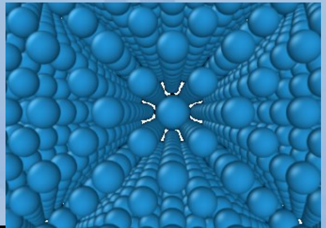
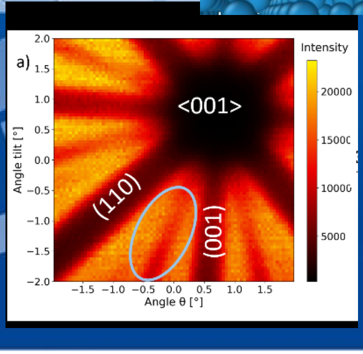
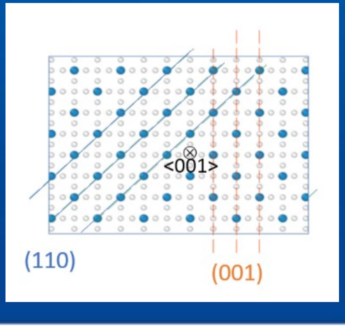
Detection of DEfects and HYDROgen by ion beam analysis in Channeling mode for fusion – DeHydroC
Project code: ENR-MAT-01-JSI







Sabina Markelj on behalf of the project team

Jožef Stefan Institute (JSI), Ljubljana, Slovenia

Final report meeting, 23-24. October 2024

Jožef Stefan Institute
F2 / Department of Low and Medium Energy Physics

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Jožef Stefan Institute

MAX-PLANCK-INSTITUT FÜR PLASMAPHYSIK

Project team workshop in February 2023

UNIVERSITY OF HELSINKI

cea

Strategy of the project

- Analysis by state of the art analysis techniques by electron microscopy and positron annihilation

- Detection of **defects** by **Rutherford Backscattering Spectroscopy** in **Channeling** configuration (RBS-C) + modelling

- Detection of **deuterium** location by **Nuclear Reaction Analysis** in **Channeling** configuration (NRA-C) + modelling

- Conclusion

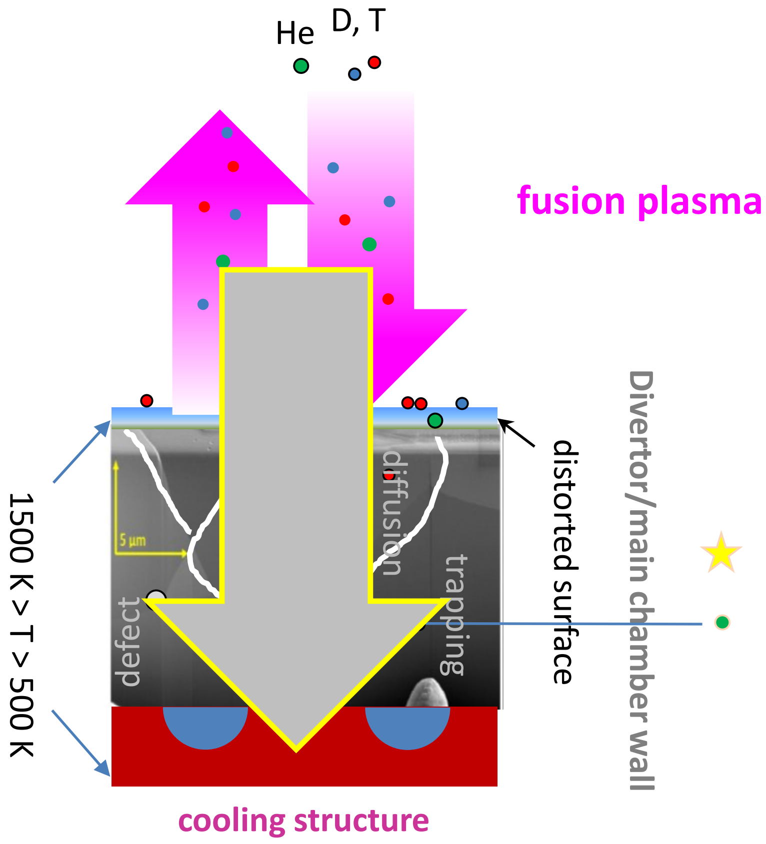
Motivation: tritium loss in displacement damage

Simplified plasma-wall interaction

Tungsten – plasma facing material – first wall and divertor

$10^{24} m^{-2} s^{-1} > j > 10^{18} m^{-2} s^{-1}$

eV < E < keV



- We need to be able to predict **tritium loss in the first wall** of a future fusion reactor
- Focus on the bulk and the influence of neutrons
- Last ten years the focus was on displacement damage

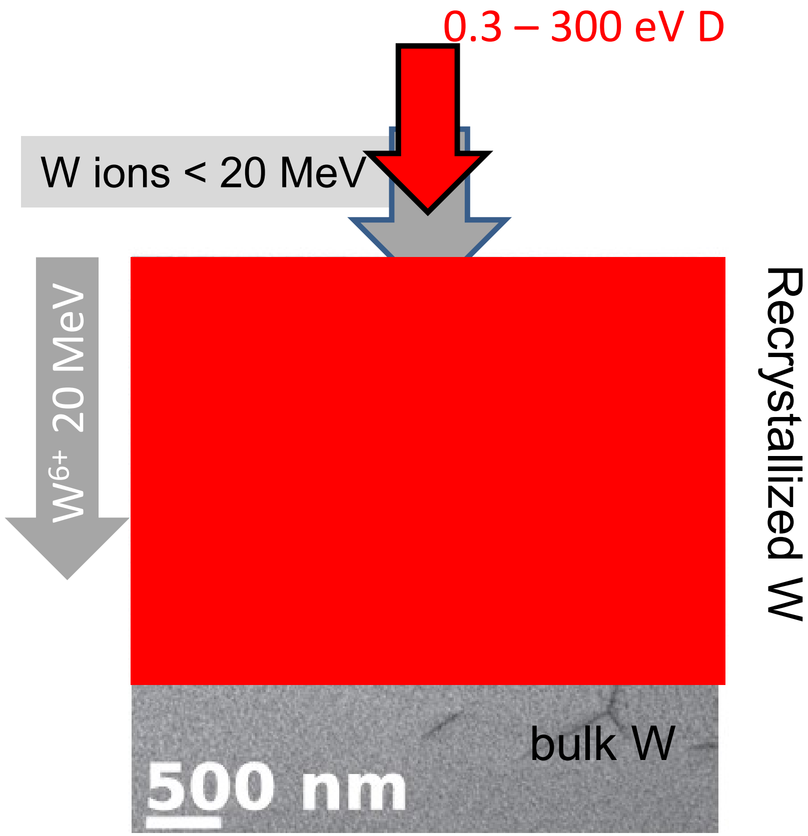
★ neutron damage – 5 dpa/fpy [1]

● He production

Transmutations,…

[1] Federici et al., Nucl. Fusion 57 092002, 2017

Separating individual aspects of the interaction



Damaged layer characterization by Scanning Transmission Electron Microscopy (STEM) [Založnik et al. Phys Scr. T167 (2016) 014031]

W ion irradiation by MeV W ions

- Creation of displacement damage
- Dense cascades

- ➢ Exposure to D atoms/ions – to only populate the existing traps without producing new ones
- ➢ Open volume defects are traps for hydrogen isotopes [S. M. Myers et al., JNM 165 (1989) 9-64]

Methodology to quantify D retention, defect evolution and defect concentration:

- ➢ **Measure D concentration by nuclear reaction analysis (NRA) via $D(^3He,p)^4He$**
- ➢ **Desorption kinetics by thermal desorption spectroscopy (TDS)**
- ➢ **Use macroscopic rate equation modelling**

Which defects are really responsible for hydrogen isotope retention?
Where does hydrogen sit?

Project objectives

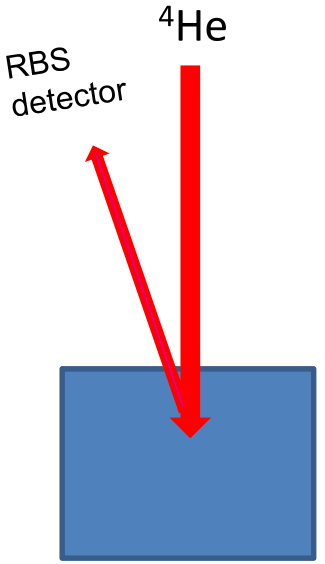
The main goal of this project is to develop an experimental setup and analysis procedure that will enable detection of individual types of defects and the amount of hydrogen trapped in the defects.

- **Objective 1: To differentiate defect structures in the channeling-RBS spectra: to separate small from large defects.**

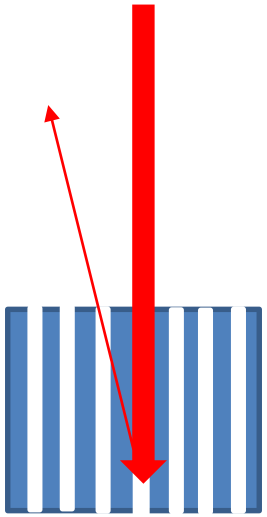
- **Objective 2: To perform NRA in channeling mode on a quantitative level to allow for determination of absolute deuterium amounts inside individual defects.**

Methodology

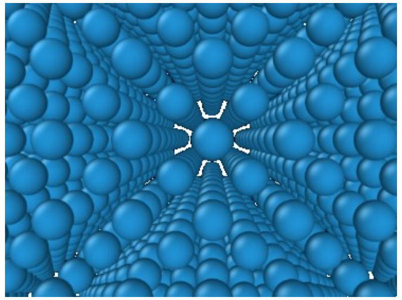
Rutherford Backscattering Spectroscopy (RBS)

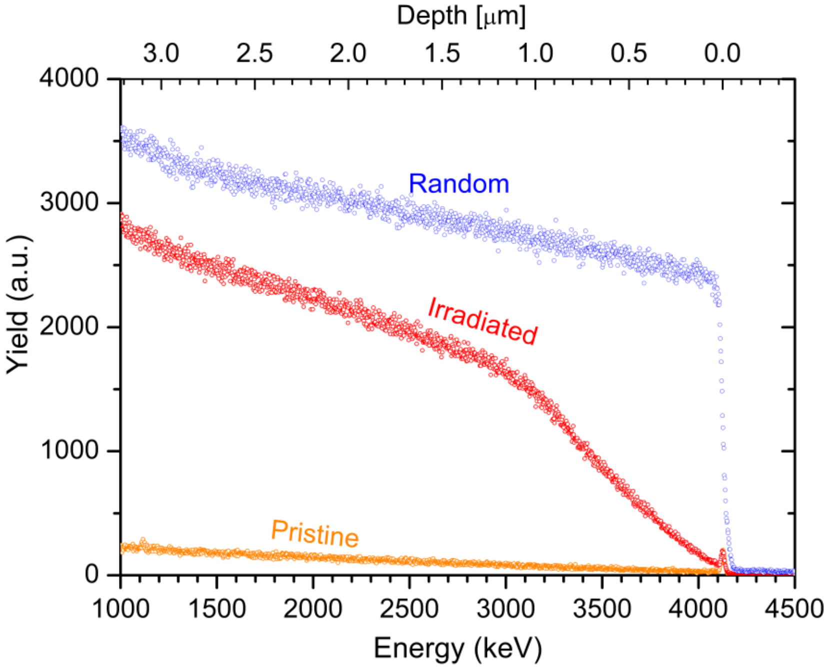


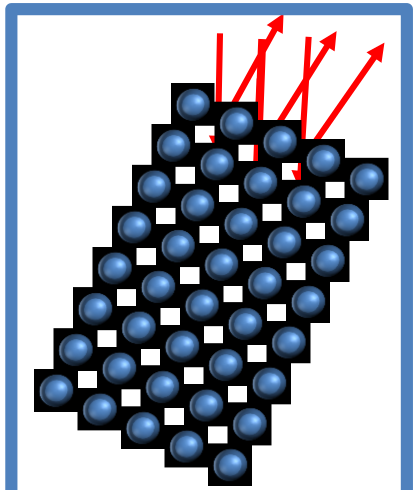
In Channeling (RBS - C)



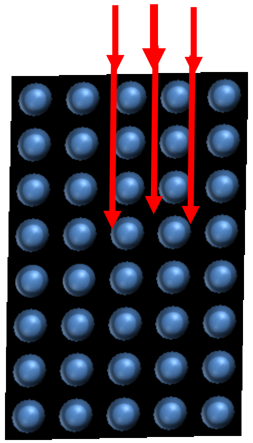
- Ion beam technique
- Non-destructive!
- In situ!
- Study disorder in materials due to irradiation (depth resolved)
- Defect type? Sensitive mainly to dislocation structure (loops, lines)



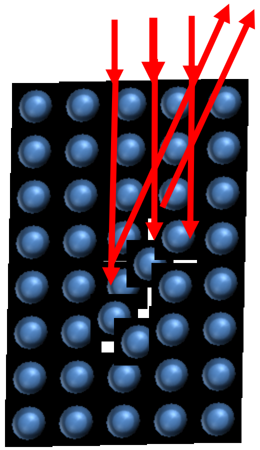




Amorphous material
Random direction



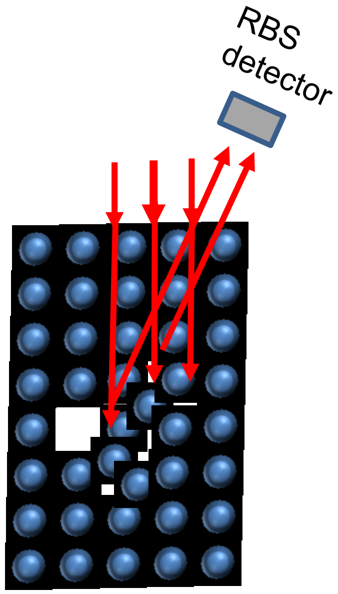
Pristine crystal - aligned



Dis-ordered crystal - aligned

Methodology

Channeling Rutherford Backscattering Spectroscopy (RBS - C)



- Disorder in materials due to irradiation (depth resolved)

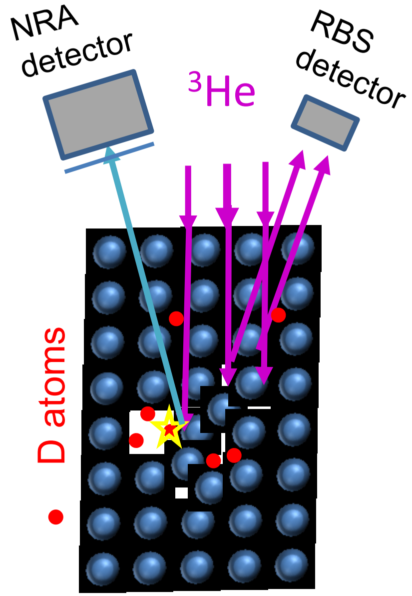
Defect type?

- Sensitive mainly to dislocation structure (loops, lines)

- Ion beam techniques
- Non-destructive!
- In situ!

Nuclear Reaction Analysis (NRA - C)

$D(^{3}He,p)^{4}He$



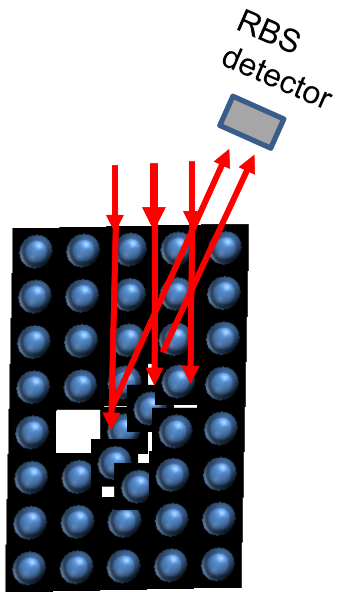
- Deuterium populates defects in materials – analysis depth resolved

Defect type?

