

First Principles Calculations of PtN and MAX phases

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Outline

- Experiment on PtN
- PtN calculations
- About MAX phases
- MAX phases - calculations
- Conclusions

Experimental synthesis of PtN

Experimental Synthesis and characterization of a binary noble metal nitride

E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Giquet, H-K. Mao, and R. J. Hemley, Nat. Mat. 3, 294 (2004).

Although numerous metals react with nitrogen there are no known binary nitrides of the noble metals. We report the discovery and characterization of platinum nitride (PtN), the first binary nitride of the noble metals group.

This compound can be formed above 45–50 GPa and temperatures exceeding 2,000 K, and is stable after quenching to room pressure and temperature.

It is characterized by a very high Raman-scattering cross-section with easily observed second and third-order Raman bands.

Synchrotron X-ray diffraction shows that the new phase is cubic with a remarkably high bulk modulus of $372(\pm 5)$ GPa.

Structure of experimental PtN

Data is taken from two samples once with N as the pressure medium and once with He as the pressure medium.

All patterns at different pressure are consistent (see Fig. 3) and PtN can be indexed as f.c.c. ($a = 4.8041(2) \text{ \AA}$ at 0.1 MPa) at all pressures.

Although the Rietveld refinement is complicated by the strong Pt signal, the refinement agrees with the non-centrosymmetric space group $F4-3m$, to which the zinc-blende structure belongs, as well as the rock-salt structure ($Fm3-m$); the large mass difference between Pt and N makes it impossible to distinguish between these two structures from the diffraction intensities.

The rock-salt structure does not have a first-order Raman spectrum and can therefore be ruled out. The zinc-blende structure has two Raman active peaks, consistent with the two strong first-order bands observed (see Fig. 1).

X-ray diffraction of PtN

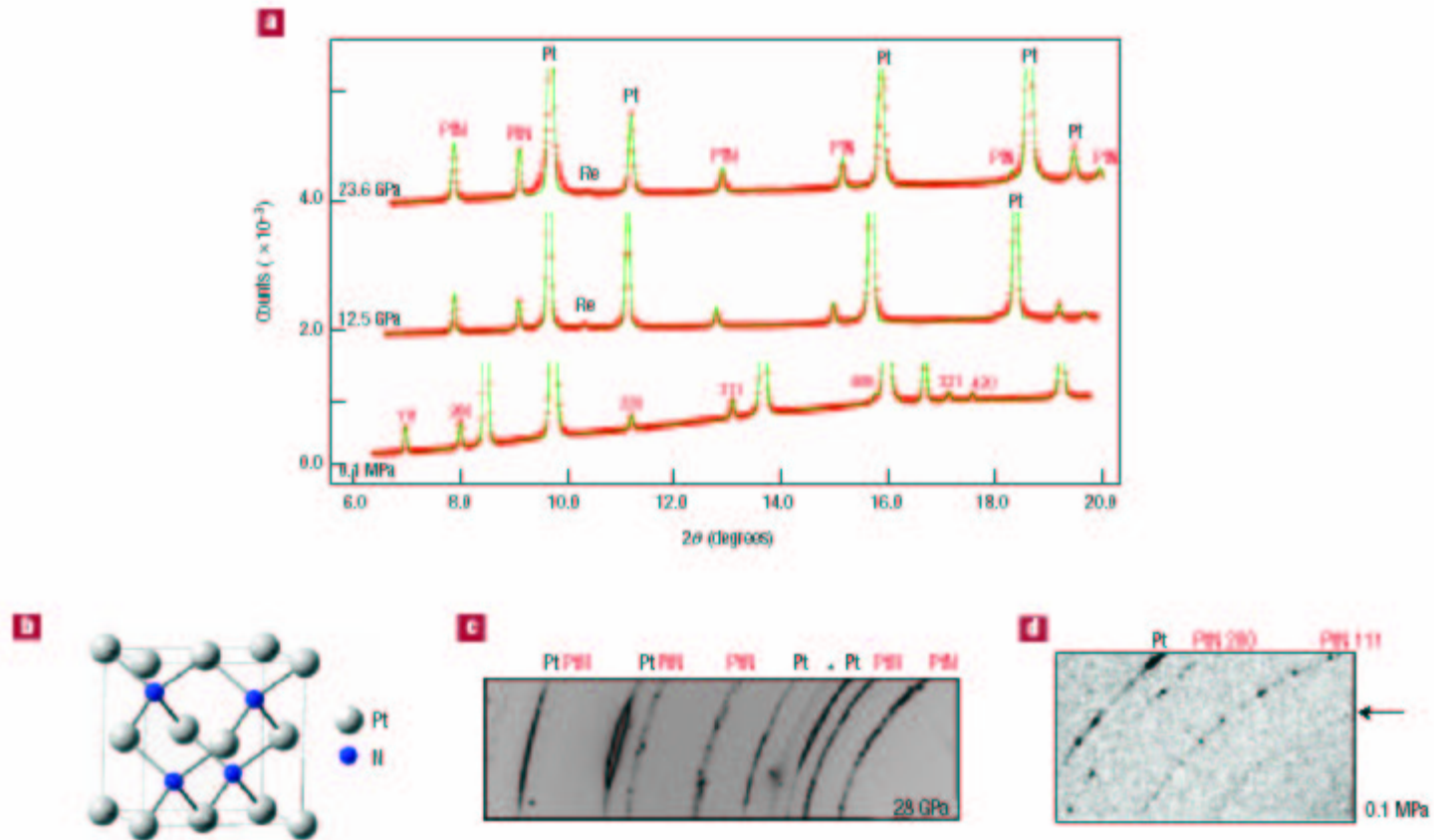


Figure 3 *In situ* X-ray diffraction data. **a**, X-ray spectra of PtN taken at different pressures. At ambient pressure the spectrum was taken with wavelength $\lambda = 0.3311 \text{ \AA}$ and others with $\lambda = 0.3738 \text{ \AA}$. Red crosses: data; green line: GSAS fit. **b**, Zinc-blende structure of PtN. **c**, Section of the CCD image at 28 GPa showing the powder-like texture; the asterisk indicates a rhenium diffraction ring. **d**, Detail of the inner section of the charged-coupled device image (shown in **c**) at ambient pressure with the arrow pointing at one of the two weak rings in addition to Pt and PtN signal.

PtN stoichiometry and back-scattered electron image

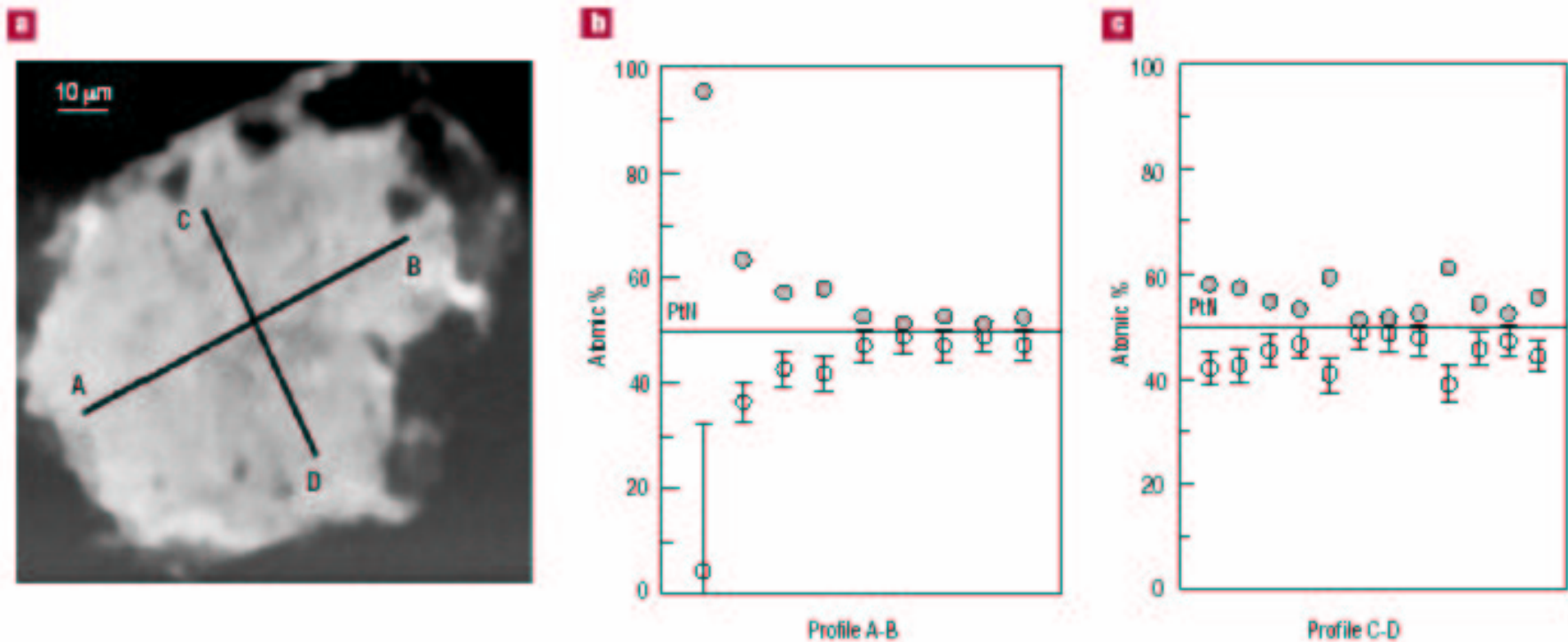
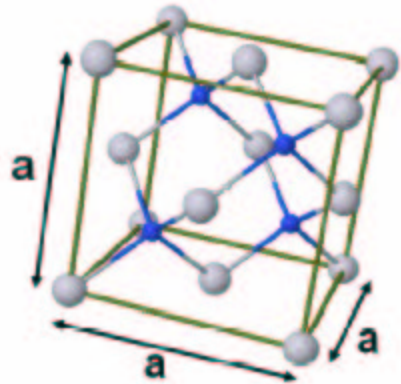


