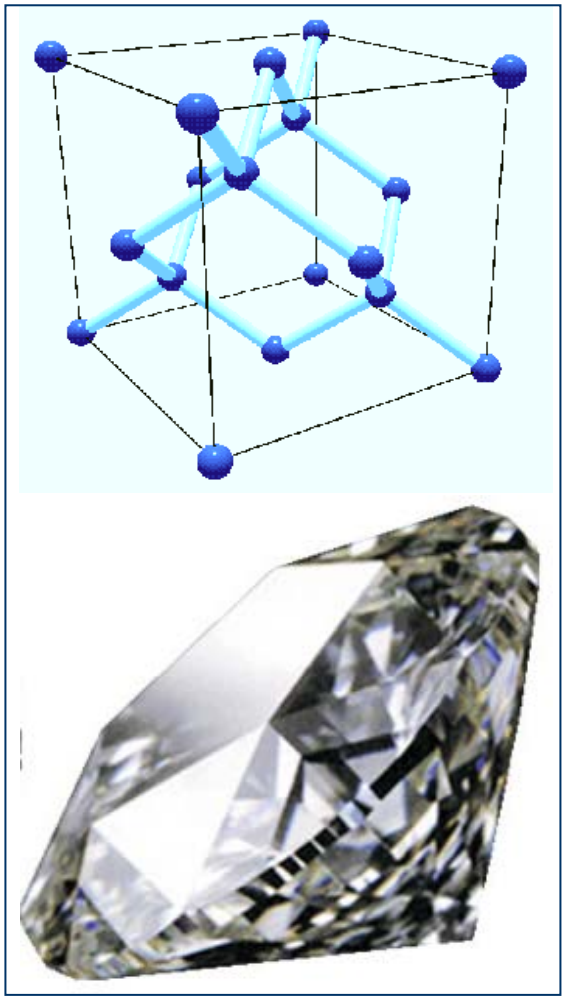
2.2 Superhard Materials

The 0th Law" of Relative Hardness

If A can scratch B, A is harder than B.

The Hardest Known Material

Diamond



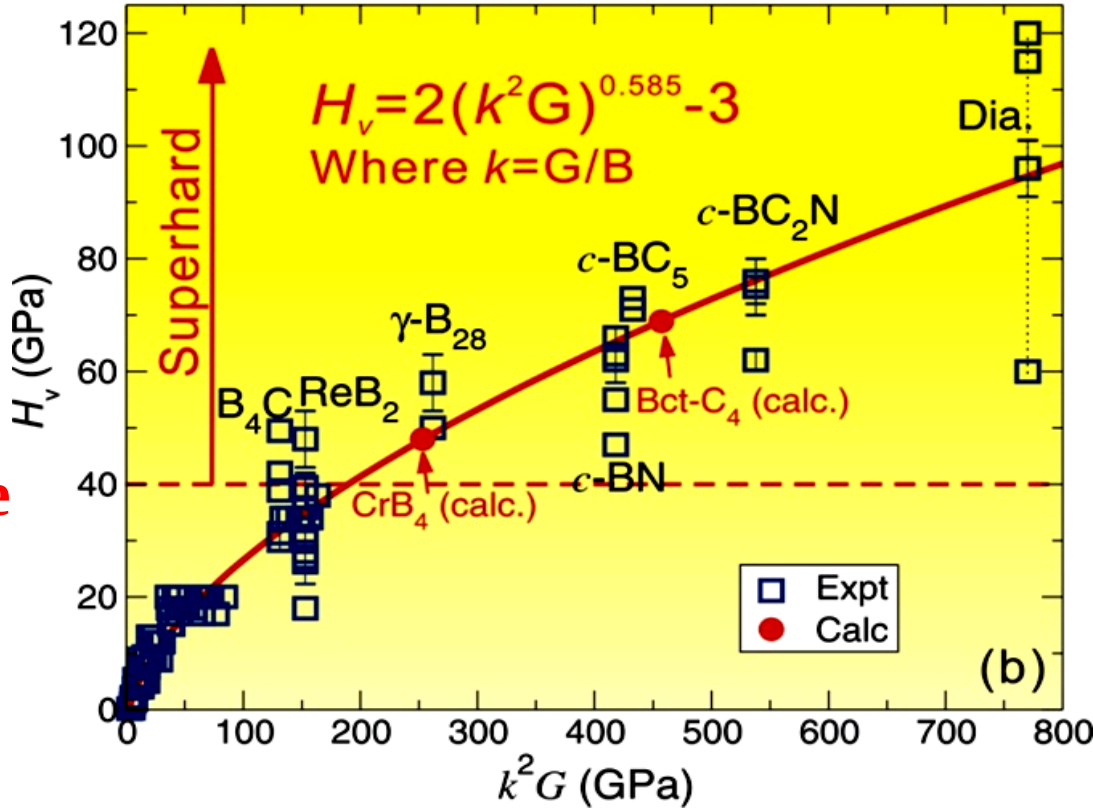
Mohs Hardness for Minerals (Friedrich Mohs, 1812)

The Mohs scale of mineral hardness is based on the ability of one natural sample of matter to scratch another.

Mohs hardness	Mineral	Chemical formula	Absolute hardness
1	Talc	$Mg_3Si_4O_{10}(OH)_2$	1
2	Gypsum	$CaSO_4 \cdot 2H_2O$	3
3	Calcite	$CaCO_3$	9
4	Fluorite	CaF_2	21
5	Apatite	$Ca_5(PO_4)_3(OH^-,Cl^-,F^-)$	48
6	Orthoclase Feldspar	$KAlSi_3O_8$	72
7	Quartz	SiO_2	100
8	Topaz	$Al_2SiO_4(OH^-,F^-)_2$	200
9	Corundum	Al_2O_3	400
10	Diamond	C	1600

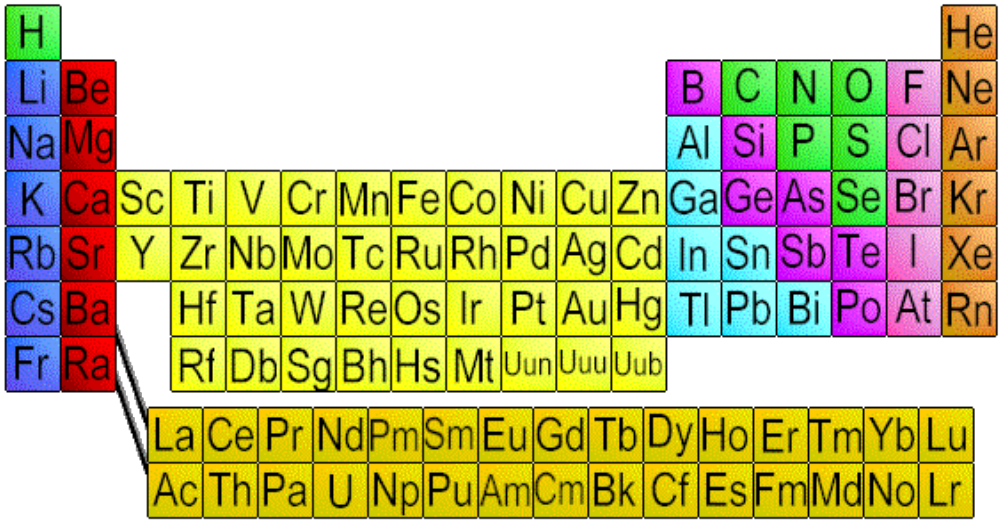
Known Natural or Manmade Superhard Materials

- **Diamond** (natural, C)
- **Cubic boron nitrides** (manmade, *c*-BN)
- **Cubic boron carbon nitride** (manmade, *c*-BC_2N)



Candidates for Superhard Materialss

- **Hardness: a mechanical property, but dictated by the electrons**
  (not too few e: no inert, alkali, or alkali earth elements)



Candidates for Superhard Materials

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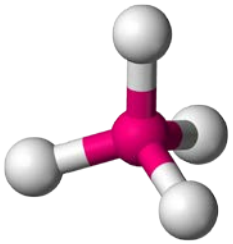

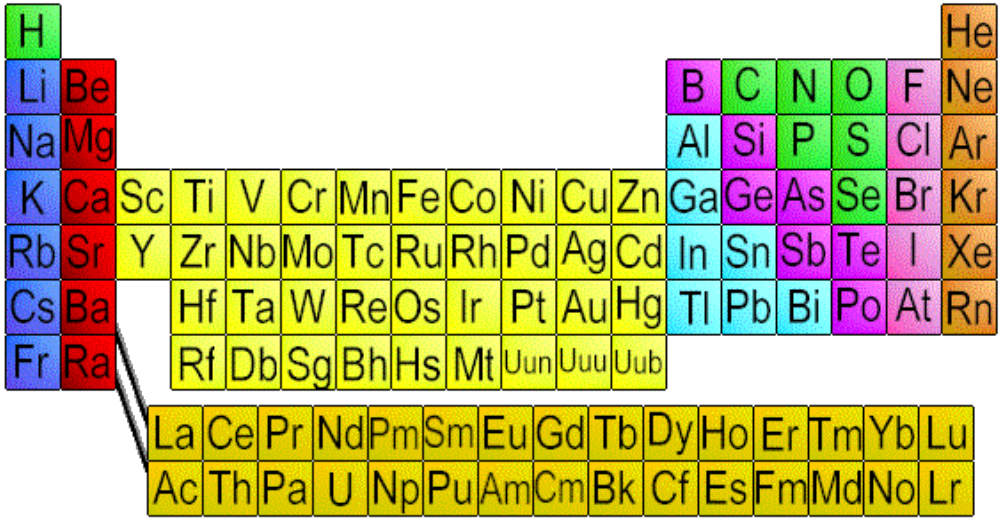

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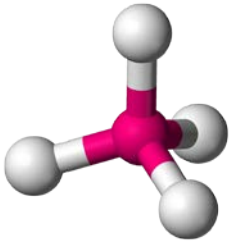

