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

NETL Project DE-FE0004007

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Outline

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II. Project outline and objectives

III. Technical approach and methods used

IV. Results on Mo-based alloys

a. Electronic structure and bonding

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I. Background

♠ Current materials used in fossil energy conversion are all based on transition metal alloys .

♠ Alloys of refractory metals (Nb, Mo, W etc.) have show great promise due to their high melting temperature.

♠ new materials envisioned are likely to be more complex both in structure and composition and contain defects and microstructures.

♠ Computational studies can lead the way in the search for novel materials or for significant improvements in existing materials without costly laboratory tests.

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

♠ Specifically aims are:

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

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II. Project outline and tasks

Task 1.0 Effective management of the research project through the 3 year period

Task 2.0 - Fundamental properties of the main phases in the Mo-Si-B system.

2.1 Elastic and mechanical properties of: $MoSi_2$,Mo_3Si,Mo_2B,Mo_5Si_3,Mo_5SiB_2.

2.2 Lattice phonon calculation of the same five crystalline phases.

2.3 Calculation of the electronic structure, bonding and charge distributions.

Task 3.0 – Development of new method for thermomechanical properties at high T&P.

3.1 Formulation and the calculation of Helmholtz free energy for one crystal (Mo_3Si).

3.2 Computer programing, code testing and implementation of the new scheme.

3.3 Extensive tests of codes and monitor performance on supercomputers.

Task 4.0 – *Ab initio* supercell modeling of Mo-Si-B alloys with different compositions.

4.1 Construction of several supercell models with different compositions $Mo_xSi_yB_z$.

4.2 Zero temperature mechanical properties of the modeled supercell composites.

4.3 Calculation of electronic structures of the modeled composites.

Task 5.0 – Investigation of the high T and high P properties of Mo-Si-B alloys.

5.1 Refine and improve codes for high T simulations to ensure stability & efficiency.

5.2 Investigate T and P dependent mechanical properties composite models.

Task 6.0 – Exploration of new phases and new materials.

6.1 Explore new phases or materials. Substitution of Mo with Nb, varying Si/B ratio.

6.2 Investigation of microstructures and defects in a few selective Mo-Si-B alloys .

Task 7.0 – Establishing effective collaborations.

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Technical approach and methods used

A. Methods

♠ **OLCAO** (Orthogonalized linear combination of atomic orbitals) developed by us. Used for electronic structure, bonding, optical properties, XANES/ELNES calculations.

♠ **VASP** (Vienna *Ab initio* Simulation Package): Used for structural relaxation, mechanical properties and tensile experiment using supercomputers.
For mechanical properties calculations, a strain (ε_i) vs. stress (σ_i) analysis is used according to obtain the elastic constants C_{ij} (or the compliance tensor S_{ij}).
From the C_{ij}, the bulk modulus (K), shear modulus (G), Young's modulus (E), and Poisson's ratio (η) are evaluated using the Voigt-Reuss-Hill (VRH) approximation

♠ ***Ab initio* phonon** and thermodynamic calculations. This is done within the quasi harmonic approximation (QHA) valid for temperatures < 1800K-2000K. The computational effort for *ab initio* phonon calculations is extremely demanding.

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More on the OLCAO method

OLCAO (orthogonalized linear combination of atomic orbitals)

A. Use LDA approximation.

B. Basis expanded in term of atomic orbitals consisting of Gaussians: minimal basis (MB), full basis (FB), or extended basis (EB) for different purposes.

C. Economic basis expansion is the key to large complex systems.

1) Effective Charge:
(for charge transfer)

$$Q_\alpha^* = \sum_i \sum_{n,occ} \sum_{j,\beta} C^{*n}_{i\alpha} C^n_{j\beta} S_{i\alpha,j\beta}$$

2) Bond Order:
(for bond strength)

$$\rho_{\alpha\beta} = \sum_{n,occ} \sum_{i,j} C^{*n}_{i\alpha} C^n_{j\beta} S_{i\alpha,j\beta}$$

: the eigenvector of the n^{th} band state.

: overlap matrix between Bloch functions.

α and β represent atoms, and the i and j represent the orbitals.

3) Site-decomposed density of states (PDOS).

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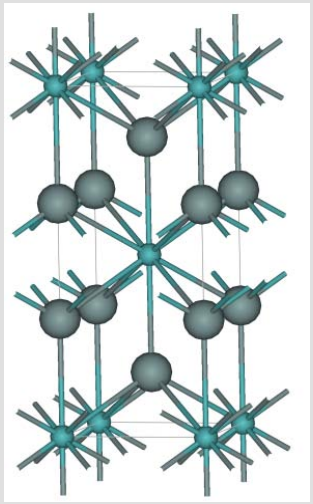
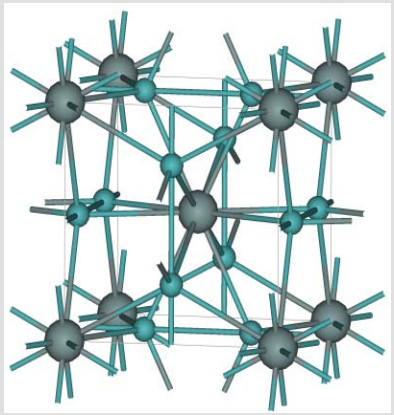
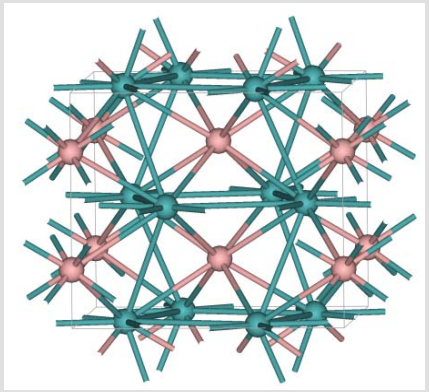
$MoSi_2$



