Rate Theory Analysis of Growth Process of Helium Bubbles in F82H Irradiated at SINQ

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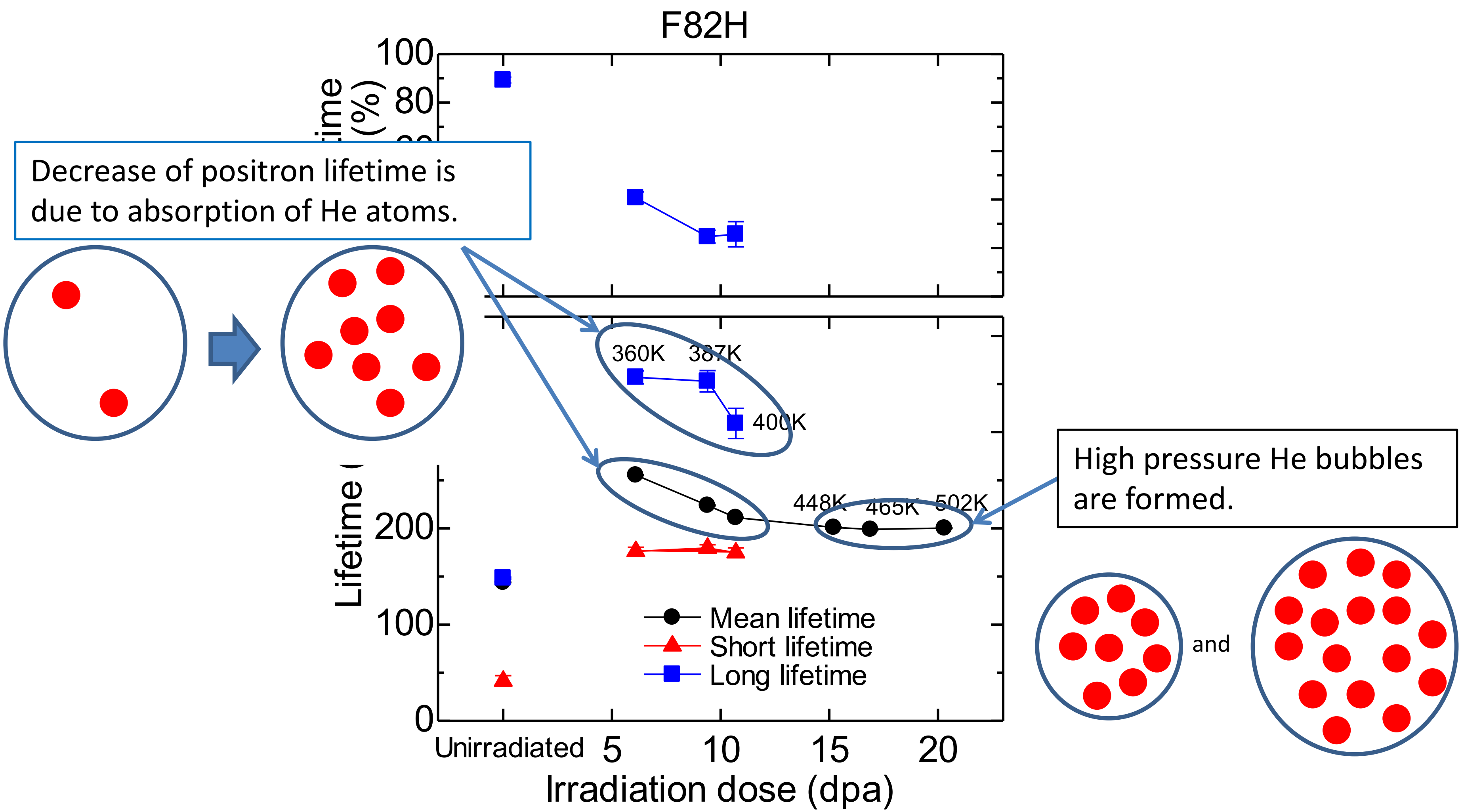
Background

- The study of irradiation effects on the reduced activation ferritic/martensitic steels is important for the structural materials of spallation neutron source.
- One of features of spallation neutron source is high production rate of gas atoms, which leads to the formation of a large amount of He bubbles. He bubbles have great influence on mechanical properties of structural materials.
- Clarifying the growth mechanism of He bubbles is important for the development of nuclear materials.

Positron annihilation spectroscopy



[Sato et al., J. Nucl. Mater. 431 (2012) 52.]

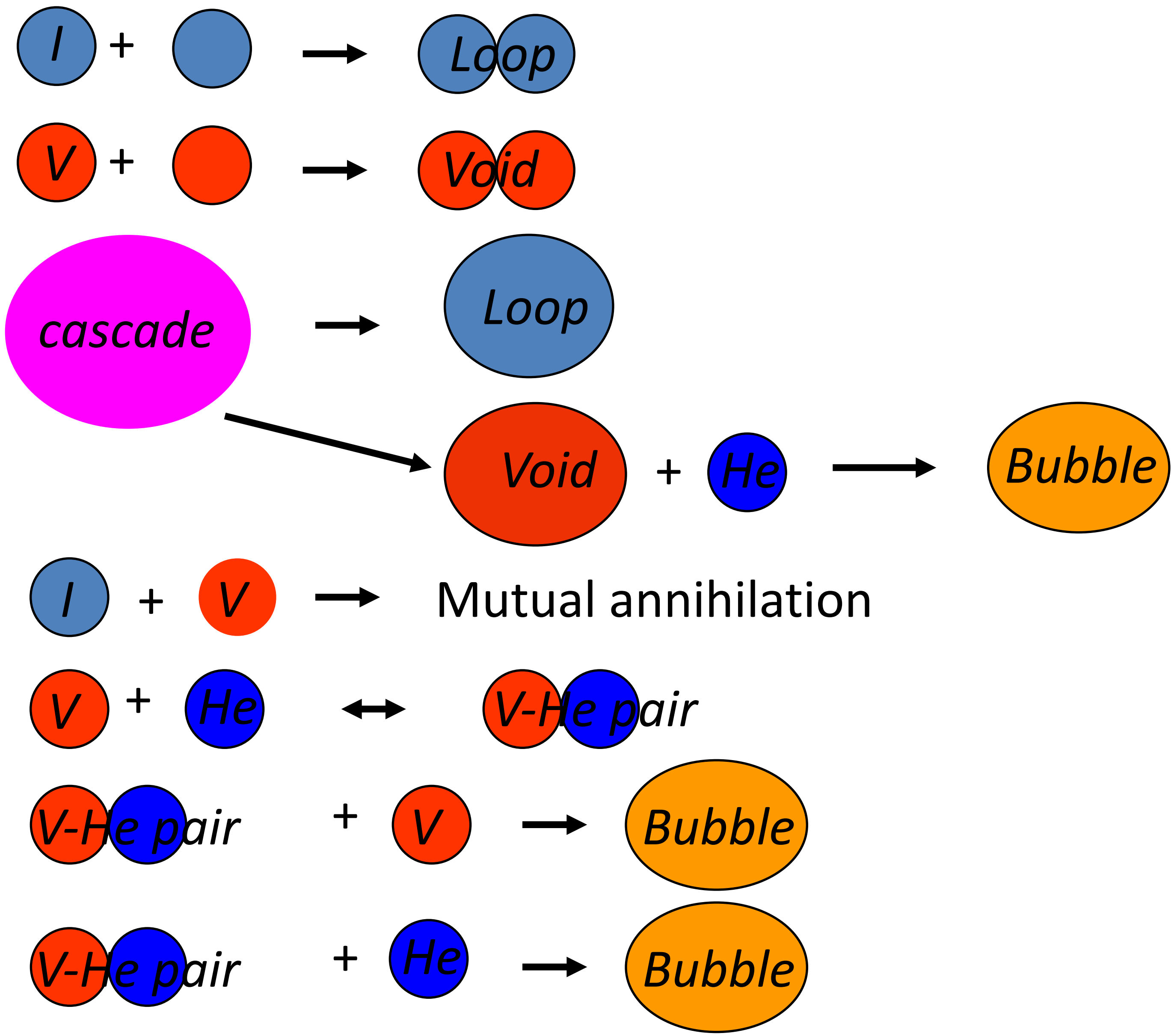
Long lifetime decreased with increasing irradiation dose and temperature.

Purpose of this study

- We explained that the change in positron annihilation lifetimes was caused by the absorption of He atoms by He bubbles.

- In this study, the change in He-to-vacancy ratio of He bubbles was obtained by rate theory analysis.

Calculation model (1)

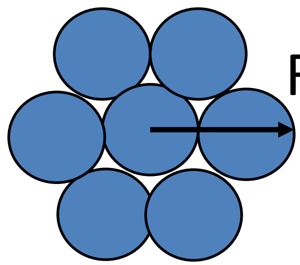


Calculation model (2)

- Mobile defects: interstitials, vacancies, He
- Clusters: interstitial type dislocation loops, voids, bubbles, vacancy-He pairs
- Damage: protons, neutrons
- Gas atom production: helium (no hydrogen)
- Thermal dissociation: vacancy-helium pairs, dissociation of interstitials, vacancies and helium atoms from bubbles
- No interaction of helium with interstitials and dislocation loops
- Nucleation of clusters: di-interstitials, di-vacancies and directly in cascades.
- Materials parameters: Fe (F82H)

Calculation model (3)

Concentration of interstitial type dislocation loops; C_{IC}

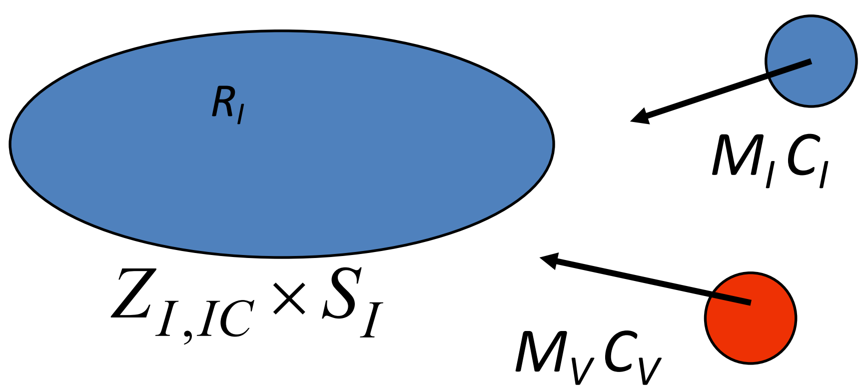


Total sink efficiency of interstitials in dislocation loops : S_I

$$S_I = C_{IC} \times 2\pi L_I$$

Total interstitials in interstitial type dislocation loops : R_I

$$R_I = C_I \times \pi L_I^2$$



Rate equations (1)

The change in concentration of interstitial C_I (fractional unit).

C_V: vacancy concentration

Z: cross section of the reaction

M: mobility of point defects

$$\frac{dC_I}{dt} = P_I - 2Z_{I,I}M_I C_I{}^2 - Z_{I,V}(M_I + M_V)C_I C_V$$

damage production   I-I recombination   mutual annihilation

$$- Z_{I,IC}M_I C_I S_I - Z_{I,VC}M_I C_I S_V - Z_{I,B}M_I C_I S_B - Z_{I,VHe}M_I C_I C_{V,He}$$

absorption by loops   absorption by voids   absorption by bubbles   absorption by vacancy-He pairs

$$- M_I C_I C_S - N_I P_{IC} + C_B D_{B,I}$$

annihilation at permanent sinks   direct production of loops   dissociation from bubbles

Rate equations (2)

The change of vacancy concentration: C_V

$$\frac{dC_V}{dt} = P_V - 2Z_{V,V}M_V{C_V}^2 - Z_{I,V}(M_I + M_V)C_I C_V - Z_{He,V}M_{He}C_V C_{He}$$
$$- Z_{V,V}M_V C_V S_V - Z_{V,IC}M_V C_V S_I - Z_{V,B}M_V C_V S_B - Z_{V,He}M_V C_V C_{He}$$
$$+ M_{He}D_{VHe,V}C_{V,He} + Z_{I,VHe}M_I C_I C_{V,He} - M_V C_V C_S - N_V P_{VC} + C_B D_{B,V}$$

The change of He concentration: C_{He}

$$\frac{dC_{He}}{dt} = P_{He} - Z_{He,V}M_{He}C_V C_{He} - Z_{He,V}M_{He}C_{He}S_V - Z_{He,B}M_{He}C_{He}S_B$$
$$- Z_{He,V}M_{He}C_{He}C_{V,He} + Z_{I,VHe}M_I C_I C_{V,He} + M_{He}D_{VHe,He}C_{V,He} - M_{He}C_{He}C_S + C_B D_{B,He}$$

Determination of parameters

Advantages of rate theory analysis:

Easy calculation of defect structural evolution from low to high dose.

Disadvantages:

To obtain accurate results, the number of parameters increases.

Parameters were determined to fit experimental results

F82H: X. Jia, Y. Dai, J. Nucl. Mater., 318 (2003) 207-214.

Dose (dpa)	He (appm)	Irr. Temp. (K)	Loops		Bubbles	
			Size (nm)	Density (m^3)	Size (nm)	Density (m^3)
9.9	560	448	3.3	3×10^{22}	0.7	5.1×10^{23}

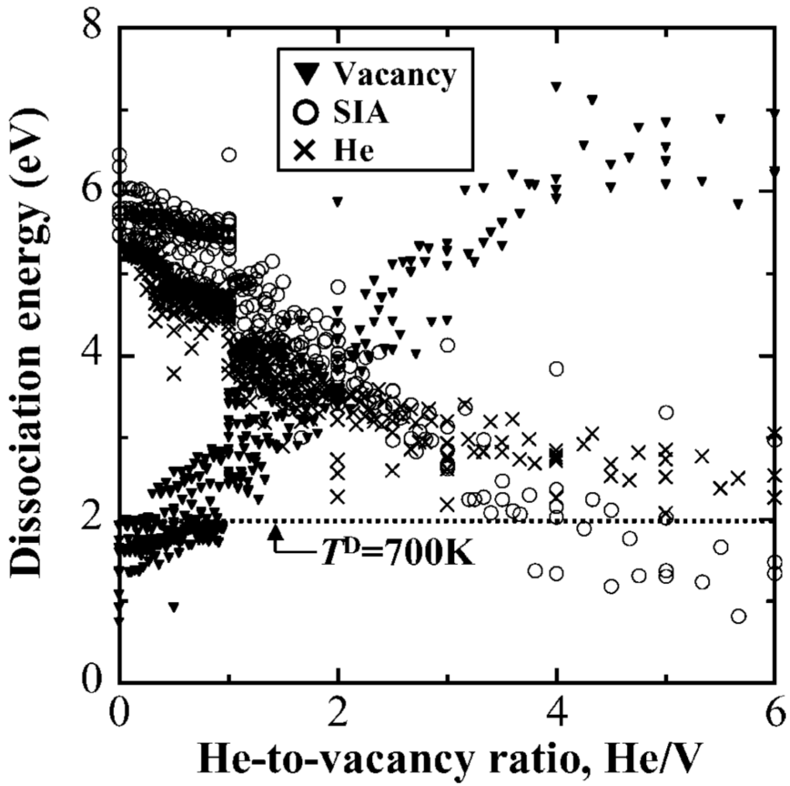
Defects in F82H were assumed to be interstitial type dislocation loops.

Parameters used in this simulation

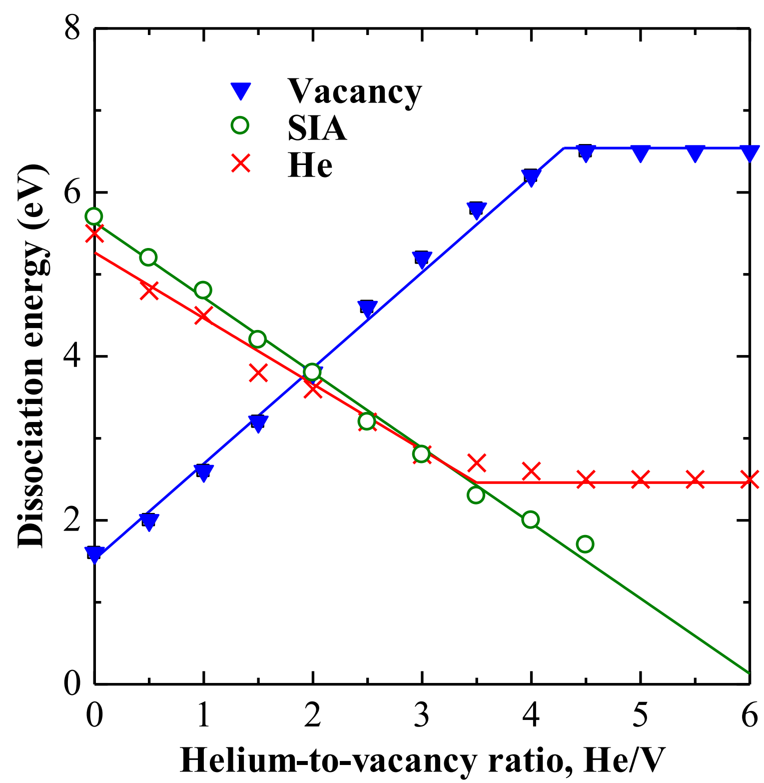
P_{ic}	1.07×10^{-14} /s
P_{vc}	3.76×10^{-16} /s
$E_m^{\ i}$	0.26 eV
$E_m^{\ v}$	1.26 eV
$E_m^{\ He}$	0.08 eV
$E_B^{\ V\text{-}He}$	3.9 eV
C_s	10^{-8}
$C_{s,He}$	10^{-10}
Z_{iv}	40
Z_{vic}	45
Z_{ib}	1
Z_{vb}	25
Z_{ivc}, Z_{hevc},Z_{vvc}, Z_{vvhe}	10
ν	10^{13} /s

Dissociation energy from bubbles

Molecular Dynamics simulation

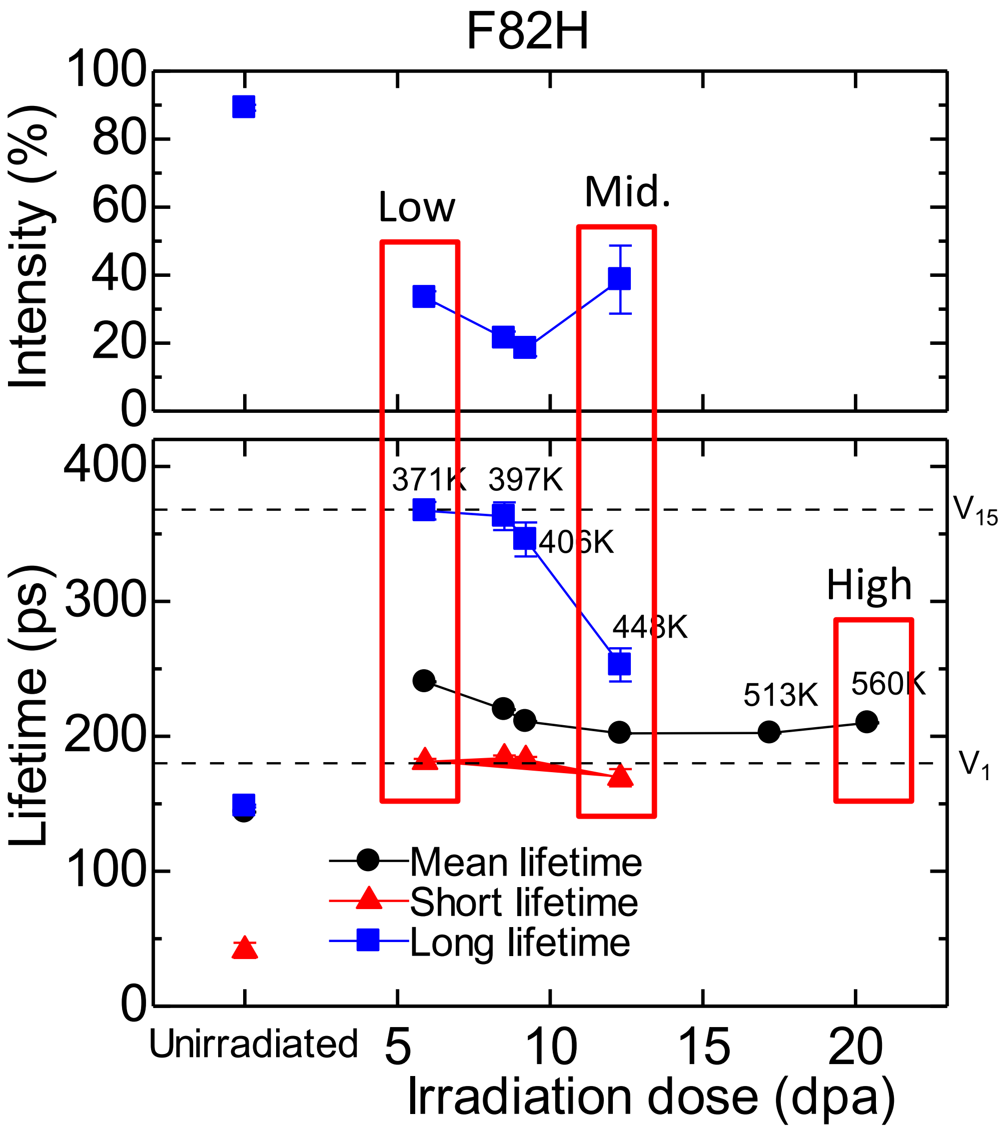


[Morishita, J. Plasma Fusion Res. 81 (2005) 13.]



Linear approximation was applied.

