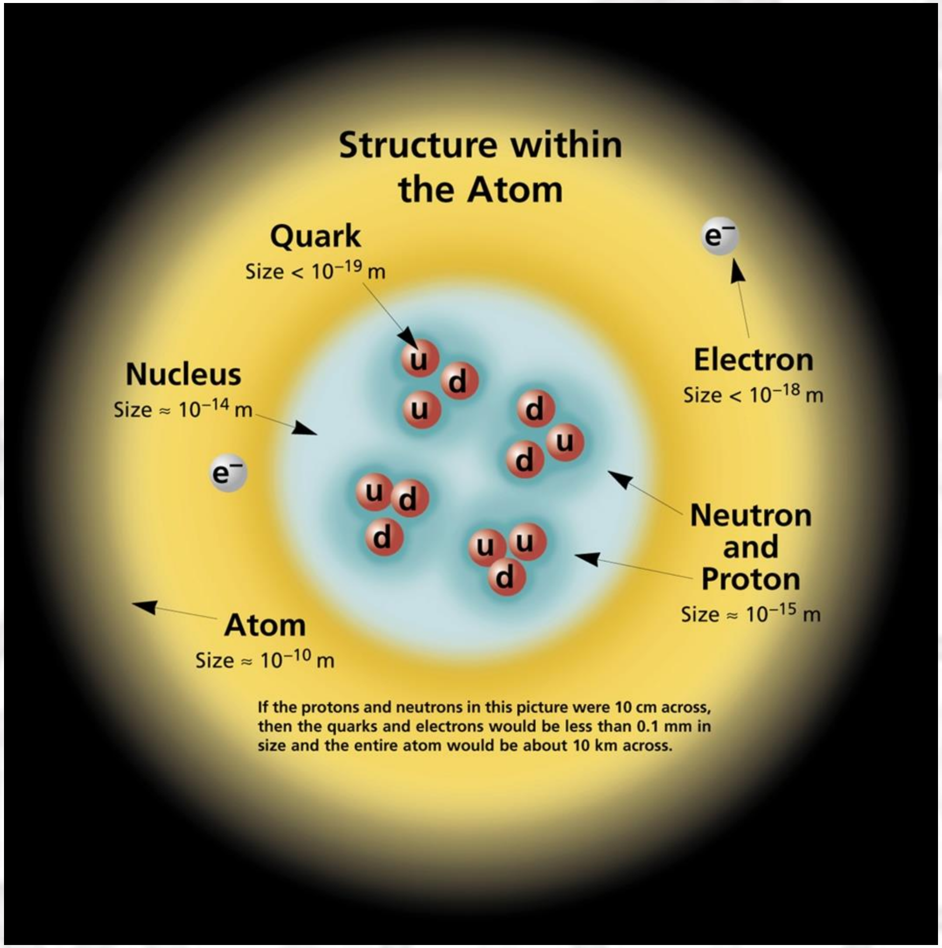
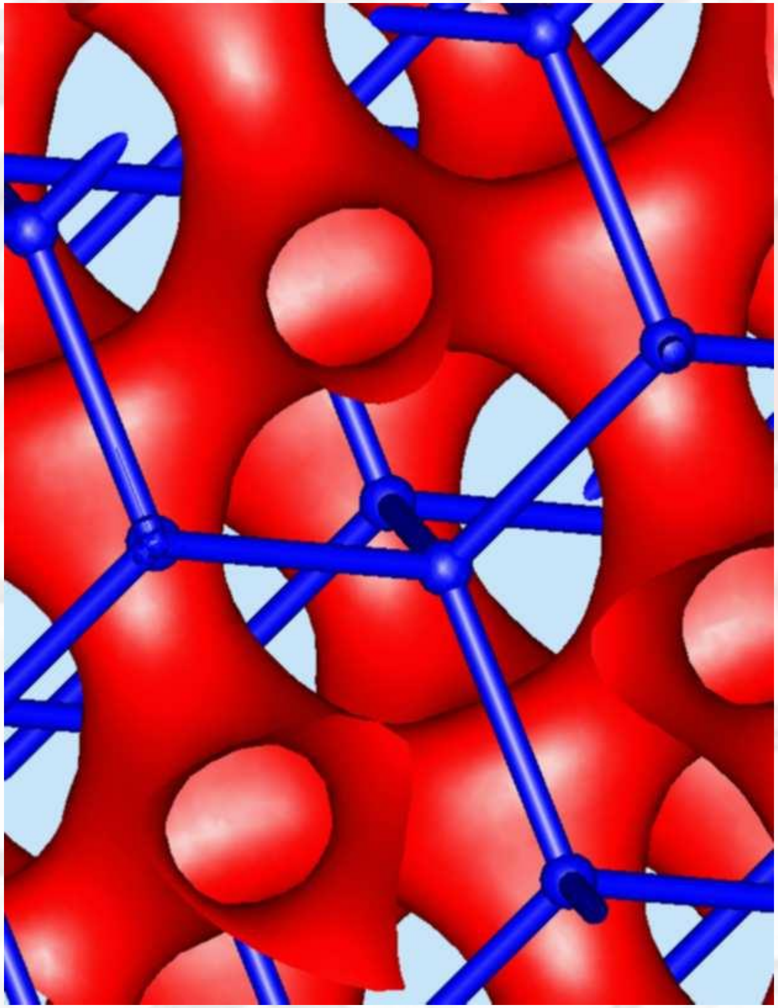