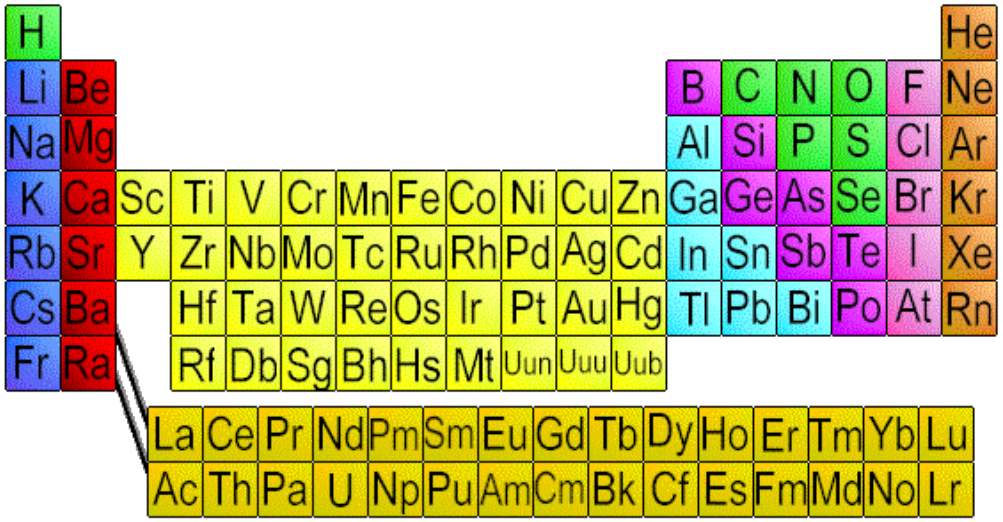

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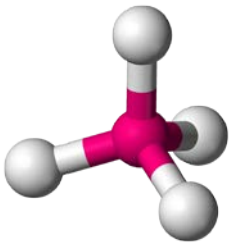
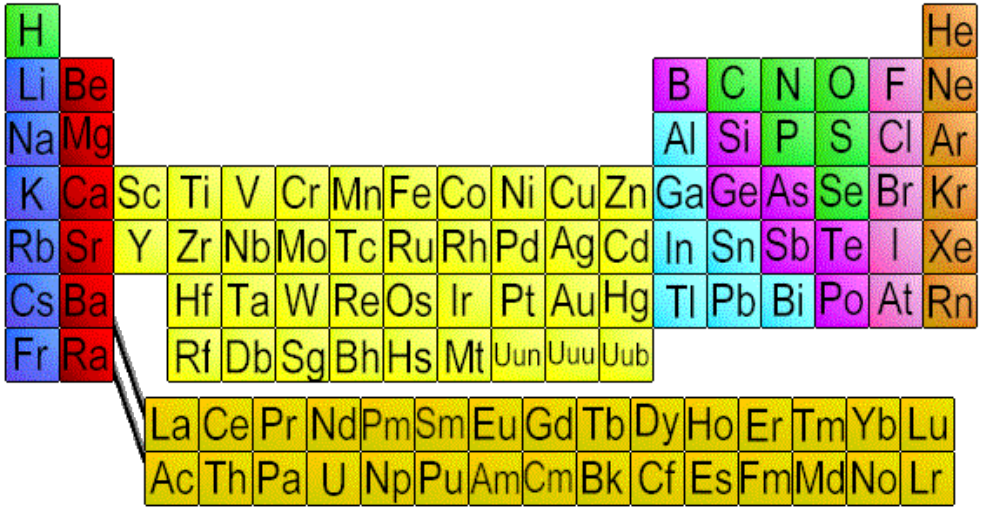
  (not too few e: no inert, alkali, or alkali earth elements)
- **High symmetry rules: hard in every direction**
  (tetrahedral symmetry preferred)
- **Metals are less stable than insulators**
  (not too many e: no F, Cl, … Q: magic element with 7 legs?)
- **Direct sticking on nuclei**
  (not too many shells: only C, BN…)





Superhard materials

courtesy of

Xing-Qiu Chen

Institute of Metal Research,

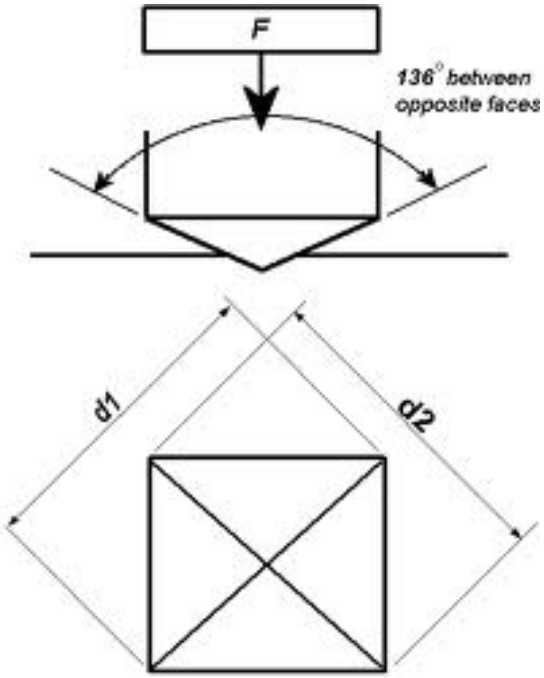
Chinese Academy of Sciences

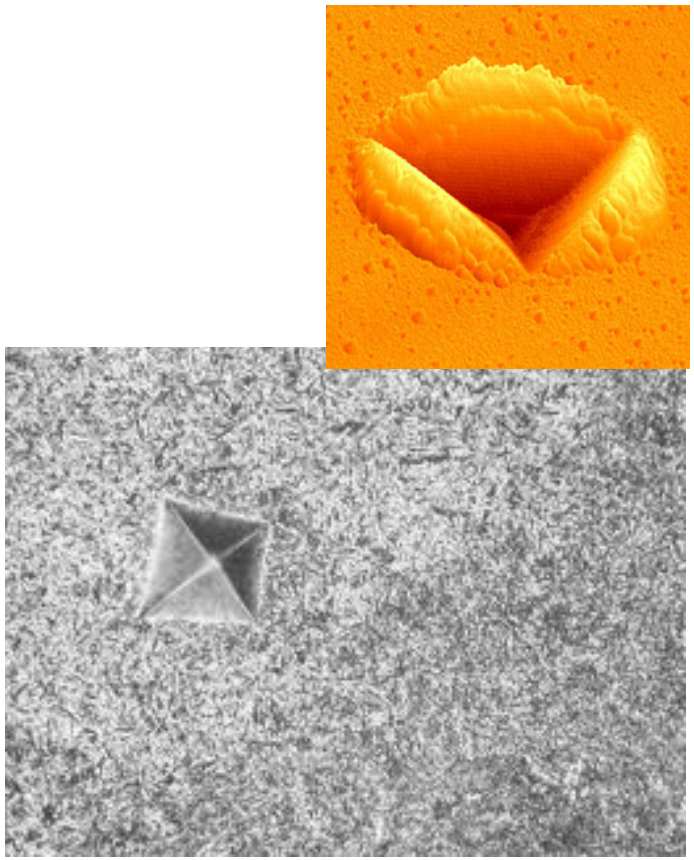
April, 2012

Vickers hardness

(Smith & Sandland, Vickers Ltd., 1921)

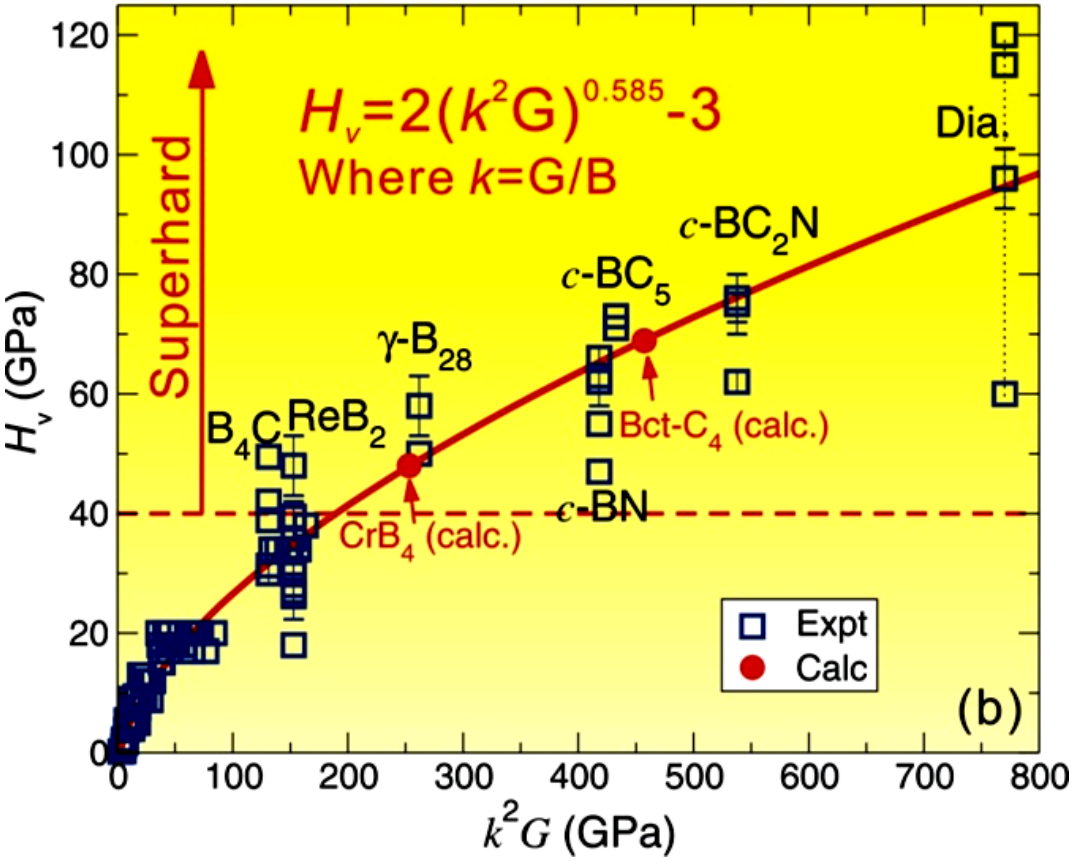
$$H_V = \frac{F}{S} = 2F\frac{Sin\left(\frac{\theta}{2}\right)}{d^2} = 0.001854\frac{F}{d^2} \quad (\mathrm{GPa})$$