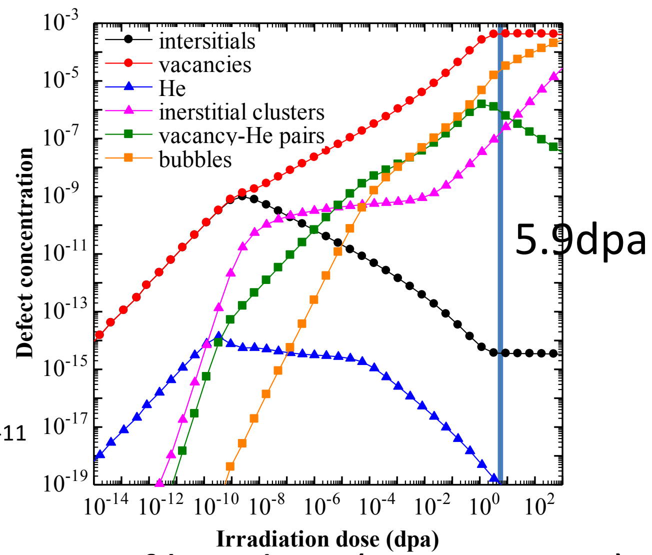
Irradiation condition calculated in this study



Temp. (K)	Irradiation dose (dpa)	He (appm)	H (appm)
371	5.9	413	1680
397	8.5	650	2530
406	9.2	715	2850
448	12.3	1015	4200
513	17.2	1505	6200
560	20.4	1795	7720

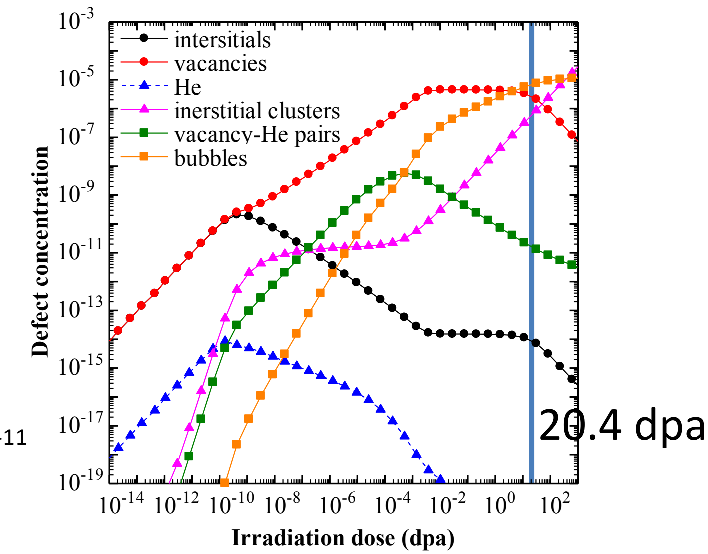
Change in defect concentration

P = 1.8×10^{-7}
P_{He} = 1.3×10^{-11}
T_{irr} = 371 K



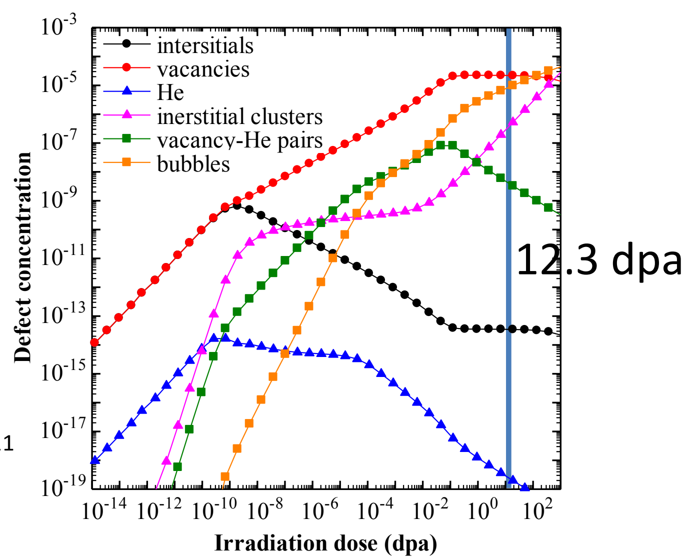
Simulation of low dose (temperature)

P = 6.2×10^{-7}
P_{He} = 5.5×10^{-11}
T_{irr} = 560 K



Simulation of high dose (temperature)

P = 3.8×10^{-7}
P_{He} = 3.1×10^{-11}
T_{irr} = 448 K

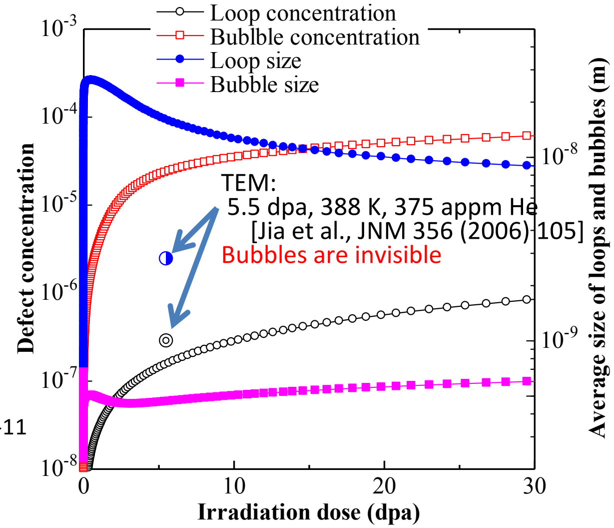


Simulation of middle dose (temperature)

Parameters (Z: cross section of reactions) are fitted to the TEM observation results. Production rate of point defects and helium and irradiation temperature are changed to the positron annihilation (PA) results.

The concentration of vacancies and bubbles is higher in lower dose/temperature. This deference is caused by the irradiation temperature.

Comparison with TEM observation

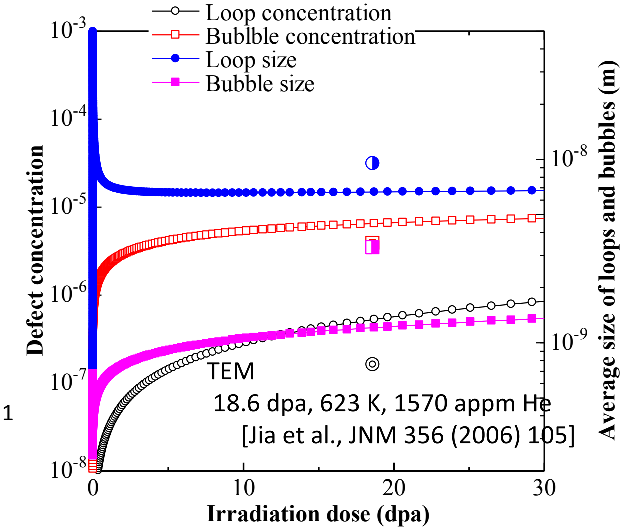


$P = 1.8 \times 10^{-7}$

$P_{He} = 1.3 \times 10^{-11}$

$T_{irr} = 371$ K

Simulation of low dose (temperature)

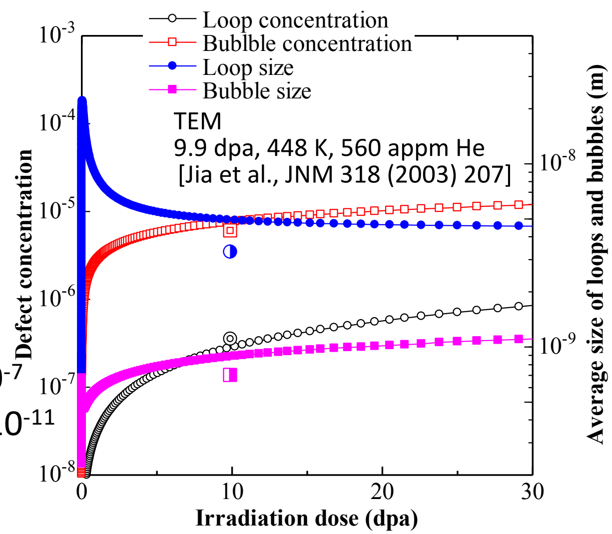


$P = 6.2 \times 10^{-7}$

$P_{He} = 5.5 \times 10^{-11}$

$T_{irr} = 560$ K

Simulation of high dose (temperature)



$P = 3.8 \times 10^{-7}$

$P_{He} = 3.1 \times 10^{-11}$

$T_{irr} = 448$ K

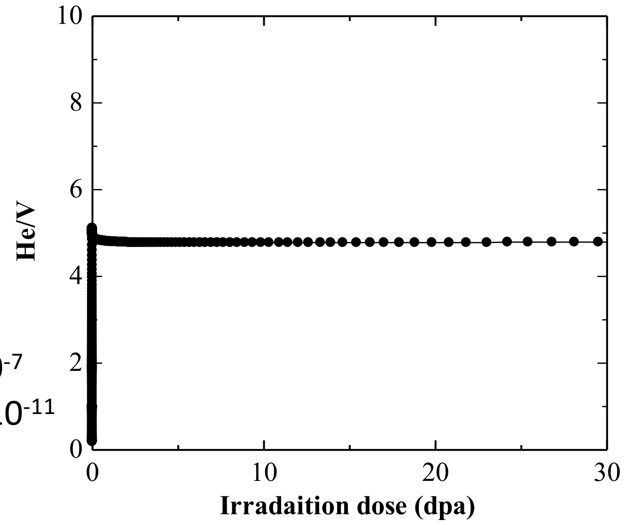
Simulation of middle dose (temperature)

Simulation results are compared with the TEM observation. Irradiation condition of TEM close to that of PA is selected.

Simulation results do not correspond with the TEM observation.

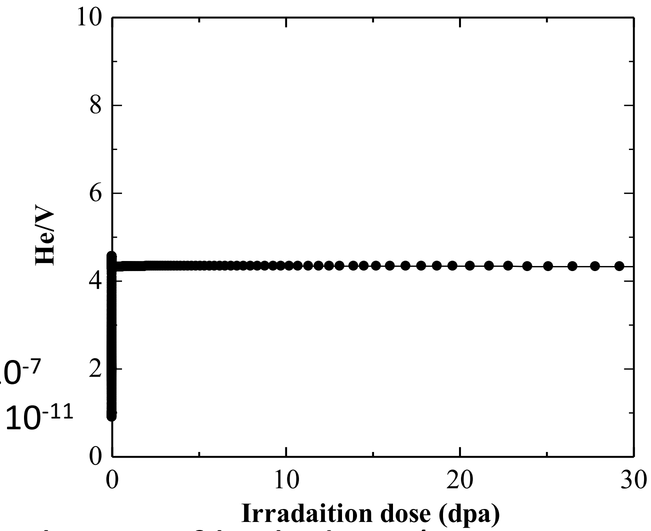
We have to find better parameters.

Helium-to-vacancy ratio



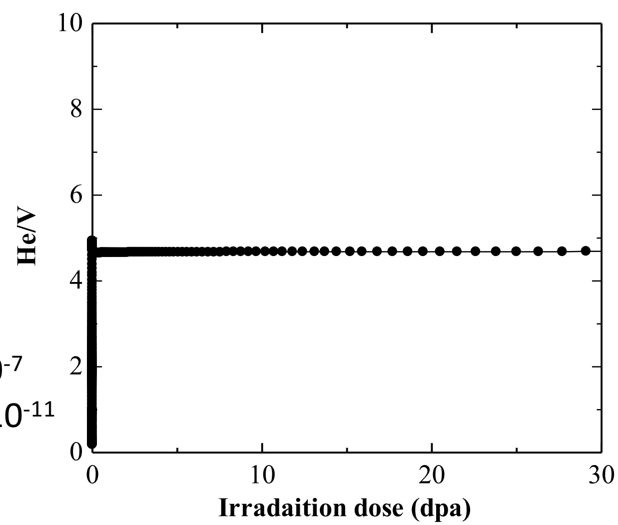
P = 1.8×10^{-7}
P_{He}= 1.3×10^{-11}
T_{irr}= 371 K

Simulation of low dose (temperature)



P = 6.2×10^{-7}
P_{He}= 5.5×10^{-11}
T_{irr}= 560 K

Simulation of high dose (temperature)



P = 3.8×10^{-7}
P_{He}= 3.1×10^{-11}
T_{irr}= 448 K

Simulation of middle dose (temperature)

He/V ratio is almost constant.
High-pressure bubbles are formed.

To explain the PA results, it is necessary that He/V ratio decreases with increasing the irradiation temperature.

Reason of high Helium-to-vacancy ratio

Reaction of helium

$$\frac{dC_{He}}{dt} = P_{He} - Z_{V,He}(M_V + M_{He})C_V C_{He} - Z_{He,VHe} M_{He} C_{He} C_{VHe}$$

production — formation of V-He pair — absorption by V-He pair

$$- Z_{He,VC} M_{He} C_{He} S_V - Z_{He,B} M_{He} C_{He} S_B + Z_{I,VHe} M_I C_I C_{VHe} + M_{He} T_{VHe} C_{VHe}$$

absorption by voids — absorption by bubbles — reaction of intersitials and V-He pair — dissociation of V-He pair

$$- M_{He} C_{He} C_{S,He} + C_B D_{B,He}$$

annihilation at permanent sinks — dissociation from bubbles

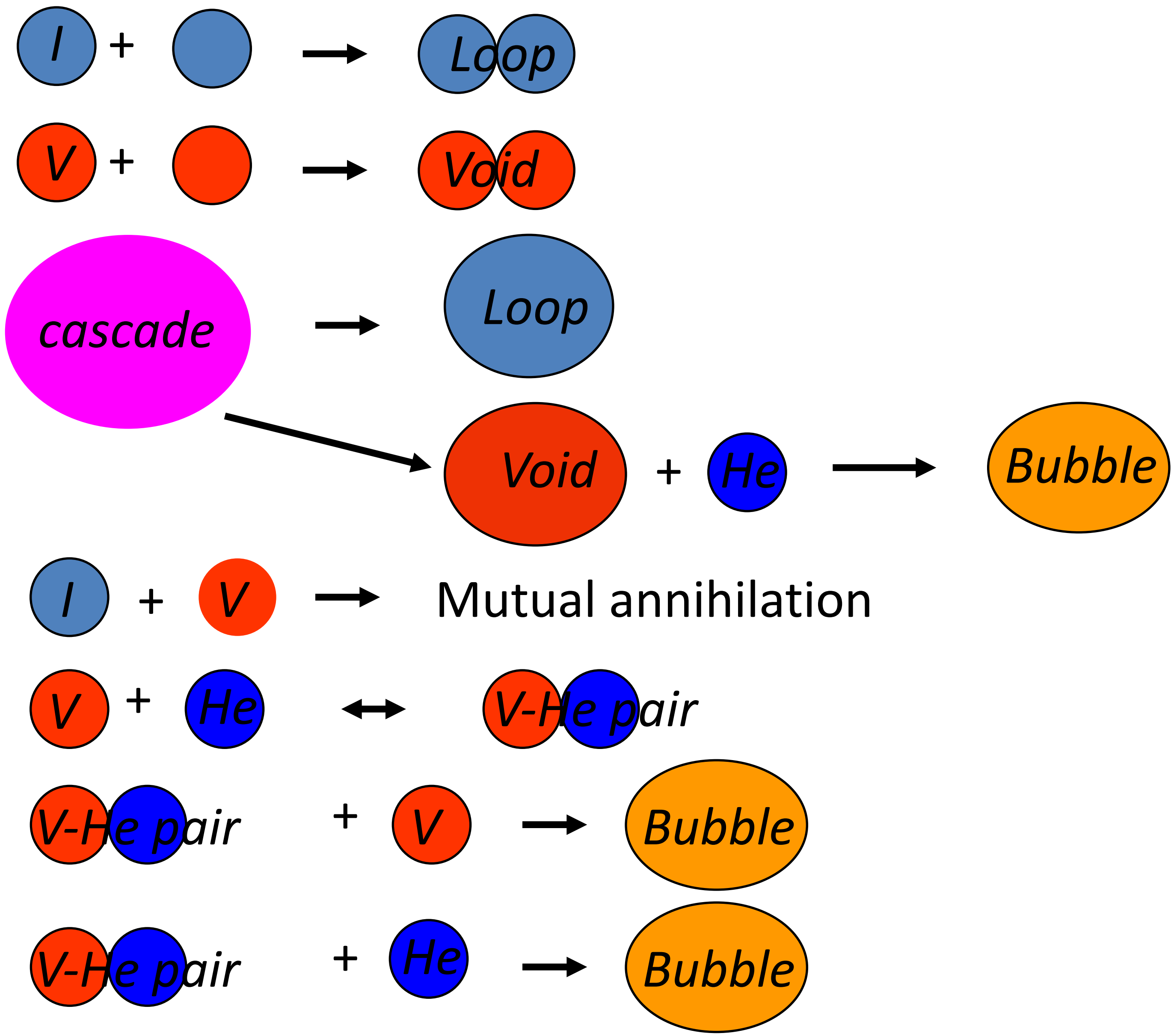
Terms marked by red squares lead to the formation of bubbles.

Only one term marked by blue square leads to the annihilation of He from matrix.

⇓

Helium atoms, which lead to the formation of bubbles, are too many.

Calculation model (1)

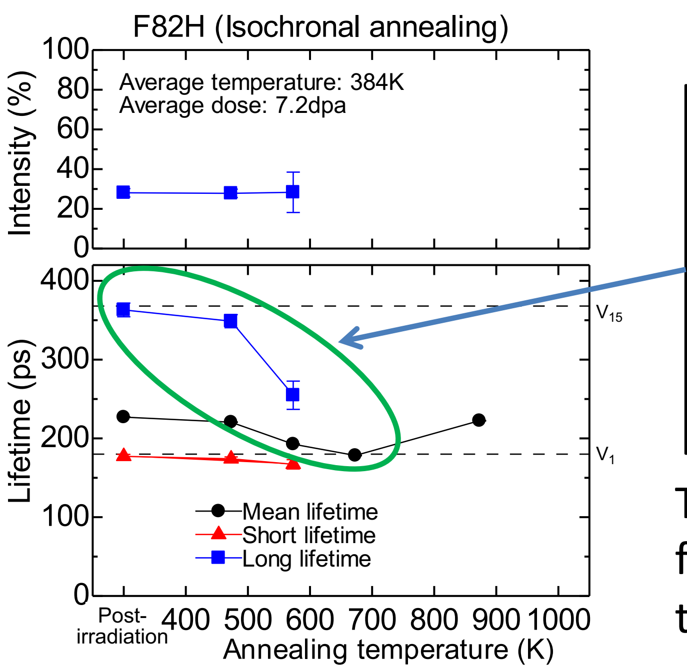


Revision of calculation model (Future plan)

- The following effects should be added.
  1. Interaction between He and interstitial clusters (loops)

     (Relatively strong trapping sites: E_b > 2 eV)
  2. Interaction between He and grain boundaries and interstitial impurities

     (Weak trapping sites: E_b= 1.2 – 1.8 eV)



We expect that the decrease of the positron lifetime is caused by the absorption of He by bubbles, and the He atoms are released from the weak trapping sites (grain boundaries and interstitial impurities).

The number of He atoms , which lead to the formation of bubbles, should decrease in the matrix.

Summary

- The growth process of helium bubbles was investigated by the rate theory analysis.

- The concentration and size of interstitial clusters and bubbles did not correspond with TEM observation. He-to-vacancy ratio was very high (～4.5), and did not change with the irradiation dose. This trend did not correspond with PA results.

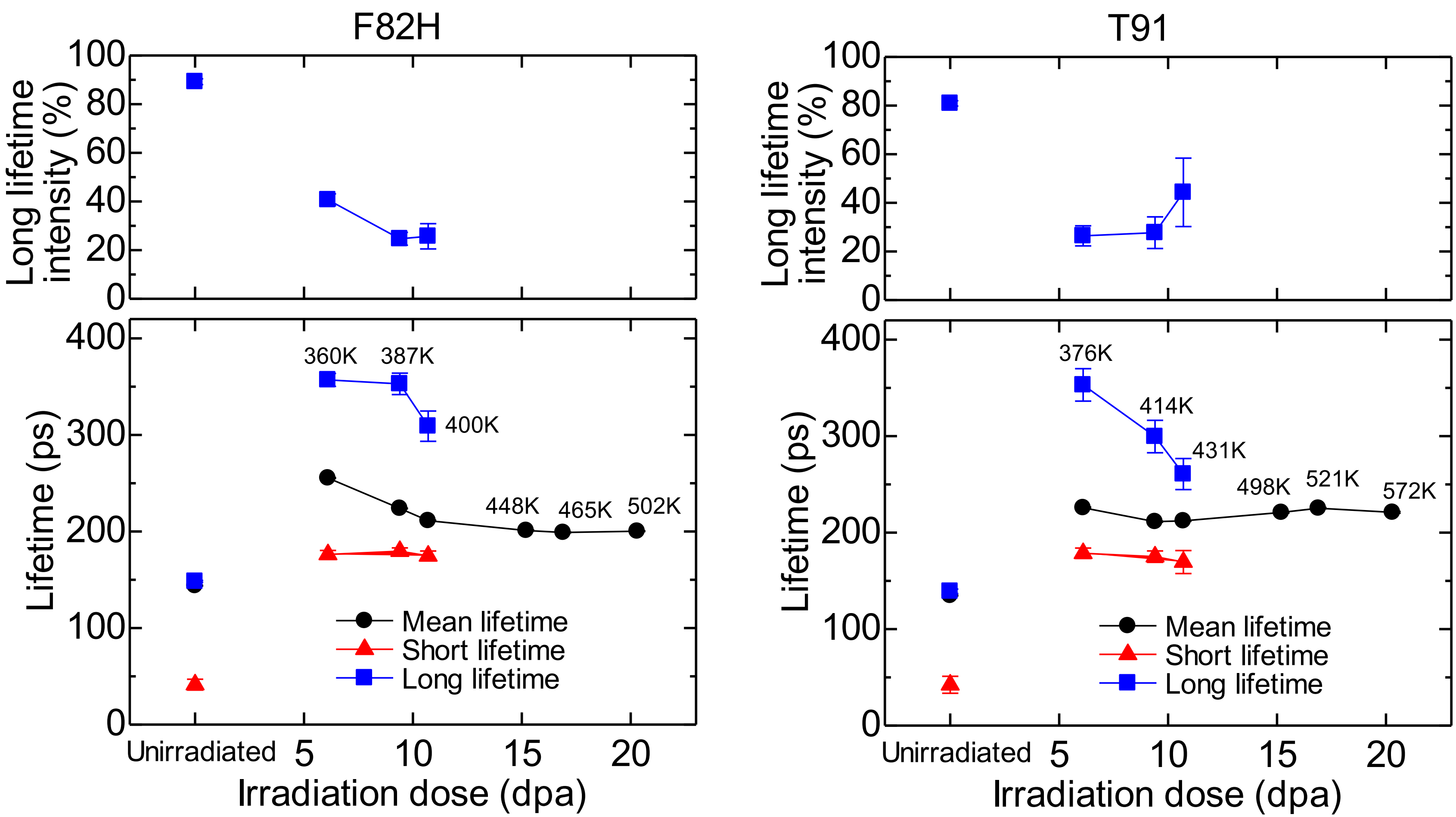
  →Parameters should be modified.

