

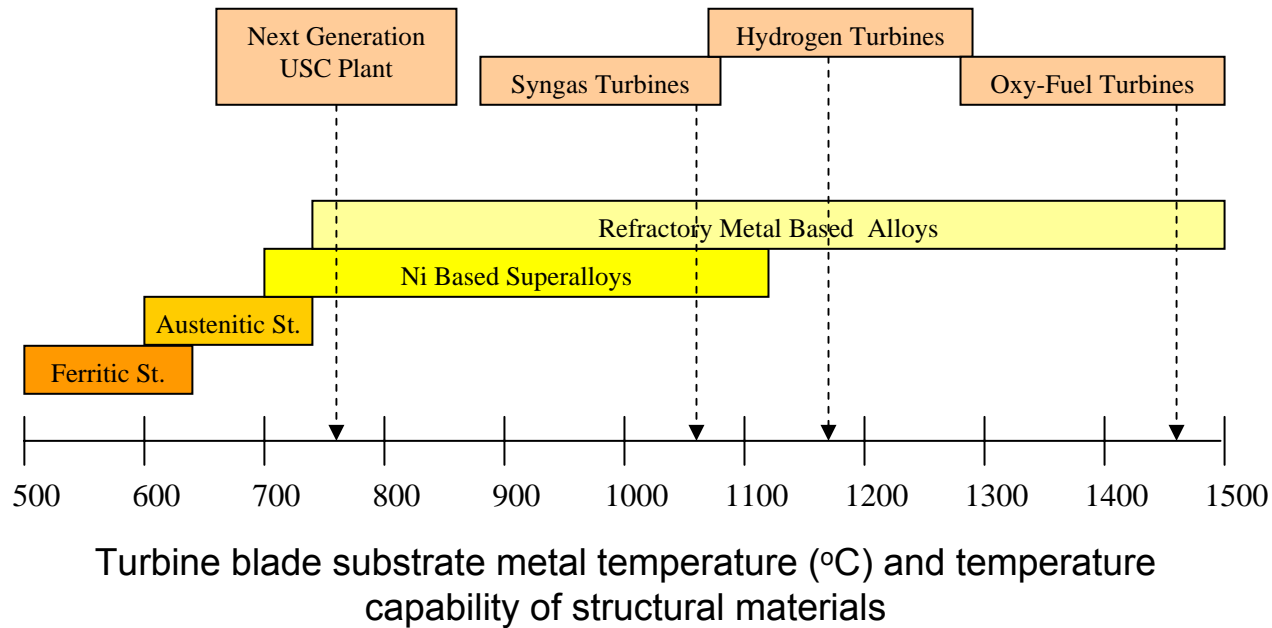


Integrated Design and Rapid Development of Refractory Metal Based Alloys for Fossil Energy Applications

Ömer Doğan, Michael Gao, Paul King



New Energy Generating Technologies and High-Temperature Structural Materials



Refractory Metals and Ni

	Melting T °C	Density g/cm ³
Ni	1455	8.9
Cr	1863	7.2
V	1910	6.1
Rh	1963	12.4
Hf	2231	13.3
Ru	2334	12.4
Ir	2447	22.6
Nb	2469	8.6
Mo	2623	10.2
Ta	3020	16.6
Os	3033	22.6
Re	3186	21.0
W	3422	19.3

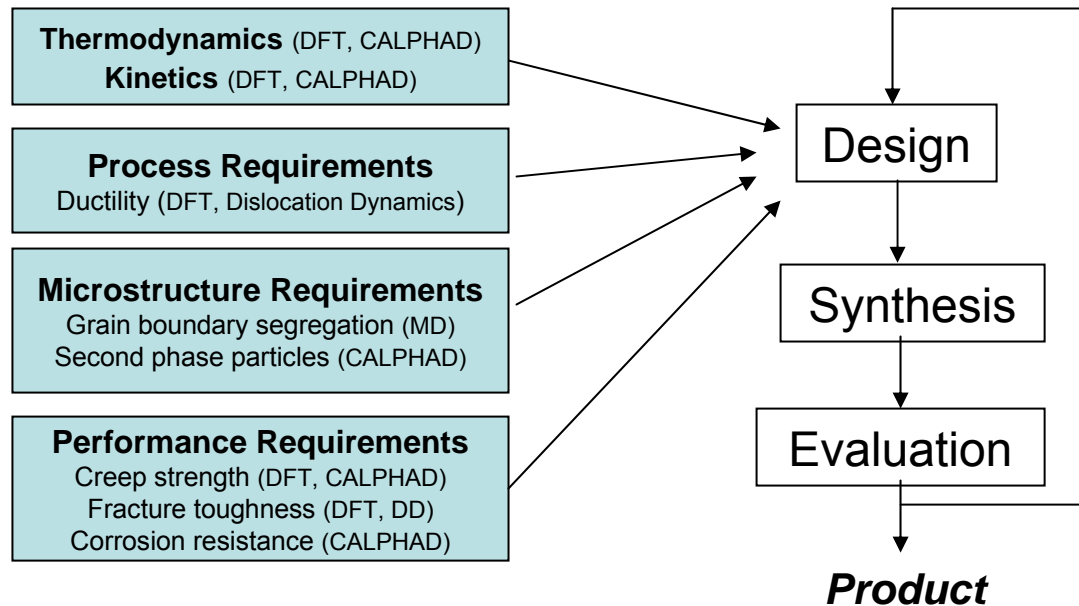
Major issues with refractory metals

- Low ductility and fracture toughness at low temperatures
- Poor oxidation resistance at high temperatures

Integrated Design of Refractory Metal Based Alloys For Fossil Energy Applications

The project goal is to develop refractory metal based alloys utilizing integrated design approach.

Integrated design uses computational methods with experimental verification and available knowledge base to design alloys according to the requirements of processing, microstructure and properties.



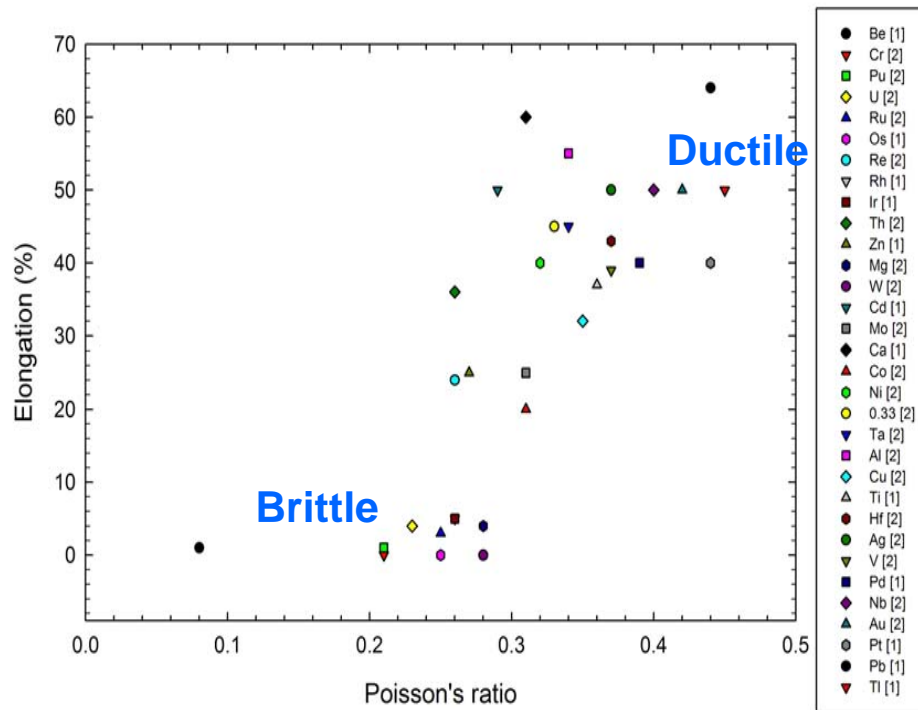
As a result of integrated design, the efficient development of materials requires much less experimental work, thus reducing the time and cost involved in alloy development.

