First principles studies of intrinsic defects in hexagonal tungsten carbide

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Outline

- **Background and motivation**
- **Computational methods**
- **Results and discussions**
- **Summary**

Background:

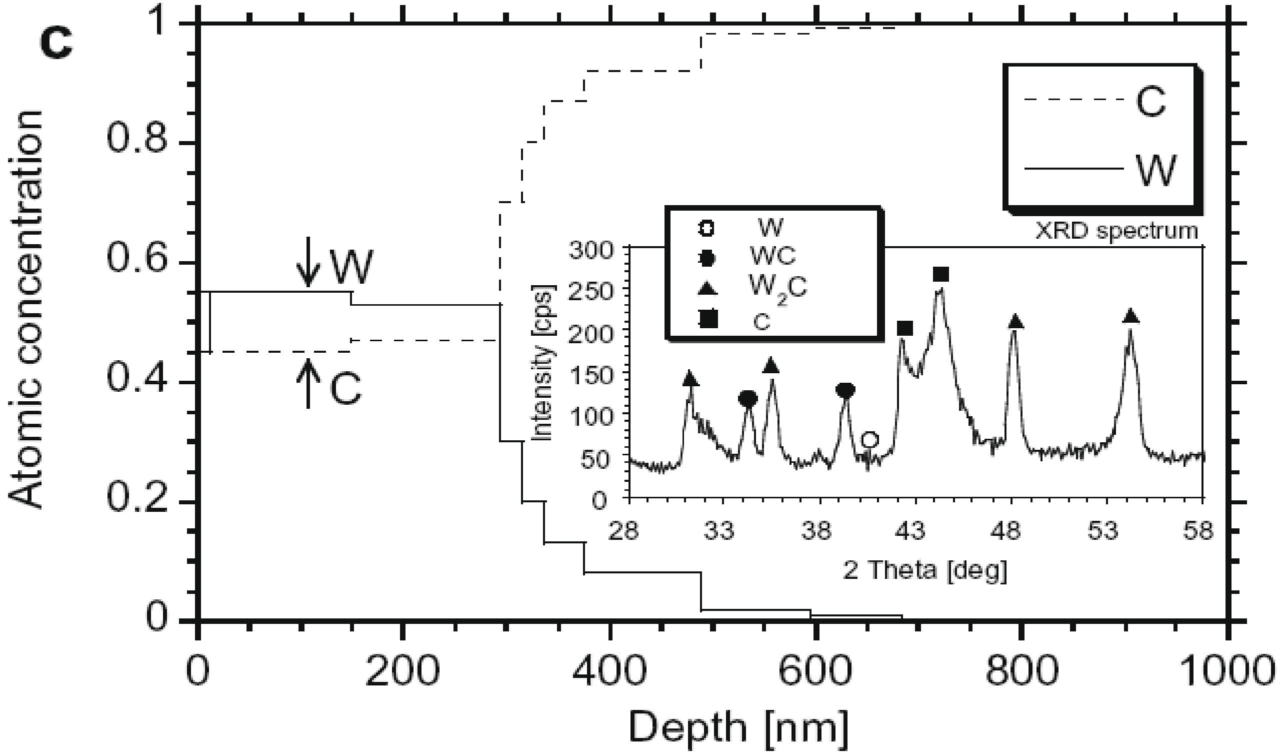
- In ITER, plasma facing materials of beryllium, carbon, and tungsten are planned to be used.
- The re-deposition of sputtered substances modifies the surface

WC is stable in a hexagonal structure, which consists of alternating simple hexagonal layers of carbon and layers of tungsten.

- For safety, periodic tritium removal is required before the in-vessel tritium inventory reaches its administrative limit, → tritium retention rate strongly affects ITER operation program in the D-T phase.
- **WC** may be used as coating materials of tungsten target of spallation neutron source.

Background: tungsten carbide

Tungsten carbide layer is formed on tungsten surface succeeding carbon impurity deposition.



Layer thickness and composition of W/C systems after annealing determined by Rutherford Backscattering Spectrometry (RBS). The XRD spectrum is shown together with RBS results. (produced by means of magnetron sputter deposition)

Sugiyama et al. J. Nucl. Mater. 390–391 (2009) 659–662

Background: intrinsic defects in WC

six types of intrinsic defects in WC:

- carbon (V_C) and tungsten (V_W) vacancy;
- carbon (C_W) and tungsten (W_C) antisite;
- carbon (I_C) and tungsten (I_W) interstitial.

The formation energy (eV) of intrinsic defects in WC calculated using different method.

	V_C	V_W	I_C	I_W	C_W	W_C
FPLMTO	1.77	2.72	–	–	–	–
MD	0.5	3	2.7	12	–	9.6

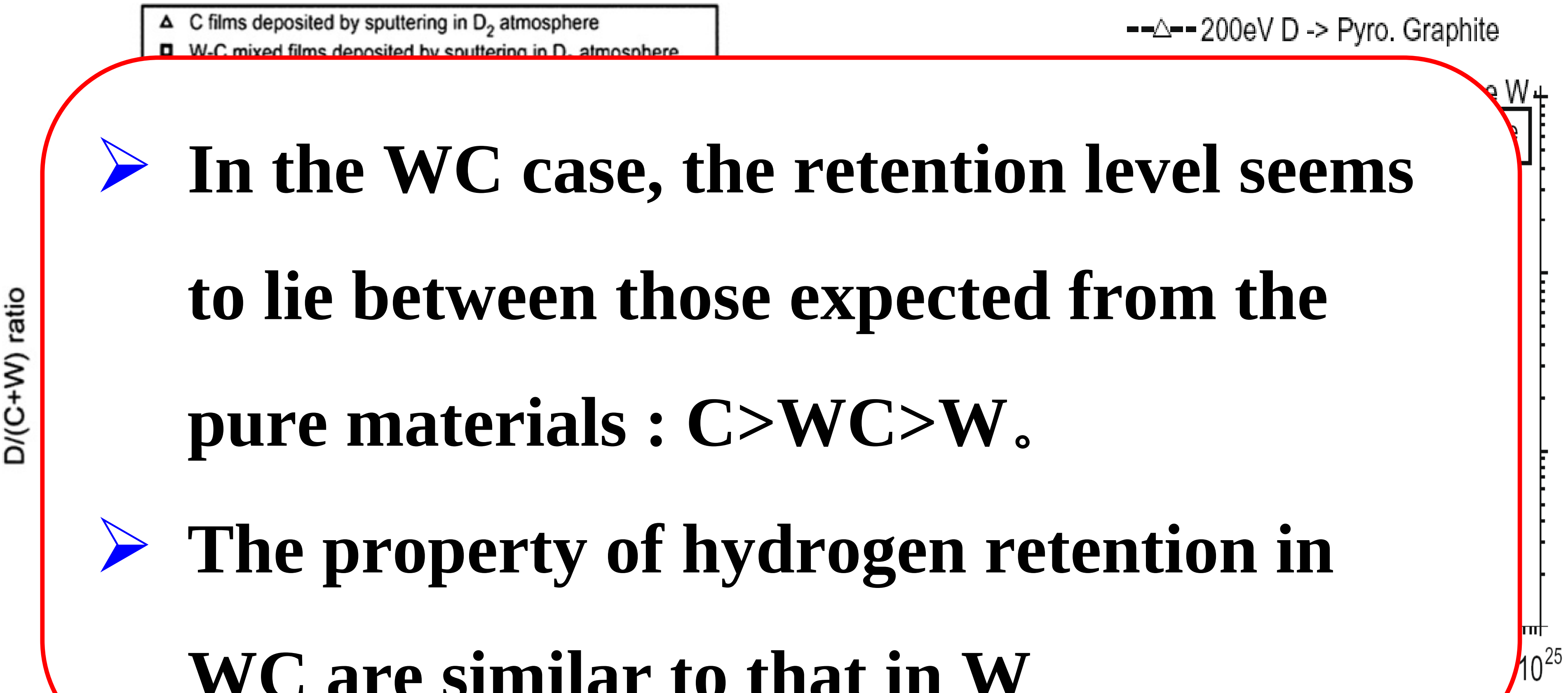
Big difference

FPLMTO: full-potential linear muffin-tin orbital approach

MD: molecular dynamic simulation

Medvedeva et al., PSS 43(2001)469; Juslin et al., JAP 98(2005)123520.

