start

Quantum chemical calculations and MD simulations for Be

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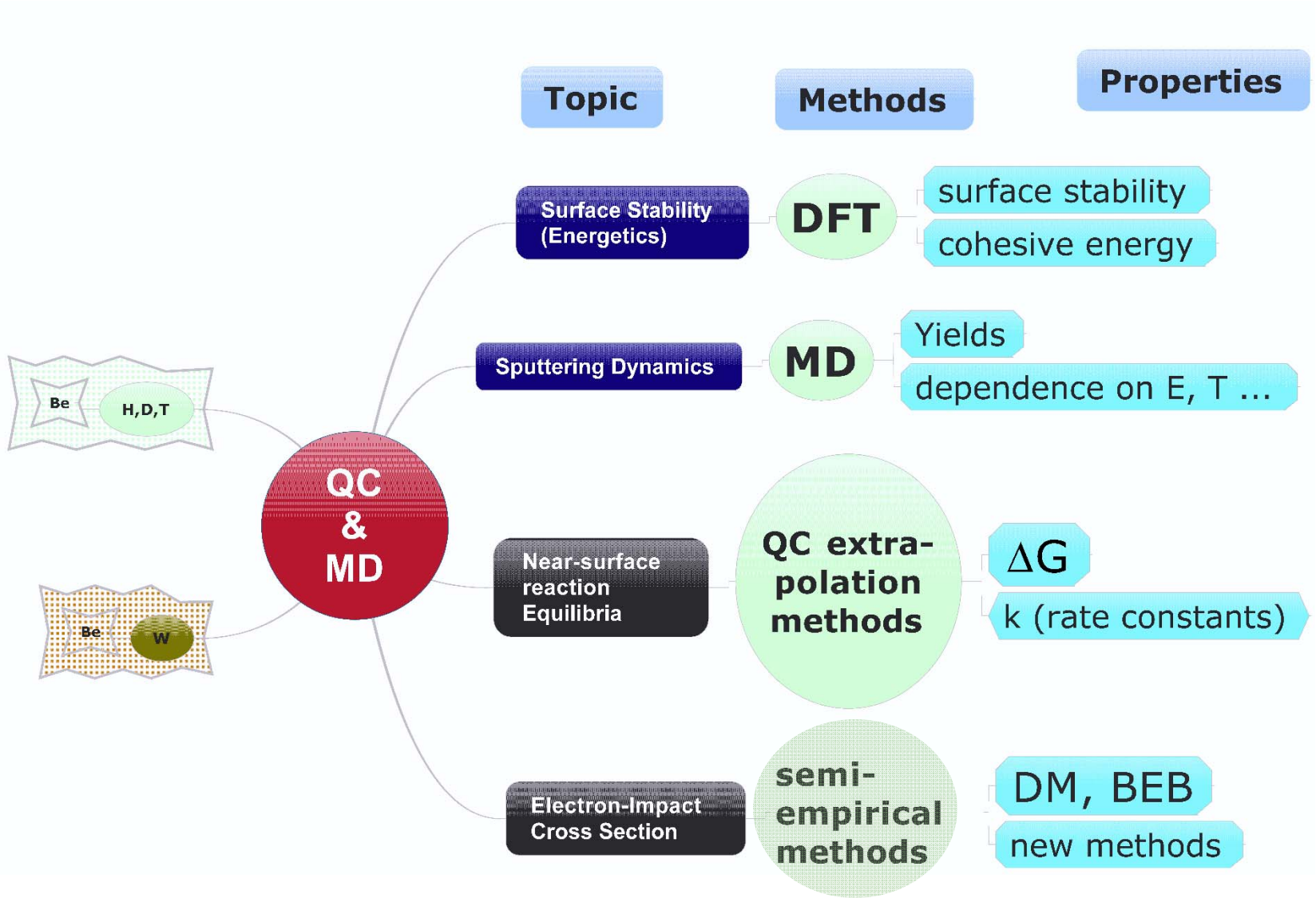
Be-CRP IAEA VIE June 15-20 2016


Topic
Methods
Properties
Surface Stability (Energetics)
DFT
surface stability
cohesive energy
Sputtering Dynamics
MD
Yields
dependence on E, T ...
Be
H,D,T
QC & MD
Be
W
Near-surface reaction Equilibria
QC extra-polation methods
ΔG
k (rate constants)
Electron-Impact Cross Section
semi-empirical methods
DM, BEB
new methods

1 Electron impact ionization cross sections (EICSs)

Electron impact ionization cross sections of beryllium-tungsten clusters

Ivan Sukuba, Alexander Kaiser, Stefan E. Huber, Jan Urban, Michael Probst

Eur. Phys. J. D (2016) 70: 11.

Last meeting: Beryllium hydride cross sections.

We wanted to modernize the EICS calculations a little bit:

- use at least 2 independent methods (BEB and DM)
- work to incorporate a third method (optical potential)
- use good global geometry optimization algorithms
- extend the EICS to cover excited states / ionic states

Example: BeW results.

DM:

- $\sigma_{DM}(u) = \sum_{n,l} g_{nl} \pi \boldsymbol{r_{nl}^2} \xi_{nl} b_{nl}^{(q)}(\boldsymbol{u})[\ln(c_{nl}\boldsymbol{u})/\boldsymbol{u}]$

$$b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2$$

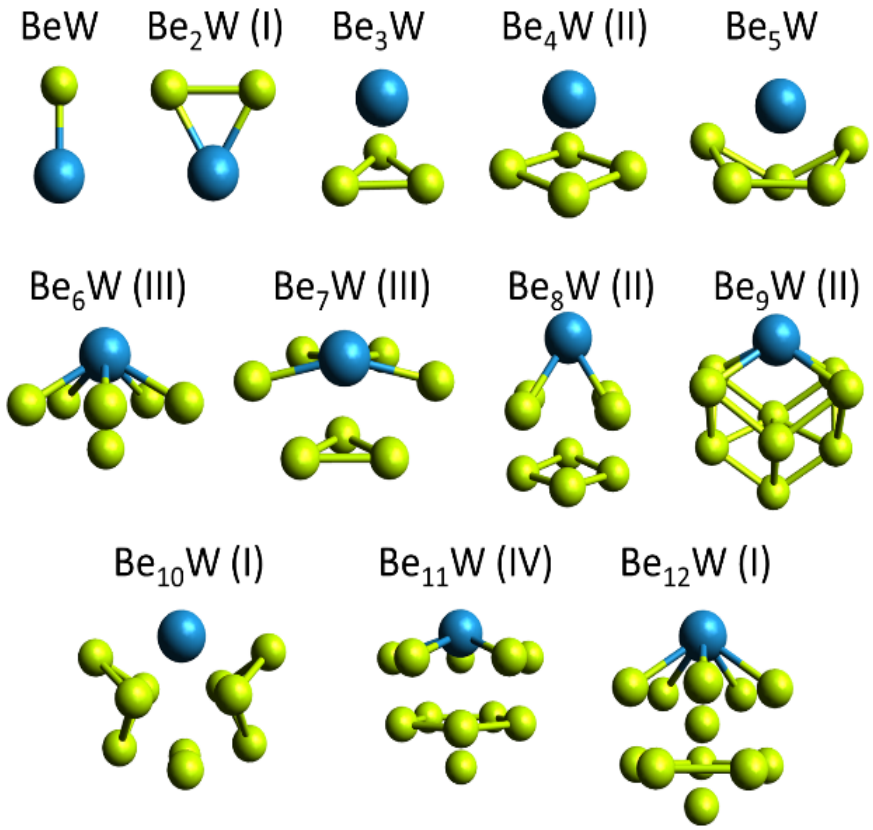
BEB:

- $\sigma_{BEB}(t) = \frac{S}{t+(u+1)/n}\left[\frac{\ln(t)}{2}\left(1 - \frac{1}{t^2}\right) + 1 - \frac{1}{t} - \frac{\ln(t)}{t+1}\right],$

$$\boldsymbol{t = T/B},\ \boldsymbol{u = U/B},\ S = 4\pi a_0^2 N R^2/B^2$$

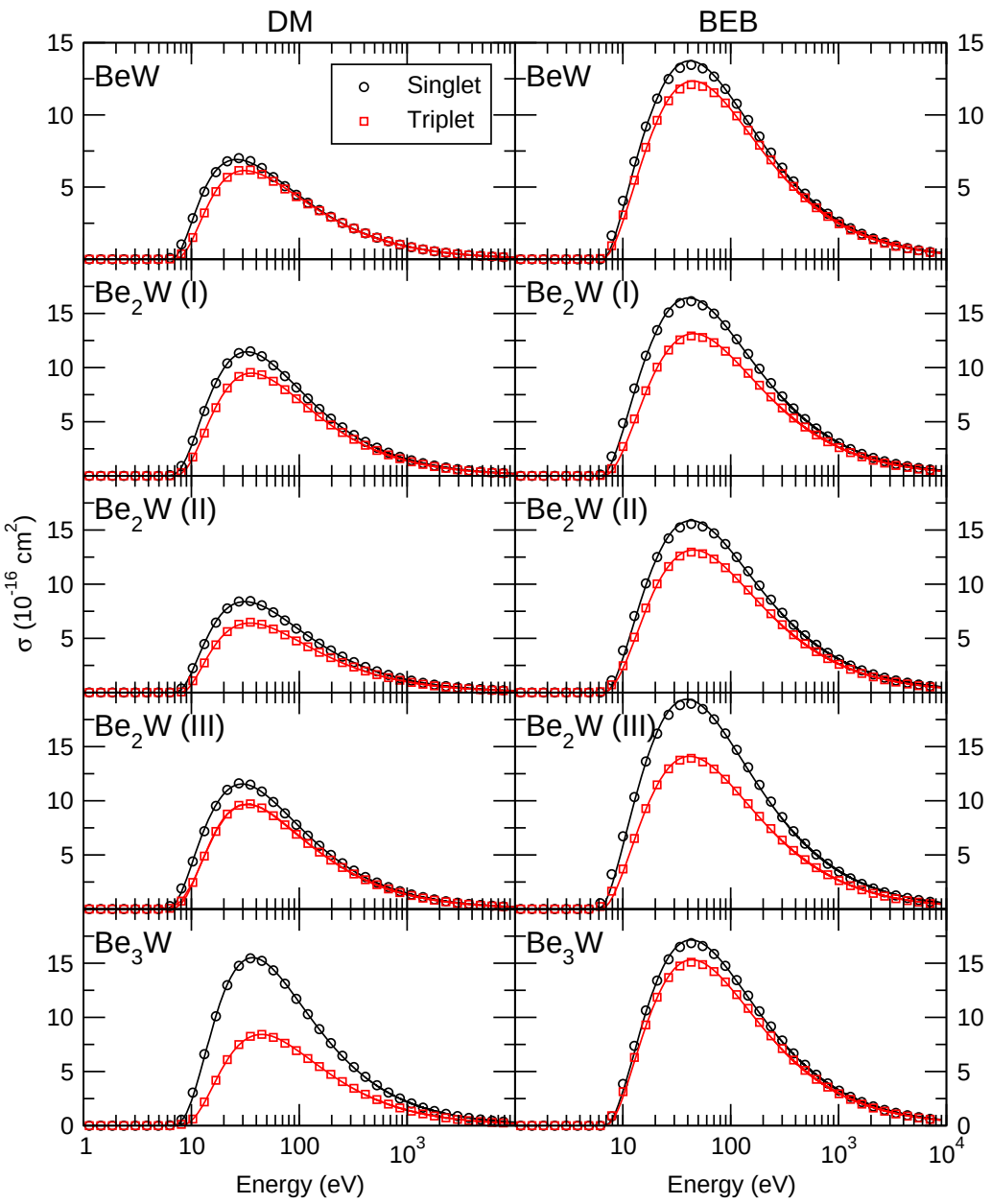
From QC calculations

- Be_nW cluster, n=1-12, all singlet states
- Optimization by simulated annealing (Born-Oppenheimer molecular dynamics with TURBOMOLE)



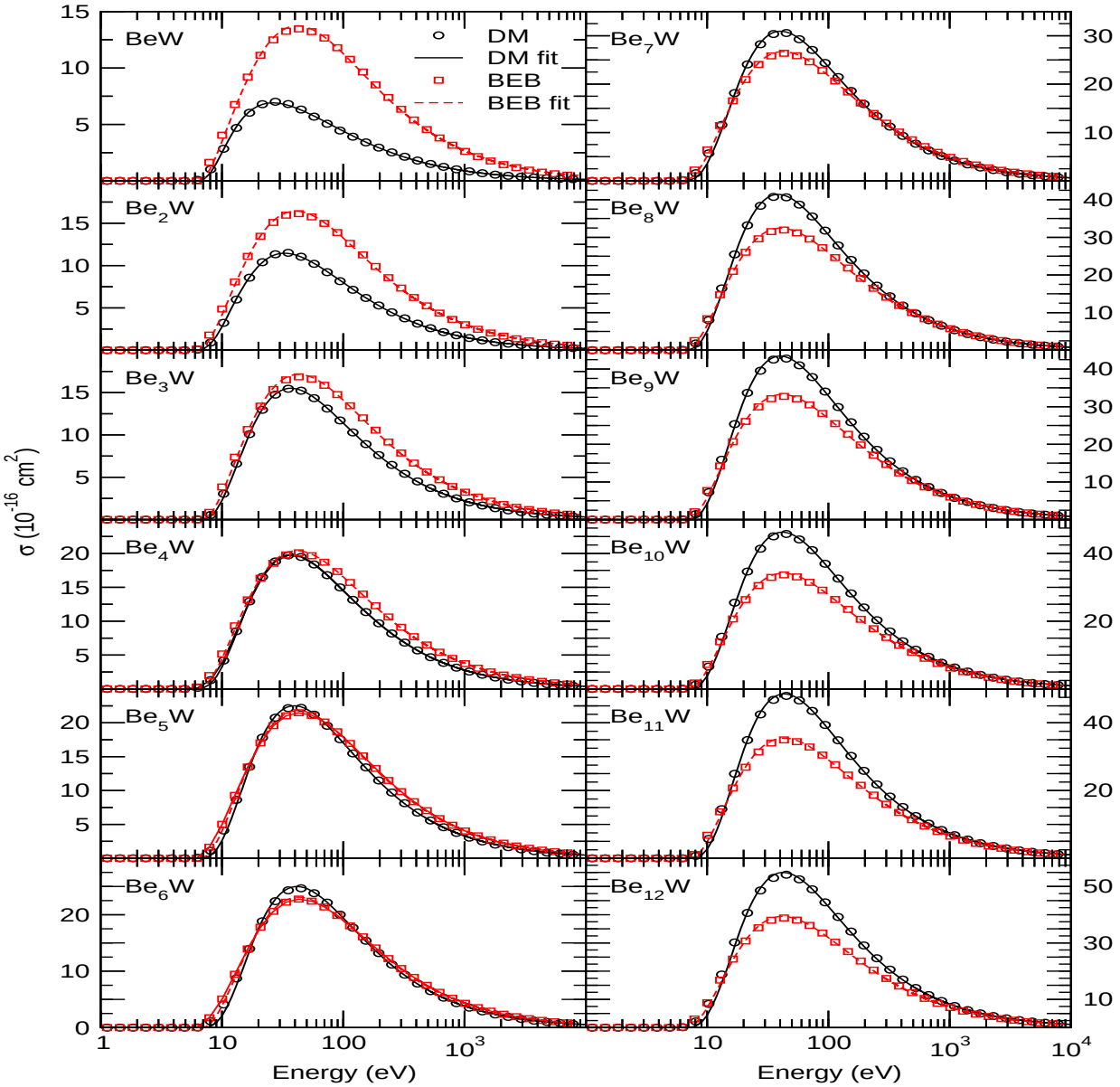
Be_nW cluster, n=1-3

Cross sections for S and T spins:

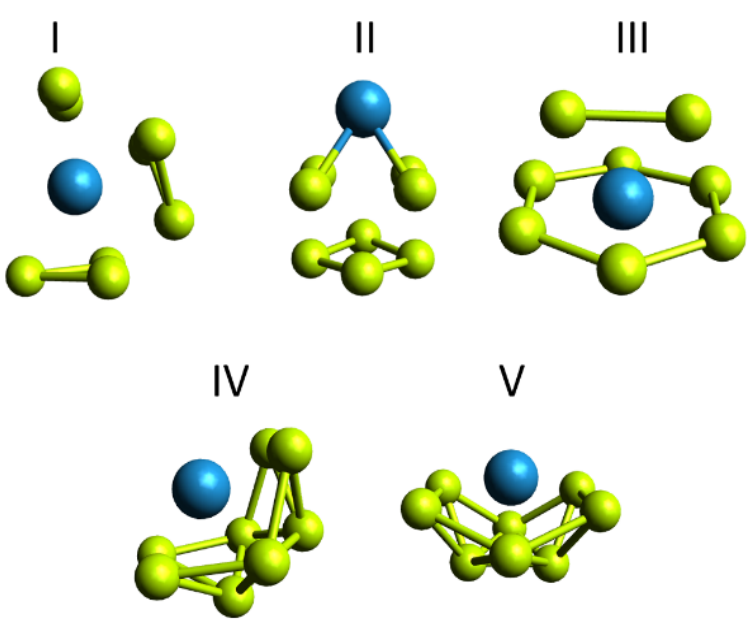


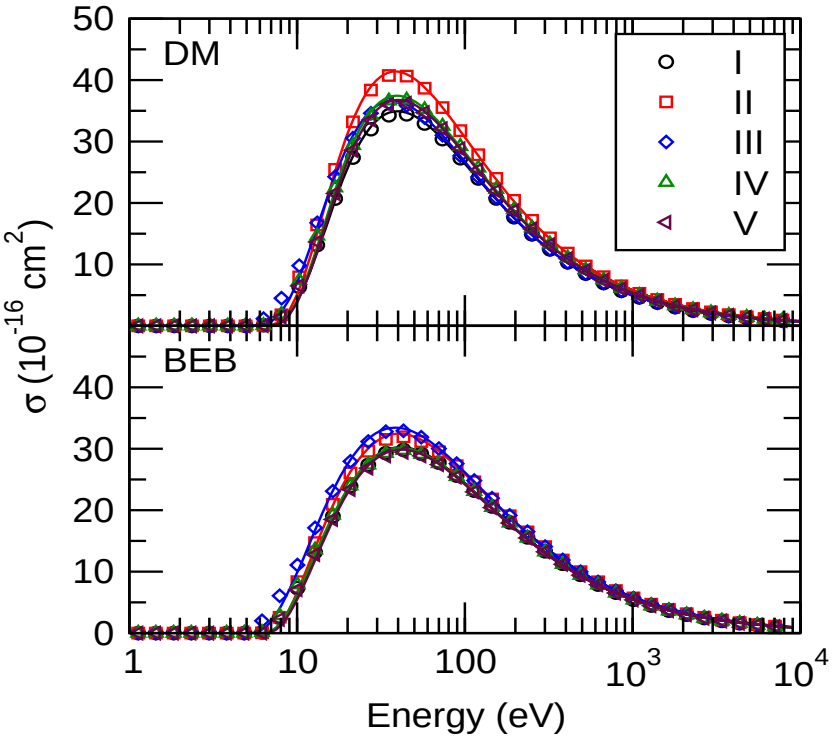
Be_nW cluster, n=1-12

Cross sections:



- In Be_8W, different geometries are close in energy. Their cross sections are similar to each other:





2 MD of Be-D sputtering

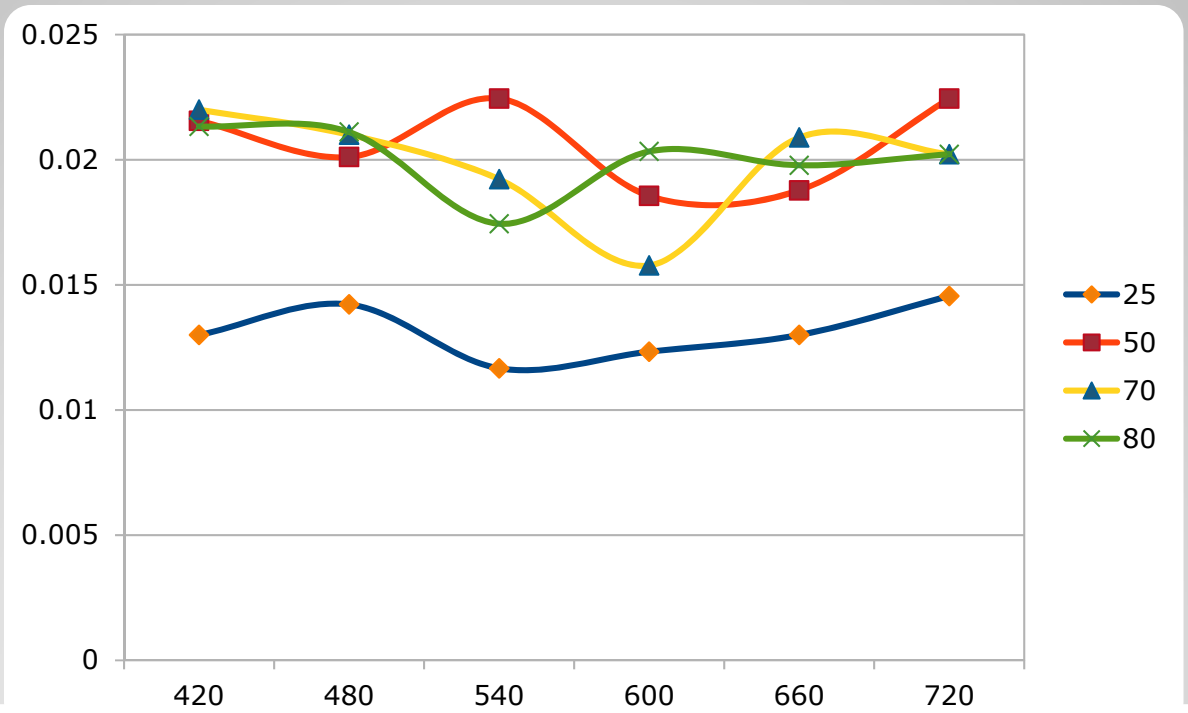
(Ivan Sukuba et al.)

