SMARTMET project: Towards breaking the inverse ductility-strength relation

B. Grabowski, C. Tasan
Inverse strength-ductility relation

increase strength $\rightarrow$ decrease ductility
increase ductility $\rightarrow$ decrease strength for a single hardening mechanism!
Break inverse relation by new hardening mechanisms!
SMARTMET idea

Phase instability + Nano-particles → combined increase in strength and ductility

High risk – high gain idea!
The ideal outcome:

Crack propagation stopped by transformed nano-particle!
Investigation of unstable phases experimentally difficult
→ close collaboration of theory and experiment required!

Requirements for ab initio part:

- inclusion of relevant finite temperature mechanisms:
  - $T=0$ K, electronic, quasiharmonic, anharmonic, magnetic
- high precision at lowest possible computational effort
- description of unstable phases
  - methodological development necessary

Approach:

- in first stage, study of (unstable) bulk phases
  simulate influence of host matrix by strain dependence

- in later stage, study explicit influence of interface and particle size
SMARTMET ab initio part

very demanding computations ➔ CPU times: days to weeks
restriction to several 100 atoms
BUT: accurate energetics and kinetics possible
Methodological development crucial

**Needed CPU time**\(^{[1,2]}\)

<table>
<thead>
<tr>
<th>Method</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular dynamics</td>
<td>1000 years</td>
</tr>
<tr>
<td>Thermodyn. Integration</td>
<td>1 year</td>
</tr>
<tr>
<td>UP-TILD</td>
<td>20 days</td>
</tr>
</tbody>
</table>

(\text{logarithmic})

**CPU:**
- AMD Opteron, 2.4 GHz, serial\(^{[1]}\)

**System:**
- aluminum, 32 atoms, pseudopotential, 14 Ry (190 eV) cutoff, 4x4x4 \(k\) points\(^{[2]}\)

\(\rightarrow\) Reasonable simulation times
1. fcc to bcc phase transition in calcium

2. heat capacity in calcium

1. phonon DOS for unstable bcc-uranium
Challenge: Extremely high accuracy needed

1 meV $\approx 0.07$ mRy $\approx 0.1$ kJ/mole

$\Delta G_{\text{bcc-fcc}}$ (meV/atom)

Temperature (K)

Ca fcc

Ca bcc

CALPHAD

$T_{\text{exp}}^{\text{bcc-fcc}}$

$T_{\text{mel}}^{\text{exp}}$
Challenge: Extremely high accuracy needed

1 meV ≈ 0.07 mRy ≈ 0.1 kJ/mole
\[ \Delta G_{\text{bcc-fcc}} \text{ (meV/atom)} \]

\[ \Delta \text{Gibbs energy bcc-fcc in Calcium} \]

Temperature (K)

Ref: Grabowski et al., PRB 84, 214107 (2011).
Δ Gibbs energy bcc-fcc in Calcium

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$\Delta$ Gibbs energy bcc-fcc in Calcium

Ref: Grabowski et al., PRB 84, 214107 (2011).
\[ \Delta G_{\text{bcc-fcc}} \text{ (meV/atom)} \]

\[ \begin{align*}
\Delta G_{\text{bcc-fcc}} &= 15 \\
&= 10 \\
&= 5 \\
&= 0 \\
&= -5 \\
&= -10 \\
&= -15
\end{align*} \]

Temperature (K)

\[ T_{\text{exp}} \]

\[ T_{\text{melt}} \]

Ref: Grabowski et al., PRB 84, 214107 (2011).
Ref: Grabowski et al., PRB 84, 214107 (2011).
Δ Gibbs energy bcc-fcc in Calcium

Ref: Grabowski et al., PRB 84, 214107 (2011).

ΔG_{bcc-fcc} (meV/atom)

CALPHAD

0K
0K + h
0K + h + q
0K + h + q + el
0K + h + q + el + ah (+ vac)

DFT shifted by -6 meV

Temperature (K)
300 600 900

T_{exp}^{fcc\rightarrow bcc} T_{melt}^{exp}

quasi

anharmomic
1. fcc to bcc phase transition in calcium

2. heat capacity in calcium

1. phonon DOS for unstable bcc-uranium
$C_P$ of calcium

Ref: Grabowski et al., PRB 84, 214107 (2011).

- Ditmars 1989
- Robie 1985
- Ulyanov 1985
- Kubaschewski 1950
- Jauch 1946
- Clusius 1930
- Zalesinski 1928
- Eastman 1924

Ref: Grabowski et al., PRB 84, 214107 (2011).
$C_p$ of calcium

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Heat capacity ($k_B$)

Temperature (K)

References:
- Ditmars 1989
- Robie 1985
- Ulyanov 1985
- Kubaschewski 1950
- Jauch 1946
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- Eastman 1924

fcc

bcc

300 $T_{exp}$

600 $T_{exp\rightarrow bcc}$

900 $T_{melt}$
$C_p$ of calcium

Heat capacity ($k_B$) vs. temperature (K) plot with data points from various sources:
- Ditmars 1989
- Robie 1985
- Ulyanov 1985
- Kubaschewski 1950
- Jauch 1946
- Clusius 1930
- Zalesinski 1928
- Eastman 1924