Background: hydrogen retention in WC



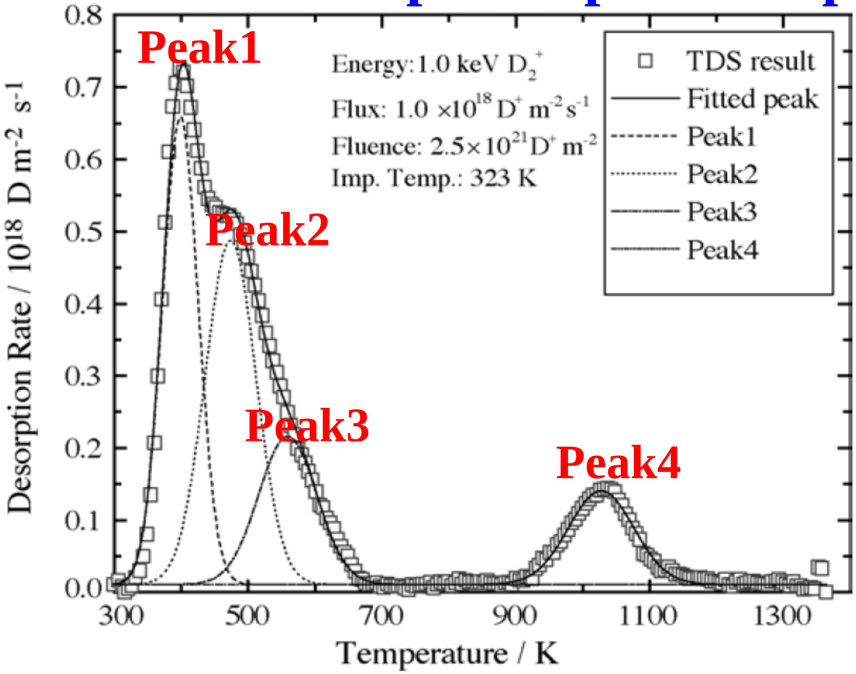
- **In the WC case, the retention level seems to lie between those expected from the pure materials : C>WC>W。**
- **The property of hydrogen retention in WC are similar to that in W**

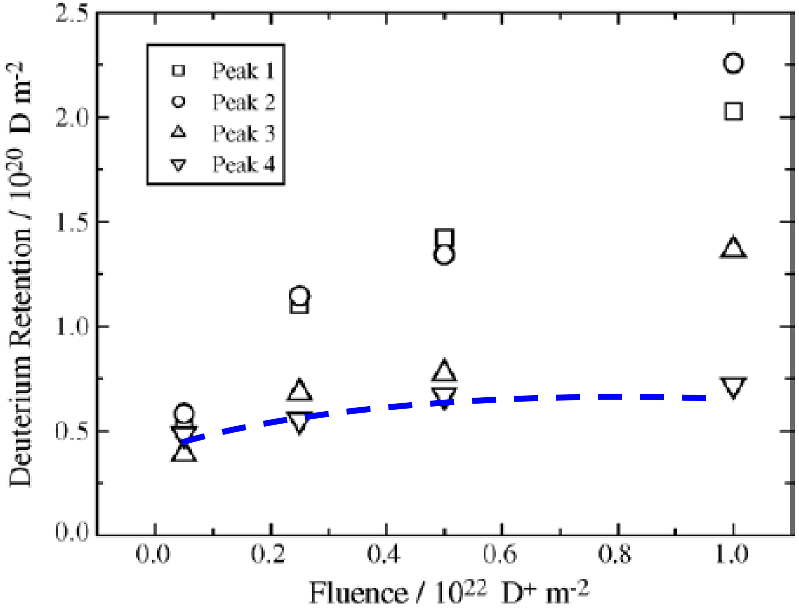
Comparison of **hydrogen isotope** retention between pure carbon and tungsten surfaces to the retention in mixed W/C material

Ogorodnikova et al. J. Nucl. Mater. 313–316 (2003) 469; Igarashi et al., 363–365 (2007) 32; Sugiyama et al., 390–391 (2009) 659

Background: the desorption of hydrogen

Thermal Desorption Spectroscopy of deuterium implanted into WC





Peak 1 and 2: two different interstitial sites
Peak 3: D trapped in C vacancy
Peak 4: D bound to C

The D contention bound to carbon is very low and saturated at the initial stage of D implantation

Horikawa et al., J. Nucl. Mater. 258-263 (1998) 1087; 266-269 (1999) 1091; Doerner et al., 363–365 (2007) 910; Kimura et al., Fusion Engineering and Design 81 (2006) 295–299

Background: motivation

- The structure and stability of intrinsic defects of WC
- The atomic-scale mechanisms of defect migration in WC
- The trapping site of hydrogen and the interaction of hydrogen with the carbon or tungsten vacancy in WC

Computational method

- DFT (density functional theory), VASP code
- The interaction between ions and electrons: PAW
- Exchange and correlation functions: PW91-GGA
- Energy cutoff: 500 eV
- Supercell: 54-atom supercell and 128-atom supercell
- K-points: 5×5×5 and 3×3×3.

Results: the ground-state properties of WC

The bulk properties and cohesiveenergy (E_c) of WC, MD and DFT mean the results obtained by molecular dynamic simulation and density functional theory, respectively.

	a_0(nm)	c_0/a_0	B_0(GPa)	E_c(eV)
Experiment	0.2907	0.976	329	-16.68
MD	0.2917	0.964	443	-16.68
DFT	0.2979	0.975	368	-15.01
Present work	0.2932	0.973	356	-16.42

Our results are in agreement with the experimental and former theoretical values

Results: vacancy and antisite defects

The formation energy of intrinsic defect:

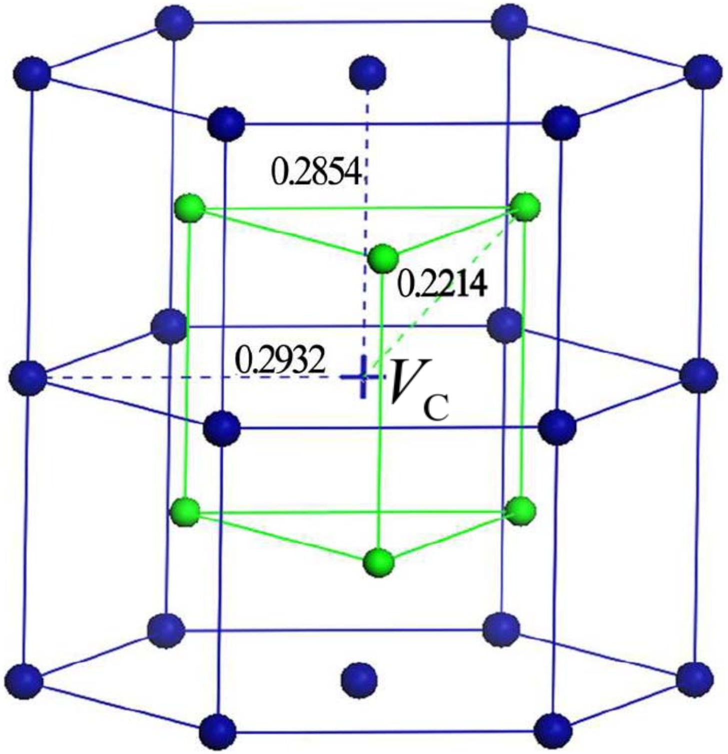
$$E_f = E - \frac{1}{2}(n_w + n_c)\mu_{wc} - \frac{1}{2}(n_w - n_c)(\mu_w - \mu_c)$$

