RAD INTERFACES

BSC

RES projects
FI/QCM

PRACE

DECI project
PRIMO

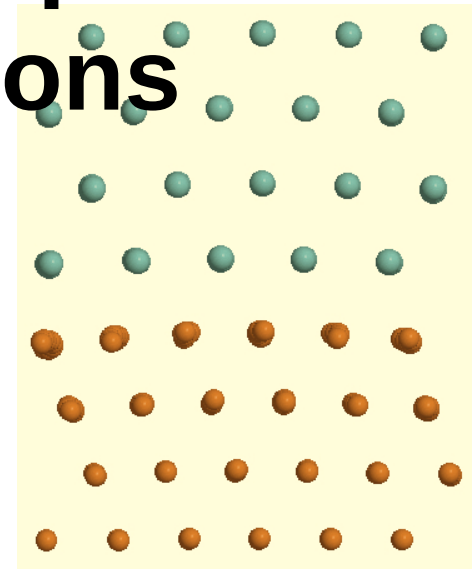
UNIVERSIDAD DE OVIEDO

SEVENTH FRAMEWORK PROGRAMME

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

NANOEXTREM/RADIAFUS

Construction and relaxation of metallic heterointerfaces including point defects for DFT simulations



C. González, M. A. Cerdeira and R. Iglesias

University of Oviedo

Outline

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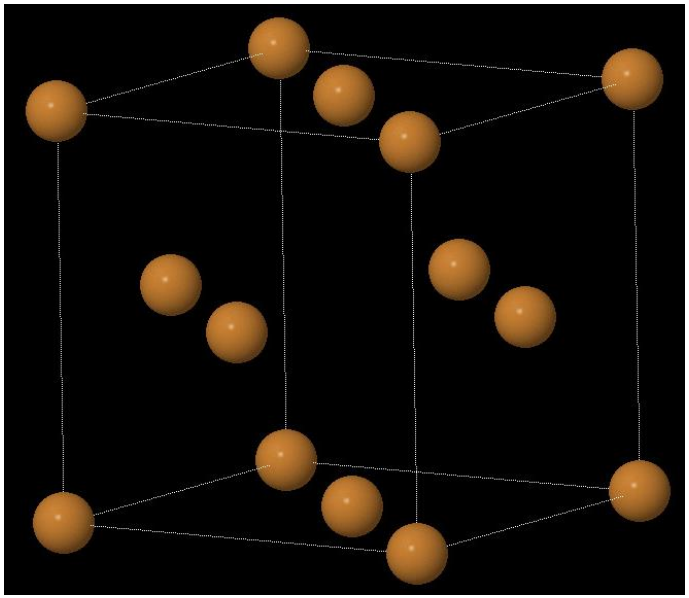
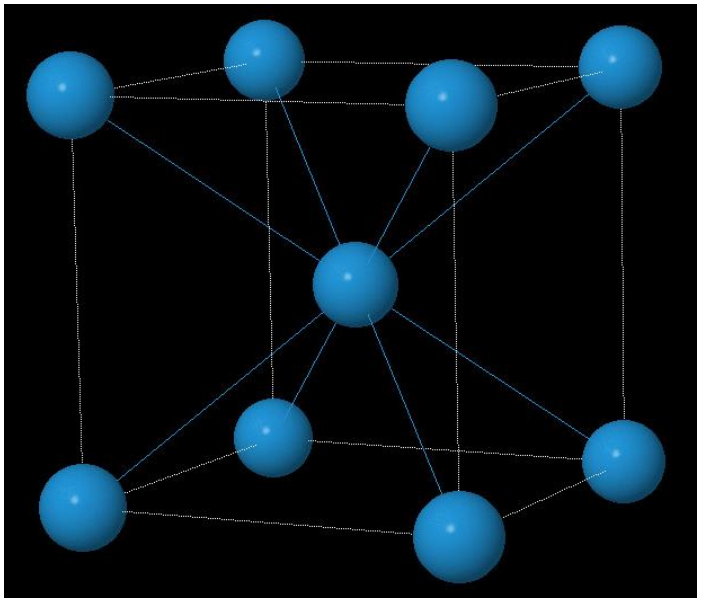
- What is an interface: Motivation
- Introduction to DFT and details of the simulations
- Creating the interface
- Applications: defects on Cu/Nb, Cu/W and W/W interfaces
- Conclusions.

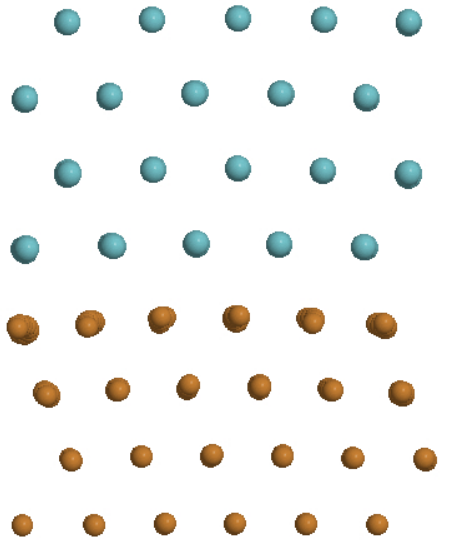
The perfect crystal

FCC structure: Cu



BCC structure: Nb





A surface is created when the bulk is truncated
An interface is created by adjoining two different surfaces

Motivation

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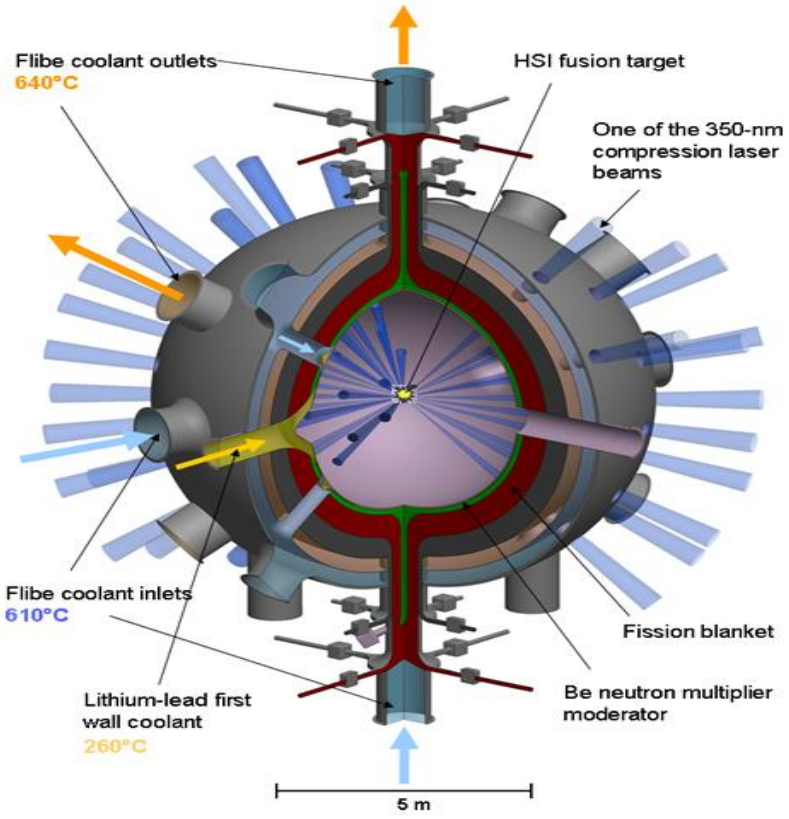
Future fusion energy reactor: ICF vs MCF

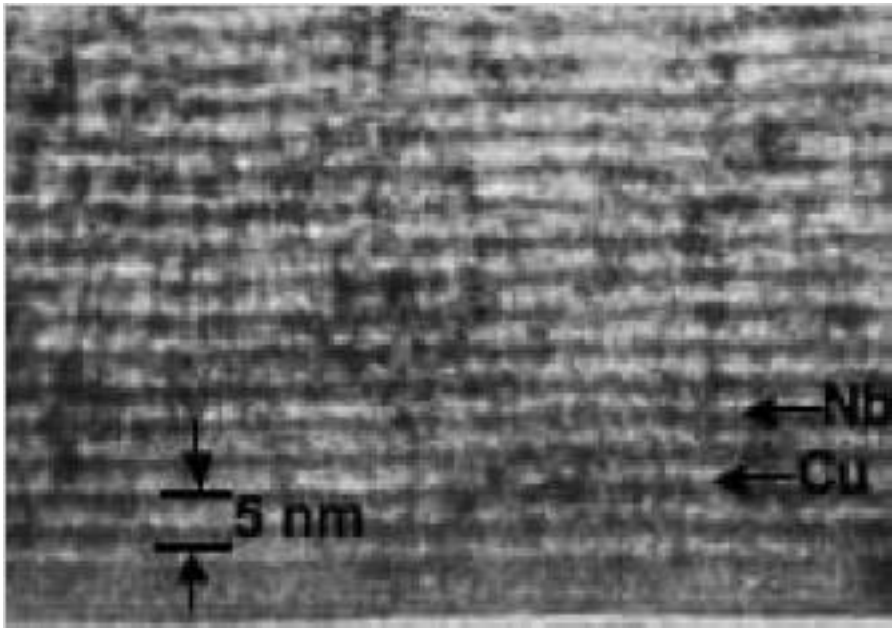


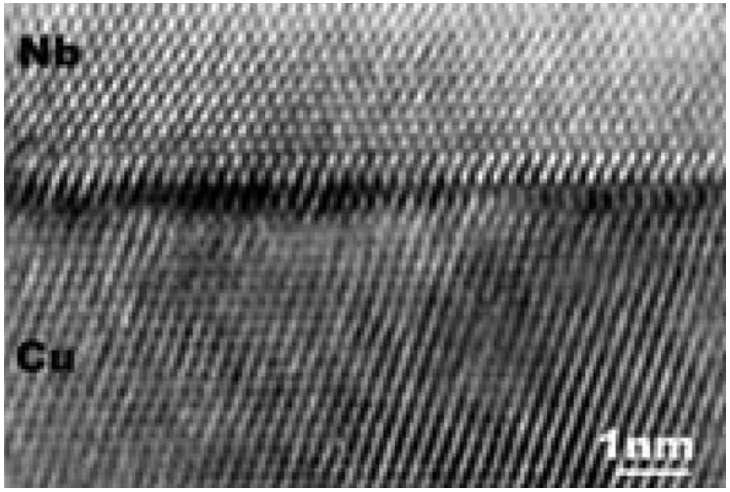
Metallic multilayers proposed as PFMs: Cu/Nb-Cu/W-W/W…

Point defect analysis: H/He, vacancies and SIAs.

Introduction

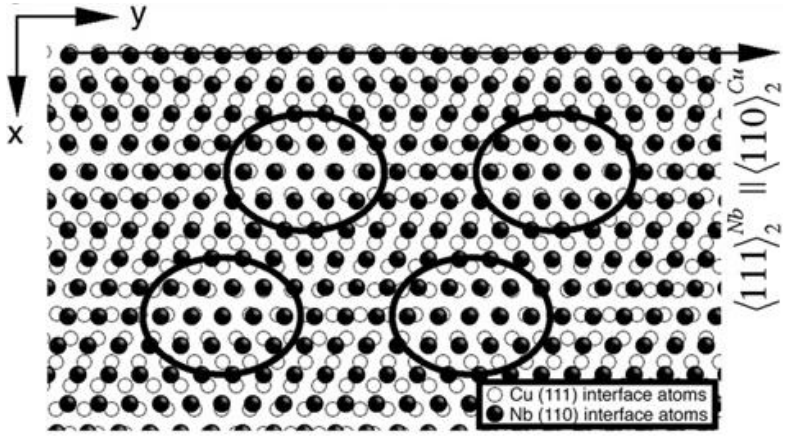
TEM experiments

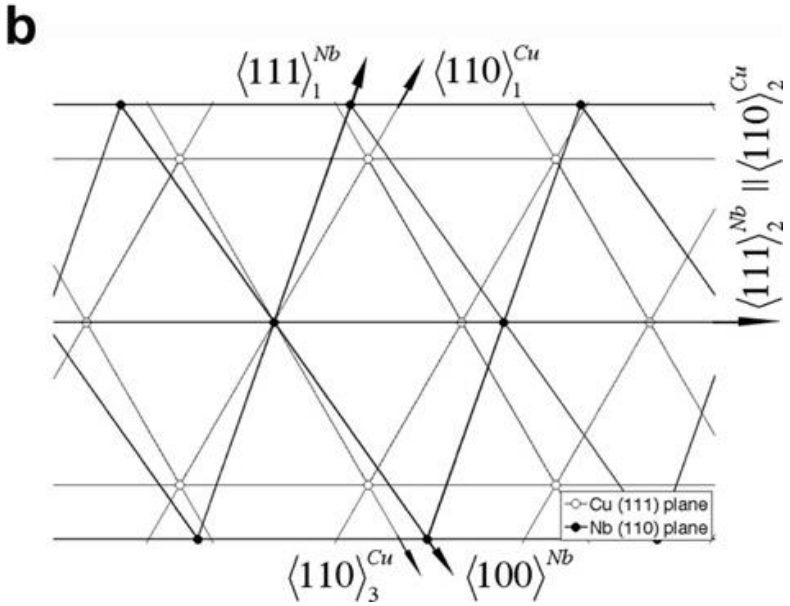




A. Misra, M.J. Demkowicz, X. Zhang and R.G. Hoagland, JOM 2007

KS_1 interface





M.J. Demkowicz and R.G. Hoagland JNM 372 45 (2008)

Introduction

TEM experiments

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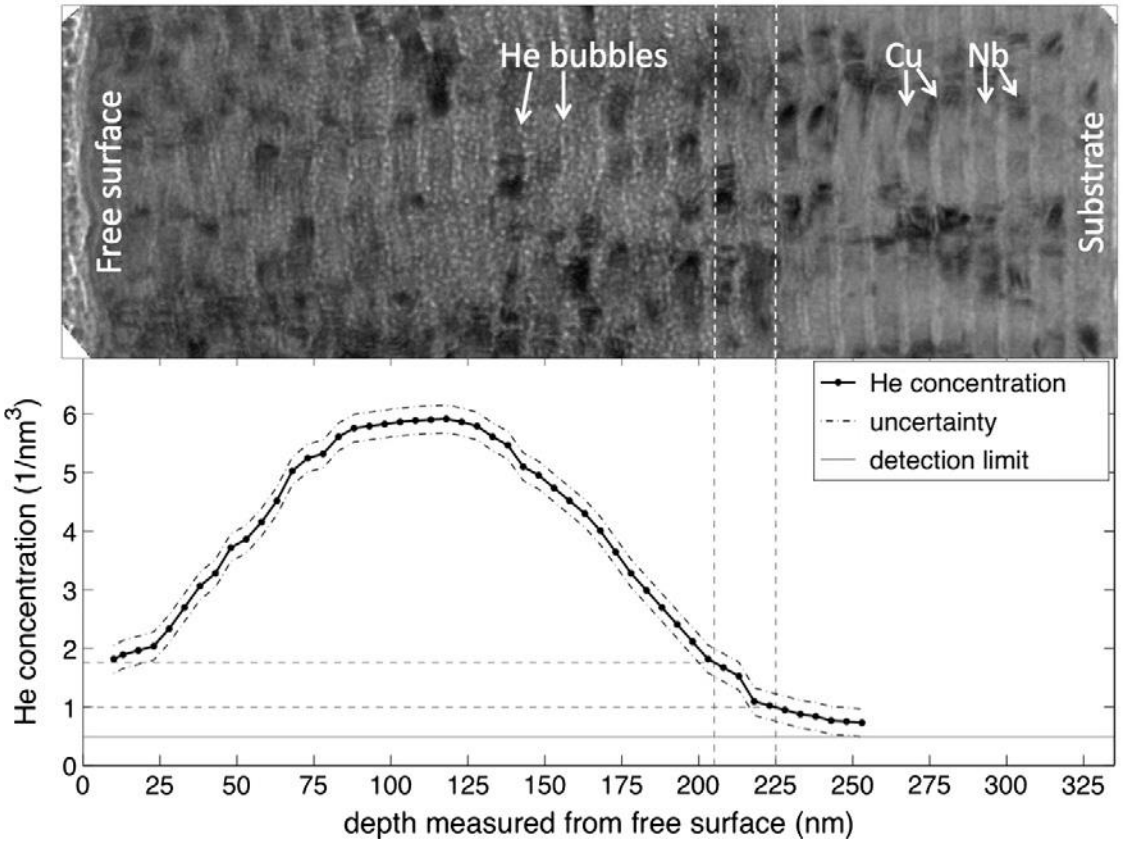
M. J. Demkowicz et al *Curr. Opin. Solid State. Mater. Sci.* **16**, 101 (2012)