Ref: Grabowski et al., PRB 84, 214107 (2011).
$C_P$ of calcium

- Anharmonic (PBE)
- Quasi-harmonic
- Harmonic

Heat capacity ($k_B$) vs. Temperature (K)

References:
- Grabowski et al., PRB 84, 214107 (2011).
- Ditmars 1989
- Robie 1985
- Ulyanov 1985
- Kubaschewski 1950
- Jauch 1946
- Clusius 1930
- Zalesinski 1928
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Temperature ($T_{exp}$) and $T_{exp \rightarrow bcc}$
$C_p$ of calcium

Heat capacity ($k_B$)

+ electronic (PBE)
- anharmonic
- quasiharmonic
- harmonic

Temperature (K)

Ref: Grabowski et al., PRB 84, 214107 (2011).
$C_p$ of calcium

Heat capacity ($k_B$)

- + vacancies (PBE)
- + electronic
- anharmonic
- quasi-harmonic
- harmonic

Temperature (K)

Ref: Grabowski et al., PRB 84, 214107 (2011).
$C_p$ of calcium

Heat capacity ($k_B$) vs. Temperature (K)

- LDA
- GGA-PBE

Ref: Grabowski et al., PRB 84, 214107 (2011).

- Ditmars 1989
- Robie 1985
- Ulyanov 1985
- Kubaschewski 1950
- Jauch 1946
- Clusius 1930
- Zalesinski 1928
- Eastman 1924
Ref: Grabowski et al., PRB 84, 214107 (2011).
Examples

1. fcc to bcc phase transition in calcium

2. heat capacity in calcium

1. phonon DOS for unstable bcc-uranium
Challenge: Strong instabilities in actinides at $T=0$ K
Phonon-phonon stabilization in actinides: Example of bcc uranium

bcc-U at 1113 K

→ bcc uranium fully stabilized in the experimentally observed temperature range

Details:
GGA-PBE
FPLMTO
relativistic core
SO+OP for valence
3x3x3 bcc supercell

Ref:
Söderlind, Grabowski, et al., submitted to PRB.
Phonon-phonon stabilization in actinides: Example of bcc uranium

bcc-U at 1113 K

Experiment vs. DFT

→ bcc uranium fully stabilized in the experimentally observed temperature range

Details:
GGA-PBE
FPLMTO
relativistic core
SO+OP for valence
3x3x3 bcc supercell

Ref: Söderlind, Grabowski, et al., submitted to PRB.
Conclusions – previous work

- set of efficient tools developed
  - relevant excitations can be studied up to melting point
  - numerical accuracy of 1 meV/atom can be reached

- several elements investigated with highest accuracy
  - Al, Ca, Cu, Cr, Mg, Si, Th
  - generally excellent agreement with experiment
  - \textit{ab initio} allows to distinguish set of experiments

- phonon-phonon coupling in phase transition studied
  - can be of substantial importance
  - for Ca change of 400 K in transition temperature

- first investigations for actinides started
  - phonon-phonon interaction can stabilize unstable phases
  - for U a good agreement with experimental DOS achieved
SMARTMET outlook

SMARTMET
ERC advanced grant
3.8 Mio Euro for 5 years
(Raabe/Neugebauer)

Adaptive Structural Materials group at MPIE

finite $T$ ab initio elastic maps
optimize strength and ductility simultaneously
multiscale in situ tensile tests

finite $T$ ab initio
B. Grabowski +
7 members

multiscale in situ experiments
C. Tasan +
7 members
Vacancies in copper

Gibbs energy of formation (eV) vs. Temperature (K)

Standard ab initio range

Experimental range

PAS

DD

60% T_{melt}

\%T_{melt}
Vacancies in copper

Gibbs energy of formation (eV) vs. Temperature (K)

- Standard ab initio range
- Experimental range

Concentration vs. $T_{melt}/T$

- Experimental range
- Standard and ab initio range

$S_f = 0.0 \text{ kJ mol}^{-1}$
Vacancies in copper

Gibbs energy of formation (eV) vs Temperature (K)

- Experimental range
- Standard ab initio range
- Ab initio range

$S_f = 0.0 \text{ k}_B$

Concentration vs $T_{melt}/T$

- Experimental range
- Standard range
- Ab initio range

$60\% T_{melt}$
## Vacancies in copper

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Gibbs energy of formation (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>300</td>
<td>1.2</td>
</tr>
<tr>
<td>600</td>
<td>1.1</td>
</tr>
<tr>
<td>900</td>
<td>1.0</td>
</tr>
<tr>
<td>1200</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The graph shows the Gibbs energy of formation (Gibbs energy of formation (eV)) as a function of temperature (K). The experimental range is indicated by the shaded area. The standard range is shown as a dashed line, and the ab initio range is shown as a solid line. The extrapolated range is indicated by the dotted line. The concentration is shown on the right side of the graph. The transition temperature (T_melt) is indicated by the dashed line. The concentration is expressed as a ratio of T_melt/T, where T_melt is the melting temperature. The concentration is shown on a logarithmic scale, with concentrations ranging from $10^{-3}$ to $10^{-6}$. The graph also includes a inset showing the experimental range and the extrapolation of the data. The standard deviation (SD) of the data is shown for both the PAS and DD ranges.