Electronic Structure and Mechanical Properties of 20 MAX-Phase Compounds

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

NETL Project DE-FE0005865 (Technical Manager: Richard Dunst)

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I. Background of the project
II. Project outline and significance
III. Statement of project objectives (OSPO)
IV. The project team
V. Technical approach and methods used
VI. Some preliminary results

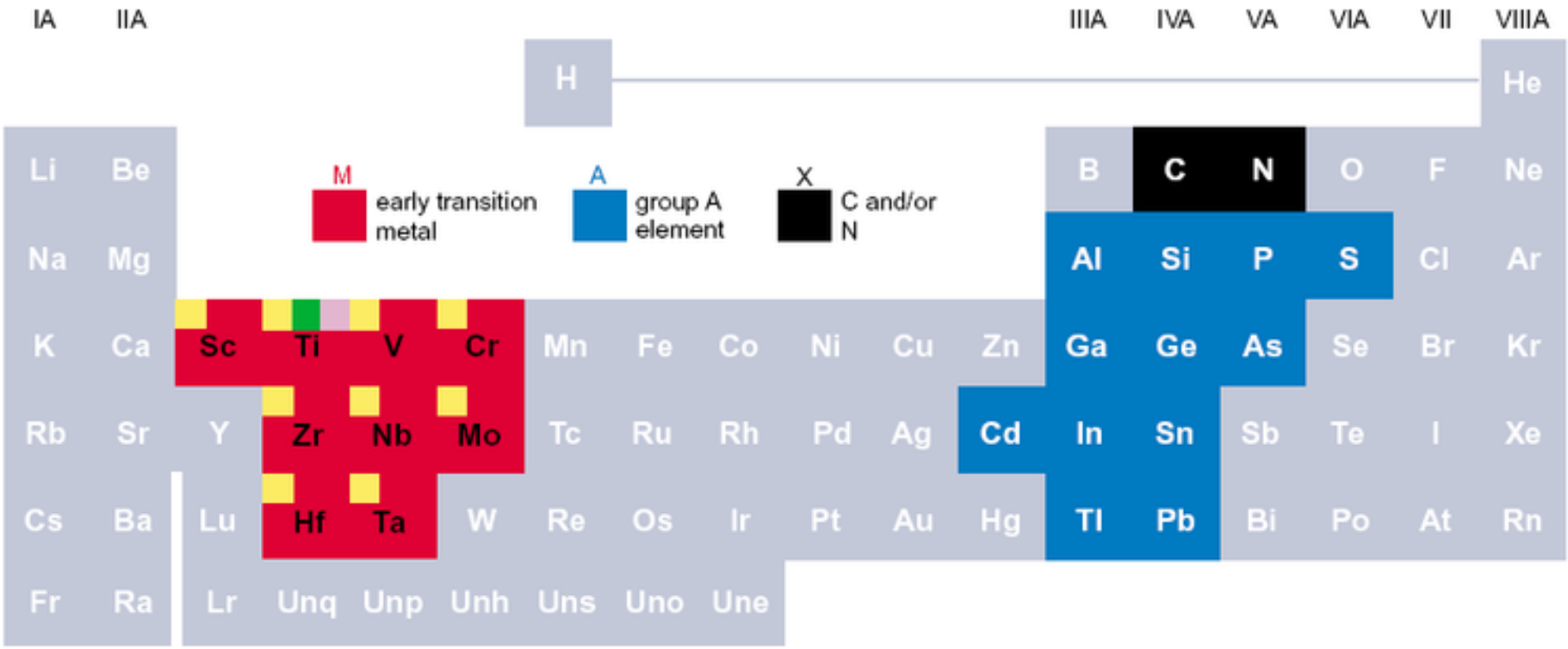
What I present today at the 26th ACFEM is essentially a Report

OUTLINE:

1. Introduction to MAX phase compounds
2. Why MAX compounds
3. **Results on 20 MAX phases**
    - **a. Electronic and optical properties**
    - **b. Mechanical and elastic properties**
4. Implication of results
5. Summary
6. Work in progress or planned

Introduction to MAX Phase

What is MAX? Layered Ternary Transition Metal Carbides and Nitrides
Formula: $M_{n+1}AX_n$ where **M** — Early Transition **M**etal; **A** — **A**-group element; **X** — Carbide or Nitride, n = 2-5. n=1 also possible.
Most phases are 211 or 312 compounds; 413 and 514 are very rare.



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	$Cr_{0.5}Al_{0.5}N$
	V_2SiC	Ta_6AlC_5	Solid Solutions
	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		$Ti_3Si(Al)C_2$

Many phases have not been synthesized. This list is rapidly increasing!

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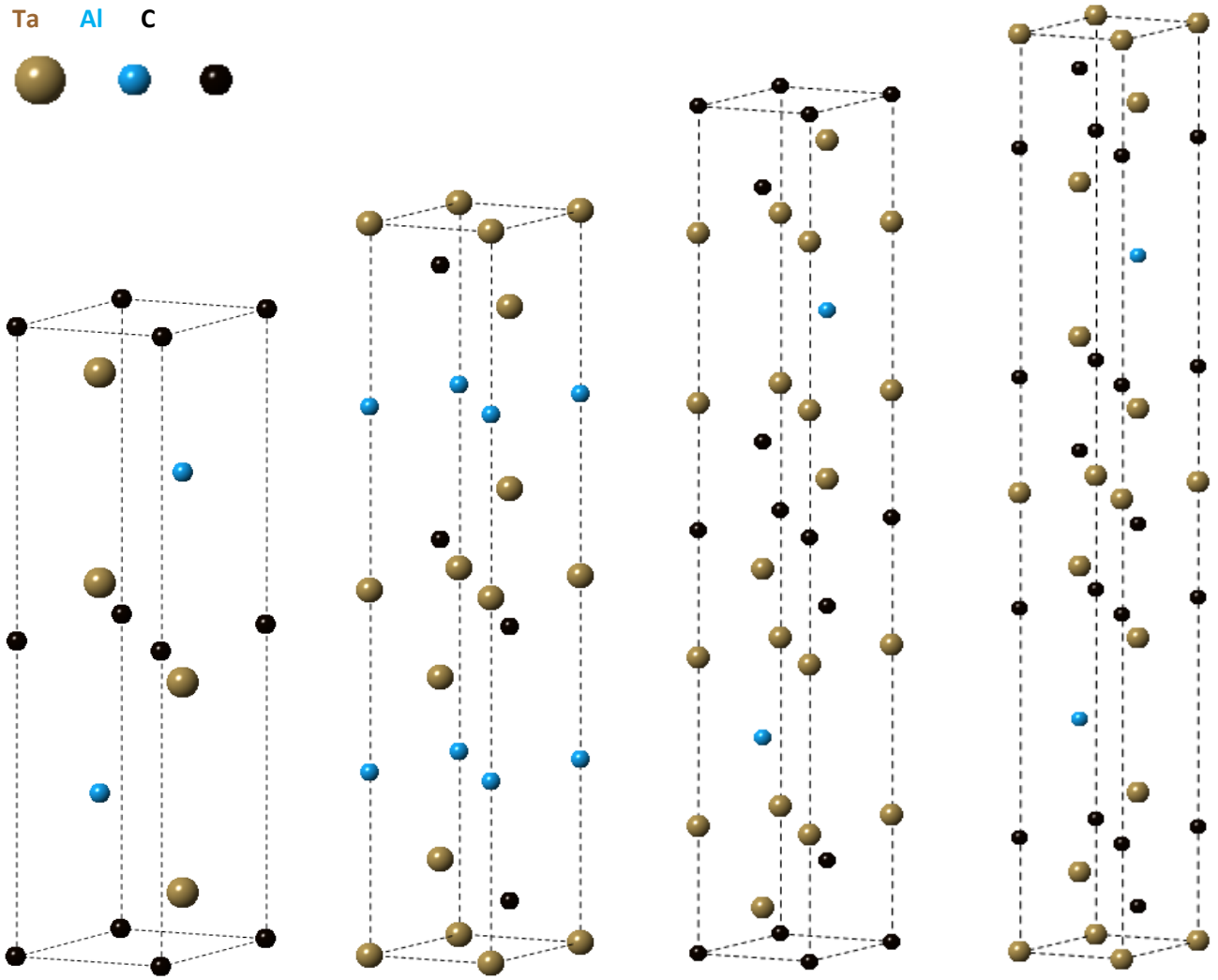
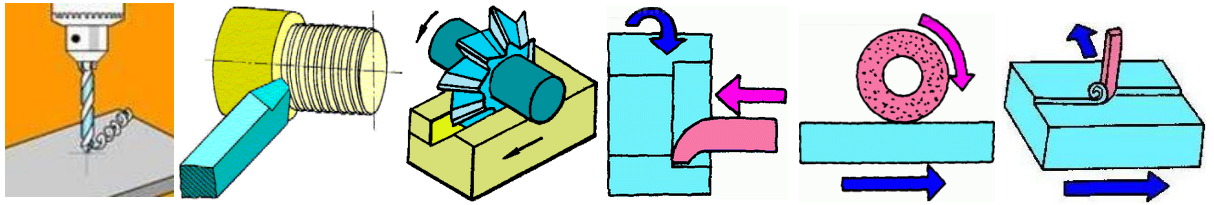
Crystal structures of 211, 312, 413, 514 MAX phases



Special properties of MAX phases compounds

Advanced Properties:

Like a Metal: thermally and electrically conductive, thermal-shock resistantant, machinable, and damage tolerant;



Images from the Internet

Like Ceramics: light weighted, stiff, refractory and oxidation resistant, not too expensive.

Mechanical properties of MAX phases are very complicated!!

Some are very promising, others are detrimental, depending on structure, composition and interatomic bonding.

Applications (realized and projected):

- **High-temperature structural applications;**
- **Porous exhaust gas filters for automobiles;**
- **Heat exchangers;**
- **Heating elements;**
- **Wear and corrosion protective surface coatings;**
- **Electrodes, resistors, capacitors, rotating electrical contacts;**
- **Nuclear applications;**
- **Bio-compatible materials;**
- **As sensor materials;**
- **Cutting tools, nozzles, tools for die pressing;**
- **Impact-resistant materials; projectile proof armor, bullet proof vest, etc.**

As Advanced Materials in Fossil energy power plants?

This is the one of the main goals for this project!

==> Using ab initio computation to explore new materials systems for advance applications based on fundamental understanding!

