DMREF/Collaborative Research: Nitride Discovery - Creating the Knowledge Base for Hard Coating

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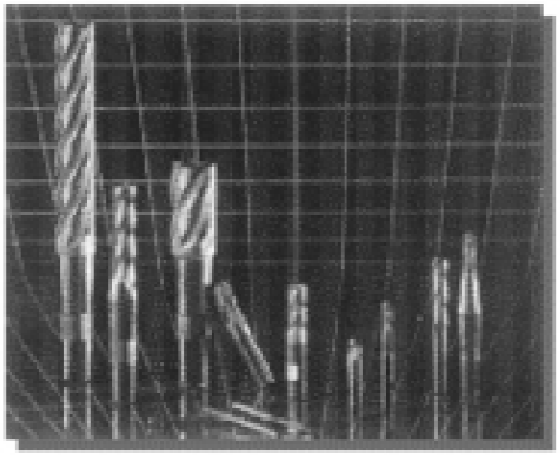
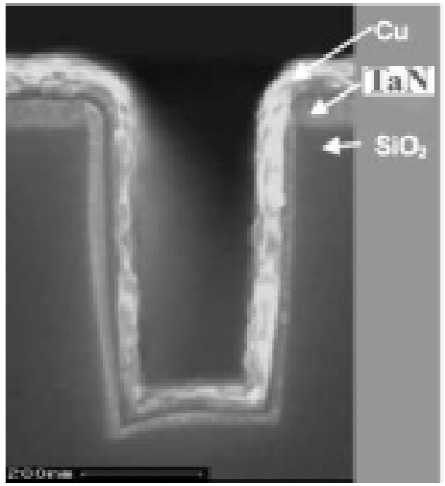
Outline

- Transition metal nitrides (TMNs)
- Coatings By Design Approach
- Experimental approaches
- Theoretical Approaches
- *Ab initio* method
- Results for Cubic structures – zincblende, rocksalt, CsCl, NbO
- Structural, mechanical and electronic properties
  - Lattice constants and bulk modulus (B)
  - Elastic constants, C_{11}, C_{12}, C_{44}
  - Ductility indicators
  - Vicker's hardness (H_V)
  - Correlation of H_V with θ_D
  - Correlation of H_V with TDOS
  - LDOS
  - Bader analysis
- Conclusion
- Future

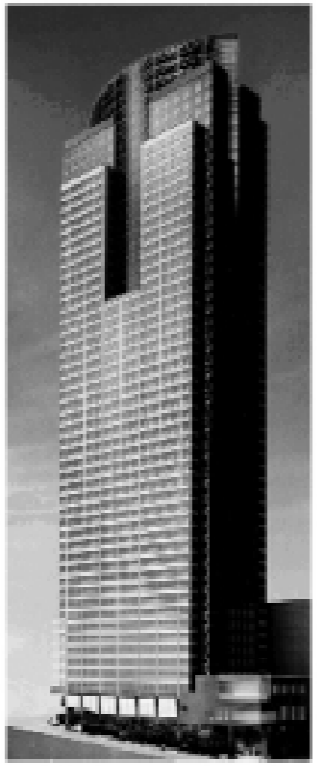
Transition-metal nitrides: applications



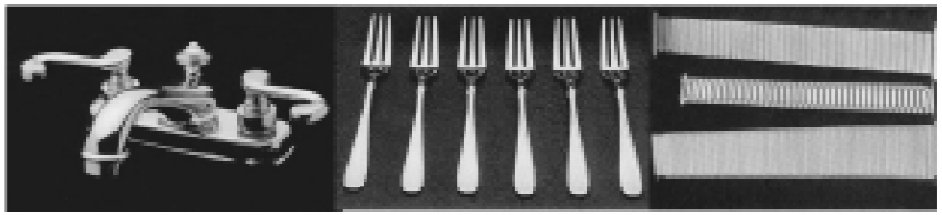
Hard wear-resistant coatings
(TiN, ZrN, CrN, TaN)



Diffusion barriers
(TiN, TaN)



Optical coatings
(TiN, ZrN)



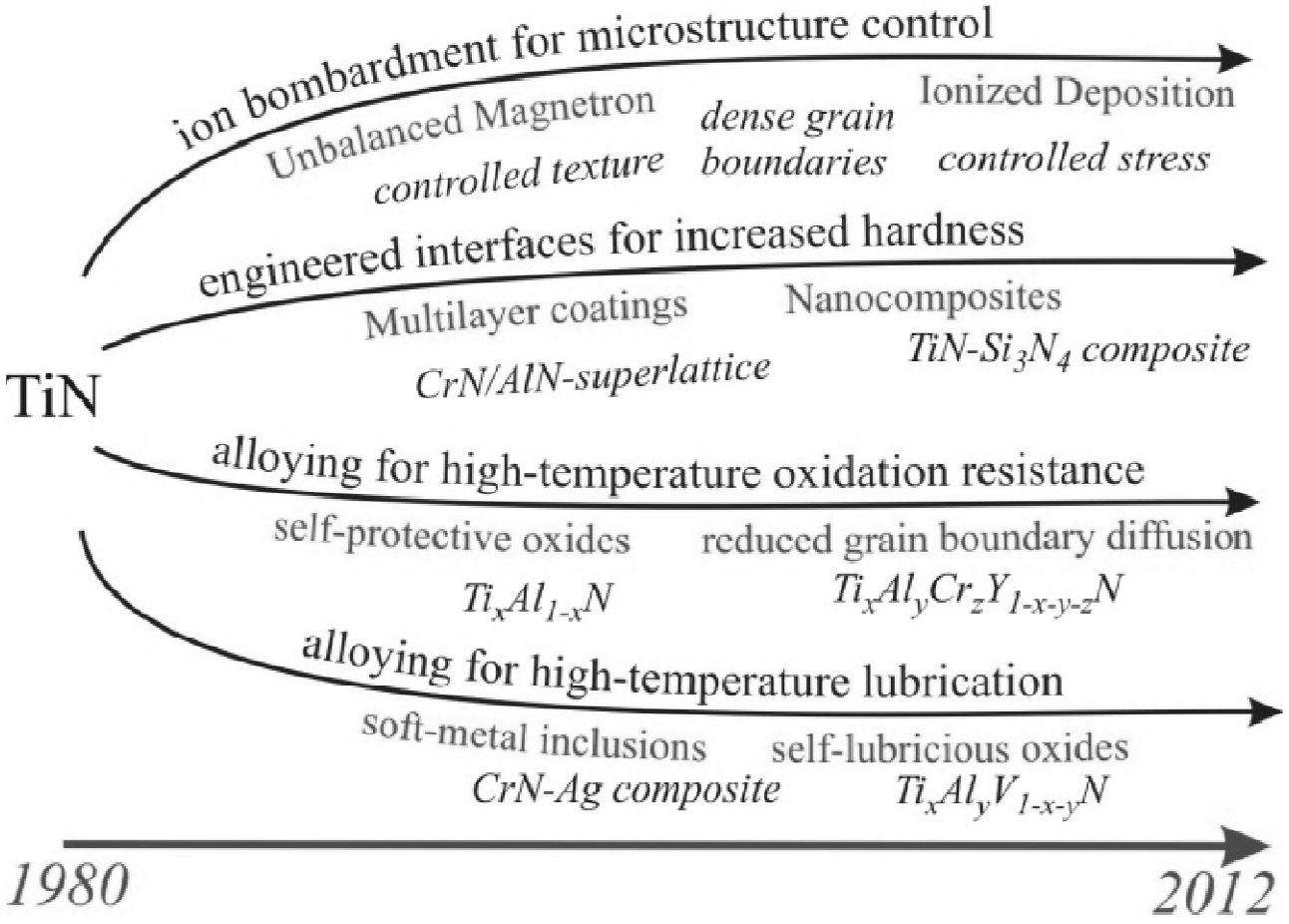
Decorative coatings (TiN, ZrN)

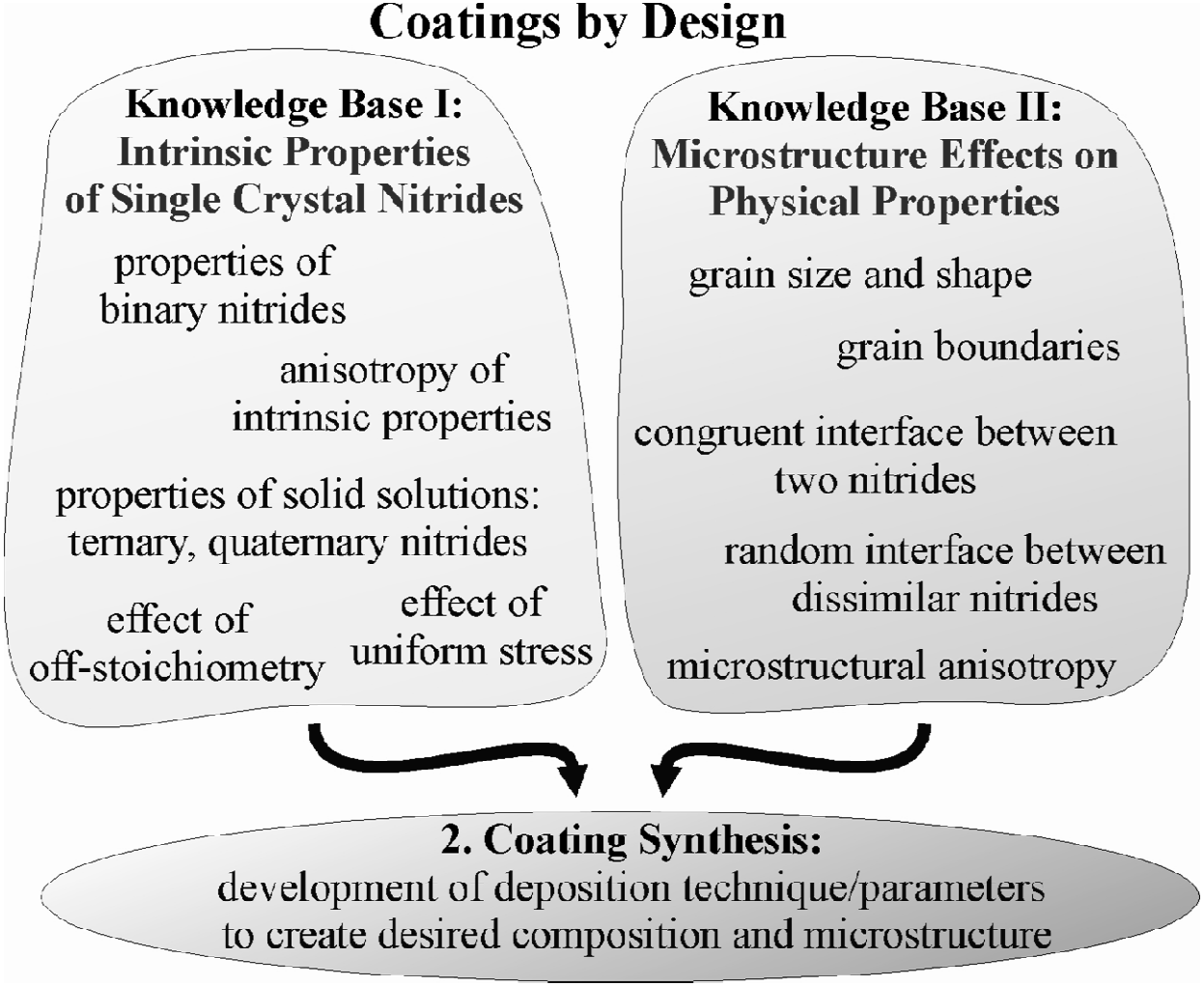

Buy Now & Save!
3 PC.
LOT NO. 91616/8873
TITANIUM NITRIDE COATED
M2 HIGH SPEED STEEL
STEP DRILLS
Includes (A) 3/16" to 1/2" six step bit, (B) 1/4" to 3/4" nine step bit and (C) 1/8" to 1/2" thirteen step bit.
DRILL MASTER
A
B
C
$14.99
Item 8873 shown
REGULAR PRICE $29.99
SAVE 50%

Transition Metal Nitrides (TMNs)

- Refractory hard materials
- Extremely high hardness – wear resistance
- High melting points – thermal resistance
- Good electrical and thermal conductivity
- Good corrosion resistance

Evolutionary Development of Nitride Hard Coatings




Coatings by Design
Knowledge Base I:
Intrinsic Properties
of Single Crystal Nitrides
properties of
binary nitrides
anisotropy of
intrinsic properties
properties of solid solutions:
ternary, quaternary nitrides
effect of
off-stoichiometry
effect of
uniform stress
Knowledge Base II:
Microstructure Effects on
Physical Properties
grain size and shape
grain boundaries
congruent interface between
two nitrides
random interface between
dissimilar nitrides
microstructural anisotropy
2. Coating Synthesis:
development of deposition technique/parameters
to create desired composition and microstructure

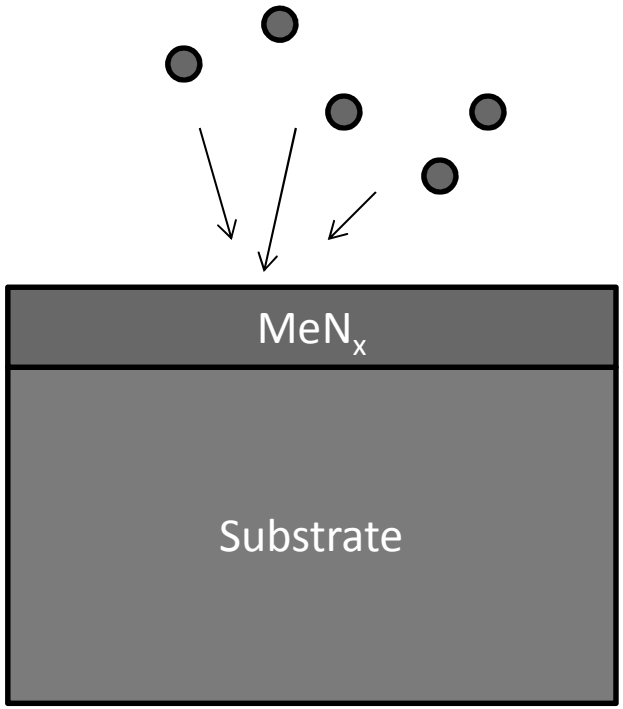
Knowledge Base II

Microstructure Effects on Physical Properties

Experimental work of Prof. Daniel Gall at RPI

Experimental Approach

Brian Ozsdolay and Daniel Gall
Rensselaer Polytechnic Institute



Epitaxial layer deposition
by reactive magnetron sputtering

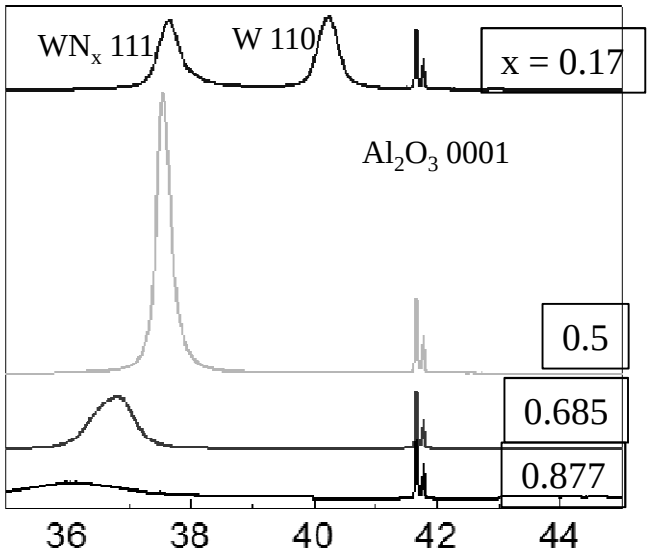
Measurement of properties:

- Lattice constants
- Elastic constants
- Mechanical properties
- Temperature stability
- Oxidation stability

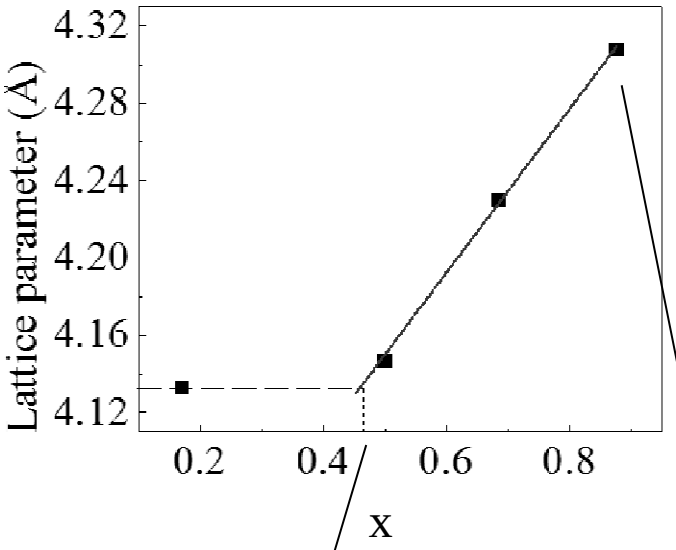
First studied material system: WN_x

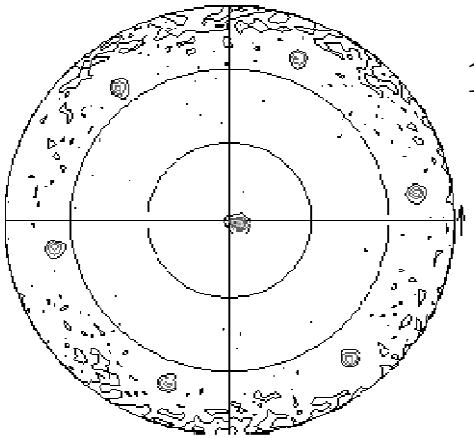
X-ray Diffraction

Lattice constant vs composition



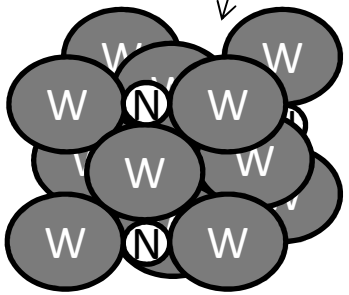
WN_x lattice parameter vs x



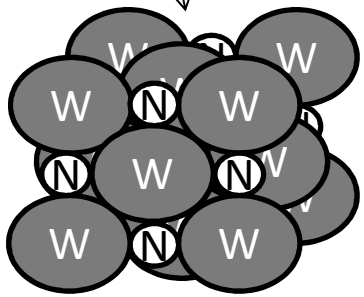


111 pole figure

WN (111) || Al_2O_3 (0001)
WN <110> || Al_2O_3 <11$\bar{2}$0>



x = 0.45



x = 1

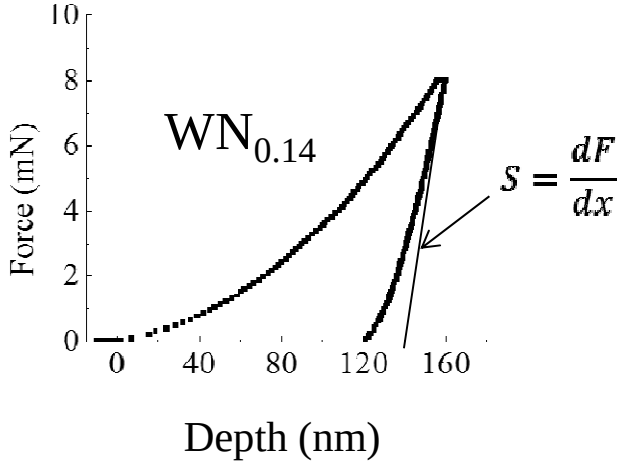
➔ **WN_x is epitaxial (two domains)**

➔ **Large single phase field in WN_x (~0.45≤x<1)**

Mechanical Properties Measurements

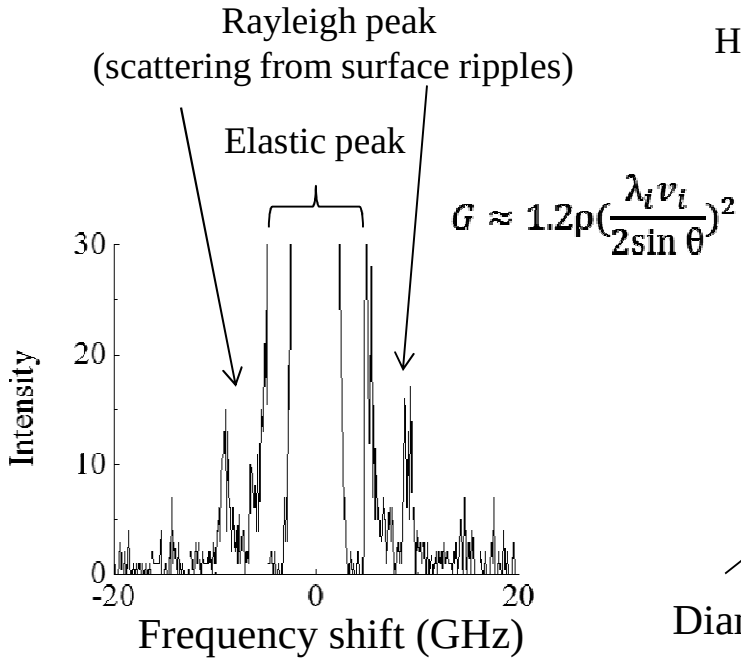
Nanoindentation

$$H = \frac{F}{A} \qquad E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}}$$



➔ Hardness
➔ Elastic modulus

Surface Brillouin Scattering (SBS)

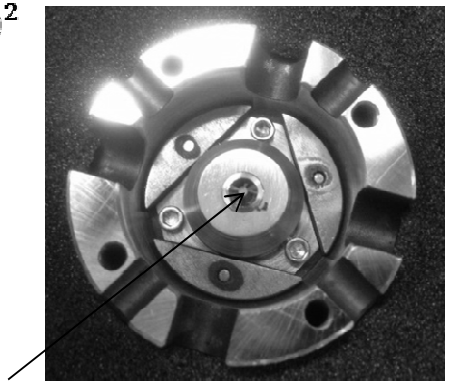


$$G \approx 1.2\rho\left(\frac{\lambda_i v_i}{2\sin\theta}\right)^2$$

➔ Shear modulus
➔ C_{11}, C_{12}, C_{44}

Diamond Anvil Cell (DAC)

High Pressure XRD and SBS
(0-10 GPa)



Diamond facet - 1mm diameter

➔ Bulk modulus
➔ Bonding asymmetry
➔ Phase transitions

Direct comparison to first principles calculations

Knowledge Base I

Intrinsic Properties of Single Crystal Nitrides

Theoretical work by Sanjay V. Khare with students Terence Liu, Xiuquan Zhou, S. K. R. Patil and others

The General Program

Prepare input files of a series of TMNs for DFT computations

Ab initio computation

Lattice constant, elastic constants, DOS

Effective medium theory

Bulk modulus, shear modulus, Young's modulus

Poisson's ratio, Pugh's ratio, Vicker's hardness

Visualization

Visualization

Recognize **trends** and **correlations** between trends

Identify promising ones and eliminate the opposite

Applicability of *Ab Initio* Methods

Pros

Very good at predicting structural properties:

(1) Lattice constant good to 1-3%

(2) Elastic constants good to 1-10%

(3) Very robust relative energy ordering between structures

(4) Good pressure induced phase changes

Good band structures, electronic properties

Good phonon spectra

Good chemical reaction and bonding pathways

Cons

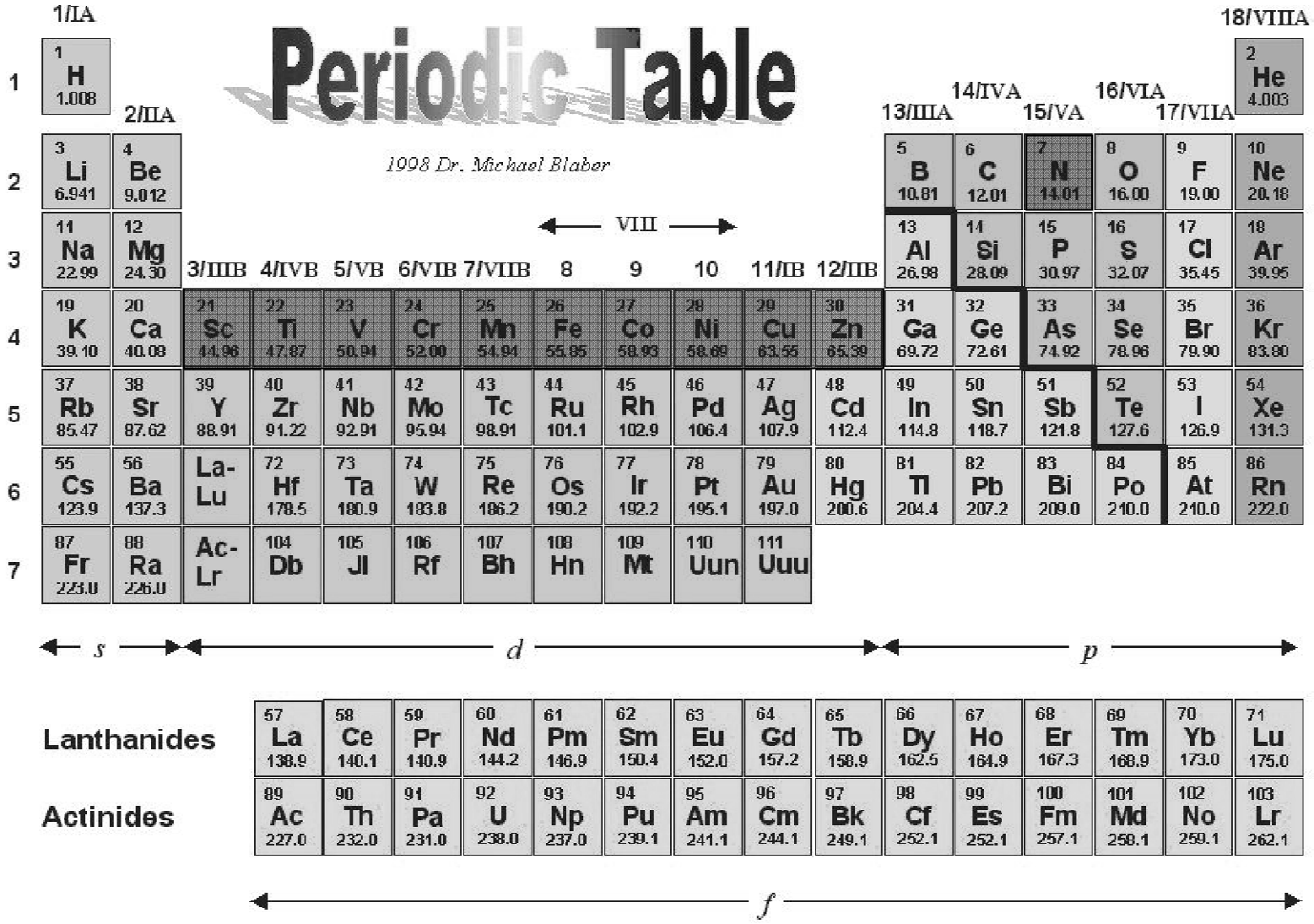
Computationally intensive

Band gaps are wrong

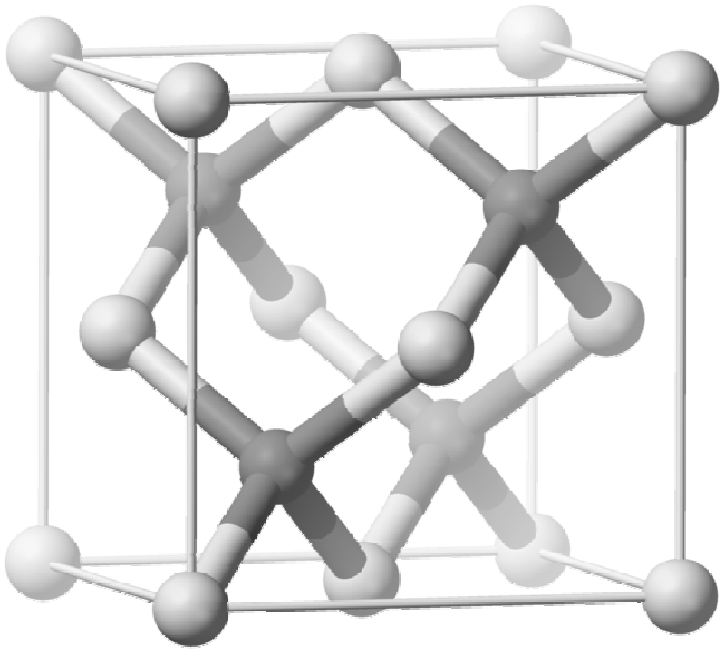
Excited electronic states are difficult

Structural, mechanical and electronic properties of 3d transition metal nitrides in cubic zincblende, rocksalt and cesium chloride structures

Periodic Table 3d highlight
Combine with previous slide



Structure – zincblende (MN)



Lattice Vectors

$\mathbf{A}_1 = \frac{1}{2}\,a\,\mathbf{Y} + \frac{1}{2}\,a\,\mathbf{Z}$

$\mathbf{A}_2 = \frac{1}{2}\,a\,\mathbf{X} + \frac{1}{2}\,a\,\mathbf{Z}$

$\mathbf{A}_3 = \frac{1}{2}\,a\,\mathbf{X} + \frac{1}{2}\,a\,\mathbf{Y}$

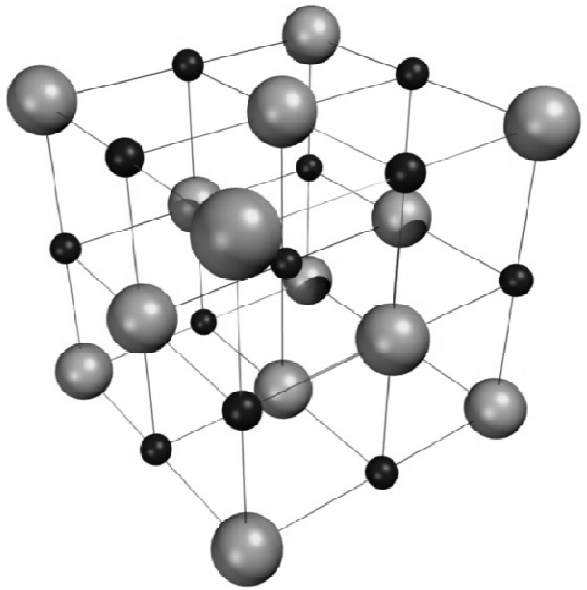
Basis Vectors

$\mathbf{B}_1 = 0$

$\mathbf{B}_2 = \frac{1}{4}\,\mathbf{A}_1 + \frac{1}{4}\,\mathbf{A}_2 + \frac{1}{4}\,\mathbf{A}_3 = \frac{1}{4}\,a\,\mathbf{X} + \frac{1}{4}\,a\,\mathbf{Y} + \frac{1}{4}\,a\,\mathbf{Z}$

http://en.wikipedia.org/wiki/File:Sphalerite-unit-cell-depth-fade-3D-balls.png

Structure – rocksalt (MN)



Lattice Vectors

$\mathbf{A}_1 = \frac{1}{2}\,a\,\mathbf{Y} + \frac{1}{2}\,a\,\mathbf{Z}$

$\mathbf{A}_2 = \frac{1}{2}\,a\,\mathbf{X} + \frac{1}{2}\,a\,\mathbf{Z}$

$\mathbf{A}_3 = \frac{1}{2}\,a\,\mathbf{X} + \frac{1}{2}\,a\,\mathbf{Y}$

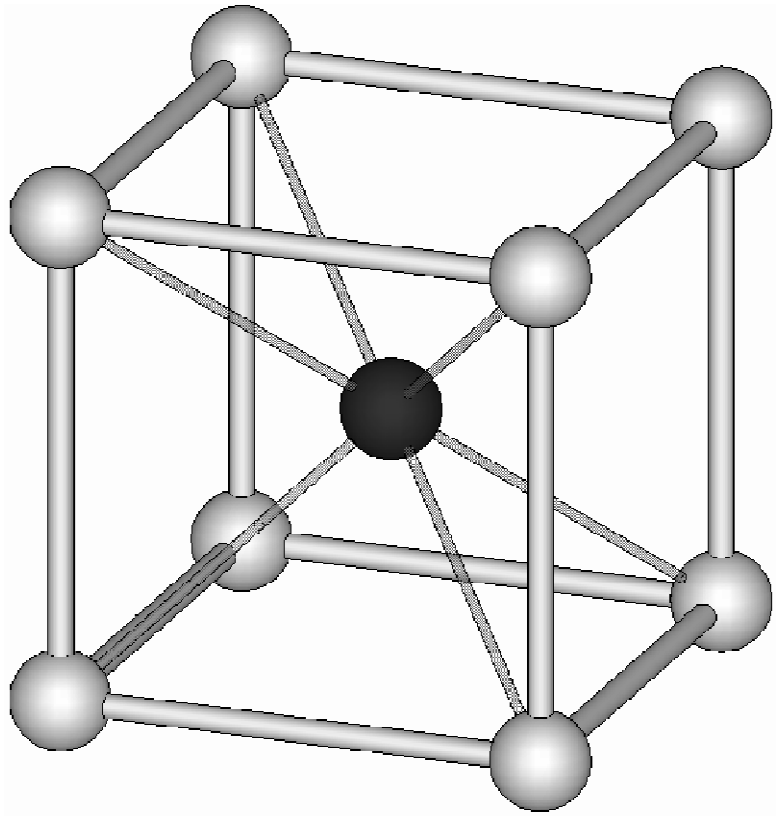
Basis Vectors

$\mathbf{B}_1 = 0$

$\mathbf{B}_2 = \frac{1}{2}\,\mathbf{A}_1 + \frac{1}{2}\,\mathbf{A}_2 + \frac{1}{2}\,\mathbf{A}_3 = \frac{1}{2}\,a\,\mathbf{X} + \frac{1}{2}\,a\,\mathbf{Y} + \frac{1}{2}\,a\,\mathbf{Z}$

http://commons.wikimedia.org/wiki/File:Nacl-structure.jpg

Structure – cesium chloride (MN)



Lattice Vectors

$\mathbf{A}_1 = a\,\mathbf{X}$

$\mathbf{A}_2 = a\,\mathbf{Y}$

$\mathbf{A}_3 = a\,\mathbf{Z}$

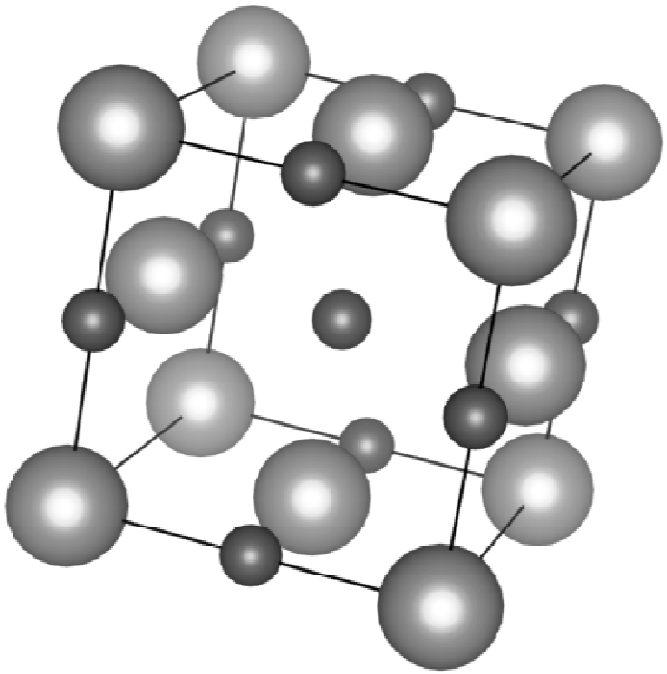
Basis Vectors

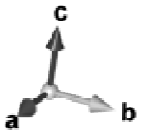
$\mathbf{B}_1 = 0$

$\mathbf{B}_2 = \frac{1}{2}\mathbf{A}_1 + \frac{1}{2}\mathbf{A}_2 + \frac{1}{2}\mathbf{A}_3 = \frac{1}{2}a\,\mathbf{X} + \frac{1}{2}a\,\mathbf{Y} + \frac{1}{2}a\,\mathbf{Z}$

http://meatfighter.com/puls/

Structure – NbO (MN)





Lattice Vectors

$\mathbf{A}_1 = a\,\mathbf{X}$

$\mathbf{A}_2 = a\,\mathbf{Y}$

$\mathbf{A}_3 = a\,\mathbf{Z}$

Basis Vectors

$\mathbf{B}_1 = 0$

$\mathbf{B}_2 = \frac{1}{2}\mathbf{A}_1 + \frac{1}{2}\mathbf{A}_2$

$\mathbf{B}_3 = \frac{1}{2}\mathbf{A}_1 + \frac{1}{2}\mathbf{A}_3$

$\mathbf{B}_4 = \frac{1}{2}\mathbf{A}_2$

$\mathbf{B}_5 = \frac{1}{2}\mathbf{A}_3$

$\mathbf{B}_6 = \frac{1}{2}\mathbf{A}_1 + \frac{1}{2}\mathbf{A}_2 + \frac{1}{2}\mathbf{A}_3$

M	a (Å)			C_{11} (GPa)			C_{12} (GPa)			C_{44} (GPa)			Mechanical Stability		
	zb	rs	cc	zb	rs	cc	zb	rs	cc	zb	rs	cc	zb	rs	cc
Sc	4.883	4.503	2.768	179.6	434.7	502.8	132.9	97.7	42.2	71.8	160.9	-119.2	S	S	**U**
		4.516[a]			390[a]			105[a]			166[a]				
		4.48[b]			386.4[b]			101[b]			171.7[b]				
		4.44[c]													
Ti	4.569	4.221	2.607	307.2	657.7	619.6	165.2	121.0	106.2	99.2	165.4	39.6	S	S	S
		4.253[a]			560[a]			135[a]			163[a]				
		4.218[b]			591.8[b]			123.4[b]			184.7[b]				
		4.241[c]			625[d]			165[d]			163[d]				
					507[e]			96[e]			163[e]				
V	4.407	4.095	2.521	328.1	685.8	969.5	213.0	172.8	33.6	42.8	121.5	160.3	S	S	S
		4.127[a]			660[a]			174[a]			118[a]				
		4.088[b]			695.9[b]			146.7[b]			152.8[b]				
		4.139[c]			533[d]			135[d]			133[d]				
Cr	4.302	4.025	2.477	341.1	636.0	894.3	240.2	218.1	102.1	-66.2	7.0	17.0	**U**	S	S
		4.048[b]			510.5[b]			217.2[b]			6.8[b]				
Mn	4.229	3.985	2.459	352.0	616.0	898.6	257.6	229.7	98.2	33.5	-10.9	38.3	S	**U**	S
Fe	4.201	3.968	2.459	356.9	485.9	825.9	258.7	281.4	110.0	112.4	-37.2	29.4	S	**U**	S
Co	4.221	3.971	2.485	322.5	468.0	542.2	242.9	258.1	191.8	68.2	65.7	17.8	S	S	S
Ni	4.289	4.029	2.520	255.5	434.1	529.5	223.5	212.4	151.0	46.7	87.7	-5.5	S	S	**U**
Cu	4.398	4.136	2.585	202.7	352.3	356.0	180.0	171.0	160.8	39.4	62.6	7.5	S	S	S
Zn	4.530	4.258	2.674	161.3	288.7	231.5	143.0	139.2	150.7	45.0	67.3	-39.0	S	S	**U**

a GGA, D. Holec *et al.*, Phys. Rev. B **85,** 064101 (2012).
b Avg. of LDA & GGA, M. G. Brik *et al.*, Comput. Mater. Sci. **51**, 380 (2012).
c Exp., Powder diffraction files: ScN 00-045-0978, TiN 03-065-0565, VN 00-035-0768.
d Exp., J. O. Kim *et al.*, J. Appl. Phys. **72**, 1805 (1992).
e Exp., W. J. Meng *et al.*, Thin Solid Films **271**, 108 (1995).

Comparison of direct *ab initio* results with experimental values

M	a (Å)			C_{11} (GPa)			C_{12} (GPa)			C_{44} (GPa)		
	zb	rs	cc	zb	rs	cc	zb	rs	cc	zb	rs	cc
Sc	4.883	4.503	2.768	179.6	434.7	502.8	132.9	97.7	42.2	71.8	160.9	-119.2
		4.44[a]										
Ti	4.569	4.221	2.607	307.2	657.7	619.6	165.2	121.0	106.2	99.2	165.4	39.6
		4.241[a]			625[b]			165[b]			163[b]	
					507[c]			96[c]			163[c]	
V	4.407	4.095	2.521	328.1	685.8	969.5	213.0	172.8	33.6	42.8	121.5	160.3
		4.139[a]			533[b]			135[b]			133[b]	

a Powder diffraction files: ScN 00-045-0978, TiN 03-065-0565, VN 00-035-0768.

b J. O. Kim *et al.*, J. Appl. Phys. **72**, 1805 (1992).

c W. J. Meng *et al.*, Thin Solid Films **271**, 108 (1995).

Polycrystalline properties

B (bulk modulus), *G* (shear modulus) and *E* (Young's modulus)

M	B (GPa)			G (GPa)			E (GPa)		
	zb	rs	cc	zb	rs	cc	zb	rs	cc
Sc	148.5	210.0	195.7	45.8	163.9	**U**	124.7	390.2	**U**
Ti	212.6	299.9	277.3	86.8	200.9	93.2	229.1	492.8	251.4
V	251.4	343.8	345.6	48.2	164.7	250.5	135.9	426.1	605.2
Cr	273.9	357.4	366.2	**U**	49.6	98.1	**U**	142.1	270.3
Mn	289.1	358.5	365.0	38.4	**U**	121.5	110.4	**U**	328.1
Fe	291.4	349.5	348.6	80.6	**U**	103.6	221.5	**U**	282.8
Co	269.5	328.0	308.6	55.0	79.3	54.2	154.4	220.2	153.7
Ni	234.2	286.3	277.1	30.4	96.3	**U**	87.5	259.8	**U**
Cu	187.6	231.5	225.9	24.0	72.6	27.7	69.1	197.3	79.8
Zn	149.1	189.1	177.6	24.1	70.2	**U**	68.6	187.3	**U**

zb (zincblende)
rs (rocksalt)
cc (cesium chloride)

Polycrystalline properties

P_C (Cauchy's pressure), v (Poisson's ratio) and k (Pugh's ratio)

M	P_C (GPa)			v			k		
	zb	rs	cc	zb	rs	cc	zb	rs	cc
Sc	61.1	-63.3	U	0.36	0.19	U	0.31	0.78	U
Ti	66.0	-44.4	66.6	0.32	0.23	0.35	0.41	0.67	0.34
V	170.2	51.3	-126.7	0.41	0.29	0.21	0.19	0.48	0.72
Cr	U	211.1	85.1	U	0.43	0.38	U	0.14	0.27
Mn	224.1	U	59.9	0.44	U	0.35	0.13	U	0.33
Fe	146.3	U	80.6	0.37	U	0.36	0.28	U	0.30
Co	174.7	192.4	174.1	0.40	0.39	0.42	0.20	0.24	0.18
Ni	176.8	124.7	U	0.44	0.35	U	0.13	0.34	U
Cu	140.6	108.4	153.3	0.44	0.36	0.44	0.13	0.31	0.12
Zn	98.1	72.0	U	0.42	0.33	U	0.16	0.37	U

zb (zincblende)
rs (rocksalt)
cc (cesium chloride)

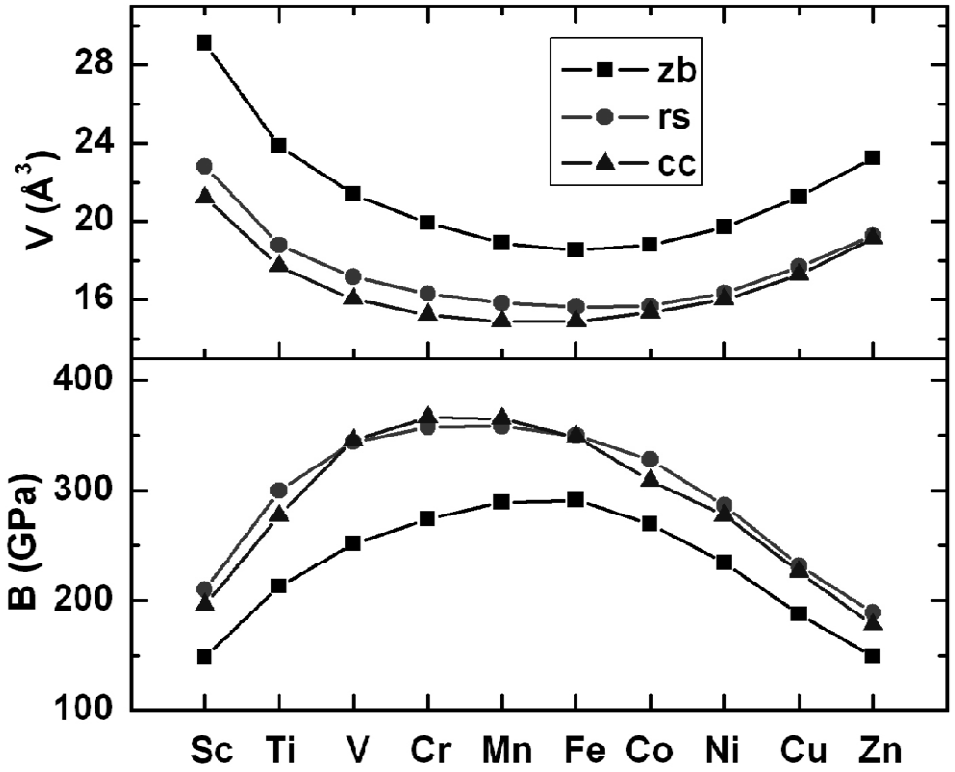
Polycrystalline properties

H_V (Vicker's hardness) and θ_D (Debye temperature)

