Computational Studies of Mechanical Properties of Nb-Si Based Alloys

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Goal

- Develop a software package to facilitate the first principles calculations of physical properties of crystals and solid solutions commonly found in alloys.

- Compute thermodynamic and mechanical properties of various phases found in the Nb-Si-Cr-X alloy systems.

Methods: G(P, T) package

- First principles calculations based on DFT (VASP)
- Born-Oppenheimer approximation
- Harmonic model for vibrational free energy
- Quasi-harmonic approximation for first order anharmonicity
- Berry phase approach for polarization
- RPA for optical properties

Crystal Free Energy

- Helmholtz free energy $F(\{\mathbf{a}\},T)$

$$F(\{\mathbf{a}\},T) \approx E^{c}(\{\mathbf{a}\}) + F^{el}(\{\mathbf{a}\},T) + F^{v}(\{\mathbf{a}\},T)$$

- Electron excitation free energy:
  - Mermin's finite temperature DFT: $F = \underset{n(r,T)}{Min}\{E - TS\}$
  - Non-interacting reference frame

$$F^{el}(\{\mathbf{a}\},T) \approx \sum_i \left\{ (\boldsymbol{\varepsilon}_F - \boldsymbol{\varepsilon}_i) - k_B T \ln\left(1 + e^{(\boldsymbol{\varepsilon}_F - \boldsymbol{\varepsilon}_i)/k_B T}\right) \right\}$$

- Vibrational free energy:
  - Quantum harmonic oscillators: (non-interacting phonon model)
  - *Anharmonic effect through phonon perturbation theory*

$$F^{v}(\{\mathbf{a}\},T) \approx \sum_i \left\{ \tfrac{1}{2}\hbar\boldsymbol{\omega}_i - k_B T \ln\left(1 - e^{-\hbar\boldsymbol{\omega}_i/k_B T}\right) \right\}$$

- Potential energy due to external fields:
  - *electric field, magnetic field*

Phonon

- **Harmonic Model:** non-interacting reference frame

$$\mathsf{H} = \frac{1}{2}\sum_i \left\{p_i^2 + \omega_i^2 q_i^2\right\}$$

- **Quasi-Harmonic Approximation**

$$\omega_i(\{\mathsf{a}\},T) \approx \omega_i(\{\mathsf{a}\})$$

- **Dynamical matrix**
  - *finite difference approximation*

$$D_{\mu\nu}\begin{pmatrix}\vec{q}\\ k\,k'\end{pmatrix} = \frac{1}{\sqrt{m_k m_{k'}}}\sum_l \Phi_{Ok_\mu, lk'_\nu} e^{i\,\vec{q}\bullet(u_{l\,k'} - u_{0k})}$$

$$\Phi_{lk_\mu, l'k'_\nu} = -\frac{\partial F_{lk_\mu}}{\partial u_{l'k'_\nu}} \approx -\frac{\Delta F_{lk_\mu}}{\Delta u_{l'k'_\nu}}; \qquad \Phi_{lk,l'k'} = 0 \quad for \quad |r_{lk} - r_{l'k'}| > R_{cutoff}$$

- **LO/TO splitting**
  - *Born effective charge calculated using Berry phase method*
  - *LO/TO splitting calculated using Born effective charge*

Supercell finite difference approach:

$$\Phi_{lk,l'k'} = 0 \quad for \quad |r_{lk} - r_{l'k'}| > R_{cutoff}$$

Density functional perturbations theory:

$$D_{\mu\nu}\begin{pmatrix}q\\ kk'\end{pmatrix} = \frac{1}{\sqrt{m_\mu m_\nu}}\frac{\partial^2 E}{\partial u_{\mu k}^q \partial u_{\nu k'}^q}$$

Physical properties

- **Physical properties**
  - *Energies: $F(\{\mathbf{a}\},T)$, $U(\{\mathbf{a}\},T)$*
  - *1st order derivatives: $\boldsymbol{\sigma}(\{a\},T)$, $S(\{a\},T)$*
  - *2nd order derivatives: $C_V(\{a\},T)$, $\mathbf{C}(\{a\},T)$, $\boldsymbol{\alpha}(\{a\},T)$, $\boldsymbol{\gamma}(\{a\},T)$*
  - *Higher order derivatives …*

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G(P,T) Module: Elastic tensor C_{ij}

General case:

$$C_{ij}(\{\mathbf{a}\},T) = \frac{\partial^2 F(\{\mathbf{a}\},T)}{\partial \boldsymbol{\varepsilon}_i \partial \boldsymbol{\varepsilon}_j}$$

Challenges:

- *seven parameters:* $\{\mathbf{a}\},T$
- *instability zone*

Hydrostatic case:

$$C_{ij}(P,T) = \left. \frac{\partial^2 F(\{\mathbf{a}\},T)}{\partial \boldsymbol{\varepsilon}_i \partial \boldsymbol{\varepsilon}_j} \right|_{\frac{\partial F(\{\mathbf{a}\},T)}{\partial \boldsymbol{\varepsilon}_i} = -P\boldsymbol{\lambda}_i} \quad where\ \boldsymbol{\lambda}_i = \begin{cases} 1, i = 1,2,3 \\ 0, i = 4,5,6 \end{cases}$$

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Continue

For small finite strain on a periodic structure {a}

$$F(\{a\},T) = F(\{a\}_0,T) - V_0\sum_i \boldsymbol{\sigma}_i(\{a\}_0,T)\boldsymbol{\varepsilon}_i + \tfrac{1}{2}V_0\sum_{ij} C_{ij}(\{a\}_0,T)\boldsymbol{\varepsilon}_i\boldsymbol{\varepsilon}_j + O[\boldsymbol{\varepsilon}^3]$$

$$S(\{a\},T) = S(\{a\}_0,T) + V_0\sum_i \frac{\partial\boldsymbol{\sigma}_i(\{a\}_0,T)}{\partial T}\boldsymbol{\varepsilon}_i - \tfrac{1}{2}V_0\sum_{ij}\frac{\partial C_{ij}(\{a\}_0,T)}{\partial T}\boldsymbol{\varepsilon}_i\boldsymbol{\varepsilon}_j + O[\boldsymbol{\varepsilon}^3]$$

$$C_V(\{a\},T) = C_V(\{a\}_0,T) + V_0T\sum_i \frac{\partial^2\boldsymbol{\sigma}_i(\{a\}_0,T)}{\partial T^2}\boldsymbol{\varepsilon}_i - \tfrac{1}{2}V_0T\sum_{ij}\frac{\partial^2 C_{ij}(\{a\}_0,T)}{\partial T^2}\boldsymbol{\varepsilon}_i\boldsymbol{\varepsilon}_j + O[\boldsymbol{\varepsilon}^3]$$

For a local quadratic energy expansion:

$$if\ \{a\}_{P,T} \sim \{a\}_0$$

$$\rightarrow \quad V_0C_{ij}(\{a\}_0,T) \approx V(P,T)C_{ij}(\{a\}_{P,T},T)$$

where

$$\{a\}_{P,T} = \{a\}_0(I + \boldsymbol{\varepsilon}(P,T))$$

$$\boldsymbol{\varepsilon}_i(P,T) = \sum_j S_{ij}(\{a\}_0,T)(P\boldsymbol{\lambda}_j - \boldsymbol{\sigma}_j(\{a\}_0,T))$$

Algorithm

For each sampling volume V_k falls within the targeted P and T range:

1. Geometry optimization at $T=0K$ to obtain $\{a\}_0^k$:

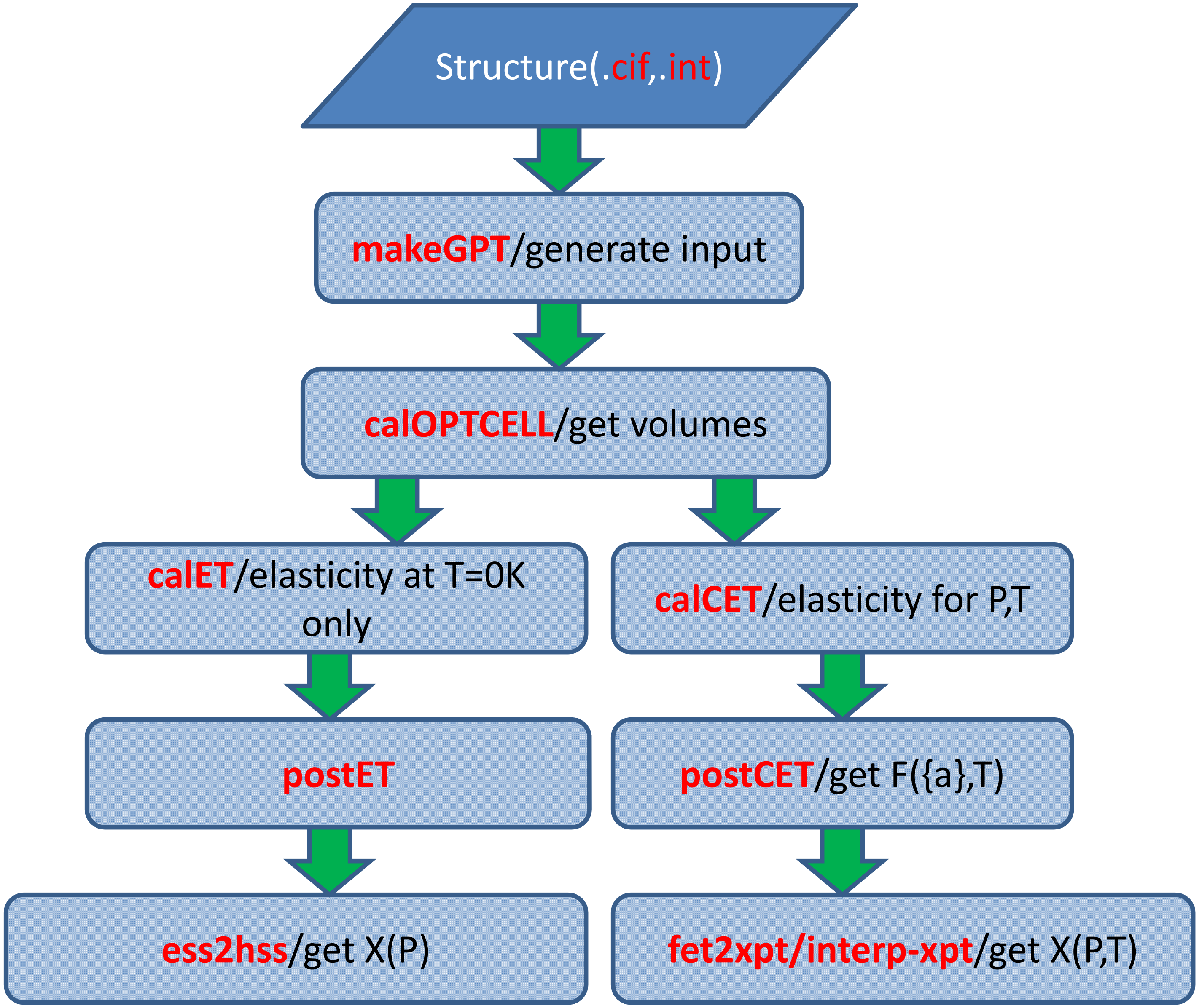
2. Applied a set of small strains $\{ \boldsymbol{\varepsilon}^i \}$ to $\{a\}_0^k$: ($\{a\}_i^k$)
   symmetry constrains applied to reduce # of strains

3. Calculate Helmholtz free energy for strained structure $\{a\}_i^k$:

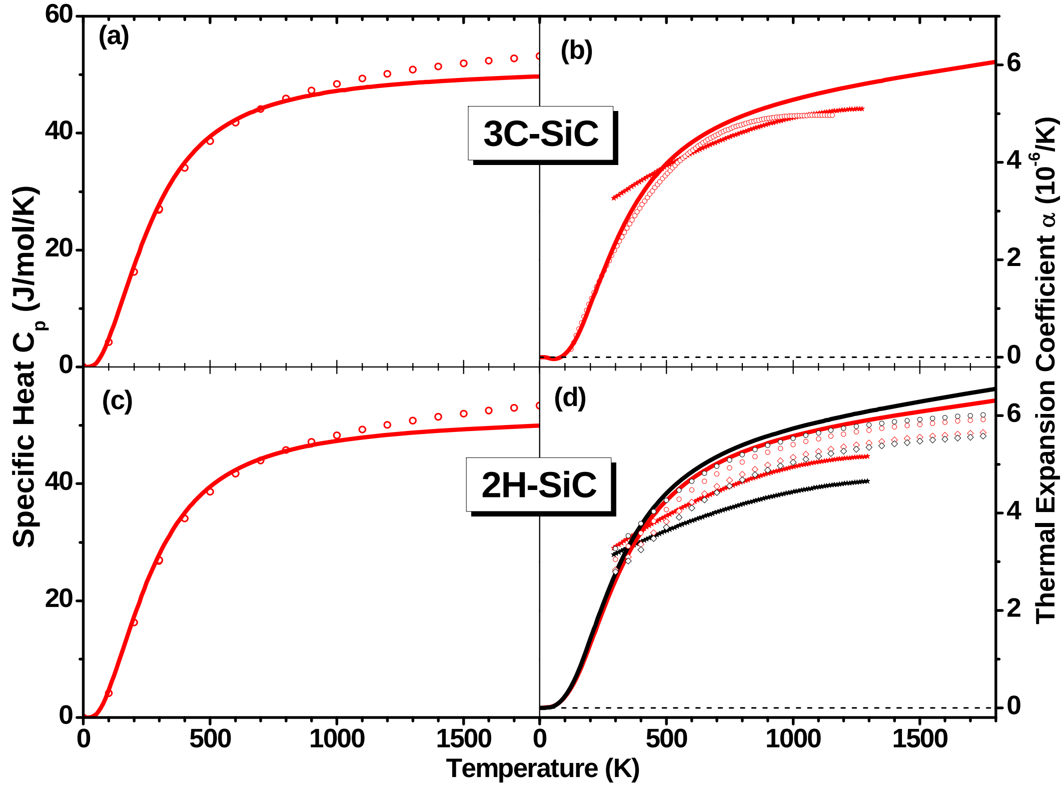
4. **Symmetry constrained fitting** of $F(\{a\}_i^k,T)$, $S(\{a\}_i^k,T)$ and $C_V(\{a\}_i^k,T)$ of strained structures against the isothermal quadratic model to obtain:
   elastic constants and their temperature derivatives (2nd order)
   stress and its temperature derivatives (1st order)

