Second Sina-German Workshop on PWI, December 6-8, 2010

# Synergetic Effects of H/He on W-based PFMs In a Nuclear Fusion Tokamak

*A possible way to suppress H retention & blistering*


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# Contributors


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# Outline

- Background & motivation
- H blistering mechanism in metals
- H/He synergetic effects
- The way to mitigate H retention & suppressing H blistering
- PFMs study strategy & perspective

# Background: H blistering in W & W alloys

## Application

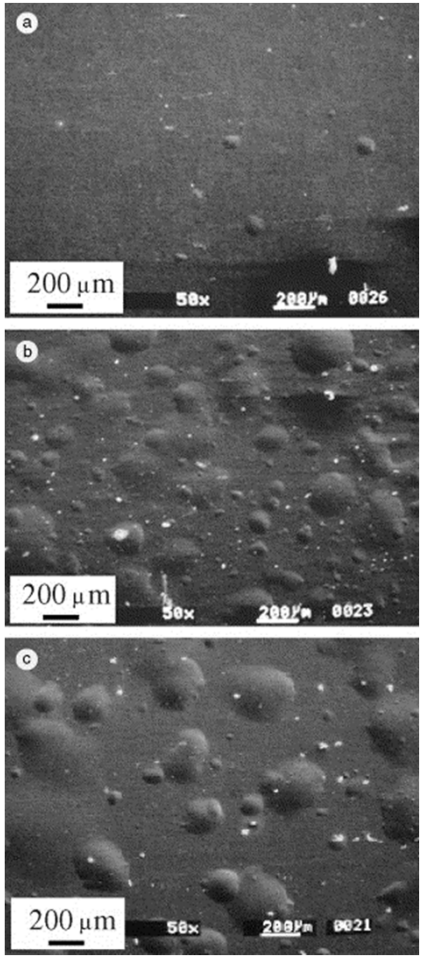
- Tungsten (W) and W-alloys are considered to be one of the most promising candidates for the PFM in Tokamak.

## Advantages

- Low sputtering erosion and good thermal properties including high thermal conductivity and high melting temperature.

## Critical issues: *H blistering*

- Higher H concentrations isotope ions on a W single crystal, as well as polycrystalline gives rise to **blistering** at the W surface.




J. Nucl. Mater. **313-316**, 72 (2003)

# Motivation

- H trapping process in W is still unclear
- Mechanism of H bubble formation in W is still not fully understood.
- Still have no effective method to suppress the H bubble formation

First Sino-German Workshop on PWI Hefei, 2009

# H blistering mechanism in metals

**Question:** What is the physical mechanism

for the H bubble formation in W?

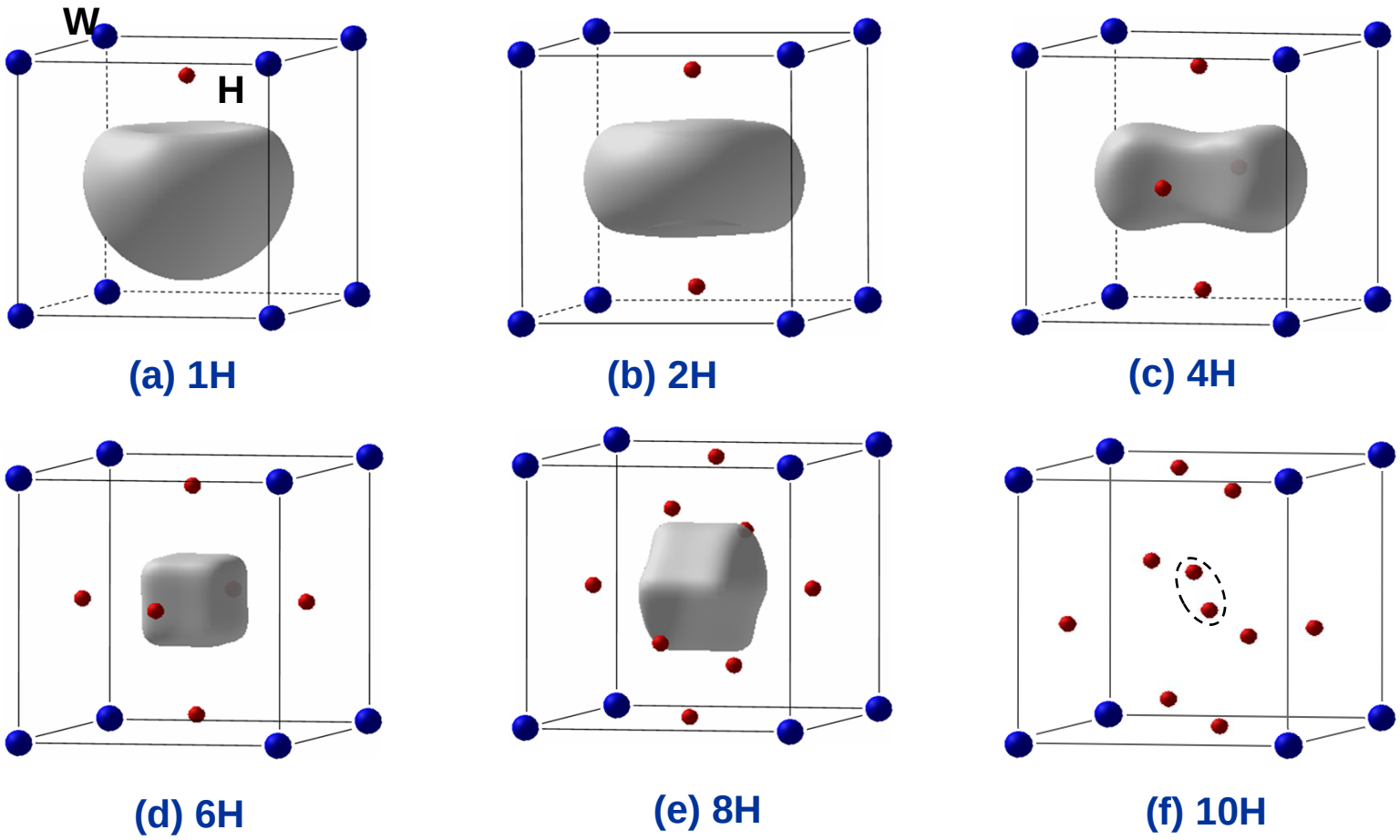
→ **H molecule ($H_2$)**

**Preliminary stage of H bubble formation**


- Y-L Liu, G.N. Luo, and Guang-Hong Lu, J. Nucl. Mater. (2009)
- Y-L Liu , G.N. Luo, and Guang-Hong Lu, PRB (2009)
- H.-B. Zhou , G.N. Luo, and Guang-Hong Lu, Nuclear Fusion (2010)