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Strategy

- Select 20 MAX phases of different components and compositions. They are: Ti_3MC_2 (M=**Al**; **Si**, **Ge**), Ti_2MC (M=**Al**, **Ga**, **In**; **Si**, **Ge**, **Sn**; **P**, **As**; **S**), Ti_2AlN, M_2AlC (M=**V**, **Nb**, **Cr**) and $Ta_{n+1}AlC_n$ (n=1~4). (Materials Genome approach!)
- Calculate the Electronic Structure, bonding and optical conductivities of these 20 MAX phases.
- Calculate the elastic and mechanical properties of the same 20 MAX phases.
- Find the property **trends** among them and predict properties of other MAX phases.
- Explore the **correlations** between properties, compositions and structures and search for new MAX phases.

Methods (brief!)

Electronic structure calculations:

First-principles orthogonalized linear combination of atomic orbitals (**OLCAO**) method.

Density Functional Theory (DFT) based using LDA, very efficient for complex systems.

Effective Charge Q* on each atom, **Bond Order** values for each pair of atoms, are evaluated according to:

$$Q_{\alpha}^{*} = \sum_{i} \sum_{n,occupied} \sum_{j,\beta} C_{i\alpha}^{m^{*}} C_{j\beta}^{m} \langle b_{i\alpha}(\vec{k},\vec{r}) | b_{j\beta}(\vec{k},\vec{r}) \rangle$$

$$\rho_{\alpha\beta} = \sum_{n,occupied} \sum_{j,\beta} C_{i\alpha}^{n^{*}} C_{j\beta}^{n} \langle b_{i\alpha}(\vec{k},\vec{r}) | b_{j\beta}(\vec{k},\vec{r}) \rangle$$

The real part of the **Optical Conductivity** is obtained by $\sigma_1 = \frac{\varepsilon_2 \omega}{4\pi}$, after evaluating

$$\varepsilon_2(\omega) = \left(\frac{e^2}{\pi m E \omega}\right) \times \int d\vec{k} \sum_{n,l} \left| \langle \psi_n(\vec{k},\vec{r}) | \vec{P} | \psi_l(\vec{k},\vec{r}) \rangle \right|^2 f_l(\vec{k}) \times \left[1 - f_n(\vec{k})\right] \delta\left[E_n(\vec{k}) - E_l(\vec{k}) - E\right].$$

Mechanical properties Calculations:

Use Vienna *Ab initio* Simulation Package (**VASP**) with high accuracy, a stress- strain analysis of under linear elastic theory, and RVH approximation for poly-crystals.

These methods have bee successfully used by us in many crystals and non-crystalline materials in recent years.

3. Results on 20 MAX phases

Show what have been accomplished so far, not into details for each of the 20 MAX phases compounds.

a. Electronic and optical properties

Band structures

Density of states (DOS) and Partial DOS (PDOS)

Effective charge and bonder order values

Optical conductivities

XANES spectra

b. Mechanical and elastic properties.

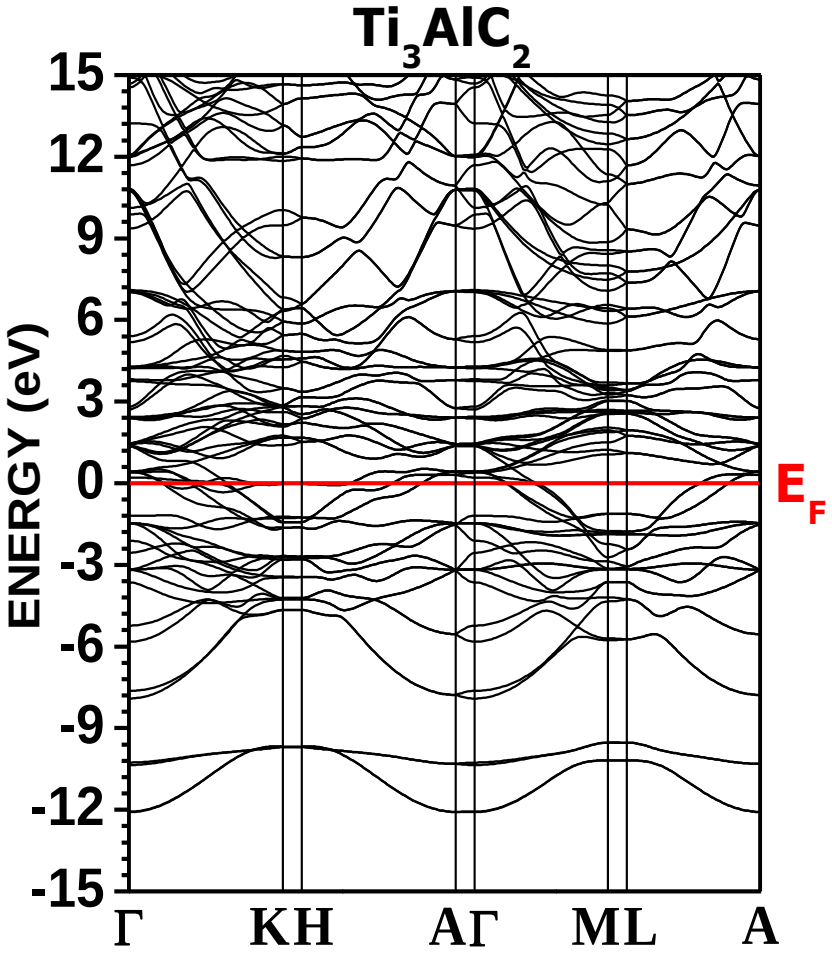
Elastic coefficients

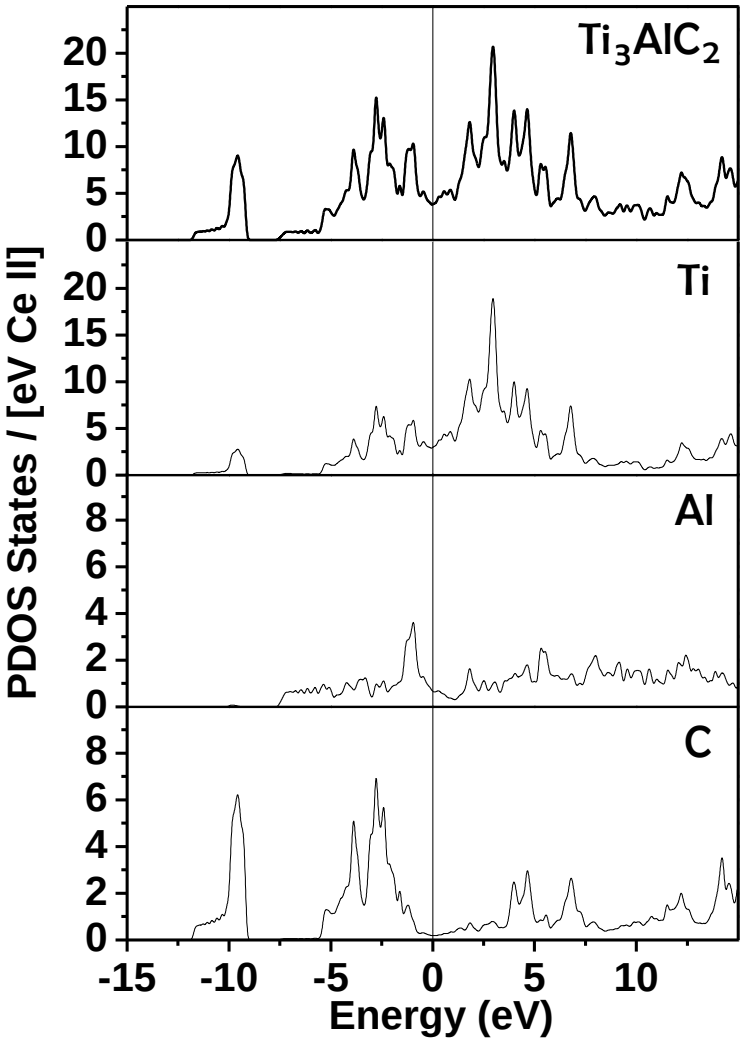
Mechanical parameters (K,G,E,η, k=G/K)

Additional analysis

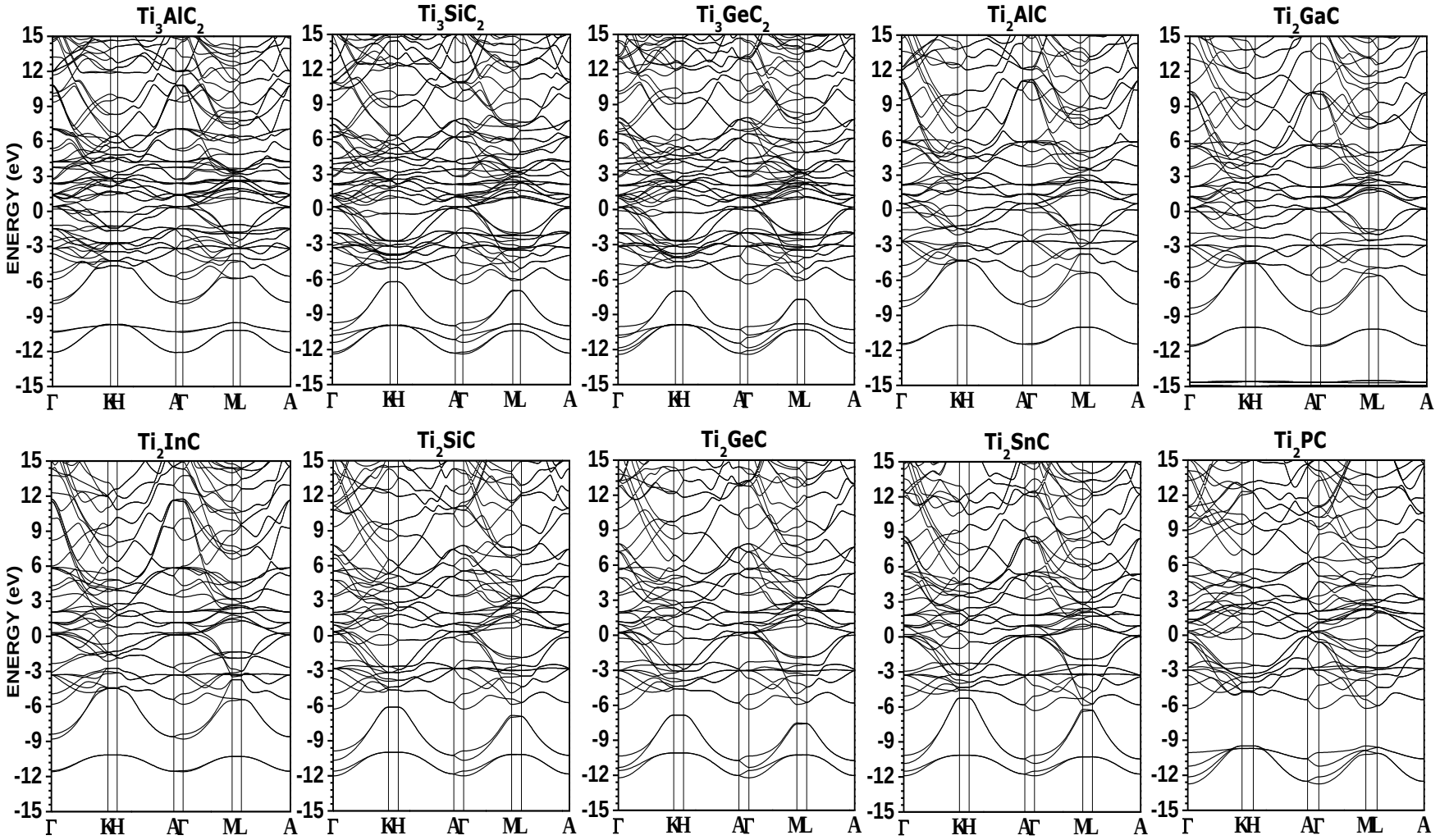
Example on the results for the electronic structure of MAX:

Band Structure and Density of states in Ti_3AlC_2

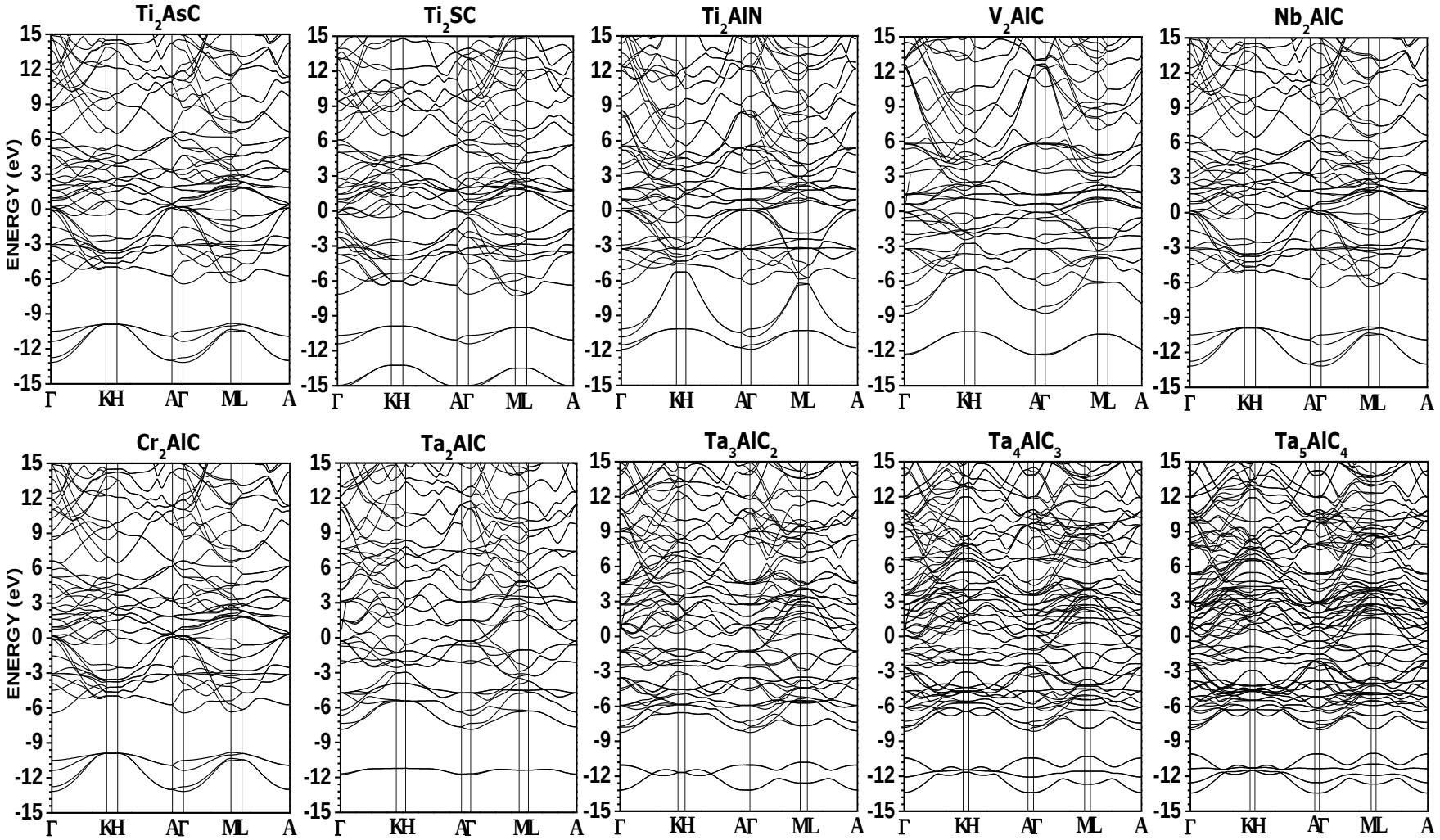




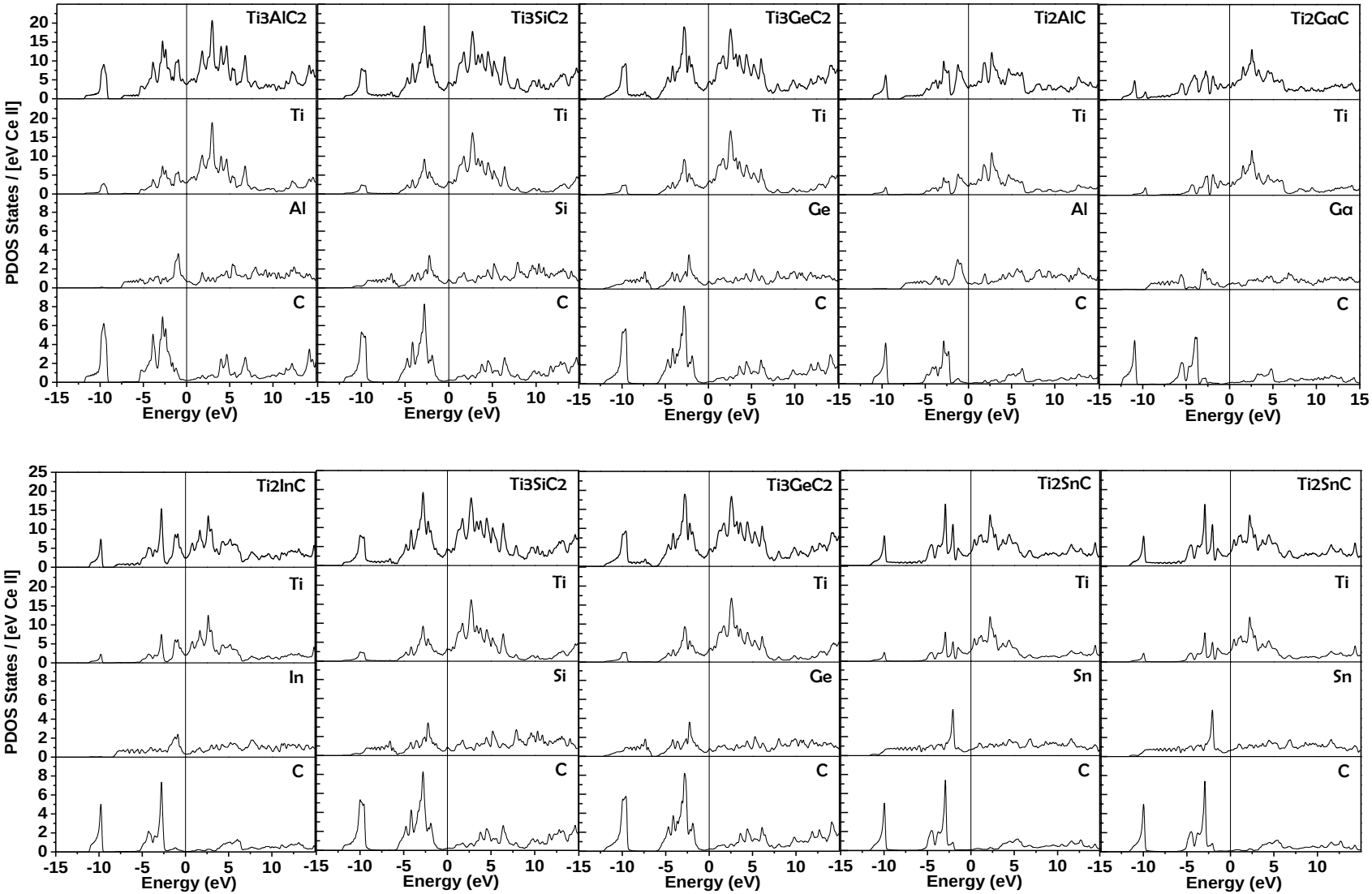
Band structure of MAX phases: 1-10



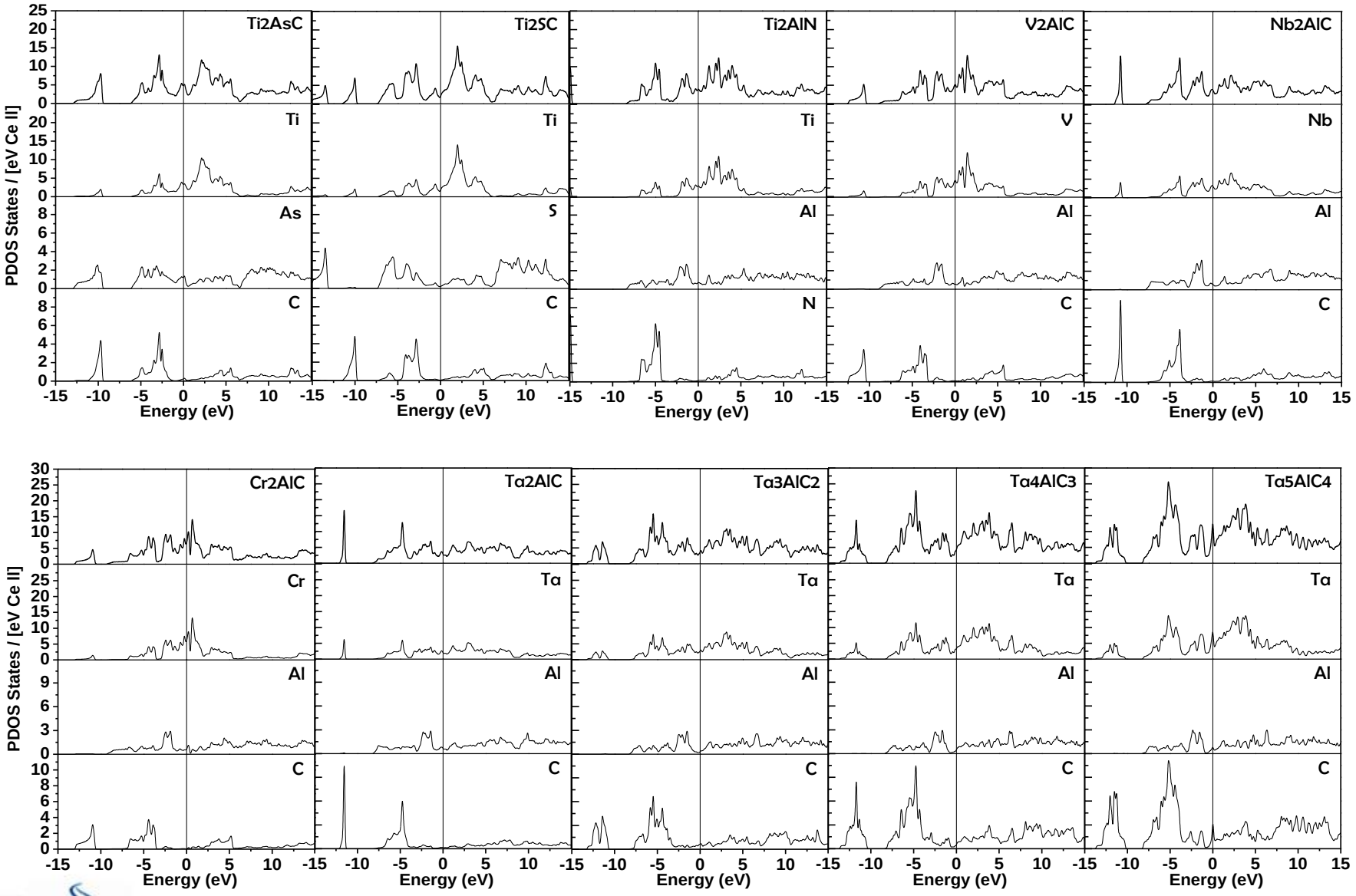
Band structure of MAX phases: 11-20



DOS and PDOS of MAX phases: 1-10



DOS and PDOS of MAX phases: 11-20



Total and partial (atom-resolved) DOS at Fermi-level

Crystal	TDOS (Fermi level)	$N(E_f)$ M	$N(E_f)$ A	$N(E_f)$ X
Ti_3AlC_2	3.826	2.97	0.67	0.19
Ti_3SiC_2	4.453	3.32	0.89	0.24
Ti_3GeC_2	4.331	3.33	0.78	0.22
Ti_2AlC	2.867	2.24	0.55	0.08
Ti_2GaC	3.274	2.76	0.44	0.08
Ti_2InC	2.537	2.14	0.34	0.06
Ti_2SiC	3.152	2.36	0.69	0.10
Ti_2GeC	3.592	2.76	0.73	0.10