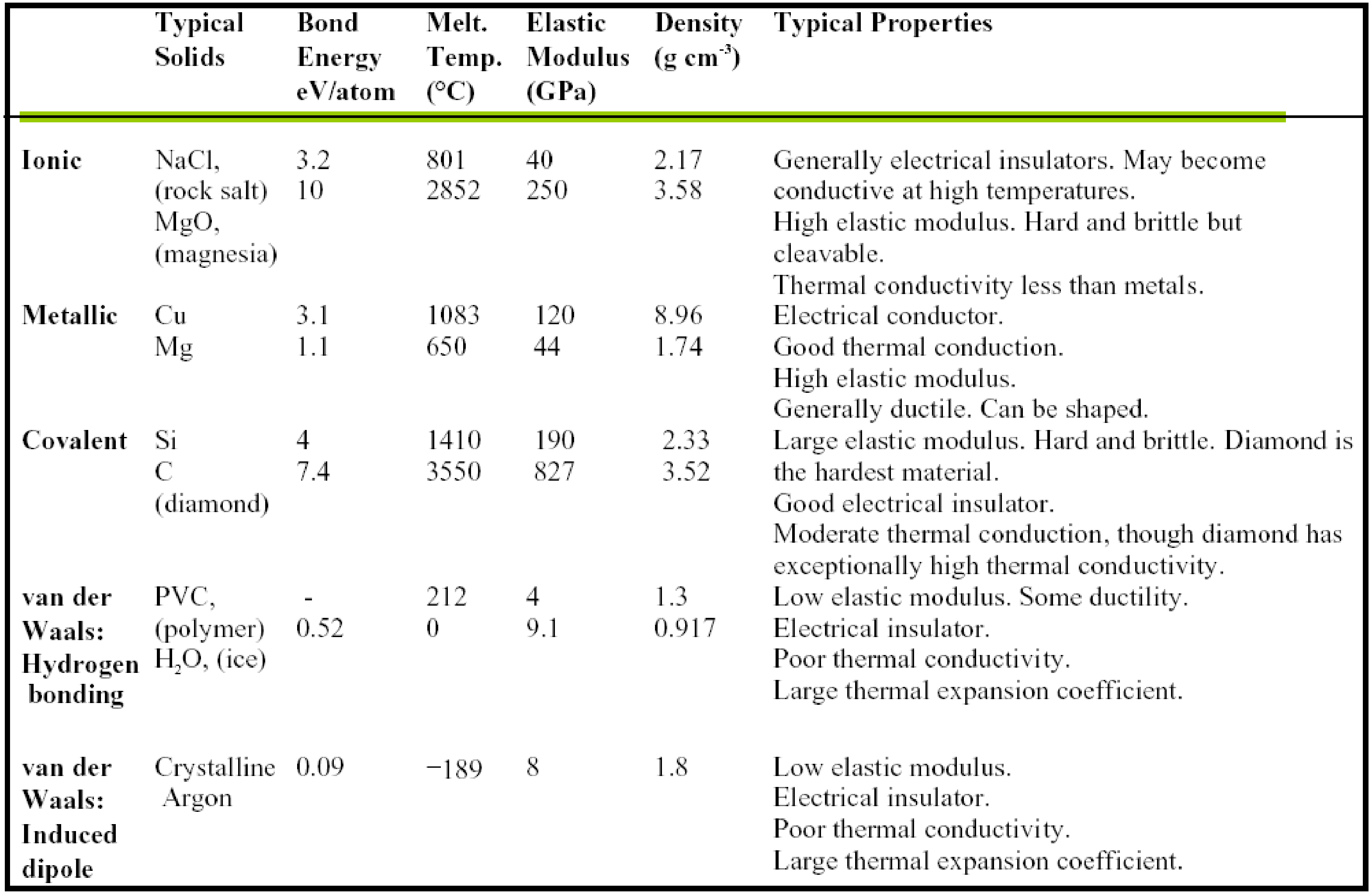
Chapter 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING



INTERATOMIC BONDS

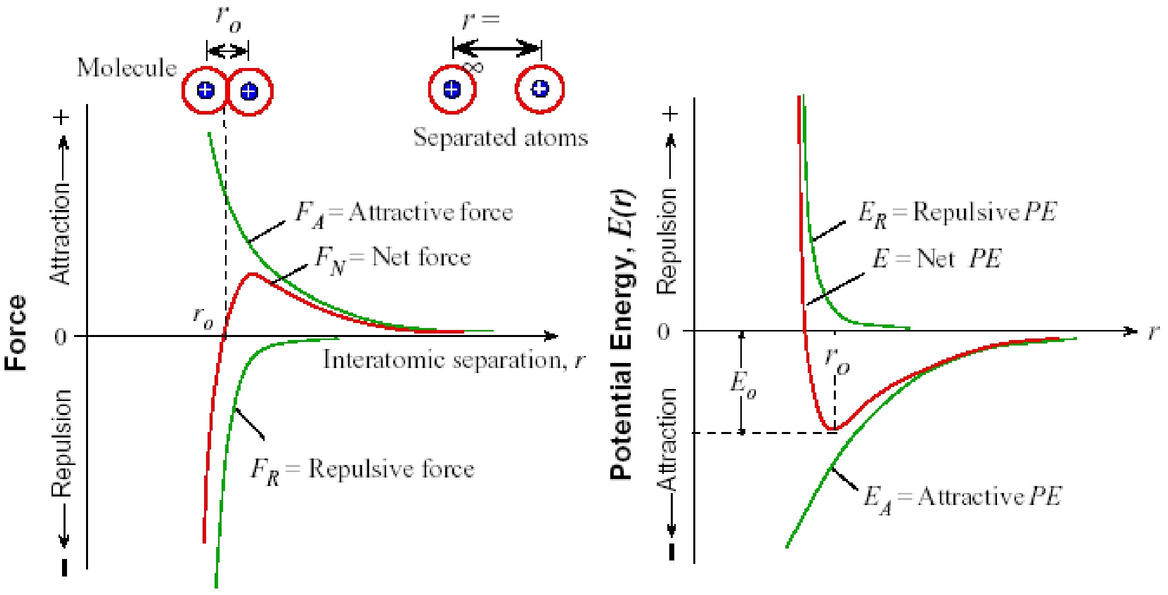
Comparison of Different Atomic Bonds



	Typical Solids	Bond Energy eV/atom	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm^{-3})	Typical Properties
Ionic	NaCl, (rock salt) MgO, (magnesia)	3.2 10	801 2852	40 250	2.17 3.58	Generally electrical insulators. May become conductive at high temperatures. High elastic modulus. Hard and brittle but cleavable. Thermal conductivity less than metals.
Metallic	Cu Mg	3.1 1.1	1083 650	120 44	8.96 1.74	Electrical conductor. Good thermal conduction. High elastic modulus. Generally ductile. Can be shaped.
Covalent	Si C (diamond)	4 7.4	1410 3550	190 827	2.33 3.52	Large elastic modulus. Hard and brittle. Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
van der Waals: Hydrogen bonding	PVC, (polymer) H_2O, (ice)	- 0.52	212 0	4 9.1	1.3 0.917	Low elastic modulus. Some ductility. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
van der Waals: Induced dipole	Crystalline Argon	0.09	−189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

