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Technical Meeting

Hydrogen Supersaturation and Defect Stabilization

Thermodynamics Models based on DFT data for Hydrogen Supersaturation and Defects Stabilization

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Outline

1 . The basic ingredients

- Density Functional Theory
- Statistic Thermodynamics (Gibbs free energy)

2 . Thermodynamic models for vacancies

3 . Supersaturation and vacancy stabilization

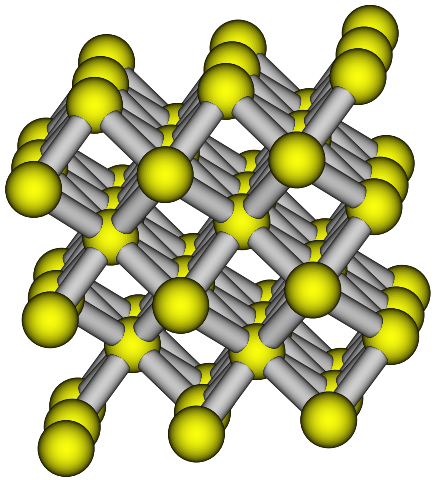
4 . Discussion

1. The Basic Ingredient

Density Functional Theory – *electronic energy*

⇒ Calculating the **electronic energy** of a system of electrons and nuclei

- Should be done using Quantum Mechanics
- Achieved through solving the Schrödinger equation
- Solutions not known, approximation, Hartree-Fock
- Limitation: the wave-function depends on too many variables $\Psi(r_1, r_2, \ldots, r_N)$ for a system of N electrons



⇒ An alternative: the **Density Functional Theory**

- The electronic density $\rho(r)$ only depends on three space variables
- The idea is to compute $E[\rho]$
- The question is how ?

1. The Basic Ingredient

Density Functional Theory – *total energy*

$$E^{elec}[\rho] = E_{kin}[\rho] + E_{electron-nuclei}[\rho] + E^{Coulmob}_{electron-electron}[\rho] + E^{XC}_{electron-electron}[\rho]$$

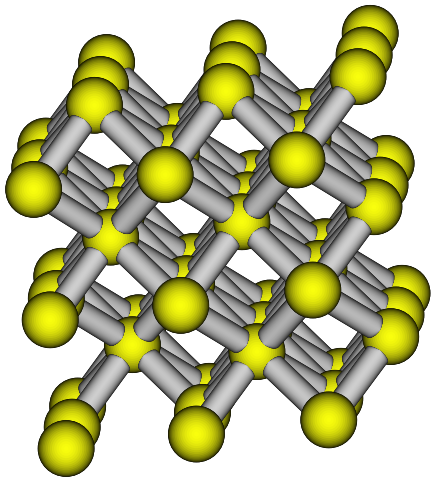
Classical terms

Quantum terms :

$E_{kin}[\rho]$ – Known for *non-interacting* electrons

$E^{XC}_{electron-electron}[\rho]$ – approximation

eXchange-Correlation functional



Total energy:

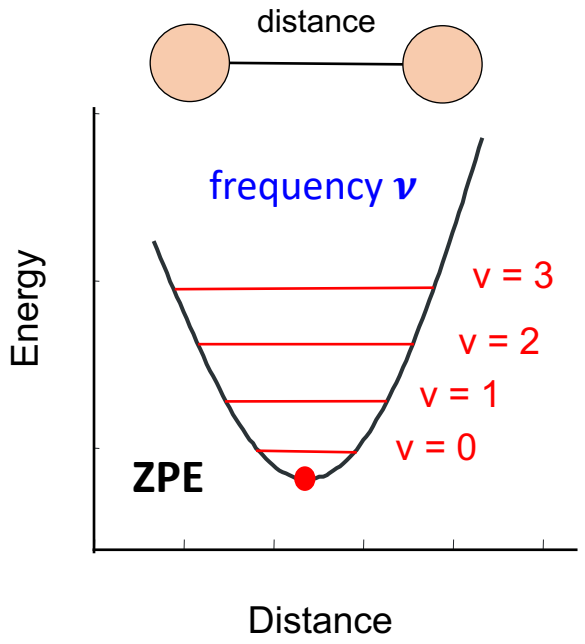
$$E^{DFT} = E^{elec}[\rho] + \mathrm{E}_{\mathrm{nuclei-nuclei}}$$

Ground state energy

Does not include the Temperature

1. The Basic Ingredient

Density Functional Theory – *vibrational frequencies*



At T = 0K, only v=0 is populated.

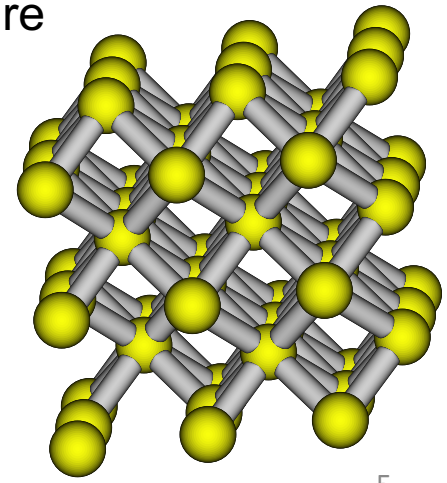
Then, energy levels v populated with increasing temperature.

Bulk system of N atoms

3N – 3 frequencies ν_j (phonons)

Energy levels are populated with increasing temperature

Vibrational energy depending on the temperature



The energy of the system is made temperature dependent

$$E_{tot}(T) = E^{DFT}(0K) + E\_vib(T)$$

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- Statistic Thermodynamics

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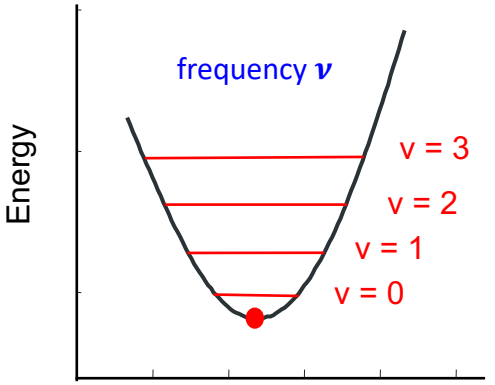
1. The Basic Ingredient

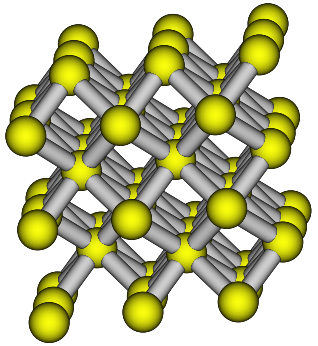
Statistic Thermodynamics – *State function Energy*

Large number of particles $\sim 10^{23}$

$$E_{tot}(T) = E^{DFT}(0K) + E_{vib}(T) + \cancel{E_{elec}(T)} + E_{trans}(T) + E_{rot}(T) + \dots$$

Bulk materials — Gas Phase





Two levels

$$E_{mean}(T) = p_1(T)\,E_1 + p_2(T)\,E_2$$

p_1(T) Boltzmann statistic

$$\boldsymbol{E_{mean}(T) = \sum_j p_j(T).E_j}$$

$$E^{vib}(T, \boldsymbol{\nu_j}) = \sum_{j=1}^{n_{vib}} h\boldsymbol{\nu_j}\left(\frac{1}{2} + \frac{1}{\exp\left(\frac{h\boldsymbol{\nu_j}}{k_B T}\right) - 1}\right)$$

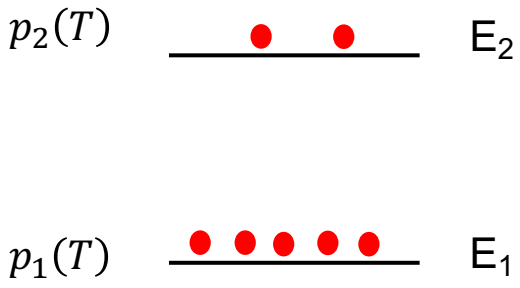
$$E_{tot}(T) = E_{tot}^{DFT}(0K) + E_{vib}(T)$$

1. The Basic Ingredient

Statistic Thermodynamics – *Toward equilibria*

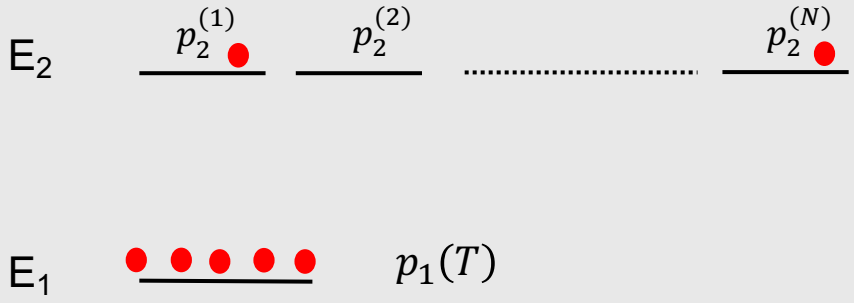
Criterion for stability ?

$p_1(T) > p_2(T)$



Is E the criterion for stability ?

$p_1(T)$? $p_2(T)$



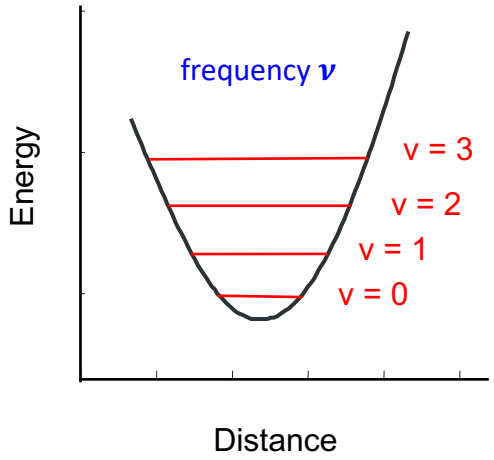
$$p_2(T) = \sum_j p_2^{(j)}(T)$$

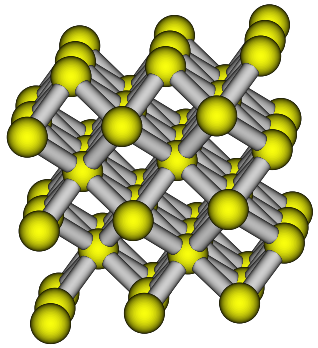
Because of the degeneracy, E_2 might be most populated depending on T

Entropy $$S(T) = -k_B \sum_j p_j(T) \ln p_j(T)$$

1. The Basic Ingredient

Statistic Thermodynamics – *State function Entropy*





$$S(T) = -k_B \sum_j p_j(T) \ln p_j(T)$$

Vibrational entropy

$$S^{vib}(T, \boldsymbol{\nu_j}) = k_B \sum_{j=1}^{n_{vib}} \left[\frac{h\boldsymbol{\nu_j}}{k_B T} \frac{1}{\exp\left(\frac{h\boldsymbol{\nu_j}}{k_B T}\right) - 1} - \ln\left(1 - \exp\left(-\frac{h\boldsymbol{\nu_j}}{k_B T}\right)\right) \right]$$