Ti_2SnC	3.527	2.80	0.63	0.10
Ti_2PC	5.464	3.95	1.22	0.29
Ti_2AsC	4.845	3.36	1.24	0.25
Ti_2SC	1.981	1.72	0.20	0.06
Ti_2AlN	3.915	3.06	0.72	0.14
V_2AlC	5.191	4.56	0.53	0.10
Nb_2AlC	3.838	3.14	0.57	0.13
Cr_2AlC	6.647	5.96	0.63	0.06
Ta_2AlC	2.918	2.08	0.68	0.16
Ta_3AlC_2	3.646	2.70	0.30	0.64
Ta_4AlC_3	4.217	3.24	0.48	0.50
Ta_5AlC_4	12.403	8.52	0.80	3.08

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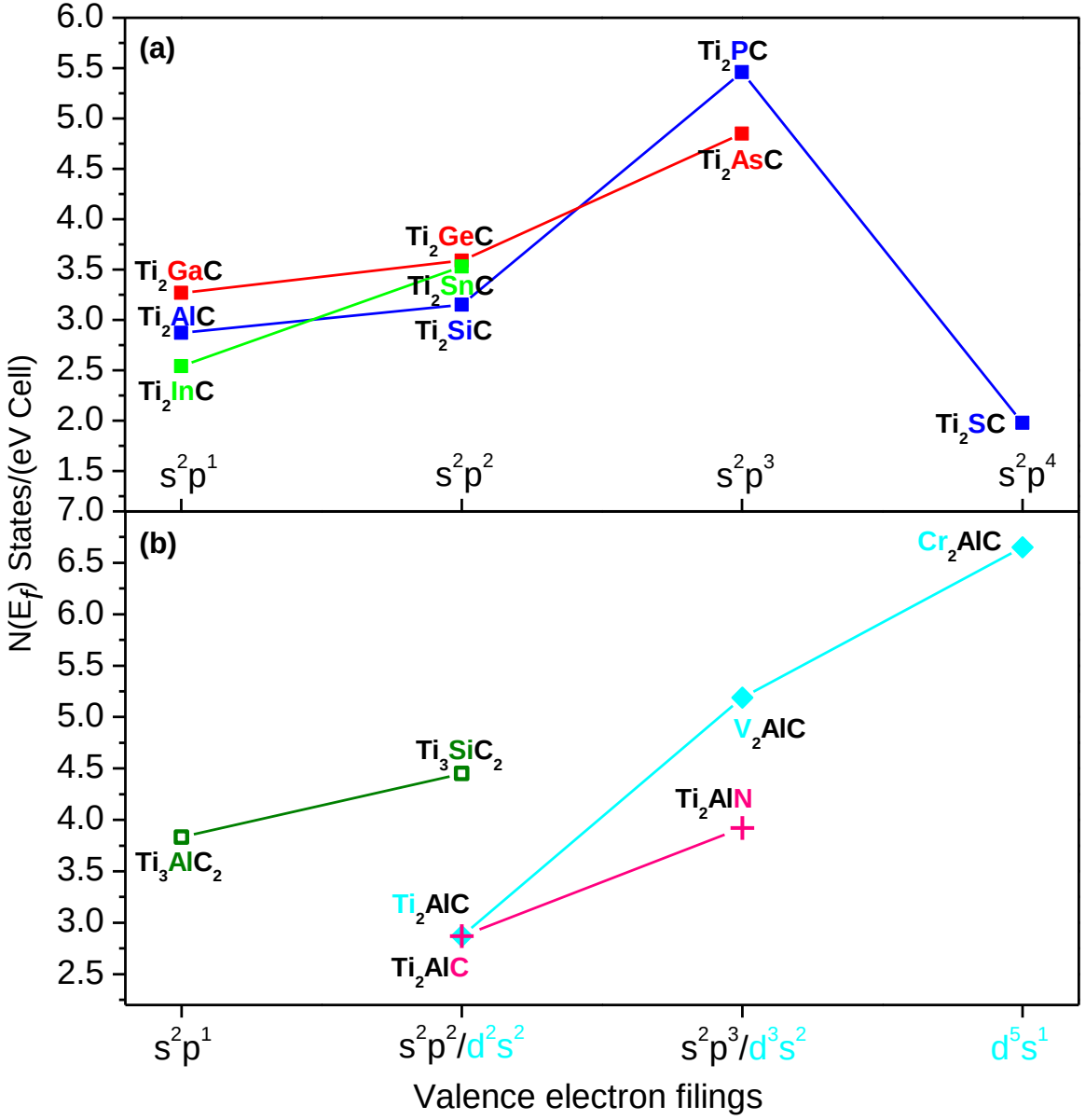
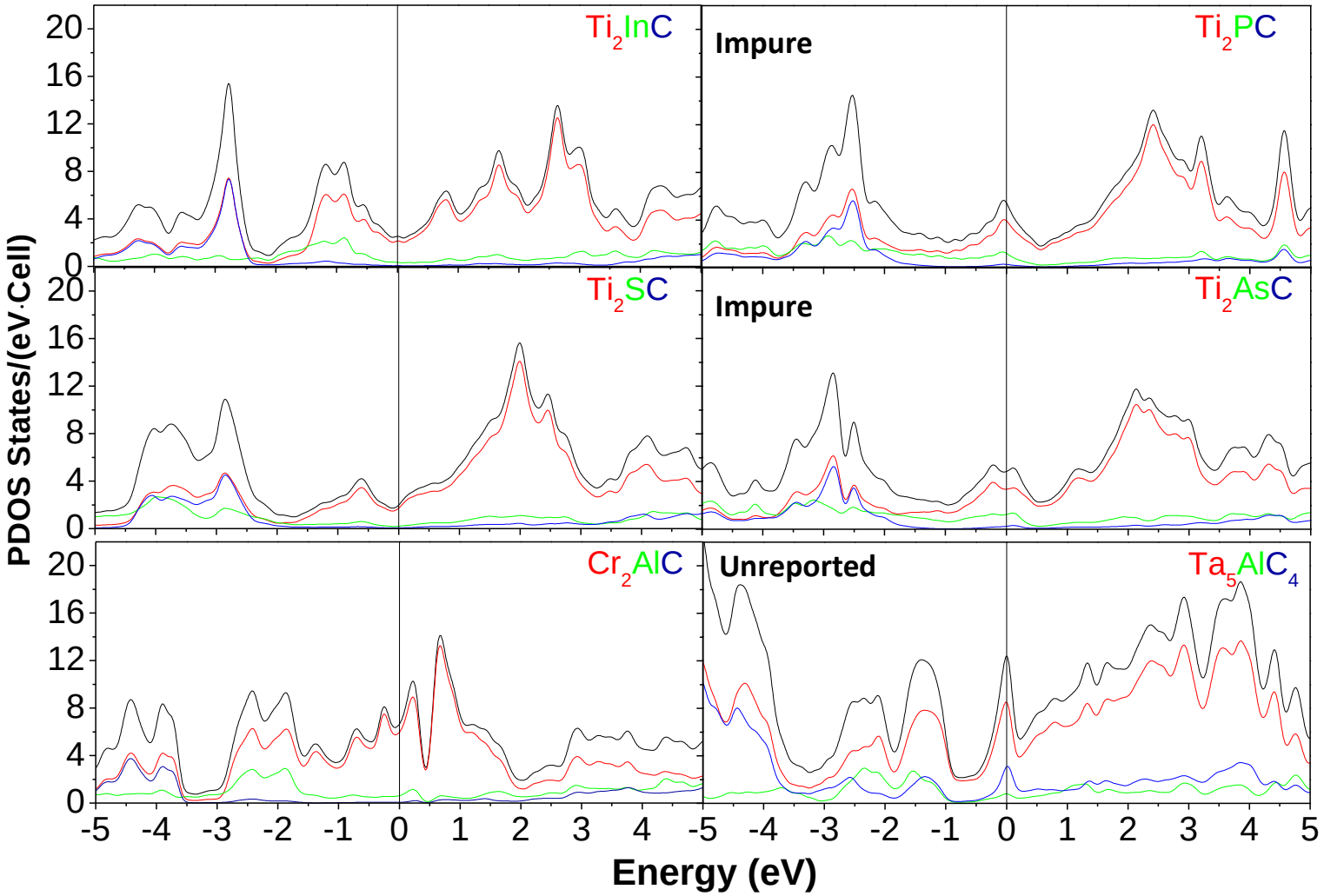
The trend of $N(E_f)$ with respect to valence electron filings



Hug G. *Electronic structures of and composition gaps among the ternary carbides Ti_2MC.* Physical Review B 2006;74:184113.