Sputtering yield as a function of the temperature of a Be surface

hcp - Be surface (0001), 32x32x45(60)A^3
~4700 atoms for 25 and 50 eV impact energies and
~6300 atoms for 70 and 80 eV energies.
9000 impacts .

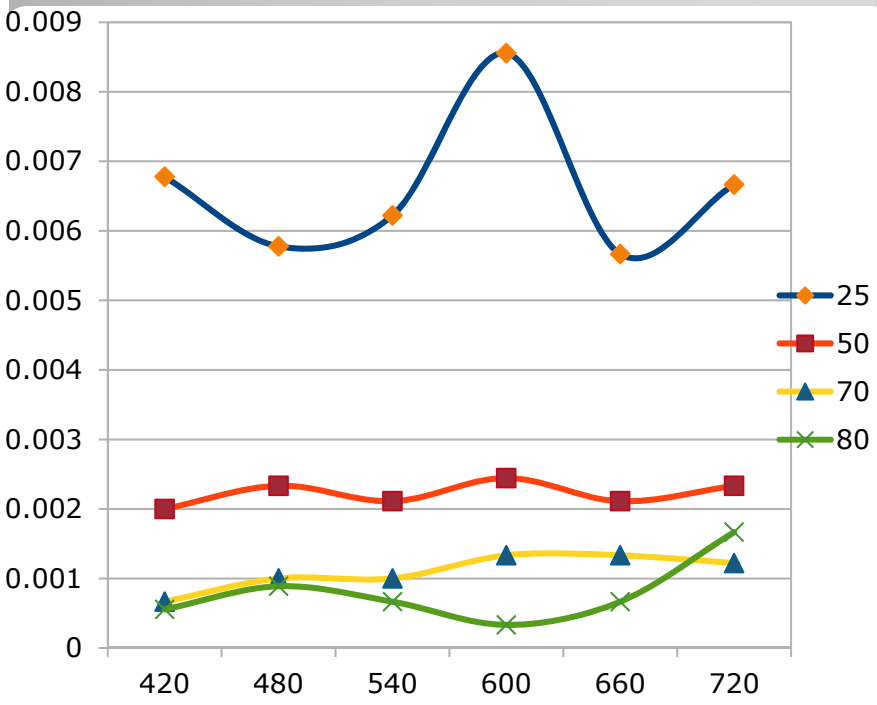
Sputtering yield as a function of the temperature of a Be surface

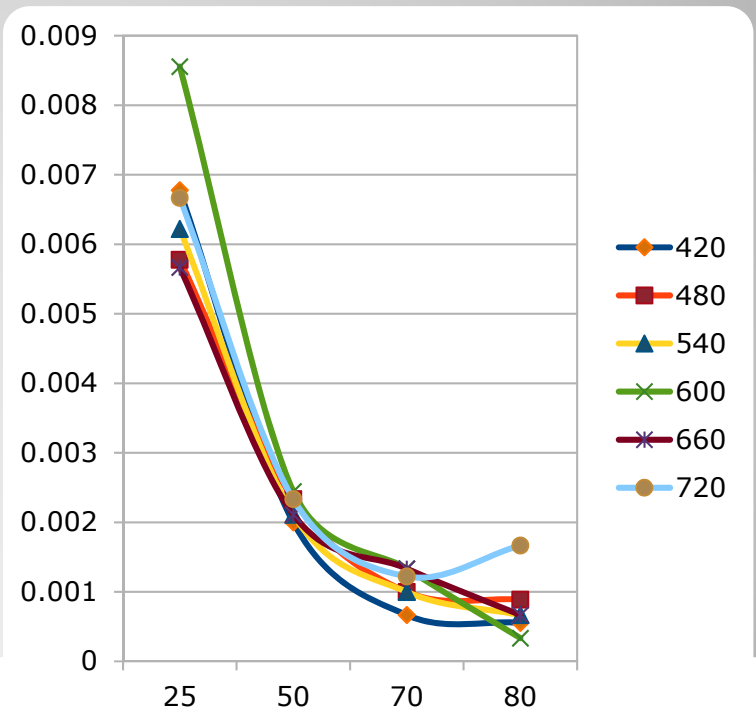
1) Be sputtering. 9000 non-cumulative events
Impact energies: 25, 50, 70, 80 eV



Sputtering yield as a function of the temperature of a Be surface

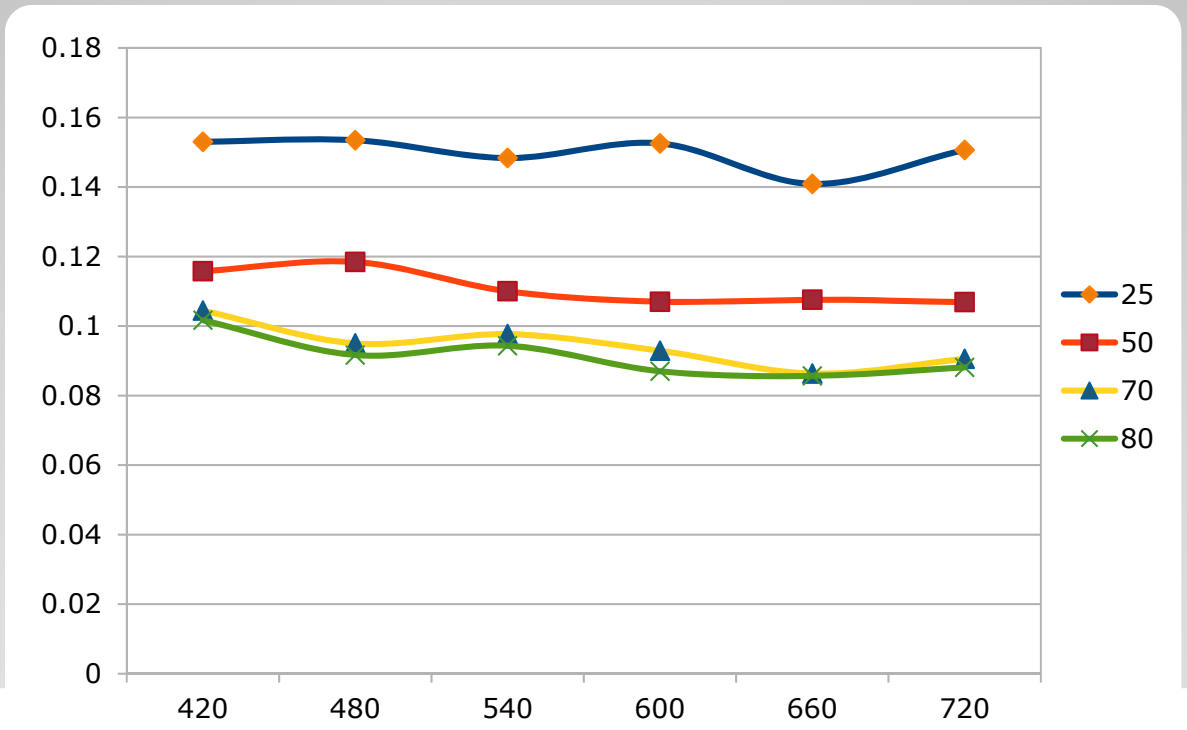
1) BeD sputtering. 9000 non-cumulative events
Impact energies: 25, 50, 70, 80 eV