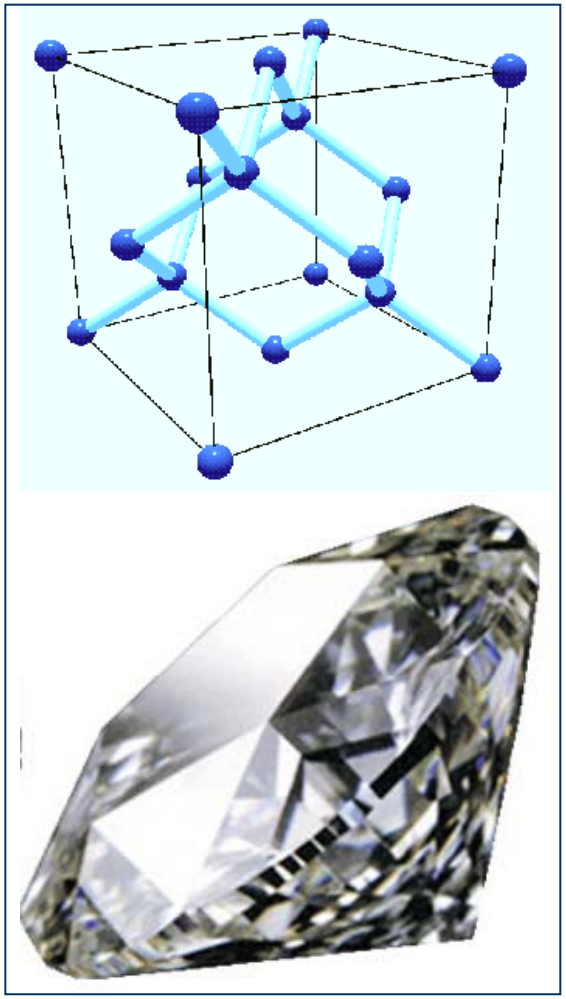




Typical Superhard Materials

- **Diamond**, the hardest material known,
- **Cubic boron carbon nitride**, *c*-BC_2N,
- **Cubic boron nitrides**, *c*-BN.





Diamond

X.-Q. Chen *et al*, Intermetallics,19, 1275 (2011); Phys. Rev. B, 84, 121405(R) (2011)

Deficiencies of superhard materials

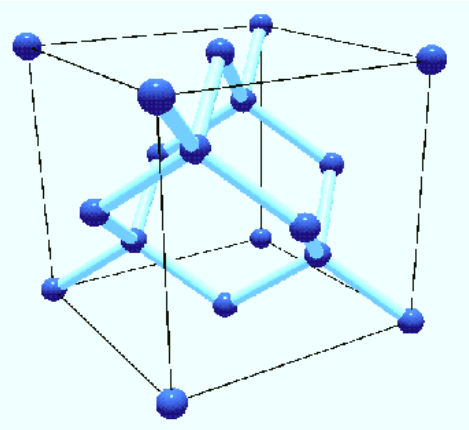
Diamond	It is not effective for cutting ferrous (Fe^{2+}) metals, including steel, because of a chemical reaction that produces iron carbide.
***c*-BN** ***c*-BC_2N**	They do not occur naturally and must be synthesized under conditions of extreme pressure and temperature or CVD, making them quite expensive.

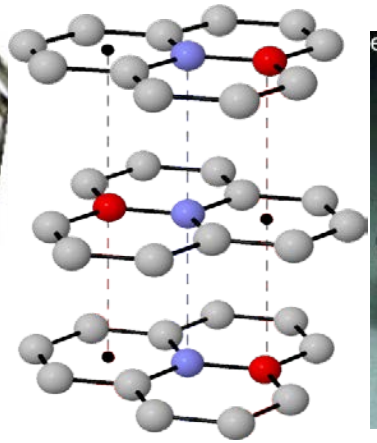
Therefore, new superhard materials, in particular, without the need of high-pressure synthesis, are not only of great scientific interest, but also could be very useful.

What makes diamond hardest?

In diamond, tetrahedrally bonded sp^3 carbon atoms form a three-dimensional, covalent network of high symmetry.

The trigonal sp^2 bonds in graphite form sheets with shorter and stronger carbon-carbon bonds. But only weak van der Waals interactions hold the sheets together, allowing layers of graphite to cleave readily. Therefore, graphite is soft.





Superhardness: Dream and Reality

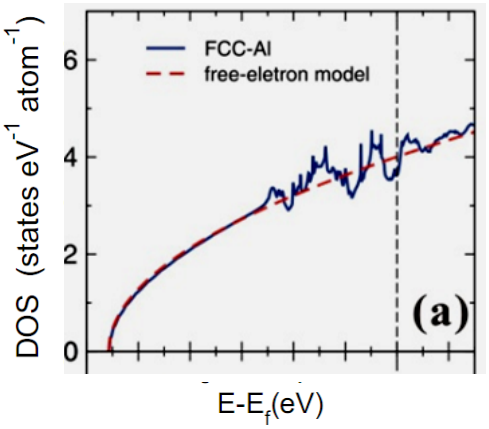
New superhard materials

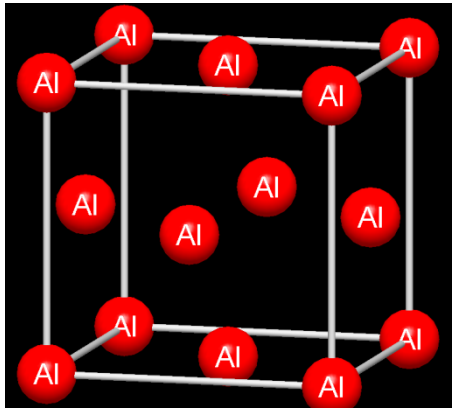
by combining high hardness with chemical inertness and low-cost synthesis as well as without the need of high pressure, could quickly yield practical benefits, for example, by providing a replacement for cubic boron nitride for cutting and polishing steel.

Inspiration by XAl_{12}

Strength and ductility have always been one of the crucial issues to study for metal materials.

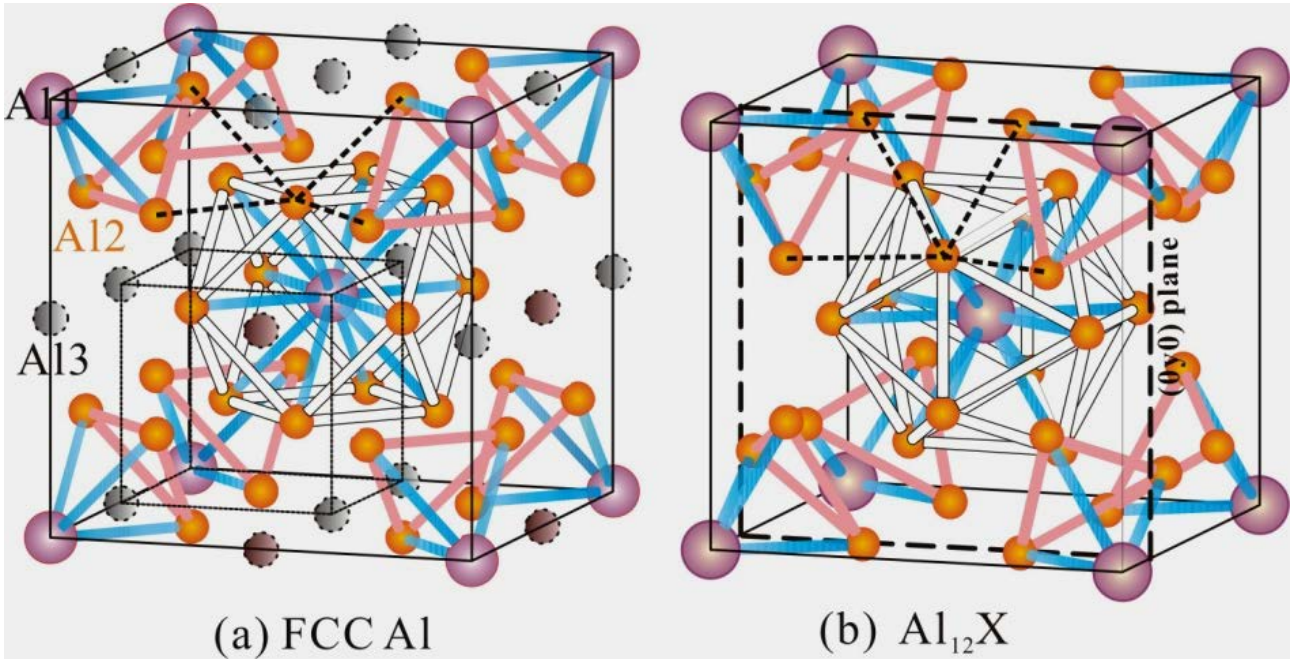
Aluminum is regarded as a typical ***sp***-bonded metal with electronic structure described totally by free-electrons model. Pure aluminum exhibits good ductility and plastic-deformation properties.



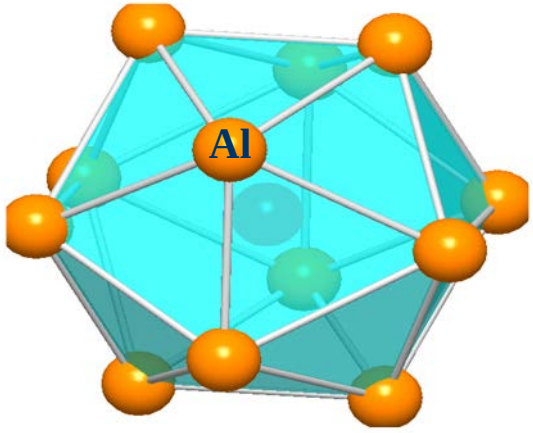


How about the Al-enriched compounds XAl_{12}（*X*=Cr, Mo, W, Mn, Tc, Re）?

$Al_{12}X$ and FCC-Al: Similarity and Difference?