Configurational entropy

Creating vacancies

N lattice sites

N_{at} atoms at lattice sites
n_V vacancies at lattice sites

$N = N_{at} + n_V$

Number of configuration $\Omega = \frac{(N_{at}+n_v)!}{N_{at}!\, n_V!}$

Entropy (Boltzmann definition)

$$S(T) = k_B \ln \Omega$$

1. The Basic Ingredient

Statistic Thermodynamics – *Equilibrium conditions*

Helmoltz Free Energy

$F(T) = E(T) - T\,.S(T)$

Bulk: $F(T) \approx G(T)$

Gibbs Free Energy

$G(T) = H(T) - T\,.S(T)$

Potential

Combines criterion on **energy** and **entropy**

Conditions for equilibrium - *system of N components*

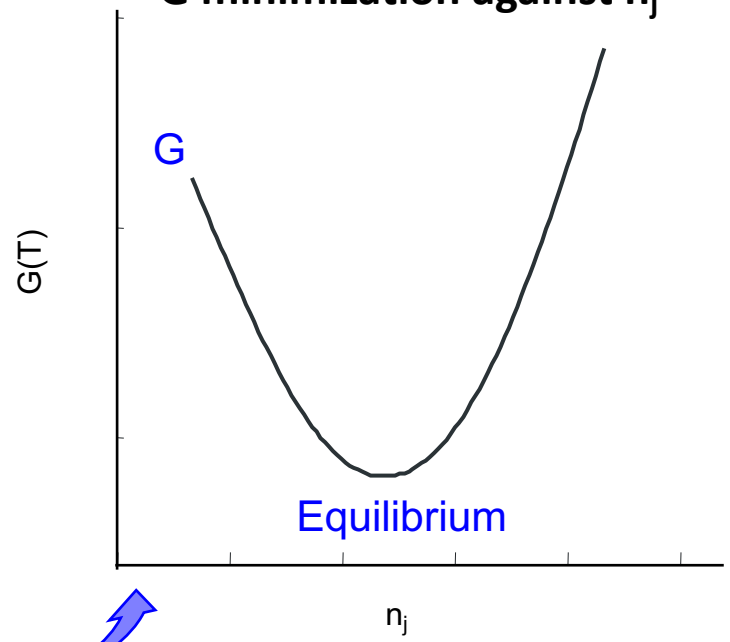
Gibbs free energy per particle for each j sub-system

$g_j = e_j - T.s_j \qquad e_j(T) = e_j^{DFT} + e_j^{vib}(T) \qquad s_j(T) = s_j^{vib}(T)$

$G(T, p, n_1, n_2, \ldots, n_N) = \sum_j n_j.g_j(T) - T\,.S^{conf}(T)$

μ_j chemical potential

G minimization against n_j



Minimization

Provides $n_1^{eq}, n_2^{eq}, \ldots, n_N^{eq}$

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2 . Thermodynamic models for vacancies

- The model
- Results of the model
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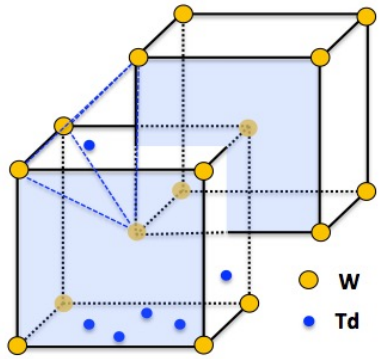
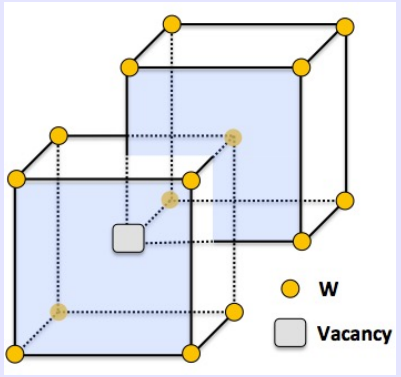
2. Thermodynamics model for Vacancies

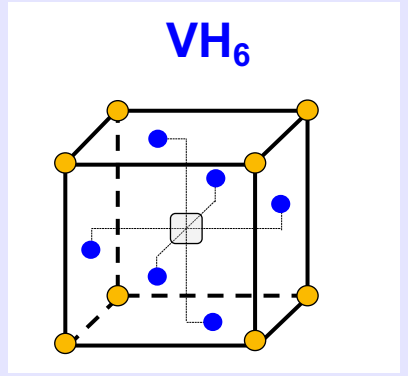
Perfect

H—H



Defects





Electronic structure DFT calculations

Molecule H_2 $e_{H_2}^{DFT}$

Interstitial H_i $e_{H_i}^{DFT}$

Vacancy V e_{V}^{DFT}

VH_j with j = 0 - 12 $e_{VH_j}^{DFT}$

Vibrational frequencies DFT calculations

ν_{H_2}

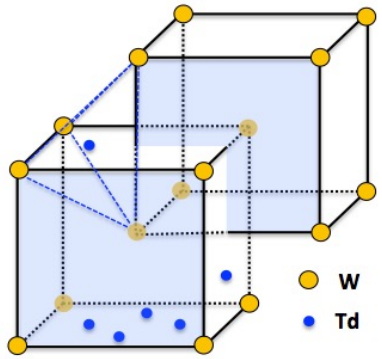
$\sum_{k=1}^{3} \nu_k$

$\sum_{k=1}^{3j} \nu_k$

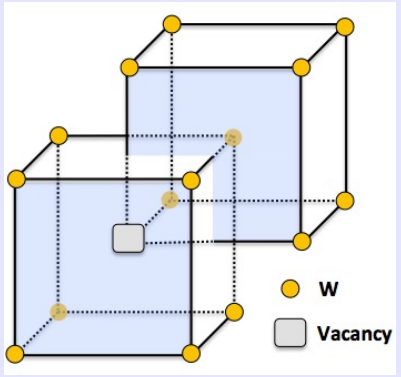
2. Thermodynamics model for Vacancies

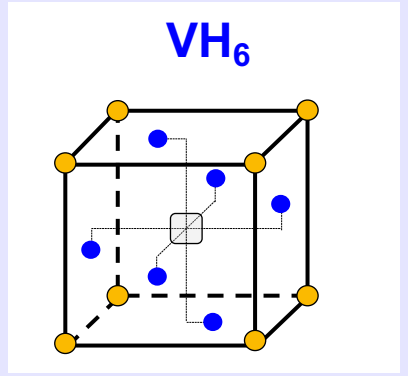
Perfect

H—H



Defects





$g_j = e_j - T.s_j$

$$G\left(T, p, n_{H_2}, n_{H_i}, n_V, n_{VH_1} \ldots, n_{VH_{12}}\right) = \sum_j n_j . g_j(T) - T\,.S^{conf}(T)$$

H_2 Gas *ideal gas*

$$g_{H_2} = g^{\circ}_{H_2} + k_B T \ln \frac{P}{P^{\circ}}$$

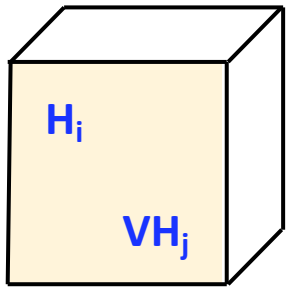
$$g^{\circ}_{H_2} = \left(e^{DFT}_{H_2} + e^{vib}_{H_2} + e^{rot}_{H_2} + e^{trans}_{H_2} + PV\right) - T\left(s^{vib}_{H_2} + s^{rot}_{H_2} + s^{\circ trans}_{H_2}\right)$$

High pressure : Tkacz and Litwiniuk, J. Alloys Compounds 330-332 (2002) 89-92

The minimizing against $n_{H_2}, n_{H_i}, n_V, n_{VH_1} \ldots, n_{VH_{12}}$

2. Thermodynamics model for Vacancies

Composition of the system at equilibrium



Reservoir μ

H_2

Minimization

$$G = \frac{1}{2}\left(\mathrm{N_H} - n_{int} - \sum_{j=0}^{12} j\, n_j\right)\mu_{H_2} + n_{int}\; g_{int} + \left(\sum_{j=0}^{12} j\, n_j\; g_j\right) - T\, S_{conf}$$

$$x_{H_i}(T) \approx \gamma \exp\left[-\frac{g_{H_i} - \mu}{k_B T}\right]$$ **H at interstitial**

$$x_{VH_j}(T) \approx \omega_j \exp\left[-\frac{g_{VH_j} - j\,\mu}{k_B T}\right]$$ **H in VH_j vacancies**

$$\mu = \frac{1}{2} g_{H_2} = \frac{1}{2}\left(\mathrm{g}^{\circ}_{H_2} + k_B T \ln \frac{P}{P^{\circ}}\right)$$ Chemical potential H_2 ideal gas

High pressure : Tkacz and Litwiniuk, J. Alloys Compounds 330-332 (2002) 89-92

The chemical potential defines
- The fraction of H interstitial
- The fraction of VH_j vacancies

Reversely H_{int} defines
- The the chemical potential
- The fraction of VH_j vacancies

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2. Thermodynamics model for Vacancies

Formation of vacancies induced by interstitial H atoms

N. Fernandez, Y. Ferro, D. Kato, Acat Mater 94 (2015) 307-318

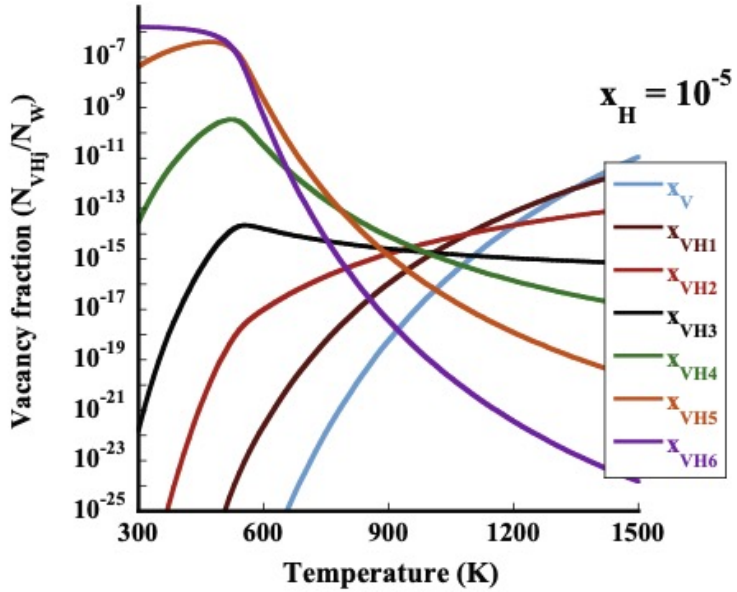
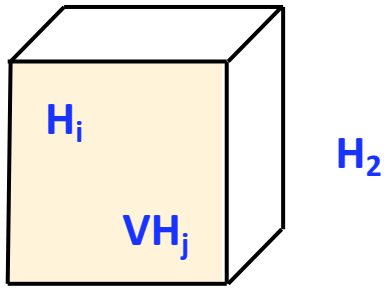