- D traps mainly in open volume defects (vacancies, vacancy clusters)

Methodology

Channeling Rutherford Backscattering Spectroscopy (RBS - C)



- Ion beam techniques
- Non-destructive!
- In situ!

- Disorder in materials due to irradiation (depth resolved)

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Nuclear Reaction Analysis (NRA - C)

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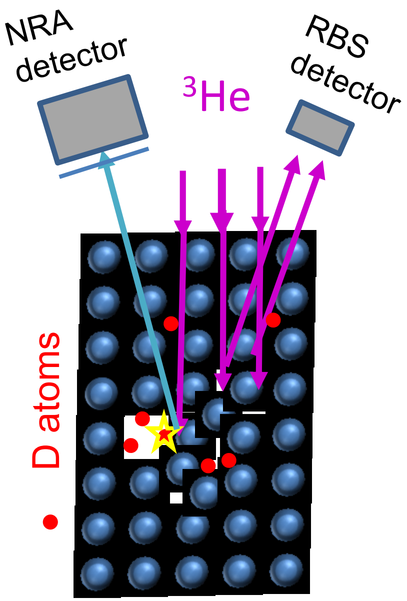
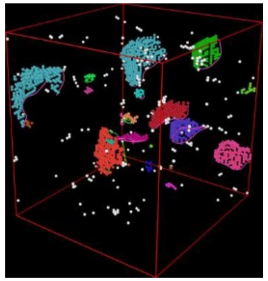


- Deuterium populates defects in materials – analysis depth resolved

Defect type?

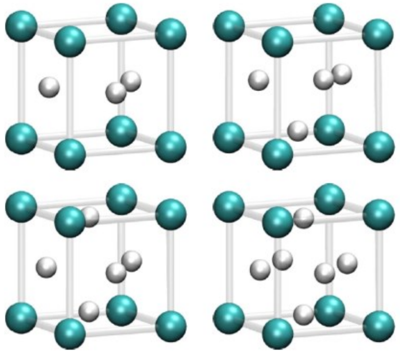
- D traps mainly in open volume defects (vacancies, vacancy clusters)

Molecular Dynamics (MD)



- Collision cascades (~10−100 nm)
- High radiation dose

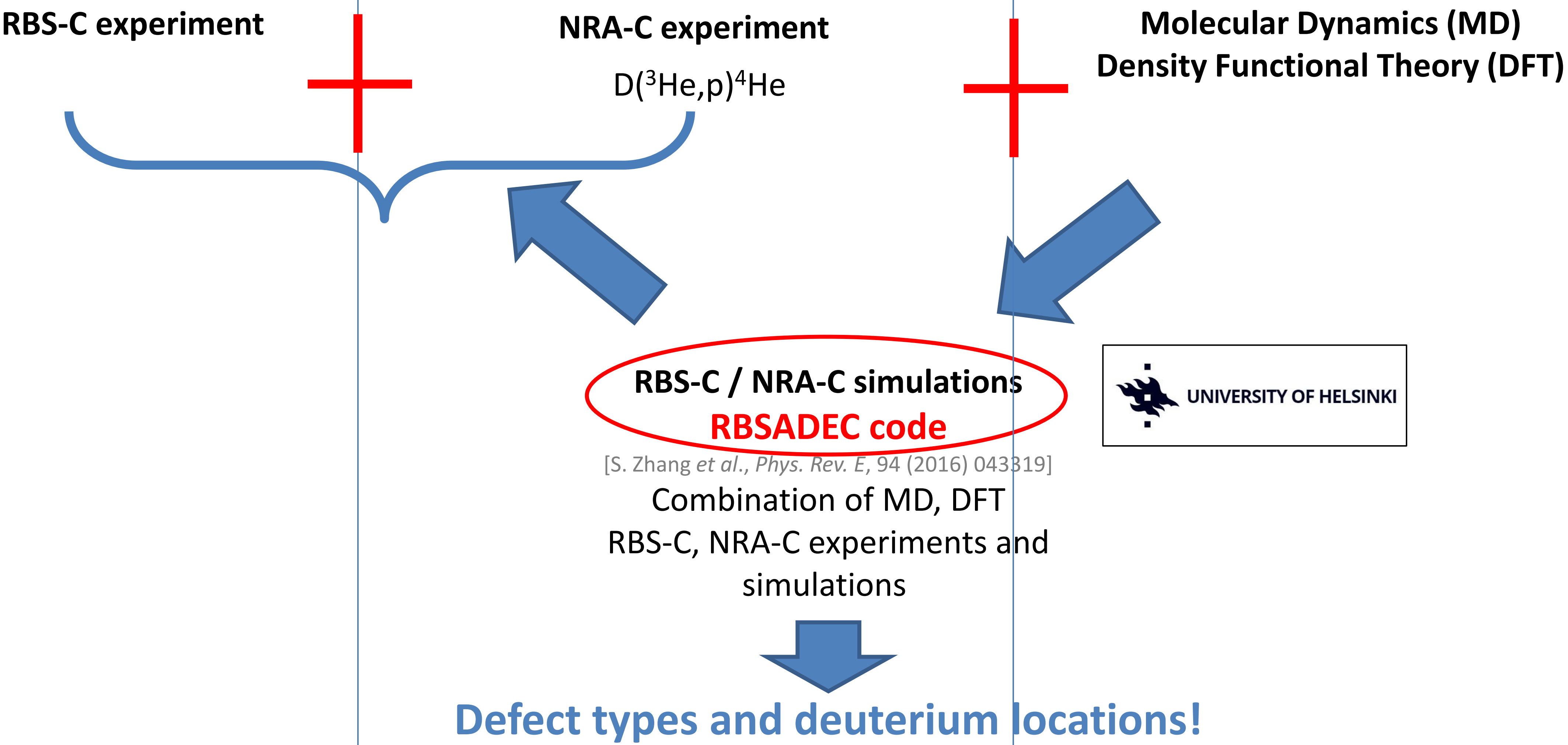
Density Functional Theory (DFT)



Heinola et al. PR B (2010)

- Hydrogen atom positions around vacancy/vacancy cluster

Methodology



RBS-C experiment

NRA-C experiment

D(^{3}He,p)^{4}He

Molecular Dynamics (MD)
Density Functional Theory (DFT)

UNIVERSITY OF HELSINKI

RBS-C / NRA-C simulations
RBSADEC code

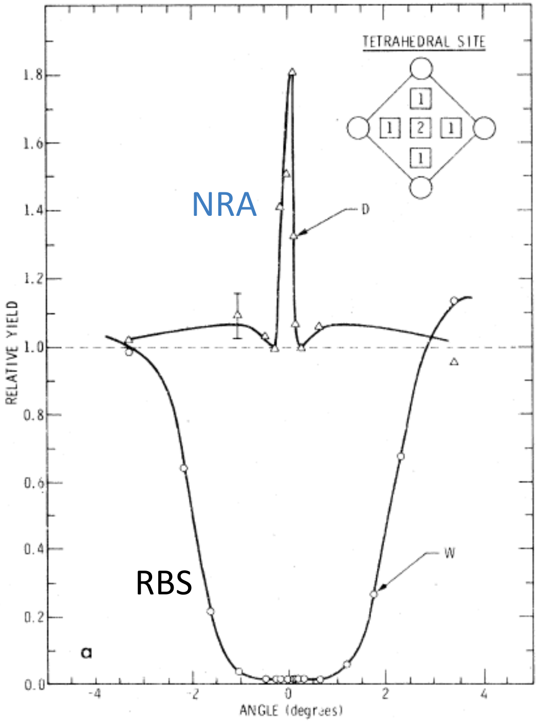
[S. Zhang *et al.*, *Phys. Rev. E*, 94 (2016) 043319]

Combination of MD, DFT
RBS-C, NRA-C experiments and simulations

Defect types and deuterium locations!

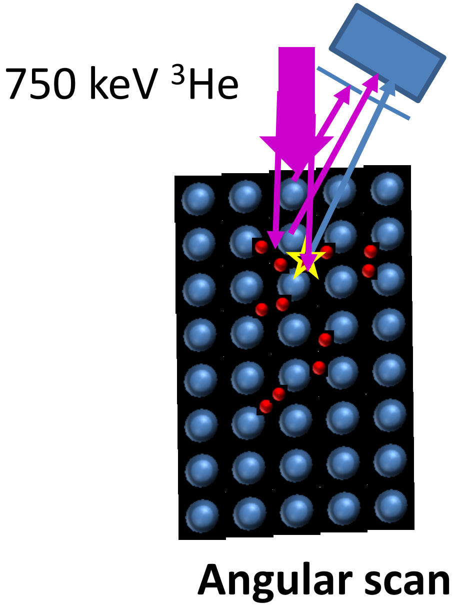
Location of D inside W (defects) - NRA channeling

- Method to determine hydrogen interstitial sites in metals in 70’s/80’s
  [Fukai, The metal-hydrogen systems, Springer 2005]
- Example of detection of hydrogen in metals by group of Picraux and Myers in Sandia National Laboratories (SNL), New Mexico; Implantation by keV D ions!



Angular scans through the <100> axis on W
- ➢ *Deuterium sitting in tetrahedral sites*

Picraux, S. T. & Vook, F. L. Deuterium lattice location in Cr and W. Phys. Rev. Letters 33, 1216 (1974).



But:

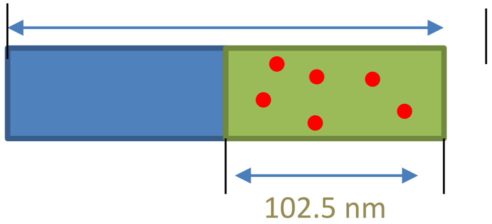
- ➢ Academic case of defect-free (?) tungsten
- ➢ Only qualitative measurement
- ➢ 30 keV D ions created vacancies by themselves:
  - Is it even possible to determine position of solute atoms?
  - Signal should be dominated by trapped D!

Incorporation of NRA-C into RBSADEC code

Incorporation of NRA-C into binary collision approximation code RBSADEC = Monte Carlo simulation code

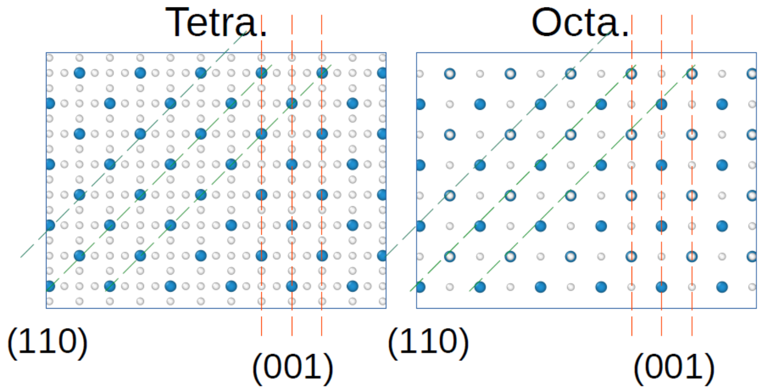
[Zhang, S. et al. Physical Review E ***94****, (2016)]*

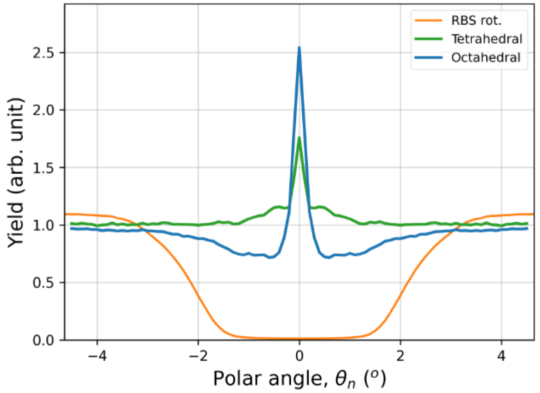
- RBS-C: a pristine W target
- NRA-C:

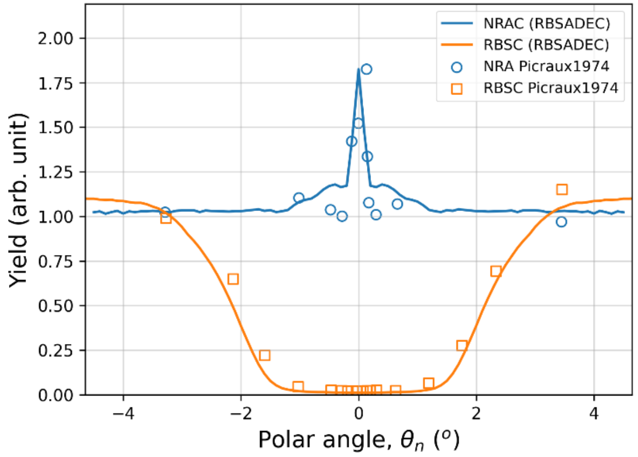


- 0.1 % of D at tetrahedral sites

<001>







S. Picraux, Phys. Rev. Lett., 33, 1974

3×10^{15} cm^{-2} 30 keV D on W

Difference between experiments and simulations: Not exactly at tetrahedral sites?

- Hydrogen in vacancies, some position close to tetrahedral sites, etc.

