Wir schaffen Wissen – heute für morgen

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SUMMARY OF THE RECENT POSITRON ANNIHILATION EXPERIMENTS ON STIP SAMPLES

OUTLINE

- **WHY** WE USE POSITRONS TO PROBE SPALLATION SAMPLES
- **HOW** DO WE DO THAT
- **WHAT** INFORMATION (ON HELIUM) CAN WE PROVIDE – OVERVIEW OF EXPERIMENTAL DATA
- SUMMARY AND CONCLUSIONS

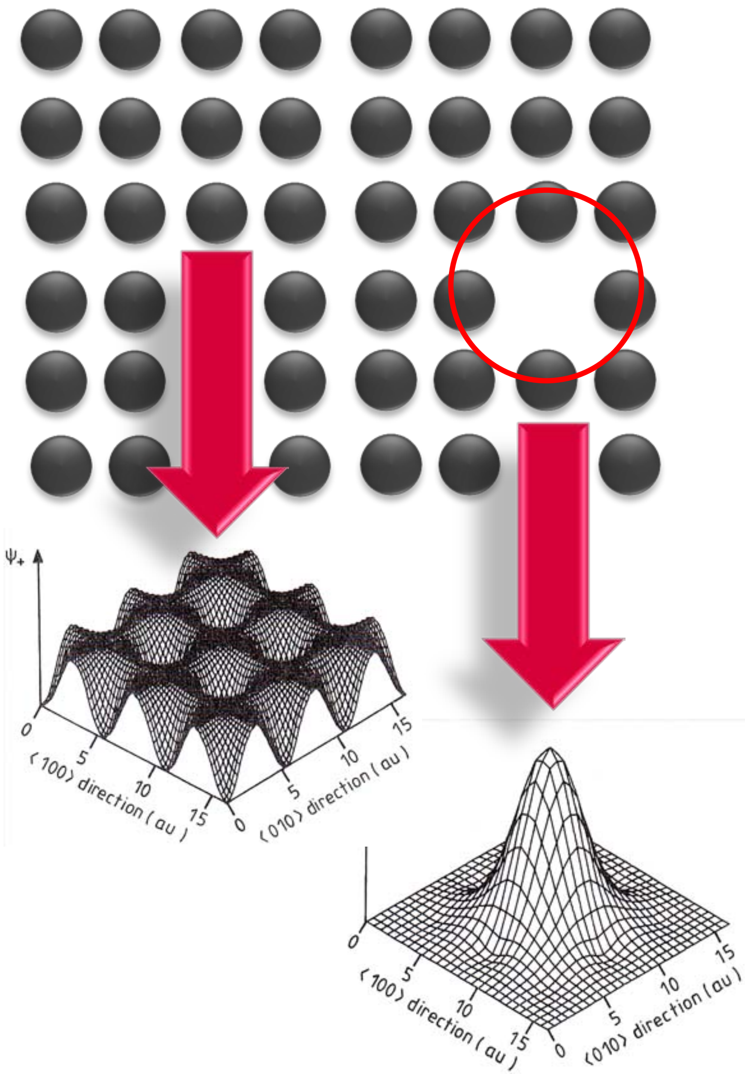
MOTIVATION

1) requirement of reliable accelerator-driven systems (ADS) for an effective transmutation of long-lived radioisotopes in the nuclear fuel;
2) requirement of affordable neutron sources for the neutron scattering and imaging techniques;
3) requirement of irradiation facilities that enable greatly accelerated irradiation studies with fusion-relevant transmutation rates.

To understand **HELIUM embrittlement** means to understand the helium-vacancy interaction at sub-nm scale level

Problem! Spatial resolution limits (and/or sampling of small area) and low sensitivity to helium at most experimental methods.

WHY POSITRON ANNIHILATION?



Self-Seeking

(positron diffuse typically ~100nm in metals and seek for sites with higher positron affinity than bulk i.e. it is attracted by certain type of defects!)

Non destructive

Sensitive

Defect type	Sensitivity range (detection limit vs. saturated trapping)
neutral vacancies	**5×10^{21}… 10^{25} m^{-3}**
dislocations	**10^{12} … 5×10^{15} m^{-2}**

Macroscopic samples

Information on sub-nm scale features from a large volume (few mm^3)

He - sensitive

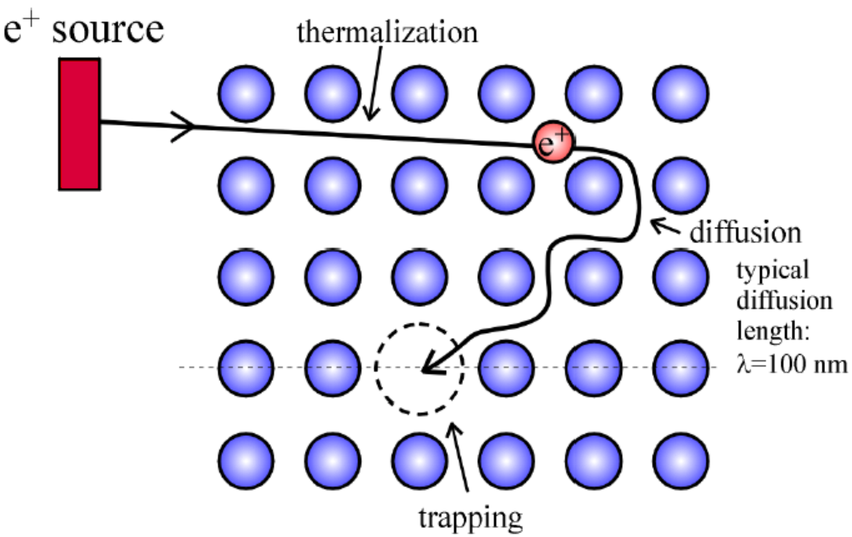
Helium presence in defects affect positron lifetime and changes the electron momentum distribution

HOW DO WE DO THAT

Positron
Annihilation
Lifetime
Spectroscopy

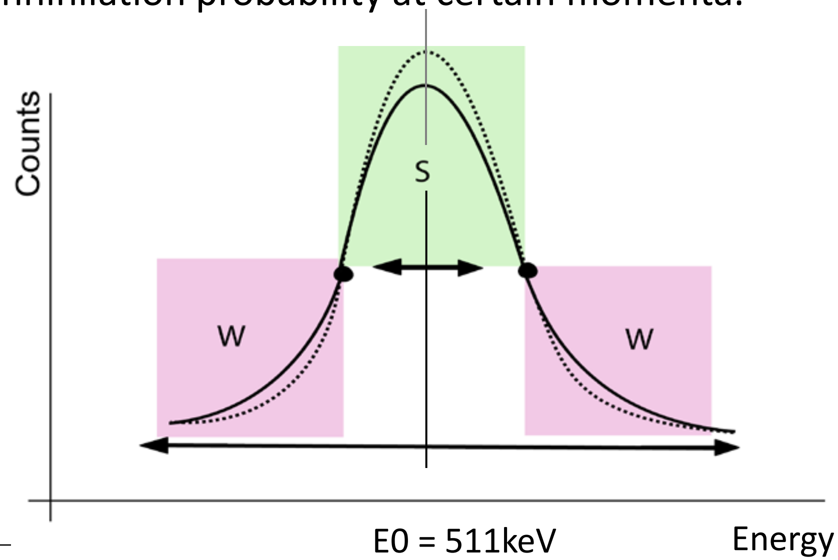
Two techniques of positron annihilation spectroscopy, based on different physical principles, have been widely established in the material research.

Coincidence
Doppler
Broadening
Spectroscopy



After thermalization (~ 3ps), positron diffuse through the lattice until trapping / annihilation. Diffusion time and trapping rate are a function of the microstructure and they can be measured.

Positrons annihilate mainly with the electrons of the outermost shell due to the repulsion of the nucleus. Such annihilation results in $E\gamma \cong 511keV$. But the annihilation occurs also with core electrons (electrons with higher momentum). Several factors determine the increase of the positron–electron annihilation probability at certain momenta.



