Defect Structures of F82H and T91 Irradiated at SINQ Using Positron Annihilation Spectroscopy

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Background

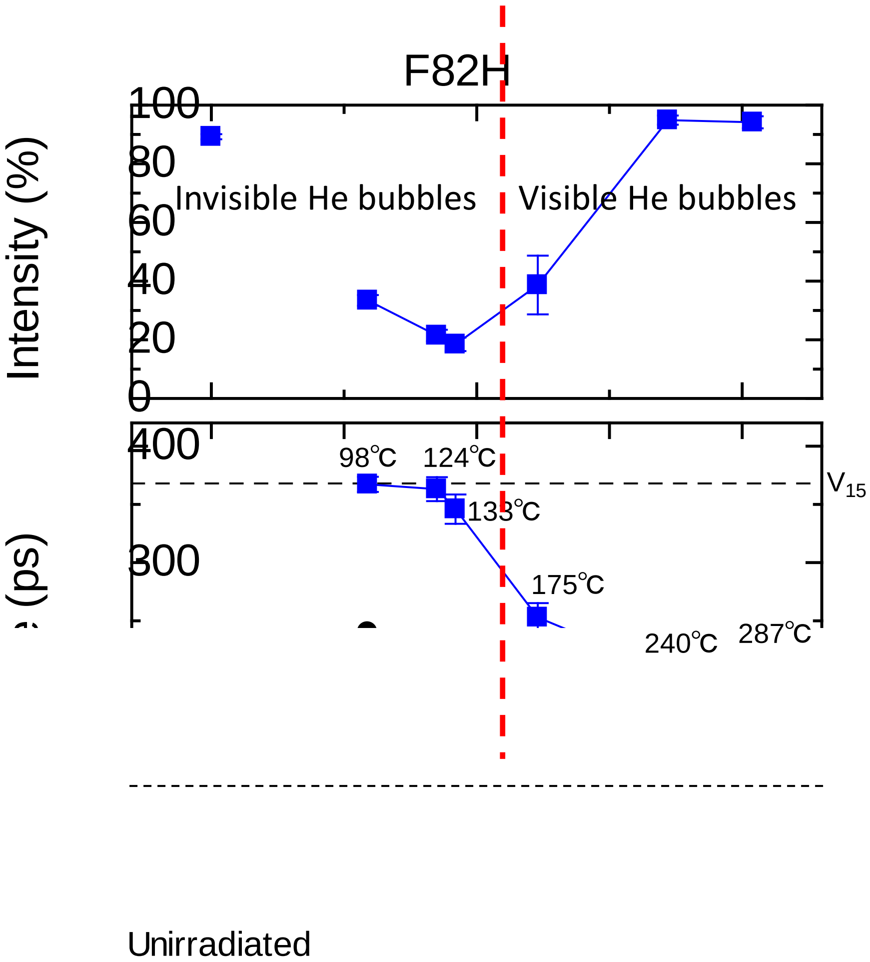
- The study of irradiation effects on the reduced activation ferritic/martensitic steels is important for the structural materials of fusion reactor and spallation neutron source including accelerator driven system.

- 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.

Purpose of this study

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



- Positron annihilation spectroscopy is very powerful tool to detect "small" vacancy type defects.
- The defect structures in F82H and T91 irradiated with protons and neutrons were investigated using positron annihilation spectroscopy
- The growth process of helium bubbles were considered.

Experimetal

- Sample: F82H, T91
- Irradiation condition (STIP-II)

Sample	Sample ID	Average temperature [K]	Irradiation dose [dpa]	He production [appm]	H production [appm]
F82H	K69L/K72L	360	6.1	460	1690
	K69H/K72L	387	9.4	735	2905
	K70L/K73L	400	10.7	850	3435
	K70H/K73H	448	15.2	1305	5365
	K71L/K73L	465	16.9	1475	6100
	K71H/K74H	502	20.3	1790	7700
T91	F37L/F40L	376	6.1	460	1690
	F37H/F40L	414	9.4	735	2905
	F38L/F41L	431	10.7	850	3435
	F38H/F41H	498	15.2	1305	5365
	F39L/F42L	521	16.9	1475	6100
	F39H/F42H	572	20.3	1790	7700

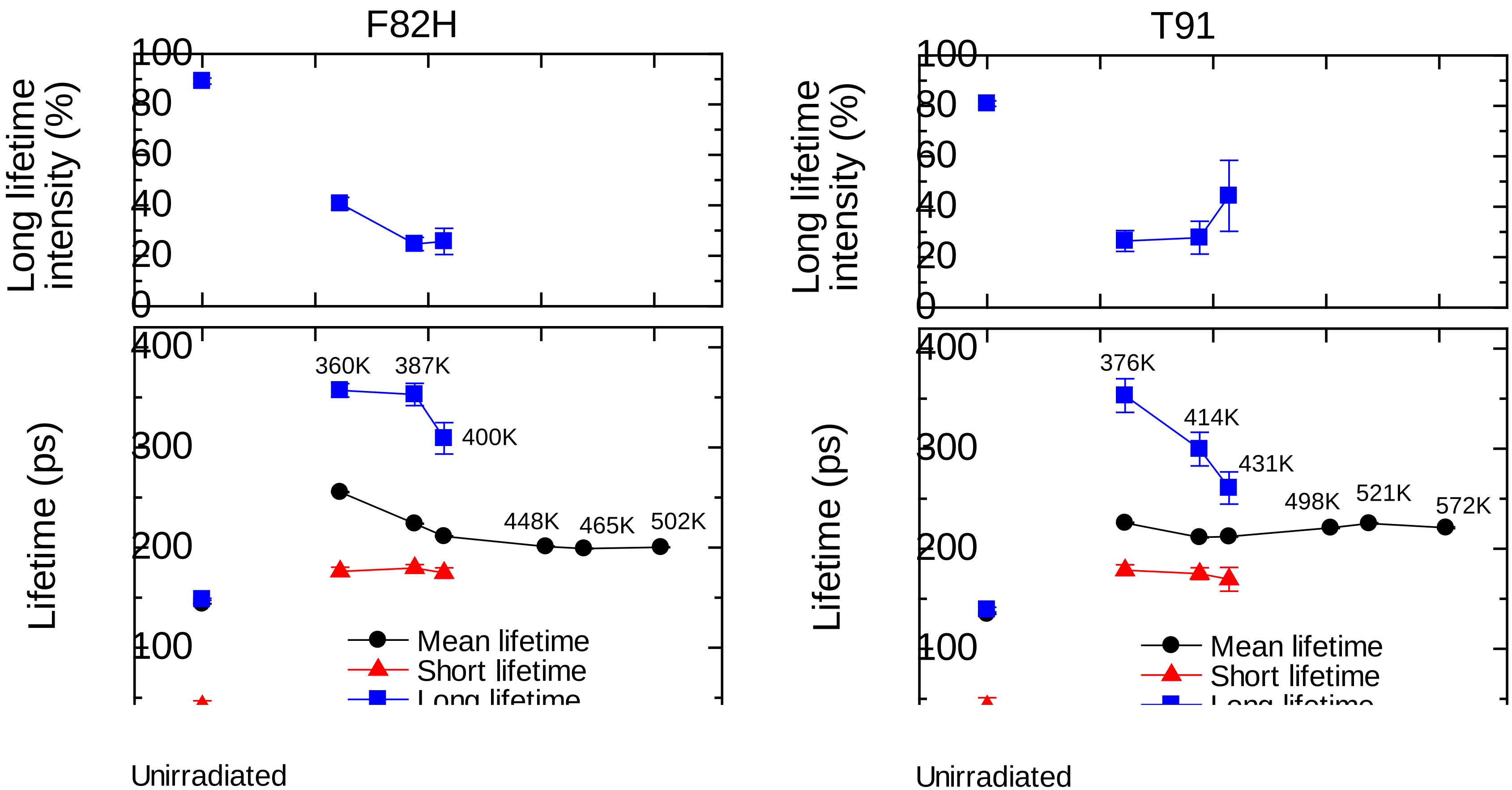
Isochronal annealing test sample

Sample	Sample ID	Average temperature [K]	Irradiation dose [dpa]	He production [appm]	H production [appm]
F82H	L11, L12	385	7.2	531.5	2105

- Positron annihilation lifetime (PAL) measurements
  Positron annihilation coincidence Doppler broadening (CDB) measurements

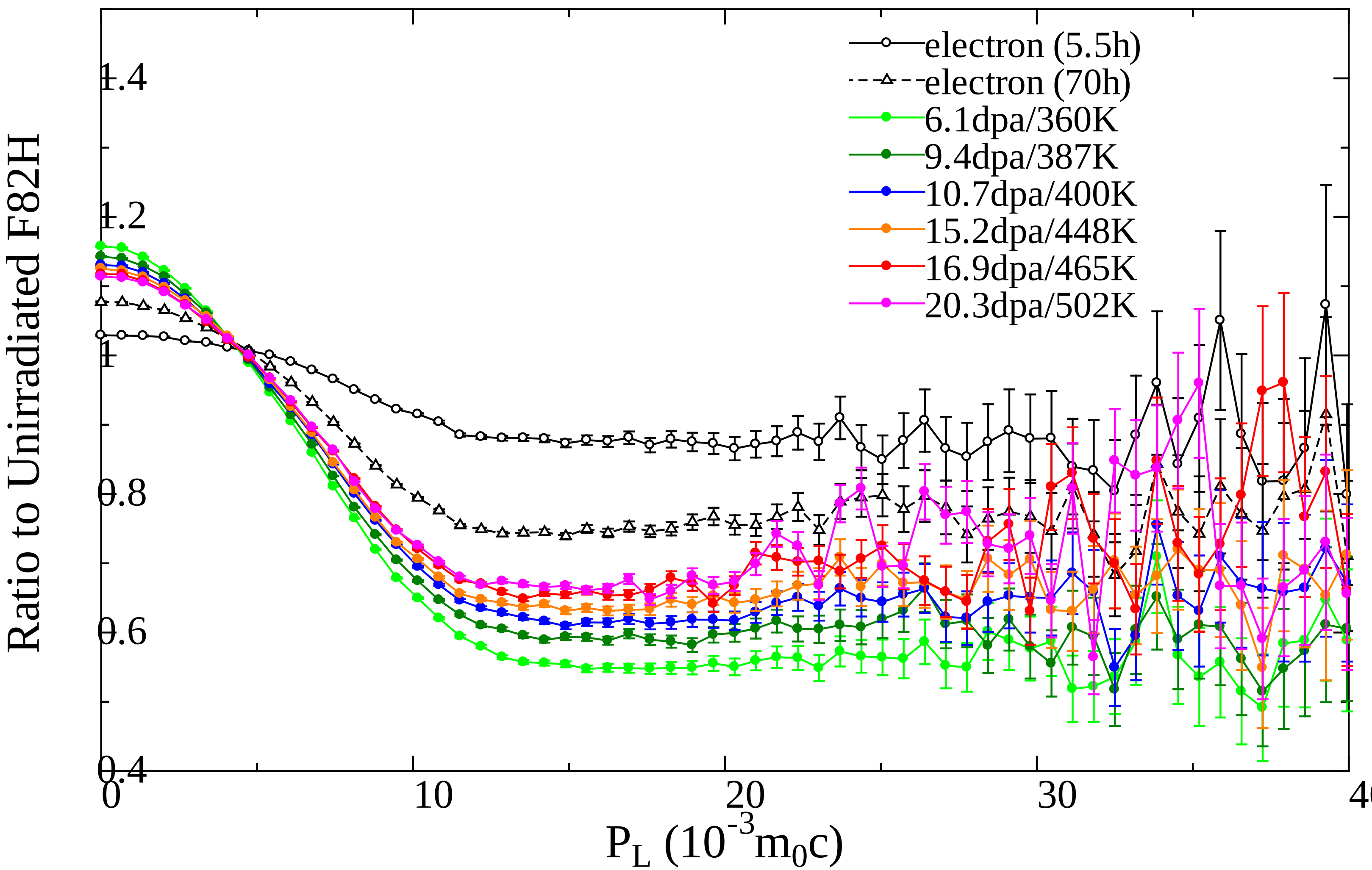
Dose dependence

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

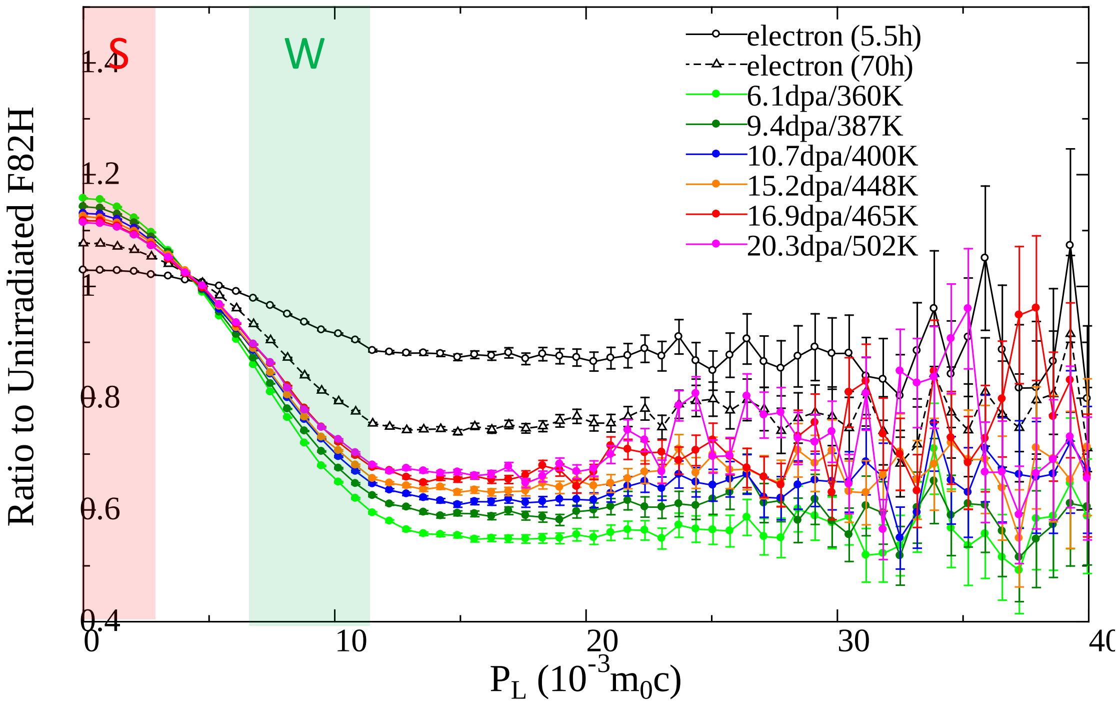
S-parameter: Ratio of the low-momentum ($|P_L|<2.5\times10^{-3}\,mc$) area to the total area

The amount of vacancy type defects

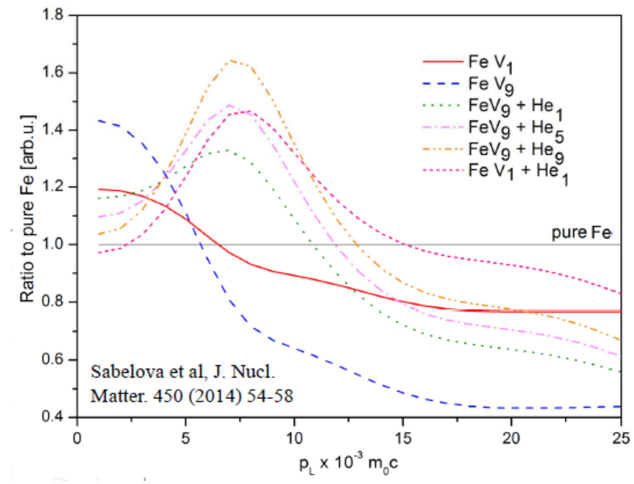
W-parameter: Ratio of high-momentum ($7\times10^{-3}\,mc < |P_L| < 12\times10^{-3}\,mc$) areas to the total area

The amount of precipitates or bubbles

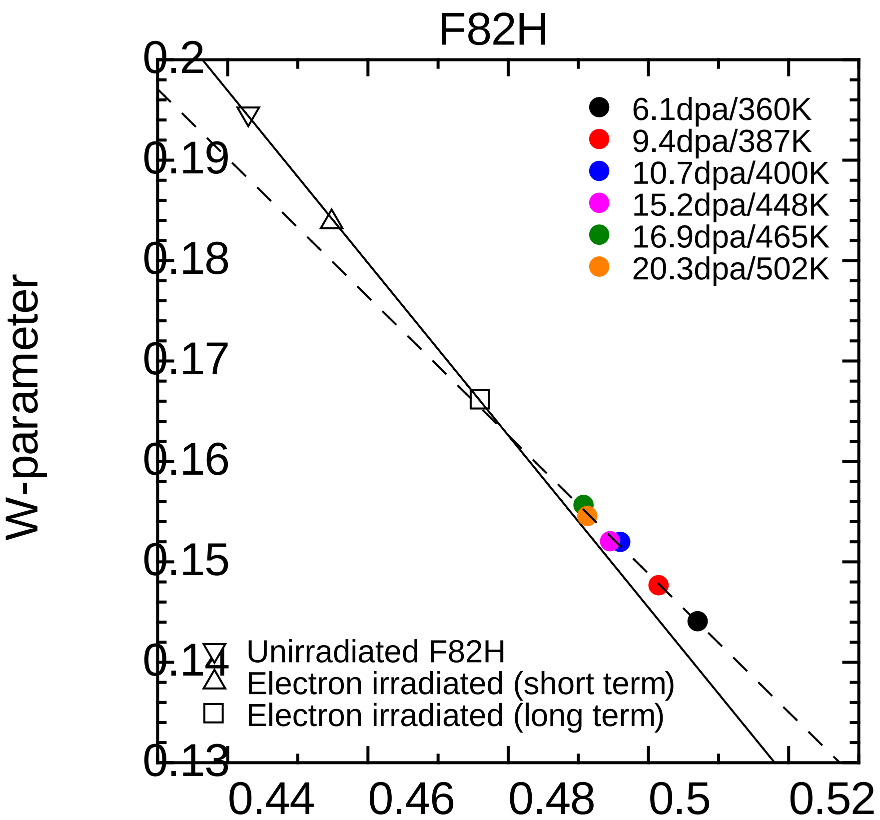
This region was decided from the previous study [Sabelova et al., J. Nucl. Mater. 450 (2014) 54.].



