AB INITIO MODELING OF THERMOMECHANICAL PROPERTIES OF Mo-BASED ALLOYS FOR FOSSIL ENERGY CONVERSION

NETL Project DE-FE0004007

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(Presented by Paul Rulis)

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Outline

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II. Review of milestones

III. Accomplishments in Year 1 & 2 (July 1, 2011 to June 30, 2012)

IV. Results for Year 3 (July 1, 2012 to June 30, 2013)

a. Development of a method for temperature dependent mechanical properties using *ab initio* molecular dynamics.

b. Investigation of thermo-mechanical properties of composite alloys for the T1 phase (Mo_5Si_3).

c. Continuation on the construction of failure envelopes of Mo_5Si_3 and Mo_5SiB_2.

V. Conclusions on the work for Year 3

VI. Plan for the future

I. Background

♠ The main objective of this 3-year project is to carry out extensive computational modeling of Mo-based alloys that can be used in a high temperature and high pressure environment.

♠ Specific aims are:

1. To develop new methods for calculating thermomechanical properties at extreme conditions.
2. To explore material properties within the Mo-Si-B system using a supercell approach.
3. To understand the enhanced properties at the fundamental level.
4. To establish effective collaborations with other research groups.

VI. Review of milestones and time line

Four milestones to be reached in 3 years for this project based on the tasks and subtasks outlined in the statement of project objectives (SOPO).

[1] Mechanical properties and electronic structure of the 5 crystalline phases in the Mo-Si-B system. Milestone date: to be finished in first year.
Status as of June 2013: work completed, paper published, **milestone reached!**

[2] Development of the new computational method. Test of the computational codes on crystals. Milestone date: to be completed by the end of 2nd year.
Status as of June 2013: new method development, results reported and paper published! **Milestone reached!**

[3] Supercell modeling of composite alloys and identification of those with promising properties. Milestone date: to be completed by the end of 2nd year.
Status as of June 2013: Composite alloys completed with substantial results. Research direction reevaluated based on these results. **Milestone reached.**

[4] Application of new method to supercell models of composite alloys and exploration of new materials. Milestone date: to be completed by the end of 3rd year.
Status as of June 2013: Substantial results obtained (this talk). Results will be analyzed and submitted for publication. **Milestone reached.**

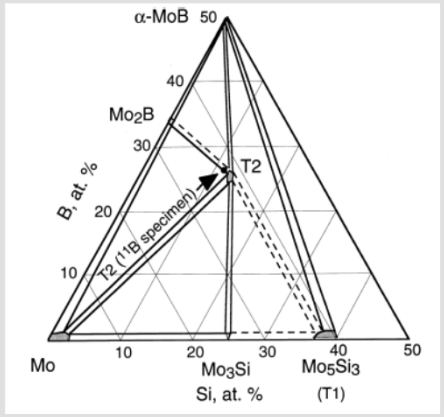
III. Accomplishments in Year 1 and Year 2
(reported at the last review meetings)

♠ Electronic structure and interatomic bonding calculations in 5 crystals within the Mo-Si-B system: $MoSi_2$, Mo_3Si, Mo_2B, Mo_5Si_3 and Mo_5SiB_2.

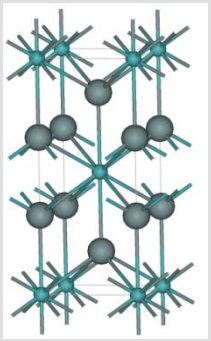
♠ Mechanical properties of the same 5 crystals.

♠ Calculations on the phonon spectra of the these crystals.

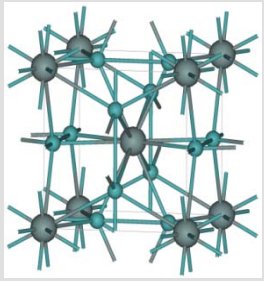
♠ Computational development for uniaxial tensile experiments.



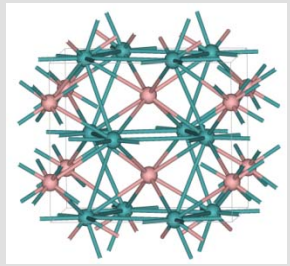
Portion of the Mo-Si-B phases diagram.



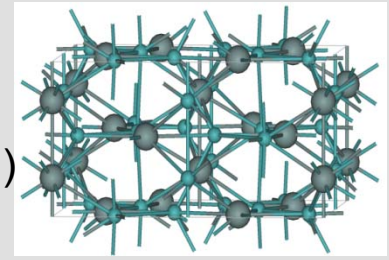
$MoSi_2$



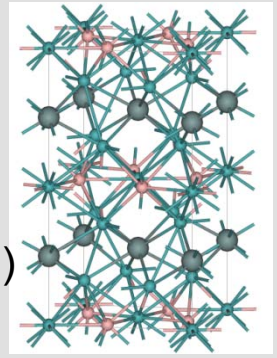
Mo_3Si



Mo_2B



Mo_5Si_3(T1)



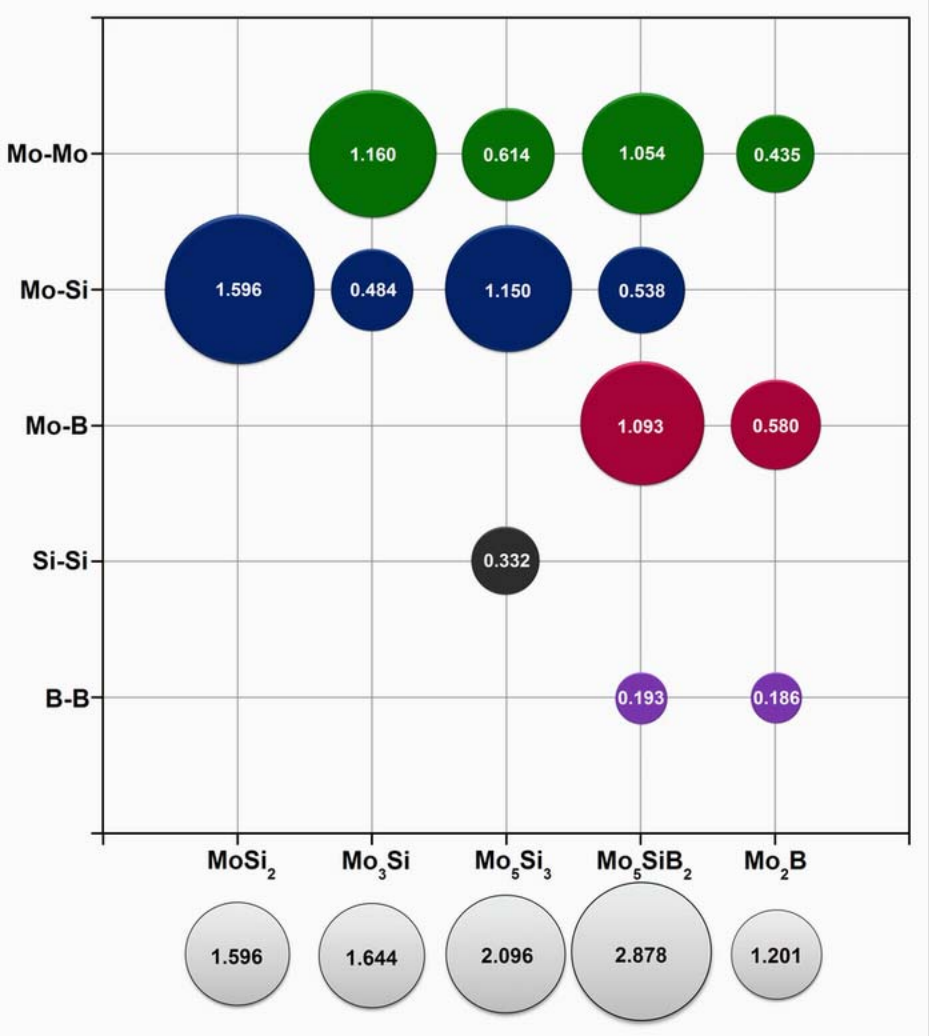
Mo_5SiB_2(T2)