HOW DO WE DO THAT

Positron
Annihilation
Lifetime
Spectroscopy

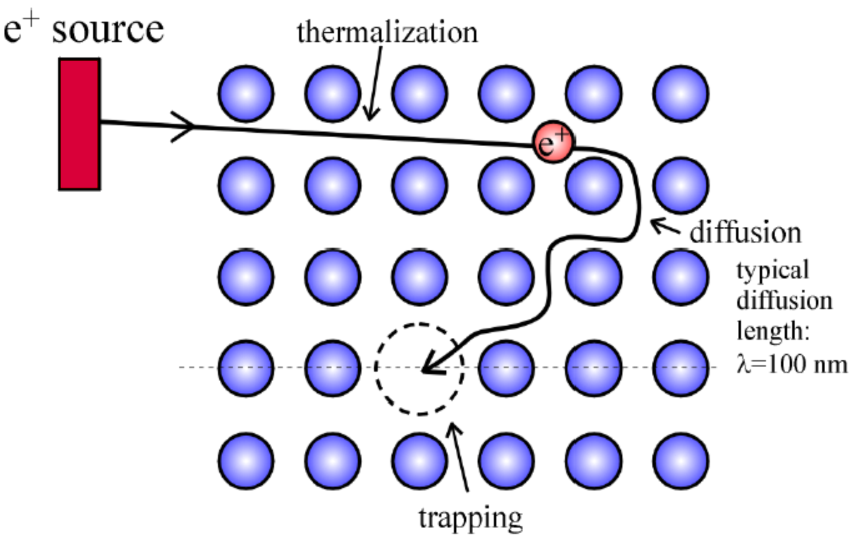
Open volume defects

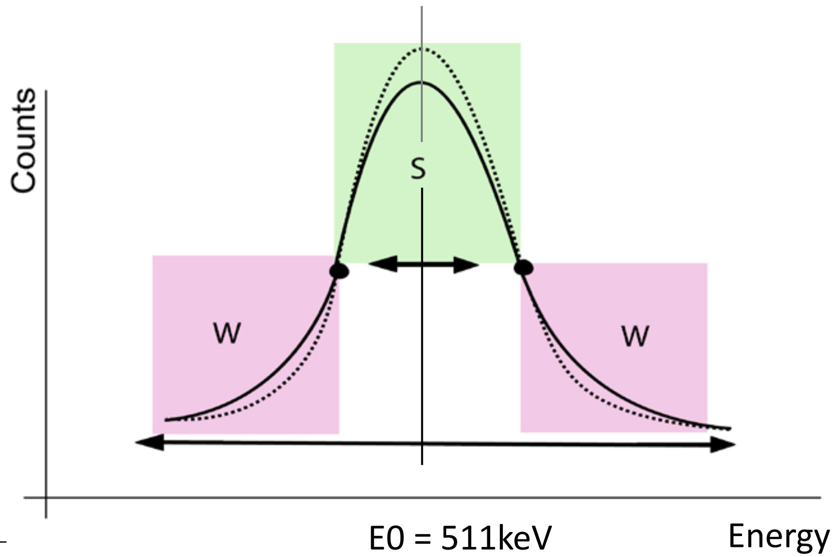
localization of positrons in open-volume defects

Coincidence
Doppler
Broadening
Spectroscopy

fraction of valence electrons (low momentum) taking part in the annihilation process is increased comparing to core electrons (high momentum)

The momentum distribution curve is narrower than that of defect-free reference material





Positron lifetime increases due to trapping at sites with reduced electron density

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HOW DO WE DO THAT

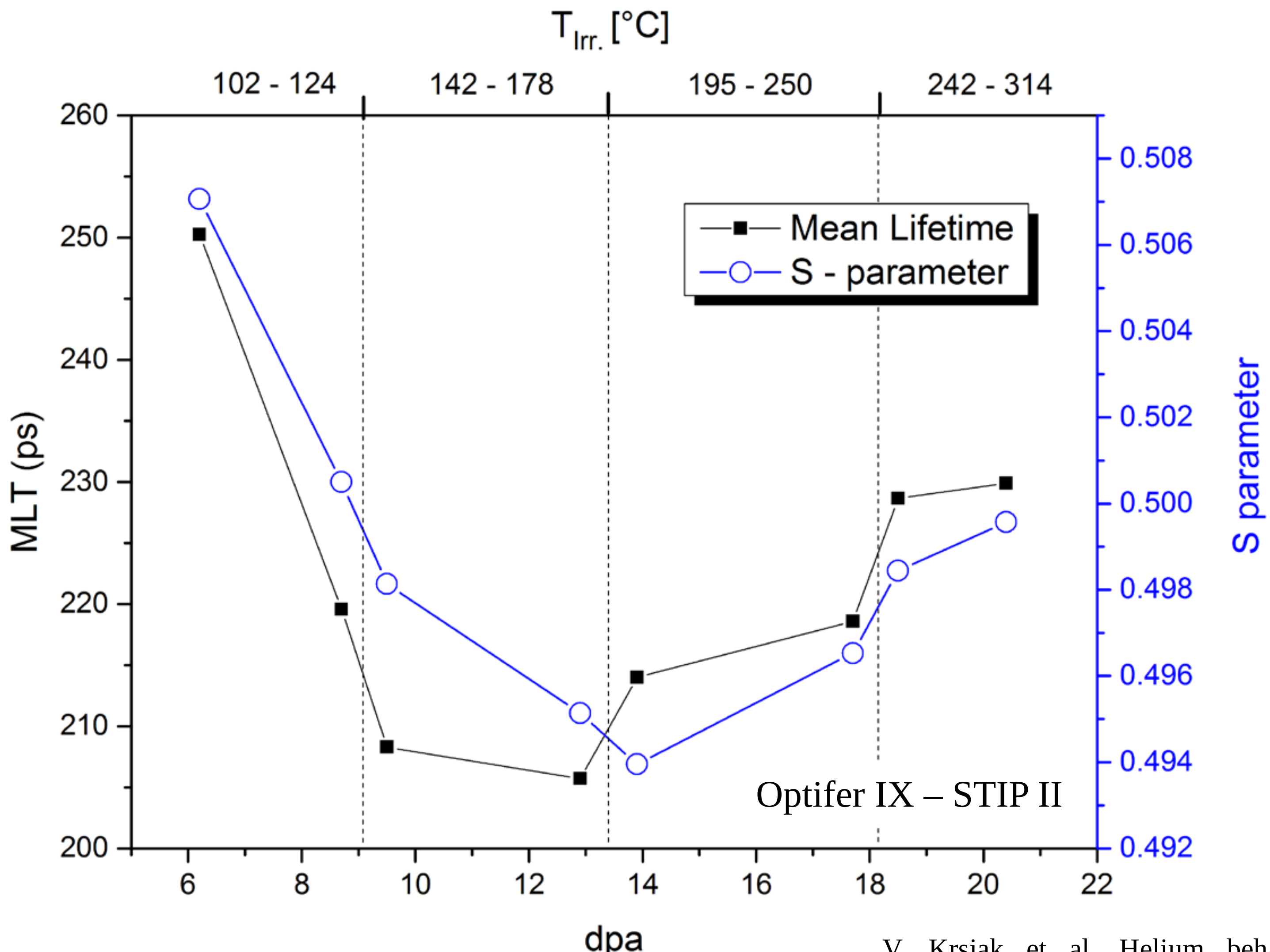
Materials: (EM10, CLAM, Eurofer 97, F82H, Optifer, MA956, ODS Eurofer, T91 …)

Irradiation doses: (5 – 21dpa)

Irradiation temperatures: (100 – 600° C)

Annealing temperatures: (200 – 800° C)

RESULTS

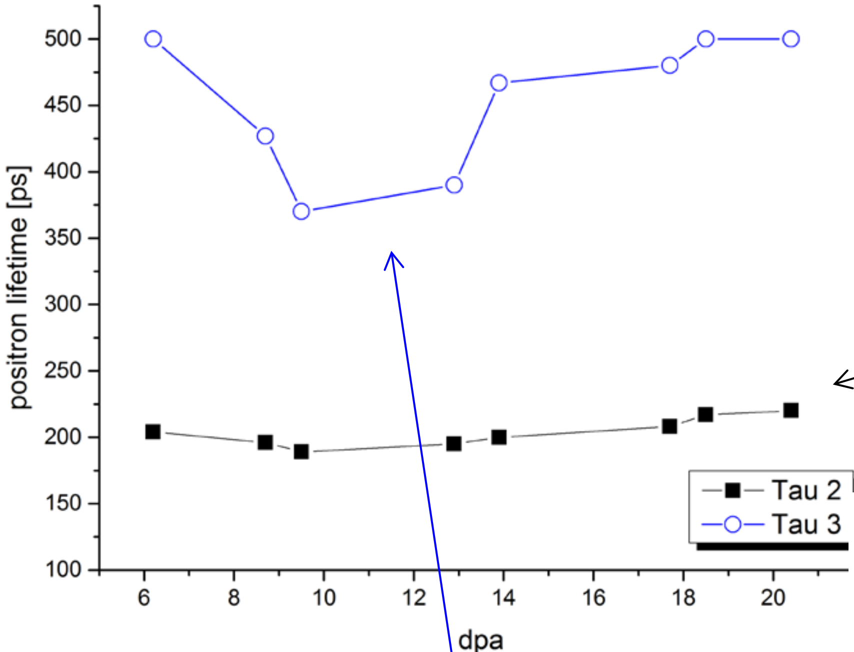


A good correlation between PASL and CDBS results were observed in all samples

V. Krsjak et al, Helium behaviour in ferritic/martensitic steels irradiated in spallation target, J. Nucl. Mater, DOI: 10.1016/j.jnucmat.2014.10.014