** For systems with large anisotropy, larger strains will be needed.*

Software implementation

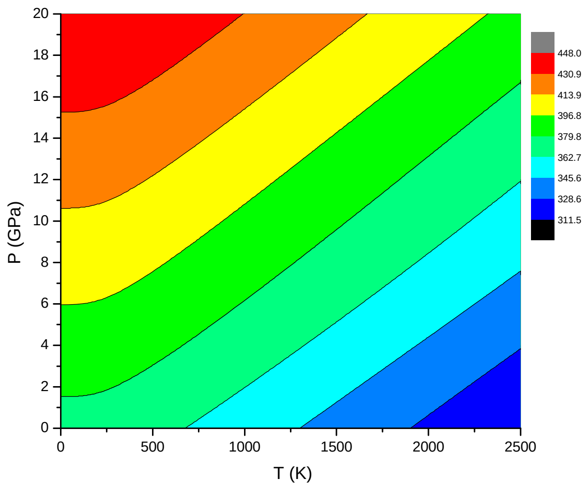


SiC: Specific heat and thermal expansion

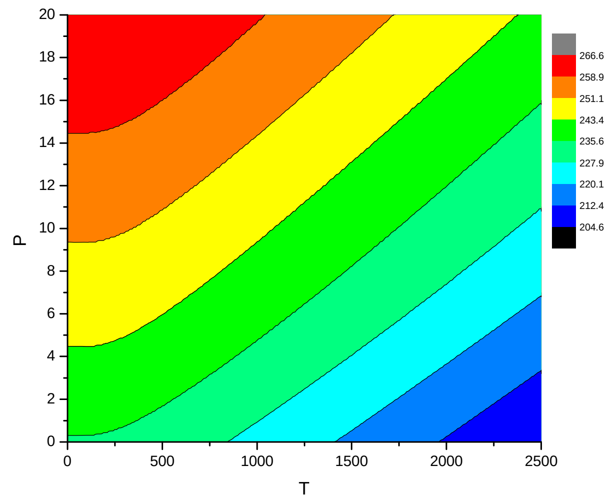


Thermodynamic properties at P=0 up to 1800 K. Solid lines represent the calculated results. (a) Specific heat Cp of 3C. Empty circles are plotted using the experimental data. (b) Thermal expansion coefficient of 3C. Empty circles and solid starts are experimental values respectively. (c) Specific heat Cp of 2H. Empty circles are the experimental data from Ref. 10 (d) Thermal expansion coefficient of 2H. The red symbols are α11 and the black symbols are α33. The circles and diamonds are recent data from Ref. 14 for undoped single crystals of 6H-SiC and 4H-SiC, respectively. The solid stars are from Ref. 13

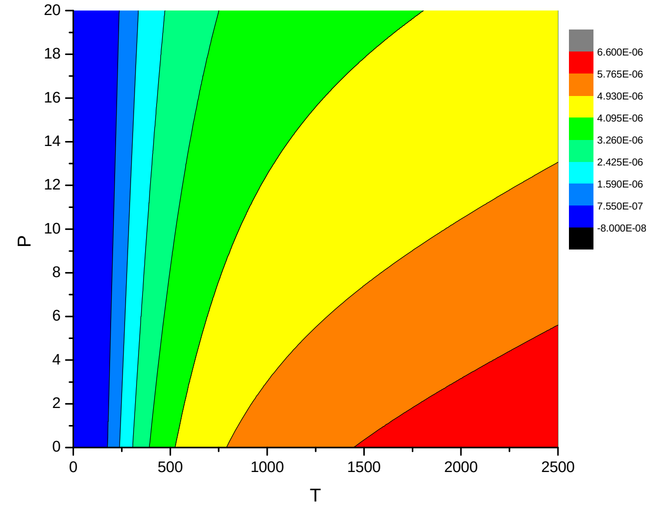
SiC: Elastic constants



C_{11}(P,T)-3C-SiC



C_{44}(P,T)-3C-SiC



α(P,T)-3C-SiC

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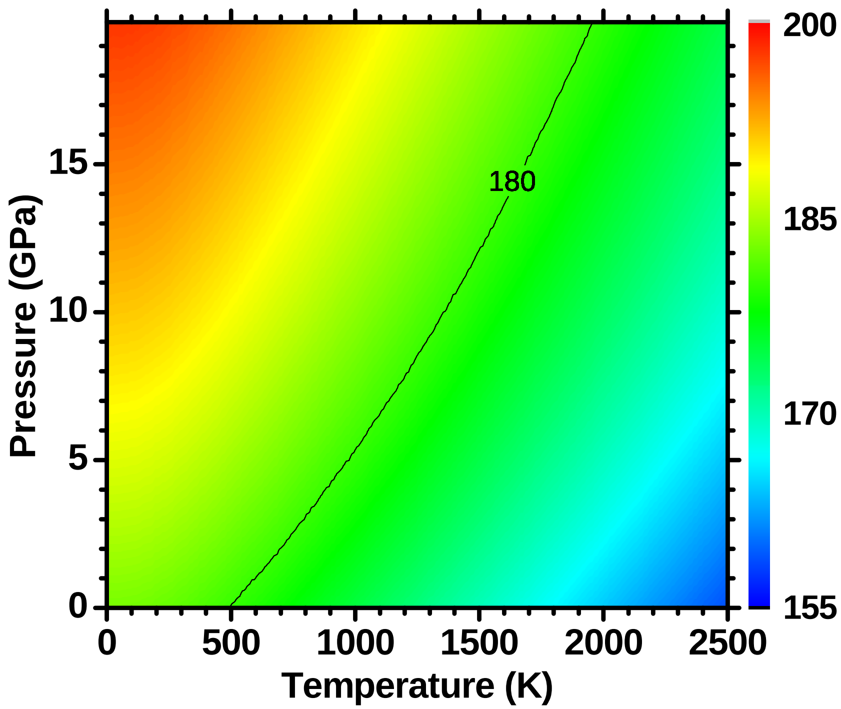
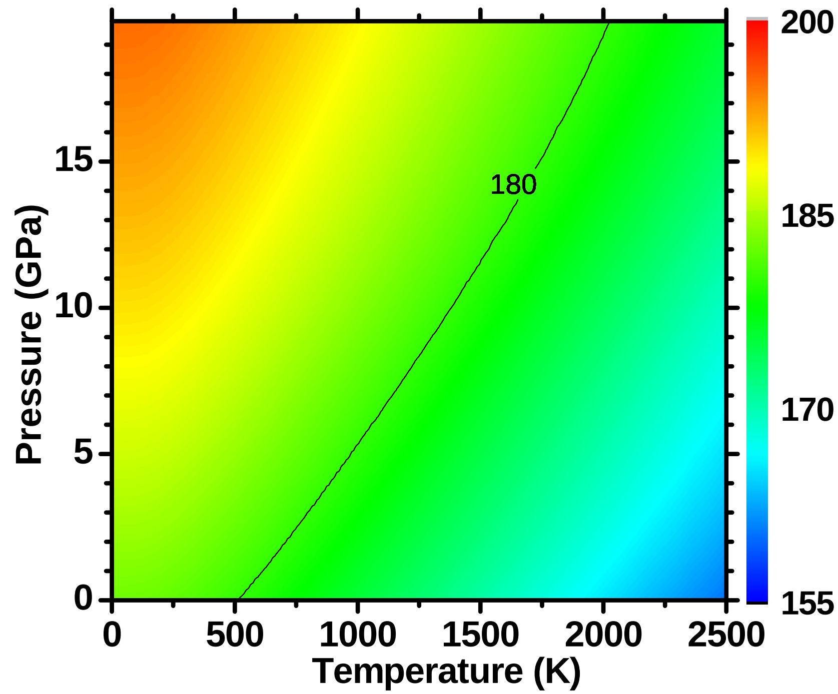
SiC: Shear modulus