# *First-principles calculation:*

## Optimal trapping sites for H in W

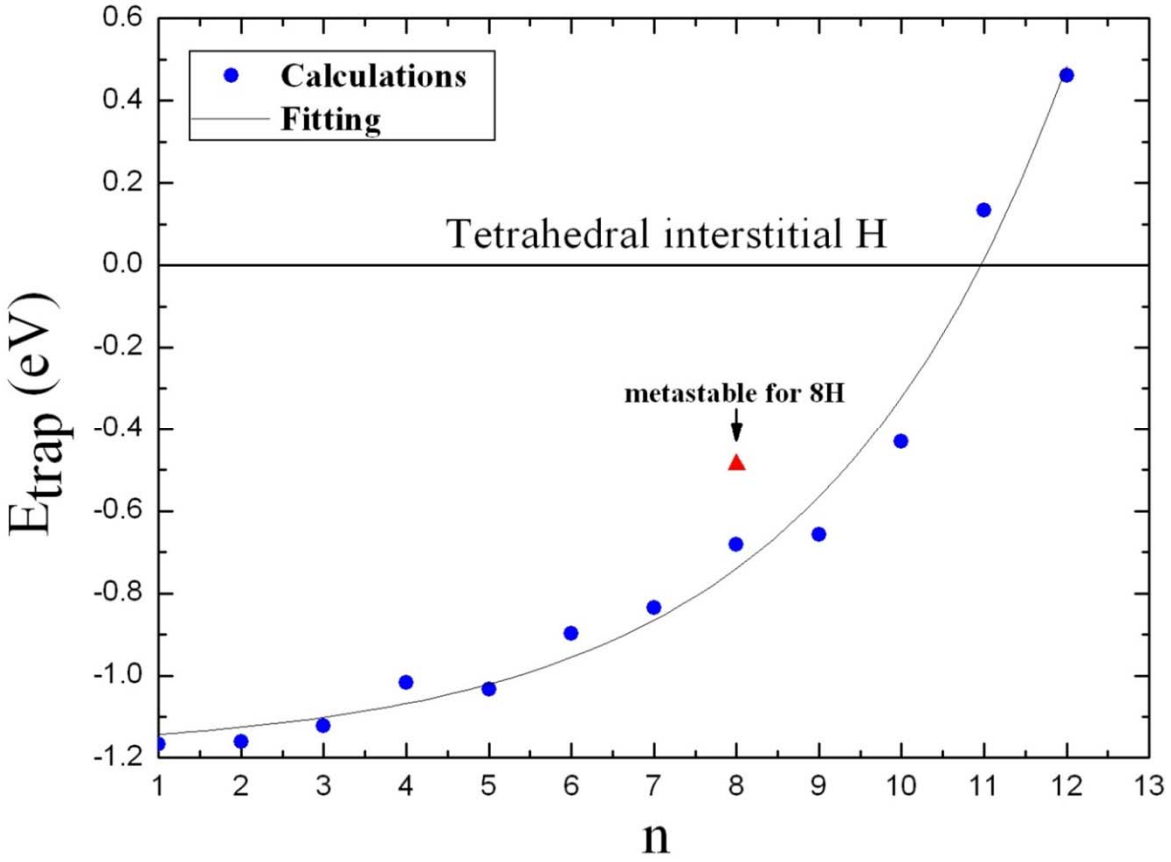



A vacancy trapping mechanism

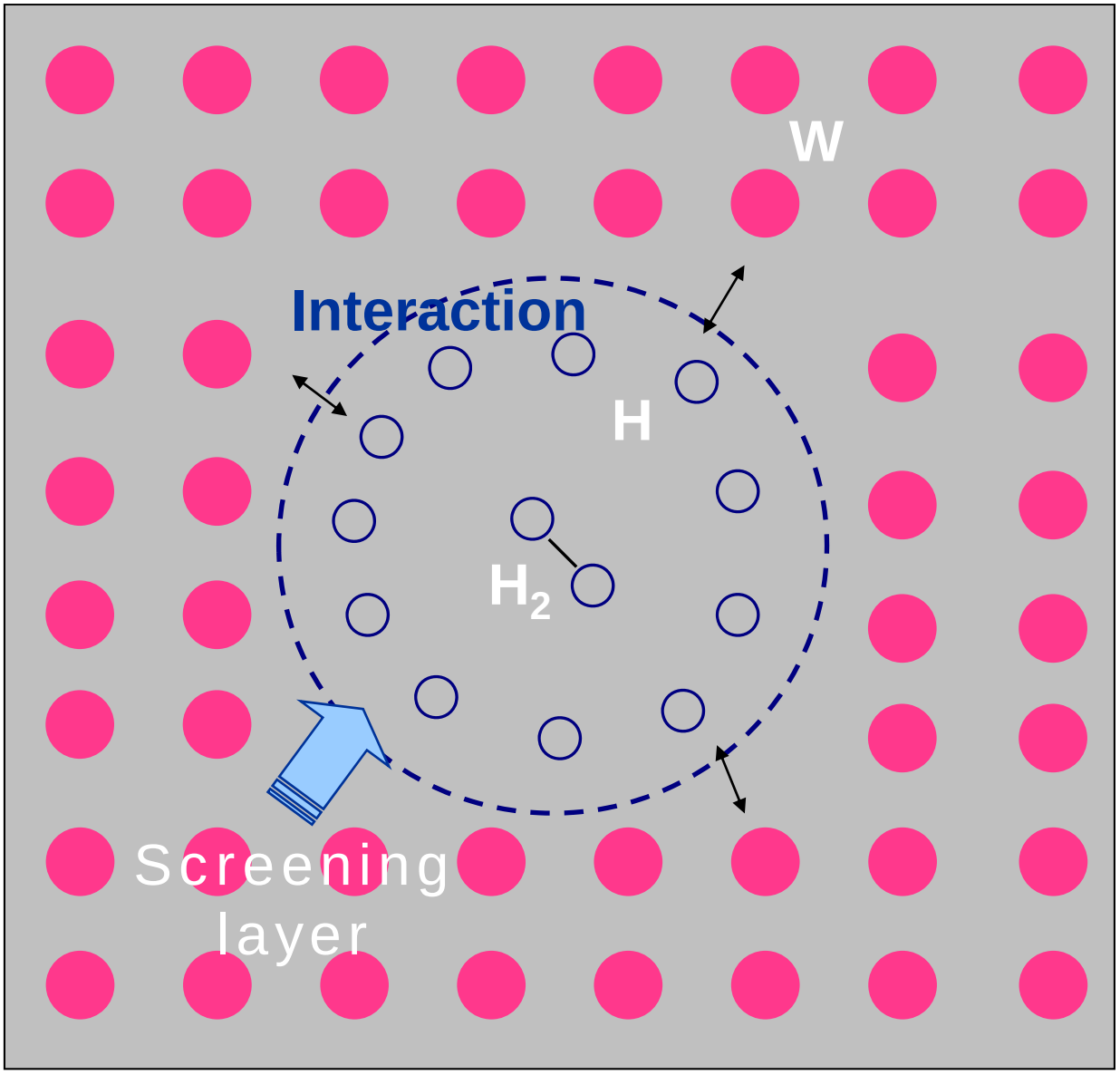
- Atomic configuration and the iso-surface of optimal charge for H with different number of trapped H atoms at the monovacancy.

First-principles calculation:

## H trapping energy at the vacancy




- Monovacancy traps up to 10 H.
- H trapping energy inside a vacancy is lower than that at the tetrahedral interstitial site far away from the vacancy.




**A vacancy trapping mechanism ( PRB, 2009 )**

# Generalization of the trapping mechanism

## A general mechanism

- Polycrystalline of W (grain boundary or other defects)
- Other metals and alloys

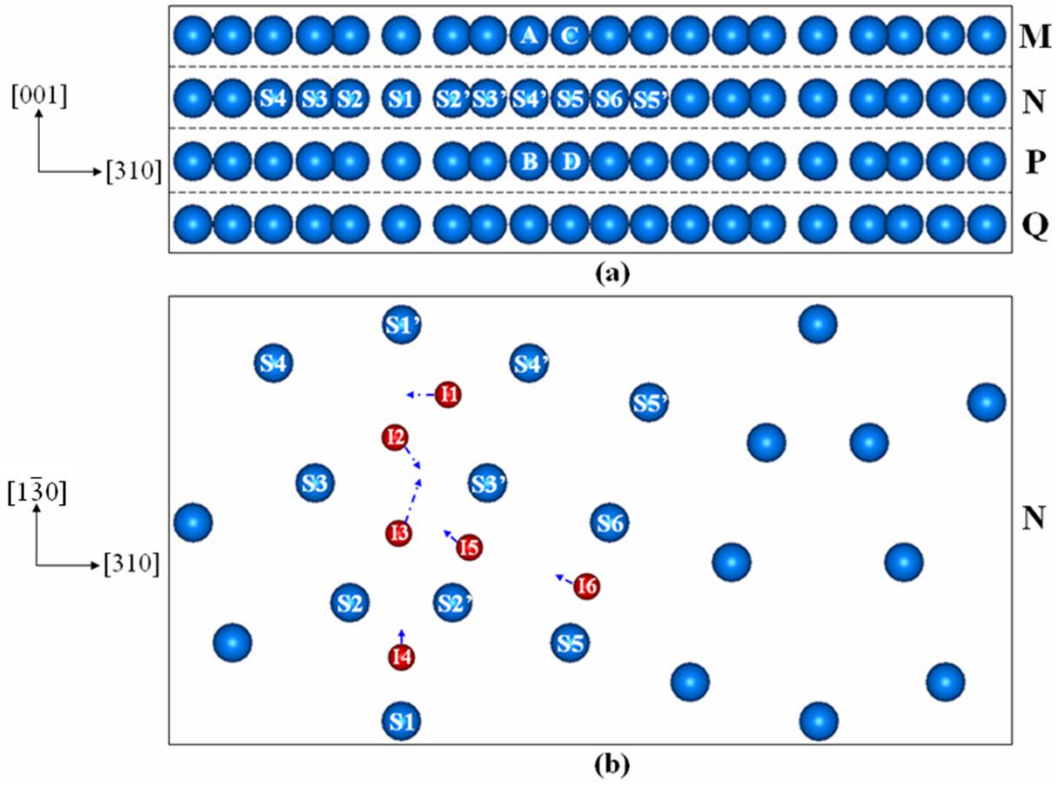
## Essence of the mechanism:

- Enough space to provide an optimal charge density

# H at grain boundary

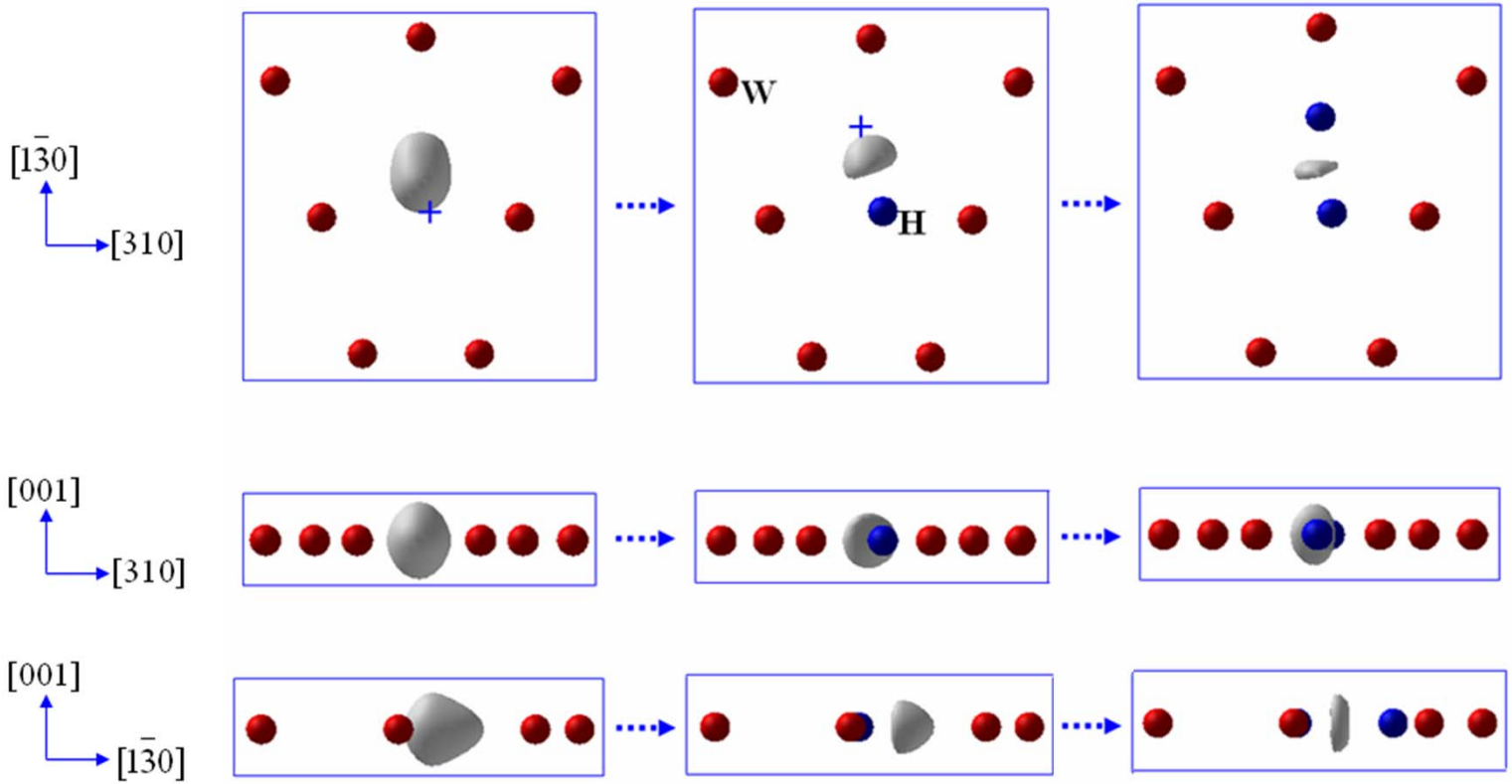
- H-B Zhou, G.-N. Luo, and Guang-Hong Lu, **Nuclear Fusion** (2010)

# Grain boundary of W




**Σ5 grain boundary: 20.87 Å × 9.97Å × 6.29 Å**

# Optimal charge density for H in grain boundary




- The H-H binding energy -0.13 eV (repulsion), equilibrium distance 2.15 Å.
- Second H atom addition makes isosurface of optimal charge density almost disappear.

# GB-vacancy trapping mechanism

| | Grain boundary | Bulk |
|---|---|---|
| H solution energy at vacancy | -1.74 eV | -1.43 eV |
| Optimal charge density | 0.10 electron/Å$^3$ | 0.11 electron/Å$^3$ |
| Vacancy formation energy | 1.72 eV | 3.11 eV |
| Coordination number of W atoms | 8 | 8 |

- The vacancy formation is much easier in the GB as compared with the bulk.
- The H bubble formation in the W GB should be via a vacancy trapping mechanism.

