start
Quantum chemical calculations and MD simulations for Be

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QC & MD

Topic
- Surface Stability (Energetics)
- Sputtering Dynamics
- Near-surface reaction Equilibria
- Electron-Impact Cross Section

Methods
- DFT: surface stability, cohesive energy
- MD: Yields, dependence on E, T ...

Properties
- QC extrapolation methods
- \( \Delta G \): k (rate constants)
- 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
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:

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

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

BEB:

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

\[ t = T/B, \ u = U/B, \ S = 4\pi a_0^2NR^2/B^2 \]

From QC calculations
• Be\textsubscript{n}W cluster, n=1-12, all singlet states

• Optimization by simulated annealing (Born-Oppenheimer molecular dynamics with TURBOMOLE)
Be$_n$W cluster, $n=1-3$

Cross sections for S and T spins:
$Be_nW$ cluster, $n=1-12$

Cross sections:
In Be$_8$W, 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)Å³
~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:

- \( \Delta G_f \) and \( \Delta H_f \) – values (free formation energies and - enthalpies) for various neutral, cationic and anionic \( \text{Be}_x\text{H}_y \) – species.
- \( \Delta \Delta G \) – values (free energies of \textit{reactions}) and equilibrium constants at different temperatures for the various interconversion reactions of neutral and ionic \( \text{Be}_x\text{H}_y \) – 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:

\[ \Delta G = \Delta G^0 + RT \ln(Q_r) = RT \ln\left(\frac{Q_r}{K_{eq}}\right) \]

- $Q_r$ ... reaction quotient
  - initial concentrations

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

\[ \ln\left(\frac{Q_r}{K_{eq}}\right) \text{ determines the direction of the reaction} \]

Eyring equation for rate constants
\[ k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\Phi}{RT}\right) \]

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 $\Delta G$ 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+E vib+E rot+E trans
TCEnthalpy           0.006677  0.00668 ZPE+E vib+E rot+E trans+RT
TCGibbs              -0.01407
Eelec+ZPE            -15.26341
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 $\Delta G_r^0$ (Ochterski approach from gaussian calculations)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>BeD → BeD⁺</th>
<th>BeD₂ → BeD⁺₂</th>
<th>BeD₂ → BeD⁺ + D⁻</th>
<th>Be⁺ + D → Be⁺ + D⁻</th>
<th>Be⁺ + D⁻ → Be⁺⁺ + D⁻</th>
<th>Be⁺⁺ + D⁻ → Be⁺⁺⁺ + e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>207.58</td>
<td>159.43</td>
<td>393.56</td>
<td>601.14</td>
<td>237.98</td>
<td>154.44</td>
</tr>
<tr>
<td>100.00</td>
<td>202.52</td>
<td>148.48</td>
<td>380.10</td>
<td>582.61</td>
<td>233.07</td>
<td>148.79</td>
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<tr>
<td>200.00</td>
<td>195.72</td>
<td>135.26</td>
<td>364.37</td>
<td>560.09</td>
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<td>140.30</td>
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<tr>
<td>298.15</td>
<td>188.42</td>
<td>121.56</td>
<td>346.20</td>
<td>536.62</td>
<td>219.30</td>
<td>131.03</td>
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<tr>
<td>300.00</td>
<td>188.28</td>
<td>121.29</td>
<td>347.89</td>
<td>536.17</td>
<td>219.17</td>
<td>130.85</td>
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<tr>
<td>400.00</td>
<td>180.43</td>
<td>106.93</td>
<td>331.01</td>
<td>511.43</td>
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<td>120.89</td>
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<tr>
<td>500.00</td>
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<td>486.16</td>
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<td>600.00</td>
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<td>62.89</td>
<td>279.18</td>
<td>434.61</td>
<td>187.38</td>
<td>95.09</td>
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<tr>
<td>900.00</td>
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<td>244.15</td>
<td>382.23</td>
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<td>75.83</td>
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<tr>
<td>1000.00</td>
<td>129.28</td>
<td>18.48</td>
<td>226.56</td>
<td>355.83</td>
<td>162.32</td>
<td>65.74</td>
</tr>
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</table>
The reaction network. Free energies as function of temperature