Fig. 8. Fractions x_j of vacancy type VH_j in tungsten at thermodynamic equilibrium for a total fraction of hydrogen $x_H = 10^{-5}$.



$$x_{H_i}(T) \approx \gamma \exp\left[-\frac{g_{H_i} - \mu}{k_B T}\right]$$

$$x_{VH_j}(T) \approx \omega_j \exp\left[-\frac{g_{VH_j} - j\,\mu}{k_B T}\right]$$

Interstitial H atoms impose a high chemical potential

This induces a high fraction of VHj vacancies

High temperature entropy favors interstitials

➔ Vacancies are depopulated

2. Thermodynamics model for Vacancies

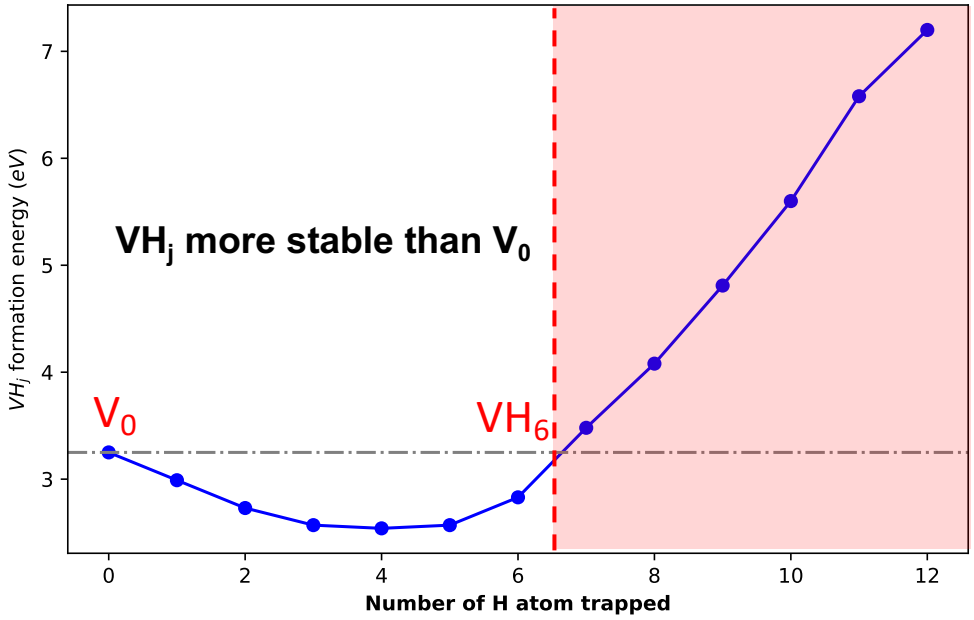
Driving forces for the formation of Super Abundant Vacancies

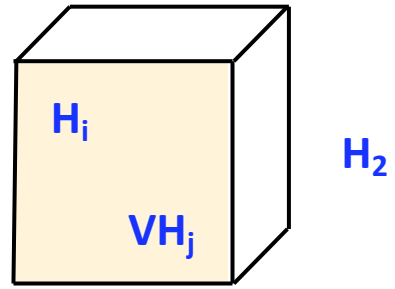
Sites	Energies (eV)
e_{int}	0.93
e_0	3.25
e_1	2.99
e_2	2.73
e_3	2.57
e_4	2.54
e_5	2.57
e_6	2.83
e_7	3.48
e_8	4.08
e_9	4.81
e_{10}	5.60
e_{11}	6.58
e_{12}	7.20

E. A Hodille et al. PRMat 2 (2018) 093802

SAV in Pd under High pressure

Y. Fukai and N. Okuma, PRL 73 (1994) 1640



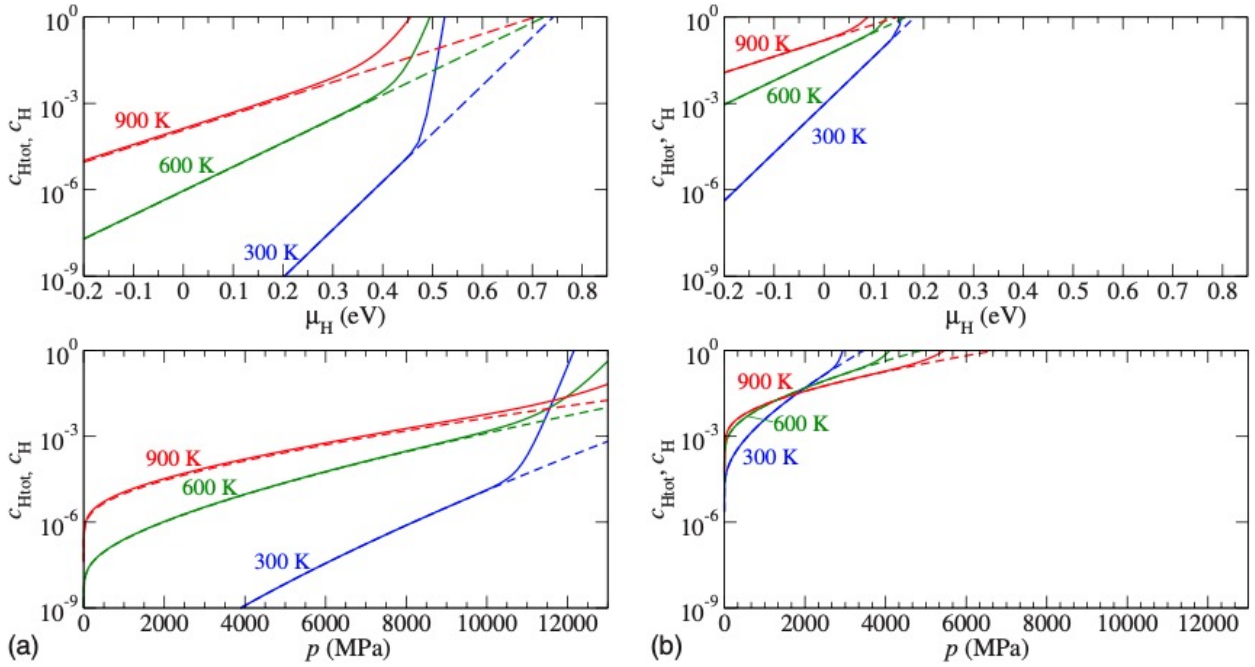


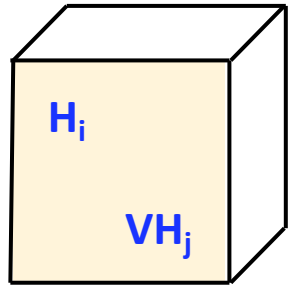
Formation energy of VH$_j$ is lower than empty V up to j=6

2. Thermodynamics model for Vacancies

Pioneering works on Mg and Al - Ismer et al. PRB 80 (2009) 184110

Aluminium **Magnesium**





Reservoir μ

H_2

Dotted lines x_{H_i}

Bold lines $x_{H_{tot}} = x_{H_i} + \sum_{j=0}^{12} j \; ; x_{VH_j}$

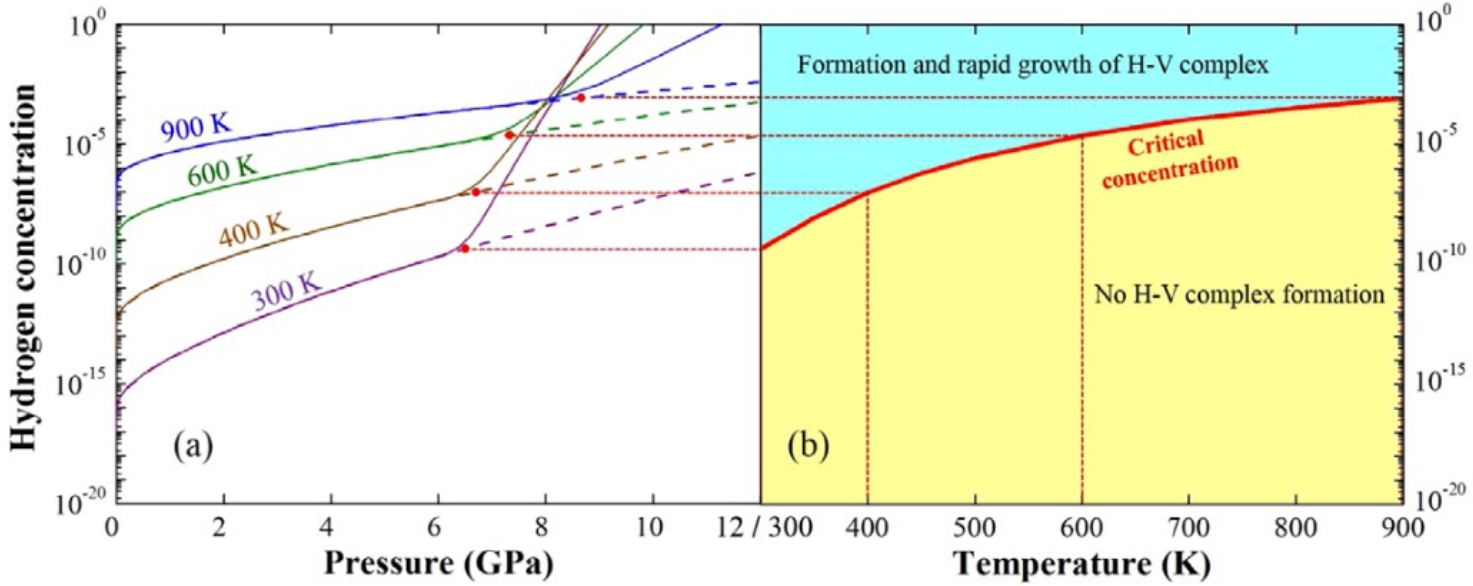
Ismer et al. PRB 80 (2009) 184110

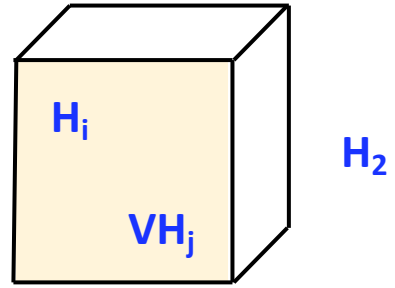
Chemical potential from Sugimoto & Fukai, Acta. Metal. Mater 40 (1992) 2327

2. Thermodynamics model for Vacancies

VHj formation in W

Lu Sun et al. J. Phys: Condensed Matter 26 (2014) 395402





Reservoir μ

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Chemical potential from Sugimoto et Fukai, Acta. Metal. Mater 40 (1992) 2327