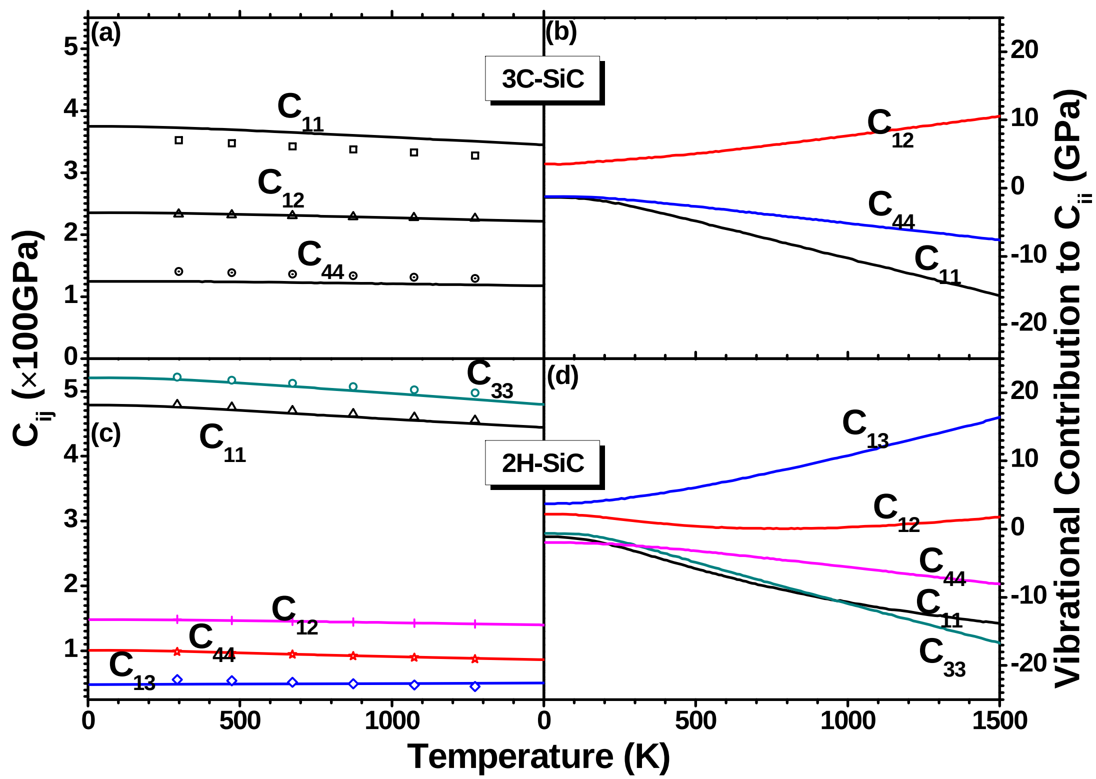
Contour plots of shear modulus for (a) 3C-SiC and (b) 2H-SiC.
The difference is very small. Shear modulus at high temperature and high pressure region is almost the same as that at ambient condition.

Under ambient pressure,

$G_{2H\text{-}SiC}$ (T=298K) =181 GPa   Experiment 179±5 GPa

$G_{2H\text{-}SiC}$ (T=1773K) = 166 GPa   Experiment 165±5 GPa

SiC: Elastic Constants



Temperature-dependent elastic constants at ambient pressure. Solid lines are the calculated properties and the symbols are from experimental measurements. (a) and (b) plot the elastic constants and thermal excitation contribution to elastic constants of 3C-SiC. (c) and (d) show the elastic constants and thermal excitation contribution to elastic constants of 2H-SiC.

Solid Solution

- **Free energy calculations**
  - *Supercell Approaches*
    - *Ensemble Average of Supercells:* $$F(\vec{\sigma},T) \approx \sum_{i\in\vec{\sigma}} w_i(T)F_i(T)$$

      supercells are local snapshots in the infinite solid solution lattice $\vec{\sigma}$

  - *Cluster Expansion Methods*
    - *Weighted average of clusters:* $$F(\vec{\sigma},T) \cong \sum_{\alpha,s} K_\alpha^s(T)\Phi_\alpha^s$$

      α,s are cluster indices and cluster order indices
      clusters are local structures in the infinite solid solution lattice $\vec{\sigma}$
    - *Mathematically rigorous*

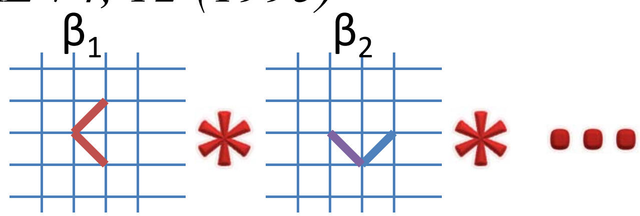
G(P,T) Module: UnitCell Expansion

Cluster Expansion Method for multi-component multi-sublattice systems:

P.D. Tepesch, et al PRL 74, 12 (1995)

$$F(\vec{\sigma}, T) \cong \sum_{\alpha, s} K_{\alpha}^{s}(T)\Phi_{\alpha}^{s},$$

$$\Phi_{\alpha}^{s} = \prod_{i} \Phi_{\beta_i}^{s_i}; \alpha = \bigcup_{i} \beta_i$$



Challenge: number of cluster expansion terms n

$$n \sim (N_{sublattice} - 1)^{|\alpha| Nsublattice}$$

UnitCell Expansion Method for multi-component multi-sublattice systems:

$$F(\vec{\sigma}, T) \cong \sum_{\gamma, s} K_{\gamma}(T)\Phi_{\gamma}^{s},$$

Rational: Coarse grained cluster expansion, unitcells are treated as pseudo atom types

- Simplify lattice
- Expected must faster cluster interaction decaying over distance (*up to pair)*

- Much larger number of components (pseudo atoms) (*unitcell types*)

Discrete Chebyshev Basis

- **Orthogonal discrete Chebyshev basis for Multi-components system**
  - $\boldsymbol{\sigma}=\{\sigma_1, \sigma_2, \ldots, \sigma_N\}$: N (number of lattice sites), σ_i (site occupation)

    $\sigma_i = \{-1, -(m-1)/m, \ldots, 1\}$: M (number of components) M=2m *or* 2m+1
  - *Discrete chebyshev polynomial* Θ_n *:*

$$\Theta_n(\sigma) = \sum_k c_{n,k}\sigma^k, \qquad \left\langle \Theta_n(\sigma), \Theta_m(\sigma) \right\rangle_{all\,\sigma} = \delta_{nm}$$

  - *Cluster function* Φ*:* $\Phi_\alpha^s = \prod_{\substack{s=\{n_1,\ldots\} \\ \alpha=\{p_1,\ldots\}}} \Theta_{n_i}(\sigma_{p_i})$

  - *Orthogonal cluster functions:*

$$\left\langle \Phi_\alpha^s, \Phi_\alpha^t \right\rangle_{all\,\vec{\sigma}} = W\delta_{st}$$

Algorithm

First principles calculations of all possible unitcells to locate group of unitcells with lower energies

•To reduce the number of unitcell types to be included in further calculations.

↓

First Principle calculations on small supercells built from selected unitcells

•To generate datasets for evaluating effective cluster interaction parameters (ECI)

↓

Solve the over determined equations to find out the effective cluster interactions (ECI)

•To obtain ECI from the supercell calculations.

↓

Do Monte Carlo simulations to calculate free energy of much large systems based on ECI

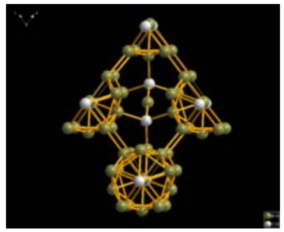
The large supercell's energy is calculated by ECI instead of first principle calculation

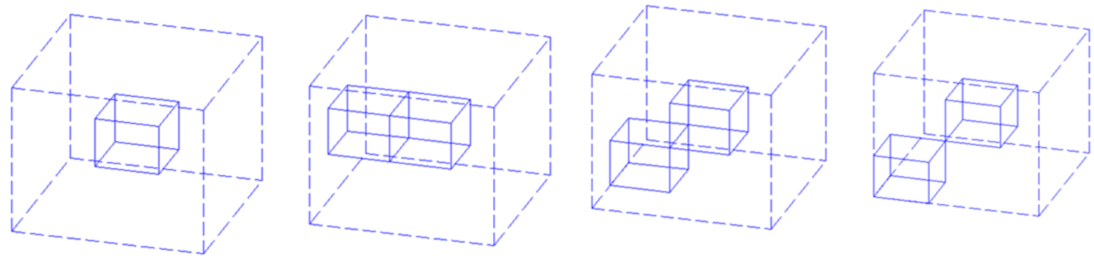
•To estimated configuational free energy.

