Investigation of open volume in photochromic YH_xO_y thin films by positron annihilation lifetime spectroscopy

Ziying Wu[1,*], Tom de Krom[1], Gijs van Hattem[1], Giorgio Colombi[2], Bernard Dam[2], Henk Schut[1], Marcel Dickmann[3], Werner Egger[3], Christoph Hugenschmidt[4], and Stephan W.H. Eijt[1]

[1]*Department of Radiation Science and Technology, Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands*
[2]*Materials for Energy Conversion and Storage, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Delft, The Netherlands*
[3]*Institut für angewandte Physik und Messtechnik, Bundeswehr Universität München, Germany*
[4]Physics Department and Heinz Maier-Leibnitz Zentrum (MLZ), TU München, Germany

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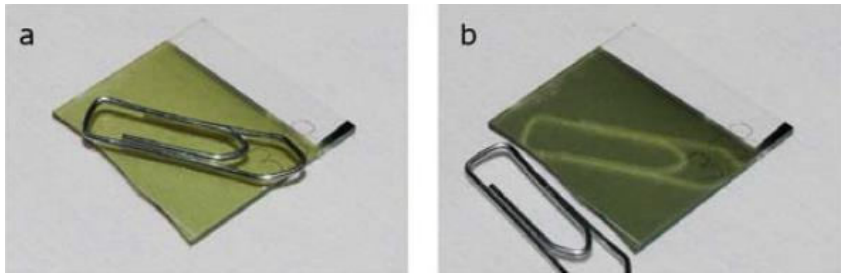
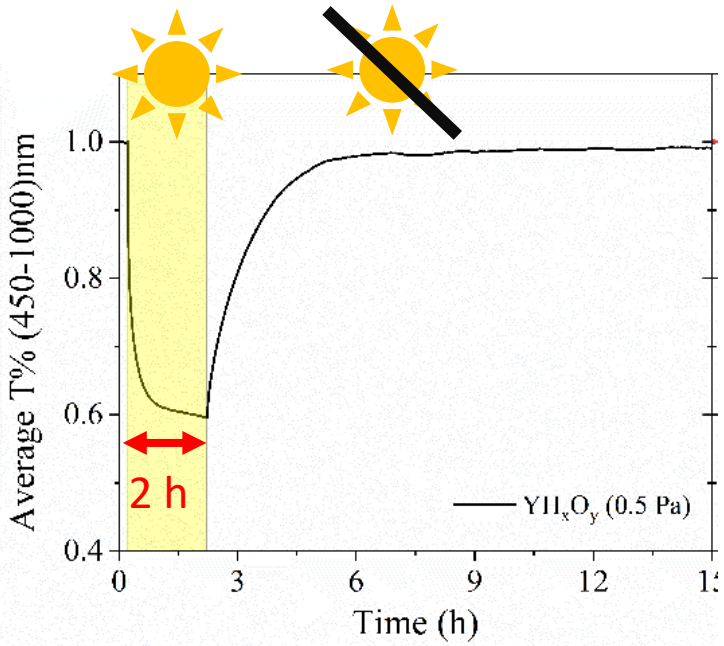
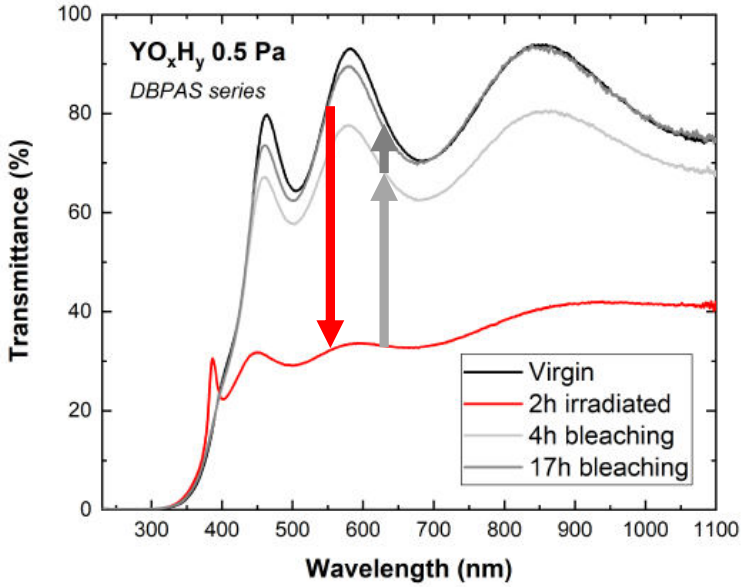
- Conclusions

Photochromic YH_xO_y thin films



Picture: **T. Mongstad *et al***. "A new thin film photochromic material: Oxygen-containing yttrium hydride", *Sol. Energy Mat. Solar Cells* (2011)



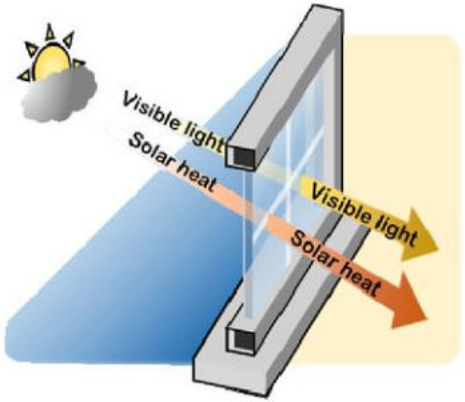


Picture: **S.W.H. Eijt *et al***. "Photochromic YOxHy Thin Films Examined by in situ Positron Annihilation Spectroscopy", *ACTA PHYS POL A* (2020)

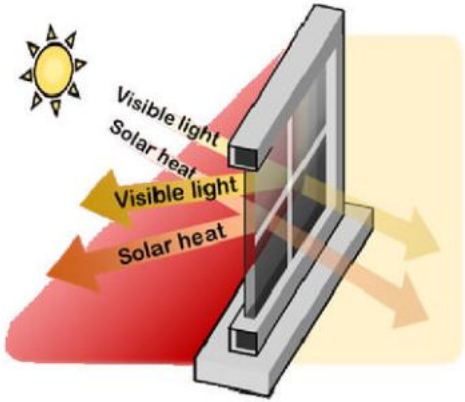
Photo-darkening:
Reduced sub-bandgap transmission

Bleaching: nearly full recovery

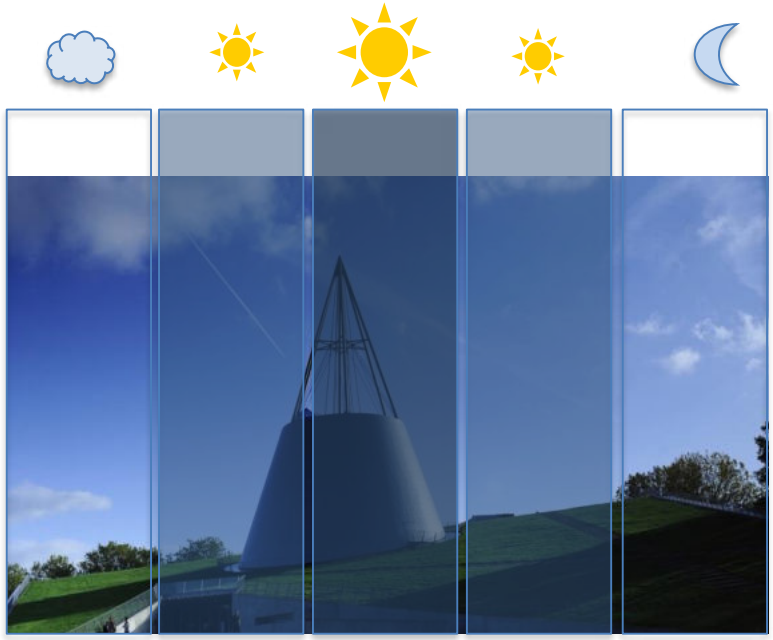
Smart windows for energy-saving



Transparent
Weak sunlight



Opaque
Strong sunlight

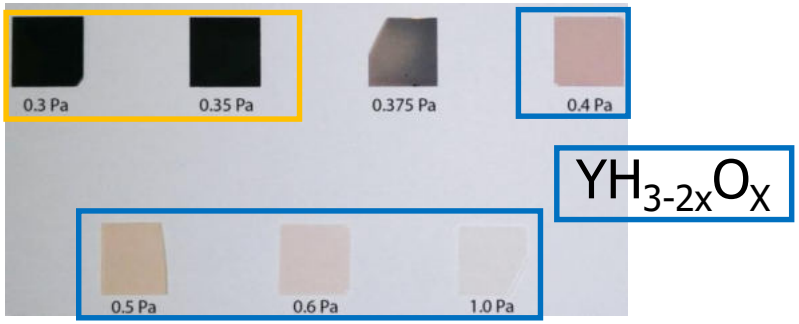


Picture: Proc. SPIE 10555, Emerging Liquid Crystal Technologies XIII, 1055516 (2018)

Synthesis of YH_xO_y thin films

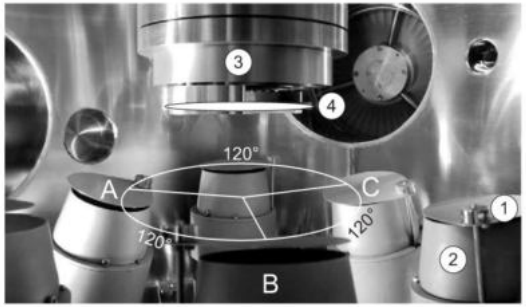
Sputtered $YH_{\sim 2}$ films (300-500 nm) —Oxidized in air→ photochromic YH_xO_y films