♠ Electronic structure and bonding: 5 types of bonding (Mo-Mo, Mo-Si, Mo-B, Si-Si, B-B) in 5 crystals.

♠ Total bond order (BO)(represented by the size of the circles in the **figure** on the right) for five different types of the bonds in the 5 crystals. The total bond order for the crystal is shown at the bottom (x 1/2).
Mo_5SiB_2 has the largest circle, or strongest total bonding.

♠ These and other results suggest that addition of B can enhance the bonding and significantly improve the alloy properties.

♠ We focus our studies on the 2 crystals: Mo_5Si_3 (T1) and Mo_5SiB_2(T2). Both have b.c.t structure.



♠ Electronic structure and mechanical properties of supercell composite models between Mo_5Si_3 & Mo_5SiB_2

Calculated DOS at Fermi level in composite models of Mo_5SiB_2 in States/(eV-supercell).

Model	Total	Mo	Si	B
Mo_5Si_3	145.05	122.93 (84.7)	22.12 (15.3%)	-
$Mo_{160}Si_{64}B_{32}$	188.01	164.60 (87.6%)	19.74 (10.5%)	3.68 (1.9%)
$Mo_{160}Si_{56}B_{40}$	179.75	158.02 (87.9%)	17.18 (9.6%)	4.55 (2.5%)
$Mo_{160}Si_{48}B_{48}$	173.81	153.31 (88.2%)	14.92 (8.6%)	5.58 (3.2%)
$Mo_{160}Si_{40}B_{56}$	170.19	151.47 (89.0%)	12.36 (7.3%)	6.36 (3.7%)
Mo_5SiB_2	153.41	136.74 (89.1%)	10.00 (6.5%)	6.66 (4.3%)

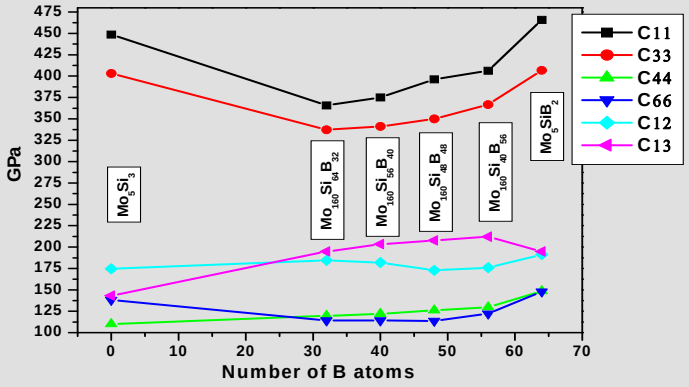
Comments on composite models:

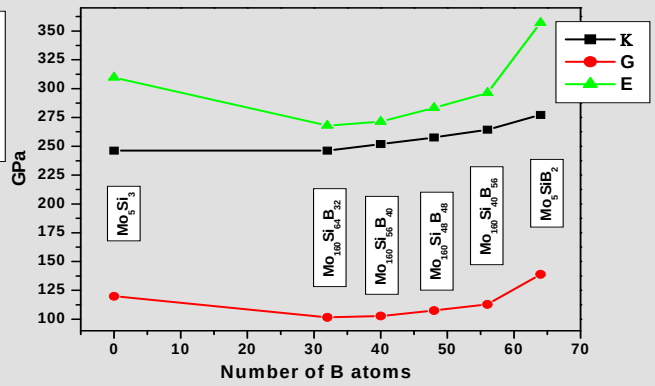
1. Both crystalline phases have lower $N(E_F)$ => stability of pure crystalline phases.
2. $N(E_F)$ dominated by states from Mo.
4. $N(E_F)$ components of B and Si do not scale with B concentration.

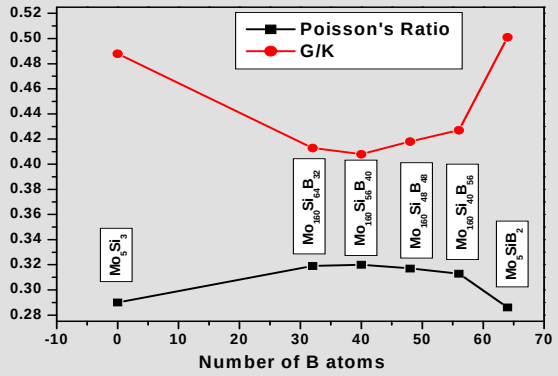
Calculated elastic constants and bulk properties of composite models $Mo_5(Si_1\text{-}yBy)_3$. (in GPa).

Models	C_{11}	C_{33}	C_{13}	C_{12}	C_{44}	C_{66}	K	G	E	η	G/K
$Mo_{160}Si_{96}$	448.8	403.1	143.1	174.7	0.00	138.3	246.9	83.64	225.5	0.348	0.339
$Mo_{160}Si_{64}B_{32}$	365.8	337.3	194.9	184.5	119.7	114.2	246.2	101.6	268.0	0.319	0.413
$Mo_{160}Si_{56}B_{40}$	375.1	341.2	203.3	181.9	122.1	114.3	251.9	102.7	271.3	0.320	0.408
$Mo_{160}Si_{48}B_{48}$	396.2	349.9	207.9	172.8	126.0	113.7	257.6	107.6	283.4	0.317	0.418
$Mo_{160}Si_{40}B_{56}$	406.2	366.7	212.3	176.0	129.8	122.3	264.4	112.8	296.2	0.313	0.427
$Mo_{160}Si_{32}B_{64}$	465.9	406.9	194.8	191.3	148.6	148.2	277.3	138.9	357.0	0.286	0.501

Variations of the mechanical properties as a function of B content in composites







Some conclusions on these composite model studies:

(1) $C_{11} = C_{22}$ is larger than C_{33} and both much larger than the C_{ij}s in the non-axial directions.