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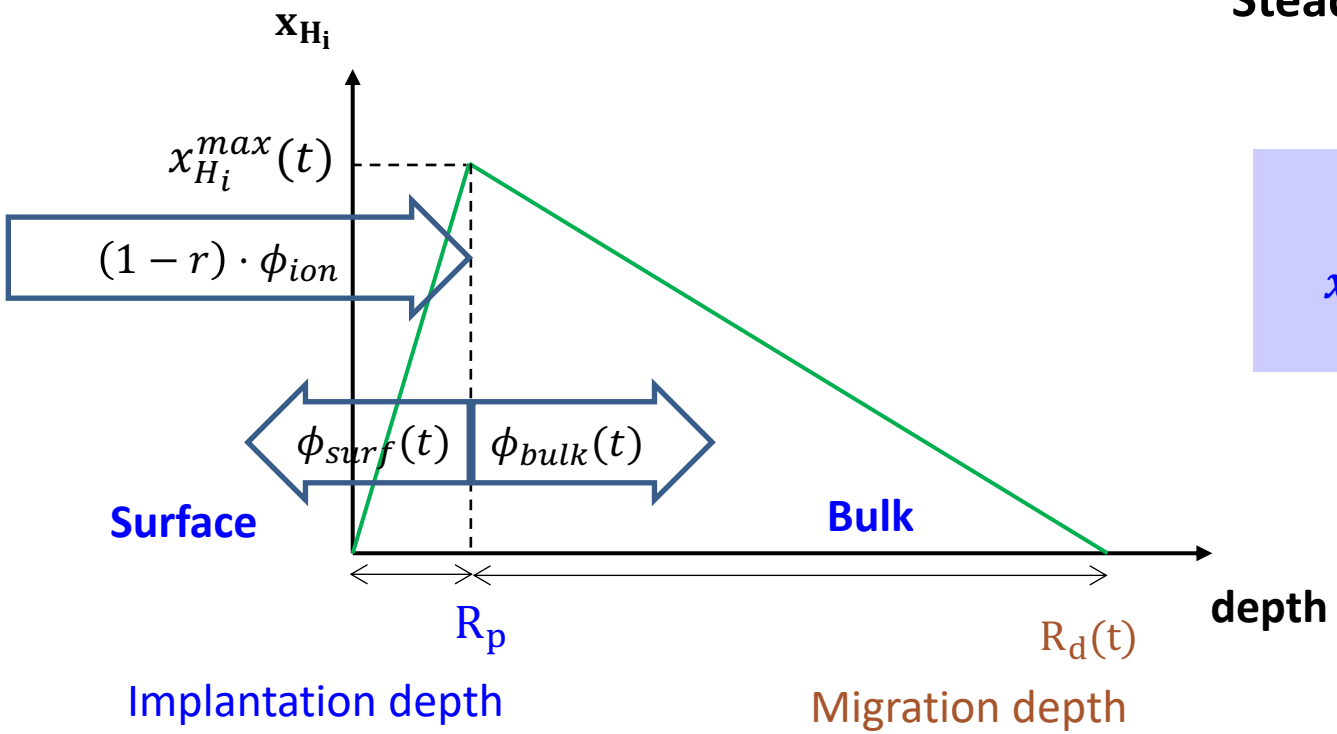
Chemical potential fixed by the flux in the sub-surface

E. A Hodille, N. Fernandez, Z. A. Piazza, M. Ajmalghan, Y. Ferro et al. PRMat 2 (2018) 093802



Steady state *Flux balance*

Experimental conditions

$$x_{H_i}^{MAX}{}_{t\to\infty} = R_p \cdot (1-r) \cdot \frac{\phi_{ion}}{\rho_W} \cdot \frac{1}{D(T)}$$

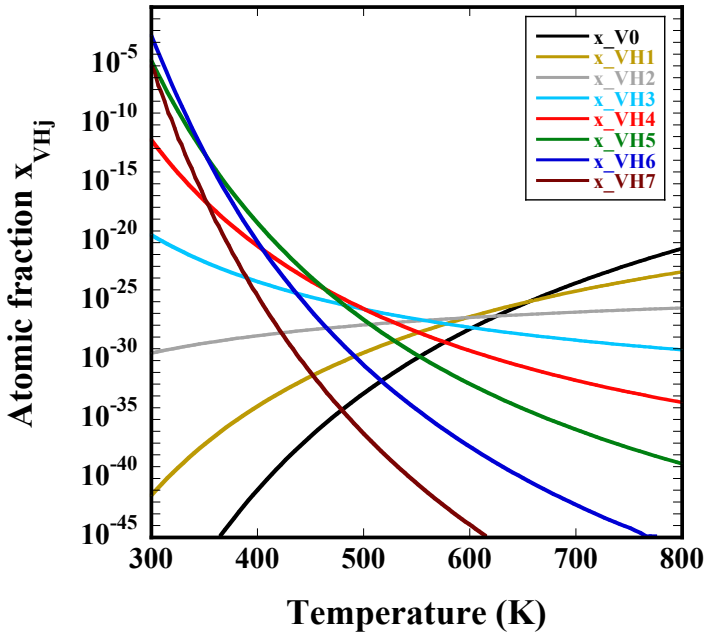
TRIM - depends on E_{ion} **DFT**

2. Thermodynamics model for Vacancies

Chemical potential fixed by the flux in the sub-surface

E. A Hodille, N. Fernandez, Z. A. Piazza, M. Ajmalghan, Y. Ferro et al. PRMat 2 (2018) 093802

Atomic fraction of VHj vacancies in the 10 nm the sub-surface



Incident flux $\phi_{inc} = 10^{19}\mathrm{m}^{-2}\mathrm{s}^{-1}$
Incident ion energy E_{inc} = 500 eV/ion.

The flux fixes H_{int} …

- H_{int} fixes the chemical potential…
- … and the fraction of VH_j vacancies

$$x_{H_i} = R_p \cdot (1 - r) \cdot \frac{\phi_{ion}}{\rho_W} \cdot \frac{1}{D(T)}$$

$$x_{H_i}(T) \approx \gamma \exp\left[-\frac{g_{H_i} - \mu}{k_B T}\right]$$

$$x_{VH_j}(T) \approx \omega_j \exp\left[-\frac{g_{VH_j} - j\,\mu}{k_B T}\right]$$

Vacancy depopulation with increasing temperature

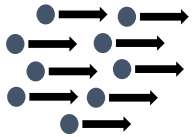
2. Thermodynamics model for Vacancies

Chemical potential fixed by the flux in the sub-surface

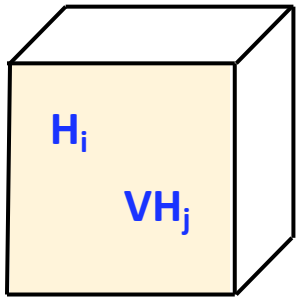
Flux

$$x_{H_i} = R_p \cdot (1 - r) \cdot \frac{\phi_{ion}}{\rho_W} \cdot \frac{1}{D(T)}$$

H/D



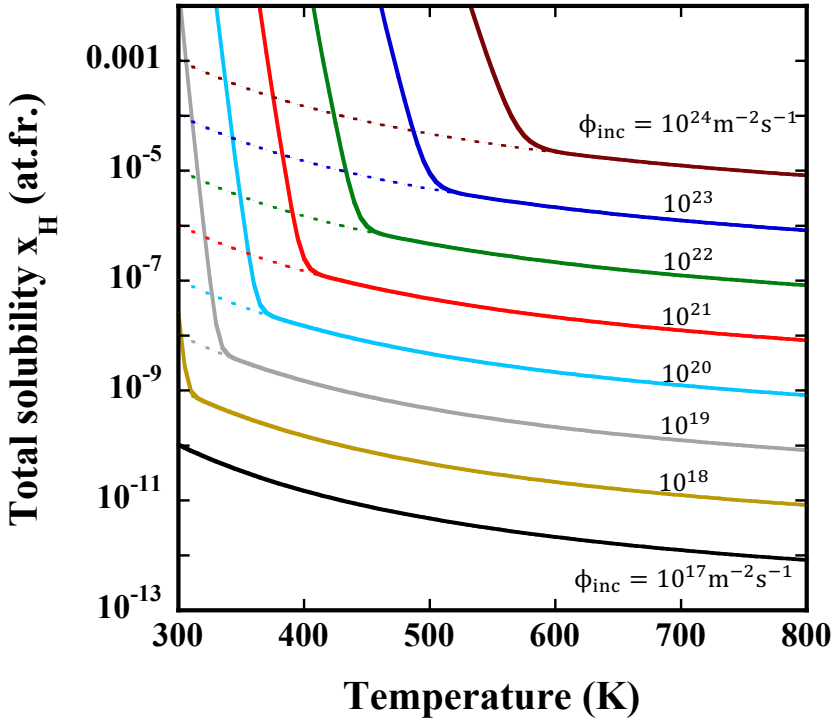
μ



Response of the sub-surface

$$x_{H_i}(T) \approx \gamma \exp\left[-\frac{g_{H_i} - \mu}{k_B T}\right]$$

$$x_{VH_j}(T) \approx \omega_j \exp\left[-\frac{g_{VH_j} - j\,\mu}{k_B T}\right]$$

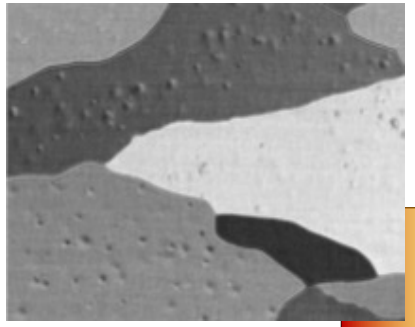


Dotted lines x_{H_i}

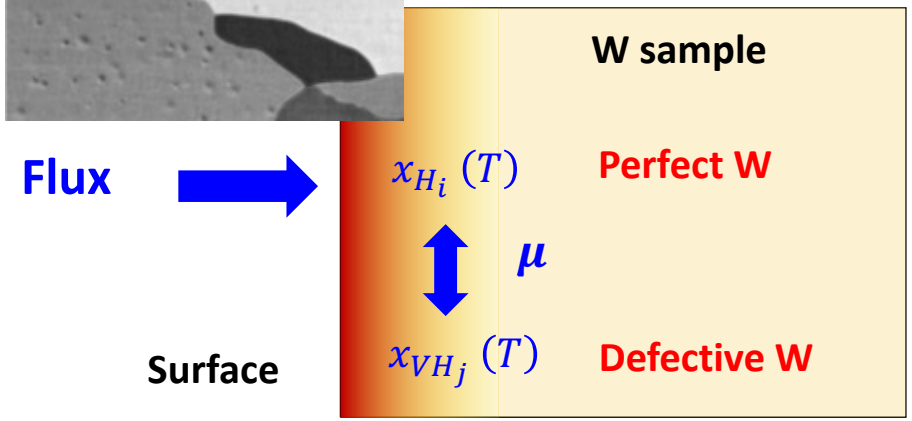
Bold lines
$x_{H_{tot}} = x_{H_i} + \sum_{j=0}^{12} j \,.\, x_{VH_j}$

Incident fluxes ranging from $\phi_{inc} = 10^{17}m^{-2}s^{-1}$ to $\phi_{inc} = 10^{24}m^{-2}s^{-1}$
Incident energy of E_{inc} = 500 eV/ion.
The fraction of hydrogen **interstitial** sites is plotted in dotted lines