$YH_{\sim 2}$



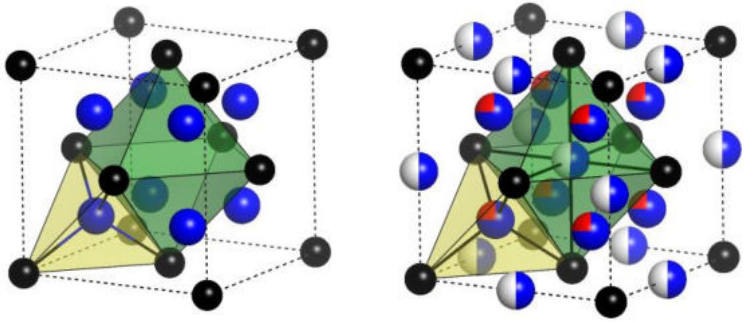
$YH_{3-2x}O_X$

Color changes



Reactive magnetron sputtering

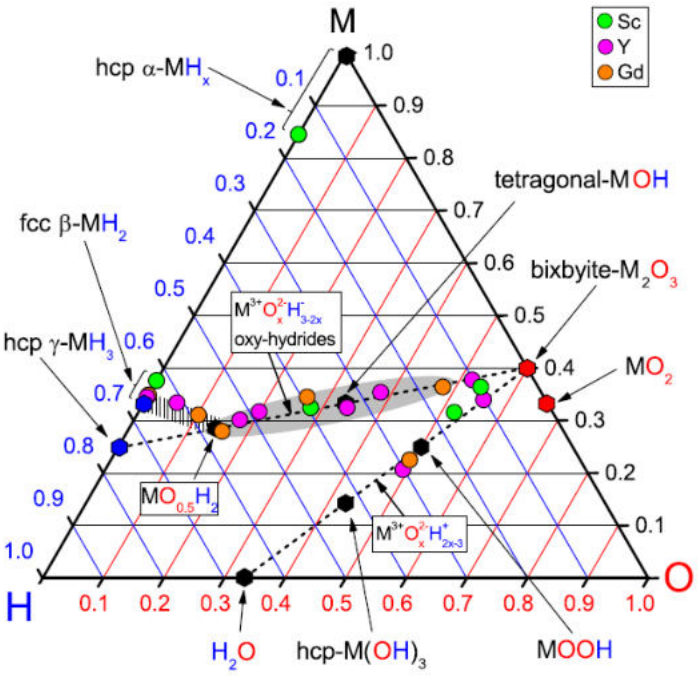
Metal-to-semiconductor change

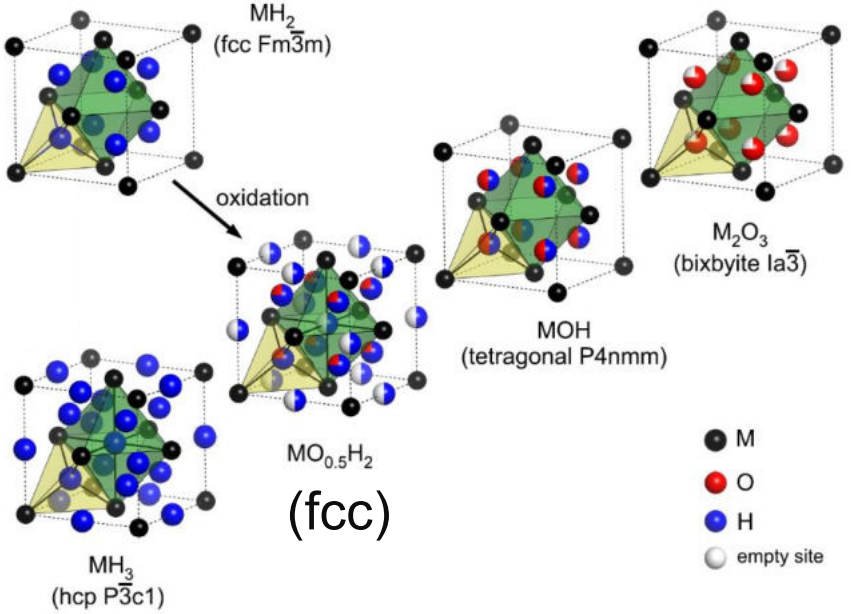


MH_2 (fcc) → $MH_{3-2x}O_x$ (0.5<x<1) (fcc)

Phase diagram of YH_xO_y thin films

Pictures: Cornelius et al., J. Phys. Chem. Lett. 10 (2019) 1342−1348

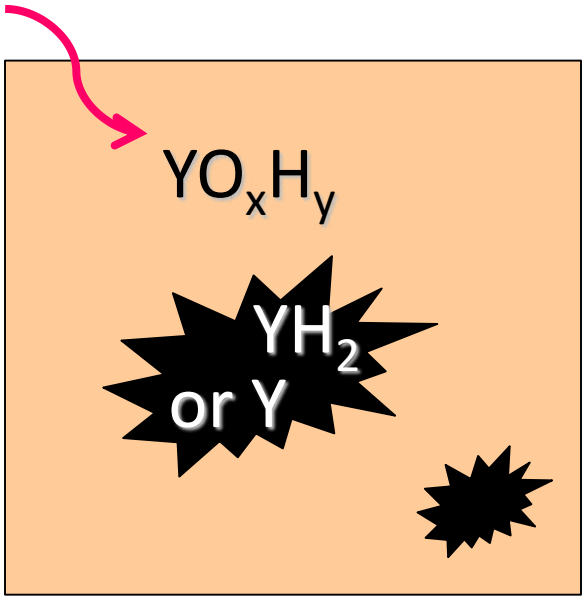


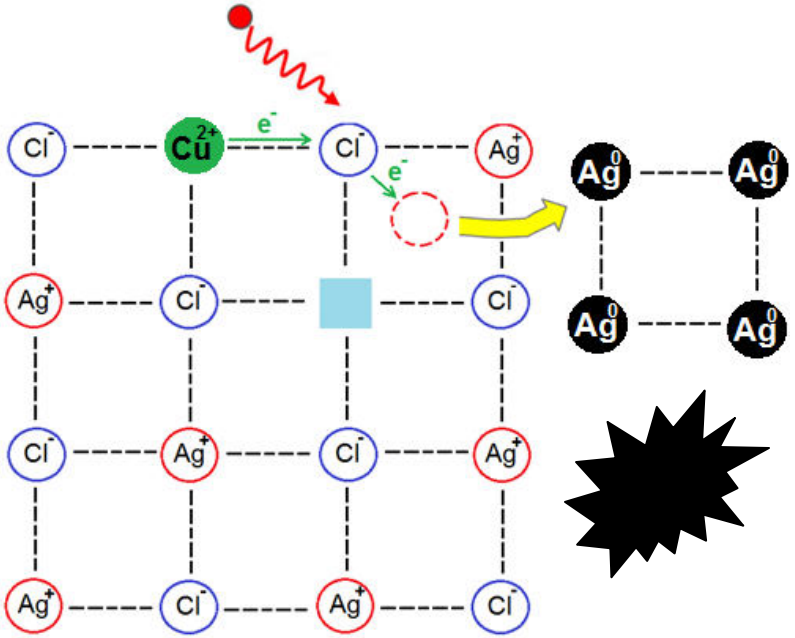


Grey area ($MH_{3-2x}O_x$): photochromic

Why are these films photochromic?

Mechanism: similar to Ag-based photochromism?



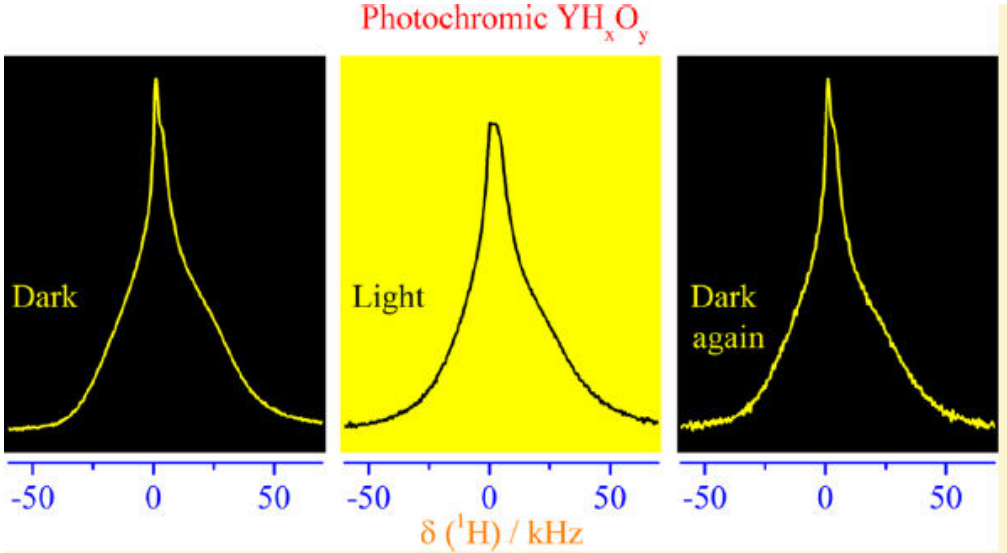


Pictures: F. Nafezarefi, docteral thesis, TU Delft, 2020

Yttrium (dihydride) domains growth?

Photochromic Cu^+ doped AgCl glass: formation of Ag metal clusters

Mechanism: Role of Hydrogen?

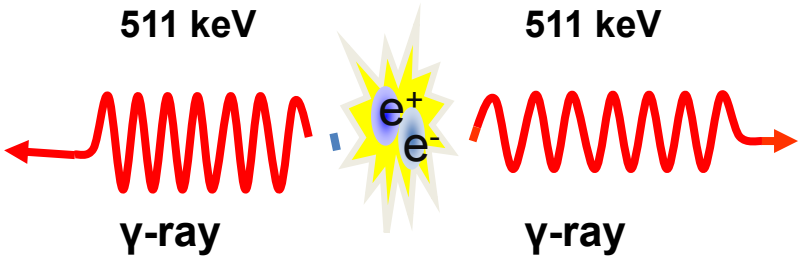


Picture: **C. Vinod Chadran *et al***. "Solid-State NMR Studies of the Photochromic Effects of Thin Films of Oxygen-Containing Yttrium Hydride", J. Phys. Chem. C 118 (2014) 22935 - 22942

NMR:

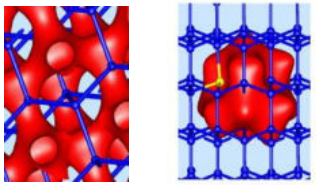
- mobile hydrogen 'disappears' upon UV illumination
- reversible!

Positron annihilation spectroscopy



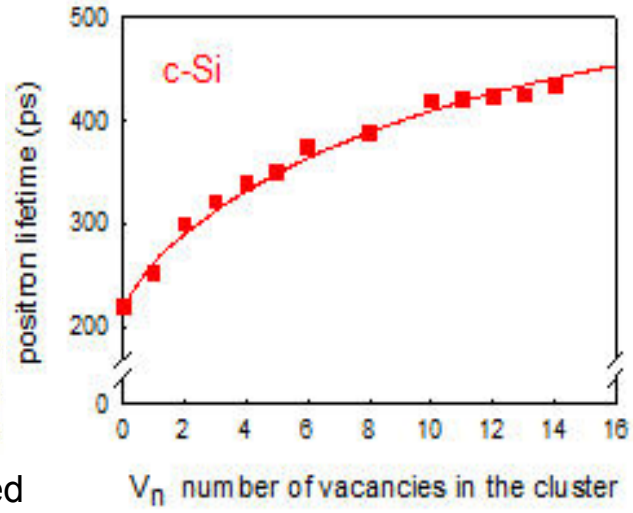
Annihilation: creation of 2 γ–rays (most common process)

$$e^+ + e^- \rightarrow 2\gamma$$



lattice

e⁺ trapped at vacancy

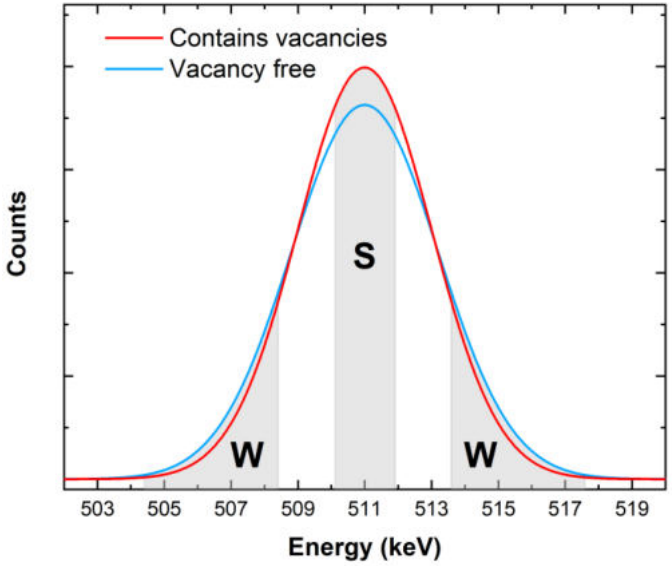


- Positron Annihilation Lifetime Spectroscopy (PALS):

  the size and concentration of vacancies

- Doppler Broadening Positron Annihilation Spectroscopy (DB-PAS):

  Vacancies
  electronic structure



Motivations:

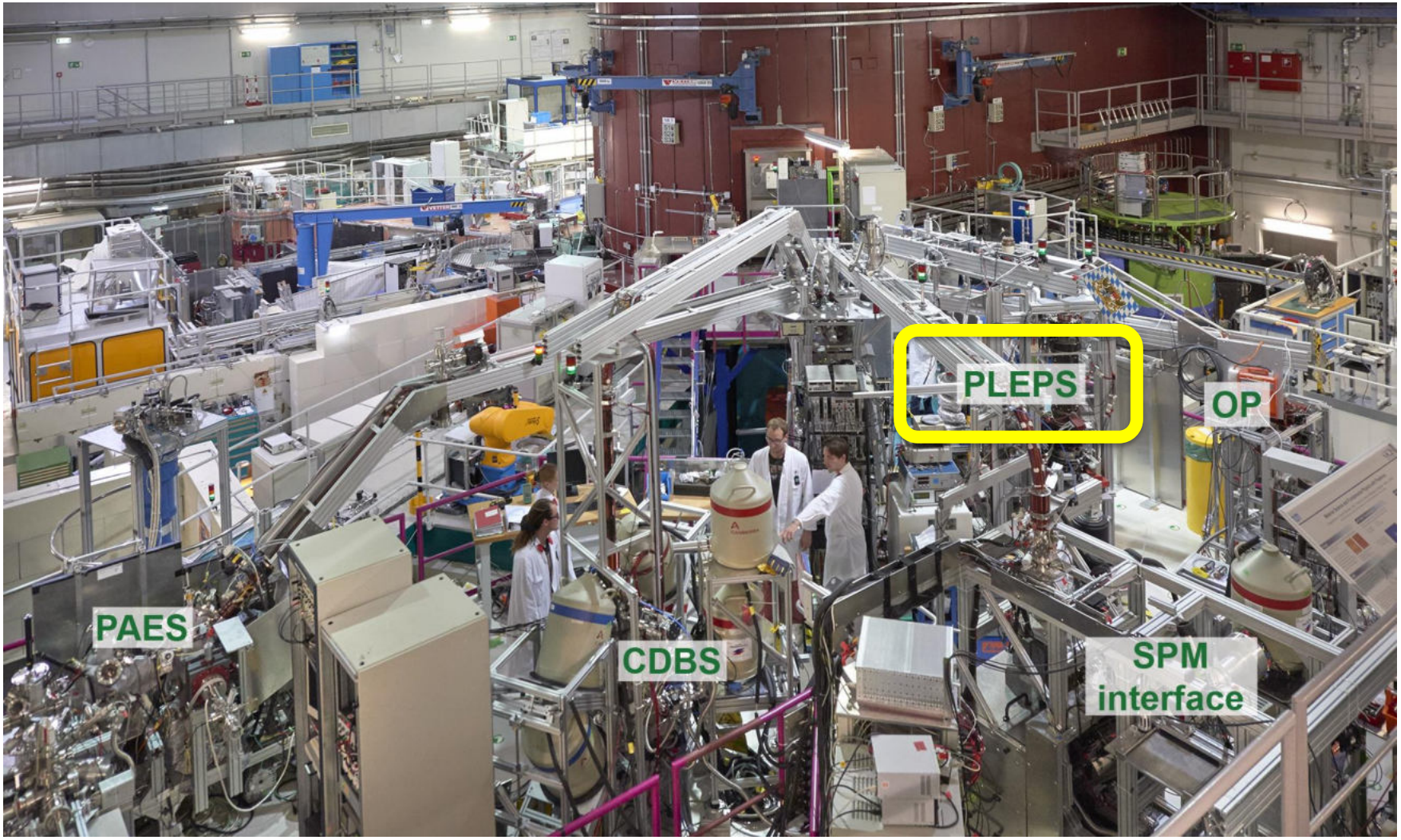
- What are the sizes and concentrations of vacancies in as-deposited YH_xO_y and Y, $YH_{\sim 2}$, Y_2O_3? ------ by PALS

- The variation of electronic structure------ by DB-PAS

- Do vacancies and electronic structure change upon illumination? Its relationship with photochromic effect?

------ by in-situ DB-PAS

PALS @ MLZ Garching

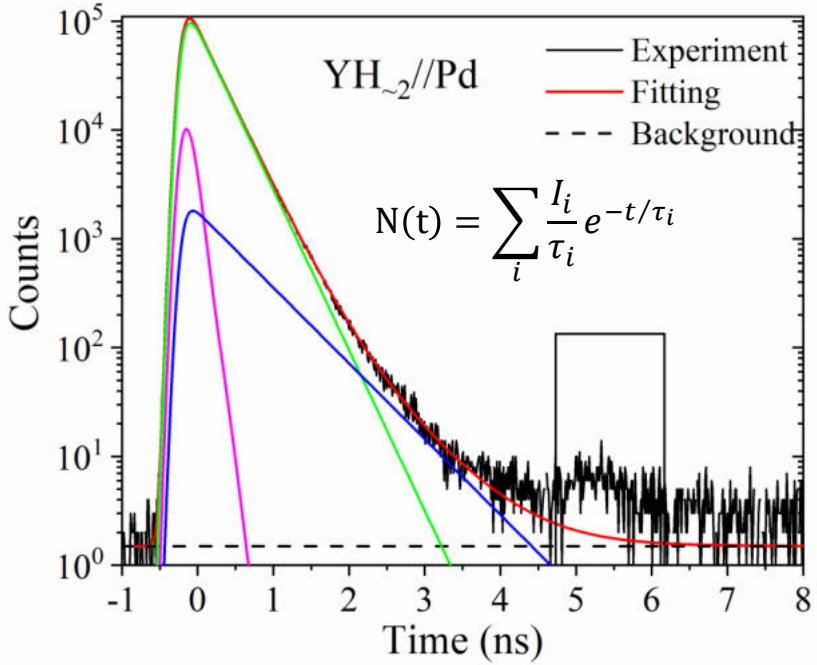


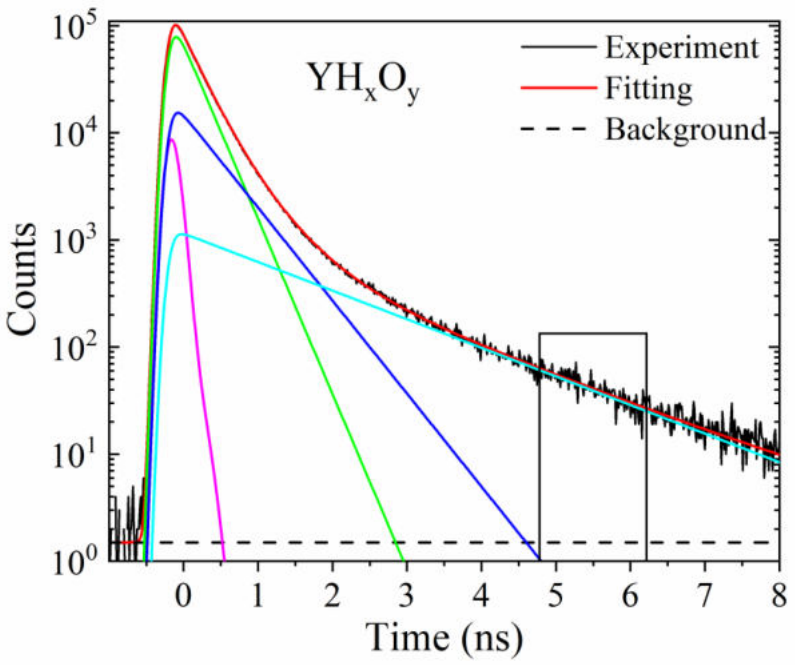
Picture from https://mlz-garching.de/nepomuc

The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS

Positron lifetime spectra @ 4 keV

POSWIN analysis





$YH_{\sim 2}$:

τ_1 : 65±3 ps
τ_2 : 279±1 ps I_2: 92±0.2
τ_3 : 683±22 ps

YH_xO_y:

τ_1 : 47±5 ps
τ_2 : 266±4 ps I_2: 71±2
τ_3 : 500±20 ps I_3: 22±2
τ_4 : 1.63±0.03 ns

TU Delft

Two-defect trapping model [2]

For extracting the bulk lifetime (τ_b), positron trapping rate (k_{di}), and defect concentrations (C_i).

Main equations of this two-defect trapping model:

$$k_{d1} = \mu C_1 = I_2\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)$$

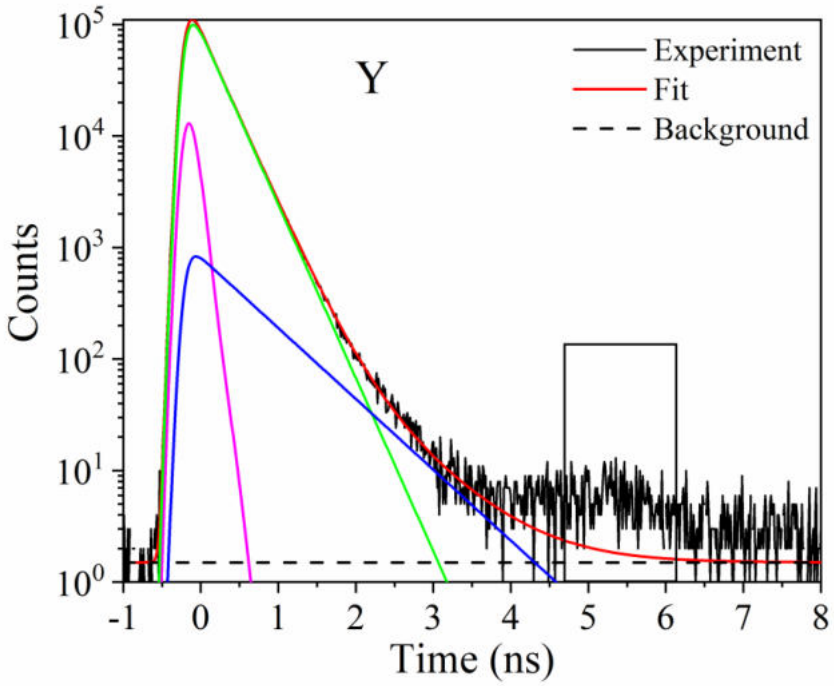
$$k_{d2} = \mu C_2 = I_3\left(\frac{1}{\tau_1} - \frac{1}{\tau_3}\right)$$

$$\tau_b^{cal.} = \left(\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} + \frac{I_3}{\tau_3}\right)^{-1}$$

Assuming $\mu = 10^{15} s^{-1}$

[2] H.S.L. Reinhard Krause-Rehberg, Positron Annihilation in Semiconductors - Defect Studies, Springer-Verlag Berlin Heidelberg1999.