- New effects will be added in this rate theory analysis.

  →Helium trapping sites (Interstitial clusters, grain boundaries, interstitial impurities etc.)

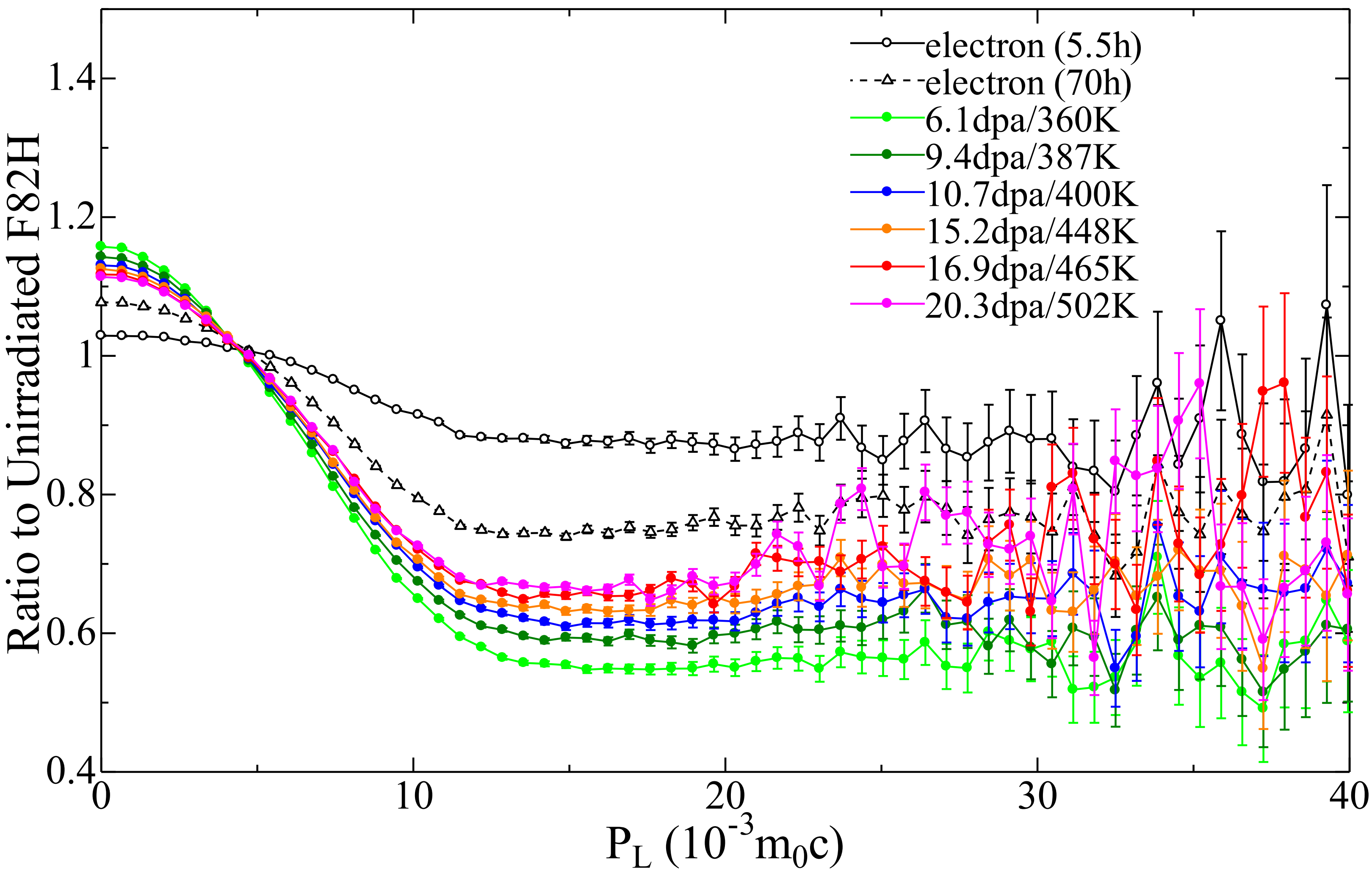
Dose dependence

Results of PAL measurements



- The long and mean lifetimes decrease with increasing the irradiation dose below 12 dpa.
- Spectra are not decomposed into two components above 12 dpa.

CDB ratio curves



We cannot see the conspicuous peak caused by the He atoms in all range.

Definition of S- and W-parameter

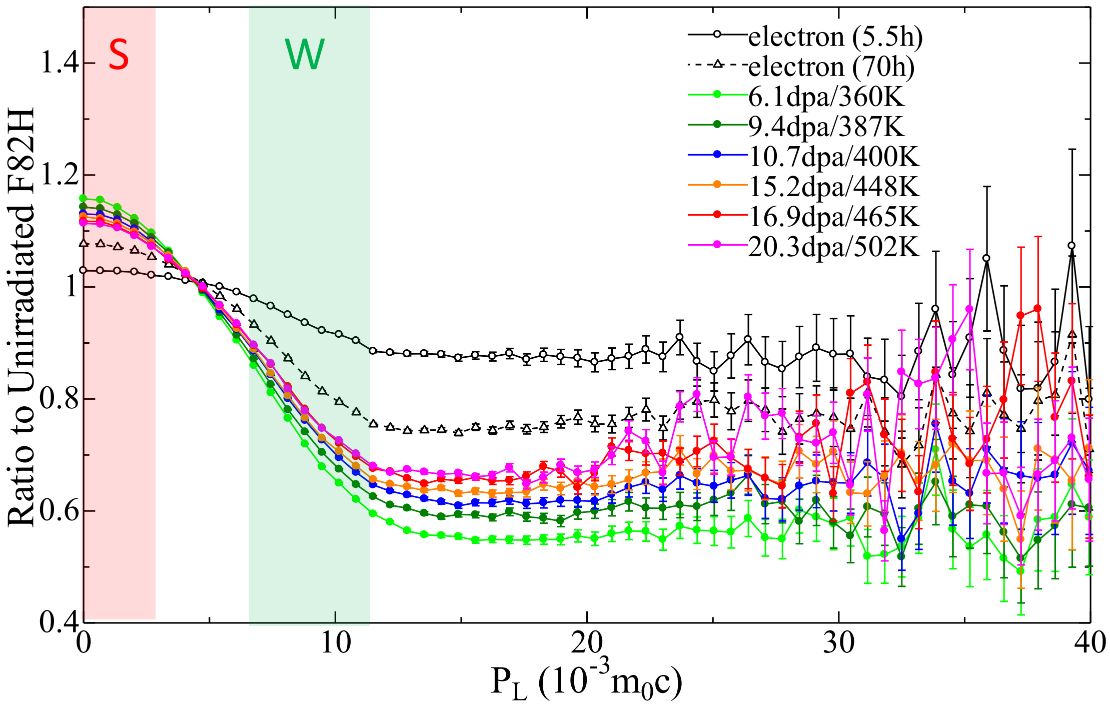
S-parameter: Ratio of the low-momentum ($|P_L|<2.5\times10^{-3}\,mc$) area to the total area

The amount of vacancy type defects

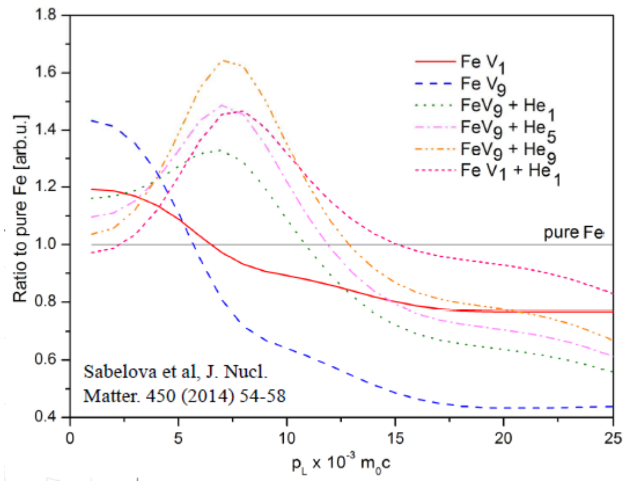
W-parameter: Ratio of high-momentum ($7\times10^{-3}\,mc < |P_L| < 12\times10^{-3}\,mc$) areas to the total area

The amount of precipitates or bubbles

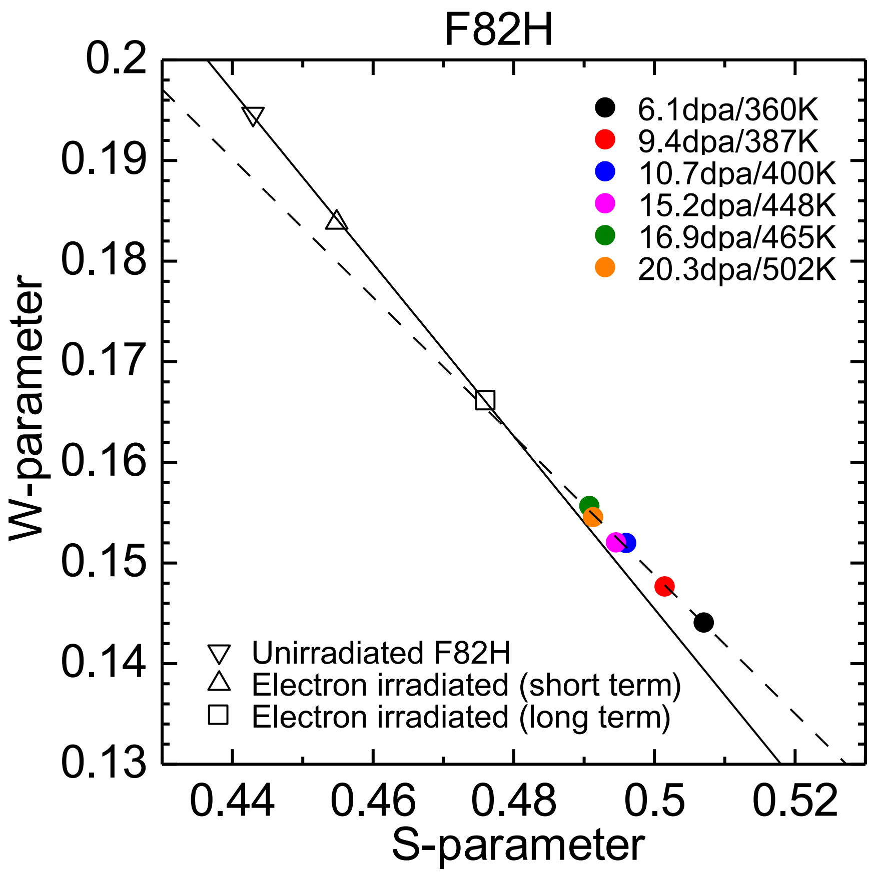
This region was decided from the previous study [Sabelova et al., J. Nucl. Mater. 450 (2014) 54.].



They reported that He atoms affect CDB ratio curves in the momentum of 5–12x10^{-3} mc by simulation.



S-W plots of F82H



Solid line denotes the change in electron irradiation.
Broken line denotes the change in STIP.

- Electron irradiation introduces only defects. Therefore, solid line denotes the change in *S*- and *W*-parameter only by the defect formation.
- Vacancy clusters contain He atoms in STIP samples.

Positron trapping rate into He bubbles is smaller than that into empty voids. So , the change in *S*- and *W*-parameter should be different between electron irradiation and STIP.

Difference of gradient of two lines is due to the He effect.

PAL of vacancy clusters-He complexes in Fe

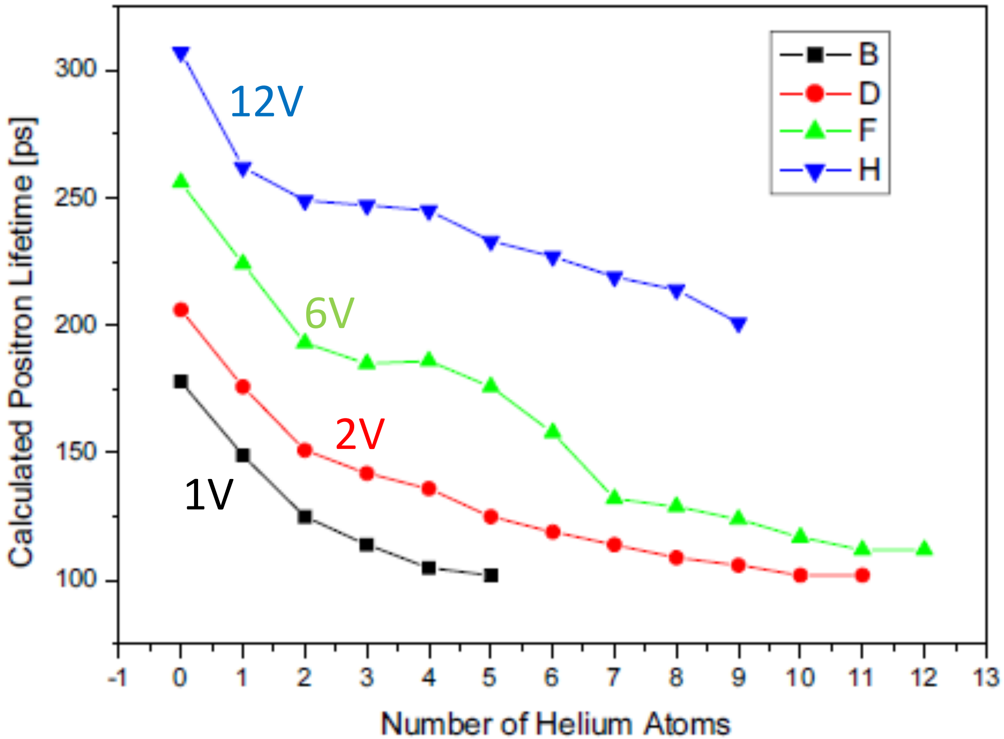


Figure 4 Correlation between positron lifetime and the number of helium atoms in nano-void (B) 1V+nHe, (D) 2V+nHe, (F) 6V+nHe, (H) 12V+nHe.

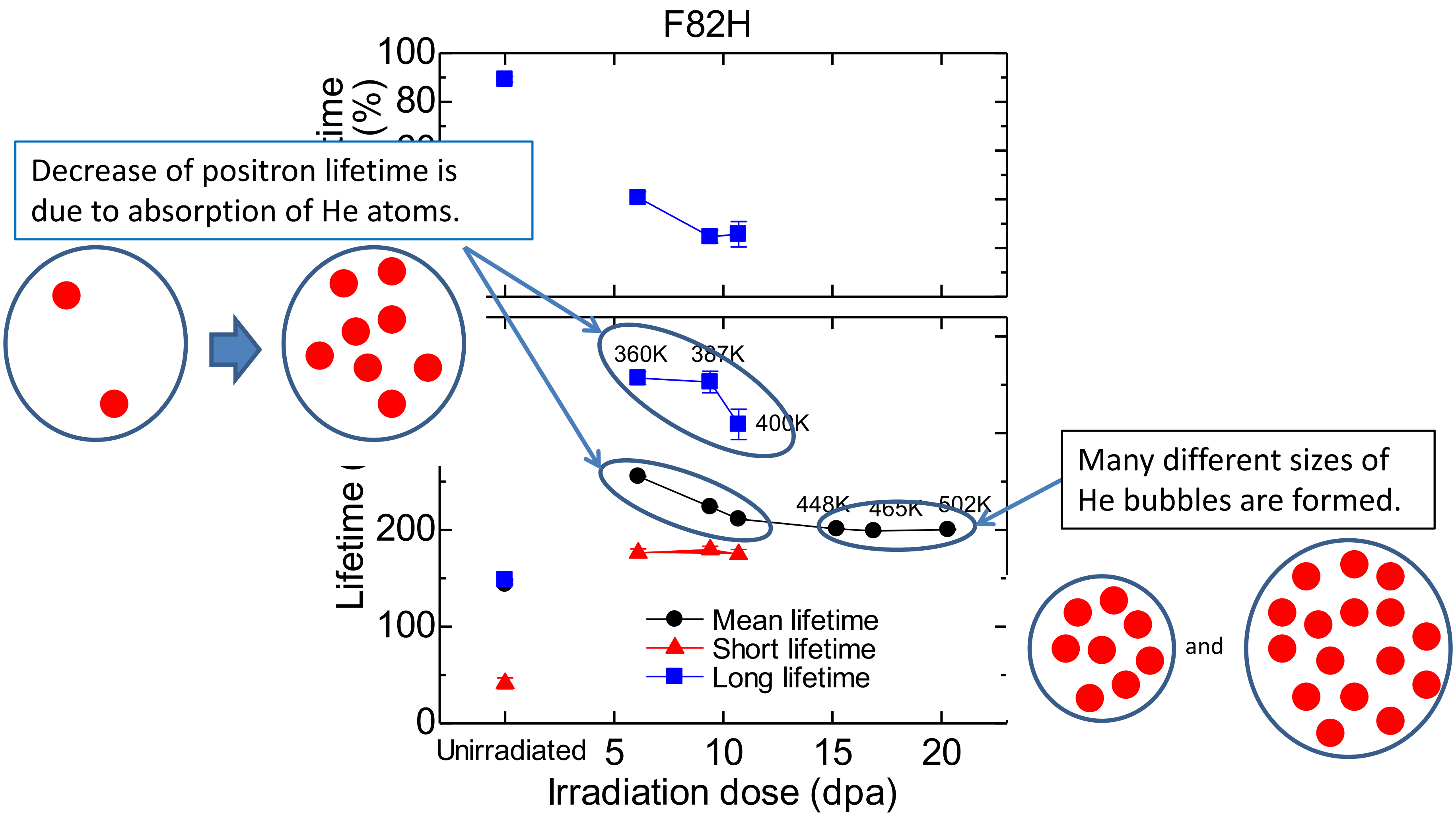
[Troev et al., Phys. Status Solidi C 6 (2009) 2373]

Change in PAL by He effect

From S-W plot, change in PAL is due to He absorption process.

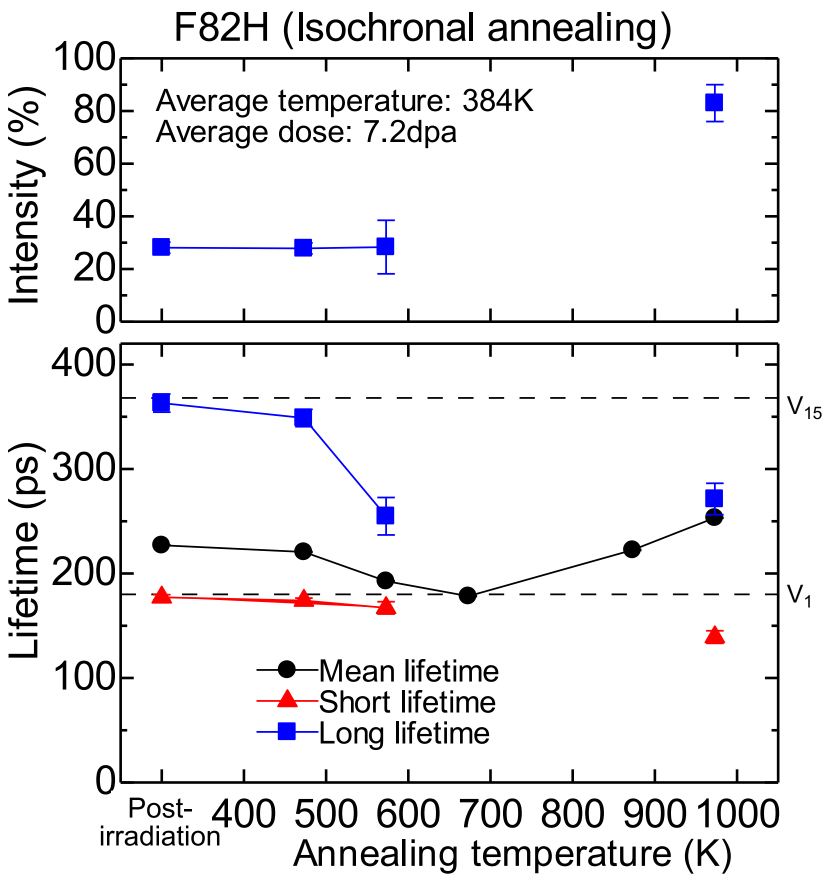
Decrease of positron lifetime is due to absorption of He atoms.

Many different sizes of He bubbles are formed.