# Prediction: How to suppress H blistering

**Two ways according to vacancy trapping mechanism.**

- **Removing all the vacancy-related defects in W**
- **Doping the elements that can change the charge distribution to make it “not optimal” for H**

**Helium $1s^2$**

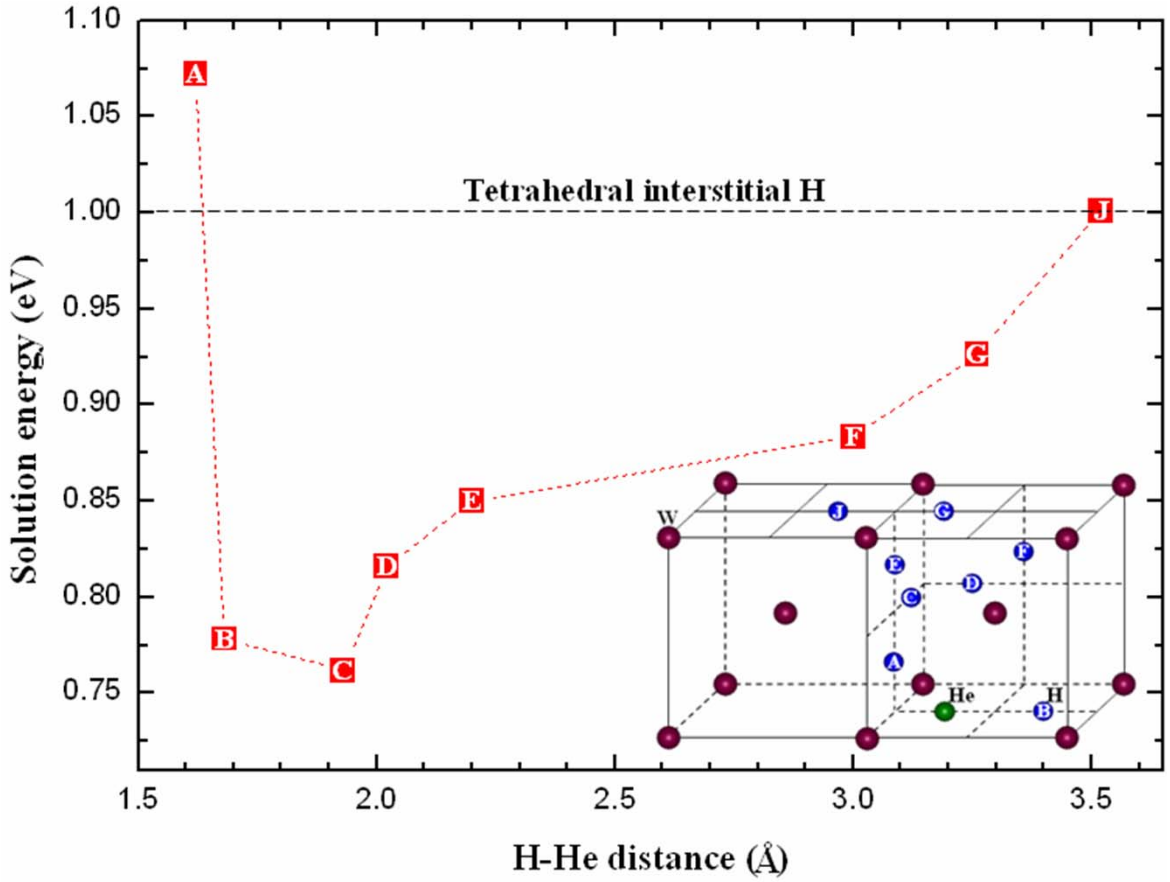
**a close-shell structure element**

# H/He synergetic effects

- H-B Zhou, G-N Luo, and Guang-Hong Lu, **Nuclear Fusion** (2010)

# Interaction of He and H in W: attractive

**Intrinsic W**




- Solution energy of H: 0.76 eV, 0.23eV lower than that of TIS in W without He.

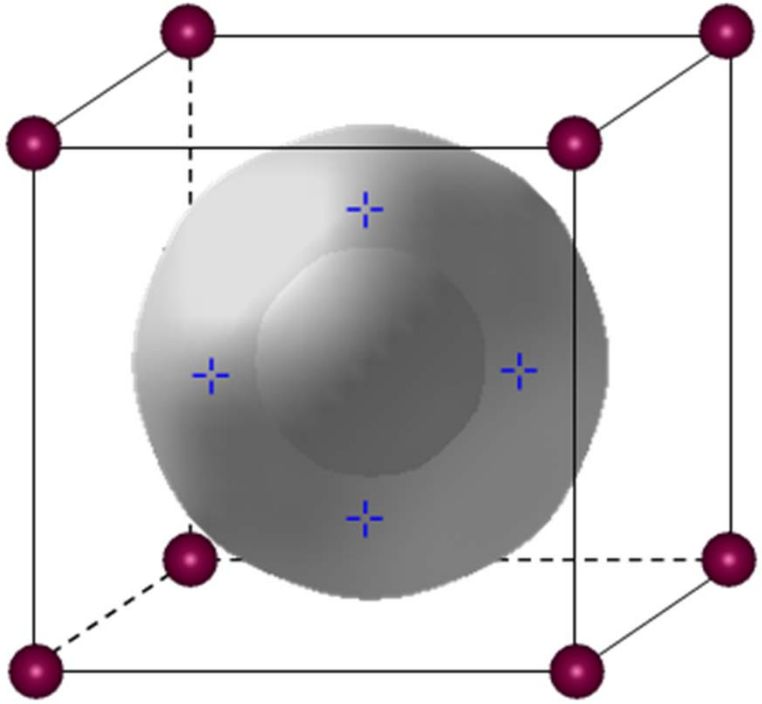
- Distortions of lattice induced by He
- Optimal charge density 0.27 →0.21 electron/ Å$^3$

**H-He binding energy in intrinsic W: 0.23 eV**

# Optimal charge density for H in W with He

**vacancy**

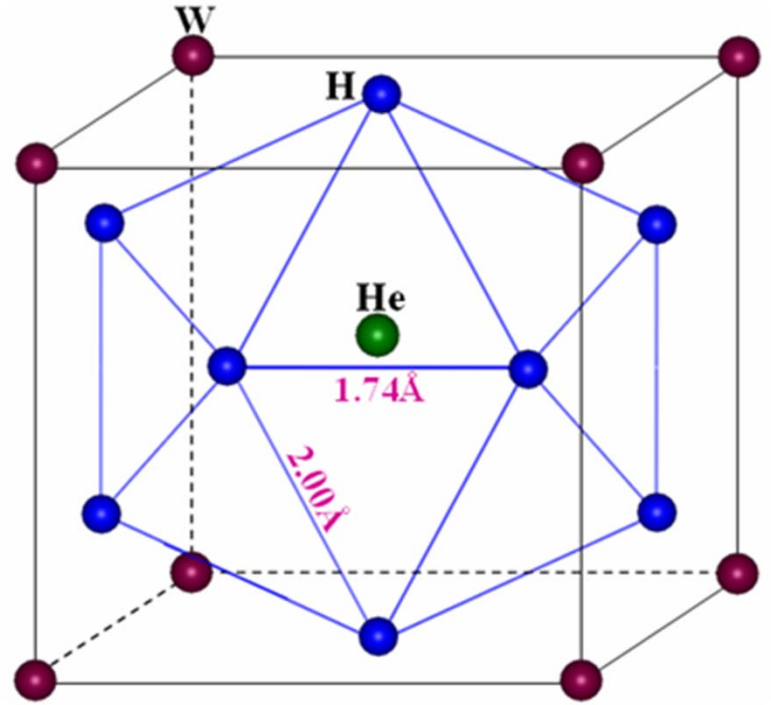
- H prefers to be embedded into a sphere-like region with the same charge density of 0.16 electron/Å$^3$.
- Vacancy without He: 0.11 electron/Å$^3$.



Optimal charge for single H embedded at a vacancy.

He-vacancy complex can be treated as a possible trapping center of H.

# Atomic configuration of H in vacancy with He




**No $H_2$ molecule formation**

H-B Zhou, G.N. Luo, G-H Lu, **Nuclear Fusion** (2010).

W.-T. Geng, **PRB** (2010)

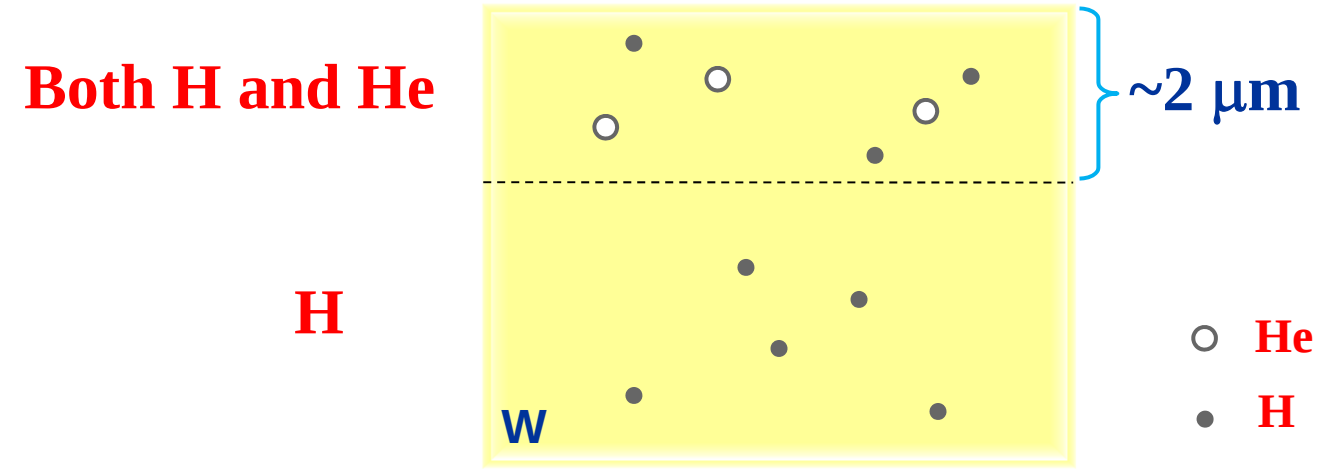
- The distance between H and its 1NN (H) is ~1.74 Å, and that between H and its 2NN (H) is ~2.00 Å.
- The icosahedron consists of 12 isoceles and 8 equilateral triangles.

- **How to suppress H blistering in W**

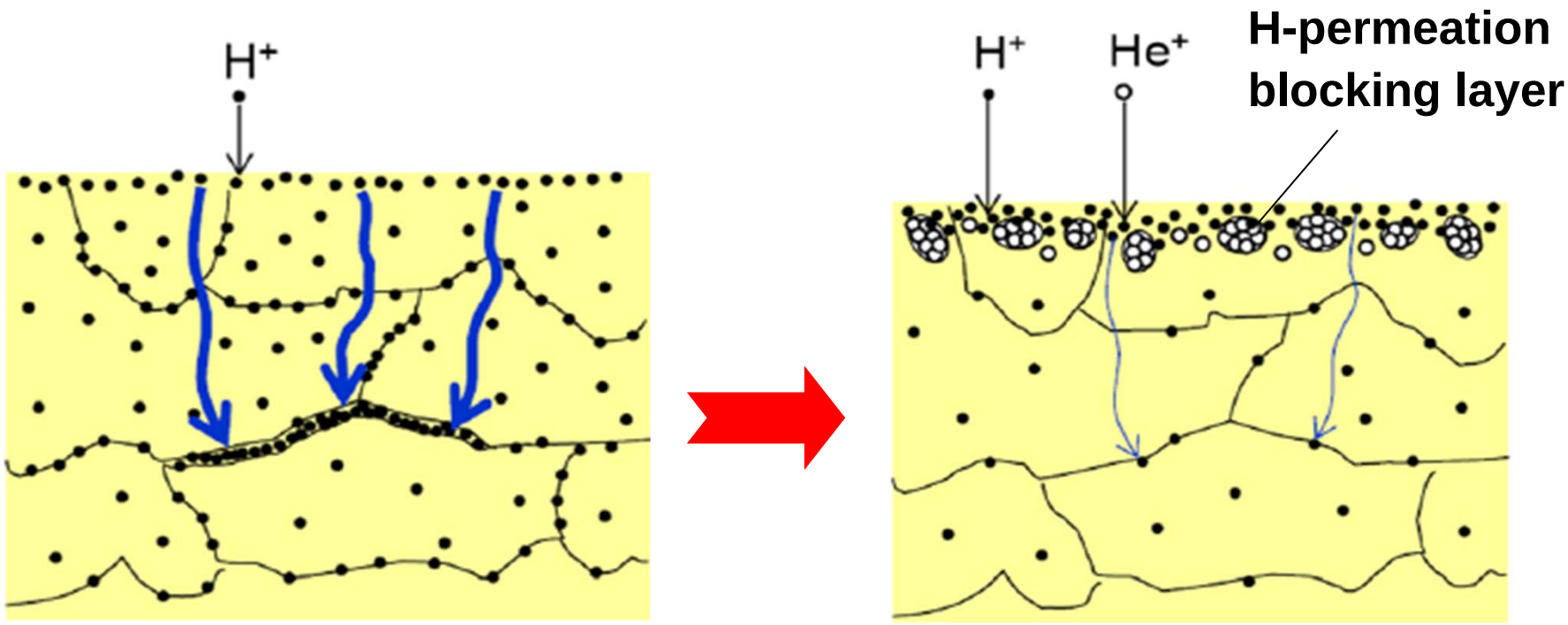
**What is the role of He on the H blistering in W?**

# The trapping depth of H and He in W

- The depth for the trapped H can be divided into three zones:
  - Near-surface layer (up to a depth of ~0.2 μm)
  - Sub-surface layer (from ~0.5 to ~2 μm)
  - Deep layer (>5 μm).
- For He, it forms bubble at the near surface at a range of 0~2 μm.