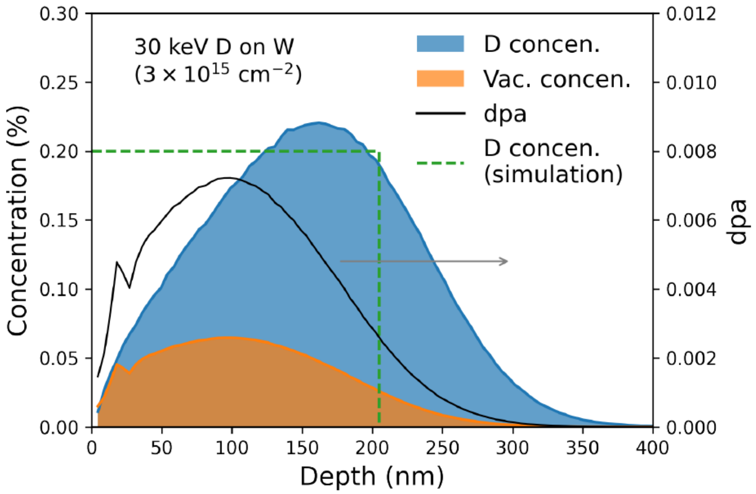
➢ Effect of damage dose: D sites change

➢ Improving the fit: adjust D locations,
D location according to DFT calculations

Development of C-NRA simulation and detection of D by RBSADEC code

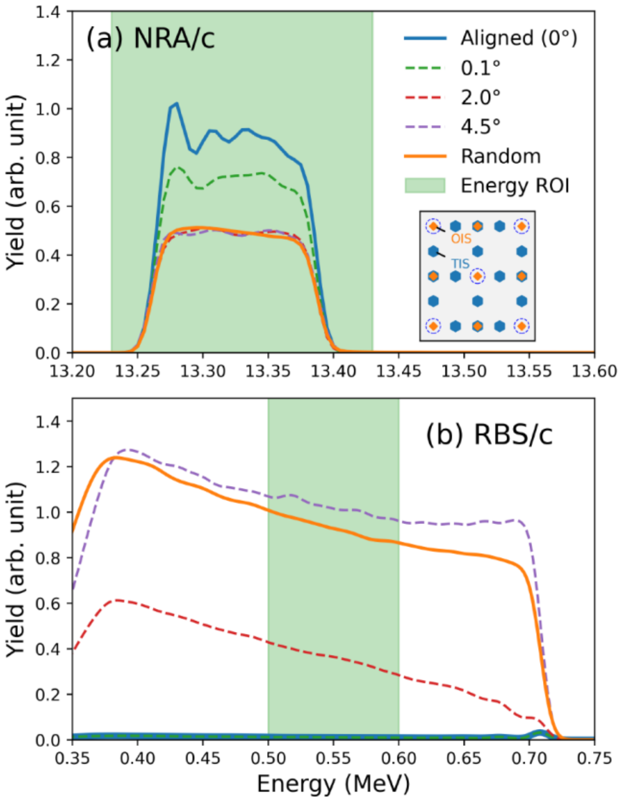
- ☐ SRIM calculation of vacancy distribution for 30 keV D ions in W for Picraux experiment

(S. Picraux, Phys. Rev. Lett., 33, 1974)

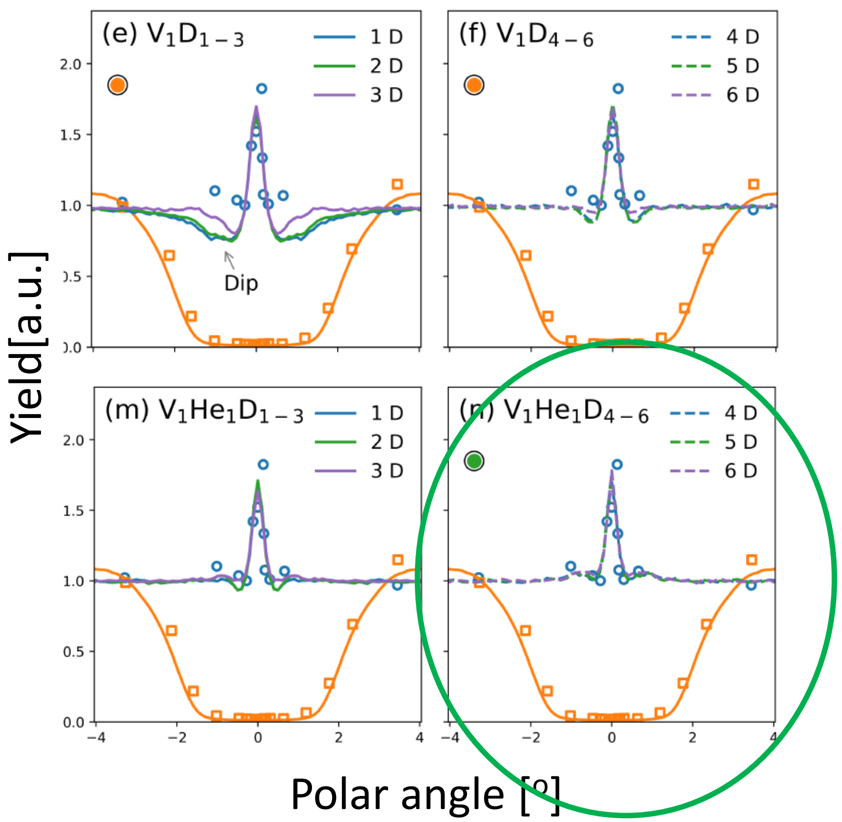


- Creation of vacancies
- Multiple hydrogen atoms in a single vacancy [Heinola et al. PR B (2010), Fernandez et al. Acta Materialia (2015)]

- **Calculating the NRA and RBS yield**



- **Best agreement obtained for He-filled vacancy with 5 H atoms**



[Jin et al. Phys. Rev. Materials 8, 043604 (2024)]

This study shows the strength of NRA-C
Picraux interpretation was wrong

Effort to detect defects and D location in W containing defects

Samples: tungsten single crystals (111) and (100)

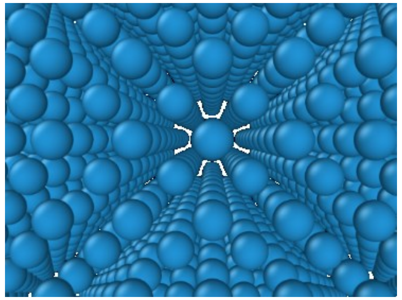
Irradiation: 10.8 MeV W ions

- **Two damage doses:**

Low ($5.8\times10^{16} m^{-2}$) & High($5.8\times10^{17} m^{-2}$)

SRIM-KP

0.02 dpa **0.2 dpa**



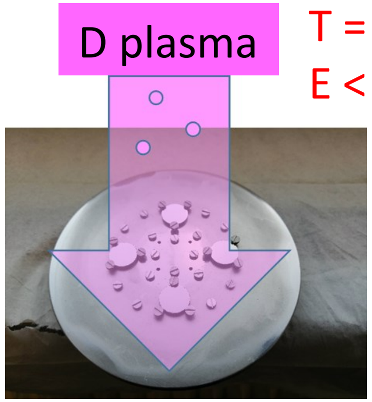
W (100)

Two temperatures:

290 K & 800 K

Single vacancies @ low dose

Large vacancy clusters



T = 370 K,
E < 5 eV/D

'gentle' loading = 'decoration' of defects
ion flux: 6 ×10^{19} D/(m^2s)
ion fluence: 1·10^{25} D/m^2 (48 h)

Based on *Hu et al. JNM 556 (2022) 153175* – open volume type defects

Sample	Irradiation conditions	Predominant defect expected
78g / 78a / #1	0.02 dpa, 290 K	single vacancies
78f / 78e / #5	0.2 dpa, 290K	heavily damaged standard
78c / 78h / #3	0.02 dpa, 800 K	small vacancy clusters
78b / 78d / #2	0.2 dpa, 800 K	big vacancy clusters

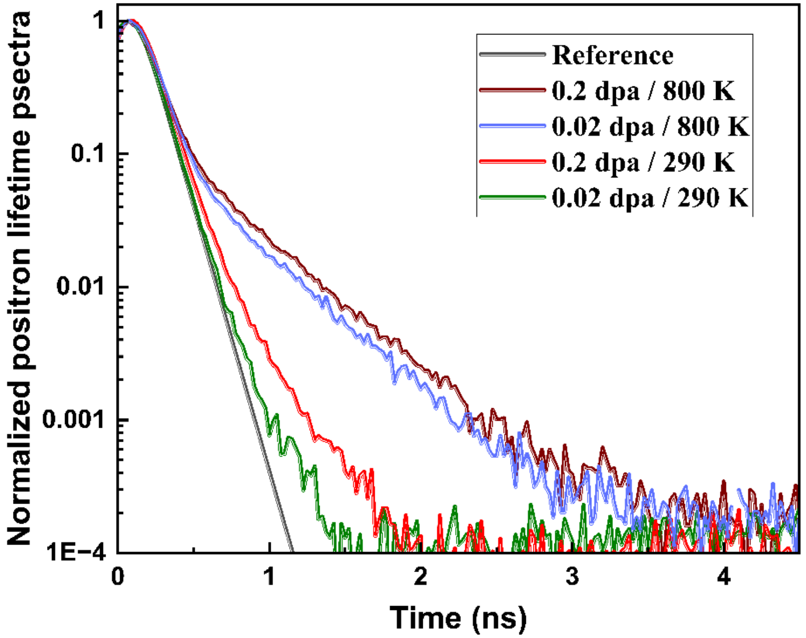
Four batches of samples produced:

1. RBS-C, TEM – re-polished RBS-C @ JSI
2. PAS, NRA
3. NRA-C

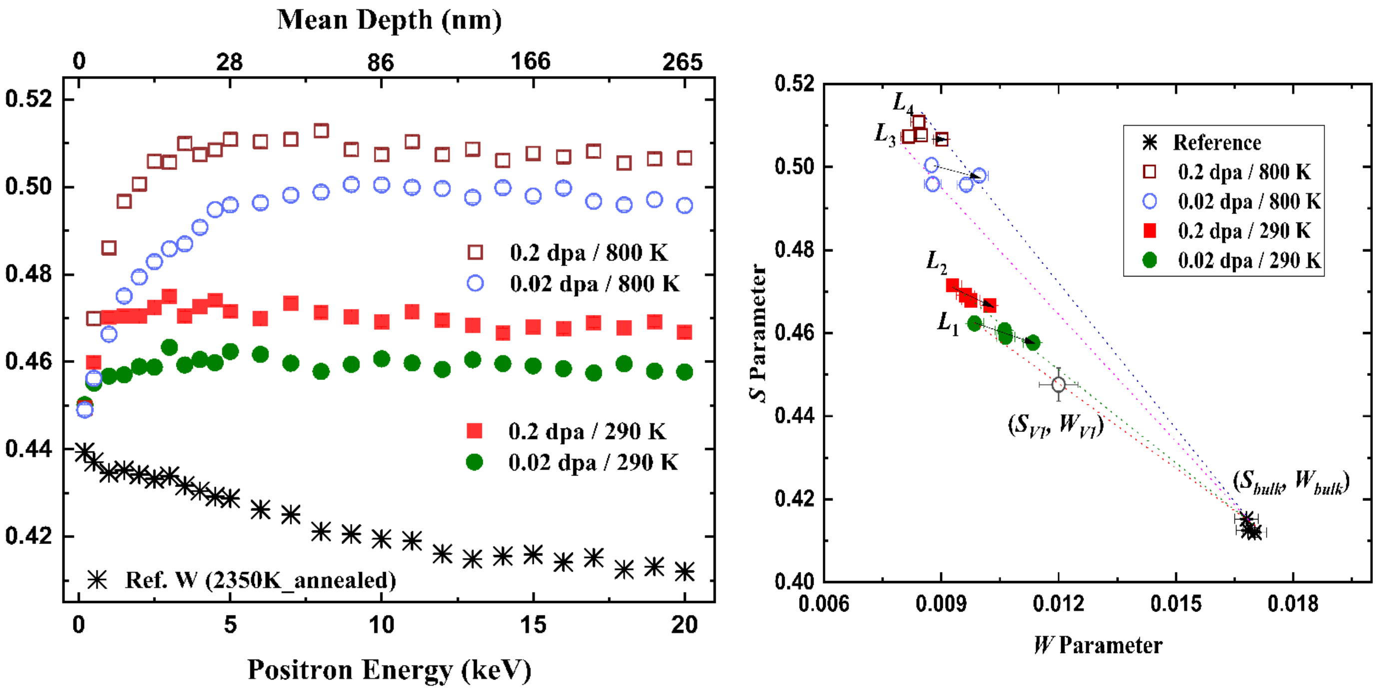
[Markelj et al. NME 39 (2024) 101630]
[Markelj et al. Acta Materiallia 263 (2024) 119499]

Positron annihilation measurements – open volume defects

Positron Lifetime measurements



Positron Doppler Broadening



Sample irrad. conditions	Vacancy cluster size
0.02 dpa / 290 K	v = 2
0.2 dpa / 290 K	v = 2 - 4
0.02 dpa / 800 K	v = 25
0.2 dpa / 800 K	v = 50

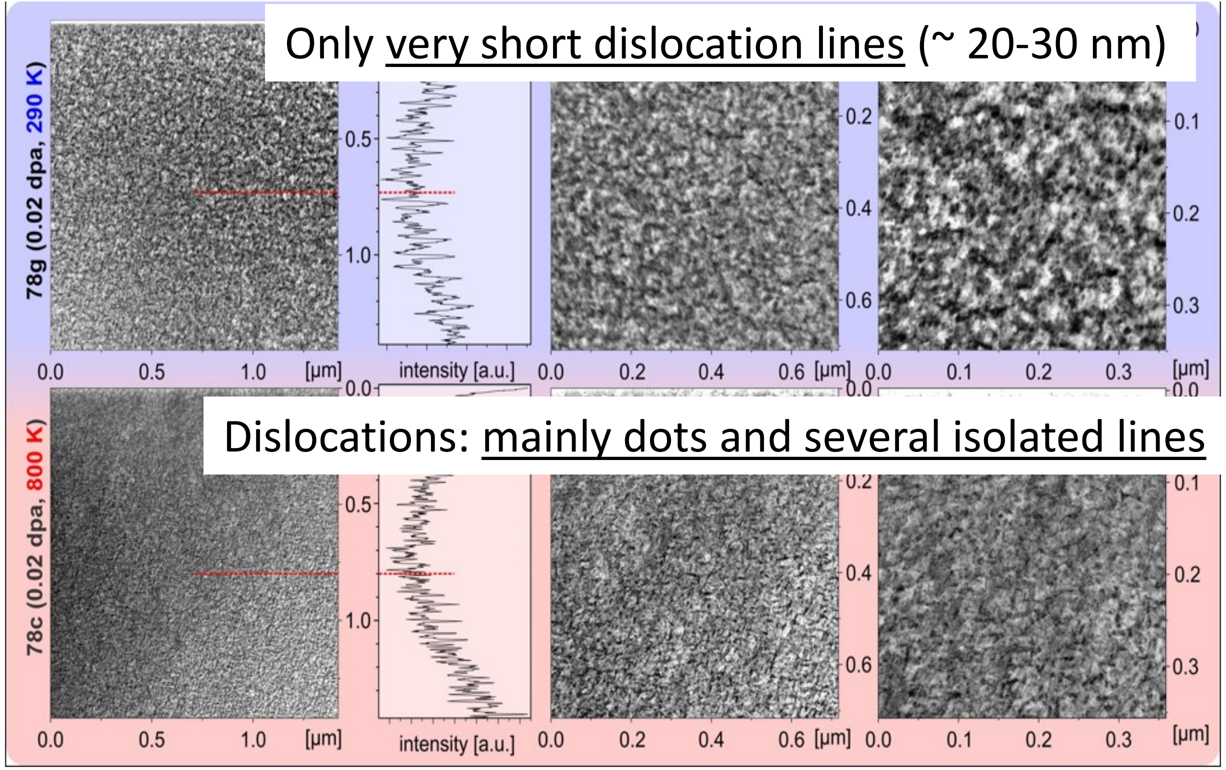
- Both methods give the same vacancy cluster size
- Proves the initial assumptions