M	H_V (GPa)			θ_D (K)		
	zb	rs	cc	zb	rs	cc
Sc	3.6	25.7	**U**	506.8	901.5	**U**
Ti	7.8	24.9	6.6	654.9	947.1	648.4
V	2.2	14.8	31.9	473.6	830.9	1002.8
Cr	**U**	1.5	5.3	**U**	457.0	630.4
Mn	1.2	**U**	7.9	403.5	**U**	681.4
Fe	4.8	**U**	6.2	573.8	**U**	626.2
Co	2.6	4.1	2.2	466.8	542.6	448.9
Ni	1.0	6.8	**U**	352.1	600.1	**U**
Cu	0.8	5.1	0.9	306.8	511.9	318.3
Zn	1.1	6.0	**U**	307.6	502.9	**U**

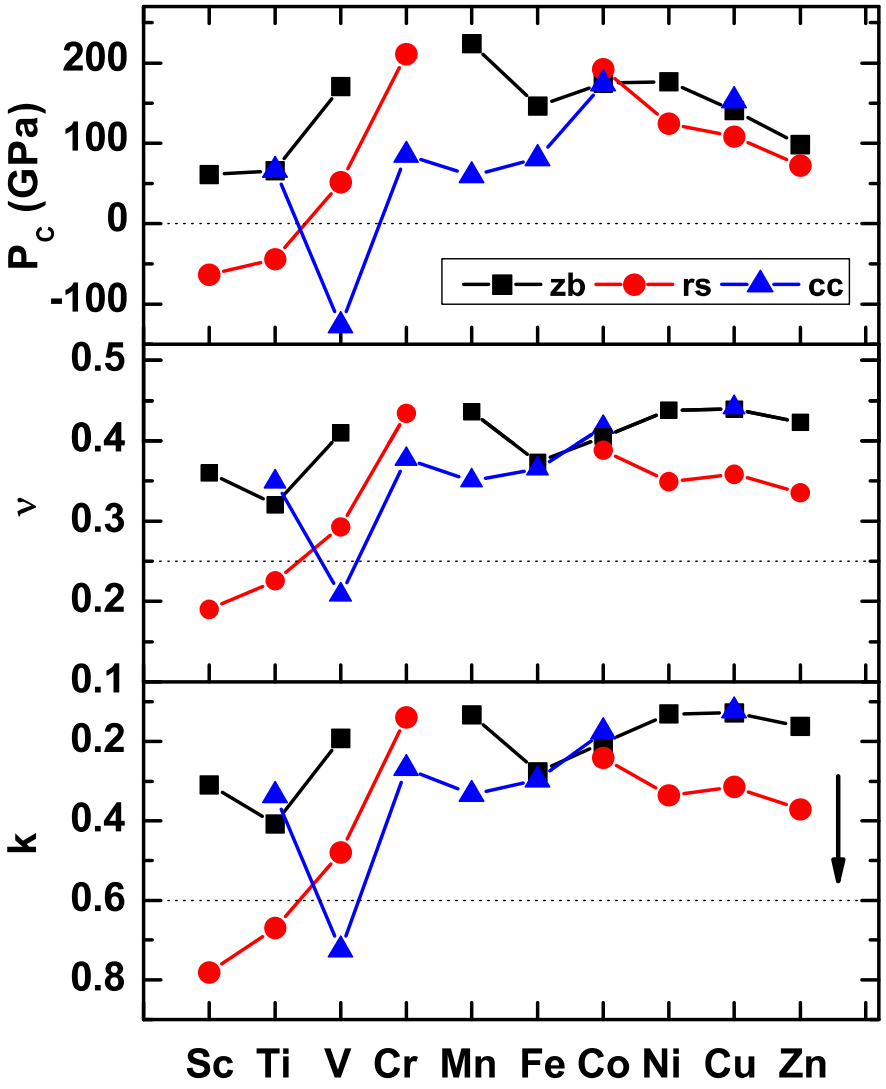
zb (zincblende)
rs (rocksalt)
cc (cesium chloride)

V (unit cell volume) and *B* (bulk modulus)



$$B = (C_{11} + 2C_{12})/3$$

P_C, ν and k

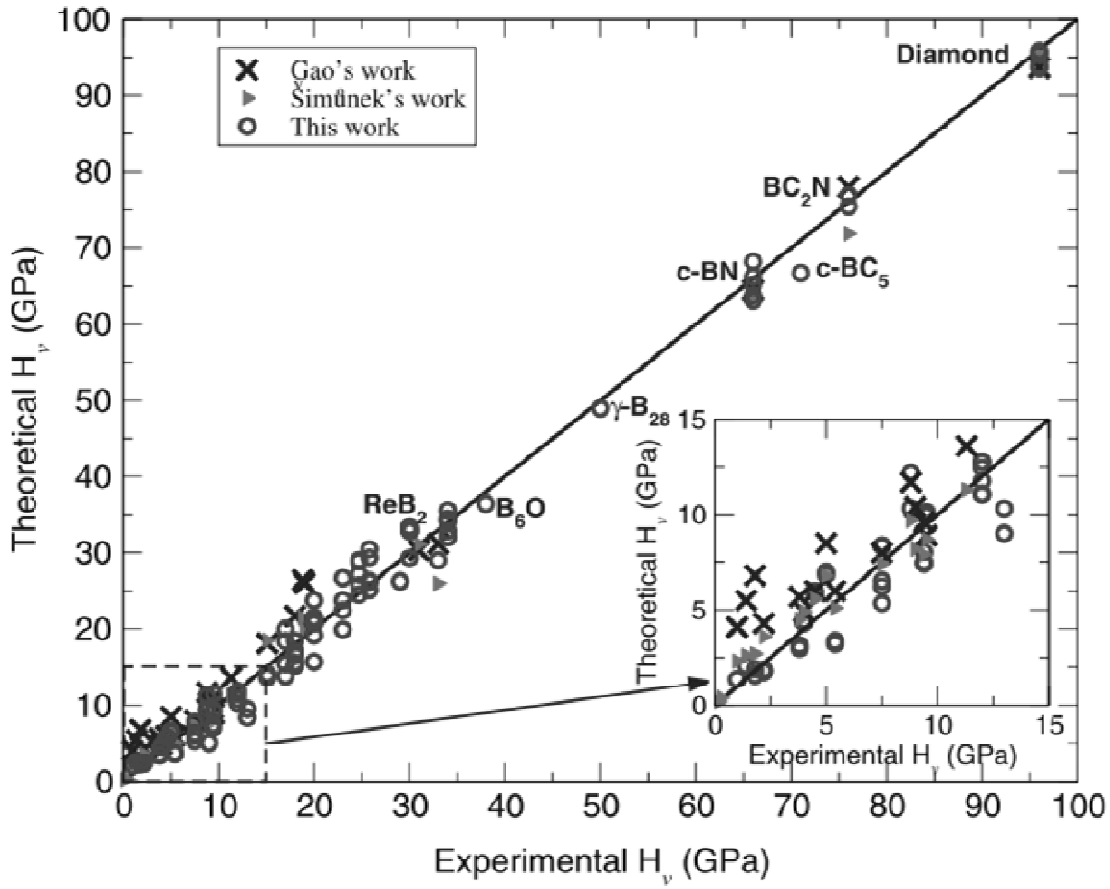


P_c (Cauchy's pressure)
$P_C = C_{12} - C_{44}$

ν (Poisson's ratio)
$\nu = (3B - 2G)/[2(3B + G)]$

k (Pugh's ratio)
$k = G/B$

Chen's formulation for calculating H_V (Vicker's Hardness)



$$B = (C_{11} + 2C_{12})/3$$

$$G_V = [(C_{11} - C_{12}) + 3C_{44}]/5$$

$$G_R = [5(C_{11} - C_{12})C_{44}]/(4C_{44} + 3C_{11} - 3C_{12})$$

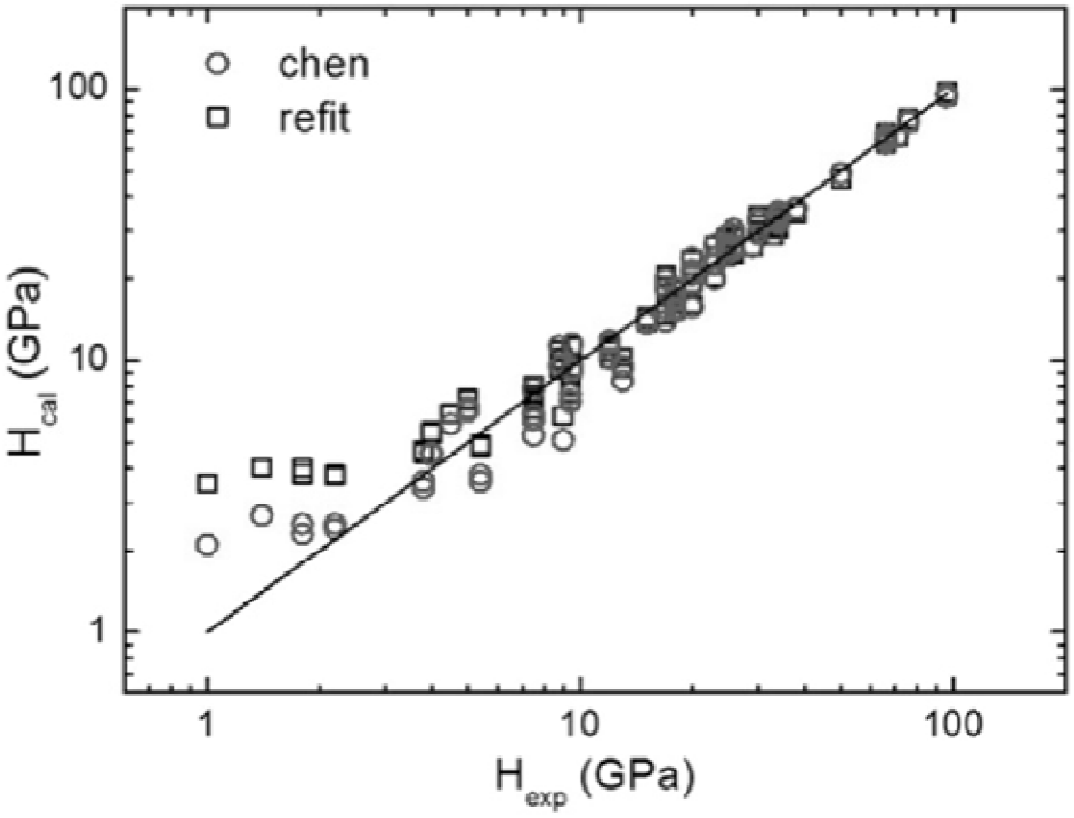
$$G = G_{VRH} = (G_V + G_R)/2$$

$$k = G/B$$

$$H_V = 2\left(k^2 G\right)^{0.585} - 3$$

X. Q. Chen *et al.*, Intermetallics **19**, 1275 (2011)

Tian's alternative for calculating H_V (Vicker's Hardness)



$B = (C_{11} + 2C_{12})/3$

$G_v = [(C_{11} - C_{12}) + 3C_{44}]/5$

$G_R = [5(C_{11} - C_{12})C_{44}]/$
$(4C_{44} + 3C_{11} - 3C_{12})$

$G = G_{VRH} = (G_v + G_R)/2$

$k = G/B$

$$H_V = 0.92k^{1.137}G^{0.708}$$

Y. Tian *et al.*, Int. J. Refract. Met. Hard Mater. **33**, 93 (2012).

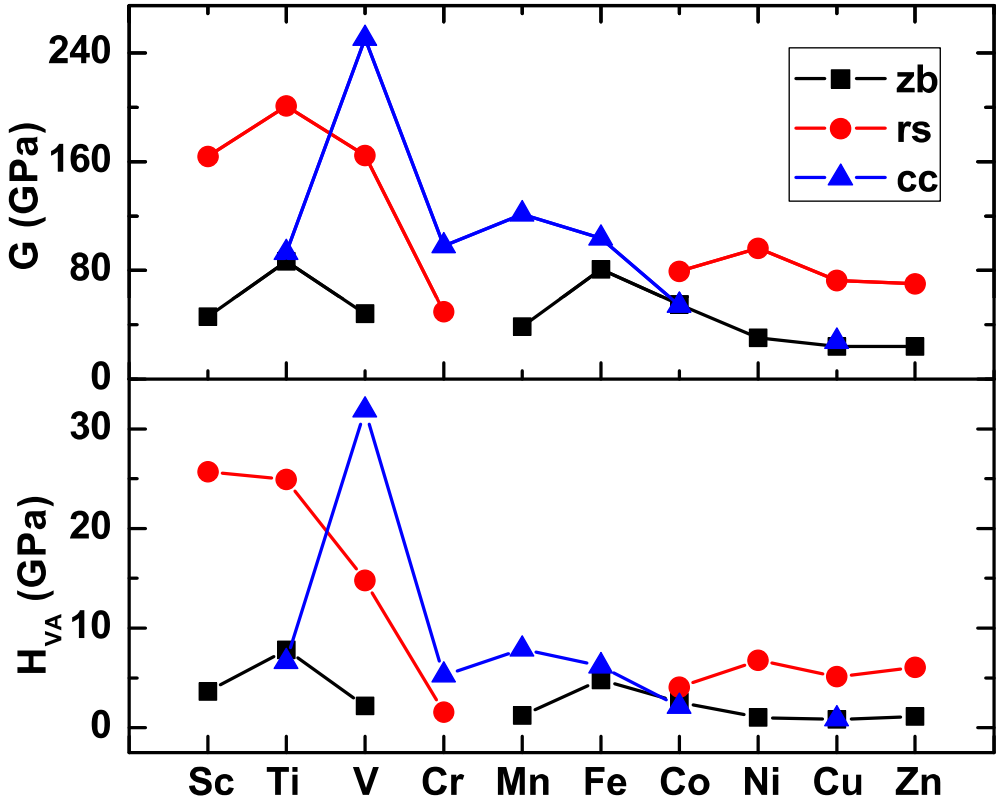
Crystal	H_{Exp} (GPa)	H_{Tian} (GPa)	$H_{Simunek}$ (GPa)	H_{Xue} (GPa)	H_{Chen} (GPa)
C	96[a]	93.6	95.4[b]	90[e]	94.6[f]
Si	12[a]	13.6	11.3[b]	14[e]	11.2[f]
Ge	8.8[b]	11.7	9.7[b]	11.4[e]	10.4[f]
SiC	31[b]	30.3	31.1[b]	27.8[e]	33.8[f]
BN	63[a]	64.5	63.2[b]	47.7[e]	65.3[f]
BP	33[a]	31.2	26[b]	24.9[e]	29.3[f]
BAs	19[b]	26	19.9[b]	21.1[e]	–
AlN	18[a]	21.7	17.6[b]	14.5[e]	16.8[f]
AlP	9.4[a]	9.6	7.9[b]	7.4[e]	7.2[f]
AlAs	5.0[a]	8.5	6.8[b]	6.3[e]	6.6[f]
AlSb	4.0[a]	4	4.9[b]	4.9[e]	4.4[f]
GaN	15.1[a]	18.1	18.5[b]	13.5[e]	13.9[f]
GaP	9.5[a]	8.9	8.7[b]	8[e]	9.9[f]
GaAs	7.5[a]	8	7.4[b]	7.1[e]	7.8[f]
GaSb	4.5[a]	6	5.6[b]	4.5[e]	5.8[f]
InN	9[a]	10.4	8.2[b]	7.4[e]	7.4[f]
InP	5.4[a]	6	5.1[b]	3.9[e]	3.7[f]
InAs	3.8[a]	3.8	5.7[b]	4.5[e]	3.3[f]
InSb	2.2[a]	4.3	3.6[b]	2.2[e]	2.4[f]
ZnS	1.8[b]	6.8	2.7[b]	2.4[e]	2.4[f]
ZnSe	1.4[b]	5.5	2.6[b]	1.8[e]	2.7[f]
ZnTe	1[b]	4.1	2.3[b]	0.9[e]	2.1[f]
TiC	32[c]	34	18.8[b]	23.9[e]	27[f]
TiN	20.6[c]	21.6	18.7[b]	23.8[h]	23.3[f]
ZrC	25[c]	21	10.7[g]	15.7[h]	27.5[f]

Y. Tian *et al.*, Int. J. Refract. Met. Hard Mater. **33**, 93 (2012).

Crystal	H_{Exp} (GPa)	H_{Tian} (GPa)	$H_{Simunek}$ (GPa)	H_{Xue} (GPa)	H_{Chen} (GPa)
ZrN	15.8[c]	16.7	10.8[g]	15.9[h]	–
HfC	26.1[c]	26.8	10.9[g]	15.6[h]	–
HfN	16.3[c]	18	10.6[g]	15.2[h]	19.2[f]
VC	27.2[c]	23	25.2[g]	17.5[h]	26.2[f]
VN	15.2[c]	14.9	26.5[g]	16.5[h]	–
NbC	17.6[c]	16.1	18.3[b]	12.8[h]	15.4[f]
NbN	13.7[c]	13.6	19.5[b]	12[h]	14.7[f]
TaC	24.5[c]	26	19.9[g]	14.7[h]	–
TaN	22[c]	20	21.2[g]	14.3[h]	–
CrN	11[c]	11	36.6[g]	19.2[h]	–
WC	30[c]	31	21.5[b]	20.6[e]	31.3[f]
Re_2C	17.5[j]	19.7[j]	11.5[g]	16.2[h]	26.4[i]
Al_2O_3	20[c]	18.8	13.5[g]	18.4[h]	20.3[i]
MgO	3.9[d]	4.5	4.4[g]	5.4[h]	24.8[i]
LiF	1[d]	0.8	2.2[g]	–	8.5[i]
NaF	0.6[d]	0.85	1[g]	–	5.7[i]
NaCl	0.2[d]	0.4	0.4[b]	–	2.4[i]
KCl	0.13[d]	0.18	0.2[b]	–	2.3[i]
KBr	0.1[d]	0.23	0.2[g]	–	0.1[i]

[a] Reference [34].
[b] Reference [37].
[c] Reference [32].
[d] Reference [60].
[e] Reference [58].
[f] Reference [30].
[g] Calculated by authors using method [36].
[h] Caculated using [35].
[i] Calculated with [30].
[j] Referenece [52].

G (shear modulus) and H_{VA} (Tian's)



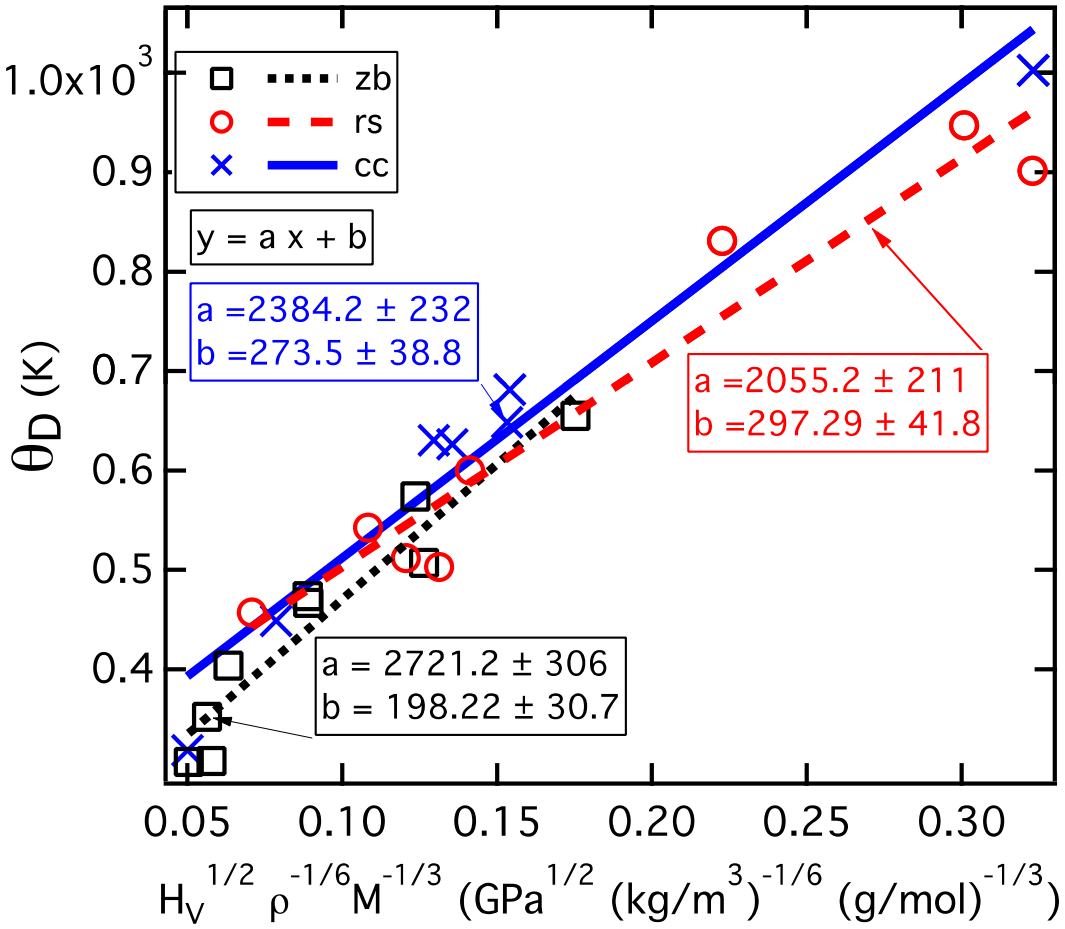
$G_V = [(C_{11} - C_{12}) + 3C_{44}]/5$

$G_R = [5(C_{11} - C_{12})C_{44}]/$
$(4C_{44} + 3C_{11} - 3C_{12})$

$G = G_{VRH} = (G_V + G_R)/2$

$H_{VA} = 0.92\ k^{1.137}\ G^{0.708}$

θ_D (Debye temperature) vs $f(H_{VA})$



$$\theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m$$

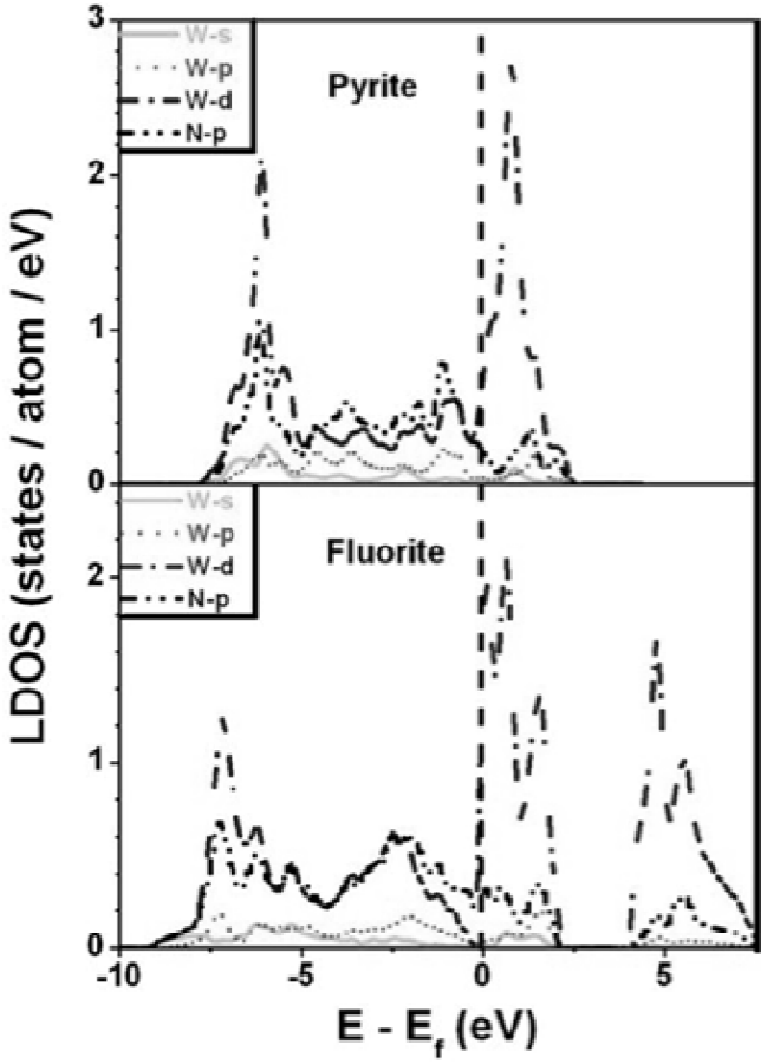
where $v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}$