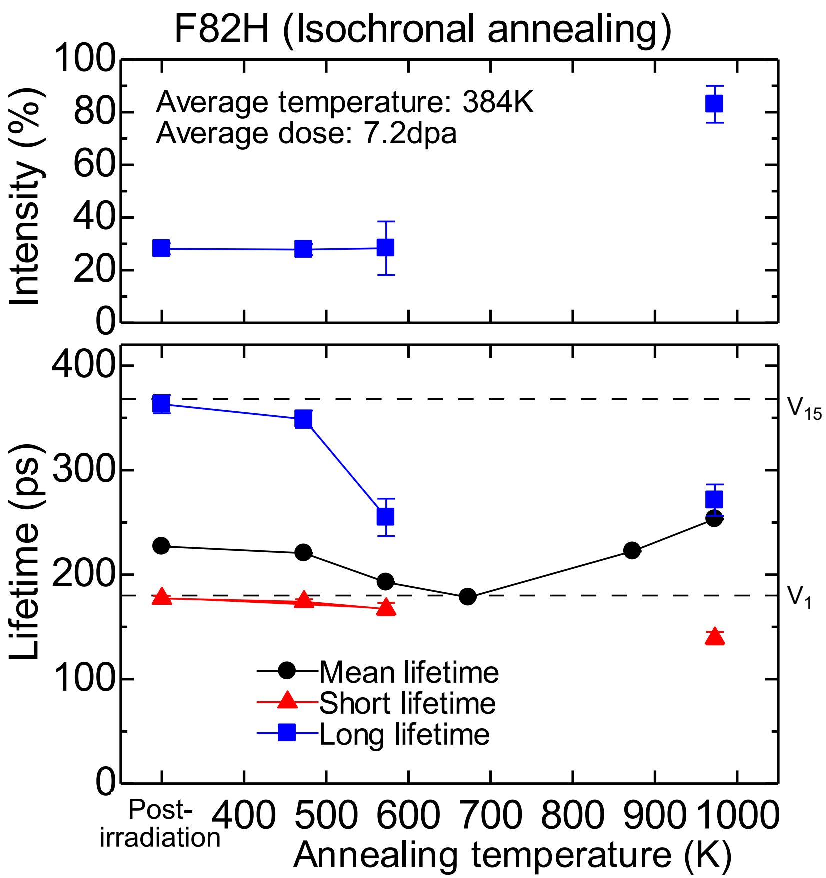
Isochronal annealing

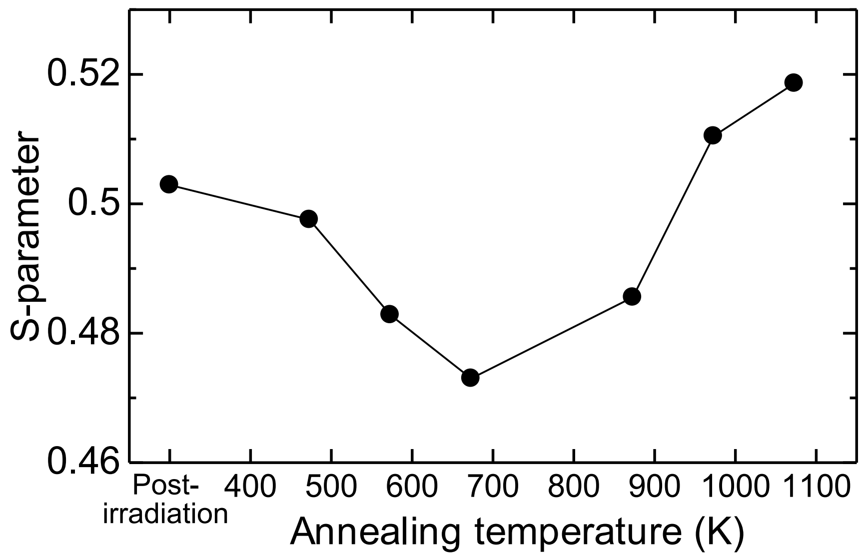
Change in PAL



- The long and mean lifetimes decrease as the annealing temperature is increased up to 673 K.
- Lifetime spectra are not decomposed into two components after annealing at 673 K.
- Spectrum is decomposed into two components in 973 K annealing again.

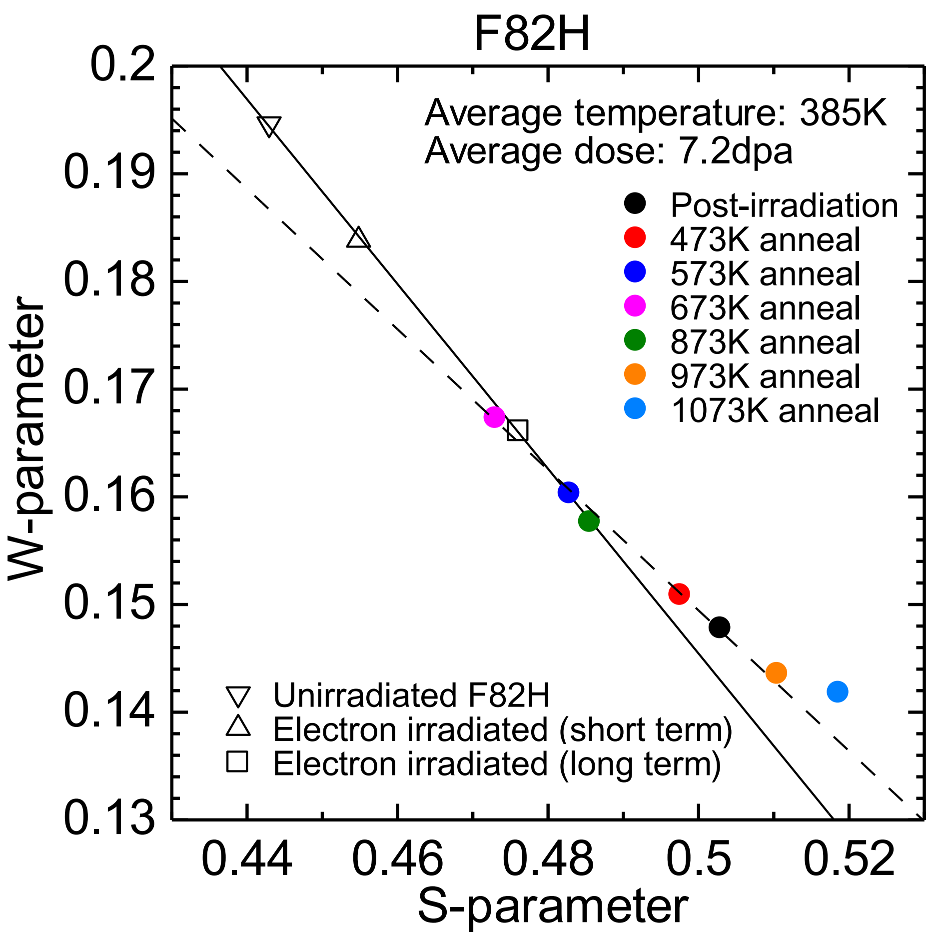
Change in PAL and S-parameter





Variation in *S*-parameter is almost the same as that in mean positron lifetime.

S-W plots of F82H



Solid line denotes the change in electron irradiation.

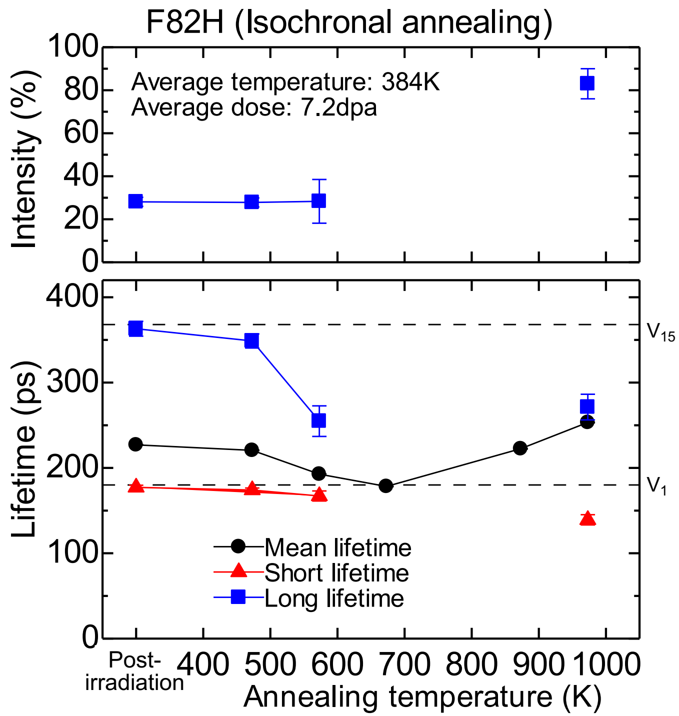
Broken line denotes the change between post-irradiation and samples annealed up to 673 K.

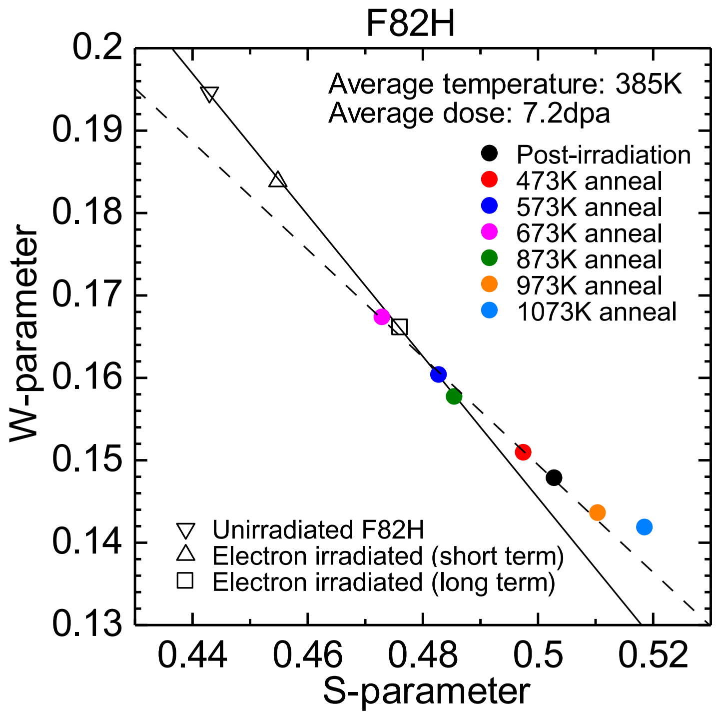
These data points in STIP(from post-irrad. to 673K annealing) are clearly on broken line.

Data points for 873K and 973 K annealing start to shift, and a data point for 1073K shift obviously.

Change from post-irrad. to 673K is due to the He effect.
After that, different process started.

S-W plots of F82H





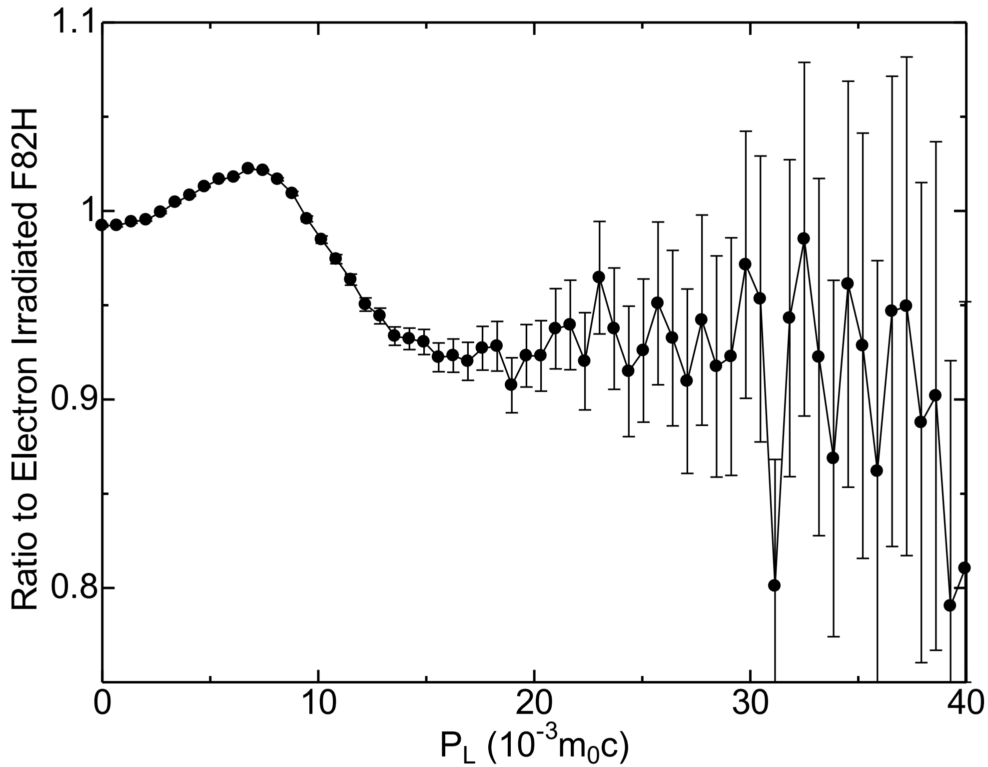
Below 673 K: Size of He filled vacancy clusters does not change, and they absorb He atoms weakly trapped in the matrix.

Above 873 K: He filled vacancy clusters absorb vacancies and release H atoms. The size of He filled vacancy clusters increases.

He filled vacancy clusters dissociate above 773 K.
[R. Sugano et al., J.Nucl. Mater. 329–333 (2004) 942]

This process is well known, however, we can detect it using positron annihilation spectroscopy.

Detection of He peak in CDB ratio curve



CDB ratio curve of F82H irradiated in STIP-II and annealed at 673 K to F82H irradiated with electrons for 70 h

The peak in the range of 5−12 x 10^{-3} *mc* can be detected.
This result agrees with previous study [Sabelova et al., J. Nucl. Mater. 450 (2014) 54.].

Summary

- PAL and CDB measurements of F82H and T91 irradiated with protons and neutrons at SINQ were performed.

- The change in PAL can be explained by the He effect.

  Dose dependence

  - In low dose region, vacancy clusters absorb He atoms, and PAL decreased.
  - In high dose region, the vacancy clusters containing a large amount of He atoms are formed.

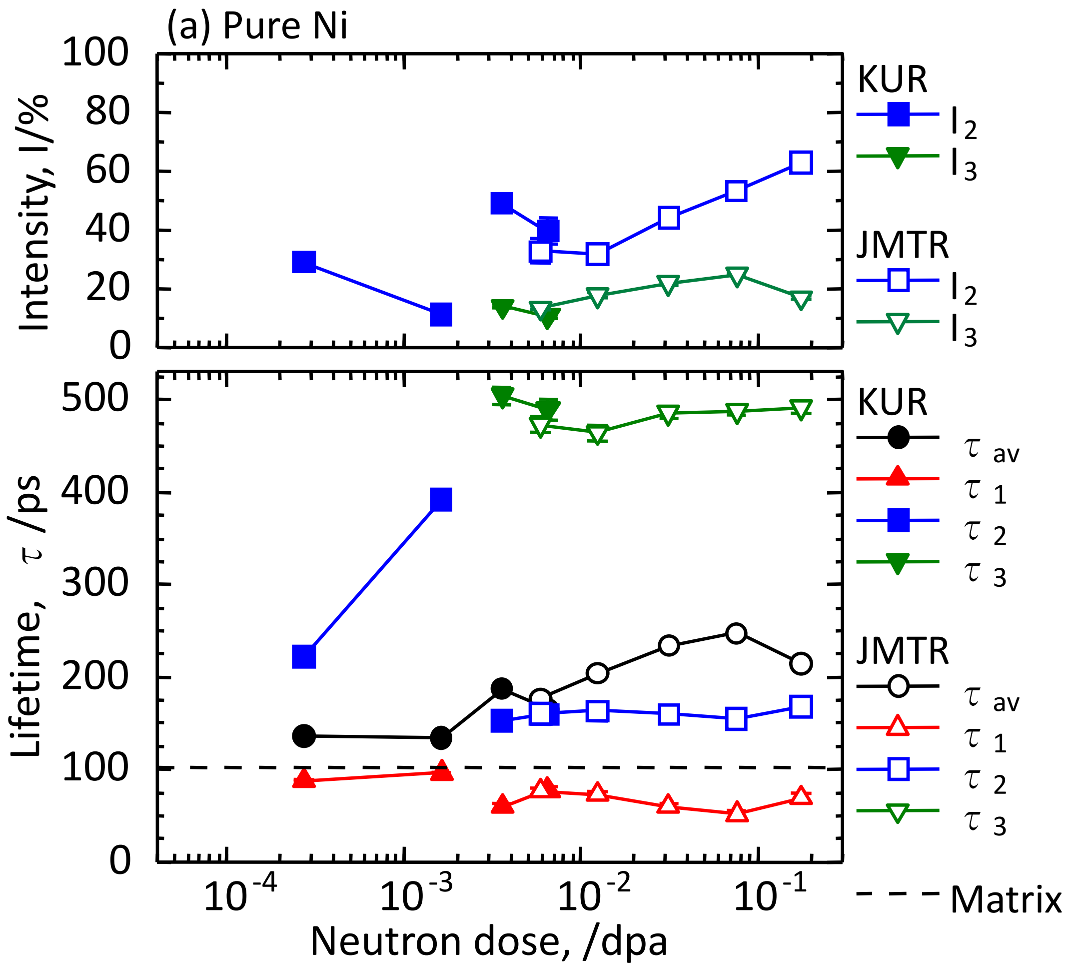
  Isochronal annealing

  - Below 673 K, He filled vacancy clusters absorbed more He atoms.
  - Above 873 K, He filled vacancy cluster size increased.

- The effect of He atoms on the CDB ratio curves was also detected.

- We could obtain a better understanding of He bubble growth by performing both PAL and CDB measurements.

PAL in fission neutron-irradiated Ni

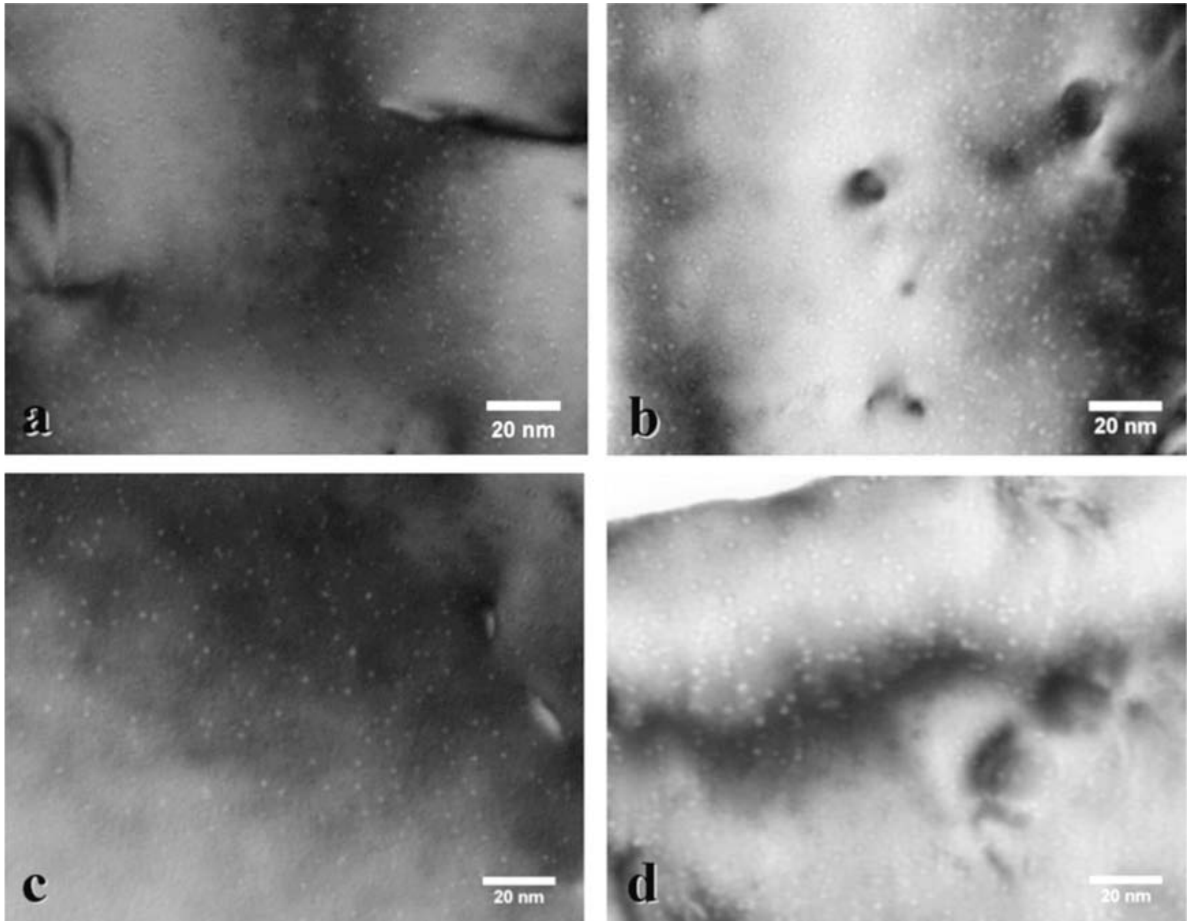


In more than 0.01dpa, positron lifetime is saturated, but void growth is observed by TEM.