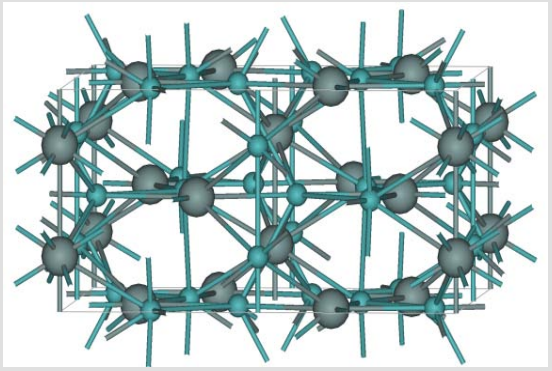
Mo_3Si



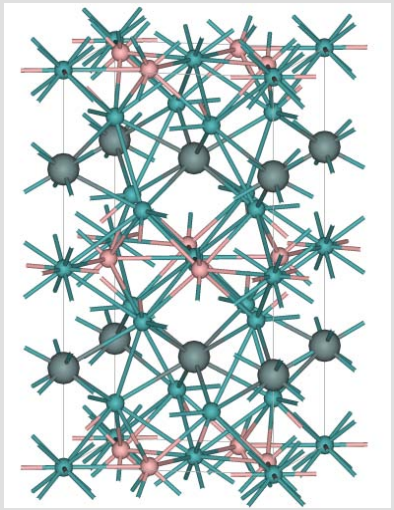
Mo_2B

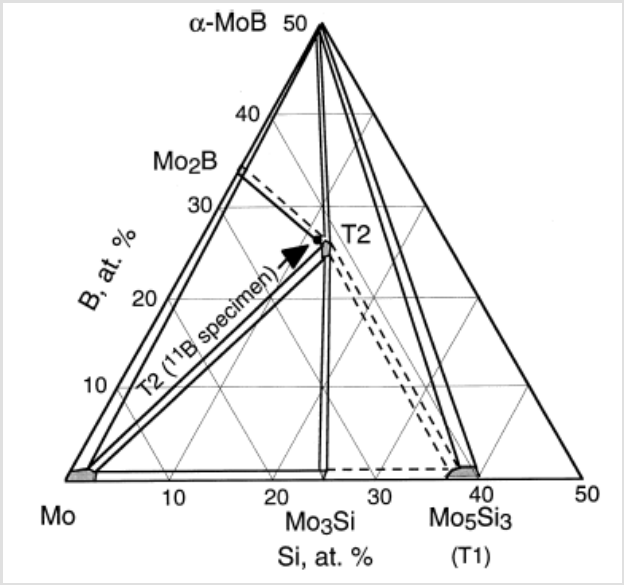


Mo_5Si



Mo_5SiB_2





Portion of the Mo-Si-B phases diagram.

Crystal structure information of five Mo-based alloys

Crystal	**$MoSi_2$**	**Mo_3Si**	**Mo_5Si_3**	**Mo_5SiB_2**	**Mo_2B**
a, b, c (Å)	3.206, 7.848	4.8900,	9.62, 4.90	6.027,11.067	5.543. 4.735
Space group	*I4/mmm*	*Pm3n*	*I4/mcm*	*I4/mcm*	*I4/mcm*
Cell	b.c.t.	b.c.c	b.c.t.	b.c.t.	b.c.t.
#atoms/cell	3	4	16	16	6
#atoms/full cell	6	8	32	32	12
Atom types	Mo, Si	Mo, Si	Mo1,Mo2, Si1,Si2	Mo1,Mo2,Si,B	Mo1,Mo2, B
Coordination (<3.2 Å): "/" separates the coordinations for two types of atoms (Mo1, Mo2) or (Si1,Si2).					
Mo-Mo	4	10	9 /10	8/11	8/11
Mo-Si	10	4	6/4	2/2	2/2
Mo-B	-	-	-	4/3	4/3
Si-Mo	5	12	10/8	10	-
Si-Si	5	-	2/2	-	
B-Mo	-	-	-	8	8
B-B	-	-	-	1	2
$N(E_F)$ (States/eV-cell) or gap:	0.31(eV)	3.90	11.0	9.6	4.2

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a. Electronic structure and bonding

Crystal	$MoSi_2$	Mo_3Si	Mo_5Si_3	Mo_5SiB_2	Mo_2B
Effective charge Q* (electrons):					
Mo	6.346	6.002	6.021, 6.048	6.026, 5.729	5.743
Si (B)	3.827	3.994	3.946, 3.977	4.025, (3.516)	(3.515)
Bond order (cut off < 0.09) (Bond length in Å and no of bonds)					
Mo-Mo		0.227(2.445)(2) 0.0898(2.995)(8)	0.108(2.834)(2) 0.165(2.762)(1) 0.199(2.450)(2)	0.102(2.733)(8) 0.121(2.798)(1) 0.117(2.845)(1)	0.181(2.613)(1) 0.127(2.704)(2)
Mo-Si	0.153 (2.610)(8) 0.186 (2.631)(2)	0.121(2.734)(4)	0.184(2.515)(1) 0.174(2.563)(1) 0.124(2.571)(2) 0.136(2.617)(4)	0.123(2.767)(2) 0.146(2.562)(2)	
Mo-B	-	-	-	0.172 (2.396)(4) 0.135 (2.394)(1) 0.135 (2.329)(2)	0.146(2.381)(4)
Si-Si	-	-	0.166 (2.450)(2)	-	
B-B	-	-	-	0.193 (2.073)(1)	0.093(2.367)(2)

