Ab Initio Simulations of Martensitic Phase Transformations in NiTi-based Shape Memory Alloys: From Binaries to Ternaries

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Computational SMA Goal

**Given:** SMA alloy:

\[ \text{Ni}_x \text{Ti}_y \text{M}_z \]

Ternary metal: \( M = \text{Pd, Pt, Hf, Zr, Fe, etc} \)
Composition: \( (x,y,z) \)

**Predict:** SMA ("martensitic") transition temperature:

\[ T_M(\text{Ni}_x \text{Ti}_y \text{M}_z) \]

*Computational tool to design SMA with tunable \( T_M \)*
Mechanical Phase Stability

- Stability indicated by $d^2E/dX^2$
- Stable systems vibrate about single minimum
- Unstable systems vibrate and hop between multiple minima

$X = $ atomic displacements
MD Simulation Scatter Plot: B2

- Atomic displacements relative to ideal B2
- High T scatter plot shows B2 stabilization

Haskins, Thompson and JL, PRB (2016)
Phonon Spectra: B2

- T=0 negative phonons indicate B2 instability
- All phonons are positive by 300K
- Entropic stabilization of B2

Haskins, Thompson and JL, PRB (2016)
Free Energy vs Monoclinic Angle

- *Ab initio* thermodynamic integration
- B2, B19' stabilized; B33 destabilized
- Monoclinic angle temperature dependent

Haskins, Thompson and JL, PRB (2016)
Free Energy $F(T, \gamma)$ Contours

- Free energy $F(T, \gamma)$ contours (blue=low, red=high)
- Stability basins with stability lines

Haskins, Thompson and JL, PRB (2016)
Electronic FE reduces MTT by 65 K for NiTi

Z. Wu et al., (2022), in preparation
Binary Transition Temperatures

- Agreement between theory and experiment very good
- Other binaries have much larger transition temperatures than NiTi
- Low temperature phases (B19, B33) correctly predicted

Ternary Transition Temperatures: NiTiPd

- **Differential scanning calorimetry (DSC) data, stress free**

- **Expt. \((M_s+A_f)/2\)**

- **Averaged Data**

- **Theory**

- **MAE = 38.6 K**

- **Compare the computed MTTs with those DSC measurements.**

- **Very good agreement with experimental data.**

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Z. Wu et al., (2022), in preparation
Excellent agreement with recent measurements ($x \geq 0.3$) by NASA scientists.

For $x \leq 0.2$, MTTs are overestimated by ~100 K, similar to that in NiTi.
Summary and Future Work

- First-principles calculations can accurately predict martensitic transitions in SMAs
  - Including electronic FE reduces errors in predicted MTTs of binaries.
  - Small cells (48 atoms) greatly speed up calculations with acceptable accuracy.
  - Applicable to ternary SMAs: the computed MTTs are within about 100 K compared with measurements

- Thermodynamics integration remains expensive
  - Fast screening before carrying out TI
  - More efficient methods: such as P4, FE from higher-order terms
  - Machine learning

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