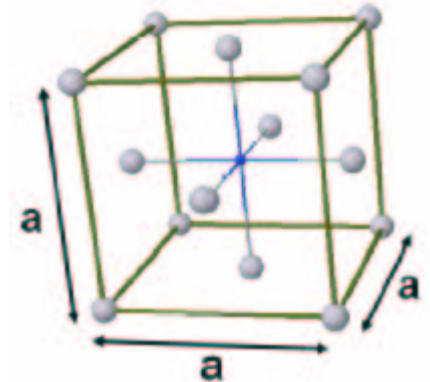
Figure 2 Chemical analysis of a reacted sample. **a**, Back-scattered electron image of an unloaded sample. **b, c**, Compositional profiles of the sample analysed by electron probe. Open circles: N content; closed circles: Pt content (the error bar on Pt is 0.55%).

Forms of PtN in our study

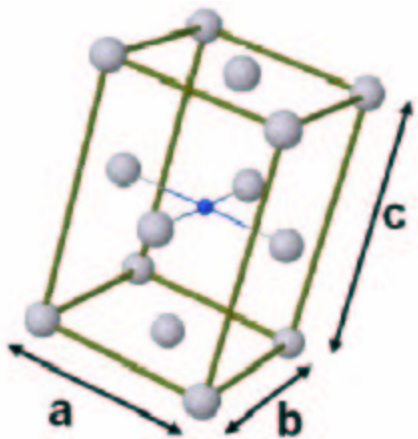


Zinc Blende

Rock Salt

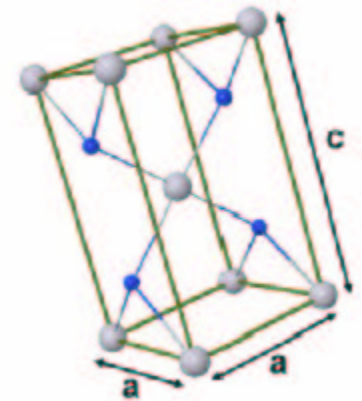


Pt:N ratio 1:1 in all forms



Face centered
Orthorhombic

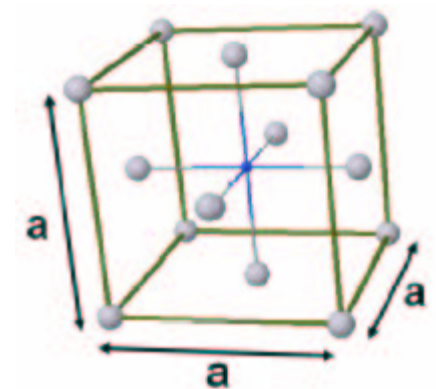
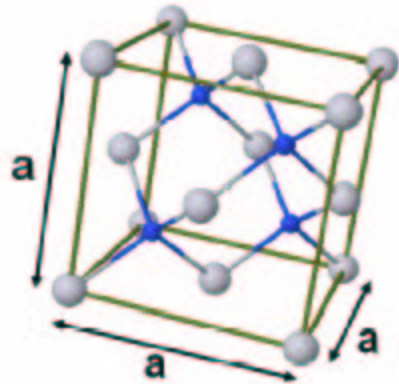
Cooperite
(PtS form)



***Ab initio* method details**

- LDA, Ceperley-Alder exchange-correlation functional as parameterized by Perdew and Zunger
- Used the VASP code with generalized ultra-soft Vanderbilt pseudo-potentials and plane wave basis set
- Bulk supercell approach with periodic boundary conditions in all three dimensions
- Cut-offs of 224 eV for PtN, 300 eV for MAX phases, dense k-point meshes
- Forces converged till < 0.03 eV/Å
- Used AMD Athlon dual processors at UT and OSC

Lattice constants for zb and rs forms of PtN



Theory with VASP

Zinc Blende

$a = 0.4699 \text{ nm}$ (LDA)
 0.4781 nm (GGA)
 $B = 230 \text{ GPa}$ (LDA)
 192 GPa (GGA)

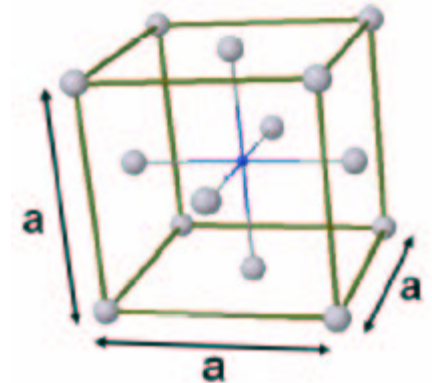
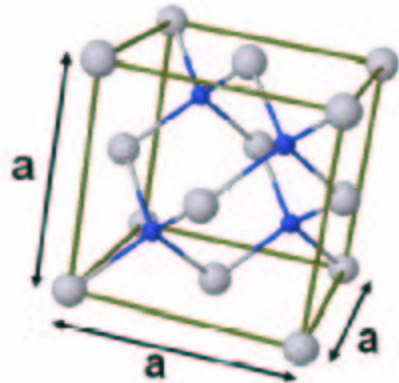
Rock Salt

$a = 0.4407 \text{ nm}$ (LDA)
 0.4504 nm (GGA)
 $B = 284 \text{ GPa}$ (LDA)
 226 GPa (GGA)

Experiment, Gregoryanz et al. Nat. Mat. 3, 294 (2004)

$a = 0.4801 \text{ nm}$
 $B = 372 \text{ GPa}$

No effect of N vacancies on bulk modulus of PtN



Theory with VASP

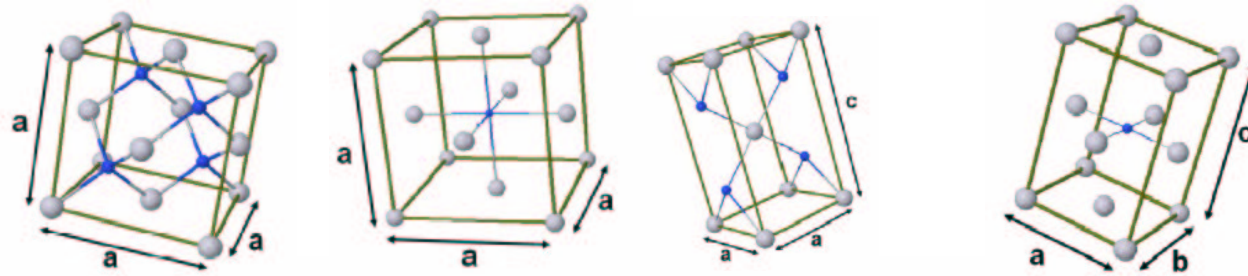
Zinc Blende

Rock Salt

No significant change in bulk modulus was found by introducing vacancies. We used $\text{Pt}_1\text{N}_{1-x}$, where $x = 0, 0.037, \text{ and } 0.125$. Use $2 \times 2 \times 2$ or $3 \times 3 \times 3$ fcc supercells.