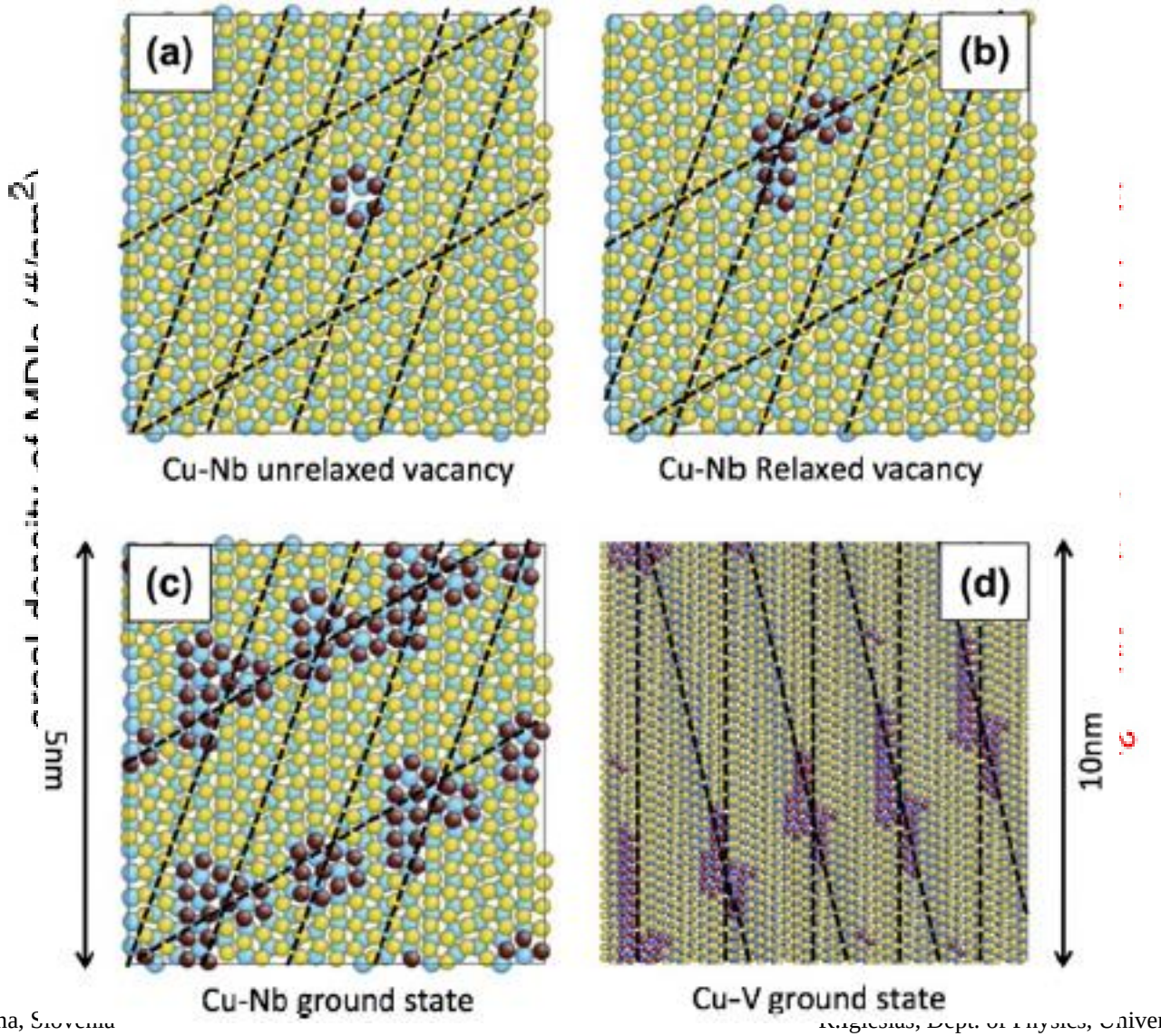


He at the interfaces

Introduction

MDIs

M. J. Demkowicz et al *Curr. Opin. Solid State. Mater. Sci.* **16**, 101 (2012)



Introduction

MD and kMC simulations

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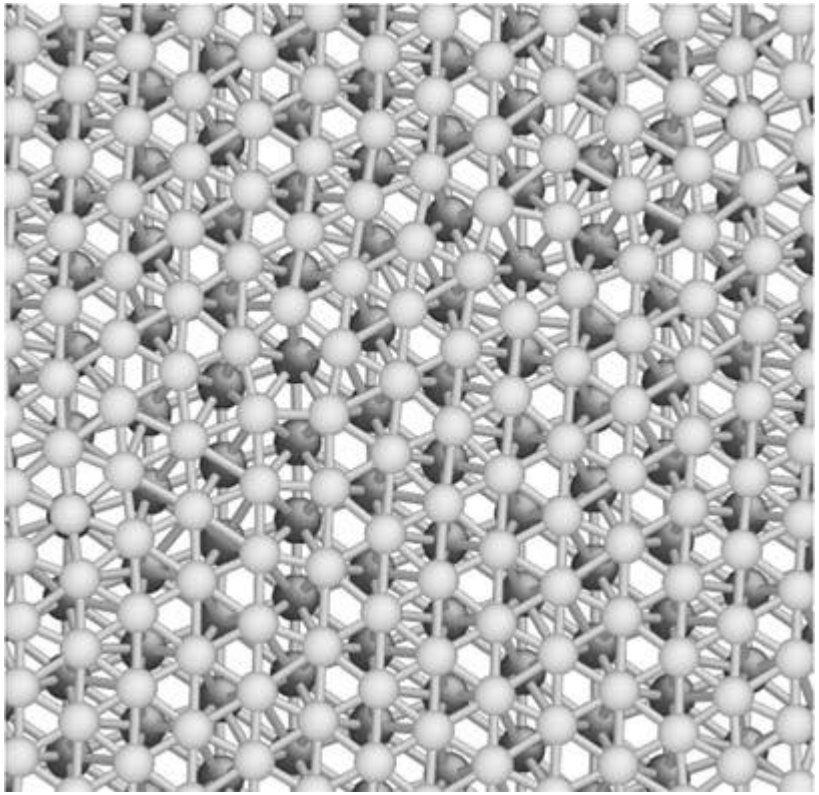

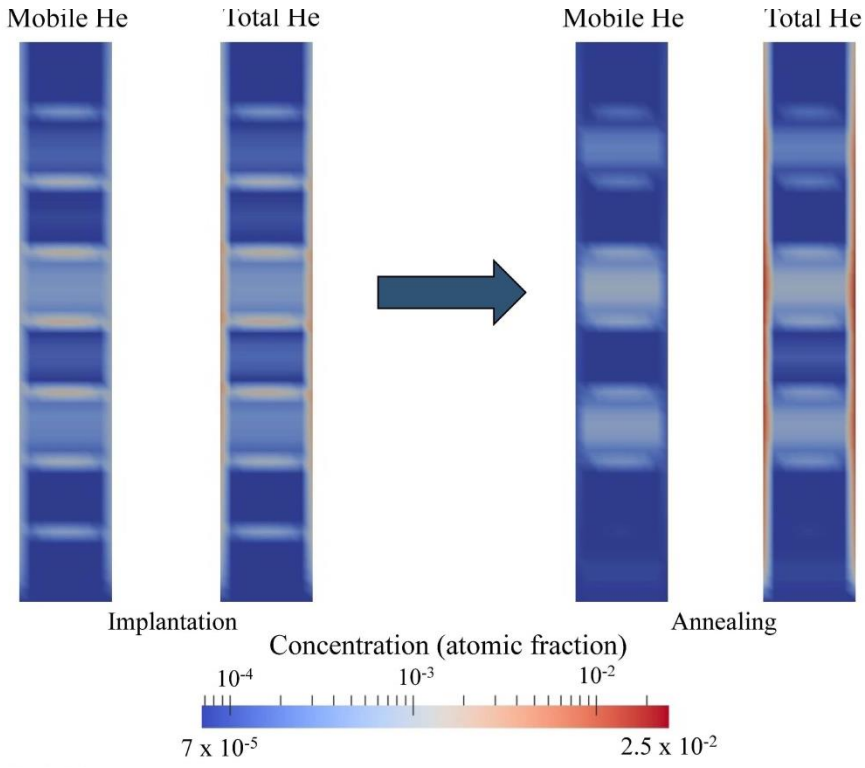

MD calculations good for one (two) elements. Problems with the potential generation for three elements

M. J. Demkowicz et al *Curr. Opin. Solid State. Mater. Sci.* **16**, 101 (2012)

Parametrized with bulk or MD data

A. Y. Dunn et al *J. Nucl. Mater*. **435**, 141 (2013)

Introduction to DFT

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Schrödinger equation (Quantum Mechanics)

$$\hat{H}_S \Phi = E_{TOT} \Phi$$

Approximations:

Born-Oppenheimer: Separates electrons and ions (Ehrenfest)

Electron treated QM as a electronic density/Ions classically

Khon-Sham equations and one electron approximation:

$$E[\rho] = \int v(\vec{r})\rho(\vec{r})d\vec{r} + E_{ee}[\rho] + T_S[\rho] + E_{XC}[\rho]$$

Pseudo-potential: only valence electrons in the calculation, cutoff

Introduction to DFT

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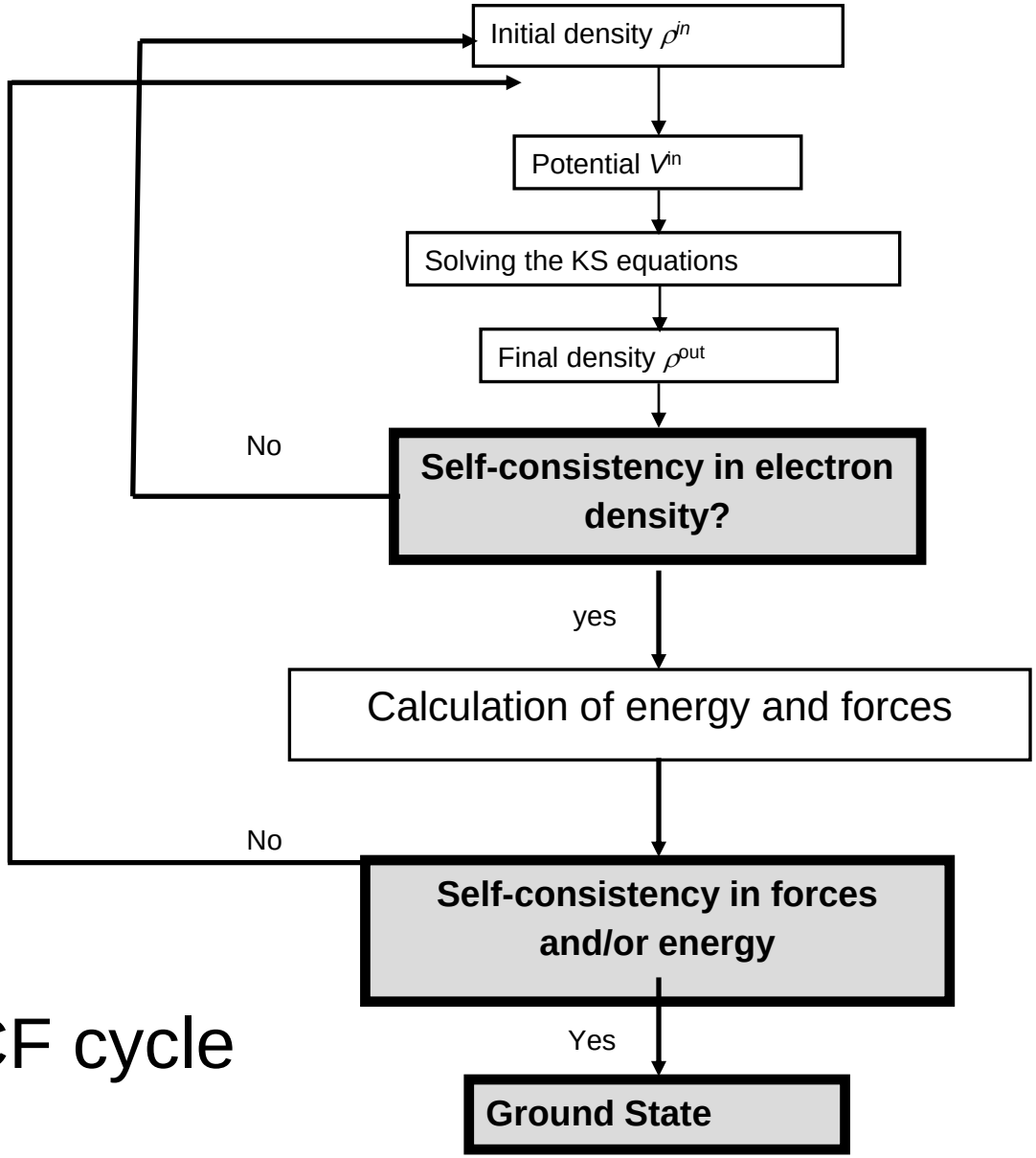

SCF cycle

Details of the calculation

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- DFT calculations performed with VASP code.
- PBE XC functional.
- VASP-PAW pseudopotentials.
- Cutoff energy: 479 eV (He atoms)
- **Migration energies calculated with NEB method**

The perfect crystal

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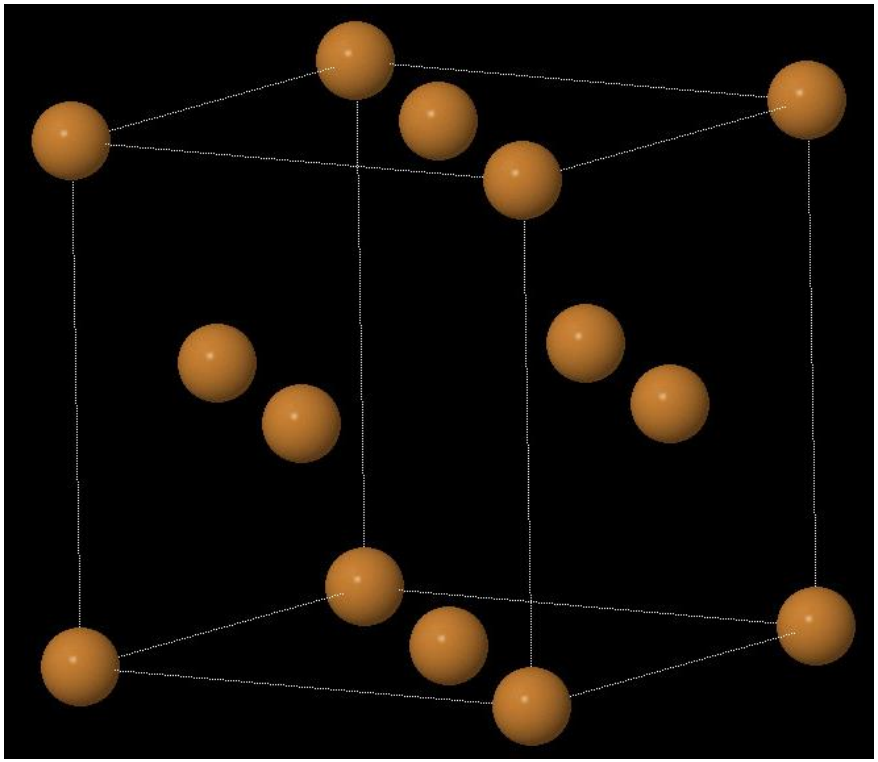
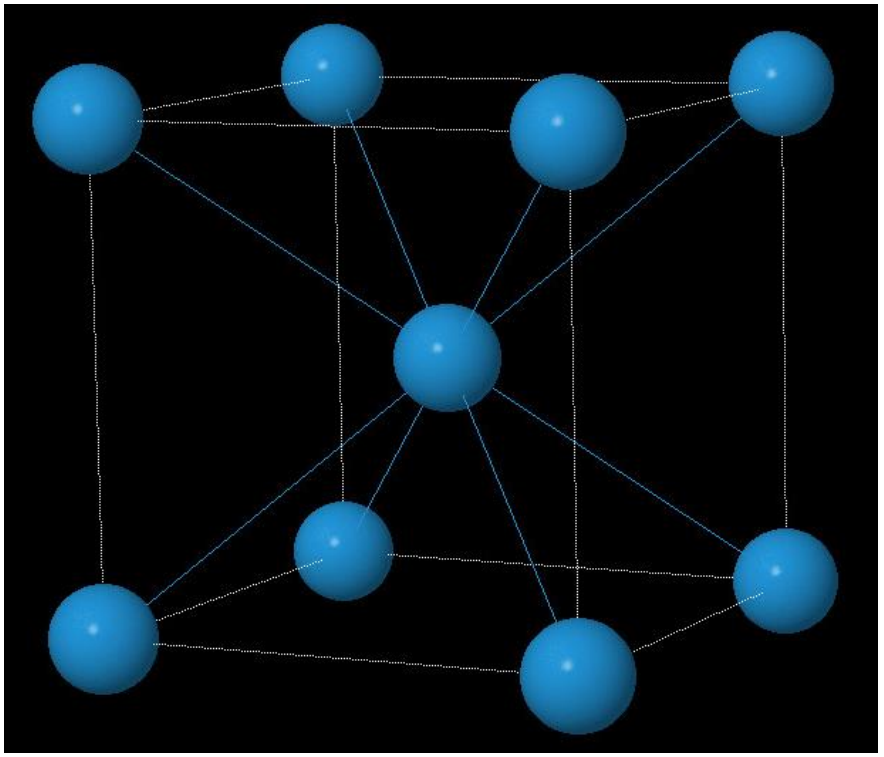
FCC structure: Cu