Cohesive energy of supercell

Chemical potential of WC, W, C

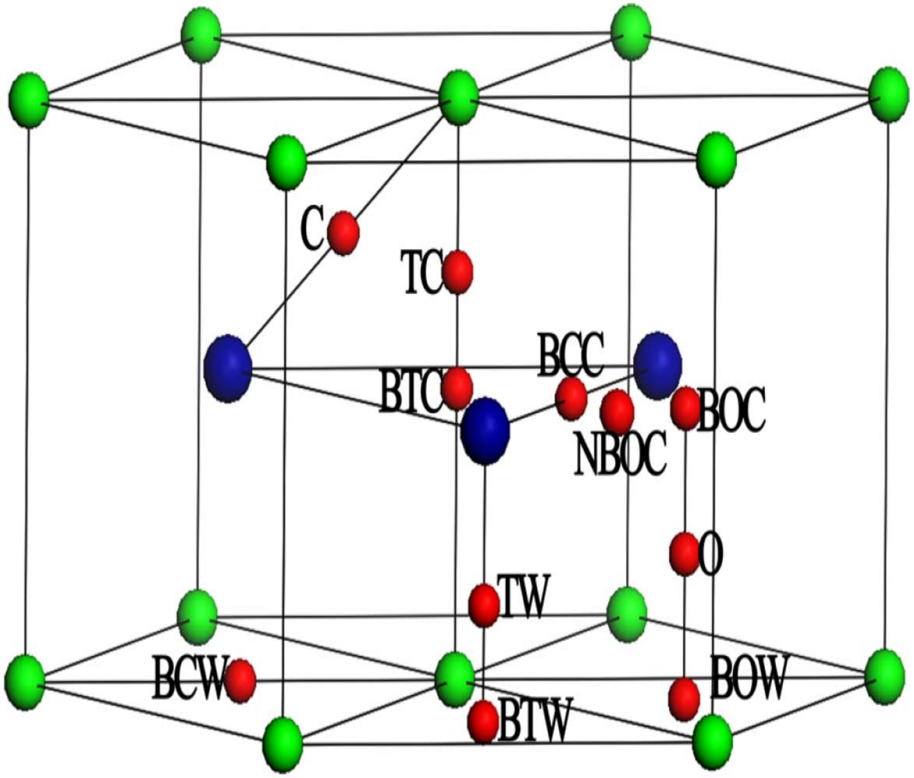
The formation energies (eV) of vacancies and antisites in WC

	V_C	V_W	C_W	W_C
FPLMTO	1.77	2.72	–	–
MD	0.5	3	–	9.6
DFT	0.39	4.14	8.81	8.69



C: blue
W: green

Results: interstitial defect



Interstitial sites: red ball

octahedral site: O

↓

carbon or tungsten basal plane projection of O site: BOC, BOW

two different tetrahedral site: TC, TW

↓

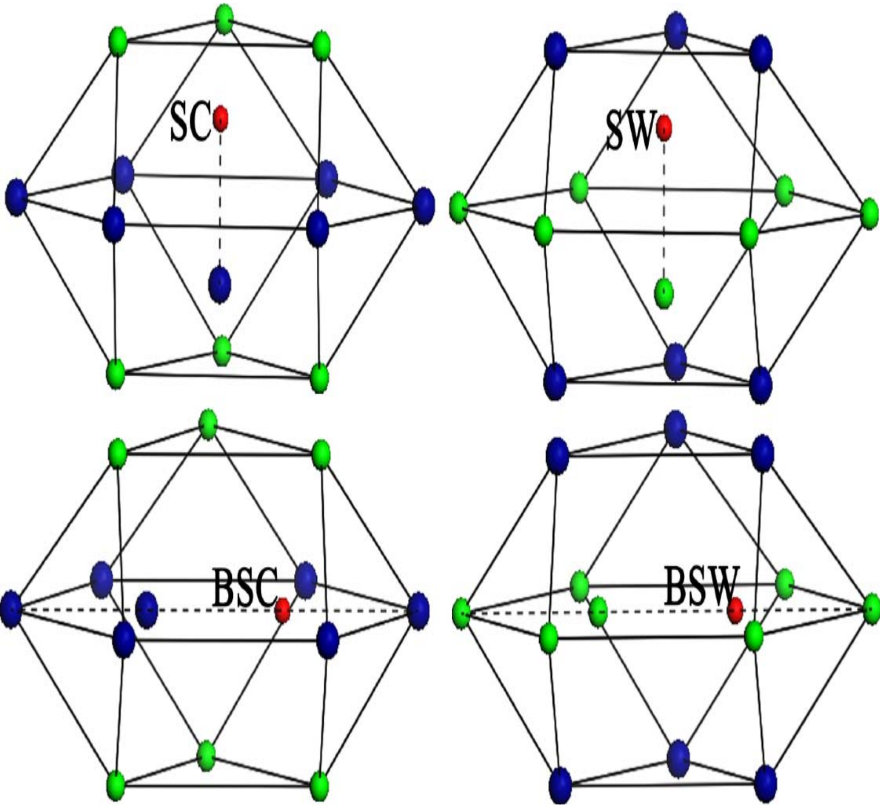
BTC, BTW

center of the nearest-neighbor tungsten and carbon: C

center of the nearest-neighbor carbon/tungsten in carbon/tungsten basal plane: BCC, BCW

Results: interstitial defect

Four possible carbon/tungsten split-interstitial configurations



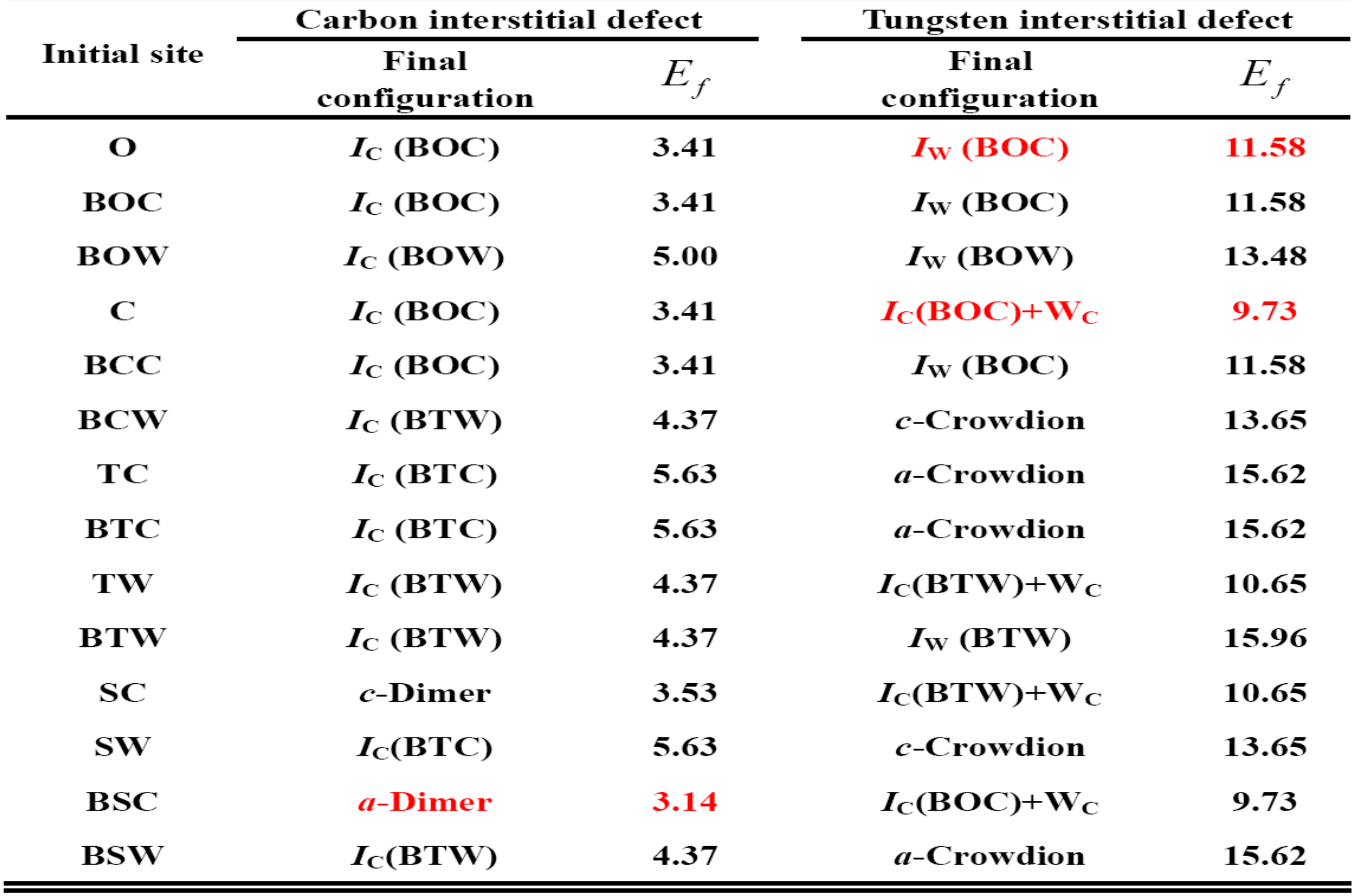
Two carbon/tungsten atoms are symmetrically split in the *c* direction: SC/SW