TEM images of T91 irradiated in STIP-III

9.5dpa

13.6dpa



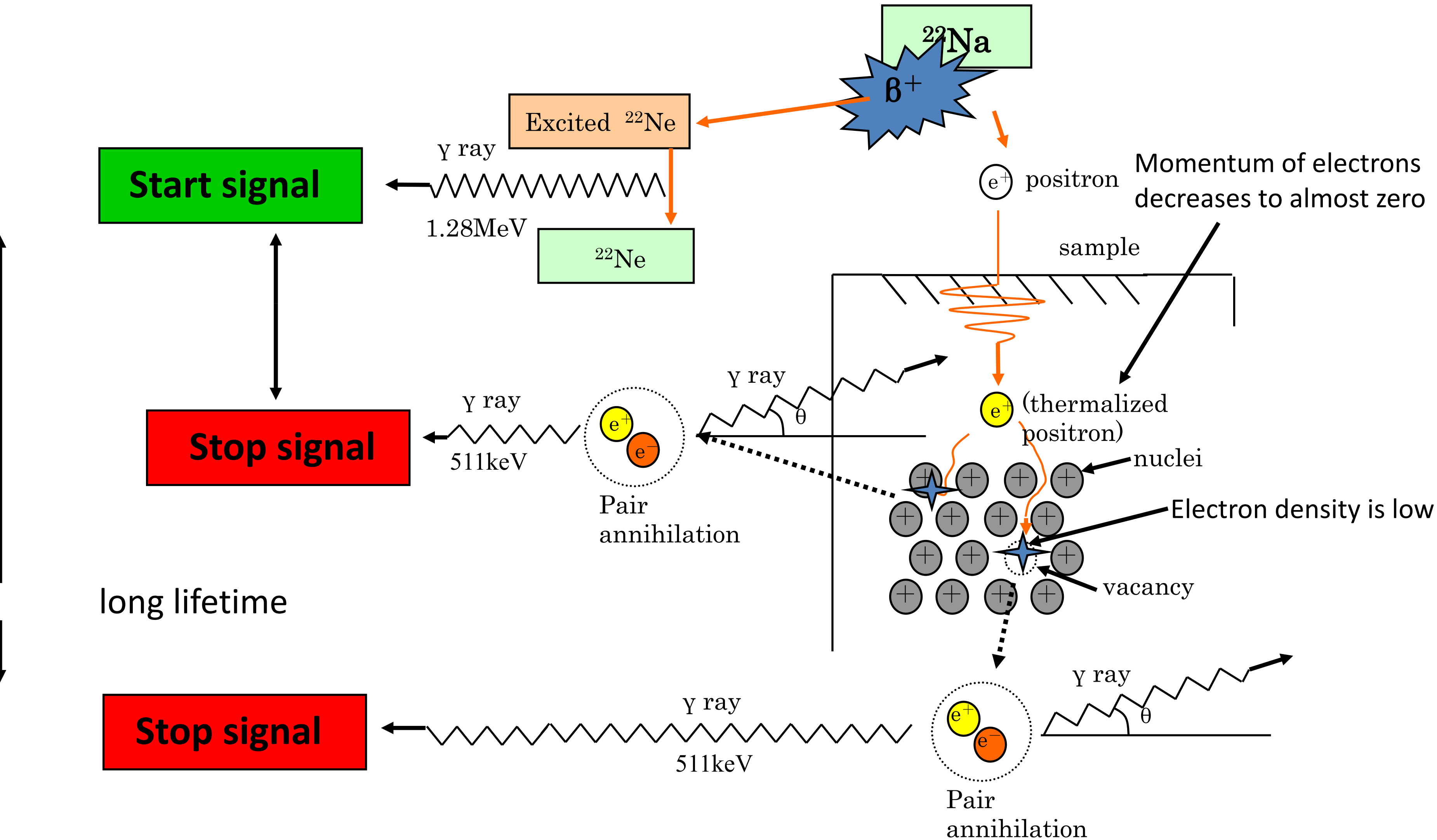
17.3dpa

20.3dpa

[Tong et al., J. Nucl. Mater. 398 (2010) 43]

Helium bubbles grow.

Positron annihilation lifetime measurement



Calculated positron annihilation lifetime

Table 1
The calculated positron lifetimes and binding energies for vacancy clusters in Ni, Cu, and Fe as a function of the cluster size

Ni			Cu			Fe		
Defect	τ (ps)	E_b (eV)	Defect	τ (ps)	E_b (eV)	Defect	τ (ps)	E_b (eV)
Bulk	100	0.00	Bulk	110	0.00	Bulk	104	0.00
V_1	169	3.34	V_1	173	2.35	V_1	180	3.56
V_2	188	3.82	V_2	196	2.74	V_2[a]	187/202	3.86/4.11
V_4	246	4.66	V_4	255	3.36	V_5	246	4.89
V_7	265	4.92	V_7	274	3.57	V_9	280	5.32
V_{13}	341	5.54	V_{13}	348	4.07	V_{15}	368	6.01
V_{19}	371	5.77	V_{19}	377	4.28	V_{27}	396	6.27
V_{43}	410	6.15	V_{43}	413	4.62	V_{51}	419	6.55
V_{55}	420	6.28	V_{55}	421	4.74	V_{59}	426	6.69
V_{79}	427	6.42	V_{79}	428	4.86	V_{65}	427	6.72
V_{177}	435	6.60	V_{177}	436	5.02	V_{137}	435	6.91

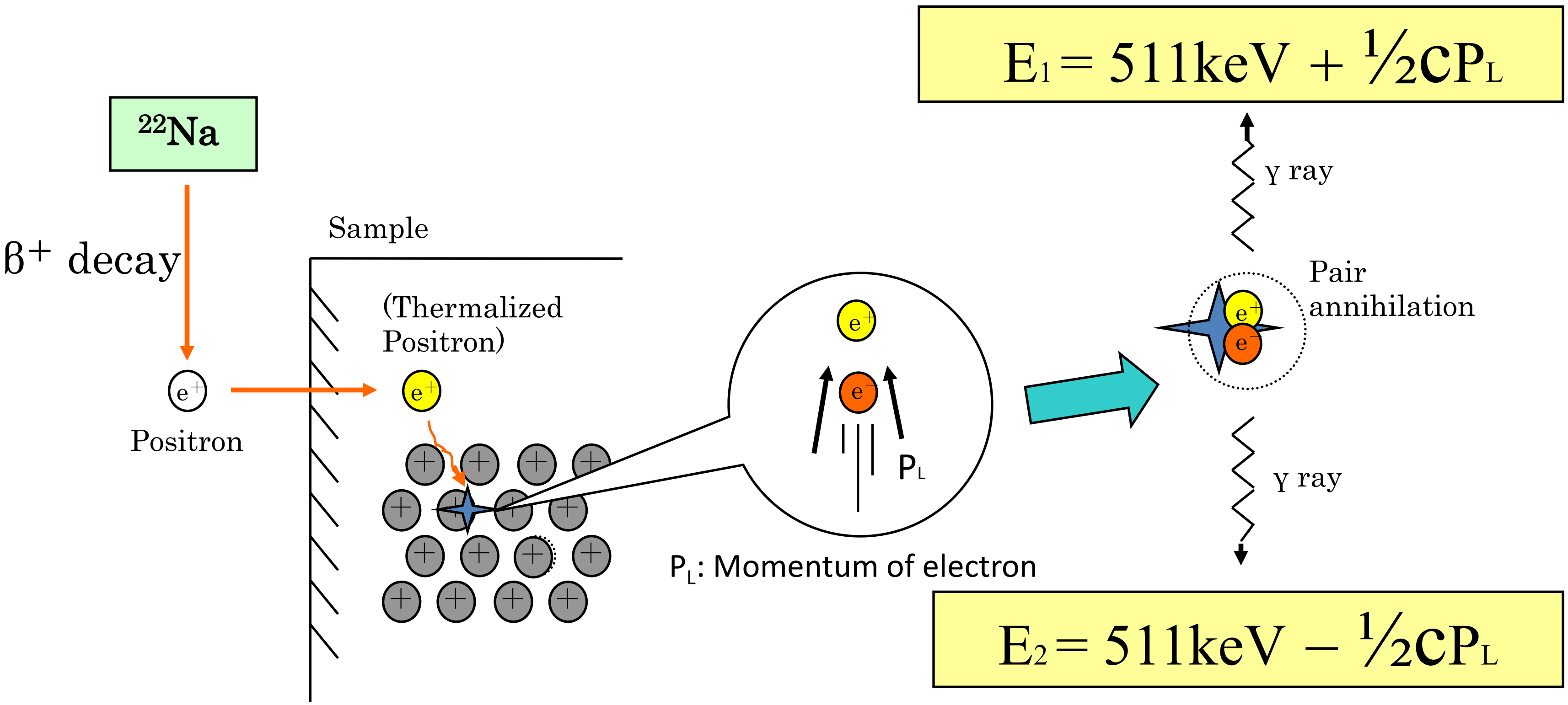
[a] The values are listed for two distinct divacancy geometries, i.e. V_2 along [111] and [100] directions.

[H. Ohkubo et al., Mater. Sci. Eng. A350 (2003) 95.]

- Positron lifetime is proportional to the size of vacancy clusters.

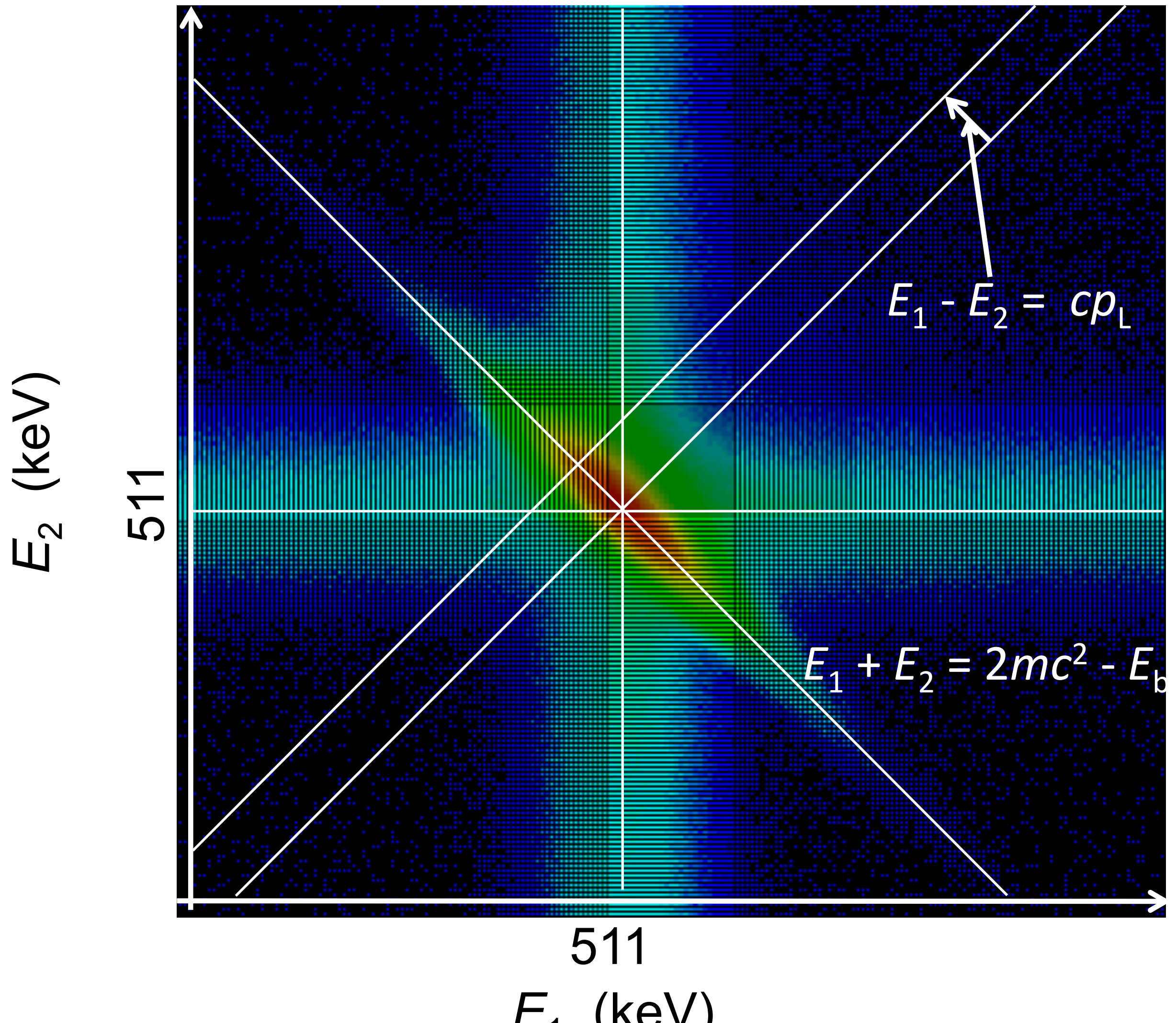
- In metallic system, positron lifetime is less than 500ps.
  500ps is saturation value of positron lifetime.
  Even if voids grow and are observed by TEM, positron lifetime of voids is less than 500ps.

CDB measurement

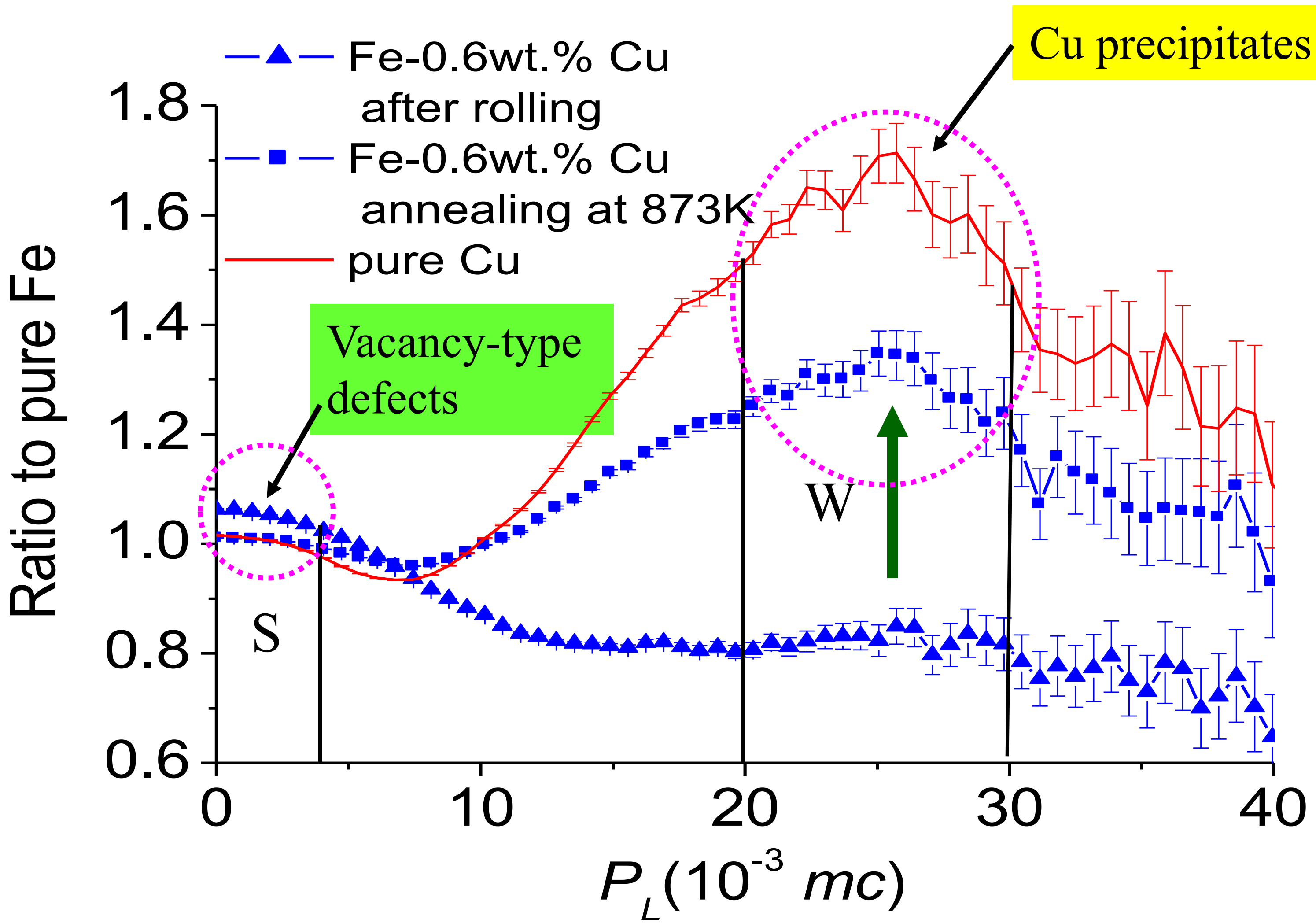


※c: light velocity

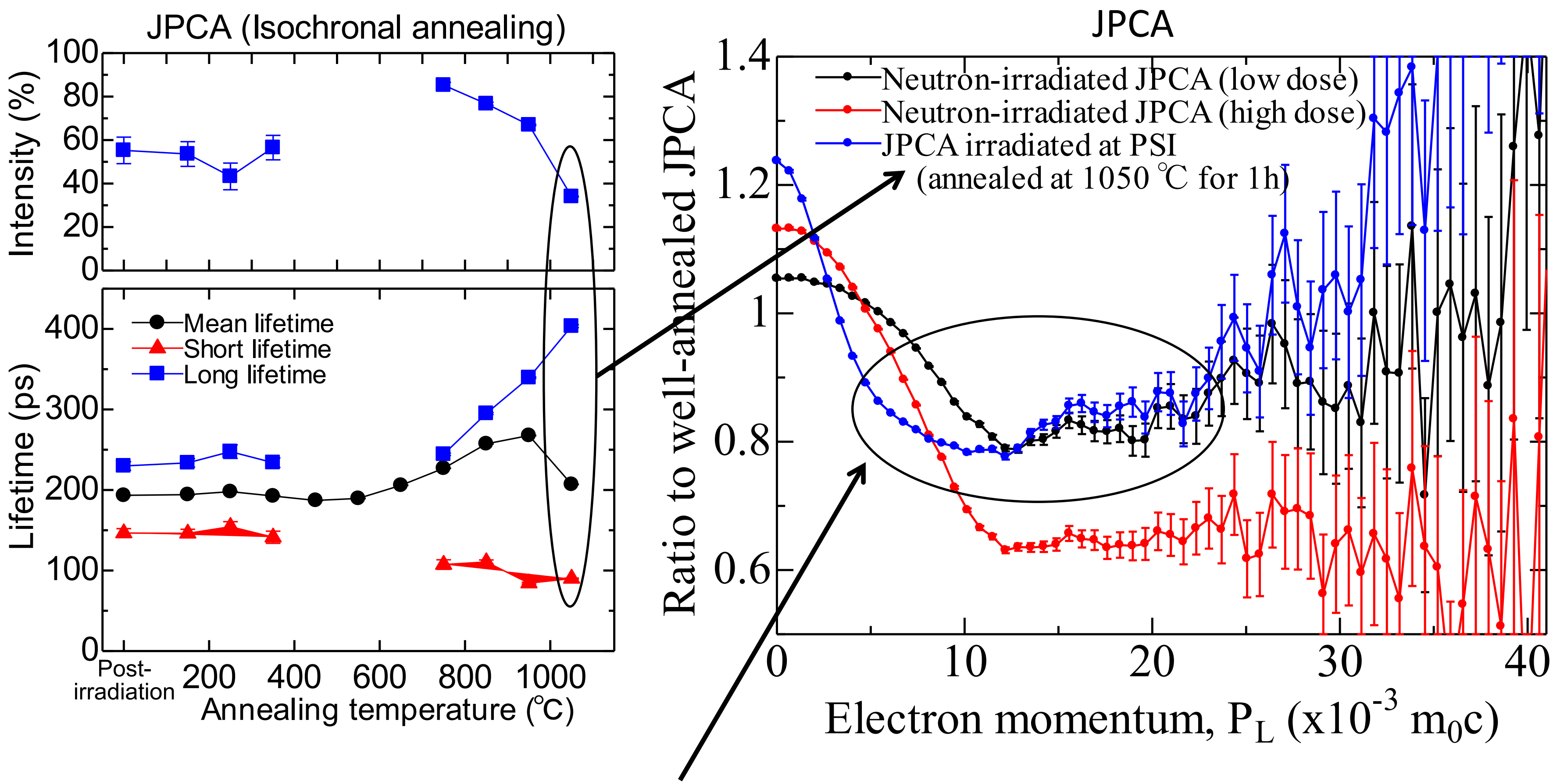
CDB spectrum



CDB ratio curve of Fe-Cu alloy



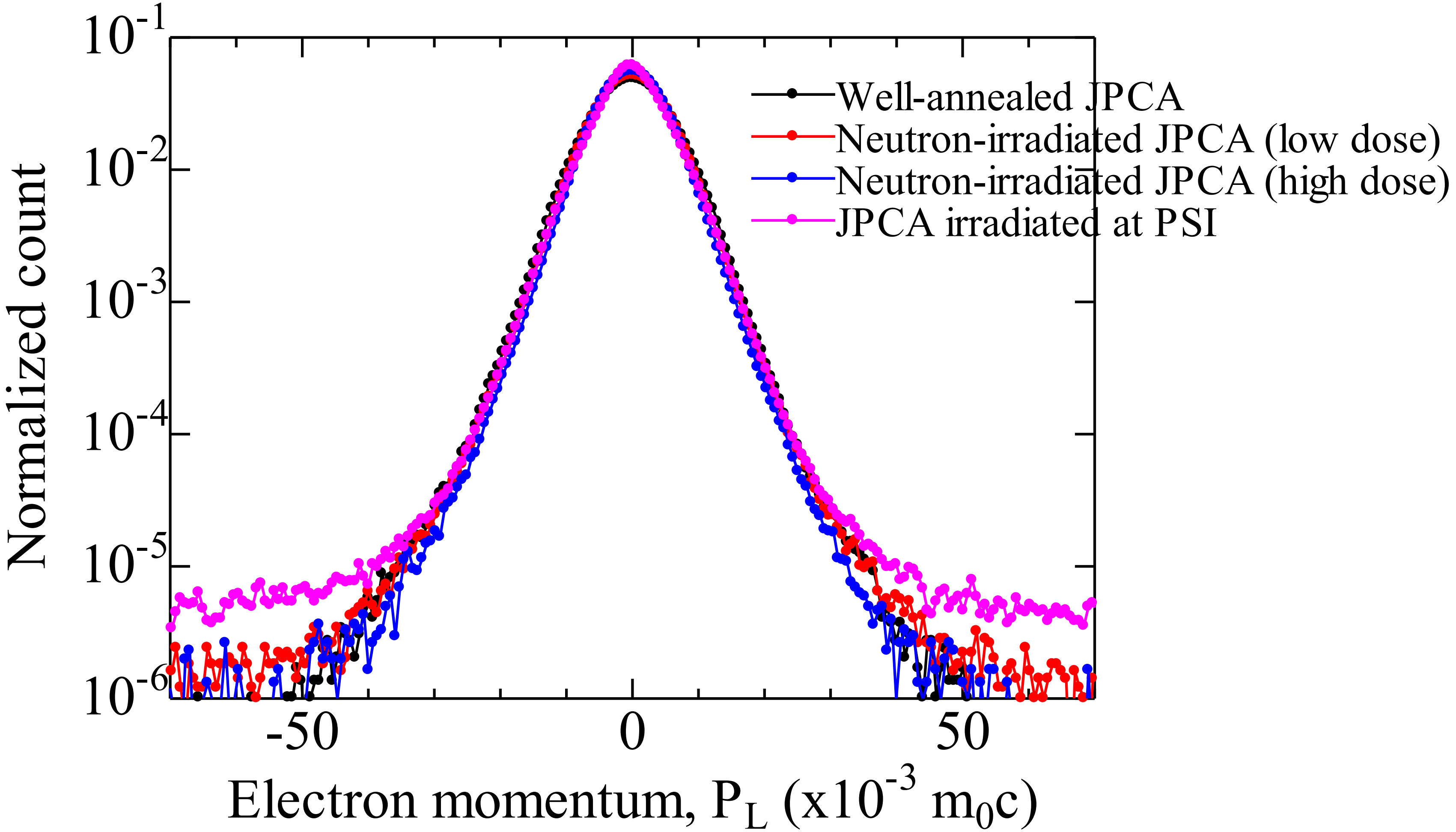
CDB ratio curves



Usually, when low momentum region increases, high momentum region decreases.
But high momentum region of JPCA irradiated at PSI was higher than other samples.
This is due to helium effect??

