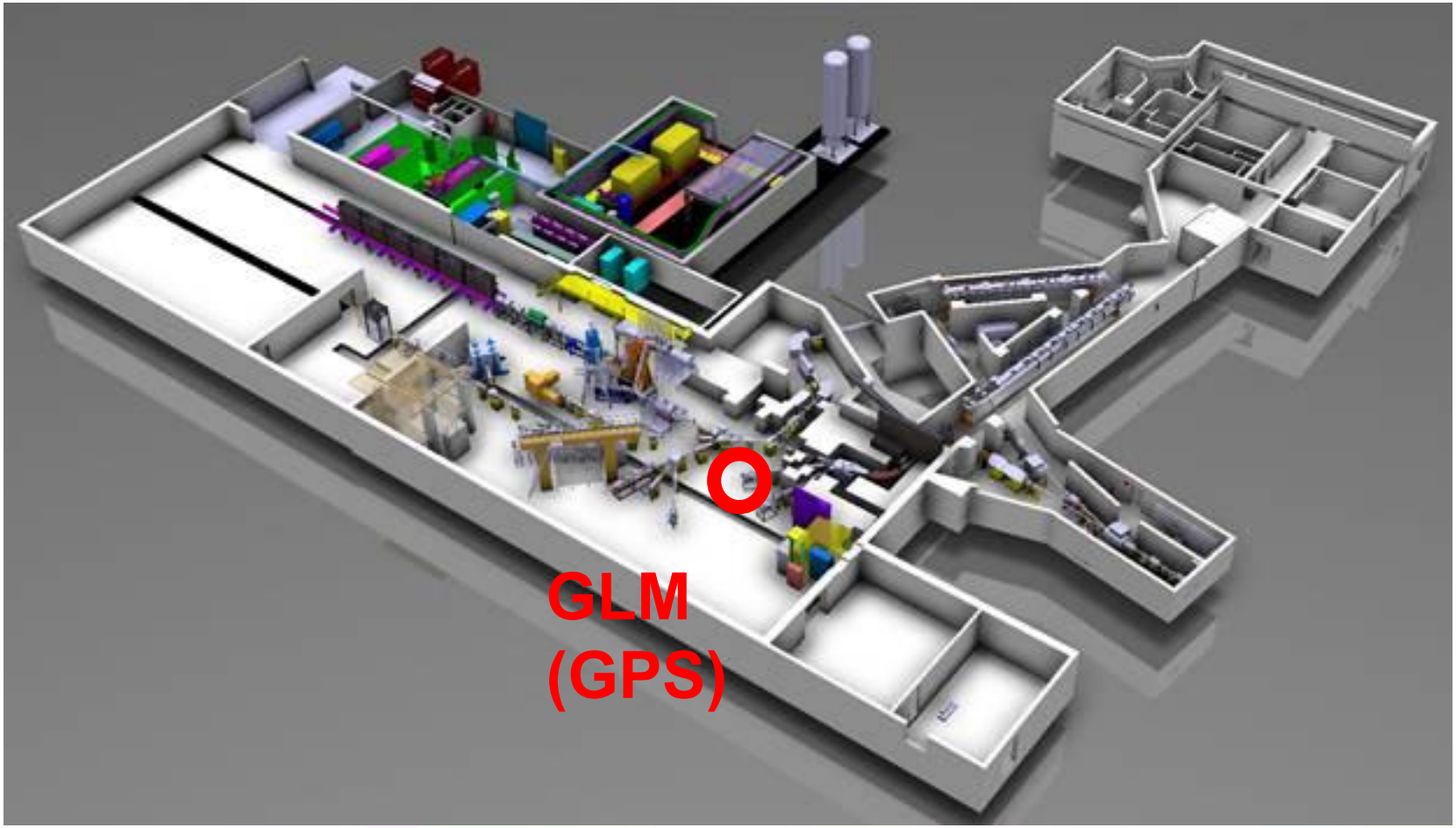


Isotope production

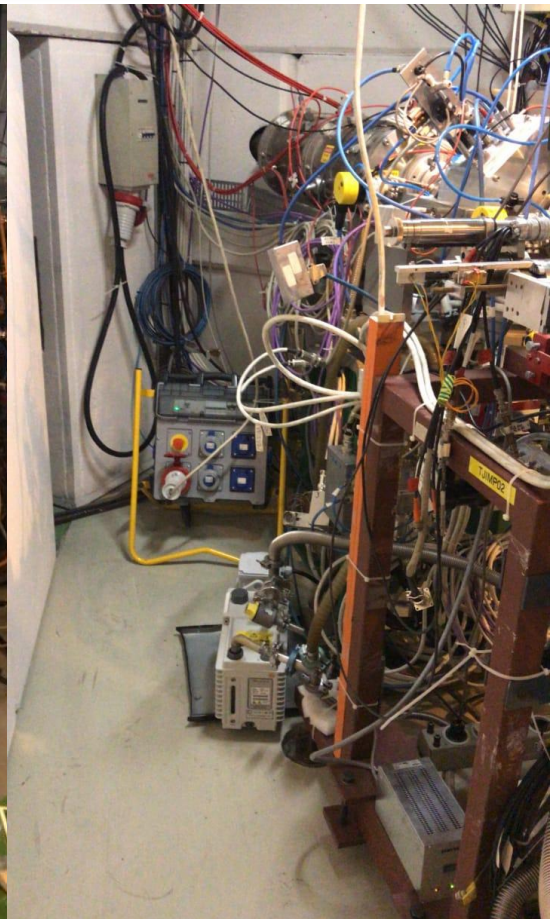


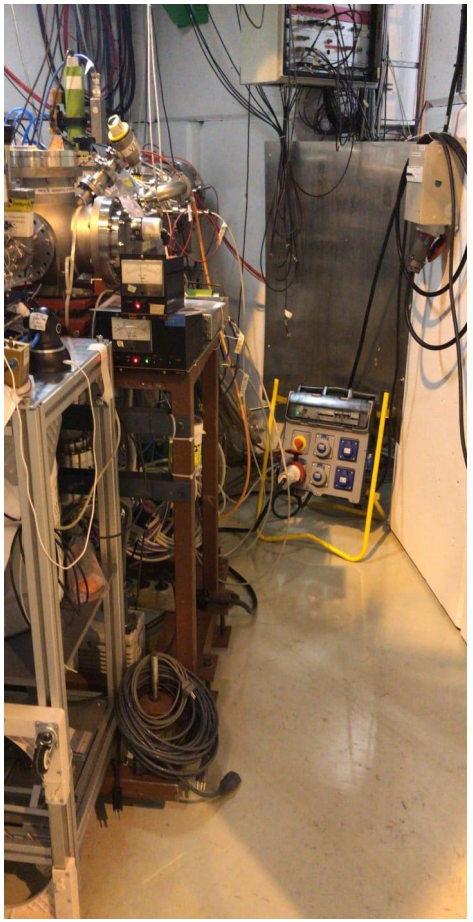


Setup chamber at ISOLDE/CERN

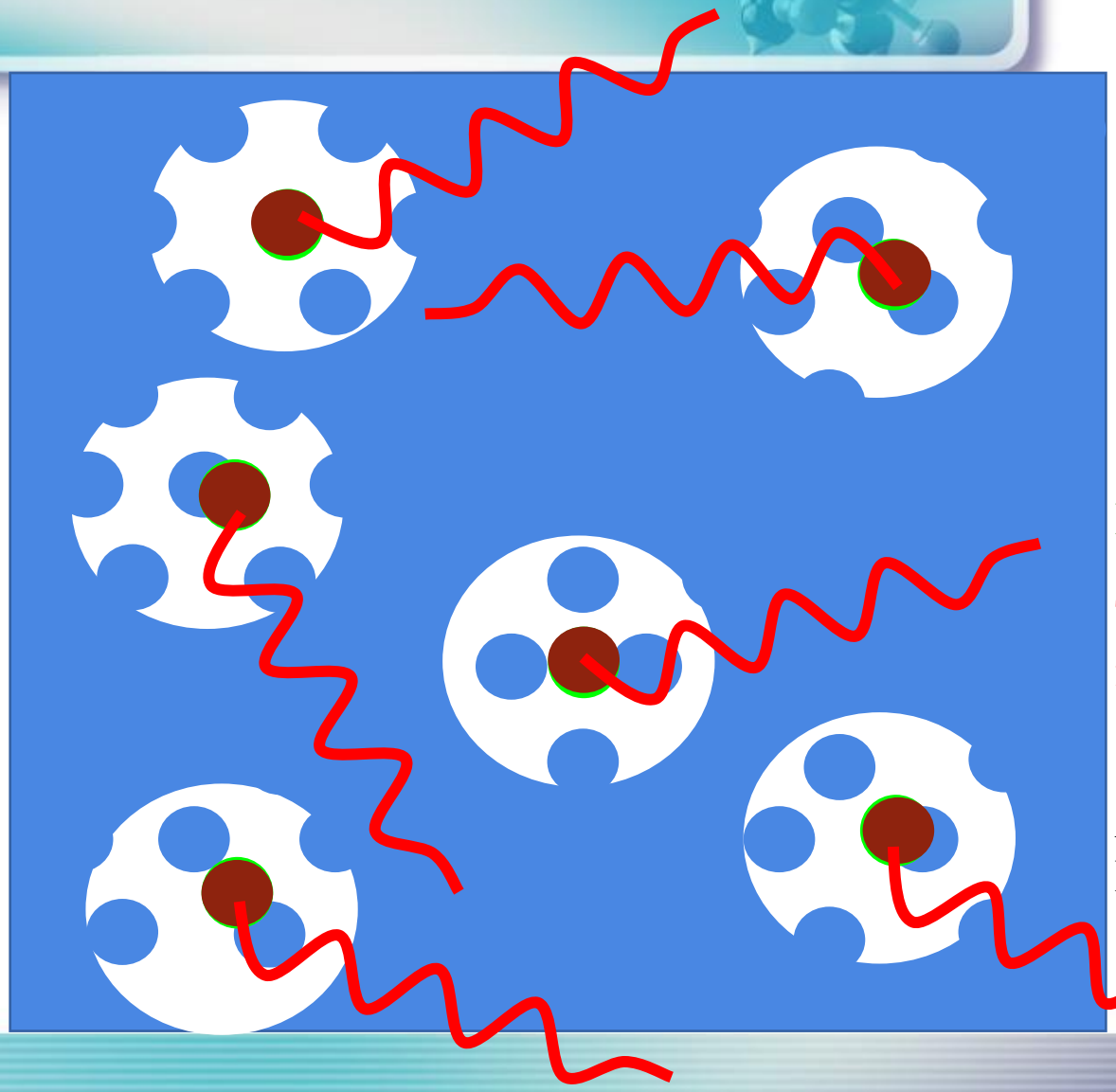


GLM beam line





Information about solid

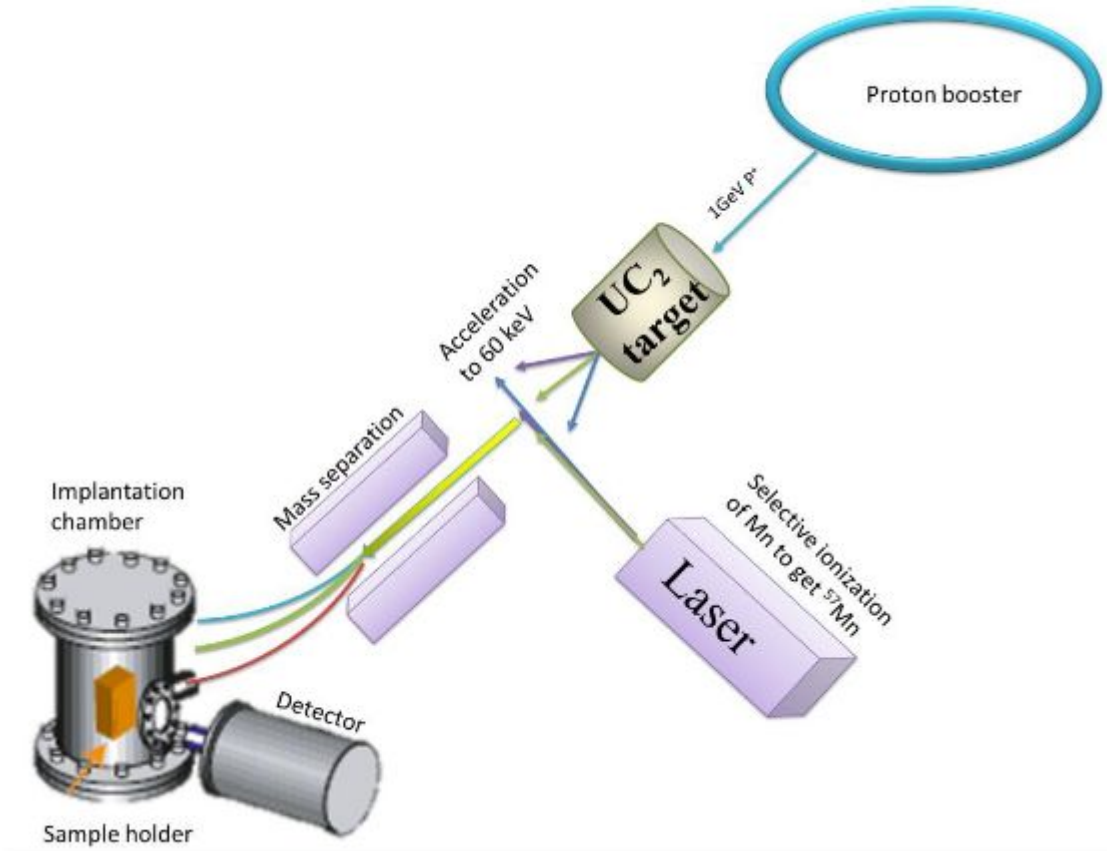


Implant Radioactive probes

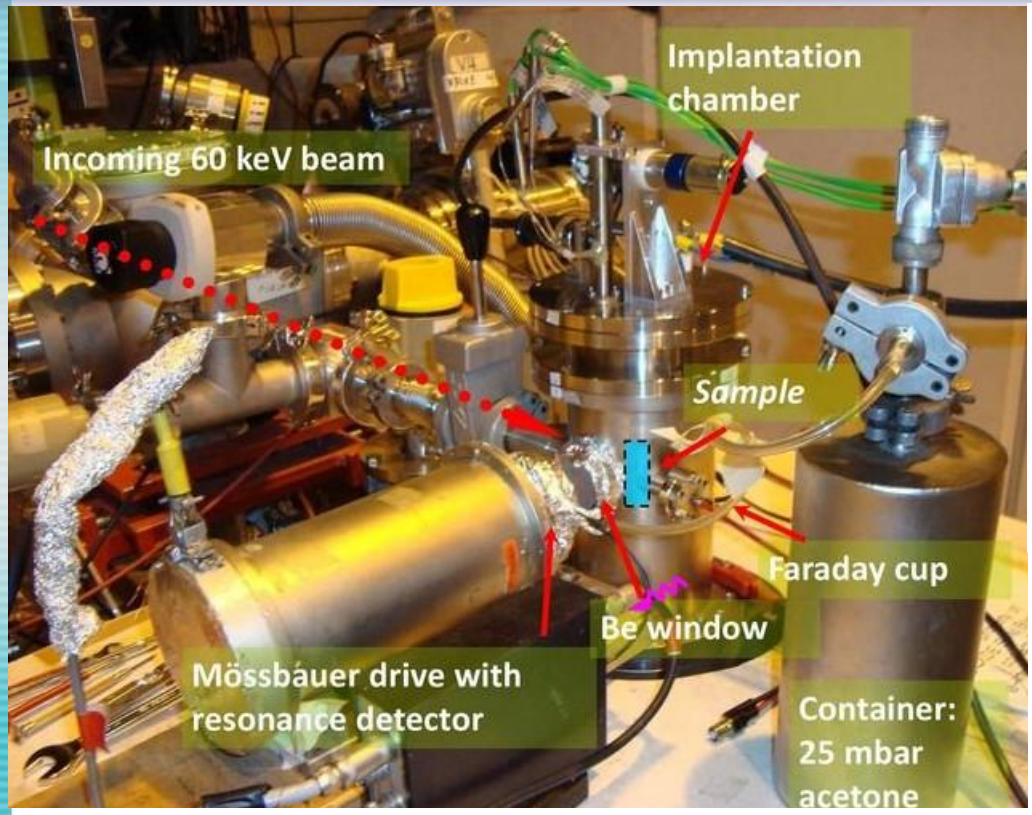