Two carbon/tungsten atoms are symmetrically split in the dense *a* direction about a carbon/tungsten vacant site : BSC, BSW

Interstitial site: red ball

Results: interstitial defect

The final configurations of interstitial defect in WC and corresponding formation energies (E_f), the stable configuration are highlighted in red



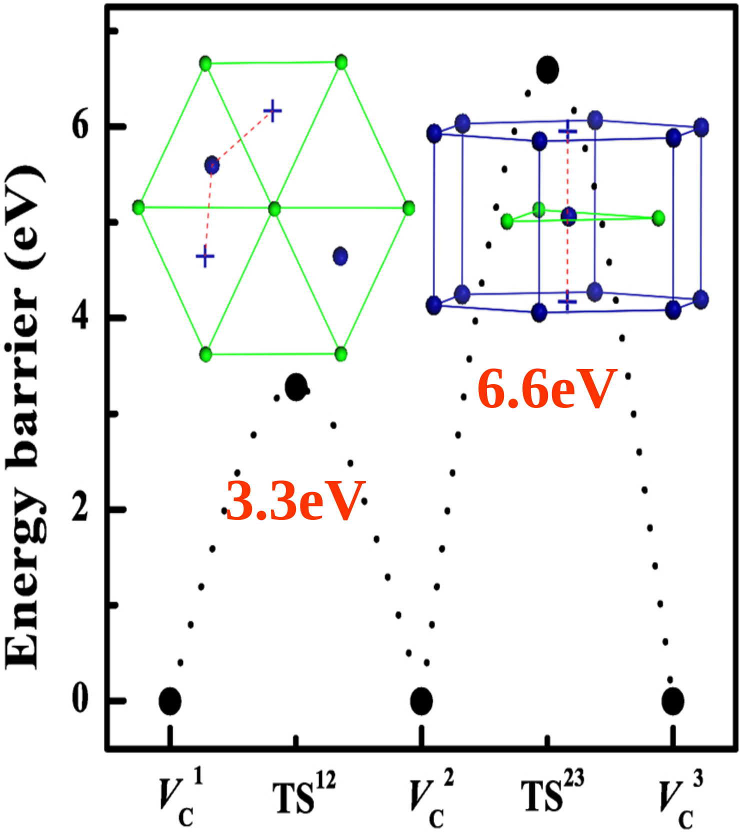
Initial site	Carbon interstitial defect		Tungsten interstitial defect	
	Final configuration	E_f	Final configuration	E_f
O	I_{C} (BOC)	3.41	I_{W} (BOC)	11.58
BOC	I_{C} (BOC)	3.41	I_{W} (BOC)	11.58
BOW	I_{C} (BOW)	5.00	I_{W} (BOW)	13.48
C	I_{C} (BOC)	3.41	I_{C}(BOC)+$\mathrm{W_C}$	9.73
BCC	I_{C} (BOC)	3.41	I_{W} (BOC)	11.58
BCW	I_{C} (BTW)	4.37	*c*-Crowdion	13.65
TC	I_{C} (BTC)	5.63	*a*-Crowdion	15.62
BTC	I_{C} (BTC)	5.63	*a*-Crowdion	15.62
TW	I_{C} (BTW)	4.37	I_{C}(BTW)+$\mathrm{W_C}$	10.65
BTW	I_{C} (BTW)	4.37	I_{W} (BTW)	15.96
SC	*c*-Dimer	3.53	I_{C}(BTW)+$\mathrm{W_C}$	10.65
SW	I_{C}(BTC)	5.63	*c*-Crowdion	13.65
BSC	*a*-Dimer	3.14	I_{C}(BOC)+$\mathrm{W_C}$	9.73
BSW	I_{C}(BTW)	4.37	*a*-Crowdion	15.62

Results(1): a brief summary

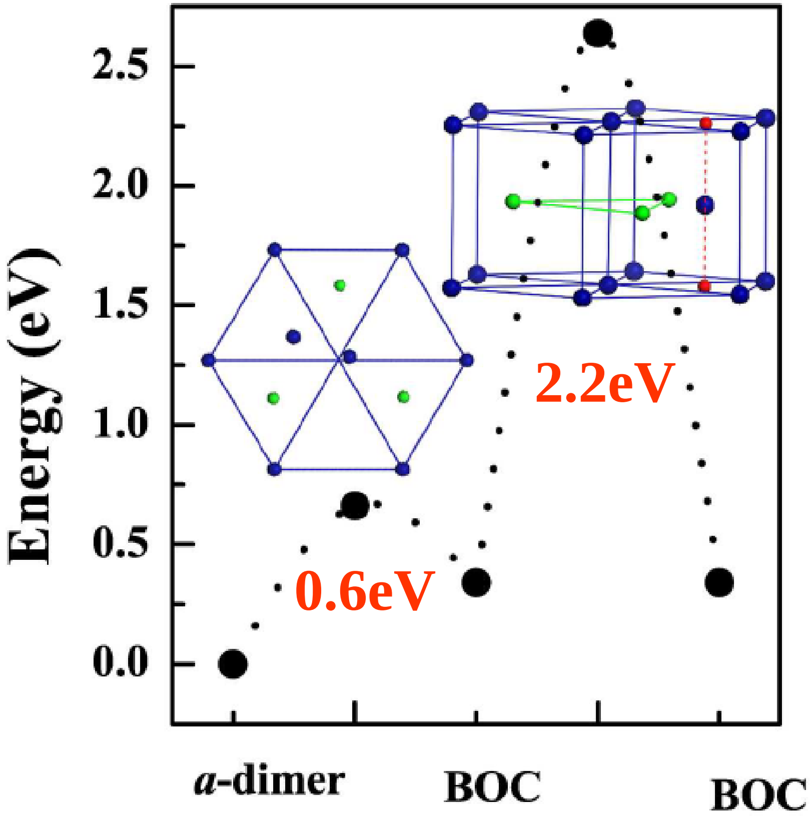
- The defect formation energy of carbon are much lower than that of tungsten.
- The carbon vacancy is the dominant defect in tungsten carbide.
- The concentration of tungsten vacancy is considerably low and the tungsten interstitial defects are energetically less favorable.
- The C-C dimer configuration along the dense *a* direction is the most stable configuration of carbon interstitial defect.