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

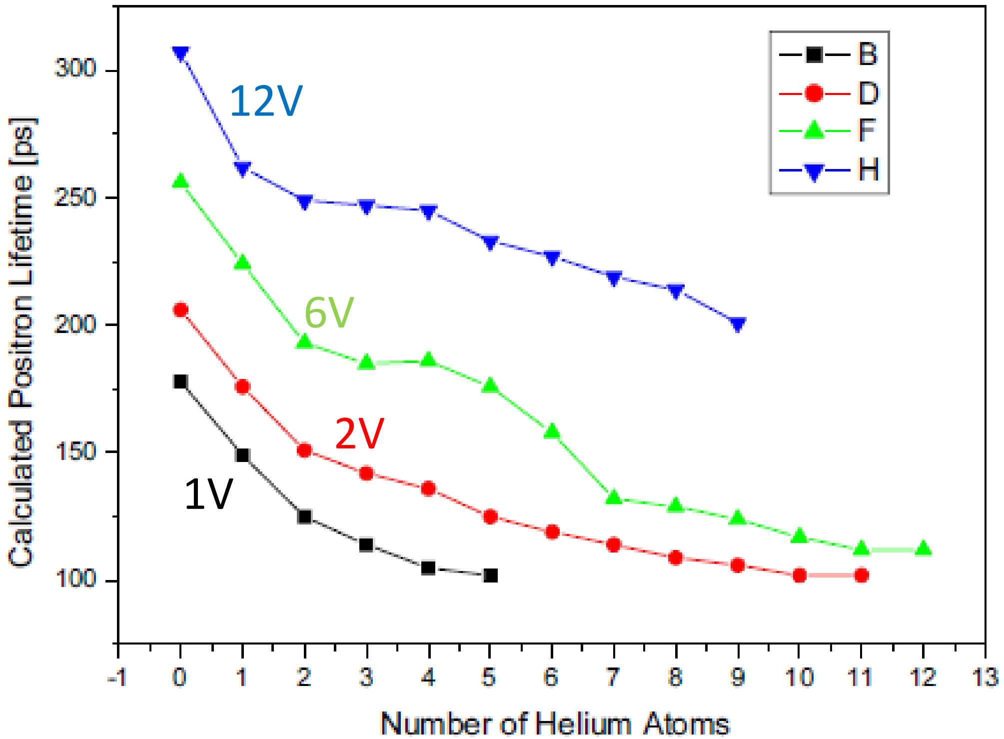
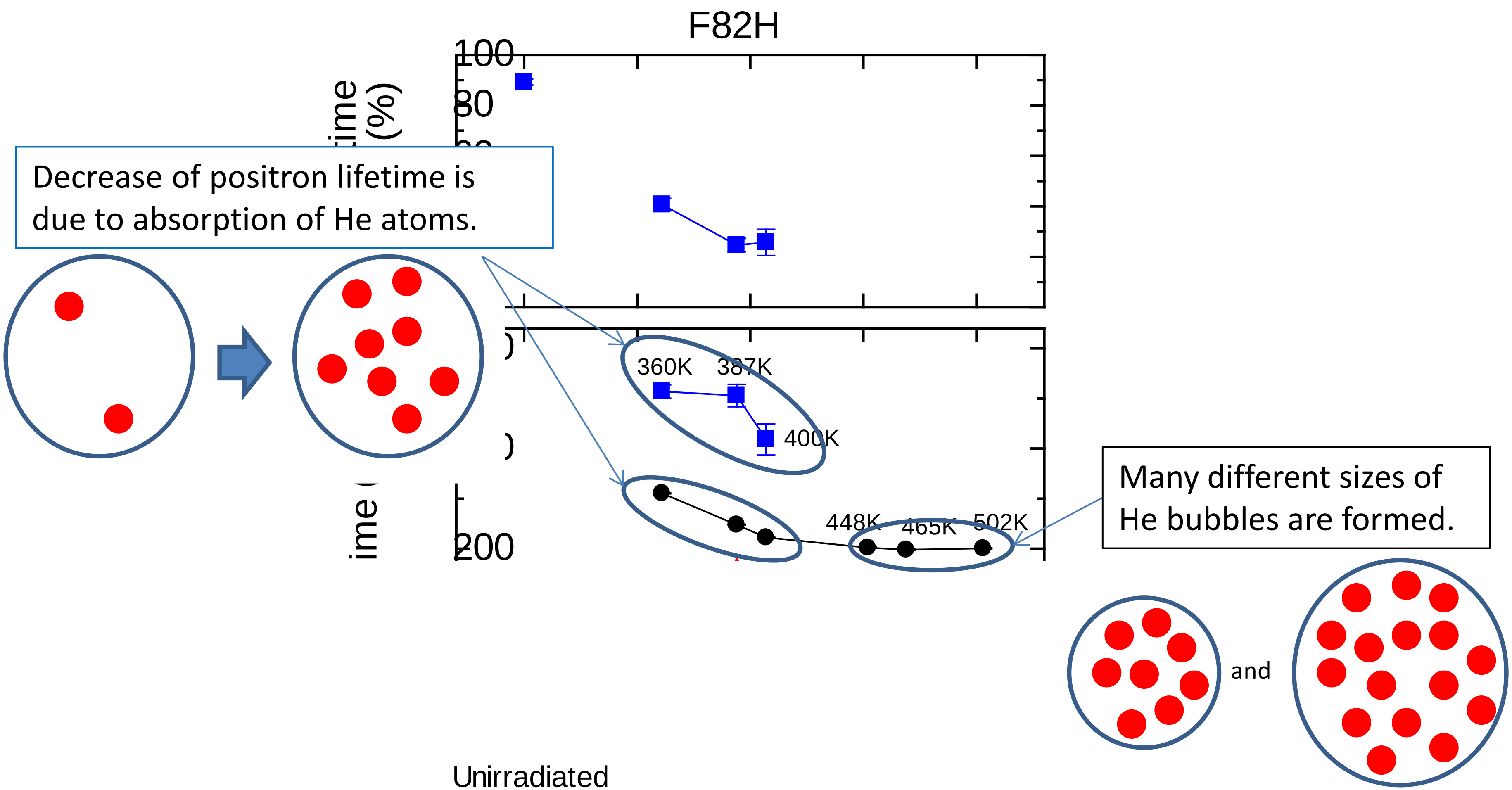


Figure 4 Correlation between positron lifetime and the number of helium atoms in nano-void (B) 1V+nHe, (D) 2V+nHe, (F) 6V+nHe, (H) 12V+nHe.

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

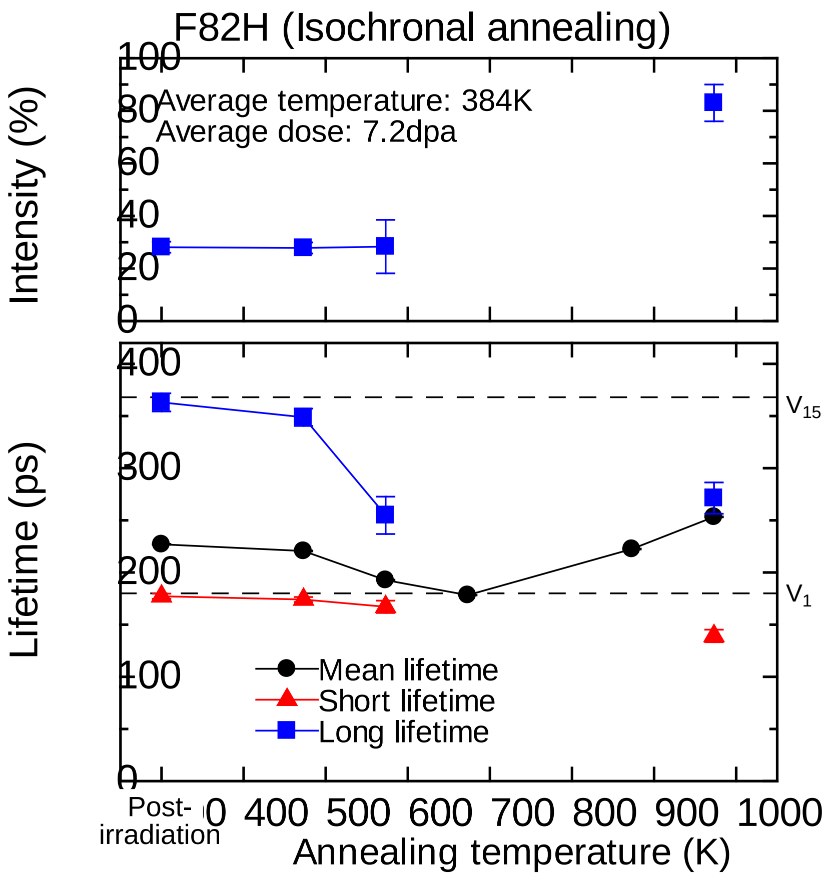
Change in PAL by He effect

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



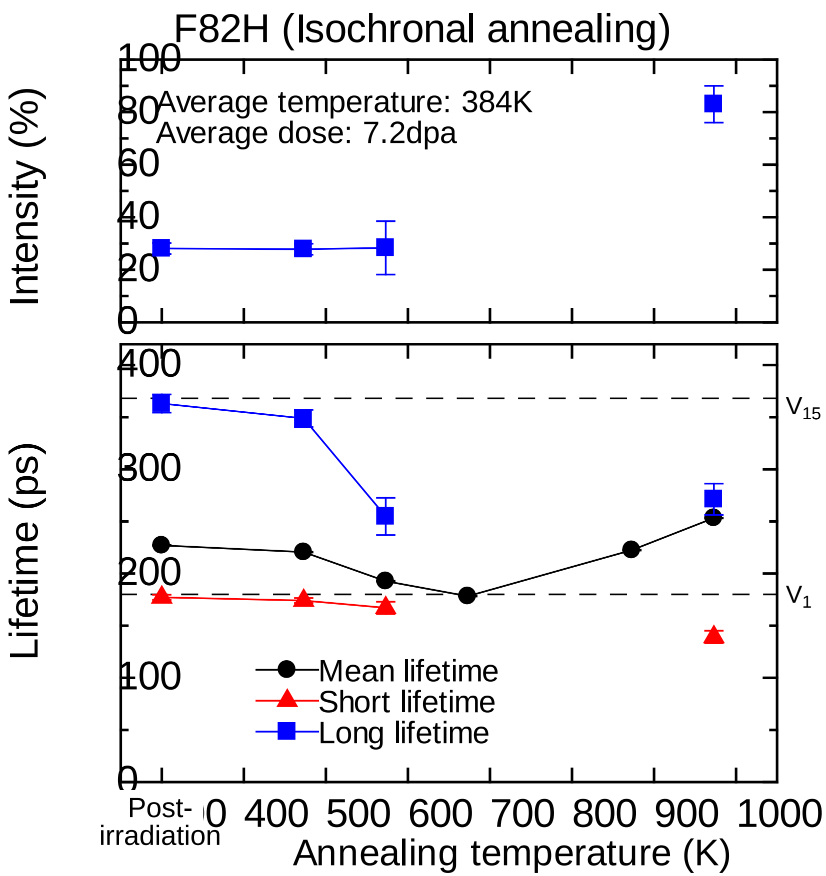
Isochronal annealing

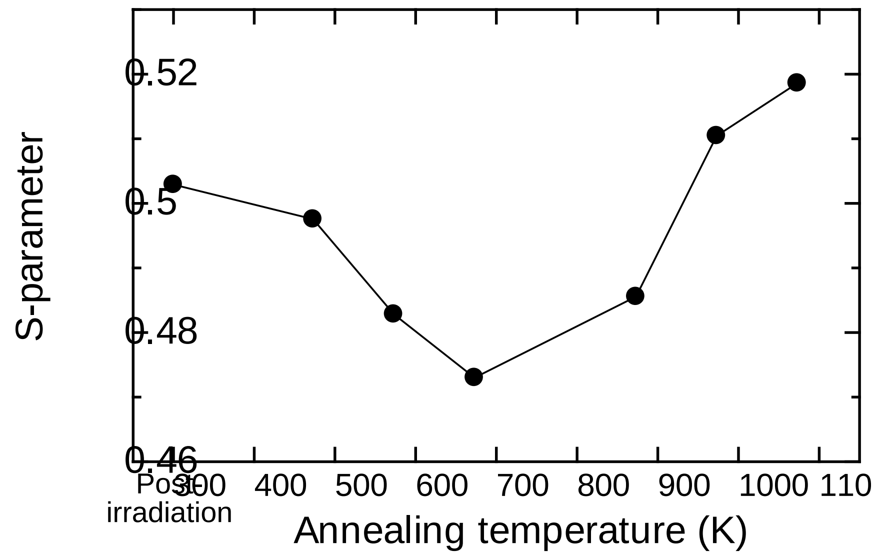
Change in PAL



- 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.