The radioactive decay gives information about the probe sites

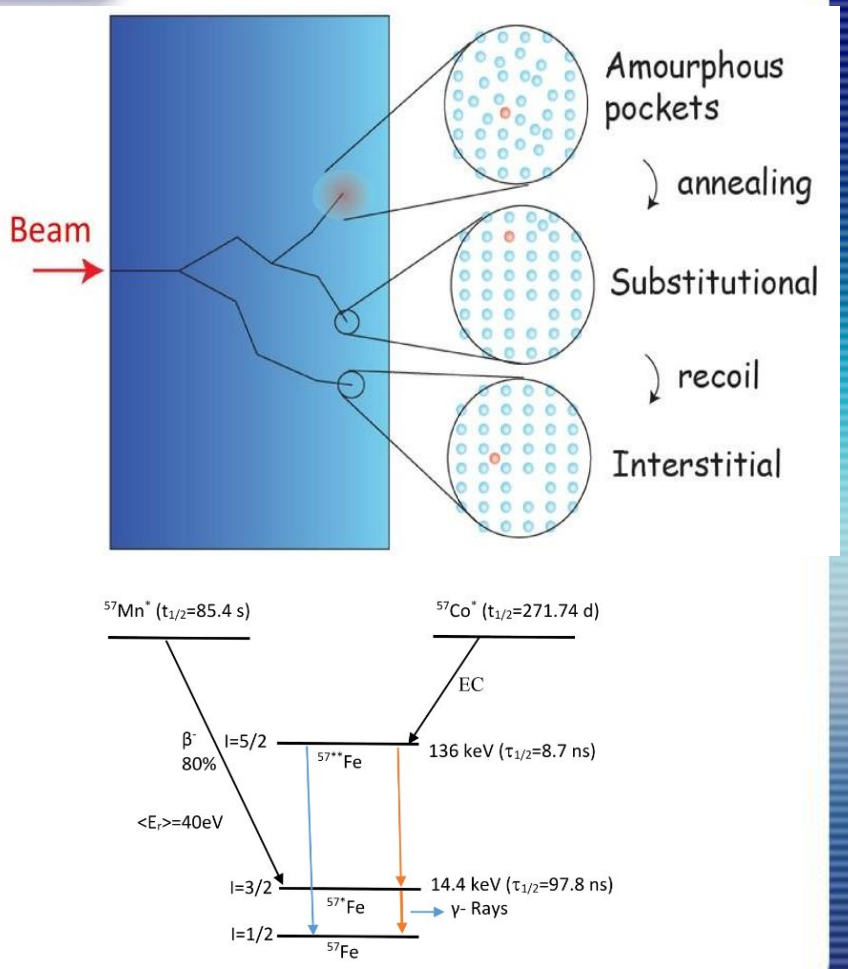
Analysis of Spectra → The Hyperfine parameters

The production of ^{57}Mn radioactive isotope



Mössbauer Experimental setup





Hyperfine parameters

Hyperfine parameters

Quadrupole splitting

Isomer shift

$$\Delta E_Q = \frac{eQV_{zz}}{2}\left[1+\frac{1}{3}\eta^2\right]^{1/2}$$

