LARGE SCALE SIMULATIONS OF THE MECHANCIAL PROPERTIES OF LAYERED TRANSITION METAL TERNARY COMPOUNDS FOR FOSSIL ENERGY POWER SYSTEM APPLICATIONS

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I. Technical background of the project

Advanced materials with applications in extreme conditions such as high temperature, high pressure, and corrosive environments play a critical role in the development of new technologies to improve the performance of different types of power plants.

Computational studies can lead the way in the search for novel materials or for significant improvements in existing materials that can meet the DOE requirements without incurring costly trial and error laboratory tests.

The **UMKC** project focuses on the computational studies of a new class of materials called MAX phases, or $M_{n+1}AX_n$ (M = a transition metal, A = Al, X = C or N).

The MAX phases are layered transition metal carbides or nitrides with the rare combination of metallic and ceramic properties.

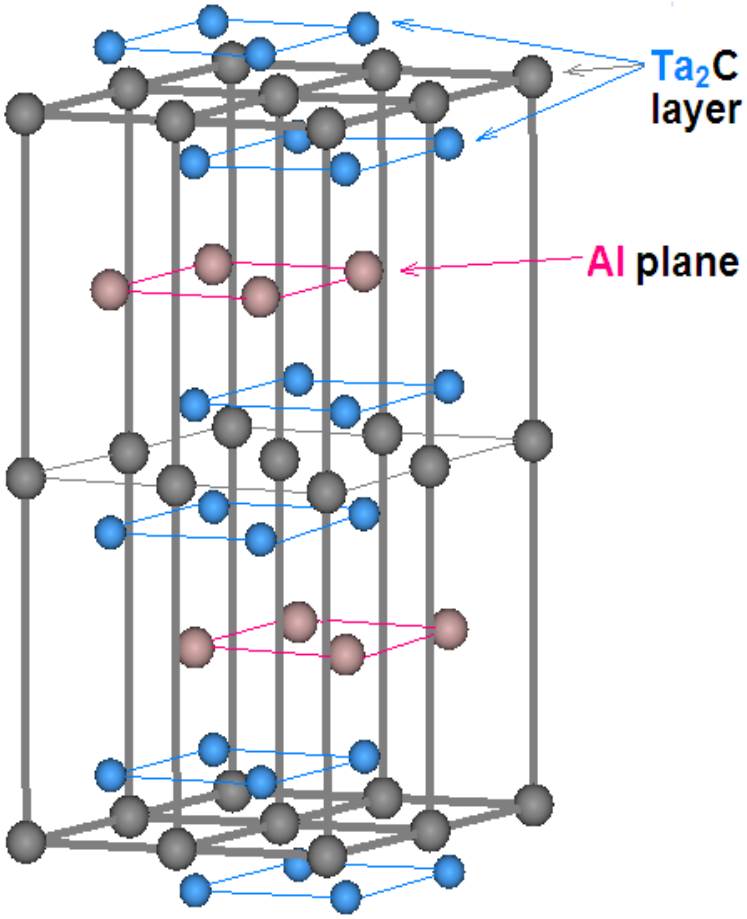


Fig. 1: Ball and stick model of a typical MAX phase (Ta_2AlC) showing the layered structure in a 2x2x1 supercell.

The unique structural arrangements and directional bonding (both covalent and ionic) in MAX phases result in some outstanding properties:

Thermodynamic stability,

damage-resistance,

oxidation resistance,

excellent thermal and electric conductivity,

machinability,

fully reversible dislocation-based deformation,

and more.

These properties can be explored in the search for new phases and their composites that can meet performance goals set by DOE for applications in the next generation of fossil energy power systems.

List of major MAX ($M_{n+1}AX_n$) phases

M: **Ti**, **Cr**, V, Nb, Ta, Hf, Zr, Mo, W, ..

A: **Al**, **Si**, Ge, Sn, P, S.

X: **C**, **N**, or O

n = 1, **2**, **3**, 4, 5, 6, ?

List of 70 MAX Phases			
(1 1 1) Phases	**(2 1 1) Phases**	**(3 1 2) Phases**	**"Irregular" Phases**
ScAlC	Ti_2AlC ♣	Ti_3SiC_2	$HfAl_3C_3$
VAlC	Ti_2AlN ♣	Ti_3SiC_2 ♣	$Hf_2Al_3C_4$
TiAlC	Ti_2SiC	Ti_3AlC_2 ♣	$Hf_3Al_3C_5$
CrAlC	Ti_2GeC	Ti_3GeC_2	$Hf_2Al_4C_5$
ZrAlC	Ti_2SnC	Ta_3AlC_2	$Hf_3Al_4C_6$
NbAlC	Ti_2PbC	Ti_3SnC_2	$ZrAl_3C_3$
MoAlC	Ti_2PC	α-V_3SiC_2	$Zr_2Al_3C_4$
HfAlC	Ti_2SC	β-V_3SiC_2	$Zr_3Al_3C_5$
WAlC	Ti_2GaC	**(4 1 3) Phases**	$Zr_2Al_4C_5$
TaAlC	Ti_2InC	α-Ta_4AlC_3	$Zr_3Al_4C_6$
	Ti_2TlC	β-Ta_4AlC_3	$Zr_3La_3C_5$
	Ti_2AsC	Ti_4AlN_3	$ZrAl_4C_4$
	Cr_2AlC ♣	V_4AlC_3	$Zr_2Al_3C_5$
	Cr_2SiC	Nb_4AlC_3	γ-$Y_2Si_2O_7$
	Cr_2PC	**(5 1 4) Phases**	Al_4SiC_4
	Cr_2SC	Ta_5AlC_4	$La_2Zr_2O_7$
	V_2AlC	**(6 1 5) Phases**	**"Hybrid" Phases**
	V_2SiC	Ta_6AlC_5	$Cr_{0.5}Al_{0.5}N$
	V_2PC		$Zr_2[Al(Si)]_4C_5$
	V_2SC		$Zr_3[Al(Si)]_4C_6$
	Nb_2AlC		$Ti_3Si_{0.75}Al_{0.25}C_2$
	Nb_2AsC		$Ti_3Si_{0.9}Al_{0.1}C_2$
	Ta_2AlC		$Ti_3Si(Al)C_2$

Outline of the UMKC project

Initially, the UMKC team will investigate five MAX phase crystals: Ti_3AlC_2, Ti_2AlC, Ti_3SiC_2, Ti_2AlN, and Cr_2AlC.

Next, we will shift to newly discovered compounds of Hf(Zr)-Al(Si)-C and Nb-based MAX phases.

A systematic computational study of a large number of these phases using accurate *ab initio* methods will be carried out.

Carefully designed large-scale multi-axial simulations will be conducted on DOE supercomputers.

Project designed to be flexible and may change depending on actual progress.

Outline of the UMKC project (continue)

New computational methods and algorithms in the materials and engineering will be developed.

These methods are based on fundamental quantum mechanics and will have superior predictive power on the mechanical properties.

The approach adopted bridges physics/chemistry and engineering/materials science in concepts and methodologies, and for materials over different length scales.