INTERATOMIC BONDS (1)

Bonding: Molecules



(a) Force vs r

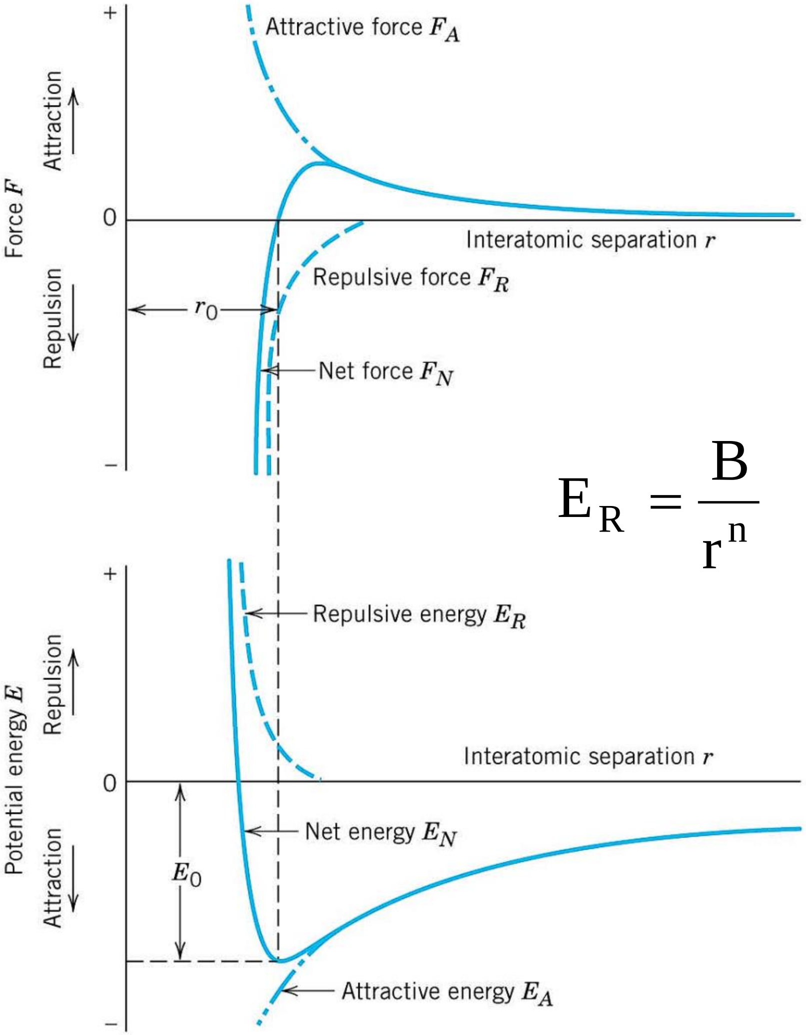
(b) Potential energy vs r

Bonding length r_0

Bonding energy $E_0>0$

$F_N=0$
or
$dE/dr=0$

INTERATOMIC BONDS (2)



$$E_R = \frac{B}{r^n}$$

F_A – attractive force is defined by the nature of the bond (e.g. Coulomb force for the ionic bonding)

F_R – atomic repulsive force, when electron shells start to overlap

Thus the net force $\mathbf{F_N (r) = F_A + F_R}$

In equilibrium: $\mathbf{F_N (r_0) = F_A + F_R = 0}$

Let us consider the same conditions

but in the term of potential energy, E.

By definition:

$$E = \int F dr$$

$$E_N = \int_{\infty}^{r} F_N dr = \int_{\infty}^{r} F_A dr + \int_{\infty}^{r} F_R dr = E_A + E_R$$

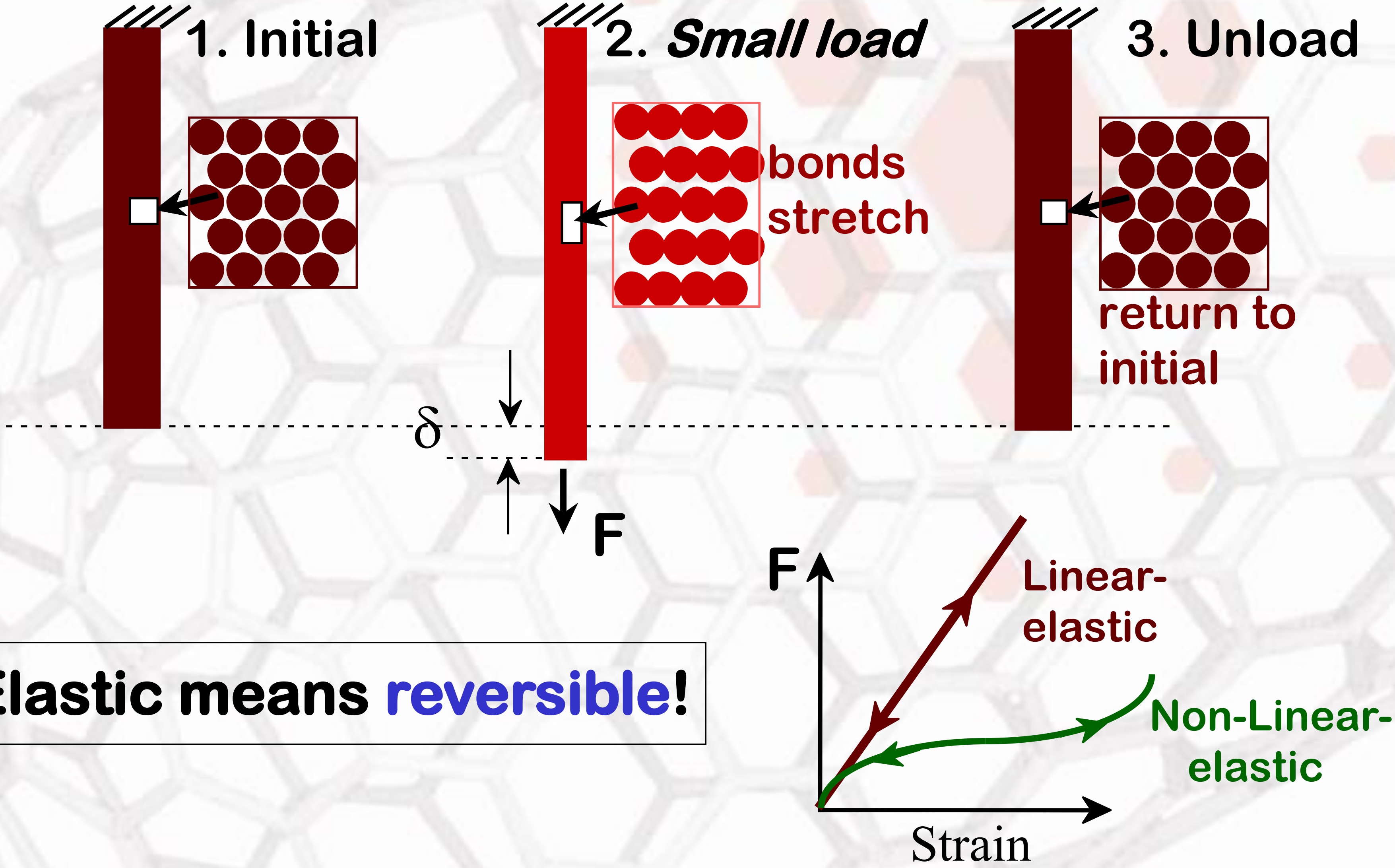
$$if \;\; F_N = 0 \quad \frac{dE_N}{dr} = 0 \Rightarrow E_N \text{ has extremum}$$