Integrated Design of Refractory Metal Based Alloys for Fossil Energy Applications

- **Improving ductility and fracture toughness through substitutional alloying**
- **Thermodynamic evaluation of promising systems**
- **Kinetic evaluation of relevant alloy systems**
- **Grain boundary segregation of C, N, O, and S in the refractory alloys**
- **Ductile – Brittle transition (DBT) in refractory alloys**
- **Improving creep strength**
- **Improving high temperature oxidation resistance**

Improving ductility and fracture toughness through substitutional alloying

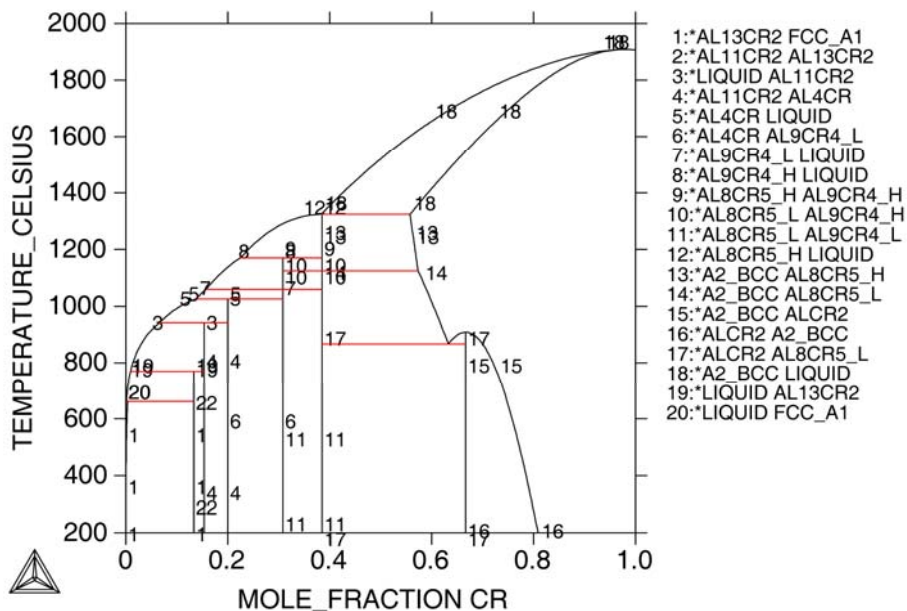
- First principles quantum mechanical calculations
- Experimental verification: tensile & fracture toughness



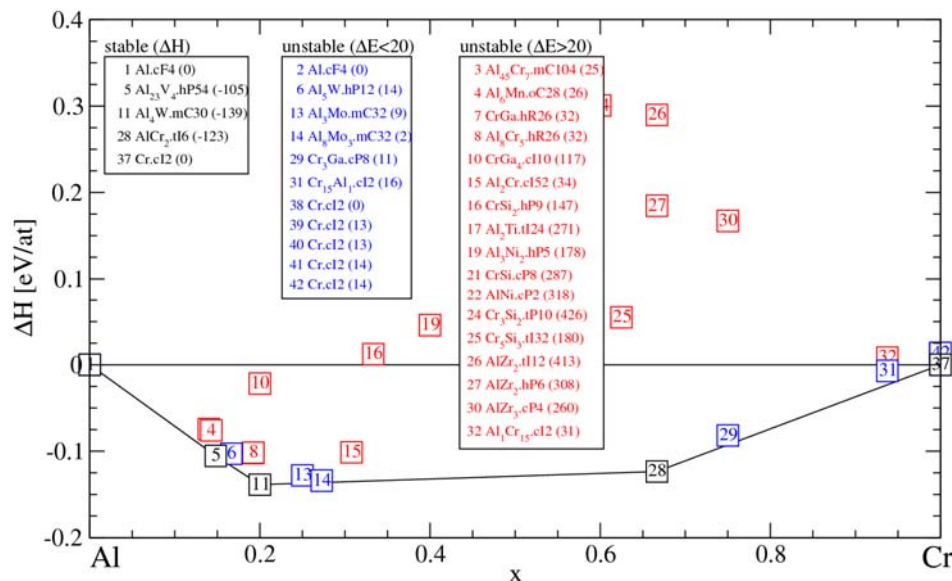
Thermodynamic evaluation of promising systems

- DFT calculations & CALPHAD modeling
- Experimental verification: Thermal analysis, XRD, TEM, SEM

THERMO-CALC (2008.06.18:14.20) :AL-CR
 DATABASE:SSOL4
 N=1, P=1E5;



Al-Cr from CALPHAD modeling



Enthalpy convex hull plot of Al-Cr from first principles DFT calculations

An efficient and reliable way to study phase diagrams is to combine first principles DFT calculations, critical experiments and CALPHAD modeling.

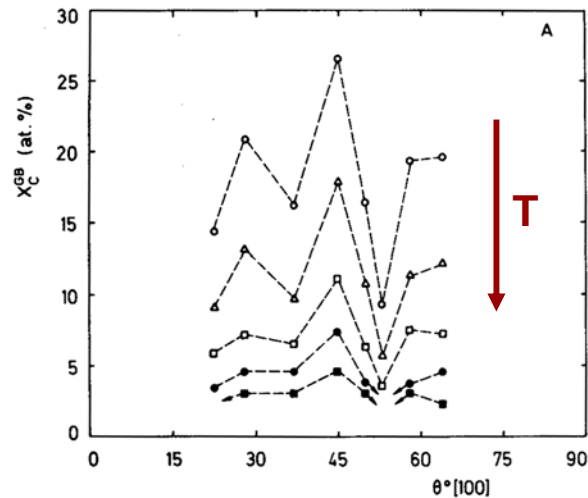
Kinetic evaluation of relevant alloy systems

- **DFT calculations of diffusivities (CMU)**
 - Interstitial (O, N and C) diffusion in refractory metal based alloys will be studied using first-principles quantum-mechanical calculations
- **Experimental diffusivity measurements (CMU)**
 - Substitutional diffusion coefficients for promising systems will be measured and incorporated into the DICTRA kinetic database

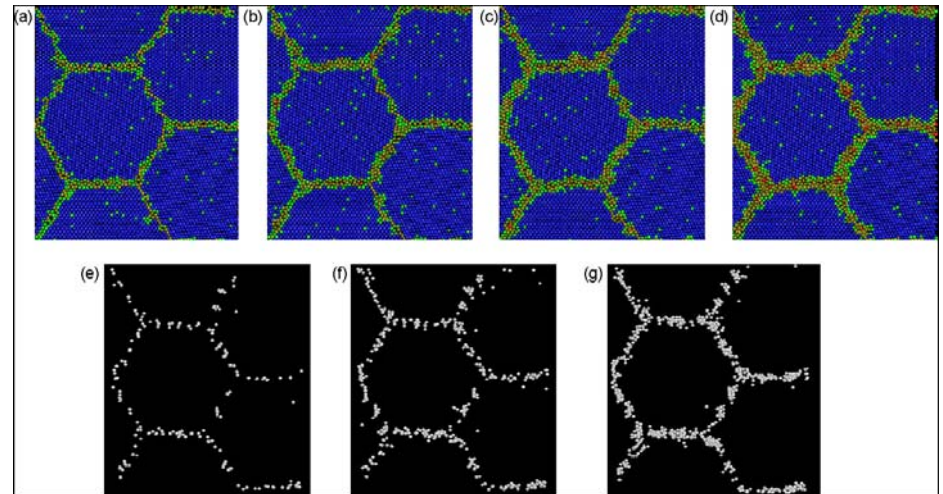
Grain boundary segregation of C, N, O, and S in the refractory alloys

- Molecular dynamic simulations coupled with DFT calculations
- Experiments: HRTEM, Analytical TEM

Carbon concentration as a function of misorientation of adjacent grains



Hofman: Surf interf Ana 19 (1992) 601



(a–d) Simulations of Al-Pb microstructures for 0–3 at.% Pb, respectively. (e–g) The Pb atom positions highlighted for frames (b–d), respectively.