Results: the diffusion of carbon defect

The diffusion of carbon vacancy



The diffusion of carbon interstitial



- The energy barrier of carbon vacancy is greatly larger than that of carbon interstitial
- Both carbon vacancy and interstitial prefer to diffuse in the carbon basal plane

Results(2): a brief summary

- Formation energy: $E_f(V_C) < E_f(I_C)$;
- But diffusion energy barrier: $E_D(V_C) > E_D(I_C)$

- The carbon vacancy stay for a wide range of temperature because of extremely high diffusion barriers, while carbon interstitial migration is activated at lower temperatures for its considerably lower activation energy. Both of them prefer to diffuse in carbon basal plane.

Results: single H atom in WC

The defect formation energy: to identify the energy favorable trapping site of H in WC.

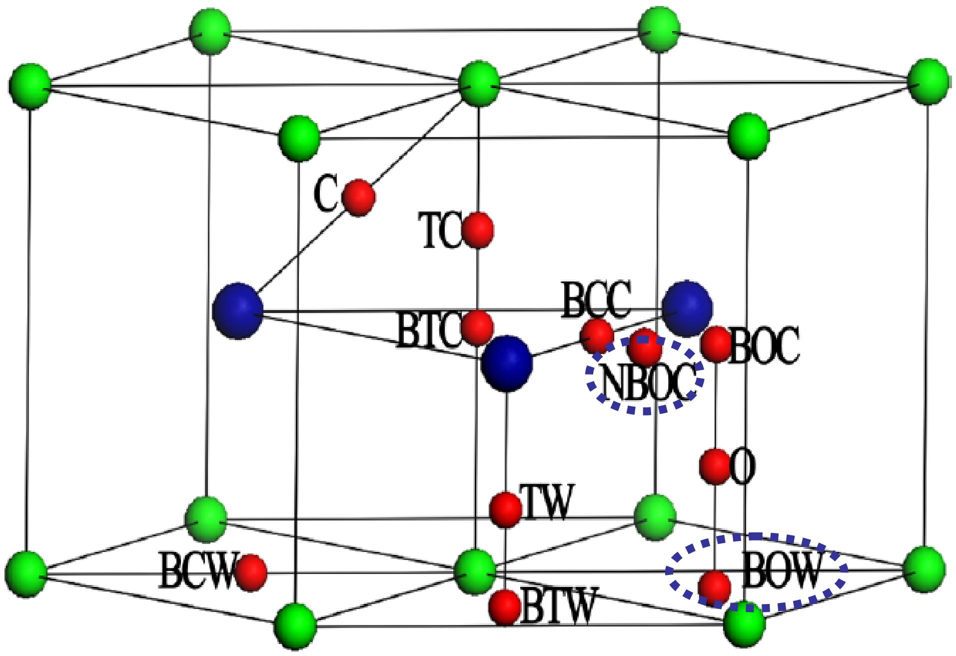
$$E_f = E_{tot}^{H} - E_{tot} - \mu_H$$

E_{tot}: the total enengy of defect-free system

E_{tot}^{H}: the total energy of system with single H atom

μ_H: the hydrogen chemical potential

Results: single H atom in WC



- ◆ Two relative stable interstitial sites for H in WC: BOW and NBOC, which are different from the experimental guess (BTW and BTC). **Igarashi et al., JNM 363–365 (2007) 32**

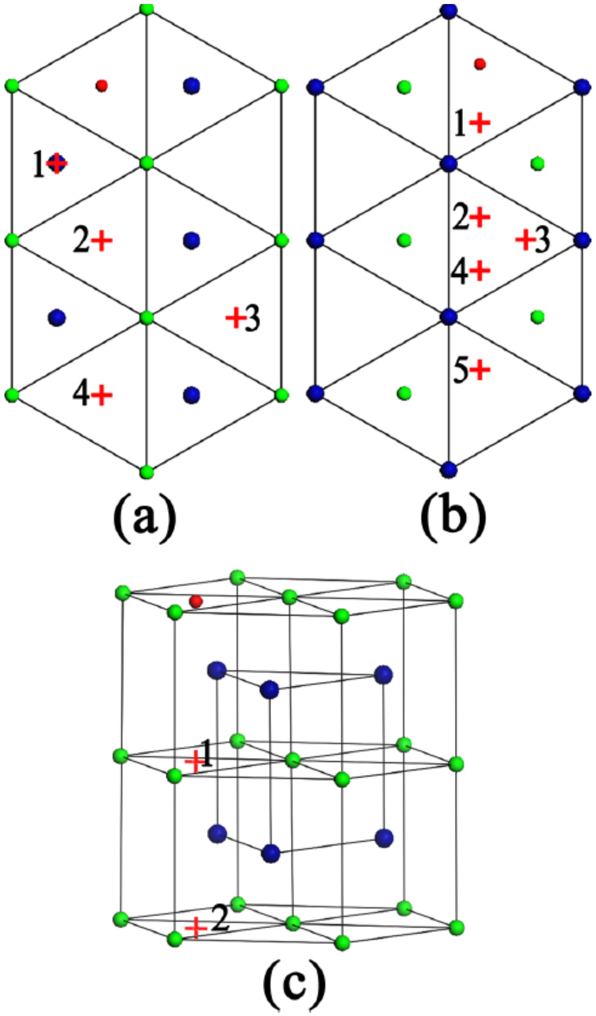
Results: Double interstitial H atoms in WC

The first H: red ball;
The second H: the red +
1~5, denote the different sites occupied by the second hydrogen atom.

(a)The first H is placed in the BOW site, and the second H is inserted at other interstitial site in the same tungsten basal plane;

(b)The first H sits in the NBOC site, and the second H occupies other interstitial site in the same carbon basal plane;

(c)Two interstitial H atoms along the *c* axis.



Results: Double interstitial H atoms in WC

The binding energy: to investigate the interaction of double interstitial H in WC and they form a hydrogen molecule?

negative bonding energy: repulsion between hydrogen atoms;