Sputtering yield as a function of the temperature of a Be surface

1) D reflected. 9000 non-cumulative events
Impact energies: 25, 50, 70, 80 eV



Sputtering yield as a function of the temperature of a Be surface

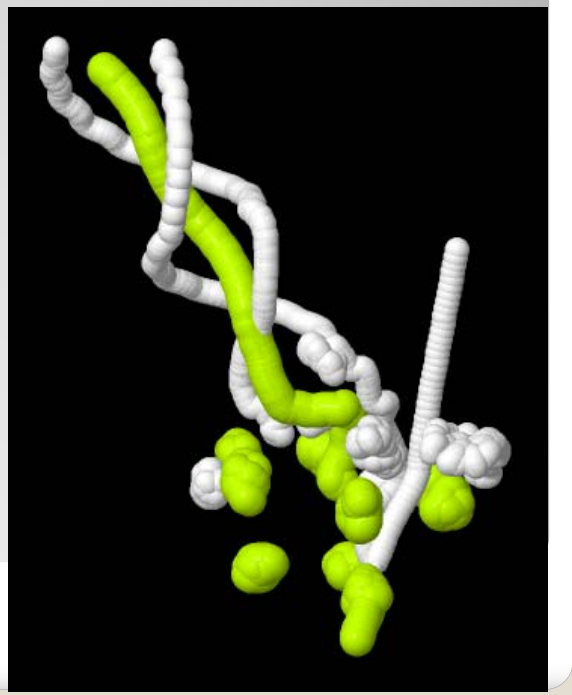
For D, Be and BeD leaving the surface there is little, if any effect of the surface temperature T, at least if T is in the range 420 to 720K.

Compare:
1eV corresponds to 11000K
Be boils at 3240K (cohesive energy)

Experiments show a definite T-dependence
Mechanism of T influencing sputtering ?

Further MD-related works:

- surface dependence trajectory analysis



3 Stability of BeH molecules

Reaction Thermodynamics
$Be \leftrightarrow BeH \leftrightarrow BeH_2$
and other equilibria

Alexander Kaiser
Ivan Sukuba
Stefan Huber
Michael Probst

Not yet published

Calculations:

- ΔG_f und ΔH_f – values
  (free formation energies and - enthalpies)
  for various neutral, cationic and anionic Be_xH_y – species.
- $\Delta\Delta G$ – values (free energies of ***reactions***) and equilibrium constants at different temperatures for the various interconversion reactions of neutral and ionic Be_xH_y – species have been calculated.
- This gives the equilibrium concentrations of these molecules
- The electron-impact cross sections of these molecules have also been calculated.

What we aimed for:

Stability analysis

Enthalpy and Free energy of reactions

Transition states (in progress)

Rate constants for various BeD_2 and BeD_3 channels

Ab initio methods:
Accuracy of the G4 method of theory is very good!
also CCSD, QCISD

Basic formulas:

$\Delta G = \Delta G^0 + RT \ln(Q_r) = RT \ln(Q_r/K_{eq})$

Q_r … reaction quotient
- initial concentrations

Sputtering yields from MD simulations and experiments (not used yet, but data available)

$\ln(Q_r/K_{eq})$ determines the direction of the reaction

Eyring equation for rate constants
$k(T) = k_B T / h \exp(-\Delta G^{\ddagger}/RT)$

All values are calculated

Motivation

Discrepancies between MD results and experiment at high temperatures (500 K)

Data for ERO (need for data in general)

Explanation of reactivity of BeD_2 and BeD_3

BeD_{1-3} molecules

Few experimental data

If, only for BeD (spectroscopic data)

Theoretical data only for BeD

Input to ∆G and k – calculations
QC data components:

BeH_298.15.log			8.31E-03	kJ/(MolK)
Eelec	-15.2667771		3.17E-06	Hartree/MolK
ZPE	0.003367			
TCEnergy	0.005733	ZPE+Evib+Erot+Etrans		
TCEnthalpy	0.006677	0.00668	ZPE+Evib+Erot+Etrans+RT	
TCGibbs	-0.01407			
Eelec+ZPE	-15.26341			
Eelec+Thermal Energy	-15.261044	-15.26104	Eelec+TCEnergy	
Eelec+thermal Enthalpy	-15.2601	-15.26010	Eelec+TCEnthalpy	
Eelec+thermal free energy	-15.280847	-15.28085	Eelec+TCGibbs	

The reaction network. Free energies as function of temperature

G4 reaction free energies ΔG_r^0 (Ochterski approach from gaussian calculations)

	1	2	3	4	5	6	7	8	9	10	11	12	13
K	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol	kJ/Mol
	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0	ΔG_r^0
T	**BeD →** **Be+D**	**BeD_2 →** **Be+D_2**	**BeD_2 →** **BeD+D**	**BeD_2 →** **Be+2D**	**BeD^- →** **Be + D^-**	**BeD^- →** **Be^- + D**	**BeD_2^- →** **Be + D_2^-**	**BeD_2^- →** **Be^- + D_2**	**BeD_2^- →** **Be + D + D^-**	**BeD_2^- →** **Be^-+2 D**	**BeD_2^- →** **BeD^- + D**	**BeD^- →** **Be + D + e^-**	**BeD_2^- →** **Be + D_2 + e-**
0.00	207.58	159.43	393.56	601.14	237.98	282.14	479.74	154.44	551.99	596.15	314.01	273.51	145.81
100.00	202.52	148.48	380.10	582.61	233.07	276.08	472.77	148.79	539.92	582.93	306.84	268.03	140.74
200.00	195.72	135.26	364.37	560.09	226.44	268.30	462.89	140.30	523.27	565.13	296.83	260.82	132.82
298.15	188.42	121.56	348.20	536.62	219.30	260.03	452.10	131.03	505.37	546.10	286.06	253.12	124.12
300.00	188.28	121.29	347.89	536.17	219.17	259.87	451.89	130.85	505.02	545.73	285.85	252.97	123.95
400.00	180.43	106.93	331.01	511.43	211.52	251.08	440.19	120.89	485.83	525.39	274.31	244.75	114.56
500.00	172.29	92.36	313.88	486.16	203.63	242.03	428.02	110.62	466.02	504.42	262.39	236.28	104.87
600.00	163.94	77.66	296.59	460.52	195.57	232.82	415.53	100.16	445.78	483.03	250.21	227.65	94.99
700.00	155.43	62.89	279.18	434.61	187.38	223.48	402.79	89.59	425.20	461.30	237.82	218.88	84.99
800.00	146.80	48.10	261.69	408.50	179.10	214.05	389.88	78.94	404.39	439.34	225.29	210.03	74.92
900.00	138.08	33.29	244.15	382.23	170.74	204.54	376.83	68.23	383.38	417.17	212.63	201.09	64.79
1000.00	129.28	18.48	226.56	355.83	162.32	194.96	363.66	57.49	362.20	394.84	199.88	192.09	54.62
						product anion unstable	**product anion unstable**	**product anion unstable**					

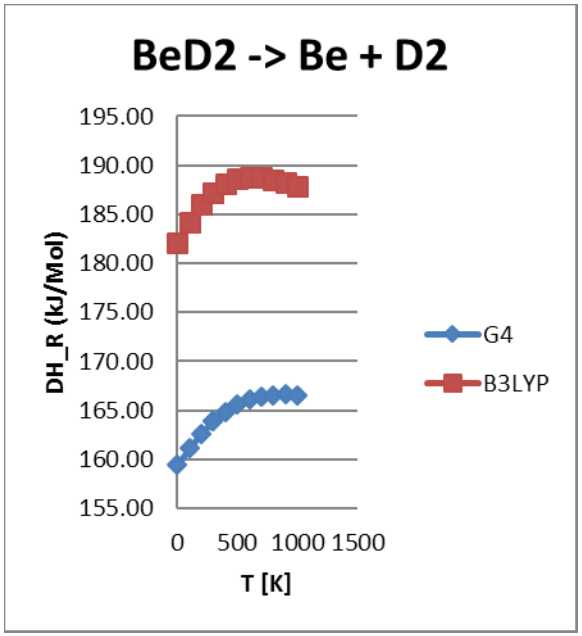
The reaction network. Free energies as function of temperature