Example: B_4C

Clusters:

(1) self
(2) face-share
(3) edge-share
(4) corner-share





Unitcell Selection:

(1) for periodic structures consisted of one type of unitcell
compute the total energy and pressure

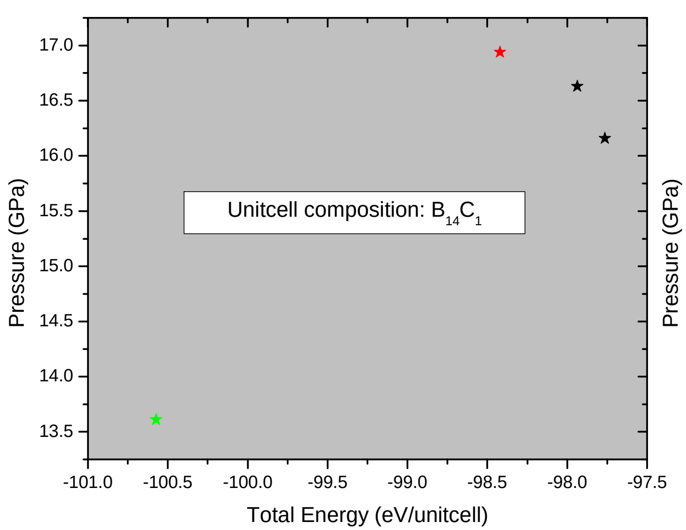
(2) group analysis of the total energies and pressures of the unitcells with the
same concentration

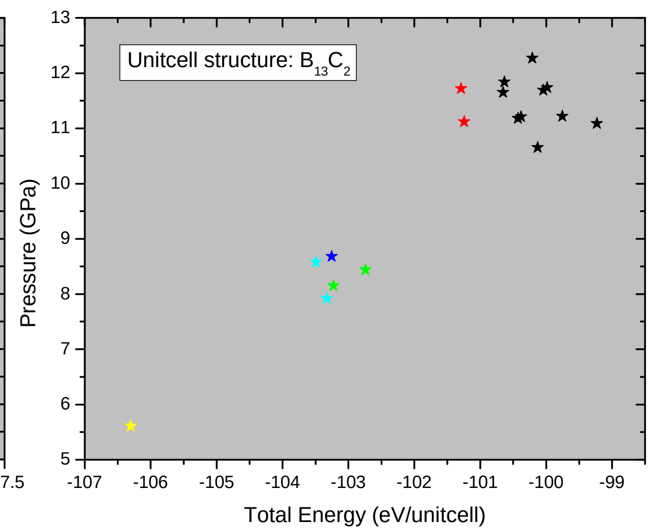
(3) select the lowest group in the total energies-pressure plot to be included in
the set of unitcells (prefers unitcells with minimal intercell interactions)

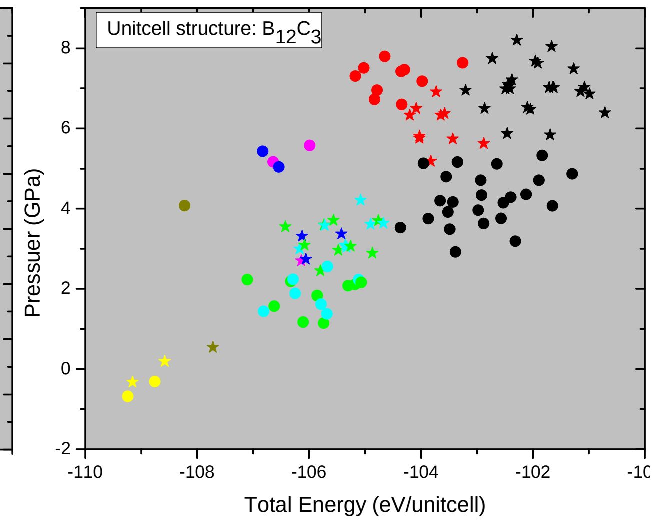
(4) it is possible to add more unitcells to the set using the criteria of
cross-validation

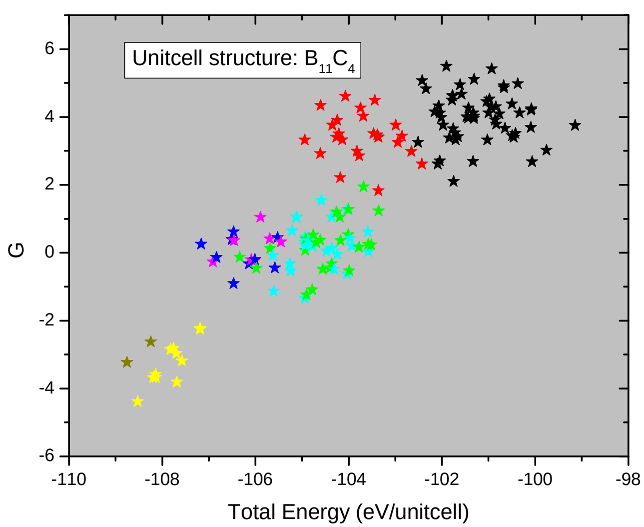
Unitcell Selection

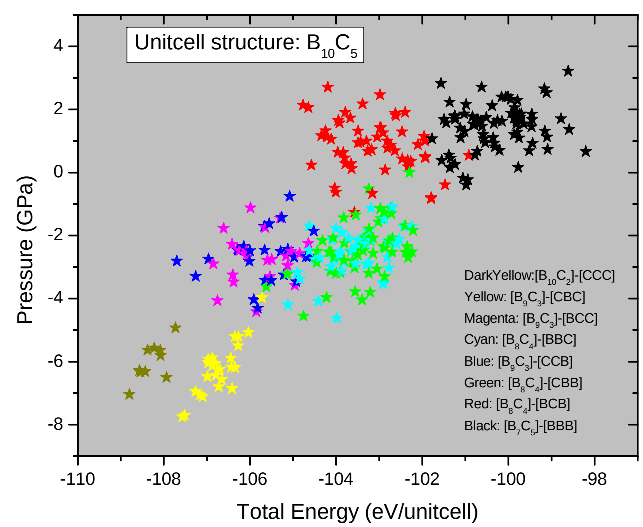
Concentration dependent energies of lattice with 1 unitcell type