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}}$$

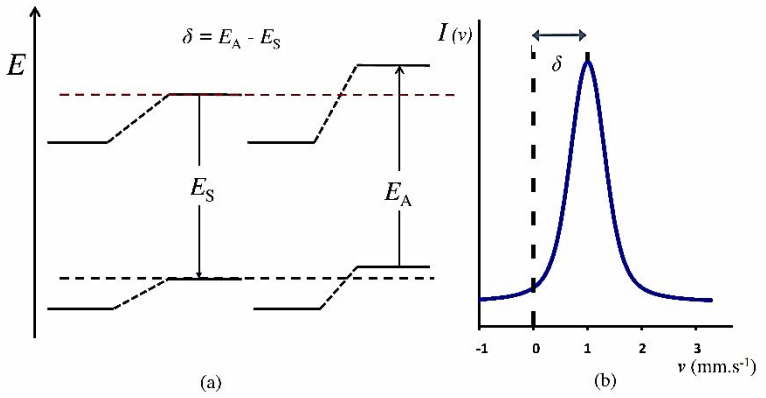
$\delta = \alpha(\rho_S - \rho_R)$, α=-0.291 au^{3}mm s^{-1}

A given charge distribution of electrons and nuclei, ρ(r), generates an electrostatic potential V(r).

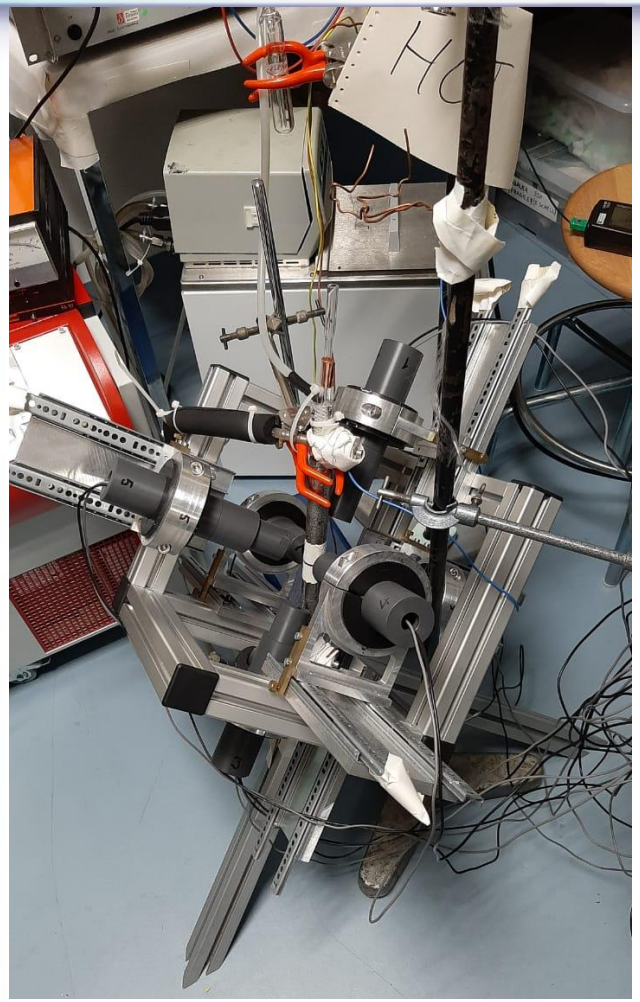
$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}$$