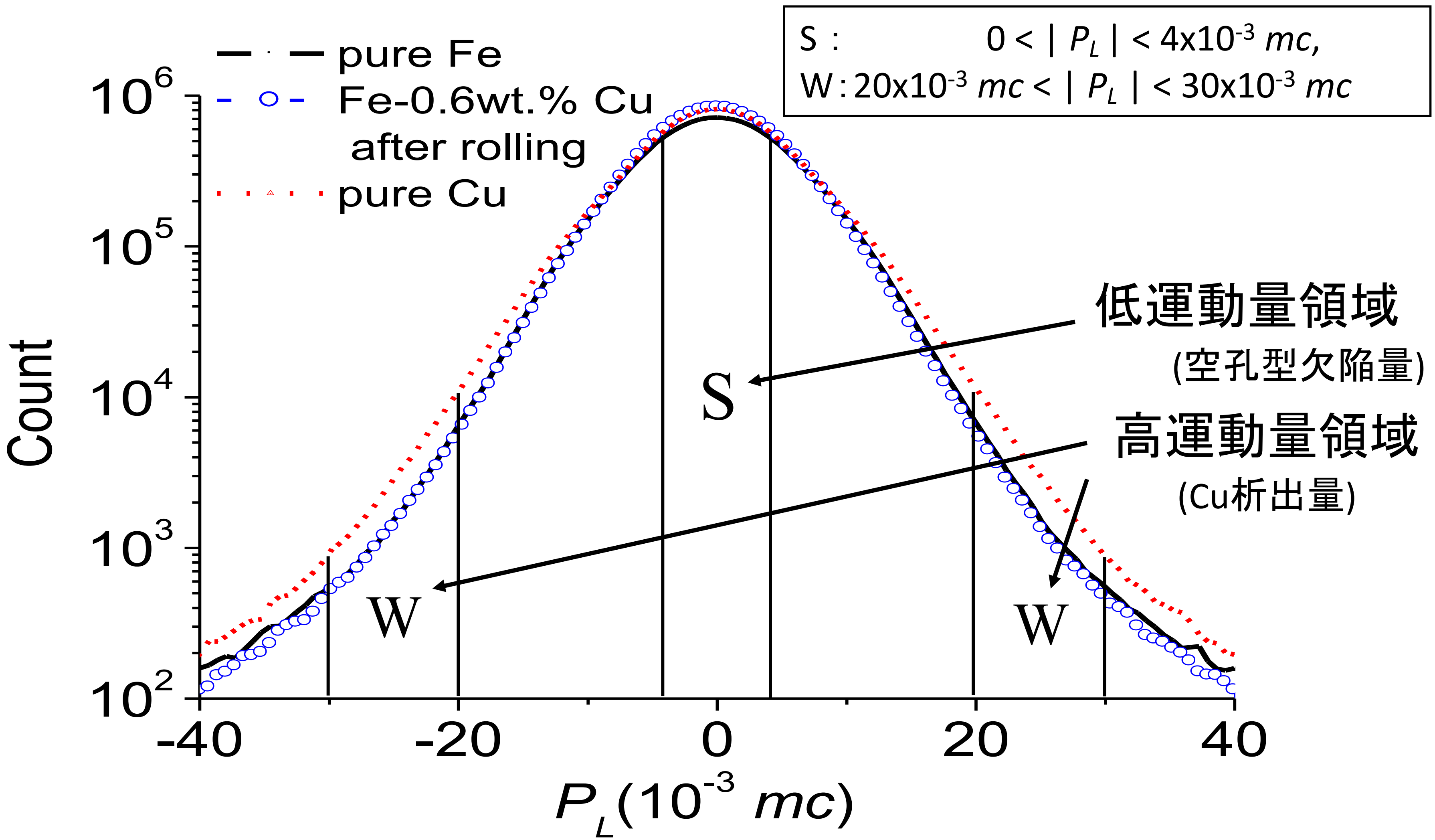
The amount of data is too small to estimate He effect.

CDB spectra



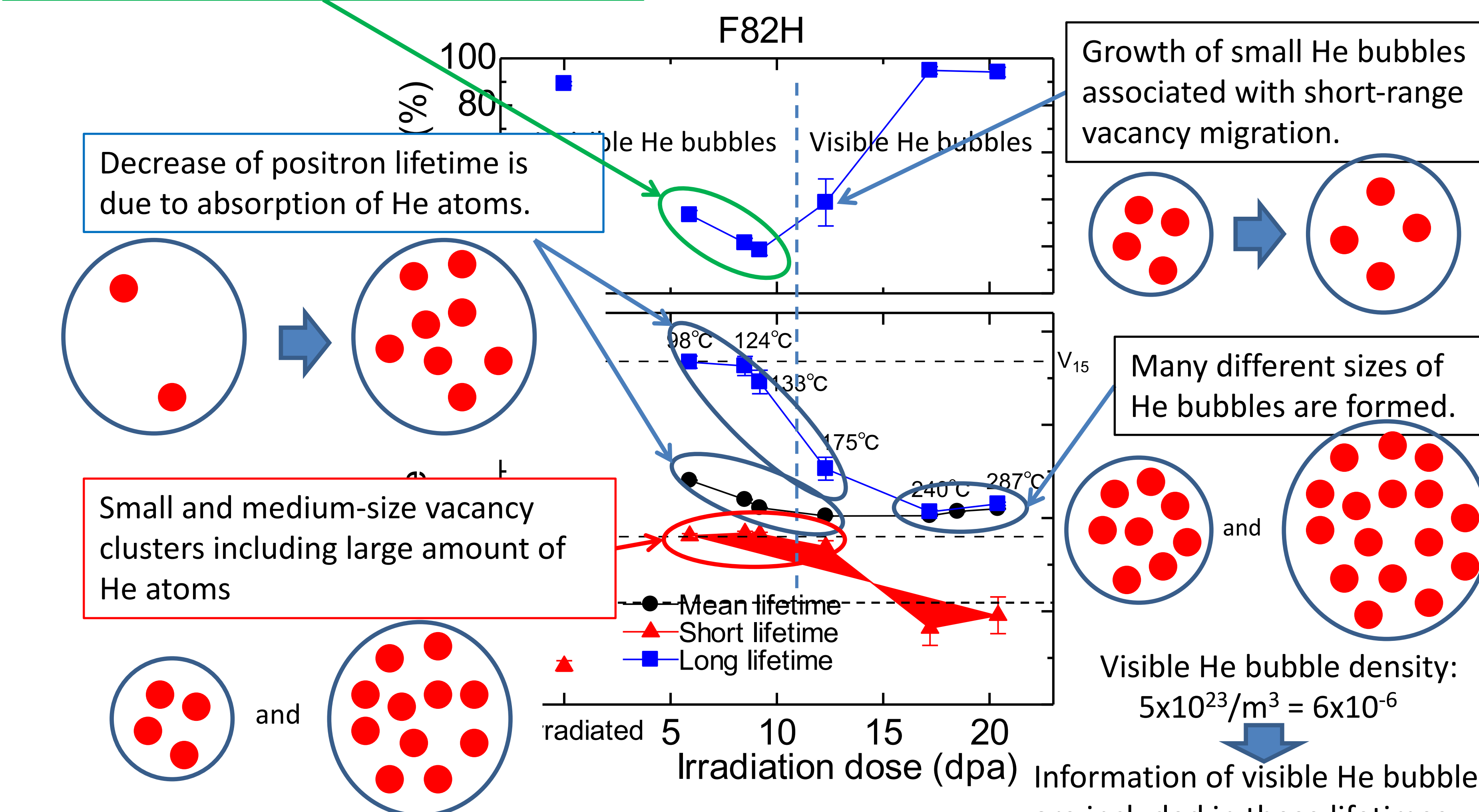
Well-annealed JPCA
Neutron-irradiated JPCA (low dose)
Neutron-irradiated JPCA (high dose)
JPCA irradiated at PSI
Normalized count
10-1
10-2
10-3
10-4
10-5
10-6
-50
0
50
Electron momentum, PL (x10-3 m0c)

Sパラメータとパラメータ（CDB測定）



Dose dependence of positron lifetime in F82H

Formation of visible He bubbles in F82H:
above about 170℃ and about 500 appm He
[X. Jia et al., J. Nucl. Mater. 305 (2002) 1.]

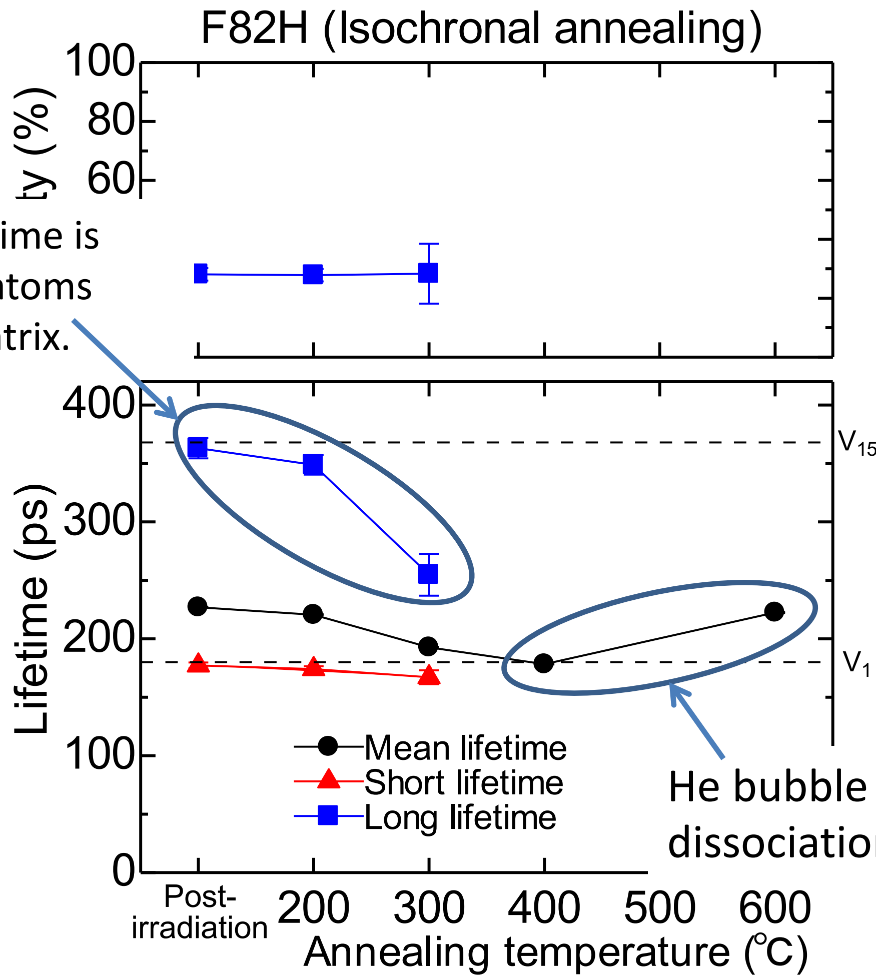


Visible He bubble density:
$5 \times 10^{23}/m^3 = 6 \times 10^{-6}$

Information of visible He bubbles are included in these lifetimes

Annealing behavior of F82H

Decrease of positron lifetime is due to absorption of He atoms weakly trapped in the matrix.



He bubble size increase because of dissociation of V-He$_n$ complexes.

500℃: V-He$_n$ complexes dissociate
700℃: V$_m$-He$_n$ complexes dissociate
1100℃: Large He bubbles dissociate

TDS measurements of Fe-Cr alloys

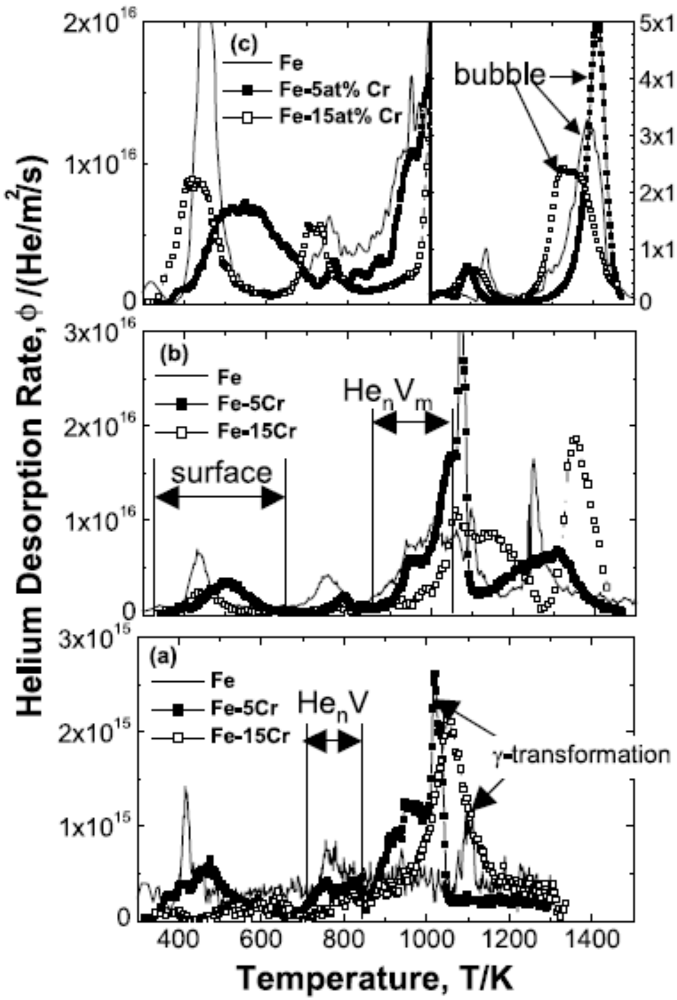
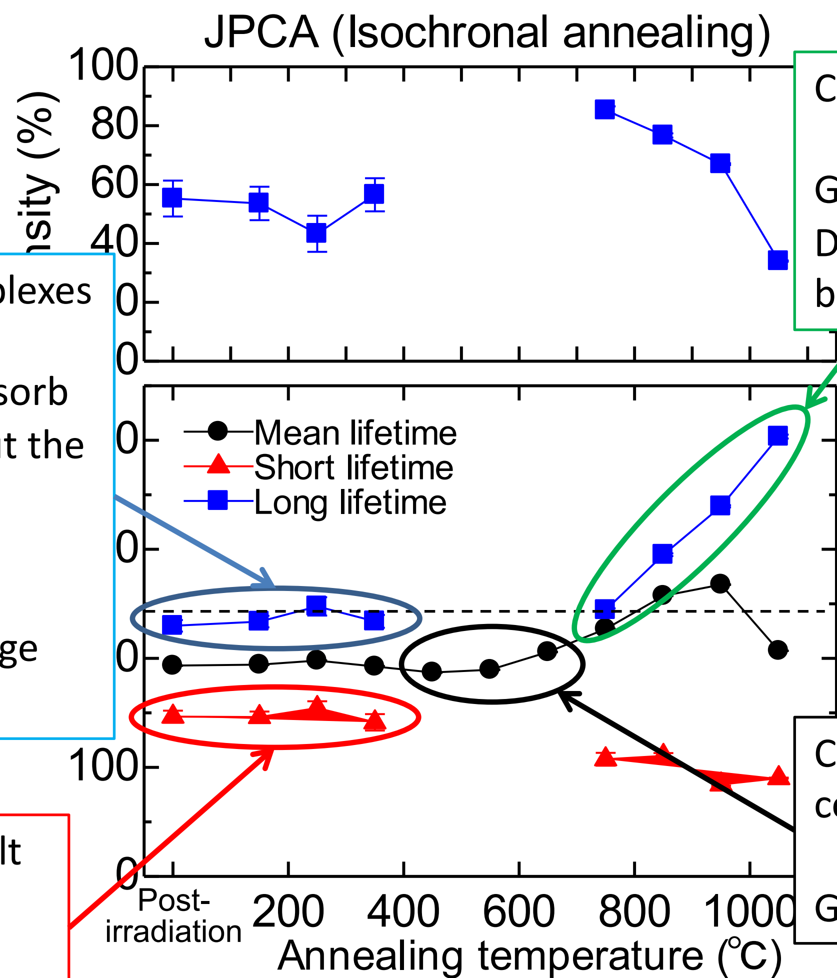


Fig. 1. He desorption spectra of Fe, Fe–5Cr and Fe–15Cr irradiated by 8 keV He+ ions at room temperature. The irradiation doses are (a) 1017, (b) 1018 and (c) 10^{19} He^+/m^2.

500℃: V-He_n complexes dissociate
700℃: V_m-He_n complexes dissociate
1100℃: Large He bubbles dissociate

[R. Sugano et al., J.Nucl. Mater. 329–333 (2004) 942]

Annealing behavior of JPCA



Formation of V_m-He_n complexes

It is expected that they absorb He atoms by annealing, but the lifetime does not change.

After irradiation, V_m-He_n complexes may include large amount of He atoms.

Formation of stacking fault tetrahedra (SFTs), dislocation loops, V-He_n complexes.

Collapse of V_m-He_n complexes

Growth of He bubbles

Density of He atoms in He bubbles decreases.