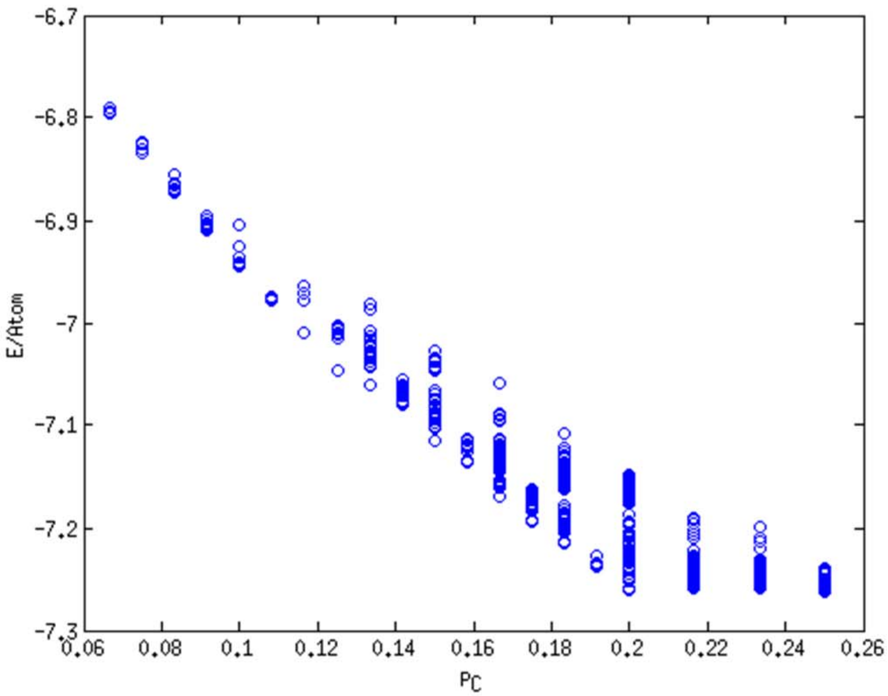


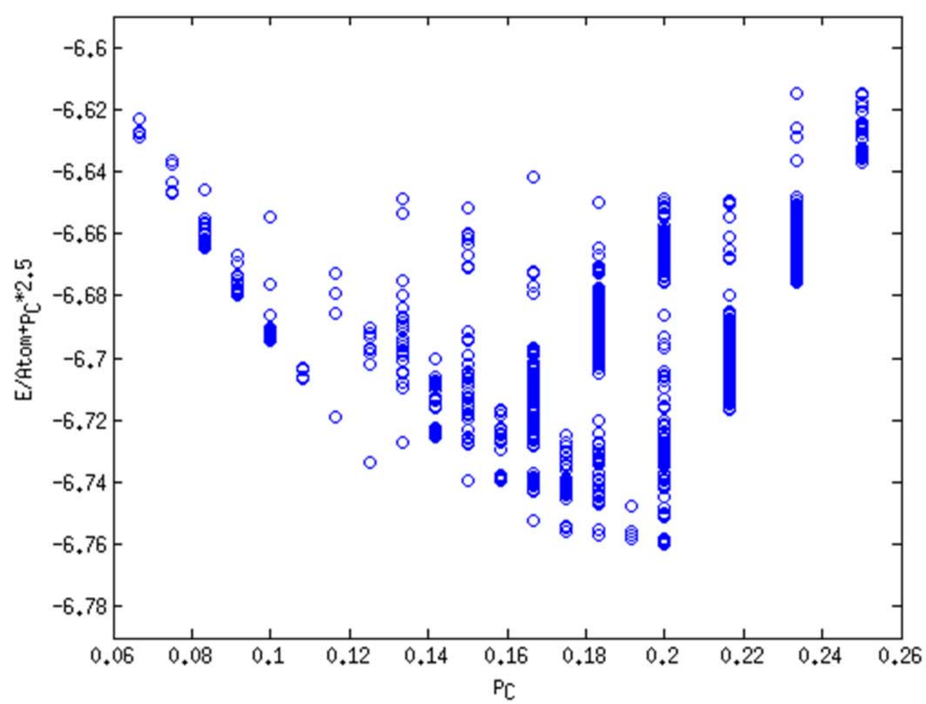




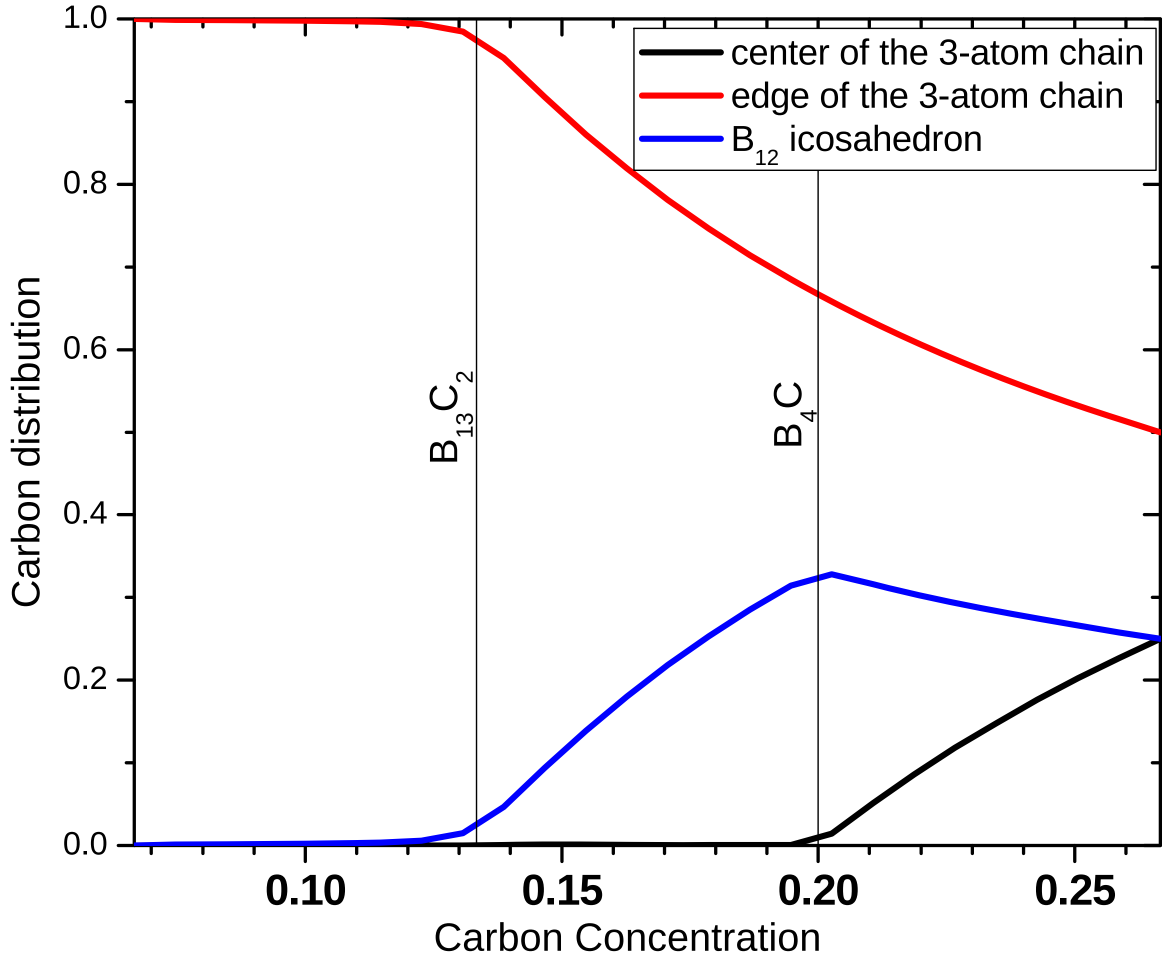


Convex Plot of Supercell Sampling



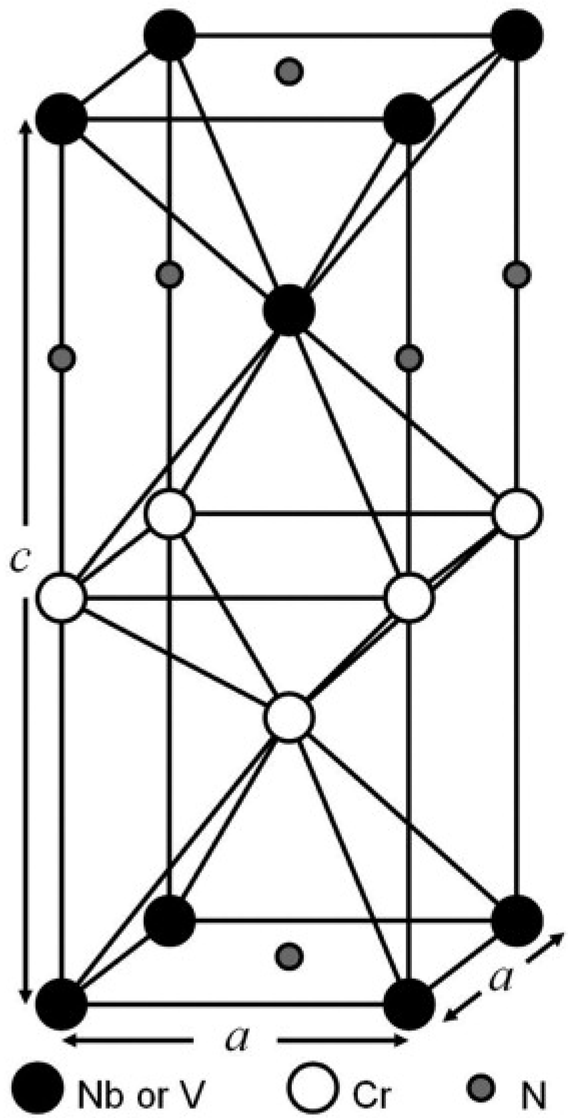


Site Occupation from Monte Carlo Simu.



Carbon distribution in Boron carbide $B_{1-x}C_x$. Red line indicates carbon percentage at two edge sites of the 3-atom chain. Blue line shows the carbon percentage