In experiment, of Gregoryanz et al. Nat. Mat. 3, 294 (2004)

$$0 < x < 0.05.$$



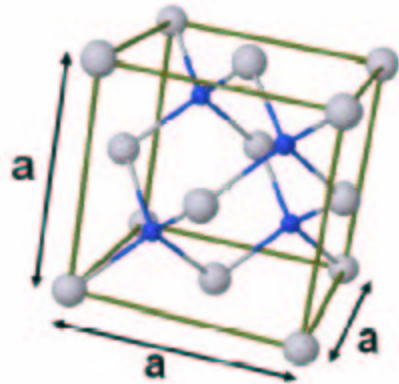
Elastic constants in GPa and stability

C_{ij} (in GPa)	Zinc blende	Rocksalt	Cooperite	Face centered orthorhombic
C_{11}	210	355	unstable	570
C_{22}	C_{11}	C_{11}	C_{11}	254
C_{33}	C_{11}	C_{11}	unstable	258
C_{44}	14	36	unstable	unstable
C_{55}	C_{44}	C_{44}	C_{44}	98
C_{66}	C_{44}	C_{44}	unstable	98
C_{12}	241	248	unstable	240
C_{13}	C_{12}	C_{12}	unstable	240
C_{23}	C_{12}	C_{12}	C_{13}	194

If $C_{11} - C_{12} < 0 \implies$
**unstable form. Also, any $C_{ij} < 0 \implies$
 unstable form. Also other conditions.**

Only stable form = rock salt.

Earlier theoretical work on PtN

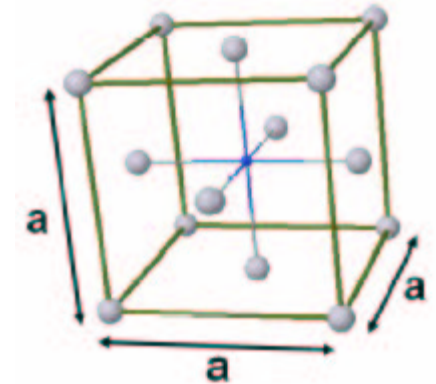


Theory with WIEN2K, Sahu et al., PRB 71, R041101 (2005).

Zinc Blende

$a = 0.4804 \text{ nm}$ (GGA)

$B = 371 \text{ GPa}$ (GGA)



Rock Salt

$a = 0.4518 \text{ nm}$ (GGA)

431 GPa (GGA)

Experiment, Gregoryanz et al. Nat. Mat. 3, 294 (2004)

$a = 0.4801 \text{ nm}$

$B = 372 \text{ GPa}$

Theory matches perfectly with experiment!

Our manuscript would have read like this

We have done first principles calculations for the newly reported noble metal nitride PtN.

Our calculations **contradict experimental findings** published in Nature Materials by a well known group.

Our calculations also **contradict theoretical findings** by another well known theoretical group published in PRB Rap. Comms.

We **think we are right**. Please accept this manuscript for publication.

More of earlier theoretical results for PtN

Lattice Structure	Present work				Ref. [9]		Ref. [8]
	LDA		GGA		LDA	GGA	GGA
	VASP	WIEN2K	VASP	WIEN2K	WIEN2K	WIEN2K	WIEN2K
zb-PtN							
Bulk modulus (GPa)	230	235	192	178	244	194	371
Lattice constant (nm)	0.4699	0.4683	0.4794	0.4781	0.4692	0.4780	0.4804
E_{r-r-t} (eV)	0.42						
rs-PtN							
Bulk modulus (GPa)	284	298	226	233	-	-	431
Lattice constant (nm)	0.4407	0.4397	0.4504	0.4496	-	-	0.4518
E_{r-r-t} (eV)	0.75						

Experiment, Gregoryanz et al. Nat. Mat. 3, 294 (2004)

$a = 0.4801\text{nm}$ and $B = 372\text{ GPa}$

[8] B. R. Sahu and L. Kleinman, Phys. Rev. B **71**, R041101 (2005).

[9] R. Yu and X. F. Zhang, Appl. Phys. Lett. **86**, 121913 (2005).

Summary of theoretical results for PtN

Lattice Structure	Present work				Ref. [9]		Ref. [8]
	LDA		GGA		LDA	GGA	GGA
	VASP	WIEN2K	VASP	WIEN2K	WIEN2K	WIEN2K	WIEN2K
zb-PtN							
Bulk modulus (GPa)	230	235	192	178	244	194	371
Lattice constant (nm)	0.4699	0.4683	0.4794	0.4781	0.4692	0.4780	0.4804
E_{f-r-t} (eV)	0.42						
rs-PtN							
Bulk modulus (GPa)	284	298	226	233	-	-	431
Lattice constant (nm)	0.4407	0.4397	0.4504	0.4496	-	-	0.4518
E_{f-r-t} (eV)	0.75						
fco-PtN							
Bulk modulus (GPa)	270						
Lattice Constants (nm)	a = 0.3972 b = 0.3977 c = 0.6022						
E_{f-r-t} (eV)	0.17						
co-PtN							
Bulk modulus (GPa)	-						
Lattice Constants (nm)	a = 0.3323 b = a c = 0.4579						
E_{f-r-t} (eV)	0						

Some evolution of the other theory

We made a mistake of a factor of 2 in the unit cell volume while calculating the bulk modulus for the zinc-blende and rocksalt structures of PtN. As a result the bulk modulus values are now half the values quoted in Table 1. The corrections in the bulk moduli, while not affecting any of the other results in the paper, invalidate the conclusion that PtN exists in the zinc-blende structure. This is made more certain by the calculations of two groups^{1,2} who find the zinc-blende structure to be unstable. Furthermore, it is now believed by those who synthesized platinum nitride³ that is more likely to be PtN₂ and not PtN. We thank Sanjay Khare and Chang-zeng Fan for suggesting to us that we had miscalculated the bulk modulus.

¹R. Yu and X. F. Zhang, Appl. Phys. Lett. 86, 121913 (2005).

²S. K. R. Patil, S. V. Khare, B. R. Tuttle, J. K. Bording, and S. Kodambaka (unpublished).

³Eugene Gregoryanz (private communication).




Erratum by B. R. Sahu et al., PRB 72, 119901 (E) (2005).