Transmission electron microscopy (TEM) analysis – dislocations, voids

Low dose 0.02 dpa

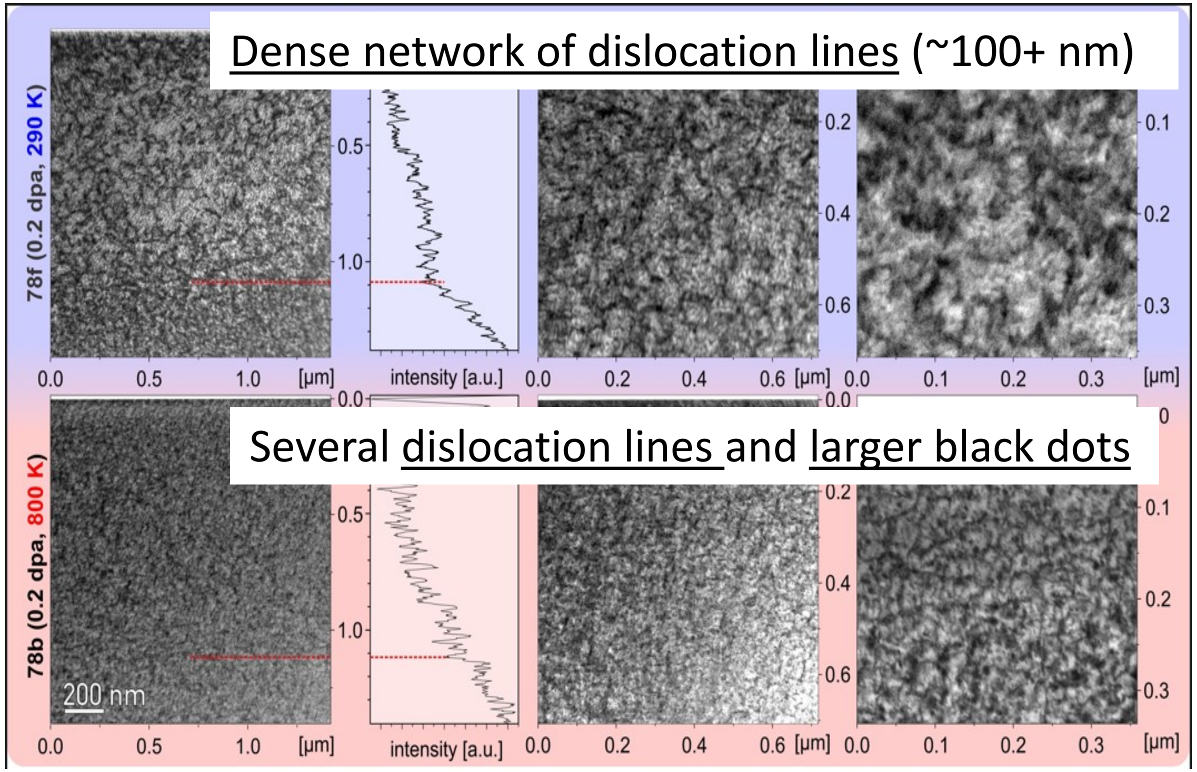
290 K

800 K


Only very short dislocation lines (~ 20-30 nm)

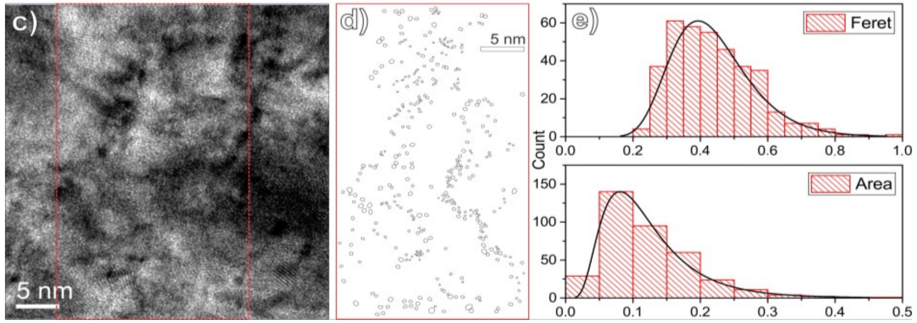
Dislocations: mainly dots and several isolated lines

High dose 0.2 dpa


Dense network of dislocation lines (~100+ nm)

Several dislocation lines and larger black dots

Detection of small voids in 0.2 dpa / 800 K sample



RBS-C measurements

- ^{4}He ions along <111> channel
- Multiple energies of He ions (3 to 4.5 MeV) – **Multi energy RBS-C**

➢ RBS-C spectra @ 4.5 MeV

Irradiation at 290 K:

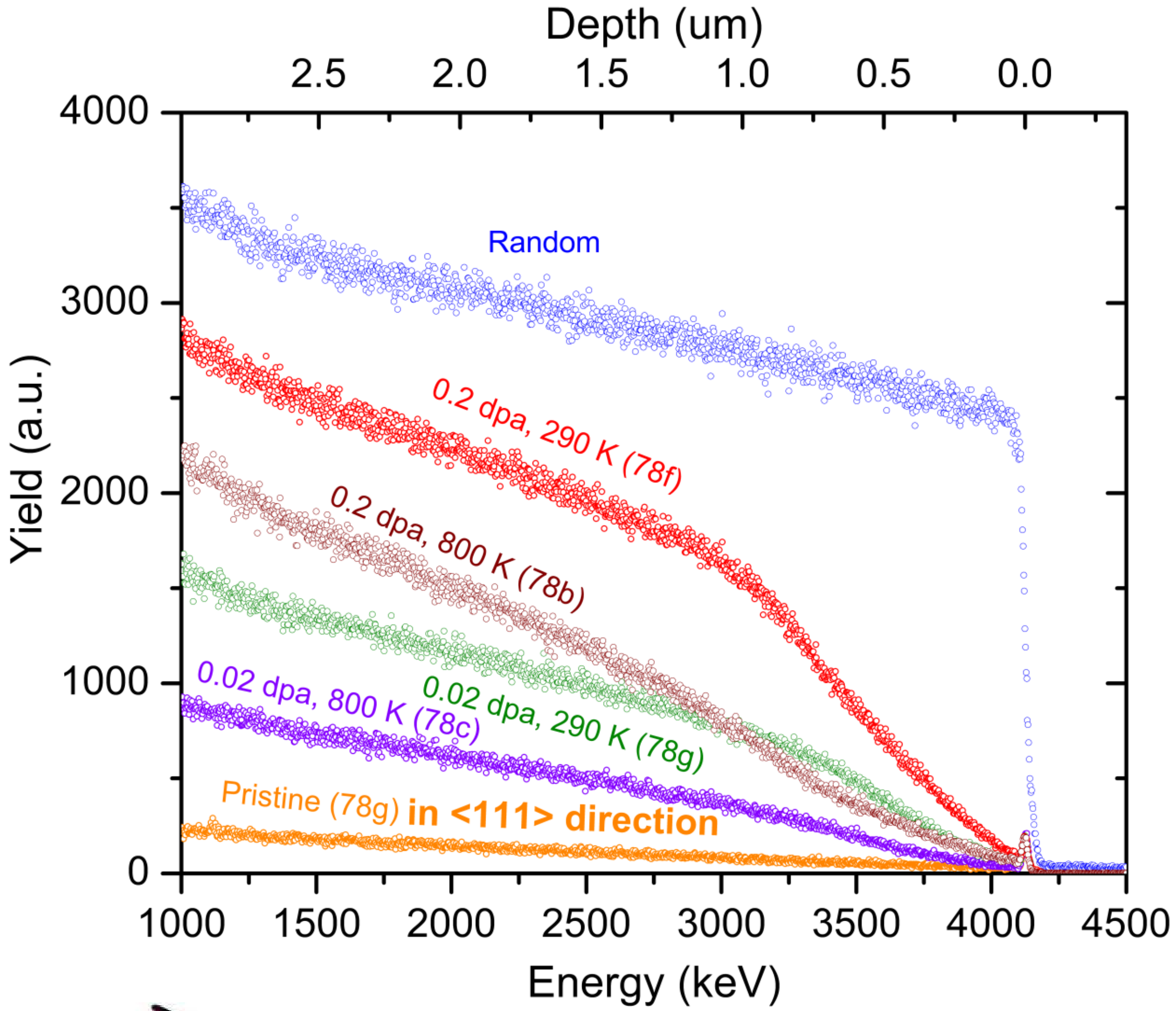
- 78f : 0.2dpa, 290 K (heavily damaged standard)
- 78g : 0.02 dpa, 290 K (single vacancies)

Irradiation at 800 K:

- 78c : 0.02 dpa 800 K (small vacancy clusters)
- 78b : 0.2 dpa 800 K (big vacancy clusters)

- **Clear differences between the irradiation damage treatments**

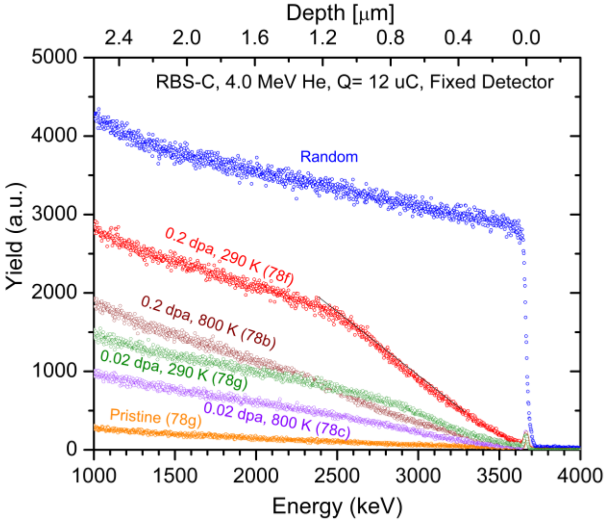
^{4}He beam E=4.5 MeV

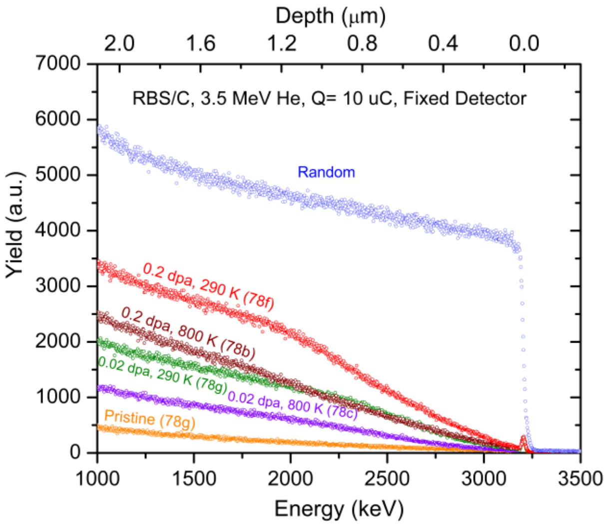


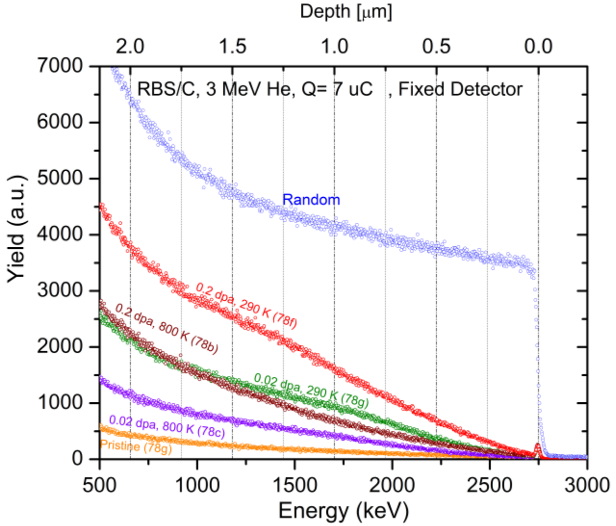
[S. Markelj et al., Acta Mater. 263 (2024) 119499]

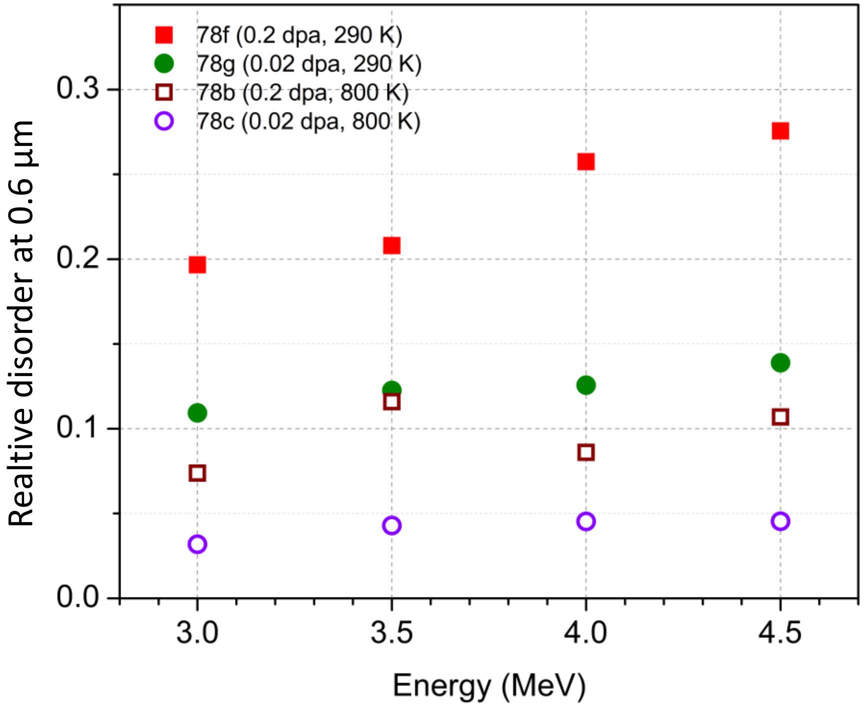
Measurements were preformed at CMAM, Madrid, Spain.

Multi-energy RBS-C









➢ Following: *FELDMAN, MATERIALS ANALYSIS BY ION CHANNELING. Submicron Crystallography, 1982, Academic press*

Dechanneling factor as a function of energy at 0.6 um

78g (0.02 dpa, 290 K): no slope – localized defects – small dislocation loops (TEM)

78f (0.2 dpa, 290 K): positive slope –extended defects – dislocation lines (TEM)

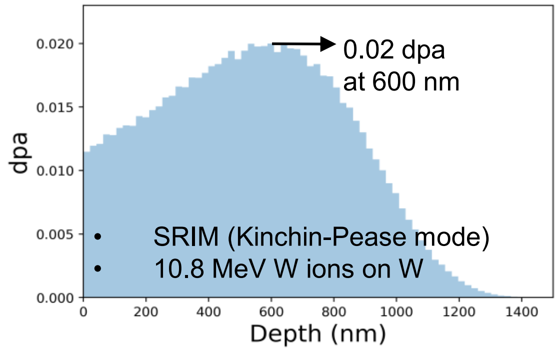
78c (0.02 dpa, 800 K): no slope – localized defects – dots and isolated lines (TEM)

78b (0.2 dpa, 800 K): no slope – localized defects – dislocation lines and black dots (TEM)

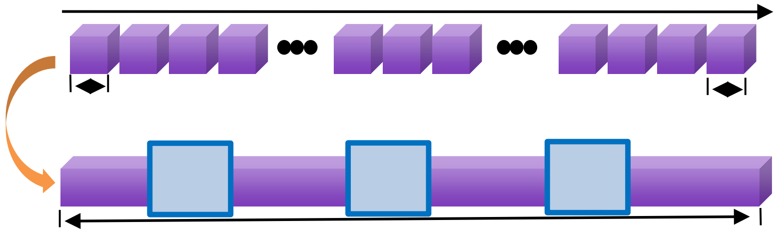
- **Good qualitative agreement with TEM**

Simulation of RBS-C spectra – samples irradiated at R.T.