in the icosahedrons. Black line depicts carbon percentage at the center of the 3-atom chain.

Example: Z-phase in steel



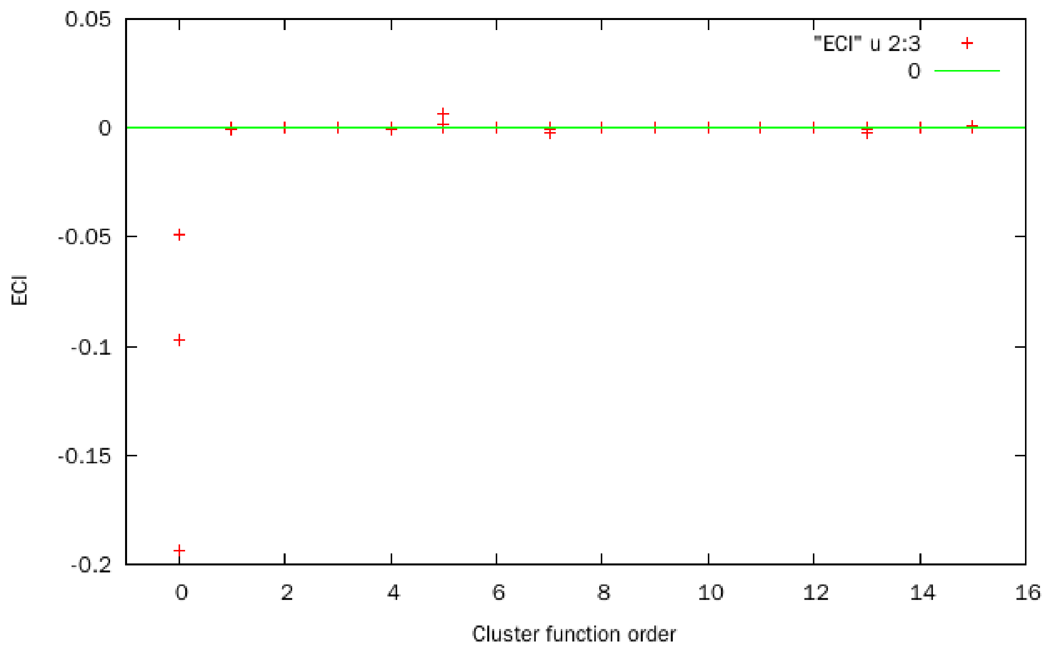
➢Based centered tetragonal lattice

➢Primitive cell contains two disordered sublattice sites that are occupied by Nb or V

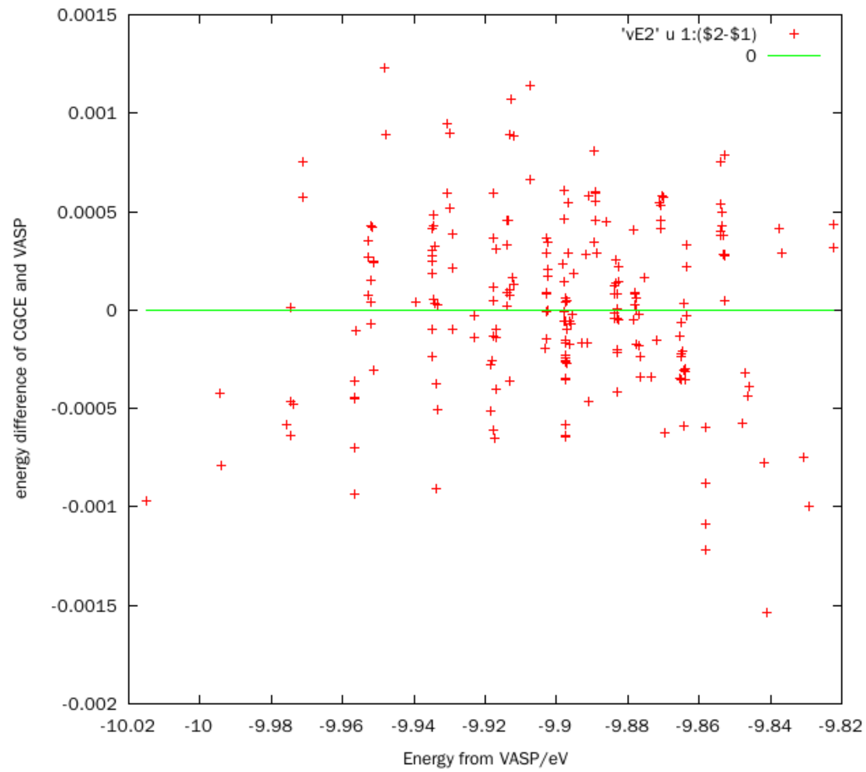
➢4 type of cells used in the UEM calculation.

➢Clusters limited no more than pairs.