II. Potential significance of the results of the work

A. **Critical outcome of the project**:

[1] An extensive database of fundamental properties of the MAX phase compounds will become available. They are used for the search of additional phases and/or their composites with even better performances.

[2] New data on multi-axial simulations for anisotropic MAX phases will be collected for the first time. This establishes a paradigm for study the mechanical properties of advanced materials. They are crucial in assessing the durability of materials under extreme conditions, over a long operation time, and under harsh environments.

II. Potential significance of the results (continue)

[3] The methods used are based on a solid theoretical underpinning of physical and chemical principles. The project extends our knowledge base of a new class of layered alloys on their electronic structure & bonding.

[4] The project provides the solid training of graduate students and postdoctoral fellows in state-of-the-art computational skills to meet the demand for a skilled and technologically competent workforce in energy science and technology.

[5] This project will lead to close collaborations between computational scientists and experimentalists in thus accelerate the development of new materials for fossil energy technology.

II. Potential significance of the results (continue)

B. **Impact:**

[1] The successful completion of this project will have significant impact on materials related to fossil energy technology. New advanced materials with unique properties will be identified and understood, and new methods developed. This project can provide useful guideline for laboratory efforts at DOE facilities.

[2] The new computational methods and algorithms developed will be used by other researchers to further computational materials research and establish a roadmap for searching new alloy systems with desirable properties. It provides an opportunity for the proper training of the next generation of scientists and engineers.

III. Statement of project objectives (SOPO)

A. Objectives:

(1) To understand the fundamental mechanical and electronic structures of the MAX phase alloys and to predict the useful new phases;

(2) To perform multi-axial compression and tensile experiments on selective MAX alloys on DOE supercomputers to understand their deformation behavior;

(3) To develop new methods for calculating thermomechanical properties at elevated temperature and pressure starting from the calculation of phonon spectra;

(4) To explore the effects of grain boundaries and interfaces of the MAX phase materials with and without segregated ions via large scale structural modeling including spectroscopic characterizations;

(5) To establish effective collaborations with experimentalists at DOE laboratories and other academic institutions to accelerate the materials development for fossil energy technology.

B. Scope: roughly divided into two phases.

Phase I (first 2 years) will cover the areas of fundamental mechanical properties, electronic structure and bonding of MAX phase alloys, and execution of the multi-axial tensile/compression simulations.

Phase II (third year) focuses on mechanical properties at high temperature, pressure, and corrosive environments. Modeling and simulation of microstructures and interfaces in MAX phases.

Development of computational algorithms and codes starts immediately and proceed through the completion of the project.

Flexible assignment of tasks depending on actual progress and unexpected difficulties during investigation.

Some routine type of the work may finish ahead of schedule.

Overall strategy: achieve as much as possible to reach the specified goals within the time frame outlined.

C. Tasks: (7 tasks)

Task 1 Project Management and Planning

The management plan is straightforward since this is essentially a computational project that does not involve any complicated instrumentation or materials processing and characterizations.

Task 2 Fundamental mechanical properties of MAX phases

These include the following MAX phase alloys: Ti_3AlC_2, Ti_2AlC, Ti_3SiC_2, Ti_2AlN, Cr_2AlC, Nb_2AsC, Nb_4AlC_3, Zr_3AlN, $Zr_3Al_3C_5$, $Zr_2Al_3C_5$, Hf_3AlN, $HfAl_4C_4$. Other crystalline phases may also be studied if deemed necessary.

Task 3 – Electronic structure and spectroscopic properties of MAX phas

Task 4 – Multi-axial tensile and compression simulations

A select group of MAX phase alloys whose mechanical properties are deemed most interesting and important will be subjected to multi-axial tensile and compression experiments.

Task 5 – Mechanical properties at high temperature and pressure

This is the main goal in the search for high performance alloys for fossil energy technology. It will depend on the progress of task 7 outlined below.

Task 6 – Modeling of microstructures and interfaces and the effect of corrosion

Construction of supercell models in MAX phase alloys containing grain boundaries, interface with oxides and models containing segregated foreign ions. The specific systems targeted for the interface modeling will be conducted only after substantial progress in Phase I.

Task 7 – Development of computational algorithms and codes

We will develop new computational methods and write efficient codes to be executed on DOE supercomputers for tasks 2 through 6 . This part of the project is labor intensive and requires the vast experience and expertise in this area.

D. Deliverables:

The deliverables for this project will be in the form of quarterly progress reports covering the tasks and subtasks outlined. These reports will be submitted in the timely manner to document the progress made, outstanding results obtained, technical difficulties encountered, potential modifications to the tasks needed and any new initiation of collaborations related to this project.

We will have frequent presentations at professional meetings. Manuscripts on the completed work will be prepared and submitted to peer-reviewed journals for publication with acknowledgments to NETL support.

There will also be a more comprehensive yearly progress report to highlight any outstanding accomplishments.

IV. The project team

Team members: Professors **Wai-Yim Ching** (PI), **Paul Rulis,** and **Lizhi Ouyang** (co-PIs), their graduate students and postdoctoral fellows.

The PI, a Curators' Professor of Physics, leads the Electronic Structure Group (**ESG**) in Physics Dept. at the University of Missouri-Kansas City.

Co-PI Rulis is a Research Assistant Professor and the Laboratory Manager. He is an expert on the OLCAO method and has extensive experience on all aspects of computer code development and their implementation on supercomputers.

Co-PI Ouyang is an Assistant Professor at Tennessee State University, a long time collaborator of PI. He is an expert in mechanical properties evaluation and algorithm development.

Other participants of this project: 2-3 Ph.D. level graduate students and 2 postdoctoral fellows.

MS level students and undergraduates may participate later.

External collaborators in both theory and experiment.

V. Technical approach to achieving the project goals

A. Methods

OLCAO (Orthogonalized linear combination of atomic orbitals)
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) can be easily 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.

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

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

$C^n_{i\alpha}$: the eigenvector of the n[th] band state.

$S_{i\alpha,j\beta}$; overlap matrix between Bloch functions.

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

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

More on Ab initio phonon and thermodynamic calculations

$F^{vib}(V,T)$: Vibrational part of free energy. Phonon frequency: $\hbar\omega_i(V,\vec{q})$

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

Helmholtz free energy: $F(V,T) = F^{el}(V,T) + F^{vib}(V,T)$.

$$F^{el}(V,T) = U^{el}(V) - TS^{el}(V,T) \sim U^{el}(V)$$

Gibb's free energy: $G(P,T) = F(V,T) + PV$; $P = -(\partial F/\partial V)T$.

Enthalpy: $H(P,T) = G(P,T) + TS^{vib}(V,T)$

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

No configurational entropy is considered at this time.

B. **Approach**

Extensive study of the MAX phases crystals and their fundamental properties.

Search for new phases within the MAX family or related families of layered compounds.

Microstructure and interface modeling of the MAX phases.

Implementation of efficient simulation schemes on supercomputers.

Development of new computational methods and algorithms.

C. Proposed research projects

Project 1:

Fundamental mechanical and vibrational properties of MAX phases.

Project 2:

Electronic structure and spectroscopic properties of MAX phases.