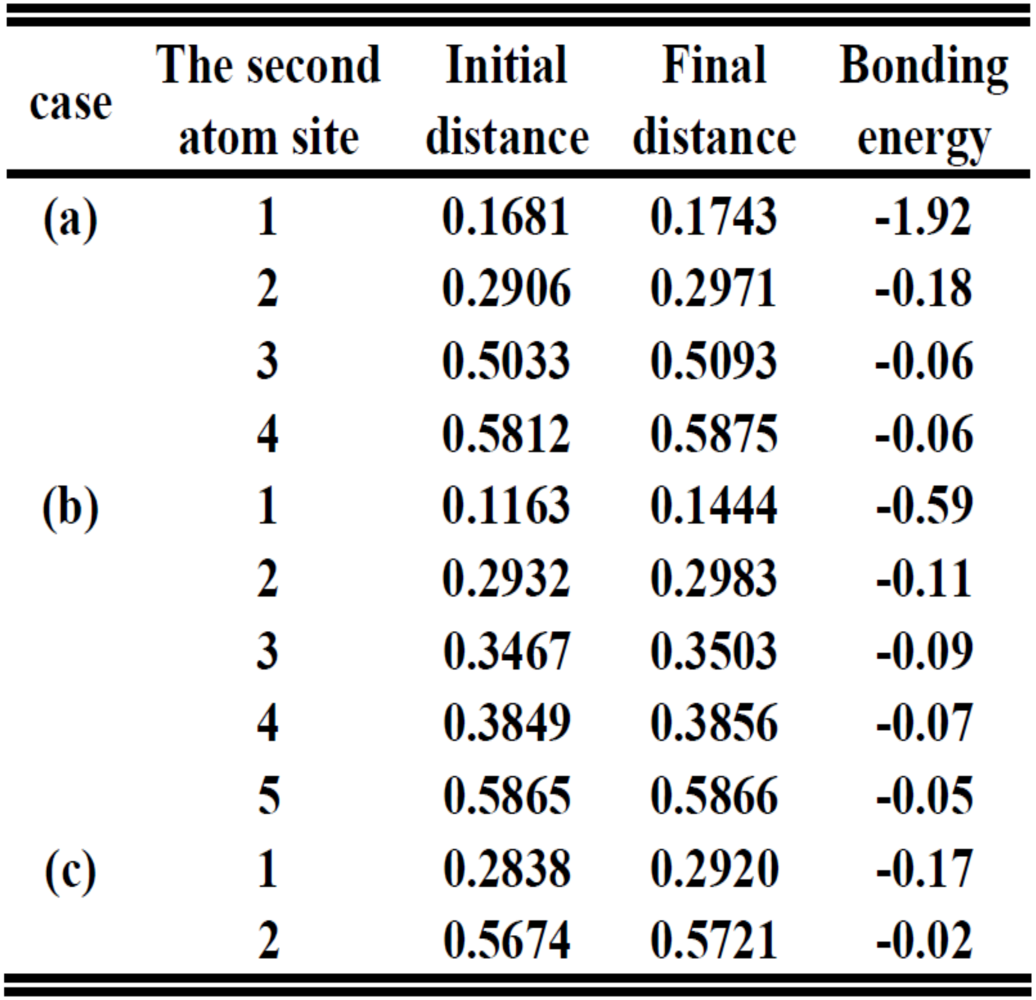
positive binding energy : attraction between hydrogen atoms.

$$E_b = 2E_{tot}^{H} - E_{tot}^{2H} - E_{tot}$$

E_{tot}^{2H}: the total energy of system with two H atoms

Results: Double interstitial H atoms in WC

The initial and final distance (before and after the relaxation, nm) between two hydrogen atoms and corresponding binding energy (eV) in three cases.



case	The second atom site	Initial distance	Final distance	Bonding energy
(a)	1	0.1681	0.1743	-1.92
	2	0.2906	0.2971	-0.18
	3	0.5033	0.5093	-0.06
	4	0.5812	0.5875	-0.06
(b)	1	0.1163	0.1444	-0.59
	2	0.2932	0.2983	-0.11
	3	0.3467	0.3503	-0.09
	4	0.3849	0.3856	-0.07
	5	0.5865	0.5866	-0.05
(c)	1	0.2838	0.2920	-0.17
	2	0.5674	0.5721	-0.02

- the distance between two hydrogen atoms increases
- the binding energy are negative

Results: Double interstitial H atoms in WC

There exists a repulsive interaction when two interstitial H atoms are close to each other.

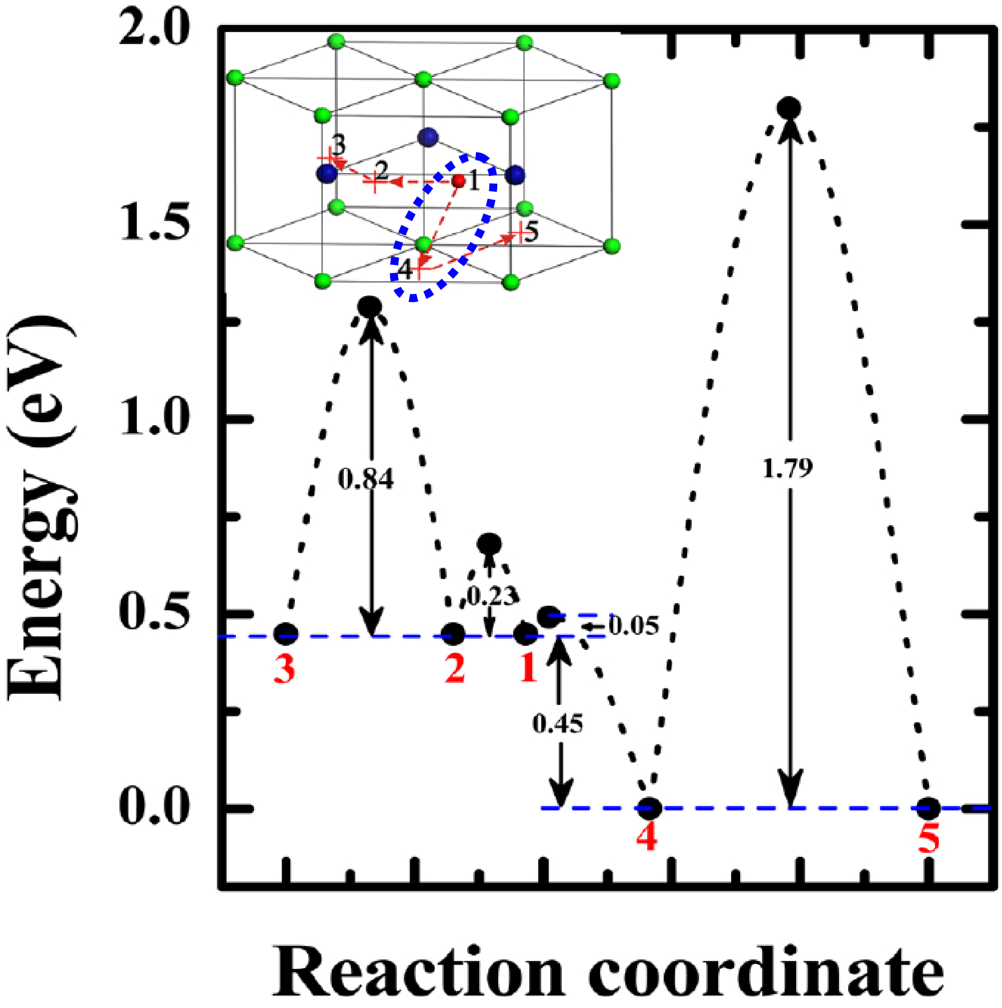
So they do not form H2

Results: the diffusion of interstitial H

Diffusion energy profile and the corresponding diffusion paths for interstitial hydrogen atom in WC.

- Site 1, 2 and 3: NBOC site
- Sites 4 and 5: BOW site

The interstitial H atom prefers to jump form NBOC to BOW along the *c* axis in WC



Results(3): a brief summary

- Two stable interstitial sites for the H atom in WC are BOW and NBOC, which may be responsible for the two low temperature desorption peaks, i.e., Peak 1 and Peak 2, respectively.
- The binding energy between two interstitial hydrogen atoms is negative, suggesting that hydrogen itself is not capable of trapping other hydrogen atoms to form a hydrogen molecule.
- The interstitial hydrogen atom prefers to diffusion along the ***c*** axis

Results: multiple H occupancy of vacancy

Cumulative H trapping energy of *m* hydrogen atoms in a carbon/tungsten vacancy

$$E_{tr}^{mH-V_C} = E_{tot}^{mH-V_C} - E_{tot}^{V_C} - m(E_{tot}^{H} - E_{tot})$$

$$E_{tr}^{mH-V_W} = E_{tot}^{mH-V_W} - E_{tot}^{V_W} - m(E_{tot}^{H} - E_{tot})$$

The trapping energy when the number of H atoms in carbon/tungsten vacancy is increased from *m*-1 to *m*