$v_t = \left(\frac{G}{\rho}\right)^{1/2}$ and $v_l = \left(\frac{3B+4G}{3\rho}\right)^{1/2}$

$H_{VA} = 0.92\ k^{1.137}\ G^{0.708}$

P. Deus *et al.*, Cryst. Res. Technol. **18**, 491 (1983).

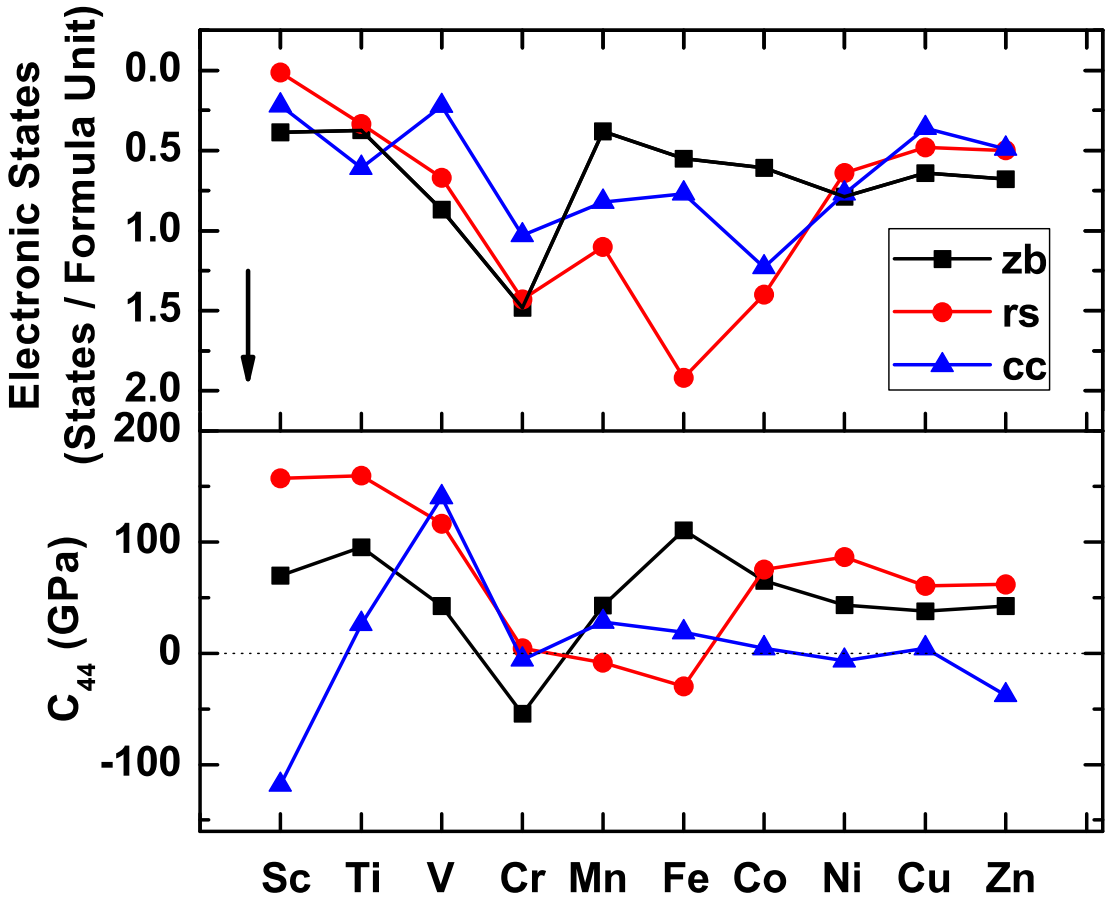
Correlation of stability with DOS



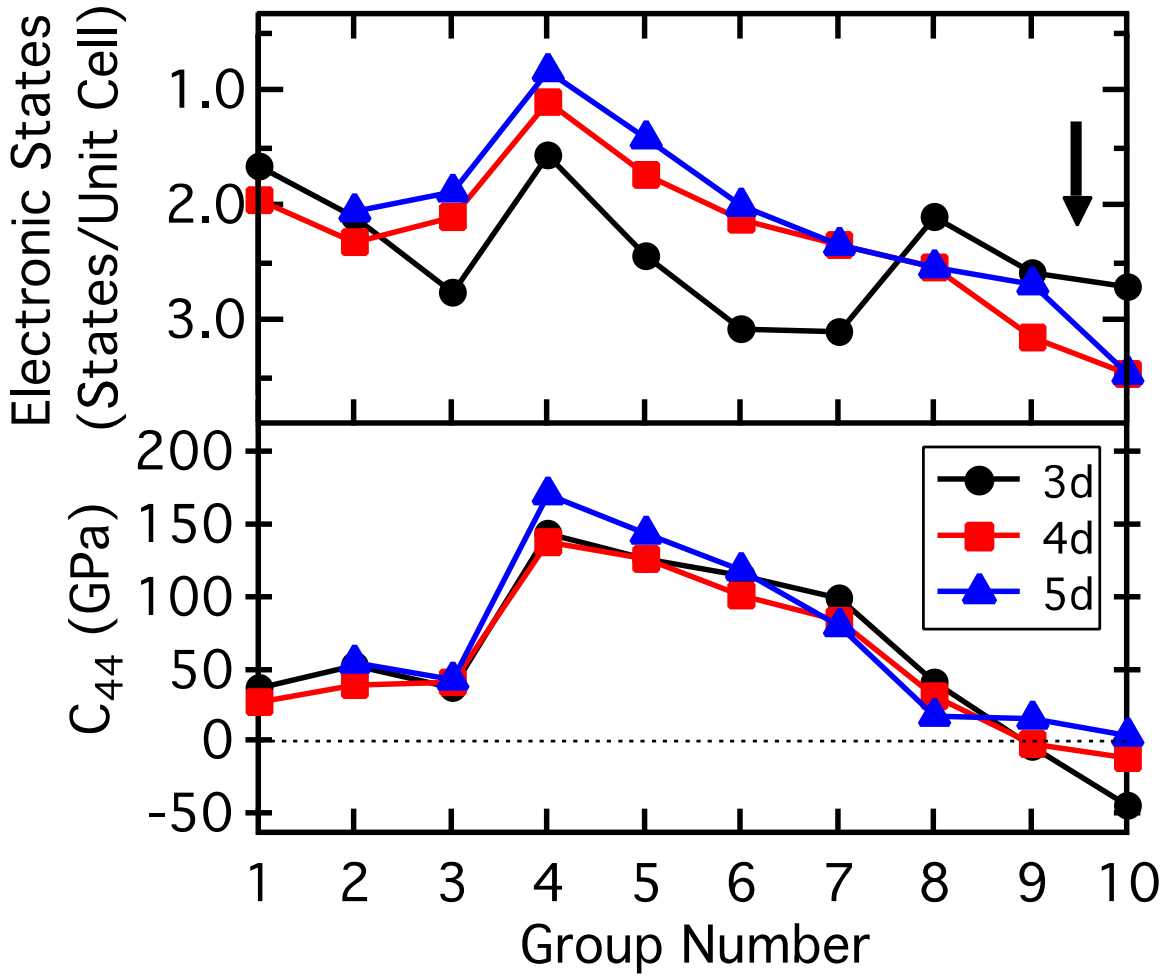
- Pyrite-structured WN_2 is stable, and DOS at E_F is small
- Fluorite-structured WN_2 is unstable, and DOS at E_F is large

S. K. R. Patil *et al.*, Thin Solid Films **517**, 824 (2008)

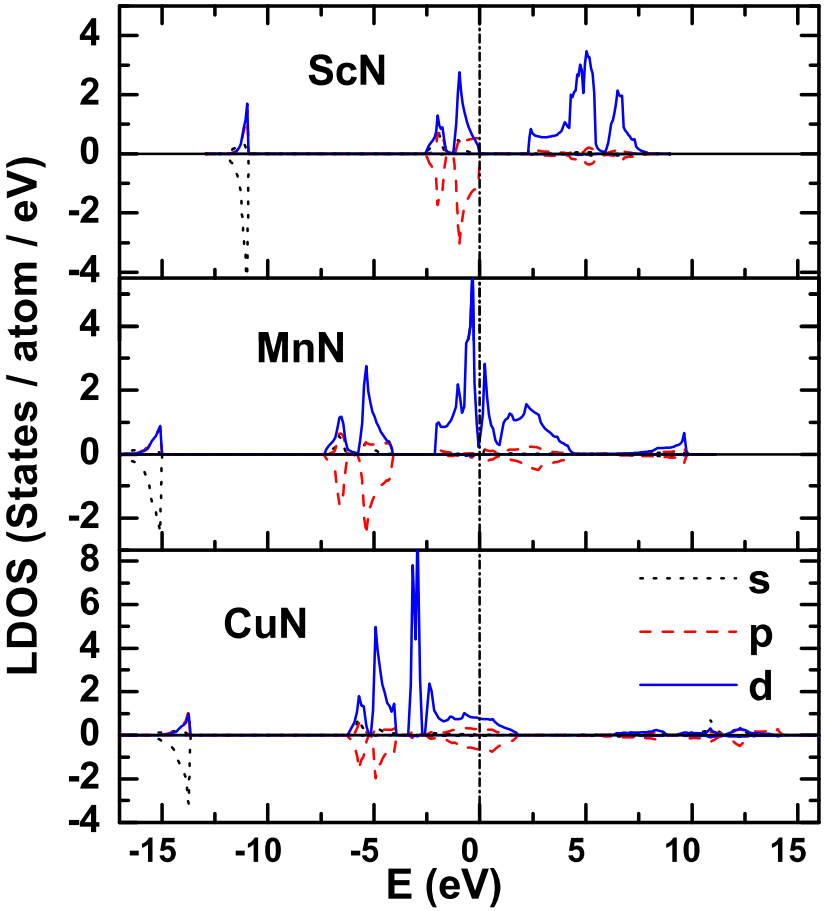
Correlation of C_{44} (indicating H_V and stability) with TDOS



Correlation of C_{44} (indicating H_V and stability) with TDOS of NbO-type

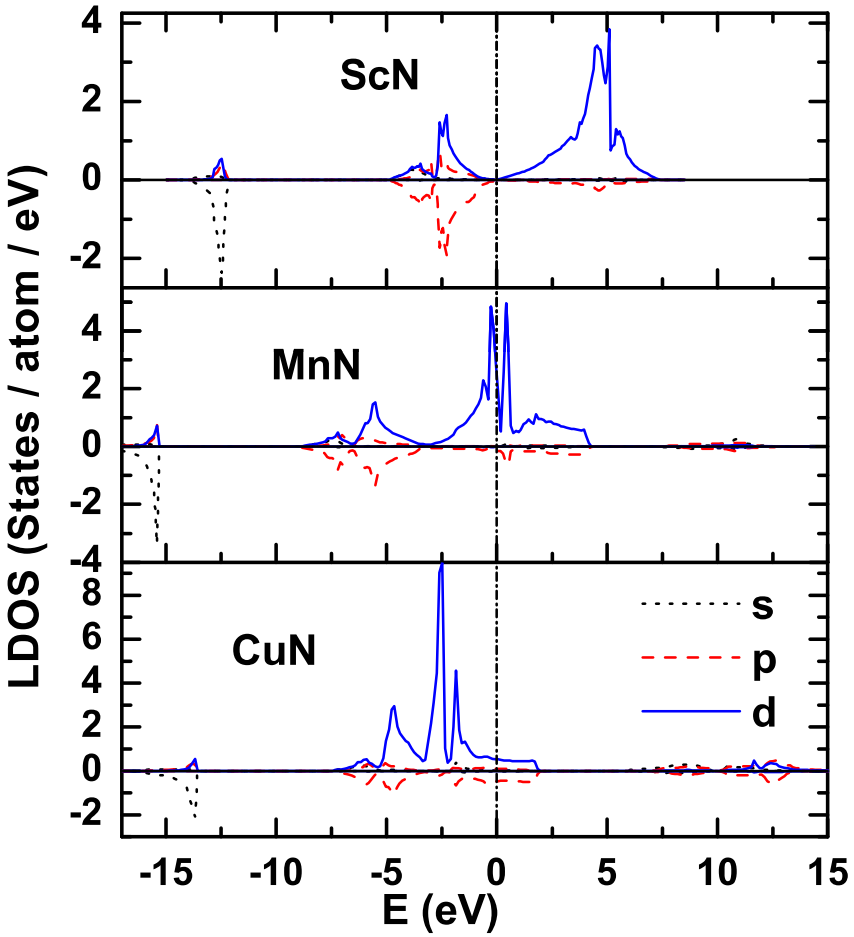


LDOS - zincblende



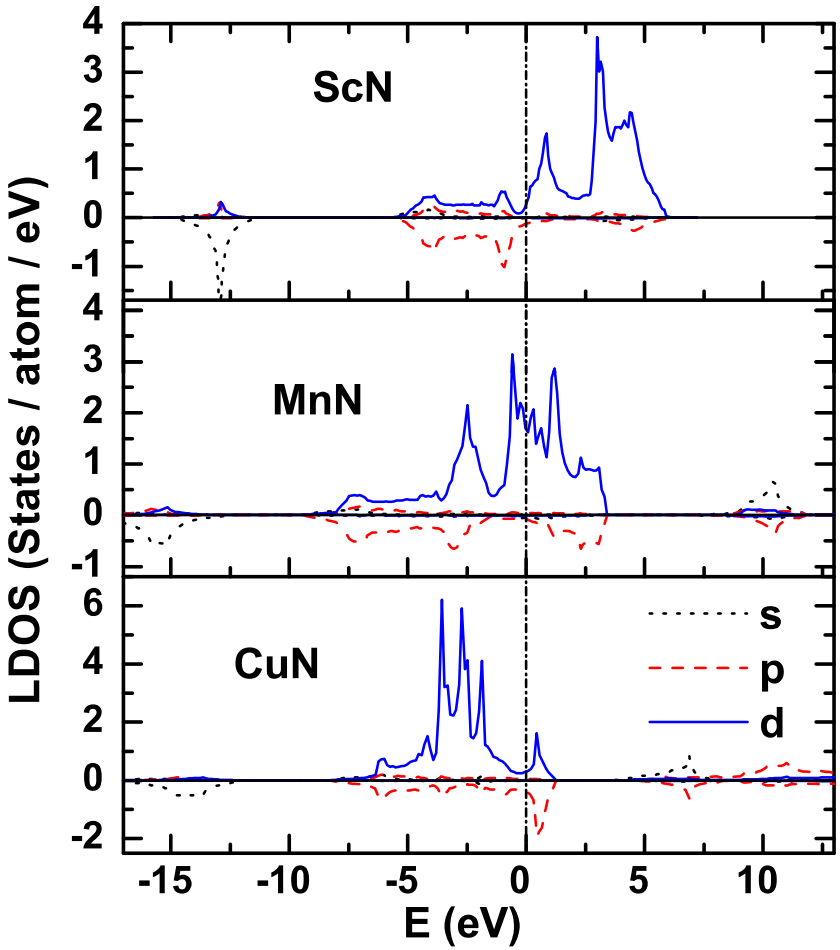
As transition metal goes from left to right in the 3d row, more states shift below E_F, peaks becoming sharper.

LDOS - rocksalt



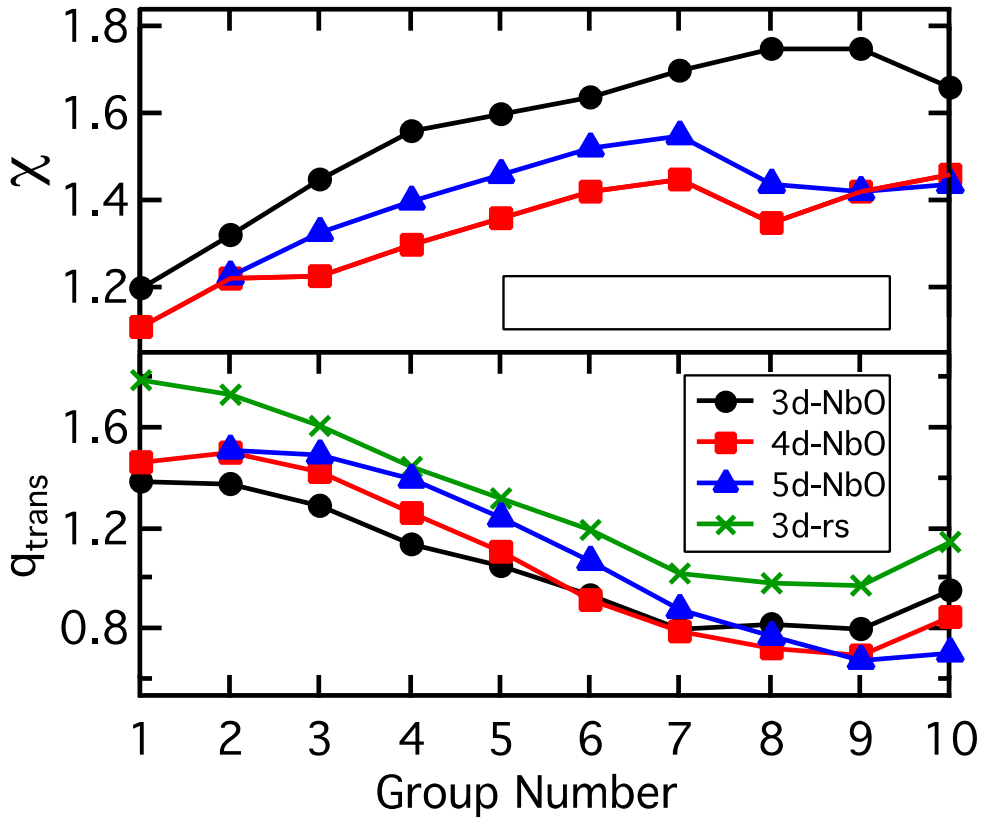
As transition metal goes from left to right in the 3d row, more states shift below E_F, peaks becoming sharper.

LDOS – cesium chloride



As transition metal goes from left to right in the 3d row, more states shift below E_F, peaks becoming sharper.

Bader analysis of NbO-type



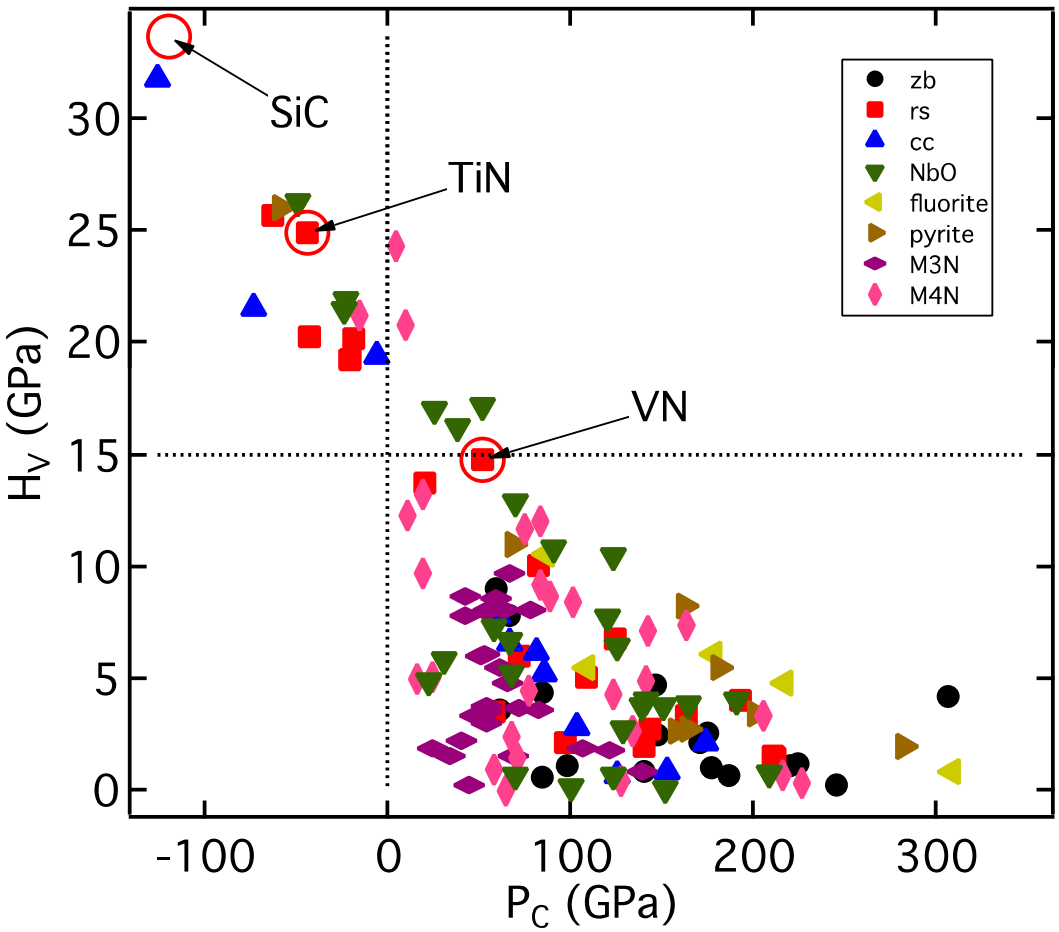
χ (nitrogen): 3.07

χ (electronegativity) from
A. L. Allred *et al.*, J. Inorg. Nucl. Chem. **5**, 264 (1958).

q_{trans} (charge transfer from transition metal to nitrogen using Bader's scheme)

Bader analysis program from
W. Tang *et al.*, J. Phys.: Condens. Matter 21, 084204 (2009)
E. Sanville *et al.*, J. Comp. Chem. 28, 899-908 (2007)
G. Henkelman *et al.*, Comput. Mater. Sci. 36, 254-360 (2006)