(2) The modulus values of the crystalline phases always larger than the composite models.

(3) Bulk modulus K, Young's modulus E and shear modulus G scale roughly as the B/Si ratio y. E > K > G.

(4) Individual variations in C_{ij} are related to the direction of applied strain to the model.

(5) The Pugh ratio G/K for the composite models show small variations, but the end members (Mo_5SiB_2 and Mo_5SiB_2) have much larger value. G/K < 0.5 is expected to be tough and G/K > 0.5 will be more brittle.

(6) It is not clear if the composite models of the two can give a tougher compound.

Composite models of replacing Mo by Nb in Mo_5Si_3 and Mo_5SiB_2.

Calculated on composite models $(Mo_{1-x}Nb_x)_5SiB_2$ and $(Mo_{1-x}Nb_x)_5Si_3$ for x = 0.05 (8 NB atoms) and x = 0.10 (16 Nb atoms). Also listed are the supercell models of Mo_5Si_3 (first line) and Mo_5SiB_2 (last line) for comparison (in GPa).

Models	C_{11}	C_{33}	C_{13}	C_{23}	C_{44}	C_{66}	K	G	E	η	G/K
$Mo_{160}Si_{96}$	468.8	403.1	143.1	174.7	0.00	138.3	246.9	83.64	225.5	0.348	0.339
$Mo_{152}Nb_8Si_{96}$	442.3	356.8	163.6	157.4	100.9	128.4	242.3	114.2	296.2	0.296	0.471
$Mo_{144}Nb_{16}Si_{96}$	426.1	346.7	158.6	162.1	104.3	126.3	238.6	114.2	295.5	0.294	0.479

Models	C_{11}	C_{33}	C_{13}	C_{23}	C_{44}	C_{66}	K	G	E	η	G/K
$Mo_{160}Si_{32}B_{64}$	465.9	406.9	194.8	191.3	148.6	148.2	277.3	138.9	357.0	0.286	0.501
$Mo_{152}Nb_8Si_{32}B_{64}$	478.2	396.2	198.2	167.5	161.8	140.1	275.1	143.5	366 .8	0.278	0.522
$Mo_{144}Nb_{16}Si_{32}B_{64}$	477.6	404.2	191.3	161.7	164.4	140.4	271.6	146.7	372.9	0.271	0.540

Some conclusions in the Nb substituting Mo composite model:

(1) Significant increase in G and E but little variation in K for both types of composite models.
(2) The increases are much larger in Mo_5Si_3-based composites than in the Mo_5SiB_2-based composites.
(3) These increase in modulus values increases with Nb content.
(4) An increase in G/K when Nb atoms are introduced with a large decrease in Poisson's ratio.
(5) G/K less than 0.5 is expected to be tough and G/K greater than 0.5 will be more brittle. It is possible that Mo/Nb composite models may be more brittle than the two crystalline phases.

Construction of failure envelope in of Mo_5Si_3 and Mo_5SiB_2. (Preliminary results, work still in progress!)

♠ What is materials failure? How to precisely define failure? open question!

♠ In engineering, materials failure is addressed by constructing empirical surfaces in stress or strain spaces for failure prediction. Construction of such surfaces difficult.

♠ Strength theories have been devised to be the essential parts of the material constitutive behavior (Mroz 2003).

♠ We proposed a method to construct the failure envelope of a crystal using data from multi-axial tensile experiment through 'theoretical' experiments using *ab initio* simulations.

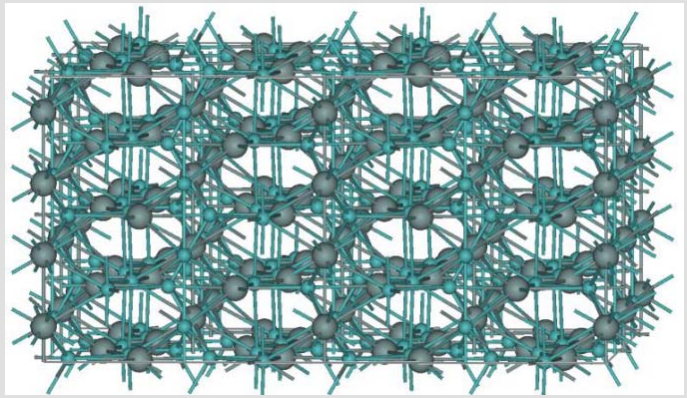
♠ This is an example of multi-scale modeling connecting microscale and macroscale properties.

♠ The strength of a material is characterized by a 3-d failure envelope (surface of failure points) in the stress space (σ_{xx}, σ_{yy}, σ_{zz}).

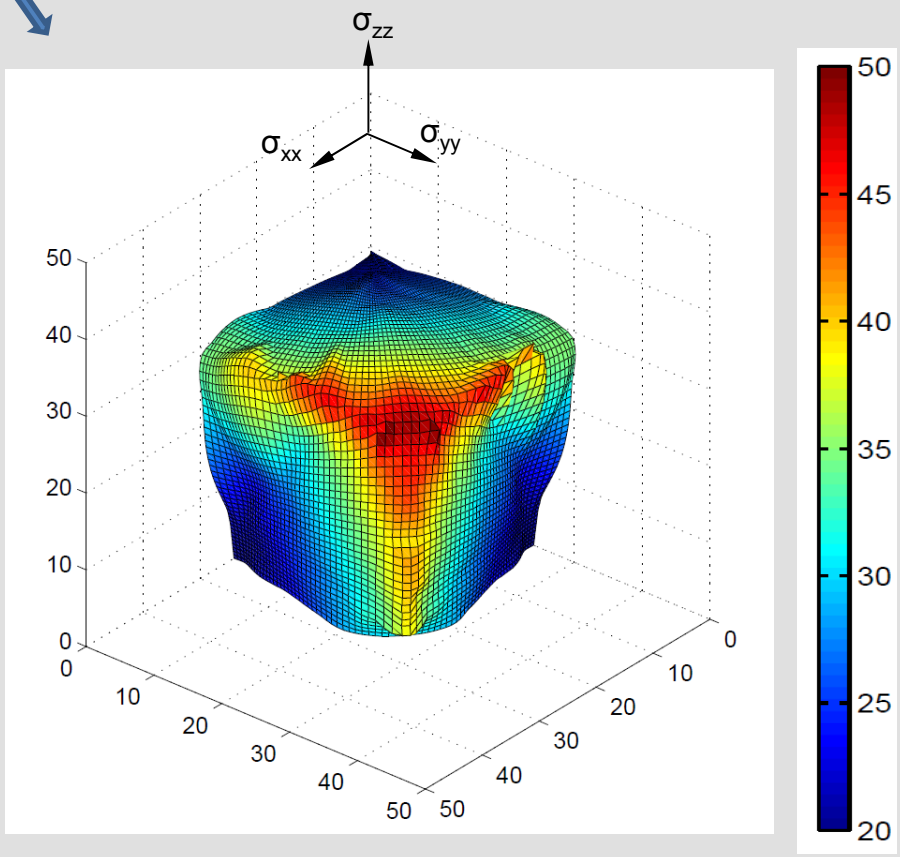
♠ The total area (or volume enclosed) of the envelope constitutes a single parameter representing the average strength of a materials under tensile deformation.