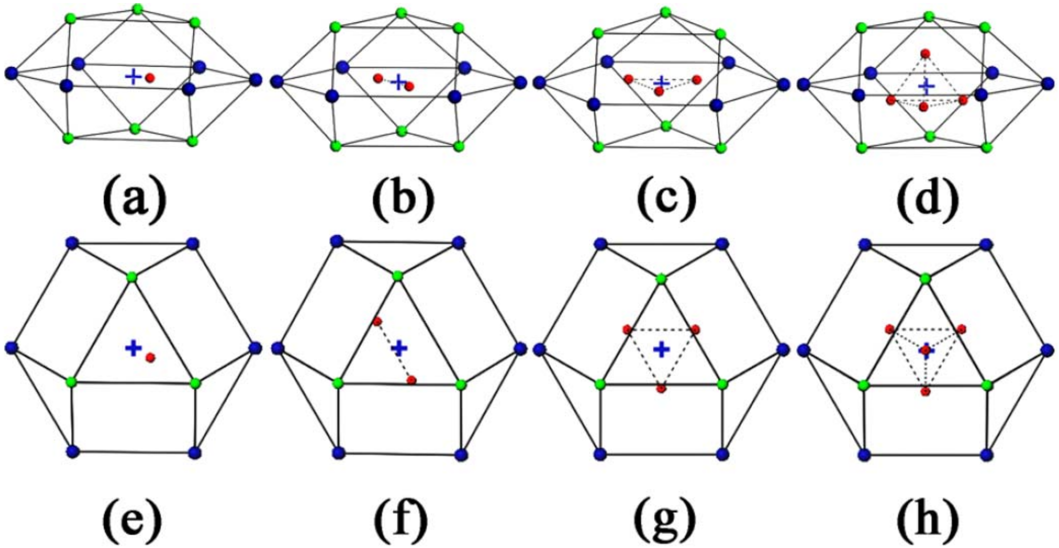
$$\Delta E_{tr}^{mH-V_C} = E_{tot}^{mH-V_C} - E_{tot}^{(m-1)H-V_C} - (E_{tot}^{H} - E_{tot})$$

$$\Delta E_{tr}^{mH-V_W} = E_{tot}^{mH-V_W} - E_{tot}^{(m-1)H-V_W} - (E_{tot}^{H} - E_{tot})$$

Negative trapping energy indicates that the addition of hydrogen atoms is energetically favorable

Results: multiple H occupancy of V_C

The schematic diagram of the lowest-energy configurations of mH-V_C and the corresponding trapping energy and cumulative trapping energy (eV)

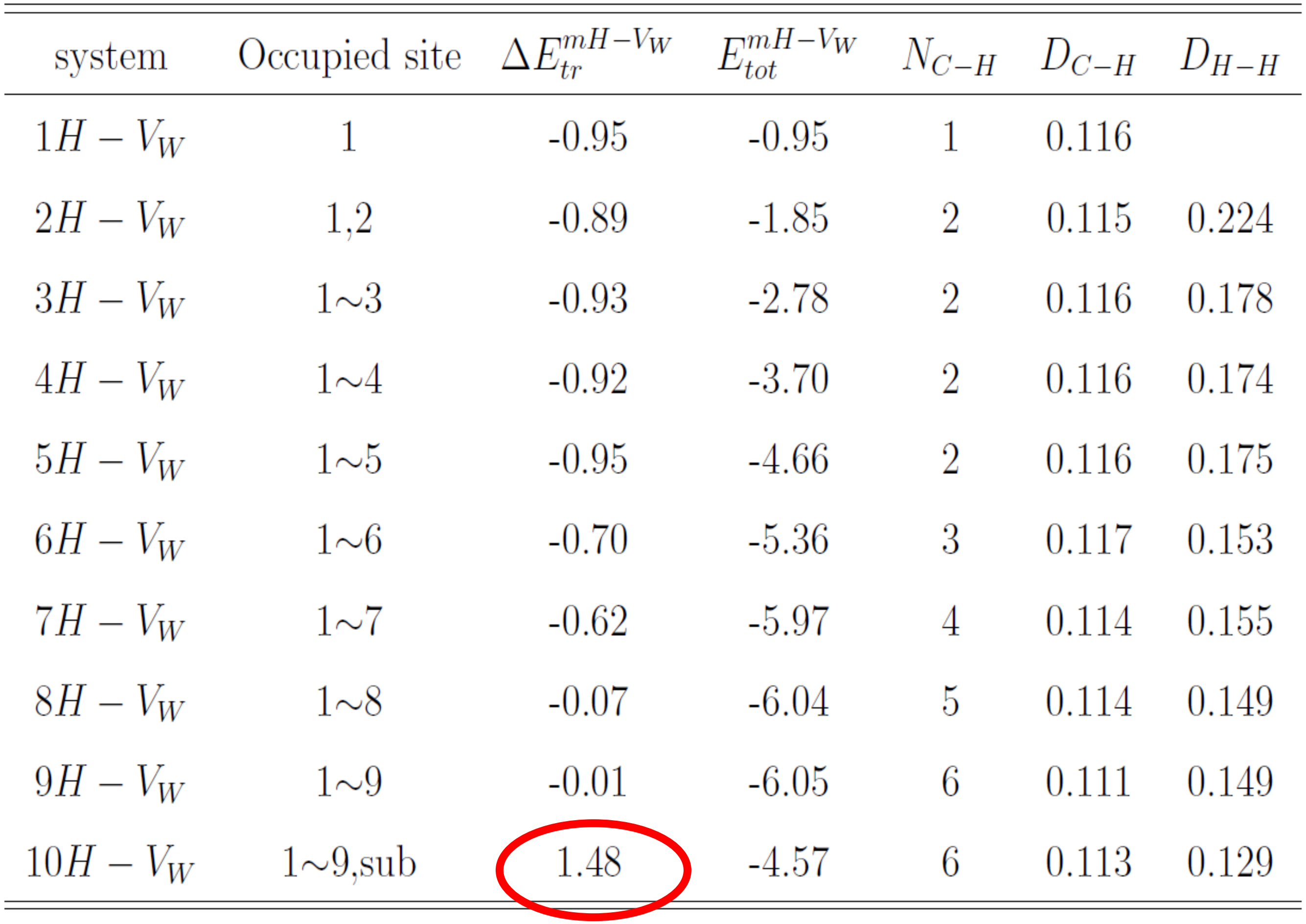


system	$\Delta E_{tr}^{mH-V_C}$	$E_{tot}^{mH-V_C}$
$1H-V_C$	-0.25	-0.25
$2H-V_C$	-0.83	-1.08
$3H-V_C$	-0.27	-1.35
$4H-V_C$	0.20	-1.15

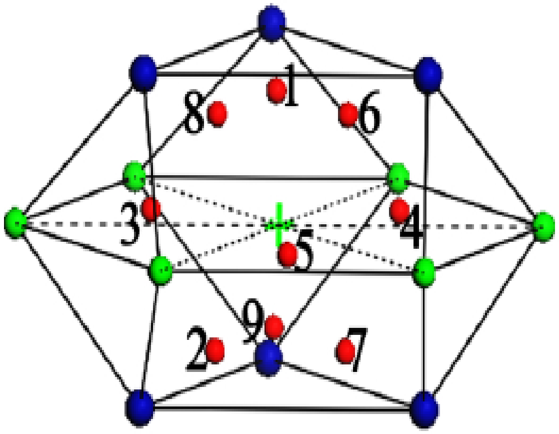
- It is energetically favorable for mono-carbon-vacancy to trap as many as 3 H atoms.
- Hydrogen atoms can not bind together to form a H_2 in mono-carbon-vacancy.