(a) FCC Al (b) $Al_{12}X$

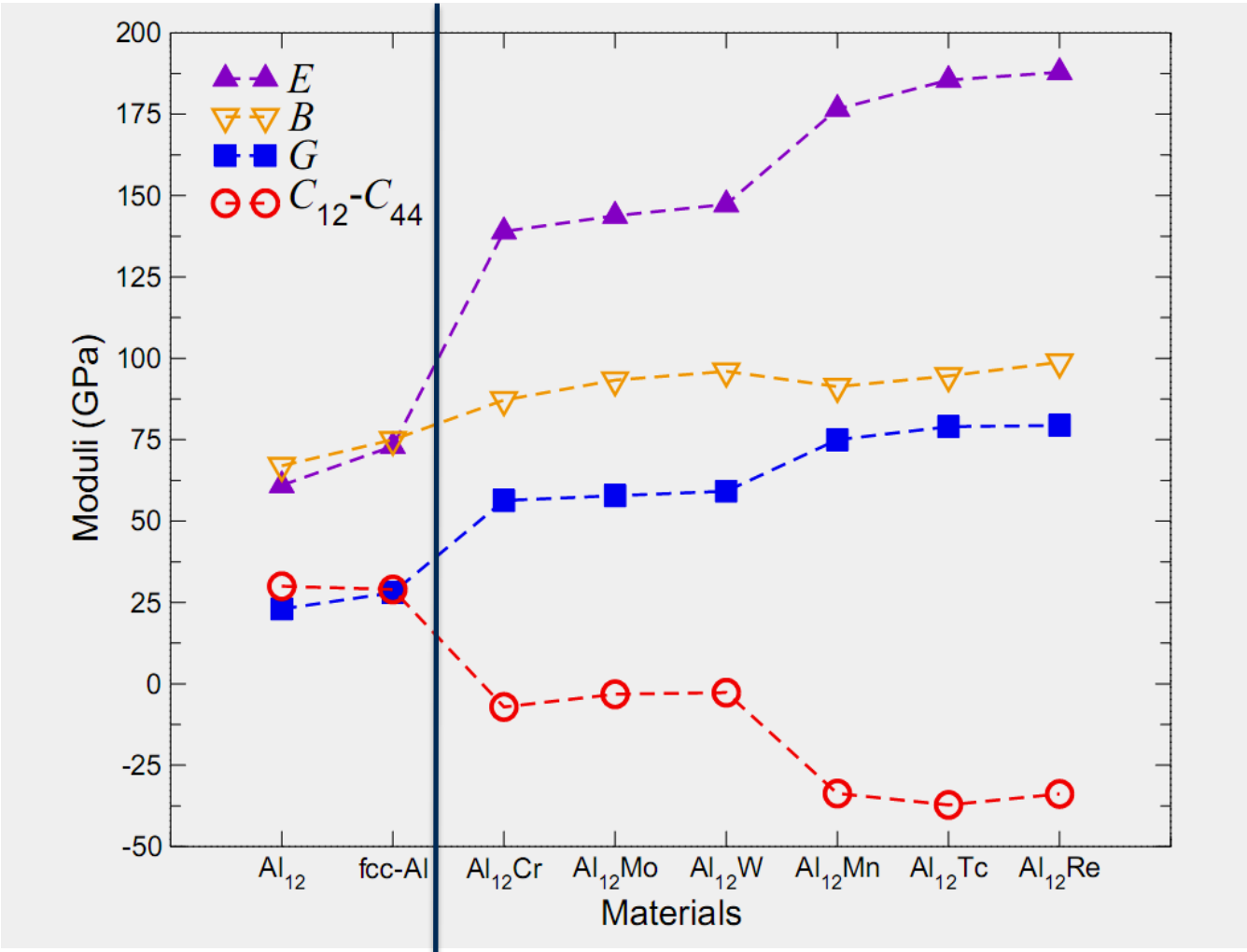


(c) Al_{12}-icosahedron

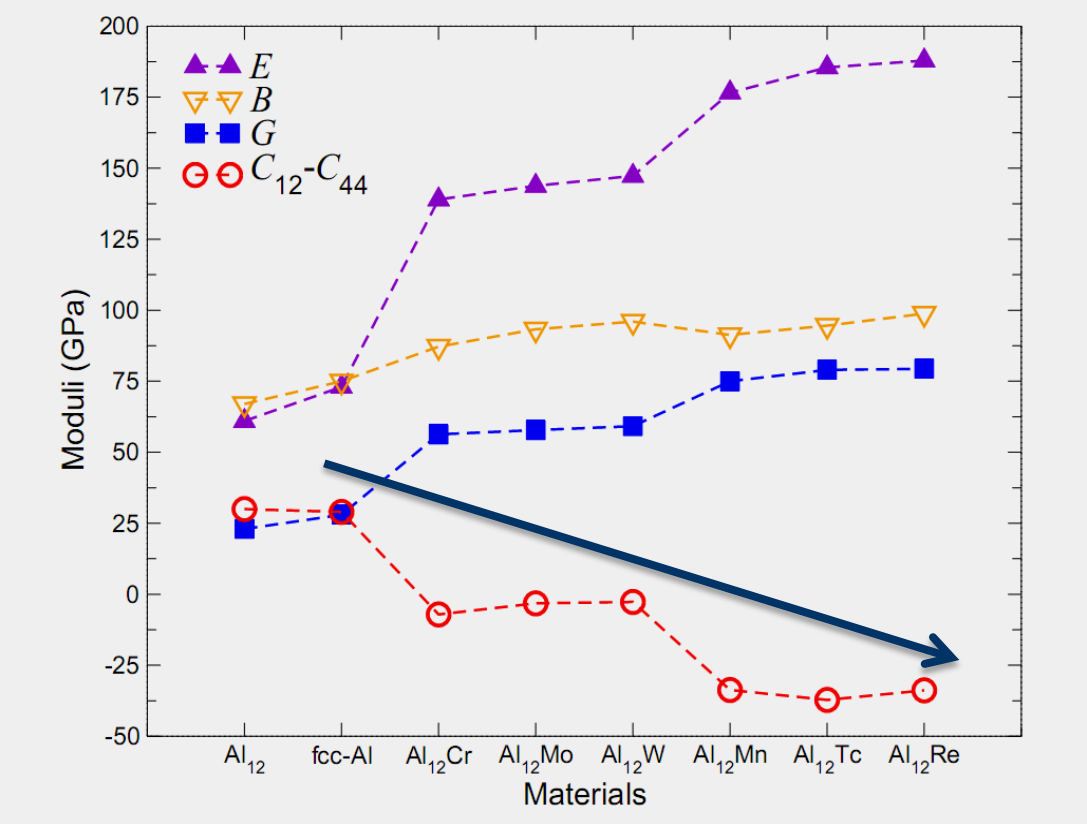
In FCC Al each Al has twelve nearest-neighbor Al atoms, forming a Al_{12} **tetradecahedron** whereas in the $Al_{12}X$ compounds each *X* atom is surrounded by an **icosahedron** of twelve Al atoms (called Al_{12}-icosahedron).

***X* = Cr, Mo, W, Mn, Tc, Re**

Strong mechanical properties in $Al_{12}X$ resulting from the emergent covalent bonds



Classical Cauchy Pressure (C_{12}-C_{44})



In the 1990s Pettifor [1] proposed this criterion:

C_{12}-C_{44} > 0

metallic bonds

C_{12}-C_{44} < 0

Covalent bonds

■ The conclusion is in agreement with our analysis of electronic structure.

[1] D. G. Pettifor, Materials Science and Technology 8, 345-349 (1992)

Classical Pugh Modulus Ratio (*G*/*B*)

Compounds	C_{11}	C_{12}	C_{44}	*G*	*B*	*E*	*v*	*G/B*	C_{12}-C_{44}
Al_{12}	99.6	50.7	10.7	15.0	67.0	41.9	**0.40**	0.22	40.0
$Al_{cal.}$	111	57	28	27.6	75.0	73.7	0.34	0.37	29.0
$Al_{exp.}$	114.3	61.9	31.6	29.3	79.4	78.3	**0.34**	0.37	30.3
$Al_{12}Cr$	153.8	53.9	61.0	56.3	87.2	139.0	0.23	0.65	-7.1
$Al_{12}Mo$	167.2	56.3	59.5	57.8	93.3	143.8	**0.24**	0.62	-3.2
$Al_{12}W$	171.8	58.1	60.8	59.2	96.0	147.3	0.24	0.62	-2.7
$Al_{12}Mn$	190.1	41.8	75.5	75.0	91.3	176.6	**0.18**	0.82	-33.7
$Al_{12}Tc$	194.7	44.6	81.8	79.0	94.6	185.5	0.17	0.84	-37.2
$Al_{12}Re$	197.1	49.6	83.4	79.4	98.8	187.9	0.18	0.80	-33.8

In as early as 1954,Pugh proposed a relation between the elastic and plastic properties of pure polycrystalline metals and stated that G/B(Called Pugh's modulus ratio)[2].

***G*/*B* < 0.571 → ductile; *G*/*B* > 0.571 → brittle**

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

Two classical criteria

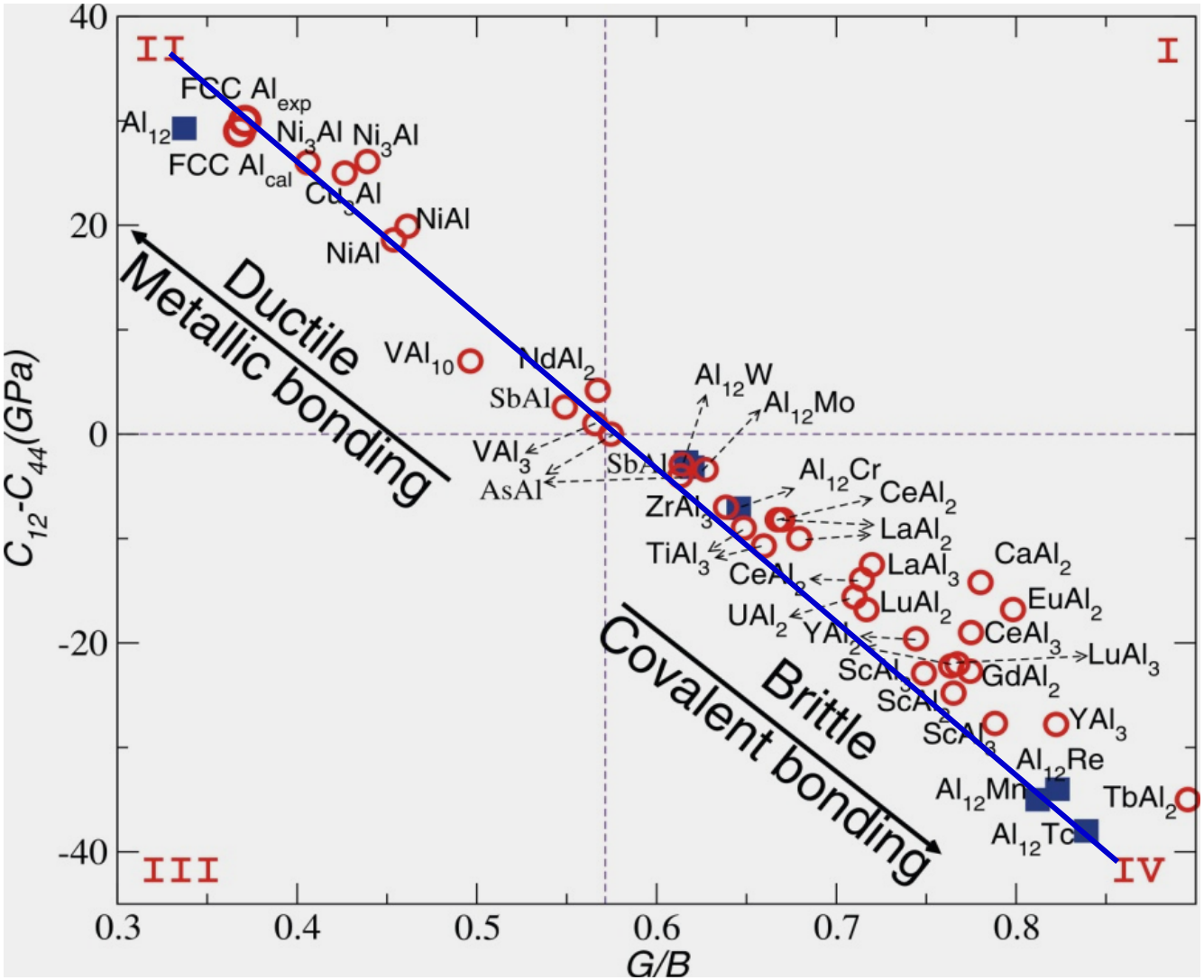
Pettifor's criterion: For metallic non-directional bonding compounds, the Cauchy pressure (C_{12}-C_{44}) value is typically positive. The larger positive value represents a more metallic bonding. The negative value signifies a covalent bonding framework.