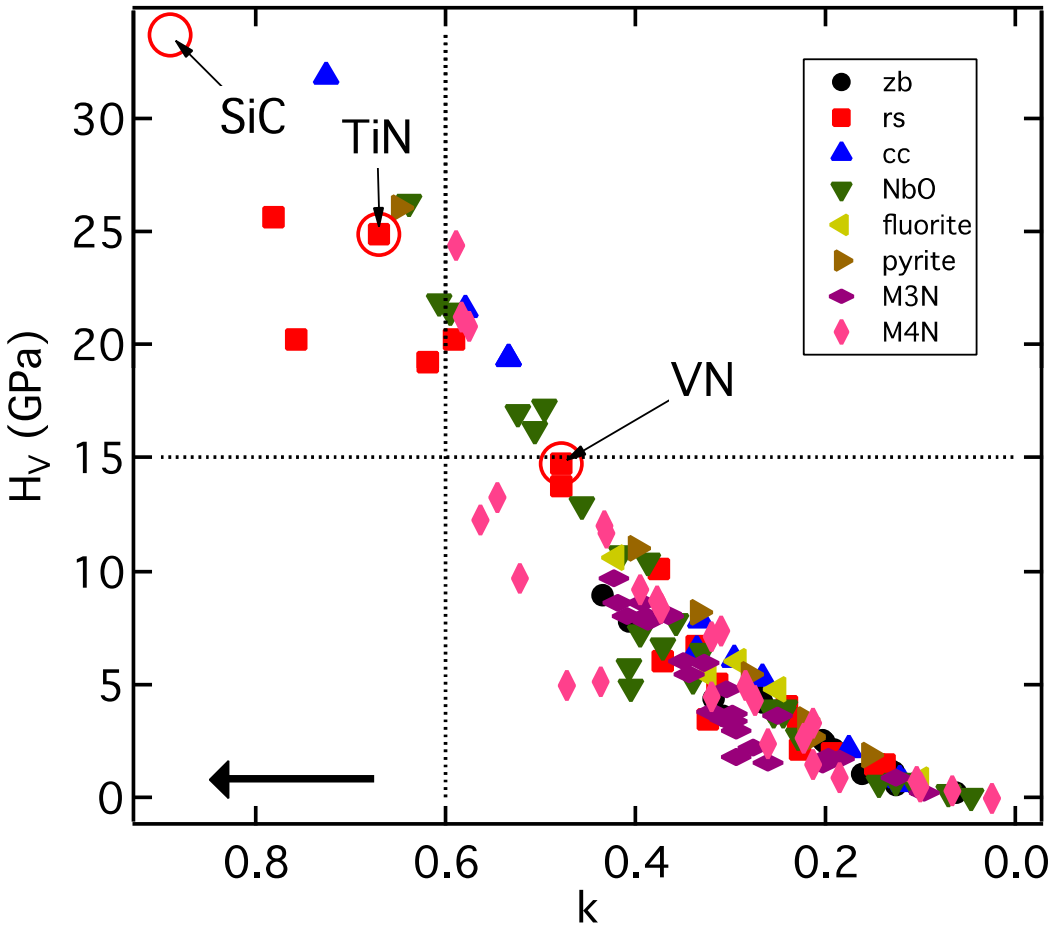
H_{VA} vs P_C (Cauchy's pressure)



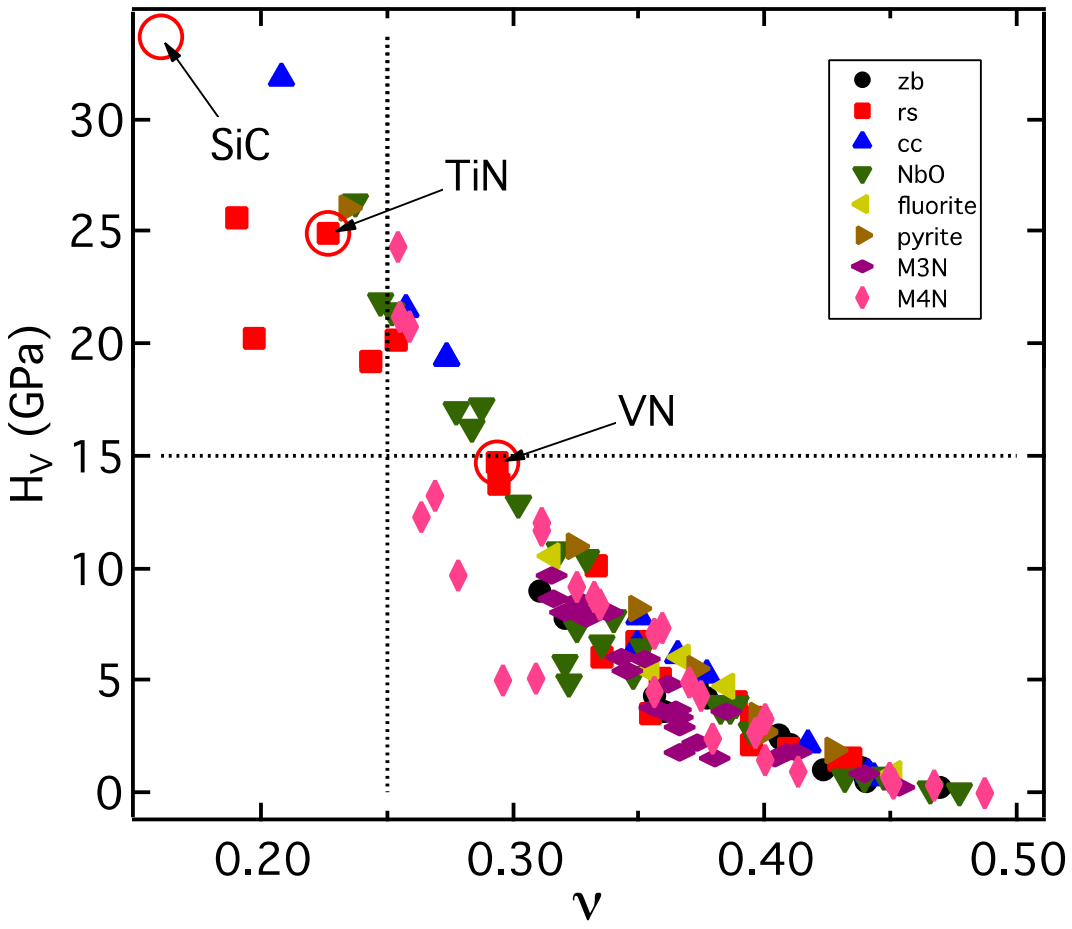
Data partly from

W. Chen *et al.*, J. Alloys Compd. **499**, 243 (2010).
E. J. Zhao *et al.*, Comput. Mater. Sci. **47**, 1064 (2010).
E. J. Zhao *et al.*, J. Solid State Chem. **181**, 2814 (2008).

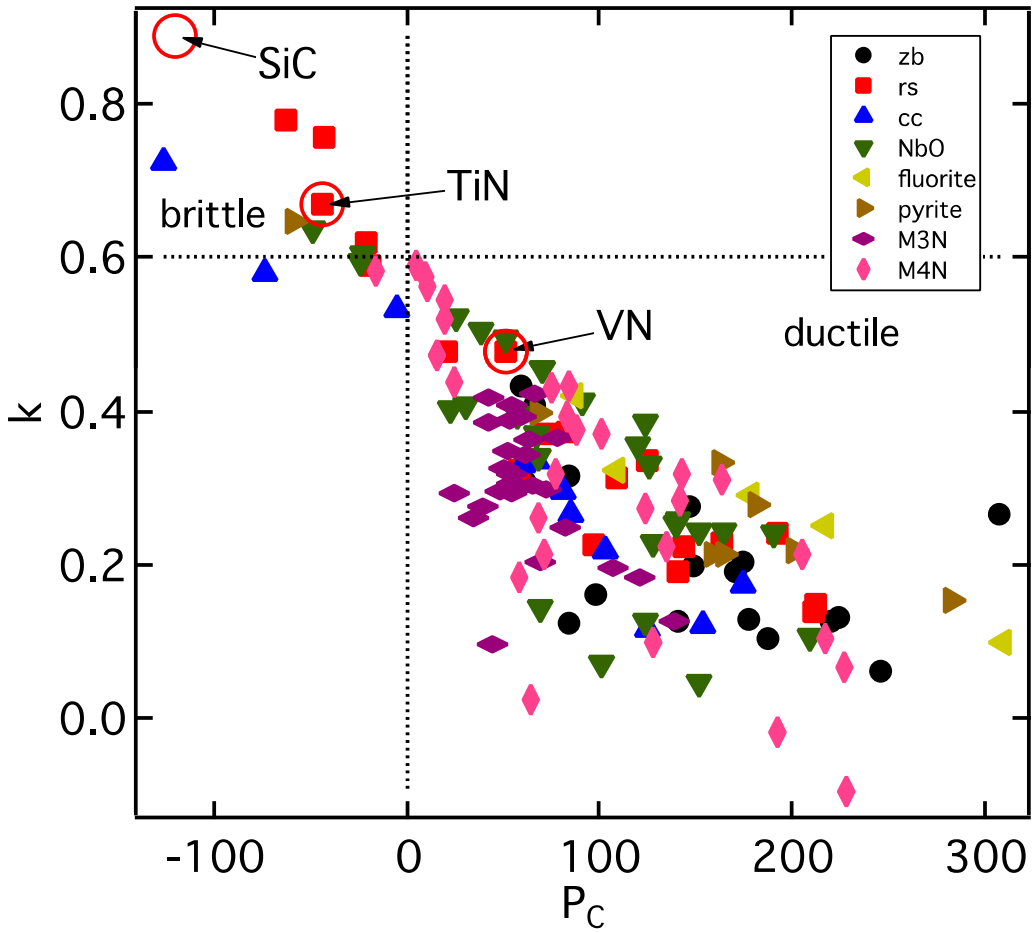
H_{VA} vs k (Pugh's ratio) x-axis inverted



H_{VA} vs v (Poisson's ratio)



k vs P_C


SiC
TiN
VN
brittle
ductile
zb
rs
cc
NbO
fluorite
pyrite
M3N
M4N
0.8
0.6
0.4
0.2
0.0
k
-100
0
100
200
300
P_C

Nitrides with $H_{VA} \geq 15$ GPa

Material	a (A)	C_{11}	C_{12}	C_{44}	B (GPa)	G (GPa)	ν	k	P_C (GPa)	H_{VA} (GPa)
diamond	3.548	1079.8	131.4	577.2	447.5	533.5	0.07	1.19	-445.80	95.80
SiC	4.345	396.5	128.5	249.2	217.8	194.3	0.16	0.89	-120.70	33.70
M_4N-Mn_4N	3.653	769.2	127.6	143.8	341.4	199.5	0.26	0.58	-16.20	21.23
M_4N-Tc_4N	3.971	670.3	184.1	174.3	346.1	199.2	0.26	0.58	9.81	20.83
M_4N-Re_4N	3.993	772.4	221.1	217.0	404.8	238.8	0.25	0.59	4.06	24.37
rs-ScN	4.503	434.7	97.7	160.9	210.0	163.9	0.19	0.78	-63.27	25.67
rs-TiN	4.221	657.7	121.0	165.4	299.9	200.9	0.23	0.67	-44.40	24.93
rs-VN	4.095	685.8	172.8	121.5	343.8	164.7	0.29	0.48	51.32	14.78
rs-YN	4.890	319.0	84.0	127.0	162.3	123.1	0.20	0.76	-43.00	20.28
rs-ZrN	4.580	563.0	101.0	122.0	255.0	158.0	0.24	0.62	-21.00	19.23
rs-HfN	4.436	704.9	111.8	131.0	309.5	182.9	0.25	0.59	-19.20	20.22
cc-VN	2.521	969.5	33.6	160.3	345.6	250.5	0.21	0.72	-126.72	31.85
cc-TaN	2.731	1006.0	33.0	107.0	357.3	207.2	0.26	0.58	-74.00	21.60
cc-ReN	2.679	900.0	122.0	128.0	381.3	203.7	0.27	0.53	-6.00	19.45
NbO-CrN	3.802	724.9	123.2	146.9	323.8	196.6	0.25	0.61	-23.72	21.94
NbO-MnN	3.744	683.9	156.9	131.4	332.6	174.3	0.28	0.52	25.55	17.04
NbO-MoN	4.096	763.6	115.3	139.6	331.4	197.1	0.25	0.59	-24.28	21.47
NbO-TcN	4.030	686.0	169.6	131.6	341.7	173.0	0.28	0.51	37.94	16.30
NbO-WN	4.092	857.9	123.1	172.5	368.1	234.7	0.24	0.64	-49.36	26.30
NbO-ReN	4.041	761.0	200.9	149.5	387.6	192.7	0.29	0.50	51.37	17.24
pyrite-PtN_2	4.792	845.0	101.0	160.0	349.0	226.0	0.23	0.65	-59.00	26.06

Database

Cubic forms of 3d, 4d and 5d transition metal nitrides in M:N ratios from 4:1 to 1:1 to 1:3. Dark green regions have completed *ab initio* results!

Structures	Formula	Stoichiometry	3d	4d	5d
M_4N	M_4N	4:1			
Anti-ReO3	M_3N	3:1			
Zincblende	MN	1:1			
Rocksalt	MN	1:1			
Cesium chloride	MN	1:1			
NbO	MN	1:1			
Spinel	M_3N_4	0.75:1			
Fluorite	MN_2	0.5:1			
Pyrite	MN_2	0.5:1			
Skutterudite	MN_3	0.33:1			

Summary

- Computed single crystal V, C_{11}, C_{12}, C_{44}, LDOS and band structures
- Multi-crystal average of B, G, E, ν, k, H_V, θ_D, T_m.
- Showed correlations of hardness and ductility
- Importance of spread out bands and bonding between M-p orbitals and N-d orbitals
- Inverse correlation of DOS at E_F and C_{44} or stability

Future

- Create Web database of 10 cubic binary nitride phases
- Some search ability will exist
- Hexagonal structures
- Ternaries

Hexagonal structures

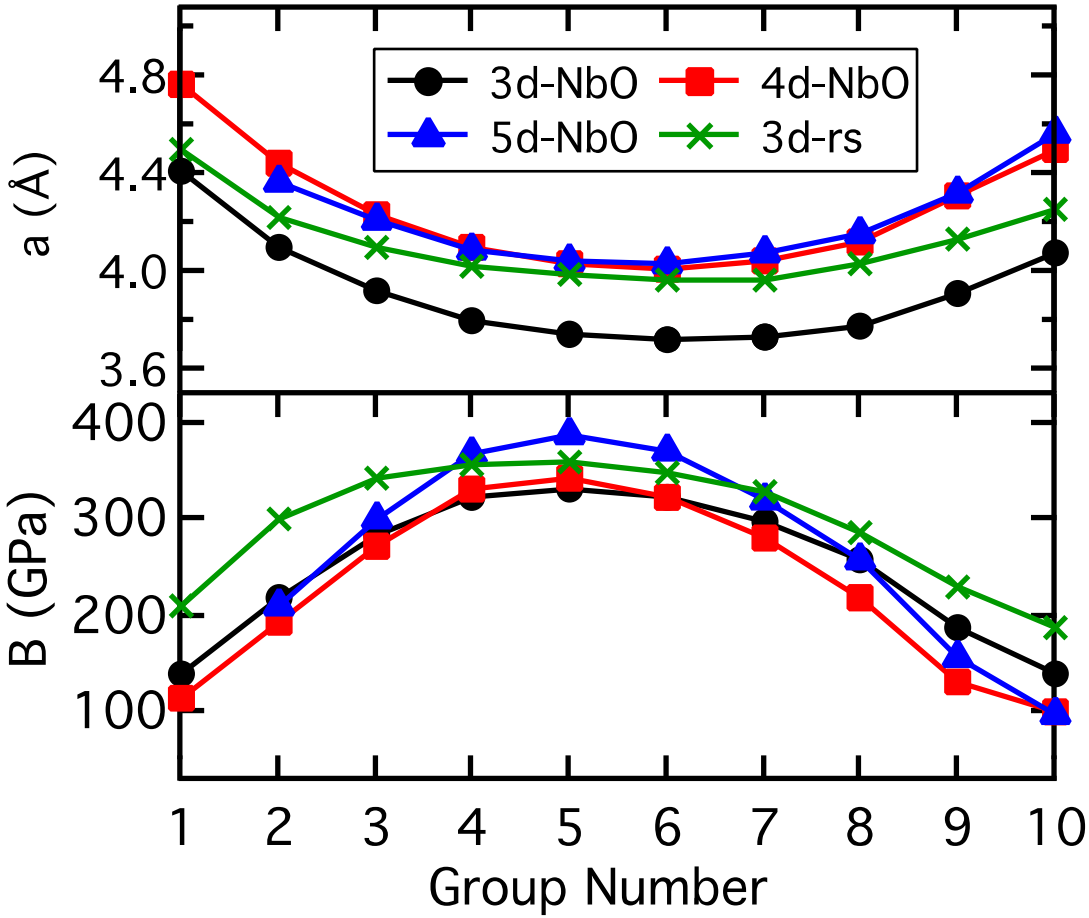
- Apart from the cubic phases, there are also **experimental** studies of hexagonal structures.
  - AlN, I. W. Kim *et al.*, Appl. Phys. Lett. **78**, 892, (2001)
  - IrN_2, A. F. Young *et al.*, Phys. Rev. Lett. **96**, 155501, (2006)
  - ReN_2, F. Kawamura *et al.*, Appl. Phys. Lett. **100**, 251910, (2012)
  - Re_3N, A. Friedrich *et al.*, Phys. Rev. B **82**, 224106, (2010)

Ternary systems

- TM-TM-N:
  - Ti-V-N, Ti-Nb-N, Ti-Mo-N, Ti-W-N, Ti-Ta-N, V-W-N, V-Mo-N, V-Ta-N, D. G. Sangiovanni *et al.*, Acta Mater. **59**, 2121, (2011).
- TM-non-TM-N:
  - Ti-Al-N, P. H. Mayrhofer *et al.*, Appl. Phys. Lett. **83**, 2049, (2003).

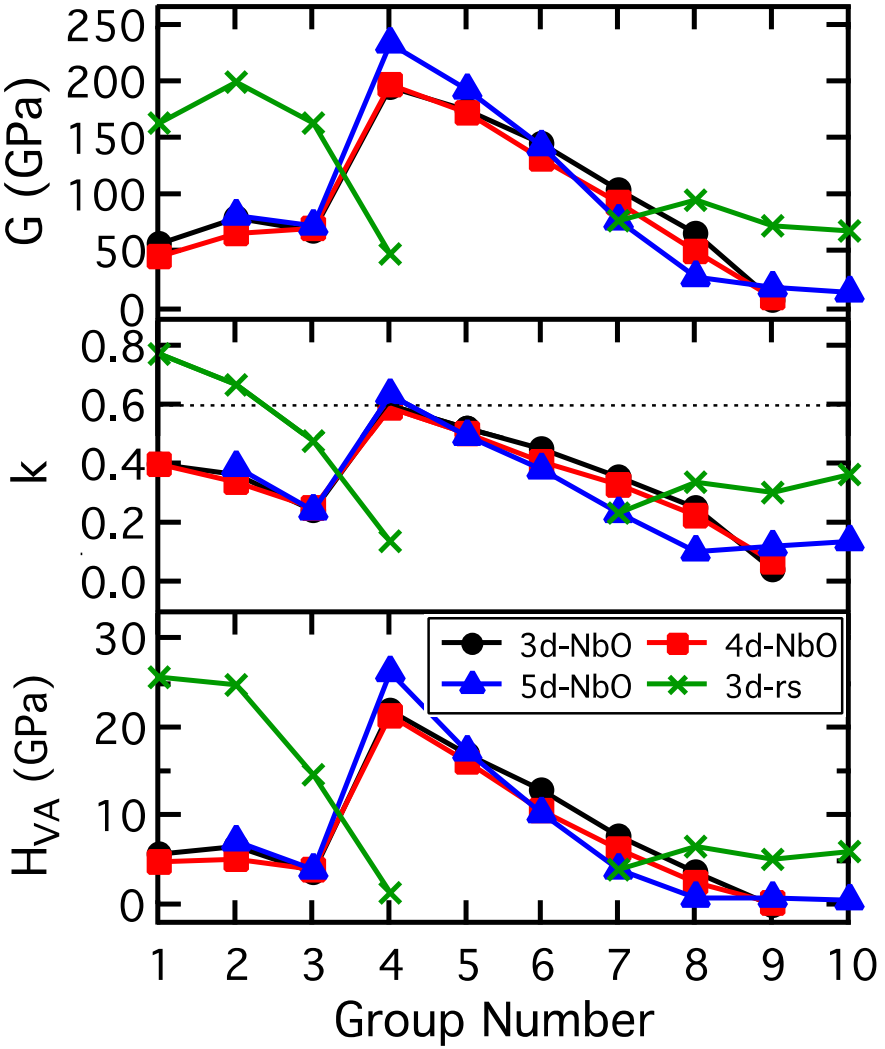
Thank you!

a (lattice constant) and *B* (bulk modulus)



$$B = (C_{11} + 2C_{12})/3$$

G, *k* and H_{VA}



G (Shear modulus)

$G_V = [(C_{11} - C_{12}) + 3C_{44}]/5$

$G_R = [5(C_{11} - C_{12})C_{44}]/(4C_{44} + 3C_{11} - 3C_{12})$

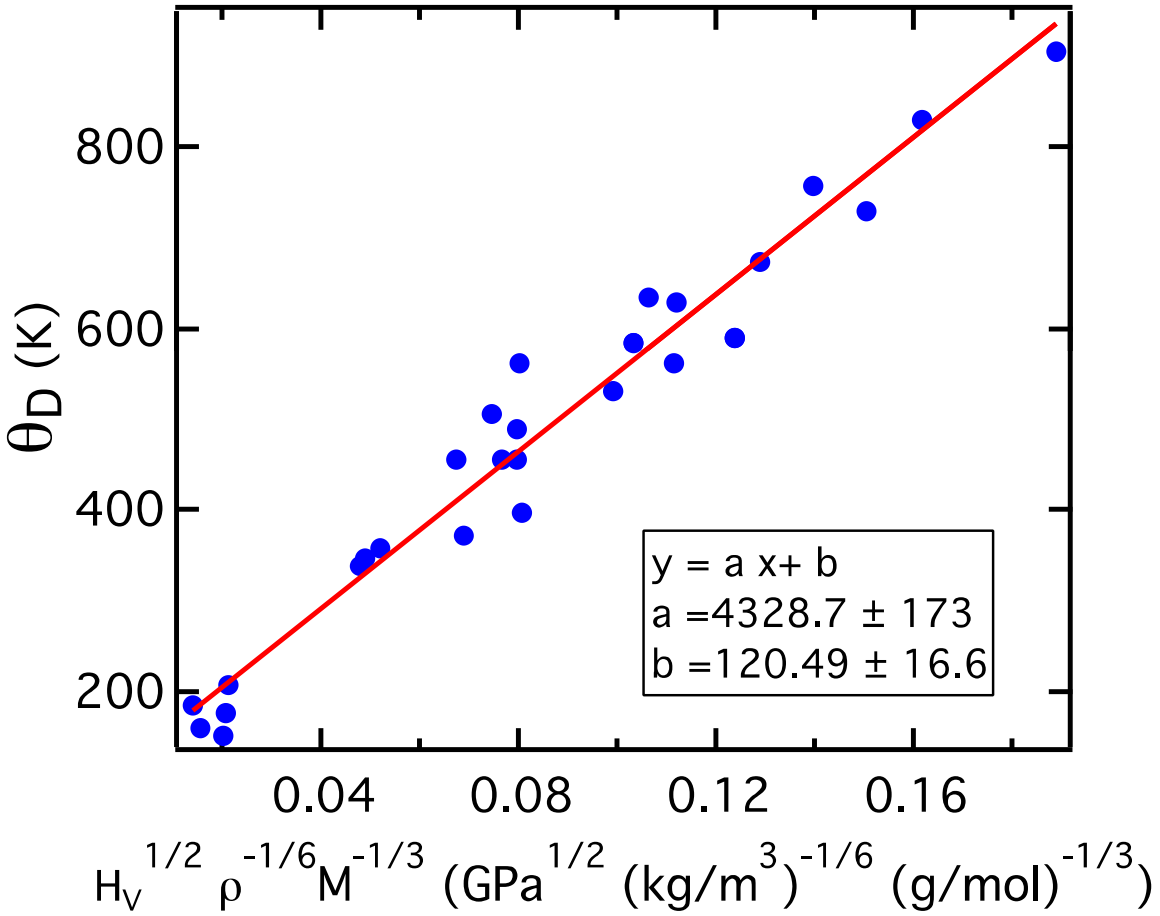
$G = G_{VRH} = (G_V + G_R)/2$

k (Pugh's ratio)