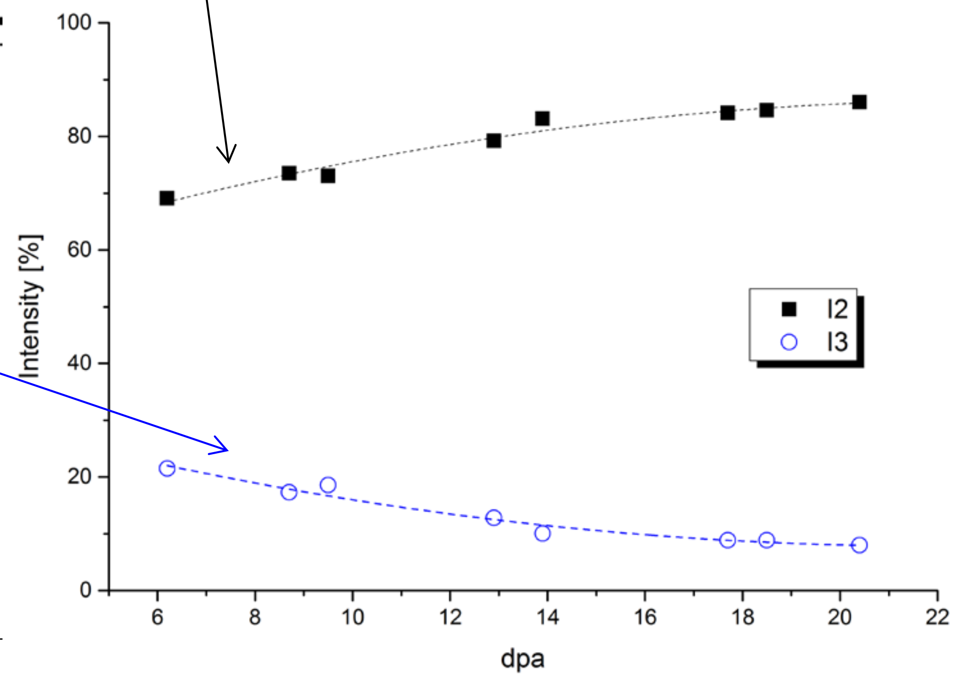
RESULTS

Lifetime spectra decomposition to 1 or 2 defect components.
(Two defect components of STIP II Optifer IX)

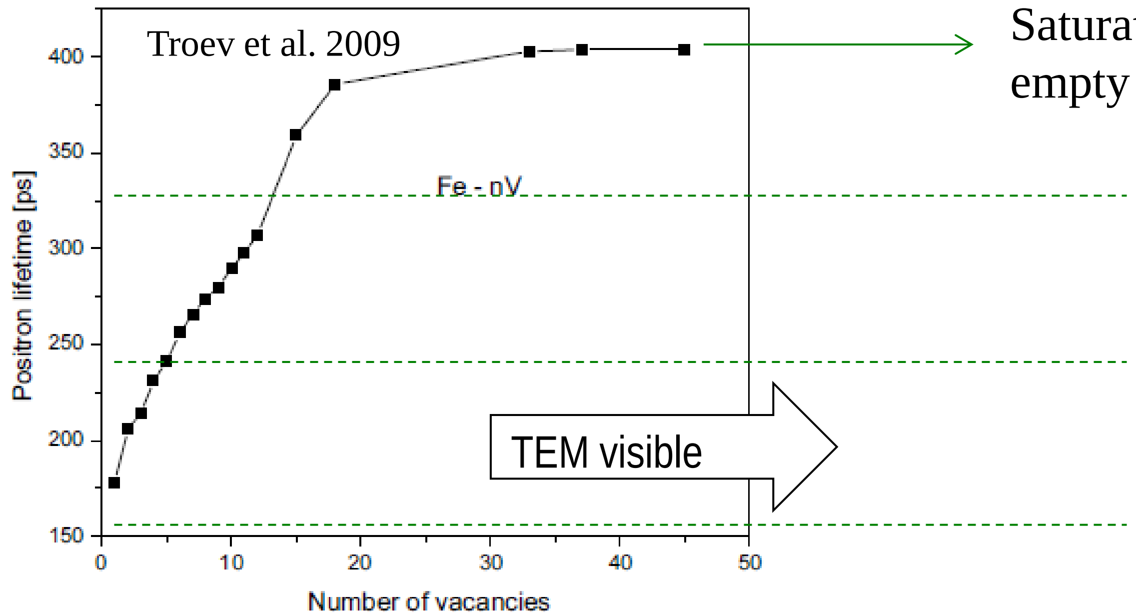


Small defects

Large defects



Large defects (lifetime ~ 450ps)



Saturated positron lifetime for an empty vacancy cluster

He/V = 0.5

He/V = 1

He/V = 2

Figure 3 Correlation between positron lifetime and the number of vacancies in a nano-void in bcc iron.

Saturated positron lifetimes for large vacancy clusters with helium
(calculations of J. Kuriplach, 2014)

Since we have observed positron lifetimes above 400ps (large vacancy clusters) in all materials, there must be **only small amount of helium** in these defects. As we have not seen by TEM vacancy clusters, they must not be much larger than ~ **30vacancies**

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RESULTS

Small defects (lifetime ~ 200ps)

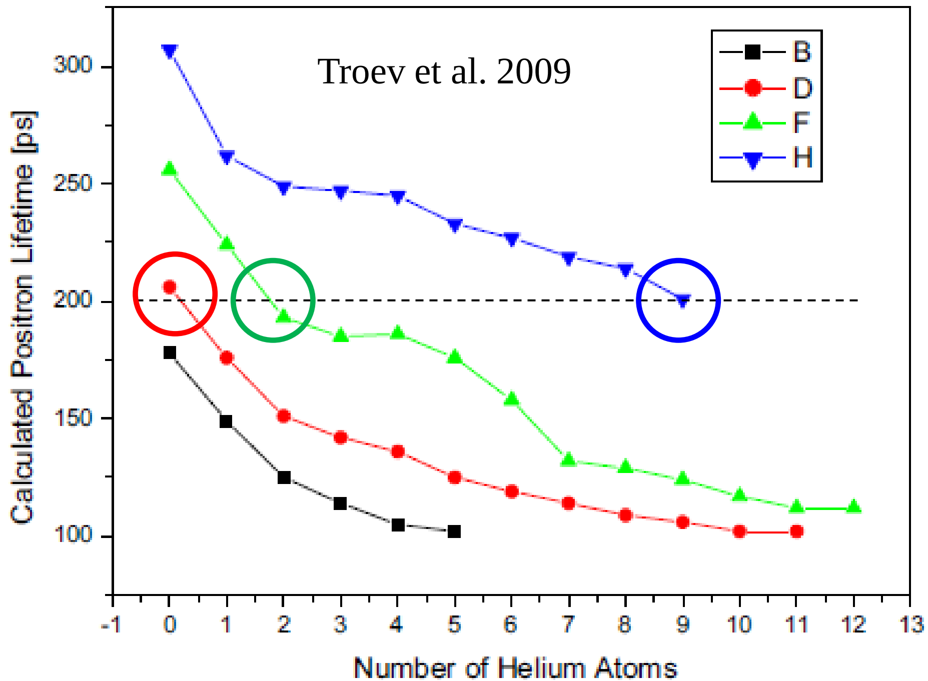


Figure 4 Correlation between positron lifetime and the number of helium atoms in nano-void (B) 1V+nHe, (D) 2V+nHe, (F) 6V+nHe, (H) 12V+nHe.