S. Jang, et al., Mater. Sci. Eng. A (2008), doi:10.1016/j.msea.2007.05.130

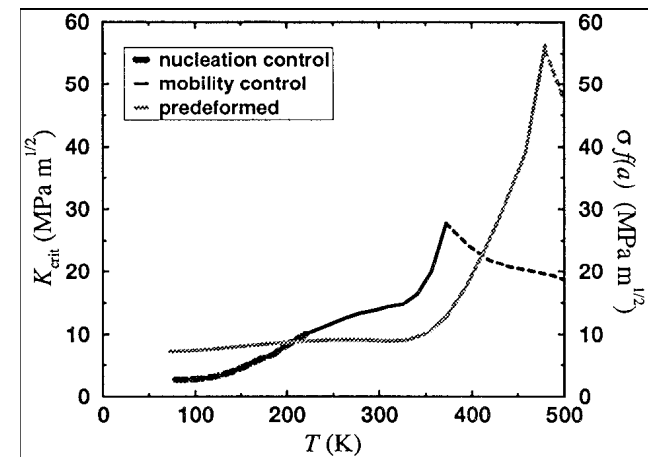
Ductile – Brittle Transition (DBT) in Refractory Metal Based Alloys

- Dislocation dynamics simulations to study interactions between the crack tip and dislocations
- Experimental study to understand the ductile-brittle transition

DBT

Is it lack of dislocation nucleation?

Is it lack of dislocation mobility?

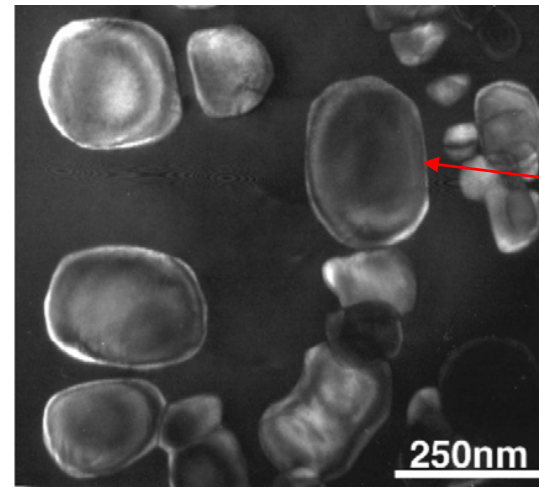
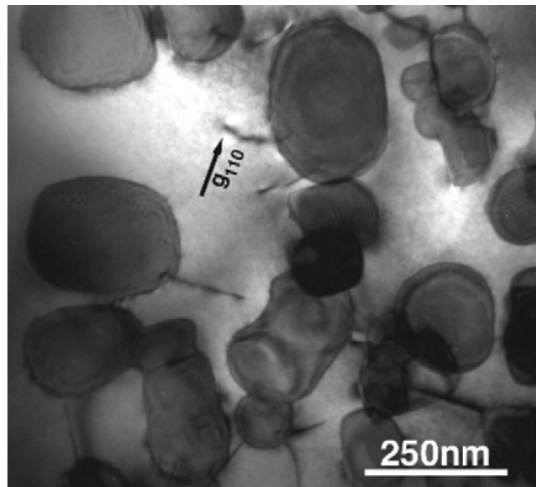


Hartmaier 1999 – *j. Comp.-Aided Mat. Des.*, 6, 145

Improving Creep Strength of Refractory Metal Based Alloys

- Explore strengthening second phase particles in terms of high temperature stability, lattice coherency, and coarsening behavior in candidate alloy systems
- Fabricate designated binary/ternary/higher degree alloys and characterize them using XRD, TEM, SEM, and optical microscopy

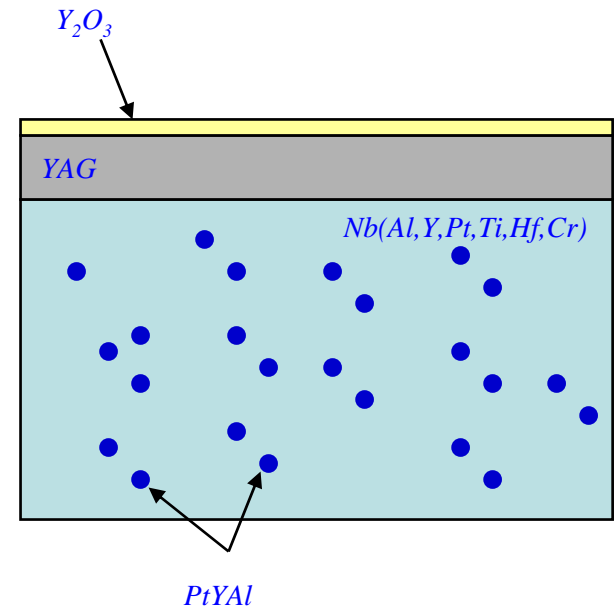
82Nb-8Al-10Ru



G. Ghosh, G.B. Olson, Acta Mat., 55, 2007, 3281-3303.

Improving High Temperature Oxidation Resistance of Refractory Metal Based Alloys

- Thermodynamic calculations to identify stable oxides at high temperatures, to determine solubility of alloying elements and elements entering from the environment both in the scale and in the bulk alloy
- Kinetic computations will be performed to determine growth rates of the oxide scales
- High temperature oxidation experiments (continuous and cyclic) will be performed and oxide scales will be characterized using XRD, ESCA, Auger spectroscopy, and SEM