Project 3:

Multi-axial tensile and compression simulations.

Project 4:

Mechanical properties at high temperature and pressure.

Project 5:

Modeling of microstructures, interfaces, and effects of corrosion.

Project 6:

Development of computational algorithms and codes.

VI. Project budget and schedule

A. Budget

	Year 1	Year 2 (x1.035)	Year 3 (x1.035)
Total direct	212,690	220,134	227,840
Indirect cost	106,345	110,067	113,920
Direct + Indirect	327,035	338,481	350,330
Subcontract to TSU	33,000	33,000	33,000
Indirect cost for subc.	12,500	0	0
Total cost for 1 year	372,535	371,481	383,330
Matching (20%)	74,507	74,296	76,666

Total cost from DOE-NETL:	**901,877**
Total cost sharing from UMKC:	**225,469**
Total budget for three years:	**1,127,346**

B. Budget explanation and justification

Bulk of the cost: Salary and benefits for:

- 1 month in summer for PI. 6 months for a co-PI.
- 2 post-doctoral fellows.
- 2 Ph.D level students
- 2 MS level students.

Minor costs:

- Travel to meetings
- Miscellaneous office and publication costs

No cost on equipments!

No cost on computations!

C. Project schedule

Four milestones and one general goal to be reached:

1. Completion of the mechanical properties and electronic structure of the specified crystalline phases in the MAX system. **Date: End of first year.**
2. Lattice dynamic and phonon calculation of the MAX phases; multi-axial deformation tests for at least 5 different MAX phase compounds; development and testing of computational codes. **Date: End of second year.**
3. Study of high temperature/high pressure properties of selected MAX phase compounds. **Date: Near the end of second year**.
4. Modeling of microstructure and interface models and evaluation of their properties. **Date: End of the third year.**

General goal: Successful development of new computational methods and codes for accurate evaluation of mechanical properties at extreme conditions.

Date: Targeted progress and validation checked at the middle and the end of each year.

VII. Project management plan

Seven specific tasks listed. (See SOPO). General plan of management:

Systematically study the electronic structure and mechanical properties of a large number of the MAX phase alloys.

Develop new computational algorithms for efficient and accurate calculations. Devise new simulation schemes that will be more accurate in predicting for the materials properties at extreme conditions and long service periods.

Extend the simulations to microstructure models both with and without the influence of doped elements. Ese spectroscopic calculations for their characterization.

Explore new material phases and their composite structures that have optimal mechanical and corrosion resistant properties.

Establish an extensive database of the structure and properties of the modeled MAX systems and provide them to our collaborators at DOE laboratories and other institutions

VIII. Project risks and risk management plan

The risks for this project are very low.

Unforeseeable technical difficulties in the development of new codes.

Possible action: Devise alternative approaches involving legitimate simplifications without loss of general accuracy and efficiency.

Insufficient computing resources for a large number of simulation tasks.

Possible action: Seek additional computing.

Lack of sufficient progress with students. (a very rare situation.)

Possible action: Replace ineffective students with more experienced ones within the same research group and within the budget constraints.

New opportunities in discovery and collaboration.

New discoveries may require immediate modification of the plan.

Possible action: In consultation with NETL manager, replace some of the compounds listed for study with the new and more promising materials.

IX. Project status

Project started on time. (January 1, 2011).

A postdoctoral fellow has been recruited.

Financial planning in good order.

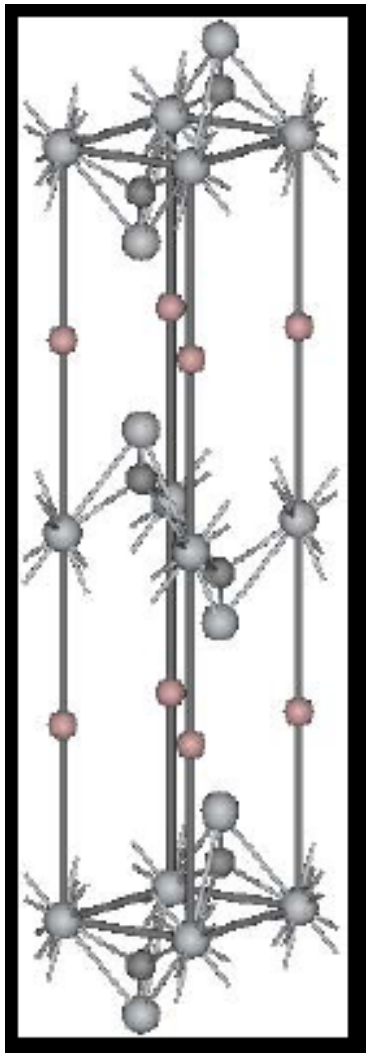
Project assignment to 2 graduate students carried out.

Some preliminary results obtained (see below).

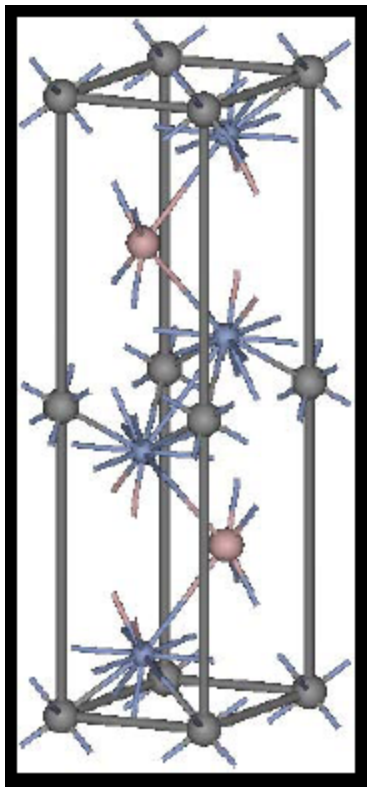
IX. Project status: some preliminary results

1. MAX phase electronic structure and bonding
2. MAX phase core level spectroscopy for characterization
3. Max phase mechanical properties
4. Multi-axial tensile experiment
5. Multi-axial failure envelope
6. MAX phase phonon dispersions
7. MAX phase theromodynamics
8. Implementation of calculations on NERSC supercomputers.