Isolated He atom has an extremely low migration energy;

He mobility drastically reduced in the vicinity of defects

Most of He is expected to be accommodated by defects (at 6dpa ~ 450appm He)

- Small defects (lifetime ~ 200ps):
  - ~~empty di-vacancy~~
  - ~~6 vacancy + 2-3 He~~
  - 12 vacancy + 12 He

Small defects τ_1 ~ 200 ps

Large defects τ_2 ~ 450 ps

DFT simulations + experiments

Small defects N_1 ~ 12 vacancies (high He)

Large defects N_2 ~ 30 vacancies (low He)

Trapping model

Three-state trapping model

$$-\frac{dn(t)}{dt} = \sum_{i=1}^{3} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_1}\right) \qquad I_1 = 1 - I_2 - I_3$$

$$\tau_1 = \frac{1}{\lambda_1} = \frac{1}{\lambda_b + \kappa_1 + \kappa_2} \qquad \tau_2 = \frac{1}{\lambda_{D1}} \qquad \tau_3 = \frac{1}{\lambda_{D2}}$$

$$\kappa_1 = \frac{I_2 I_3 (\lambda_{D1} - \lambda_{D2}) + I_2 (\lambda_b - \lambda_{D1})}{I_1} = \mu_{D1} N_{D1} \qquad \kappa_2 = \frac{I_2 I_3 (\lambda_{D2} - \lambda_{D1}) + I_3 (\lambda_b - \lambda_{D2})}{I_1} = \mu_{D2} N_{D2}$$

$\tau_{1,2,3}$ – lifetime components
$I_{1,2,3}$ – components intensities
$\tau_b = 1/\lambda_b$ – lifetime in defect-free bulk
D_1, D_2 (indexes) – defect 1, defect 2
$\kappa_{D1,D2}$ – positron trapping rate at defect (proportional to defect concentration N and positron trapping coefficient of the given defect μ).

Small defects number density ~ 10^{24}

Large defects number density ~ 10^{22}

RESULTS

Small defect – 12vacancy cluster with 12 helium atoms (He/V = 1) ~ 10^{24} m^{-3}
Large defect – 30 vacancy cluster with 3 helium atoms (He/V = 0.1) ~ 10^{22} m^{-3}

Material	dpa / t [°C]	He appm	N_1 [m^{-3}]	N_2 [m^{-3}]	He in defect 1 [m^{-3}]	He in defect 2 [m^{-3}]	He total PALS [m^{-3}]	He total Theory [m^{-3}]
Optifer (STIP 2)	6.1 99	450	2.7×10^{24}	2.3×10^{22}	3.3×10^{25}	5.3×10^{22}	3.3E+25	3.8E+25
Optifer (internal source)	6.1 99	450	3.1×10^{24}	1.5×10^{22}	3.8×10^{25}	4.6×10^{22}	3.8×10^{25}	3.8×10^{25}
EM10 (STIP 2)	6.1 93	450	3.4×10^{24}	5.1×10^{21}	4.0×10^{25}	1.2×10^{22}	4.0×10^{25}	3.8×10^{25}
F82H (STIP 2)	6.2 115	465	3.1×10^{24}	1.5×10^{22}	3.7×10^{25}	3.3×10^{22}	3.7×10^{25}	4.0×10^{25}
Eurofer (STIP V)	5.8 116	~ 450	2.5×10^{24}	1.8×10^{22}	3.0×10^{25}	5.5×10^{22}	3.0×10^{25}	3.8×10^{25}

RESULTS

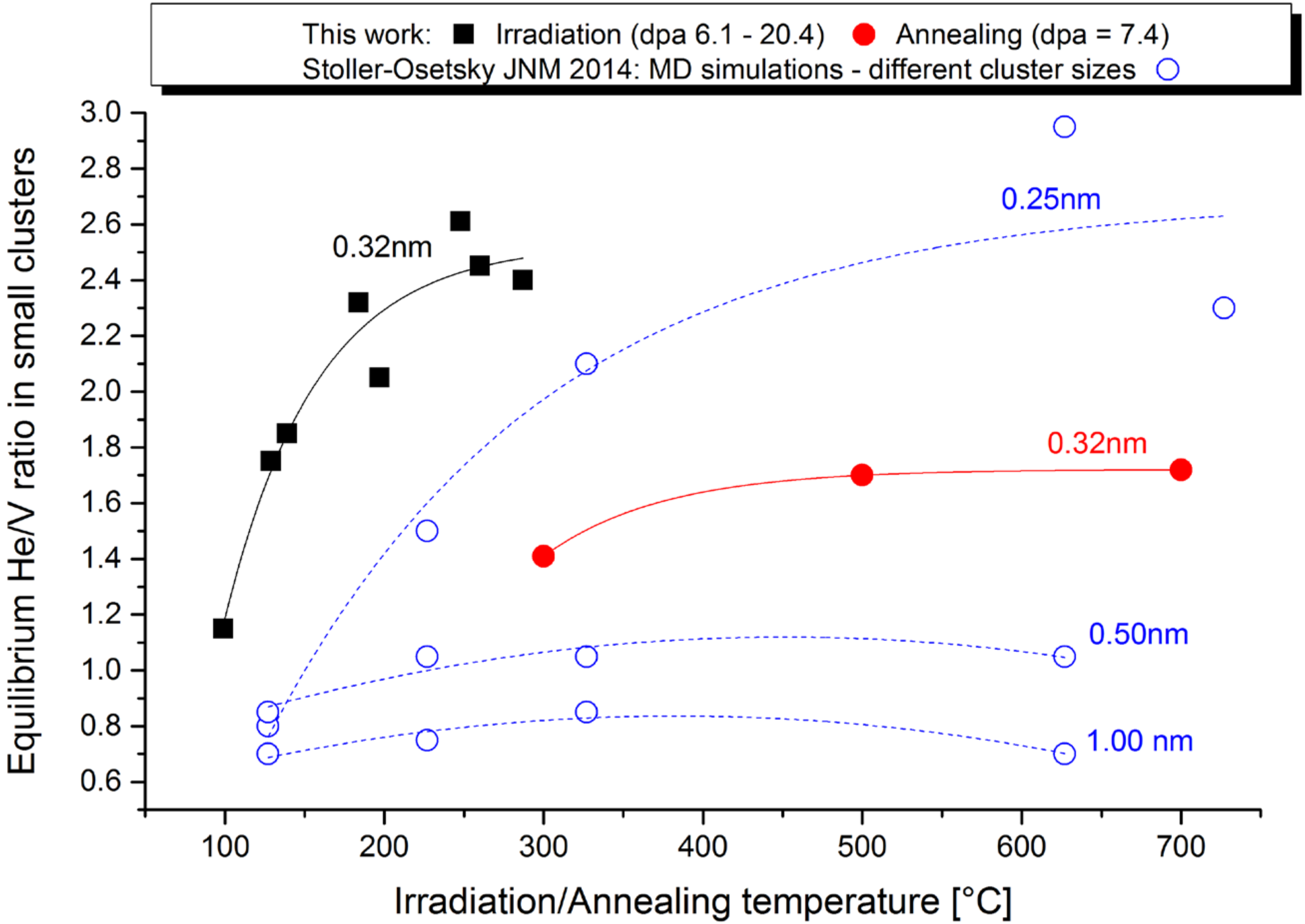
Lets take low dpa sample and lets assume that all helium is in small vacancy clusters:

- We know the helium concentration (400 – 500 appm for low-dose STIP sample)