--- D. G. Pettifor, Materials Science and Technology 8, 345-349 (1992)

Pugh's criterion: If G/B>0.57, the materials behaves in a brittle manner. The higher the value of G/B, the more brittle the materials.

--- S. F. Pugh, Phil. Mag., 45 823(1954)

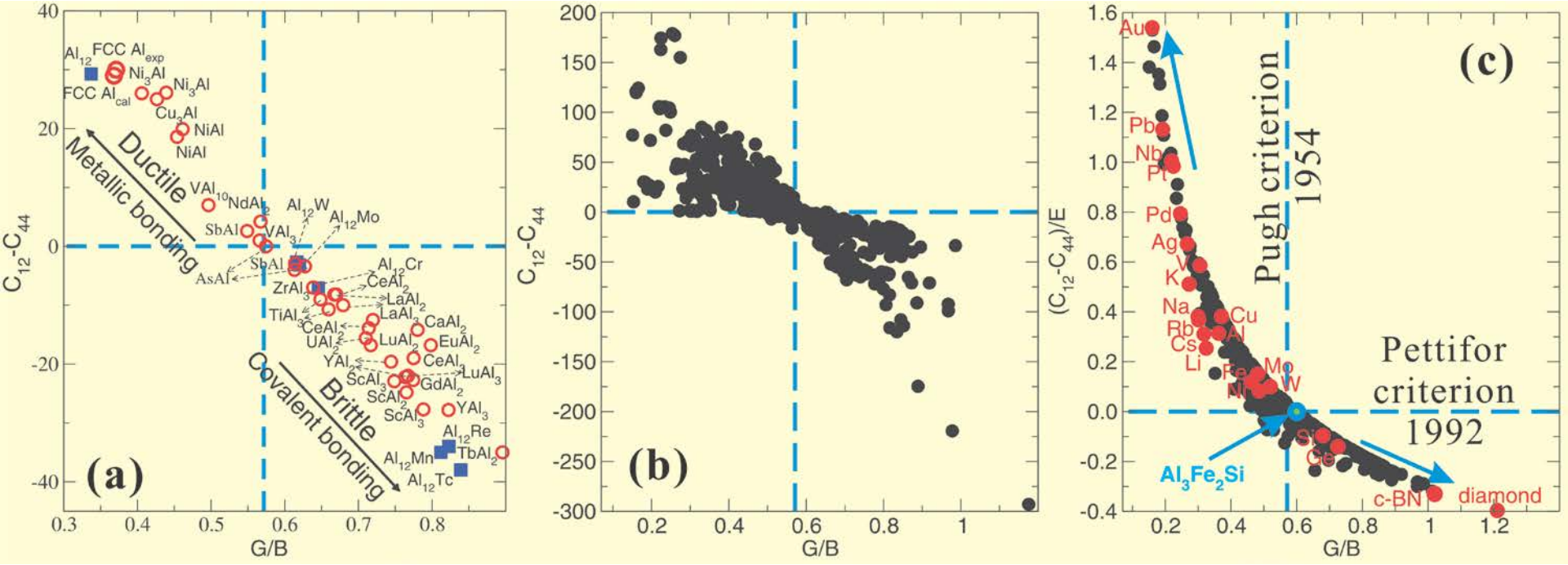
C_{12}-C_{44} Versus *G*/*B*



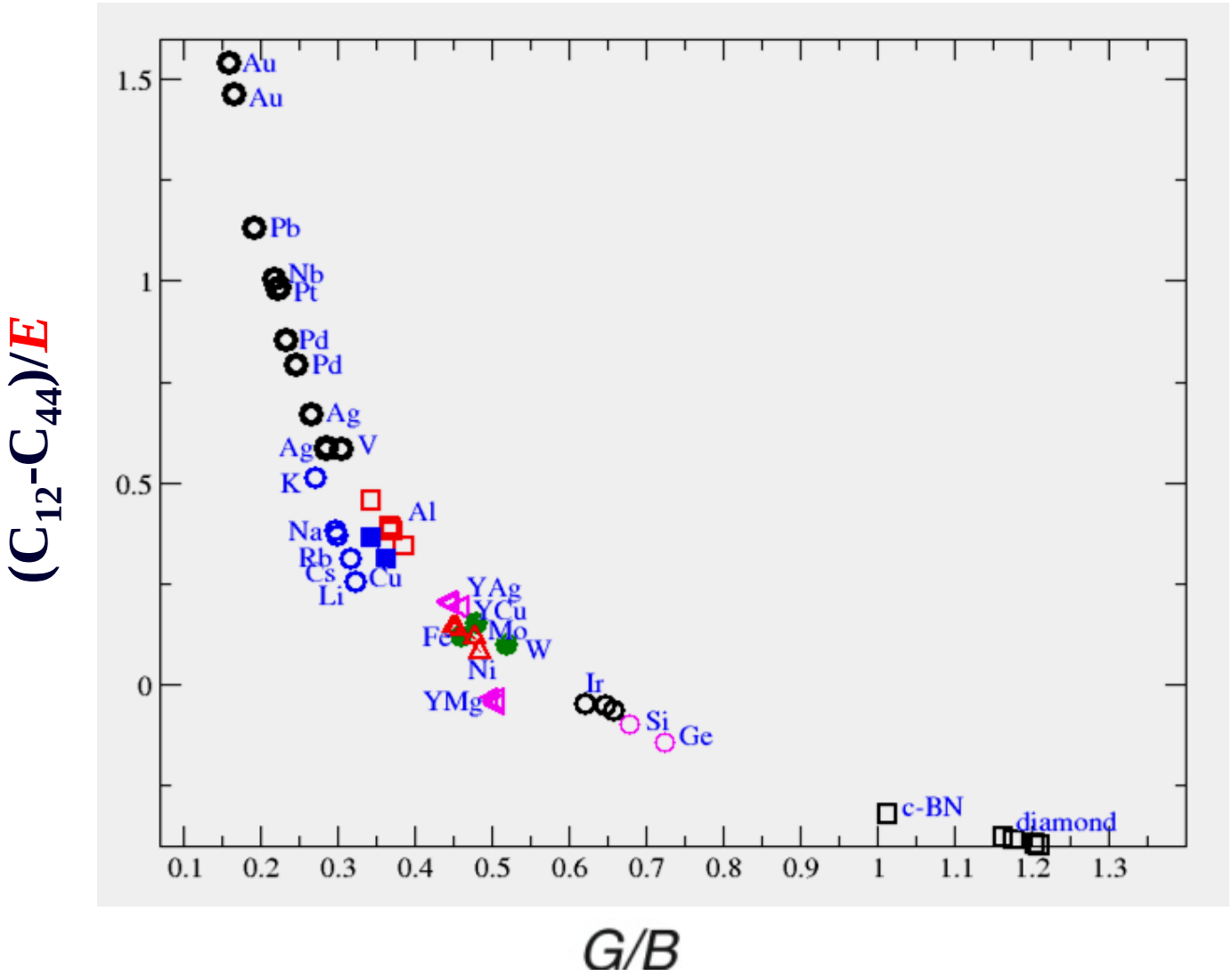
Correlation between C_{12}-C_{44} and G/B for 35 aluminides