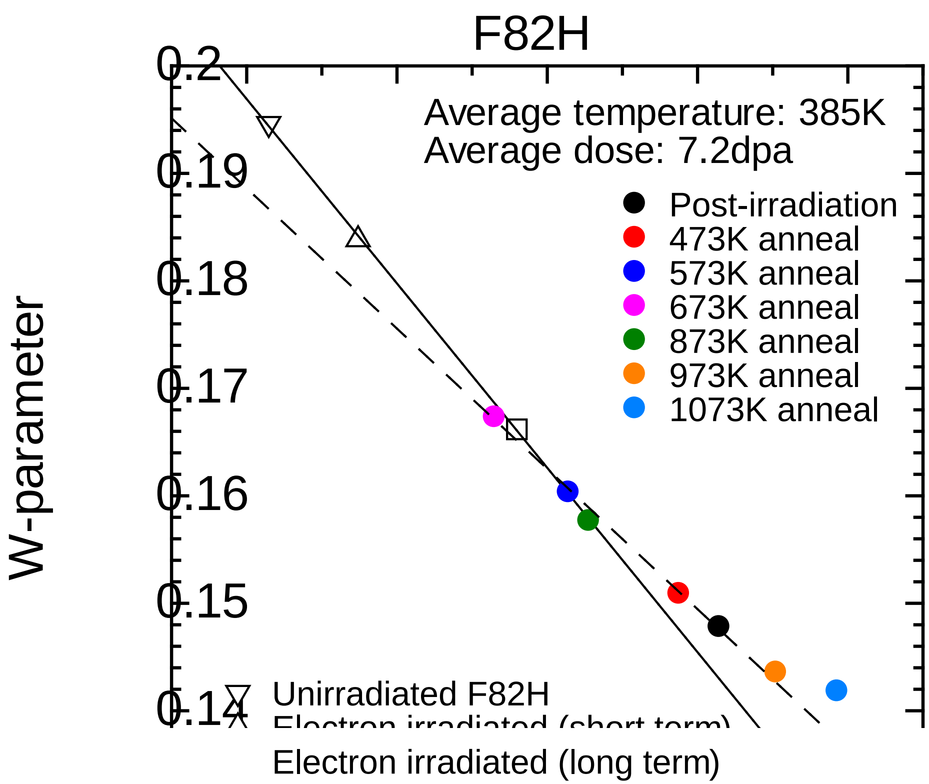
Change in PAL and S-parameter





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.

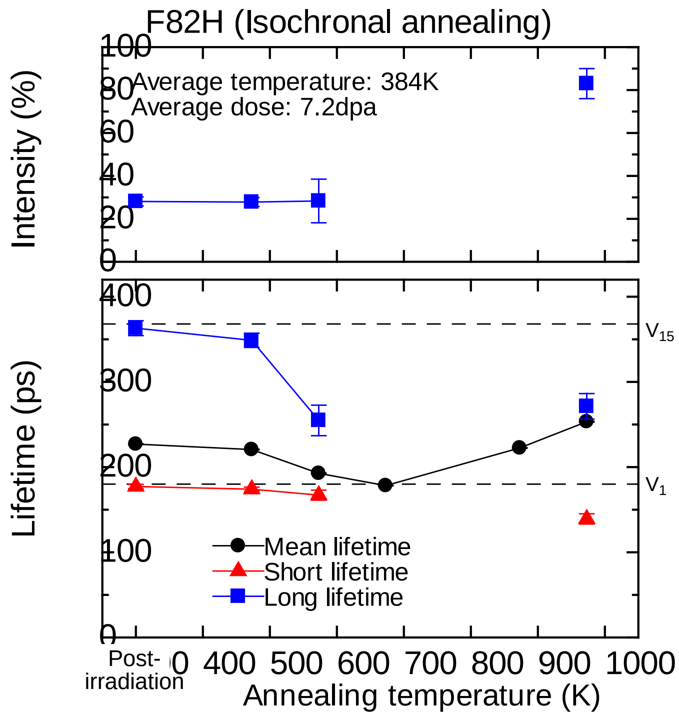
Broken line denotes the change between post-irradiation and samples annealed up to 673 K.

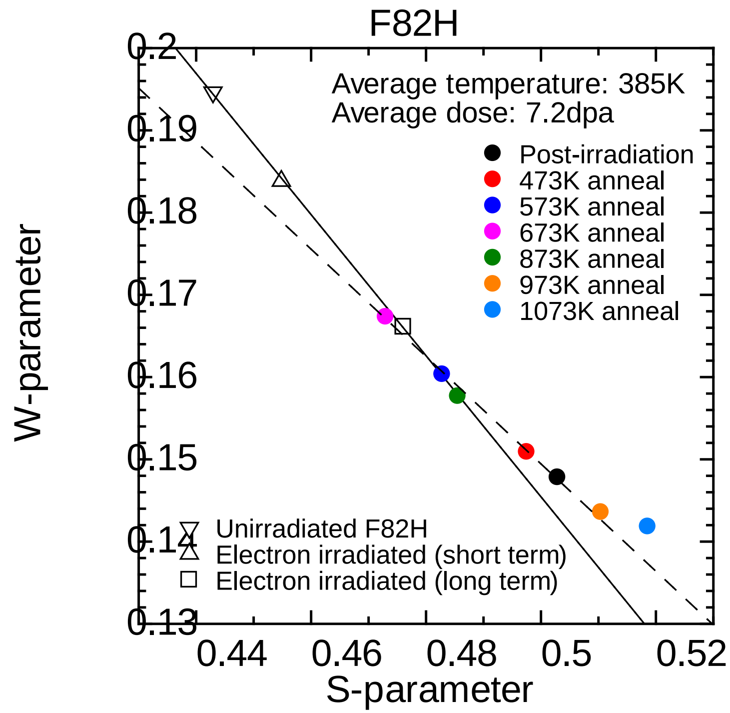
These data points (from post-irrad. to 673K annealing) are clearly on broken line.

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





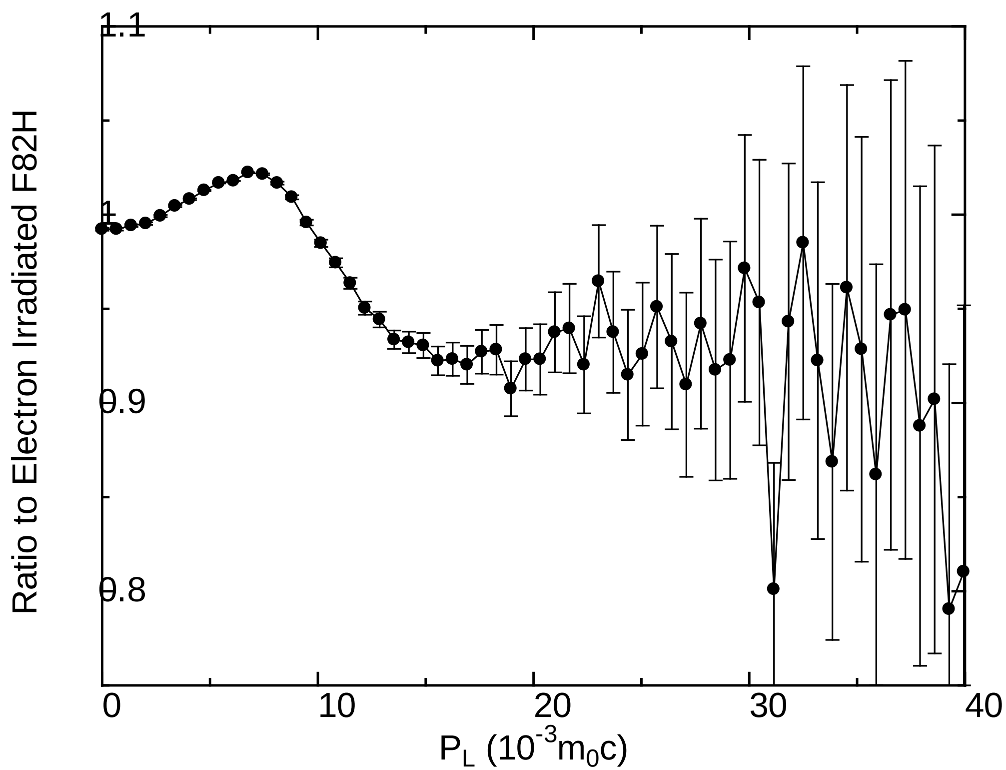
Below 673 K: Size of He filled vacancy clusters does not change, and they absorb He atoms weakly trapped in the matrix.

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.

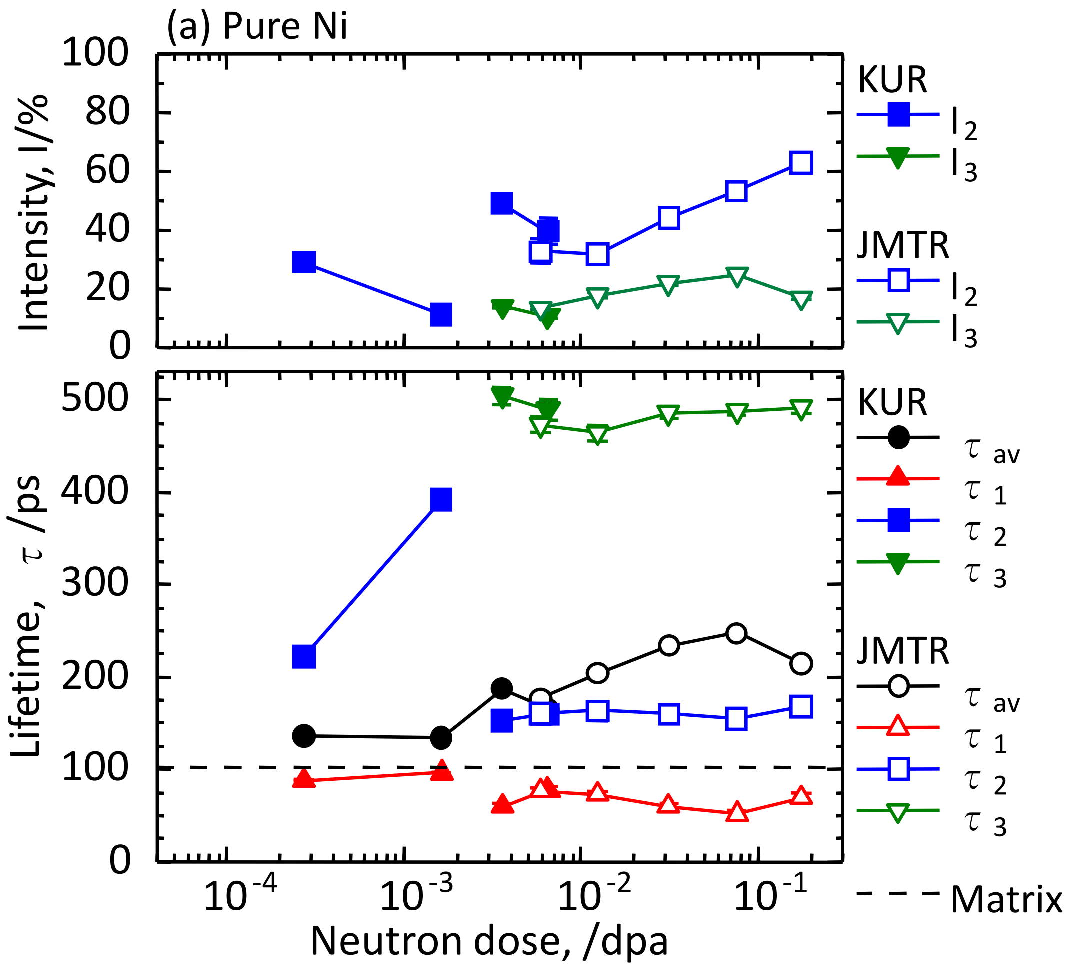
  Isochronal annealing

  - 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

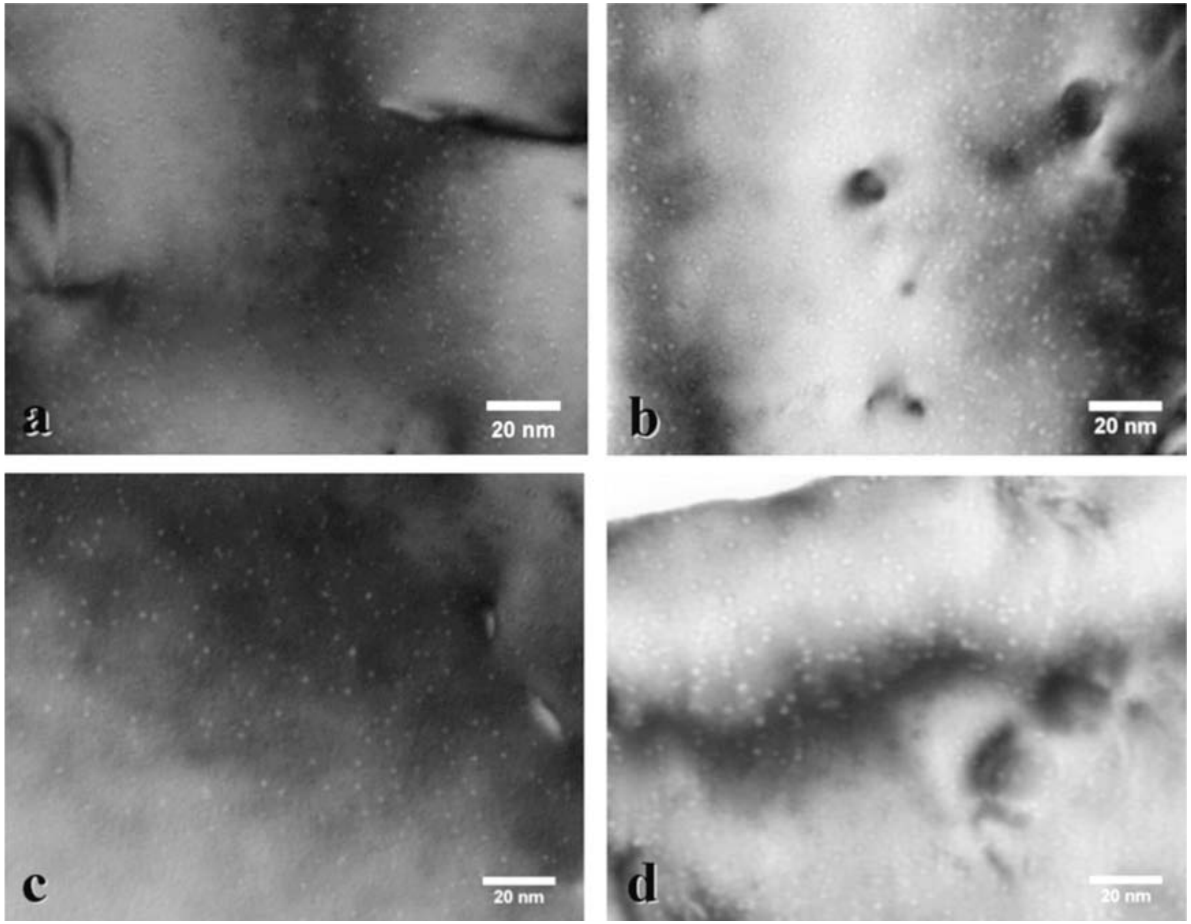


In more than 0.01dpa, positron lifetime is saturated, but void growth is observed by TEM.