C. González et al MSMSE **22** 035019 (2014)

BCC structure: Nb



M. A. Cerdeira et al J. Nucl. Mater. **478** 185 (2016)

4x4x4 (256 at) and 5x5x5 (128) cubic unit cells for Cu and Nb, resp.
27 kpoints in the first Brillouin zone

Details of the calculation

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- Formation energy expression:

$$E_f(\{n_{vac} n_{He}\}) = E(VASP) - (NCu - n_{vac}) E_{Cu}^{ref} - n_{He}\, E_{He}^{ref}$$

$$E_f(\{nvac n_{He}\}) = E(VASP) - E(slab) + n_{vac} E_{Cu/Nb}^{bulk} - n_{He}\, E_{He}^{ref}$$

Computational resources

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RES project:
FI-2014-1-0008
Supernova

WCSS

Universidad Santander

ICHEC
Fionn

DECI project
PRIMO

Searching for a good interface

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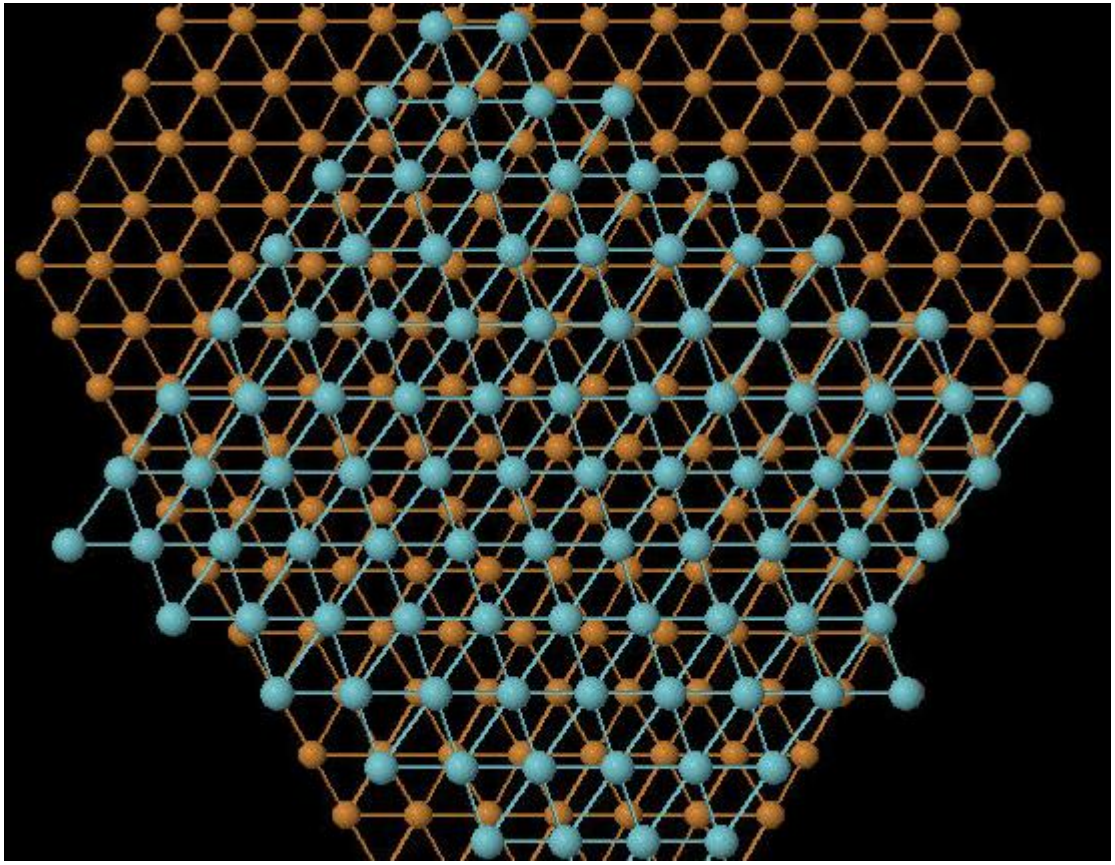

1 layer of each metal
Rotate one against the other
Find the possible coincidence sites and periodicities:
are they manageable using DFT?

Searching for a good interface

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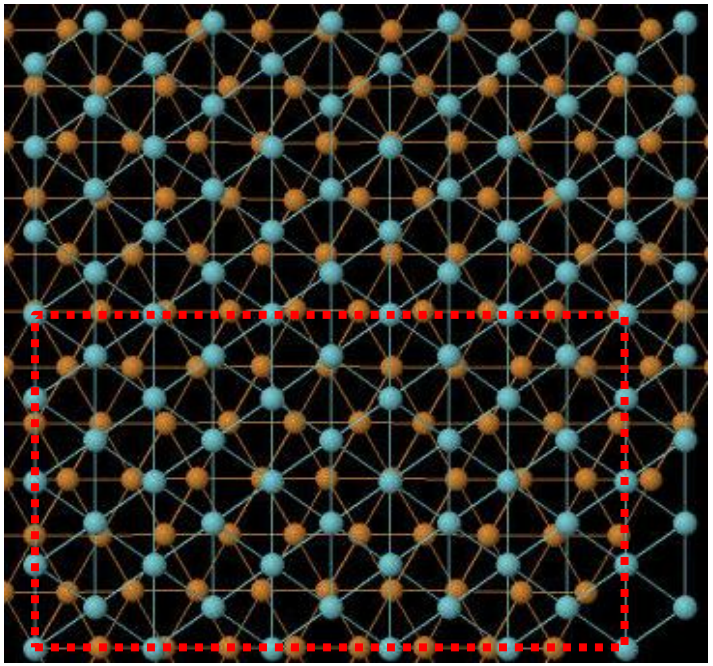
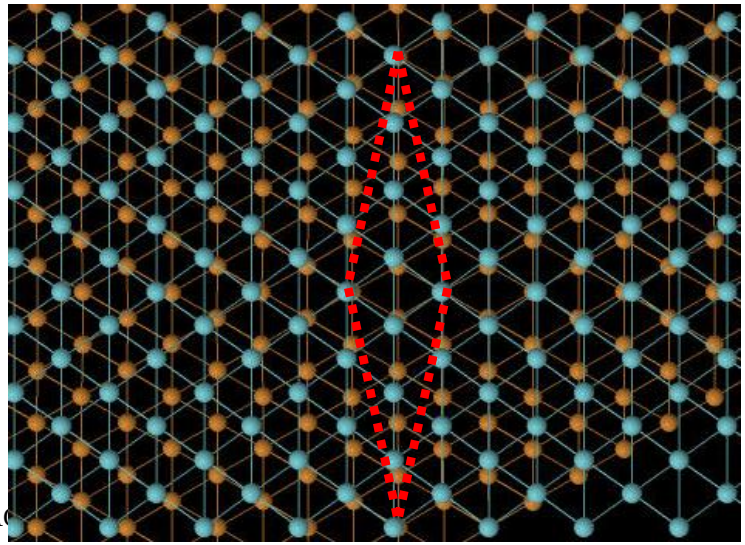
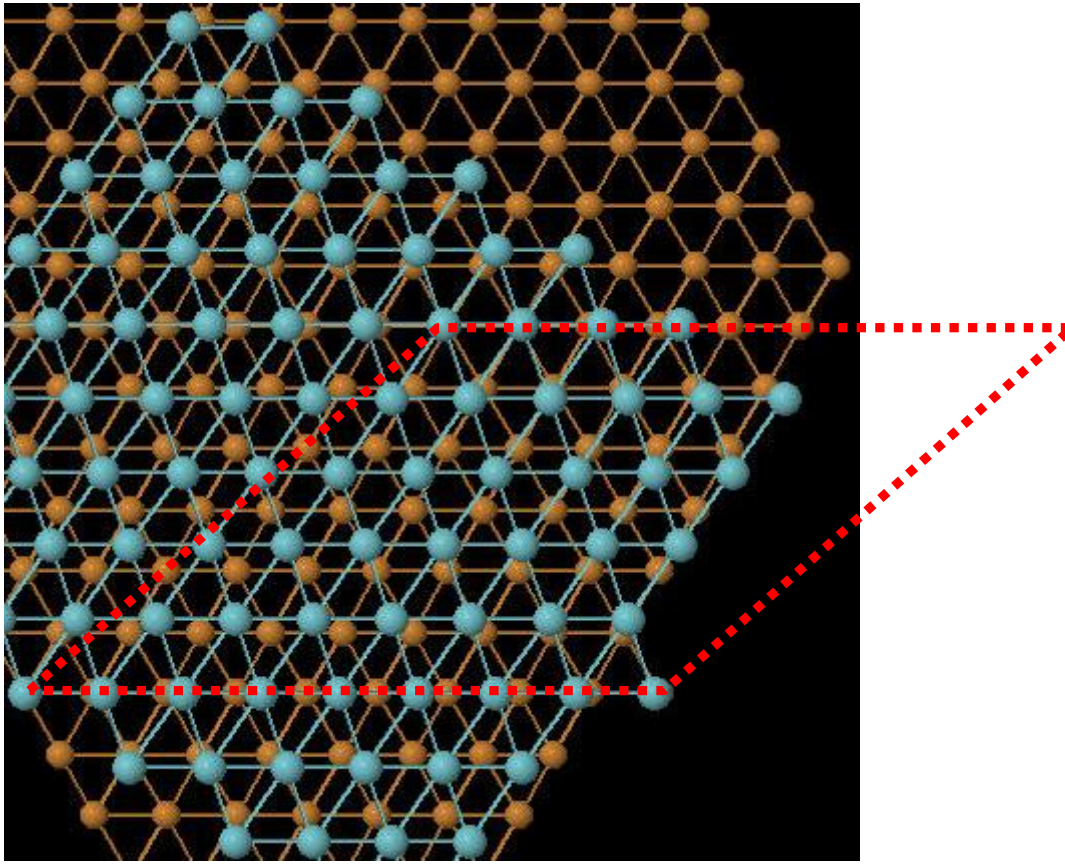




Cu/Nb KS interface



Cu-Nb IF relaxation (upside view)

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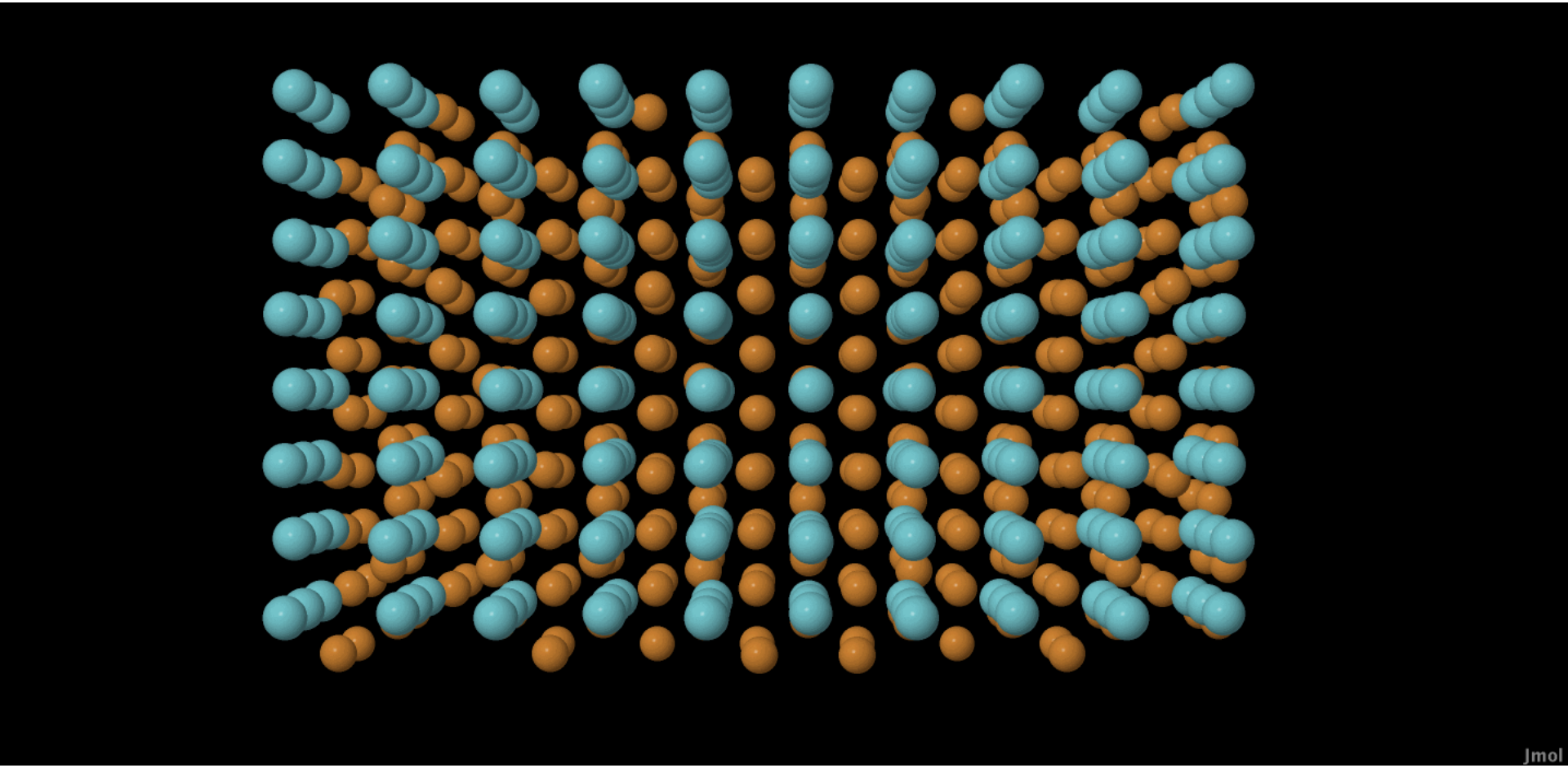

González/Iglesias 2015

Cu-Nb IF relaxation (side view)

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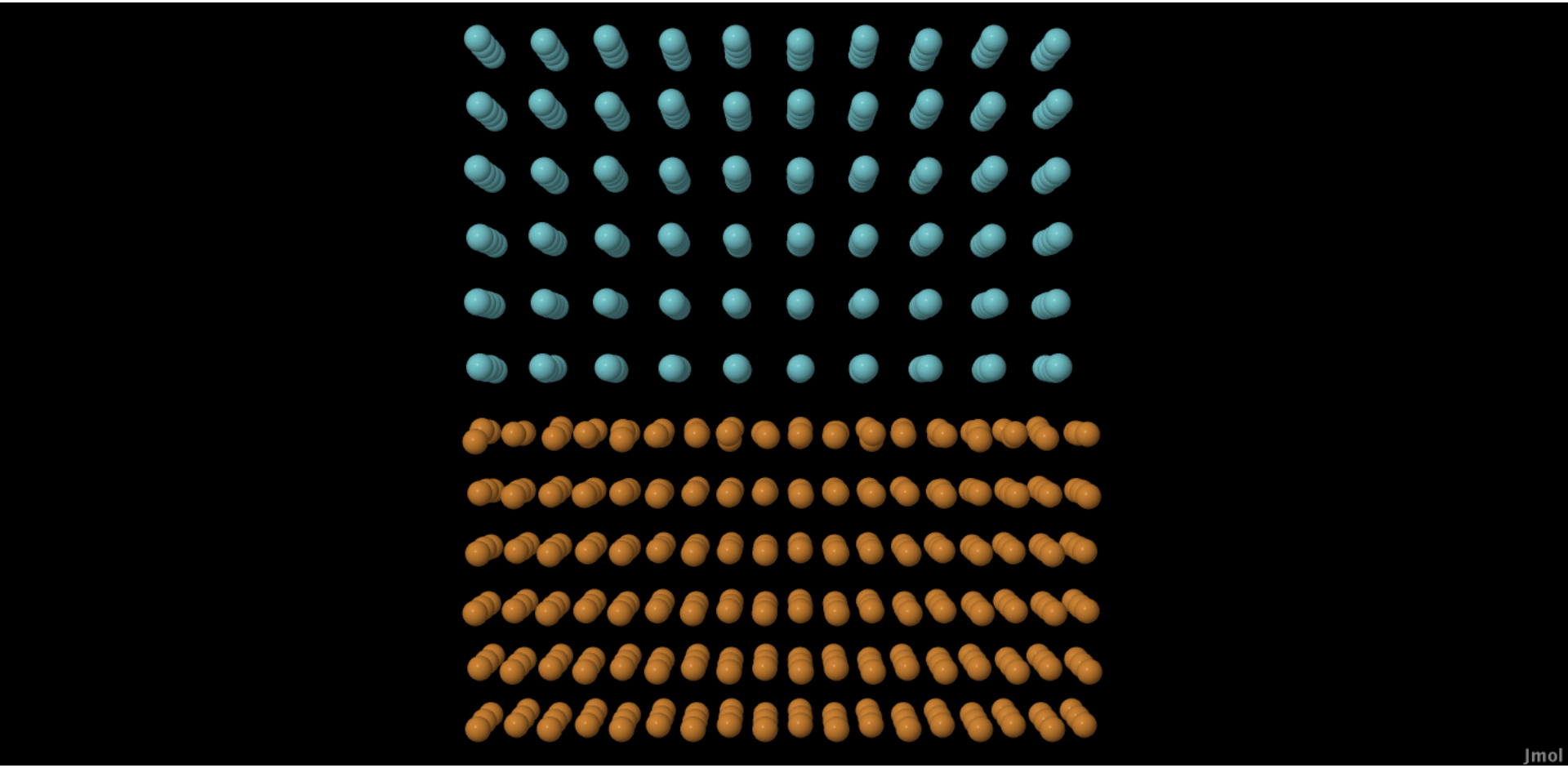