Summaries for a wide variety of materials

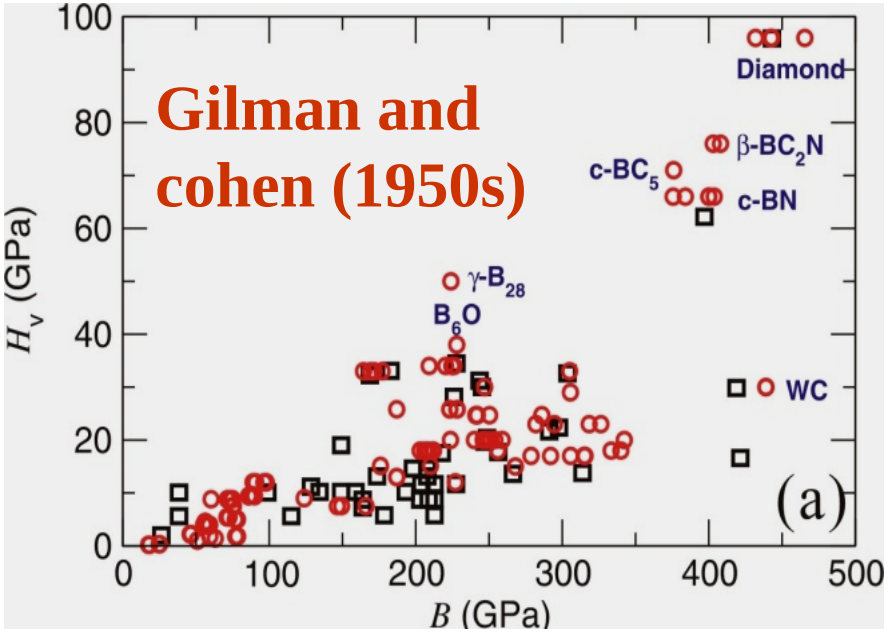
572 Groups

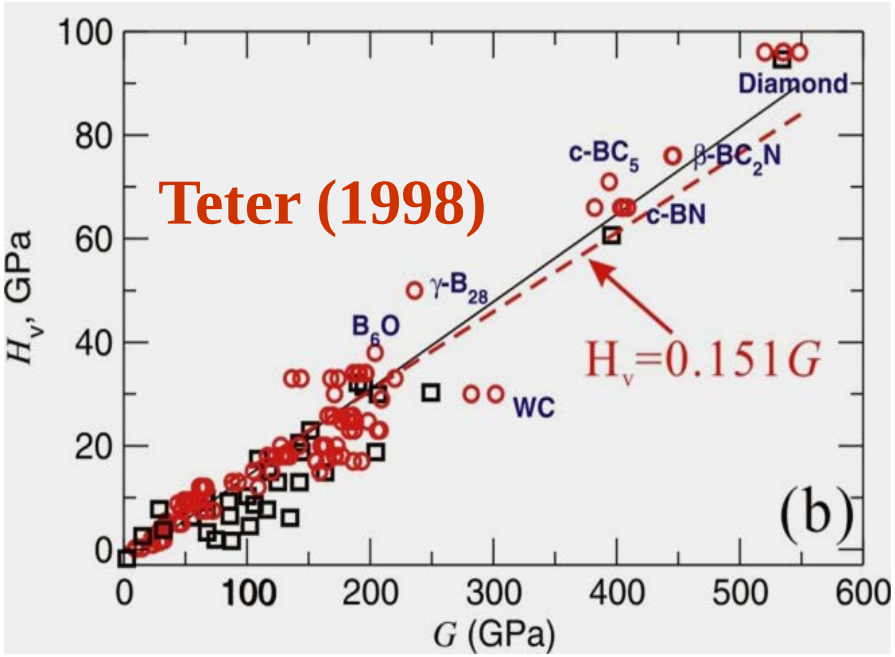


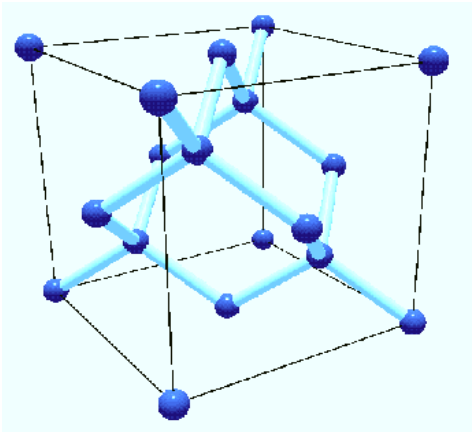
Pure elements: C_{12}-C_{44} versus G/B

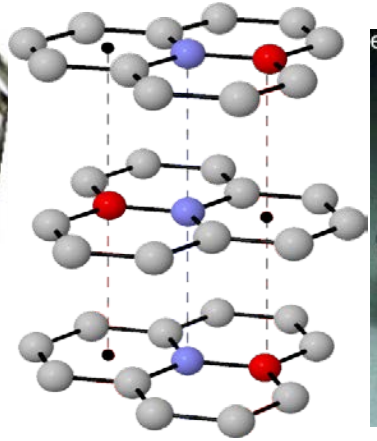


Classic correlations between Hardness and elastic moduli

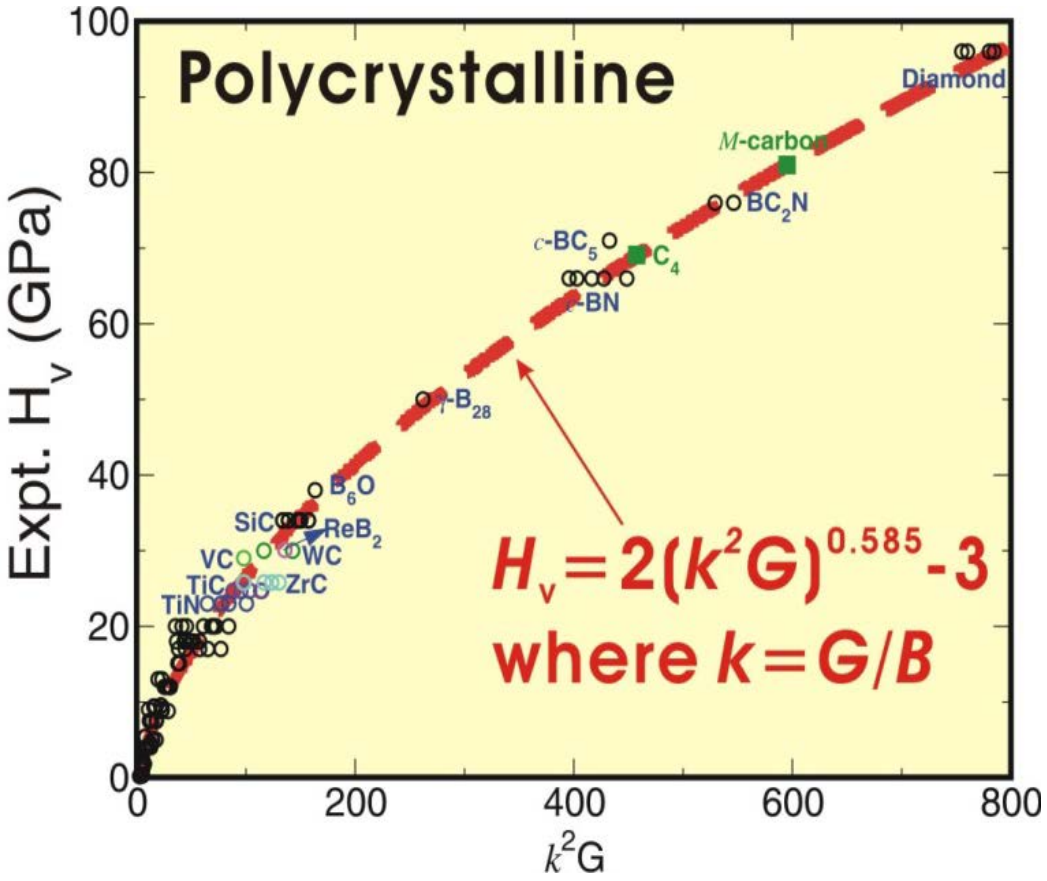






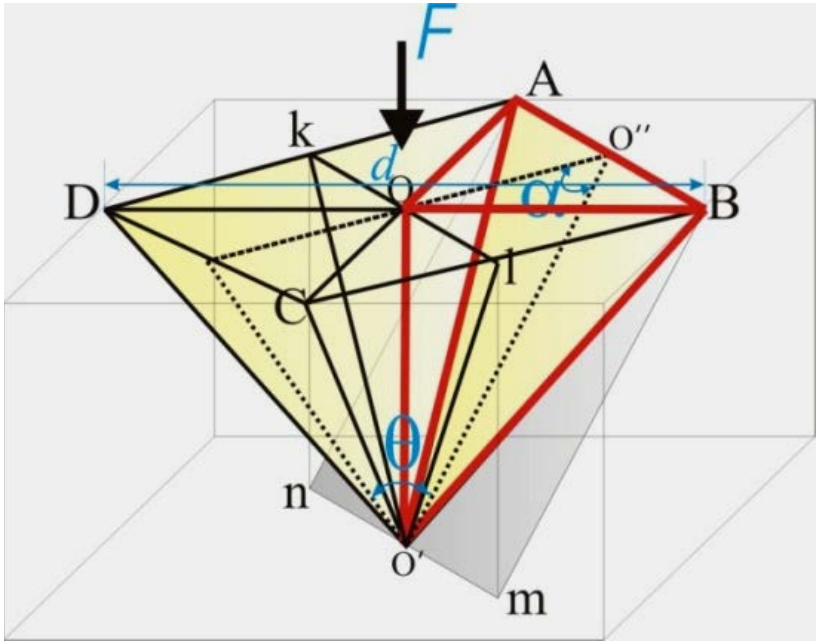


New correlation of hardness with *G*/*B*



Assuming materials fail in the elastic scale

Hardness?



$$H_v = \frac{2F\sin(\theta/2)}{d^2} \quad (1)$$

$$G = \frac{F}{4A\tan(\alpha)} \quad (2)$$

- The indenter can be divided into four triangular based pyramid indenters.
- The Vickers hardness is measured within the elastic scale.