We will start with the two MAX phase compounds: Ti_3AlC_2 and Cr_2AlC



	Ti_3AlC_2	Cr_2AlC
Cell: hexagonal		
a (Å)	3.0753	2.858
b (Å)	3.0753	2.858
c (Å)	18.578	12.818
Space group:	#192	#194
# atoms/cell:	12	
Atomic sites:	Ti1,Ti2, Al,C	Cr,Al, C



MAX phase band structures

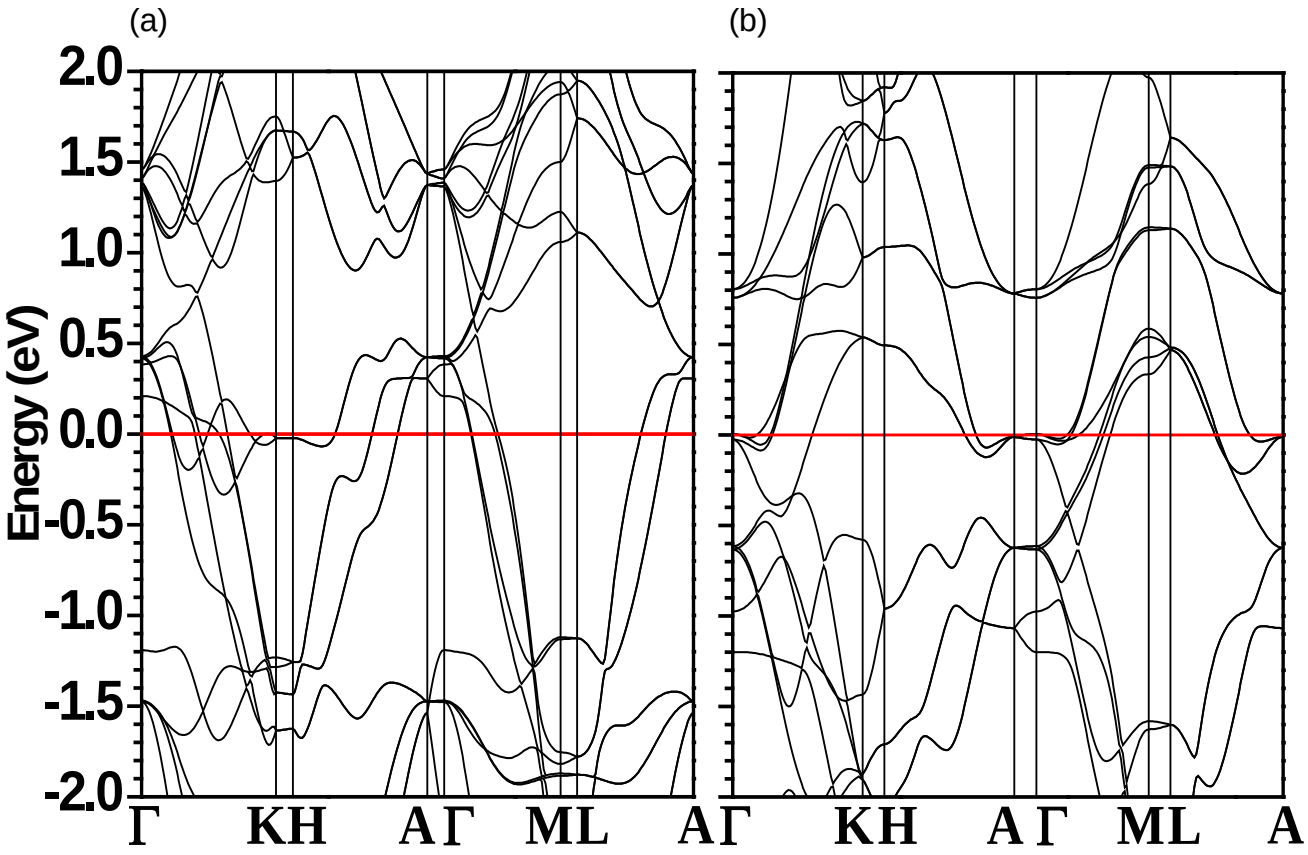


Fig. 2: Band structure near the Fermi level (red line at zero eV) for (a) Ti_3AlC_2 and (b) Cr_2AlC.

Density of states (DOS) and partial DOS

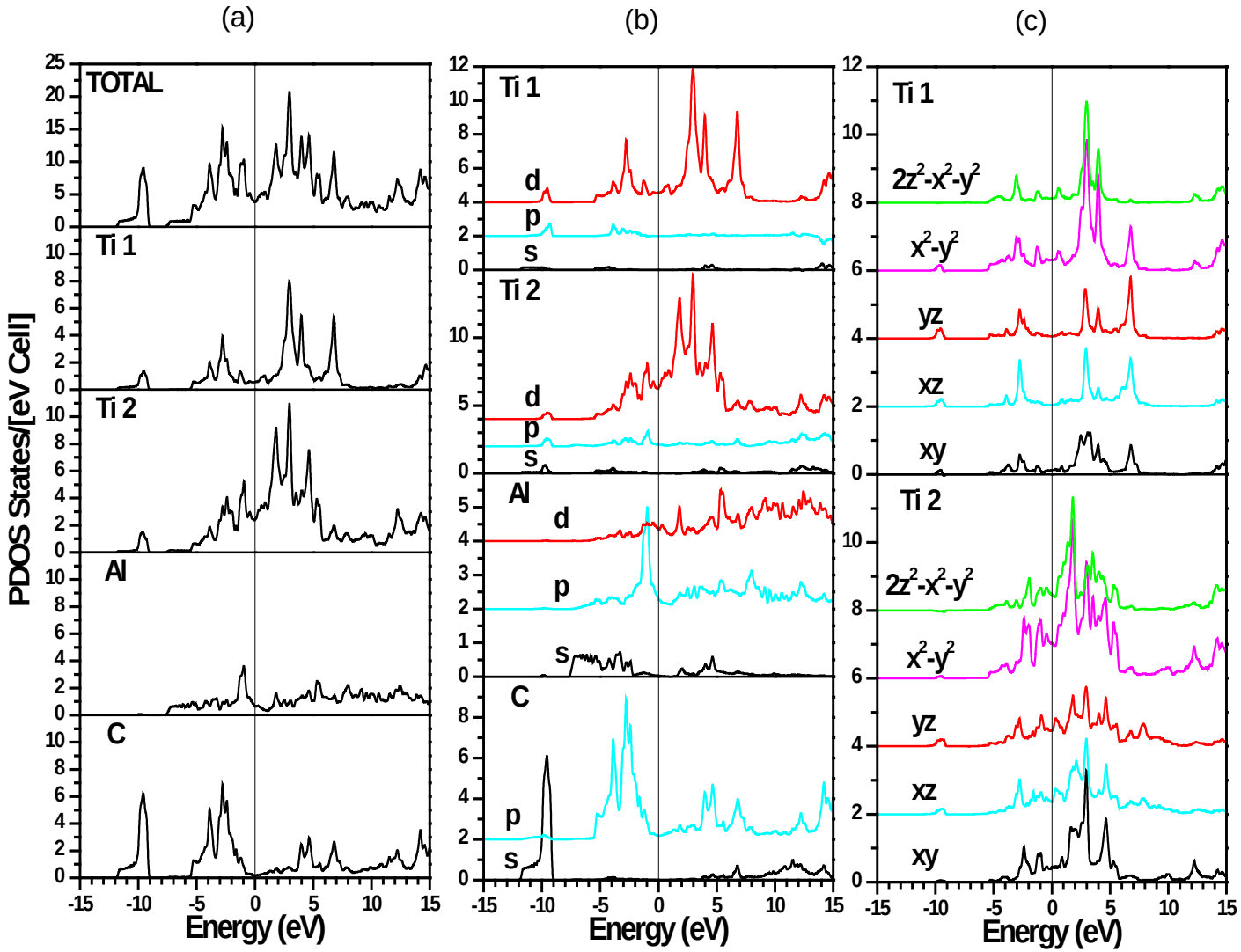


Fig. 3: DOS and PDOS of Ti_3AlC_2. (a) Total DOS and (b) atom-resolved PDOS; (c) e_g and t_{2g} resolved d orbitals Ti1 and Ti2.