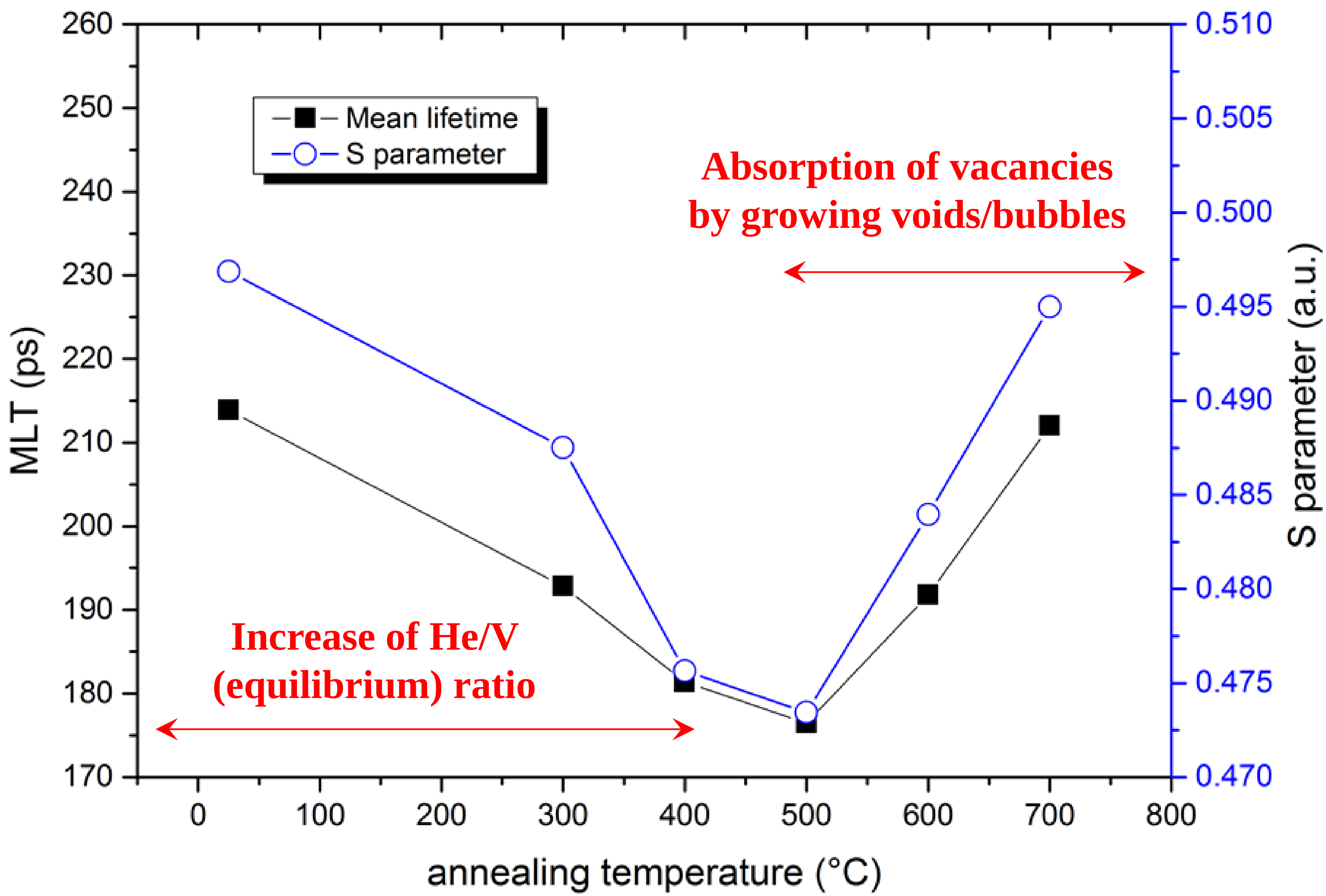
- We know the vacancy clusters number density

What happens to the actual He/V ratio at different temperatures?

RESULTS

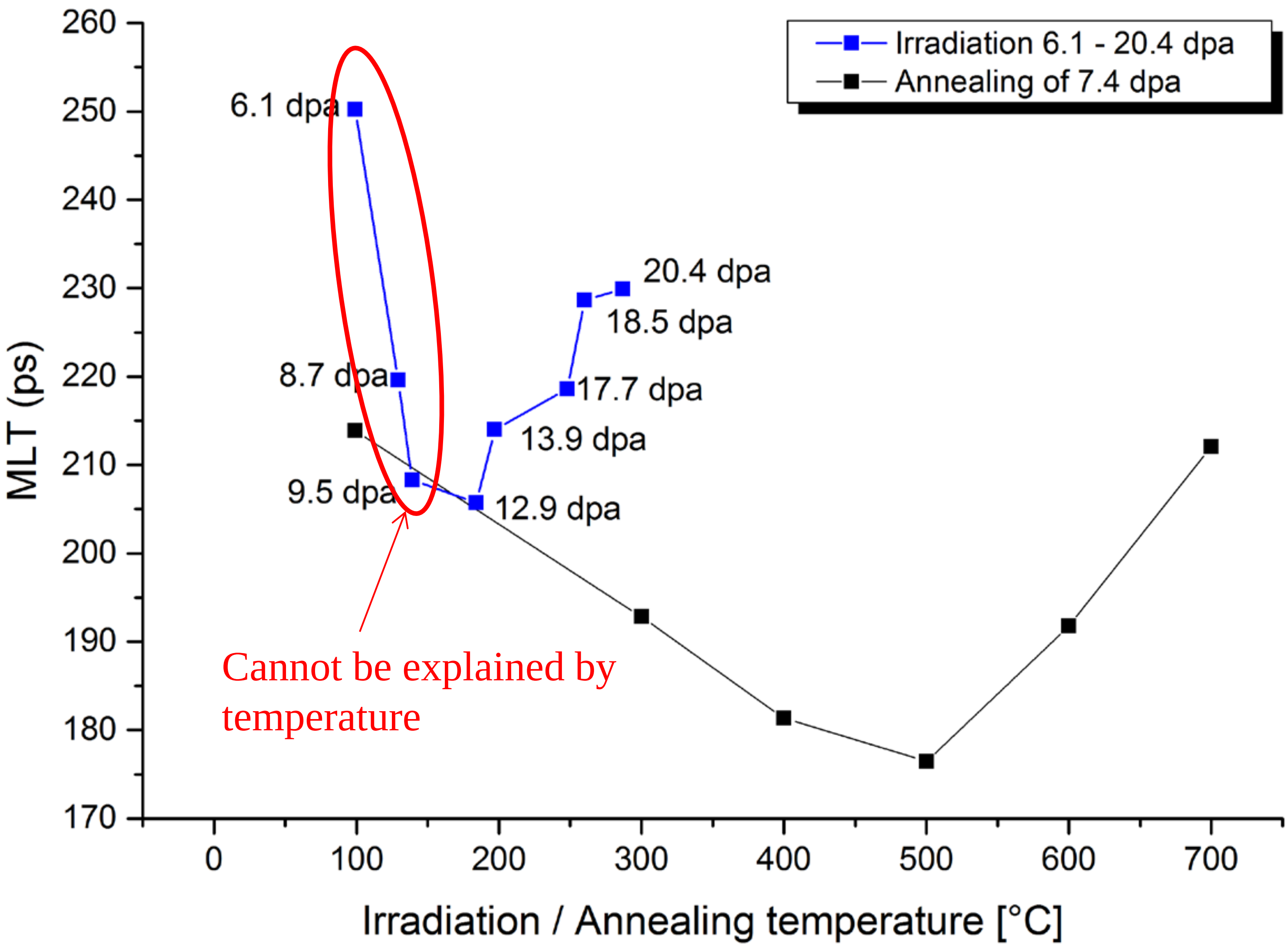

This work: Irradiation (dpa 6.1 - 20.4) Annealing (dpa = 7.4)
Stoller-Osetsky JNM 2014: MD simulations - different cluster sizes
Equilibrium He/V ratio in small clusters
Irradiation/Annealing temperature [°C]
0.32nm
0.25nm
0.32nm
0.50nm
1.00 nm
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
100
200
300
400
500
600
700