A. Get depth distribution of damage level (SRIM)



B. MD simulations and assemble of MD cells



Creation of radiation defects by Molecular Dynamics (MD) calculation

MD cells with certain number of collision cascades

Primary knock-on atom: 10 keV

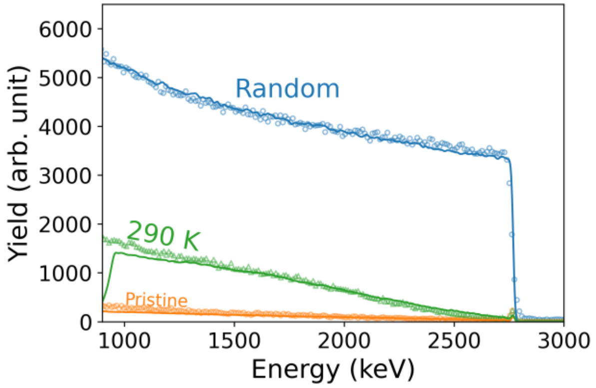
Size of MD cells: ~ 20nm

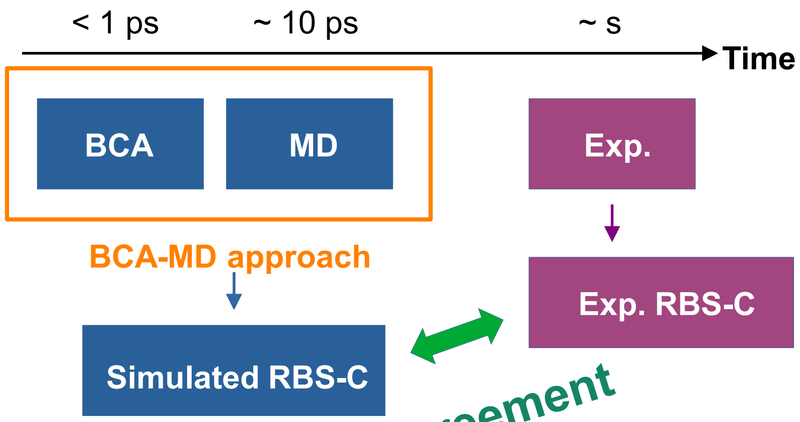
Overlapping of cascades: High damage dose (evolution of defects)

[F. Granberg et al., J. Nucl. Mater. 556 (2021) 153158]

Incorporation of merged MD cells into RBSADEC simulation code

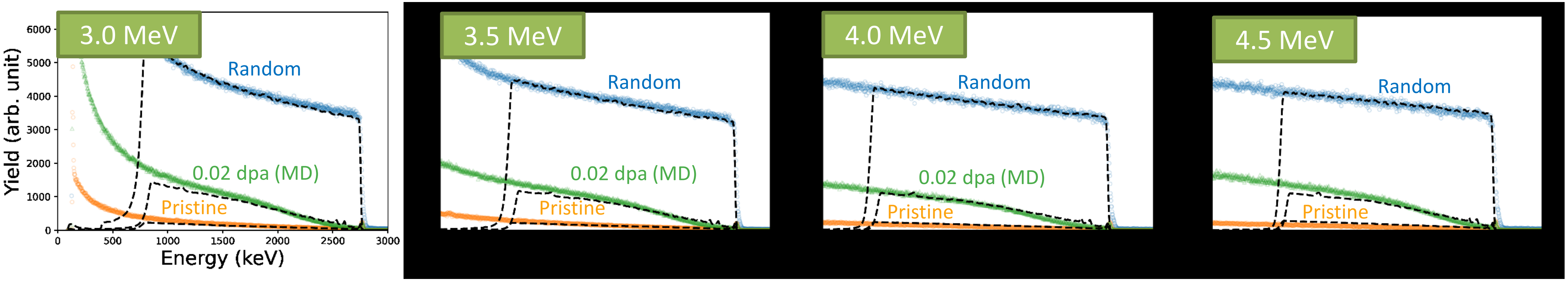
C. Simulation and comparison of RBS-C spectra

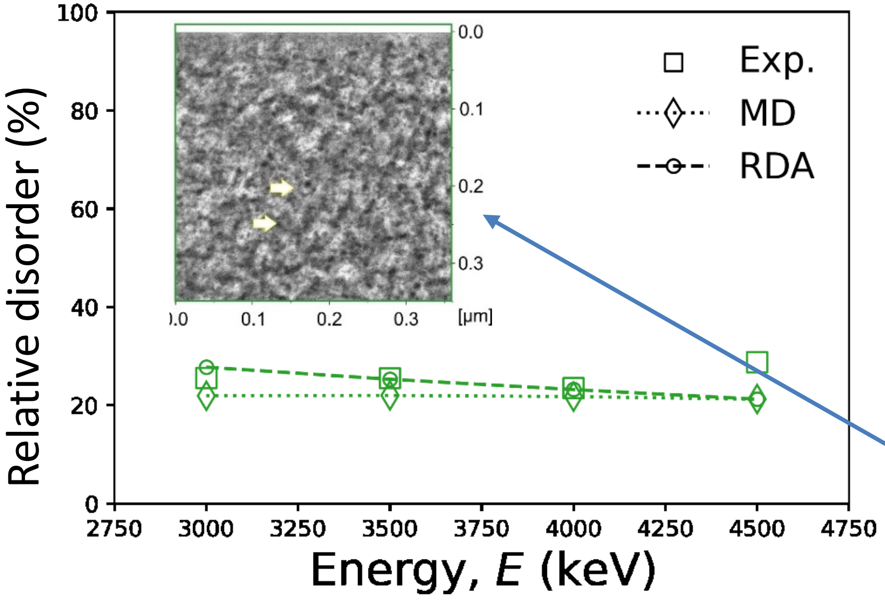




Agreement
No free parameters

Multi-energy RBS-C (0.02 dpa, 290 K)





(Dechannelling calculated at $1.2 - 1.3\ \mu m$)

[S. Markelj, et al., Acta Mater. 263 (2024) 119499]

☐ **Dechanneling (energy)**

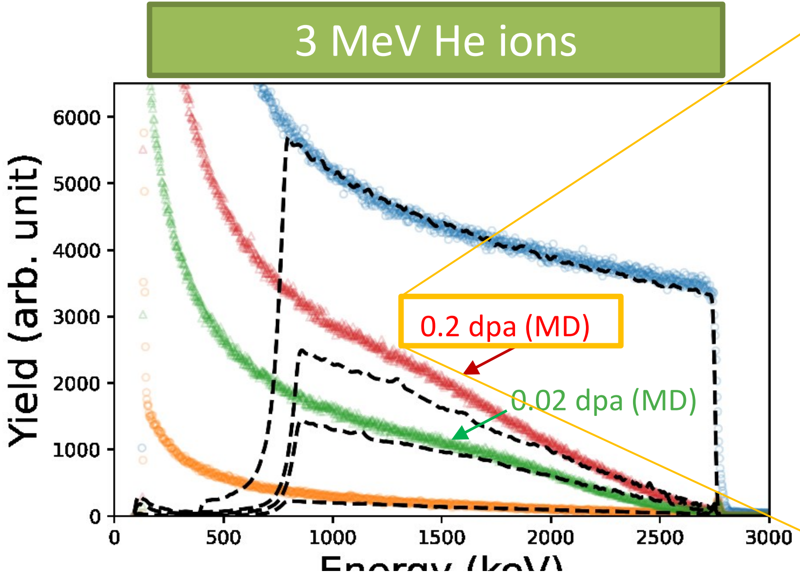
- **Experiments: No obvious trend**
- **Simulations (MD): Constant**
- Simulations (RDA): Negative slope

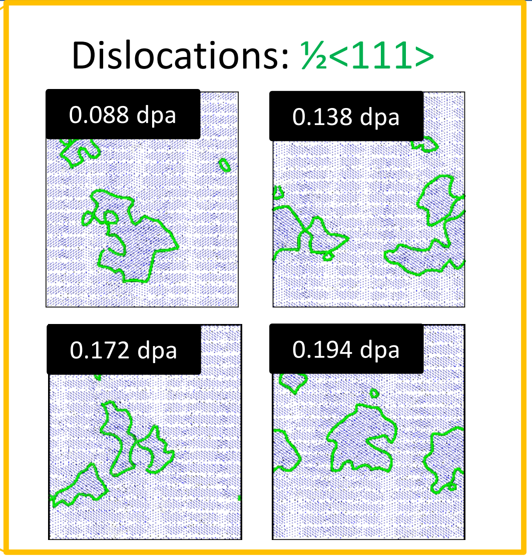
Defect nature: Dislocation loops

- **STEM results:**

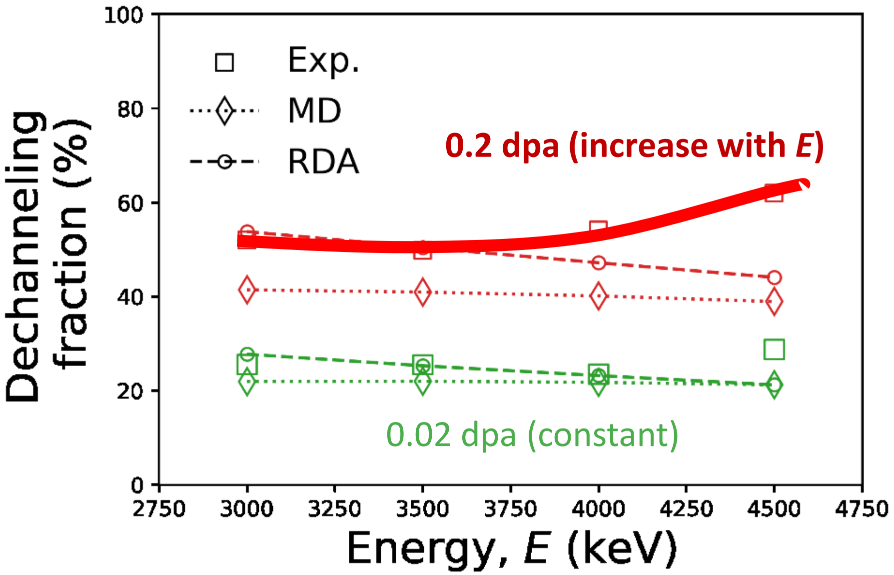
U-shaped dislocation loops around “black dots” (size ~ 10 nm).

Multi-energy RBS-C (0.2 dpa, 290 K)





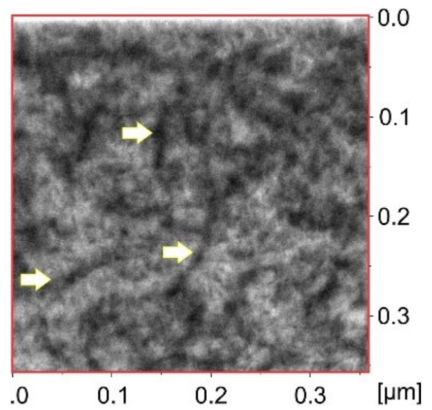
Lacking agreement between experiment and simulation due to limited size of MD cells.
Larger MD cells produced and work should be continued



(S. Markelj, et al., Acta Mater., 263 (2024) 119499)

- **RBS-C experiments (high damage, 0.2 dpa)**
  - Higher yield than that of 0.02 dpa
- **RBS-C simulations (MD cells)**
  - **Dechannelling as a function of *E***

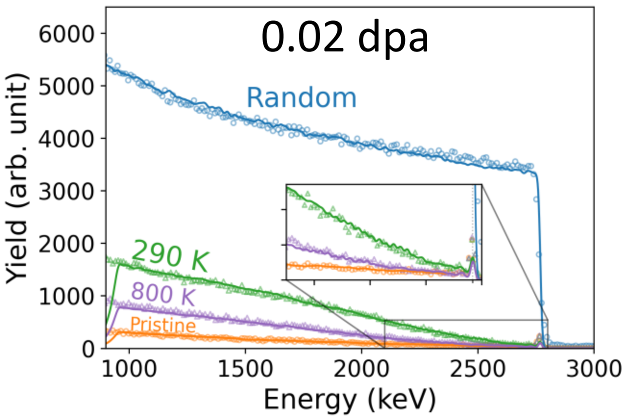
	MD	Exp.	RDA
Dechan.	Constant	Increases with E	Decrease
Defect nature	Dislocation loops	Dislocation lines	
Strain field	$1/r^3$	$1/r$	

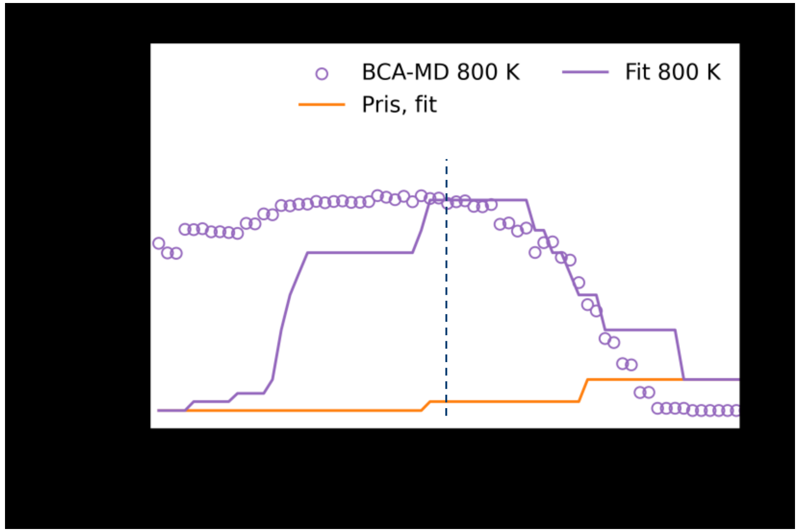


STEM results:
- Dense networks of dislocation lines (length > 100 nm).
- No lines in MD cells: limited size of cells

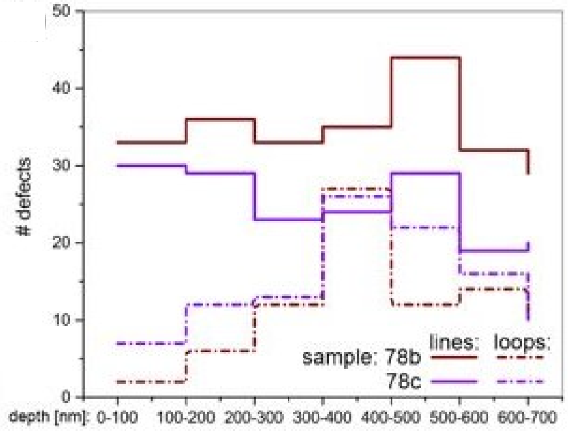
Simulation of RBS-C spectra at 800 K

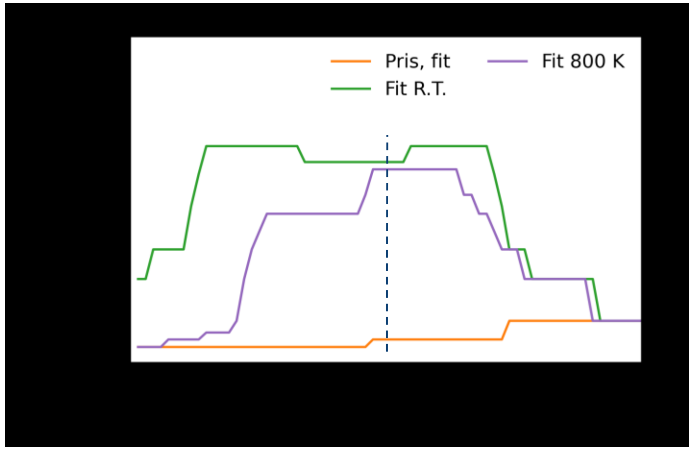
R.T. and 800 K from fitting



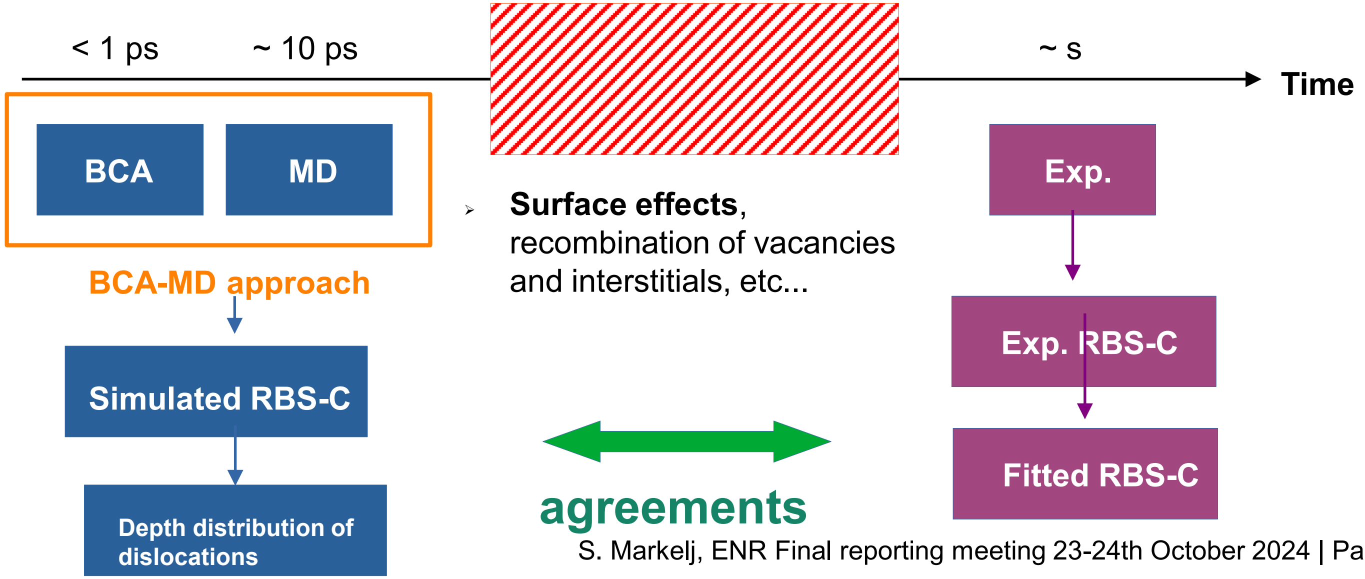


- TEM analysis indeed shows the same trend of loop distribution





- From R.T. to 800 K, the decrease of RBS-C yield is due to a significant decrease of dislocation density. (This is not reproduced in BCA-MD approach)