González/Iglesias 2015

Cu-Nb Demkowicz's KS1

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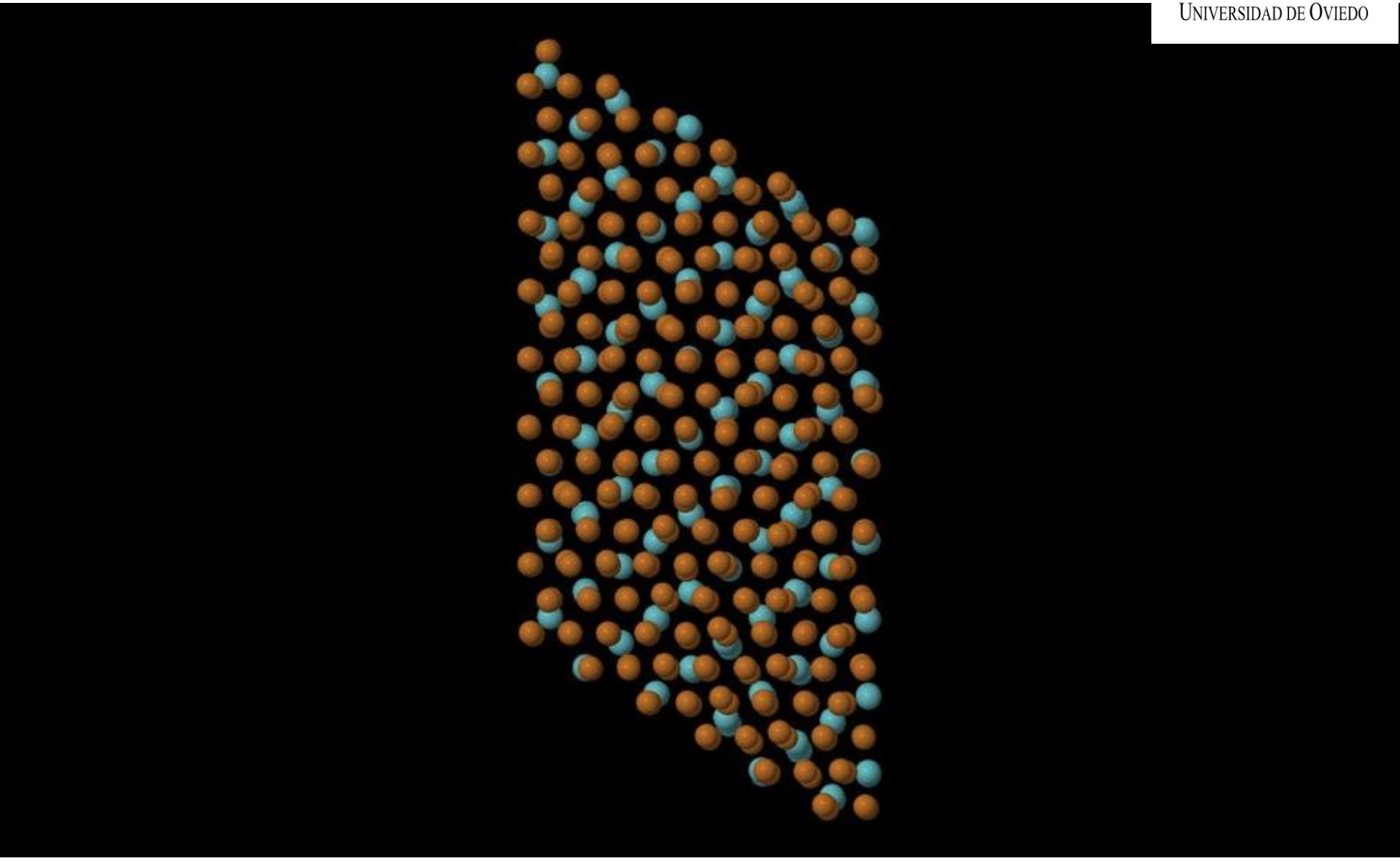

Cu-Nb Demkowicz's KS2

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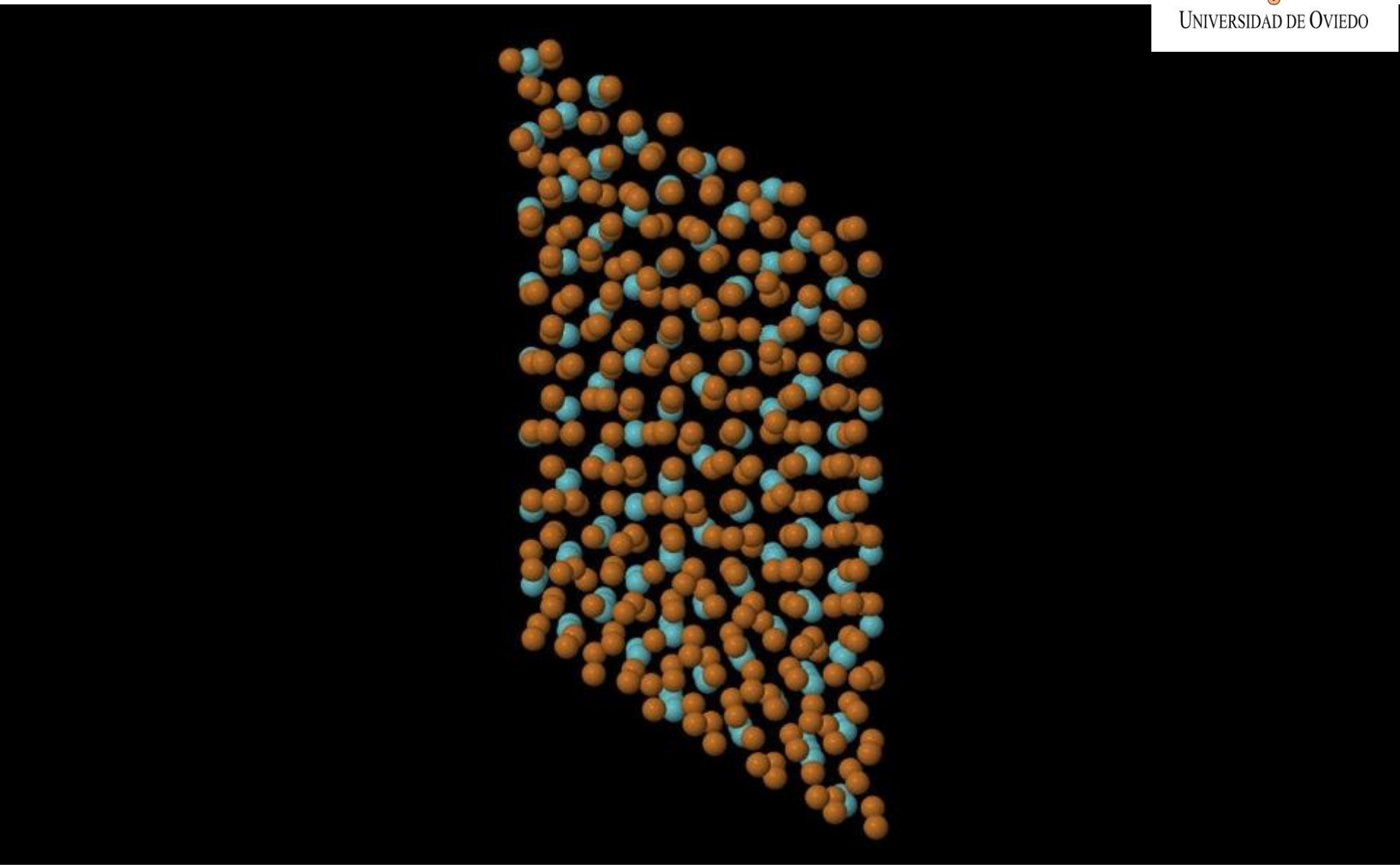
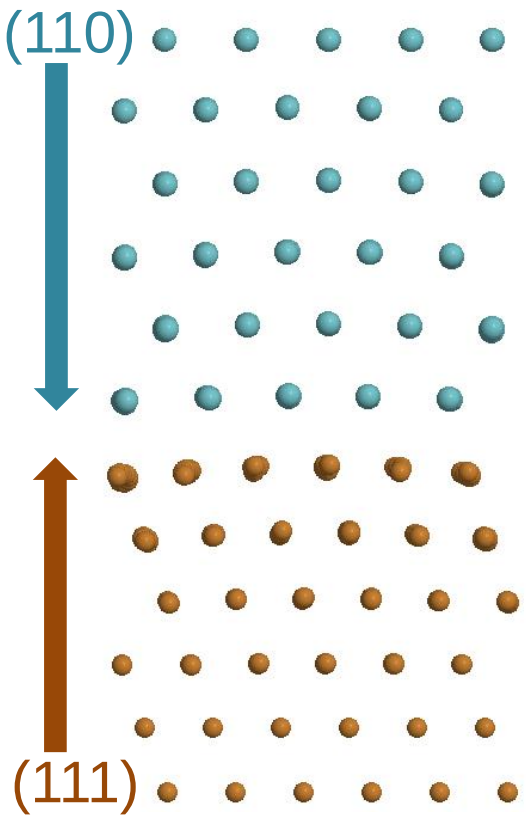


Cu/Nb-KS interface



- 6 layers of each metal
- Cu periodicity: 9x6 (324 at)
- Nb periodicity: 8x5 (240 at)
- 9 kpoints in the 1BZ of the surface
- Last layers kept fixed to simulate bulk behaviour

Cu/Nb DFT results

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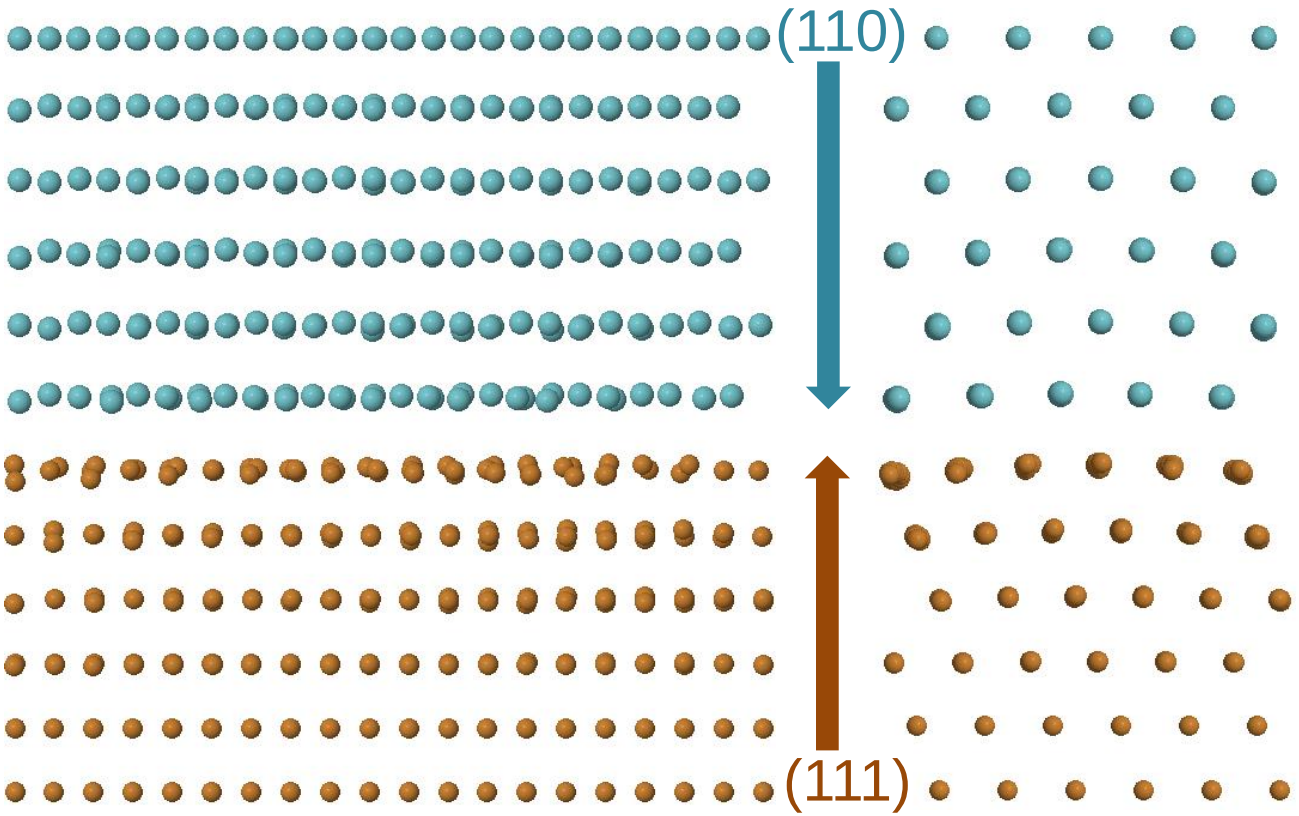

Strong reconstruction at interface but no Cu-Nb mixing
Corrugation: Cu/Nb 0.58/0.26 Å

Cu/Nb DFT results

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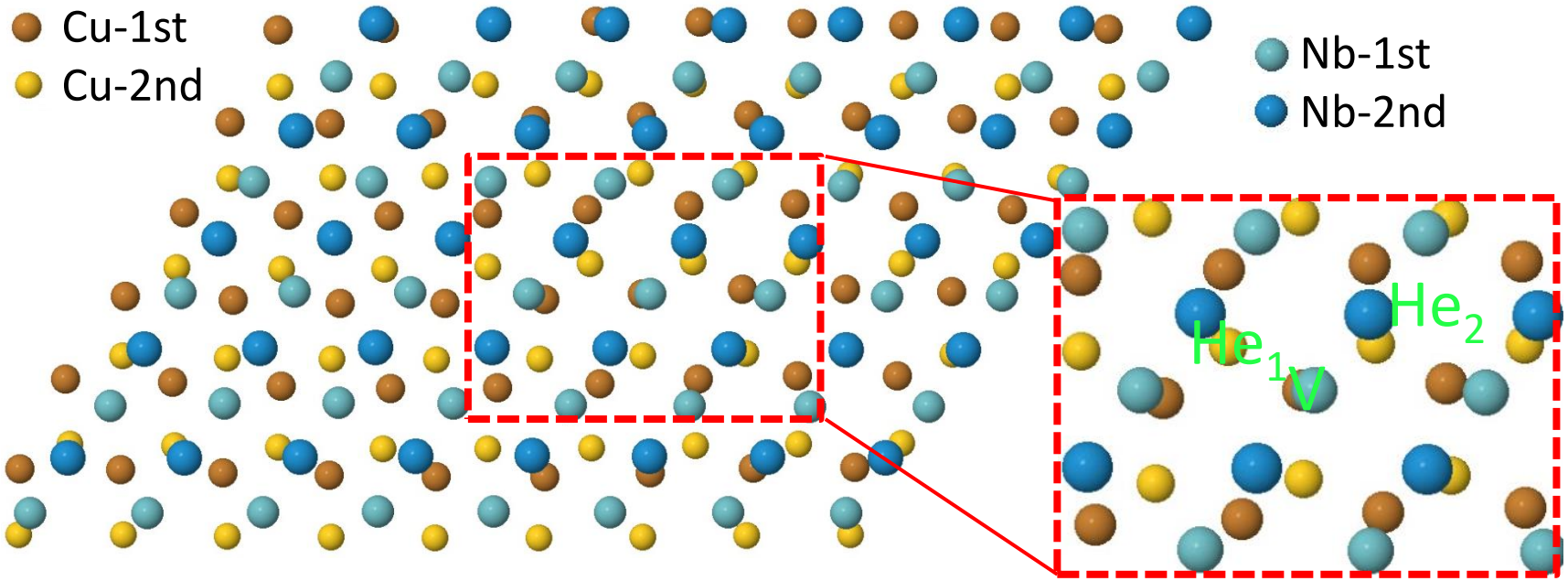