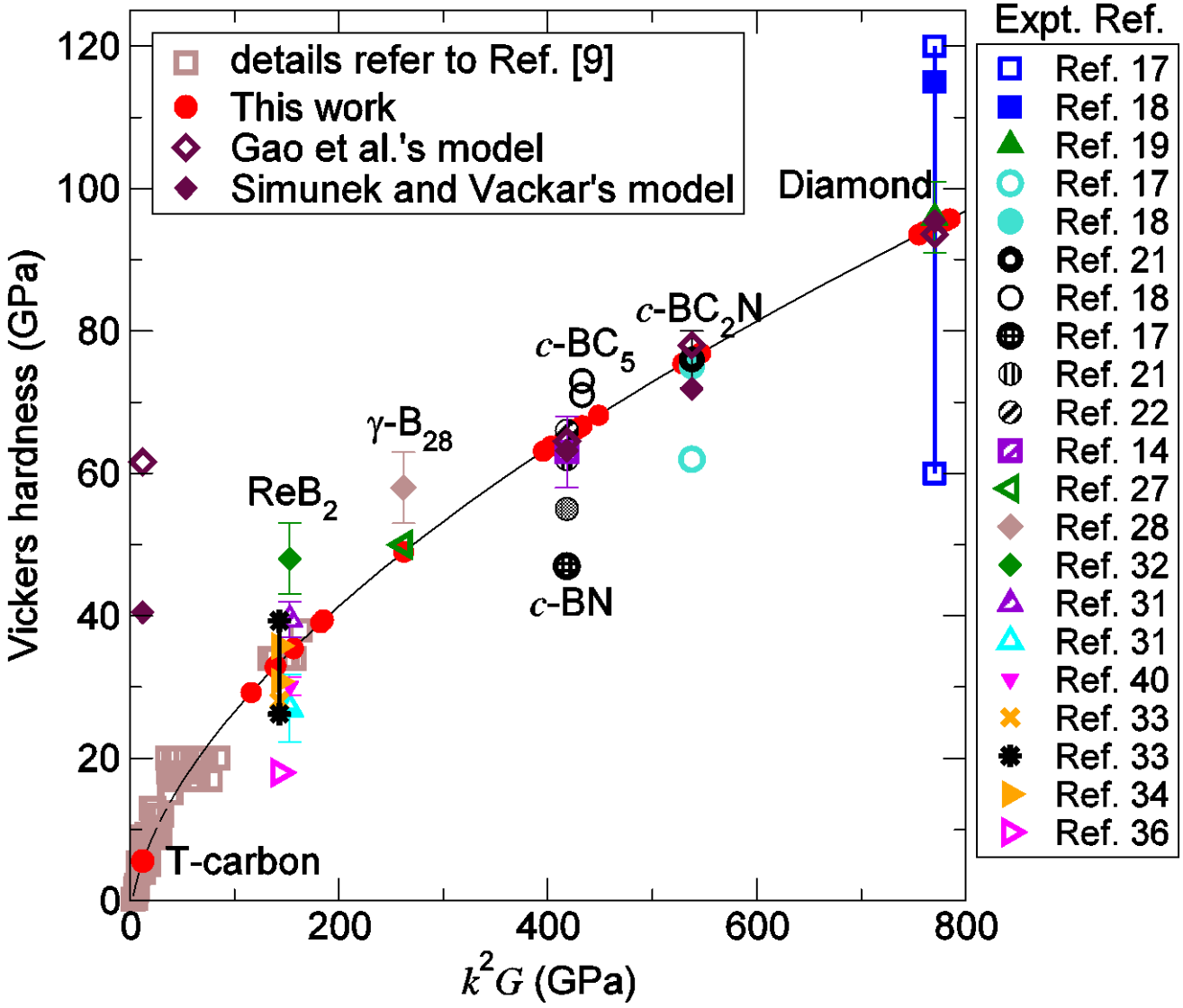
$$A = cA^* = \frac{c}{8}d^2\tan(\alpha) \quad (3)$$