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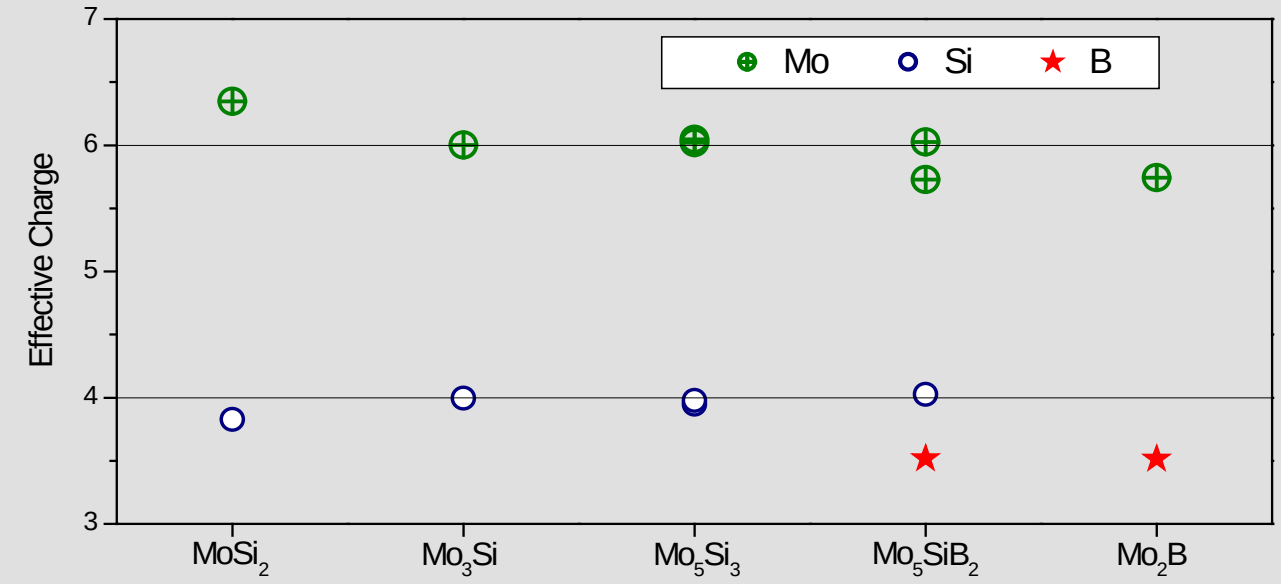
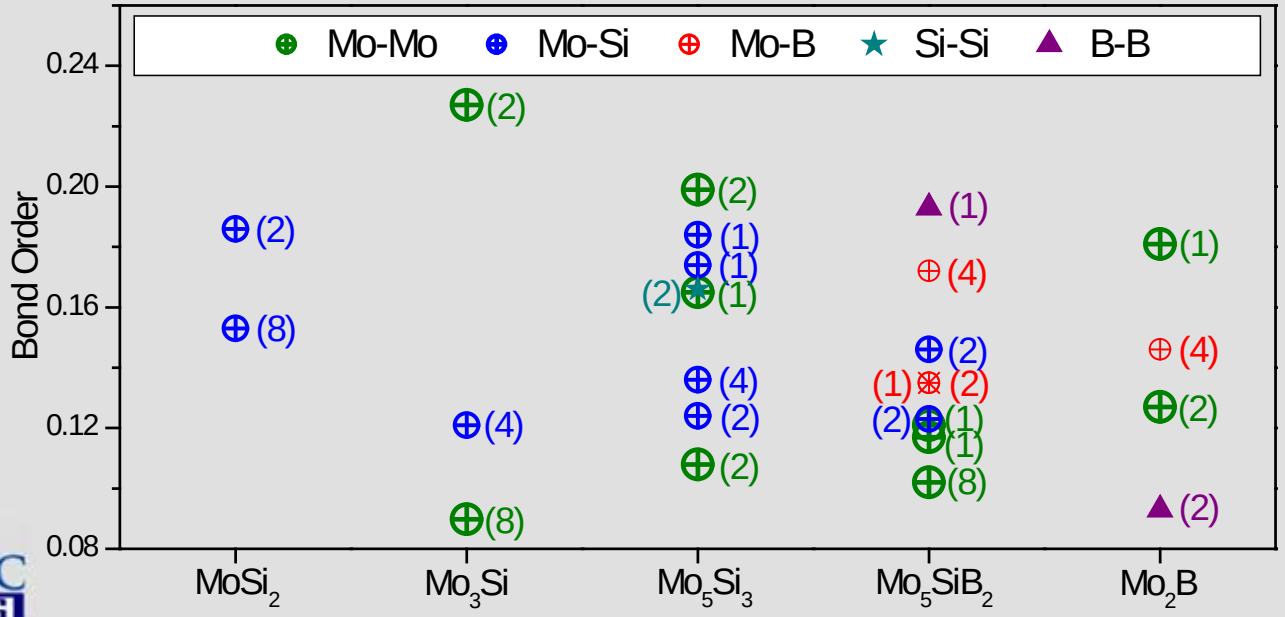
Plots of Q* and BO values from previous slide





Conclusions of the previous page

♠ Many types of bonds, especially Mo-Mo bonds. No Si-B bonds.

♠ The charge deviation from neutral atom for Mo and Si are small except in the Mo_5SiB_2 and Mo_2Si where one of the M loss ~0.1 electron which is gained by B., indicating these two crystals gain some ionic character.

♠ Cohesion in a crystal is related to the number of bonds and the strength of each bond (BO values). These values can be related to the mechanical properties of crystals.

♠ $MoSi_2$ has only 1 type of bonds (Mo-Si).

♠ Mo_3Si has 2 types of bonds (Mo-Mo, Mo-Si). Strong Mo-Mo bonds, No Si-Si bonds.

♠ Mo_5Si_3 has 3 types of bonds (Mo-Mo, Mo-Si, Si-Si). The only phases has Si-Si bonds of considerable strength. Mo-Mo bond strong.

♠ Mo_5SiB_2 has 4 types of bonds. The strongest one is the B-B bond. Mo-B bonds are also strong. All Mo-Mo bonds are weak.

♠ Mo_2B also has 4 types of bonds. B-B bond is very weak.

Thus the bonding in the 5 crystals can range from simple to very complex, many types to 1 type and they can be the same types with different BO values (not necessarily scale with bond lengths). This plethora display of the interatomic bonding make the atomic scale structure very complex, especially in Mo_5SiB_2 and Mo_5Si_3.

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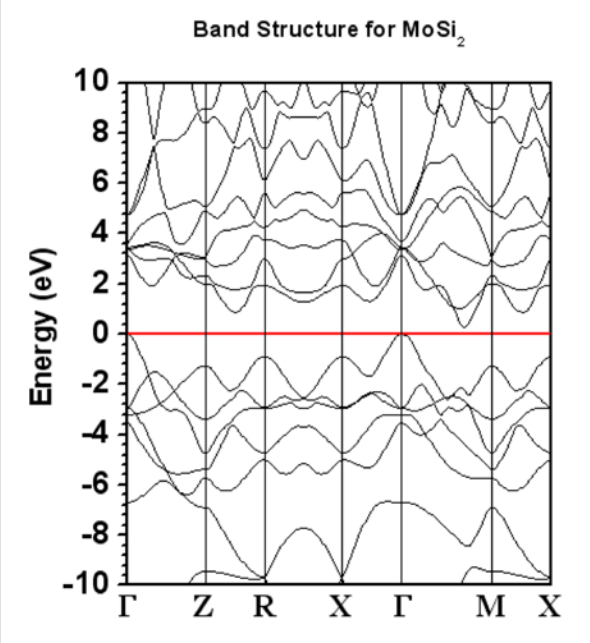
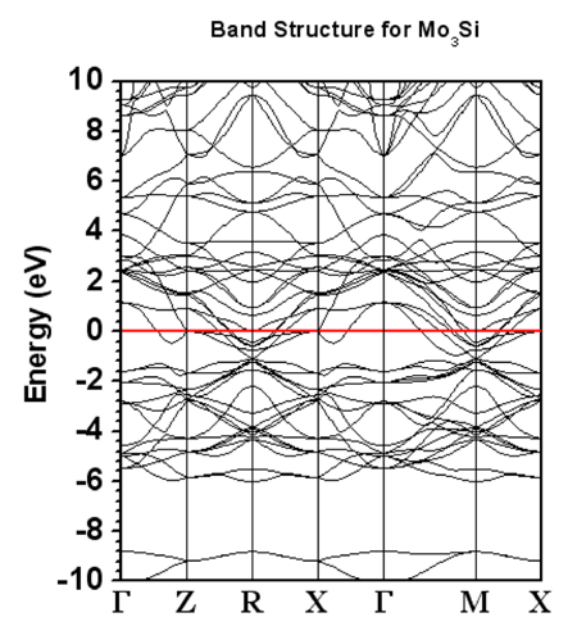
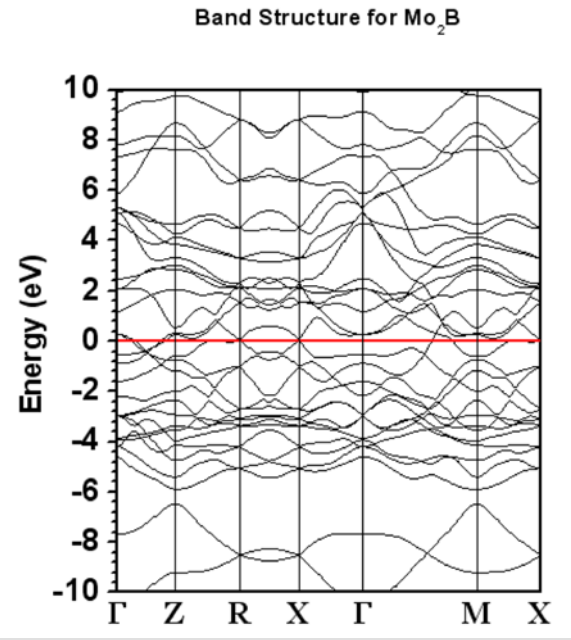
Band structures of $MoSi_2$, Mo_3Si and Mo_2B.