Vacancies and He atoms are introduced at the interface
Most stable sites for vacancy formation and He implantation are in the area where Nb and Cu atoms coincide

Cu/Nb DFT results

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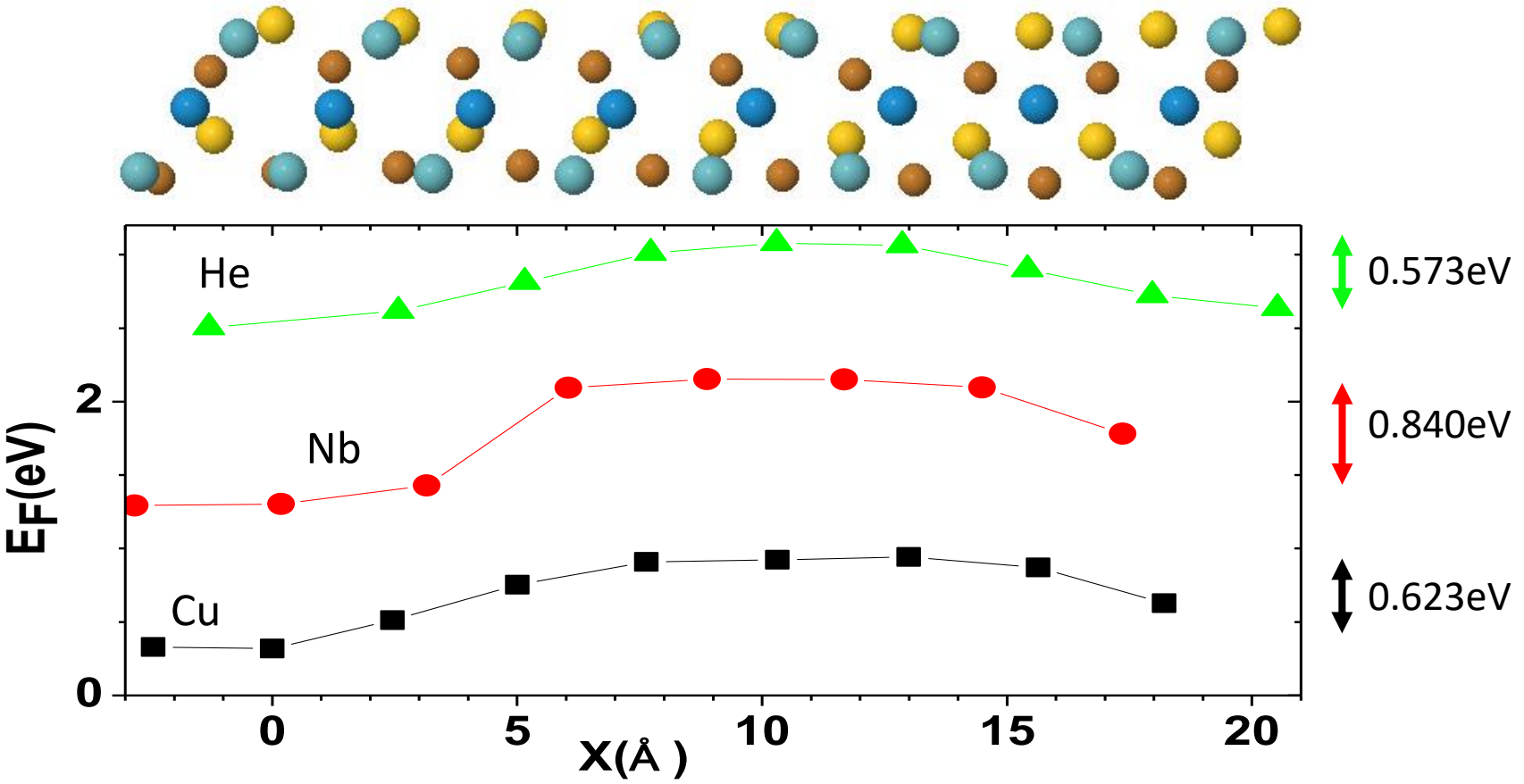

Cu/Nb DFT results: Cu vacancy

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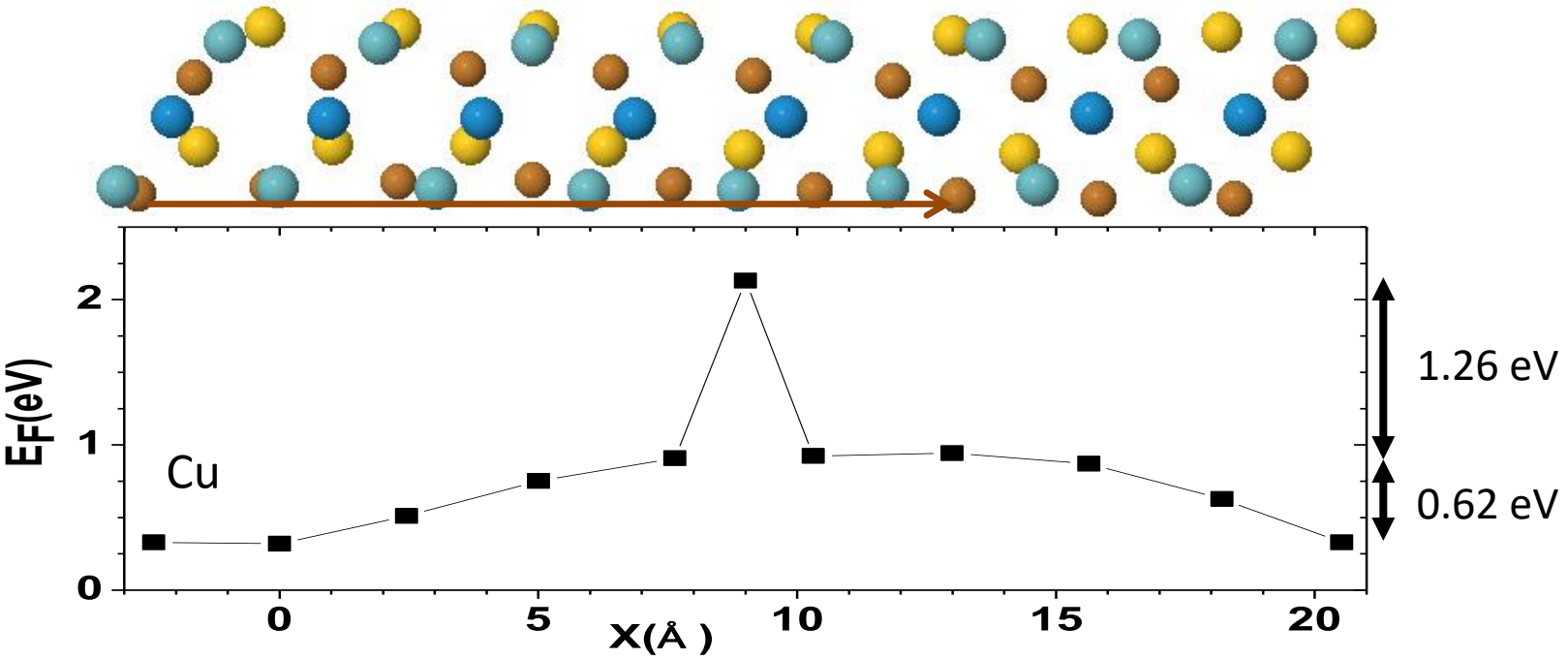

(eV)	Cu bulk	Inter Cu	Cu 2lay
E_F vac	1.08	0.32	0.78
1vac→1vac	0.73	1.88 (1.26)	0.44

Cu/Nb DFT results: Nb vacancy

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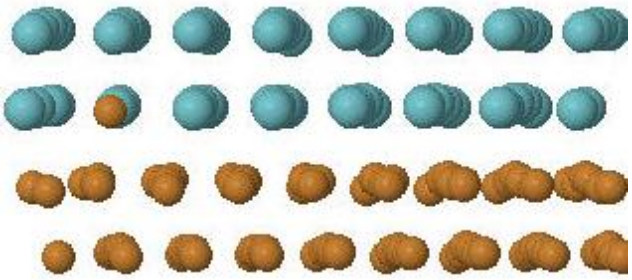
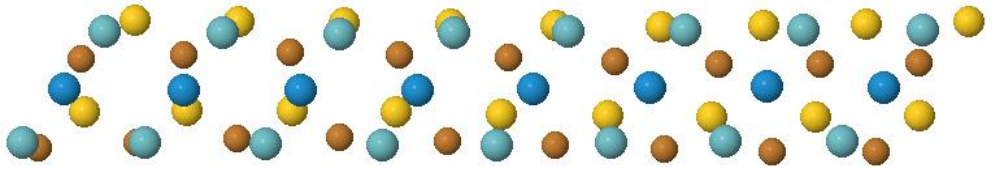
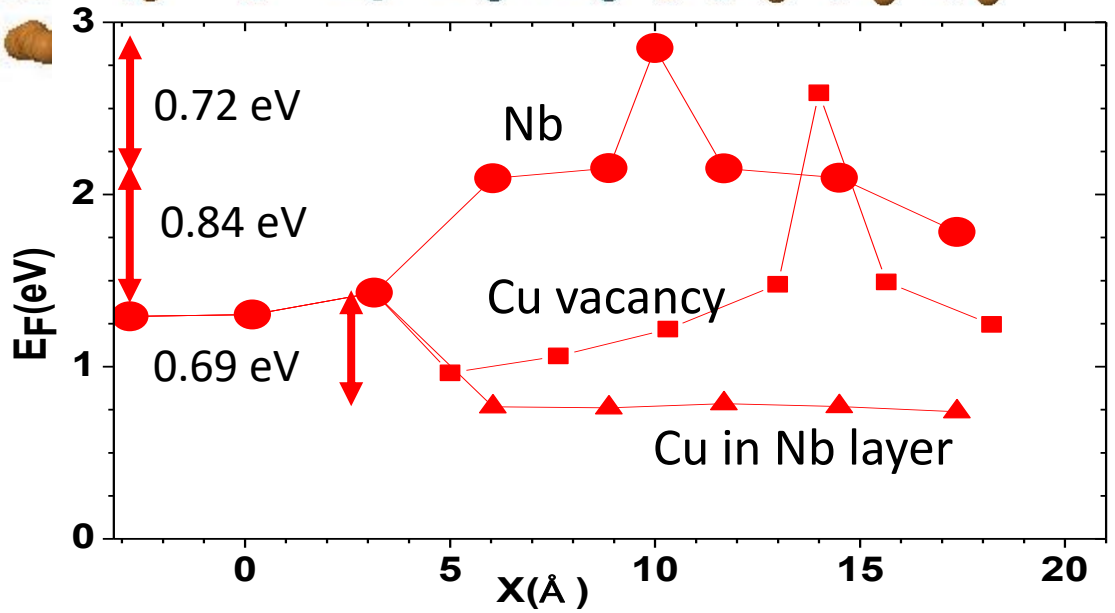




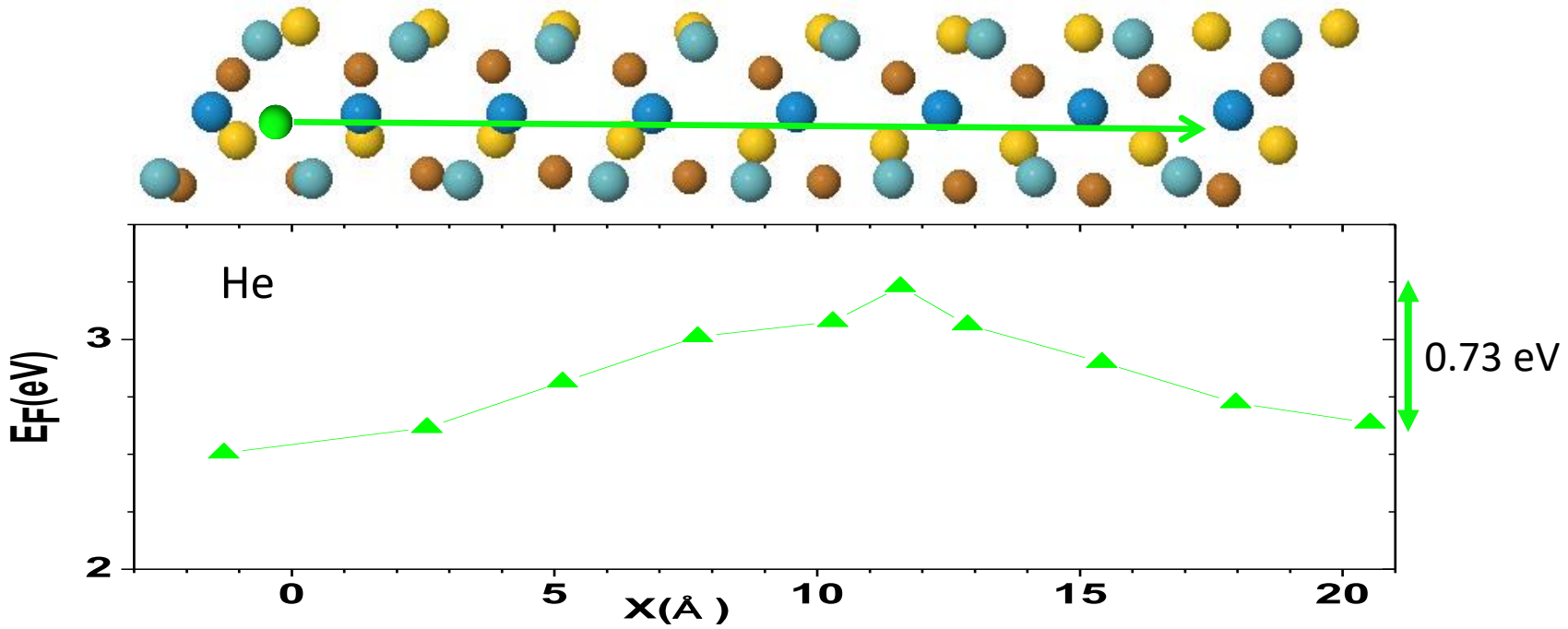
3 ways of migration

- Pure Nb atom
- Cu in Cu layer
- Cu in Nb layer



(eV)	Nb bulk	Inter Nb	Nb 2lay	Cu(v)
E_F vac	2.66	1.29	2.75	
1vac→1vac	0.59	1.56 (0.72)	0.12	1.11

Cu/Nb DFT results: He



(eV)	Cu bulk	Nb bulk	Inter	Cu 2lay	Nb 2lay
E_F tet	3.94	3.14	2.50	3.40	To Inter
1He-tet →1He-tet	0.13	0.31	0.73 (0.11)	0.14	No

Cu/Nb DFT results: He+vacancy

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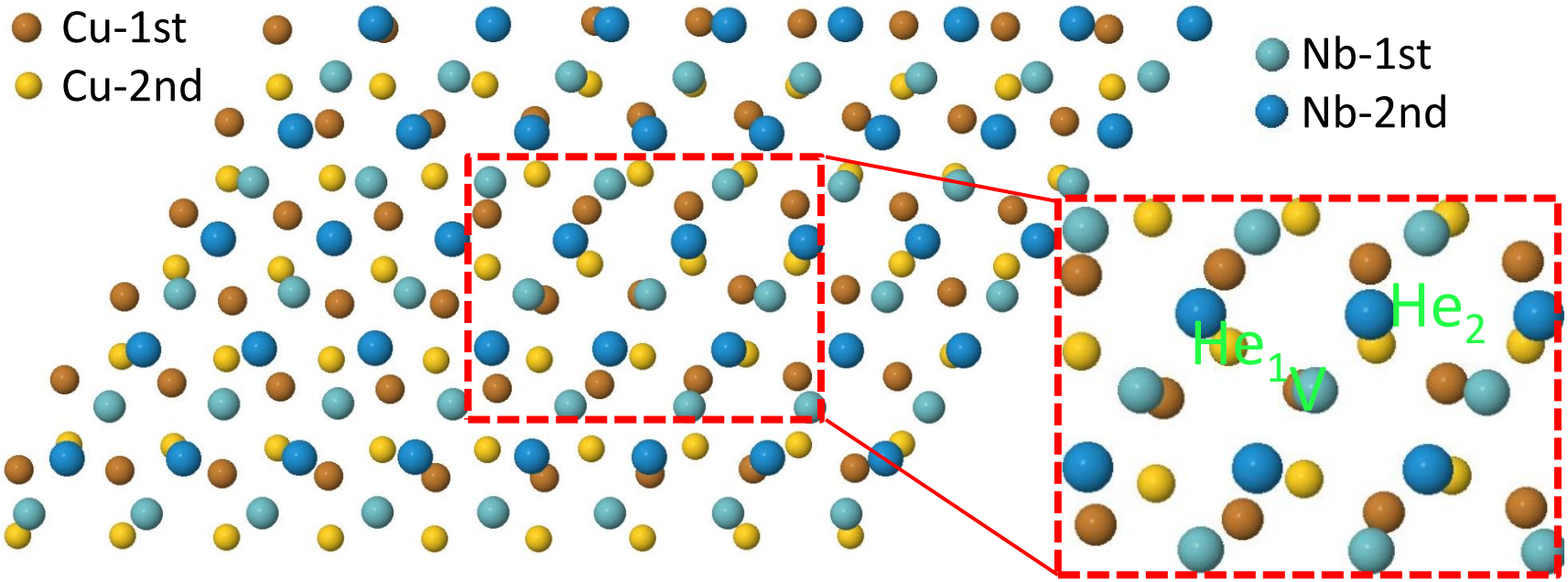