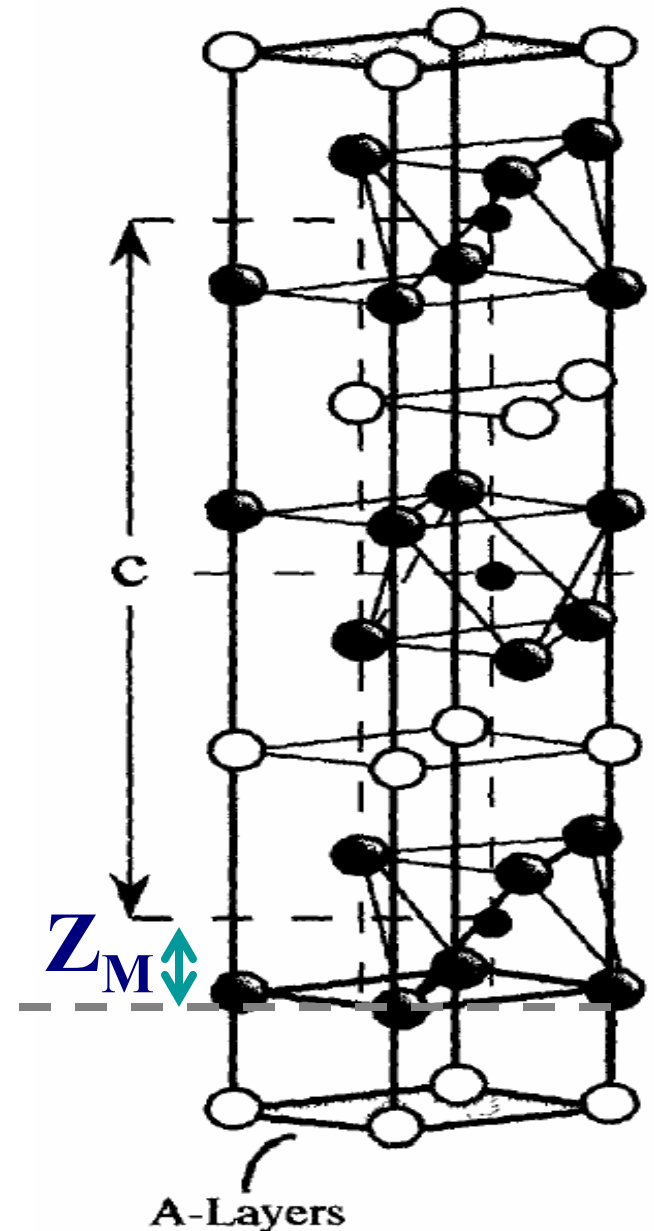
Conclusions of work on PtN

1. Zinc blende structure for PtN as claimed in experiment and an earlier theory is incorrect
2. There exists a stable form of PtN the rock salt phase. It is not superhard. Has $B < 300$ GPa. Its lattice constant is around 0.44 nm.
3. The experimental form of PtN remains unknown.
4. Published theory and experiment can match each other and **both be self-consistently wrong!**

What are MAX Phases?

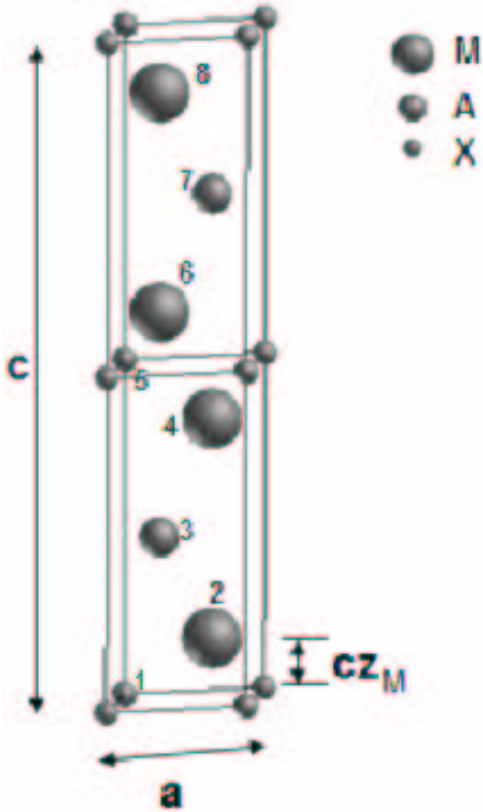


- M = transition metal = 
- A = A-group element = 
- X = C or N = 
- Electrically and thermally conductive materials
- Relatively soft
- Resistant to Thermal Shock
- Damage Tolerant
- Z_M is the internal degree of freedom



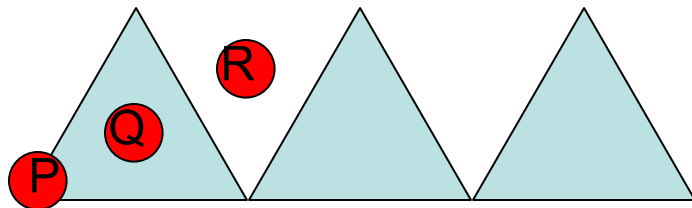
HEXAGONAL MAX 211 PHASE

Atoms in unit cell



Atom Type	Atom Number	Position Vector
X	1	0
M	2	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + z_M\mathbf{a}_3$
A	3	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + c_2\mathbf{a}_3$
M	4	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + (2c_2 - z_M)\mathbf{a}_3$
X	5	$2c_2\mathbf{a}_3$
M	6	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + (2c_2 + z_M)\mathbf{a}_3$
A	7	$c_1(\mathbf{a}_1 + 2\mathbf{a}_2) + 3c_2\mathbf{a}_3$
M	8	$c_1(2\mathbf{a}_1 + \mathbf{a}_2) + (1 - z_M)\mathbf{a}_3$

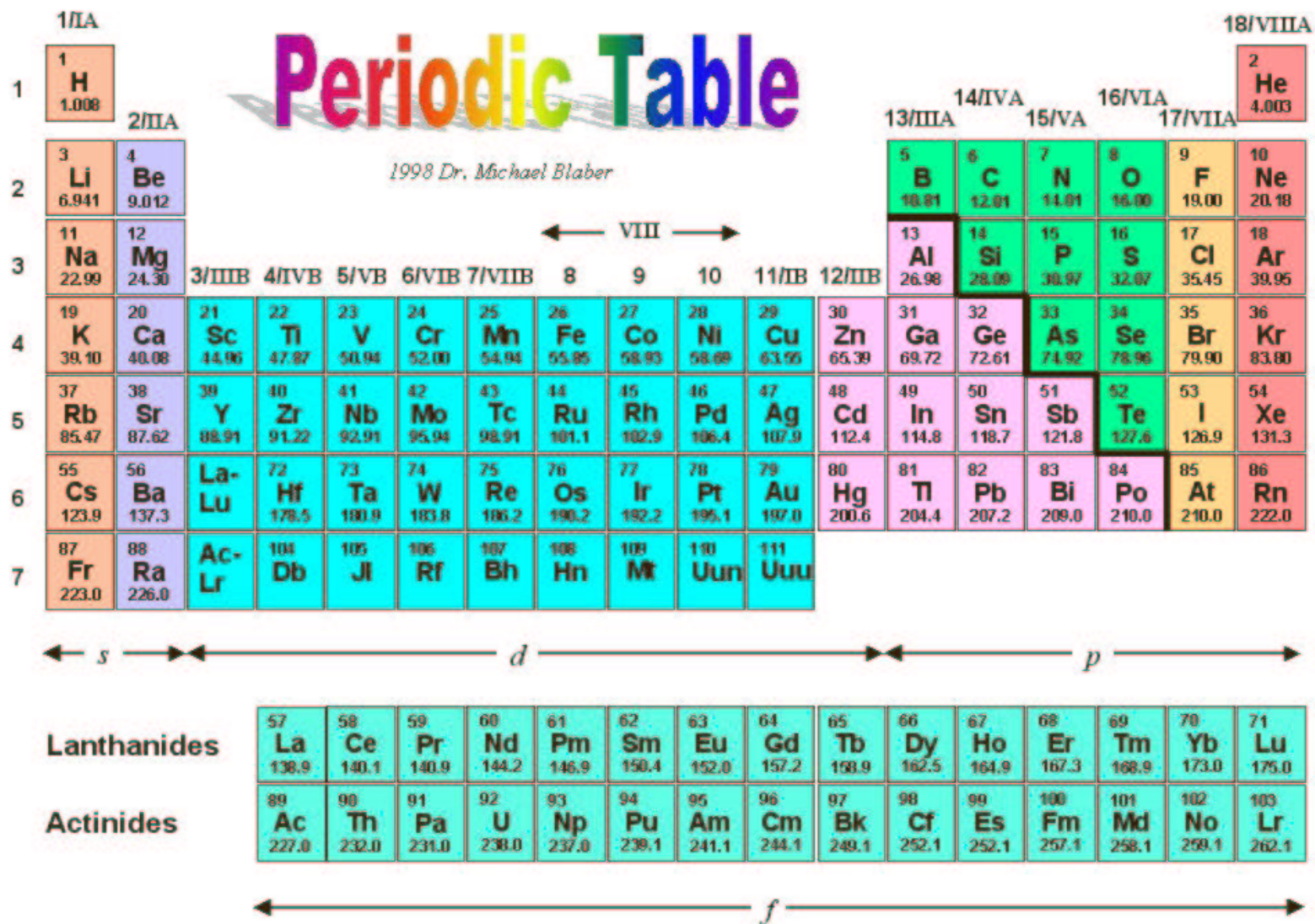
Table I. The table lists the 8 atom basis for a unit cell of M_2AX phase^{7,8,9} with $M = \text{Ti, Cr, or V}$. $X = \text{N}$ and $A = \text{Ga}$. The lattice vectors of this hexagonal unit cell with lattice constants a and c are: $\mathbf{a}_1 = 2c_2a(1, -c_3, 0)$, $\mathbf{a}_2 = 2c_2a(1, c_3, 0)$, and $\mathbf{a}_3 = c(0, 0, 1)$. The constants are $c_1 \equiv \frac{1}{3}$, $c_2 \equiv \frac{1}{4}$, and $c_3 \equiv \frac{1}{\sqrt{c_1}}$. The constant “ z_M ” corresponding to the internal degree of freedom is given in Table II for each phase. The atoms corresponding to the numbers given in the table are shown in Fig. 1.