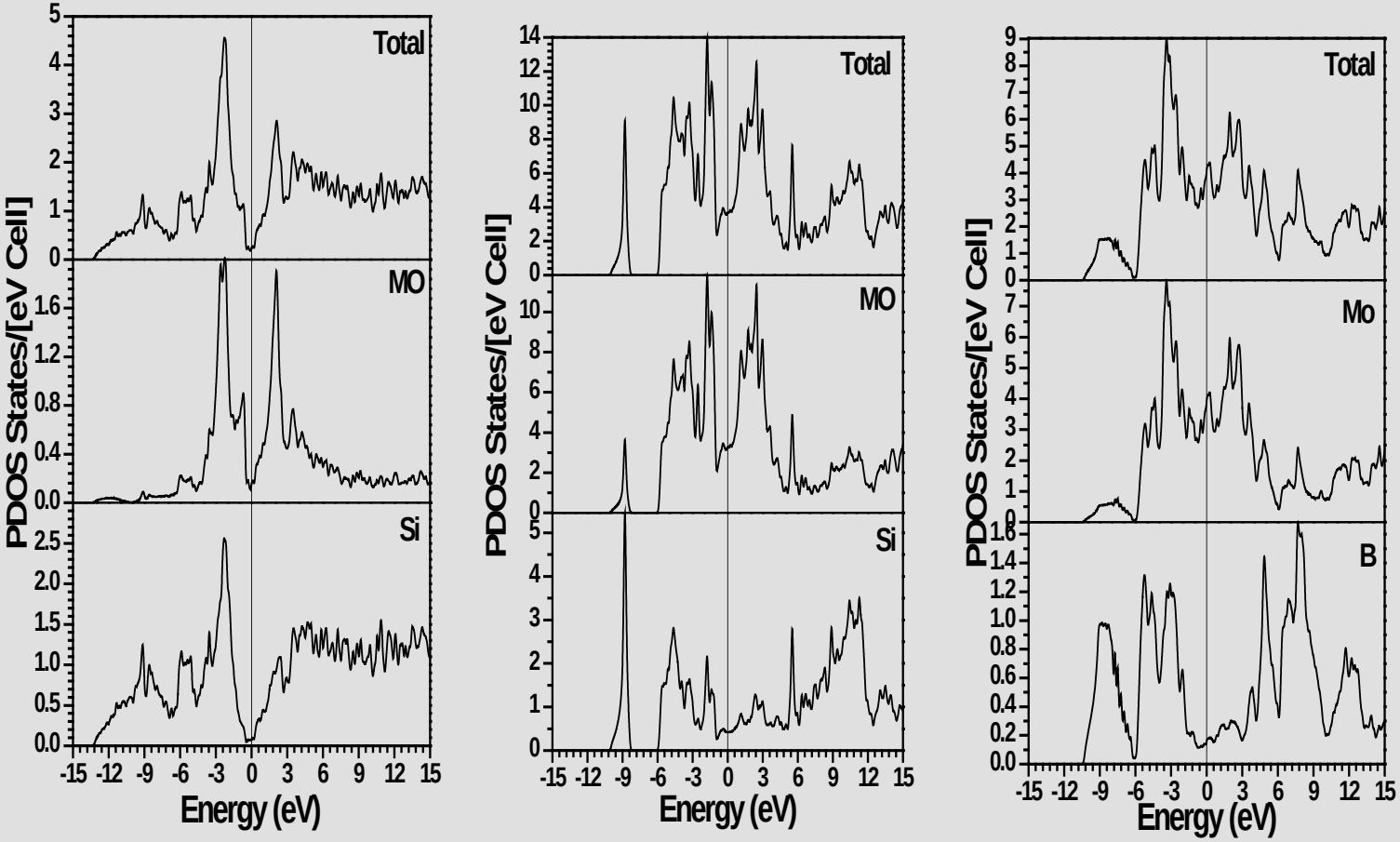




Observations:

♠ $MoSi_2$ has an indirect band gap of 0.31 eV. Mo_3Si has a near gap ~ 1 eV below E_F. In Mo_2B, E_F cross many bands. These results are reflected in DOS spectra.