The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS

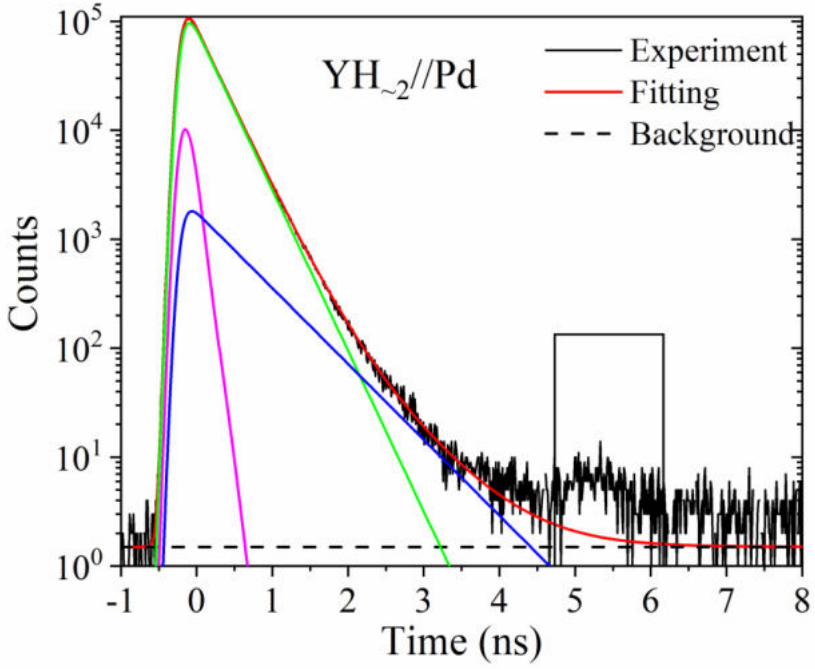


- Y thin film:

τ_b: ~235 ps, not far away from $\tau_b^{exp.}$ (249 ps) and $\tau_b^{cal.}$ (215 ps) [3]
τ_2: 279 ps, increases ~19% compare to τ_b, V_Y mono-vacancy;
I_2: 92%, concentration ~1.0×10^{-5}.

Ref [3] Robles et al., J. Phys.: Condens. Matter 19 (2007) 176222
Ref [4] Anastasopol et al., Phys. Procedia 35 (2012) 16 - 21

The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS

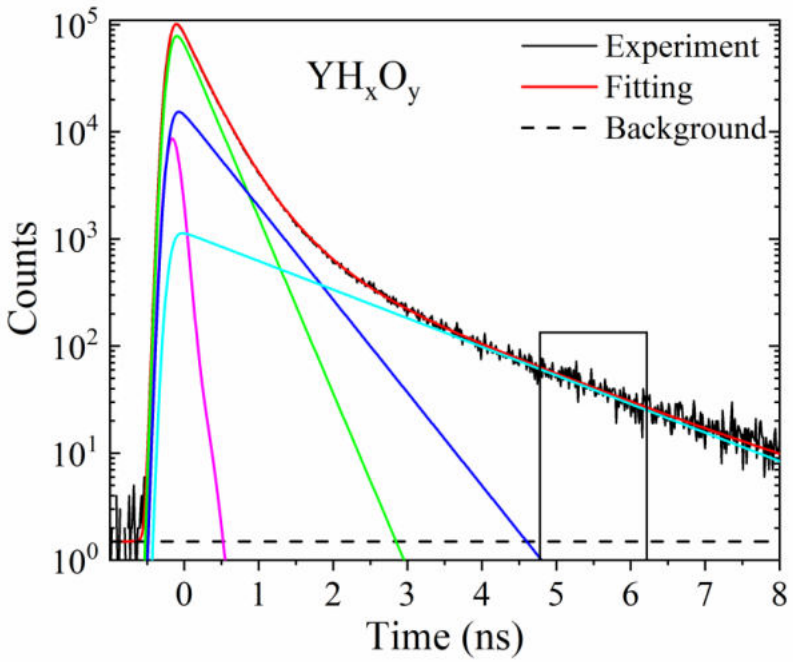


- <u>$YH_{\sim 2}$ //Pd thin film:</u>

τ_b: ~260 ps, increase ~10% compare to τ_b (Y), due to the increase of the volume per unit cell (~6%), XRD.

τ_2: 294 ps, increases ~14% compare to τ_b, V_Y mono-vacancies;
I_2: 91%, concentration ~0.8×10^{-5}.

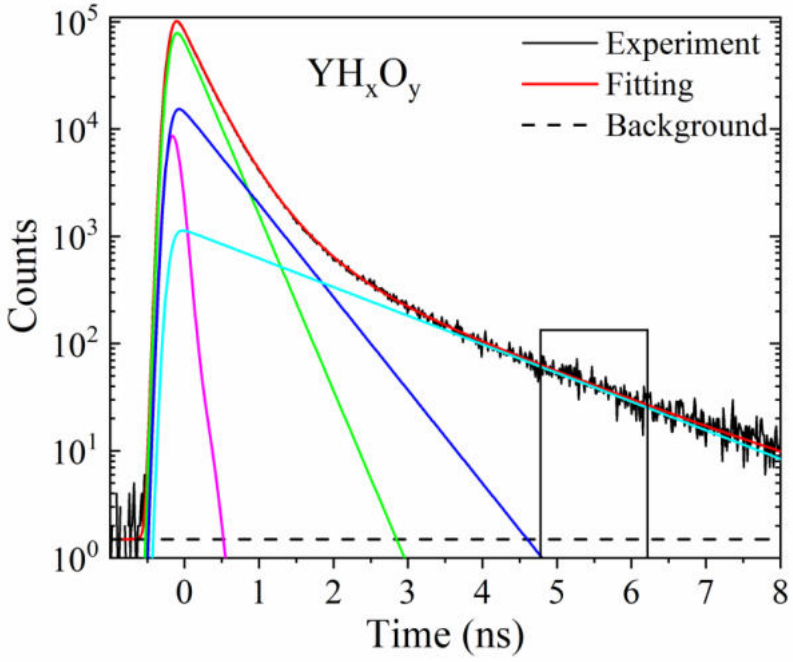
The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS



<u>YO_xH_y (0.5 Pa):</u>

τ_b: ~220 ps
τ_2: 266 ps, increases ~19% compare to τ_b, V_Y mono-vacancies, I_2: 71%, $C_{defect\ 1}$ ~1.5×10^{-5}.
τ_3: 500 ps, vacancy clusters, I_3: 22%, $C_{defect\ 2}$ ~0.5×10^{-5}.
τ_4: ~1.6 ns, o-Ps formation: presence of nanovoids

The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS



<u>YO_xH_y (0.5 Pa):</u>

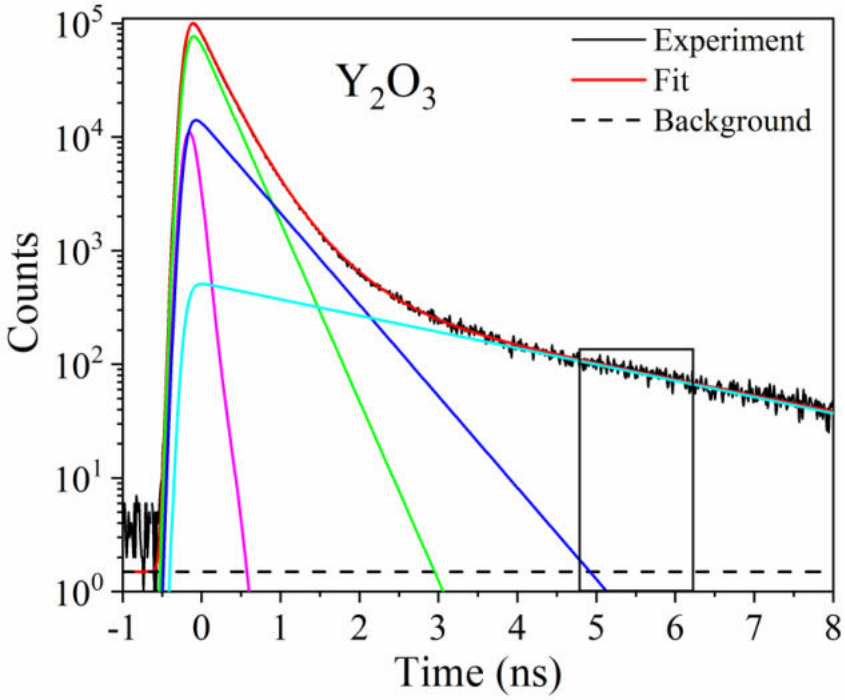
τ_3: 500 ps, vacancy clusters, $>V_5$ e.g. in GeSn and P doped Ge, $\tau \sim 450$ ps, $V_{>5}$ [7,8]

τ_4: ~1.6 ns, o-Ps formation: presence of nanovoids, radius ~0.25 nm, according to the Tao-Eldrup (TE) model [5,6]; assuming spherical pores, ~7 atoms missing in one unit cell of YH_xO_y (~V_7).

V_7 clusters could be responsible for both τ_3 and τ_4

[5] Eldrup et al., Chem. Phys. 63 (1981) 51-58.
[6] Tao, S., J. Chem. Phys. 56 (1972) 5499–5510.
[7] S. Assali et al., Appl Phys Lett 114(25) (2019).
[8] M. Elsayed et al., Acta Mater 100 (2015) 1-10.