MAX phase core level spectroscopy for characterization

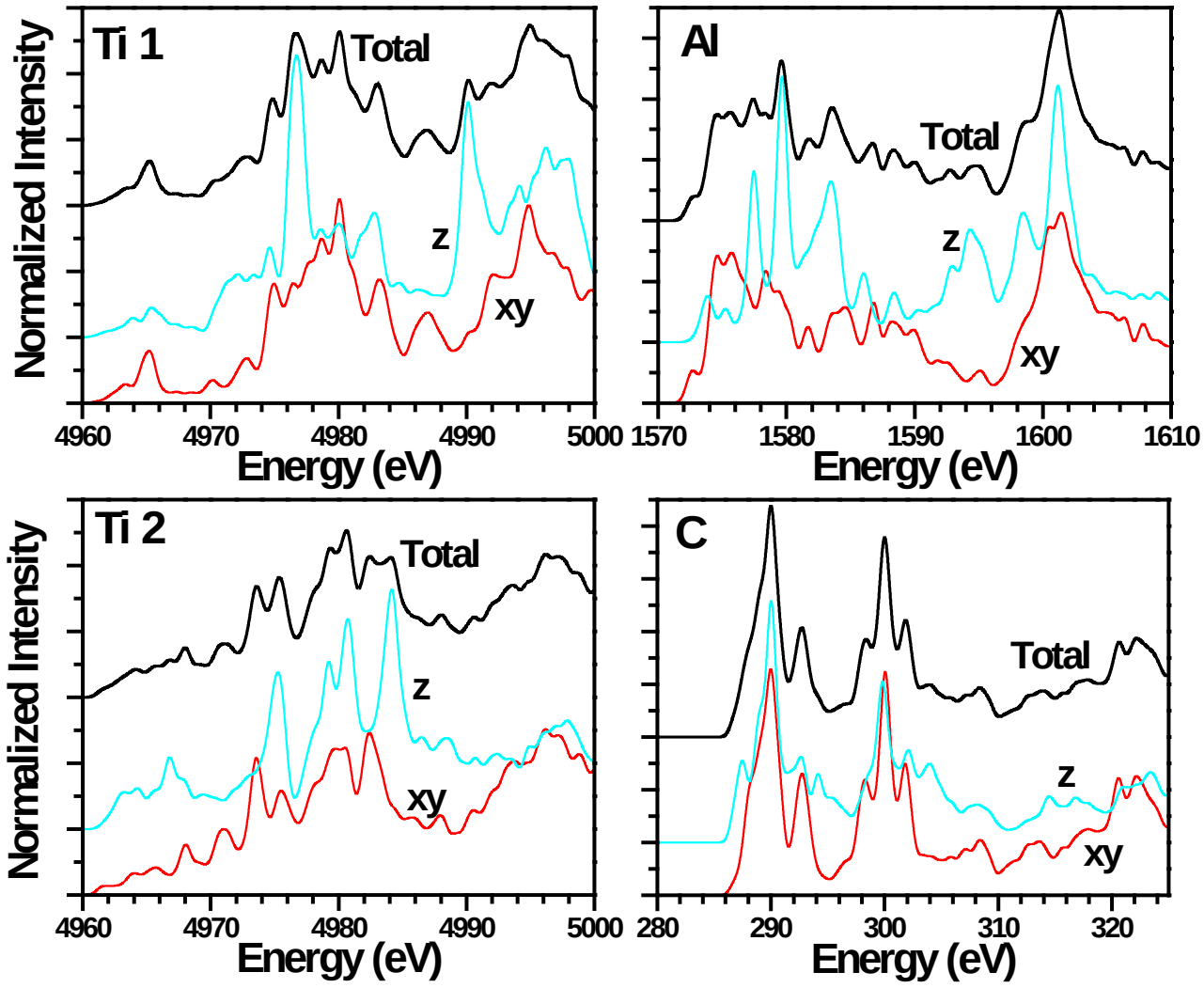


Fig. 4: (a) Ti1-K; (b) Ti2-K; (c) Al-K; (d) C-K edge XANES/ELNES spectra from Ti_3AlC_2 decomposed into planar xy and z directional components.

Table 1. Calculated effective charges Q*, BO and $N(E_F)$ in Ti_3AlC_2 and Cr_2AlC.

Crystal	Ti_3AlC_2	Cr_2AlC	
Q* (electrons):			
Ti1	3.39	-	
Ti2	3.66	-	
Cr		5.91	
Al	2.97	2.67	
C	4.66	4.52	
BO (electrons):			
Ti1-C	0.585		
Ti2-Al	0.450	Cr-Al	0.424
Ti2-C	0.644	Cr-C	0.589
Total:	3.817	6.652	
$N(E_F)$ (states/eV-cell):			
Ti-1 (s,p,d)	0.001, 0.004, 0.554		
Ti-2 (s,p,d)	0.006, 0.107, 2.288		
Cr (s,p,d)		0.000, 0.041, 5.930	
Al (s,p,d)	0.029, 0.292, 0.351	0.009, 0.222, 0.398	
C (s,p)	0.006,0.179	0.004, 0.060	

Max phase mechanical properties

Table 2 Calculated elastic constants C_{ij} and bulk parameters in Ti_3AlC_2 and Cr_2AlC in units of GPa.

	Ti_3AlC_2	Cr_2AlC
C_{11}	354.3	351.3
C_{33}	295.4	371.2
C_{13}	76.3	121.9
C_{12}	82.0	73.8
C_{44}	122.3	134.2
C_{66}	136.1	138.8
K	163.0	189.1
G	127.1	131.3
E	302.7	319.9
η	0.191	0.218