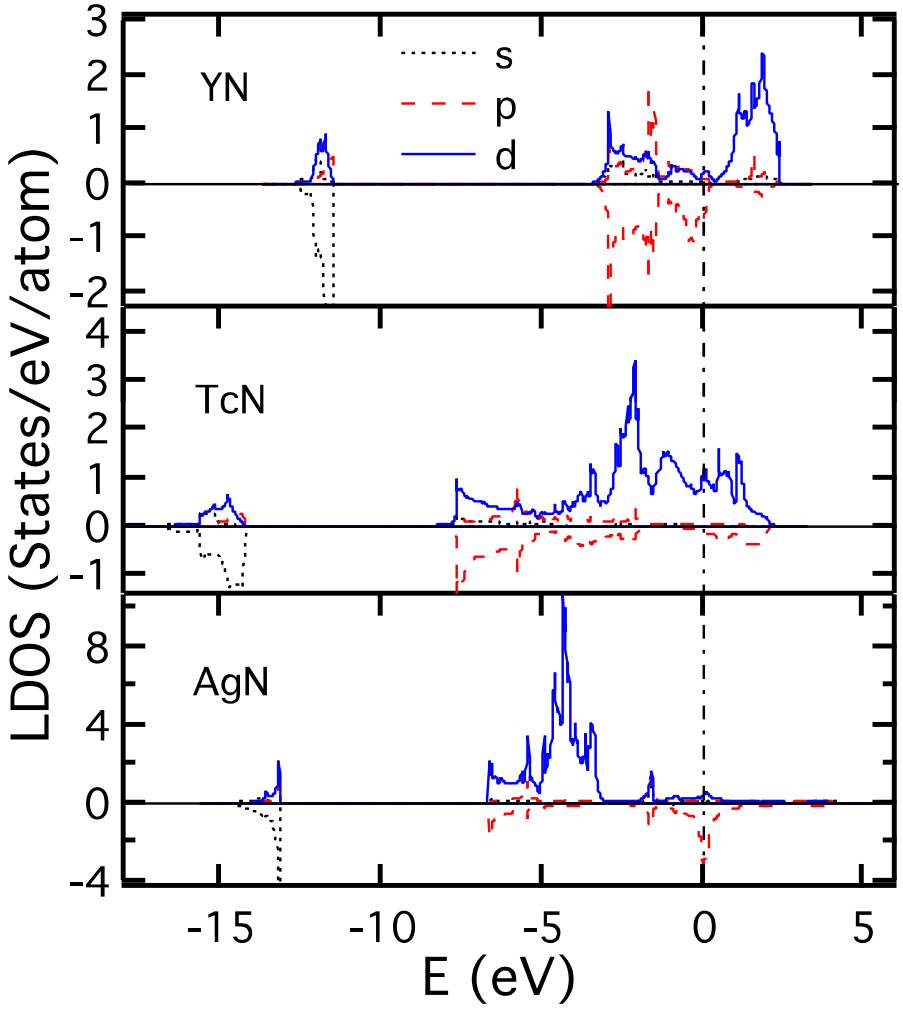
$k = G/B$

$H_{VA} = 0.92\, k^{1.137}\, G^{0.708}$

θ_D (Debye temperature) vs $f(H_{VA})$

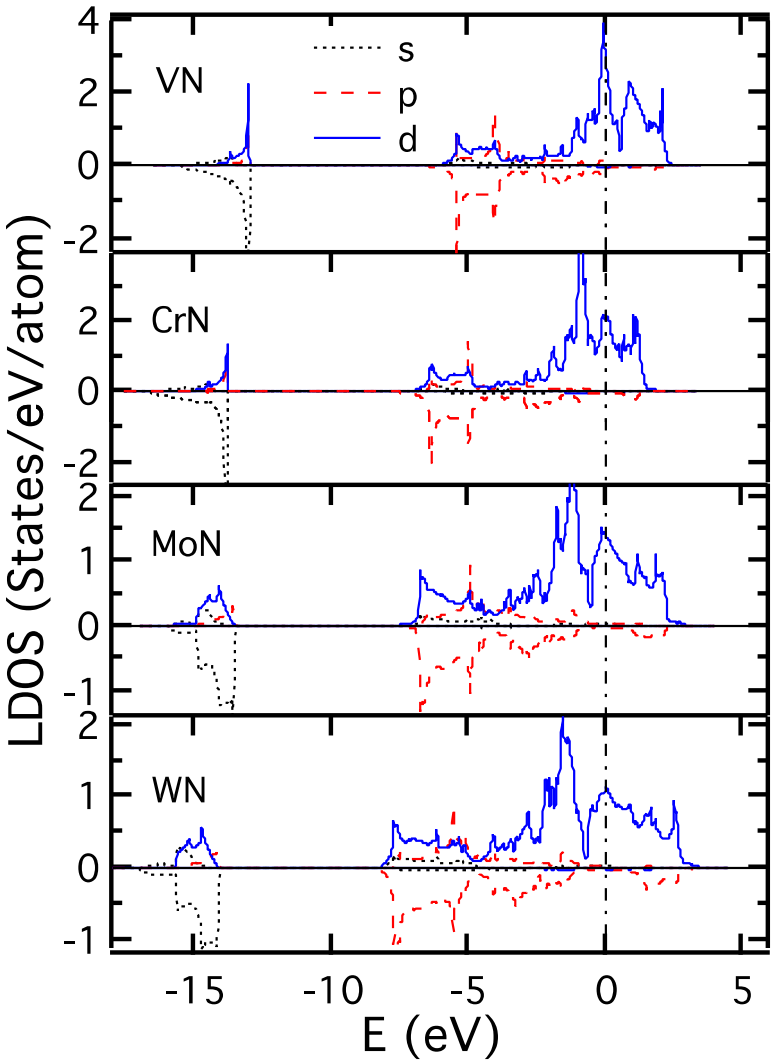


LDOS



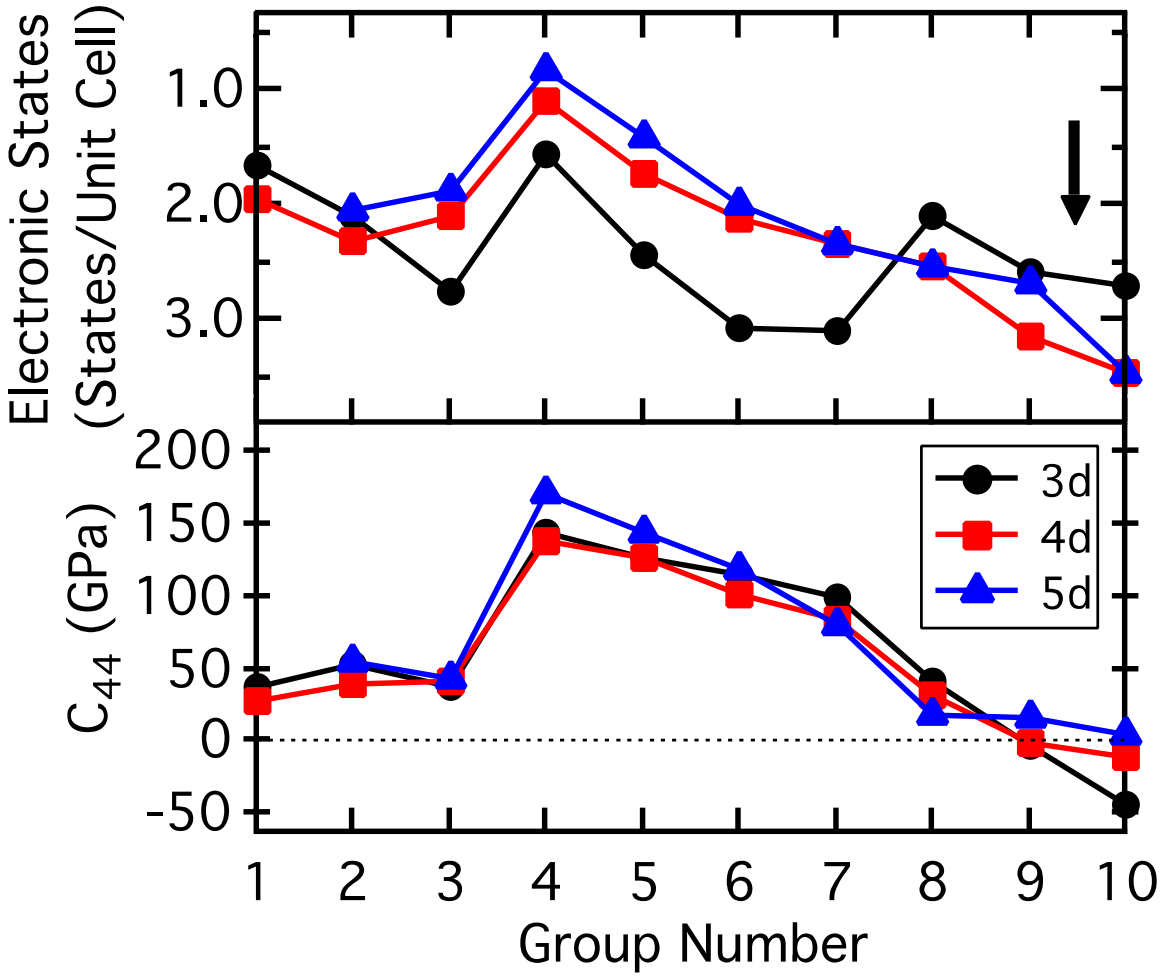
As transition metal goes from left to right in the 4d row, more states shift below E_F, peaks becoming sharper.

LDOS

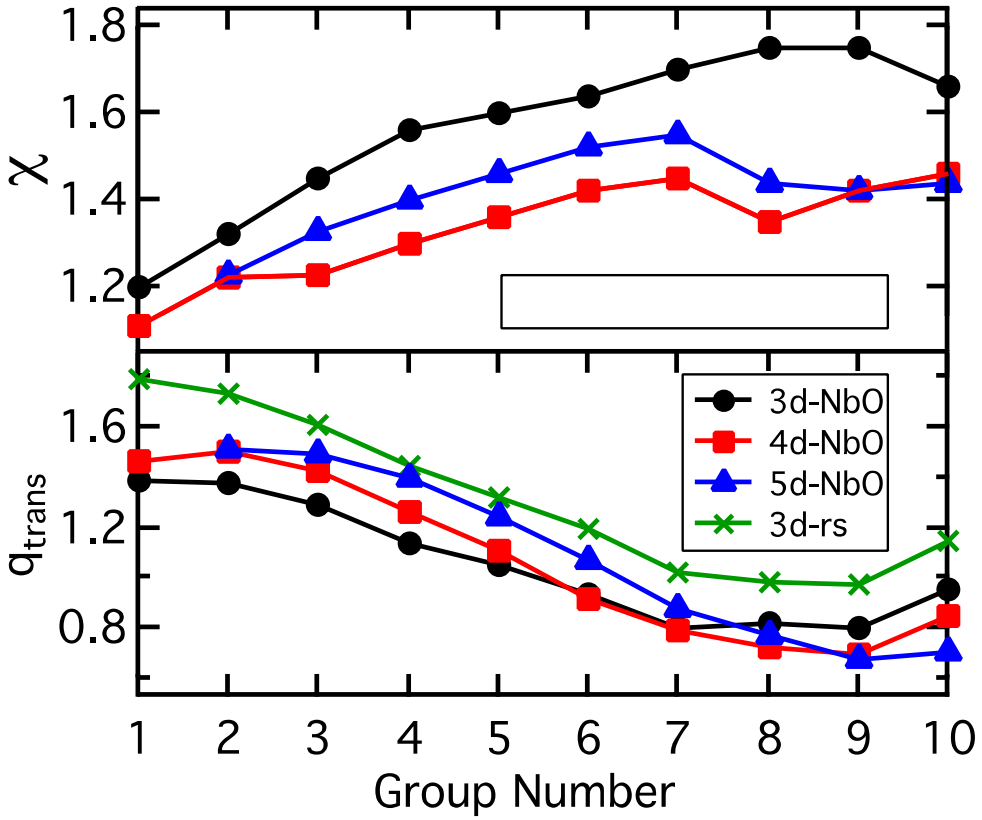


As transition metal goes from top to bottom in the group 4 column, almost nothing evident changes.

Correlation of C_{44} (indicating H_V and stability) with TDOS



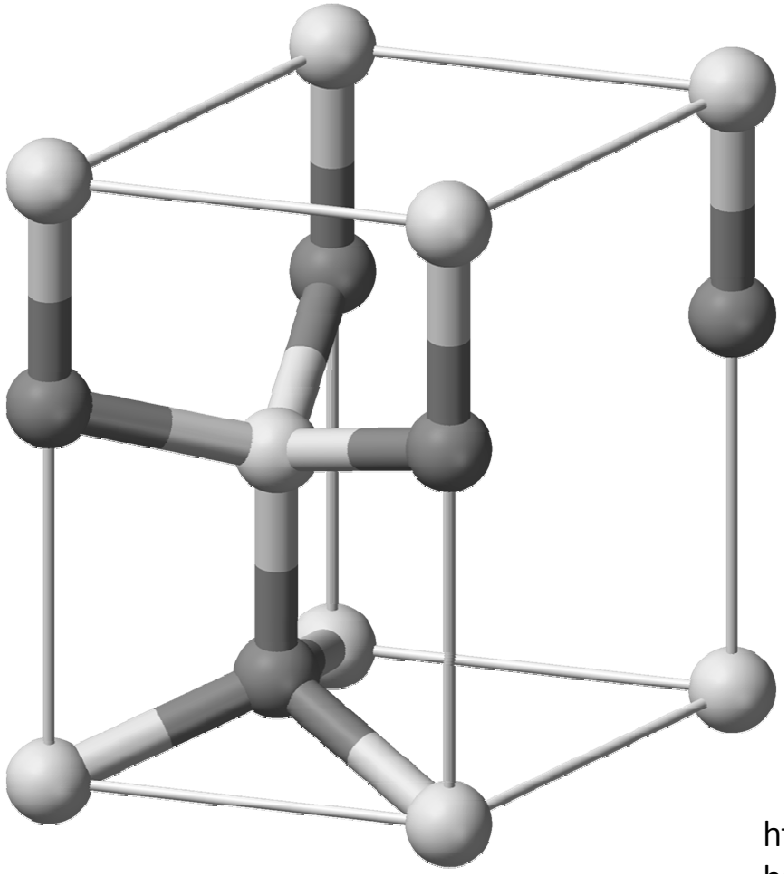
Bader analysis



χ (electronegativity)
q_{trans} (charge transfer from transition metal to nitrogen using Bader's scheme)

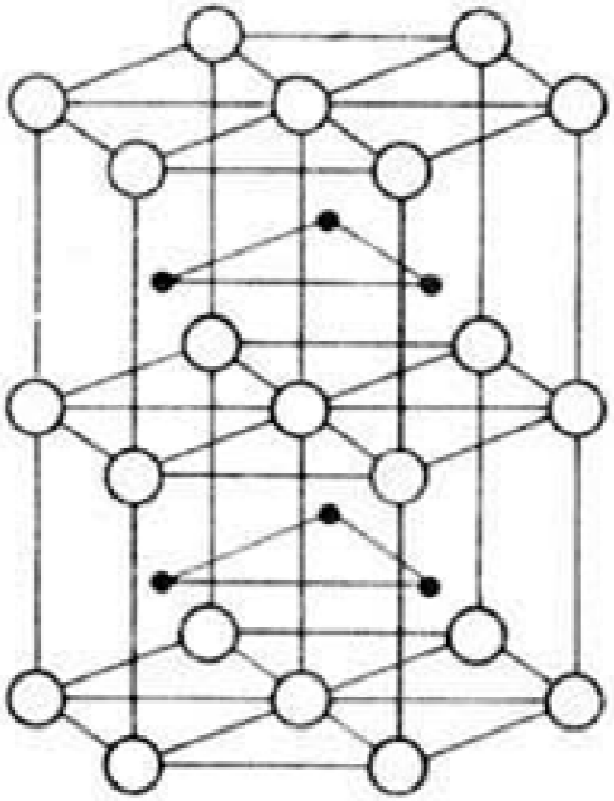
W. Tang *et al.*, J. Phys.: Condens. Matter 21, 084204 (2009)
E. Sanville *et al.*, J. Comp. Chem. 28, 899-908 (2007)
G. Henkelman *et al.*, Comput. Mater. Sci. 36, 254-360 (2006)

Hexagonal structures
Structure - wurtzite (MN)



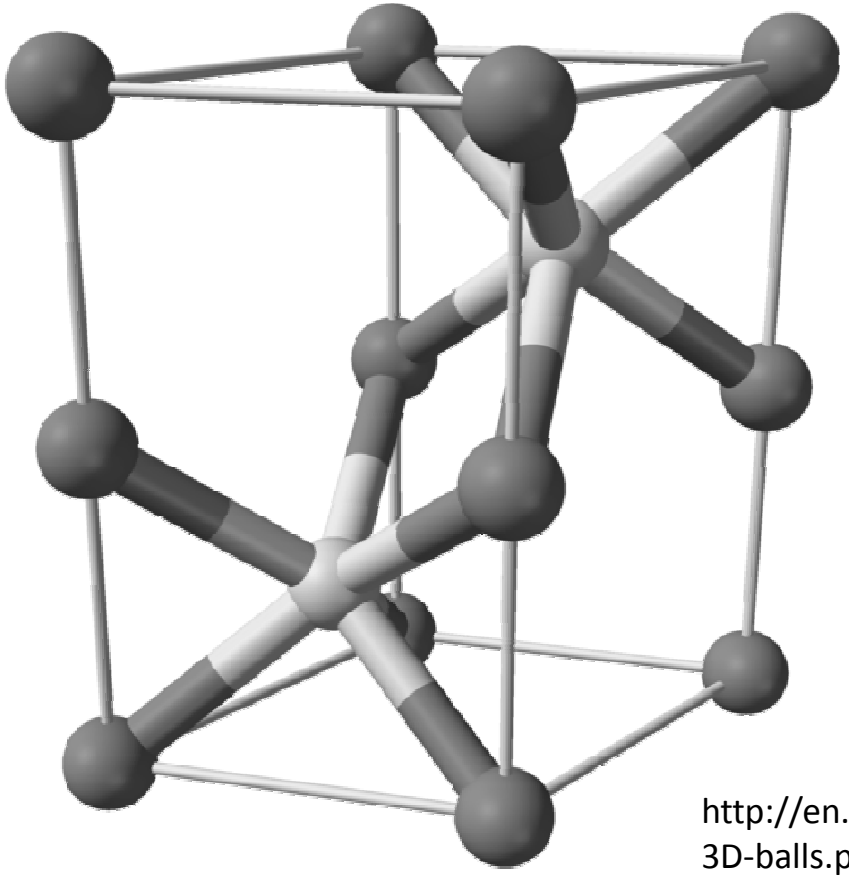
http://en.wikipedia.org/wiki/File:Wurtzite-unit-cell-3D-balls.png

Structure – WC (MN)



http://www.ls-carbide.com/About%20tungsten%20carbide.html

Structure – NiAs (MN)