Prediction of Phase Stability: Peak or valley of DOS at E_F.

Stable **Unstable**



Consistent with experimental observations!!

Correlation of $N(E_f)$ and Experimental Electrical Conductivities

Crystal	$N(E_f)$ [States/(eV·Cell)]	Electrical Conductivity ($\mu\Omega^{-1}\cdot m^{-1}$)	
Ti_3AlC_2	3.826	3.48	Acta Materialia 2002;50:3141
Ti_3SiC_2	4.453	4.5	Scripta Materialia 2006;54:841
Ti_3GeC_2	4.331	4.5	Scripta Materialia 1997;36:535
Ti_2AlC	2.867	2.8	Scripta Materialia 1997;36:535
Ti_2InC	2.537	5.0	J. Alloys Compd. 2002;340:173
Ti_2GeC	3.592	3.3	Solid State Communications 2008;146:498
Ti_2SnC	3.527	4.5	J. Euro. Ceramic Society 2000;20:2619
Ti_2SC	1.981	1.9	J. App. Phys. 2008;104:033502
Ti_2AlN	3.915	3.2	Scripta Materialia 1997;36:535
Nb_2AlC	3.838	3.4	Met. and Mater. Trans. A 2002;33A:2775
Cr_2AlC	6.647	1.4	Scripta Materialia 2006;54:841
Ta_2AlC	2.918	3.91	J. Euro. Ceramic Society 2008;28:1679

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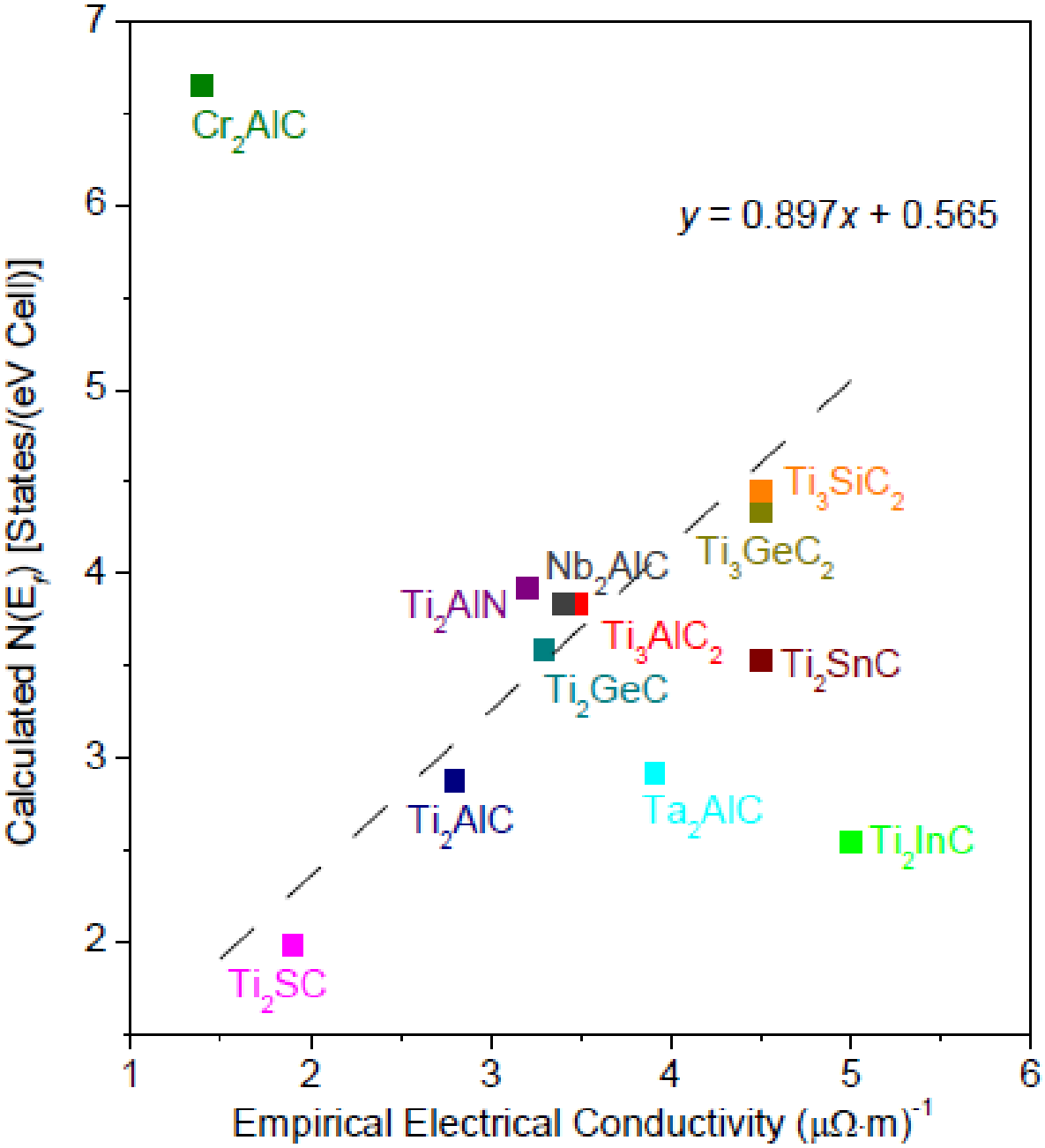
The correlation between N(E$_F$) and the electrical conductivity

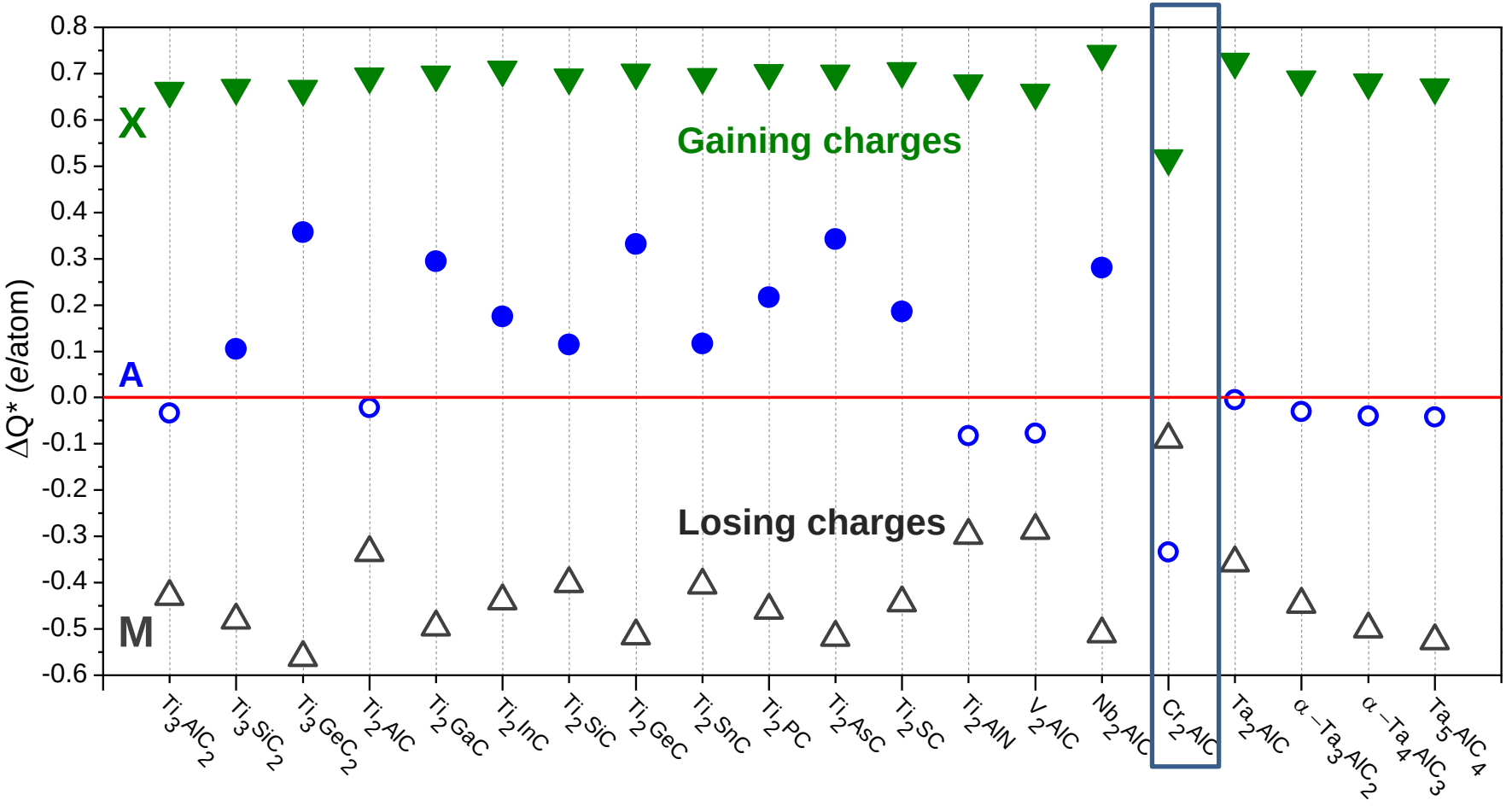


Charge transfer in MAX phases from effective charge calculations

Crystal	ΔQ* (*e*/atom) M	ΔQ* (*e*/atom) A	ΔQ* (*e*/atom) X
Ti_3AlC_2	-0.430	-0.034	0.663
Ti_3SiC_2	-0.481	0.105	0.669
Ti_3GeC_2	-0.562	0.357	0.667
Ti_2AlC	-0.335	-0.022	0.694
Ti_2GaC	-0.496	0.294	0.698
Ti_2InC	-0.439	0.175	0.708
Ti_2SiC	-0.402	0.114	0.691
Ti_2GeC	-0.515	0.332	0.702
Ti_2SnC	-0.405	0.117	0.693
Ti_2PC	-0.459	0.217	0.701
Ti_2AsC	-0.518	0.342	0.700
Ti_2SC	-0.443	0.186	0.705
Ti_2AlN	-0.298	-0.083	0.679
V_2AlC	-0.287	-0.077	0.658
Nb_2AlC	-0.511	0.280	0.742
Cr_2AlC	-0.090	-0.334	0.517
Ta_2AlC	-0.357	-0.005	0.725
α-Ta_3AlC_2	-0.447	-0.030	0.687
α-Ta_4AlC_3	-0.500	-0.040	0.681
Ta_5AlC_4	-0.525	-0.042	0.670

The charge transfer between different composing elements:

M: lose charge; X: gain charge; A: mostly losing charge, some gain charge.