Elastic tensor in Ti_3AlC_2 at different strains

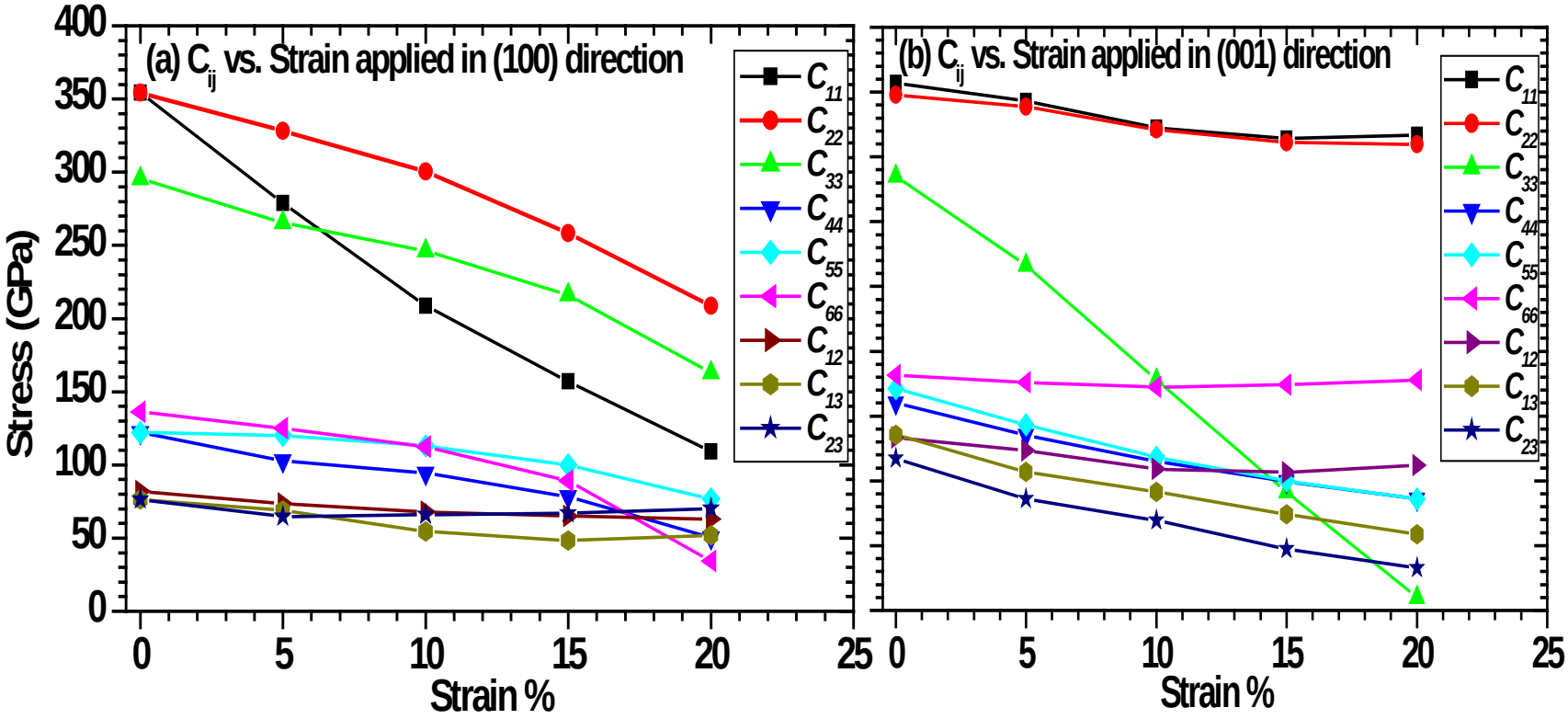


Fig. 8: The strain dependent C_{ij} from the computational tensile experiment for Ti_3AlC_2 in the (100) direction.

Multi-axial tensile experiment on Ti_3AlC_2

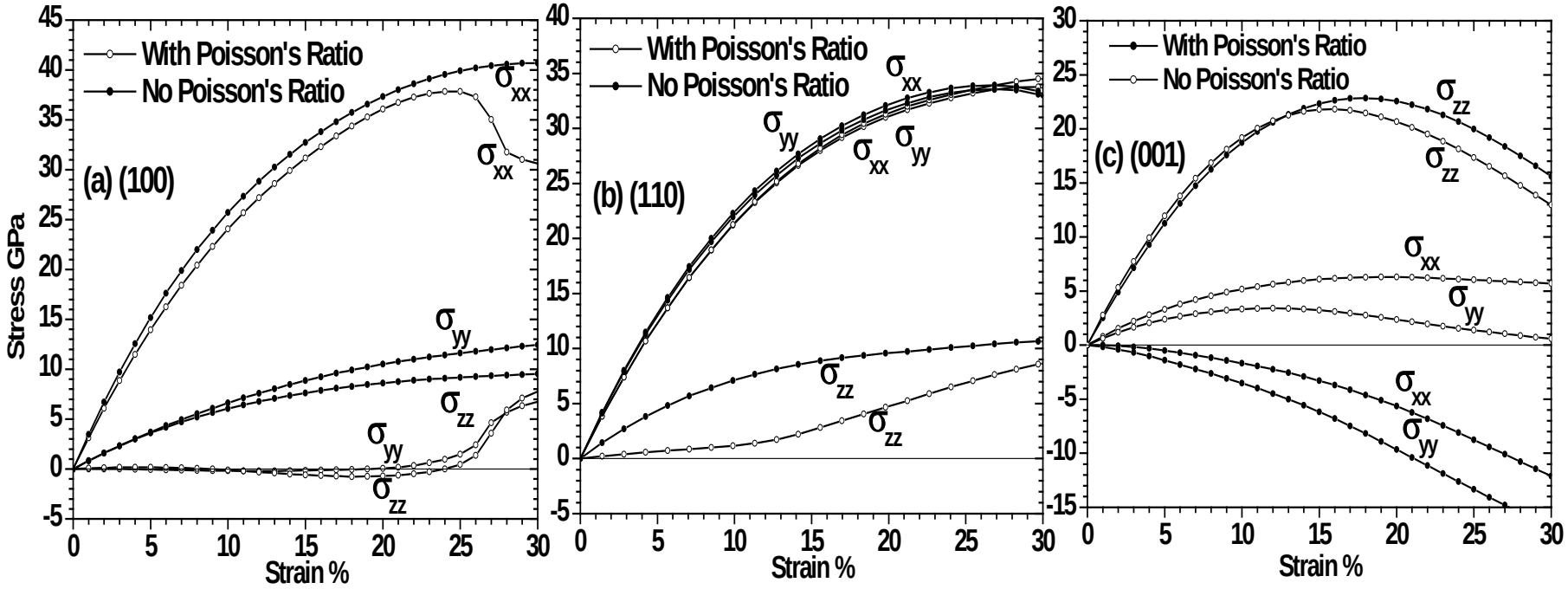


Fig. 6: Stress components $_{xx}$, $_{yy}$, $_{zz}$ vs strain for loading in three directions: (a) (100); (b) (110); and (c) (001) with (solid) and without (open) using Poisson's ratio η.