RESULTS



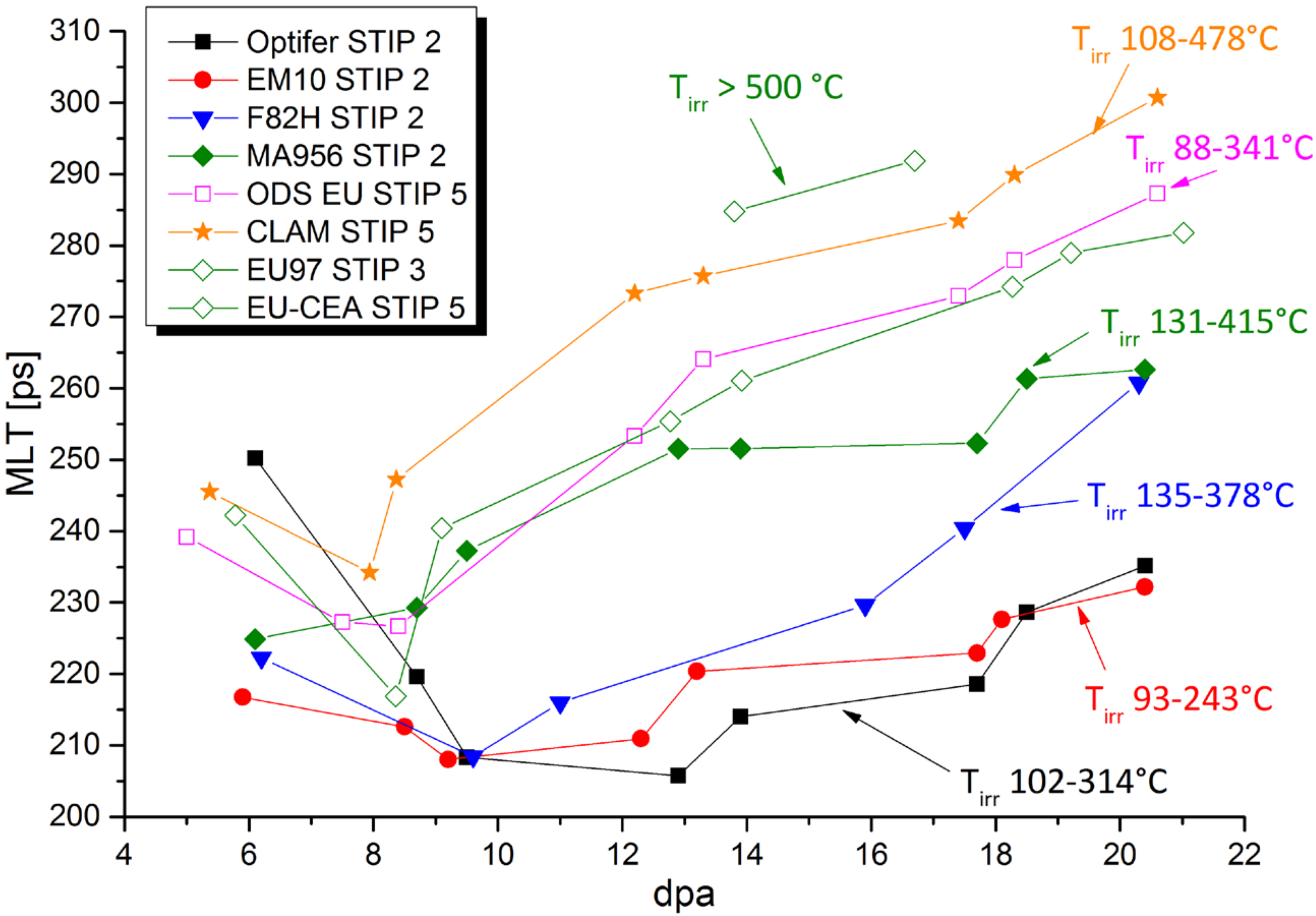
Mean lifetime
S parameter
Absorption of vacancies by growing voids/bubbles
Increase of He/V (equilibrium) ratio
MLT (ps)
S parameter (a.u.)
annealing temperature (°C)
260
250
240
230
220
210
200
190
180
170
0.510
0.505
0.500
0.495
0.490
0.485
0.480
0.475
0.470
0
100
200
300
400
500
600
700
800

RESULTS



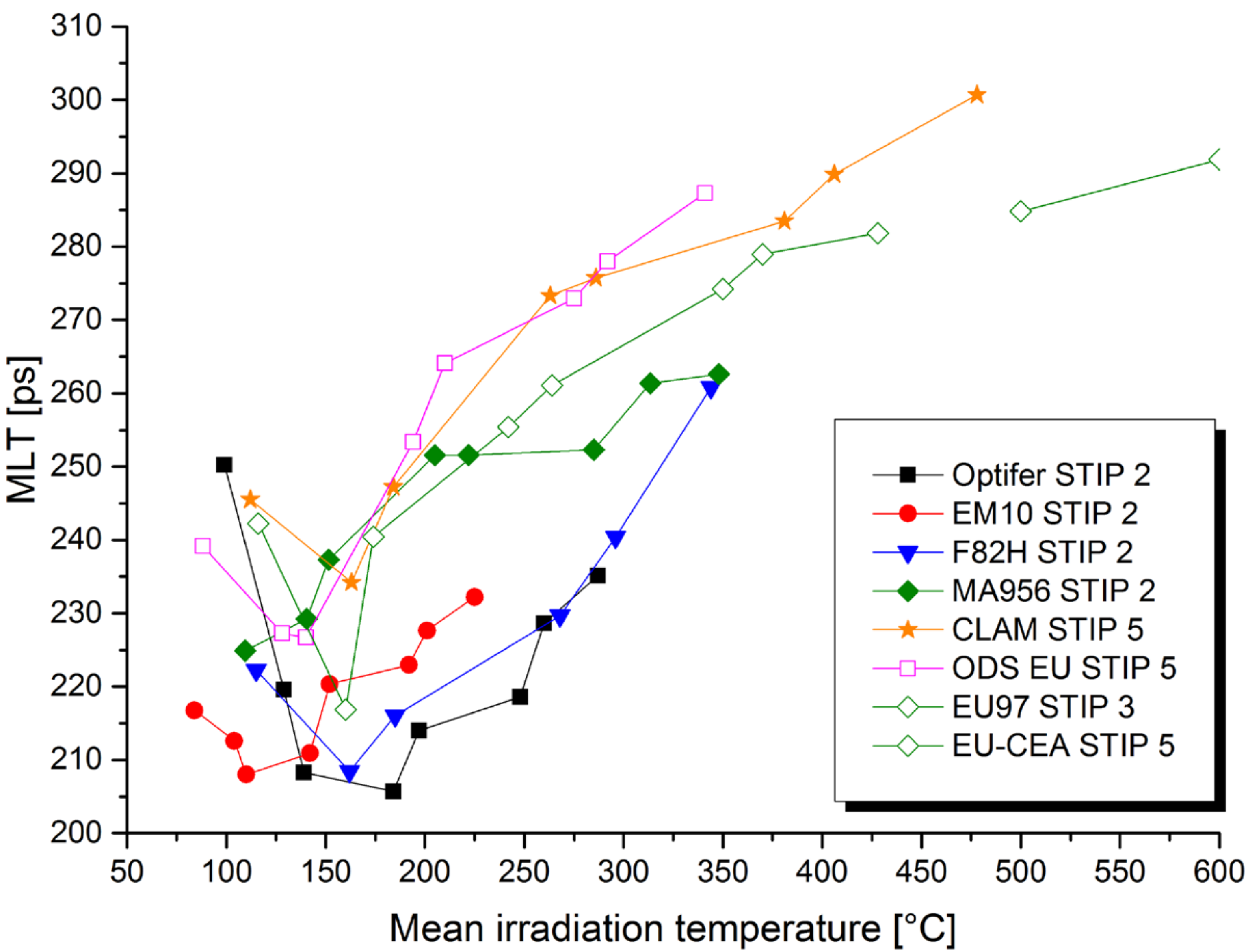
Irradiation 6.1 - 20.4 dpa
Annealing of 7.4 dpa
6.1 dpa
8.7 dpa
9.5 dpa
12.9 dpa
13.9 dpa
17.7 dpa
18.5 dpa
20.4 dpa
MLT (ps)
260
250
240
230
220
210
200
190
180
170
0
100
200
300
400
500
600
700
Irradiation / Annealing temperature [°C]
Cannot be explained by temperature