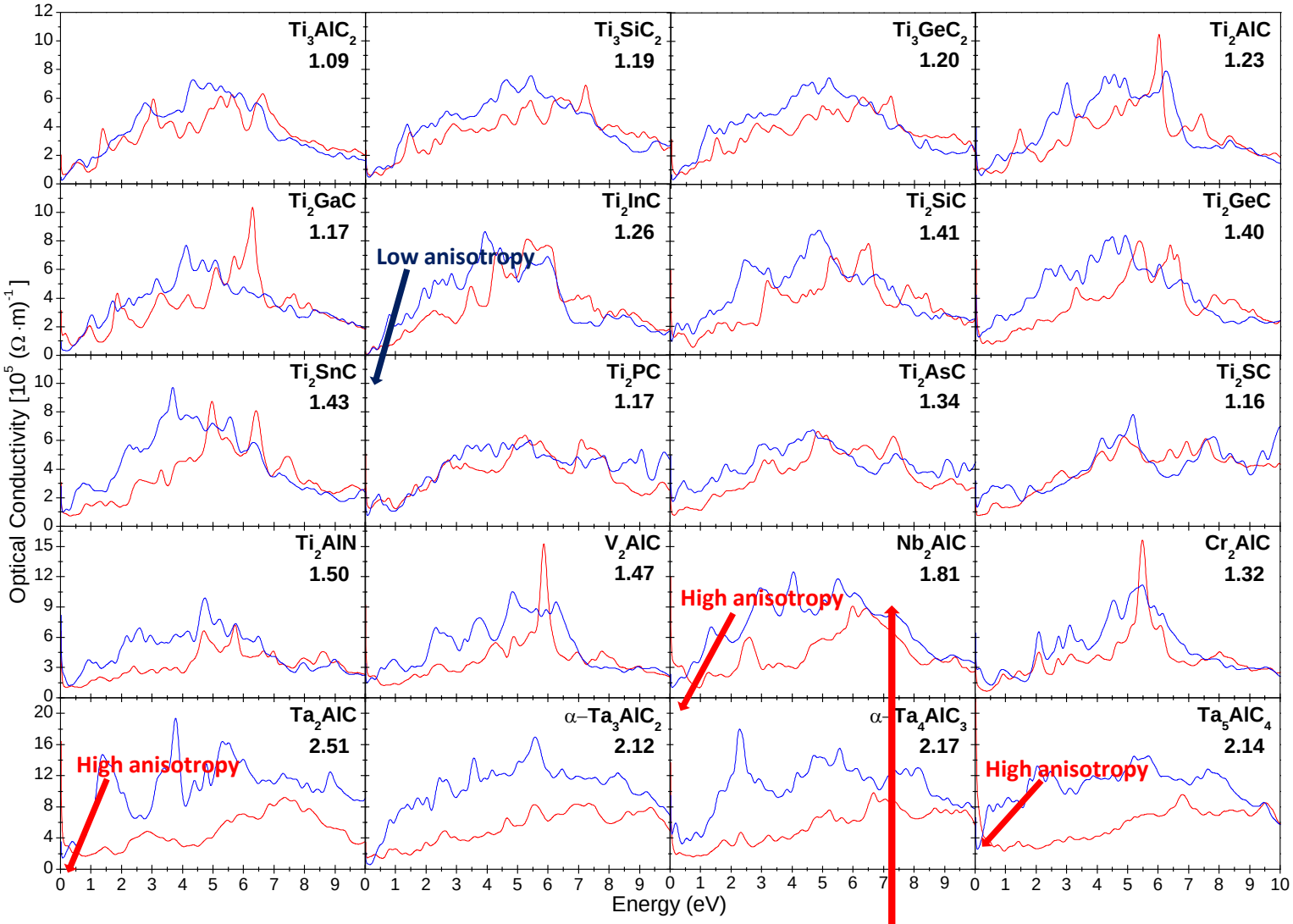


Summary of bond order values for all the bonding types:

Very complicated! They are the fundamental controlling factor of their electronic and mechanical properties (*no time to discuss in detail here!)*

Crystal	M-X	M-A	M-M		A-A
			Intra-layer	Inter-layer	
				Cross X / Cross A	
Ti_2AlC	0.212	0.159	0.069	0.050	0.063
Ti_2GaC	0.213	0.148	0.058	0.055	0.058
Ti_2InC	0.212	0.139	0.059	0.065	0.070
Ti_2SiC	0.214	0.173	0.052	0.042	0.031
Ti_2GeC	0.215	0.151	0.050	0.048	0.032
Ti_2SnC	0.214	0.152	0.054	0.056	0.040
Ti_2PC	0.216	0.199	0.029	0.041 / 0.053	
Ti_2AsC	0.216	0.171	0.029	0.052	
Ti_2SC	0.215	0.165	0.027	0.058 / 0.031	
Ti_2AlN	0.179	0.153	0.079	0.038	0.069
V_2AlC	0.205	0.152	0.070	0.037	0.072
Nb_2AlC	0.150	0.110	0.022		0.060
Cr_2AlC	0.197	0.153	0.049	0.022	0.074
Ta_2AlC	0.209	0.154	0.082	0.062	0.067
	M2-C / C-M1		M2	M1 / M1-M2	
Ti_3AlC_2	0.204 / 0.219	0.158	0.023	0.069 / 0.040	0.062
Ti_3SiC_2	0.197 / 0.230	0.175	0.033	0.045 / 0.037	0.030
Ti_3GeC_2	0.192 / 0.234	0.157	0.037	0.043 / 0.037	0.029
α-Ta_3AlC_2	0.216 / 0.206	0.145	0.020	0.096 / 0.040	0.068
α-Ta_4AlC_3	C2-Ta2 / Ta2-C1 / C1-Ta1	0.143	Ta2	Ta1 / Ta2-Ta2 / Ta2-Ta1	0.068
	0.216 / 0.218 / 0.206		0.021	0.095 / 0.025 / 0.044	
Ta_5AlC_4	Ta3-C2 / C2-Ta2 / Ta2-C1 / C1-Ta1	0.143	Ta3 / Ta2	Ta1 / Ta3-Ta2 / Ta2-Ta1	0.066
	0.219 / 0.212 / 0.216 / 0.209		0.020 / 0.022	0.096 / 0.029 / 0.042	

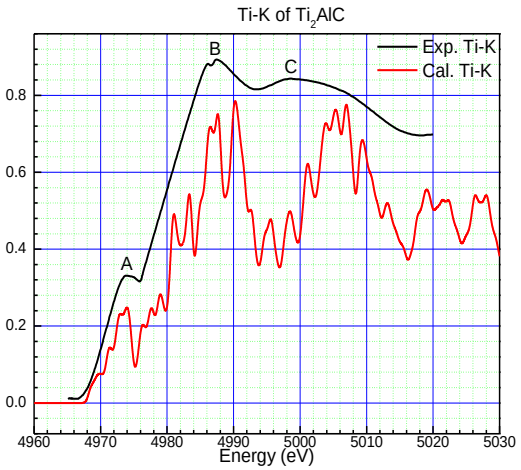
Optical Conductivities of 20 MAX phases

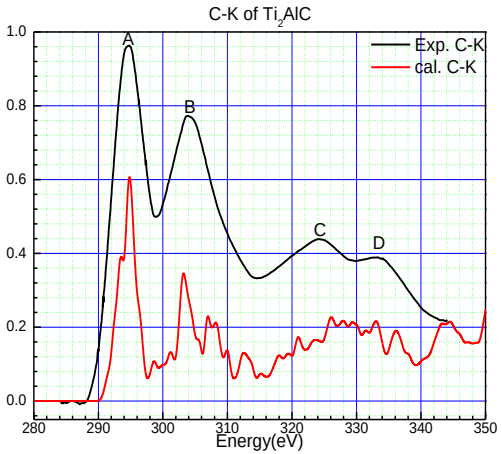


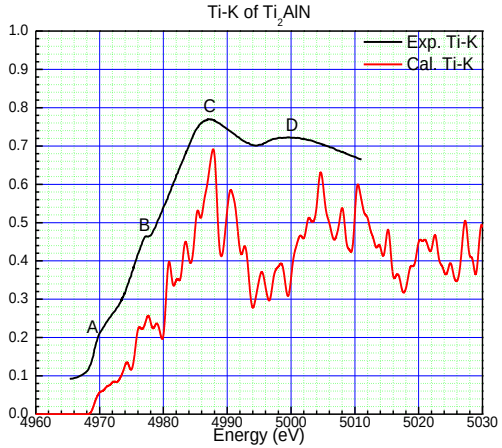
Thin Solid Films 2009;517:2920

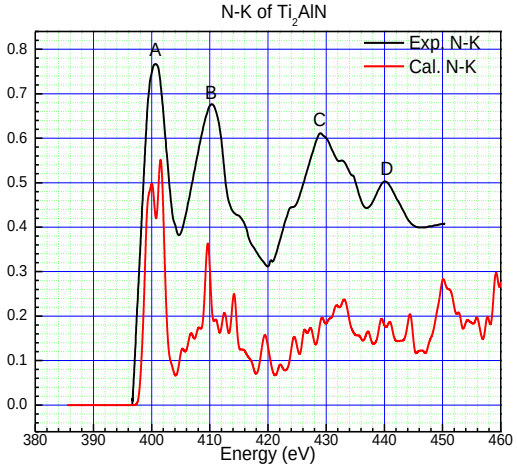
Yu, G., et al., *Photoconductivity and optical conductivity in lightly doped $Nd_2CuO_{4-\delta}$* Physica C: Superconductivity, 1992. **203**(3-4): p. 419-425

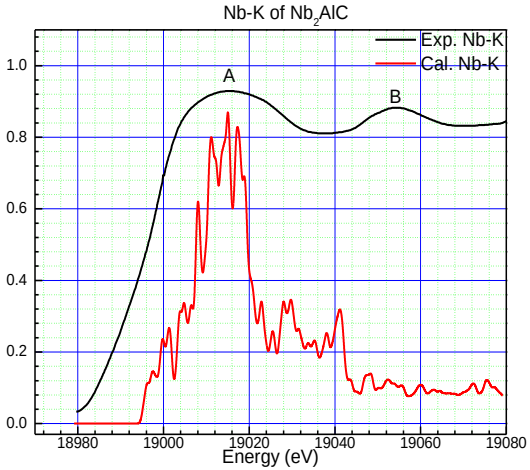
XANES spectra in MAX phases: Calculated (lower red curves) and measured (upper blue curves) for Ti-K, C-K in Ti_2AlC, Ti-K, N-K in Ti_3AlN, and Nb-K edges in Nb_2AlC crystals. Experimental data from: *G. Hag, M. Jaouen and M. W. Barsoum, Phys. Rev. B 71, 024105, (2005).*











Agreement between calculation and experiment quite good. XANES is useful for characterizing different phases and impurity contaminations. This work is part of the electronic structure results.