P Q R are three sites in hcp packing.



Motivation for M_2TIC based compounds $M = Ti, Zr, Hf$



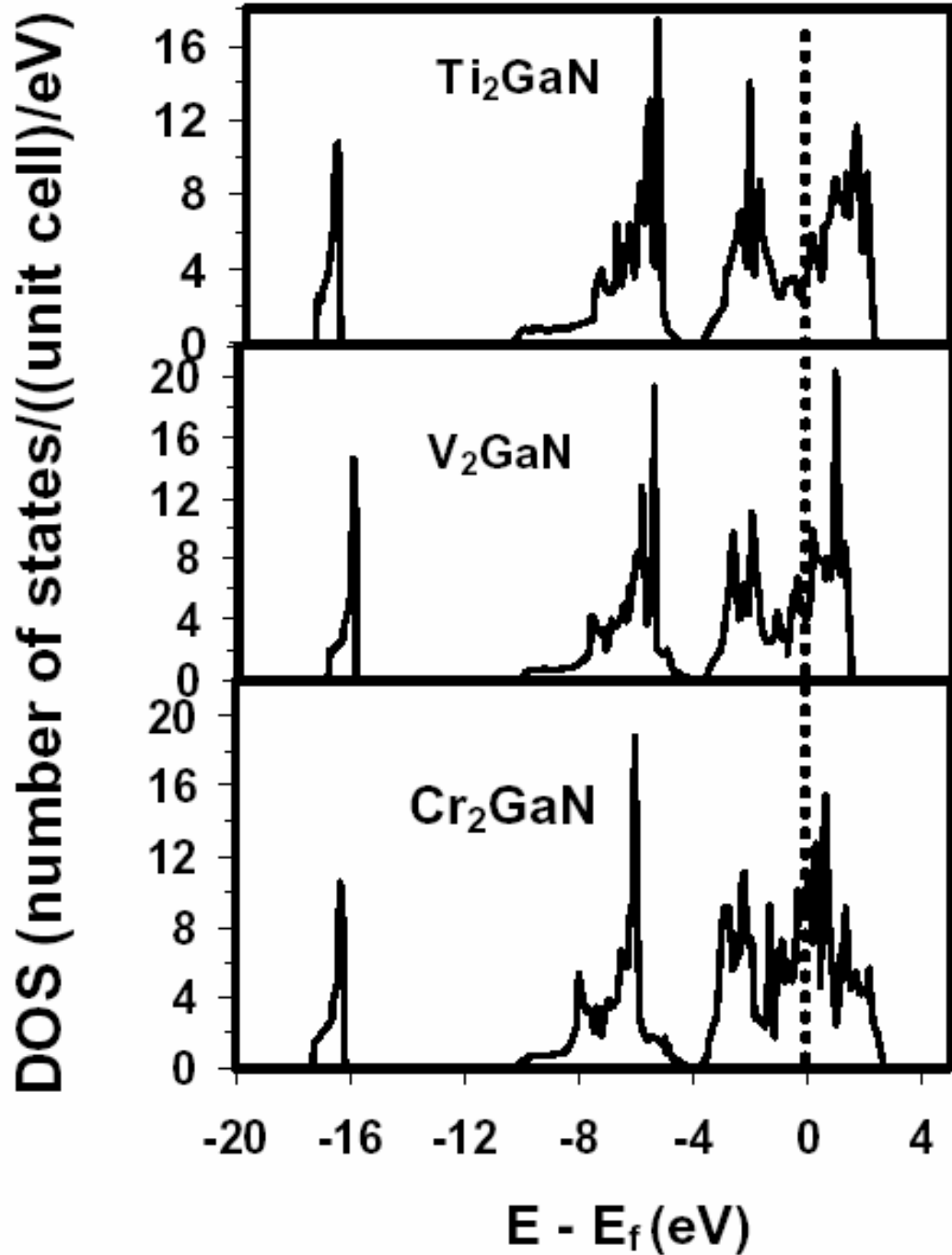
Barsoum's Table

IIB	IIIA	IVA	VA	VIA
	Al Ti₂AlC, 4.11 (3.04,13.60) V₂AlC, 4.07 (3.1,13.83) Cr₂AlC, 5.24 (2.86,12.8) Nb₂AlC, 6.50 (3.10,13.8) Ta₂AlC, 11.82 (3.07,13.8) Ti₂AlN, 4.31 (2.989,13.614) Ti₃AlC₂, 4.5 (3.075,18.578) Ti₄AlN₃, 4.76 (2.988, 23.372)	Si Ti₃SiC₂ 4.52 (3.0665,17.671)	P V₂PC 5.38 (3.077,10.91) Nb₂PC 7.09 (3.28,11.5)	S Ti₂SC, 4.62 (3.216,11.22) Zr₂SC, 6.20 (3.40, 12.13) Nb₂SC_{0.4} (3.27,11.4) Hf₂SC, (3.36, 11.99)
Zn	Ga Ti₂GaC, 5.53 (3.07, 13.52) V₂GaC, 6.39 (2.93, 12.84) Cr₂GaC, 6.81 (2.88, 12.61) Nb₂GaC, 7.73 (3.13, 13.56) Mo₂GaC, 8.79 (3.01, 13.18) Ta₂GaC, 13.05 (3.10, 13.57) Ti₂GaN, 5.75 (3.00, 13.3) Cr₂GaN, 6.82 (2.875, 12.77) V₂GaN, 5.94 (3.00, 13.3)	Ge Ti₂GeC, 5.68 (3.07, 12.93) V₂GeC, 6.49 (3.00, 12.25) Cr₂GeC, 6.88 (2.95, 12.08) Ti₃GeC₂, 5.55 (3.07, 17.76)	As V₂AsC 6.63 (3.11, 11.3) Nb₂AsC 8.025 (3.31, 11.9)	Se
Cd	In Sc₂InC Ti₂InC, 6.2 (3.13, 14.06) Zr₂InC, 7.1 (3.34, 14.91) Nb₂InC, 8.3 (3.17,14.37) Hf₂InC, 11.57 (3.30,14.73) Ti₂InN, 6.54 (3.07,13.97) Zr₂InN, 7.53 (3.27,14.83)	Sn Ti₂SnC, 6.36 (3.163,13.679) Zr₂SnC, 7.16 (3.3576, 14.57) Nb₂SnC, 8.4 (3.241,13.802) Hf₂SnC, 11.8 (3.320,14.388) Hf₂SnN, 7.72 (3.31,14.3)	Sb	Te
	Tl Ti₂TlC, 8.63 (3.15,13.98) Zr₂TlC, 9.17 (3.36,14.78) Hf₂TlC, 13.65 (3.32,14.62) Zr₂TlN, 9.60 (3.3,14.71)	Pb Ti₂PbC, 8.55 (3.20,13.81) Zr₂PbC, 9.2 3.38,14.66 Hf₂PbC, 12.13 (3.55,14.46)	Bi	

*M.W. Barsoum, Prog. Sol. Stat. Chem. 28 (2000) 201.