The open volume in YH_xO_y and Y, YH_2, Y_2O_3 by PALS

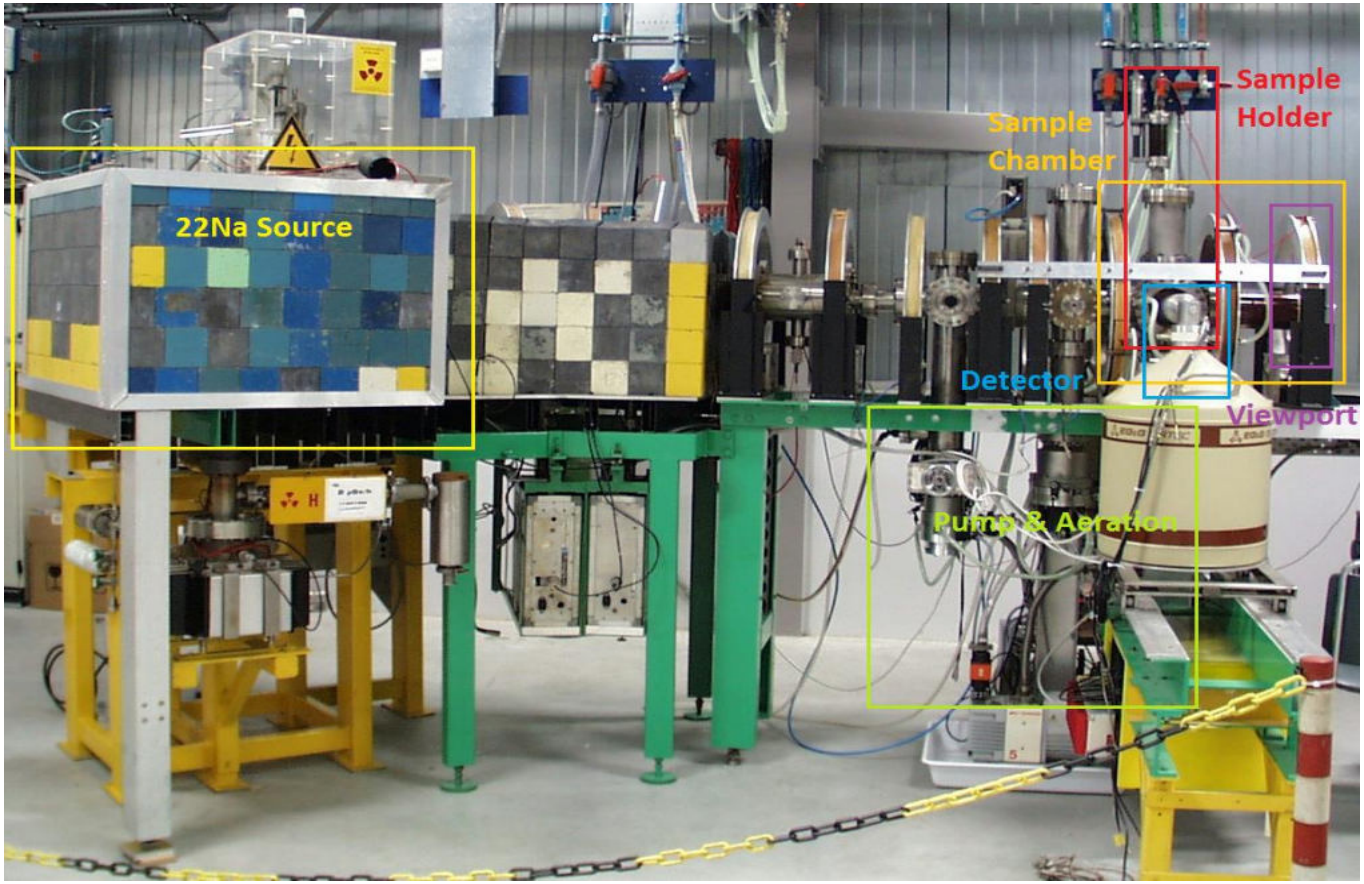


<u>Y_2O_3 thin film (0.3 Pa):</u>

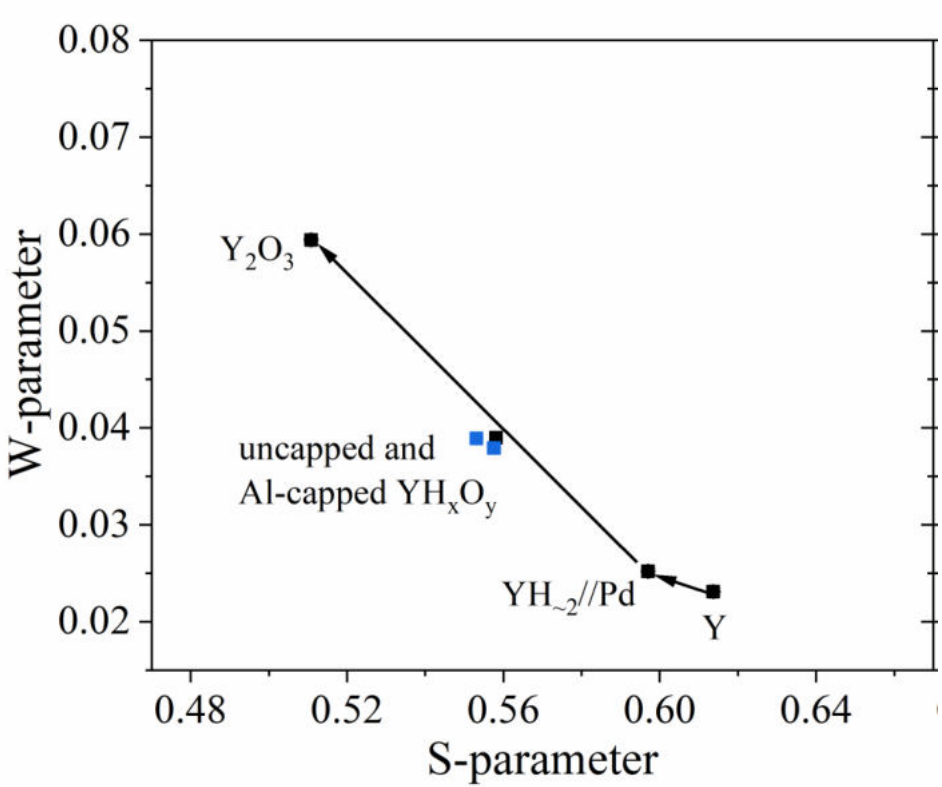
τ_b: ~237 ps, close to 239 ps for Y_2O_3 powder [9]
τ_2: 276 ps, V_Y mono-vacancy, $C_{defect\ 1}$ ~0.9×10^{-5}.
τ_3: 539 ps, vacancy clusters, $C_{defect\ 2}$ ~0.3×10^{-5}.
τ_4: ~3 ns, o-Ps formation in nanovoids, radius ~0.37 nm[5,6], ~V_{14}

[9] Damonte et al., Radiat. Phys. Chem. 76 (2007) 248–251

Doppler Broadening Positron Annihilation Spectroscopy @ TU Delft



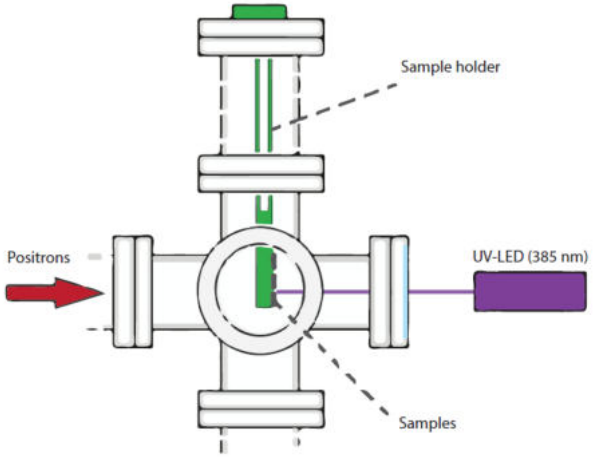
DB-PAS studies of as-deposited YH_xO_y and Y, $YH_{\sim 2}$, Y_2O_3 films

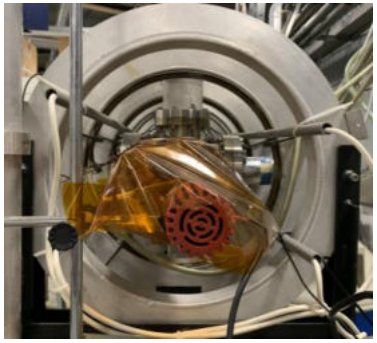


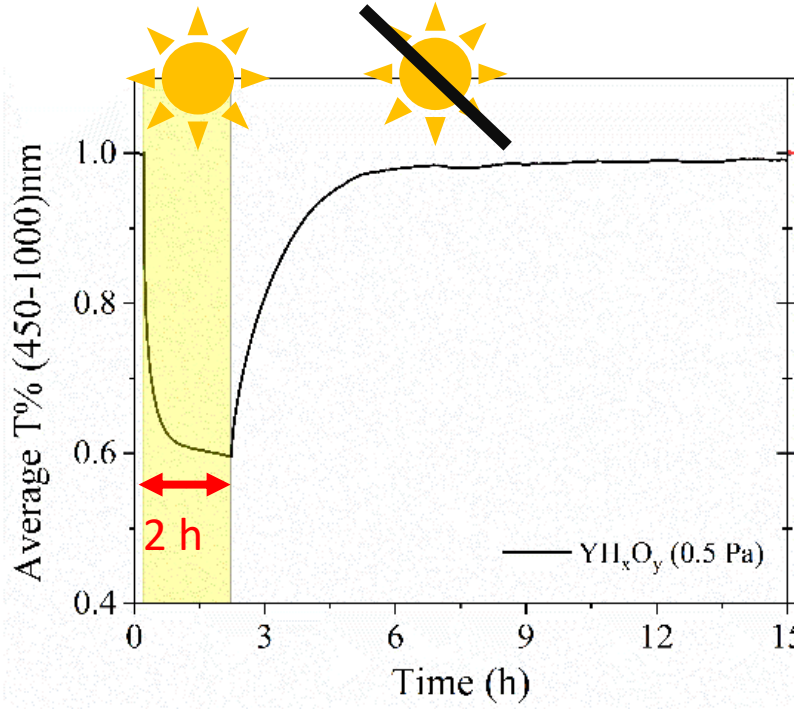
- Y: narrow electronic momentum distribution
- $YH_{\sim 2}$: more localized valence electronic orbitals due to metal-H bonds
- Y_2O_3: insulating, strong localized valence electrons of O atoms

- YH_xO_y: semiconducting, intermediate electron momentum distribution

In-situ illumination DB-PAS studies of YH_xO_y films





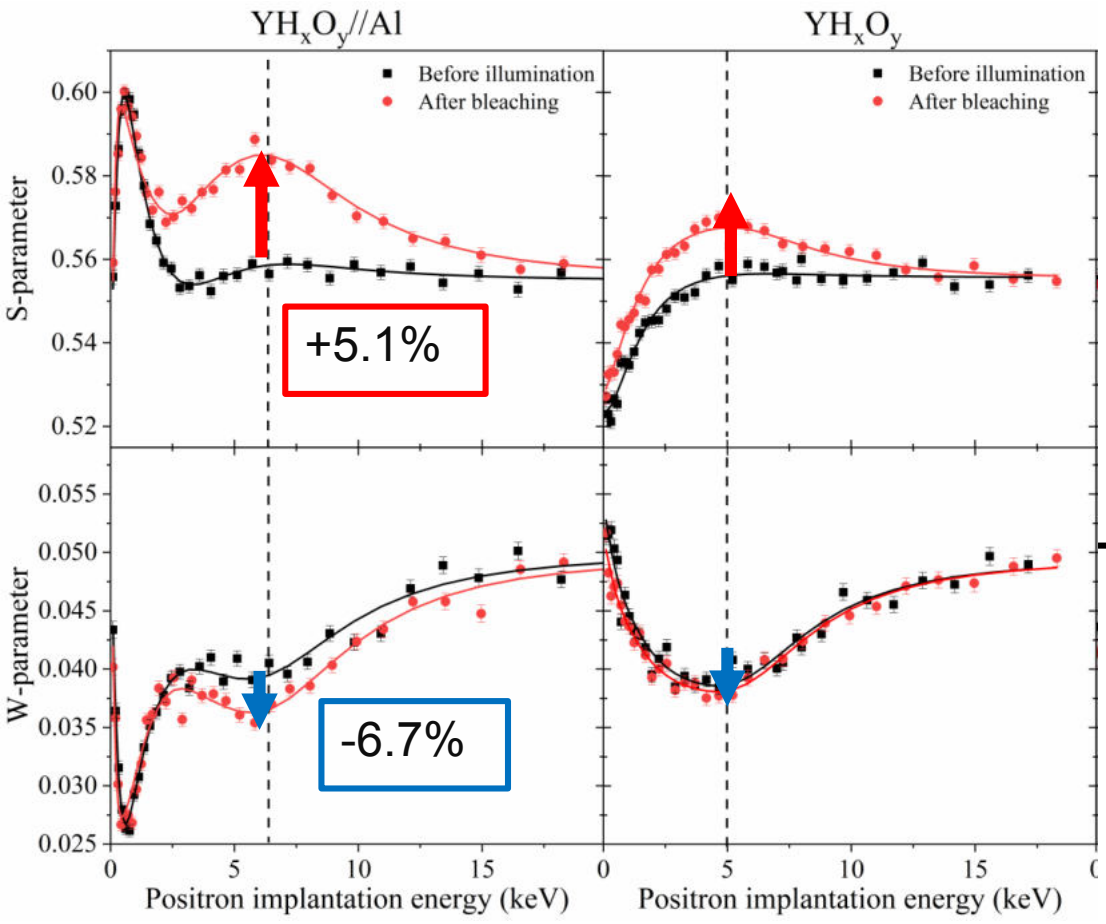


Transmittance fully recovers

In-situ illumination DB-PAS

(after ~2.5 h illumination + ~38 h bleaching)