♠ The shape and color of the envelope delineate the variations of the strength in different directions.

Multi-axial failure envelope in Mo_5Si_3 (237 data points)

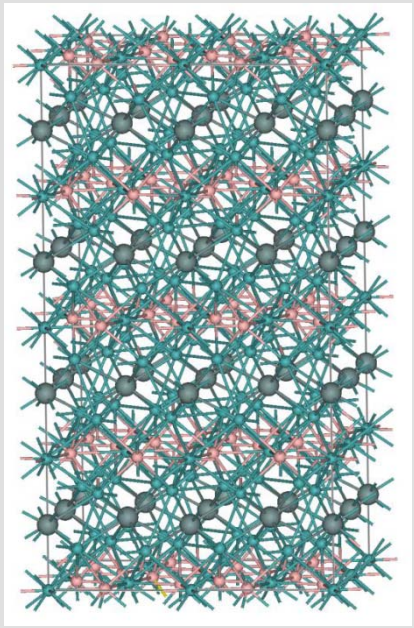


Orthorhombic 256-atom supercell model of Mo_5Si_3 used for tensile experiment for failure envelope.

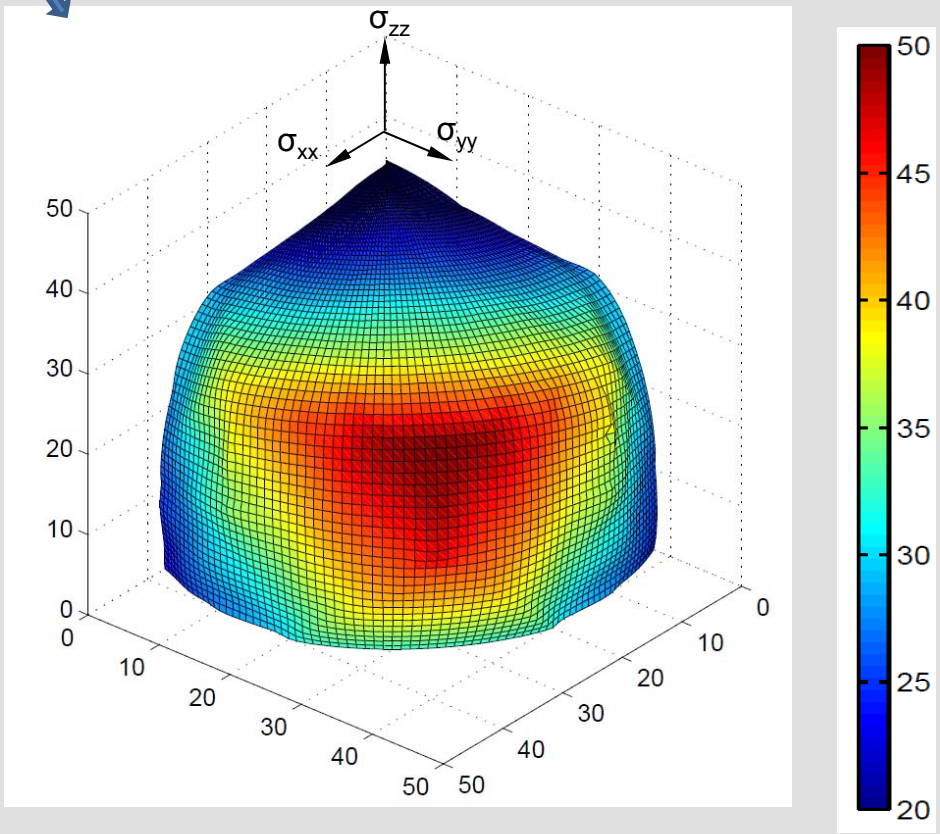


♠ Total volume enclosed: $2.800 \times 10^4 (Å)^3$;
Total surface area: $2.157 \times 10^3 (Å)^2$.

Multi-axial failure envelope of Mo_5SiB_2 (239 data points)



Orthorhombic 256-atom supercell model of Mo_5SiB_2 used for tensile experiment for failure envelope.



♠ Total volume enclosed: $5.473 \times 10^4 (Å)^3$; (95.5% **larger** than in Mo_5Si_3).
Total surface area: $3.424\ 10^3 (Å)^2$; (58.7% **larger** than in Mo_5Si_3).

♠ Mo_5SiB_2 is much stronger than Mo_5Si_3 based on failure envelope analysis.

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IV. Results for Year 3 (This presentation)

a. Development of a method for temperature dependent mechanical properties using *ab initio* molecular dynamics.

b. Investigation of thermo-mechanical properties of composite models for T1 phase (Mo_5Si_3).

c. Continuation on the construction of failure envelopes of Mo_5Si_3 and Mo_5SiB_2.

a. T-dependent mechanical properties using *ab initio* molecular dynamics (AIMD)

♠ Mechanical properties over broad temperature range are needed which are difficult to measure at ultra high T.

♠ Theoretical simulation is ideal to guide experiments.

♠ Present extrapolation techniques has only limited success at high T. AIMD can obtain high T properties far more accurately.

♠ Combination of AIMD and stress-strain methods can be used to obtain high T elastic and mechanical properties.

Method and procedures

- **Vienna *ab-initio* simulation Package (VASP):**
  - PAW-PBE potentials
  - Electronic convergence = 10^{-4} eV; Energy cutoff = 500 eV
  - Γ point only calculation
  - 2fs MD step
  - MD on the Born Oppenheimer surface (exact KS-ground state)
  - Canonical ensemble (NVT) and Nose-Hoover thermostat

$$\ddot{\tilde{\mathbf{r}}}_i = \frac{\tilde{\mathbf{F}}_i}{m_i \tilde{s}^2} - \frac{2\dot{\tilde{s}}\dot{\tilde{\mathbf{r}}}_i}{\tilde{s}},$$

$$\ddot{\tilde{s}} = \frac{1}{Q\tilde{s}} \left(\sum_i m_i \tilde{s}^2 \dot{\tilde{\mathbf{r}}}_i^2 - g k_b T_0 \right)$$