DOS and PDOS of $MoSi_2$, Mo_3Si and Mo_2B

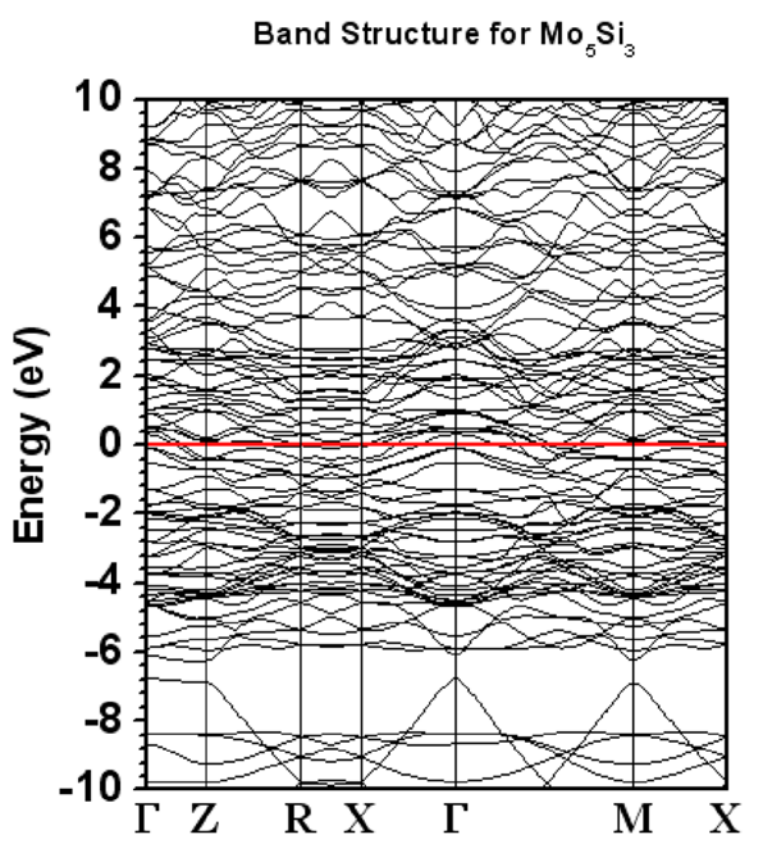


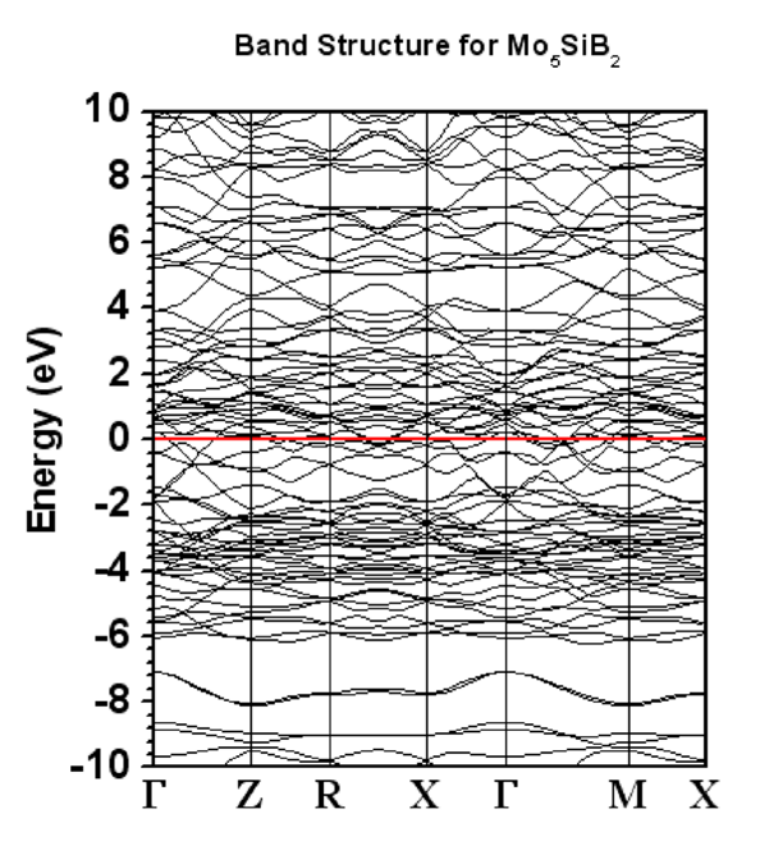
Observations:

♠ The Fermi surface for $MoSi_2$ hand Mo_3Si is at a deep valley in the DOS indicating the stability of these two phases. $MoSi_2$ actually has an indirect gap.

♠ Mo_2B has the Fermi level at a local maximum in DOS signaling potential instability.