S & W not fully recover



S increases and W decreases **permanently**

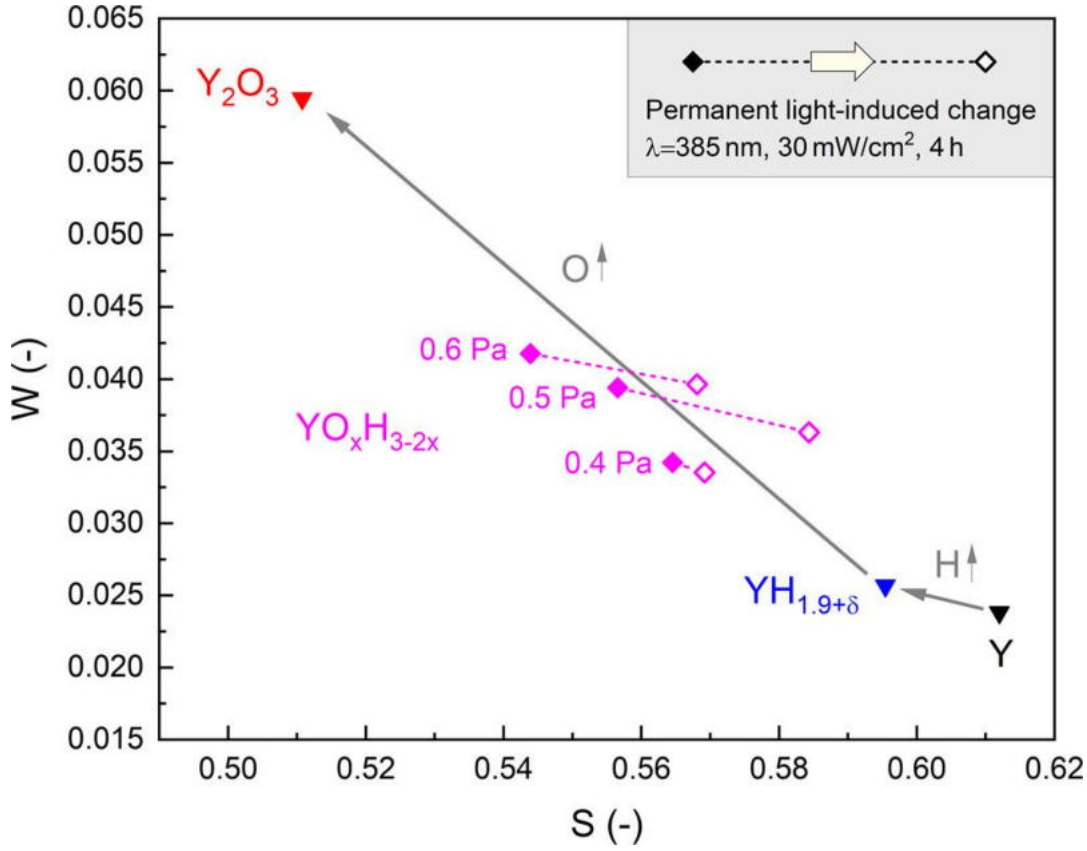
excluded: V_Y cation vacancies (near-saturation trapping of e^+ in V_Y seen by PALS)

Likely small vacancy clusters: V_Y-V_H, V_H-V_H, V_O-V_H di-vacancies

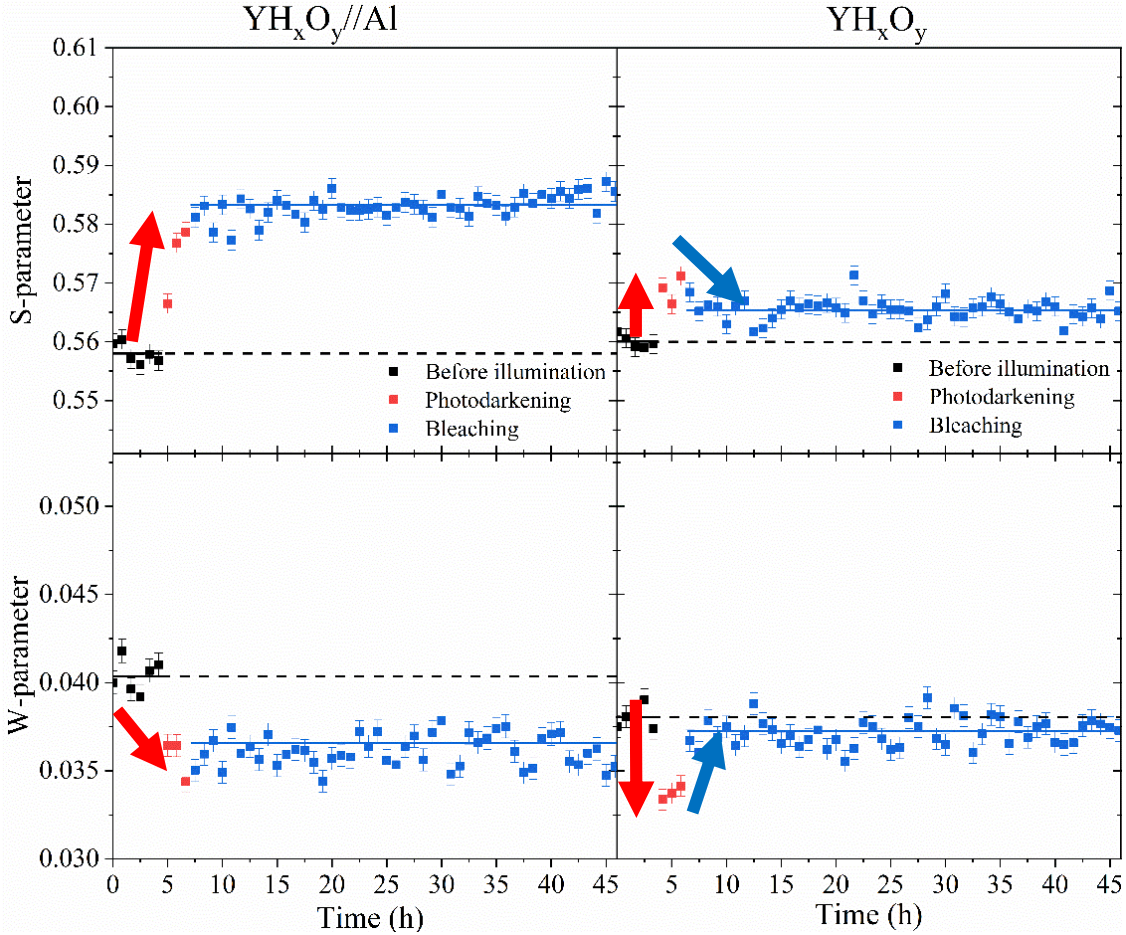
Anion mobility during illumination

In-situ illumination S-W map of Al capped YH_xO_y films

Right figure: G. Colombi et al., *ACS Photonics* 8 (2021) 709–715



Time-dependence DB-PAS under illumination

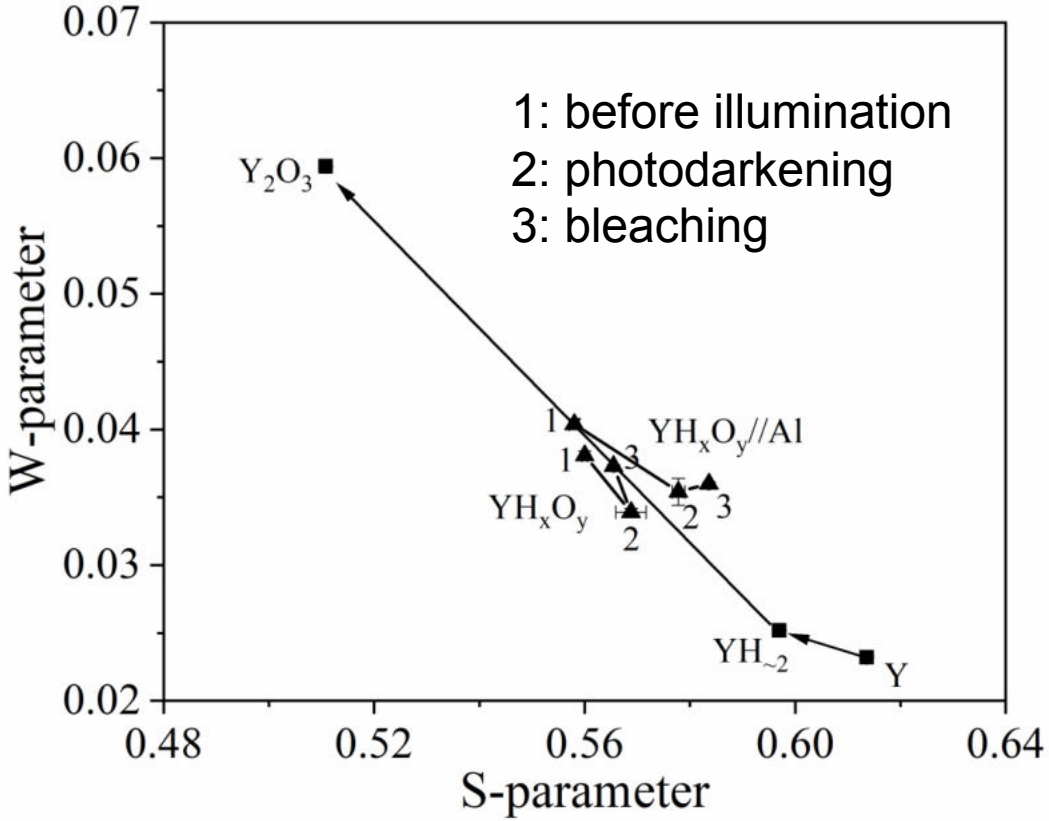


- Permanent changes after bleaching: formation of small vacancy clusters
- Larger changes of S/W during illumination

a second type of nanostructural changes

- GdHxOy: Similar behaviour

In-situ illumination S-W map of YH_xO_y films



$$R = \frac{\Delta S}{\Delta W}$$

$R(oxide \rightarrow hydride) \approx$ -2.5

YH_xO_y//Al:

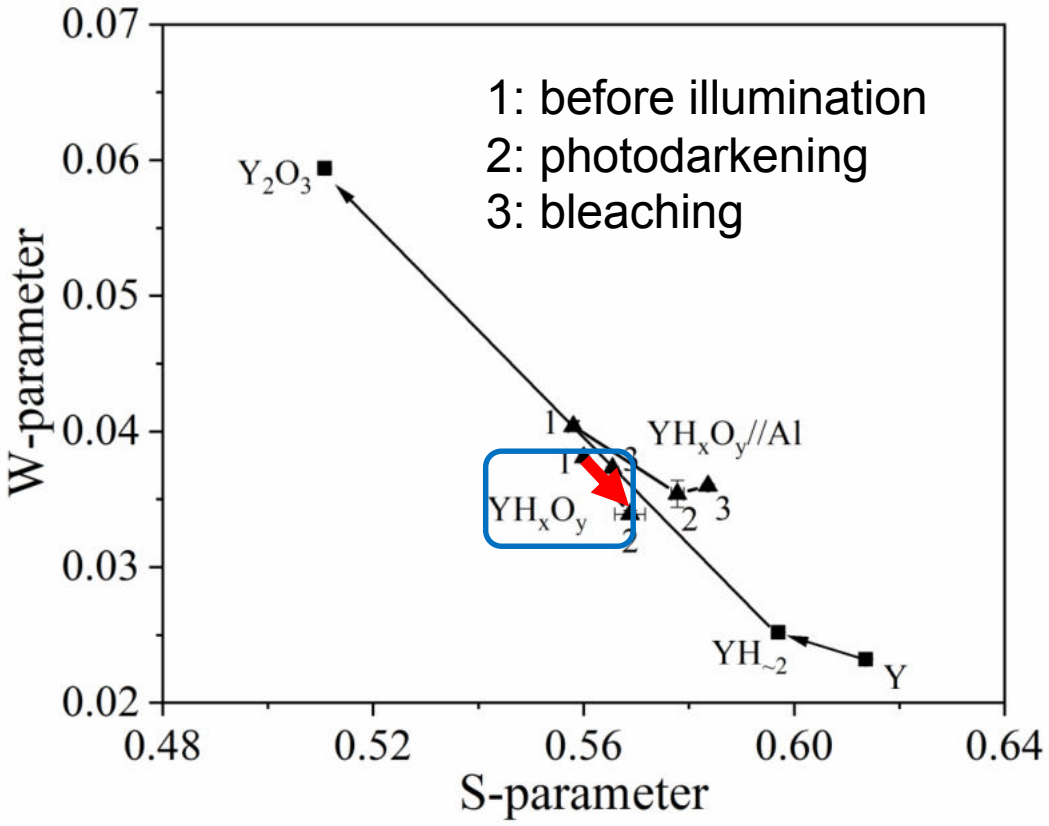
- R (1→2) ≈ -4
- irreversible formation of di-vacancies/small vacancy clusters