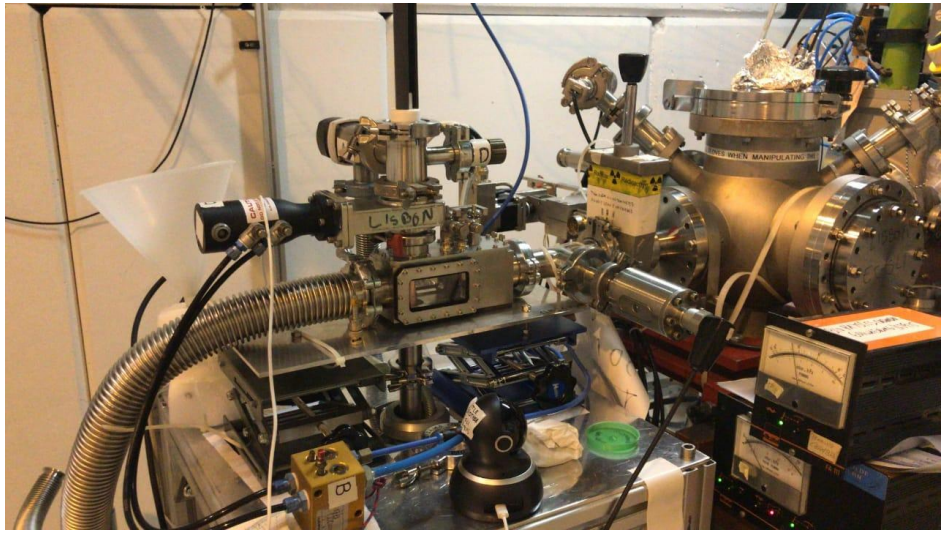
Principal component of the EFG tensor are usually defined as:

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$$

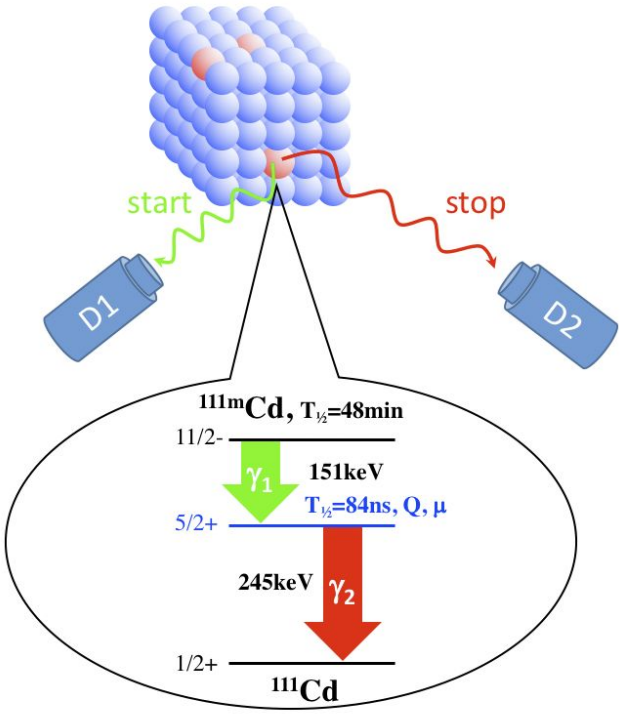


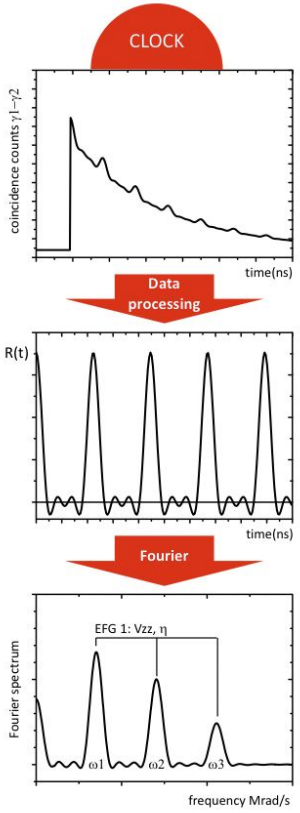
Perturbed Angular Correlation (PAC) & Chamber





Optical properties of dilute magnetic semiconductor





Calculation of hyperfine parameters using Wien2k code

Form of Potential

(non-)self consistent “Muffin-tin” MT
atomic sphere approximation (ASA)
Full potential : FP
pseudopotential (PP)

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\varphi_i^k = \varepsilon_i^k \varphi_i^k$$

Schrodinger-equation
(Kohn-sham equation)

Basis functions wavefunctions

exchange and correlation potential

Quantum chemistry:LCAO methods
plane waves : PW+pseudopotential approximation
augmented plane waves : APW
atomic orbitals. e.g. Slater (STO), Gaussians (GTO), LMTO, numerical atomic orbitals

Hartree-Fock (+correlations)
Density functional theory (DFT)

Generalized gradient approximation (GGA)
Local density approximation (LDA)
hybrid-DFT:mixing of HF+GGA, Various function
DFT+U

Structural properties

1. Total energies + forces on the atoms:
- perform structure optimization for“ real” systems
- investigate various magnetic structures ,exchange interactions

2. electronic structure:
- Band structure+DOS

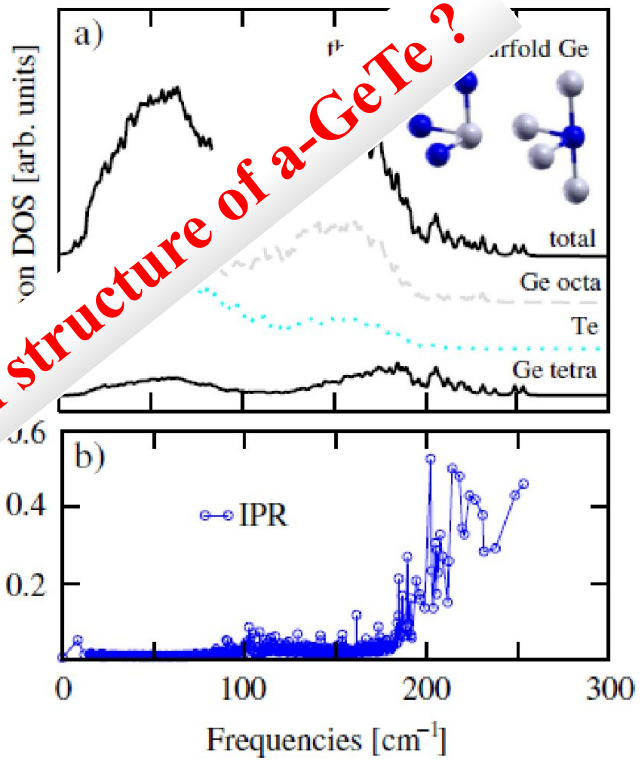
3. hyperfine parameters
- Isomer shifts, Asymmetry parameters ,electric field gradients

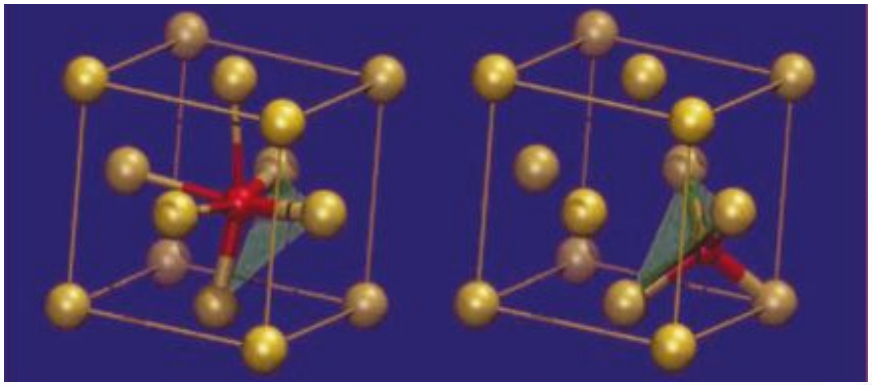
GeTe phase transition

Mazzarello et al (2010): "… based on ab initio calculations, we have provided an assignment of the Raman spectrum of a-GeTe to vibrations of specific local structures in the amorphous network which, by comparison with experimental Raman spectra, yields a compelling evidence of the existence of both tetrahedral and defective octahedral structures in a-GeTe.