Collapse of SFTs and V-He_n complexes

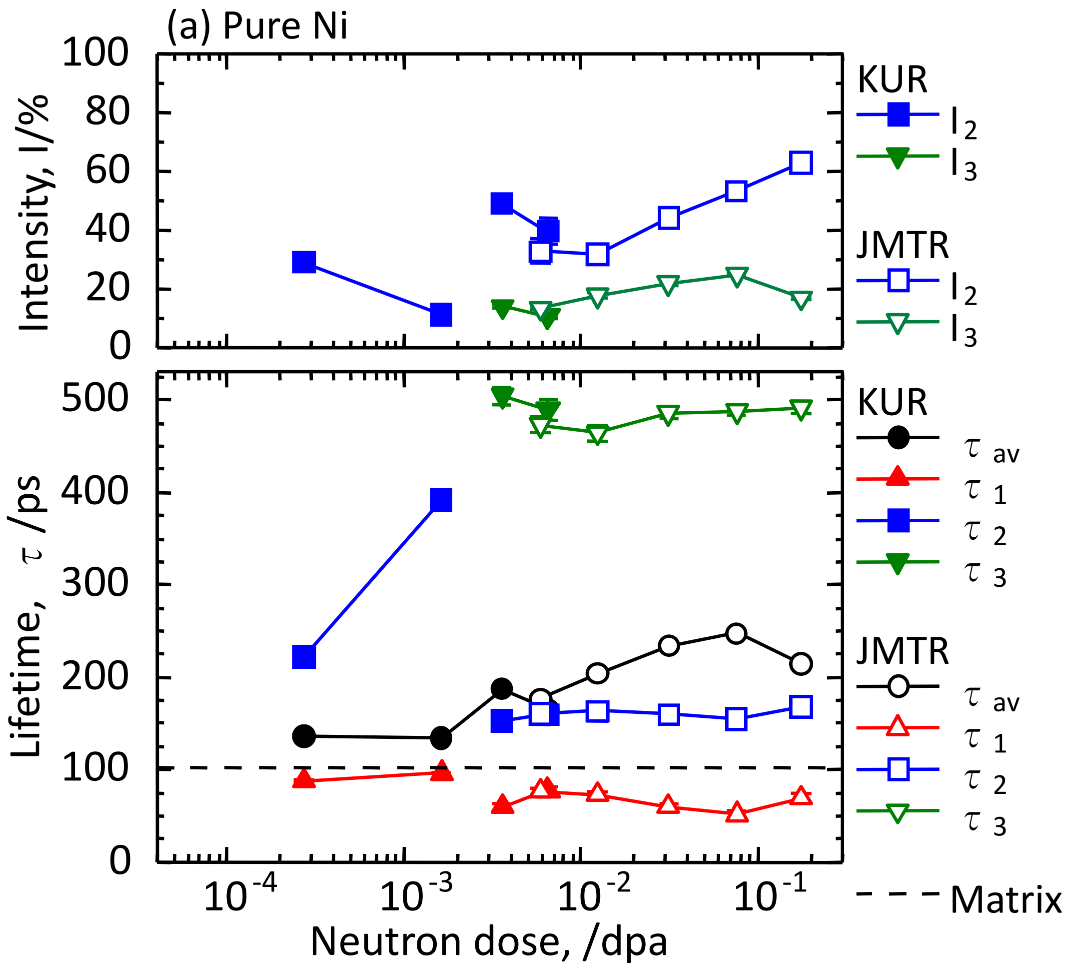
Growth of He bubbles

500℃: V-He_n complexes dissociate

700℃: V_m-He_n complexes dissociate

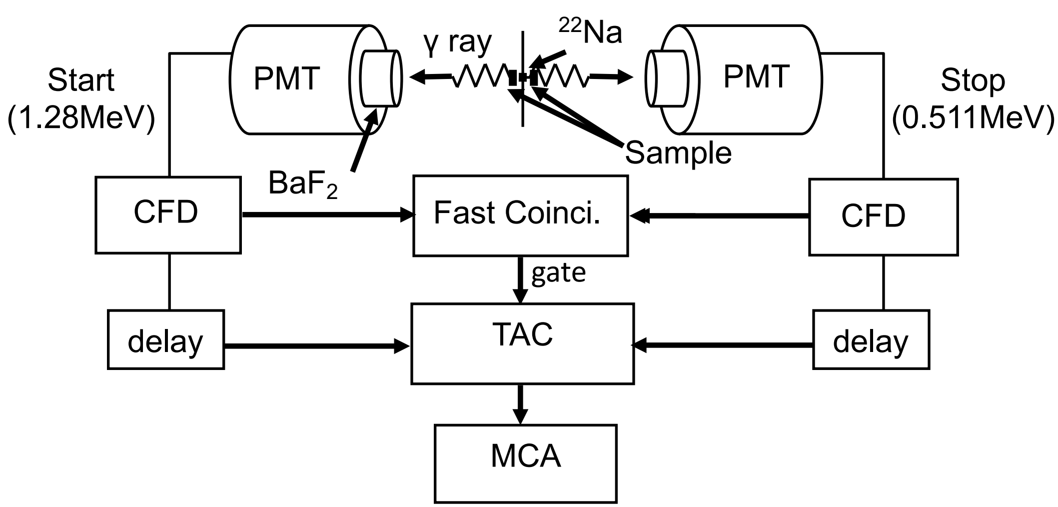
1100℃: Large He bubbles dissociate

Positron annihilation lifetimes in fission neutron-irradiated Ni

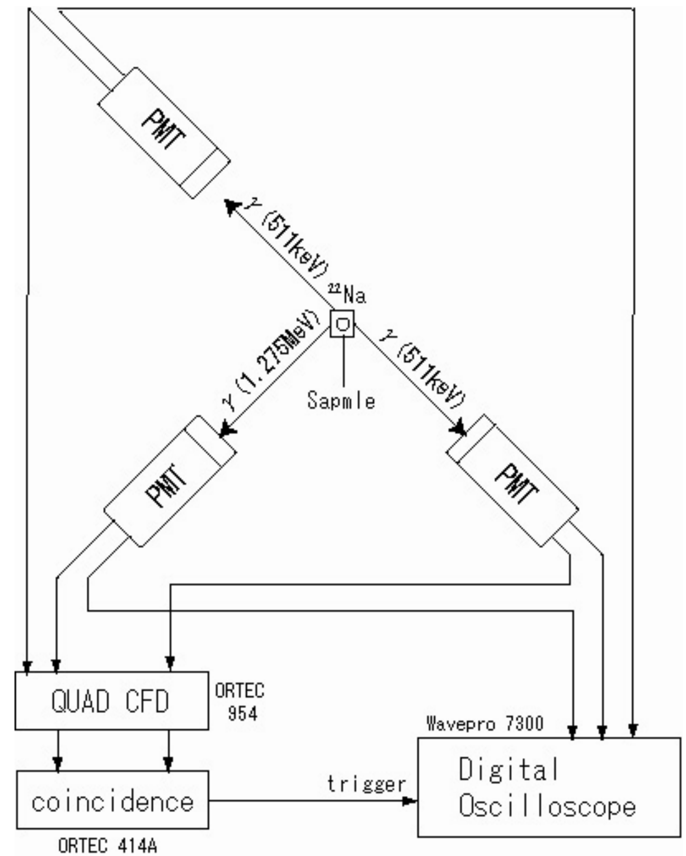


Void growth is observed by TEM in more than 0.01dpa,
but positron lifetime is saturated.

Positron annihilation lifetime measurement system



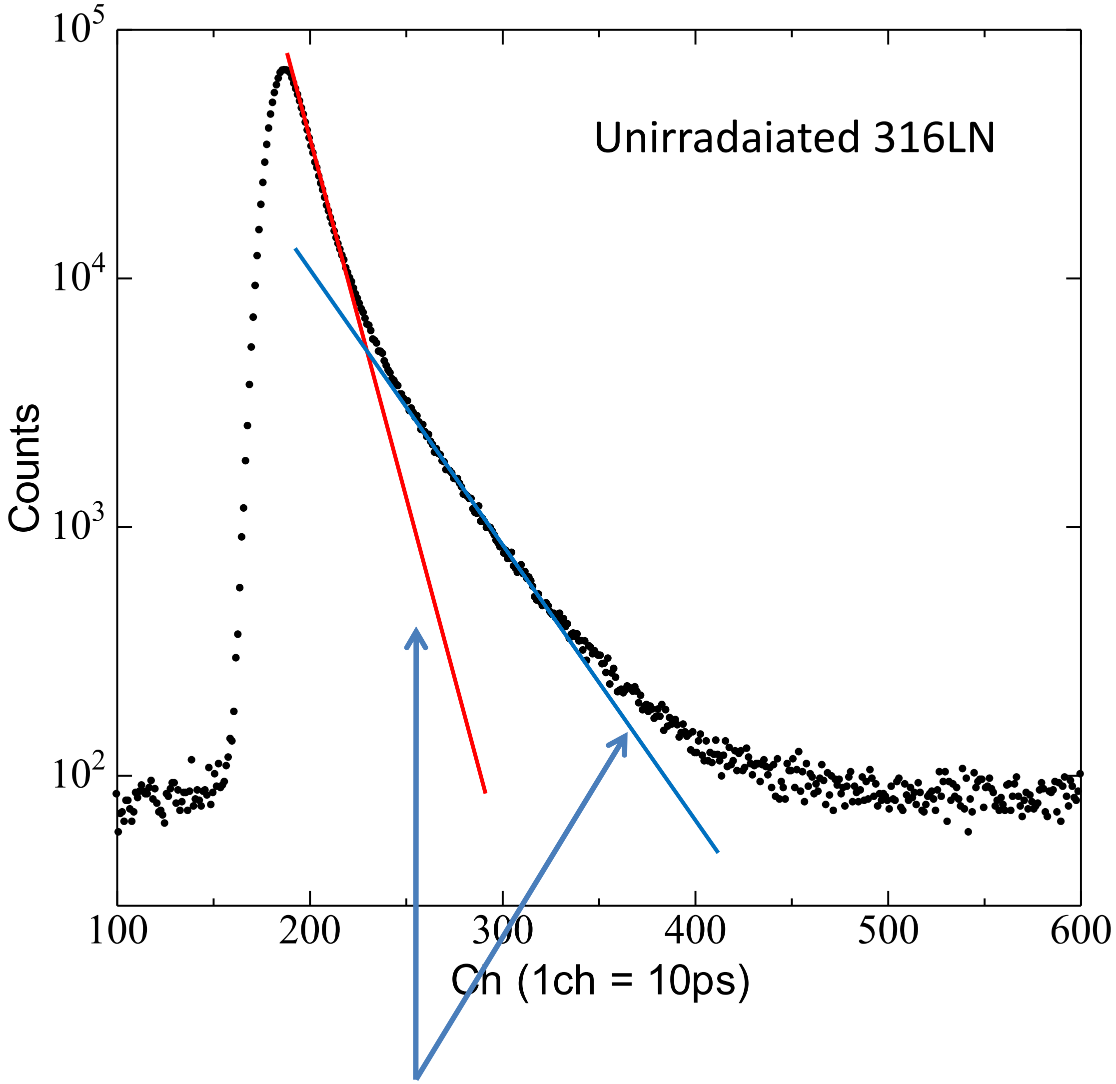
Conventional measurement system
(two-detector system)



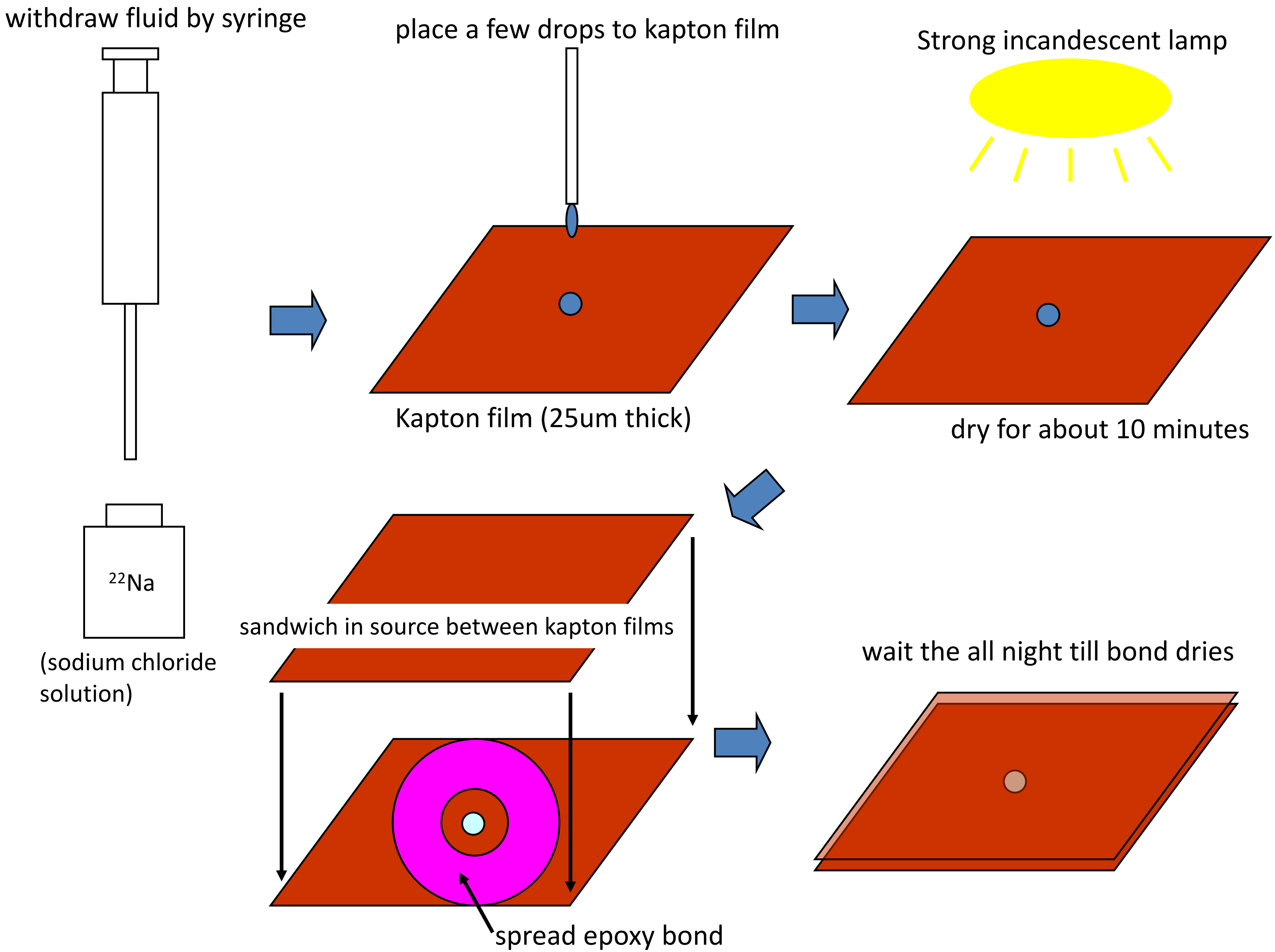
Improved measurement system
using a digital oscilloscope
(three-detector system)

Merit: Reduction of background
Demerit: Decrease of count rate

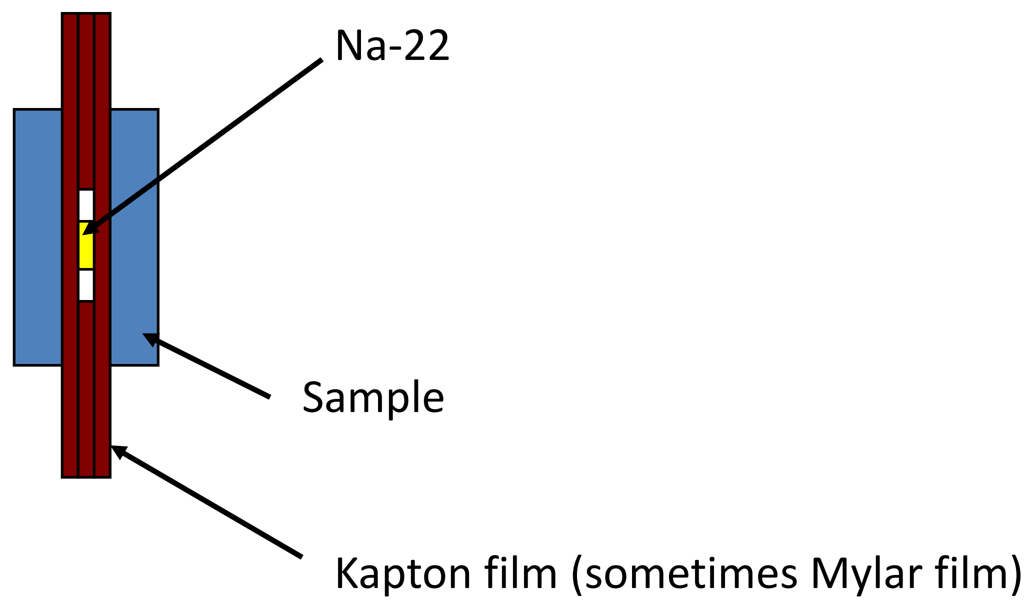
Positron annihilation lifetime spectrum



This spectrum is composed of these two curves.


withdraw fluid by syringe
place a few drops to kapton film
Strong incandescent lamp
Kapton film (25um thick)
dry for about 10 minutes
22Na
(sodium chloride solution)
sandwich in source between kapton films
wait the all night till bond dries
spread epoxy bond

Set of samples

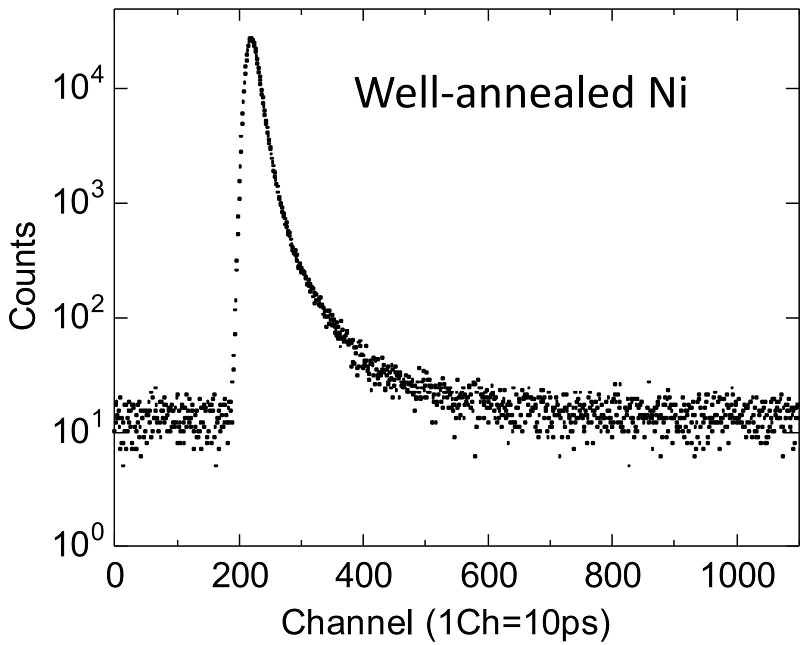


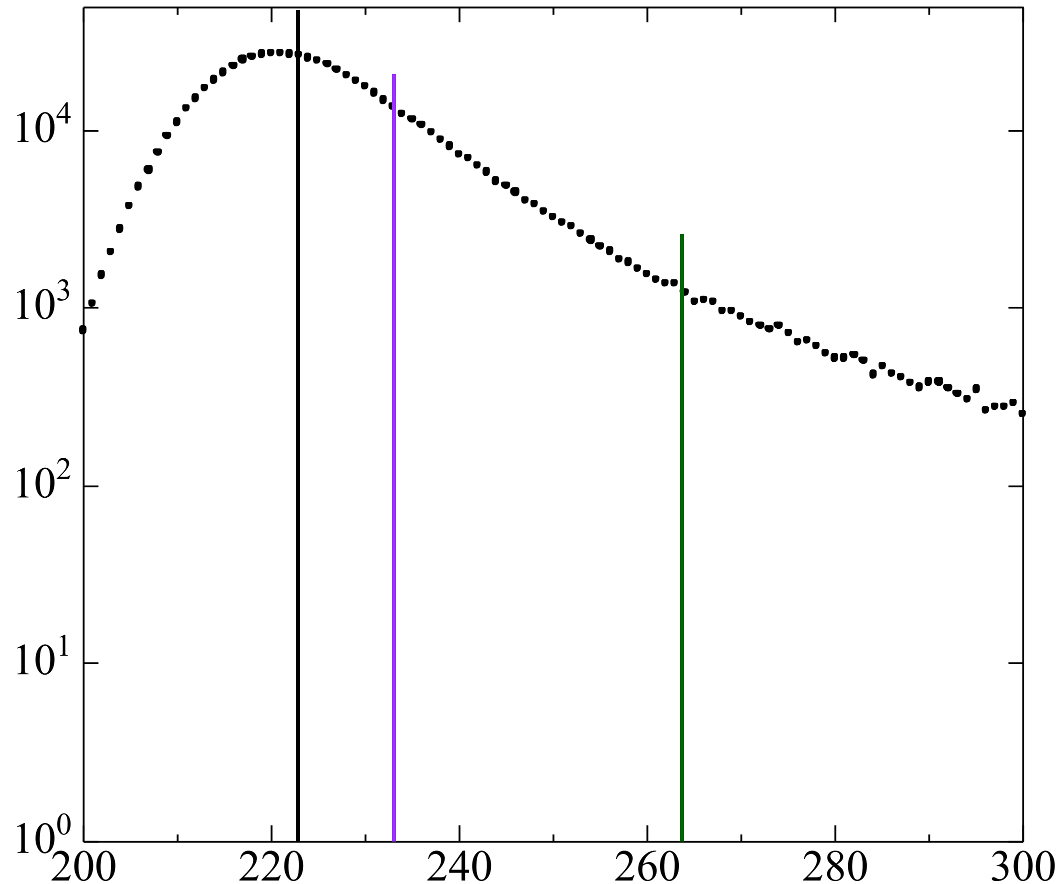
A part of positrons annihilate in the Kapton film.

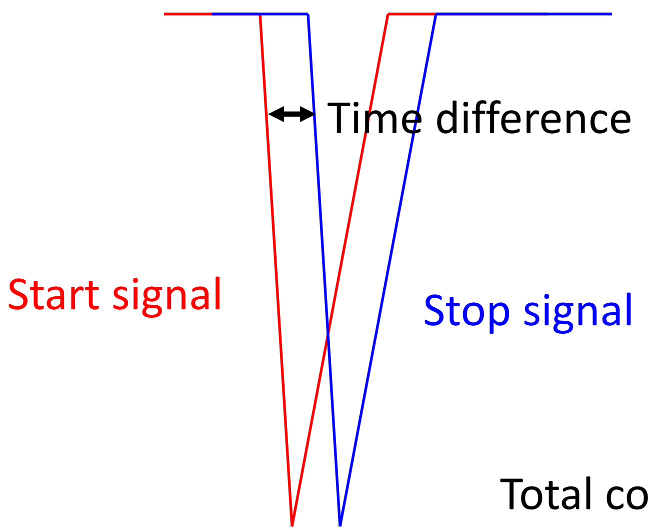
Ratio of positrons, which annihilate at Kapton film, depends on the thickness.