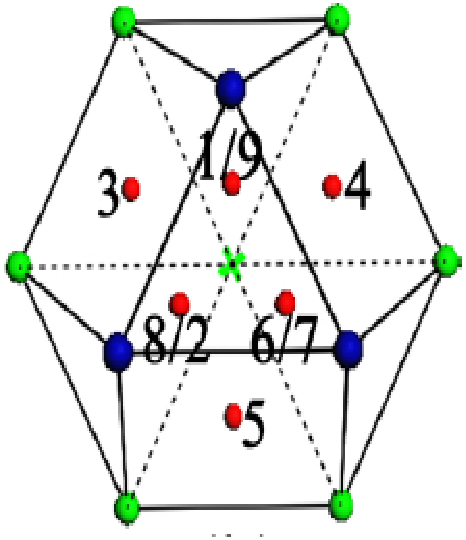
Results: multiple H occupancy of V_W

The schematic diagram of the lowest-energy configurations of mH-V_W and the corresponding trapping energy and cumulative trapping energy (eV). $N_{C\text{-}H}$ and $D_{C\text{-}H}$ (nm) are the number and length of C-H bond, respectively. $D_{H\text{-}H}$ (nm) is the smallest distance between two H atoms



system	Occupied site	$\Delta E_{tr}^{mH-V_W}$	$E_{tot}^{mH-V_W}$	N_{C-H}	D_{C-H}	D_{H-H}
$1H-V_W$	1	-0.95	-0.95	1	0.116	
$2H-V_W$	1,2	-0.89	-1.85	2	0.115	0.224
$3H-V_W$	1~3	-0.93	-2.78	2	0.116	0.178
$4H-V_W$	1~4	-0.92	-3.70	2	0.116	0.174
$5H-V_W$	1~5	-0.95	-4.66	2	0.116	0.175
$6H-V_W$	1~6	-0.70	-5.36	3	0.117	0.153
$7H-V_W$	1~7	-0.62	-5.97	4	0.114	0.155
$8H-V_W$	1~8	-0.07	-6.04	5	0.114	0.149
$9H-V_W$	1~9	-0.01	-6.05	6	0.111	0.149
$10H-V_W$	1~9,sub	1.48	-4.57	6	0.113	0.129



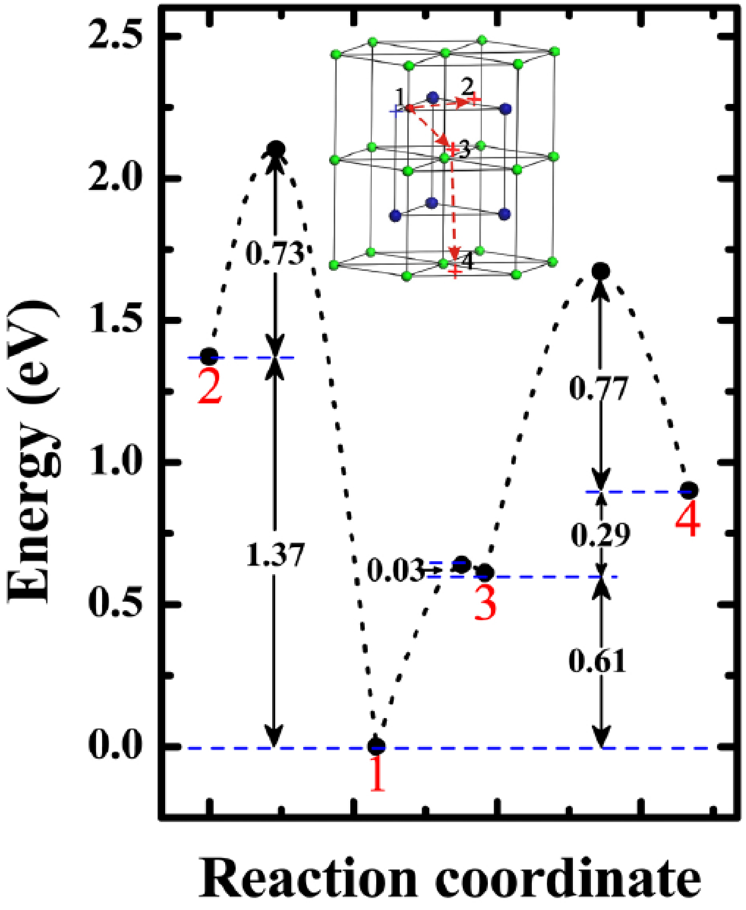


Results: multiple H occupancy of V_W

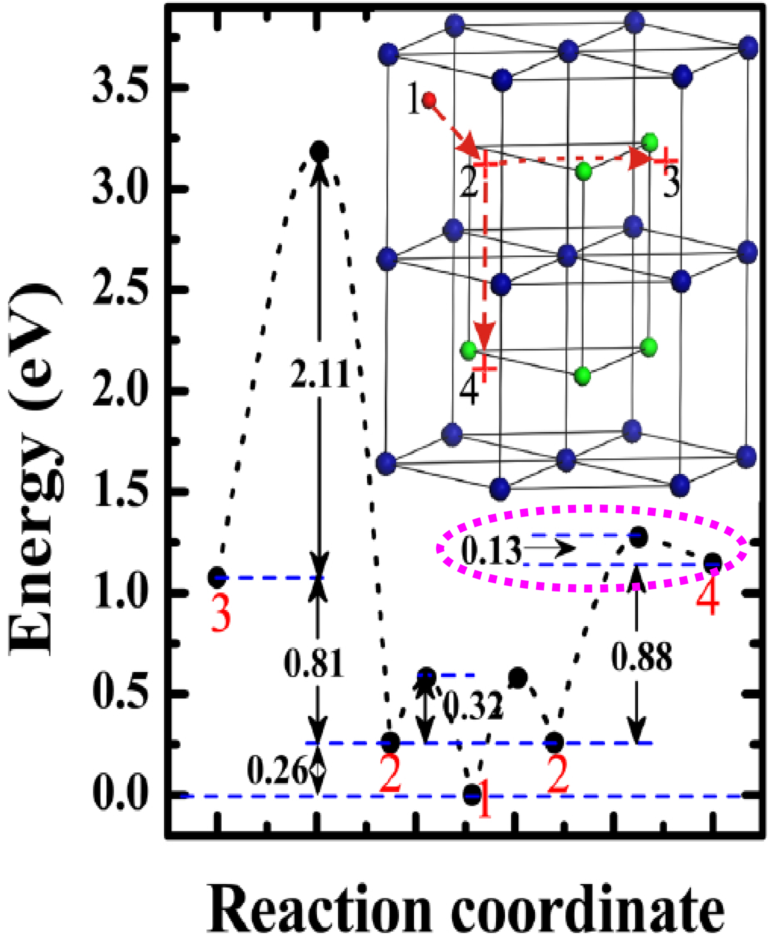
- It is energetically favorable for mono-tungsten-vacancy to trap as many as 9 H atoms.
- Hydrogen atoms can not bind together to form a H_2 in mono-tungsten-vacancy.
- The hydrogen atoms bound to carbon are only found in tungsten vacancy.

Results: the H detrapping from vacancy

H detrapping from V_C



H detrapping from V_W



Results(4): a brief summary

- It is energetically favorable for single carbon and tungsten vacancy to trap as many as 3 and 9 H atoms, respectively
- Hydrogen atoms can not bind together to form H_2 in mono-vacancy.
- The hydrogen atoms bound to carbon are only found in tungsten vacancy.
- The energy barrier of H atom jumping into the tungsten vacancy is relatively low.
- Our results provides an explanation for that the concentration of H bound to carbon is very low and saturated at the initial stage of hydrogen implantation in WC.

Summary

- The carbon vacancy is the dominant defect in tungsten carbide.
- The concentration of tungsten vacancy is considerably low.
- Two stable interstitial sites for the H atom in WC are BOW and NBOC, which are responsible for the two low temperature desorption peaks, i.e., Peak 1 and Peak 2, respectively.
- Hydrogen atoms can not bind together to form H_2 both in intrinsic WC and in mono-vacancy.
- The hydrogen atoms bound to carbon are only found in tungsten vacancy, and the energy barrier of H atom jumping into the tungsten vacancy is relatively low, which provides an explanation for that the concentration of H bound to carbon is very low and saturated at the initial stage of hydrogen implantation in WC.

Thanks for your attention!