TEM images of T91 irradiated in STIP-III

9.5dpa

13.6dpa



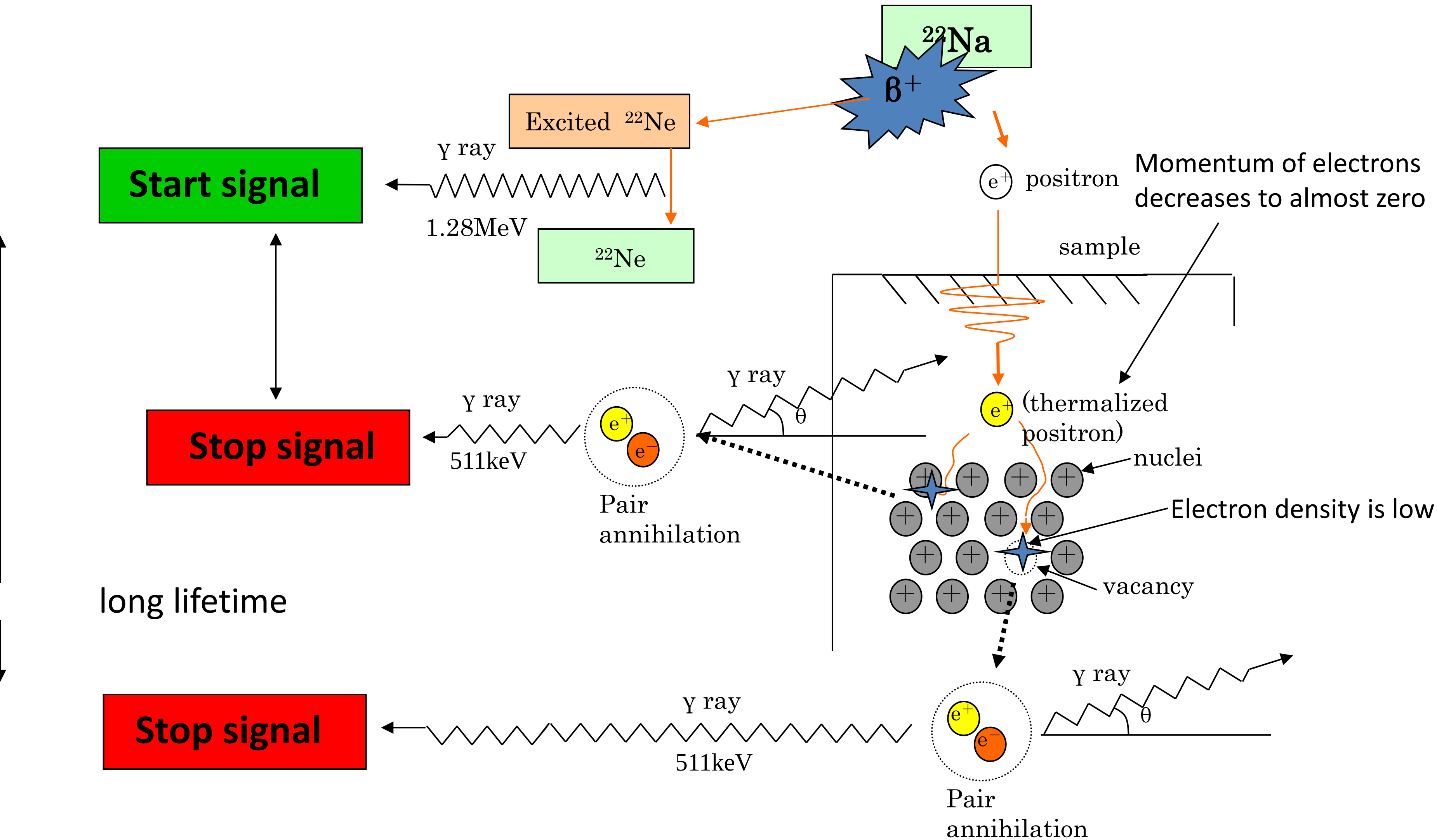
17.3dpa

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

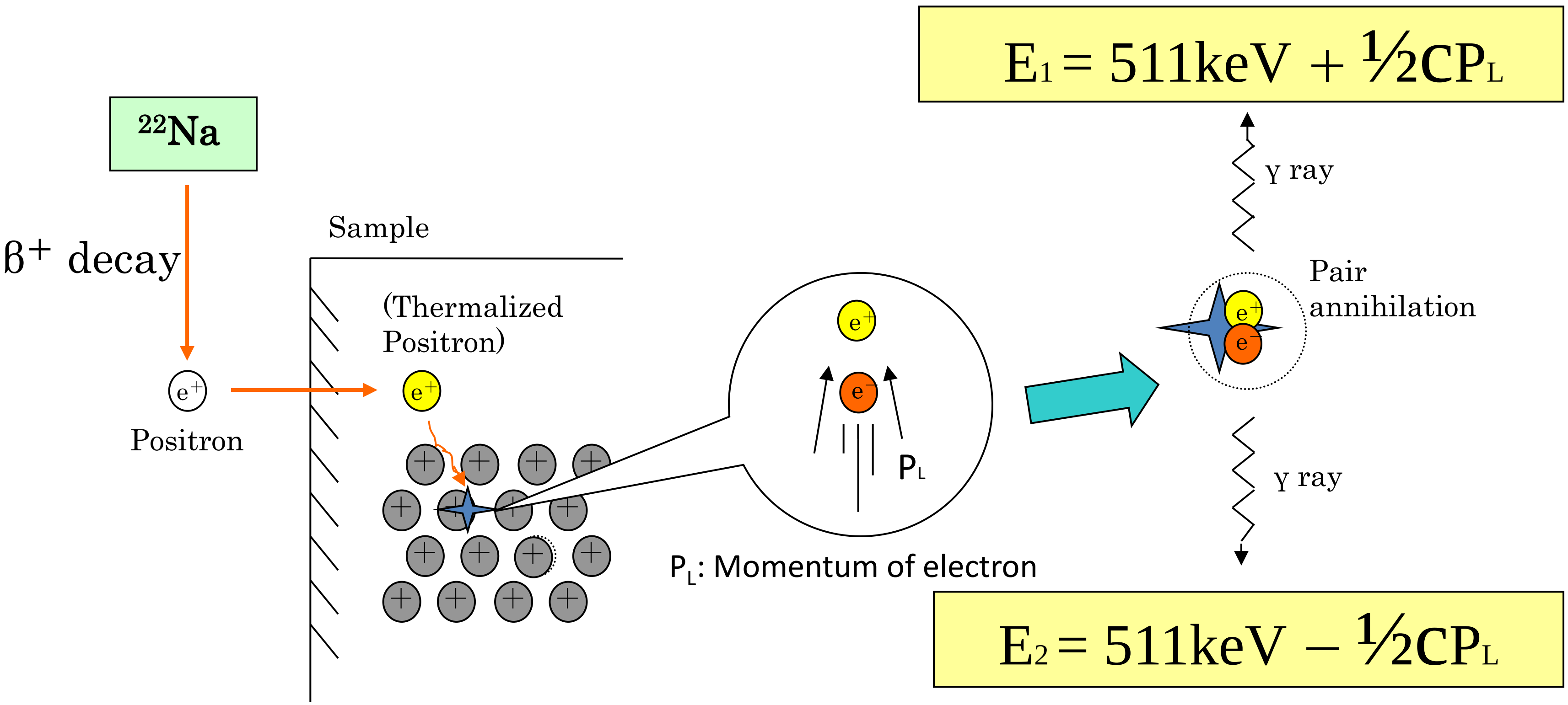
[a] The values are listed for two distinct divacancy geometries, i.e. V_2 along [111] and [100] directions.

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

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

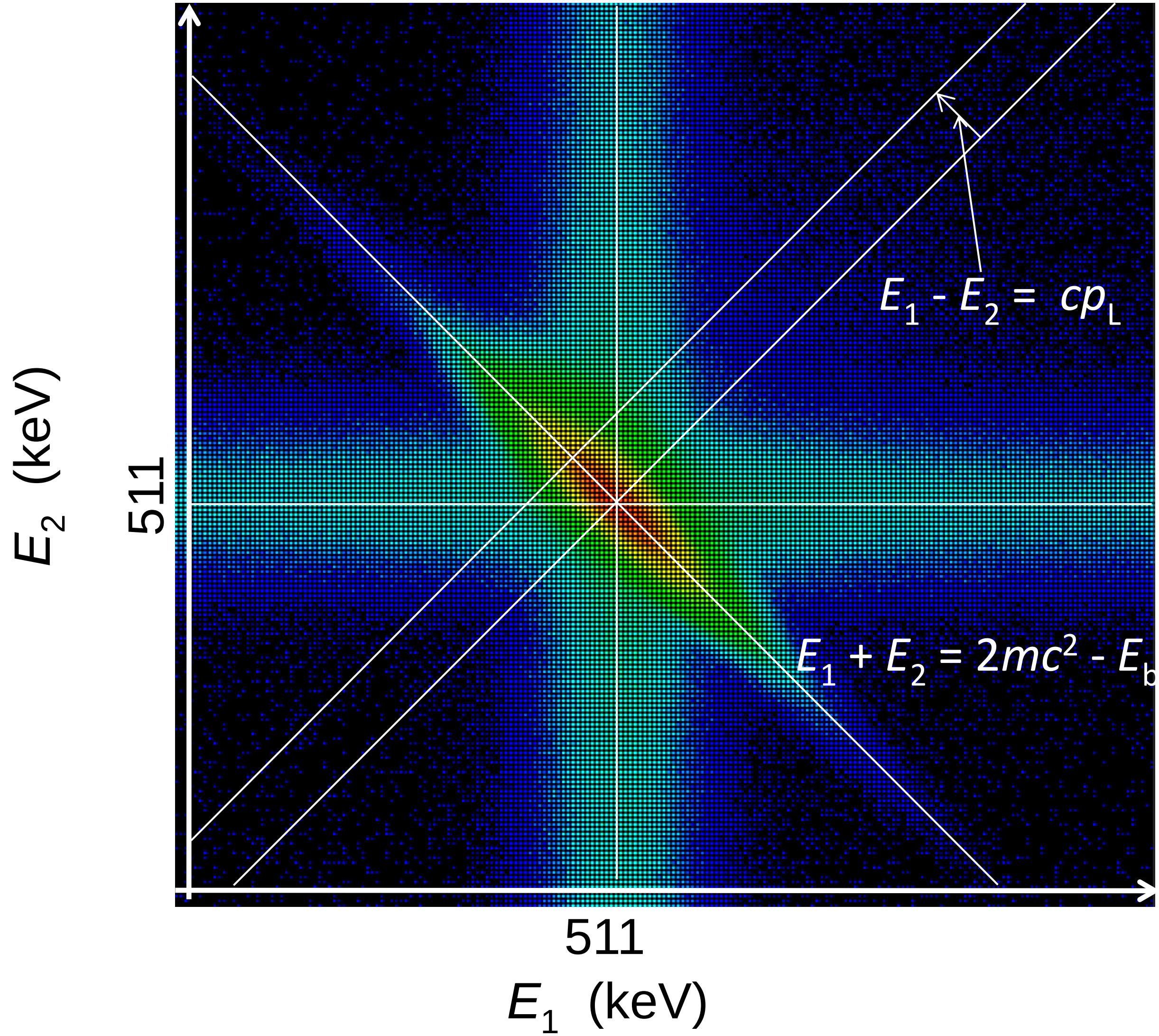
- In metallic system, positron lifetime is less than 500ps.
  500ps is saturation value of positron lifetime.
  Even if voids grow and are observed by TEM, positron lifetime of voids is
  less than 500ps.