5um: ~13%, 10um: ~20%, 25um: ~33%

How to make lifetime spectrum



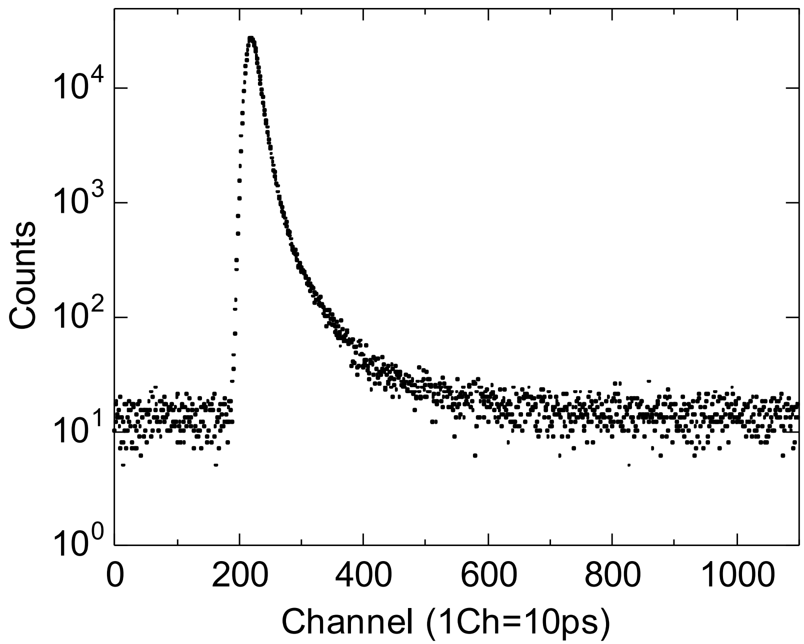




Time difference: 100ps
Time difference: 400ps

Total count of more than 1M is needed for good statistics.

Analysis of lifetime spectrum



We usually use PALSfit program, which is developed by one group of Riso DTU.

$$T'(t) = \int_{-\infty}^{\infty} T(x)G(t-x)dx + B$$

$$\int_{-\infty}^{\infty} G(t)dt = 1$$

T': Lifetime spectrum (left figure)
T: Decay function
G: Time-resolution function
B: Background

G is given by a sum of two or three Gaussians

One component

$$T(t) = \frac{I_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right)$$

Two components

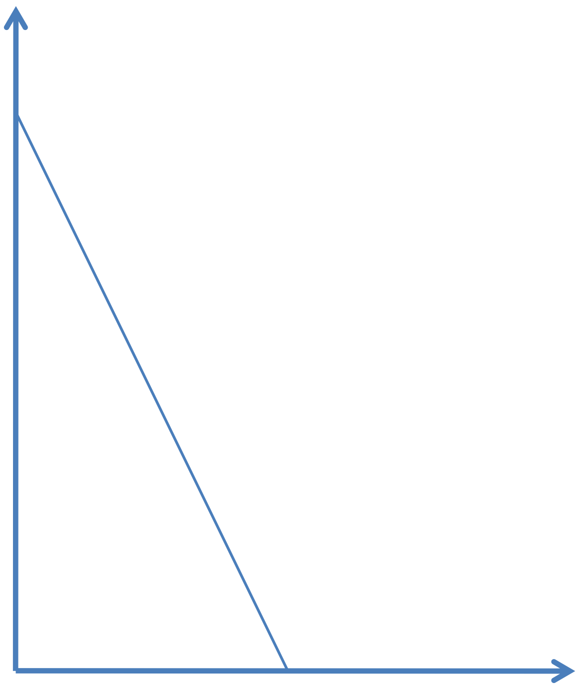
$$T(t) = \frac{I_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2}\exp\left(-\frac{t}{\tau_2}\right)$$

τ: lifetime
I : lifetime intensity

Three components

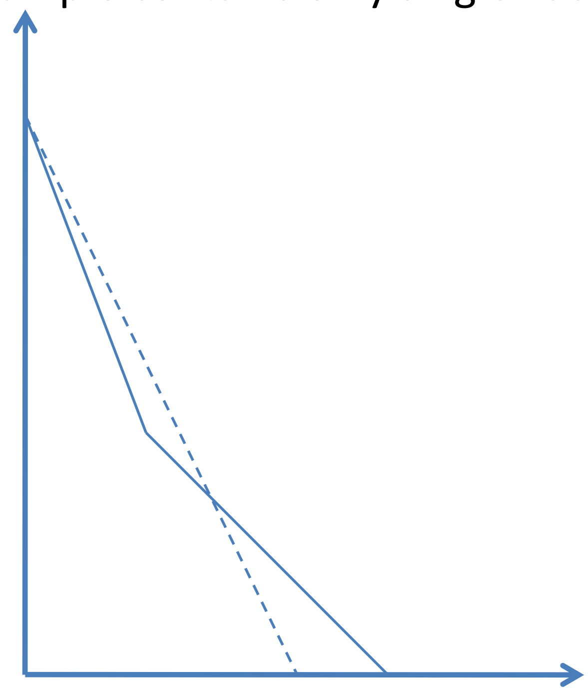
$$T(t) = \frac{I_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2}\exp\left(-\frac{t}{\tau_2}\right) + \frac{I_3}{\tau_3}\exp\left(-\frac{t}{\tau_3}\right)$$

Without any defects



$$\tau = \frac{1}{\lambda_m} \approx 100\,ps$$

With single vacancies
(sample contains only single vacancies)



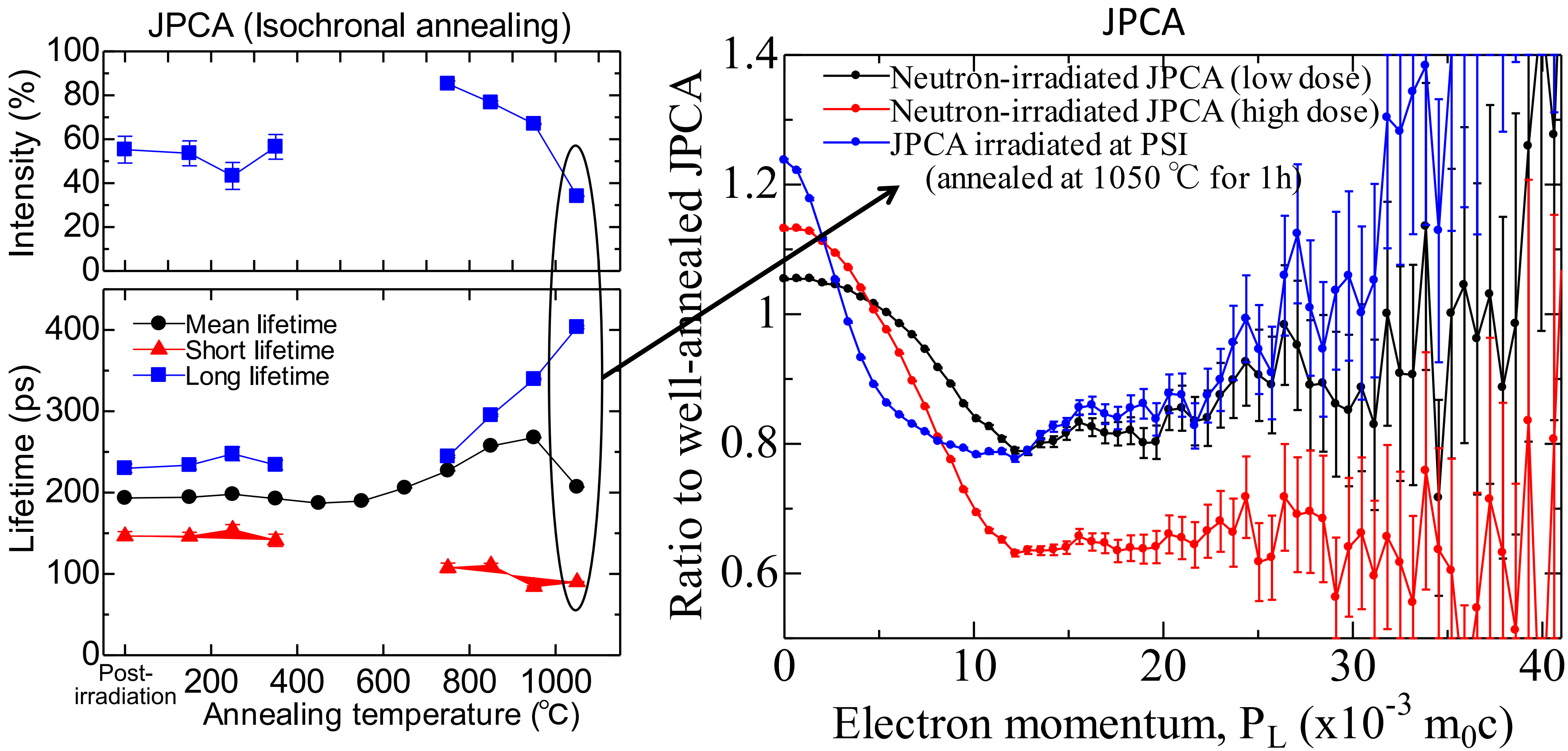
$$\tau_1 = \frac{1}{\lambda_m + \kappa} < 100\,ps$$

$$\tau_2 = \frac{1}{\lambda_d} \approx 170 - 500\,ps$$

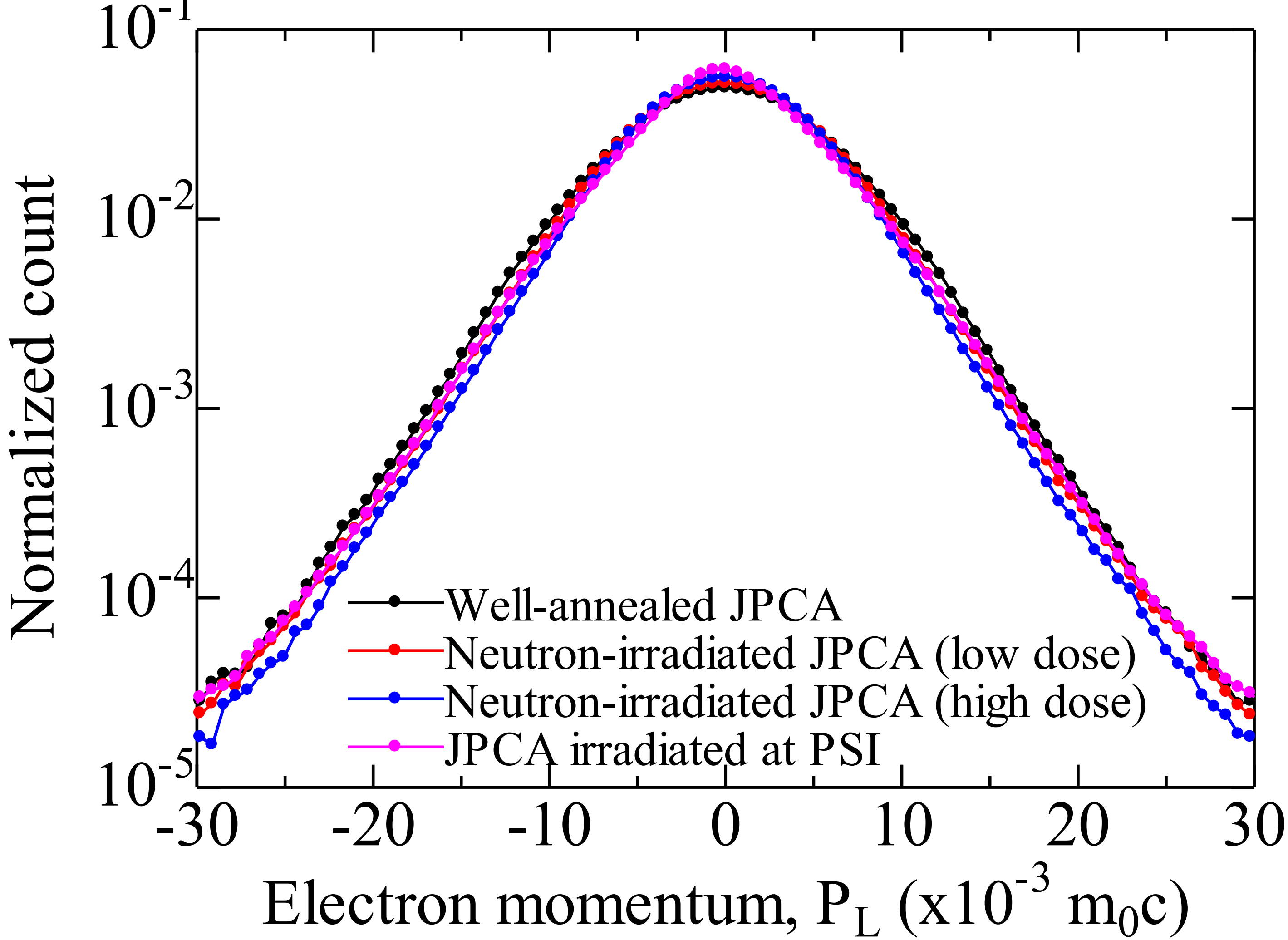
λ_m : positron annihilation rate in the matrix

λ_d : positron annihilation rate at the defect site

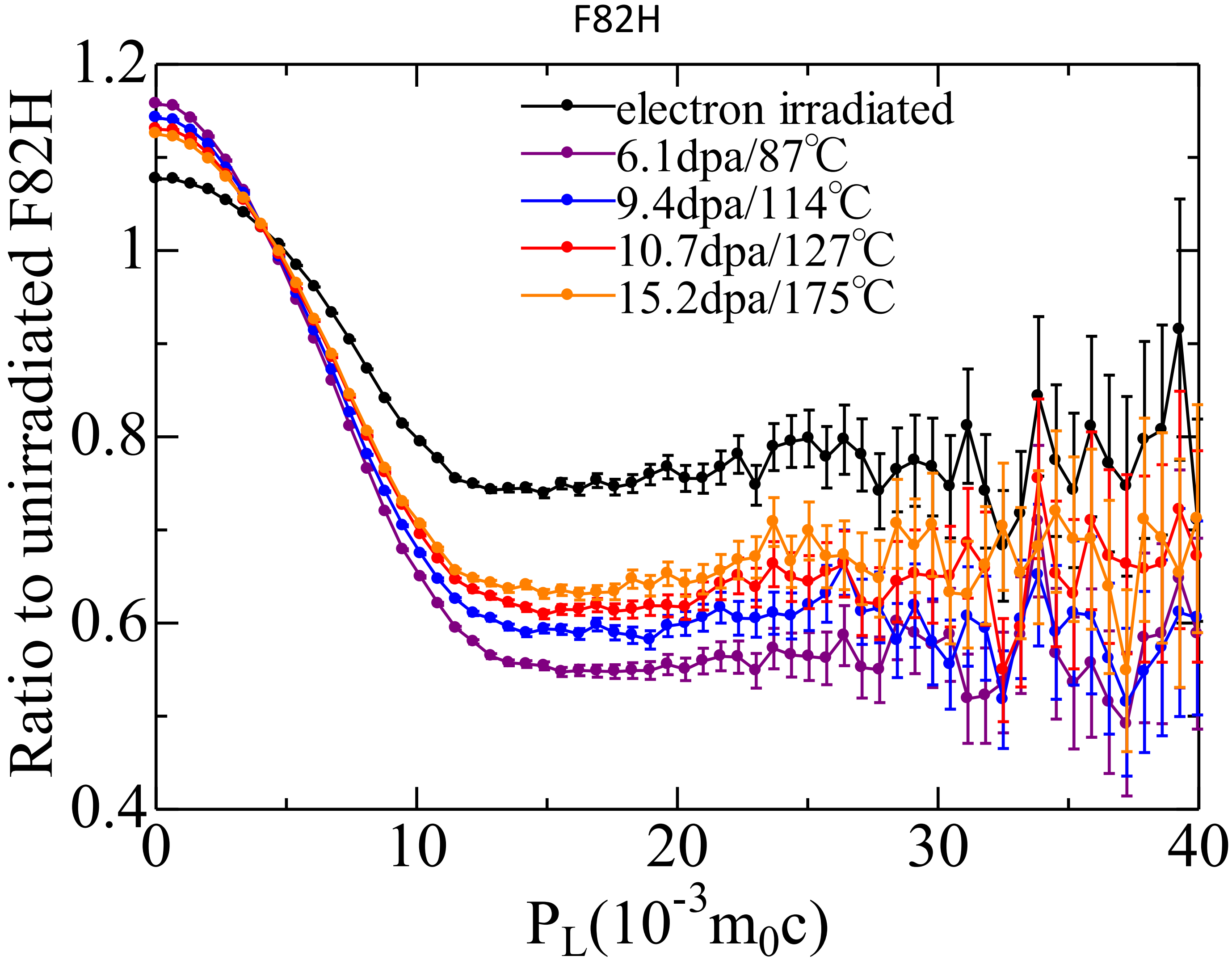
κ : positron transition rate from the matrix to the defect site



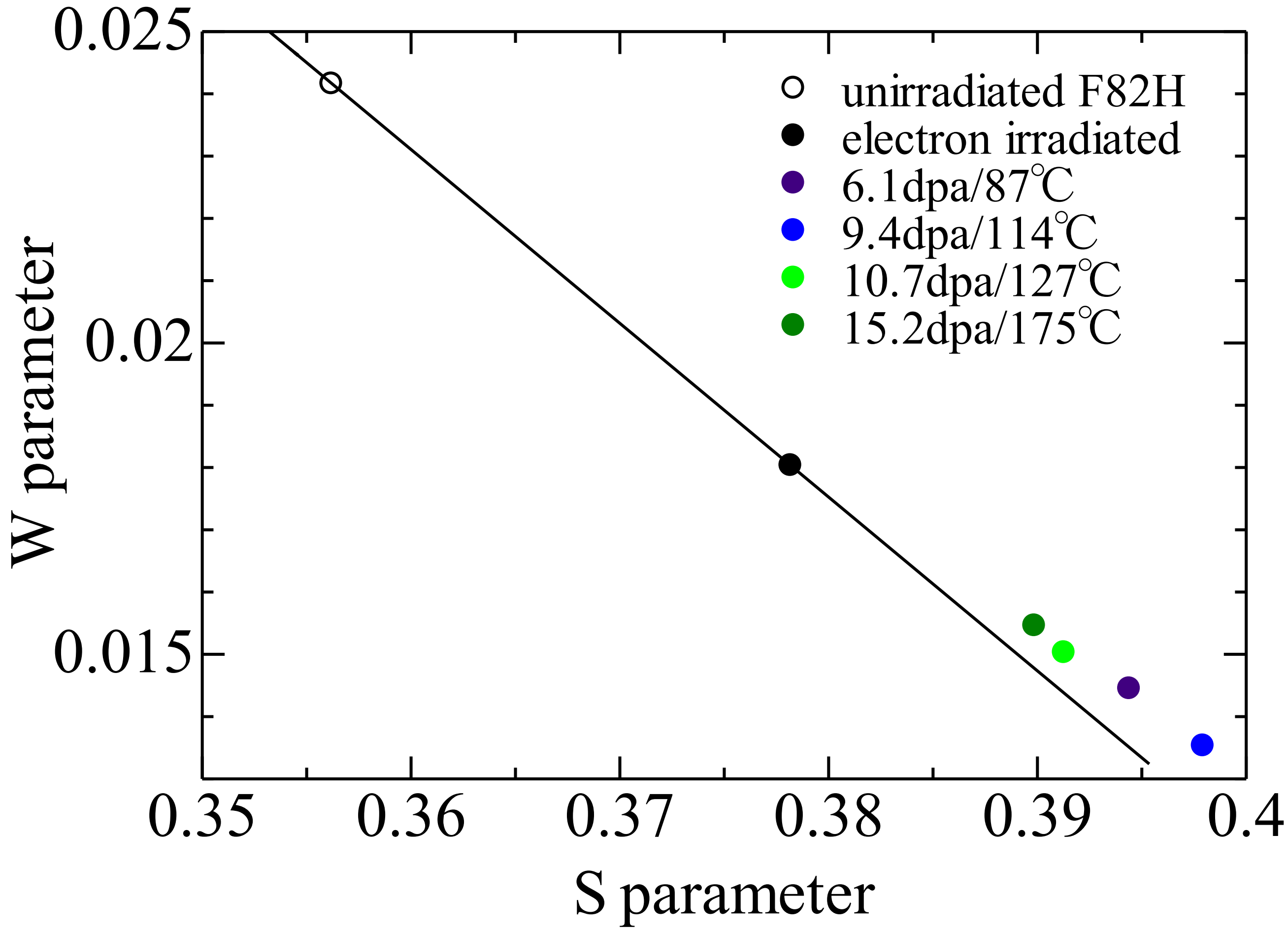
JPCA (Isochronal annealing)
Intensity (%)
Lifetime (ps)
Mean lifetime
Short lifetime
Long lifetime
Post-irradiation
Annealing temperature (℃)
JPCA
Neutron-irradiated JPCA (low dose)
Neutron-irradiated JPCA (high dose)
JPCA irradiated at PSI
(annealed at 1050 ℃ for 1h)
Ratio to well-annealed JPCA
Electron momentum, P_L ($\times 10^{-3}$ m_0c)



Normalized count
10-1
10-2
10-3
10-4
10-5
-30
-20
-10
0
10
20
30
Electron momentum, P_L (x10^-3 m_0c)
Well-annealed JPCA
Neutron-irradiated JPCA (low dose)
Neutron-irradiated JPCA (high dose)
JPCA irradiated at PSI



F82H
electron irradiated
6.1dpa/87℃
9.4dpa/114℃
10.7dpa/127℃
15.2dpa/175℃
Ratio to unirradiated F82H
1.2
1
0.8
0.6
0.4
0
10
20
30
40
$P_L(10^{-3}m_0c)$



unirradiated F82H
electron irradiated
6.1dpa/87℃
9.4dpa/114℃
10.7dpa/127℃
15.2dpa/175℃
0.025
0.02
0.015
W parameter
0.35
0.36
0.37
0.38
0.39
0.4
S parameter