$$\text{more specifically at } r = r_0,\; F_N = 0,$$

$$\text{system in equilibrium}$$

$$\text{and } E_N \text{ possesses minimum}$$

ELASTIC DEFORMATION



1. Initial

2. *Small load*

bonds stretch

3. Unload

return to initial

δ

F

F

Linear-elastic

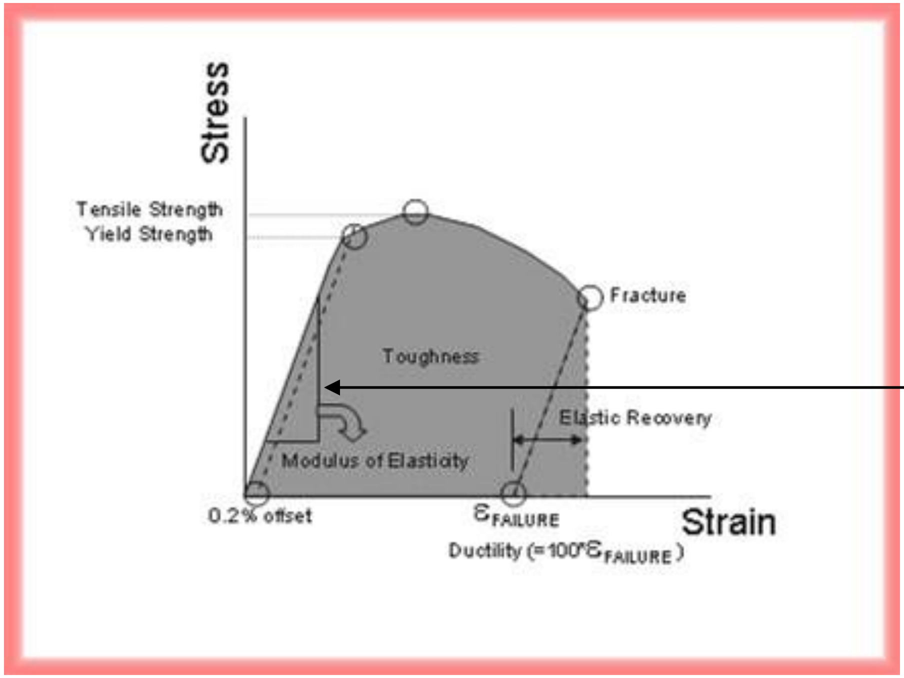
Non-Linear-elastic

Strain

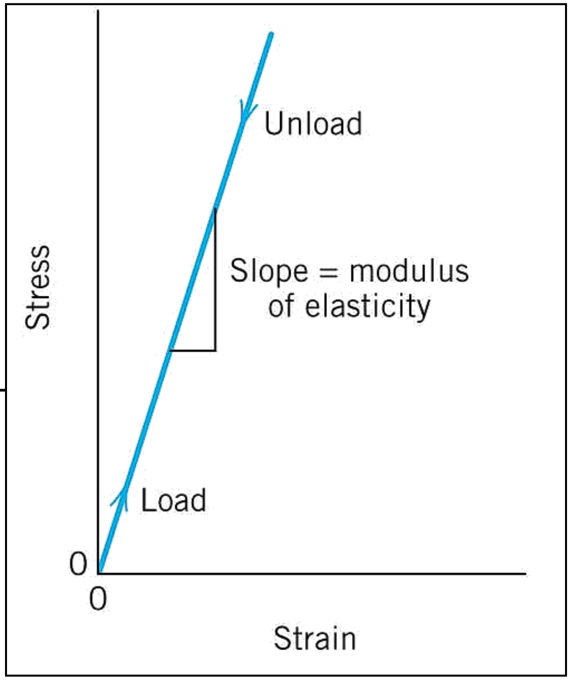
Elastic means reversible!