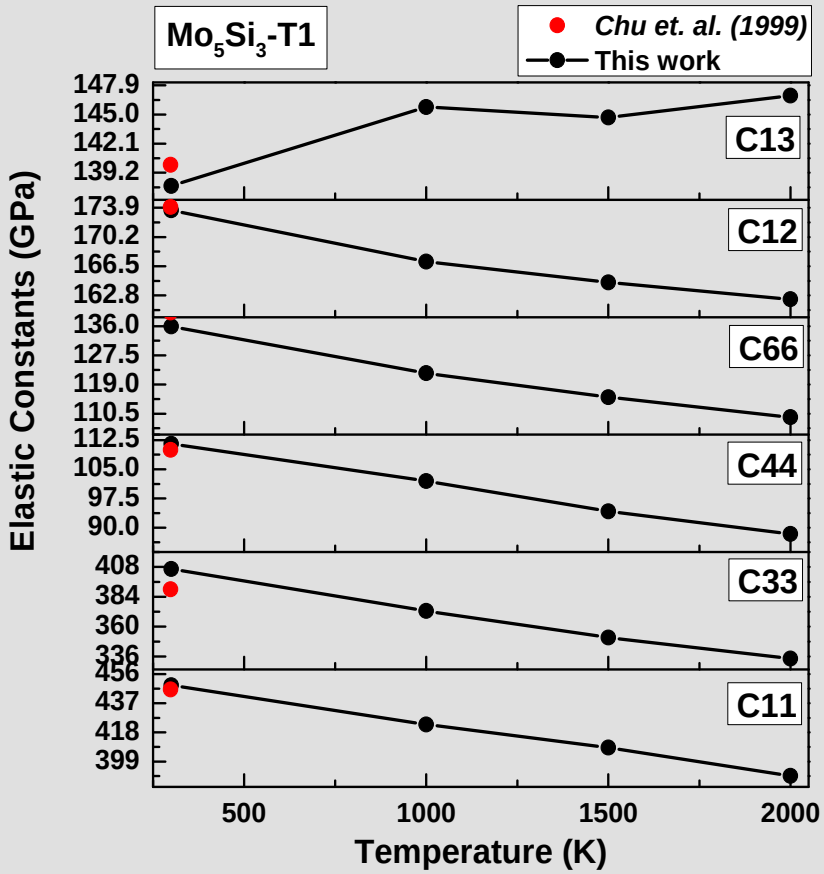
$\tilde{s}$ = time-scaling parameter

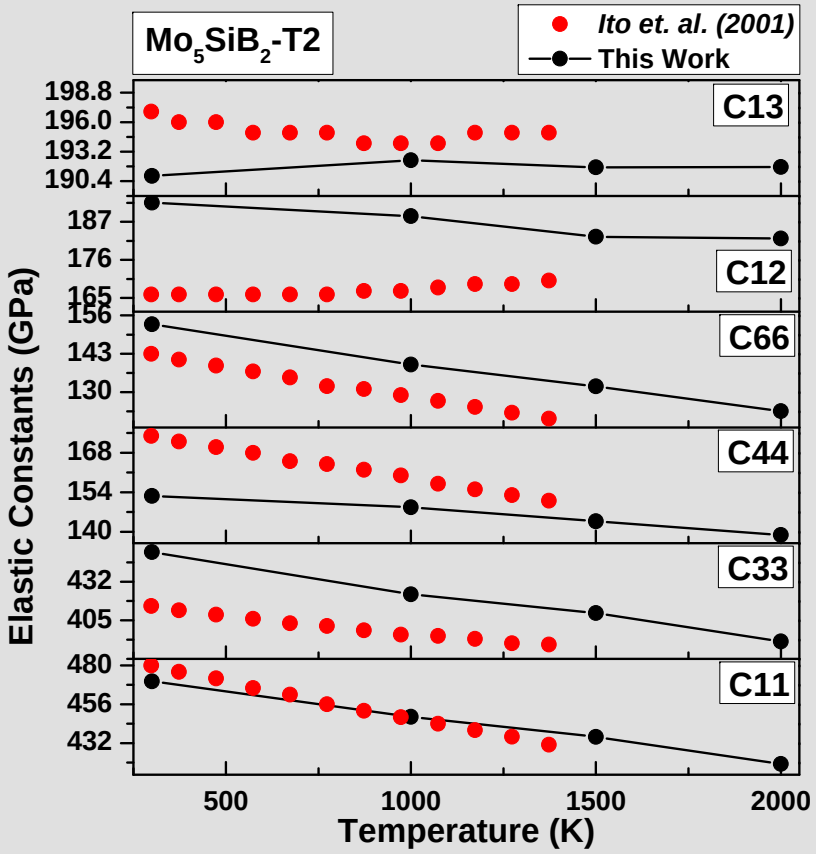
Q = "mass" = strength of coupling between the reservoir and the real system and influences the temperature fluctuations

g = N_{df} in real-time sampling

- **Elastic Property Calculations**:
  - Strain – Stress analysis approach $\sigma_j = \sum_{j=1}^{6} C_{ij}\varepsilon_j$
  - Elastic bulk Properties using Voigt-Reuss-Hill (VRH) approximation

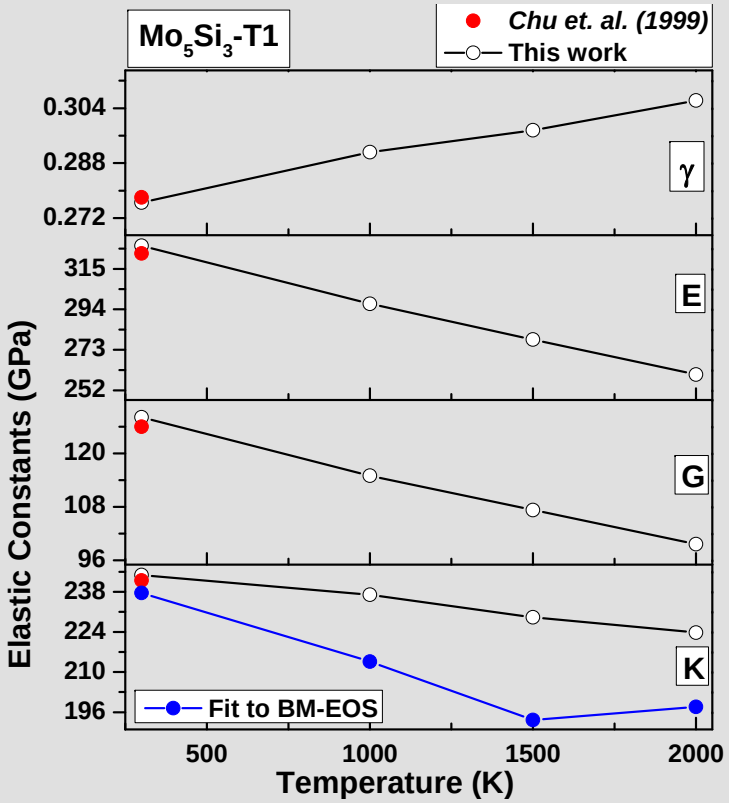
Results: T-dependent elastic coefficients and comparison with Experiment