Olson 2006, U.S. Patent No. US 2006/0172142

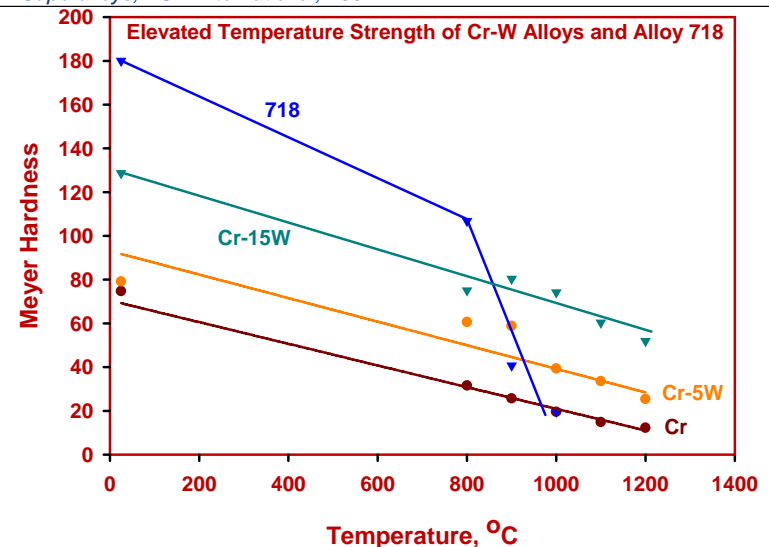
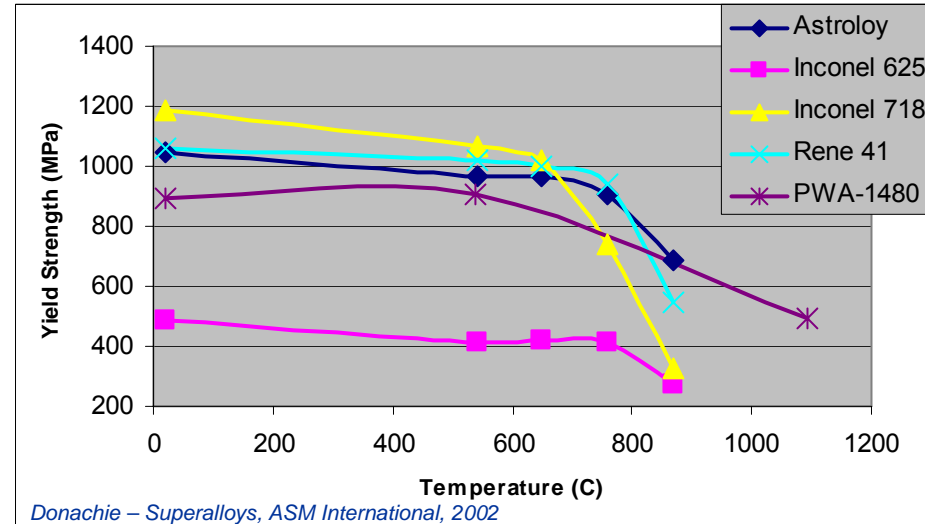
Integrated Design of Chromium Based Alloys for Fossil Energy Applications

•We selected Cr to demonstrate that integrated design methodology works well in developing new high temperature materials based on refractory metals.

•Cr based alloys show considerable promise due to

- relatively low cost
- relatively low density
- good high temperature strength

	Density g/cm ³
Ni	8.9
Cr	7.2
Nb	8.6
Mo	10.2
W	19.3



PERIODIC TABLE Atomic Properties of the Elements

NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

18
VIIIa

Frequently used fundamental physical constants
For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition

1) Binary solubility in Cr
2) Liquidus temperature

Solids
 Liquids
 Gases
 Artificially Prepared

Boltzmann constant
 k 1.3807 × 10⁻²³ J K⁻¹

Physics Laboratory physics.nist.gov		Standard Reference Data Group www.nist.gov/srd						2									
13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18												
5 B Boron 10.811 1s ² 2s ² 2p 8.2980	6 C Carbon 12.0107 1s ² 2s ² 2p ² 11.2603	7 N Nitrogen 14.0067 1s ² 2s ² 2p ³ 14.5341	8 O Oxygen 15.9994 1s ² 2s ² 2p ⁴ 13.6181	9 F Fluorine 18.9984032 1s ² 2s ² 2p ⁵ 17.4228	10 Ne Neon 20.1797 1s ² 2s ² 2p ⁶ 21.5645												
11 Na Sodium 22.989770 [Ne]3s 5.1391	12 Mg Magnesium 24.3050 [Ne]3s ² 7.6462	13 Al Aluminum 26.981538 [Ne]3s ² 3p 5.9858	14 Si Silicon 28.0855 [Ne]3s ² 3p ² 8.1517	15 P Phosphorus 30.973761 [Ne]3s ² 3p ³ 10.4867	16 S Sulfur 32.065 10.3600	17 Cl Chlorine 35.453 [Ne]3s ² 3p ⁵ 12.9676	18 Ar Argon 39.948 [Ne]3s ² 3p ⁶ 15.7596										
19 K Potassium 39.0983 [Ar]4s 4.3407	20 Ca Calcium 40.078 [Ar]4s ² 6.1132	21 Sc Scandium 44.955910 [Ar]3d ¹ 4s ² 6.5615	22 Ti Titanium 47.867 [Ar]3d ² 4s ² 6.8281	23 V Vanadium 50.9415 [Ar]3d ³ 4s ² 6.7462	24 Cr Chromium 51.9961 [Ar]3d ⁵ 4s 6.7665	25 Mn Manganese 54.938049 [Ar]3d ⁵ 4s ² 7.4340	26 Fe Iron 55.845 [Ar]3d ⁶ 4s ² 7.9024	27 Co Cobalt 58.933200 [Ar]3d ⁷ 4s ² 7.8810	28 Ni Nickel 58.6934 [Ar]3d ⁸ 4s ² 7.6398	29 Cu Copper 63.546 [Ar]3d ¹⁰ 4s 7.7264	30 Zn Zinc 65.409 [Ar]3d ¹⁰ 4s ² 9.3942	31 Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p 5.9993	32 Ge Germanium 72.64 [Ar]3d ¹⁰ 4s ² 4p ² 7.8994	33 As Arsenic 74.92160 [Ar]3d ¹⁰ 4s ² 4p ³ 9.7886	34 Se Selenium 78.96 [Ar]3d ¹⁰ 4s ² 4p ⁴ 9.7524	35 Br Bromine 79.904 [Ar]3d ¹⁰ 4s ² 4p ⁵ 11.8138	36 Kr Krypton 83.798 [Ar]3d ¹⁰ 4s ² 4p ⁶ 13.9996
37 Rb Rubidium 85.4678 [Kr]5s 4.1771	38 Sr Strontium 87.62 [Kr]5s ² 5.9949	39 Y Yttrium 88.90585 [Kr]4d ⁵ 5s ² 6.2173	40 Zr Zirconium 91.224 [Kr]4d ⁵ 5s ² 6.6339	41 Nb Niobium 92.90638 [Kr]4d ⁴ 5s 6.7589	42 Mo Molybdenum 95.94 [Kr]4d ⁵ 5s 7.0924	43 Tc Technetium (98) [Kr]4d ⁵ 5s ² 7.28	44 Ru Ruthenium 101.07 [Kr]4d ⁸ 5s 7.3605	45 Rh Rhodium 102.90550 [Kr]4d ⁹ 5s 7.4589	46 Pd Palladium 106.42 [Kr]4d ¹⁰ 8.3369	47 Ag Silver 107.8682 [Kr]4d ¹⁰ 5s 7.5762	48 Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ² 8.9938	49 In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p 5.7864	50 Sn Tin 118.710 [Kr]4d ¹⁰ 5s ² 5p ² 7.3439	51 Sb Antimony 121.760 [Kr]4d ¹⁰ 5s ² 5p ³ 8.6084	52 Te Tellurium 127.60 [Kr]4d ¹⁰ 5s ² 5p ⁴ 9.0096	53 I Iodine 126.90447 [Kr]4d ¹⁰ 5s ² 5p ⁵ 10.4513	54 Xe Xenon 131.293 [Kr]4d ¹⁰ 5s ² 5p ⁶ 12.1298
55 Cs Cesium 132.90545 [Xe]6s 3.8939	56 Ba Barium 137.327 [Xe]6s ² 5.2117	57 La Lanthanum 138.9055 [Xe]5d ¹ 6s ² 6.8251	58 Ce Cerium 140.116 [Xe]4f ¹ 5d ¹ 6s ² 5.5387	59 Pr Praseodymium 140.90765 [Xe]4f ³ 6s ² 5.473	60 Nd Neodymium 144.24 [Xe]4f ⁴ 6s ² 5.5250	61 Pm Promethium (145) [Xe]4f ⁵ 6s ² 5.582	62 Sm Samarium 150.36 [Xe]4f ⁶ 6s ² 5.6437	63 Eu Europium 151.964 [Xe]4f ⁷ 6s ² 5.6704	64 Gd Gadolinium 157.25 [Xe]4f ⁷ 5d ¹ 6s ² 6.1498	65 Tb Terbium 158.92534 [Xe]4f ⁹ 6s ² 5.8638	66 Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ² 5.9389	67 Ho Holmium 164.93032 [Xe]4f ¹¹ 6s ² 6.0215	68 Er Erbium 167.259 [Xe]4f ¹² 6s ² 6.1077	69 Tm Thulium 168.93421 [Xe]4f ¹³ 6s ² 6.1843	70 Yb Ytterbium 173.04 [Xe]4f ¹⁴ 6s ² 6.2542	71 Lu Lutetium 174.967 [Xe]4f ¹⁴ 5d ¹ 6s ² 5.4259	
87 Fr Francium (223) [Rn]7s 4.0727	88 Ra Radium (226) [Rn]7s ² 5.2784	89 Ac Actinium (227) [Rn]6d ¹ 7s ² 5.17	90 Th Thorium 232.0381 [Rn]6d ² 7s ² 6.3067	91 Pa Protactinium 231.03588 [Rn]5f ¹ 6d ¹ 7s ² 5.89	92 U Uranium 238.02891 [Rn]5f ³ 6d ¹ 7s ² 6.1941	93 Np Neptunium (237) [Rn]5f ⁴ 6d ¹ 7s ² 6.2657	94 Pu Plutonium (244) [Rn]5f ⁶ 7s ² 6.0260	95 Am Americium (243) [Rn]5f ⁷ 7s ² 5.9738	96 Cm Curium (247) [Rn]5f ⁸ 6d ¹ 7s ² 5.9914	97 Bk Berkelium (247) [Rn]5f ⁹ 7s ² 6.1979	98 Cf Californium (251) [Rn]5f ¹⁰ 7s ² 6.2817	99 Es Einsteinium (252) [Rn]5f ¹¹ 7s ² 6.42	100 Fm Fermium (257) [Rn]5f ¹² 7s ² 6.50	101 Md Mendelevium (258) [Rn]5f ¹³ 7s ² 6.58	102 No Nobelium (259) [Rn]5f ¹⁴ 7s ² 6.65	103 Lr Lawrencium (262) [Rn]5f ¹⁴ 7s ² 7p ¹ 4.9 ?	