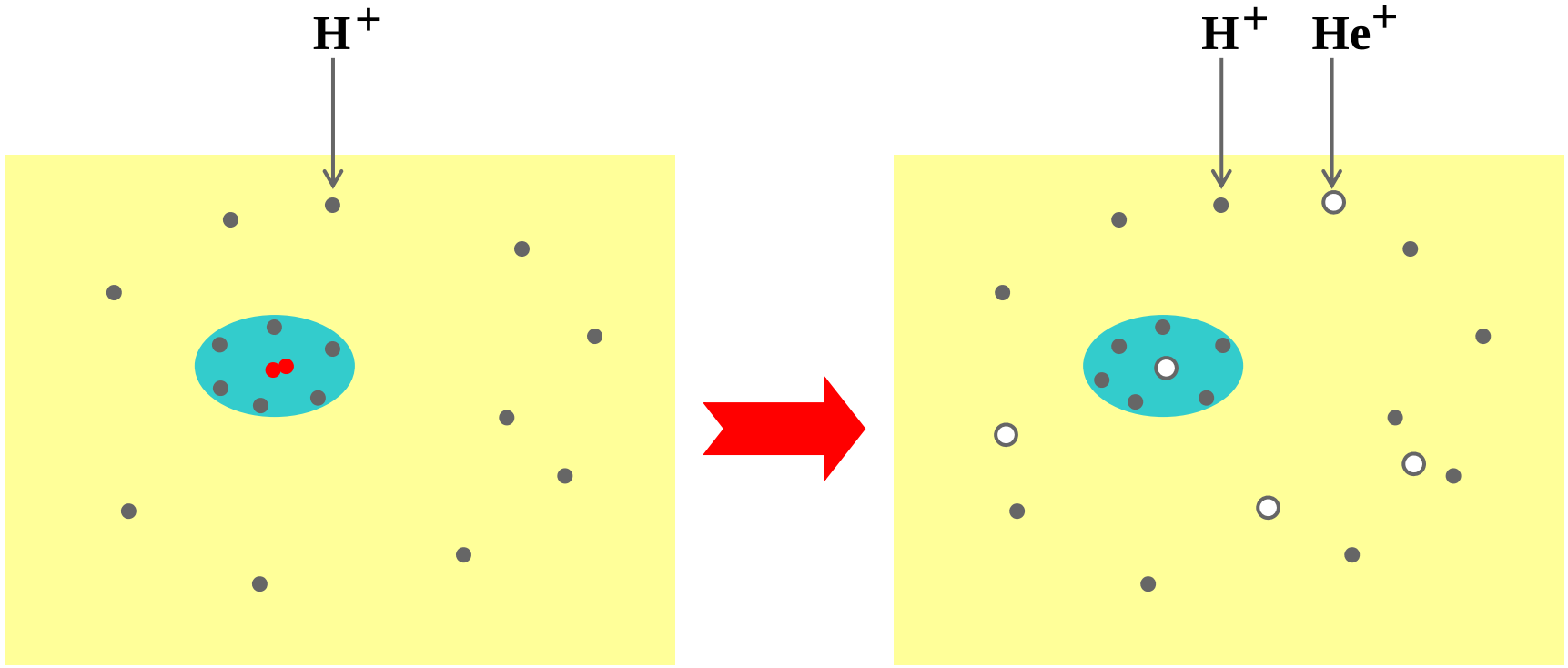


# *Role of He I:* block H permeation into deeper layers




There is a strong attraction between H and He in W originated from the charge density redistribution due to the presence of He, driving H segregating towards He. This can block the permeation of H into deeper bulk and thus suppresses the H blistering.

# *Role of He II:* block $H_2$ molecule formation



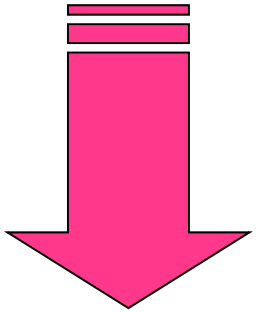

Hellium causes **a redistribution of charge density** inside the vacancy to make it “not optimal” for the formation of $H_2$ molecule, which can be treated as a preliminary nucleation of the H bubbles.

# Helium effect: experimental

| | |
|---|---|
| D retention can be reduced by as large as ~50% due to the He presence depending on the irradiation conditions. | • Fus. Eng. Des. 39-40, 227 (1998). |
| After He pre-implantation on W materials, the subsequent H has been observed to accumulate in the He saturated layer. | • J. Nucl. Mater. 307, 135 (2002).<br>• J. Nucl. Mater. 363, 898 (2007). |
| The presence of He increases D trapping at the near surface and limiting D diffusion into the W bulk. | • J. Nucl. Mater.360, 196 (2007).<br>• J. Nucl. Mater.386, 725 (2009). |

**Helium can suppress H blistering**

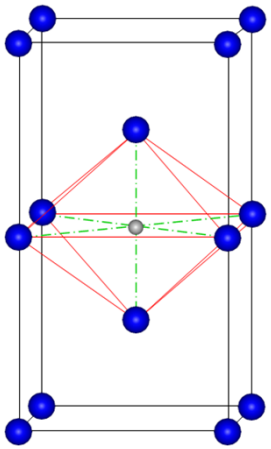
**He bubble: harmful !**



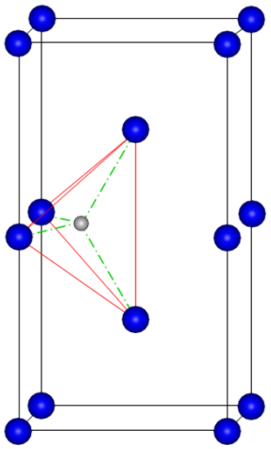
**Noble gas: Ne, Ar**

→ **Theoretical & Experimental Work**

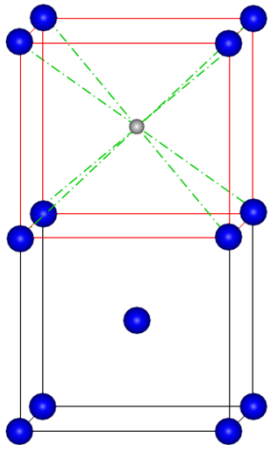
# Dissolution of noble gas in W



(OIS)



(TIS)



(SS)

**Solution energy (eV) of noble gas at octahedral interstitial site (OIS), tetrahedral interstitial site (TIS) and substitutional site (SS) in W.**

| | He | Ne | Ar | Kr |
|---|---|---|---|---|
| **OIS** | 6.44 | 11.6 | 15.3 | 17.0 |
| **TIS** | *6.13* | *11.0* | *14.3* | *16.2* |
| **SS** | 4.77 | 6.22 | 9.25 | 9.69 |