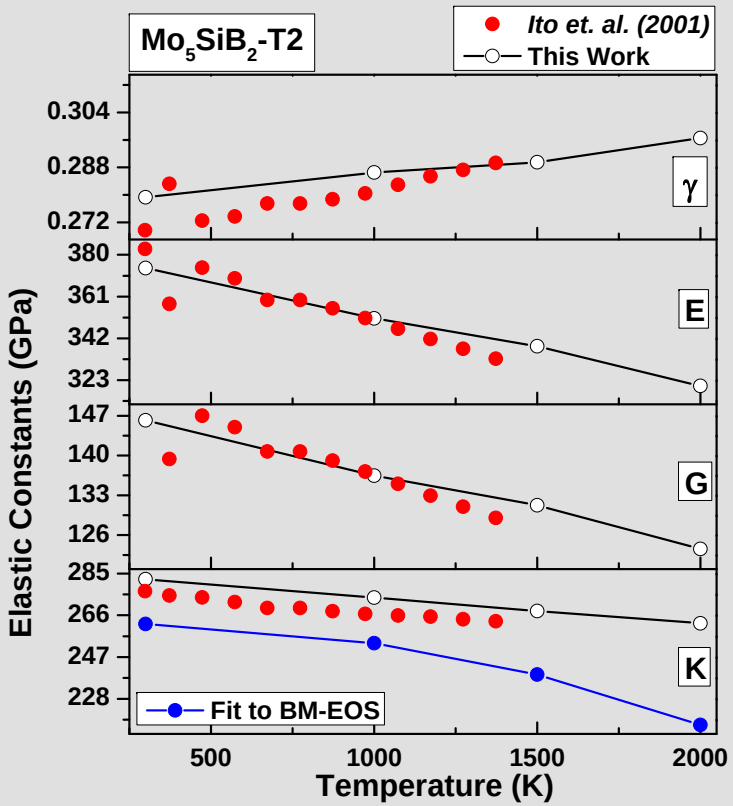




- Temperature dependence of T2 agrees well with experiment.
- No experimental data exist for T1 except at RT, which also agree well.
- $C_{11} + C_{12} > C_{33}$ for both crystals. This implies bonding in the basal plane is grater than the [001] direction

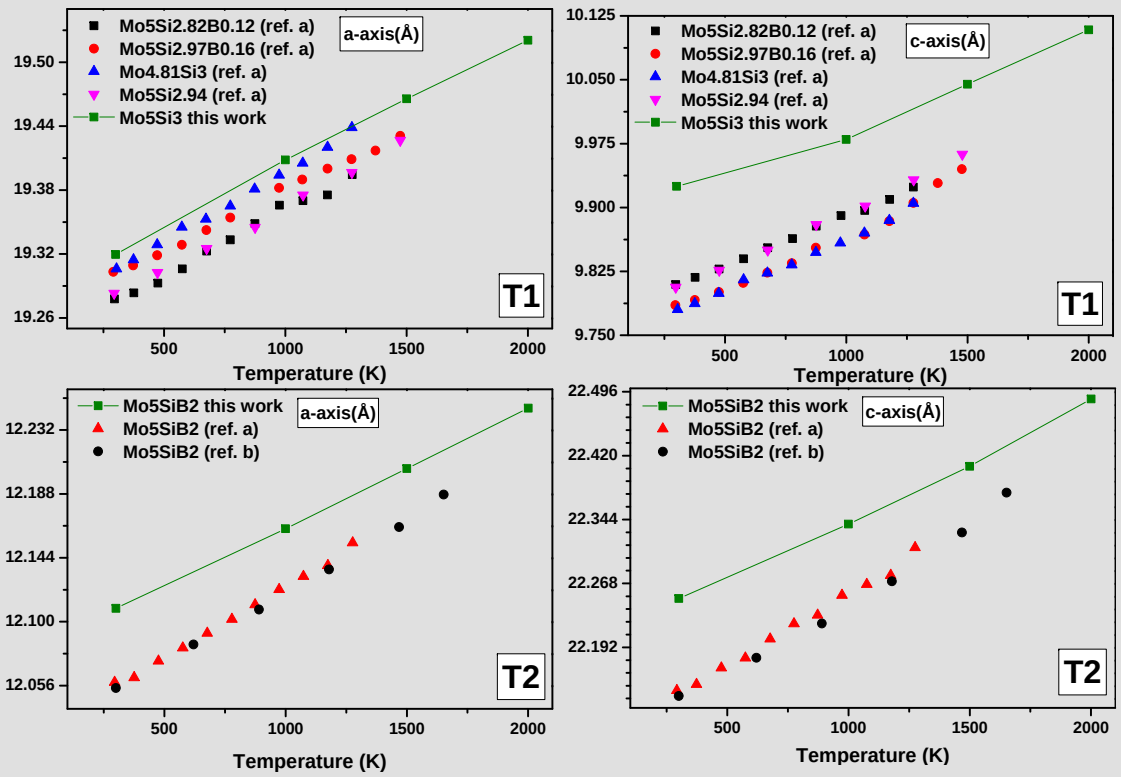
T-dependent bulk mechanical properties and comparison with experiment





- "K" obtained from fitting to 3rd order Birch–Murnaghan EOS fails at higher T
- T2 agrees well with the experimental trend from temperature dependence
- For T1 only R.T. values are found but still agrees
- Bulk properties of T2 is better than T1 which have about 20% higher K
- Temperature dependence of both crystals follow similar trend

Thermal expansion properties and comparison with experiment



- Over estimation of volume by 1.5%
- Expected within GGA

♠ Both crystals appear to expand linearly as it is shown in literature

♠ T1 in good agreement for a-axis but less for c-axis. Not finding c/a ratio accurately enough in using NVT procedure.

♠ T2 phase has less thermal expansion anisotropy, agrees well with the experiment.

♠ Assuming a linear dependence CTE and TEA can be calculated.

$$\alpha_a = \frac{1}{a_0}\frac{da}{dT}$$

♠ TEA is a excellent agreement.

[a] (*Zhao et. al. Intermetallics 12 (5), 493 (2004)*), Temperature [290 – 1475 K]
[b] (*Rawn et. al. Intermetallics 9 (3), 209 (2001)*) Temperature [300 – 1650 K]
[c] (*Chu et. al. Intermetallics **7** (5), 611 (1999)*) Temperature [310 – 745 K]

Comparison of Coefficient of Thermal Expansion and Thermal Expansion Anisotropy in T1 and T2 phases

	α_a (10^{-6} K^{-1})	α_c (10^{-6} K^{-1})	(α_c/α_a)
Mo_5Si_3(present)	6.14	11.00	1.80
$Mo_5Si_{2.82}B_{0.12}$ [a]	6.27	11.90	1.89
$Mo_5Si_{2.97}B_{0.16}$ [a]	5.72	13.90	2.43
$Mo_{4.81}Si_3$ [a]	6.89	12.64	1.83
$Mo_5Si_{2.94}$ [a]	6.27	13.48	2.15
Mo_5Si_3 [c]	5.20	11.50	2.21
Mo_5SiB_2(Present)	6.71	6.25	0.93
Mo_5SiB_2 [a]	7.72	7.20	0.93
Mo_5SiB_2 [b]	7.90	7.50	0.95

[a] (*Zhao et. al. Intermetallics **12** (5), 493 (2004)*), Temperature [290 – 1475 K]
[b] (*Rawn et. al. Intermetallics **9** (3), 209 (2001)*) Temperature [300 – 1650 K]
[c] (*Chu et. al. Intermetallics **7** (5), 611 (1999)*) Temperature [310 – 745 K]

b. Investigation of thermo-mechanical properties of composite models for T1 phase (Mo_5Si_3).