Kolobov et al., extended x-ray …on fine structure (EXAFS) experiment… …cal structure of GST and GeTe change… …amorphization. The average coordina… …Ge atoms inferred from EXAFS data …s from sixfold in the crystal to a four… …hedral coordination of Ge atoms in a-G… …a-GeTe

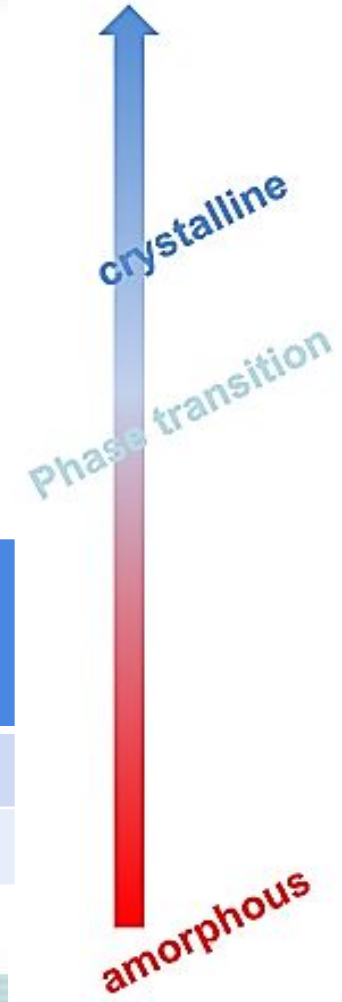
THE BIG QUESTION IS: What is the local structure of a-GeTe ?

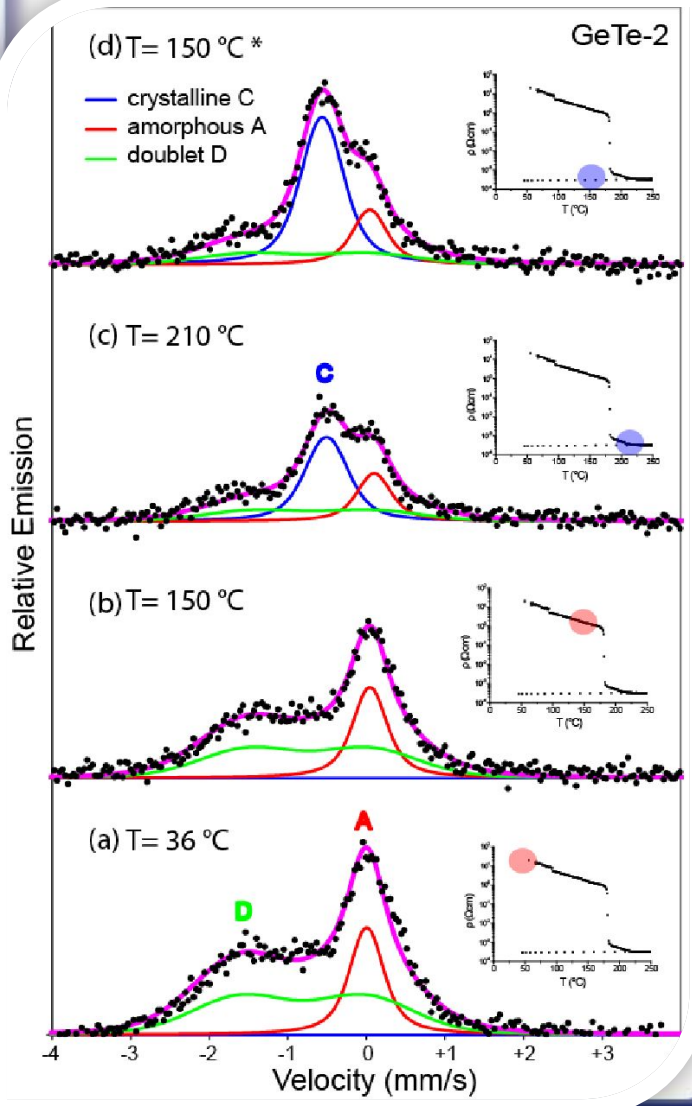




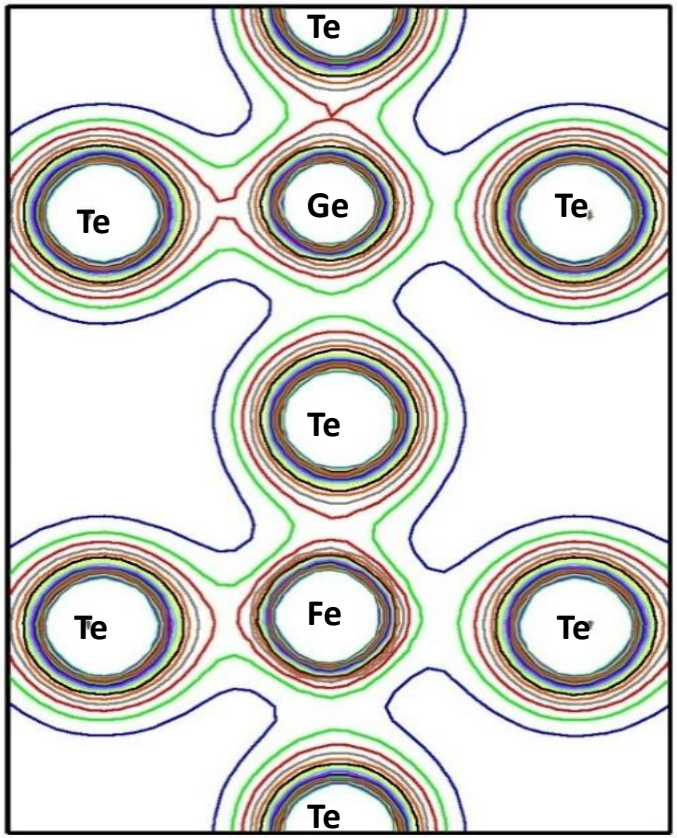
The experimental value of hyperfine parameters for $^{57}Mn \rightarrow ^{57}Fe$ implanted in GeTe