Stress Versus Strain: Elastic Deformation

Typical Stress-Strain Diagram
for one-dimensional tensile test



Elastic Region

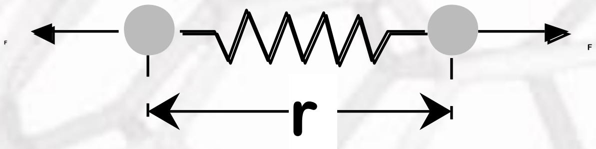


Hooke's Law: $\sigma = E\,\varepsilon$

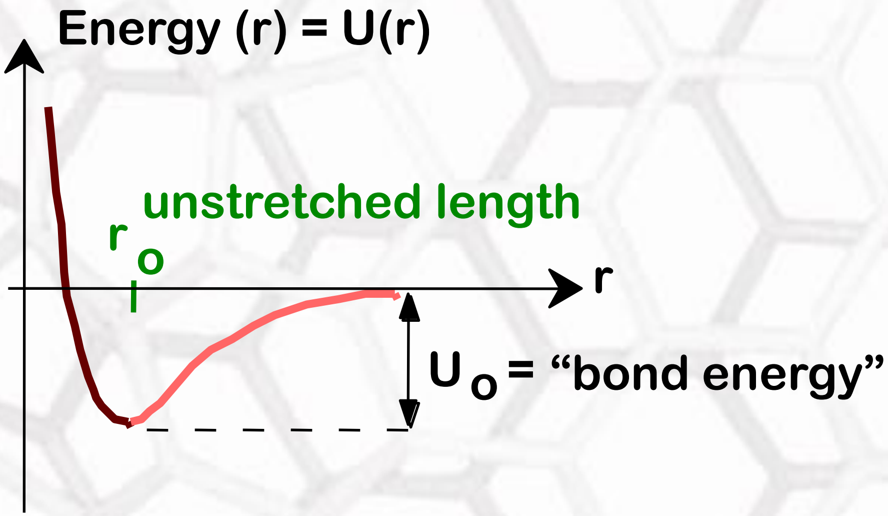
E [N/m^2; GPa] is ***Young's modulus*** or ***modulus of elasticity***

PROPERTIES FROM BONDING: E (1)

- **Bond length**, r



- **Bond energy**, U_o


Energy (r) = U(r)

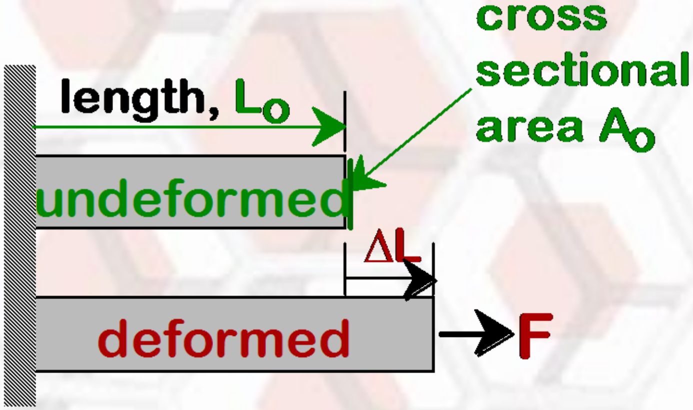
unstretched length

r_o

r

U_o = “bond energy”

- **Elastic modulus, E**


cross sectional area A_o

length, L_o

undeformed

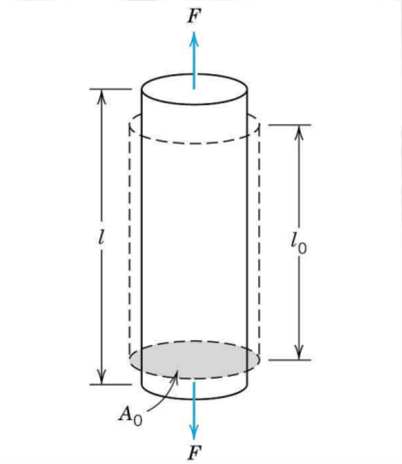
ΔL

deformed

F

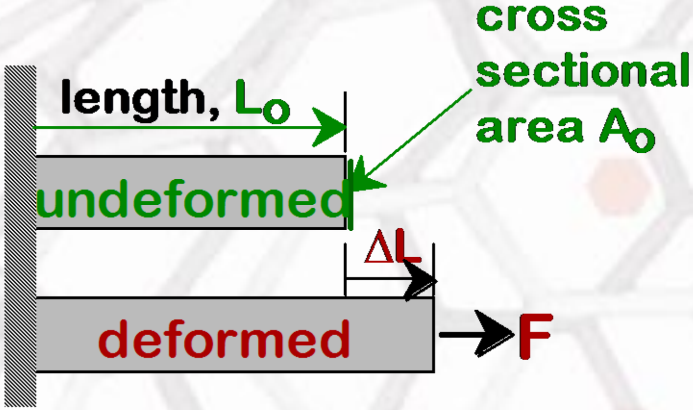
Elastic modulus

$$\frac{F}{A_o} = E \frac{\Delta L}{L_o}$$



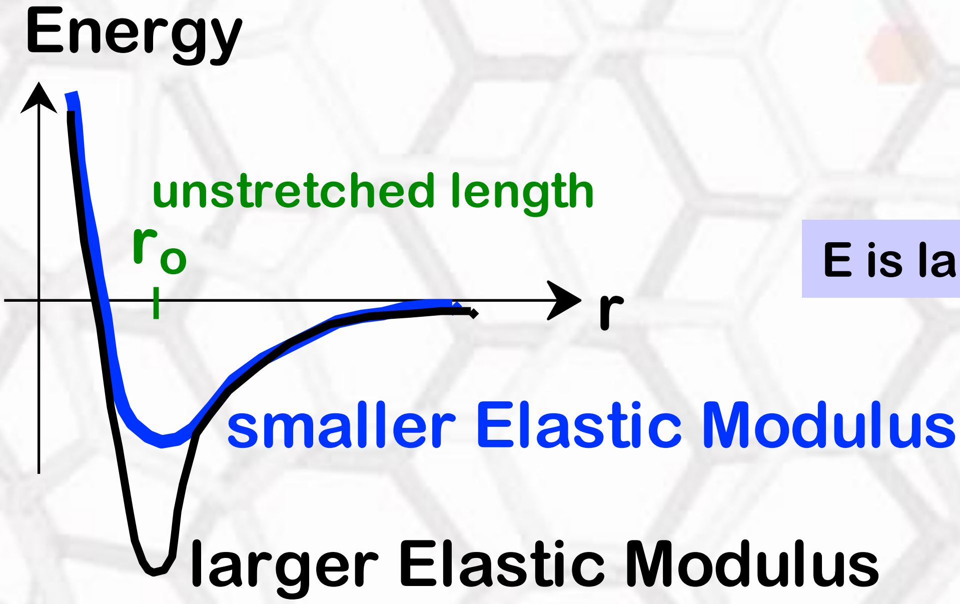
PROPERTIES FROM BONDING: E (2)