**Vacancy formation energy: 3.11 eV**

# Dissolved concentration of noble gas and H in W

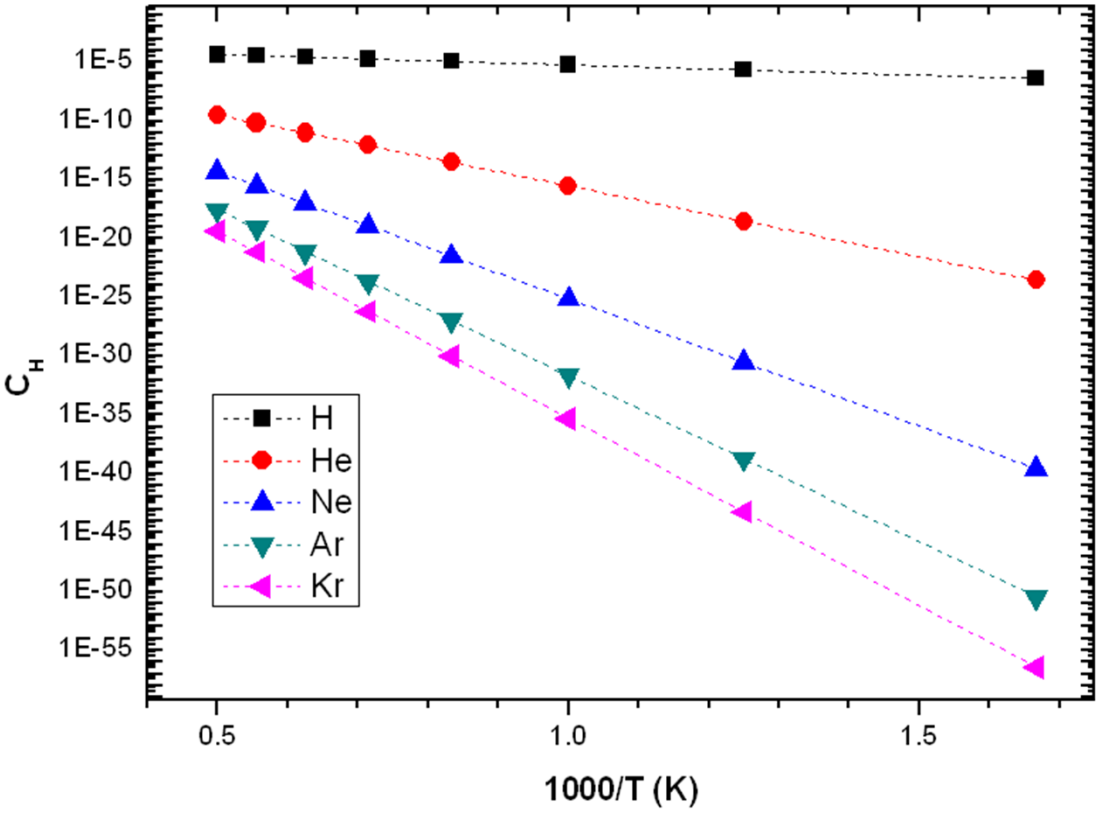
**Sieverts' law**

$$C_N = \sqrt{P/P_0}\exp[(\Delta ST + E_N^S)/KT]$$

$\Delta S$ -Solution entropy

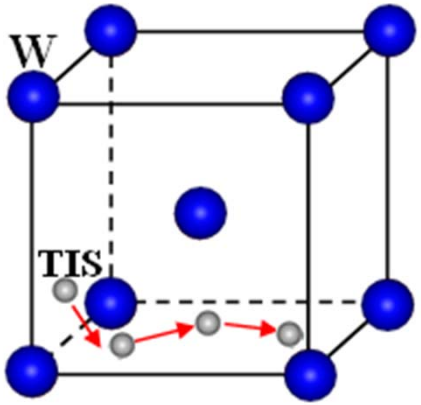
$E_N^S$ -Solution energy

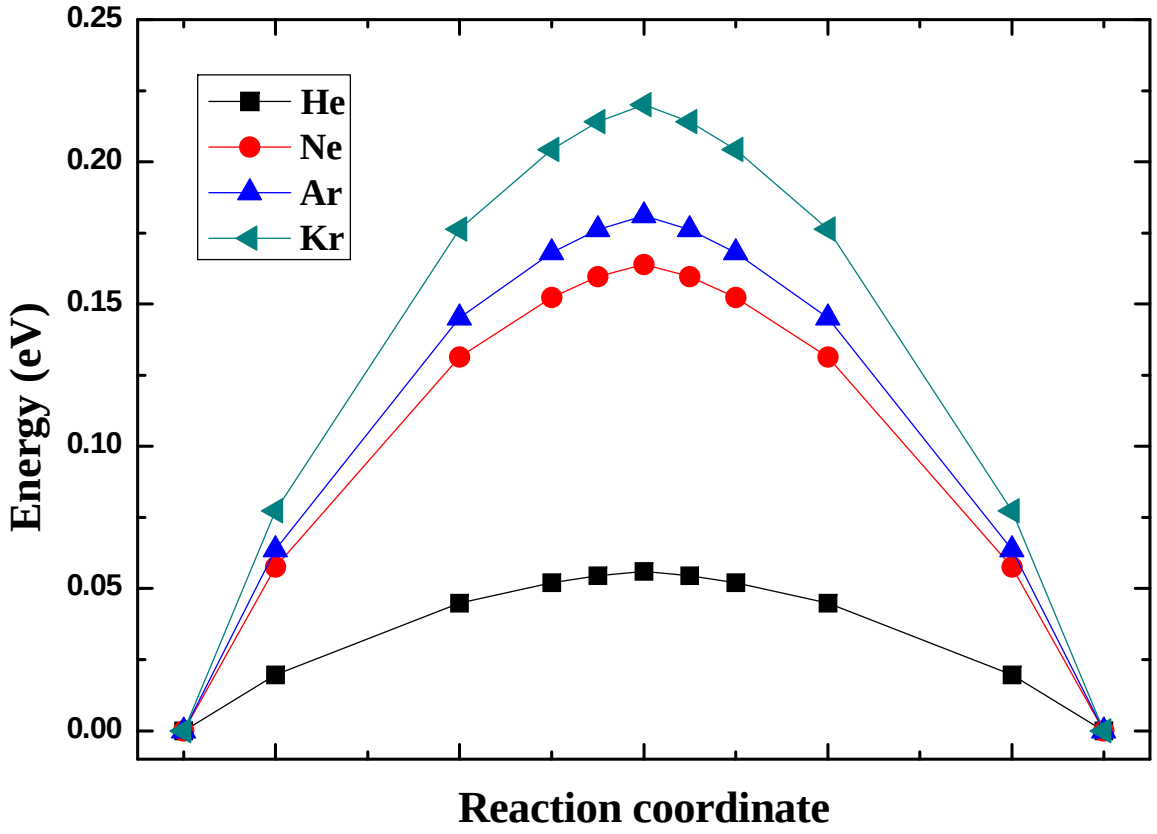
$K$ -Boltzmann constant




**The dissolved concentration of noble gas as a function of reciprocal temperature in comparison with that of H in W.**

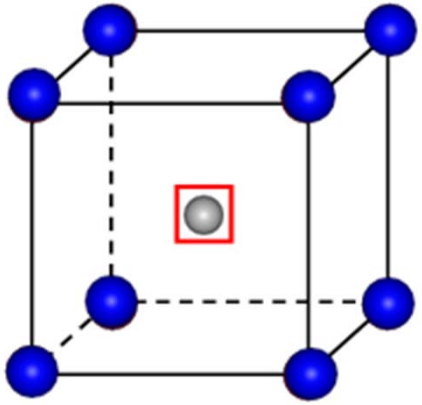
# Diffusion energy barrier of noble gas in W

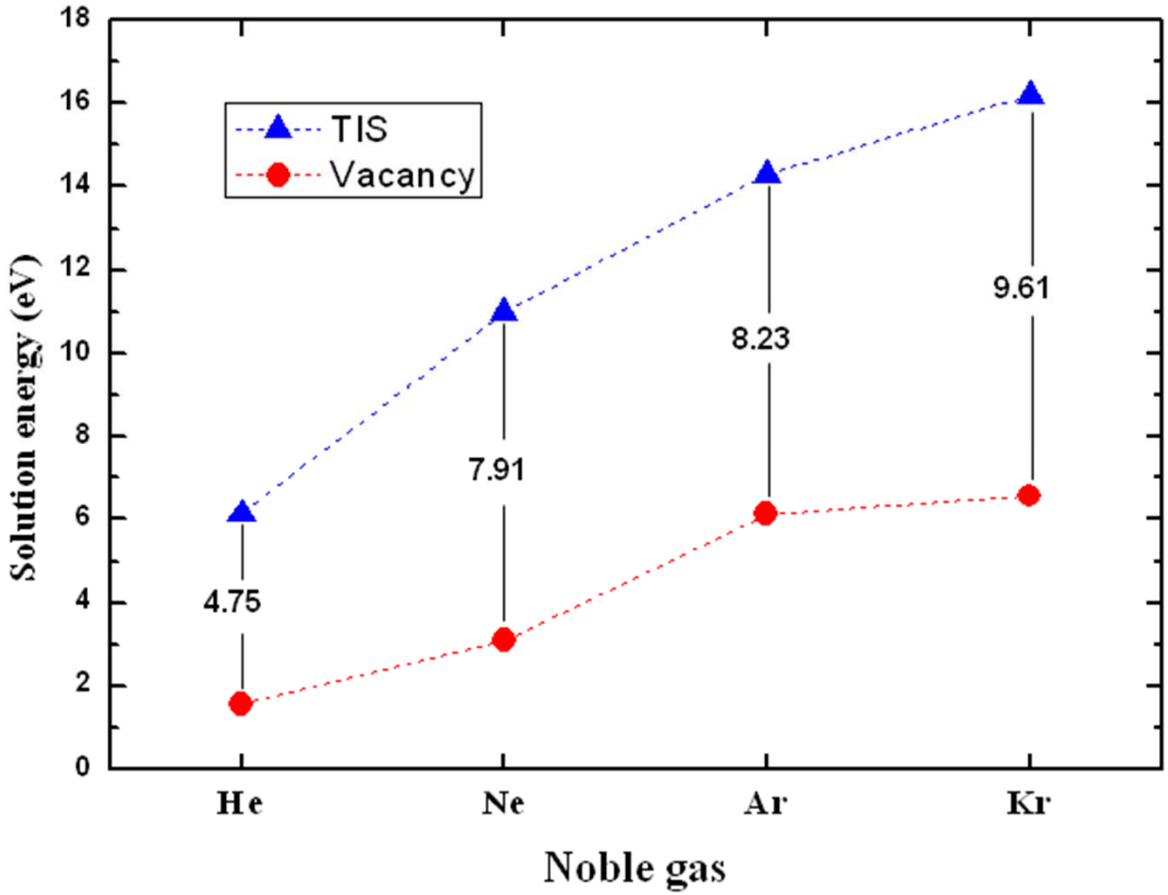



- The nudged elastic band (NEB) method.
- Diffusion energy barrier (eV), He-0.056; Ne-0.164; Ar-0.181; Kr-0.22.

# Noble gas in a vacancy





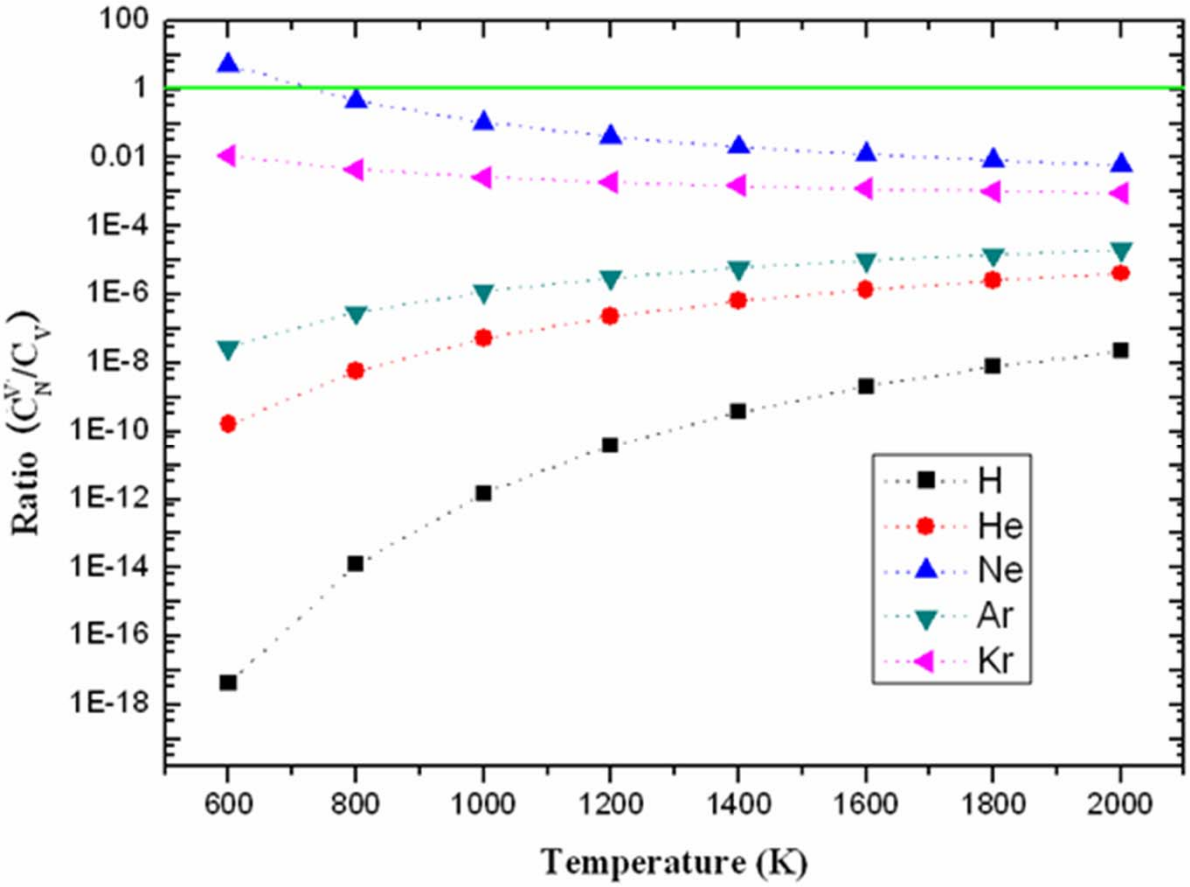

- **Compared with TIS, noble gas prefers to occupy the vacancy center with a larger segregation energy.**