< 1 ps

~ 10 ps

~ s

Time

BCA

MD

BCA-MD approach

Simulated RBS-C

Depth distribution of dislocations

- **Surface effects**, recombination of vacancies and interstitials, etc...

Exp.

Exp. RBS-C

Fitted RBS-C

agreements

Strategy of the project

- Analysis by state of the art analysis techniques by electron microscopy and positron annihilation

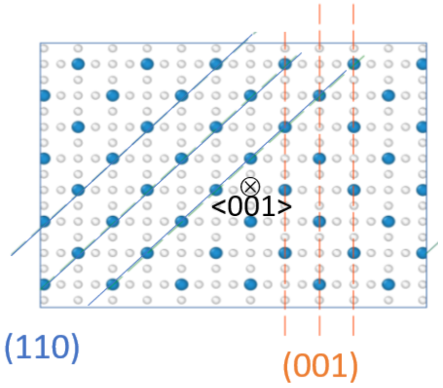
- Detection of **defects** by **Rutherford Backscattering Spectroscopy** in **Channeling** configuration (RBS-C) + modelling

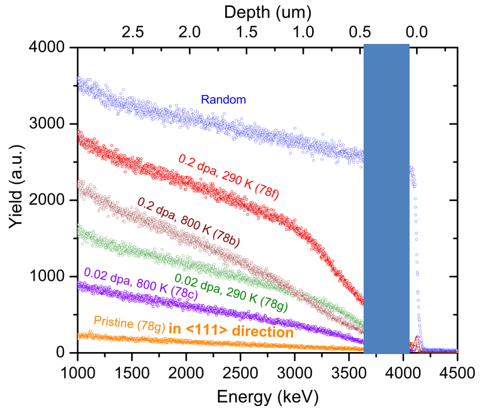
- Detection of **deuterium** location by **Nuclear Reaction Analysis** in **Channeling** configuration (NRA-C) + modelling

- Conclusion

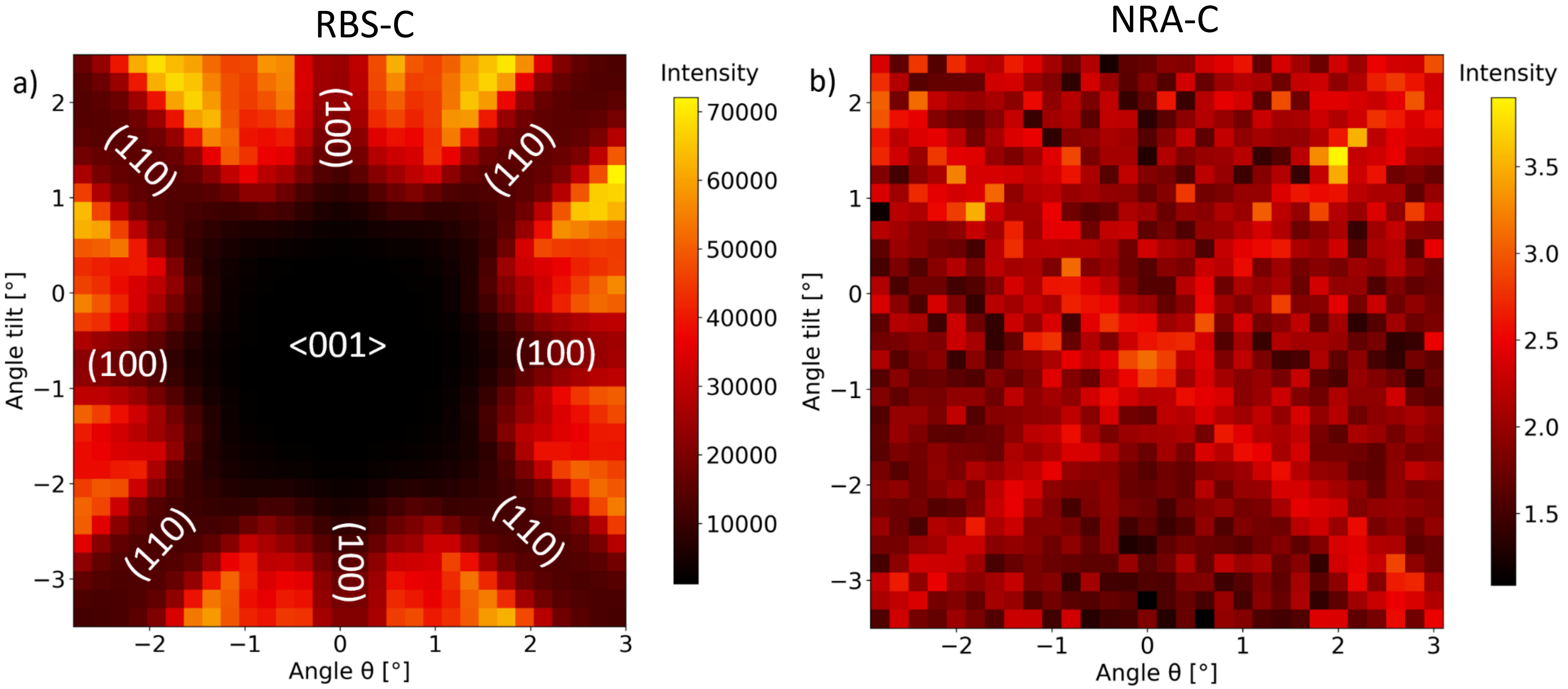
NRA-C and RBS-C on irradiated W: first DeHydroC measurements

^{3}He 0.8 MeV – simultaneous RBS-C and NRA-C 2D maps





2D map for sample: 800 K, 0.2 dpa

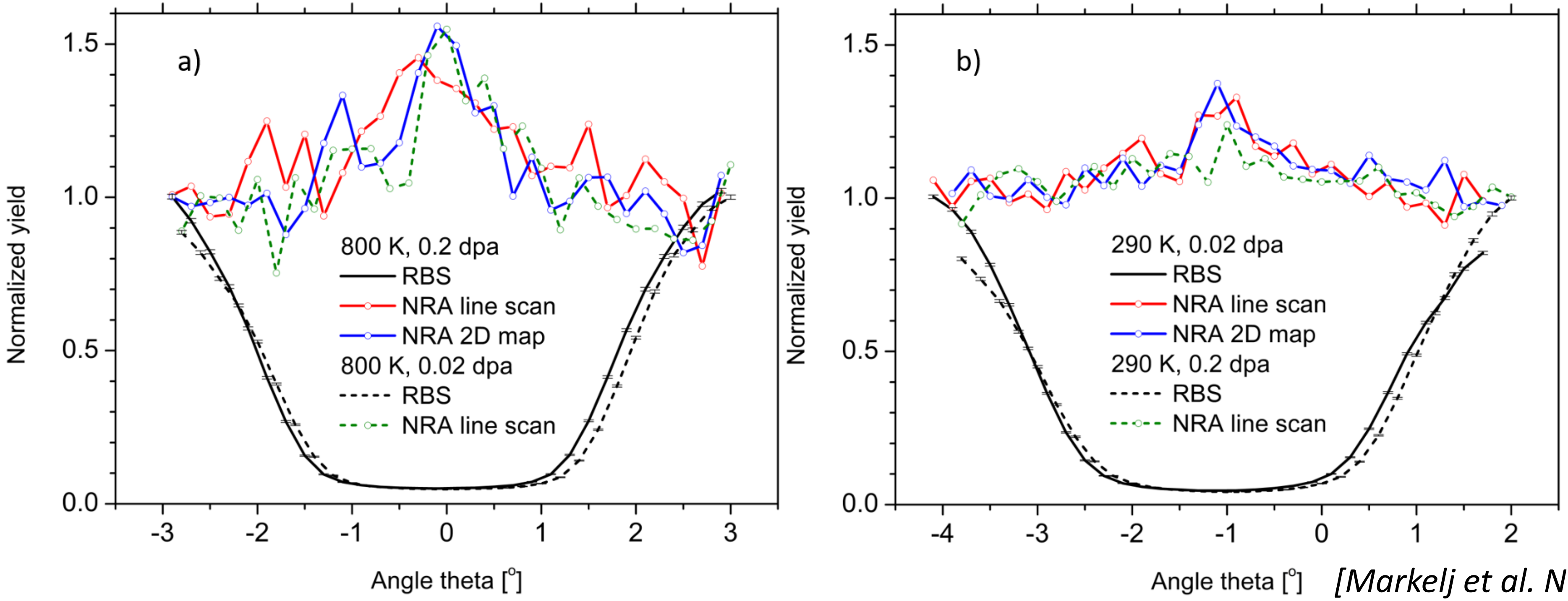


Measurements performed at the Hedgehog setup at Ion Beam Center at HZDR, Dresden, Germany.

[Markelj et al. NME 39 (2024) 101630]

NRA-C and RBS-C: angular scans

^{3}He 0.8 MeV – simultaneous RBS-C and NRA-C 2D maps

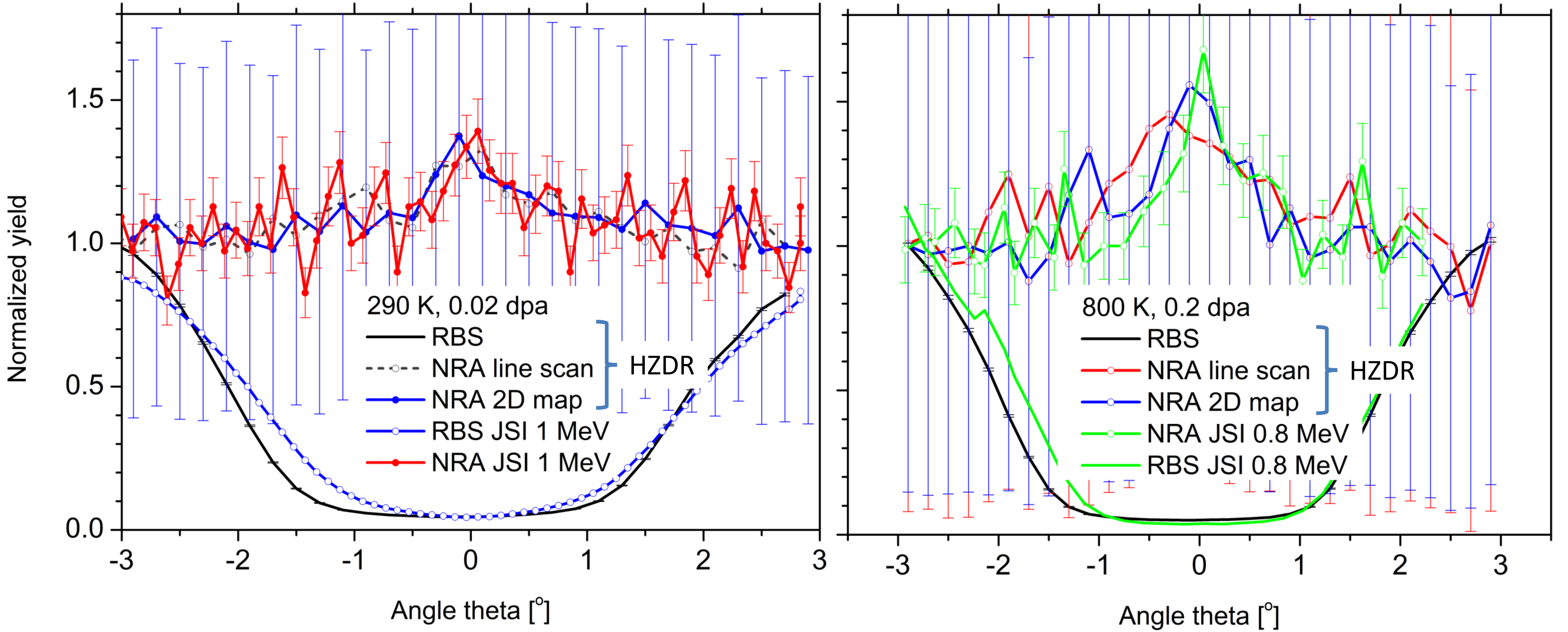


[Markelj et al. NME 39 (2024) 101630]

- 800 K irradiated samples have a wider and higher NRA signal peak than 290 K irradiated samples.
- Interpretation: deuterium is not situated at a fixed location but a broad distribution of locations in a vacancy cluster.