YH_xO_y:

- $R(1\rightarrow2)\approx$-2, Similar to $R(oxide \rightarrow hydride)$, S-W shifts to the hydride direction

Partially reversible formation of domains with low O:H ratio

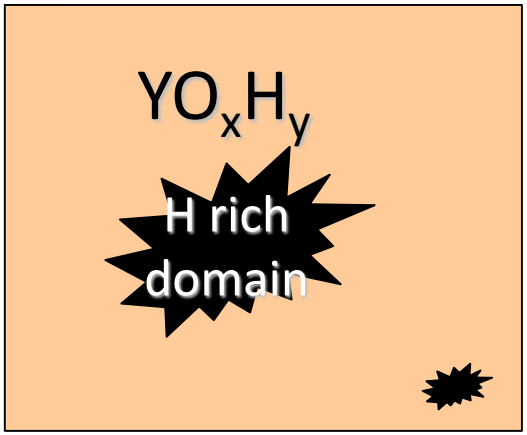
In-situ illumination S-W map of YH_xO_y films



Local composition YH_2O_x ($x<0.5$), $Y^{3+} \rightarrow Y^{2+}$

<u>metallic-like H-rich domains</u> along with mobility of H

e^+ preferentially trap in H-rich domains (e^+ affinity)



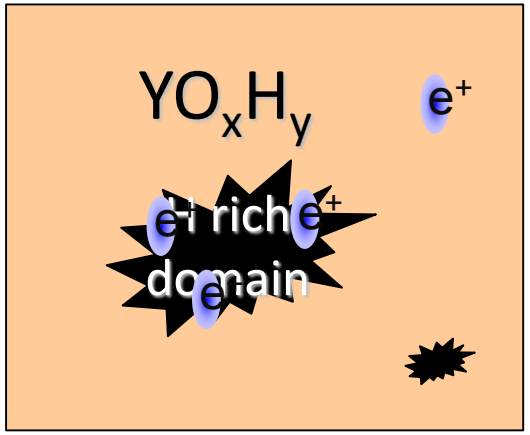
Conclusions

1. Mono-vacancies dominant Y and $YH_{\sim 2}$ films at a concentration of ~10^{-5} per Y atom, while in addition vacancy clusters and nanopores are found in YH_xO_y and Y_2O_3.

2. Variation in electronic structure of metal, metal hydride, semiconducting oxyhydride and insulating oxide.

3. In-situ illumination DB-PAS on YH_xO_y films:

   - permanent formation of small vacancy clusters;
   - partially reversible formation of H-rich domains along with the mobility of H.



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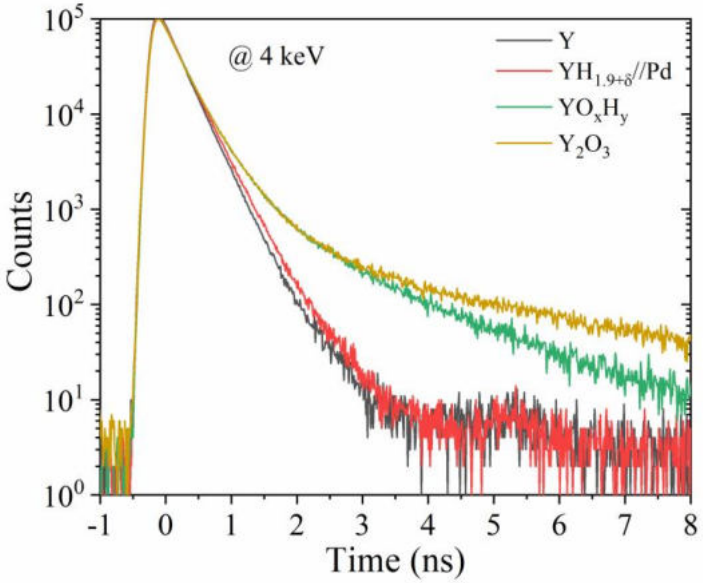
Thanks for your attention!

PALS



Thin films	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_4 (ns)	I_1 (%)	I_2 (%)	I_3 (%)	I_4 (%)	τ_{av} (ps)
Y	65±3	279±1	683±22	-	6±0.2	92±0.2	1.5±0.2	-	272±1
$YH_{\sim 2}$//Pd	73±5	294±1	624±17	-	5±0.2	92±0.2	3±0.3	-	293±3
YH_xO_y	47±5	266±4	500±20	1.63±0.03	3.8±0.2	71±2	22±2	4.2±0.2	365±17
Y_2O_3	58±5	276±4	539±16	3.03±0.06	5.1±0.3	71±2	21±2	3.4±0.1	412±13

Samples	τ_b (ps)	k_1 (10^{10} s^{-1})	k_2 (10^{10} s^{-1})	C_1 (10^{-5})	C_2 (10^{-5})
Y	235±4	1.0±0.1	0.02±0.001	1.0±0.1	0.02±0.001
$YH_{\sim 2}$//Pd	260±6	0.8±0.1	0.03±0.003	0.8±0.1	0.03±0.003
YHxOy-1	218±11	1.5±0.3	0.5±0.1	1.5±0.3	0.5±0.1
YHxOy-2	224±9	1.2±0.2	0.33±0.05	1.2±0.2	0.33±0.05
Y_2O_3	237±9	0.9±0.1	0.27±0.03	0.9±0.1	0.27±0.03

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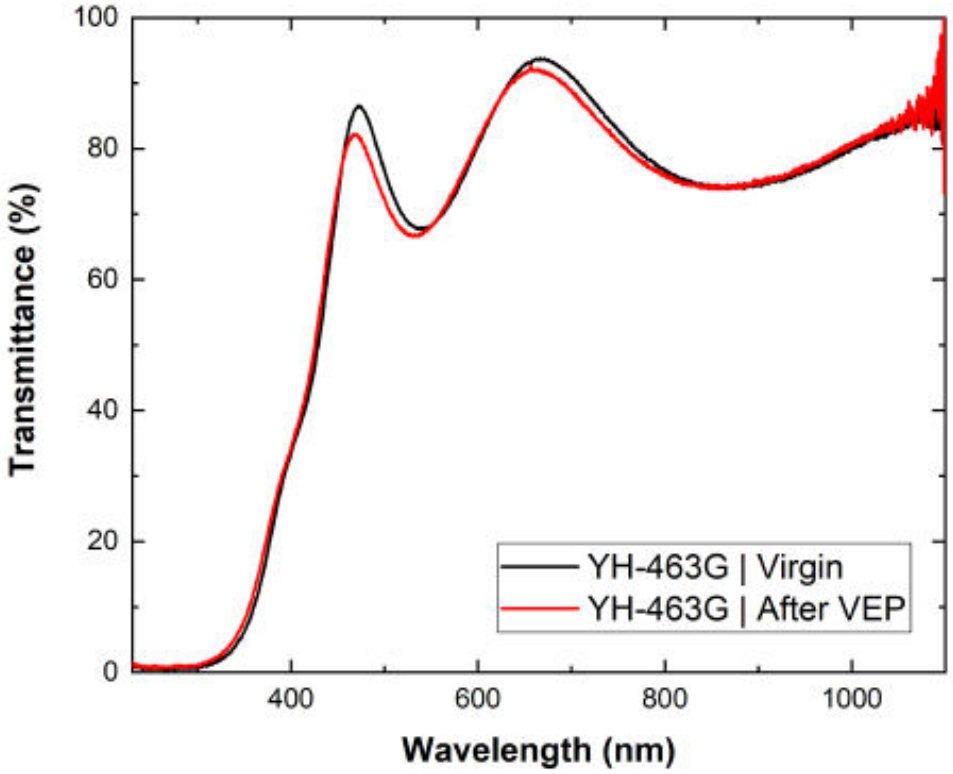
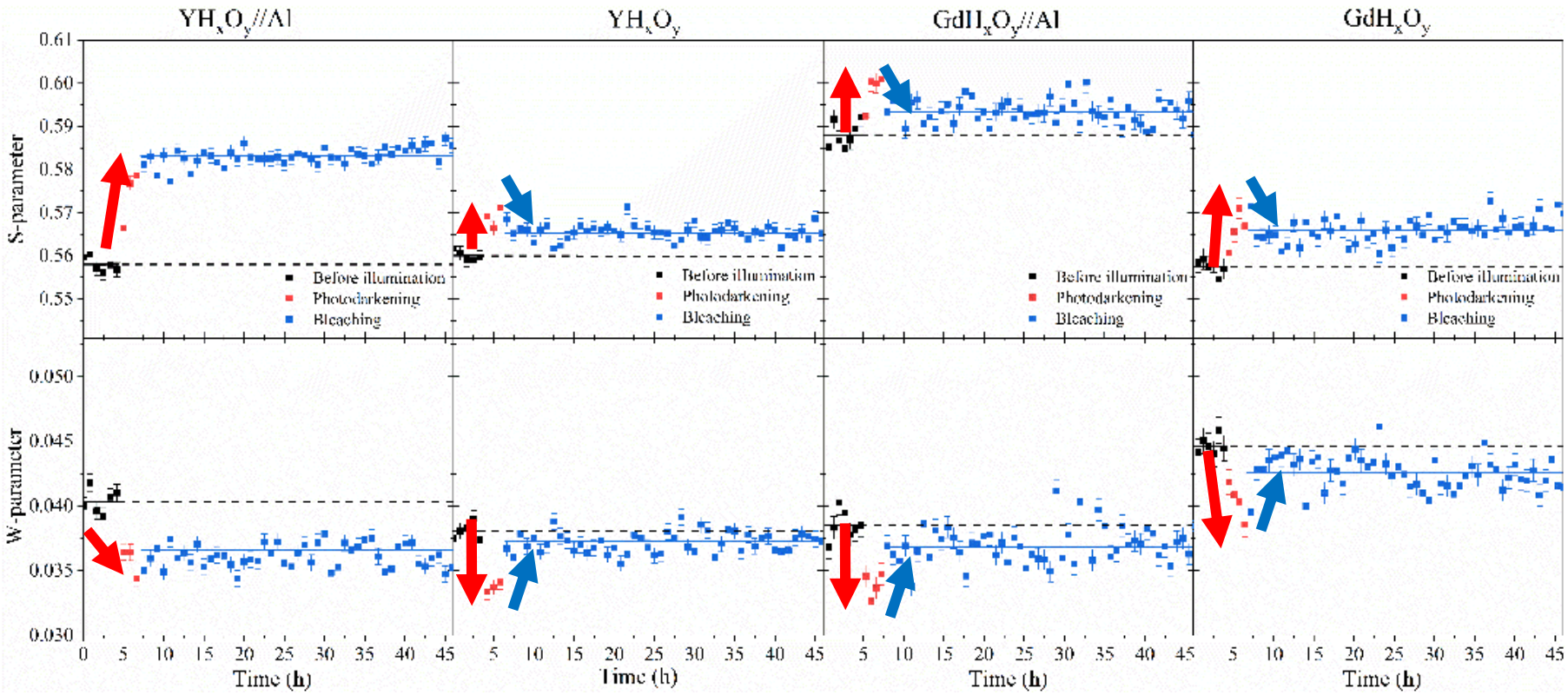
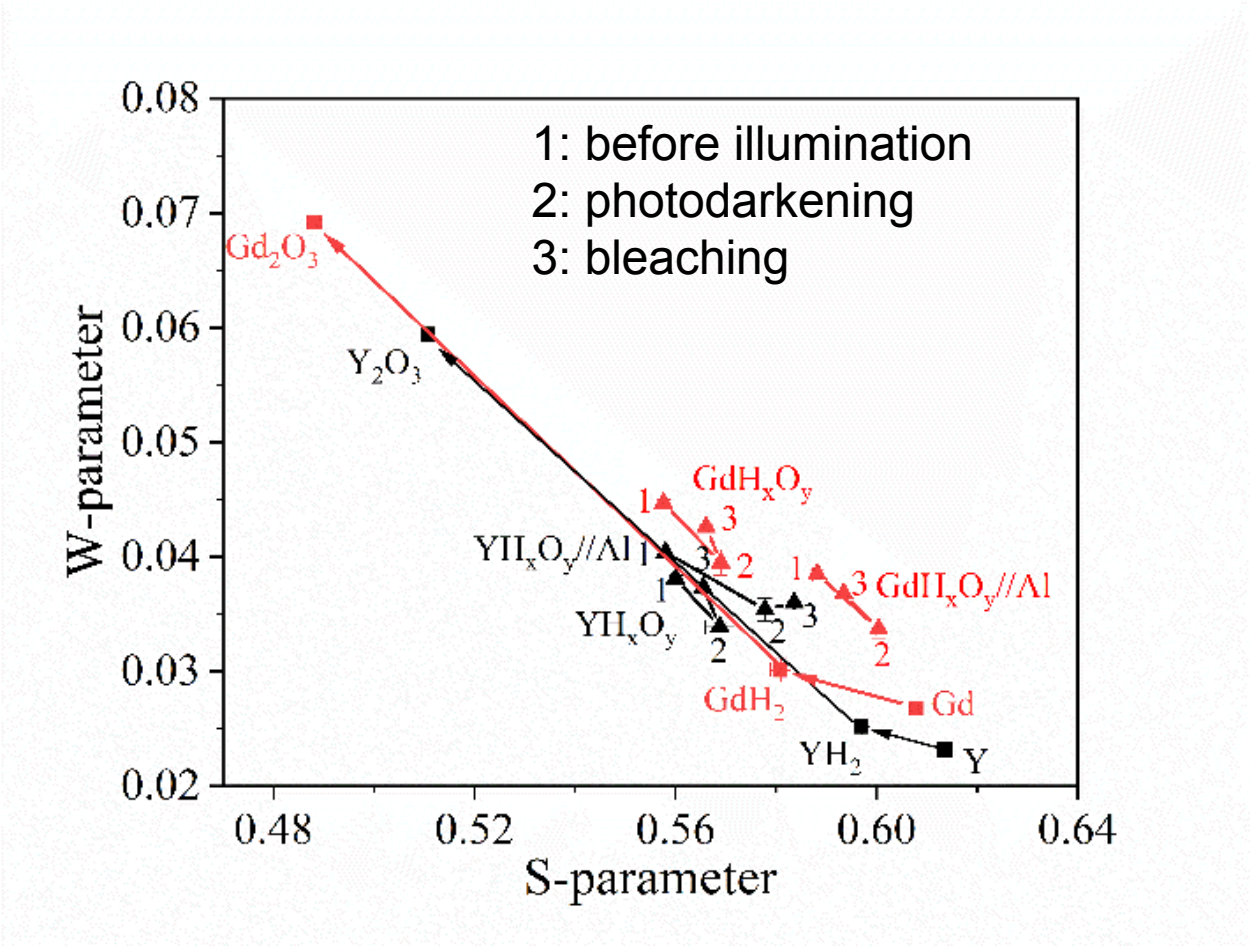
Transmittance before VEP and after VEP