Calculated elastic coefficients and mechanical properties of 20 MAX phases

Crystals	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	K	G	E	η	G/K=k
Ti_3AlC_2	355.8	81.4	75.3	293.4	120.3	137.2	162.5	126.7	301.7	0.191	0.78
Ti_3SiC_2	369.6	96.2	107.6	358.3	155.0	136.7	191.1	141.3	340.0	0.204	0.74
Ti_3GeC_2	362.0	97.2	97.7	332.0	137.3	132.4	182.2	132.2	319.3	0.208	0.73
Ti_2AlC	301.9	68.0	63.0	267.9	105.1	117.0	139.7	110.5	262.3	0.187	0.79
Ti_2GaC	300.8	79.2	63.8	246.5	92.4	110.8	139.3	101.4	244.9	0.207	0.73
Ti_2InC	284.4	69.3	55.2	235.5	83.9	107.5	128.6	96.0	230.5	0.201	0.75
Ti_2SiC	312.9	82.1	110.4	329.2	149.6	115.4	173.0	124.9	302.0	0.209	0.72
Ti_2GeC	296.6	85.7	96.8	297.1	121.5	105.5	161.0	110.0	268.8	0.222	0.68
Ti_2SnC	262.6	88.6	73.1	255.2	96.8	87.0	138.8	92.4	226.8	0.228	0.67
Ti_2PC	**256.8**	144.8	155.0	**339.5**	166.3	56.0	191.8	93.1	240.4	**0.291**	**0.49**
Ti_2AsC	**212.9**	180.4	123.7	**289.5**	146.3	16.2	150.7	57.2	152.3	**0.332**	**0.38**
Ti_2SC	339.8	101.4	109.7	361.9	159.5	119.2	186.8	134.4	325.2	0.210	0.72
Ti_2AlN	312.9	73.0	95.5	290.7	126.1	120.0	160.5	117.4	283.1	0.206	0.73
V_2AlC	334.4	71.5	106.0	320.8	149.8	131.5	172.9	132.1	315.9	0.196	0.76
Nb_2AlC	316.6	86.3	117.0	288.6	137.6	115.2	173.6	116.4	285.5	0.226	0.67
Cr_2AlC	366.3	85.8	111.3	356.9	142.9	140.2	189.6	137.0	331.2	0.209	0.72
Ta_2AlC	344.5	112.2	137.1	327.9	152.3	116.1	198.8	124.1	308.1	0.242	0.62
α-Ta_3AlC_2	453.6	130.5	135.6	388.4	175.0	161.5	232.8	161.1	392.8	0.219	0.69
α-Ta_4AlC_3	459.2	149.1	148.7	383.1	170.5	155.0	243.0	155.3	384.1	0.237	0.64
Ta_5AlC_4	481.5	149.6	158.1	423.6	188.8	165.9	257.2	169.1	416.0	0.231	0.66

Anisotropic ratio C_{33}/C_{11} correlates with G/K. Note: Ti_2PC and Ti_2AsC are outliers.

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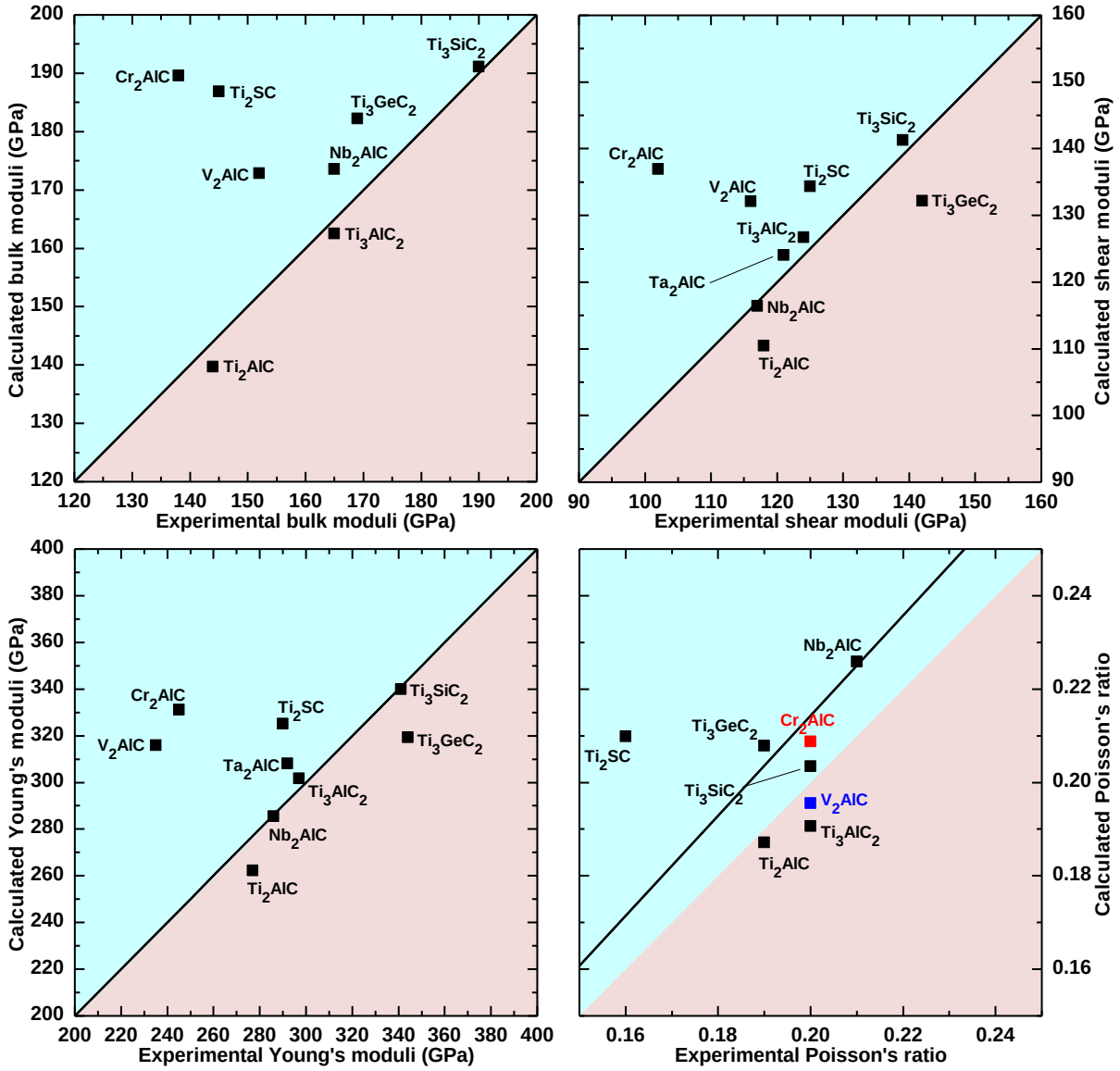
Comparison of our calculated K, G, E, and η with the experimental data from *(Barsoum & Radovic, Annu. Rev. Mater. Res. 41, 195, 2011).*

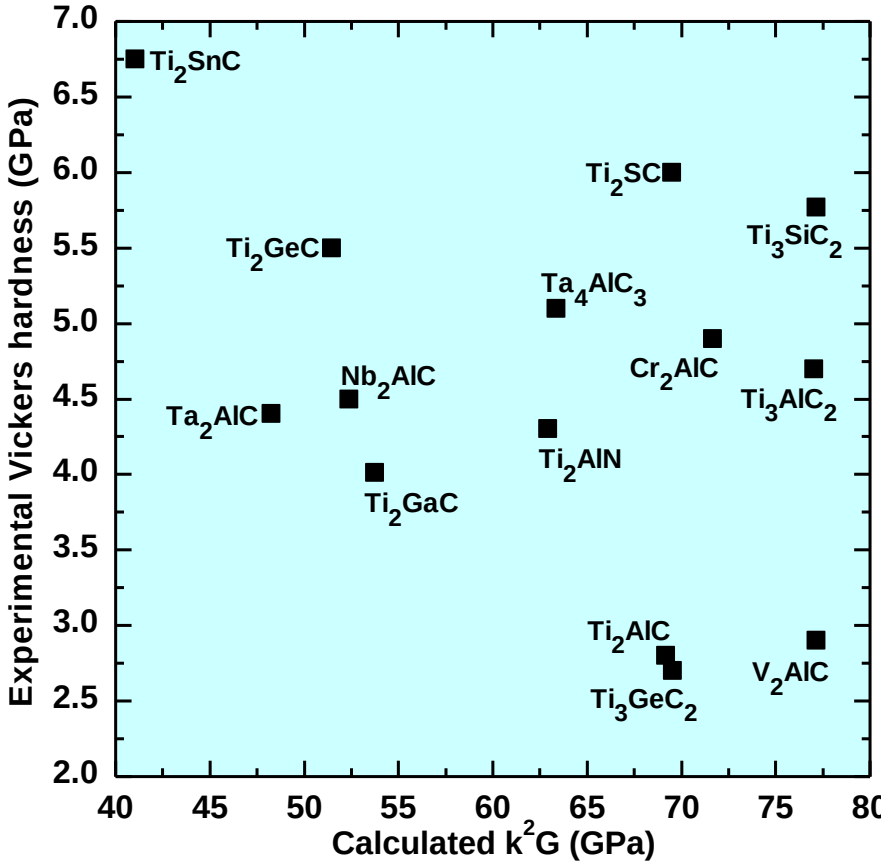


Implication of our results.