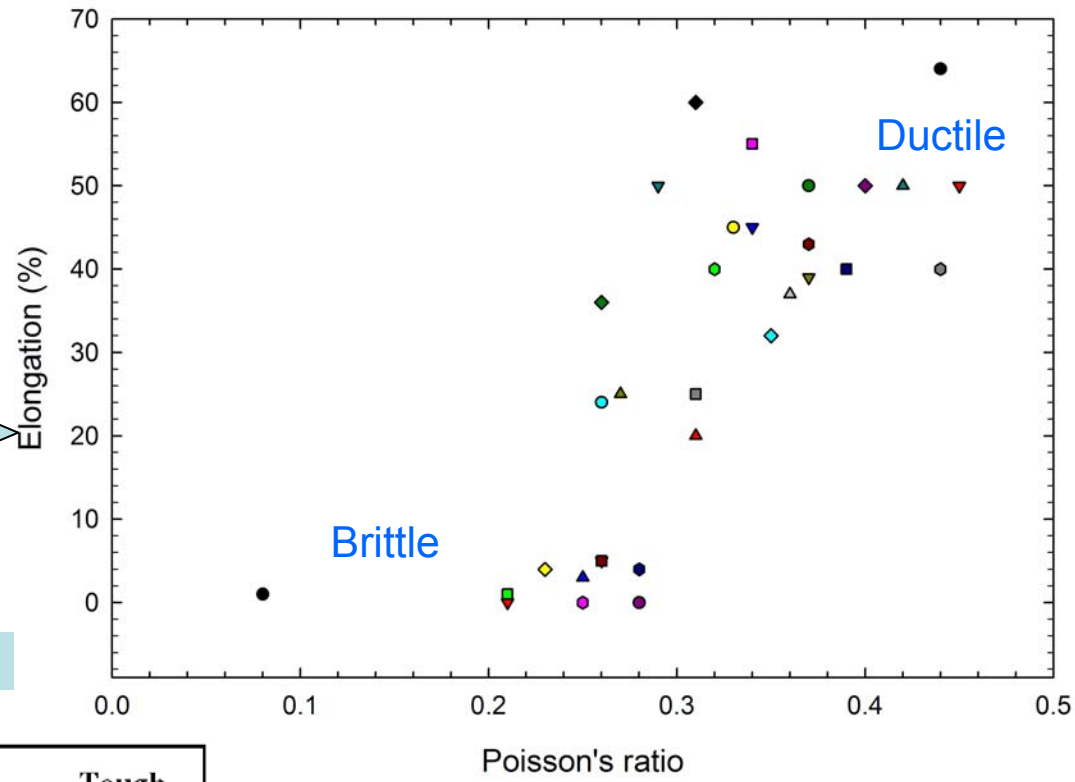
Atomic Number: 58
Ground-state Level: 1G₄
Symbol: Ce
Name: Cerium
Atomic Weight: 140.116
Ground-state Configuration: [Xe]4f¹5d¹6s²
Ionization Energy (eV): 5.5387

[†]Based upon ¹²C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

Ductility and Toughness vs. Poisson ratio

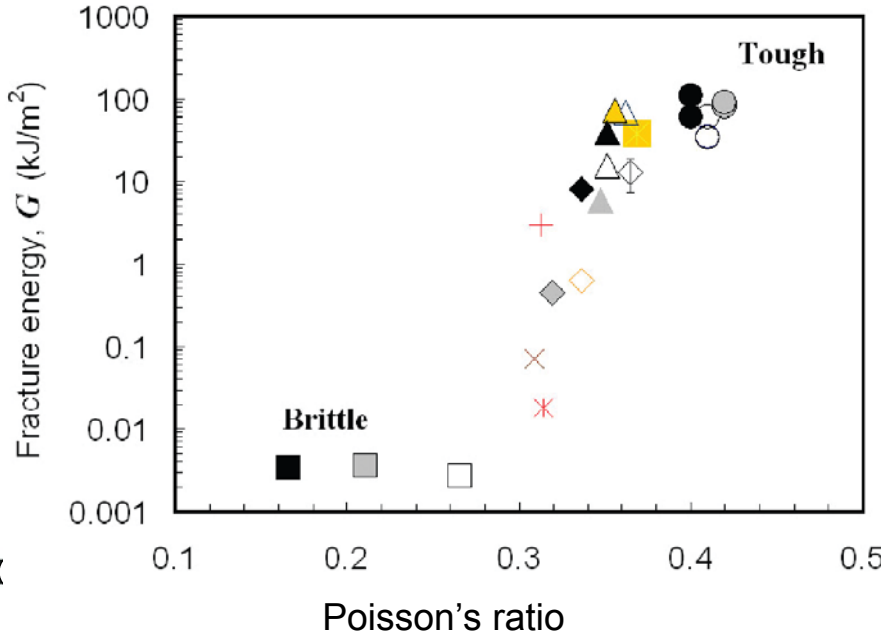
crystalline metals
(purity $\geq 99.9\%$)