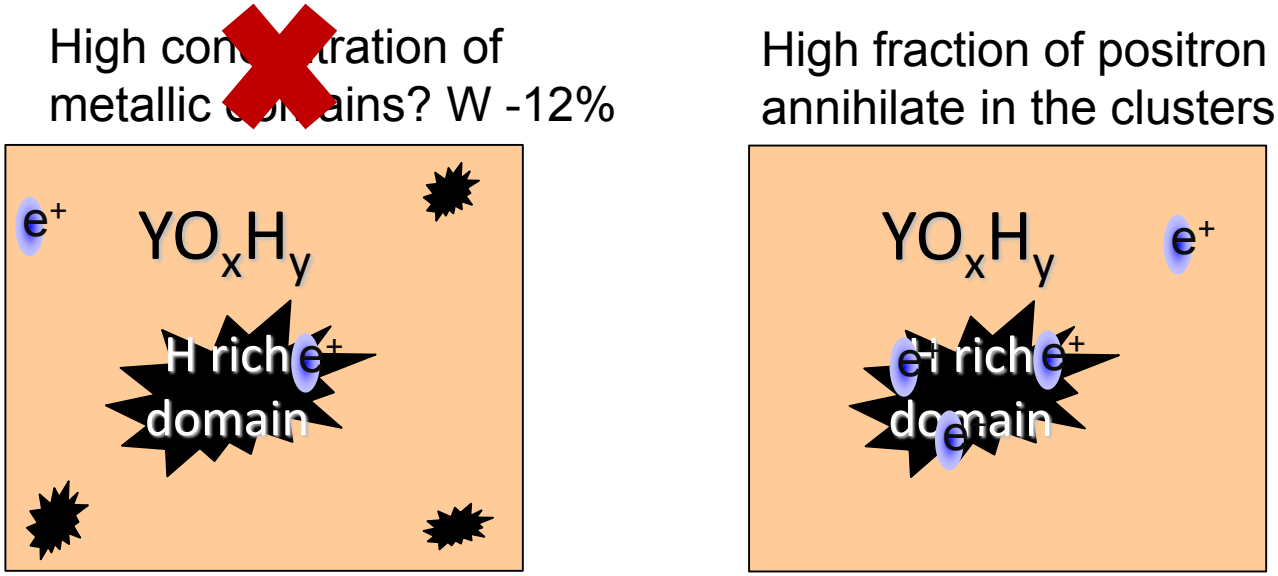
Time-dependence DB-PAS under illumination




1: before illumination
2: photodarkening
3: bleaching
W-parameter
S-parameter
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.48
0.52
0.56
0.60
0.64
Gd2O3
Y2O3
GdHxOy
YHxOy//Al
YHxOy
GdH2
YH2
Gd
Y
GdHxOy//Al

In-situ illumination S-W map of YH_xO_y films

- W: -12% during illumination with only ~6 vol. % metallic domains



The trapping fraction of Li in MgO is ~92% with Li only occupy 3 vol.% with radius of 3-7 nm [M.A. van Huis et al., 2002 PRB].

Diffusion-limited trapping model [10,11]:

The fraction of positron annihilate in H-rich domain:

$$f_{clusters} = \frac{\kappa}{\kappa+\lambda_{bulk}} = \frac{4\pi r D_+ c}{4\pi r D_+ c+\lambda_{bulk}}$$

$$L_+ = \sqrt{D_+ \tau}$$

κ is the positron trapping rate in clusters (s^{-1})
λ_{bulk} is the annihilation rate in oxyhydride (s^{-1})
r is the radius of the cluster (m)
c is the concentration of clusters (m^{-3})
D_+ is the diffusion coefficient ($m^2\ s^{-1}$)
L_+ is the diffusion length (m)
τ is the positron lifetime (s)

On the condition that:

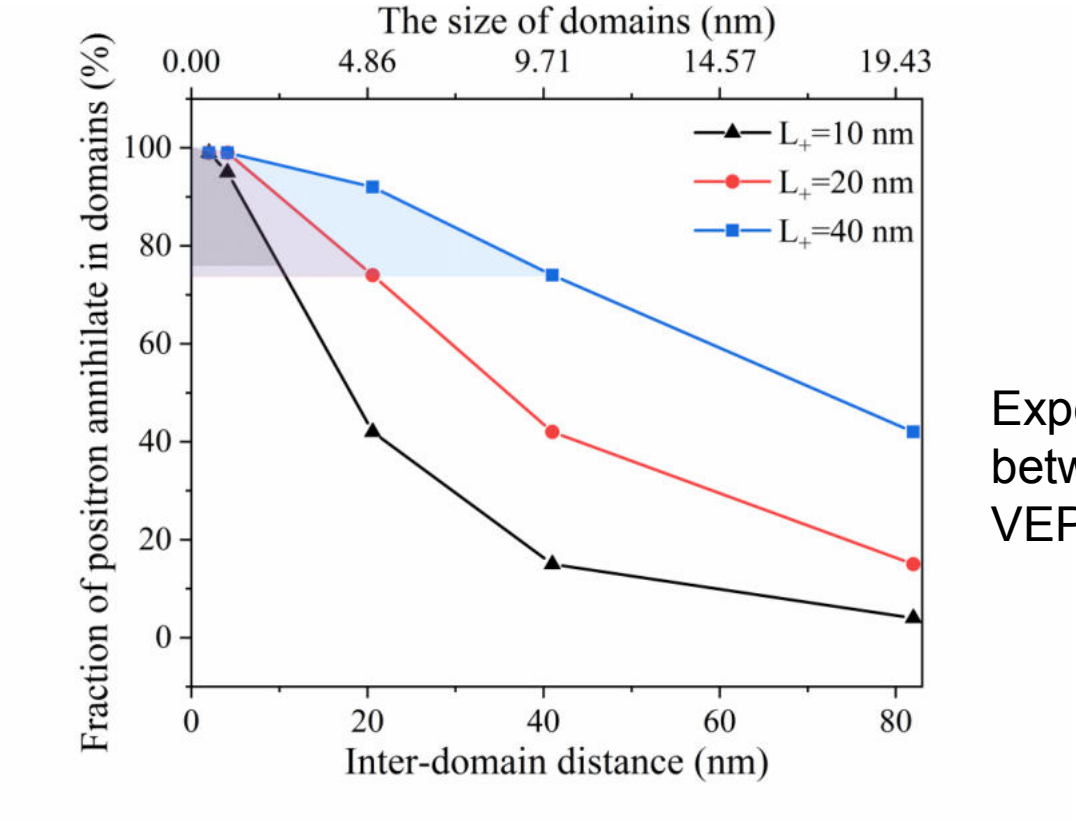
- The difference in e+ affinity is sufficient large (several tenths of eV)

Assumptions:

- The clusters are spherical and homogeneous distribute in bulk.
- De-trapping of e^+ from H-rich domains is neglected.

[10] M.A. van Huis et al., Phys Rev B 65(8) (2002).
[11] A. Dupasquier, A. Mills Jr, Positron spectroscopy of solids, IOS press1995.

Diffusion-limited trapping model



Experimental L_+ is between 10-40 nm from VEPFIT

- ~6 vol. % H-rich domains dominate >70% positron signal
- The average size of domains is ~1 to ~10 nm.