(eV)	HeV bulk	V+He-Int	V-Int+He	HeV2l	V2l-Int+He
E_F Cu	2.52	2.07	2.49	2.46	3.27
E_F Nb	4.27	2.73	3.98	4.39	5.31

He prefers the vacancy instead of the interface

HeV at second layer tends to bulk values

Cu/Nb DFT results: Summary

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E_F(eV)	Uniovi	[1]
$V(Cu)_I$	0.32	0.95±0.45
$V(Cu)_b$	1.08	1.26
$V(Nb)_I$	1.29	1.39±0.60
$V(Nb)_b$	2.66	2.75
He_I	2.50	3.15±0.34
$He(Cu)_b$	3.94	4.00
$He(Nb)_b$	3.14	3.45
$HeV(Cu)_I$	2.07	
$HeV(Nb)_I$	2.73	2.74±0.14
$HeV(Cu)_b$	2.52	2.82
$HeV(Nb)_b$	4.27	3.56

[1] MJ Demkowicz & L. Thilly, Acta Materalia **59** 7744 (2011)

Cu/W a)pNW b)GI IFs

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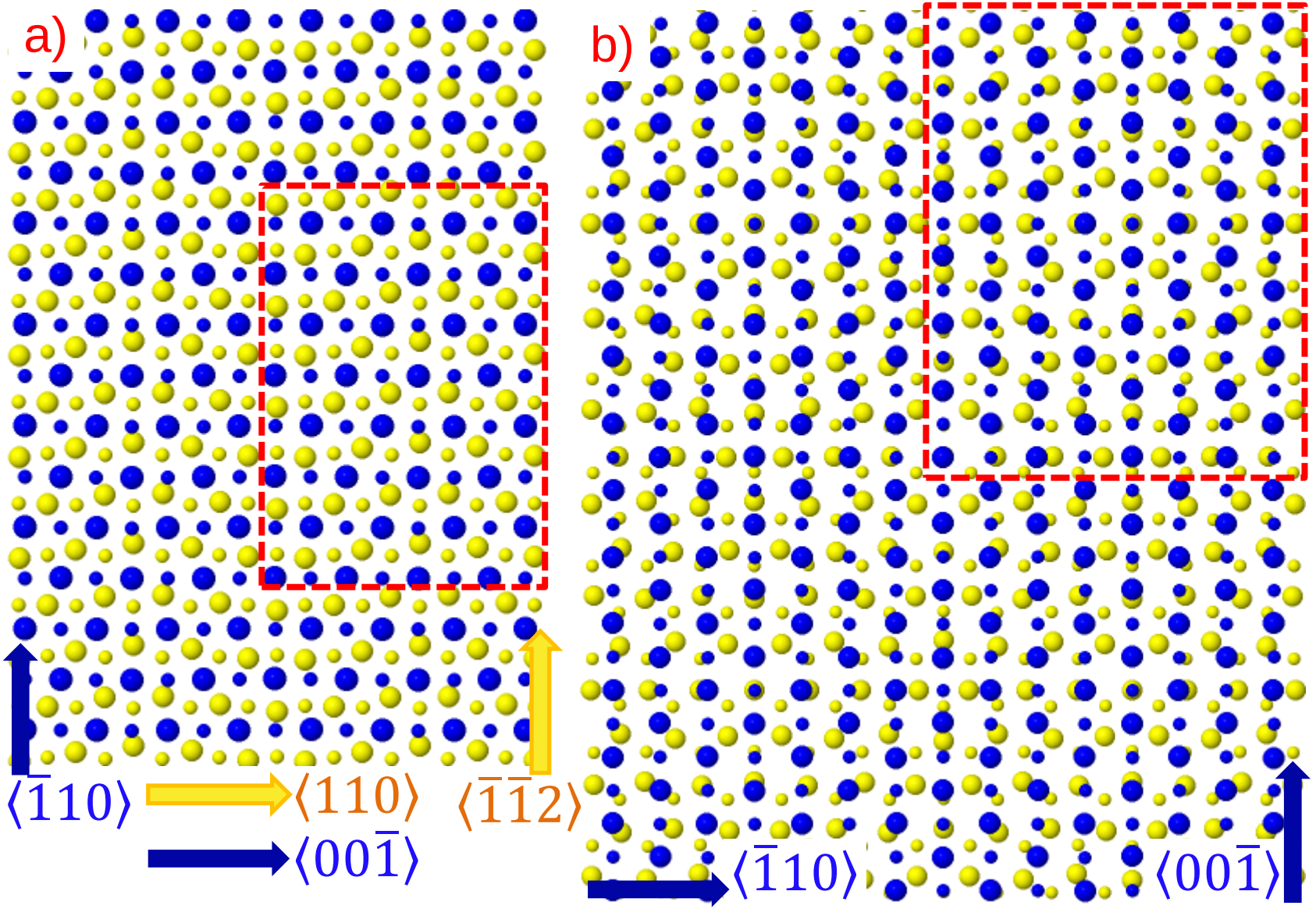

Cu/W a)pNW b)GI IFs

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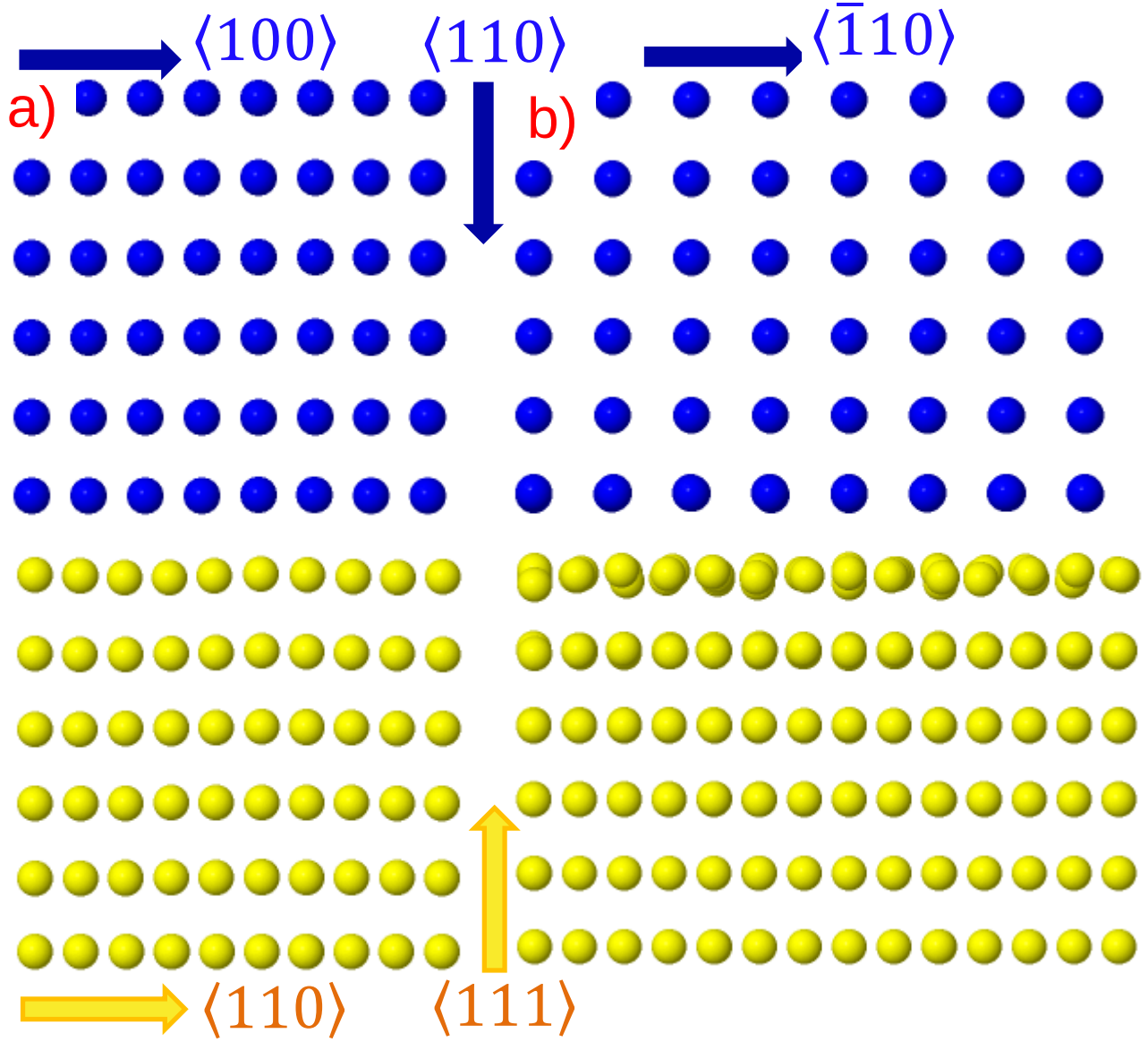

- 6 layers of each metal
- 240 (420) Cu at
- 192 (336) W at
- 9 kpoints in the 1BZ of the surface
- Last layers kept fixed to simulate bulk behaviour
- Strong reconstruction for GI, corrugation Cu/W 0.43/0.10 Å
- p-NW corrugation Cu/W 0.10/0.03 Å

Cu-W IF relaxation (upside view)

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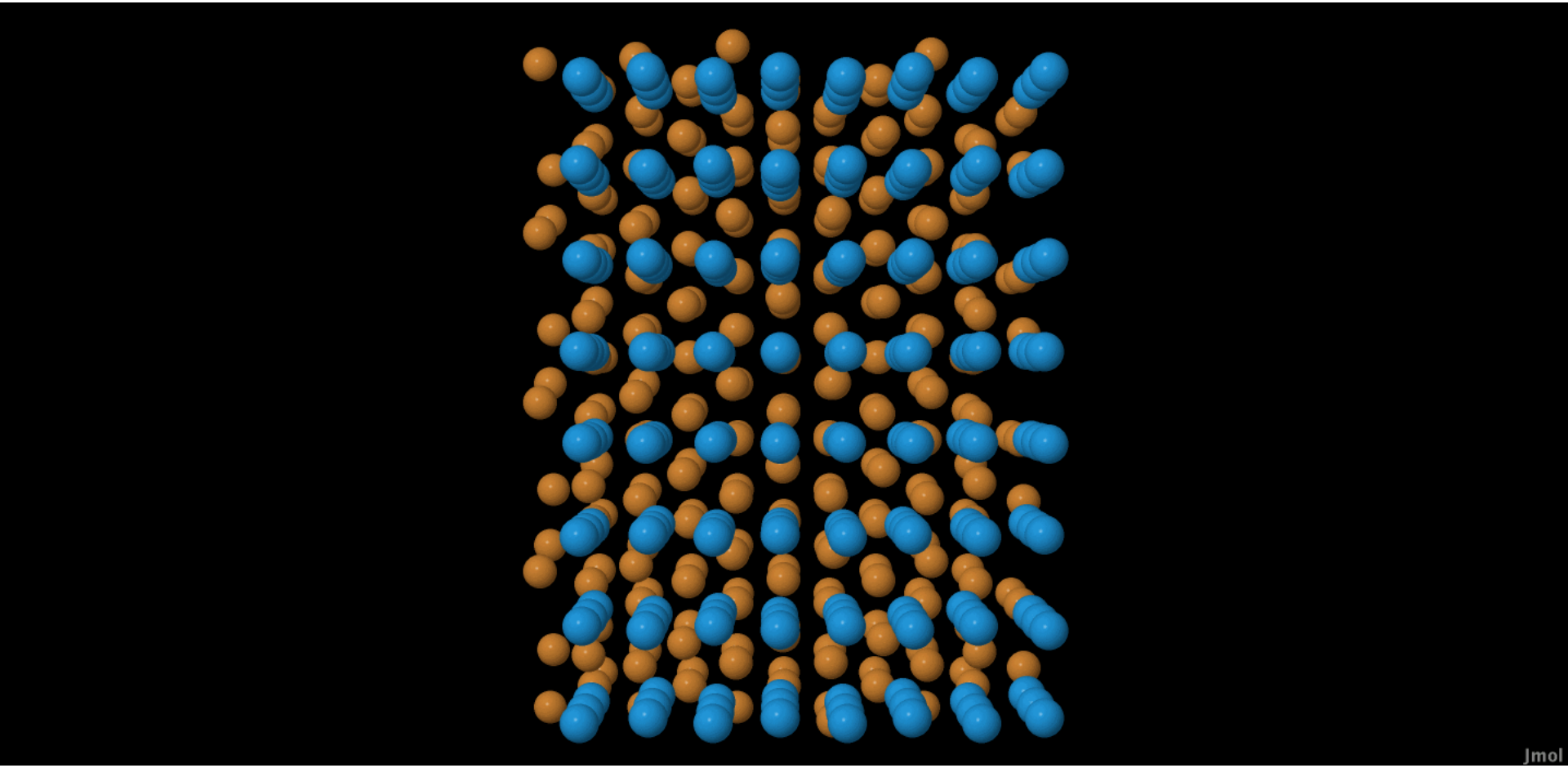

González/Iglesias 2016

Cu-W IF relaxation (side view)

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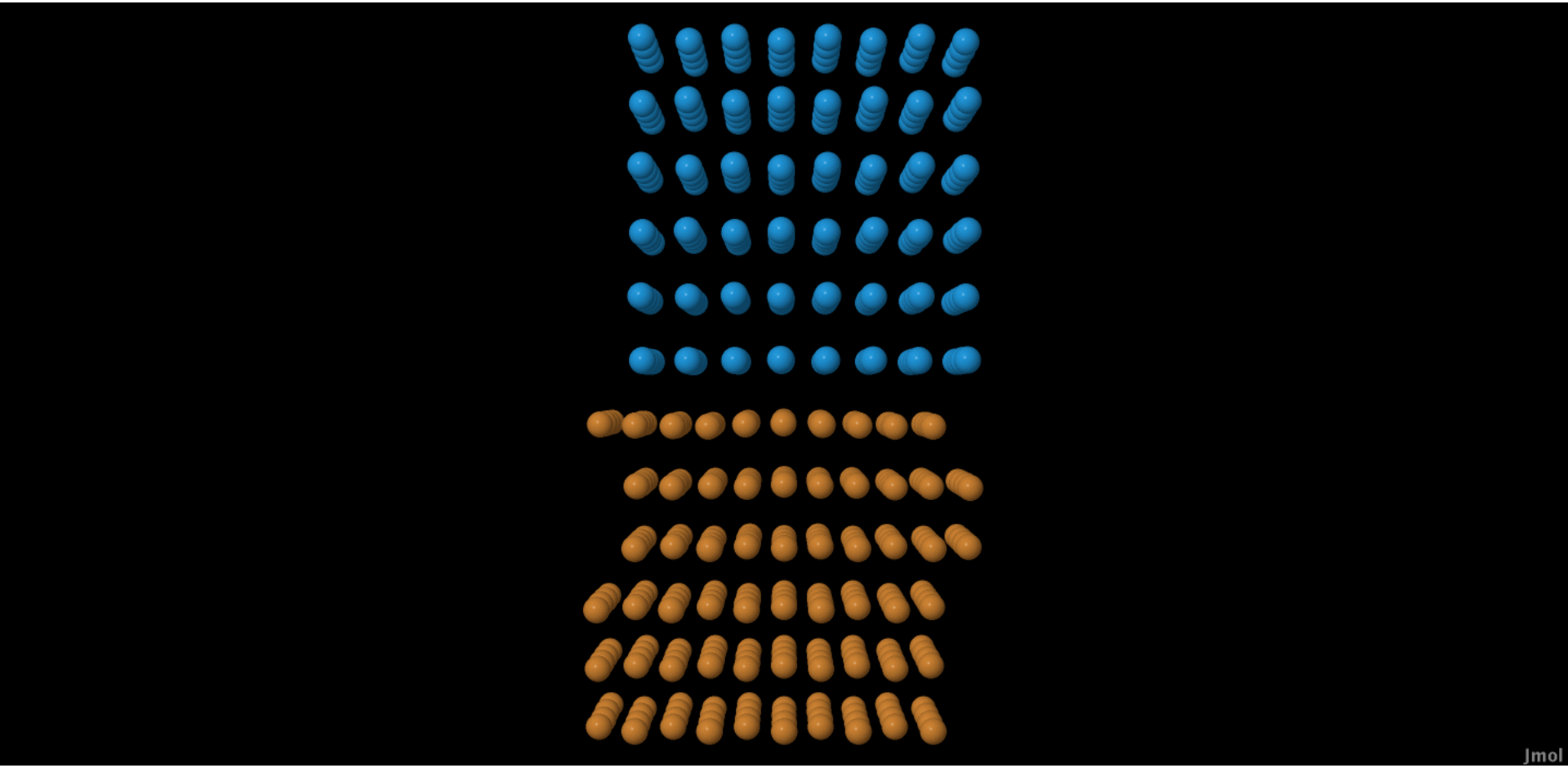