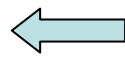
- Be [1]
- ▼ Cr [2]
- Pu [2]
- ◆ U [2]
- ▲ Ru [2]
- Os [1]
- Re [2]
- ▼ Rh [1]
- Ir [1]
- ◆ Th [2]
- ▲ Zn [1]
- Mg [2]
- W [2]
- ▼ Cd [1]
- Mo [2]
- ◆ Ca [1]
- ▲ Co [2]
- Ni [2]
- 0.33 [2]
- ▼ Ta [2]
- ◆ Cu [2]
- ▲ Ti [1]
- Hf [2]
- Ag [2]
- ▼ V [2]
- Pd [1]
- ◆ Nb [2]
- ▲ Au [2]
- Pt [1]
- Pb [1]
- ▼ Tl [1]

[1]. S.F. Pugh, *Phil. Mag.*, 45 (1954) 823

[2]. *Smithells Metals Ref. Book*, 7th Ed. 1992



Amorphous alloys
Amorphous+crystalline composite



Phil. Mag. Lett. 85 (2005) 77

What Is Poisson's Ratio?

Poisson's ratio is the ratio of the relative contraction strain, or transverse strain (normal to the applied load), divided by the relative extension strain, or axial strain (in the direction of the applied load).

Uniaxial compression

$$\nu = -\frac{\epsilon_{tran}}{\epsilon_{axial}}$$

■ is the resulting Poisson's ratio

ϵ_{tran} is transverse strain

ϵ_{axial} is axial strain.

$$\nu = \frac{3 - 2(G/B)}{6 + 2(G/B)}$$

G = polycrystalline shear modulus
B = bulk modulus

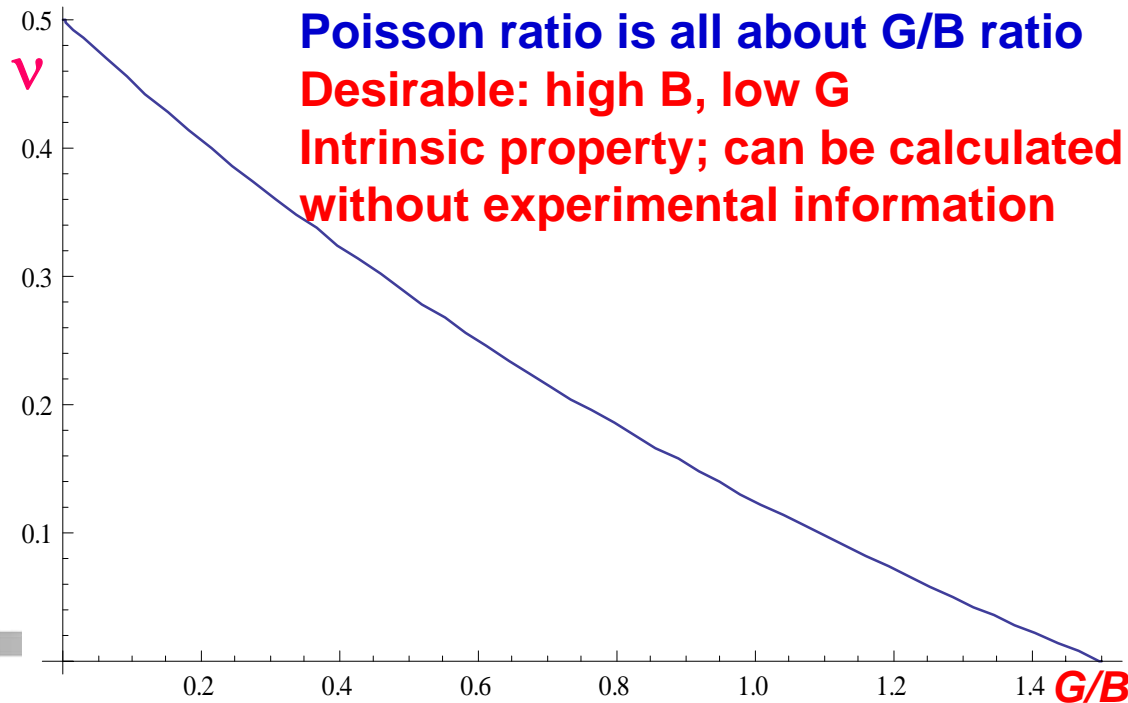
Poisson ratio is all about G/B ratio
Desirable: high B, low G
Intrinsic property; can be calculated without experimental information

General Hook's law

$$\epsilon_x = \frac{1}{E} [\sigma_x - \nu (\sigma_y + \sigma_z)]$$

$$\epsilon_y = \frac{1}{E} [\sigma_y - \nu (\sigma_x + \sigma_z)]$$

$$\epsilon_z = \frac{1}{E} [\sigma_z - \nu (\sigma_x + \sigma_y)]$$



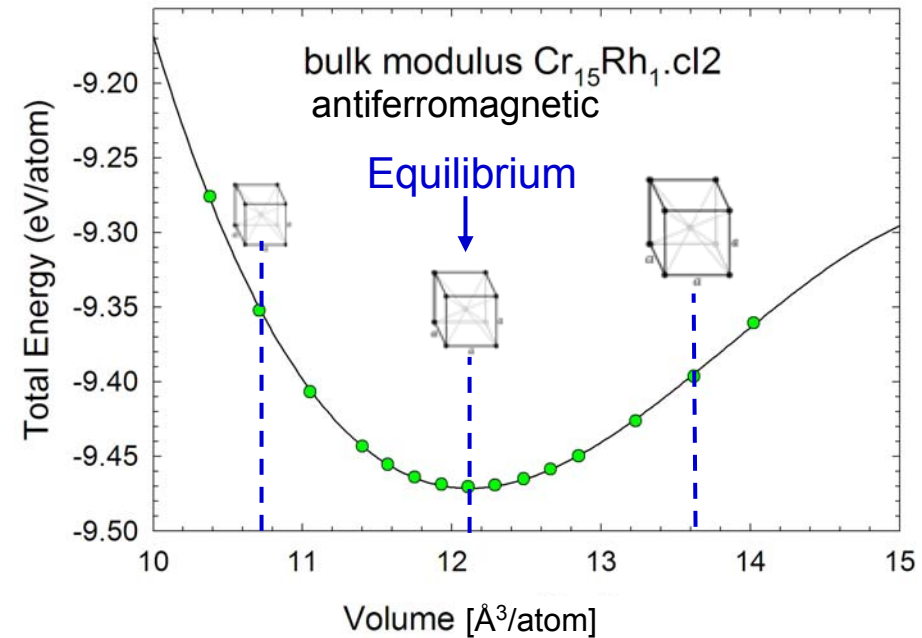
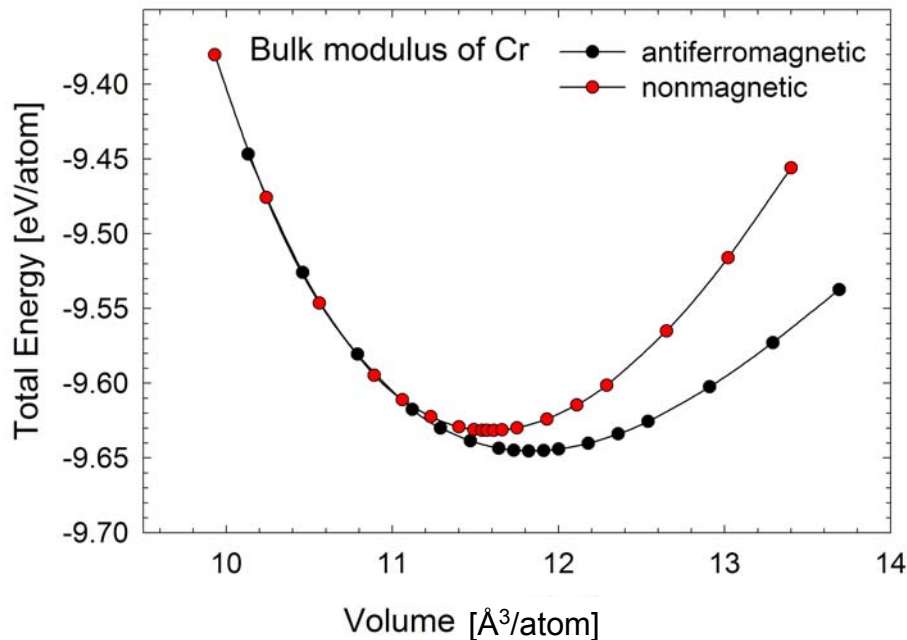
Computational Details