RESULTS



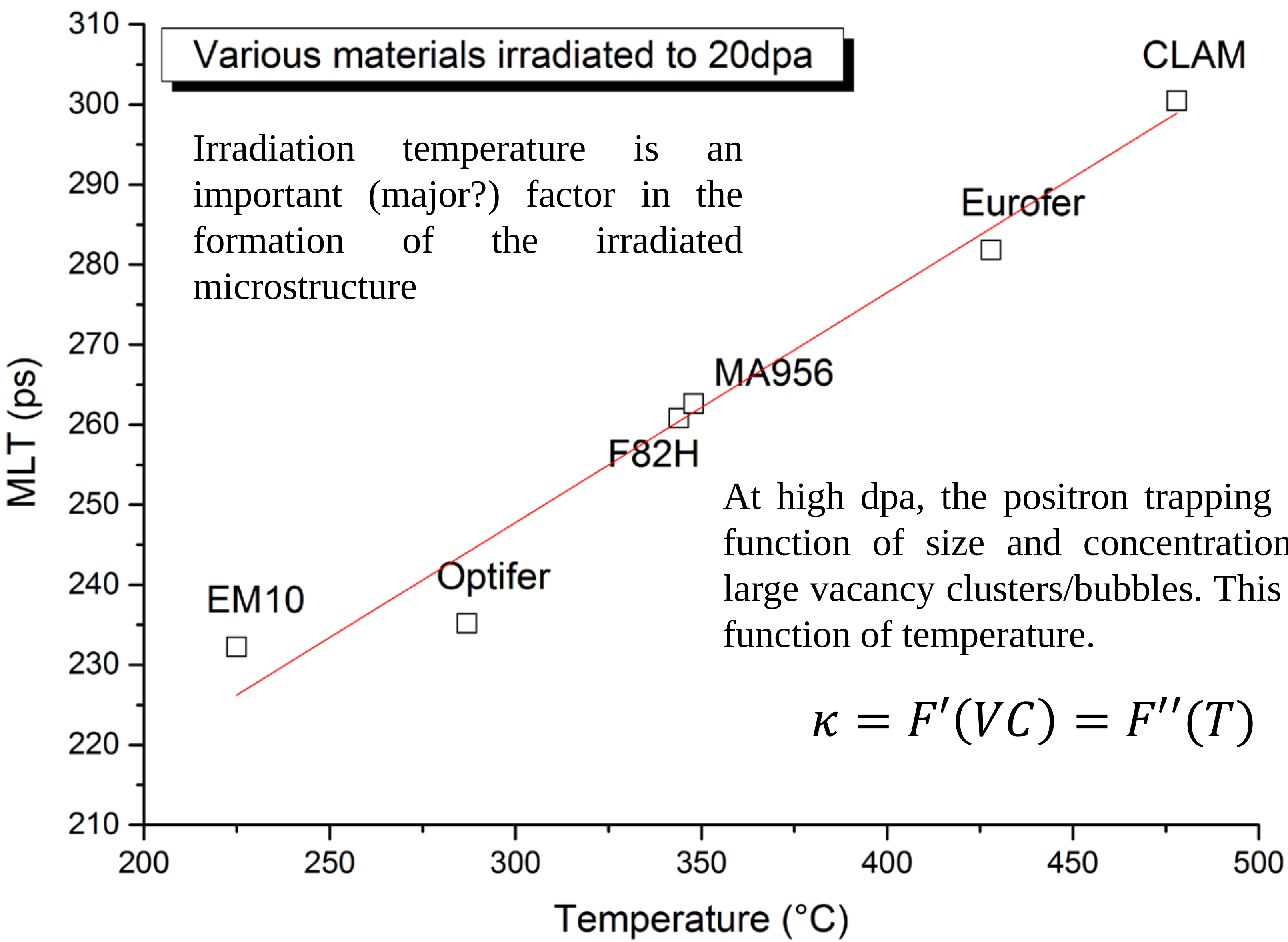
Optifer STIP 2
EM10 STIP 2
F82H STIP 2
MA956 STIP 2
ODS EU STIP 5
CLAM STIP 5
EU97 STIP 3
EU-CEA STIP 5
T irr > 500 °C
T irr 108-478°C
T irr 88-341°C
T irr 131-415°C
T irr 135-378°C
T irr 93-243°C
T irr 102-314°C
MLT [ps]
dpa
200
210
220
230
240
250
260
270
280
290
300
310
4
6
8
10
12
14
16
18
20
22

RESULTS



310
300
290
280
270
260
250
240
230
220
210
200
MLT [ps]
50
100
150
200
250
300
350
400
450
500
550
600
Mean irradiation temperature [°C]
Optifer STIP 2
EM10 STIP 2
F82H STIP 2
MA956 STIP 2
CLAM STIP 5
ODS EU STIP 5
EU97 STIP 3
EU-CEA STIP 5