Band structures of Mo_5Si_3 and Mo_5SiB_2



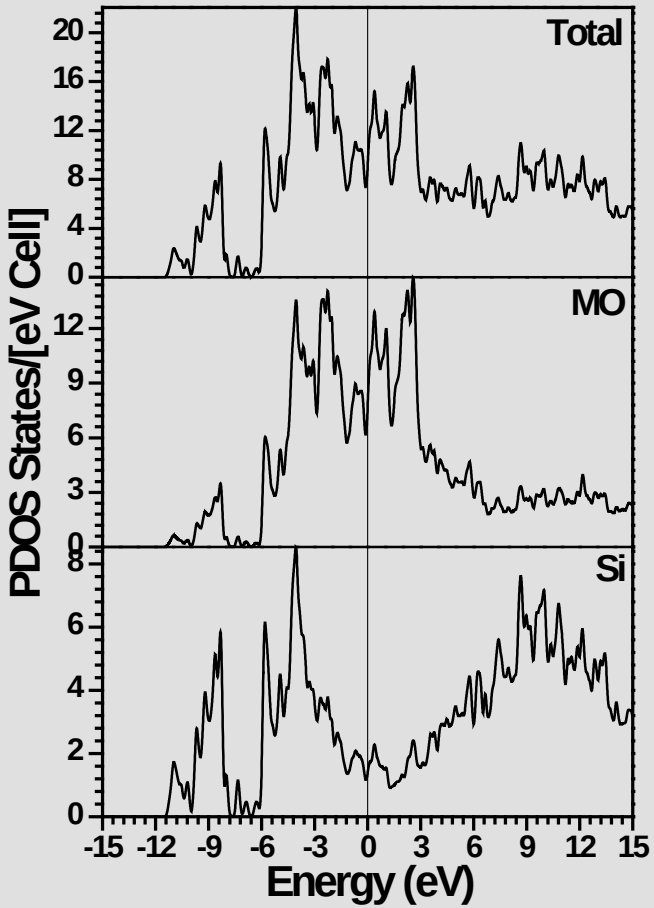


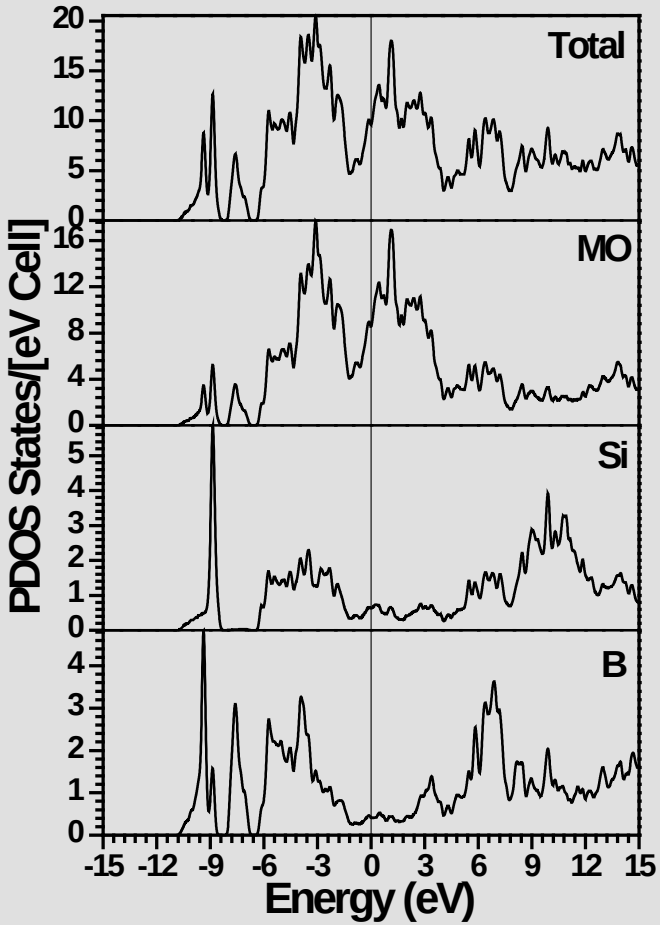
Observations:

♠ Both Mo_5Si_3 and Mo_5SiB_2 has many band near the Fermi level due to large number of atoms in the unit cell.

♠

DOS and PDOS of Mo_5Si_3, Mo_5SiB_2.





Observations:

♠ Note Mo5Si3 has its Fermi level at a local minimum but that of Mo_5SiB_2 is actually at a slope. Under a different B content, it may be possible to shift E_F to a minimum thus optimize its stability.

b. Calculated mechanical properties

Use an in-house package based on strain vs. stress applied to a crystal for C_{ij}. $\sigma_i = \sum_{j=1}^{6} C_{ij}\varepsilon_j$

Use C_{ij} to obtain bulk modulus (K), Shear modulus (G), Young's modulus (E) and Poisson's ratio η using Voigt-Reuss-Hill (VRG) approximation for polycrystals.

Crystal	C_{11}	C_{33}	C_{13}	C_{12}	C_{44}	C_{66}	K	G	E	η
$MoSi_2$	410.6	507.8	197.4	110.0	197.6	194.4	212.1	185.8	431.5	0.161
Mo_3Si	458.2	-	151.4	-	118.0	-	253.6	131.1	335.4	0.280
Mo_5Si_3	443.7 (446)	402.2 (390)	147.9 (140)	177.6 (174)	110.2 (110)	134.4 (140)	247.8	124.7	320.3	0.285
Mo_5SiB_2	463.6 (480)	370.9 (415)	215.0 (197)	176.1 (166)	152.4 (174)	127.9 (143)	278.2 (277)	129.7 (151)	336.7 (383)	0.298
Mo_2B	500.6	473.8	205.3	194.1	158.5	167.0	298.2	154.5	395.2	0.279

Observations:

♠ Mo_2B has the highest overall modulus (but may be unstable)

♠ Mo_5SiB_2 also has very high modulus values and should be the most promising compound in the Mo-Si-B system.

♠ MoS_2 which is an insulator has smallest bulk modulus but largest Young's modulus and smallest Poisson ratio.

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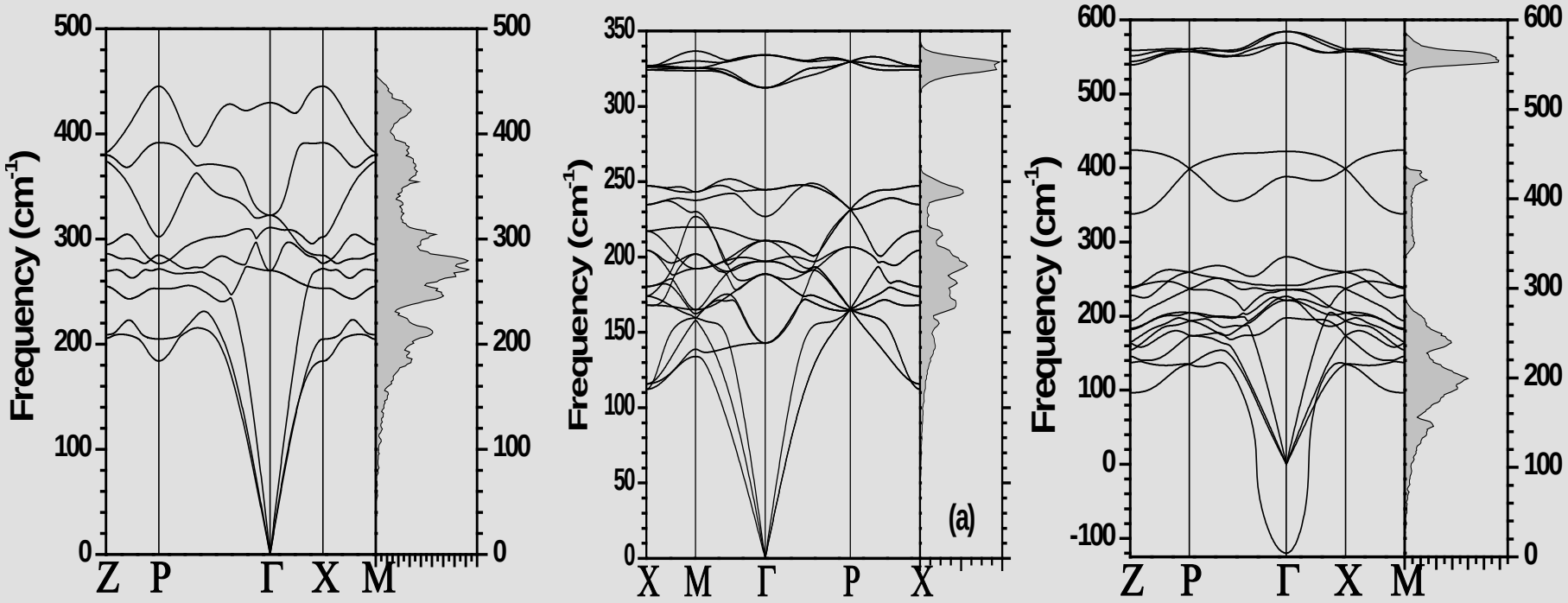
Phonon dispersion and DOS of $MoSi_2$, Mo_3Si and Mo_2B



Observations:

♠ Note the difference in the maximum frequency. Higher modes correspond to lighter atoms. Lower modes are from heavier Mo atoms.