- **VASP package is used**
- **Projector augmented-wave pseudopotentials**
- **Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional**
- **Energy cutoff = 500 eV**
- **Convergence w.r.t. K-points: 1 meV**
- **Precision “high”**
- **semi-core 3p, 4p and 5p electrons treated as valence**
- **Spin polarization considered (antiferromagnetism)**
- **2x2x2 supercell bcc lattice**
- **Binary compositions**
- **Ternary compositions in bcc structure**

Bulk Modulus Calculations

$$B = -\left(V \frac{\partial P}{\partial V}\right)_{E_{\min}} = V \left. \frac{\partial^2 E}{\partial V^2} \right|_{E_{\min}}$$

Cubic polynomial fitting. There are other EOS (equation of state) such as Murnaghan equation, Birch-Murnaghan equation.



Antiferromagnetism of Cr must be included into calculations to validate the predicated physical properties

Antiferromagnetism is considered in all bcc Cr_{15}X_1 alloys

Polycrystalline Shear Modulus

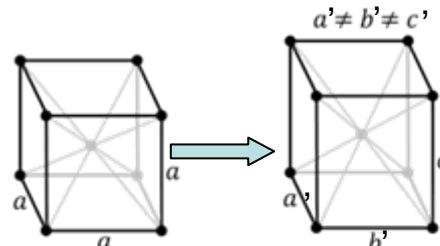
Hershey's averaging method: Taga et al. *Phys Rev B* 71 (2005) 014201

$$G^3 + \frac{9B+4C'}{8} G^2 - \frac{3C_{44}(B+4C')}{8} G - \frac{3C_{44}C'B}{4} = 0 \quad C' = \frac{1}{2}(C_{11} - C_{12}) \quad B = \frac{1}{3}(C_{11} + 2C_{12})$$

G=shear; B=bulk modulus; C_{11} , C_{12} and C_{44} are elastic constants

Applying orthorhombic strain

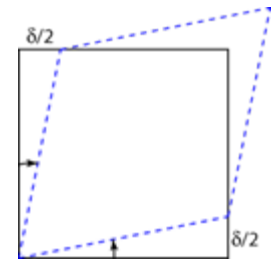
Mehl et al, *Phys Rev B* 41 (1990) 10311

$$\varepsilon_o = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2 / (1 - \delta^2) \end{pmatrix}$$


$$\Delta E(\delta) = E(0) - E(\delta) = (C_{11} - C_{12})V_0\delta^2 + O[\delta^4]$$

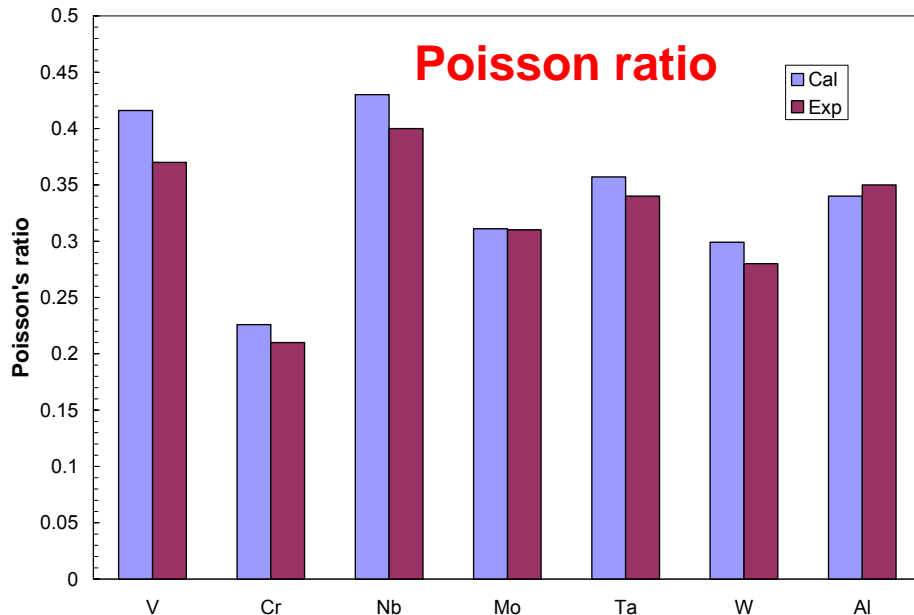
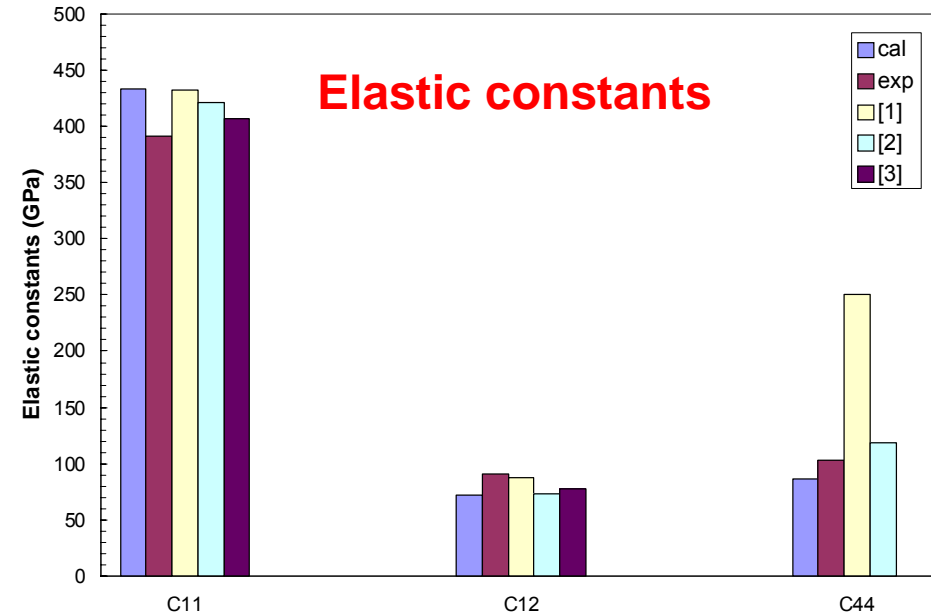
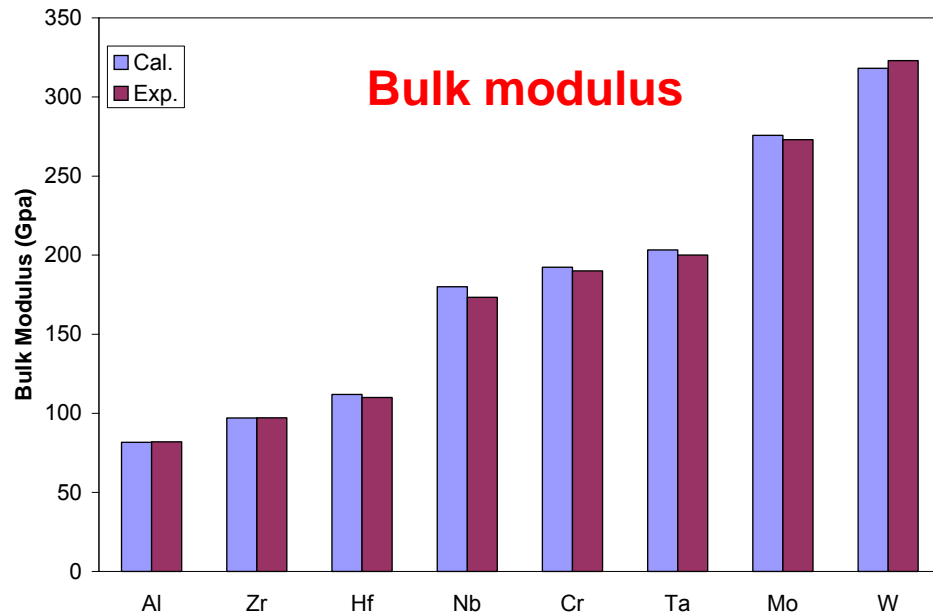
Applying monoclinic strain