- **Elastic modulus**, E



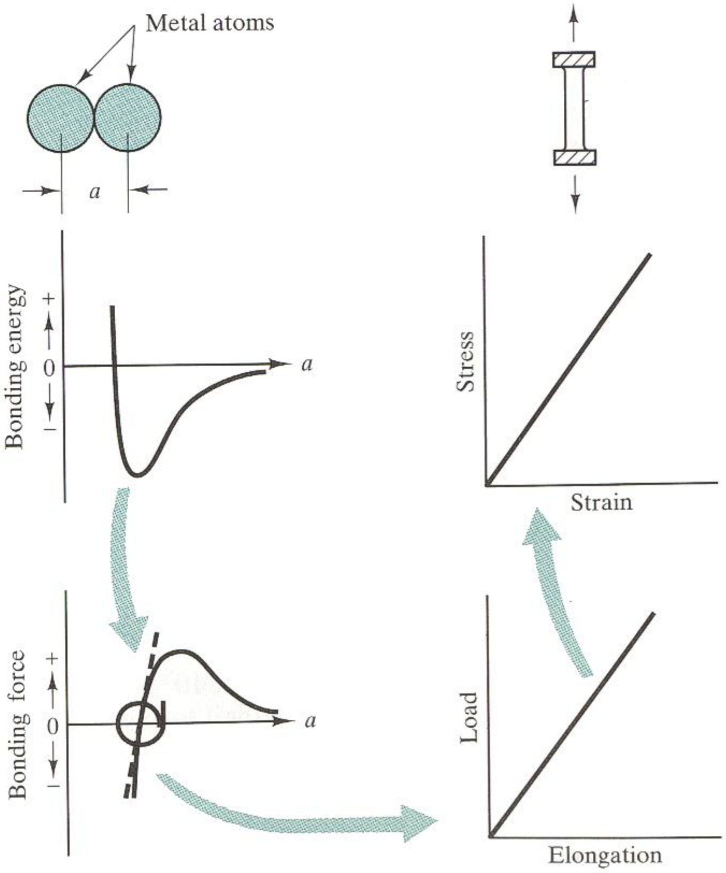
Elastic modulus

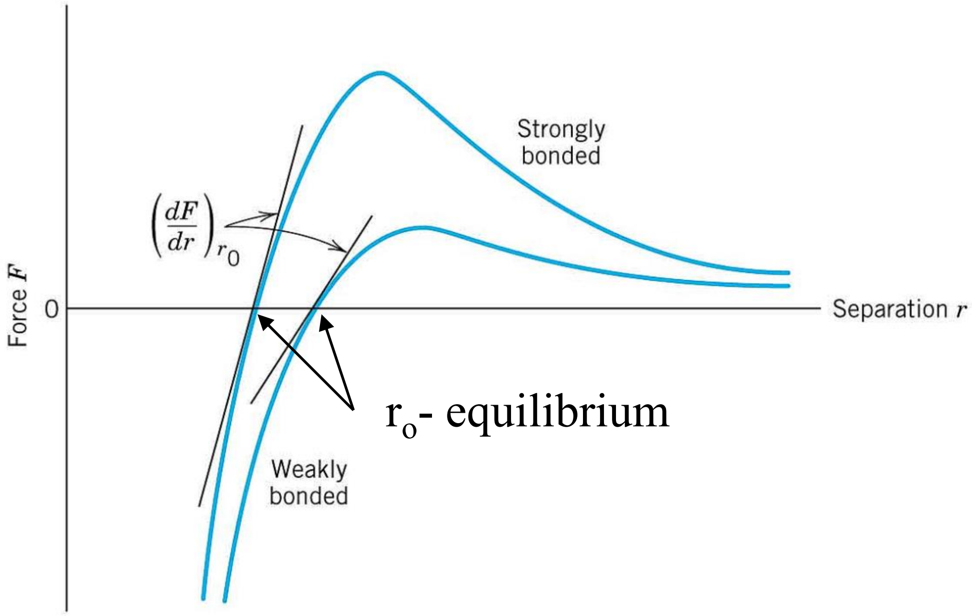
$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$



E is larger if U_o is larger.

Atomic Mechanism of Elastic Deformation





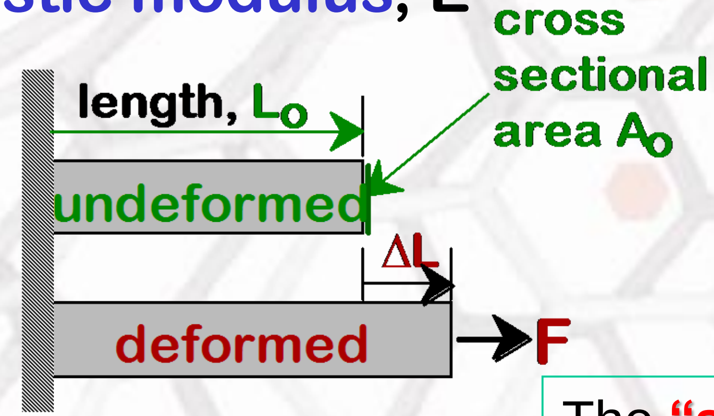
r_o- equilibrium

$E \sim (dF/dr)_{r_o}$

Weaker bonds – the atoms easily move out from equilibrium position

PROPERTIES FROM BONDING: E (3)

- **Elastic modulus**, E



Elastic modulus

$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$

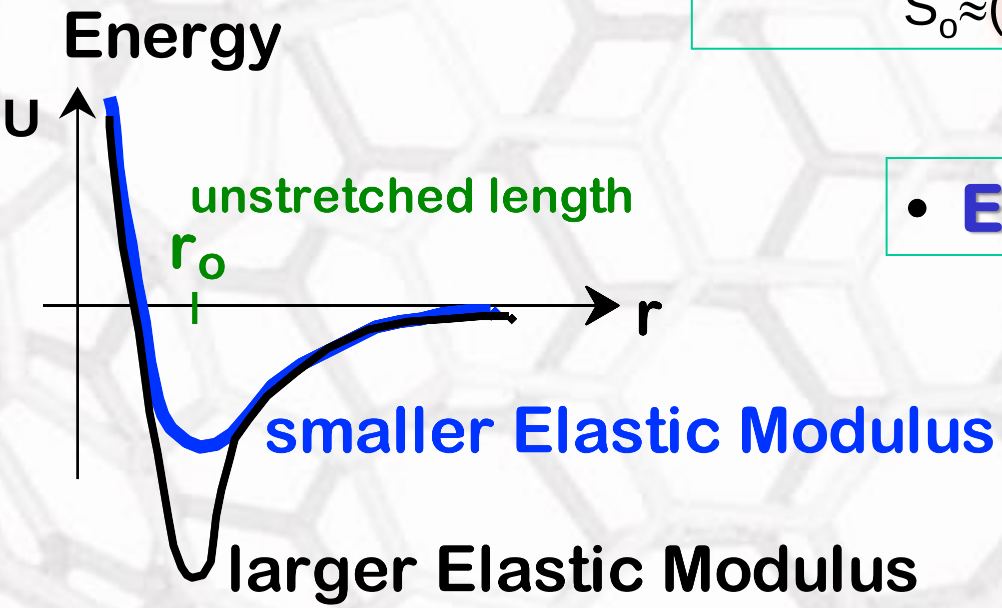
The **"stiffness"** (S) of the bond is given by:

$S = dF/dr = d^2U/dr^2$

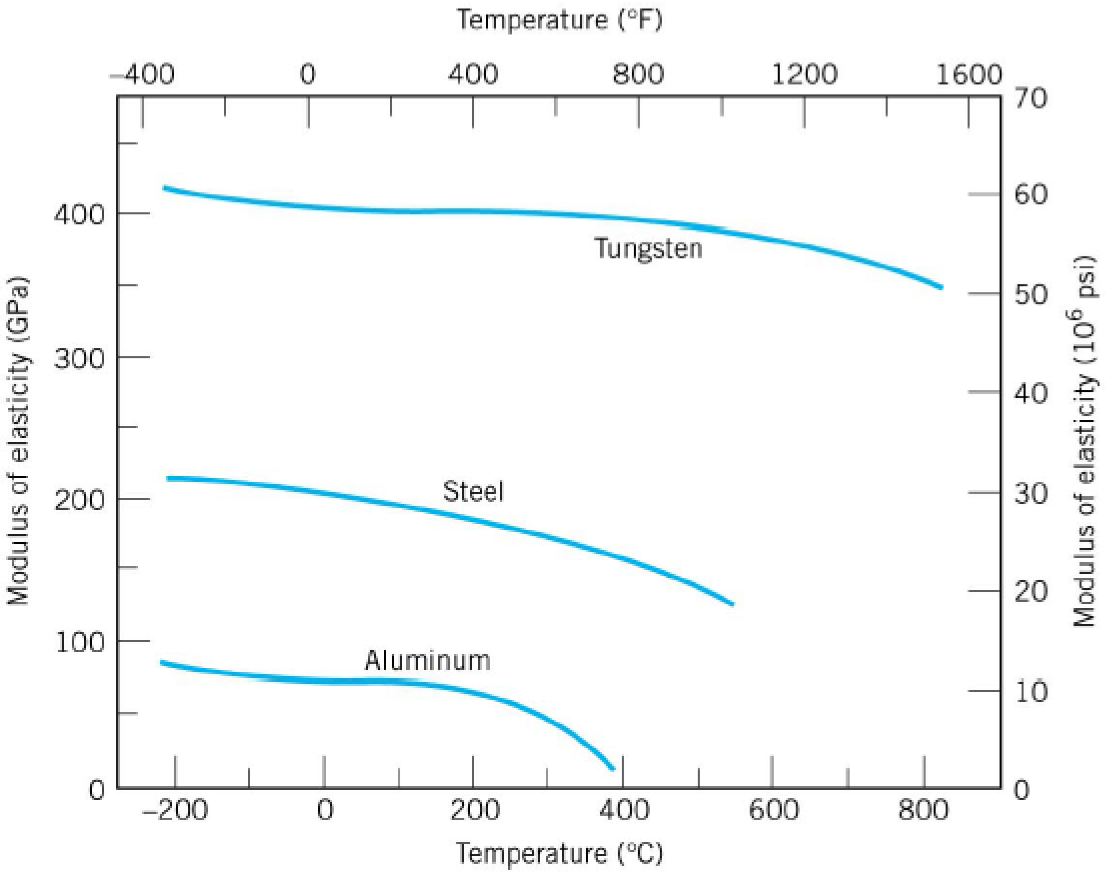
$S_o \approx (d^2U/dr^2)_{ro}$

- **E ~ S=curvature of U at r_o**

Show that $E = (S_o/r_0)$

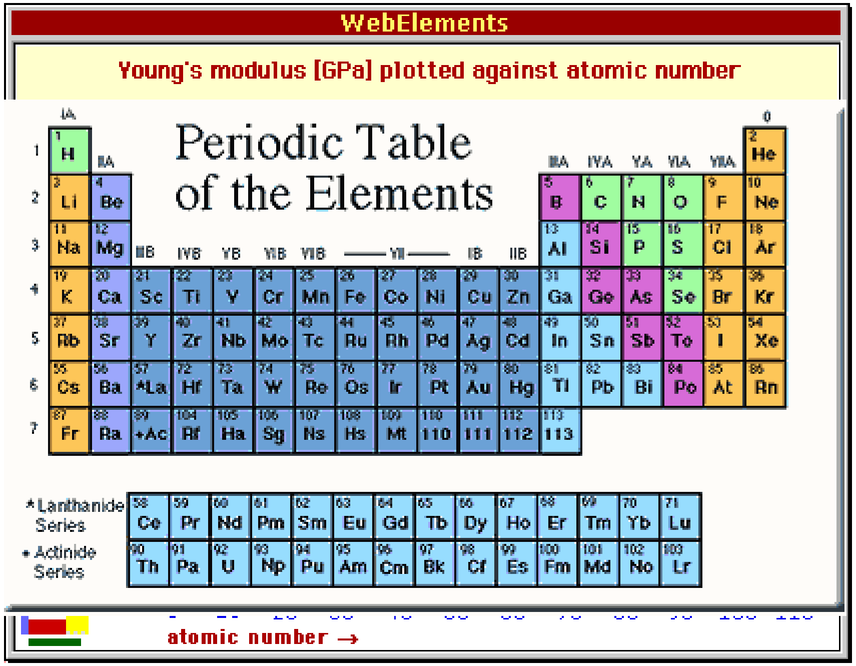


Modulus of Elasticity for Different Metals



Young's modulus

Young's modulus is a numerical constant, named for the 18th-century English physician and physicist Thomas Young, that describes the elastic properties of a solid undergoing tension or compression in only one direction.