# Concentration ratio between noble gas and vacancy

$$Ratio = C_N^V / C_V$$

$$C_N^V = C_N \exp^{(-E_{trap}/KT)}$$

$$C_V = \exp^{(-E_V^f/KT)}$$



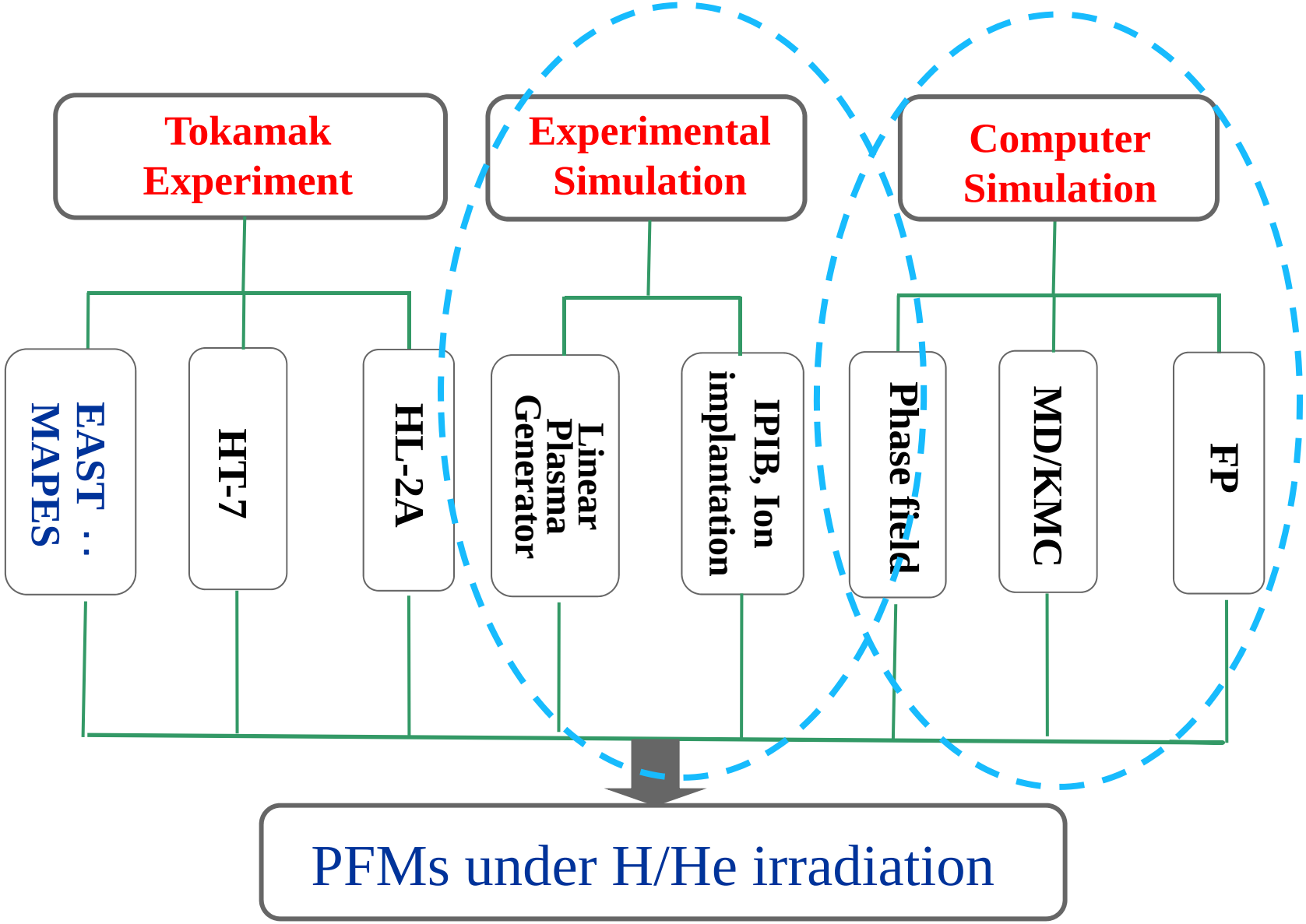

- **The ratio between noble gas concentration and vacancy concentration in W as a function of reciprocal temperature.**
- **Ne may be a good choice to reduce the vacancy concentration.**

# Summary

- **We propose a possible way to mitigate H (D/T) retention and suppress H blistering in W and W alloys.**

# PFMs study strategy & perspective

# Strategy to study PFMs



# Perspective: H Retention & blistering behavior

- Computer simulation: FP→ MD/KMC → Phase field

- Experimental simulation:

  **LPG-STEP (Prof. Kaigui Zhu)**

  **IPIB (Prof. Xiaoyun Le)**

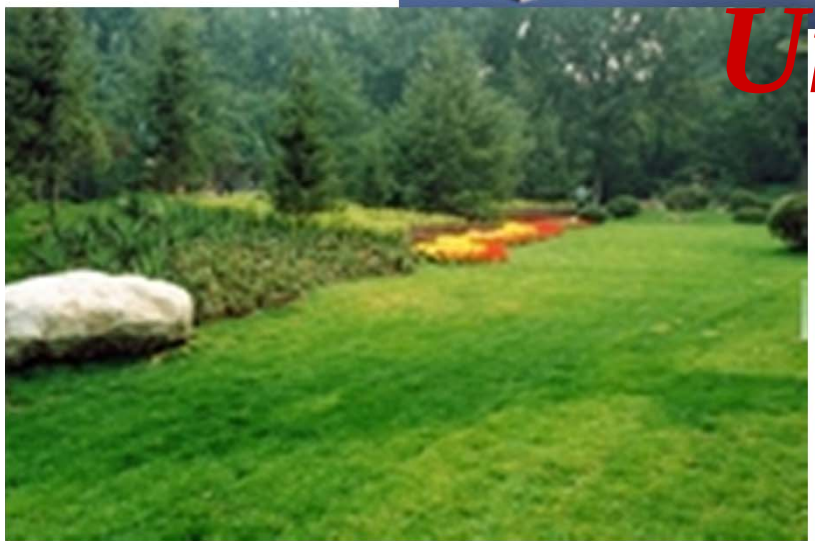
  **Ion implantation: H/He/Ar/Ne…**

- Tokamak experiments

  **EAST-MAPES**

**Collaboration:** **IPP/FZJ: PSI-II, GLADIS**

***Thanks for your attention and Welcome to visit Beihang University !***

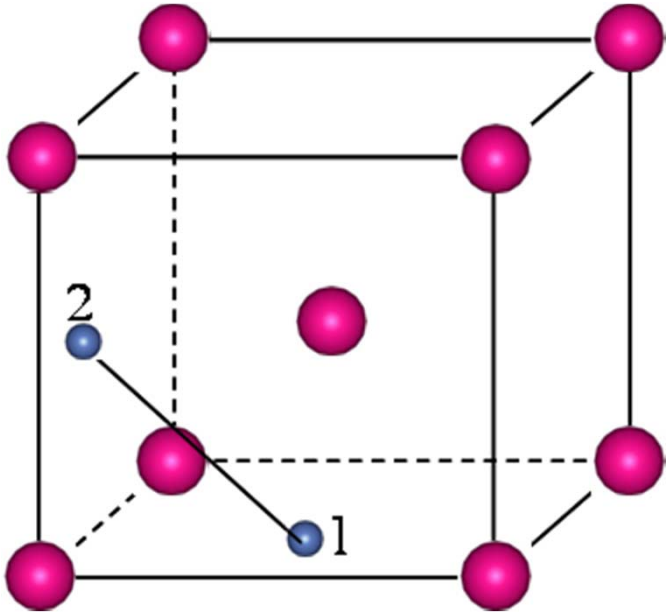


# H-H interaction in the intrinsic W

- **Single H: TIS**

- **Optimal distance of H-H: 2.22 Å**

  Double H atoms tend to pair up at two neighboring tetrahedral sites along the <110> directions with the distance of 2.22 Å and the weak binding energy of 0.02eV.

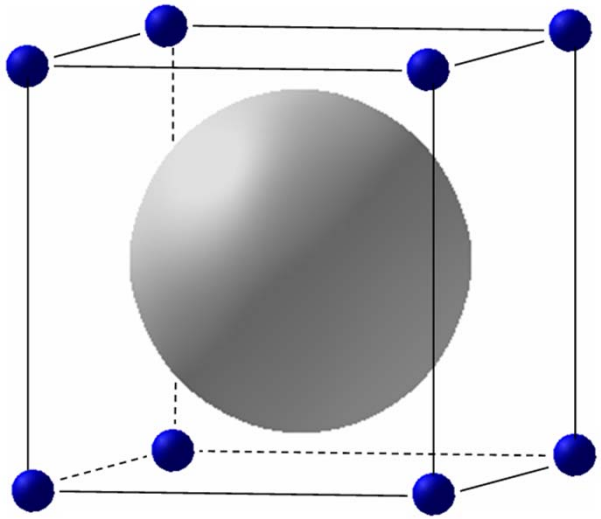



$H_2$ molecule: 0.75 Å

**$H_2$ molecule cannot be formed in the intrinsic W**

# Vacancy vs. H trapping

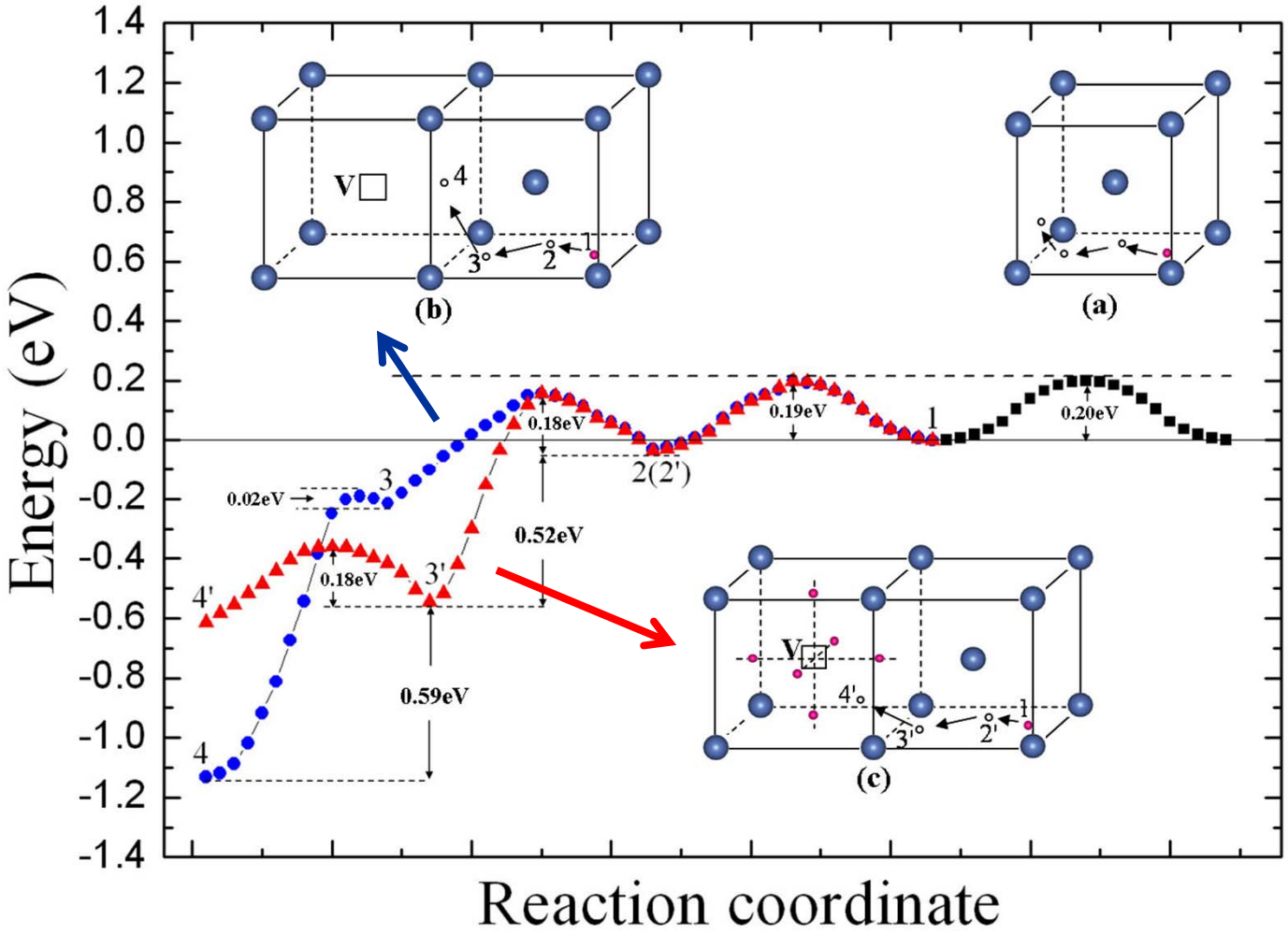
- H prefers to be embedded into a sphere-like region with the same charge density of 0.11 electron/Å$^3$.



Optimal charge density for single H embedded at a vacancy.