$$\varepsilon_m = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2 / (4 - \delta^2) \end{pmatrix}$$

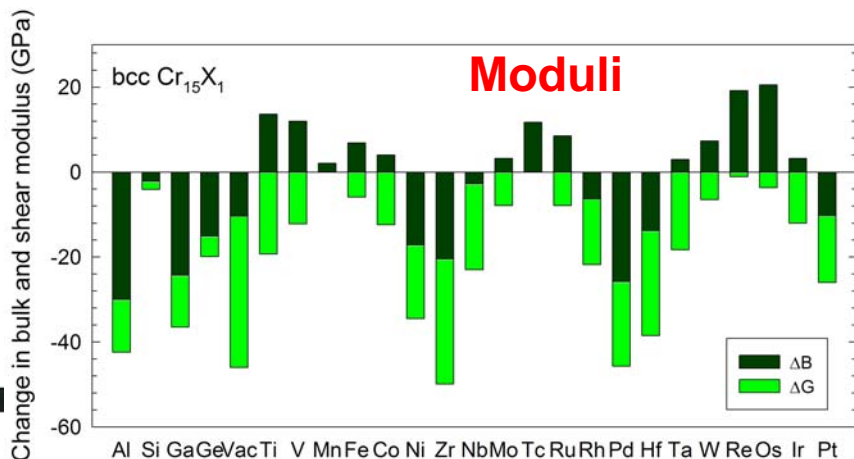
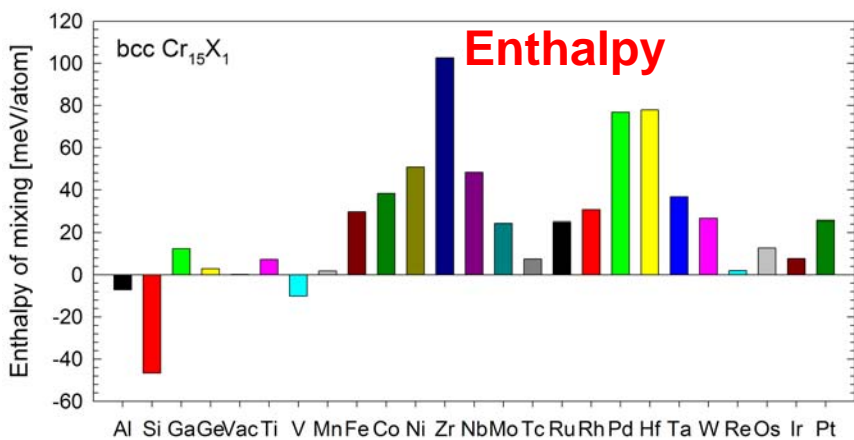
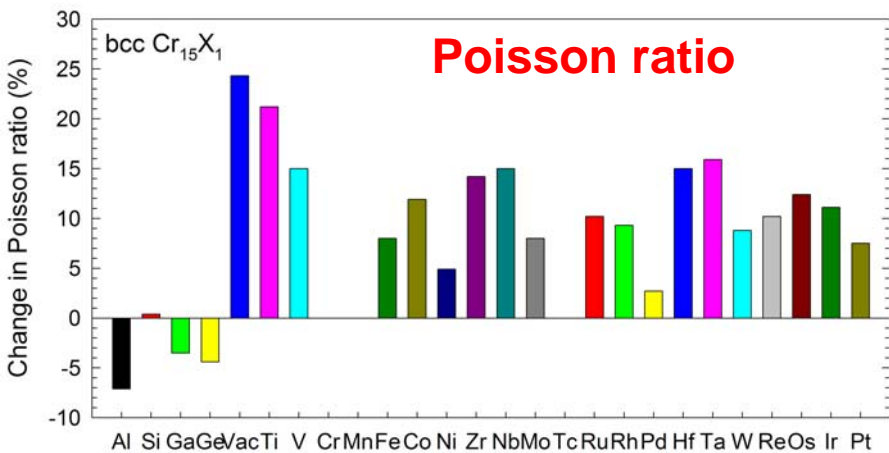


$$\Delta E(\delta) = E(0) - E(\delta) = \frac{1}{2}C_{44}V_0\delta^2 + O[\delta^4]$$

Validation of Computation



[1] Phys Rev B 54 (1996) 4519 (tight binding)
[2] Phys Rev B 62 (2000) 5136 (DFT full potential)
[3] Phys Rev B 67 (2003) 134204 (DFT full potential)



~~Al~~
~~Ga~~
~~Ge~~

Current Calculations

Ti, V, Fe, Co, Ni, ~~Zr~~, ~~Nb~~,
Mo, Ru, Rh, ~~Pd~~, ~~Hf~~, ~~Ta~~,
W, Re, Os, Ir, Pt

Solubility

Ti, V, Fe, Co, Ni, Mo,
~~Ru~~, ~~Rh~~, W, ~~Re~~, ~~Os~~, ~~Ir~~,
~~Pt~~

Economy

Ti, V, Fe, Co, Ni, Mo, W

Current status

- **We have done similar calculations on ternary systems based on the promising binaries**
- **Currently, we are working on establishing phase diagrams for the promising ternary systems**

Future Work

- **Continue thermodynamic investigation to identify a promising multi-component system**
- **Kinetic studies on the identified multi-component system**
- **Designing an alloy with sufficient creep strength within the multi-component system**
- **Further modifying the alloy composition for high-temperature oxidation resistance**

Above tasks will be accomplished utilizing various computational tools and experimental work