♠ The T1 phase (Mo_5Si_3) has undesirable high thermal expansion anisotropy (TEA). High TEA => high micro cracking => inefficient as coating material.

♠ Alloying can be used to reduce TEA while maintaining mechanical strength.

♠ Two alloys considered using AIMD.

♠ Mo substitution with Vanadium (V): (1) Experiments show Mo-V-Nb-Si alloying reduces TEA, (2) They have comparable crystal structures.

♠ Si substitution with Aluminum (Al): (1) Improve oxidation behavior, (2) Adequate mechanical properties.

Modeling of Alloy Systems

♠ Requires supercell to explore sufficient composition range.

♠ Needs high T structures. AIMD is the only choice for this task.

♠ NVT approach is too cumbersome as many compositions have to be explored and EOS is not an objective for this study.

♠ AIMD within the Isothermal–isobaric (NPT) ensemble as implemented in VASP is ideal for this problem.

♠ Langevin NPT dynamics: For a system of N particles with masses M with coordinates X(t):

$$M\ddot{X} = -\nabla U(X) - \gamma M\dot{X} + \sqrt{2\gamma k_B T M}\, R(t)$$

$U(\mathrm{X})$: Interaction potential derived from DFT calculations

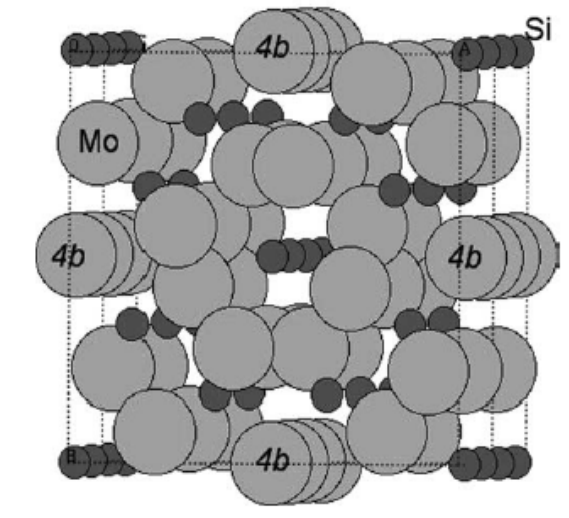
$R(\mathrm{t})$: Delta−correlated stationary Gaussian noise

γ: Friction coefficient

k_B: Bolzmann's constant

Reason for chose V substituting Mo: Mo_5Si_3 and V_5Si_3 have similar crystal structure

Compound	Structure type, space group lattice parameters	Atom	Site[a]	x	y	z
Mo_5Si_3	W_5Si_3 structure type	Mo	16k	0.0786(6)	0.2247(6)	0
	I4/mcm	Mo	4b	0	½	¼
	a = 9.650(2) Å	Si	8h	0.171(1)	0.671(1)	0
	c = 4.911(1) Å	Si	4a	0	0	¼
V_5Si_3	W_5Si_3 structure type	V	16k	0.0755(2)	0.2237(2)	0
	I4/mcm	V	4b	0	½	¼
	a = 9.4245(3) Å	Si	8h	0.1670(3)	0.6670(3)	0
	c = 4.7575(2) Å	Si	4a	0	0	¼



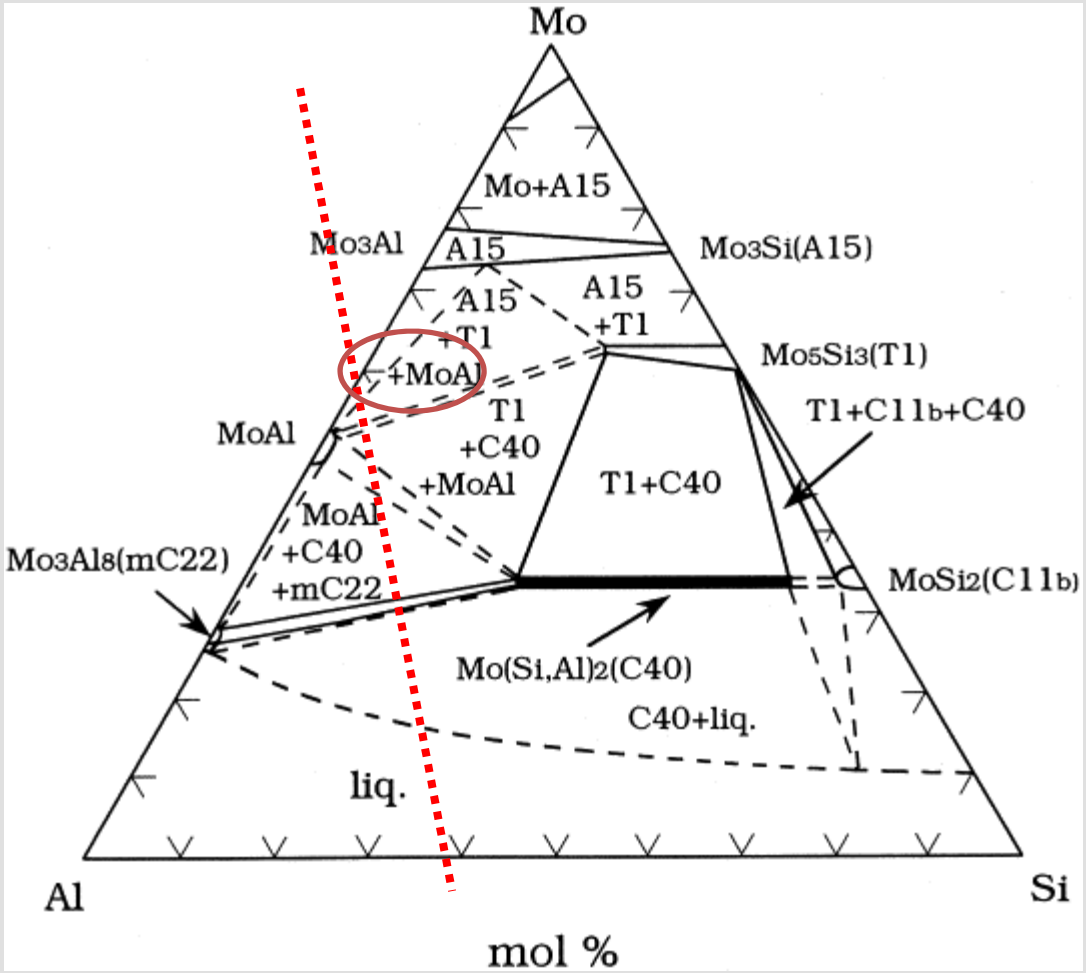
[a] Wyckoff notation indicating how often a particular site (e.g., site k) occurs in the unit cell.