CDB measurement

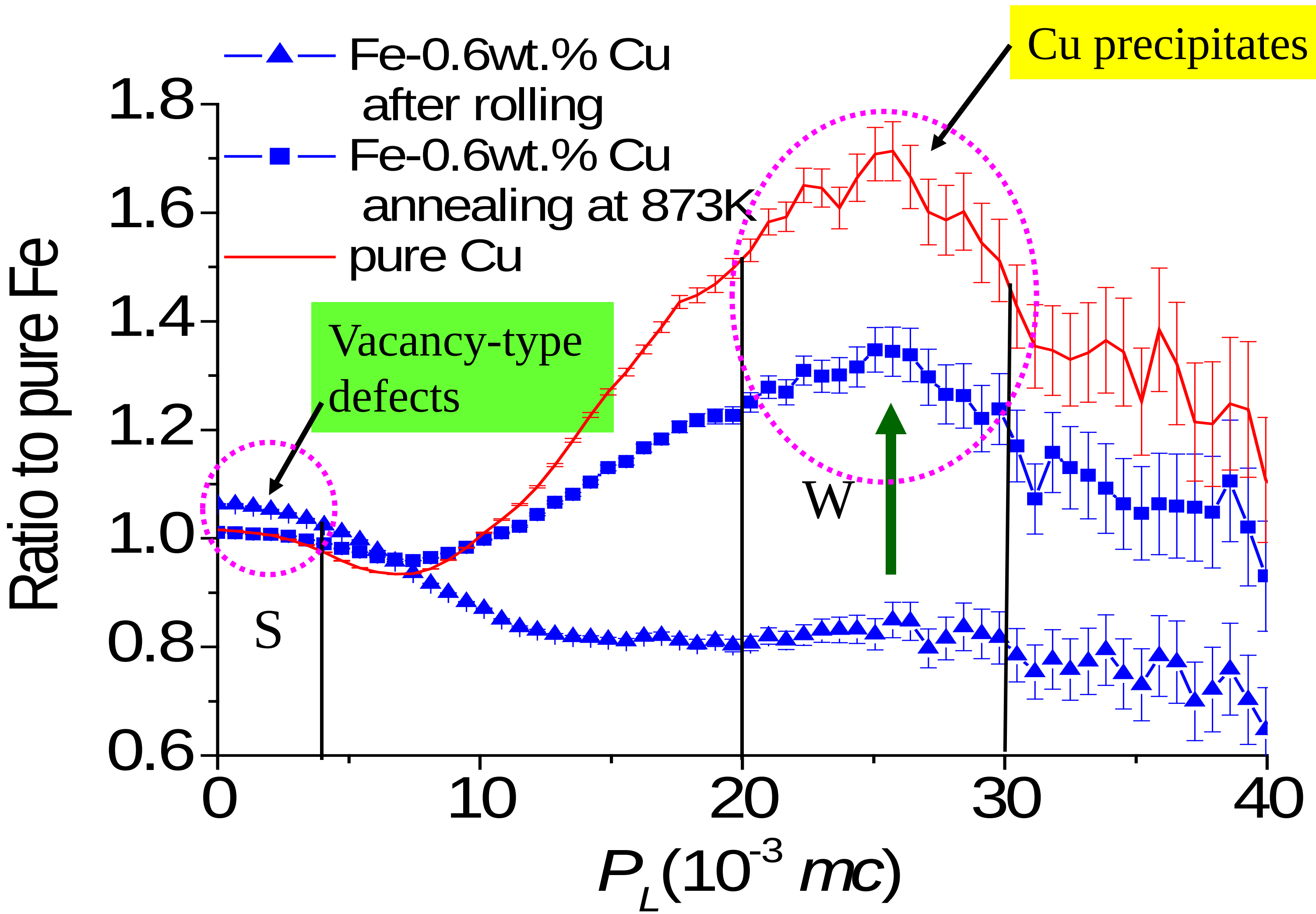


※c: light velocity

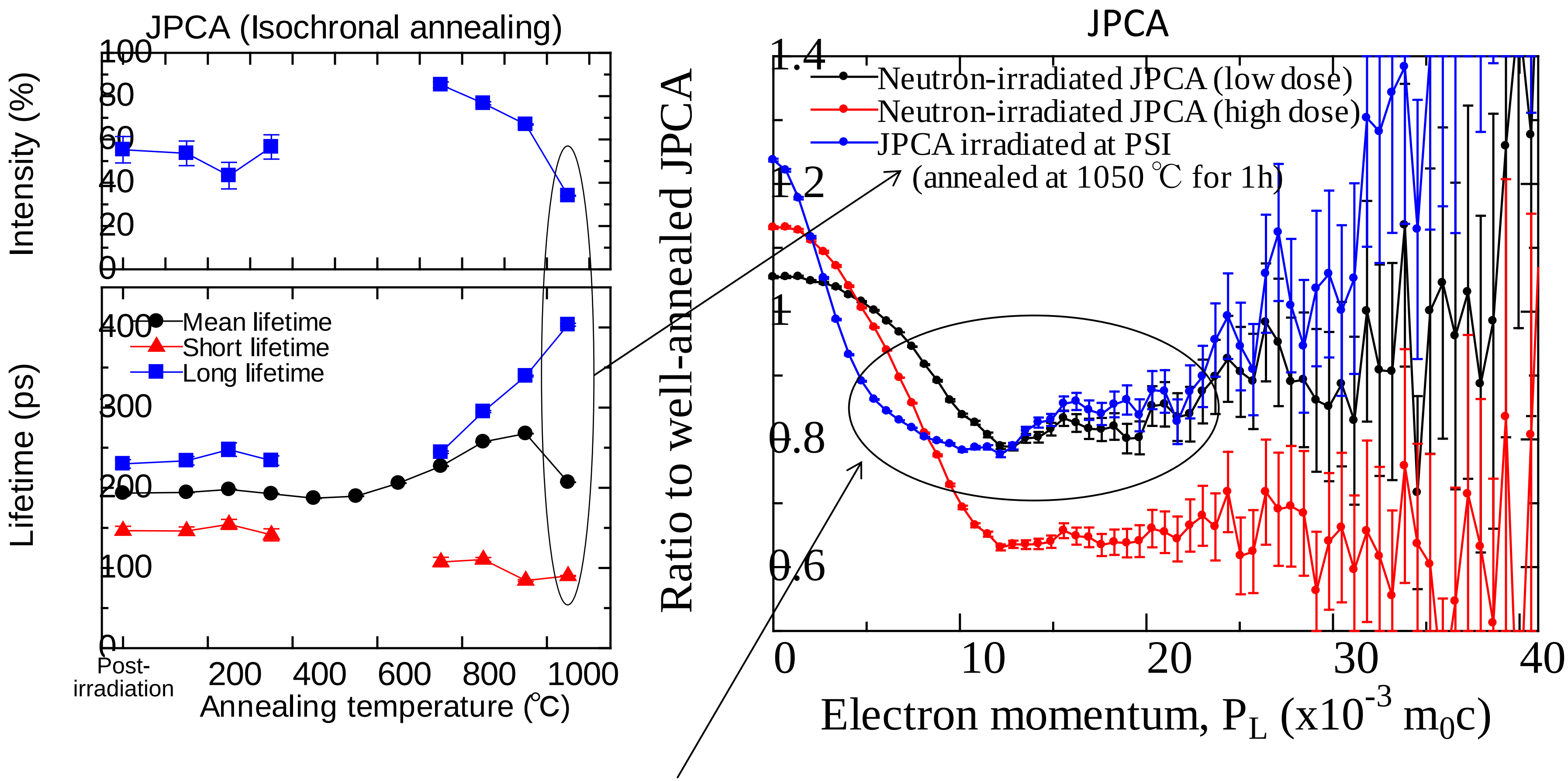
CDB spectrum



CDB ratio curve of Fe-Cu alloy



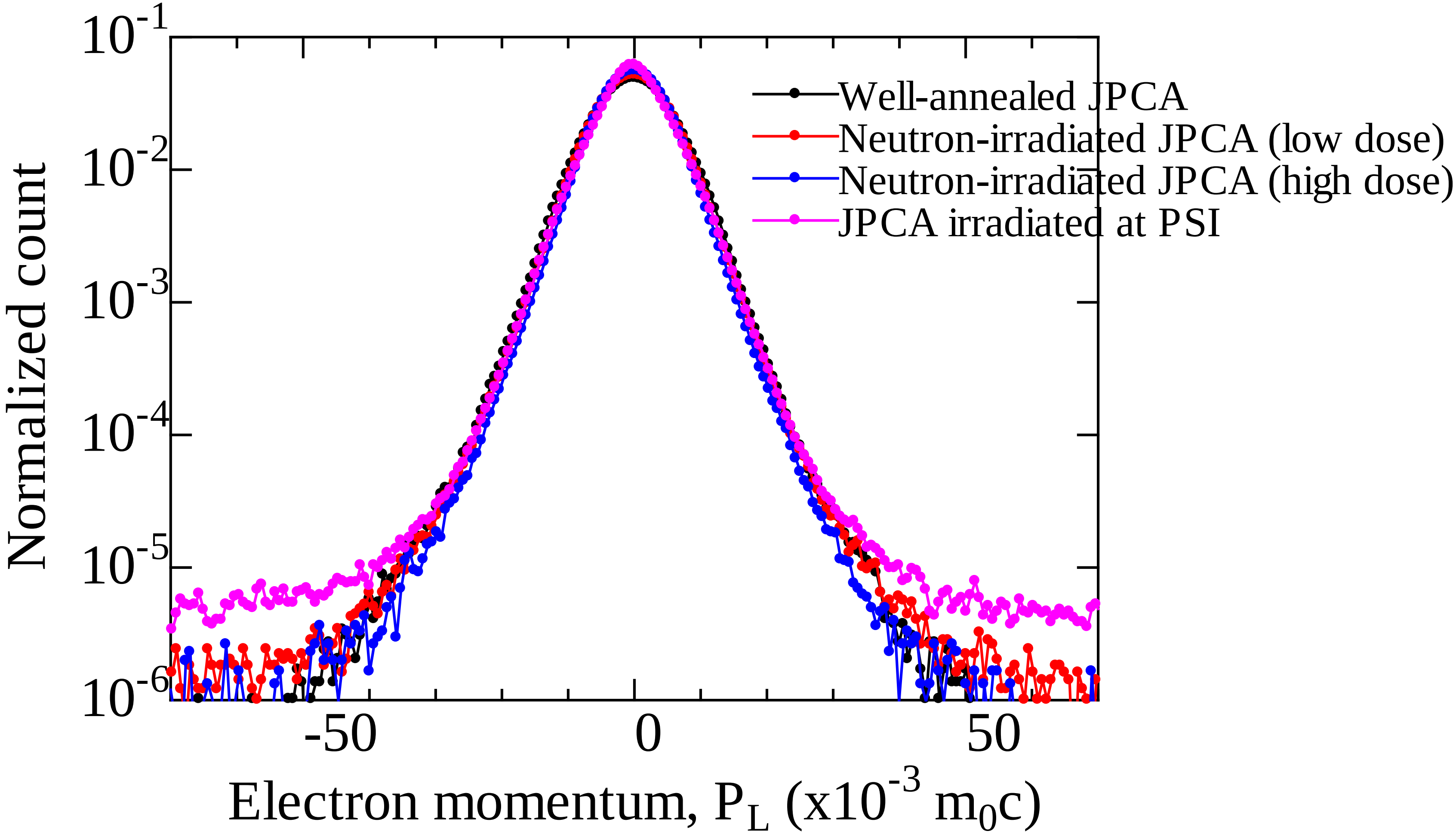
CDB ratio curves



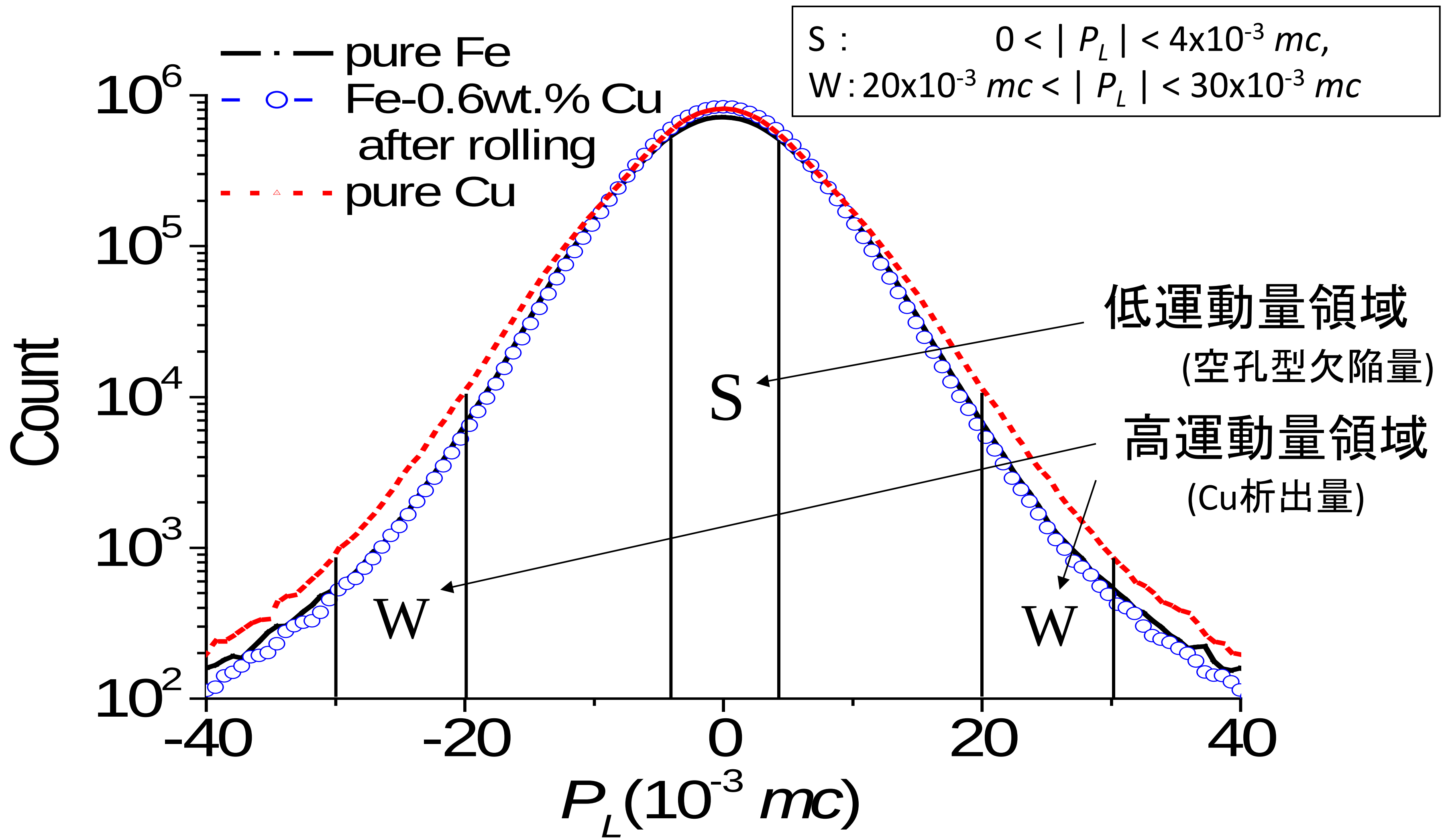
Usually, when low momentum region increases, high momentum region decreases.
But high momentum region of JPCA irradiated at PSI was higher than other samples.
This is due to helium effect??

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, P_L ($\times 10^{-3}$ m_0c)

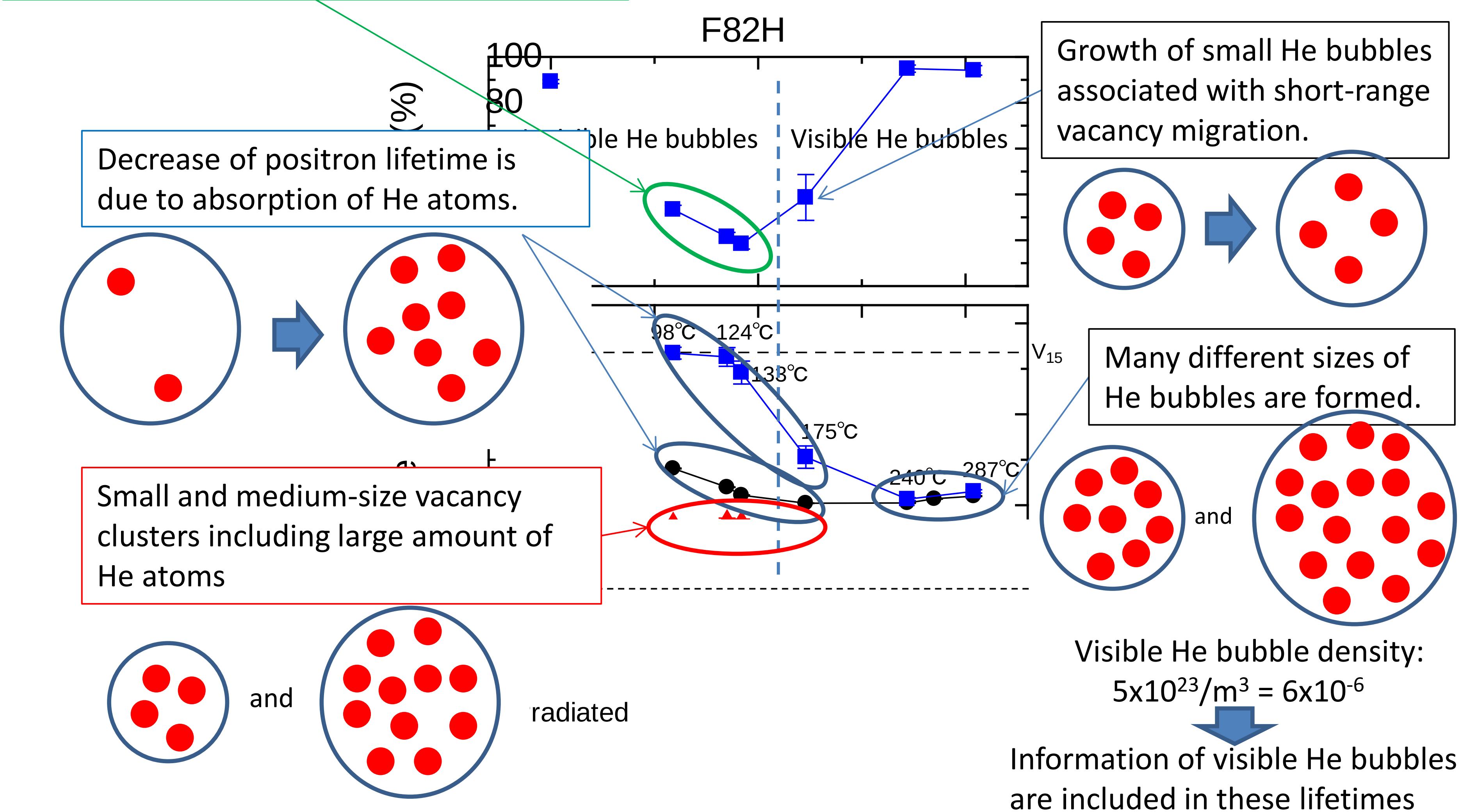
SパラメータとWパラメータ(CDB測定)



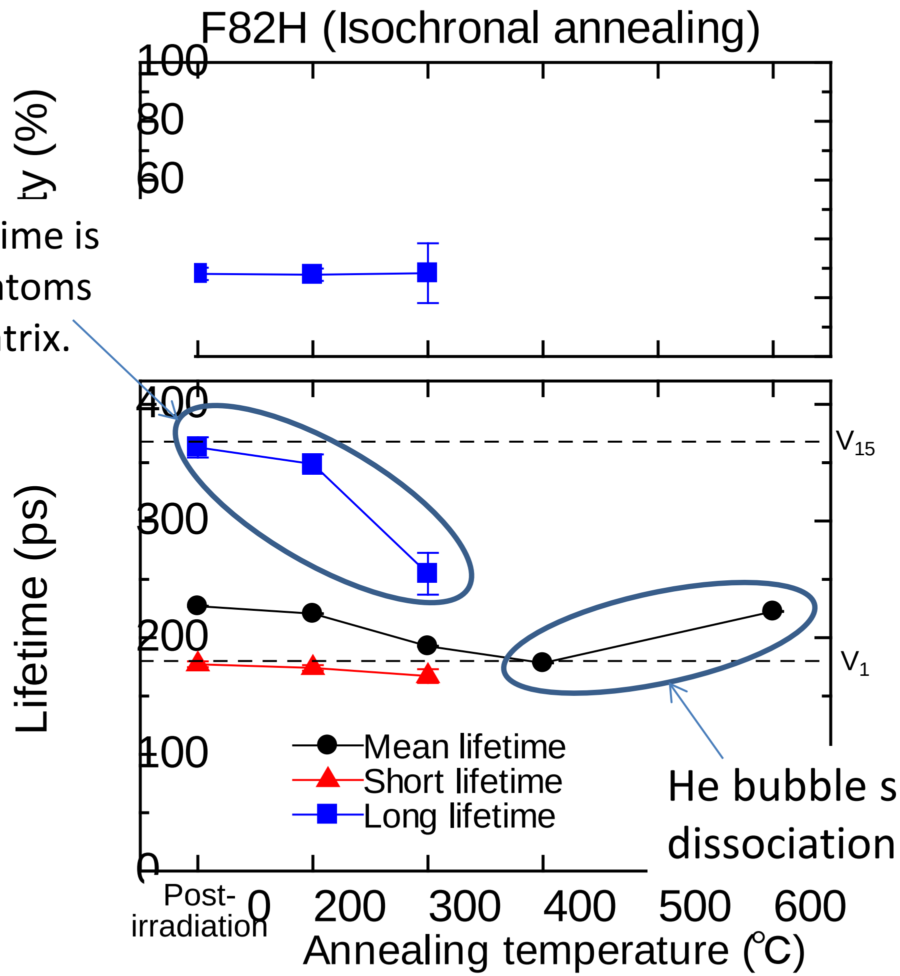
Dose dependence of positron lifetime in F82H

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.]