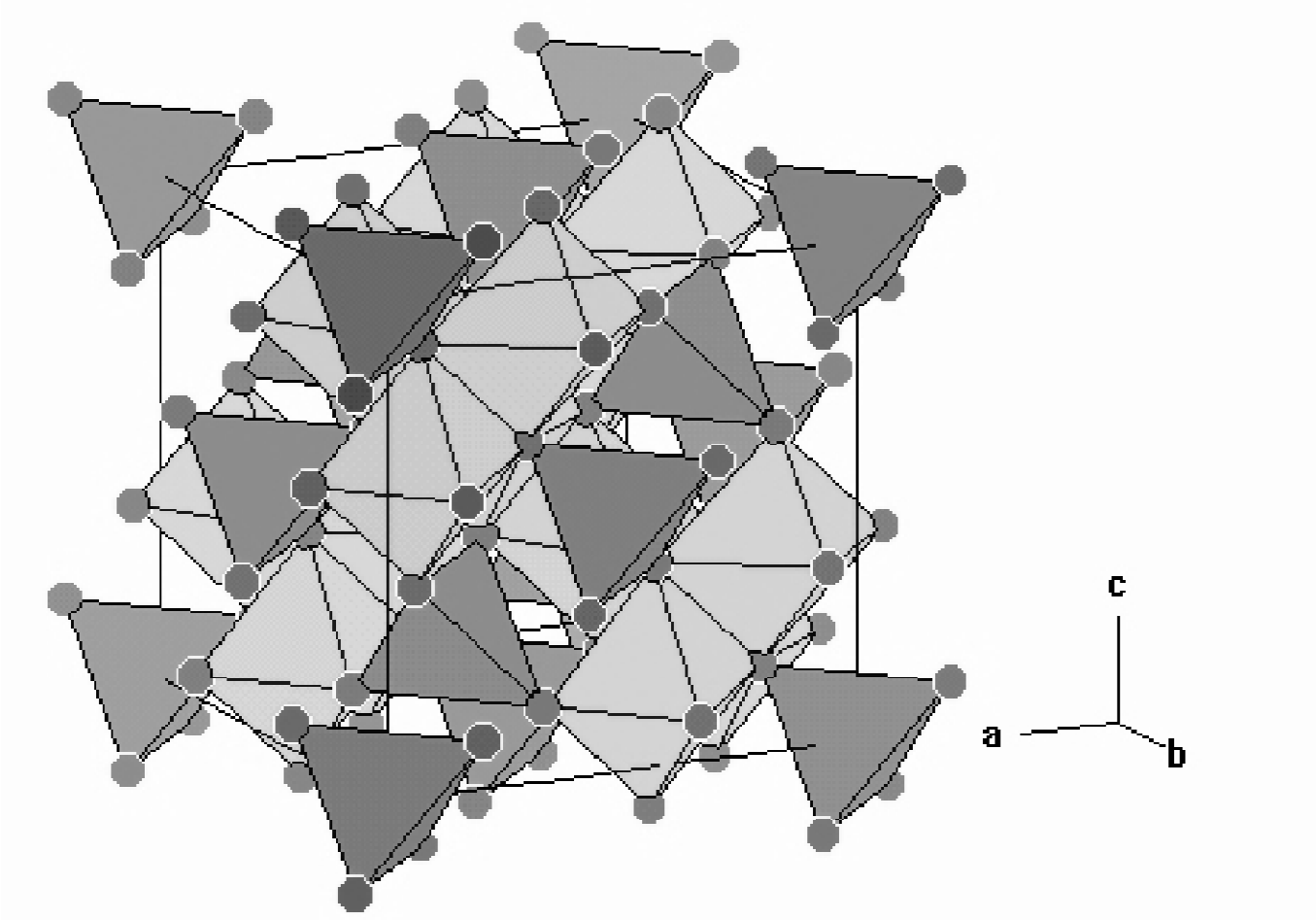


http://en.wikipedia.org/wiki/File:Iron(II)-sulfide-unit-cell-3D-balls.png

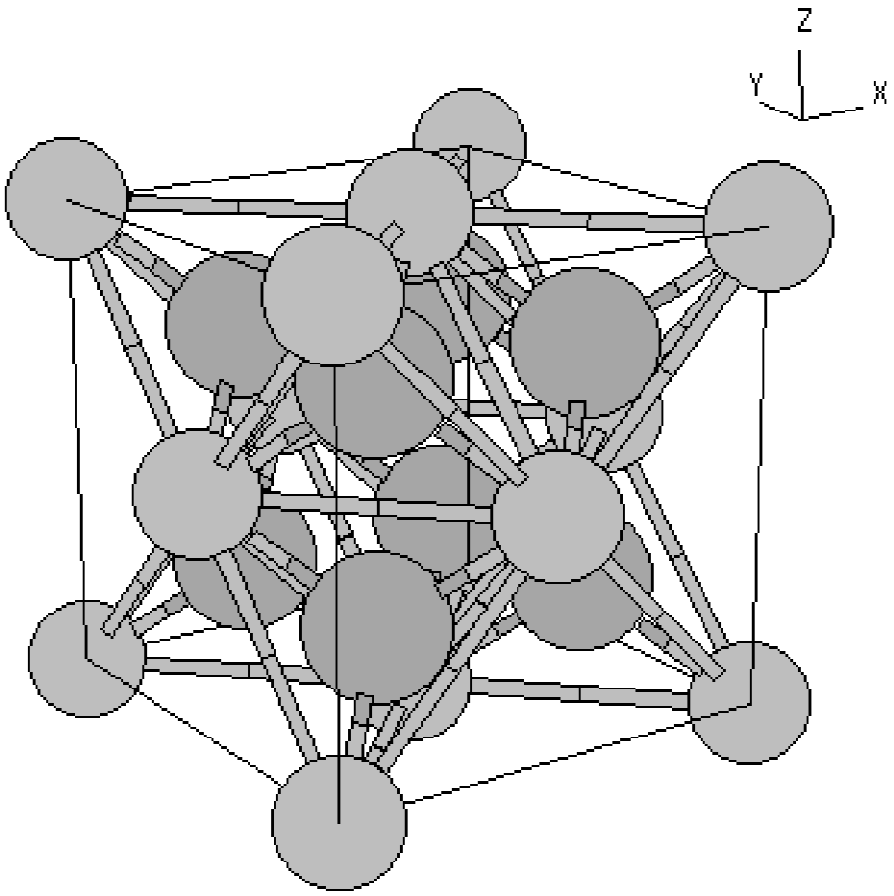
Ab initio method details

- Vienna Ab initio Simulation Package (VASP)
- Ultra-soft Vanderbilt pseudo potentials (US-PP)
- Local-density approximation (LDA) and general gradient approximation (GGA) were used and mean values used
- kinetic energy cutoff value: 450 eV
- The electronic self-consistent loops converge below 10^{-4} eV/atom
- 12 × 12 × 12 Monkhorst-Pack mesh, and denser mesh for DOS
- Murnaghan equation of state used for equilibrium lattice constant
- Three independent strains applied and a set of three equations solved for elastic constants

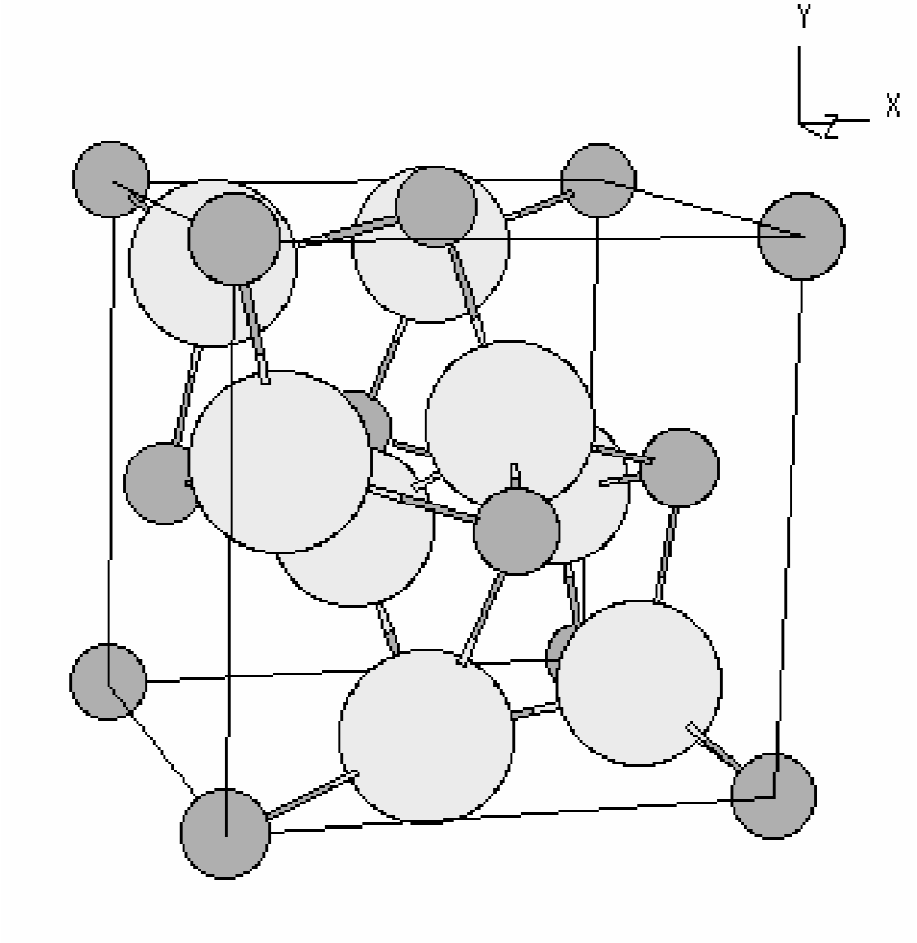
Structure – spinel (M_3N_4)



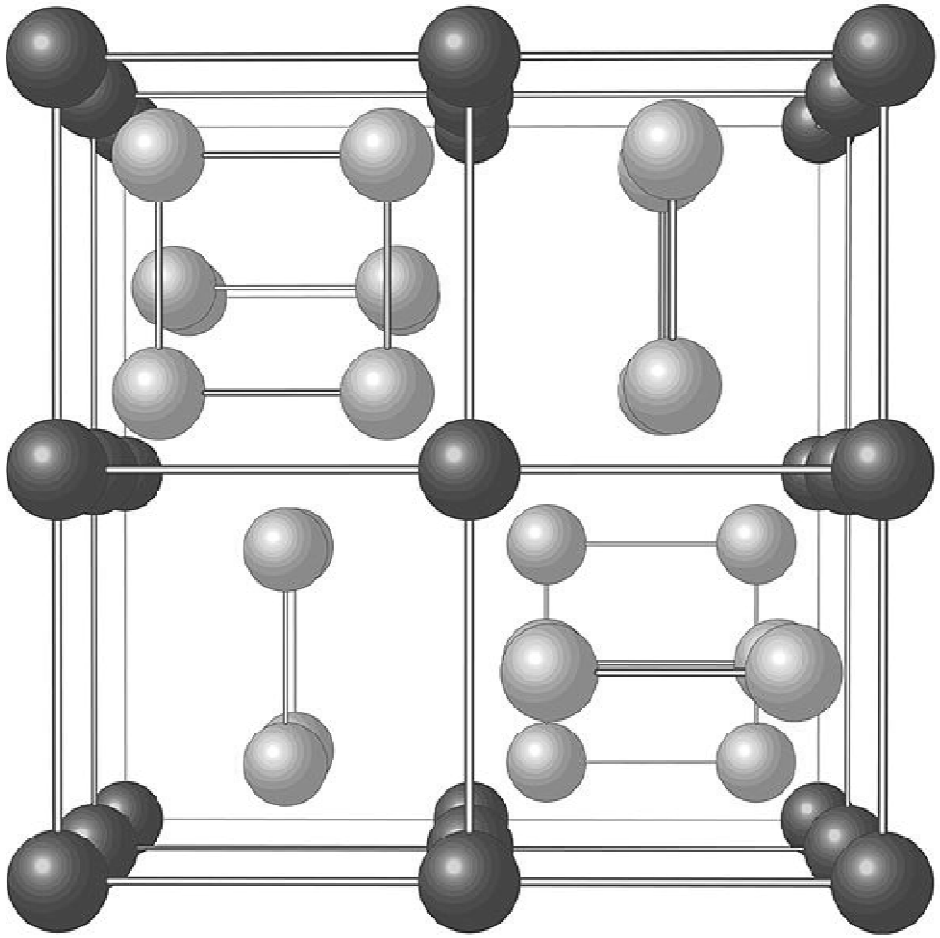
Structure – fluorite (MN_2)



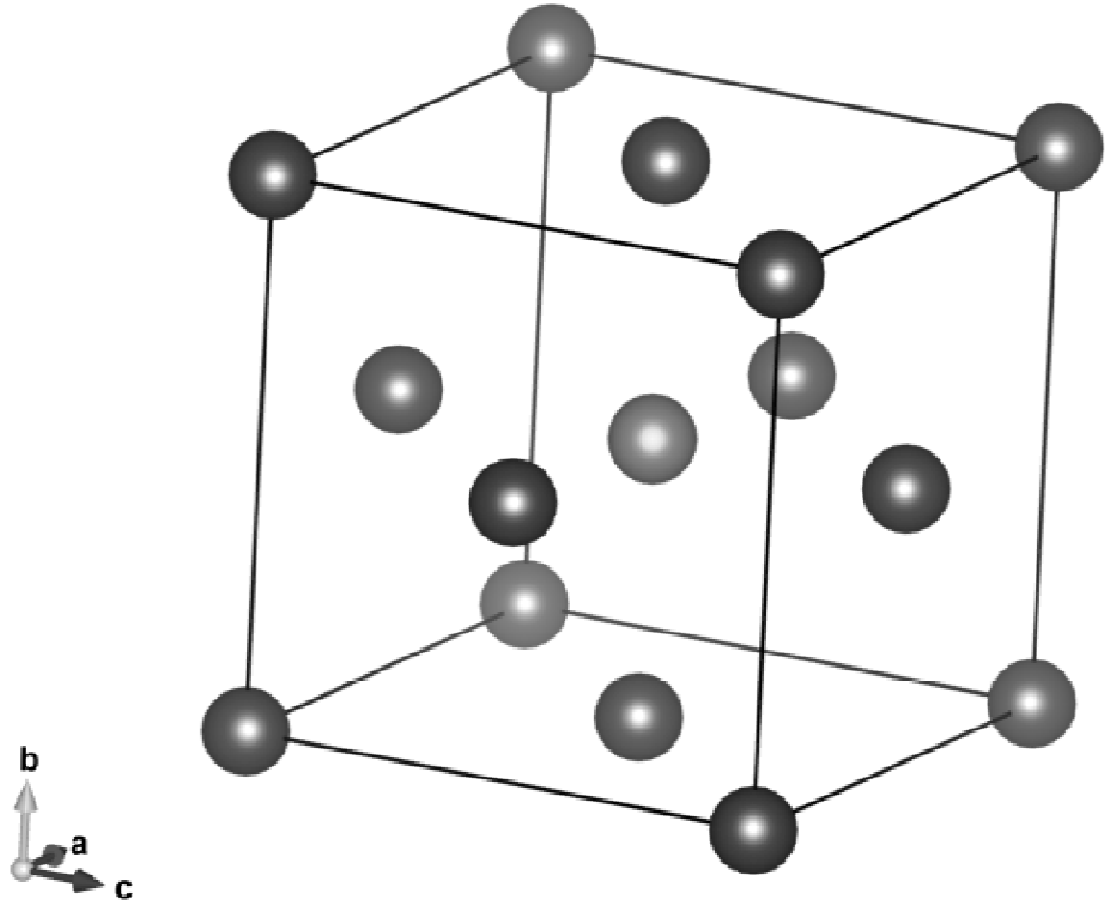
Structure – pyrite (MN_2)



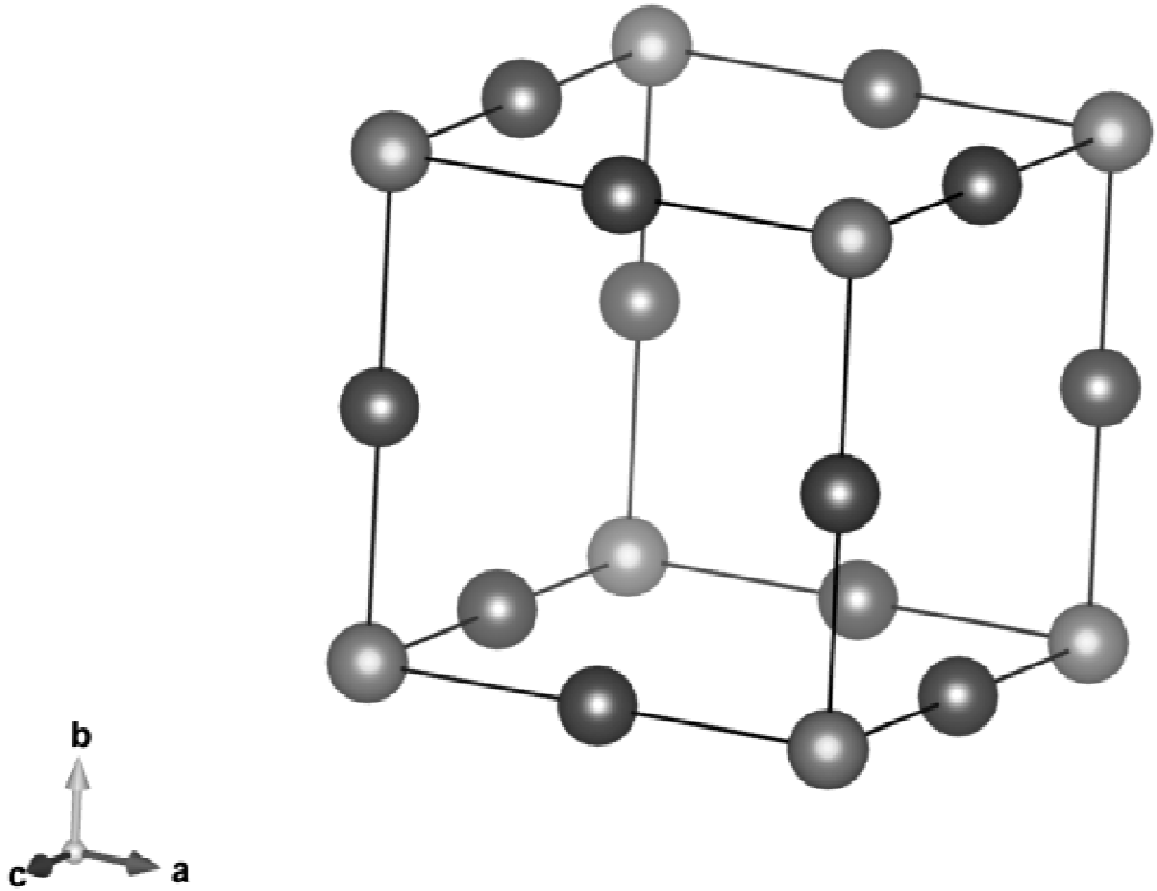
Structure – skutterudite (MN_3)



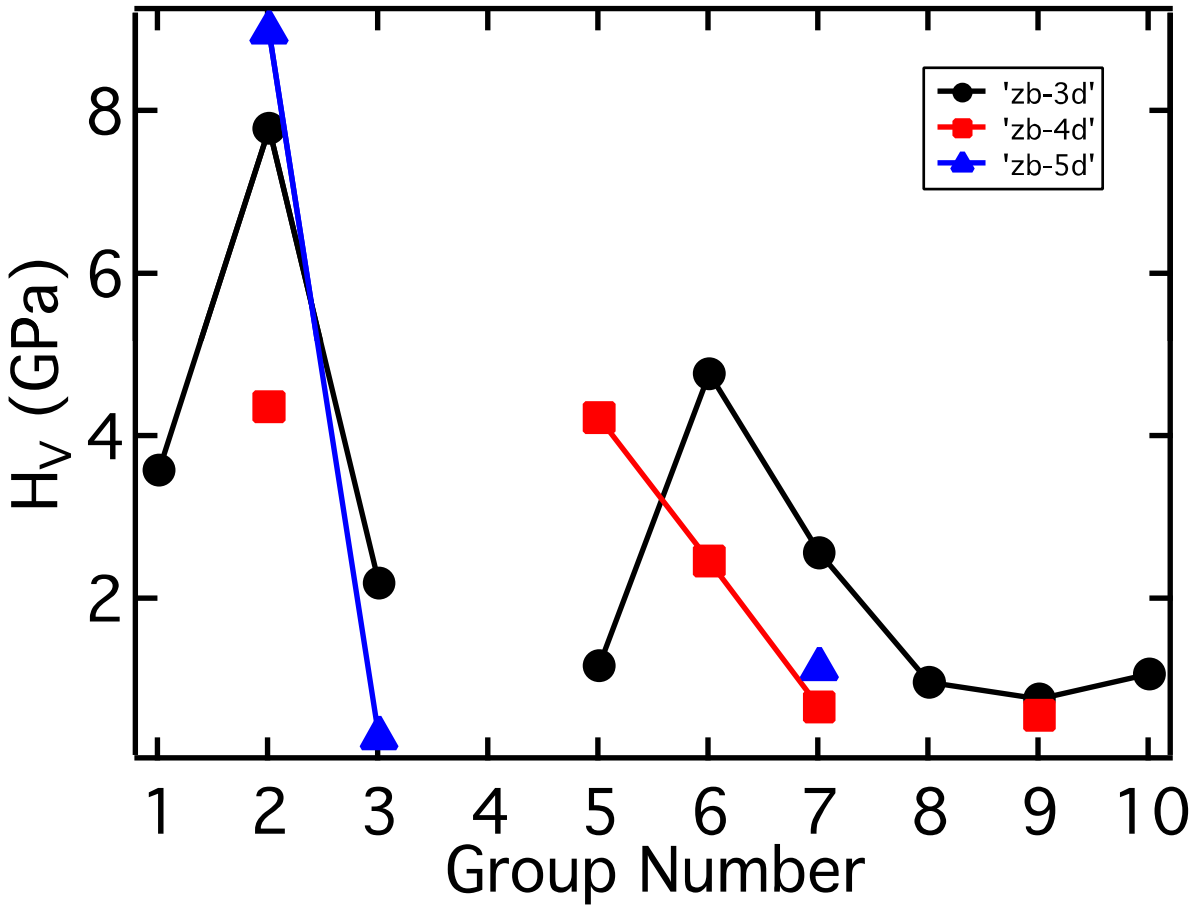
Structure – M_4N



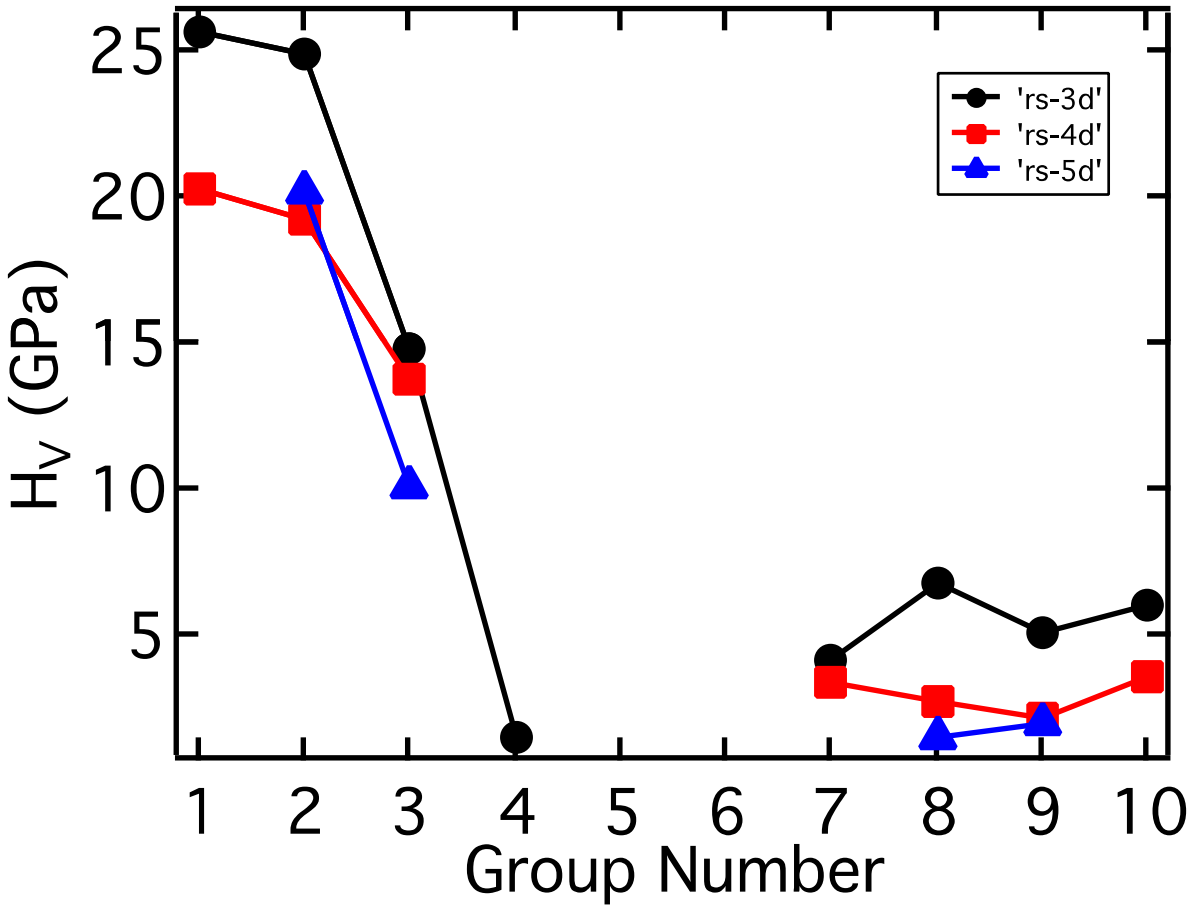
Structure – anti-ReO3 (M_3N)