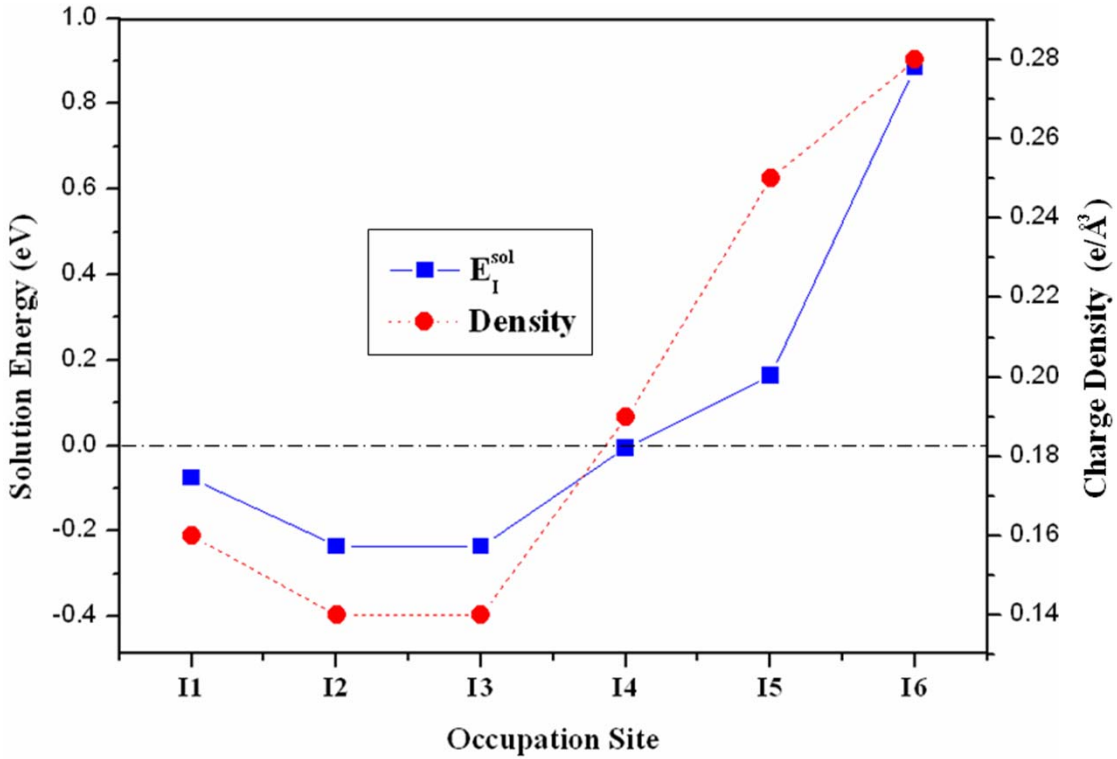
Optimal charge density for H at a vacancy in W

# H diffuses into vacancy from outside



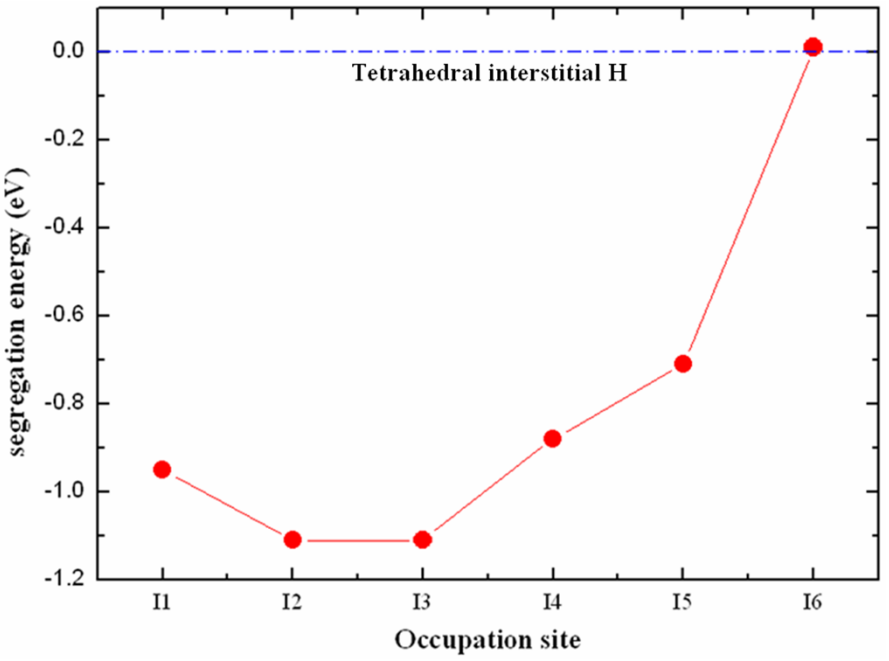

Diffusion energy profile and the corresponding diffusion paths for H in W when the vacancy is present.

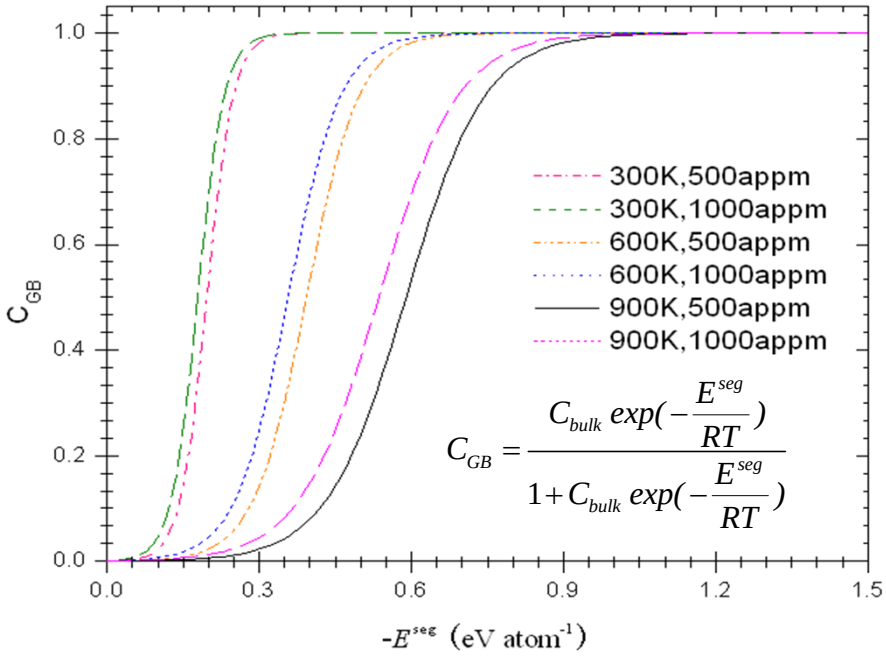
# Dissolution of single H atom in a W GB




- The order of the solution energy is *I2 (I3) < I1 < I4 < I5 < I6*, which is consistent with that of the charge density.
- The lowest solution energy of H is -0.23 eV.

# Segregation energy of H in a W GB

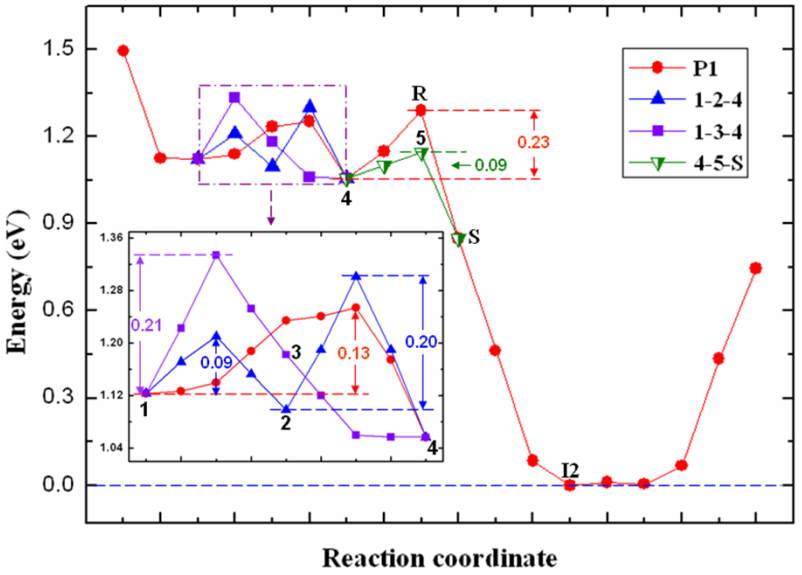


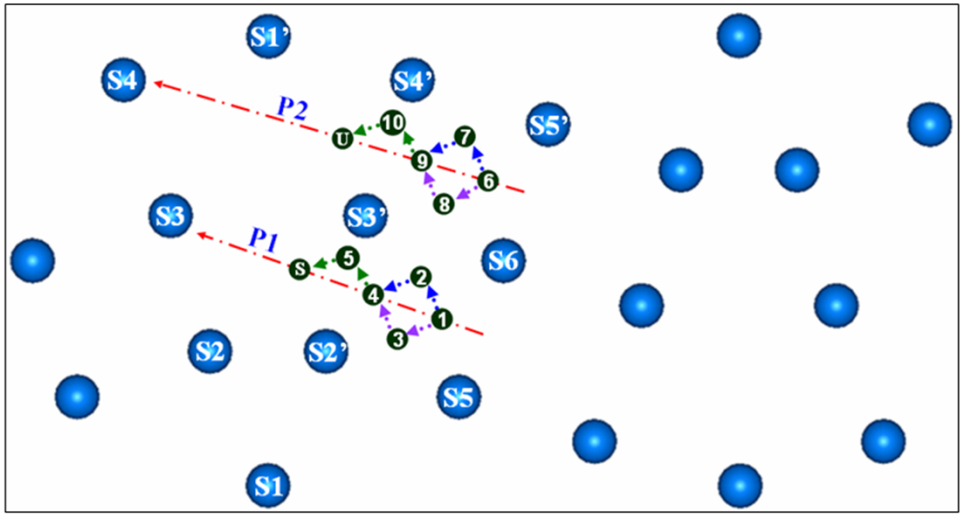



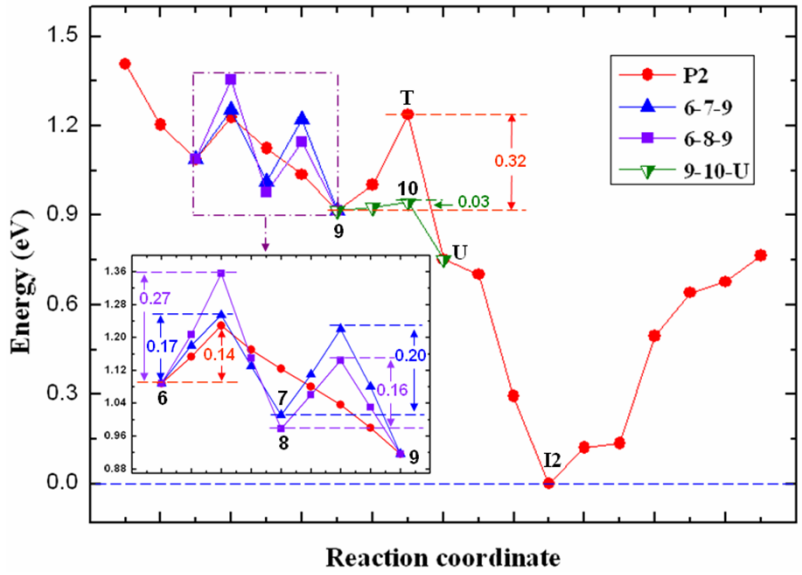

- The range of the segregation energies for the interstitial cases (*I1*-*I5*) is from -0.80 to -1.11 eV.