$$G = \frac{2F}{d^2\tan^2(\alpha)} \quad (4)$$

$$H_v = G\tan^2(\alpha)\sin(\theta/2) \quad (5)$$

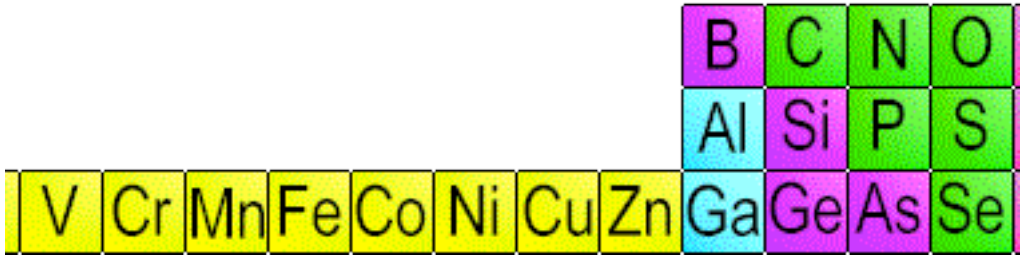
$$H_v = 0.151G.$$

Comparison with previous models

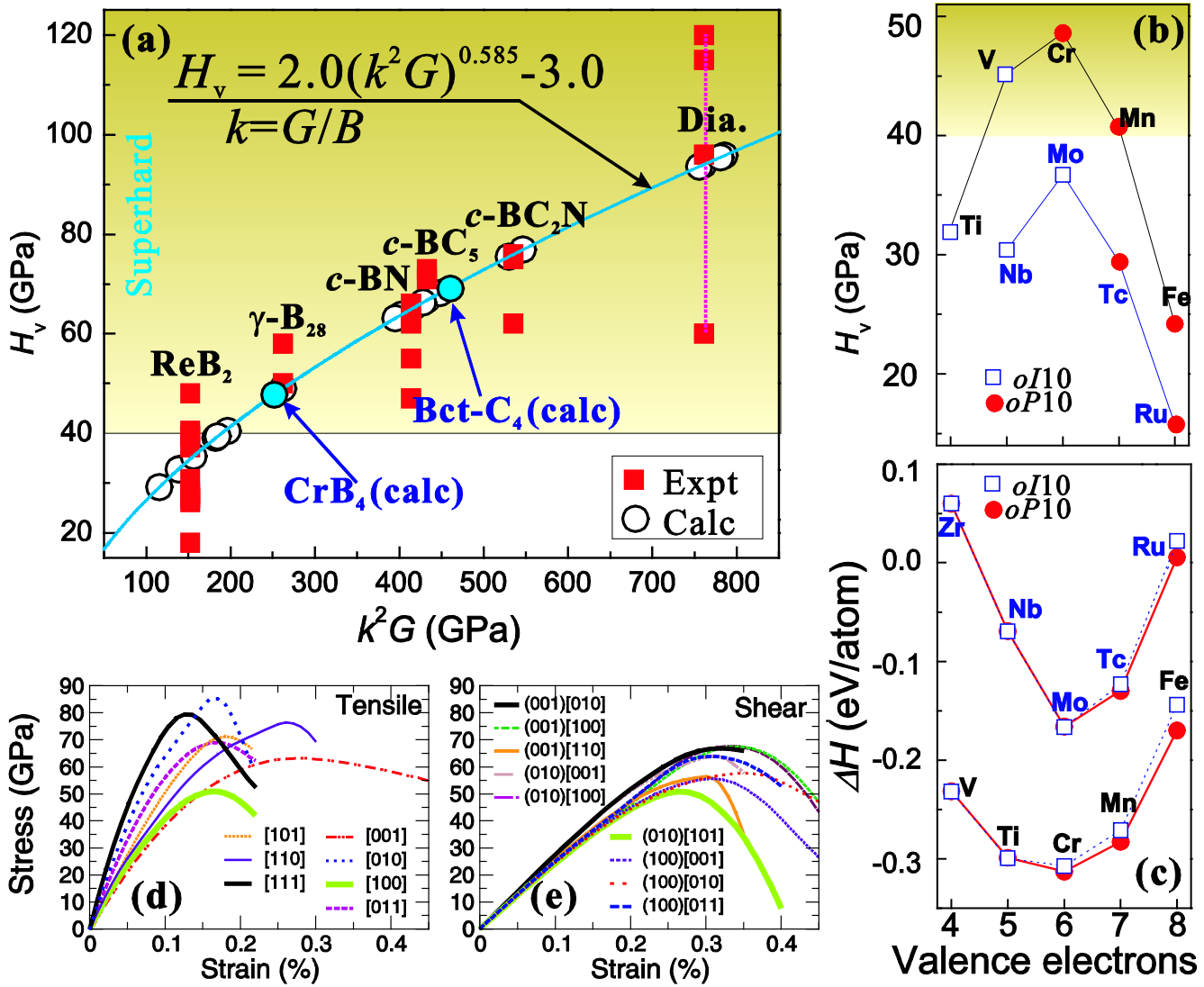


New Superhard Material without the need of high pressure

CrB4

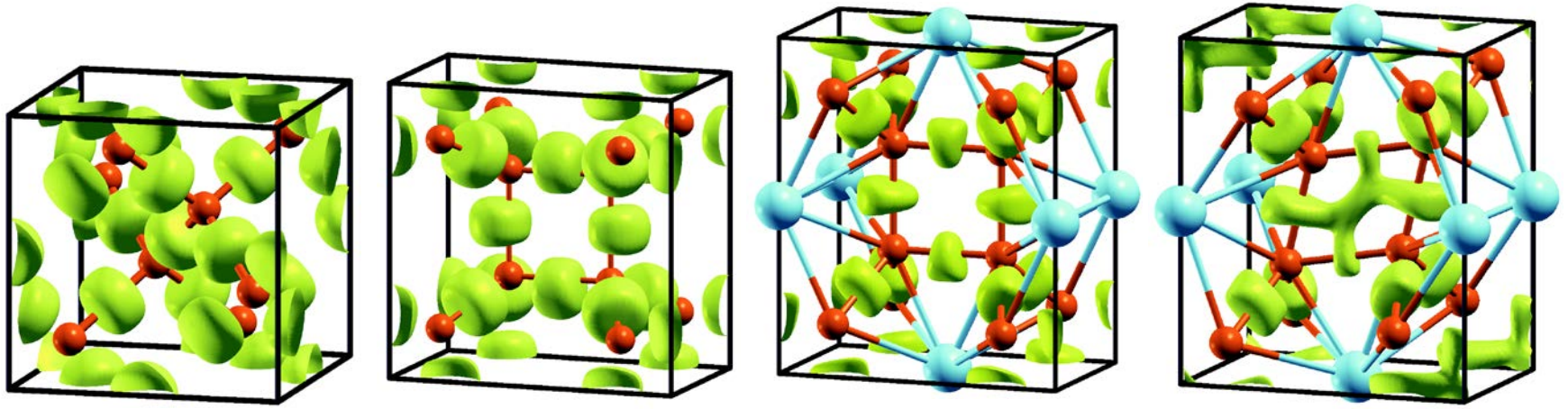


Discovery of new superhard material by design: CrB_4



Physical origin of superhardness of CrB_4

diamond **C_4** **CrB_4 (old)** **CrB_4 (new)**



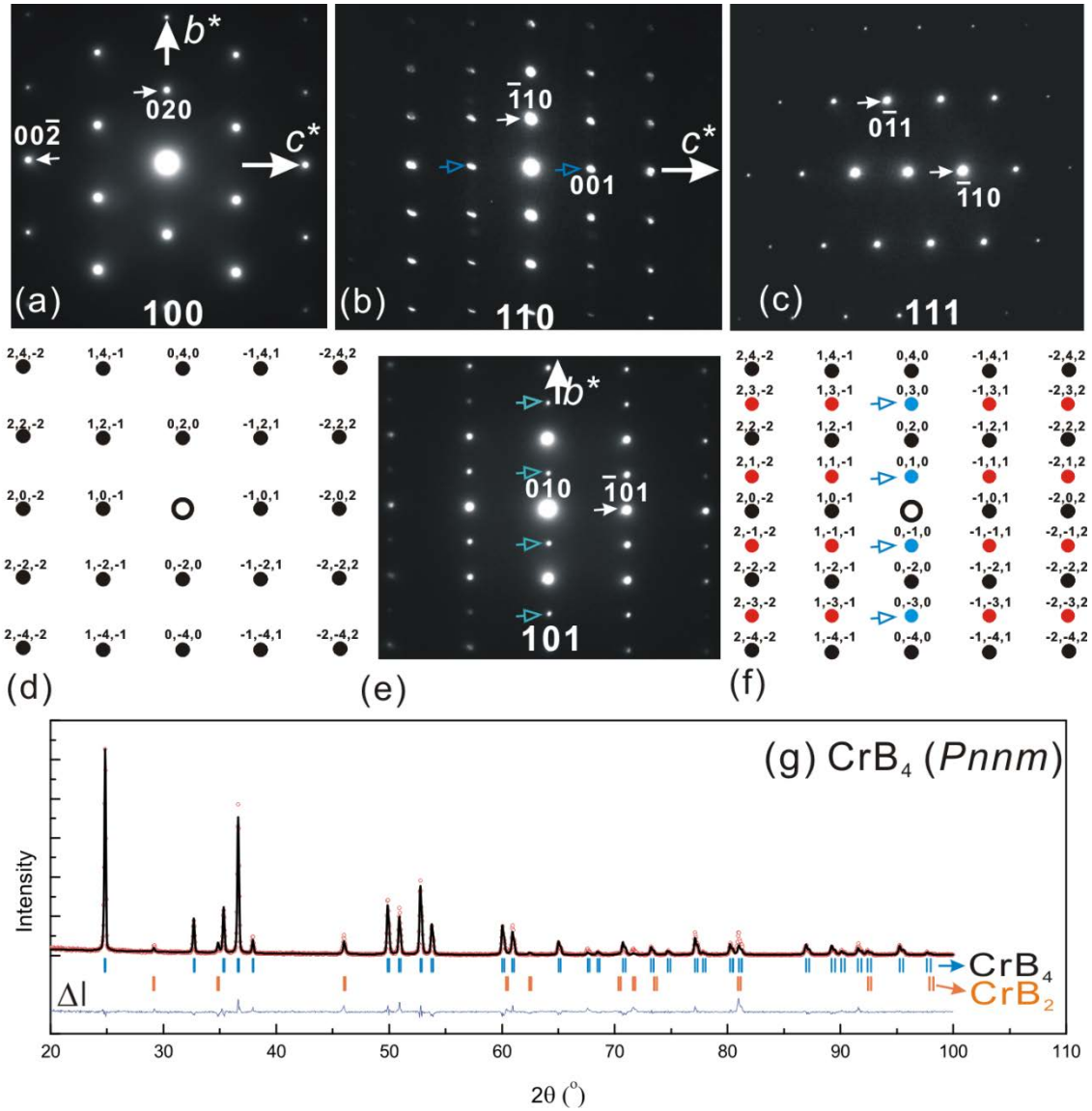
(a) $Fd\bar{3}m$ ($cF8$) (b) I_4/mmm ($tI8$) (c) $Immm$ ($oI10$) (d) $Pnnm$ ($oP10$)

Phys Rev Lett 104, 125504 (2010).

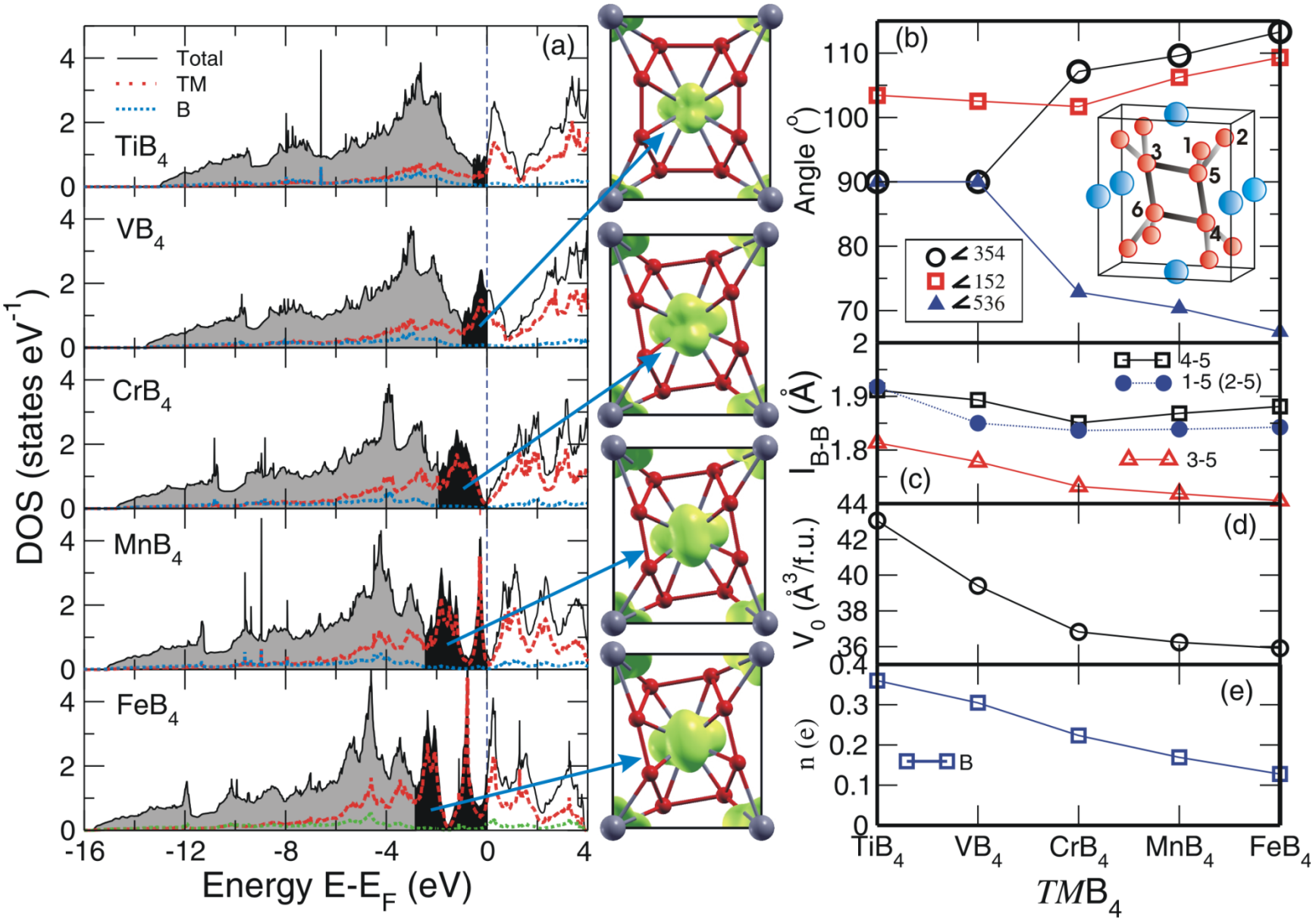
Acta Chem. Scand., 22, 3103 (1968).

Haiyang Niu, et al., Phys. Rev. B., (in press, 2012)

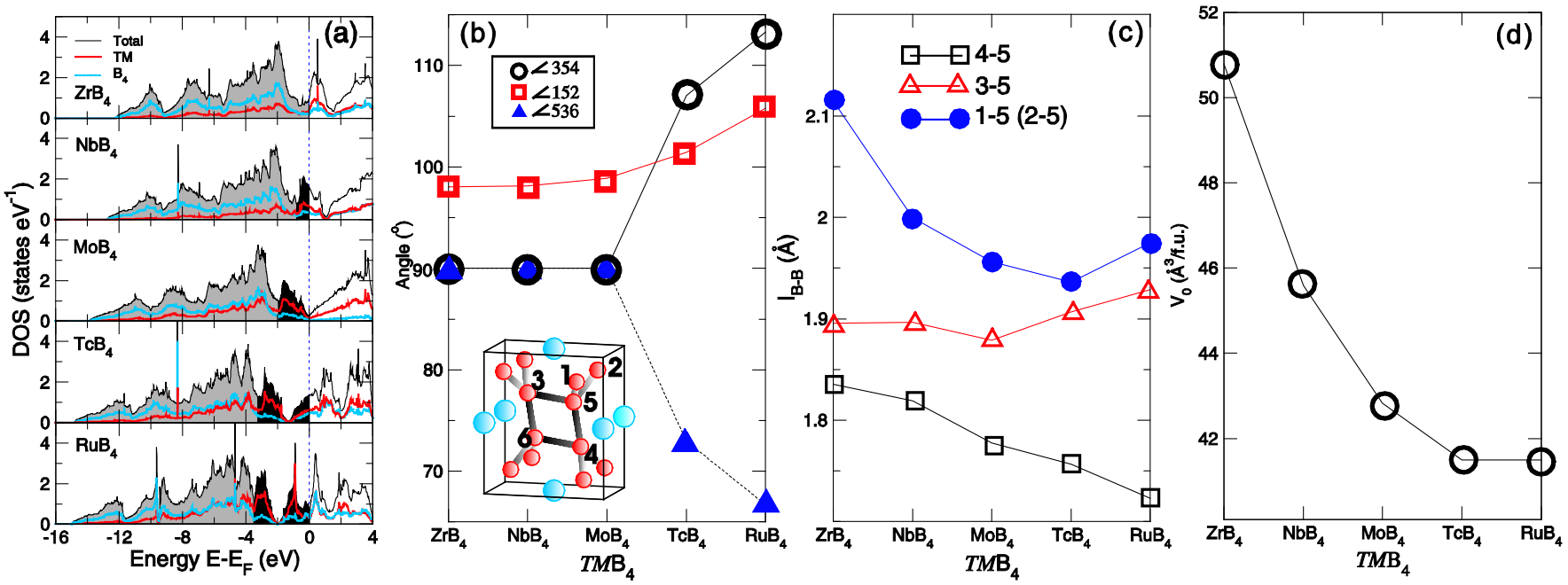
Confirmation of new structure CrB_4



Electronic origin of distortion for CrB_4



Structural distortion of 4d-*TM*B_4



Conclusions

1. **Intrinsic correlation between strength and ductility of Al-based materials**
2. **New hardness modeling of polycrystalline materials and bulk metallic glasses**

Can we ever be able to find something harder than diamond?