Multi-axial tensile experiment on Ti_3AlC_2

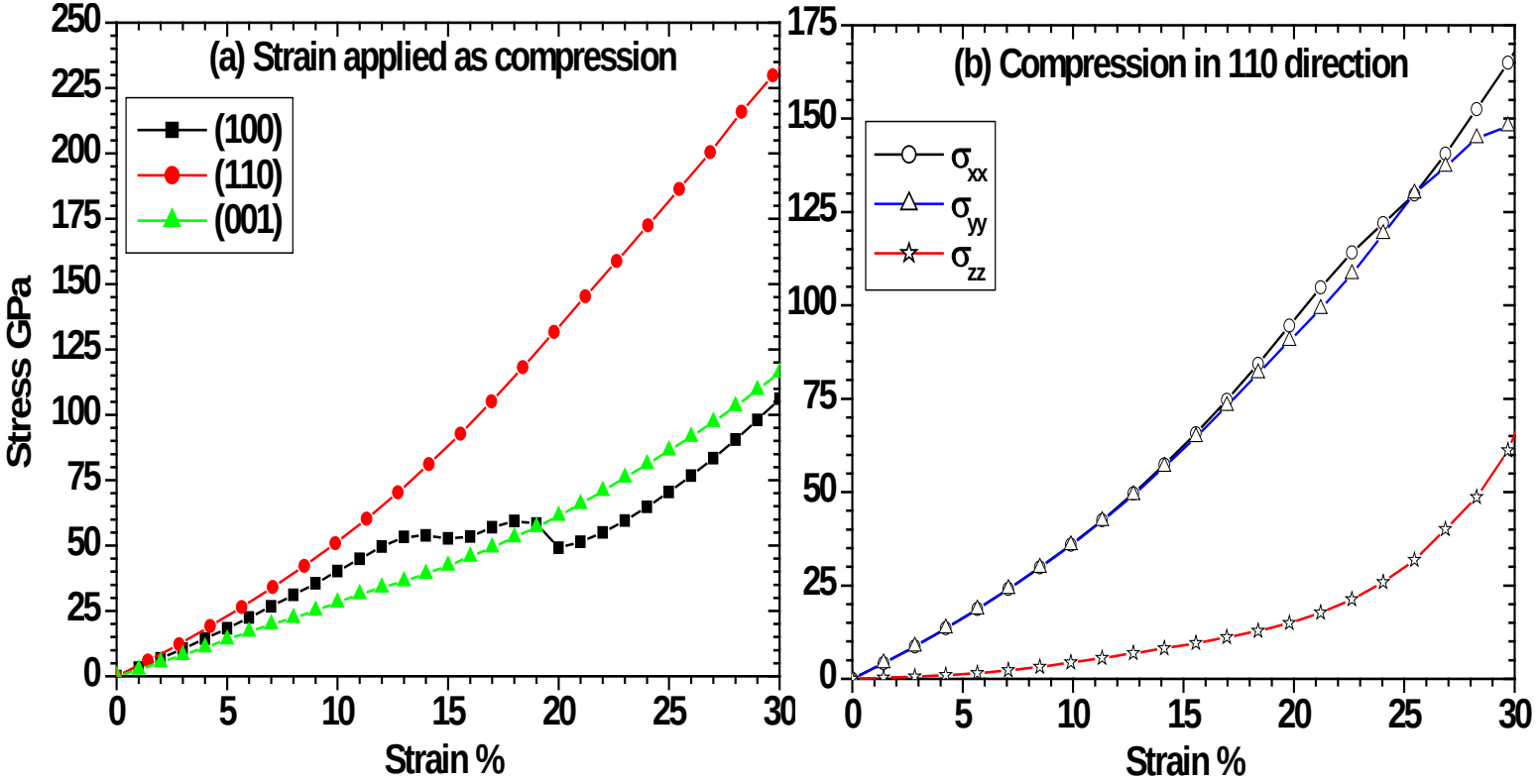


Fig. 7: (a) Total stress for compression in (100), (110), and (001) directions in Ti_3AlC_2 with Poisson ratio applied; (b) Stress components for biaxial compression applied in the (110) direction.

MAX phase phonon dispersions and theromodynamics

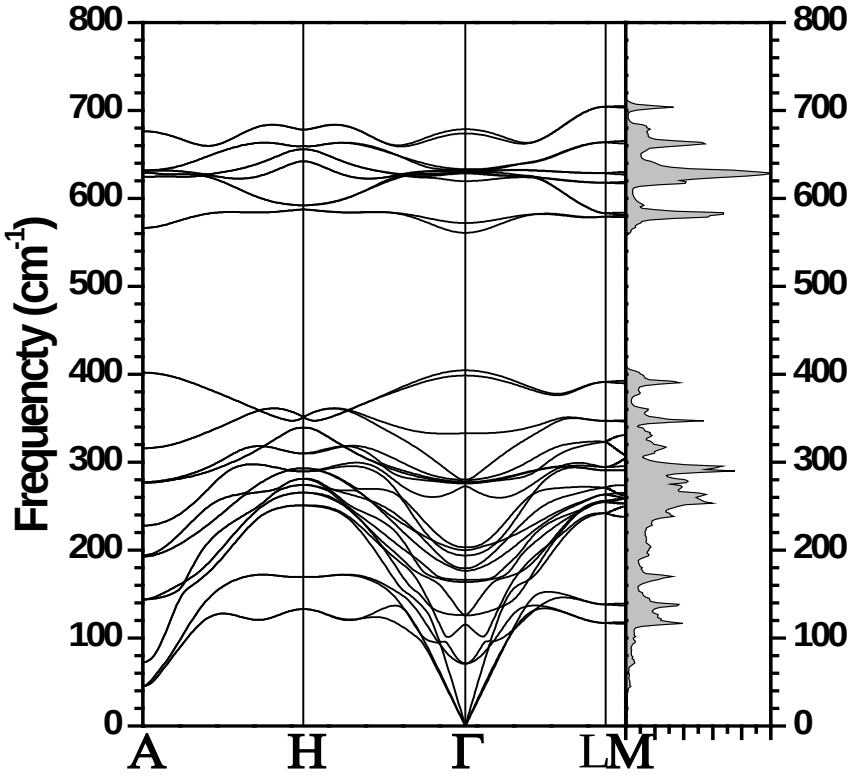


Fig. 9: Phonon dispersion and phonon DOS of Ti_3AlC_2.

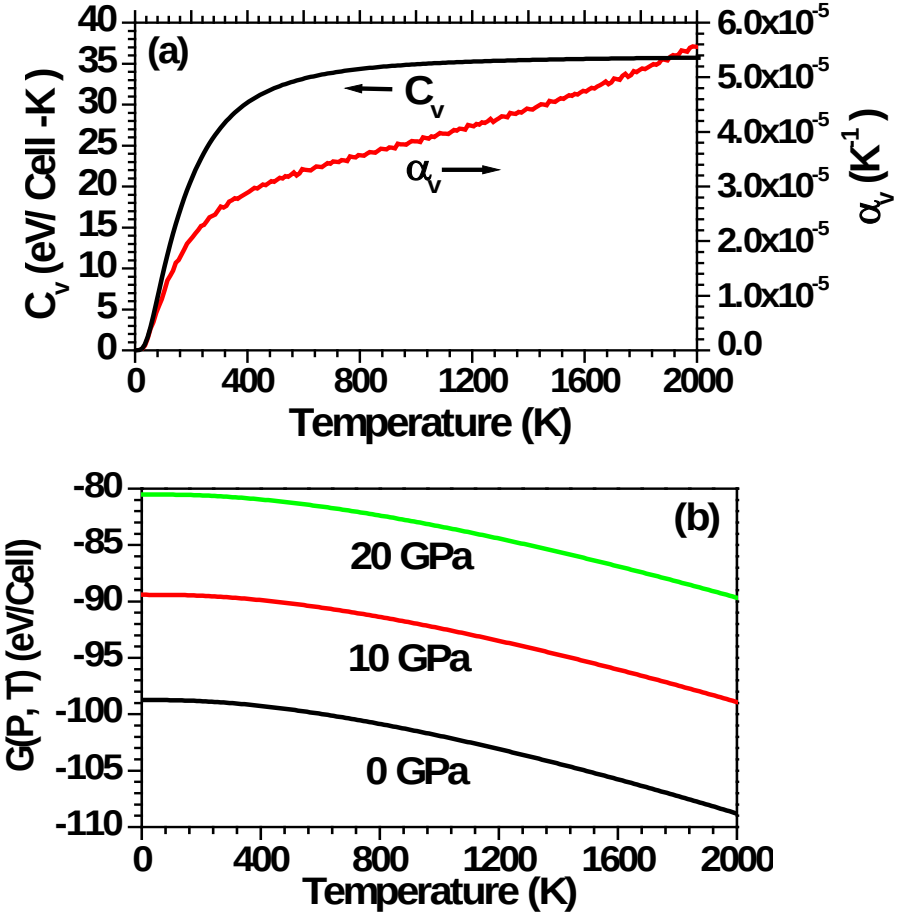


Fig. 10: (a) Specific heat at constant volume C_v; isothermal coefficient of expansion α_V in Ti_3AlC_2. (b) Gibbs free energy at 0, 10, and 20 GPa.