González/Iglesias 2016

Cu/W a)pNW b)GI IFs

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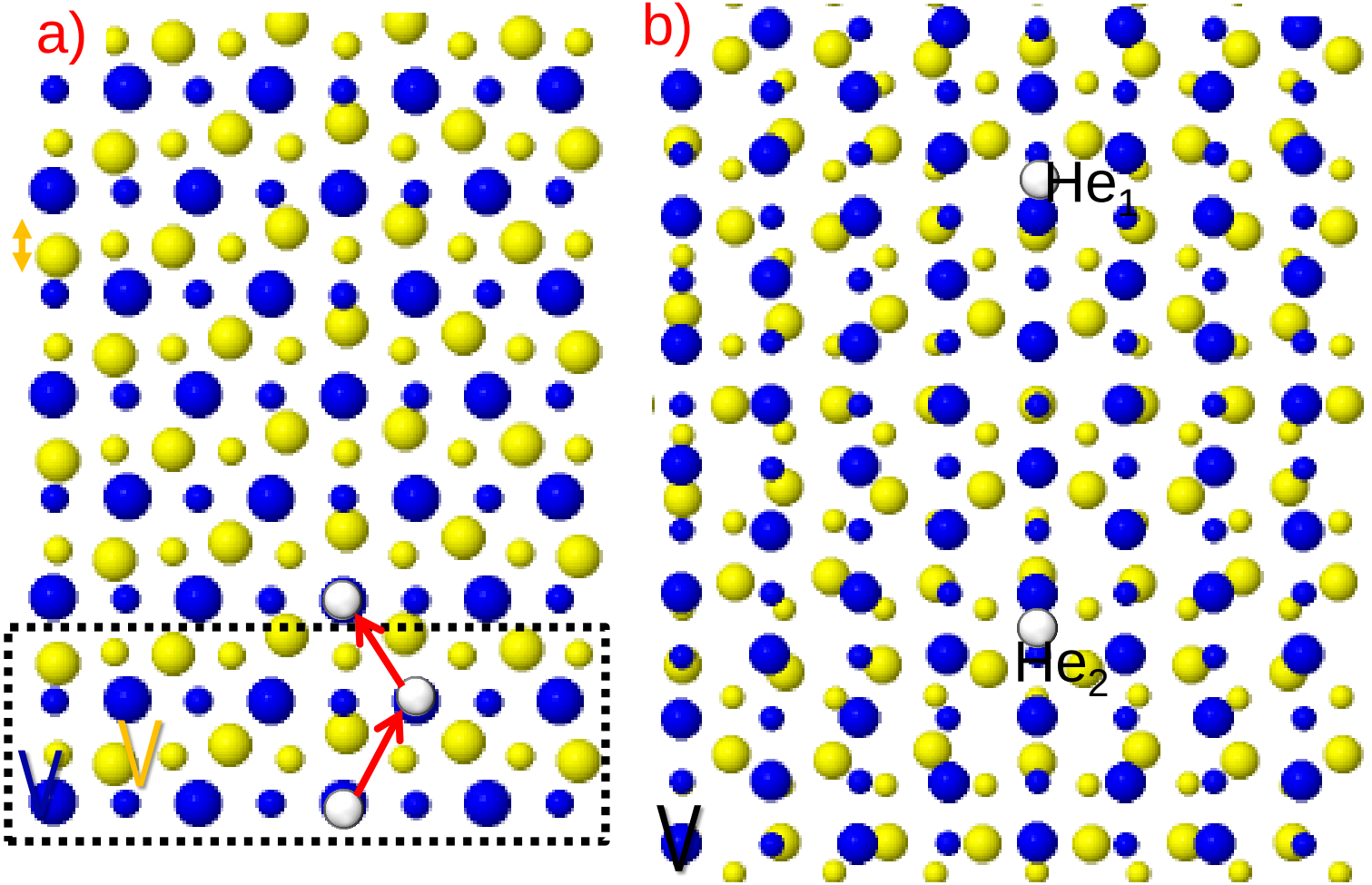
Most stable He and V sites

Atomic shift Cu atoms



- Plane structure => No MIDIs
- Low corrugation in Z direction
- Strong corrugation in Cu<112> direction.
- He atoms closer to the Cu layer by more than 1eV

Cu-W IF He10-hol-fcc (left view)

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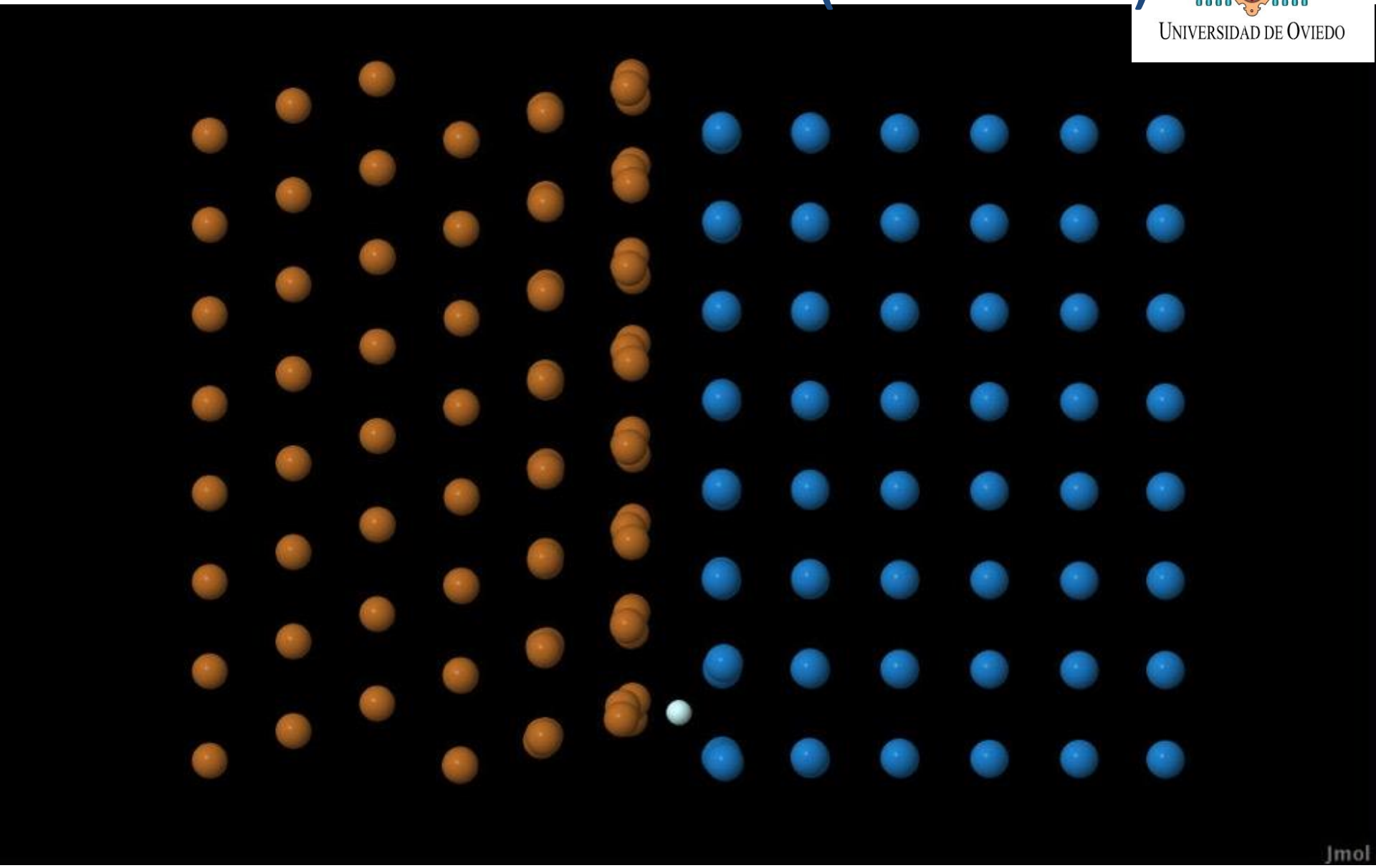

Cu/W IFs: defects at 2layer

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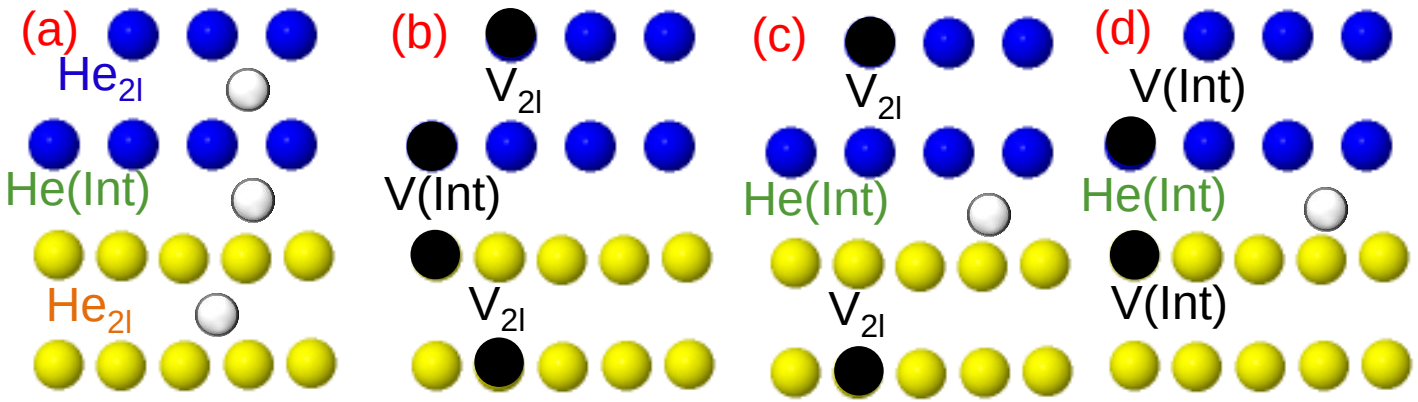


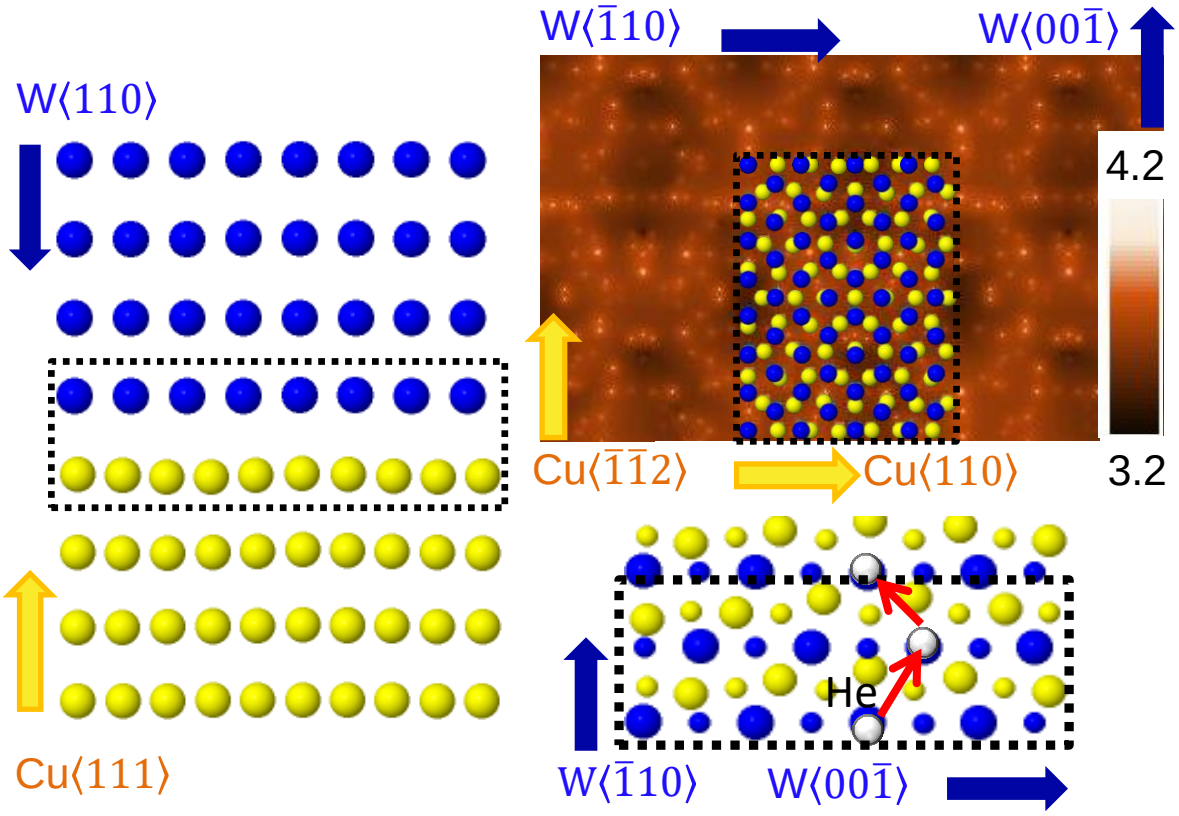
Formation energies of a He atom or a metallic Cu or W vacancy at the perfect metallic bulk, He(bulk) and V(bulk), at the second layer, He_{2I} and V_{2I}, and finally at the interface, He(Int) and V(Int). Cu1/W1 and Cu2/W2 refer to the first (p-NW) and second (GI) interfaces described in the text above. Values with an * correspond to the compressed Cu bulk.

E_f(eV)	He(bulk)	V(bulk)	He_{2I}	V_{2I}	He(Int)	V(int)
Cu1	4.30*	0.94*	2.67	0.82	2.70	−0.61
Cu2	3.95	1.08	3.90	1.00	3.31	0.50
W1	6.16	3.16	4.95	3.10	2.70	2.18
W2	6.16	3.16	–	3.14	3.31	1.40

Formation energies for different combinations of He atoms in Cu/W vacancies in the bulk, HeV(bulk), second layers, HeV_{2I}, or at the interface, HeV(Int). Cu1/W1 and Cu2/W2 refer to the p-NW and GI interfaces described in the text above. Additionally, we include the situation with a He atom and a vacancy that lie separated at the interface, V(Int)He(Int). Values with an * correspond to the compressed Cu bulk.