Decrease of the amount of vacancy clusters including small amount of He atoms



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°C: V-He_n complexes dissociate
700°C: V_m-He_n complexes dissociate
1100°C: Large He bubbles dissociate

TDS measurements of Fe-Cr alloys

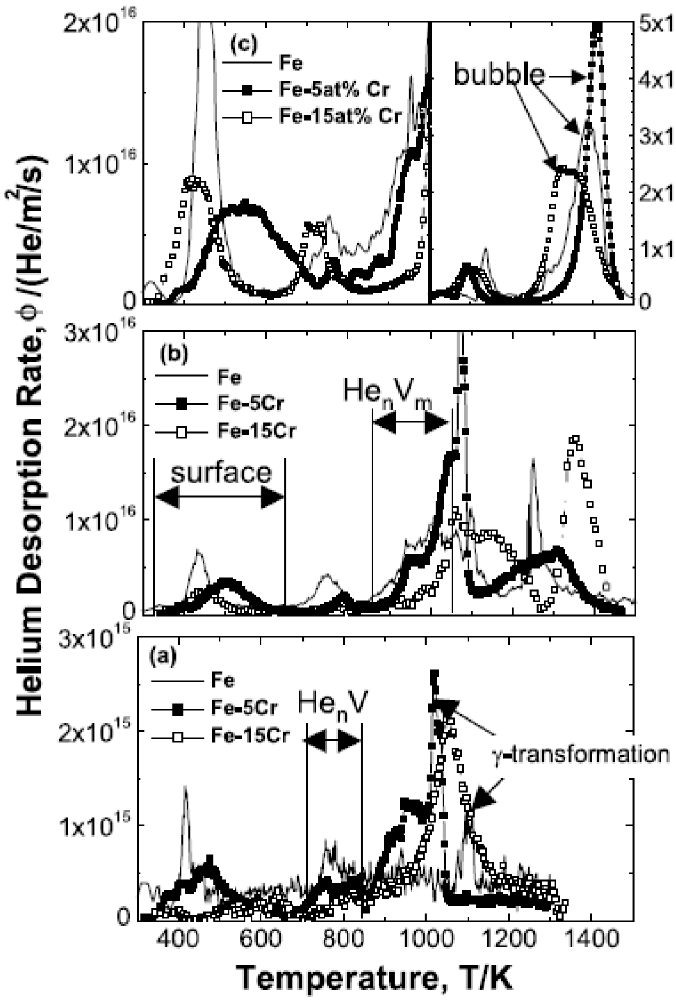
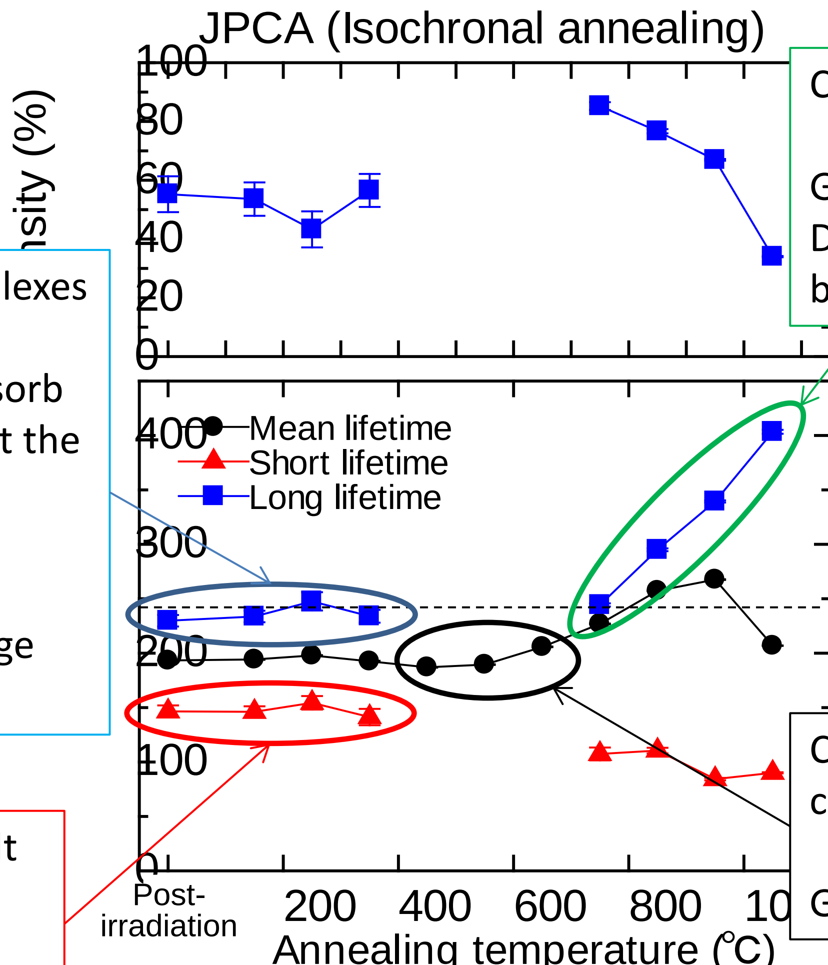


Fig. 1. He desorption spectra of Fe, Fe–5Cr and Fe–15Cr irradiated by 8 keV He+ ions at room temperature. The irradiation doses are (a) 1017, (b) 1018 and (c) 10^{19} He^+/m^2.

500°C: V-He_n complexes dissociate
700°C: V_m-He_n complexes dissociate
1100°C: 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

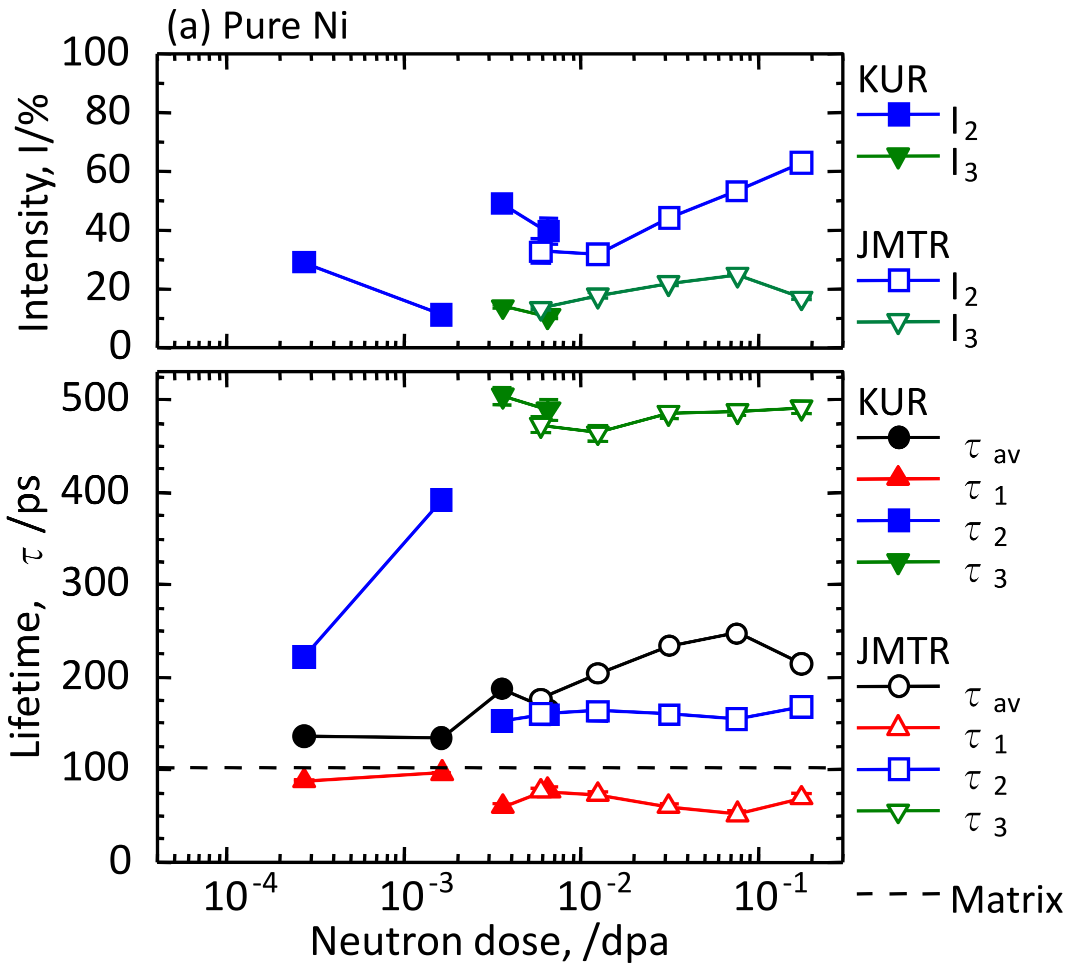
Growth of He bubbles

500℃: V-He_n complexes dissociate

700℃: V_m-He_n complexes dissociate

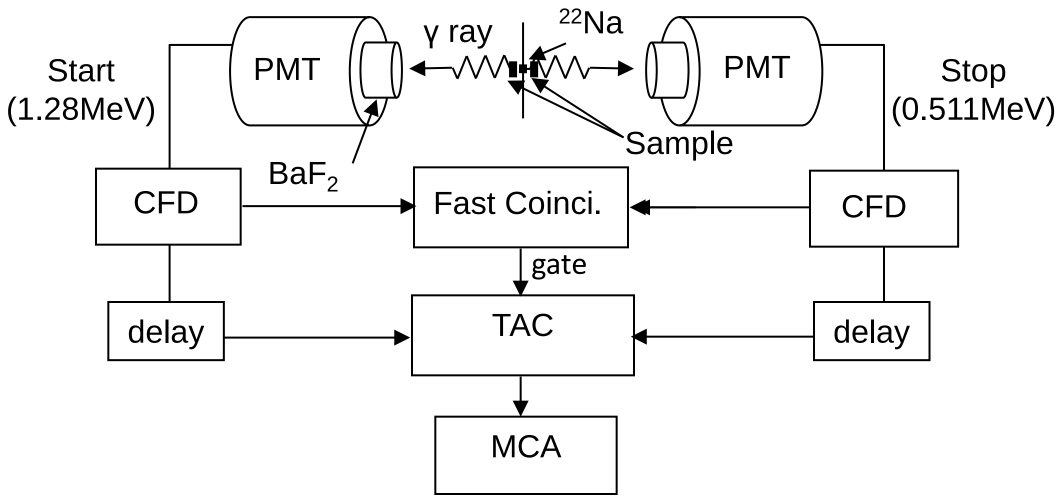
1100℃: Large He bubbles dissociate

Positron annihilation lifetimes in fission neutron-irradiated Ni

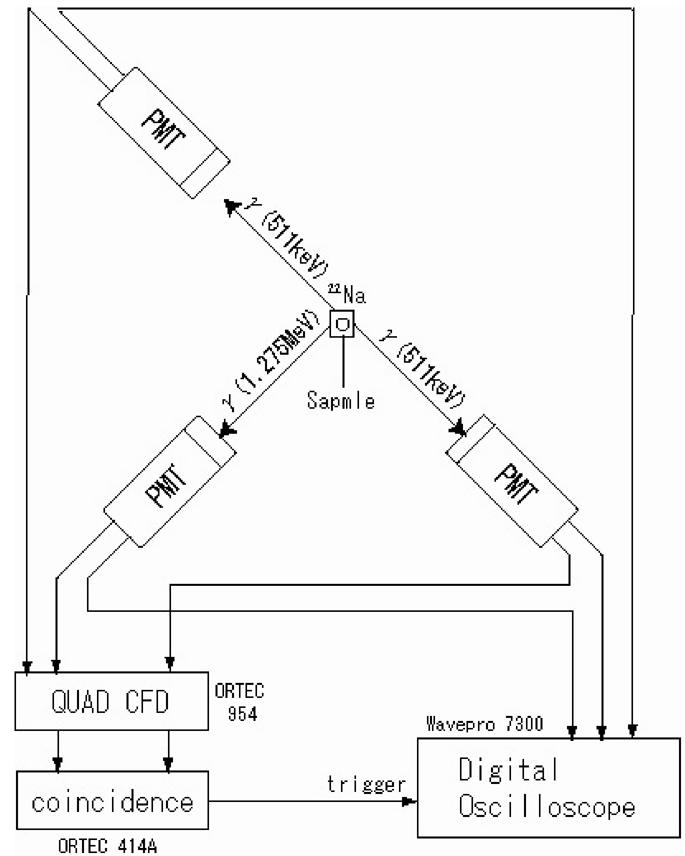


Void growth is observed by TEM in more than 0.01dpa, but positron lifetime is saturated.

Positron annihilation lifetime measurement system



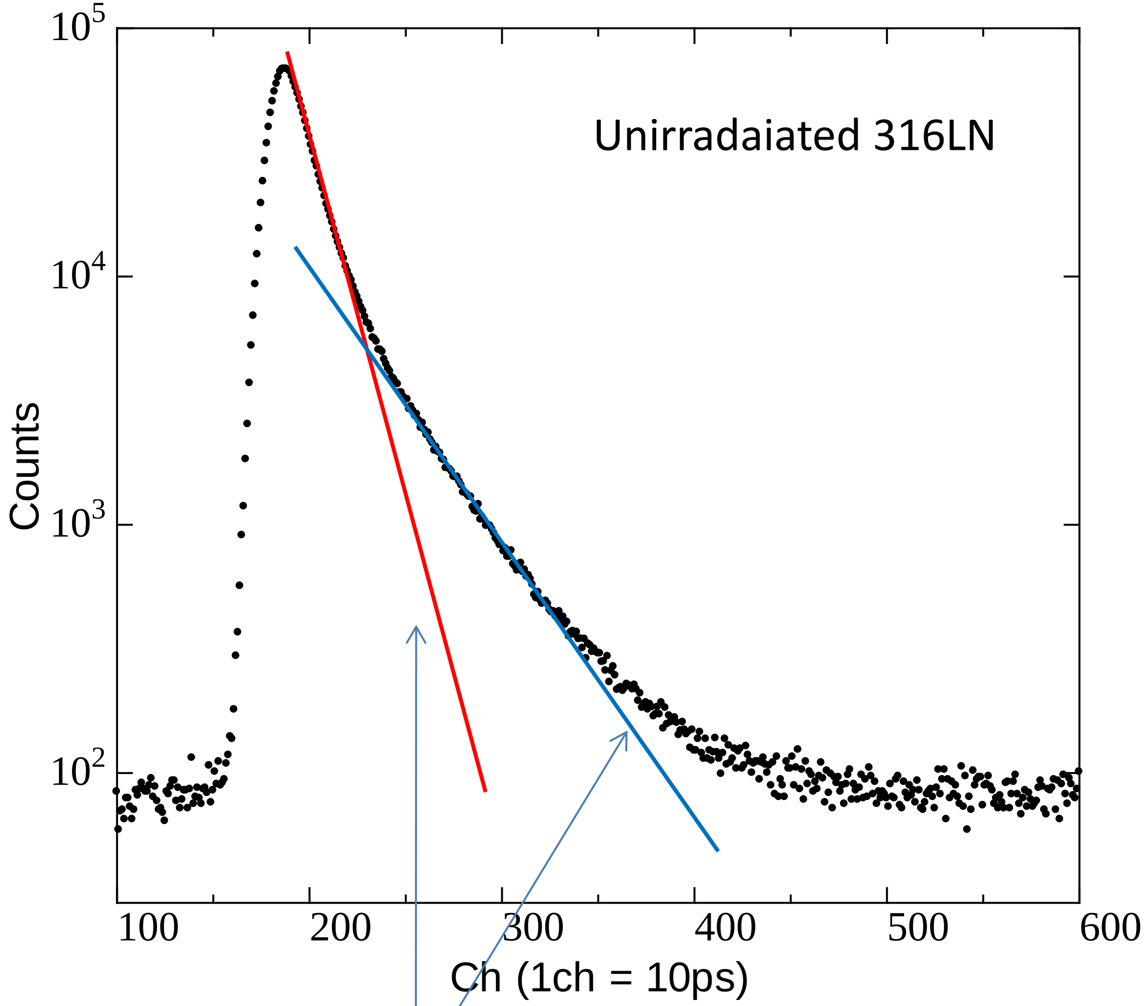
Conventional measurement system
(two-detector system)