♠ Mo_2B has a negative mode at G => lattice instability at finite temperature.

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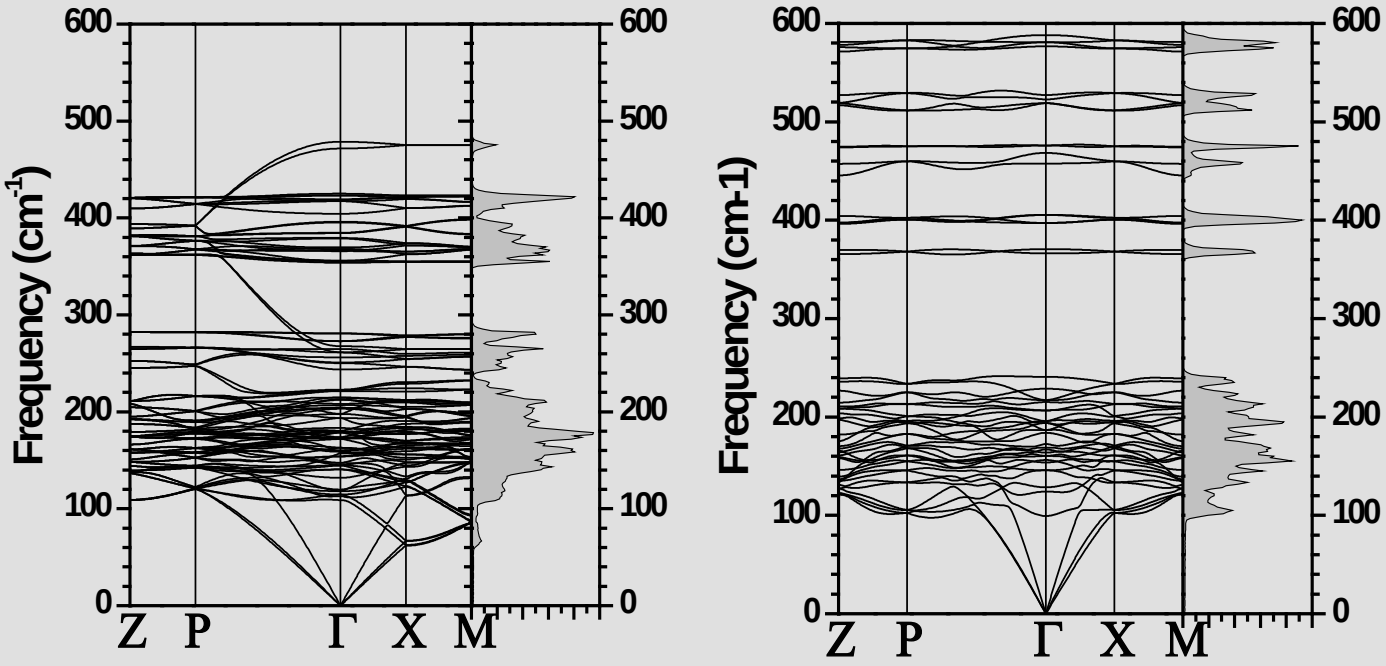
Phonon dispersion and DOS of Mo_5Si_3, and Mo_5SiB_2.



Observations:

♠ Mo_5SiB_2 has many vibrational modes at frequencies between 500-600 cm^{-1} related to the vibration of the B atoms.

♠ The phonon frequencies $\hbar\omega_j$ will be used for vibrational free energy calculation.

$$F^{vib}(V,T) = \sum_{q}^{BZ}\sum_{i}^{3N}\{\tfrac{1}{2}\hbar\omega_i(V,\vec{q}) + k_B T \ln(1-e^{-\hbar\omega_i(V,\vec{q})/k_B T})\}$$

Main conclusions

♠ The first milestone for the first year is reached with the completion of the study on the electronic structures and mechanical properties of the five crystalline phases in the Mo-Si-B system.

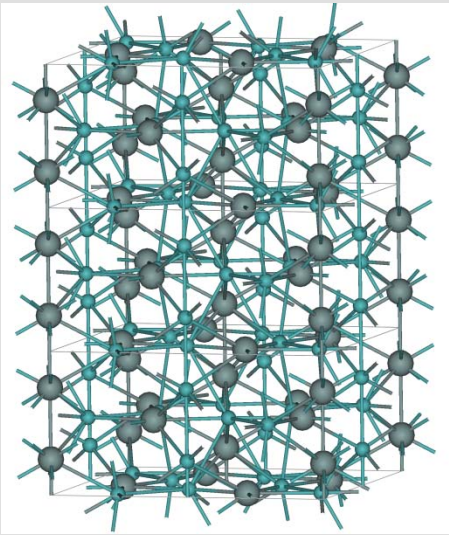
♠ Several important conclusions have been obtained on these fundamental properties which will facilitate the next phase of the project. Focus will be on the composites of Mo_5Si_3 and Mo_5SiB_2.

♠ This also us to propose two additional crystalline phases, ZrB_2 and MoB_2 to be added to the list. On the other hand, detailed and in-depth analysis of these results is in progress will later be submitted to journals for publication.