E_f(eV)	HeV(bulk)	HeV_{2I}	V_{2I} + He(Int)	HeV(Int)	V(Int)He(Int)
Cu1	2.57*	2.64	3.62	1.54	3.60
Cu2	2.54	2.57	4.35	2.05	3.94
W1	4.75	3.77	5.98	3.53	4.77
W2	4.75	4.83	6.47	3.21	4.61

Cu/W IFs: energetic maps



- He migrates through the p-NW IF (planar)
- He trapped in the GI IF (great perpendicular corrugation as Cu/Nb-KS)
- Strong influence of OR
- p-NW candidate to build up metallic MLs

W(112)/W(110) IFs

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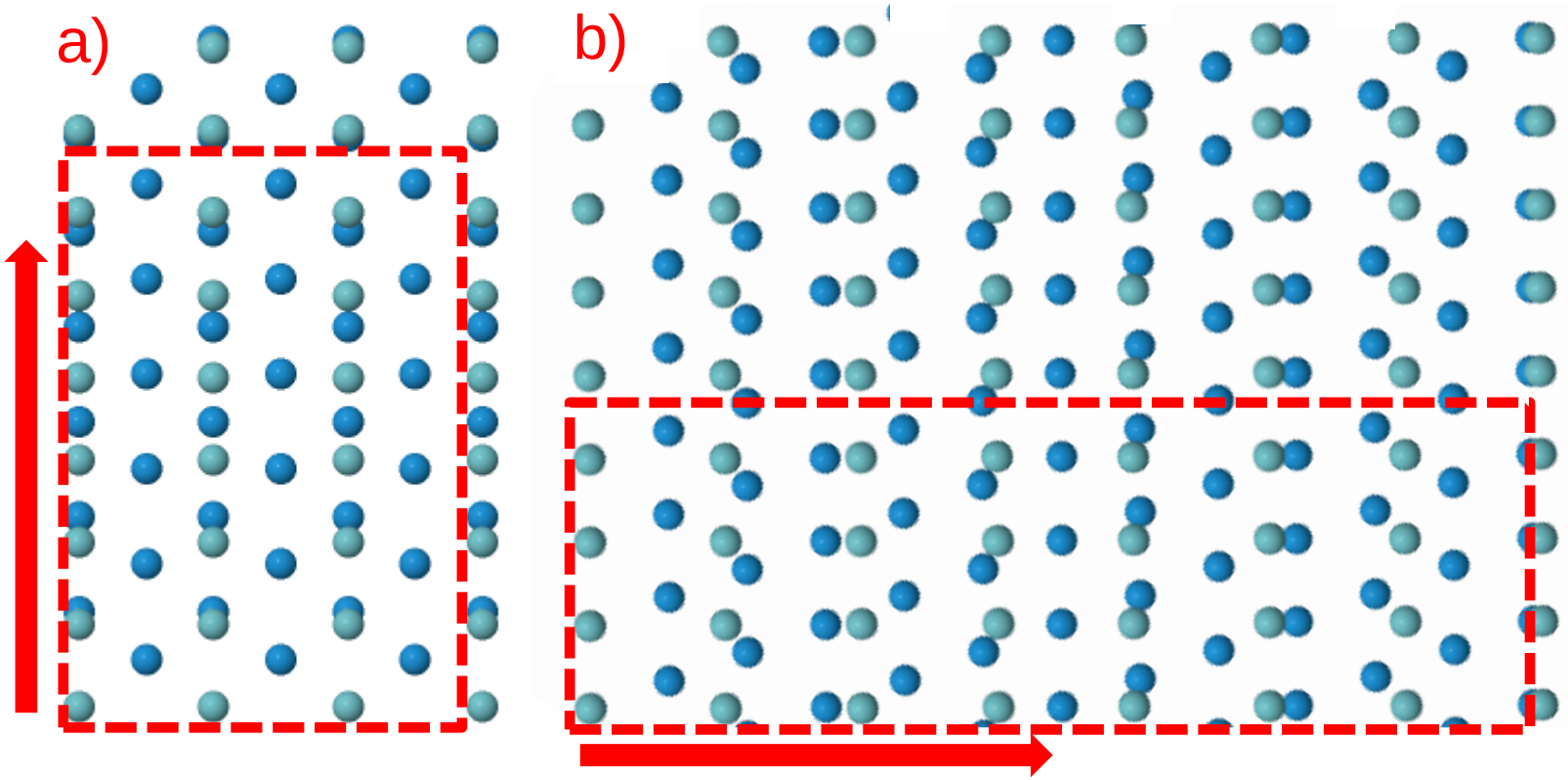

- b) rotated 55° w. r. t. a)
- (112) expanded by 1% along red arrows due to non-coherency
- Red dotted lines: 2D cells accessible to DFT
- IF b) used subsequently

W(112)/W(110) IFs: lateral view

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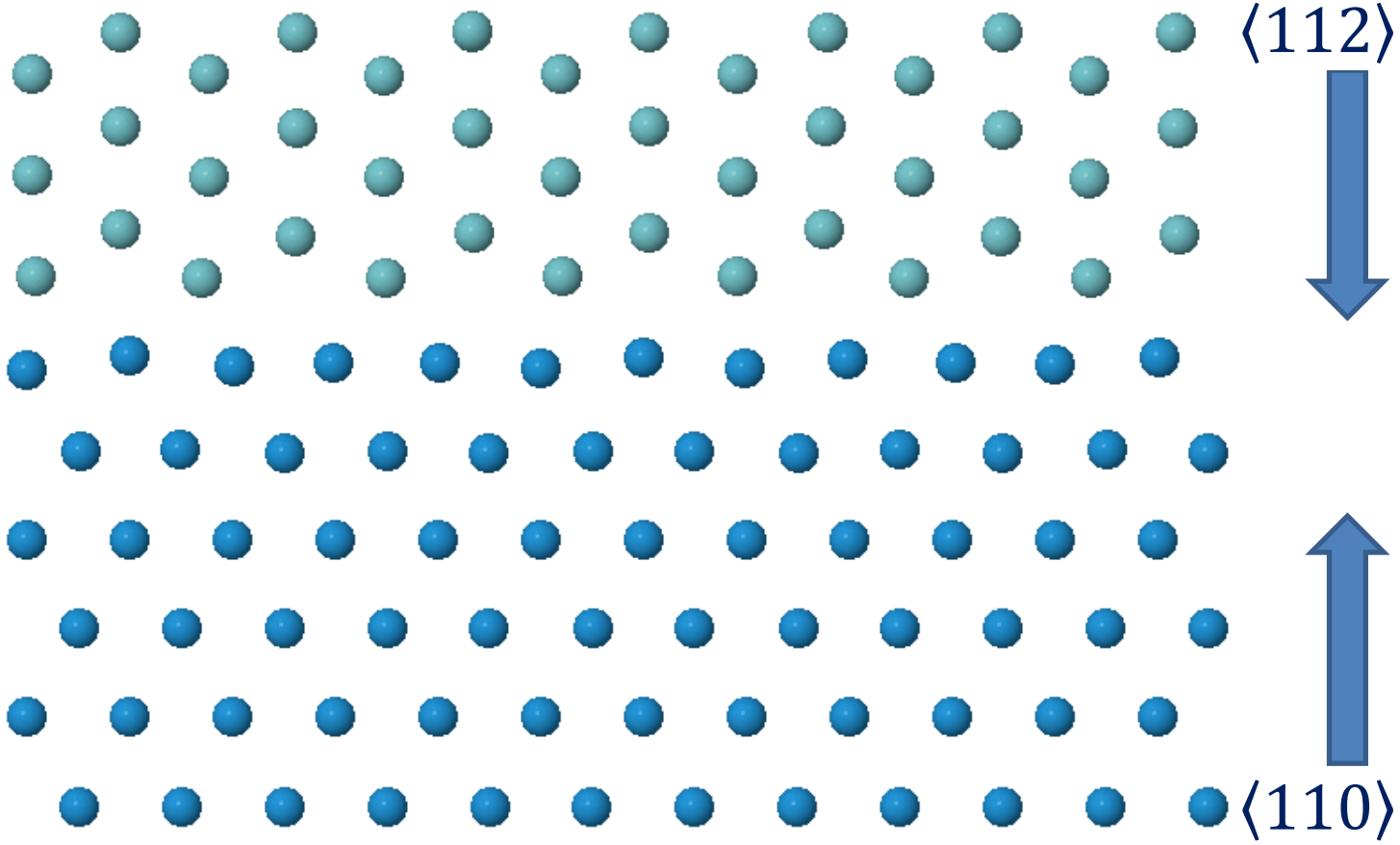

- 6 layers of each metal
- 288 (110) and 168 (112) W atoms, total 456
- 8 kpoints in the 1BZ of the surface
- Last layers kept fixed to simulate bulk behaviour
- Corrugations (110)/(112) 0.38/0.06 Å
- Decrease in the next layers of (110)/Increase for (112)

W(112)/W(110) IFs: H+vacancy

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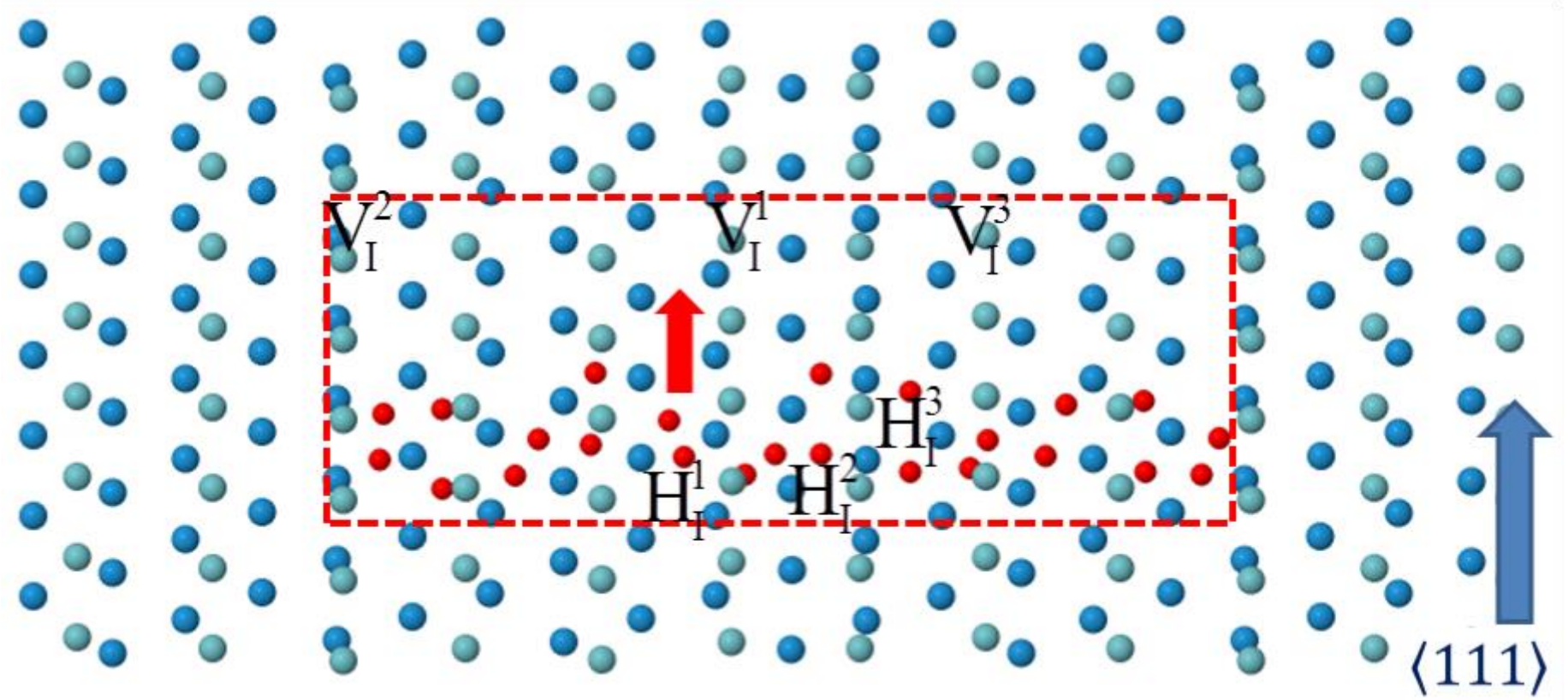

- Red dotted line: 2D cell used
- Red spheres: sites where H has been absorbed
- 3 most stable H positions shown
- H prefers to move to the less corrugated (112) surface
- 3 most stable V positions shown

W(112)/W(110) IFs: lateral view

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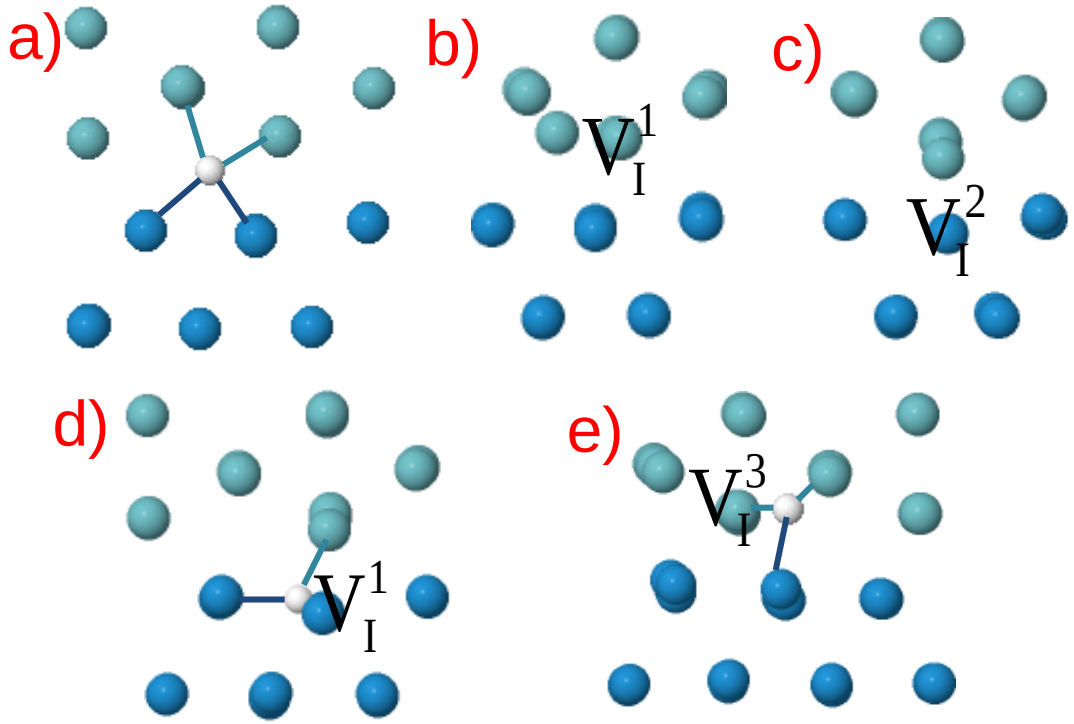

- a) Atomic reconstruction around the most stable H position
- b) and c) the same for vacancies at (112) and (110)
- d) and e) most stable H positions for vacancies V_I^2 and V_I^3

W(112)/W(110) IFs: energetics

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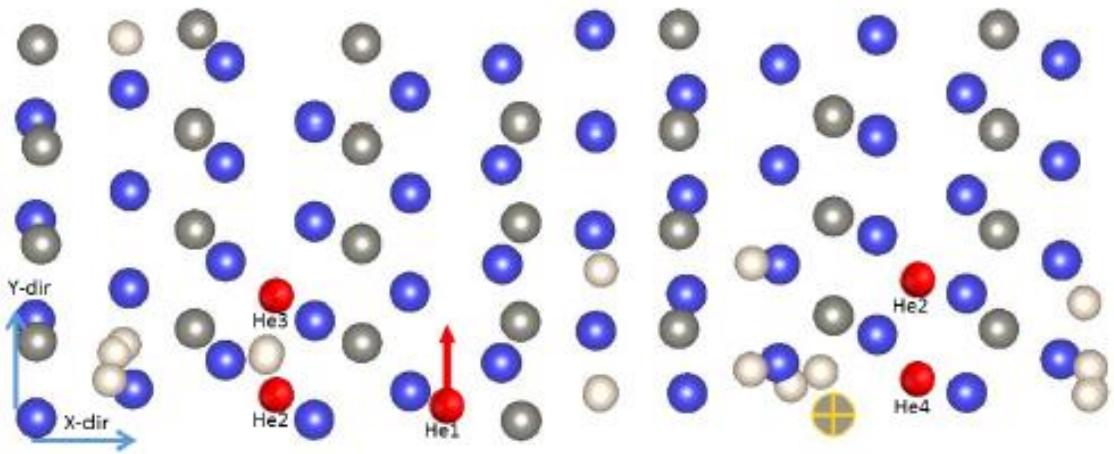
Table 1. Formation energies (in eV) of one H, one vacancy (V) and one H in a vacancy (HV) for the three most stable cases obtained at the interface (Int) as compared to bulk results (bulk) and other works (Int-bib and bulk-bib).

	Int[1, 2, 3]	Int-bib	Bulk	Bulk-bib
$E_f(H)$	− 0.09,−0.07,−0.05	− 1.73,−0.13 [49]	0.96	0.85 [49]
$E_f(V)$	1.51, 1.57, 1.64	3.66, 2.36 [35]	3.16	3.11 [63], 3.52 [58]
$E_f(HV)$	1.44, 1.21, 1.20	—	2.80	2.86 [59, 60]*
$E_S(H)$	− 0.09,−0.07,−0.05	− 0.23 [31]	0.96	0.89 [31]
$E_S(V)$	− 0.05,−0.35,−0.42	− 0.63 [31]	− 0.25	− 0.31 [31]

Note: The 1, 2, 3 indices identify the corresponding three cases analyzed here for H, V and HV. *The value was estimated combining the energies presented in both works.



	E_f(eV)			
	Interface	bulk	V-interface	V(bulk)
He1	3.07	6.25	3.33	4.65
He2	6.08	11.54	5.69	7.67
He3	9.04	16.34	8.21	10.76
He4	11.90	20.99	10.74	13.74
He5	14.80	26.86	13.09	17.75
He6	17.65	32.06	15.24	21.21
He7	20.25		17.85	25.20
He8	23.41		20.55	28.99
He9	26.20		23.17	33.12

Publications

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- C. González, R. Iglesias and M. J. Demkowicz, Point defect stability in a semicoherent metallic interface. Phys. Rev. B 91 (2015) 064103
- C. González, R. Iglesias et al., H trapping and mobility in nanostructured tungsten grain boundaries: a combined experimental and theoretical approach. Nucl. Fusion 55 (2015) 113009
- C. González and R. Iglesias, Energetic analysis of He and monovacancies in Cu/W metallic interfaces. Mater. Design 91 (2016) 171
- C. González and R. Iglesias, He accumulation in a W grain boundary. Mater. Design, in preparation.

Conclusions and future work

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- Cu/Nb, Cu/W and W/W interfaces analyzed via DFT
- Strong reconstruction but no interatomic mixing
- Defects formed preferentially in the areas of 1-2 atomic coincidence (MDIs)
- Defects prefer the interface instead of the bulk
- He prefers the vacancy instead of the interface
- Defects have to cross high barriers in the interface
- More cases should be studied: SIAs, H in Cu/X, He in W/W and vacancy clusters