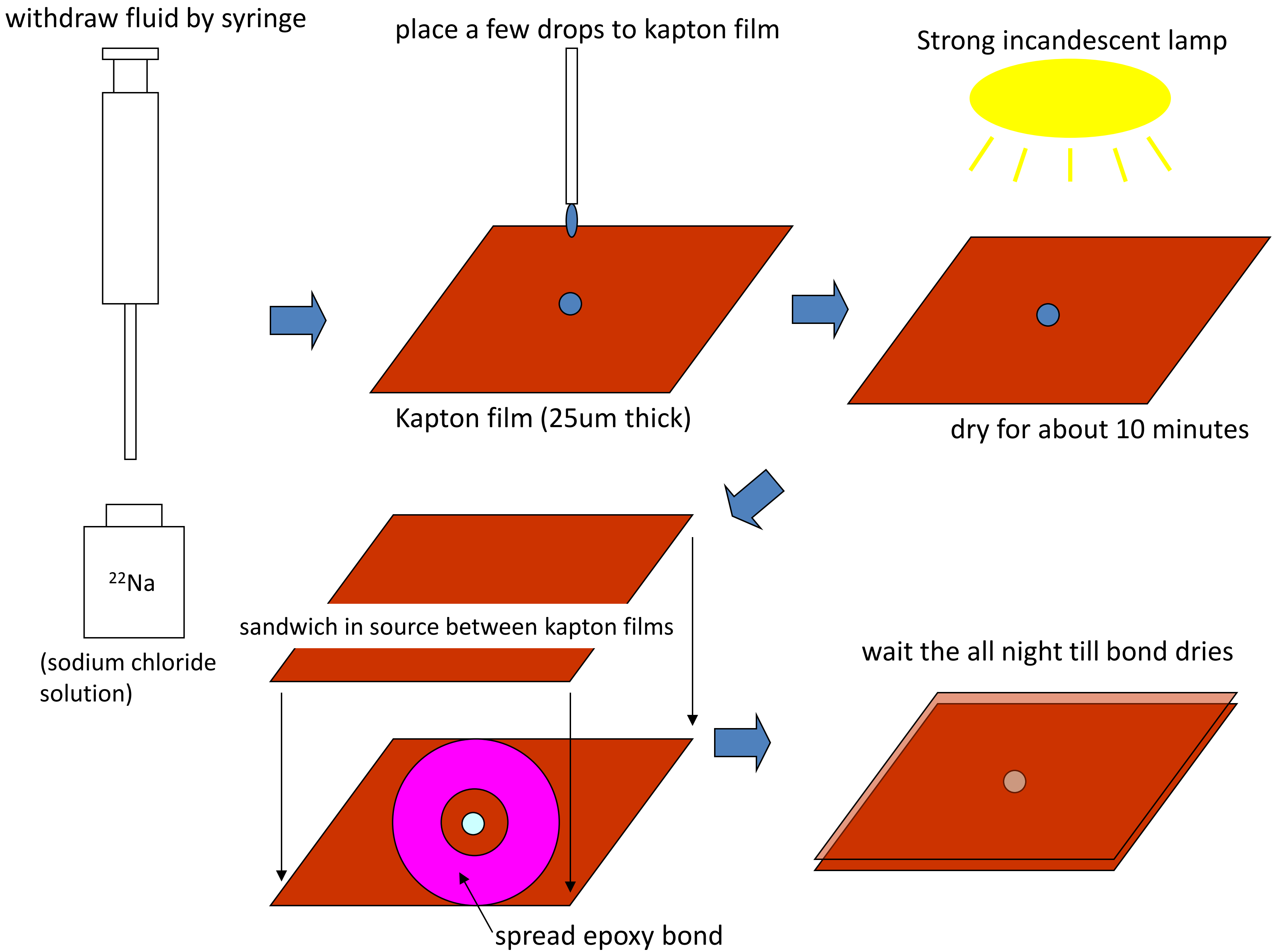
Improved measurement system
using a digital oscilloscope
(three-detector system)

Merit: Reduction of background
Demerit: Decrease of count rate

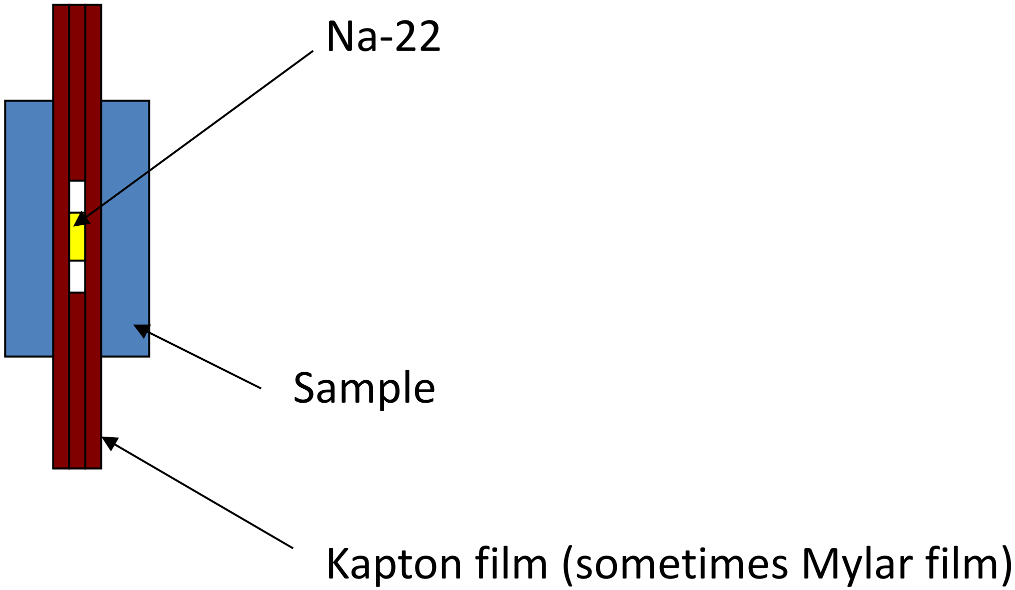
Positron annihilation lifetime spectrum



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
^{22}Na
(sodium chloride solution)
sandwich in source between kapton films
wait the all night till bond dries
spread epoxy bond

Set of samples

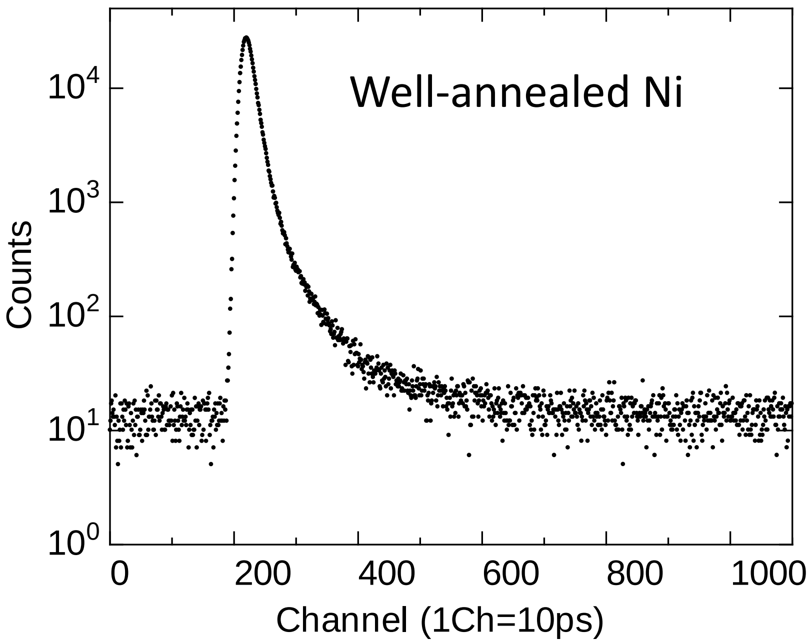


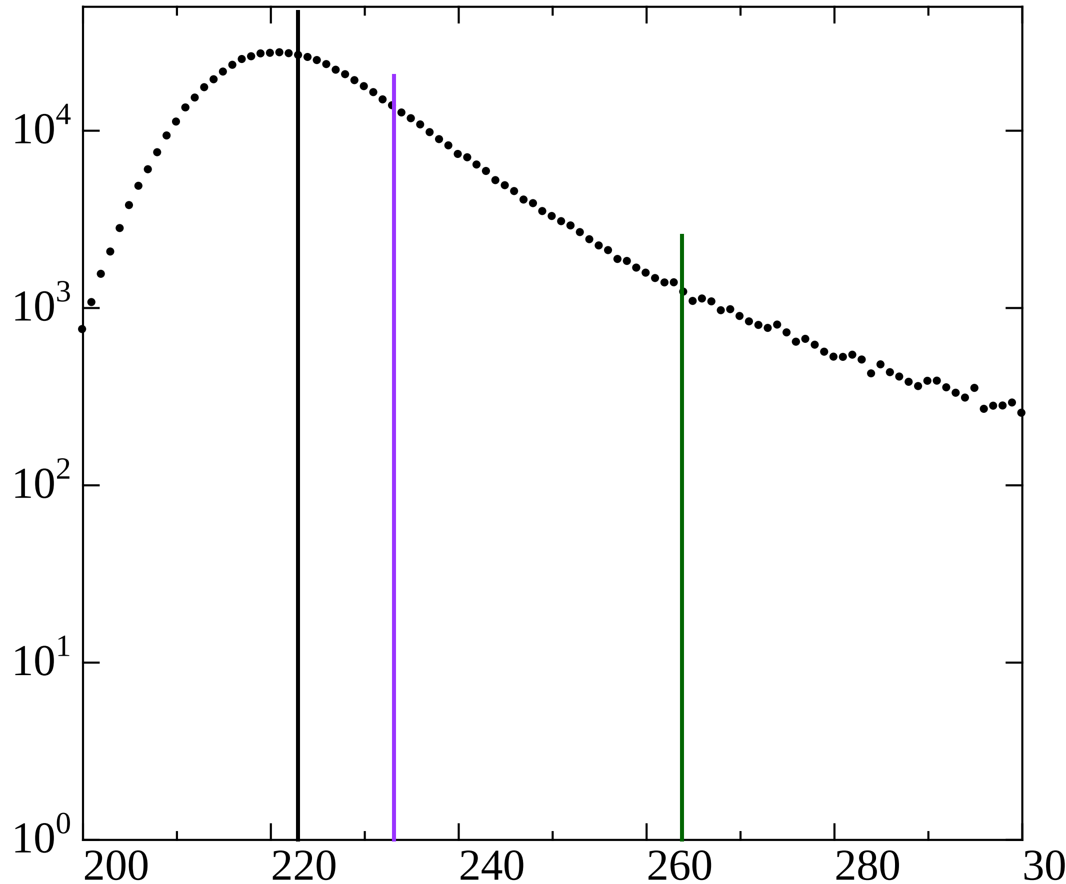
A part of positrons annihilate in the Kapton film.

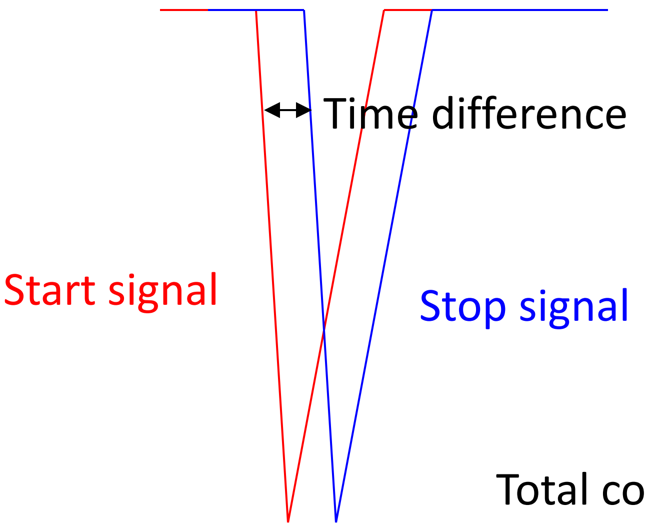
Ratio of positrons, which annihilate at Kapton film, depends on the thickness.

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

How to make lifetime spectrum





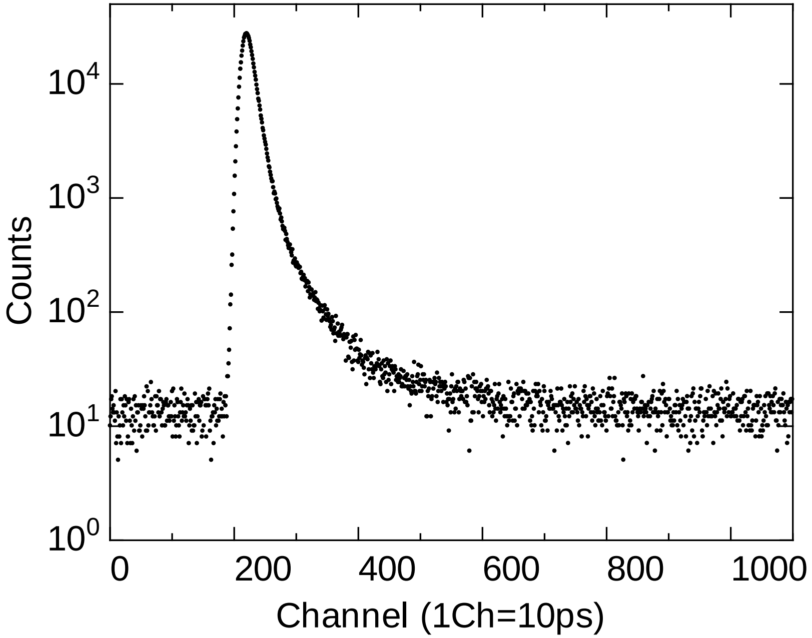


Time difference: 100ps

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

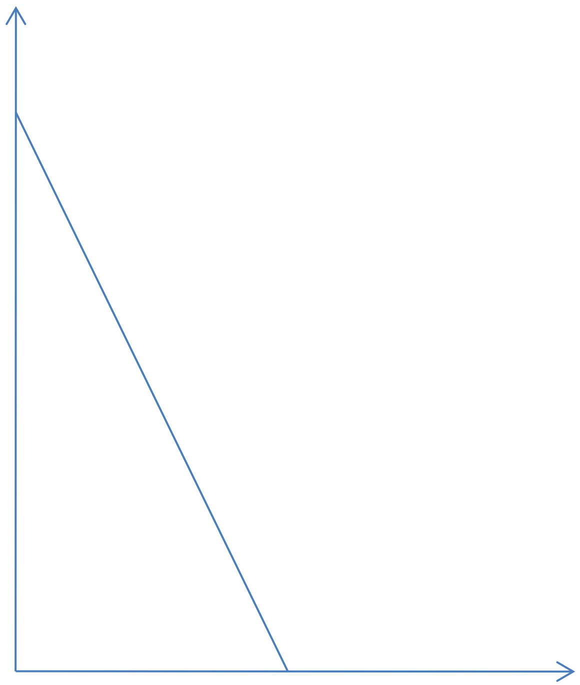
$$T(t) = \frac{I_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2}\exp\left(-\frac{t}{\tau_2}\right)$$

τ: lifetime
I : lifetime intensity

Three components

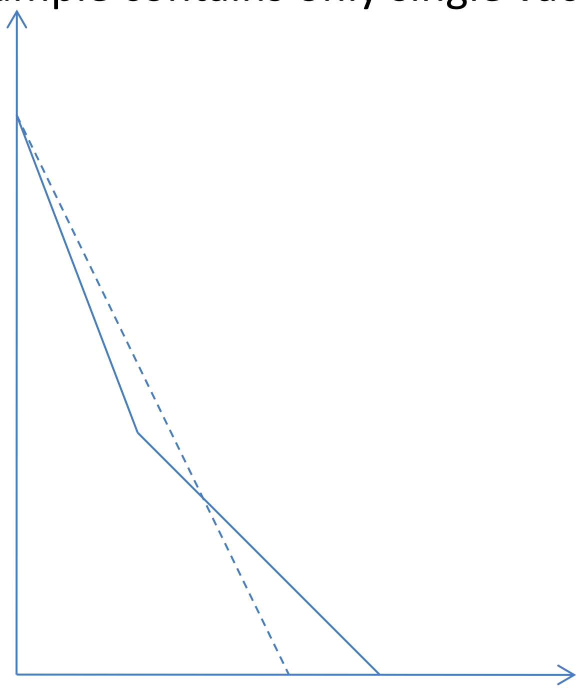
$$T(t) = \frac{I_1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2}\exp\left(-\frac{t}{\tau_2}\right) + \frac{I_3}{\tau_3}\exp\left(-\frac{t}{\tau_3}\right)$$