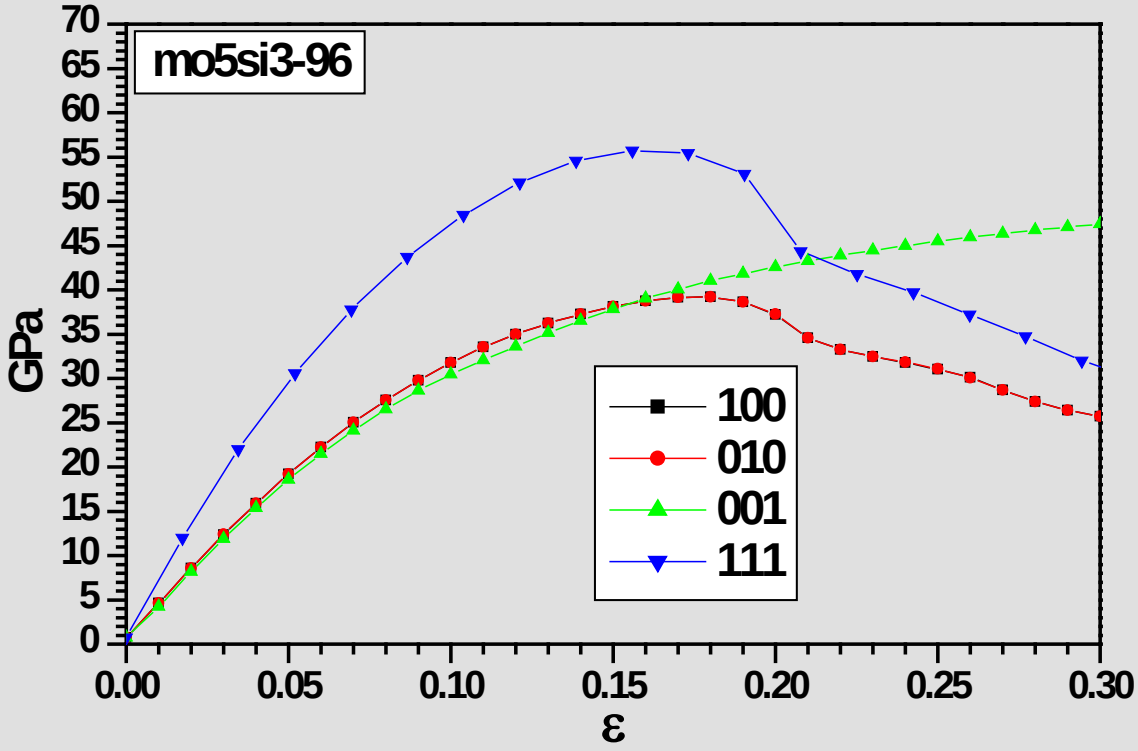
♠ New collaborations will be established especially in the area of uniaxial tensile experiments.

Our performance so far on this project is beyond our original expectation.

Uniaxial ensile experiment along principal axes in Mo_5Si_3.



1x1x3 supercell of 96 atoms



Notes:

♠ Stress-strain relations in (100), (010), and (001) directions are almost the same up to strain = 0.15. After that, stress drops in (100) and (010) directions.

♠ The (111) direction has a much higher stress at all strains below 20%.

♠ At small strain (< 0.02), stress vs. strain is approximately linear.

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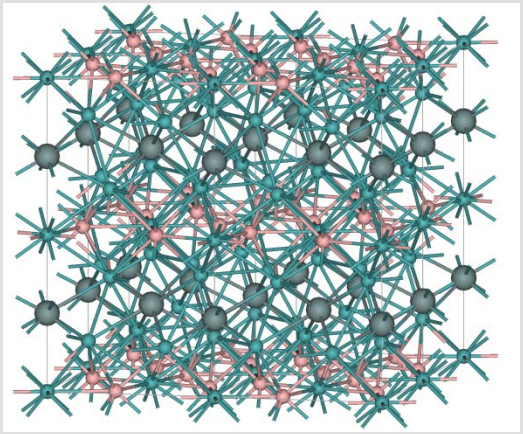
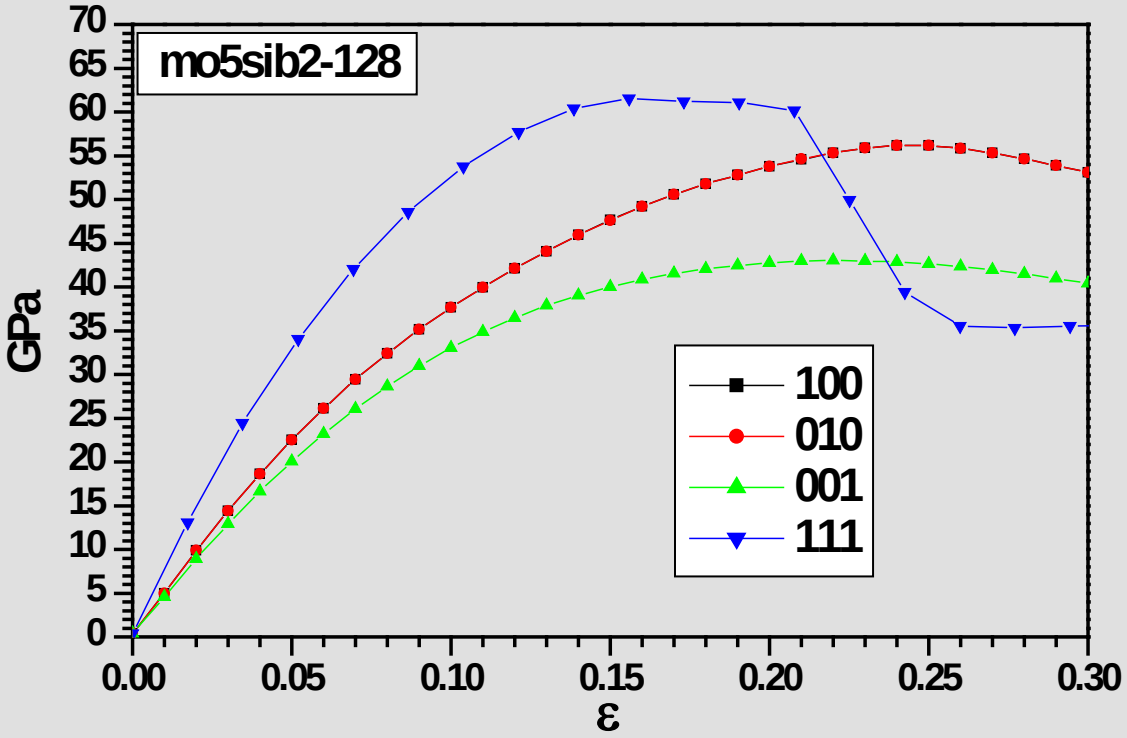
Uniaxial tensile experiment along principal axes in Mo_5SiB_2.



2x2x1 supercell of
128 atoms



Notes:

♠ (001) direction is softer than the (100) and (010) directions. (111) direction is still the hardest.

♠ The overall maximum stress is larger than that in Mo_5Si_3 indicating the beneficial effect of having B.

Review of milestones and time line

There are four milestones to be reached within 3 years based on the tasks and subtasks listed. Here are the status report.

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 2011: milestone reached!

2. Development of the new computational method. Test of the computational codes on simple crystals.
Milestone date: to be completed by the end of second year.
Status as of June 2011: new method development started!

3. Supercell modeling of composite alloys and identification of those with promising properties.
Milestone date: to be completed by the end of second year.
Status as of June 2011: will start later this year or early in 2012

4. Application of the new method to supercell models of composite alloys and exploration of new materials.
Milestone date: Targeted for completion by the end of the third year.
Status as of June 2011: Not yes started.

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THANK YOU !

WE GREATLY APPRECIATE DOE-NETL SUPPORT!

PROGRAM MANAGER: DR. RICHARD DUNST