ECI and Cross-Validation

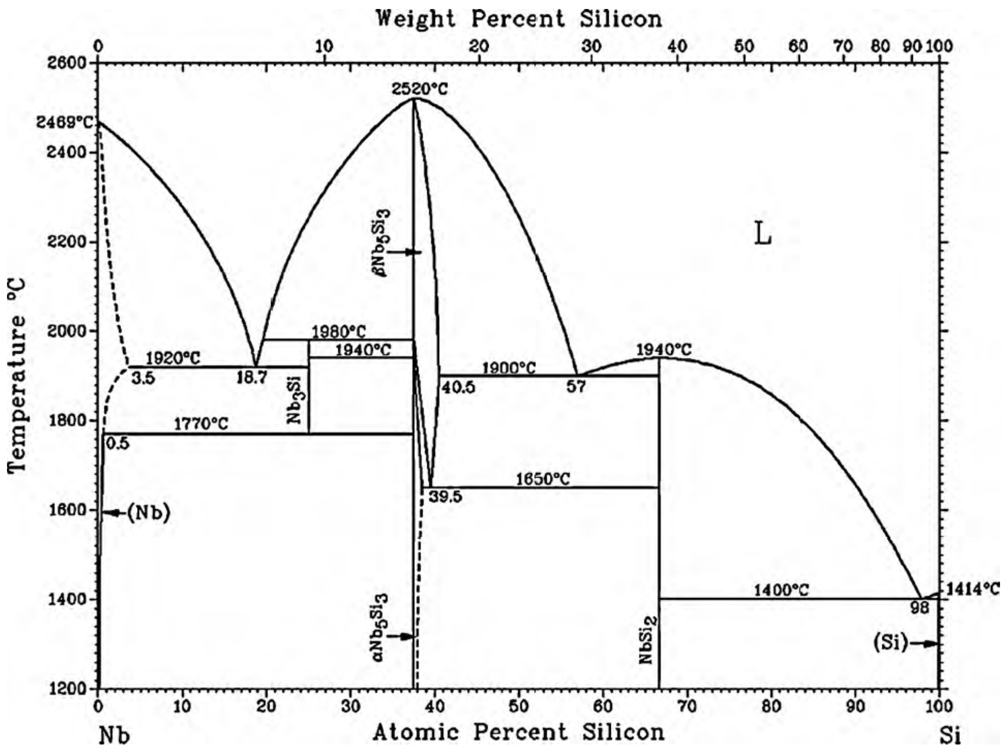


ECI vs. Cluster function order parameter *s*
Higher order negligible

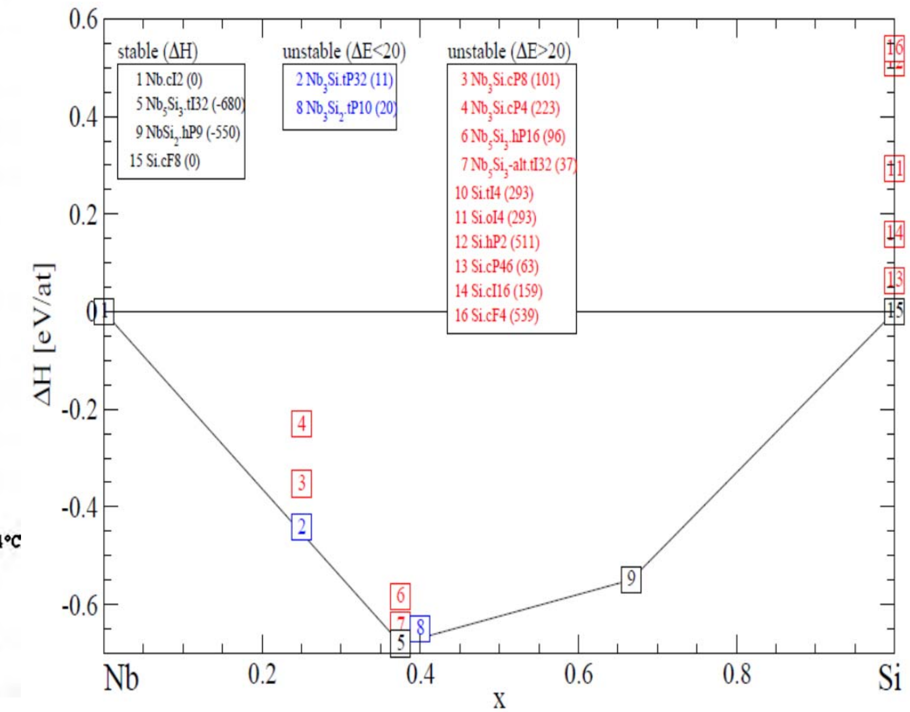


Cross-Validation: (energy difference between energies obtained from direct VASP calculations and cluster expansion) . ECIs are from obtained from different supercell set.

Application to Nb-Si Alloys



Convex Hull Plot

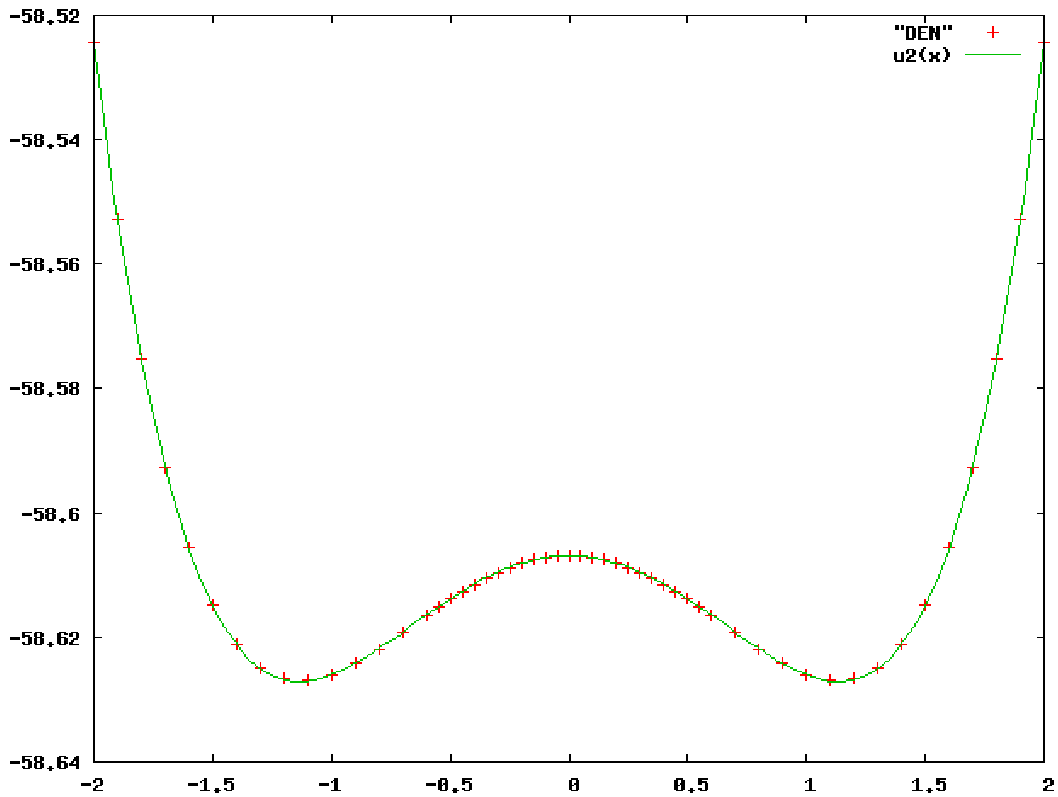


Elastic Constants

Comp.	Phase	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	K	G
Nb	cI2								
Nb_3Si	cP4	111	220			72		184	21
	cP8	323	119			68		187	81
	tP32	267	175	133	284	84	95	189	78
Nb_5Si_3	tI32	383	102	121	334	131	121	198	127
	tI32’	381	123	112	329	87	129	198	110
	~~hP16~~	~~327~~	~~153~~	~~99~~	~~359~~	~~-1132~~	~~87~~		
Nb_3Si_2	tP10	349	136	127	298	131	118	197	116
$NbSi_2$	hP9	349	76	80	442	126	136	179	138

(Unit: GPa)

Phonon Module Analysis



$$E(x) = a_0+a_2*x^2+a_4*x^4+a_6*x^6$$

a_0=-58.6±1.56×10^{-5}, a_2=-0.0306±5.51×10^{-5},

a_4=0.0110±3.78×10^{-5} a_6=4.51×10^{-4}±6.65×10^{-6}

- Mo_2B
- Negative phonon mode A_{2g} found at zone center indicate instability
- Further phonon mode analyzed indicate symmetric double well energy profile.

Summary

- Developed and tested the temperature-pressure dependent thermal expansion tensor and elastic constants module in G(P,T)

- Improved the implementation of the unitcell expansion method within the G(P,T) package.

- Developed additional modules for phonon mode analysis.

Future Plan

- Compute thermodynamic and mechanical properties of additional phases found in the Nb-Si-Cr-X alloy systems.

- Using the UEM method to study high entropy alloys

- Developing faster algorithm based on the special quasirandom structure (SQS) method for large scale material screening.

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