<table>
<thead>
<tr>
<th>Table 11 continued</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
<th>( \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>26</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>30</td>
<td>31</td>
<td>32</td>
<td>33</td>
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<tr>
<td>( K )</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
<td>kJ/Mol</td>
</tr>
<tr>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
<td>( \Delta G_0 )</td>
</tr>
<tr>
<td>( T )</td>
<td>Be( \text{D}_3 \rightarrow \text{BeD}_2 + \text{D} )</td>
<td>Be( \text{D}_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow \text{BeD} + \text{D}_2 ) | Be( \text{D}_3^+ightarrow \text{BeD} + \text{D}_2^+ ) | Be( \text{D}_3^+ightarrow \text{BeD}_2^+ + \text{D} ) | Be( \text{D}_3^+ightarrow \text{BeD}_2 + \text{D}^+ ) | Be( \text{D}_3^-ightarrow \text{BeD}_2^- + \text{D} ) | Be( \text{D}_3^-ightarrow \text{BeD} + \text{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  | 644.0858  | 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  |
| 1000              | 2.9064    | -107.8900 | 5.4610    | 672.1357  | 352.8435  | 623.2988  | 277.2580  | 244.0270  | 106.5559  |</p>

The product anion is 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$_2$W and Be$_{12}$W surfaces

Surface binding energies of beryllium/tungsten alloys
Gyoeroek, Michael; Kaiser, Alexander; Sukuba, Ivan; Urban, Jan; Hermansson, Kersti; Probst, Michael
Surfaces of Interest

- pure Be - hexagonal close packed (0001)
- pure W - body centered cubic (001)
- $\text{Be}_2\text{W} (001)$
- $\text{Be}_{12}\text{W} (001)$
VASP ...
- Density functional theory
- Widely used in materials science
- Plane waves, LAPWs as basis sets
- PBE functional
- Periodic systems
2. Methods

Surface Model

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

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

<table>
<thead>
<tr>
<th>structure</th>
<th>vacancy</th>
<th>SBE [eV]</th>
<th>no. of neighbors</th>
<th>distance [Å] (number of neighbors)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>DFT</td>
<td>ABOP</td>
<td>W-W</td>
</tr>
<tr>
<td>Be hcp (0001)</td>
<td>Be</td>
<td>5.128</td>
<td>4.26</td>
<td>- 9</td>
</tr>
</tbody>
</table>
Alloys: Geometric Arrangement

\[ \text{Be}_2\text{W} \]

\[ \text{Be}_{12}\text{W} \]
### Results

#### Surface Binding Energies

<table>
<thead>
<tr>
<th>Surface A, Be₁₂W (001)</th>
<th>vacancy</th>
<th>SBE [eV]</th>
<th>no. of neighbors</th>
<th>distances [Å] (number of neighbors in parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be (α)</td>
<td>DFT</td>
<td>W</td>
<td>8</td>
<td>2.528 (1), 2.144 (1), 2.209 (2), 2.333 (1), 2.340 (2), 2.593 (2)</td>
</tr>
<tr>
<td>Surface A, Be (γ)</td>
<td>4.12</td>
<td>1 7</td>
<td>2.595 (1)</td>
<td>2.104 (2), 2.151 (2), 2.333 (1), 2.340 (2)</td>
</tr>
<tr>
<td>Surface A, W (β)</td>
<td>6.81</td>
<td>0 12</td>
<td>2.528 (4), 2.596 (4), 2.755 (4)</td>
<td></td>
</tr>
<tr>
<td>Surface B, Be (δ)</td>
<td>4.33</td>
<td>1 5</td>
<td>2.755 (1)</td>
<td>2.104 (3), 2.209 (2)</td>
</tr>
</tbody>
</table>
Comparison DFT vs. ABOP - Be$_2$W
Comparison DFT & ABOP – Be$_{12}$W
Cohesive energy correlations

Melting Points [K]
- W: 3687
- $\text{Be}_2\text{W}$: 2523
- $\text{Be}_{12}\text{W}$: 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!