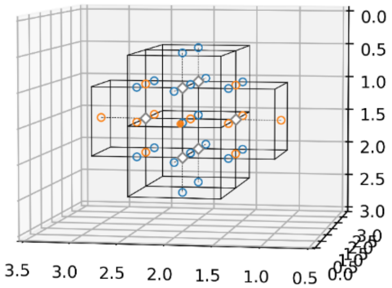
NRA channelling spectra with new goniometer at JSI

- Measurements at JSI show the same trend with better statistics



NRA-C simulations: DFT calculations – binding energy and relative positions

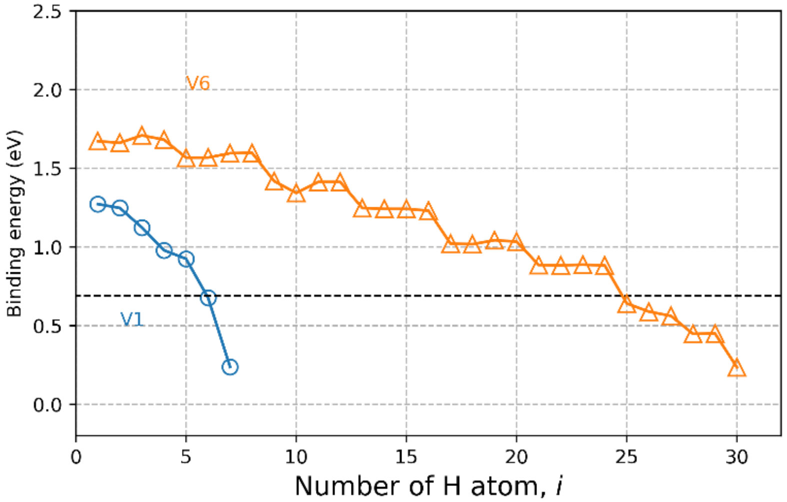
- ➢ For the NRA-C simulations we need to know the binding energy and the hydrogen position at certain fill-level (up to V_6)
- ➢ Not an easy task for position – many variations



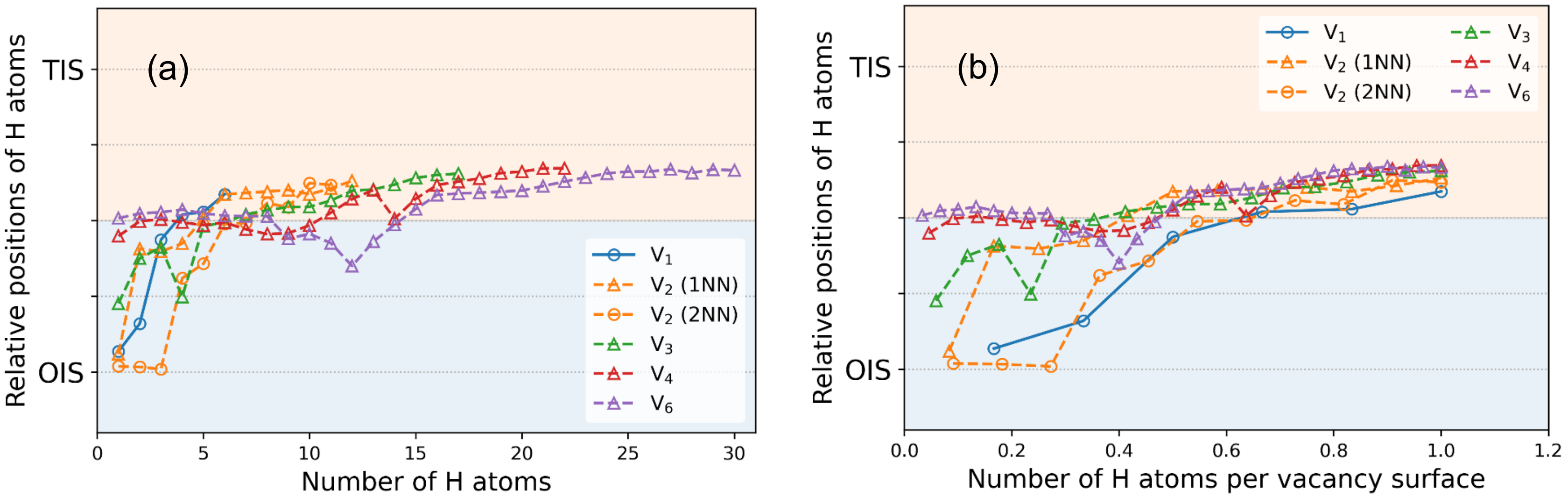
DFT calculation

- ➢ VASP
- ➢ 4 * 4 * 4 supercell
- ➢ Cut-off energy: 500 eV
- ➢ Position and volume relaxation

Binding energy for V_1 and V_6



Relative positions of H atoms between tetrahedral and octahedral sites



Change of H positions with the number of H atoms per vacancy surface:

(a) < half filled: Different positions in different vacancy

- Due to different types of vacancy surfaces clusters

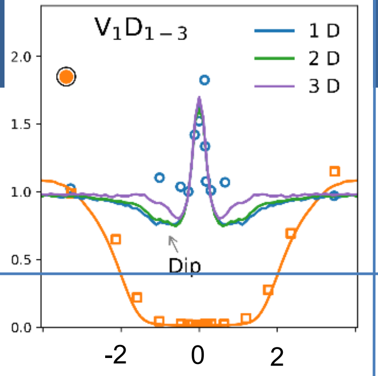
(b) > half filled: Converge and get similar behavior.

Filling level

- V1

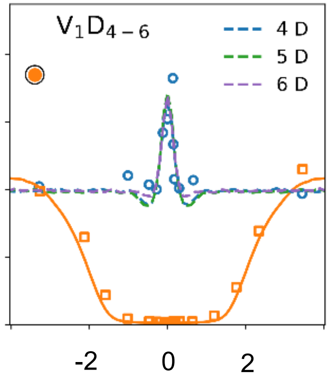
- V2-1NN

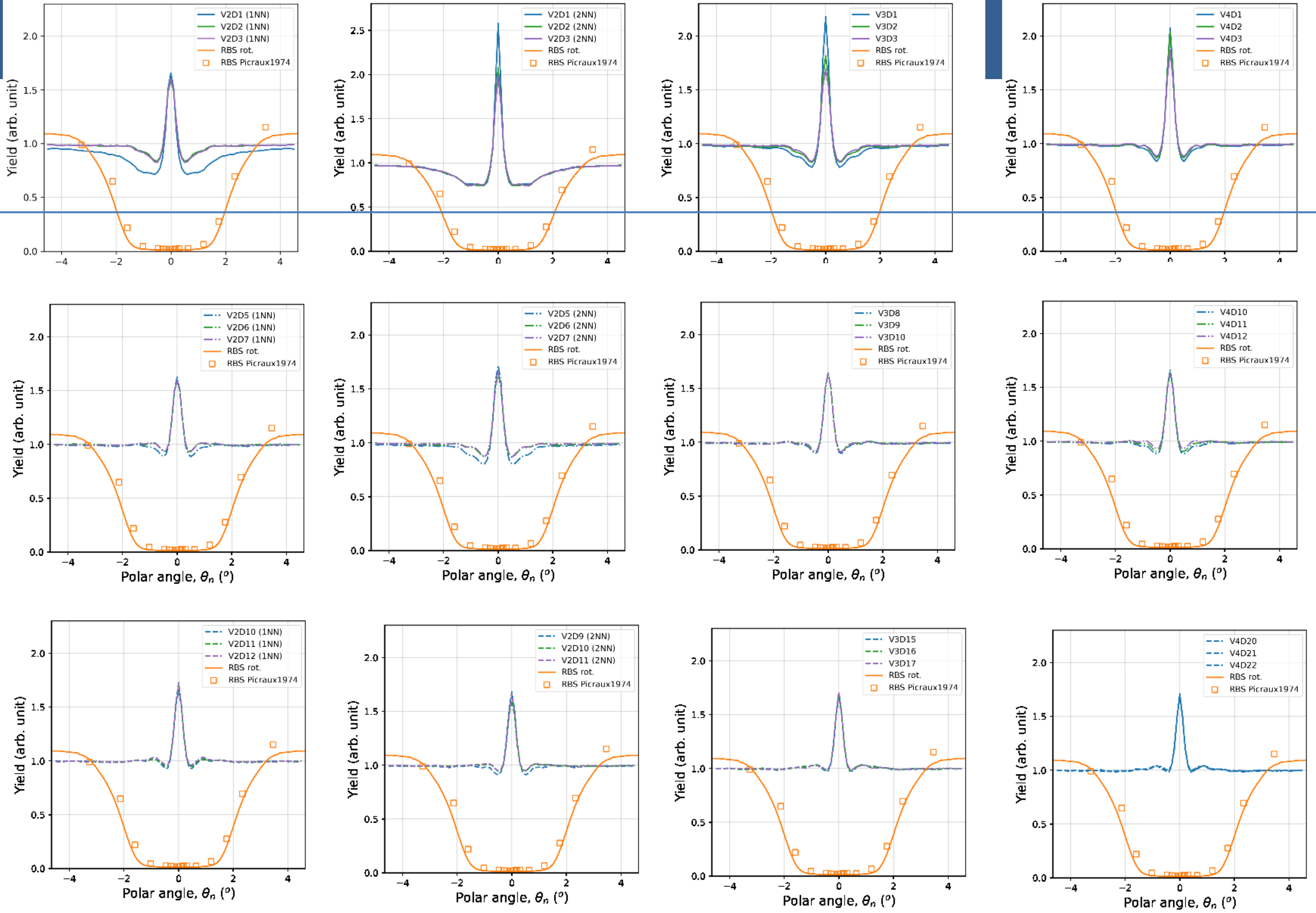
- Small



- Half

- Full





Difference

(effect of vacancy surface)

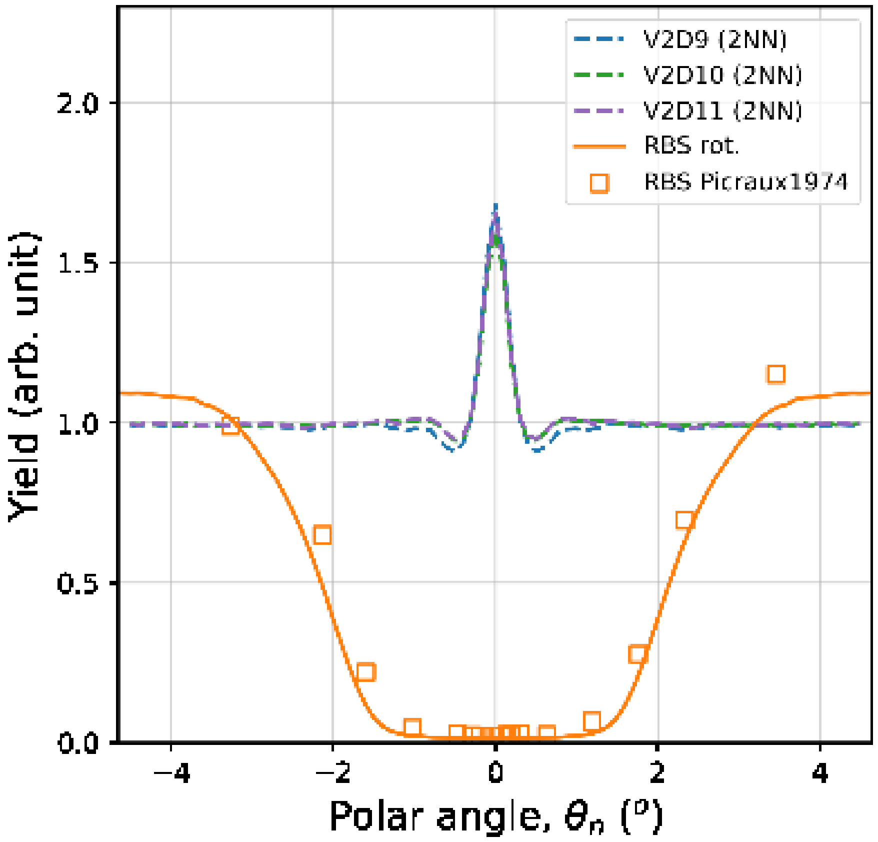
Difference (from OIS to TIS)

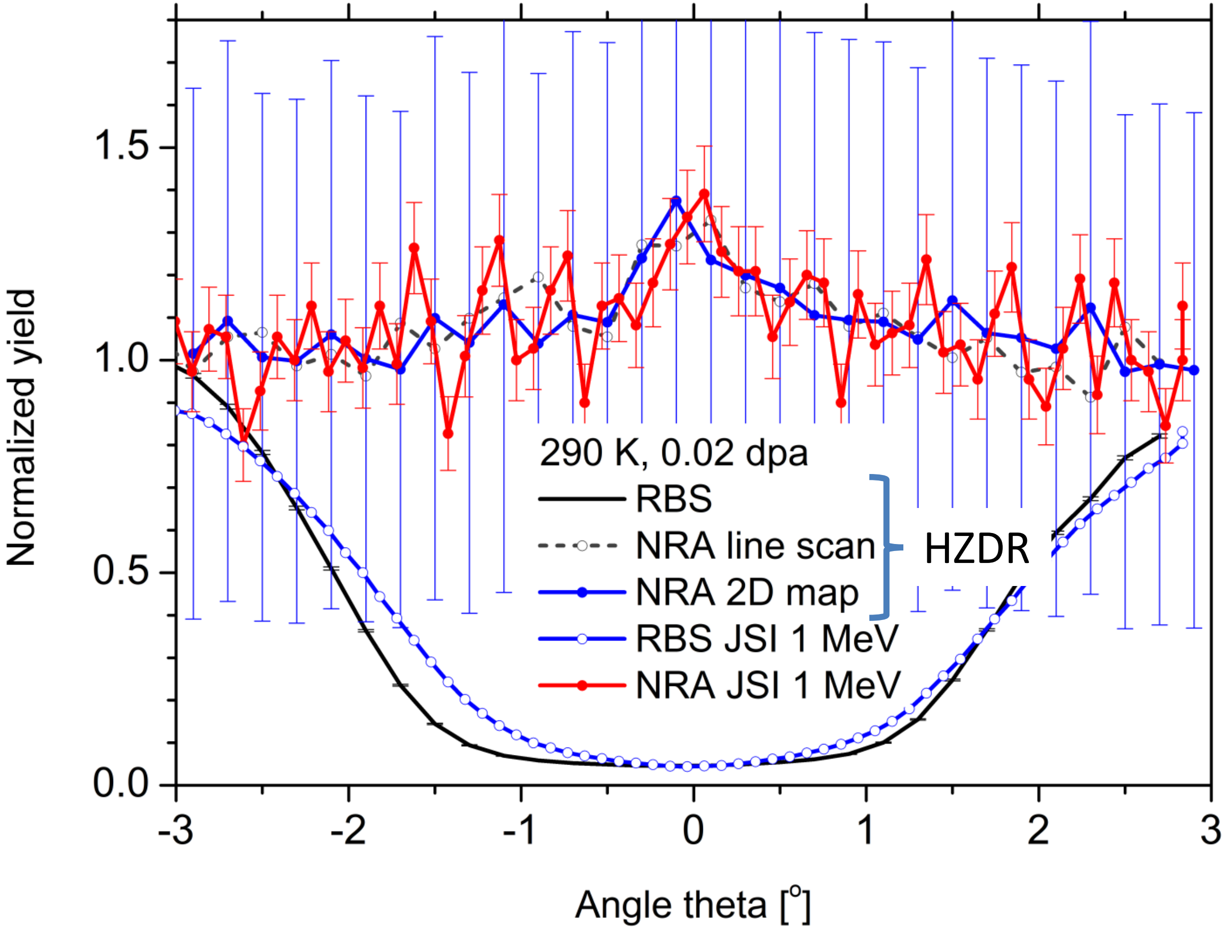
Comparison NRA-C modelling vs. experiment