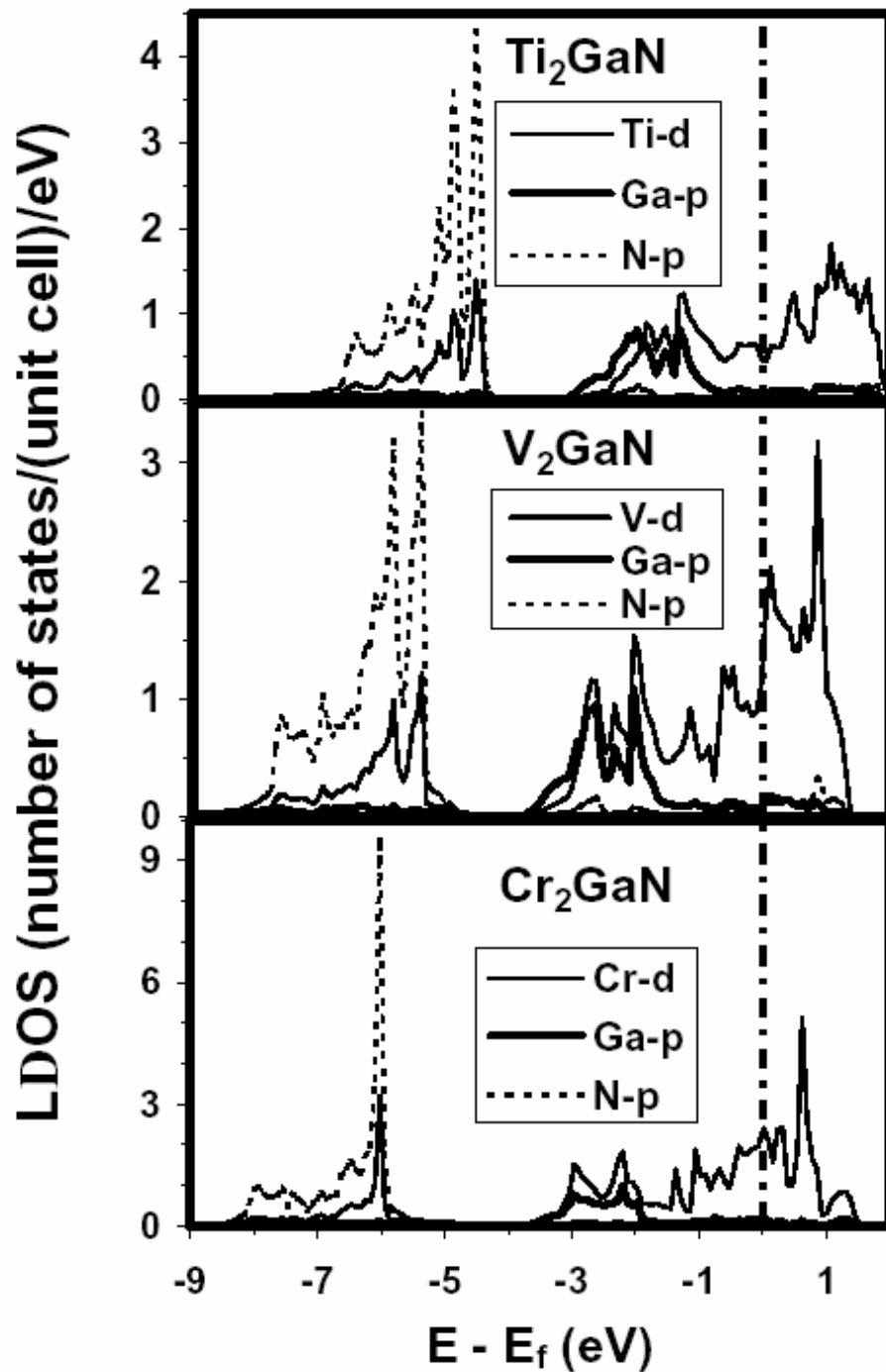
Lattice constants and B for $M_2\text{GaN}$, $M = \text{Ti, V, Cr}$

<u>Property</u>	<u>Ti₂GaN</u>		<u>V₂GaN</u>		<u>Cr₂GaN</u>	
	Theory	Expt. ^{1,5}	Theory	Expt. ^{1,20}	Theory	Expt. ^{1,6}
a (Å)	3.02	3.00	2.91	3.00	2.91	2.88
c (Å)	13.28	13.30	12.82	13.30	12.26	12.77
z_M (Å)	0.0869		0.0861			0.0860
c/a	4.40	4.42	4.41	4.42	4.22	4.43
$V = \left(\frac{\sqrt{3}}{2}\right)a^2c$ (Å ³)	104.59	103.35	93.91	103.35	89.72	91.65
B (GPa)	158		170		180	

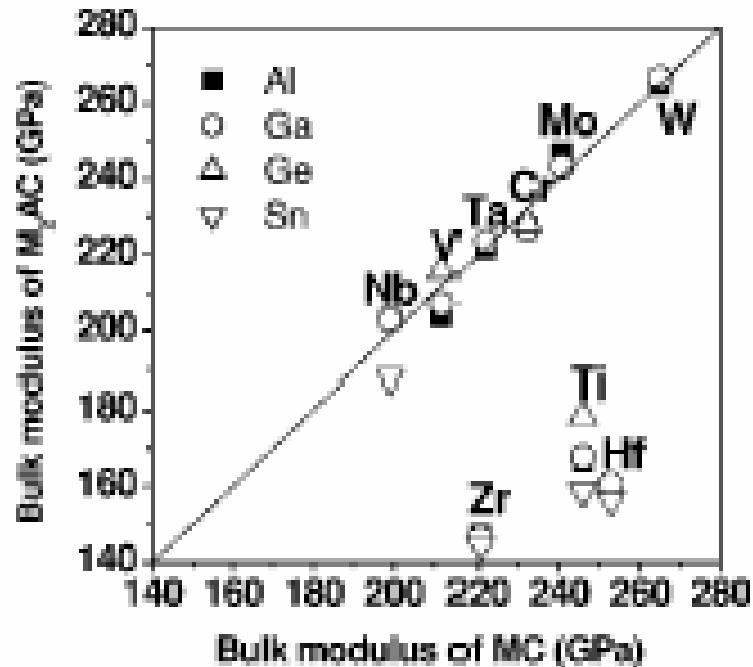


**DOS Results for
 M_2GaN ,
 $\text{M} = \text{Ti, V, Cr}$**

LDOS Results for $M_2\text{GaN}$, $M = \text{Ti, V, Cr}$



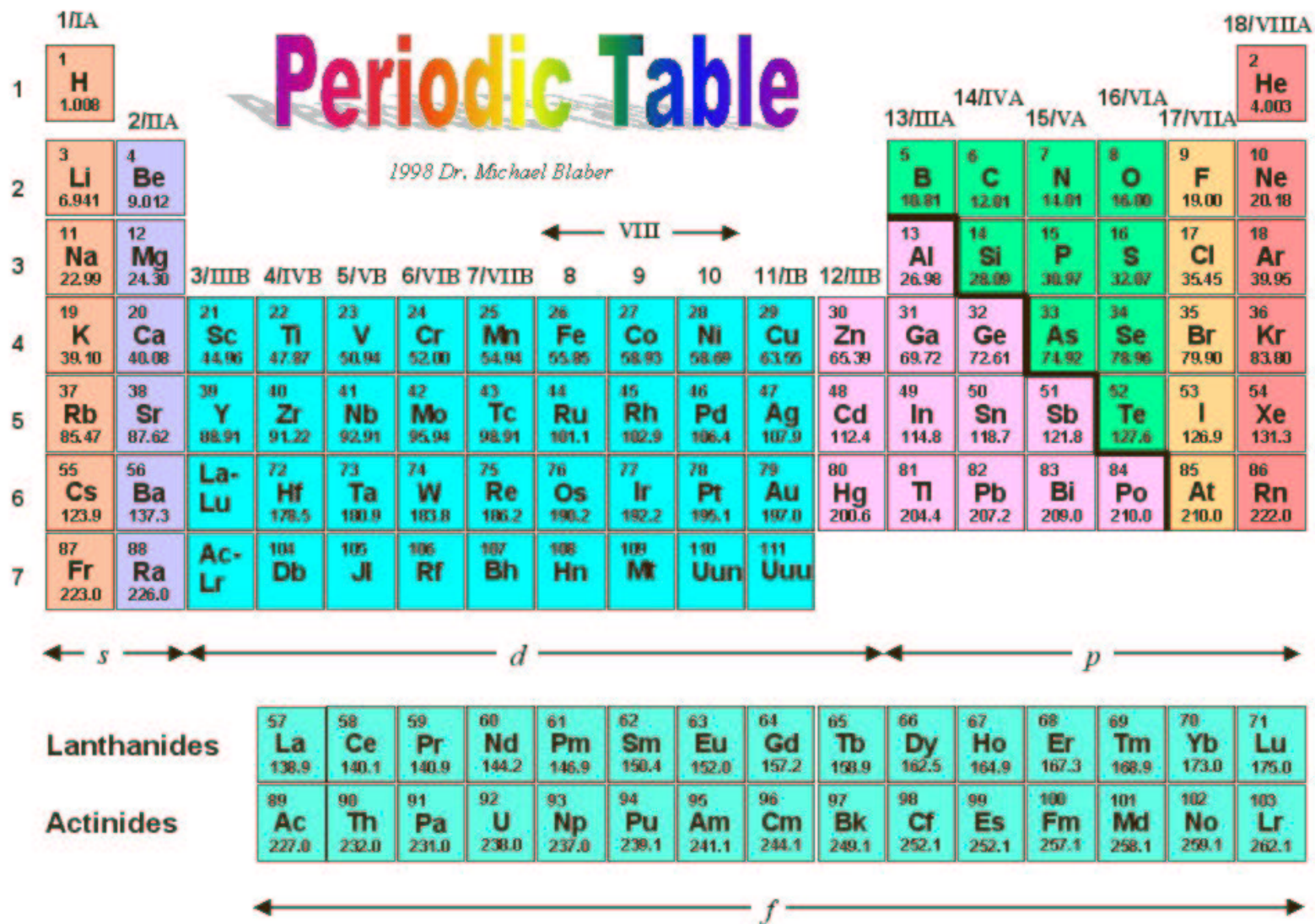
Motivation for M_2TIC based compounds $M =$ Ti, Zr, Hf