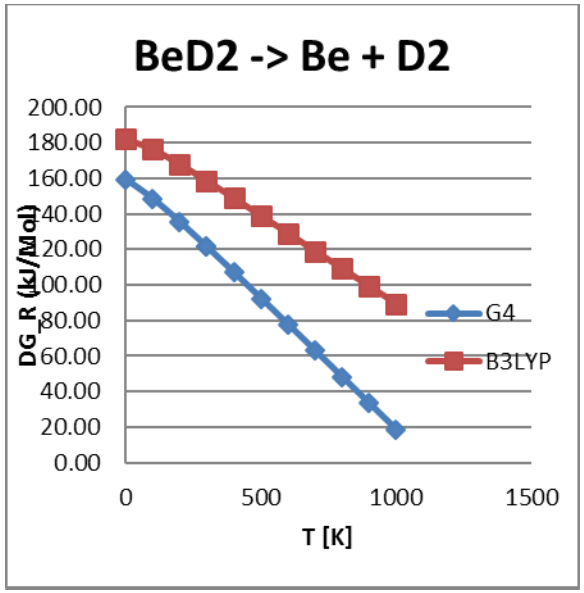
Table 11 continued
G4 calculations of reaction free energies

	25	26	27	28	29	30	31	32	33
K	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0	kJ/Mol ΔG_r^0
T	$BeD_3 \rightarrow BeD_2 + D$	$BeD_3 \rightarrow BeD + D_2$	$BeD_3^+ \rightarrow BeD^+ + D_2$	$BeD_3^+ \rightarrow BeD + D_2^+$	$BeD_3^+ \rightarrow BeD_2^+ + D$	$BeD_3^+ \rightarrow BeD_2 + D^+$	$BeD_3^- \rightarrow BeD_3 + e^-$	$BeD_3^- \rightarrow BeD_2^- + D$	$BeD_3^- \rightarrow BeD^- + D_2$
0	33.0235	-15.1281	93.2945	779.4136	462.3006	648.9368	284.7013	331.3433	203.6390
100	33.2808	-20.7546	87.4948	771.7892	454.6577	648.9920	284.4440	325.4648	198.1753
200	30.8102	-29.6524	78.8437	761.3161	444.4393	646.7393	284.0475	317.2969	189.2985
298.15	27.6964	-39.1698	69.8409	750.5174	433.7640	644.1085	283.4358	308.5671	179.5658
300	27.6360	-39.3510	69.6676	750.3100	433.5592	644.0560	283.4200	308.3990	179.3767
400	24.1940	-49.2990	60.3550	739.1542	422.3772	641.2152	282.6455	299.2098	169.0218
500	20.6443	-59.2812	51.0476	727.9591	411.0141	638.2983	281.7975	289.9313	158.5224
600	17.0684	-69.2082	41.7874	716.7640	399.5275	635.3420	280.9127	280.6501	147.9942
700	13.4951	-79.0407	32.5956	705.5767	387.9438	632.3568	280.0069	271.4058	137.5132
800	9.9401	-88.7655	23.4746	694.4052	376.2918	629.3480	279.0958	262.2191	127.1083
900	6.4115	-98.3775	14.4324	683.2600	364.5874	626.3286	278.1769	253.0929	116.7875
1000	2.9064	-107.89000	5.4610	672.1357	352.8435	623.2988	277.2580	244.0270	106.5559
								product anion unstable	

Enthalpy and Free energy

as function of temperature (kJ/mol)





At low T BeD_2 is much favoured over Be and D_2
At 1000K both BeD_2 and Be+D_2 are equally probable

4 DFT of Be_2W and $Be_{12}W$ surfaces

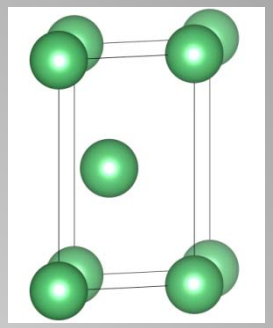
Surface binding energies of beryllium / tungsten alloys

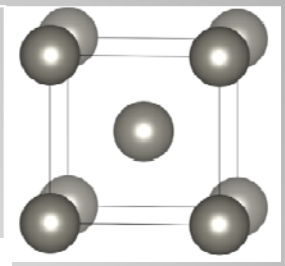
Gyoeroek, Michael; Kaiser, Alexander; Sukuba, Ivan; Urban, Jan; Hermansson, Kersti; Probst, Michael

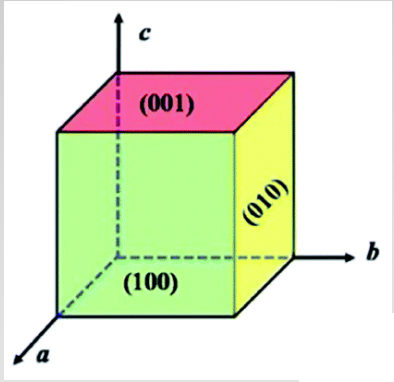
Journal of Nuclear Materials (2016), 472, 76-81.

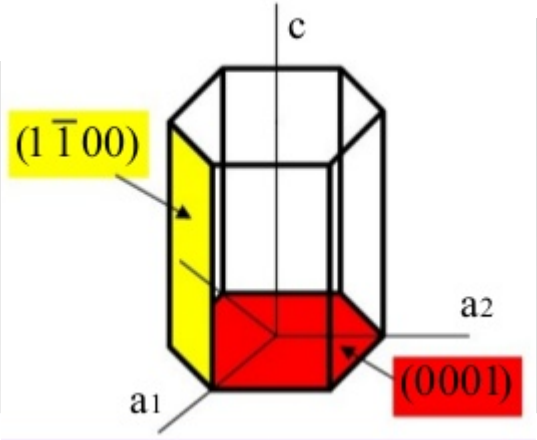
Surfaces of Interest

- pure Be - hexagonal close packed (0001)
- pure W - body centered cubic (001)
- Be_2W (001)
- $Be_{12}W$ (001)





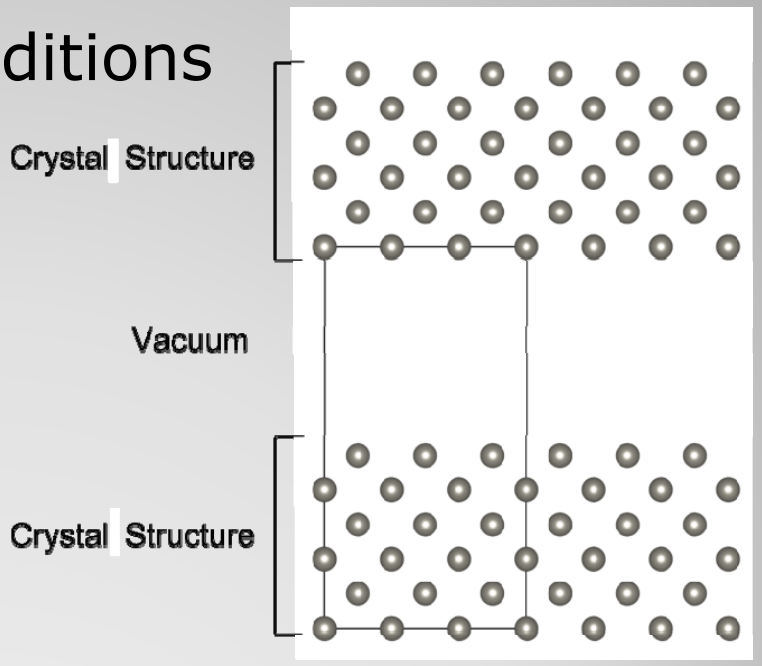




- VASP …
  - Density functional theory
  - Widely used in materials science
  - Plane waves, LAPWs as basis sets
  - PBE functional
  - Periodic systems