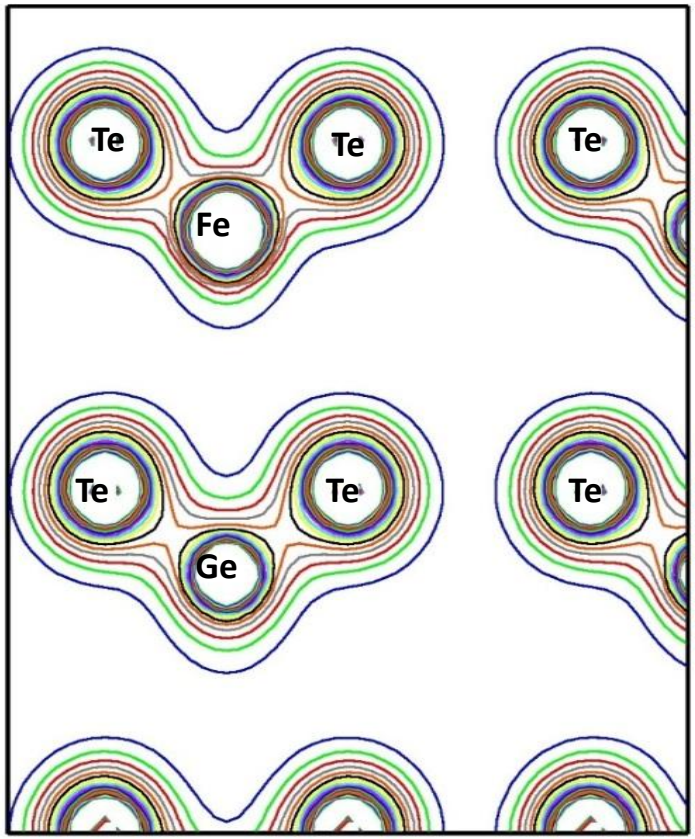
Hyp. Parameters (mm/s)	A	C
δ	0.637(5)	0.031(8)
Δ	0	0





Structure of Fe doped GeTe



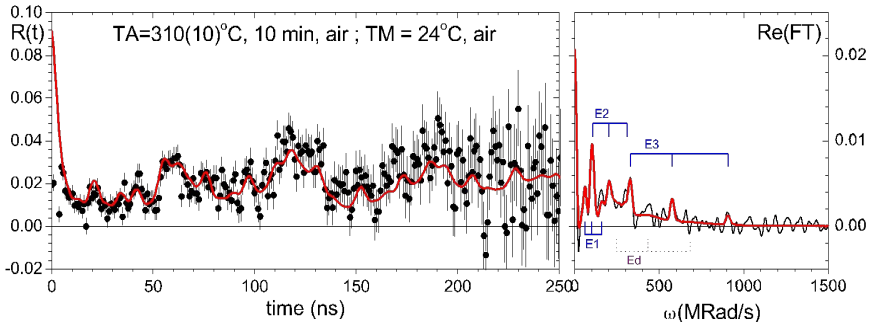


The DFT calculated value of hyperfine parameters for $^{57}Mn \rightarrow ^{57}Fe$ implanted in GeTe

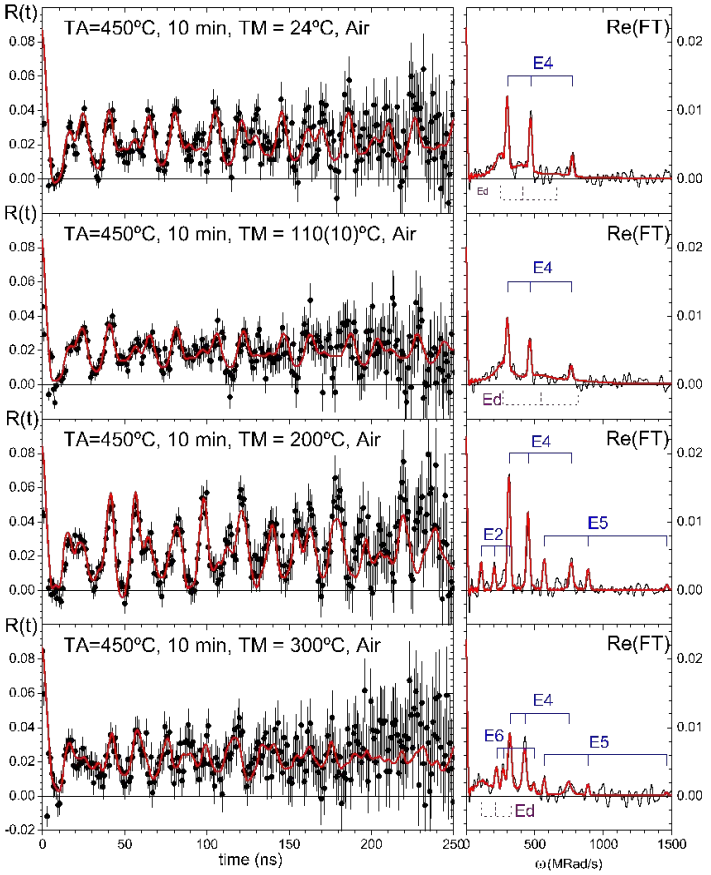
States	a-GeTe	c-GeTe
Magnetic moment	$M_{tot}(\mu_B)$	$M_{tot}(\mu_B)$
GGA	0.90	2.38
GGA+U	2.35	-----

symmetry	Phase	$V_{zz}(x10^{21}V/m^2)$	δ(mm/s)	ΔE_Q(mm/s)
Octahedral (Ge)	crystalline	0.778	0.61	0.13
Tetrahedral (Ge)	Amorphous	0.201	0.09	0

PAC spectra of Cd in α-MoO_3

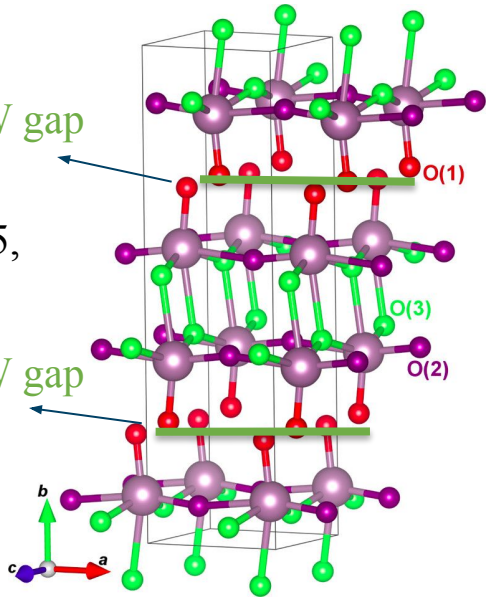


Experimental				
EFG	Vzz (V/Å^2)	η	%	ºC
EFG2	68(1)	0.19(3)	26(3)	24
EFG3	195(2)	0.32(1)	13(2)	24
EFG4	163(1)	0.484(4)	63(5)	24
EFG1	33.8(4)	0.43(3)	14(2)	24



DFT calculation with consideration of the Van der Waals forces for lattice and force optimization of α-MoO_3

- The Cd concentration of 4.16% in MoO_3 with supercell size of 3x1x2
- The radii of the muffin tin atomic spheres of Mo, O, and Cd are set to 1.65, 1.45, and 2.00 a.u., respectively.
- The energy value of -8 Ry is set as the boundary separating the core electron states and valence electron states.
- The cut-off parameter of $R_{MT} \times K_{MAX}$, which controls the size of the basis set, is set to 8.0.
- A mesh of (3x3x6) k-points in the irreducible part of the first Brillouin zone was applied to the self-consistent total energy calculation.