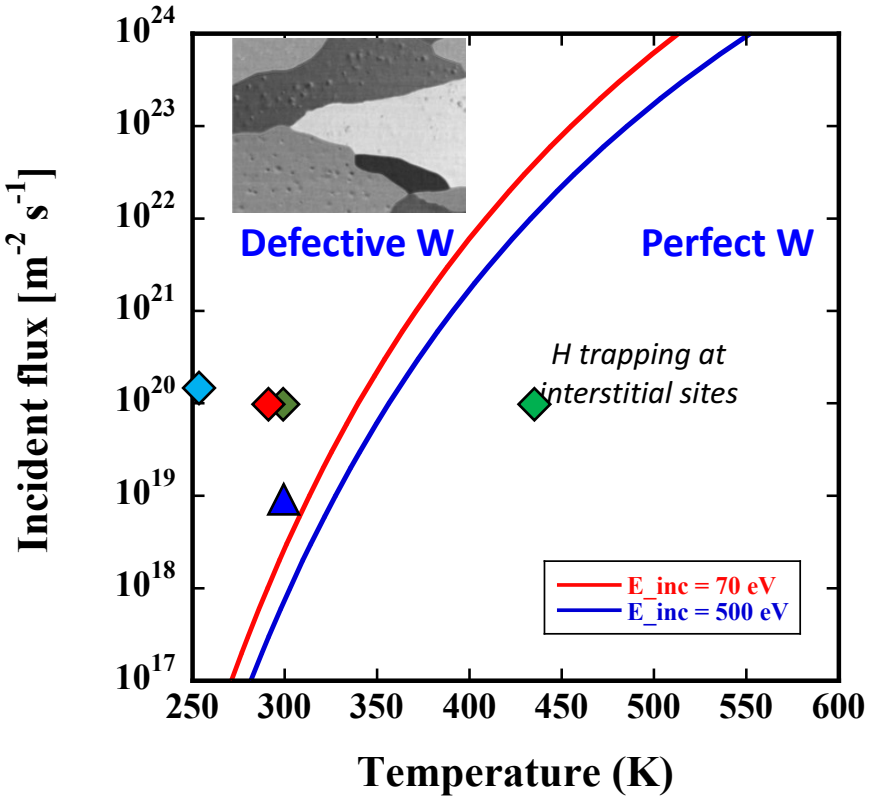
3 –Super-Abundant Vacancies



Gao et al., Nucl. Fus. **57** (2017) 016026



Phase Diagram Temp. / Flux



- ***No SSL*** *– S. Kapser et al., NF (2018)*
- ***SSL*** *– A. Manhard et al., NME (2018)*
- ***SSL*** *– S. Kapser et al., NF (2018)*
- ***SSL*** *- Gao et al., NF* (2017)
- ***SSL*** - Alimov et al., JNM (2005)

No Impact of E_i

Nishijima et al. NF 61 (2021) 116028

Outline

1 . The basic ingredients

2 . Thermodynamic models for vacancies

3 . Supersaturation and vacancy stabilization

- Super Saturated Layers
- Vacancy Stabilization

4 . Discussion

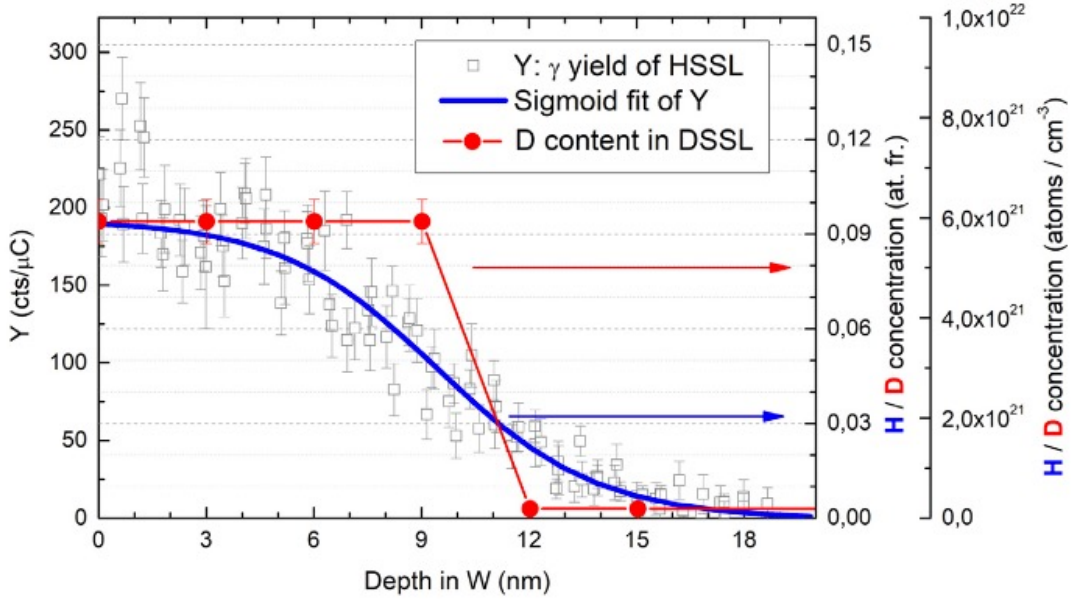
3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

215 eV/D+ or 415 eV/H+

5eV/W at., well below 9eV/W at. (displ. Thr.)

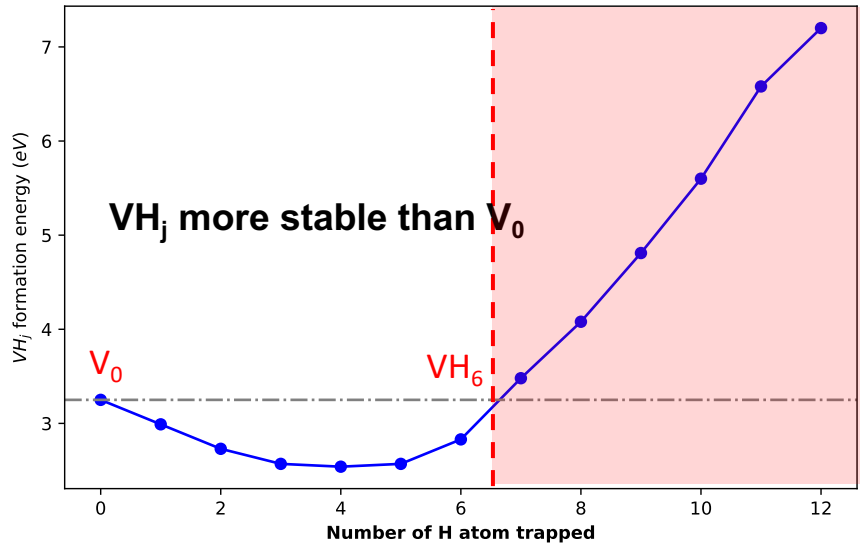


L. Gao et al. NF 57 (2017) 016026

L. Gao et al. Acta. Matter 201 (2020) 55-62

Mechanisms for vacancy stabilization ?

E. A Hodille et al. PRMat 2 (2018) 093802



Hydrogen stabilizes vacancies

3. Super-Saturation and Vacancy Stabilization

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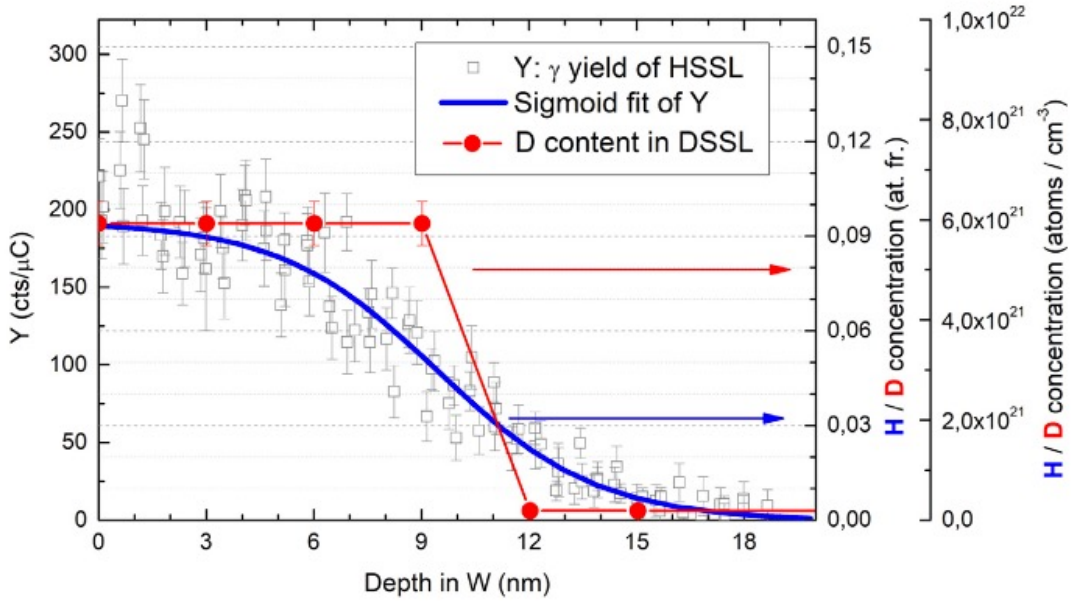

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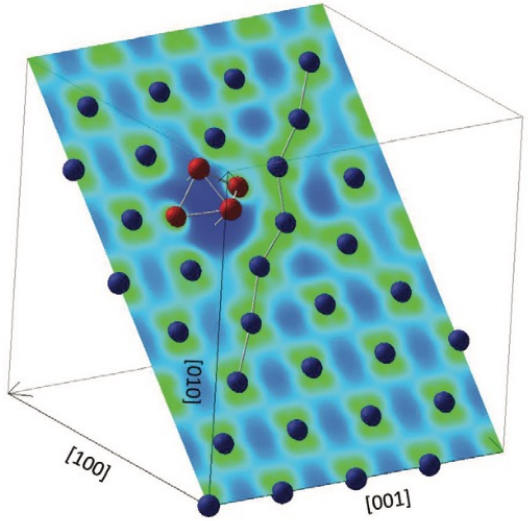


E_f (VH_6+SIA) = 12.1 eV

0.6 eV smaller than E_f (VH_6) + E_f (SIA)