UNIVERSITY OF HELSINKI

Jožef Stefan Institute

0.02 dpa/290 K – PAS observed mainly V_2





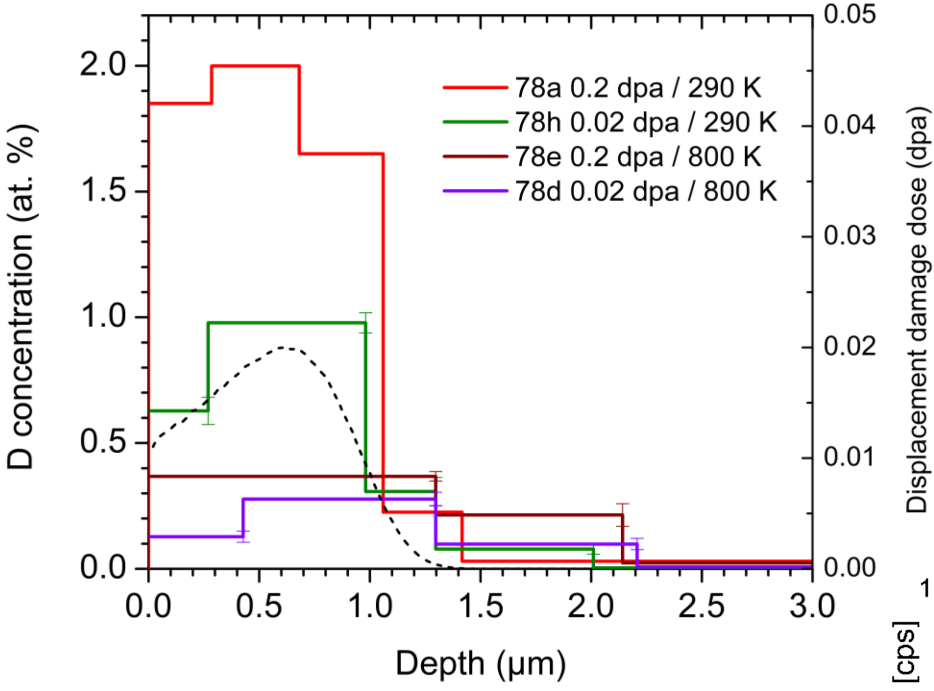
Modelling is not yet capable of describing deuterium in vacancy clusters

- no defects included in the structure only D atoms at proper locations

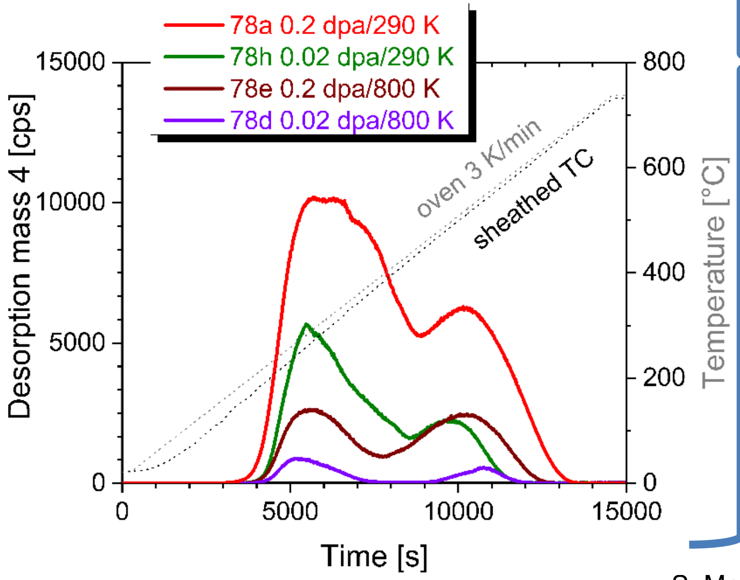
D retention in W damaged samples

W(111) samples analysed by PAS

NRA

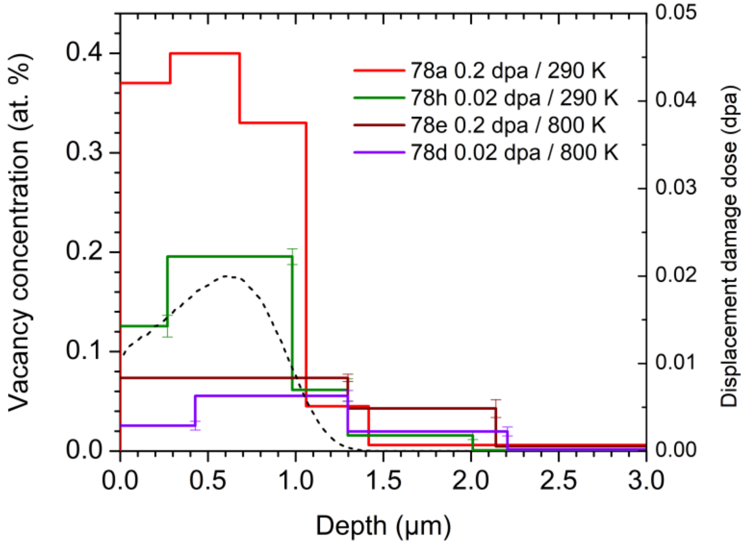


TDS



- ➢ Input for rate equation modelling

Effective vacancy concentration *[Mason (2021)]*



Conclusions

- Brought together different techniques – newer done on such quantitative level and compare the results between different methods and to state of the art modeling
- RBS-C and NRA-C fulfill their promise to detect defects and deuterium in the irradiated materials and should be used more in fusion research
- RBS-C is the method to be used to validate the creation of dislocations by state of the art modelling (test potentials and test if the size of MD cell is adequate)!!

- Revisiting old NRA-C measurements unveiled a new perspective on the strength of NRA-C (vacancies, H fill level, He in vacancy)
- **Multi-energy RBS-C** is a good tool to study interstitial type of defects in the material (in situ)
  - Combined with RBS-C simulations on W targets, containing realistic defect structures, obtained from molecular dynamics simulations, gives deeper insight into defect structure
- **First NRA-C measurements** on irradiated W samples with different defect structures show clear difference in the NRA-C response
- Further modelling with simplified experiments necessary to understand NRA-C experimental results quantitatively
- **Dedicated RBS/NRA channelling set-up established at JSI**

Perspectives EUROfusion

- RBS-C and NRA-C should be used in WP MAT – IREMEV project to further prove or falsify the state of the art modelling attempts (MD, OKMC) (now only on W but also for Fe..)

- Further modelling is necessary to understand NRA-C experimental results quantitatively – within WP MAT / PWIE

- Revisit Picraux experiment and study D filling levels by NRA-C within WP PWIE – SP C retention
  - NRA enables validation of production of vacancies and vacancy clusters by modelling

- **The results obtained at 800 K are super important to predict tritium retention and material damage evolution**

Attendance at the conferences in 2023

PFMC conference:

- E. Punzon-Quijorna et al. "Multi-Energy Rutherford Backscattering Spectroscopy in Channeling configuration for the analysis of defects in tungsten" (poster)
- X. Jin et al. Study of the lattice location of deuterium implanted into tungsten using simulations of nuclear reaction analysis in channeling mode“(poster)

IBA conference:

- S Markelj et al., Analysis of deuterium and defects in tungsten by Rutherford backscattering spectroscopy and nuclear reaction analysis in channeling configuration“ (poster)
- X. Jin et al., Deuterium trapping conditions and potential location sites in tungsten by combination of nuclear reaction analysis in channeling mode with first principle calculations" (poster)
- F. Djurabekova et al., Simulation of Rurgerford Backscattering spectrometry in channeling mode from arbitrary atomistic structures (Invited talk)

ICFRM conference:

- X. Jin et al., Analysis of radiation effects in tungsten by comparing molecular dynamics simulations to experiments of RBS-Channeling" (contributed talk)
- S Markelj et al.,"Detection of defects and hydrogen by ion beam analysis in channeling mode for fusion - DeHydroC" (poster)

MINES:

- Markelj et al., Analysis of deuterium and defects in tungsten by Rutherford backscattering spectroscopy and nuclear reaction analysis in channeling configuration (Invited talk)

Attendance at the conferences in 2024

PSI conference May 2024:

- Markelj et al. Detection of defects and deuterium in displacement-damaged tungsten by applying Rutherford backscattering spectroscopy and nuclear reaction analysis in channeling configuration (poster)
- Hodille et al., Macroscopic modelling of D trapping in self-damaged tungsten with vacancy clusters using atomistic scale modelling data (poster)

NENE conference September 2024

- Markelj et al. Detection of defects and deuterium in displacement-damaged tungsten by ion beam methods in channeling configuration for fusion application (contributed talk)

HRDP-11 conference:

- X. Jin et al., “Analysis of the depth distribution of radiation defects in tungsten with RBS in channeling mode“ (contributed talk)

COSIRES

- Djurabekova et al. – Computational approach to simulate RBS-C and NRA-C spectra for direct comparison with experiment (contributed talk)

Papers published

1. Jin et al. Effect of lattice voids on Rutherford backscattering dechannelling in tungsten, J. Phys. D: Appl. Phys. 56 (2023) 065303, https://doi.org/10.1088/1361-6463/acad12
2. Markelj, S. et al. Unveiling the radiation-induced defect production and damage evolution in tungsten using multi-energy Rutherford backscattering spectroscopy in channeling configuration. Acta Materialia 263, 119499 (2024), https://doi.org/10.1016/j.actamat.2023.119499
3. Markelj, S. et al. First study of the location of deuterium in displacement-damaged tungsten by nuclear reaction analysis in channeling configuration. Nuclear Materials and Energy 39, 101630 (2024), https://doi.org/10.1016/j.nme.2024.101630 .
4. Jin, X., Djurabekova, F., Hodille, E. A., Markelj, S. & Nordlund, K. Analysis of lattice locations of deuterium in tungsten and its application for predicting deuterium trapping conditions. Phys. Rev. Materials 8, 043604 (2024), 10.1103/PhysRevMaterials.8.043604
5. Dark, J. et al. Modelling neutron damage effects on tritium transport in tungsten. Nucl. Fusion 64, 086026 (2024) https://dx.doi.org/10.1088/1741-4326/ad56a0 .

Under review / submitted:

  - Hodille et al. "Macroscopic modelling of D trapping in self-damaged tungsten with vacancy clusters using atomistic scale modelling data“ (Nuclear Material and Energy) – under review
  - Zavasnik et al. Microstructural analysis of tungsten single crystals irradiated by MeV W ions: the effect of irradiation dose and temperature – TEM, C-RBS, PAS, NRA

- Master Thesis R. Galende Perez “Development of ion beam technique for detection of displacement damage in materials”

Acknowledgments

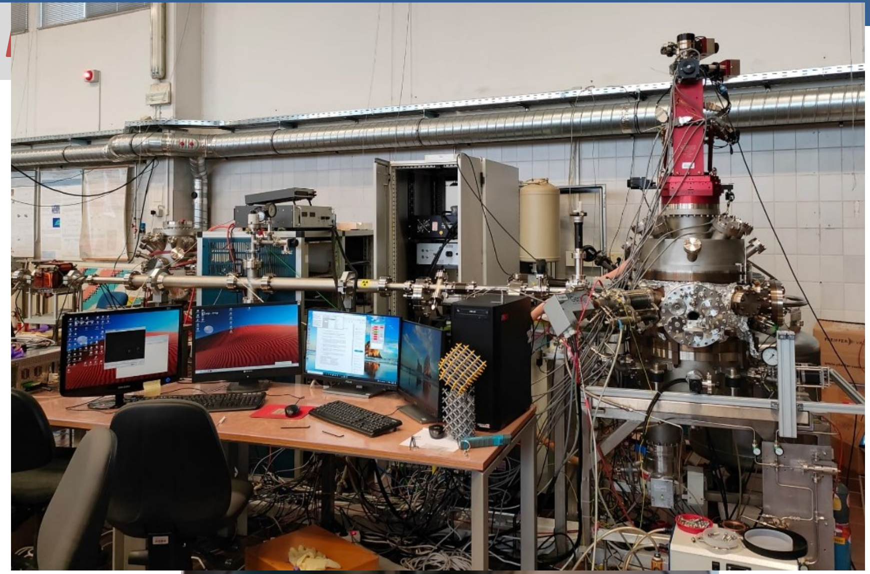
M. L. Crespillo, G. García López

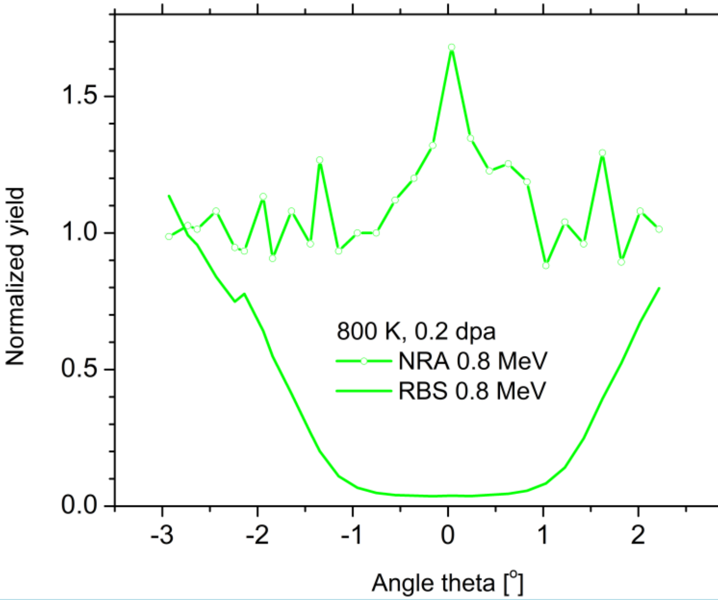
[4]Center for Micro Analysis of Materials (CMAM), Madrid, Spain

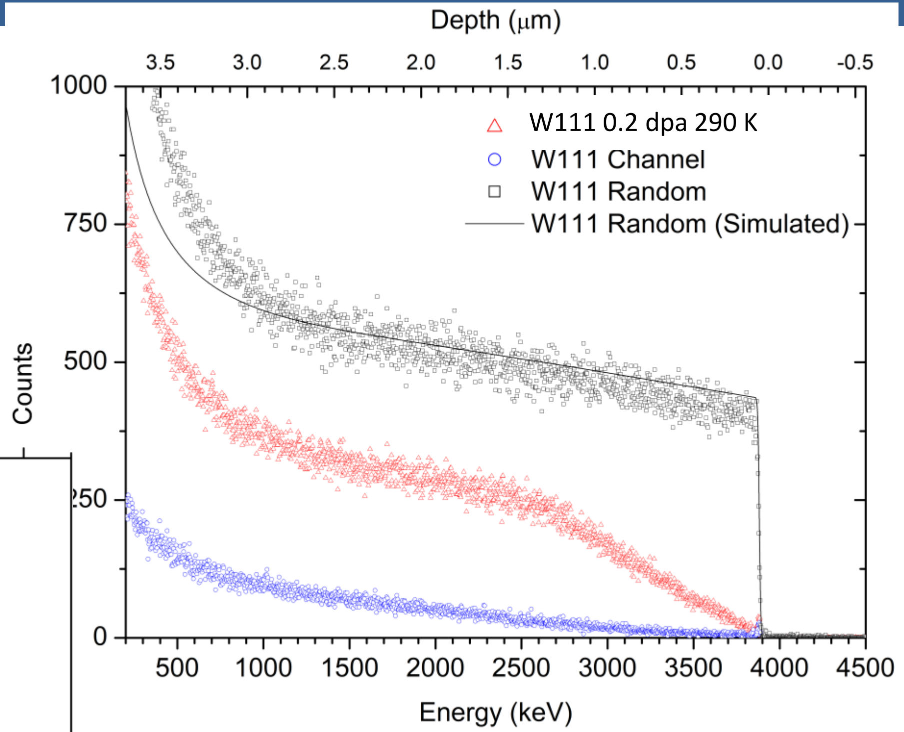
R. Heller

Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Rossendorf

Measurements at JSI with new 6 axis manipulator







Thank you for your attention

TEM analysis