RESULTS

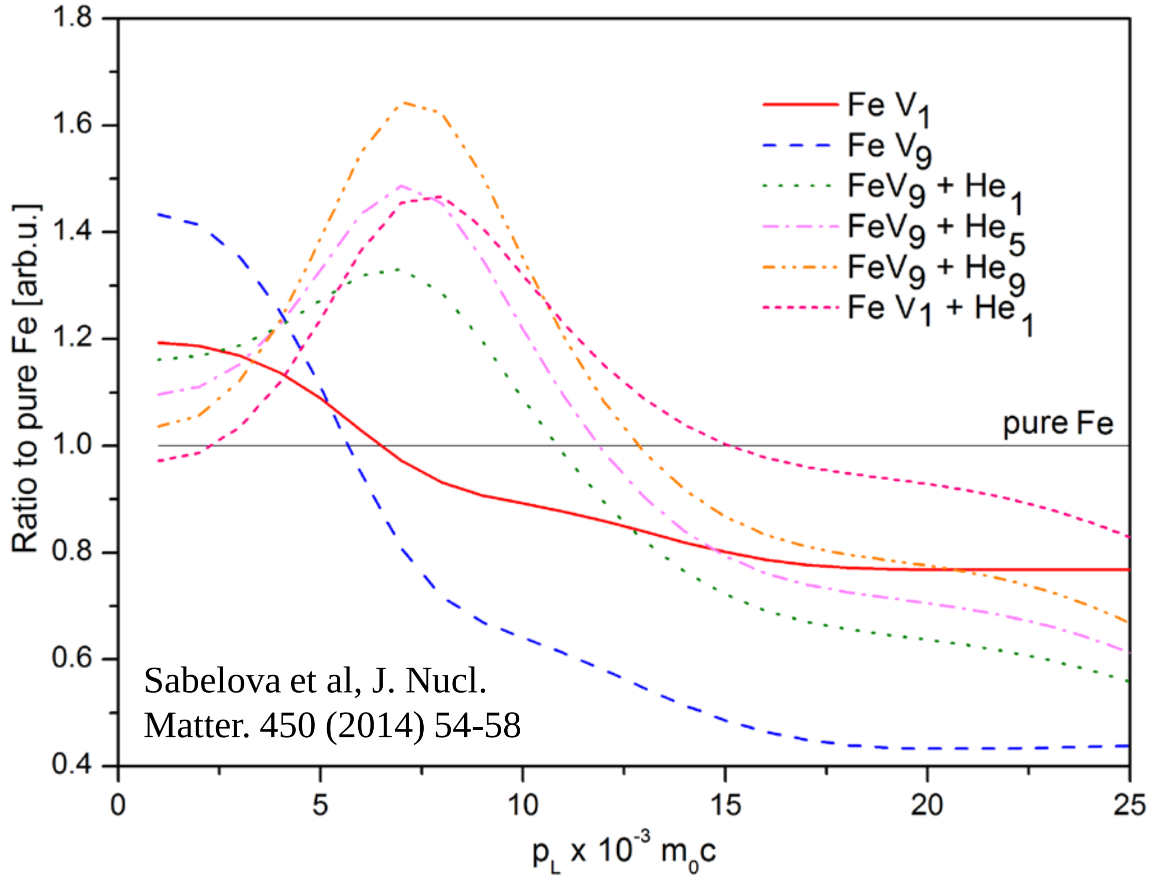


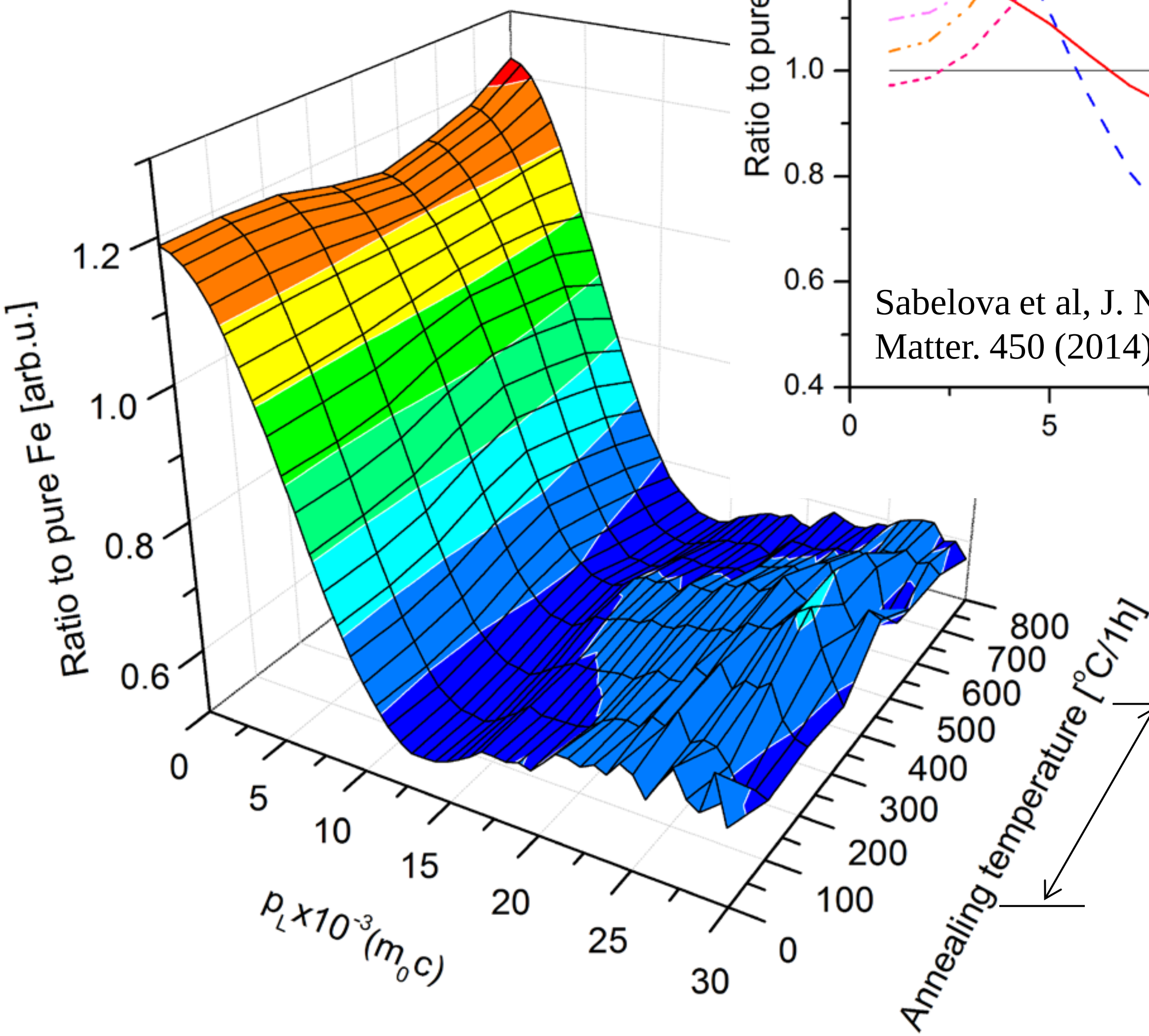
Irradiation temperature is an important (major?) factor in the formation of the irradiated microstructure

At high dpa, the positron trapping is a function of size and concentration of large vacancy clusters/bubbles. This is a function of temperature.

$$\kappa = F'(VC) = F''(T)$$

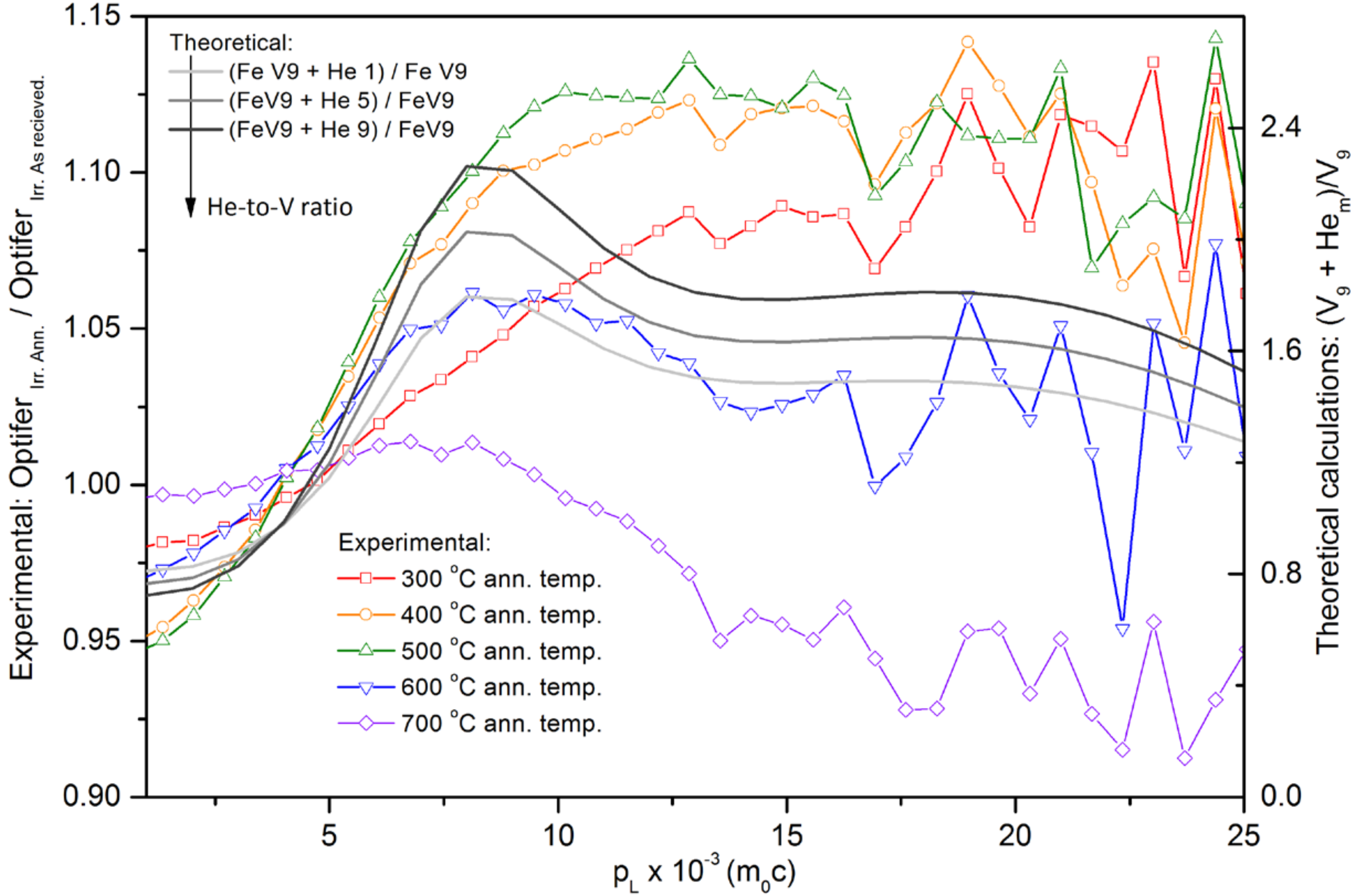
Helium reduce positron trapping at defects, thus the He peak cannot be observed directly in CDBS spectra.





Up to 500° C, He/V ratio increase with annealing temperature, while most of other "visible" features remain unchanged.

RESULTS



Sabelova et al, J. Nucl. Matter. 2014, accepted for publication

SUMMARY AND CONCLUSIONS

- 10 ferritic/martensitic steels and more than 100 samples have been investigated by means of positron annihilation spectroscopy techniques in the last 2 years. Effect of dpa, irradiation and annealing temperature was studied
- These experiments offer qualitative and quantitative information on sub-nm scale helium-vacancy clusters, which cannot be obtained by any other experimental technique
- Helium peak was clearly identified in the CDBS spectra of annealed spallation samples, which demonstrates its presence in major positron trapping sites (vacancy clusters)
- Small vacancy clusters with the mean size of 12 vacancies contains the majority of helium. He/V ratio was estimated ~1 in most as-irradiated samples and increase with annealing temperature to ~1.5.
- Large vacancy clusters (> 0.8nm), identified in all samples, contains only small amount of helium. Their size increase with irradiation/annealing via absorption of vacancies – increase of positron lifetime and CDBS S-parameter. We assume that these defects evolve eventually to helium bubbles, which can be seen by TEM at elevated temperatures/doses.

THANK YOU FOR YOUR ATTENTION