Kato et al. NF 55 (2015) 083019

Crowdion-SIA (and others) stabilizes vacancies
Prevent them from recombining

Hydrogen stabilizes vacancies

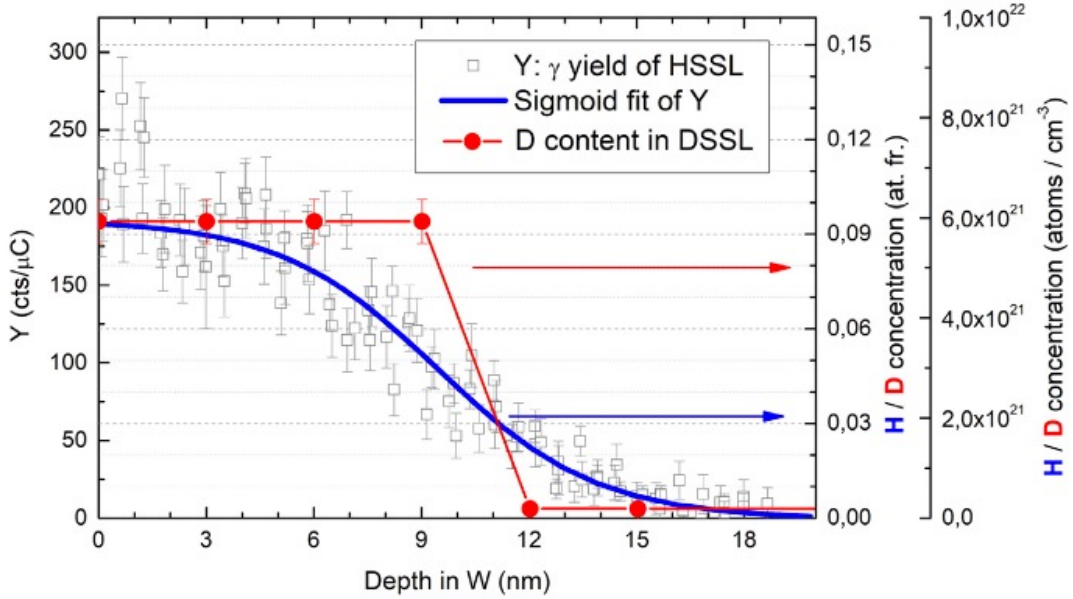
3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

SSL forms within 10 nm

215 eV/D+ or 415 eV/H+

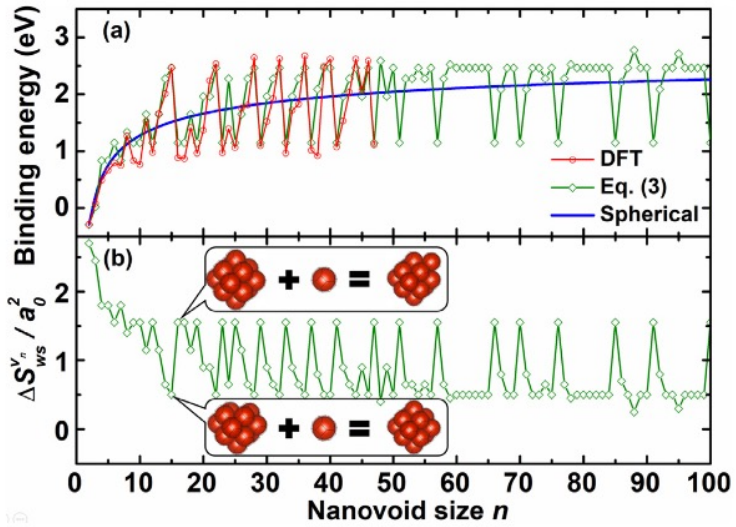
5eV/W at., well below 9eV/W at. (displ. Thr.)



L. Gao et al. NF 57 (2017) 016026

L. Gao et al. Acta. Matter 201 (2020) 55-62

Mechanisms for vacancy stabilization ?



J. Hou et al.
Acta Matter 211 (2021) 116860

Binding energy of vacancies increases when vacancies grow

Crowdion-SIA (and others) stabilizes vacancies

Hydrogen stabilizes vacancies

3. Super-Saturation and Vacancy Stabilization

Super-Saturated Layers

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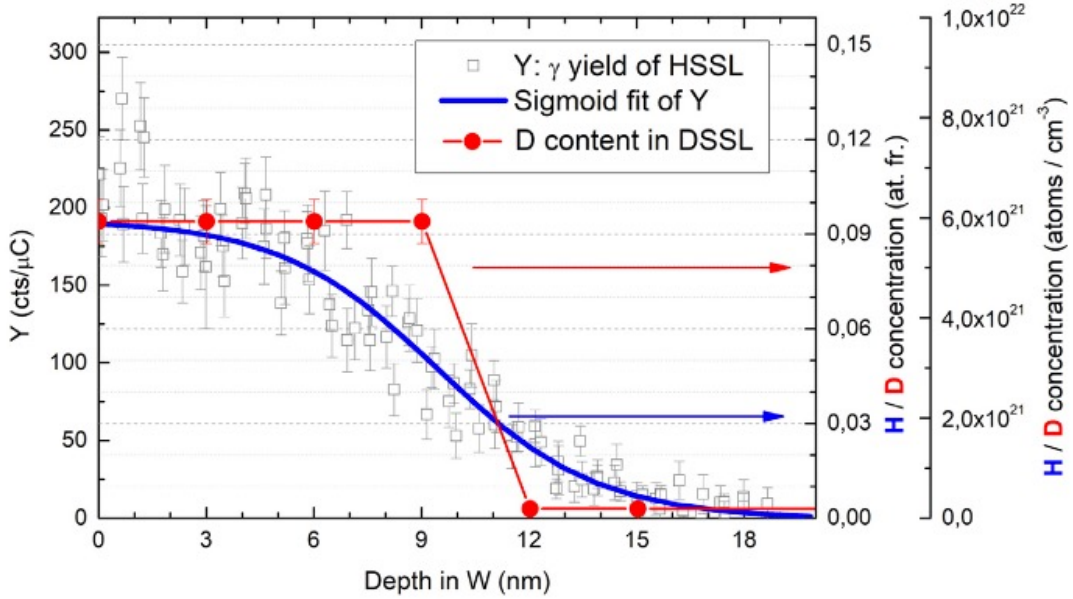
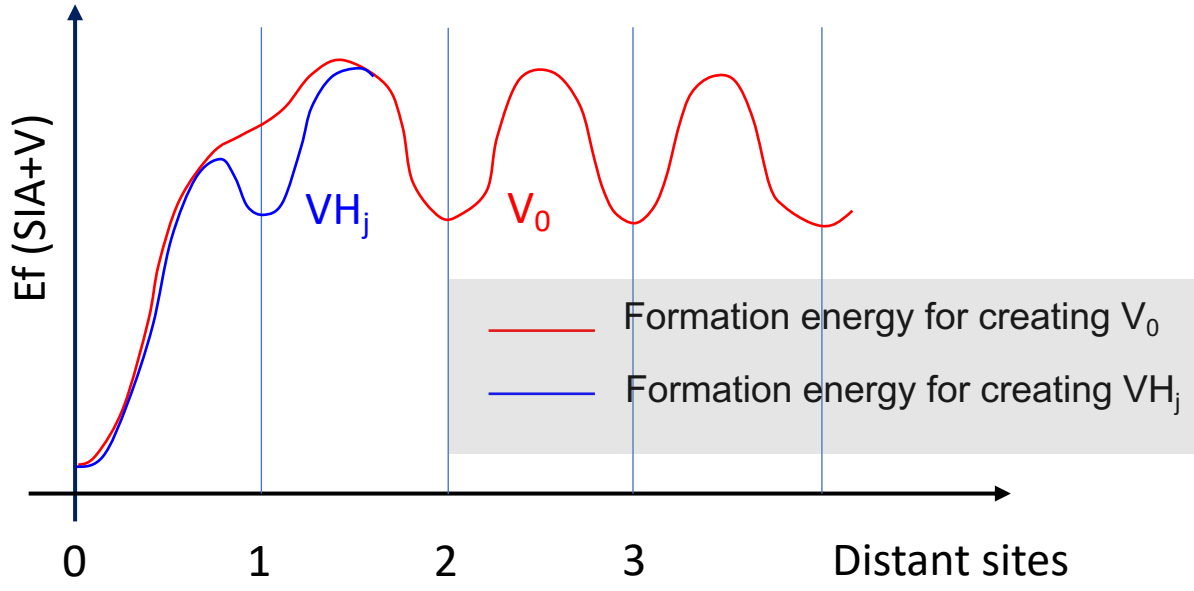


L. Gao et al. NF 57 (2017) 016026

L. Gao et al. Acta. Matter 201 (2020) 55-62

Mechanisms for vacancy stabilization ?



More energy is required to dissociate the Frenkel pair in the absence of Hydrogen

Dynamic of the process ?

Outline

1 . The basic ingredients

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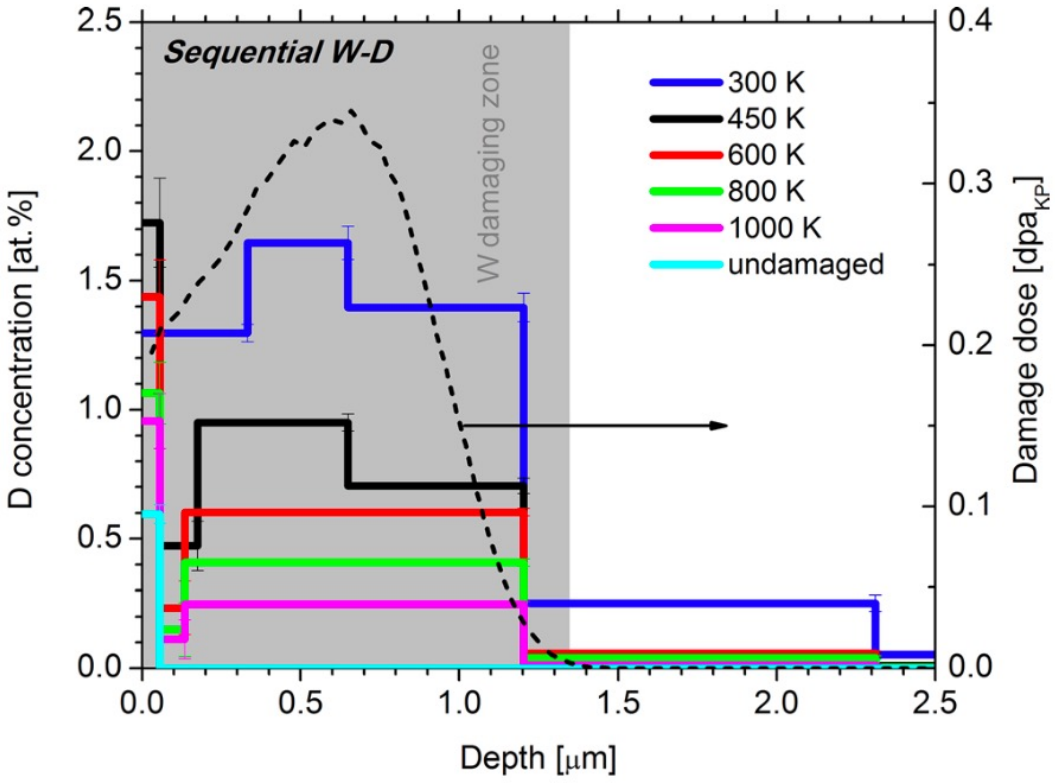
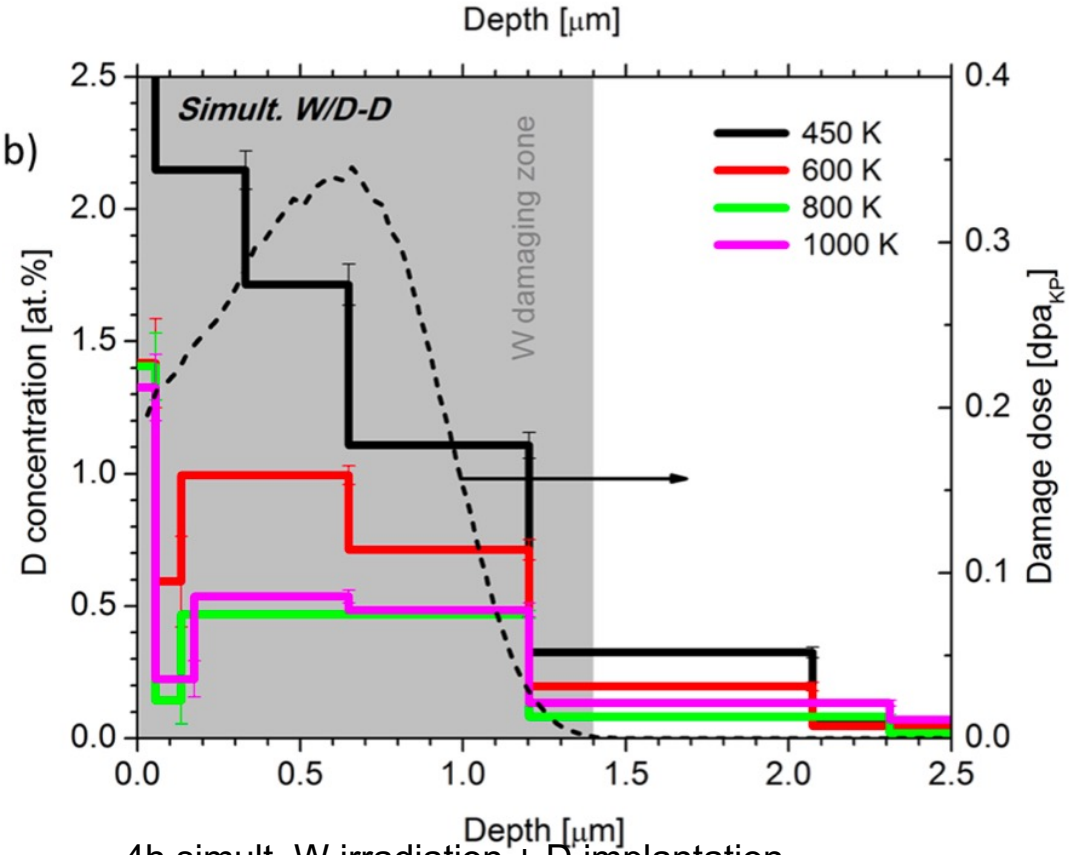
3. Super-Saturation and Vacancy Stabilization