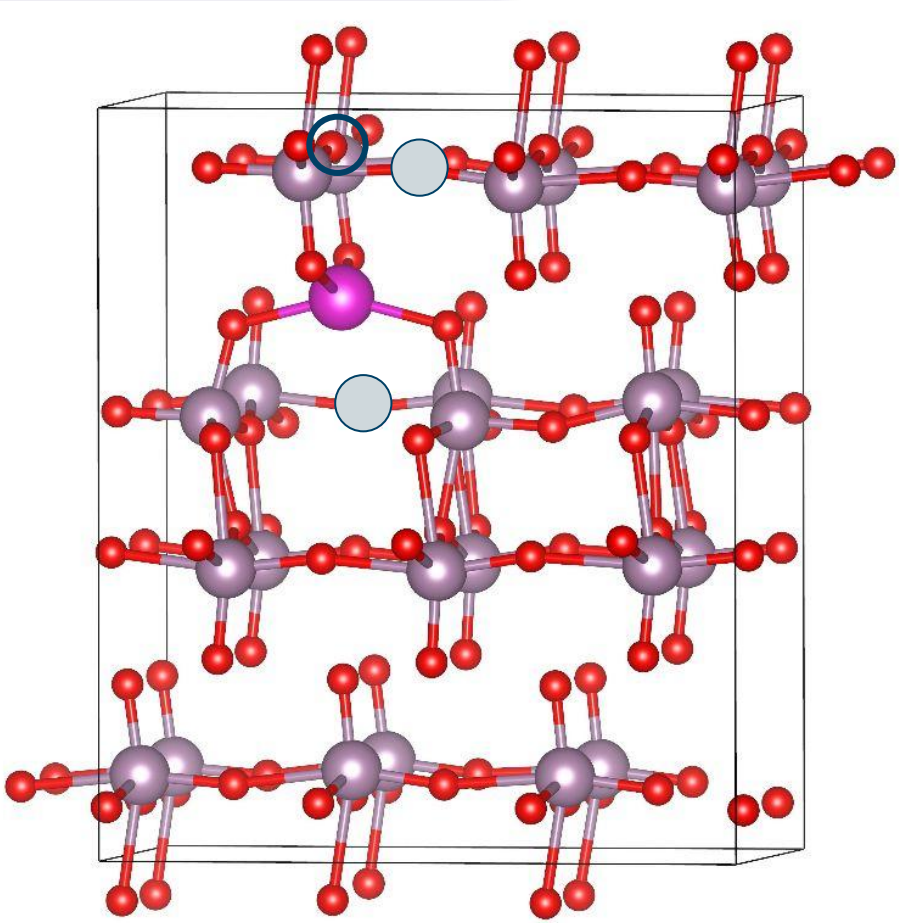
Approximation	a(Å)	%	b(Å)	%	c(Å)	%
GGA-PBE	3.9495	0.34%-	13.8086	0.33%-	3.684	0.34%-
LDA	4.002	0.99%	13.9921	0.99%	3.733	0.99%
PBE-Vdw	3.976	0.15%	13.901	0.33%	3.708	0.05%
.Exp	3.97		13.85		3.71	

The value rate of U in the calculation of DFT+U

- In the DFT+U calculations undertaken in this work(including those that made use of vdW-corrected density functionals), use was made of a value of Ueff= 6 eV.
- The value of Ueff used here is,however, considerably smaller than that suggested by Lutfalla et al(8.6 eV)[1] by fitting the experimental enthalpy for the hydrogen reduction reaction of MoO3 to MoO2: $MoO_3+H_2 \rightarrow MoO_2+H_2O$.
- The study by Ding et al[2]. use the value of≈6.0eV They obtain this value by comparing the obtained degree of charge localization in the DFT+U calculations with the HSE06 method for the same atomic geometry. By using the U=6 eV at DFT+U, they obtain the same result with the HSE06 method.
- I could try to match the bandgap with experimental value or the equilibrium lattice parameter of experiments. Or match the shape of the valence band to a higher level calculation such as hybrid method.

1.Lutfalla, S.; Shapovalov, V.; Bell, A. T. Calibration of the DFT/GGA+U Method for Determination of Reduction Energies for Transition and Rare Earth Metal Oxides of Ti, V, Mo, and Ce.J.Chem. Theory Comput.2011,7, 2218−222.
2.Ding, Hong, et al. "Computational investigation of electron small polarons in α-MoO3." *The Journal of Physical Chemistry C* 118.29 (2014): 15565-15572.

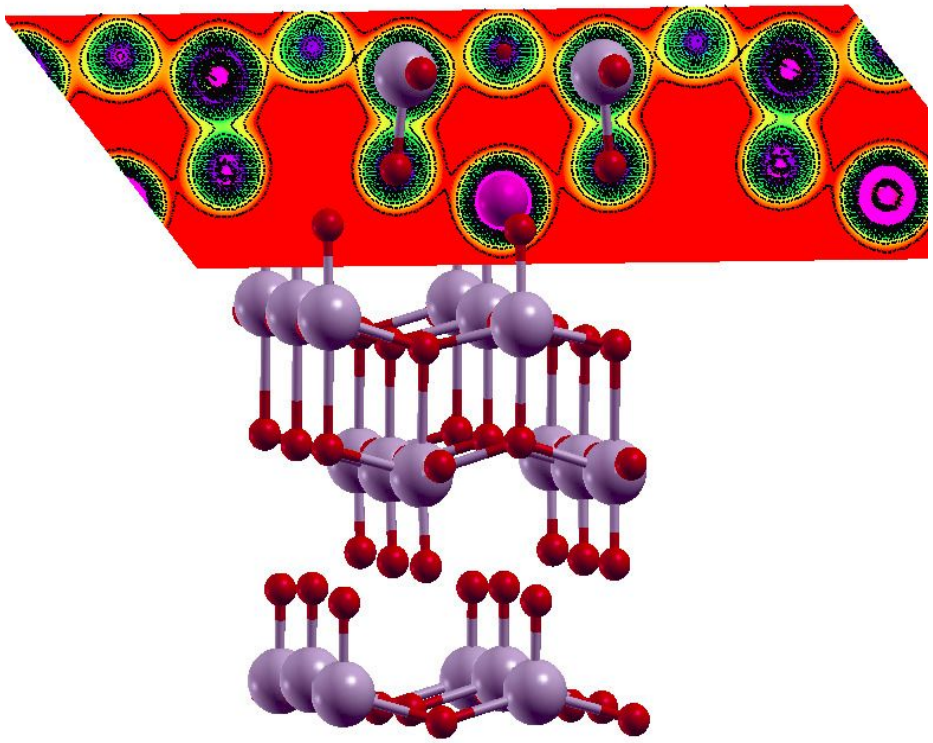
Different Configurations



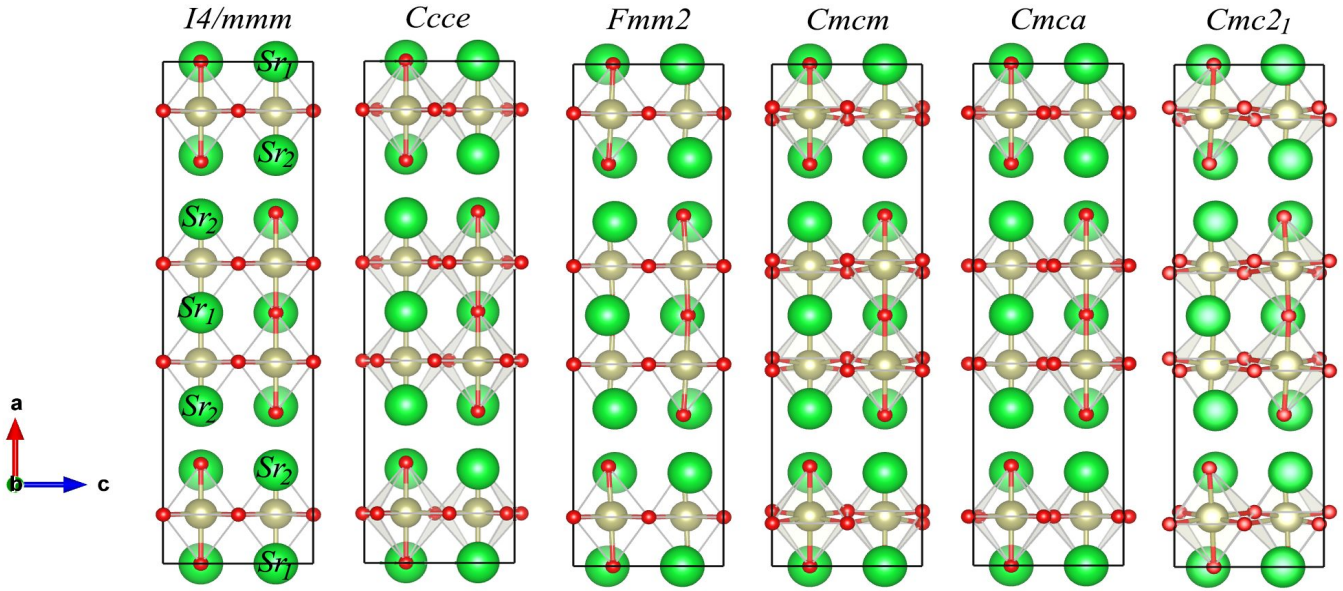
The calculated hyperfine parameters of different configuration for Cd in α-MoO_3