Surface Model

- periodic boundary conditions
- vacuum depth 8 [Å]
- orientation (001)



Surface Binding Energy & Cohesive Energy

$$E_{SBE} = E_{atom} + E_{SV} - E_S$$

$$E_{coh} = \frac{E_{bulk} - \sum_i n_i E_{atom}(i)}{\sum_i n_i}$$

E_{atom} - single atom energy

E_{SV} - total energy of the surface slab with a single surface vacancy

E_S - total energy of the slab with the clean surface

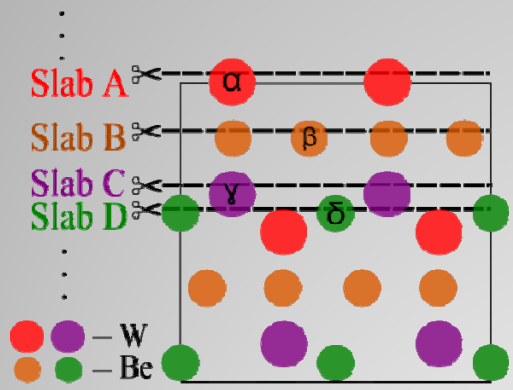
E_{bulk} - total bulk energy

n_i - number of atoms of each species

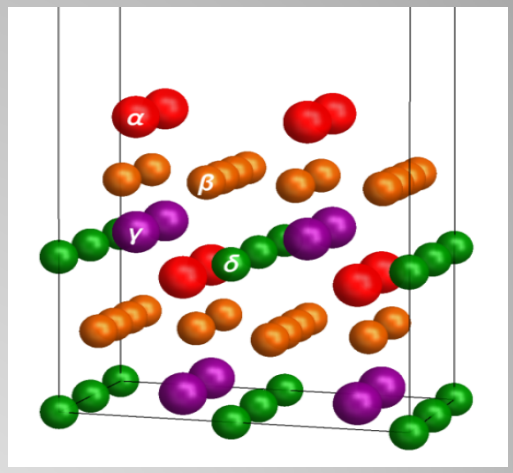
Surface Binding Energies: Pure Metals

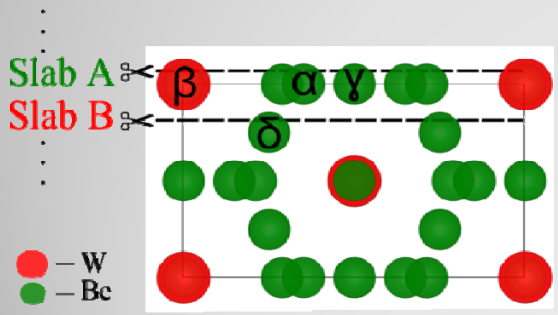
structure	vacancy	SBE [eV]		no. of neighbors		distance [Å] (number of neighbors)	
		DFT	ABOP	W	Be	W-W	Be-Be
Be hcp (0001)	Be	5.128	4.26	-	9		2.211 (3) 2.277 (6)
W bcc (001)	W	8.805	9.07	9	-	2.749 (4) 3.174 (5)	