SAV formation in damaged W – Defect Stabilization

M. Markelj et al., 59 (2019) 086050



4h W irradiation followed by 39 h D ions implantation

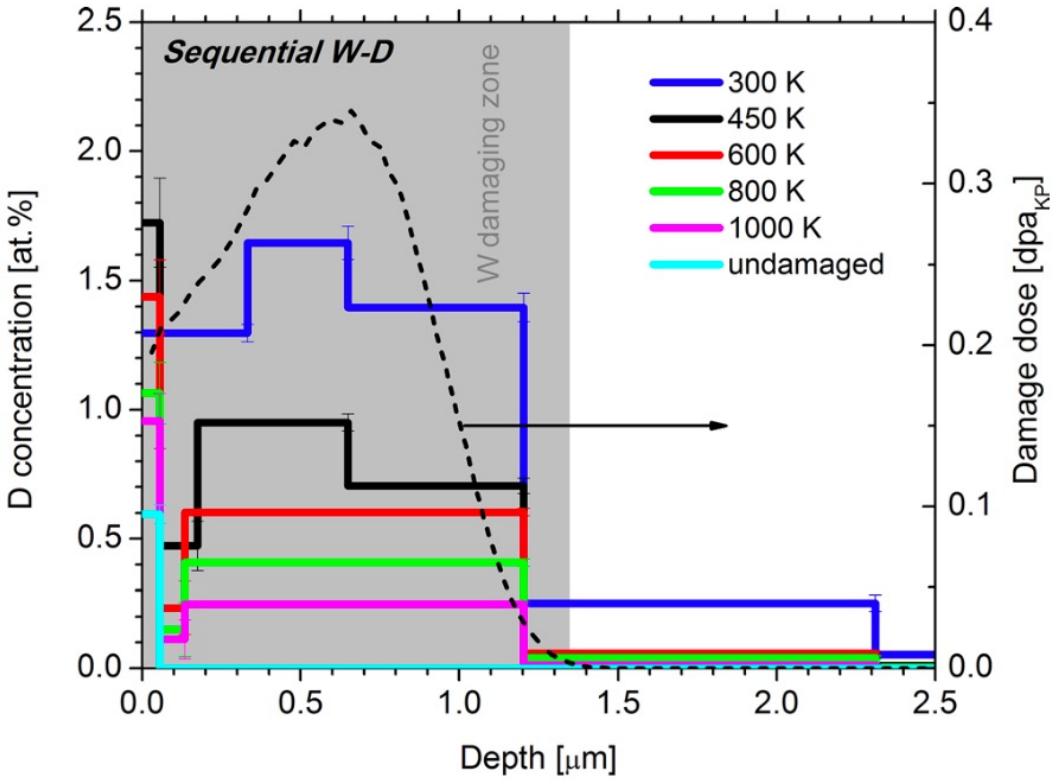


4h simult. W irradiation + D implantation followed by 35 h D ions implantation

3. Super-Saturation and Vacancy Stabilization

SAV formation in damaged W – Defect Stabilization

M. Markelj et al., 59 (2019) 086050



4h W irradiation followed by 39 h D ions implantation

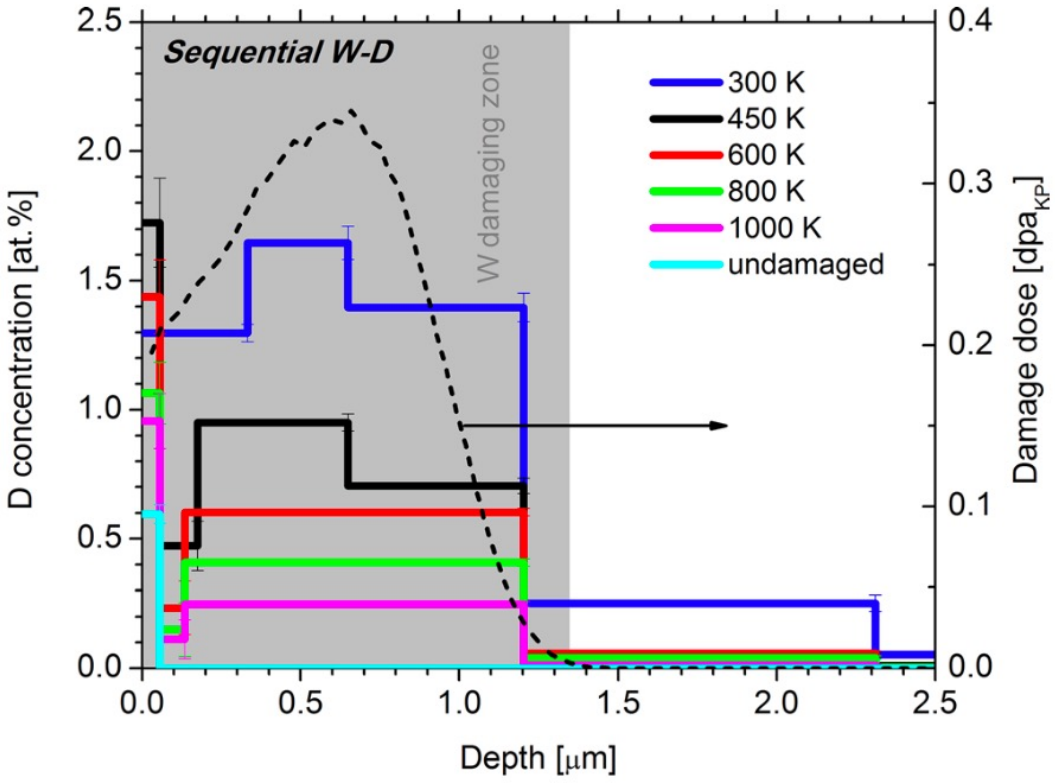
No help from the Thermo. Model

- SSL are formed in the near surface
- Vacancies annihilate with increasing T
  ➔ higher mobility of the atom
- Decoration reveals the V remaining after damaging

3. Super-Saturation and Vacancy Stabilization

SAV formation in damaged W – Defect Stabilization

M. Markelj et al., 59 (2019) 086050



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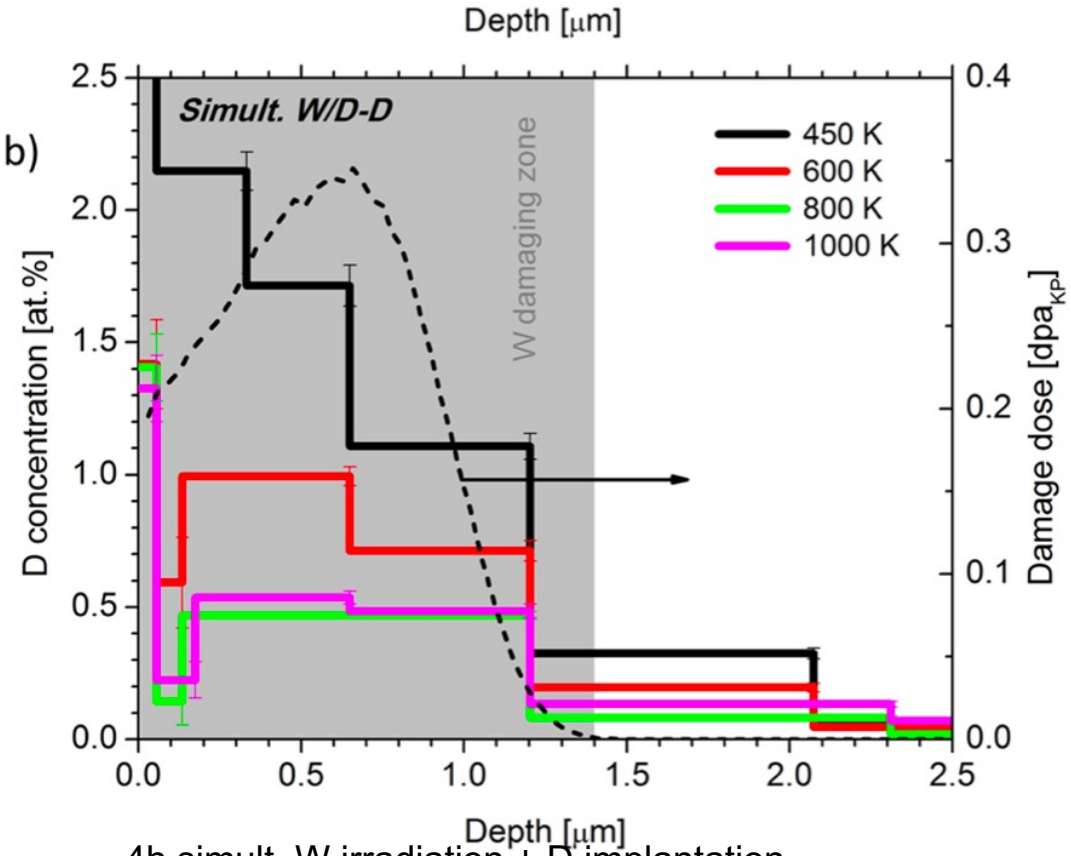