From Sun et al.,
PRB 70, 92102 (2004).

FIG. 1. The bulk moduli of M_2AC versus the bulk moduli of the corresponding MC , where M is a transition metal from group IVB, VB, and VIB, A is a IIIA and a IVA group element. Clearly, M_2AC phases can be classified into two groups: One inheriting the bulk modulus of the corresponding MC and the other with larger deviations.

Motivation for M_2TIC based compounds $M = Ti, Zr, Hf$

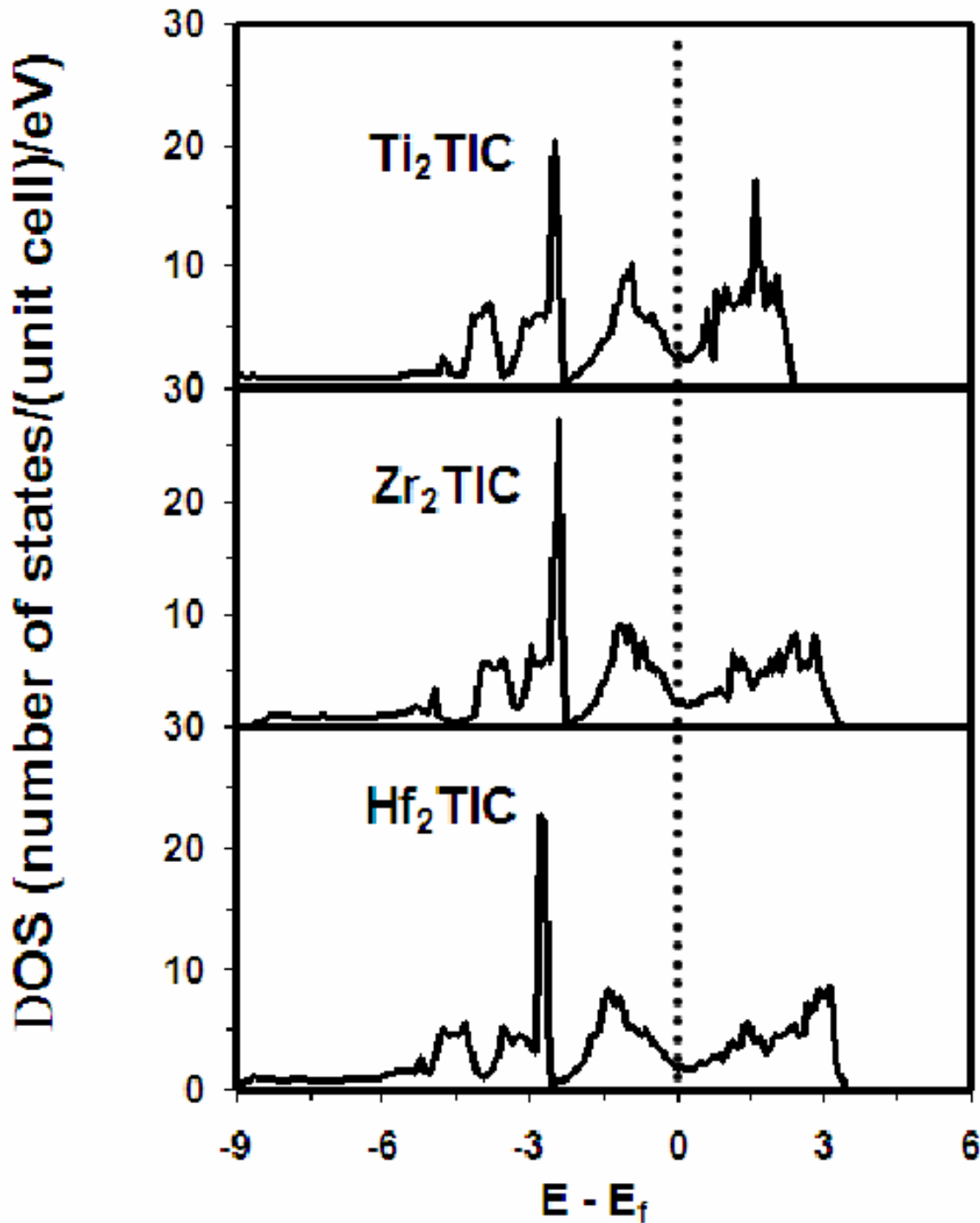


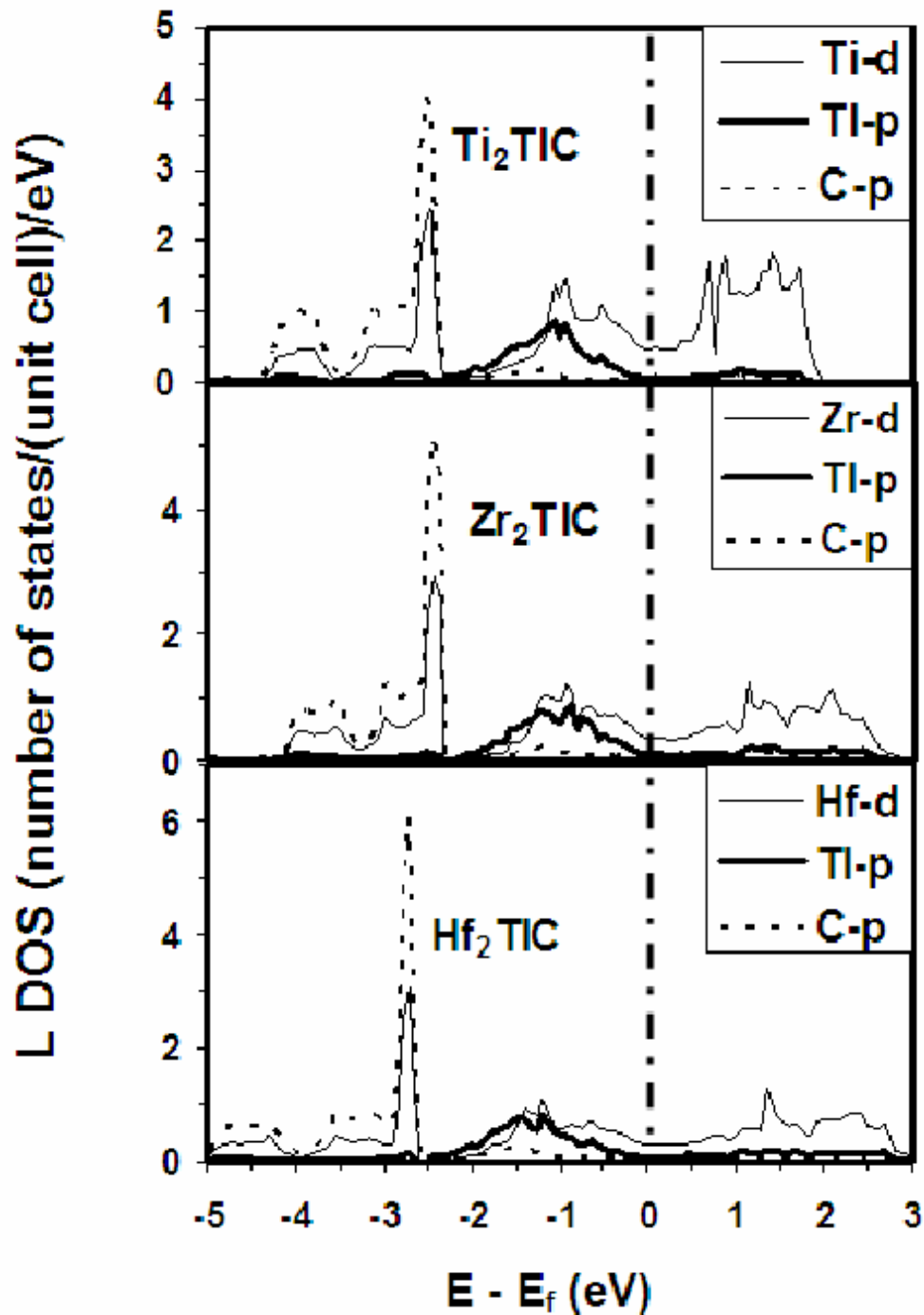
Lattice constants and B for M₂TiC, M = Ti, Hf, Zr