Is it possible to predict experimentally measurable parameters from first-principles calculations? **Yes** and **NO**!

Is there a correlation of Vickers hardness with k^2G? Answer: **NO!** (See Figure)

Is it possible to provide theoretical guidance regarding materials development? **Yes**.



There have been many attempts to predict hardness, failure behavior or other mechanical properties empirically using either experimental or calculated data. Results are mixed.

For **super-hard materials** with simple crystal structures, they are more successful.

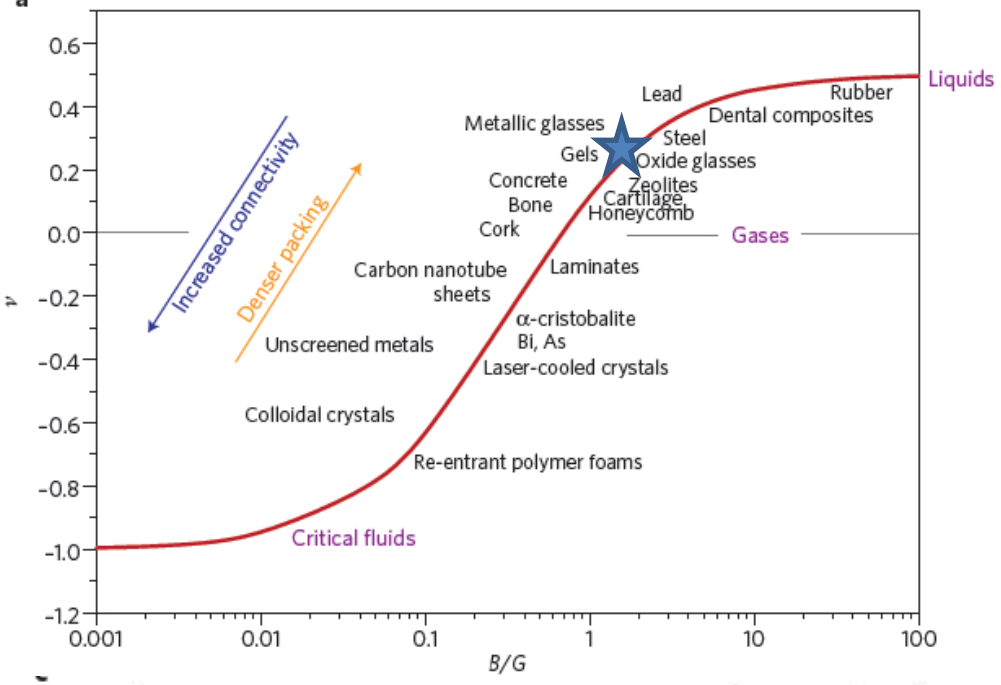
For **bulk metallic glasses**, more difficult.

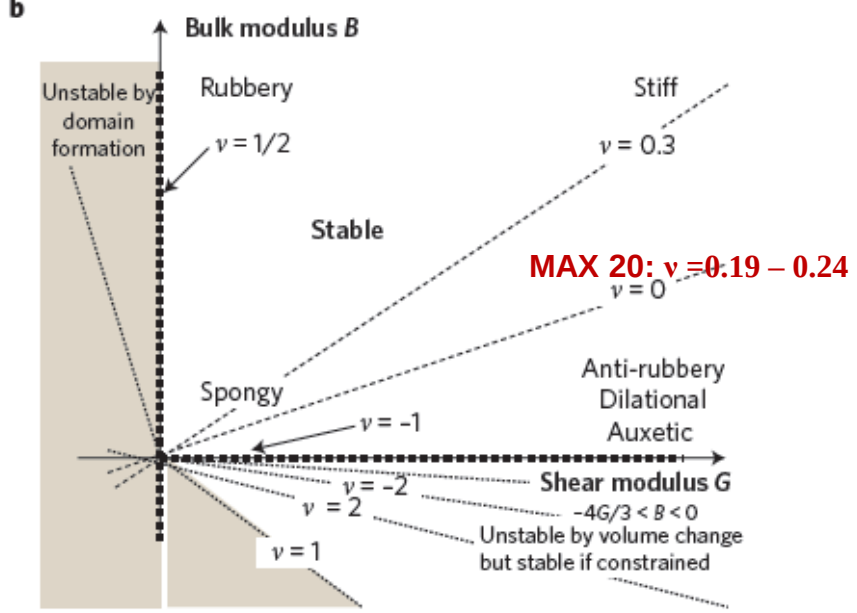
For **MAX phases**, nearly impossible.

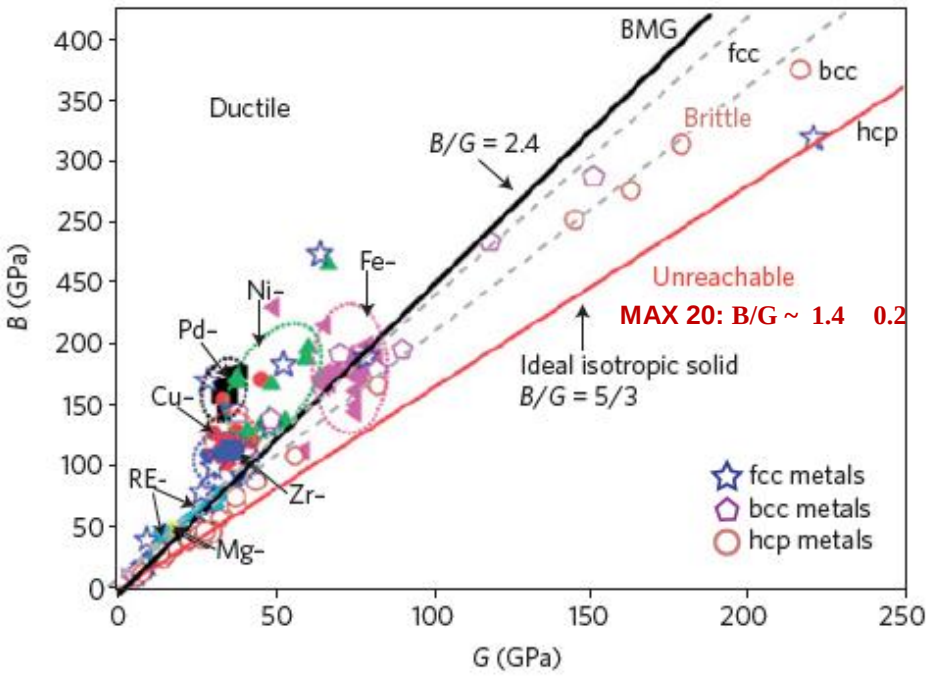
Reason: too many factors involved, and complexity of the structure and composition.

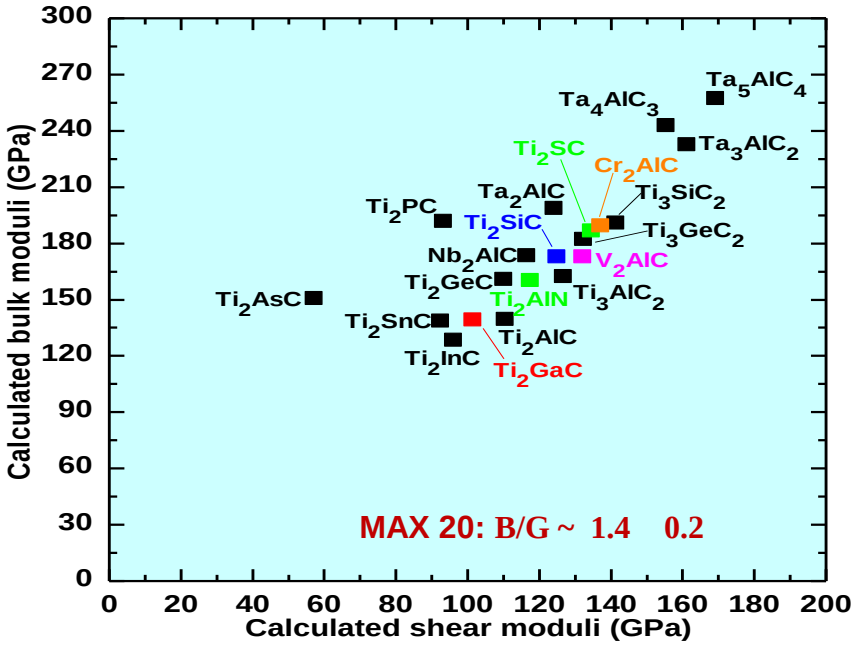
Still, we will **attempt** through fundamental studies and by understanding atomistic level interactions.

Recent empirical formula by Chan (*Intermetallic, 2011*): $H_v = 2(k^2G)^{0.585} - 3)$ for polycrystalline materials. $H_v = 0.151$ G for bulk metallic glasses.









From: G.N. Greaves et al, NM 10, 823, 2011.

Summary

- The electronic structure, interatomic bonding, interband optical properties, elastic and mechanical properties of 20 MAX phases compounds are calculated by first-principles methods.
- Some of these properties are correlated with experimentally measured data quite well and appear to be able to explain most of their properties based on fundamental electronic structure.
- However, prediction of some properties such as hardness is nearly impossible. MAX phases are a diverse group of layered compounds with considerable variations in their electronic and bonding properties.
- $N(E_f)$ has an approximately linear correlation with electrical conductivity values (except Cr_2AlC and Ti_2InC). The local feature of total DOS density near E_f can be used to predict structural stability.
- Effective charge calculation shows that M atoms always lose charge to the X (C or N) atoms whereas A-group atoms mostly gain charge.
- Bond order values are obtained and analyzed for all types of interatomic bonds in all the 20 MAX phases.
- Calculated anisotropic optical conductivities used to predict the anisotropy of electrical conductivities.

Work in progress and/or contemplated (wish list?)

- Predict or correlate hardness and toughness for MAX phases.
- Study magnetic properties of some MAX phases containing the later TM elements (Cr_2AlC, Cr_2GeC, etc.)
- Extend the list of MAX phases studied (to 60 phases) and build a more complete data base for correlated study. (Materials Genome concept.)
- Explore other properties, thermo-conductivities, electric conductivities, defects, interfaces and corrosion resistance etc.
- Explore the temperature and pressure dependent properties.
- Explore formation of composites in optimizing its properties.
- Explore new unique applications beyond those already recognized.
- Collaborative teaming with others researchers, especially experimentalists.
- Computational simulation for failure behavior => beyond elastic theory and polycrystalline assumption used in the RVH approximation.
- …… much more.

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Thank you!