Multi-axial failure envelope in Ti_3AlC_2 (139 data points)

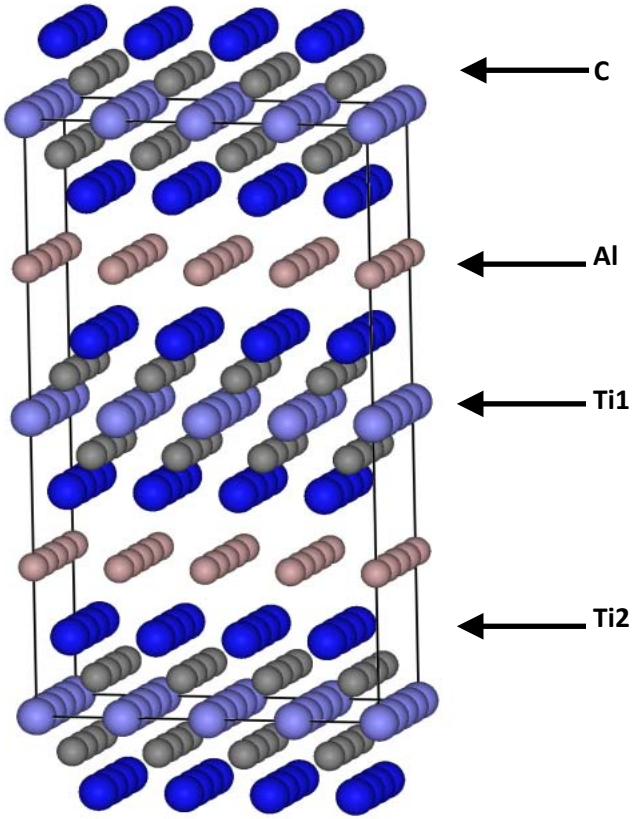
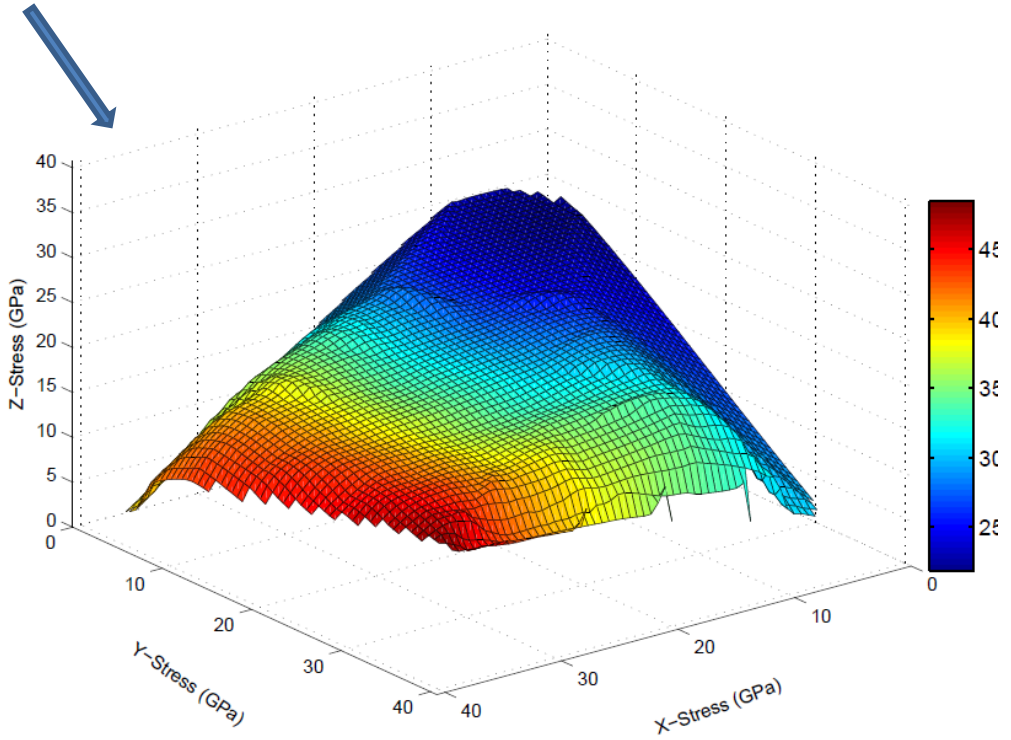


Fig.5: Orthorhombic 192-atom supercell model of Ti_3AlC_2 used for tensile and compression simulations.



From the failure envelope:

Strong anisotropy. Ti_3AlC_2 weak in the z-direction, strong in the x-direction, and intermediate in the y-direction.

Surface relatively smooth. No large peaks and valleys characteristic of metallic alloys.

Additional data points and analysis in progress.

Implementation of calculations on NERSC supercomputers.

Petasacle machines: Hopper, Franklin, Carver etc. Very powerful but require time and expertise to use effectively.

Substantial allocations obtained for our project without any cost for equipment or service rendered.

It require substantial experience and exploration to obtain meaningful results from supercomputer.

This will be the future for large scale simulations in materials research related to energy science and technology.

It is also critical to train new generation of scientists who can take advantage of new computational resources.

NERSC (National Energy Research supercomputing Center)

NERSC is the flagship high performance scientific computing facility for research sponsored by the U.S. Department of Energy Office of Science. NERSC, a national facility located at Lawrence Berkeley National Laboratory, is a world leader in providing resources and services that accelerate scientific discovery through computation.

Franklin: Cray XT4

The NERSC Cray XT4 system, named Franklin, is a massively parallel processing (MPP) system with 9,572 compute nodes. Each node has quad processor cores, and the entire system has a total of 38,288 processor cores available for scientific applications. The system is named in honor of Benjamin Franklin.

Rear Admiral Grace Murray Hopper (1906-12-09) – (1992-1-1) (aged 85)

Hopper II: Cray XE6: The fifth most powerful machine on the list of Top 500 supercomputers in the world

The Hopper II system, a Cray XE6 has been installed at NERSC. The system has a peak performance of 1.288 Peta-flops, 6384 nodes, (153,216 cores) with 217 TB of memory and 2PB of disk space

THANK YOU ALL!

AND

WE GREATLY APPRECIATE DOE-NETL SUPPORT!