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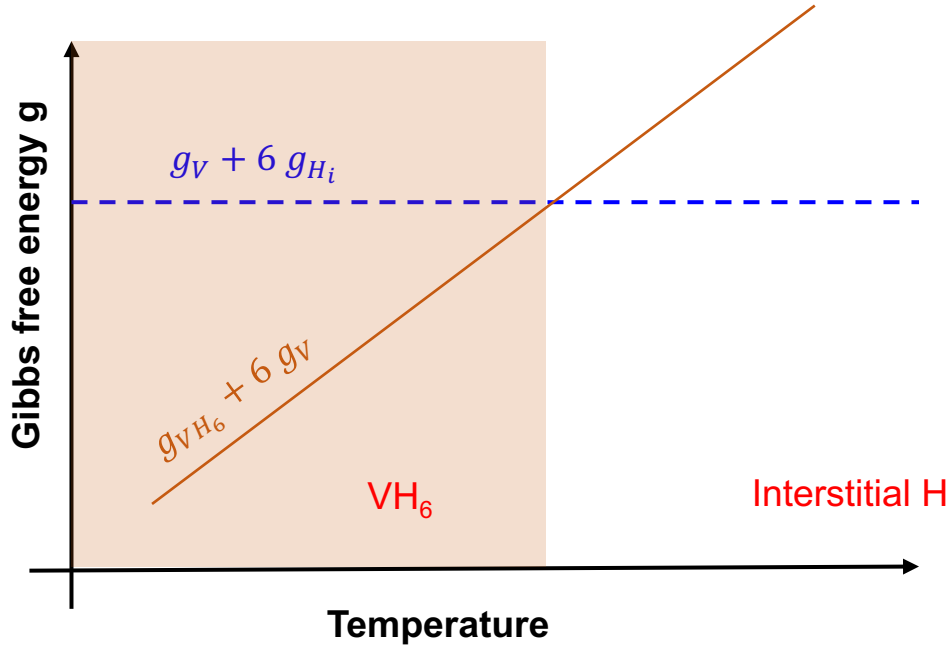


Toward VH_6 eq. during D imp. + W damage

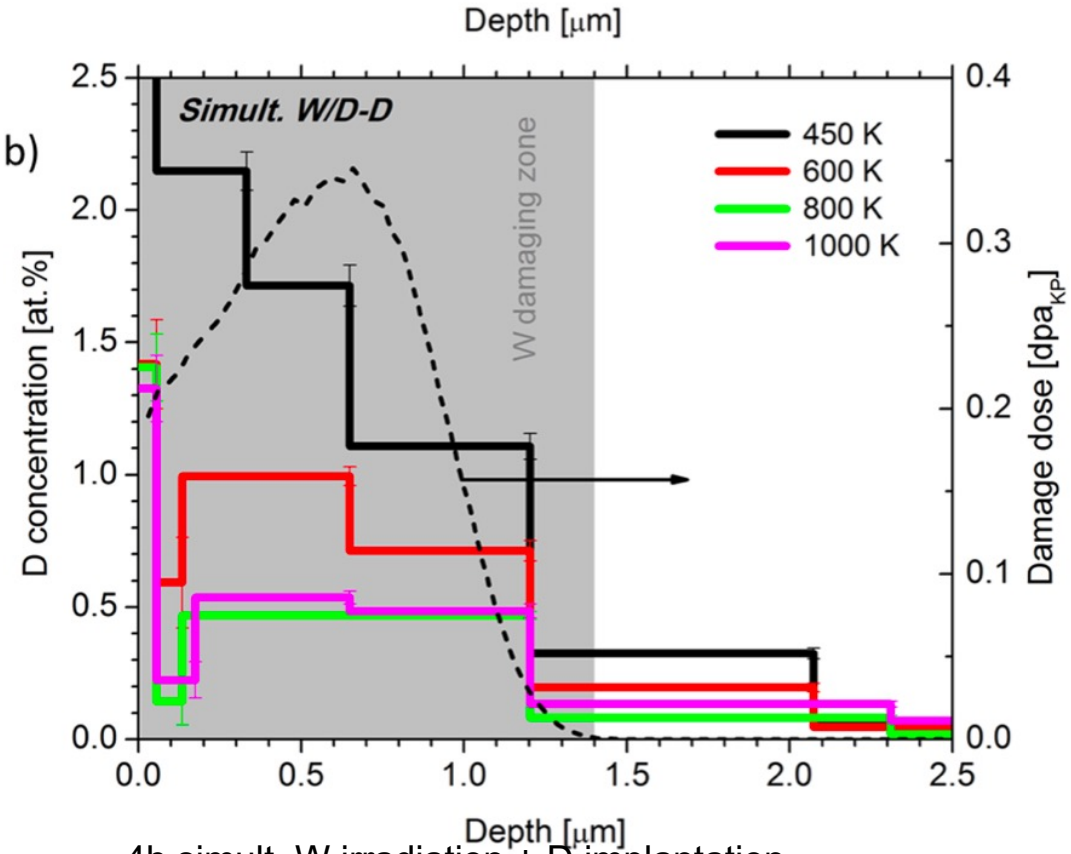
Fluence not enough for reaching eq.

➔ The near surface is more populated

After W damage, created V not filled are reveal

With temperature, mechanism for V stab less and less efficient

M. Markelj et al., 59 (2019) 086050



4h simult. W irradiation + D implantation followed by 35 h D ions implantation

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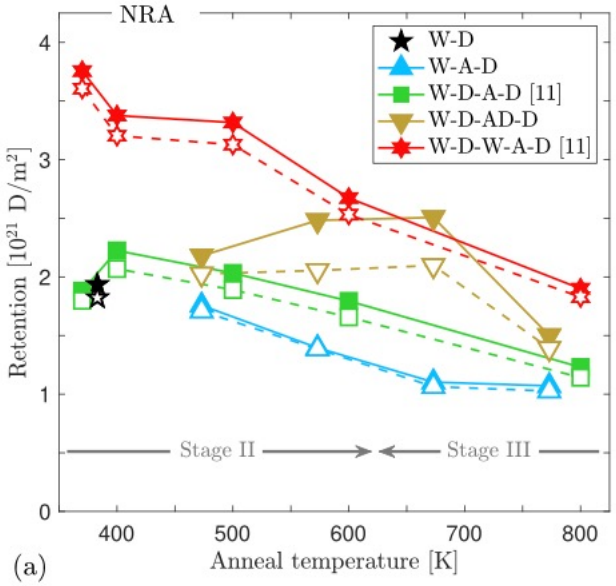
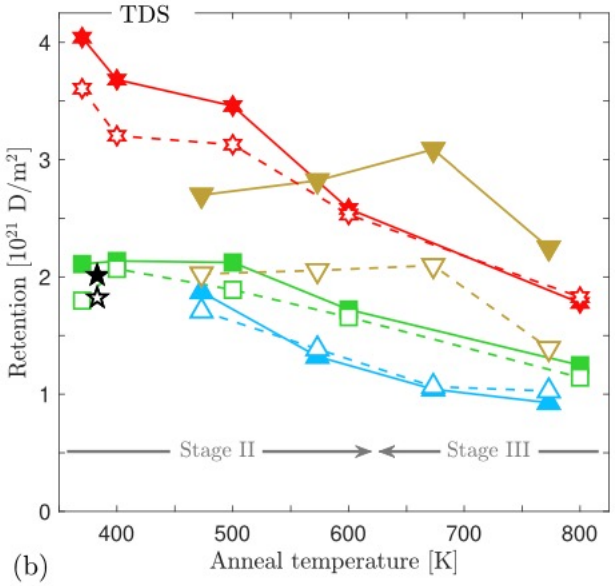
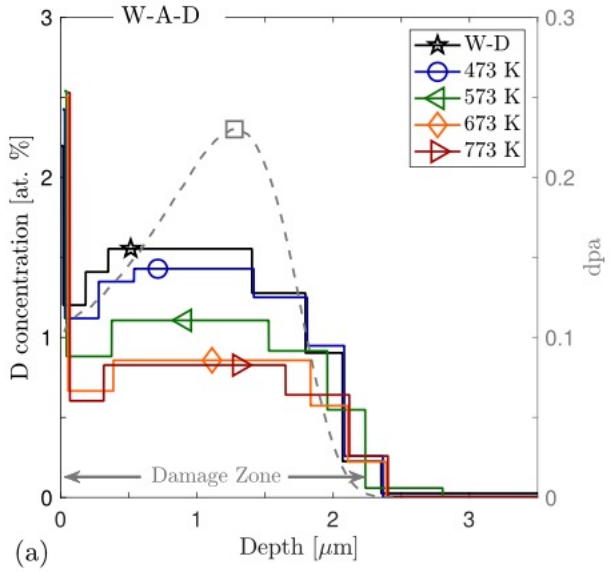
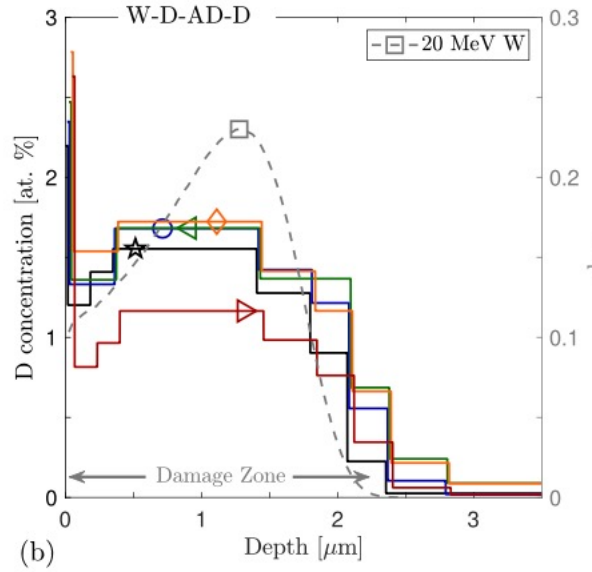
SAV formation in damaged W – Defect Stabilization

M. Simmonds et al., 59 (2019) 086050









Complies with the Thermo model

To be discussed …

Outline

1 . The basic ingredients

2 . Thermodynamic models for vacancies

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4. Discussion

- Mechanisms for SSL formation and V stab are probably the same
- H in V would stabilize a V and prevent it to recombines with SIA
- Thermal V are created at the surface. W atoms bring enough energy to create additional vacancies that would be stabilized with H. No need for collision cascade and Frankel pairs.
- The stress around VHj should be at shorter distance than around V. In addition, VHj is much less mobile the V. The cross section for VHj+SIA recombination is smaller than V + SIA.
- SSL are formed in other metals like Mo, Fe, steel, not Cu that display higher Ef for V creation
- Hy SSL are formed at T=800K. Is it because of the flux that bring μ so high ?

Thanks for your attention …

… and sorry for being that long.