Property	Ti ₂ TiC		Zr ₂ TiC		Hf ₂ TiC	
	Theory	Expt. ^{1, 23}	Theory	Expt. ^{1, 24}	Theory	Expt. ^{1, 24}
a (Å)	3.18	3.15	3.38	3.36	3.34	3.32
c (Å)	14.16	13.98	14.99	14.78	14.78	14.62
z _M (Å)	0.0777		0.0817		0.0811	
c/a	4.45	4.42	4.43	4.40	4.42	4.40
$V = \left(\frac{\sqrt{3}}{2}\right)a^2c$	124.36	119.64	148.57	144.54	142.88	139.44
B (GPa)	125		120		131	

B values lowest of all MAX phases studied so far.

**DOS Results for
 M_2TIC ,
 $M = Ti, Zr, Hf$**





**LDOS Results
for $M_2\text{TIC}$,
 $M = \text{Ti, Zr, Hf}$**

Conclusions of work on MAX phases

1. Calculated lattice constants and bulk moduli of Ti_2GaN , V_2GaN , and Cr_2GaN .
2. Calculated lattice constants and bulk moduli of Ti_2TiC , Zr_2TiC , and Hf_2TiC .
3. Calculated LDOS and DOS of Ti_2GaN , V_2GaN , and Cr_2GaN .
4. Calculated LDOS and DOS of Ti_2TiC , Zr_2TiC , and Hf_2TiC .
5. All six MAX phases are conducting. The M-A bonds are weaker than the M-X bonds.
6. Ti_2TiC , Zr_2TiC , and Hf_2TiC have the lowest bulk moduli of all MAX phases studied to date.

Collaborators

Senior

J. K. Bording (Brookhaven National Laboratory)

S. Kodambaka (T. J. Watson Research Center, IBM)

B. R. Tuttle (Penn. State. Erie Campus)

Students

S. K. R. Patil (Mechanical and Industrial Engineering, U. of Toledo)

J. A. Warner (REU at U. of Toledo 2005, U. of Wisconsin)

Institutional Support

University of Toledo URAF Summer Fellowship

Start up money University of Toledo

University of Toledo parallel computing cluster

Ohio Supercomputer cluster

NSF REU program at University of Toledo

Thank you!

Raman spectra

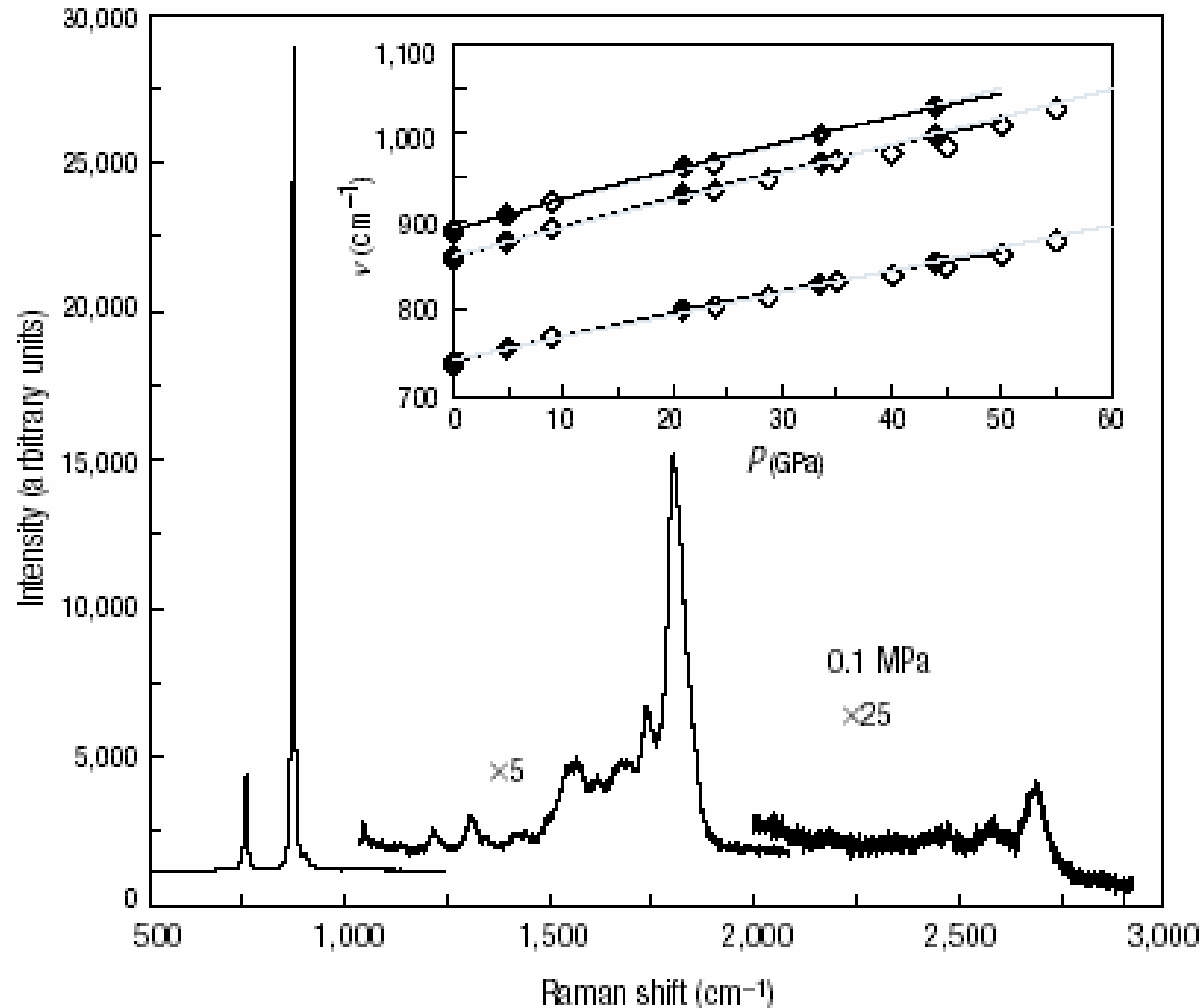


Figure 1 Representative Raman spectra (with second and third order peaks) of PtN. Measurements were done at 0.1 MPa and 300 K after quenching from 55 GPa. Inset: Pressure shifts of the first-order Raman bands of PtN. Open and filled diamonds represent different experimental runs. Solid lines are guides to the eye only.

Abstract

We will show results from ab initio calculations of bulk phases of two types of ceramics. The first part of the presentation will be about results of our computations of the structural and elastic properties of some phases of PtN. Important consequences for the recently produced PtN phase [1] will be described. The second part, will focus on properties of six MAX phases [2]. These are ternary layered compounds where X = C or N, A is an A group element, M is an early transition metal. We will show results for six of these phases $M_{\{2\}}\text{GaN}$, where M = Ti, V and Cr and $M_{\{2\}}\text{TIC}$, where M = Ti, Zr, Hf. [1] E. Gregoryanz et al., Nat. Mat. 3, 294 (2004). [2] M. W. Barsoum, Prog. Sol. Star. Chem. 28, 201 (2000).