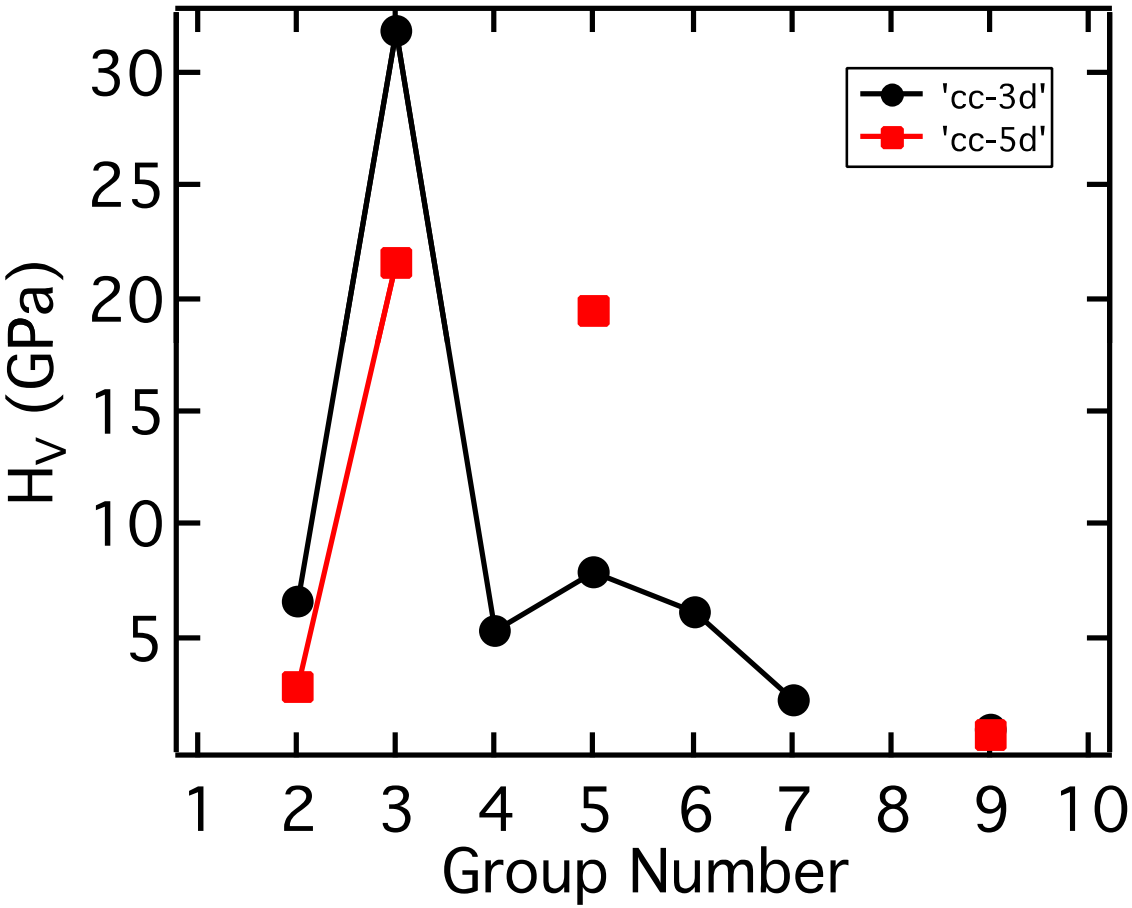
Structure - zincblende (MN)



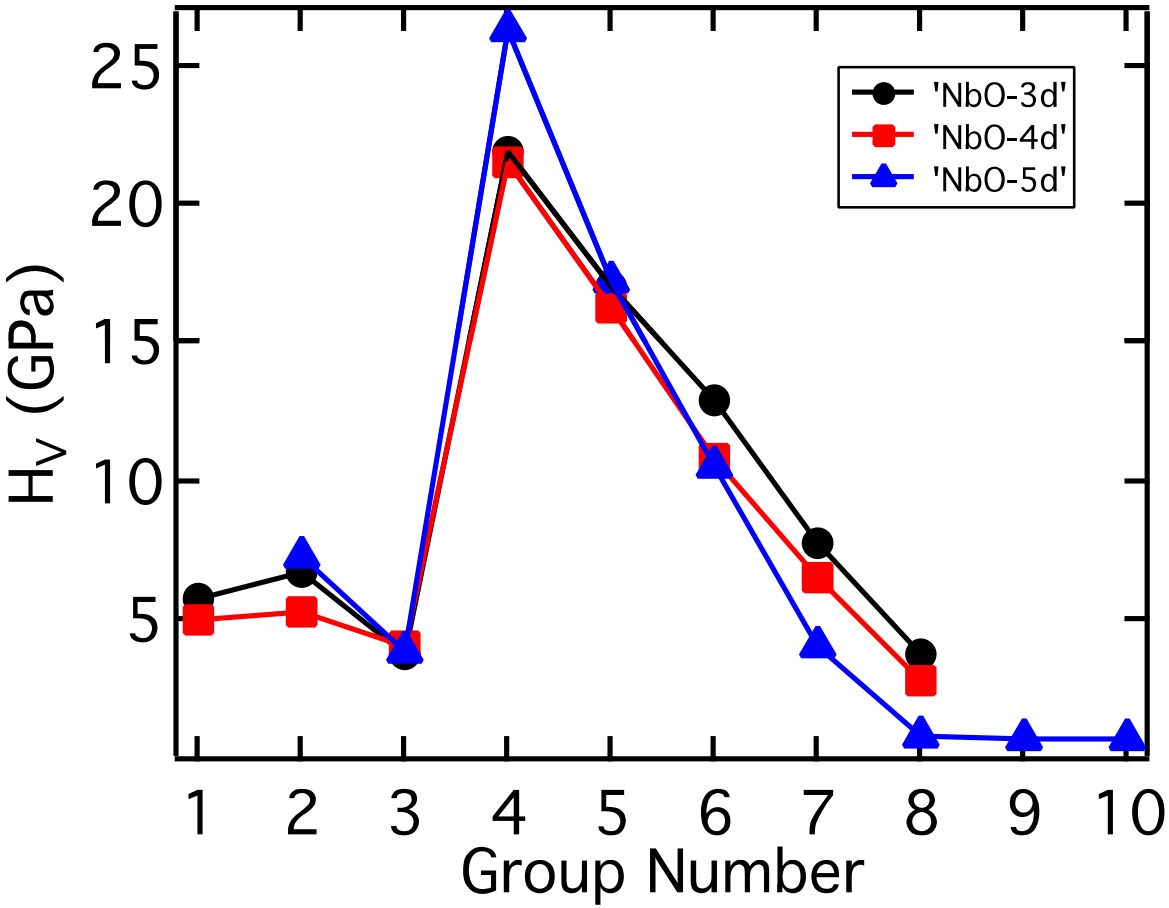
Structure - rocksalt (MN)



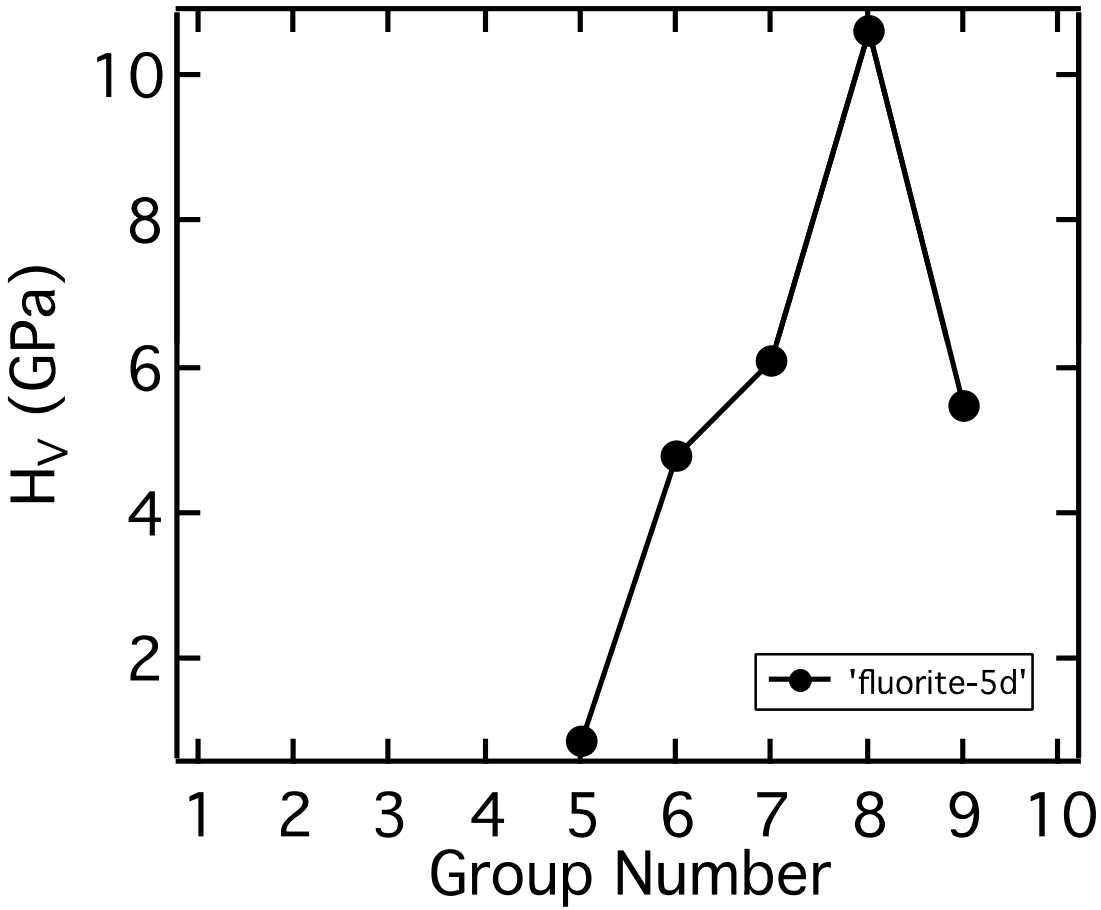
Structure - cesium chloride (MN)



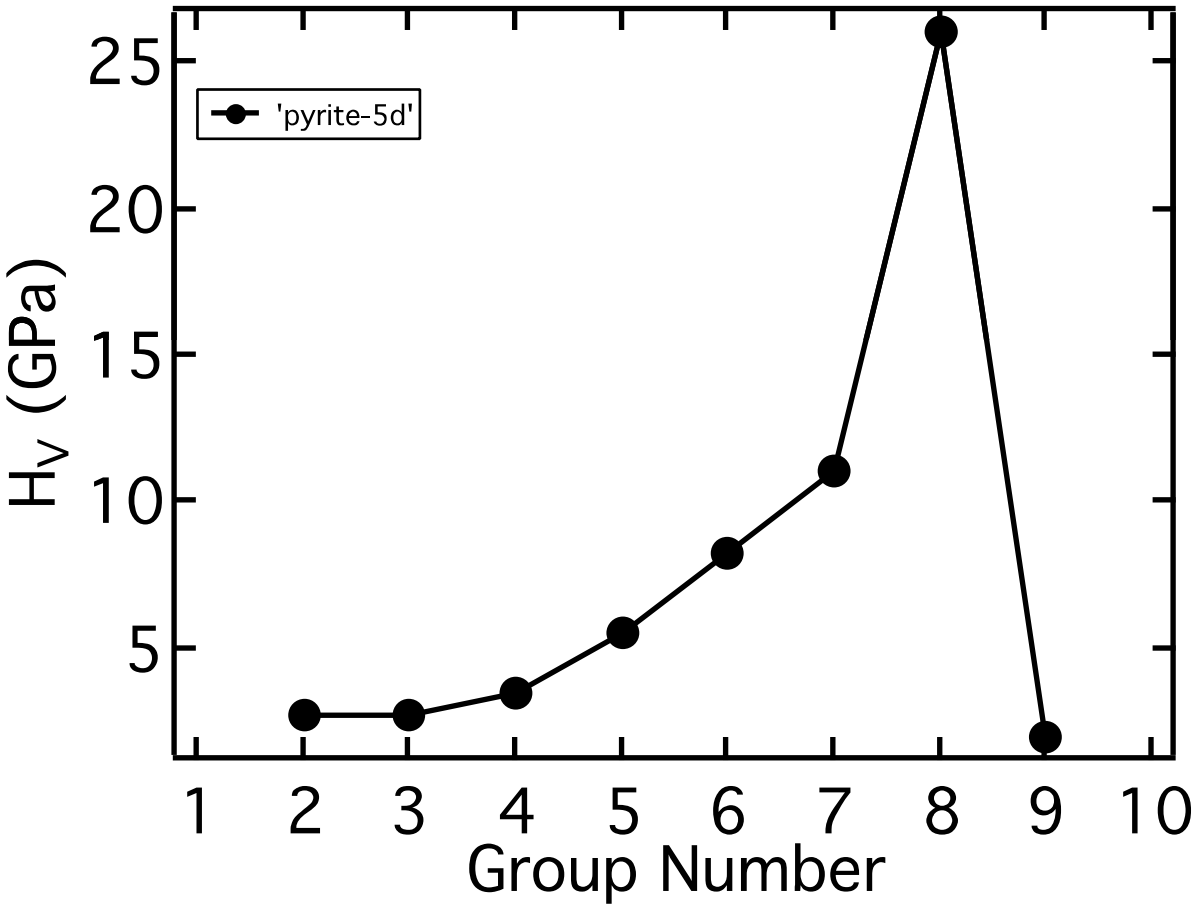
Structure - NbO (MN)



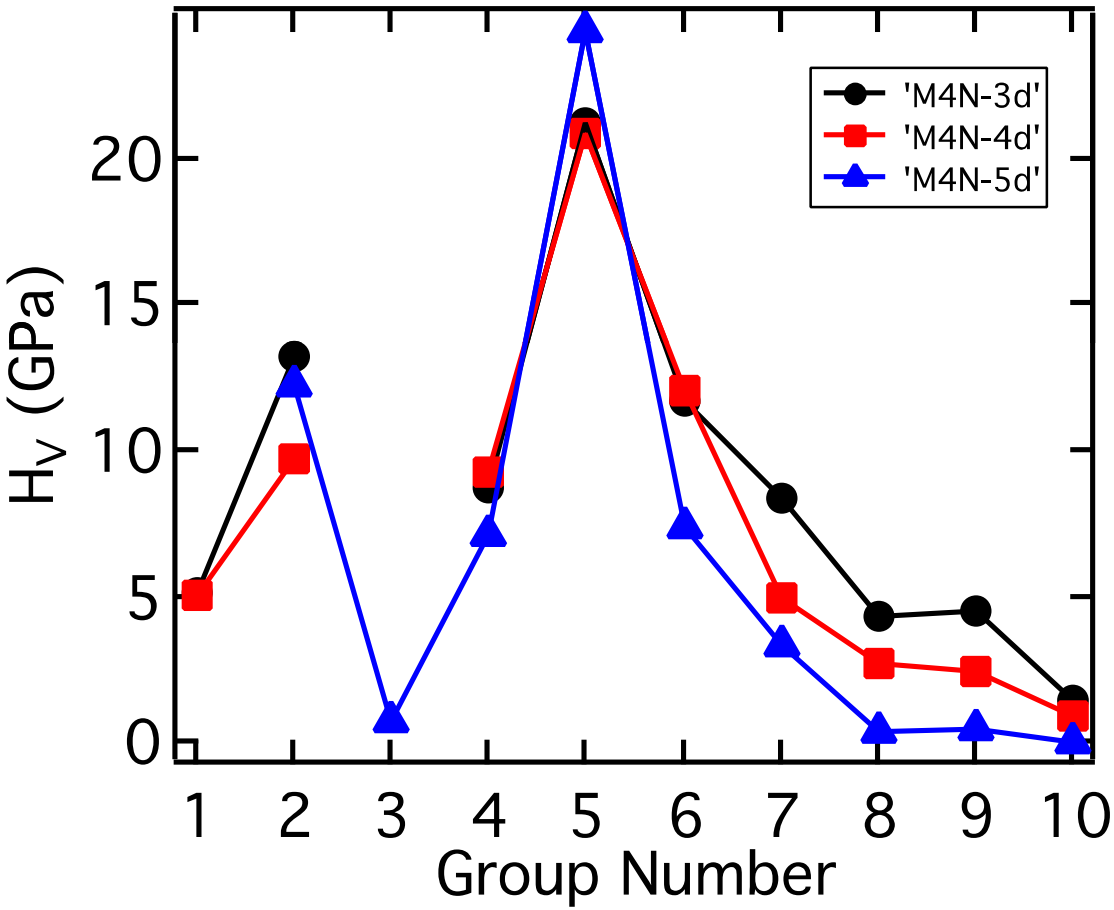
Structure - fluorite (MN_2)



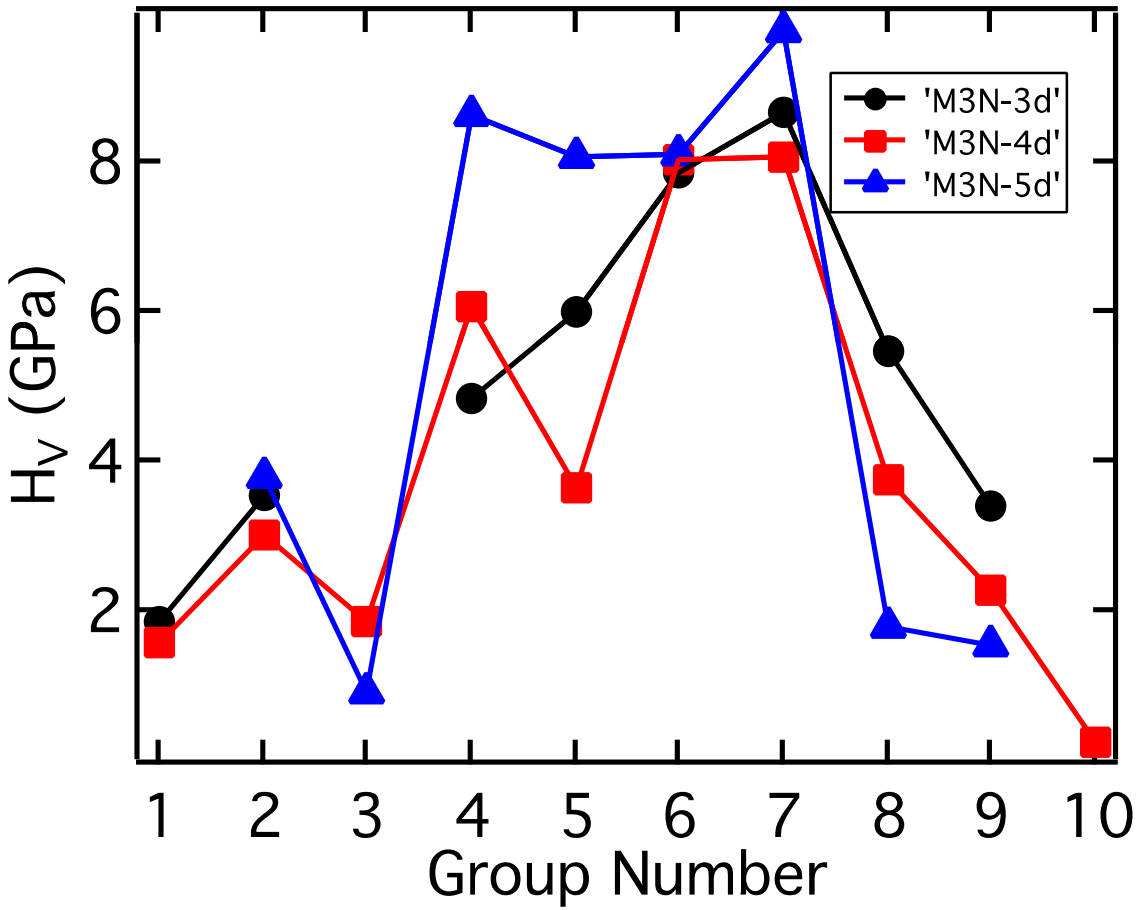
Structure - pyrite (MN_2)



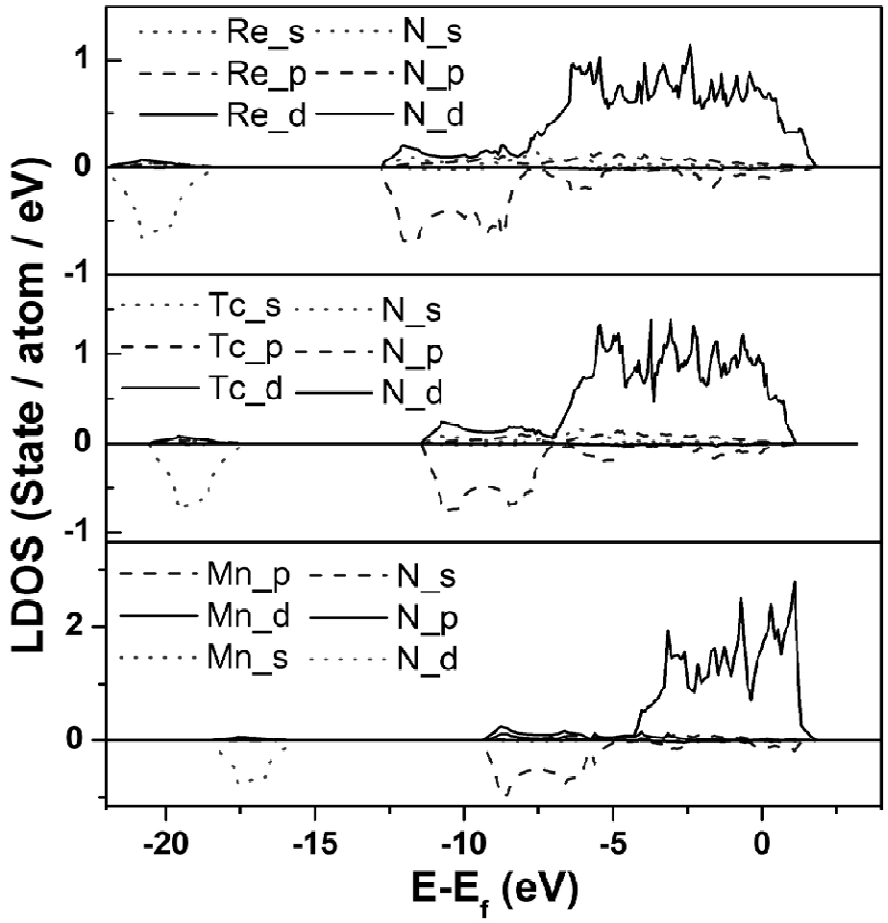
Structure - M_4N



Structure - anti-ReO_3 (M_3N)



LDOS of M_4N


Re_s
N_s
Re_p
N_p
Re_d
N_d
Tc_s
N_s
Tc_p
N_p
Tc_d
N_d
Mn_p
N_s
Mn_d
N_p
Mn_s
N_d
LDOS (State / atom / eV)
E-E$_f$ (eV)
1
0
-1
2
-20
-15
-10
-5
0

Value of *ab initio* method

- Powerful predictive tool to calculate properties of materials
- Fully first principles ==>
  - (1) no fitting parameters, use only fundamental constants (e, h, m_e, c) as input
  - (2) Fully quantum mechanical for electrons
- Thousands of materials properties calculated to date
- Used by biochemists, drug designers, geologists, materials scientists, and even astrophysicists!
- Evolved into different varieties for ease of applications
- Awarded chemistry Nobel Prize to W. Kohn and H. Pople 1998

Thank you!