Without any defects



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

With single vacancies
(sample contains only single vacancies)



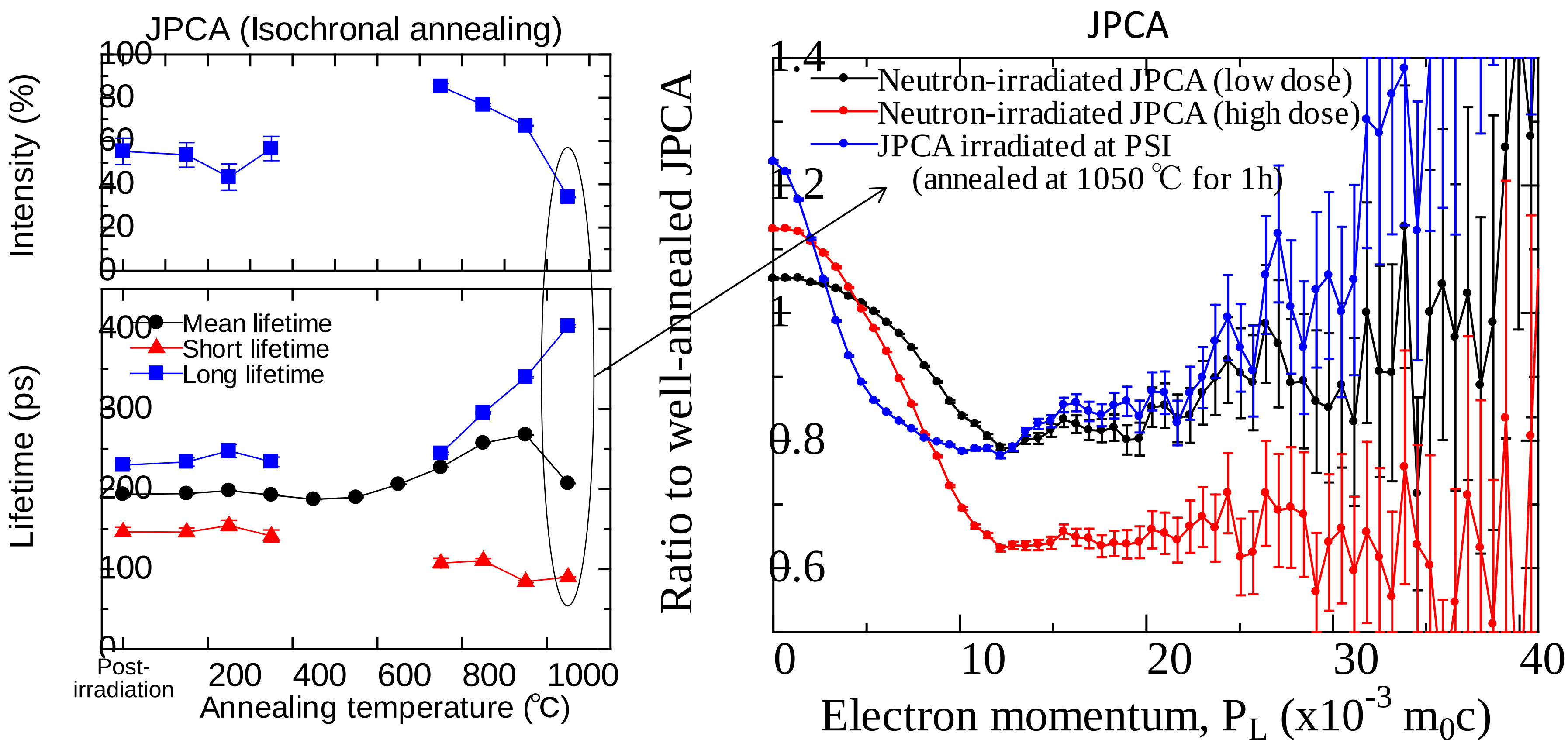
$$\tau_1 = \frac{1}{\lambda_m + \kappa} < 100\, ps$$

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

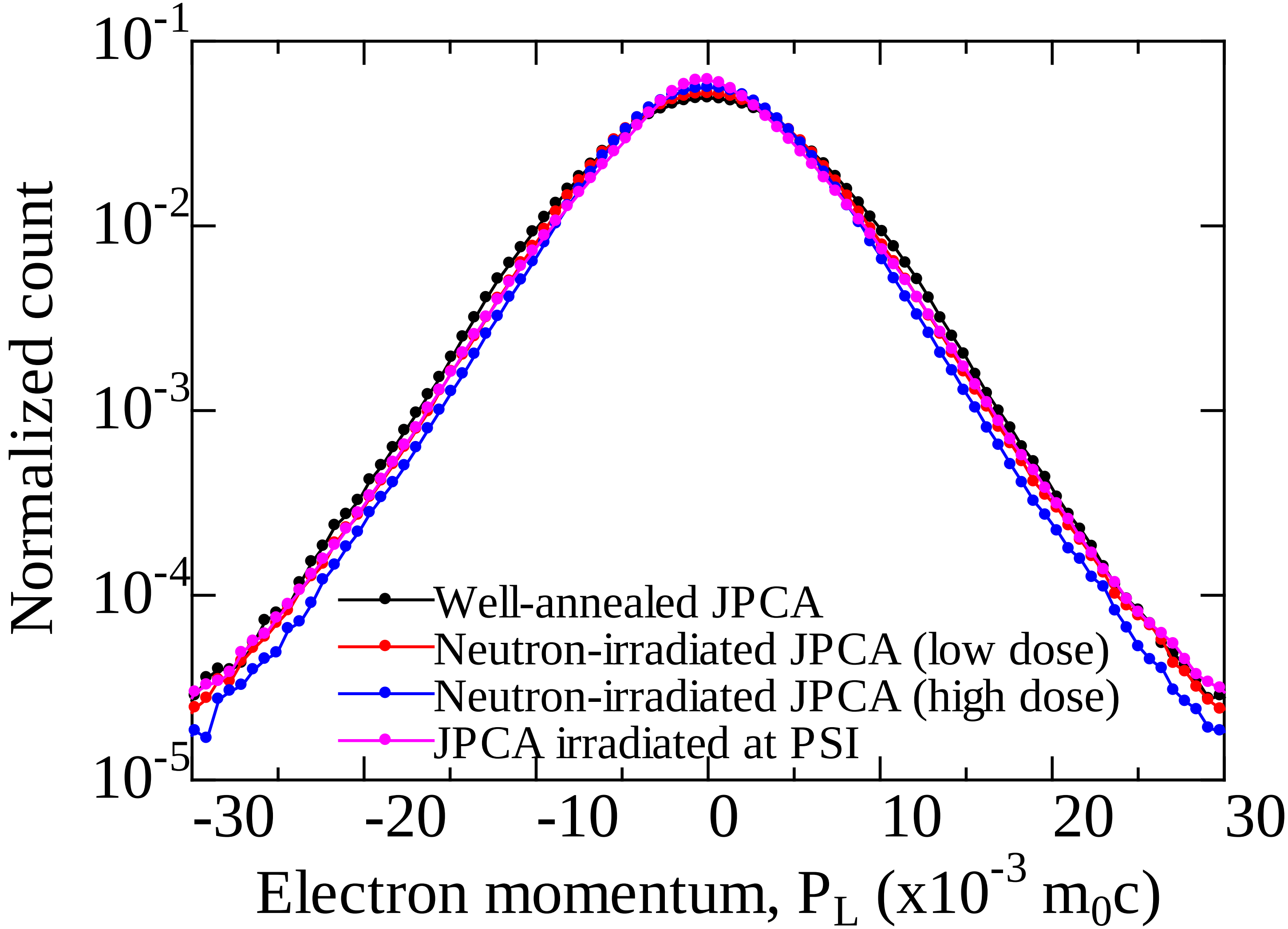
λ_m : positron annihilation rate in the matrix

λ_d : positron annihilation rate at the defect site

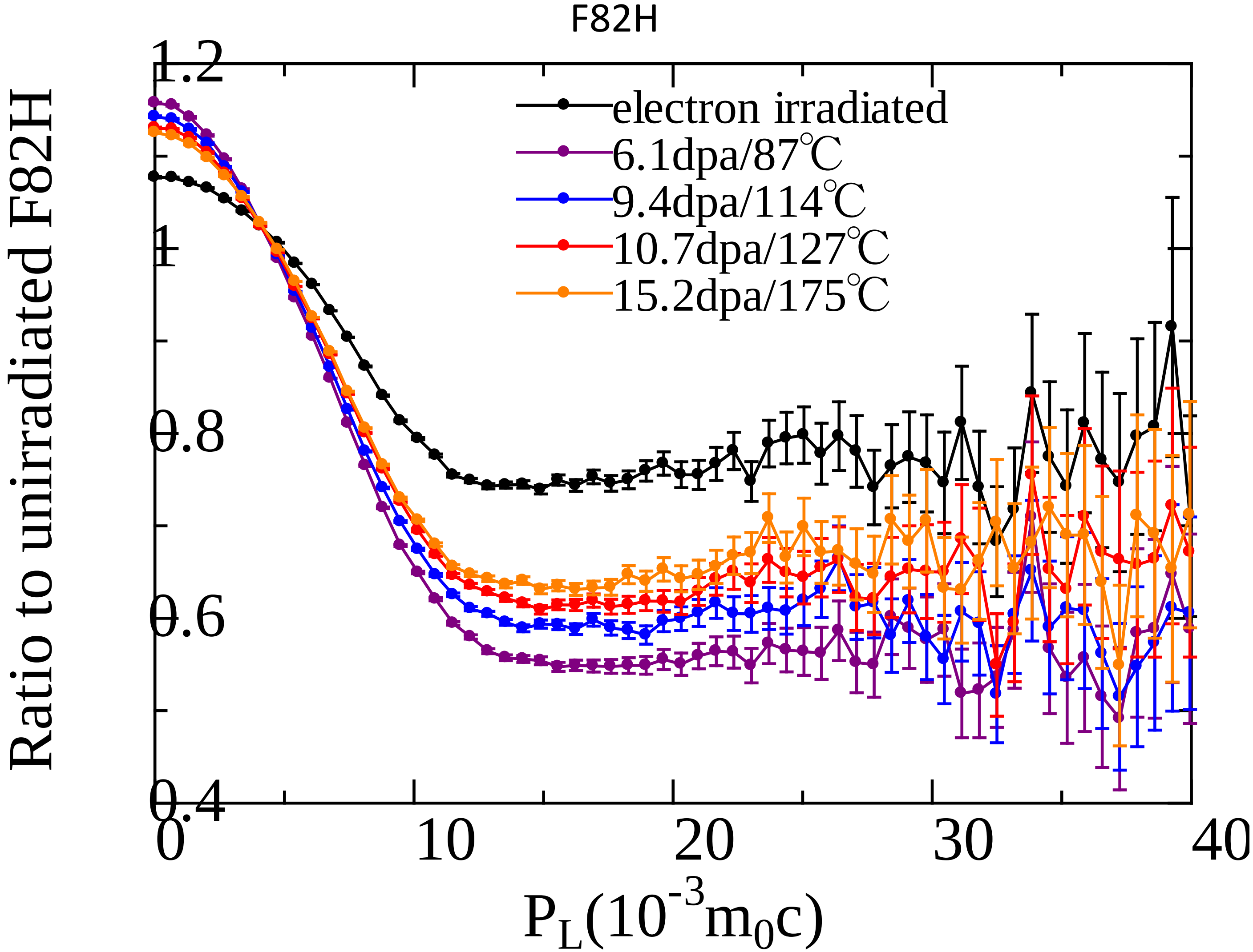
κ : positron transition rate from the matrix to the defect site



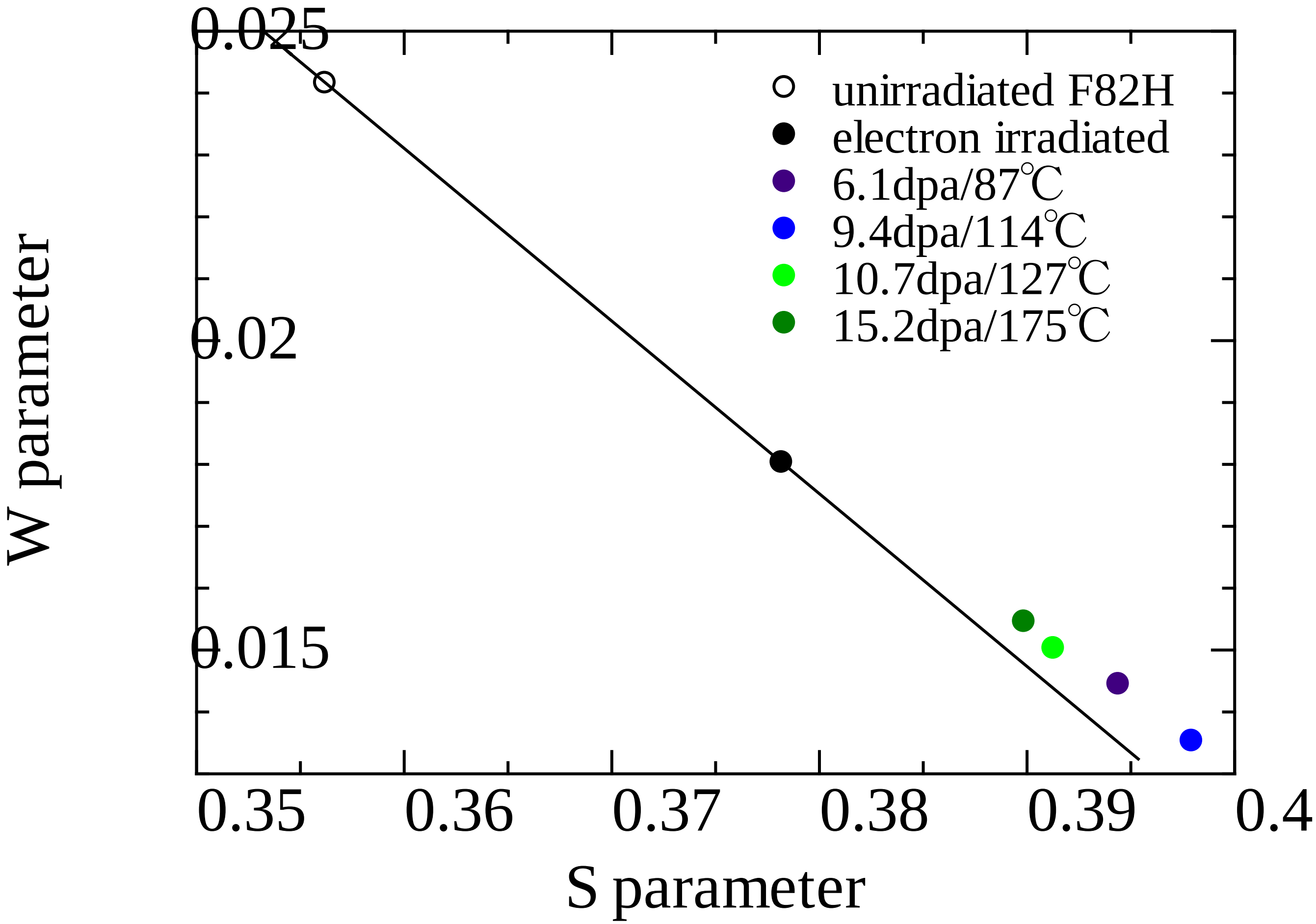
JPCA (Isochronal annealing)
Intensity (%)
Lifetime (ps)
Mean lifetime
Short lifetime
Long lifetime
Post-irradiation
200
400
600
800
1000
Annealing temperature (℃)
JPCA
Ratio to well-annealed JPCA
Neutron-irradiated JPCA (low dose)
Neutron-irradiated JPCA (high dose)
JPCA irradiated at PSI
(annealed at 1050 ℃ for 1h)
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 ($\times 10^{-3}$ 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
$P_L(10^{-3}m_0c)$



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