Alloys: Geometric Arrangement

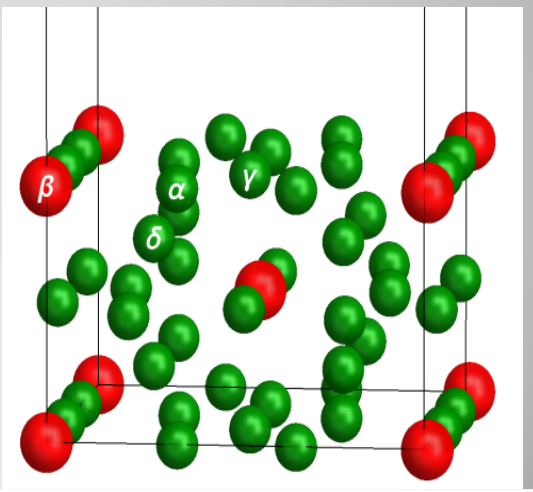


Be_2W





$Be_{12}W$

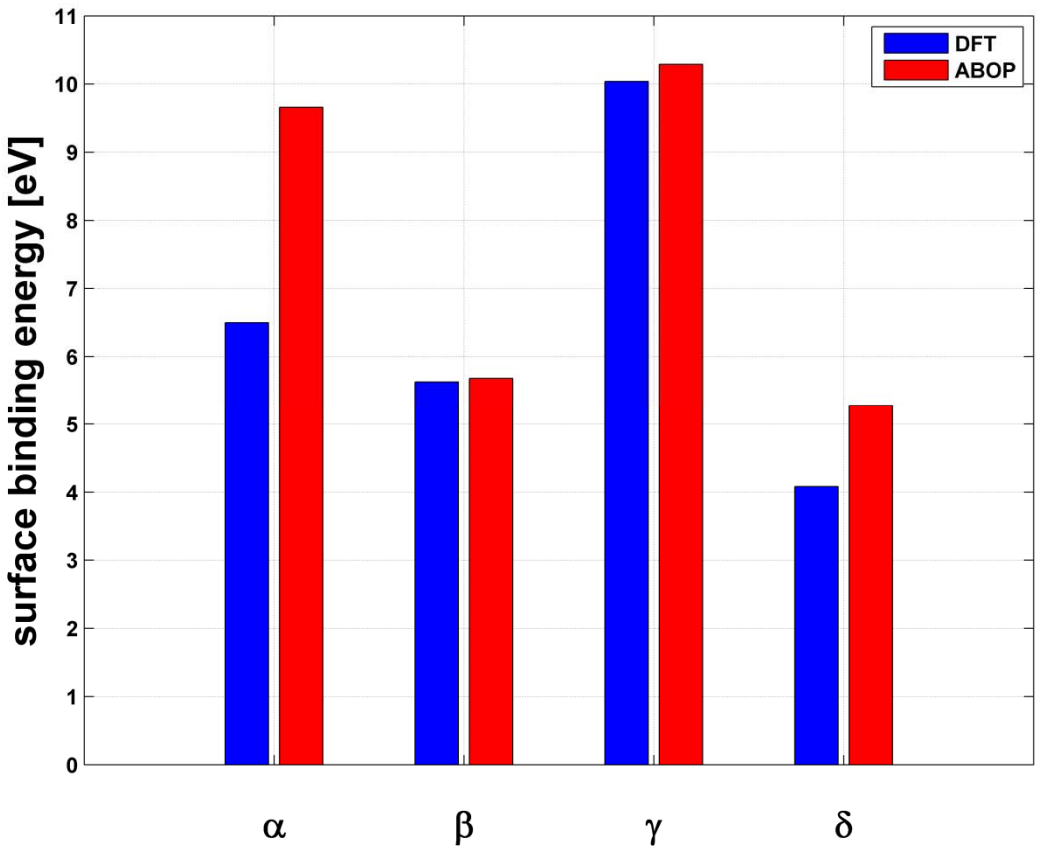


Results

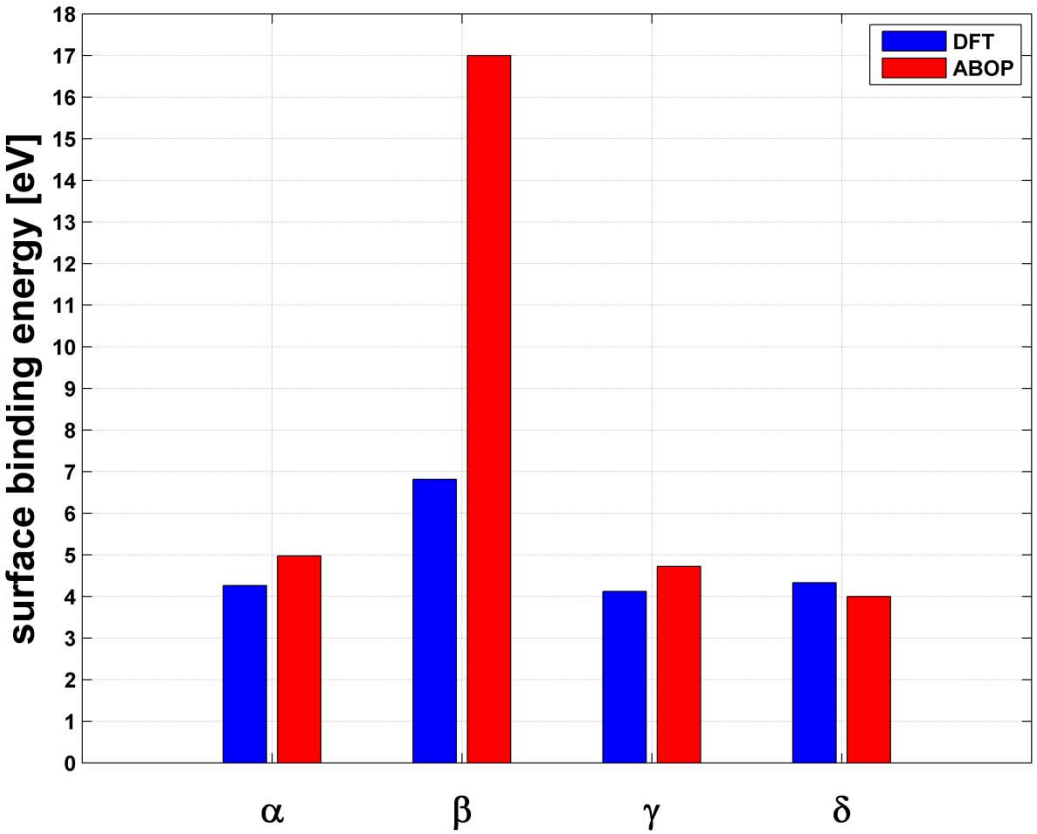
Surface Binding Energies

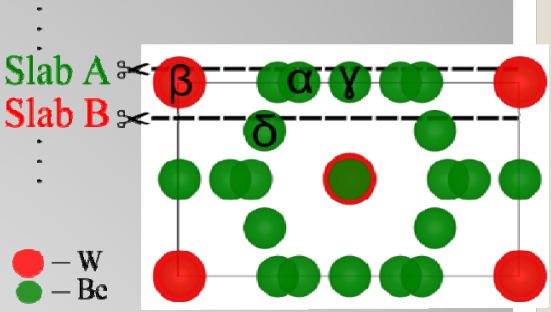
	vacancy	SBE [eV]	no. of neigh-bors		distances [Å] (number of neighbors in parentheses)	
$Be_{12}W$ (001)		DFT	W	Be	Be-W	Be-Be
Surface A	Be (α)	**4.26**	**1**	**8**	**2.528 (1)**	**2.144 (1), 2.209 (2) 2.333 (1), 2.340 (2) 2.593 (2)**
Surface A	Be (γ)	**4.12**	**1**	**7**	**2.595 (1)**	**2.104 (2), 2.151 (2) 2.333 (1), 2.340 (2)**
Surface A	W (β)	6.81	0	12	2.528 (4) 2.596 (4) 2.755 (4)	
Surface B	Be (δ)	**4.33**	**1**	**5**	**2.755 (1)**	**2.104 (3), 2.209 (2)**

Comparison DFT vs. ABOP - Be_2W

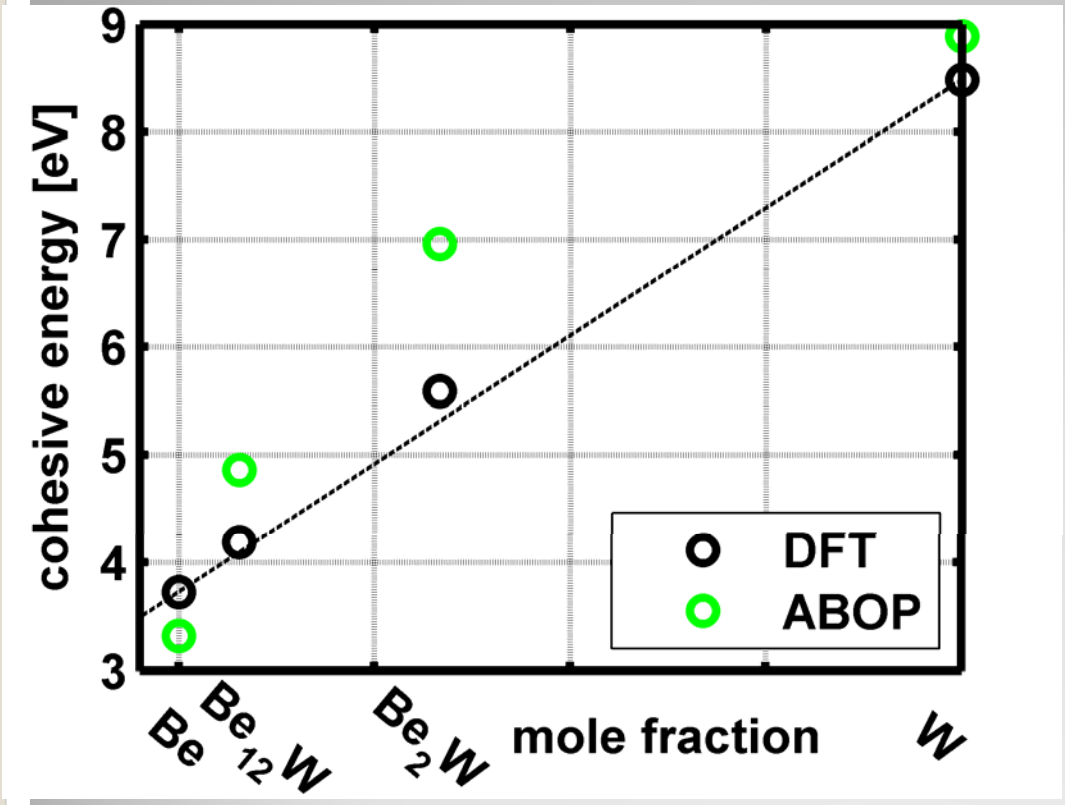


Comparison DFT & ABOP – $Be_{12}W$





Cohesive energy correlations



	Melting Points [K]
W	3687
Be_2W	2523
$Be_{12}W$	2023
Be	1560

Conclusions:

- Increasing tungsten content stabilizes the whole material (against sputtering).
- Preferential sputtering of Be (only).
- One case where there is a large discrepancy with BOP

Thank you !