Approximation: GGA/PBE with VdW D3 functional					Experimental				
	Spin polarized		PBE + U = 6eV (Mo)						
Configuration	Vzz (V/Å^2)	η	Vzz (V/Å^2)	η	EFG	Vzz (V/Å^2)	η	%	ºC
Cd_I	52.16	0.242	54.13	0.240	EFG2	68(1)	0.19(3)	24(3)	24
Cd_I - 2xV_{O1}	-156.28	0.245	-185.17	0.215					
Cd_I -V_{O1}	-111.01	0.107	-134.26	0.086					
Cd_I -V_{O2}	189.52	0.387	190.24	0.373	EFG3	195(2)	0.32(1)	13(2)	24
Cd_I - 2xV_{O2} two vacancy are in same plane	-34.02	0.343	-48.87	0.255	EFG1	33.8(4)	0.43(3)	14(2)	24
Cd_I-2xV_{O2} two vacancy are in different plane	169.49	0.549	173.96	0.545	EFG4	163(1)	0.484(4)	63(5)	24

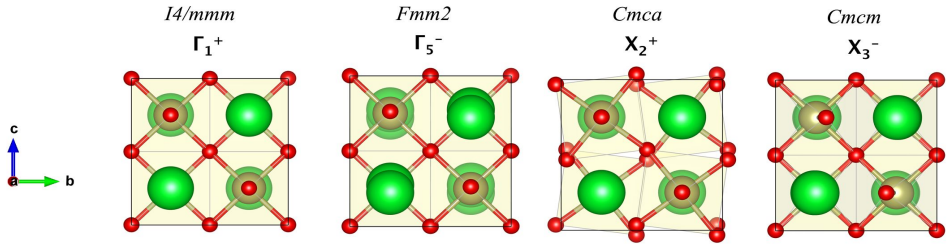
Electronic charge state of Cd_I:MoO_3



DFT calculation on $Sr_3Hf_2O_7$

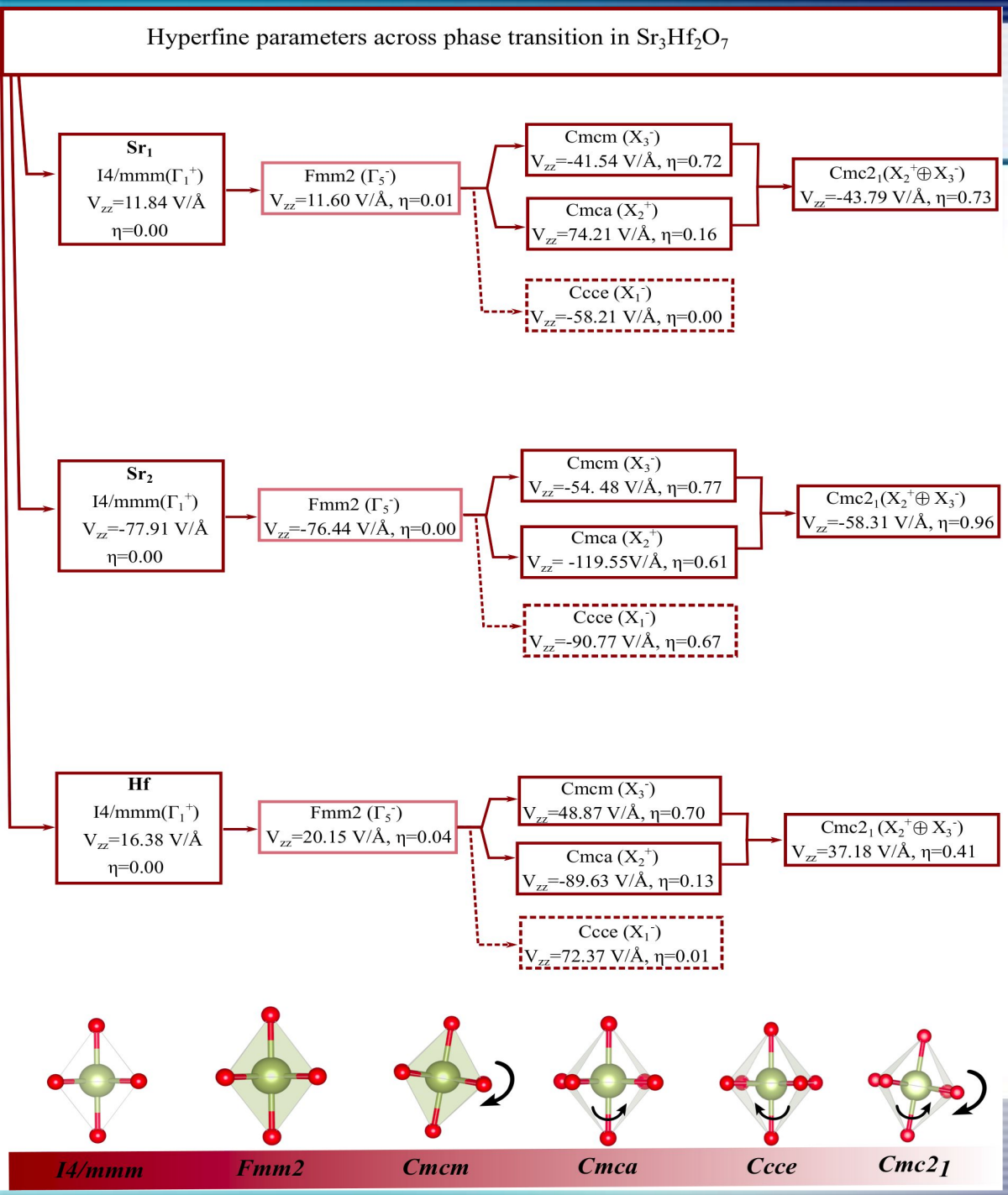


The magnitudes of Vzz and η are extremely sensitive to the octahedral rotations and tilting distortions across the phase transition path



the ^{181}Hf PAC probe is useful for studying the different phases of $Sr_3Hf_2O_7$ that is happened during the temperature variation.

Group Theory Analysis to Study Phase Transitions of Quasi-2D $Sr_3Hf_2O_7$." *Nanomaterials* 11.4 (2021): 897.



Space Group	ΔE (eV)
I4/mmm	1.946
Ccce	0.381
Fmm2	0.354
Cmcm	0.101
Cmca	0.026
Cmc2$_1$	0.000

Summary

- Radioactive measurements complement work at home laboratories
- Unique information – be it chemical or local – which is only achievable using radioactive implantations/probes.
- 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. b-NMR for biophysics

Thank You for your attention