- 300~900 K and 500~1000 appm
- -1.0 eV, independent of the temperature and concentration

# Migration of H from bulk to GB

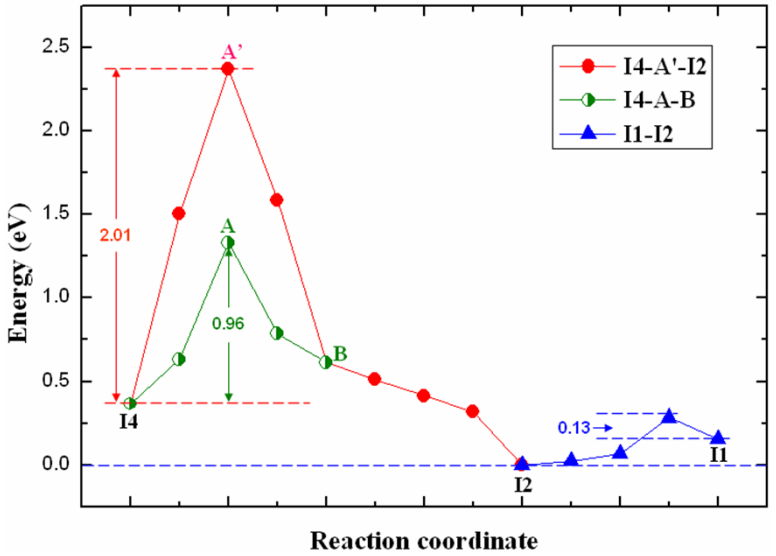


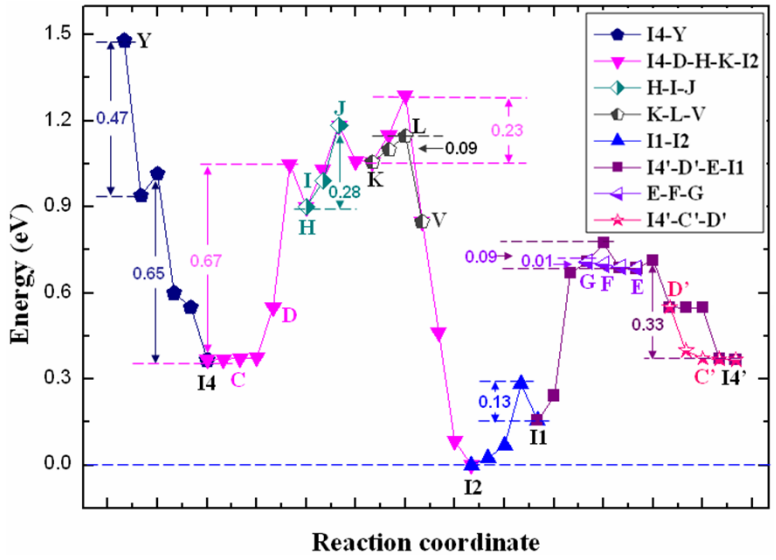



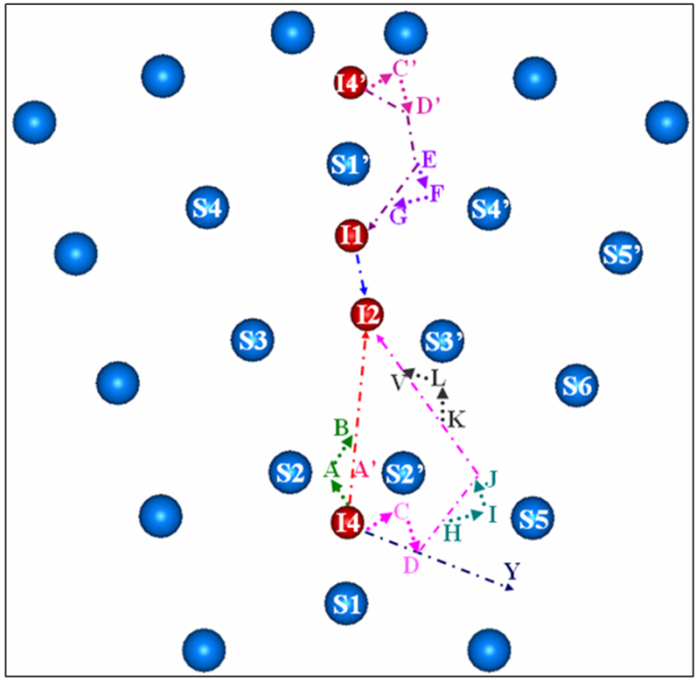




- Diffusion barrier: 0.13-0.16 eV
- A down-hill “drift” migration
- Aggregate around the vacant region at GB.

# Migration of H along GB

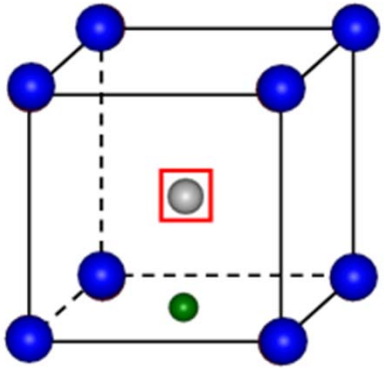


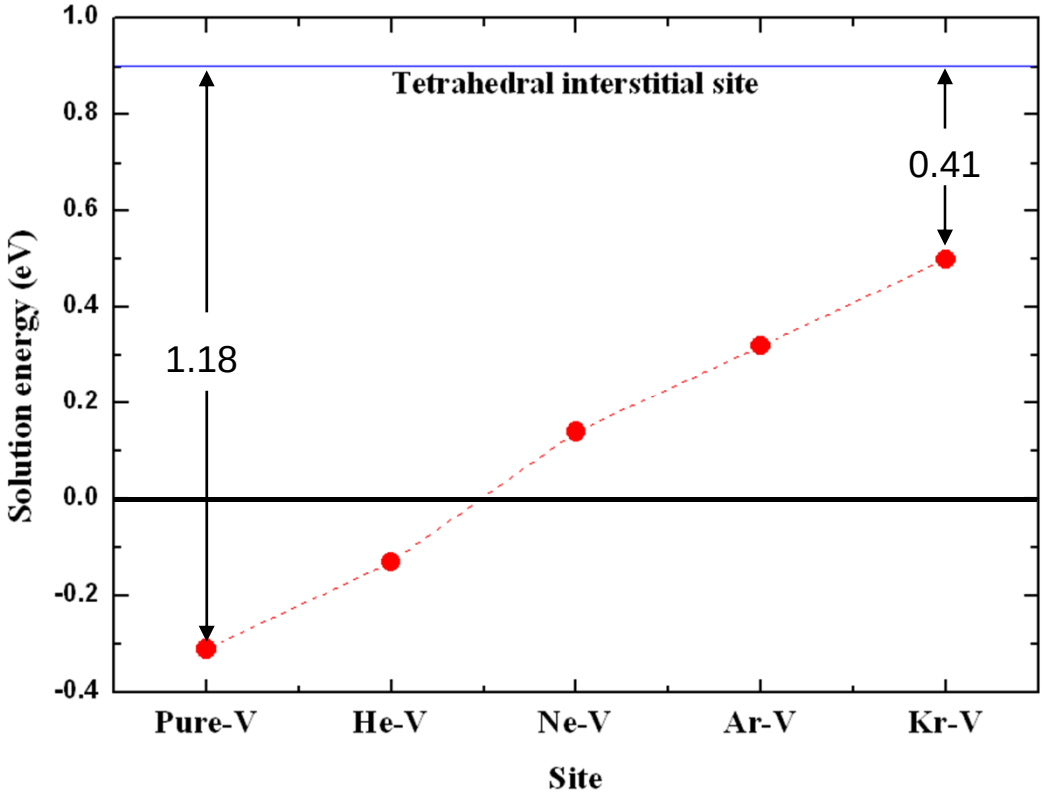




- Solution energy: I2 < I1 < I4
- Diffusion barrier: 0.13 eV and 0.33 eV
- Trapped H should be easy to aggregate in the GB.

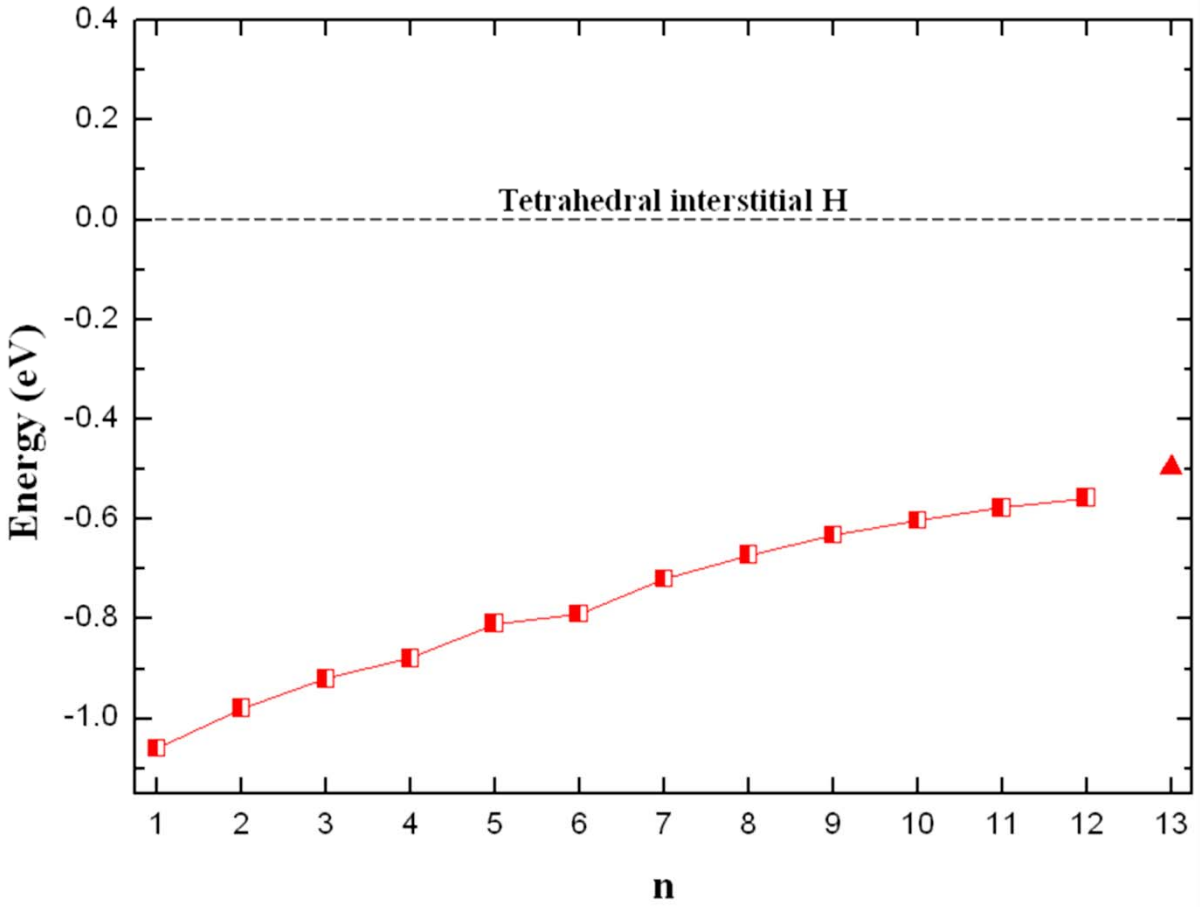
# Interaction between H and noble gas in a vacancy






- **With the radius of noble gas increasing, the solution energy of H at noble gas-vacancy will increase.**

# H trapping energy at a He-V complex




- H solution energy at a He-vacancy is lower than that at the tetrahedral interstitial site far away from the vacancy.
- He-vacancy traps up to 12 H (the 13th H stays outside vacancy).

# Blistering behavior

- Computer simulation: FP→ MD/KMS → Phase field

- Experimental simulation:

  **LPG-STEP (Prof. Kaigui Zhu)**

  **IPIB (Prof. Xiaoyun Le)**

  **Ion implantation: H/He/Ar/Ne…**

- Tokamak experiments

  **EAST-MAPES**

**Collaboration:**

**IPP/FZJ: LPG, IPIB, ASDEX-U**