Site	Mo-Mo (Å)
4b (chain site)	2.46
16k (non-chain site)	2.68
Elemental Mo	2.72

Atomic structure of Mo5Si3, showing two stacks of D8m unit cells viewed close to [001]. (Rawn et. al. 2005)

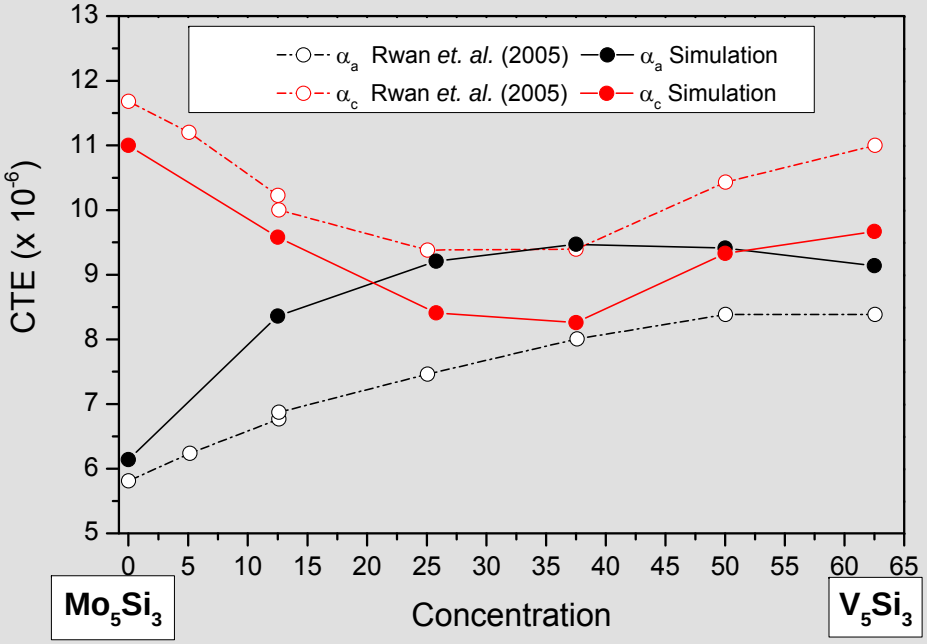
Reason for chose Al substituting Si in Mo_5Si_3: It may improve oxidation behavior and high solubility.

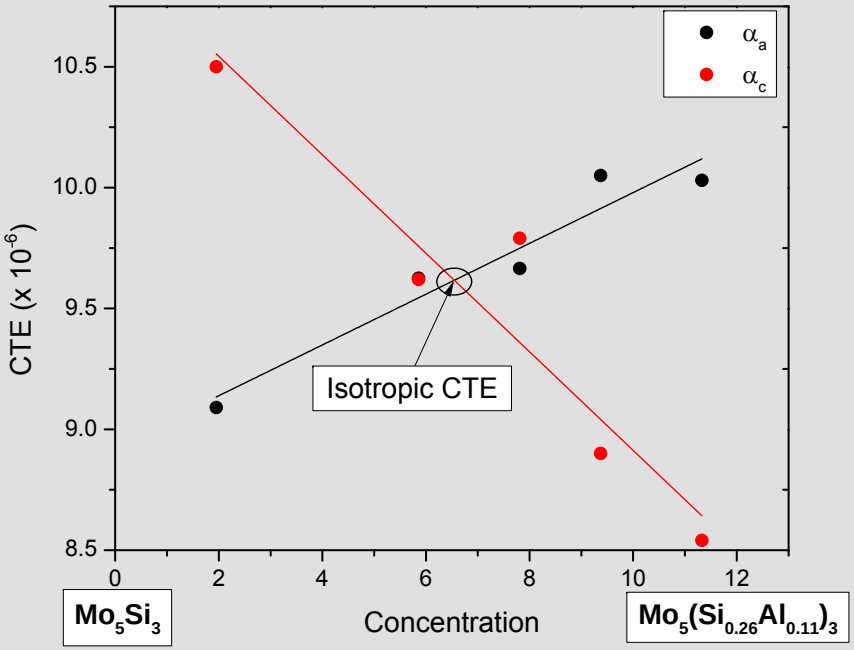
Composition	Al%
$Mo_{62.5}Si_{35.5}Al_{1.9}$	5.2
$Mo_{62.5}Si_{31.6}Al_{5.8}$	15.6
$Mo_{62.5}Si_{29.7}Al_{7.8}$	20.8
$Mo_{62.5}Si_{28.1}Al_{9.3}$	25.0
$Mo_{62.5}Si_{26.2}Al_{11.3}$	30.2



The phase diagram indicates that up to ~ 15 at. % of Al substituting for Si in T1 phase at 1600°C. Solubility may further increase at higher temperatures.

Preliminary results on the CTE in Mo-V-Si and Mo-Si-Al alloys





- Trend in Mo-V-Si (left figure) agree well with experiment.
- CTE obtained from the data at different temperatures from AIMD.
- Mo-V-Si calculations may not be sufficiently converged.
- Mo-Si-Al (right figure) show a linear behavior of CTE as a function of composition. More data points needed.

c. Continuation on the construction of failure envelopes of Mo_5Si_3 and Mo_5SiB_2.

♠ The work on the failure envelope construction has started early but is continuing effort.

♠ Most of the multi-axial simulation data have been obtained.

♠ Further analysis of the results needed in relation to the change in electronic structure.

♠ Manuscript on this work will be prepared.

V. Conclusions on the work for Year 3

♠ Proposed method is successful in capturing temperature dependent thermodynamic/mechanical properties of crystals.

♠ Calculated CTE and TEA are in excellent agreement with experiment.

♠ Temperature dependent C_{ij} for T2 is in good agreement with the experiment.

♠ The method may be applied to any materials.

♠ Mo-V-Si and Mo-Si-Al alloys can be used to reduce TEA of T1 phase.

♠ Site preference of Mo-V-Si alloy system is explicitly studies. 4b site is preferred.

♠ Mo-Cr-Si alloys affect on CTE and its relation to interatomic bonding can be investigated.

♠ We will extend the method to obtain electronic, mechanical and optical properties at high temperature.

VI. Plan for the future

- ♠ This project will be completed this year.
- ♠ Work in the same area will continue because of the opportunities offered by its successful conclusion.
- ♠ Most likely, we will engage in computational projects in other metallic systems investigating their properties under extreme conditions for specific applications of new and advanced materials.
- ♠ Extensive use of next generation of supercomputers absolutely necessary!

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THANK YOU !

WE GREATLY APPRECIATE DOE-NETL SUPPORT!

PROGRAM MANAGER: DR. RICHARD DUNST