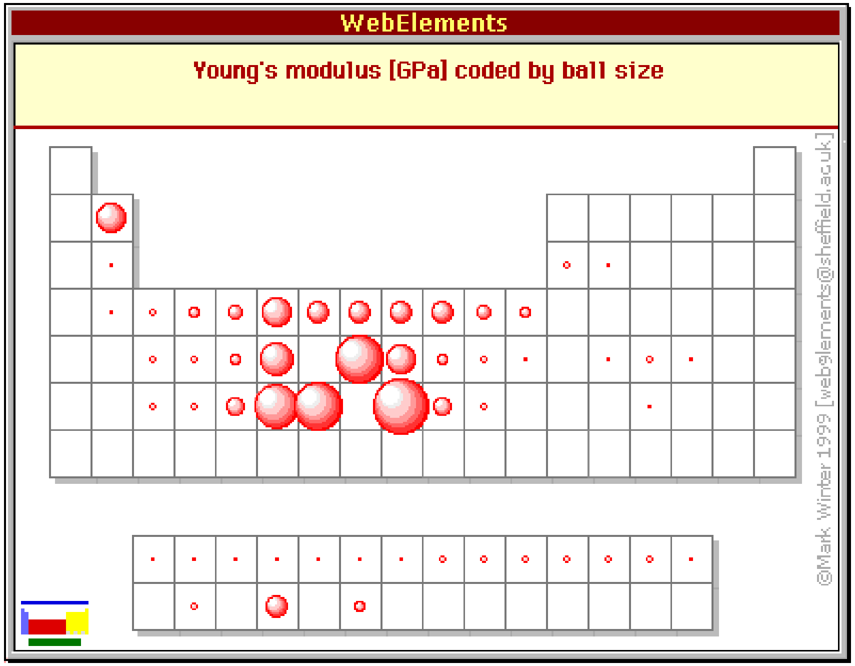
WebElements

Young's modulus [GPa] plotted against atomic number

Periodic Table of the Elements

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

*Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

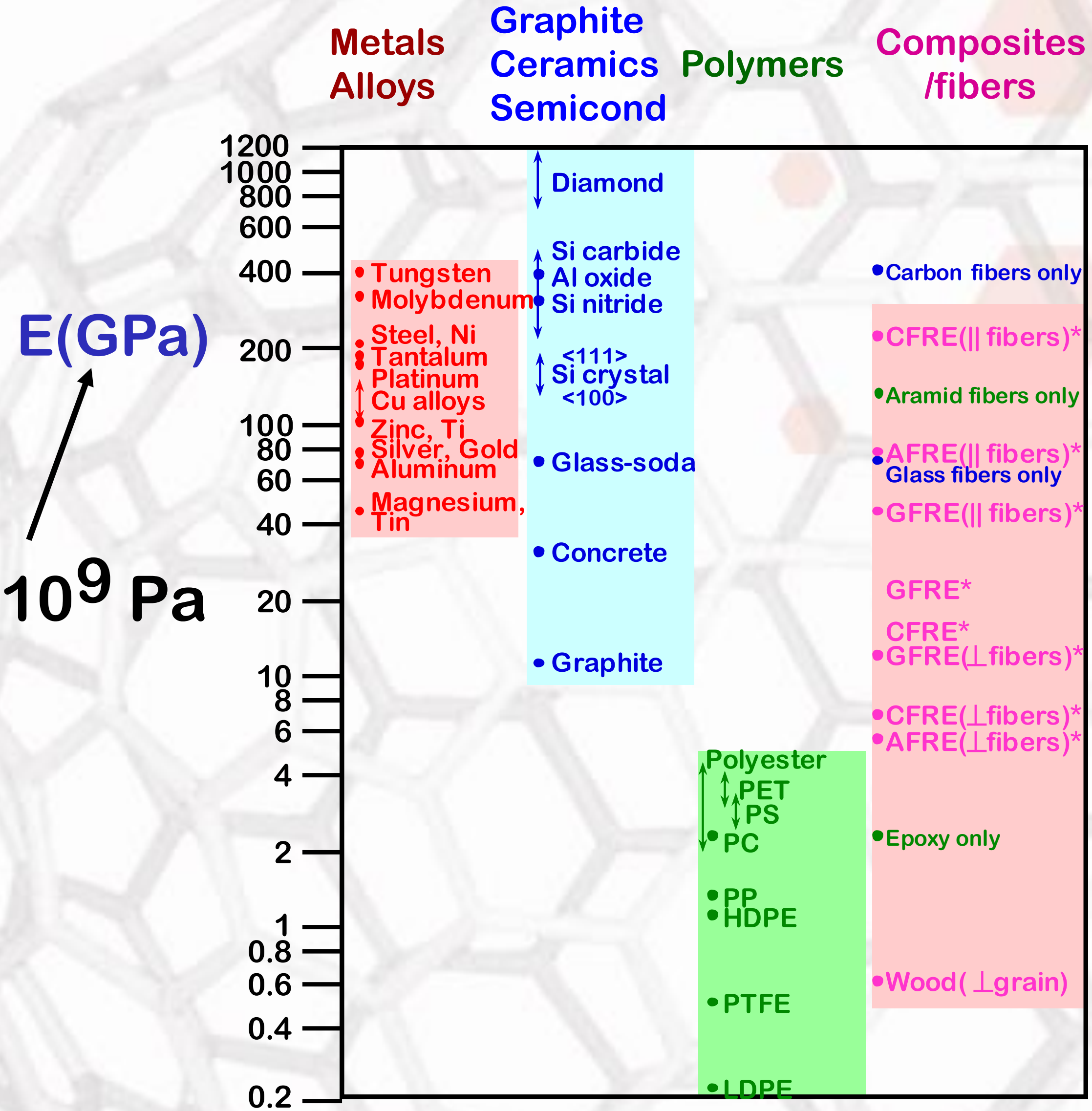


WebElements

Young's modulus [GPa] coded by ball size

Higher E – higher "stiffness"

YOUNG'S MODULI: COMPARISON



$E_{ceramics}$

$> E_{metals}$

$>> E_{polymers}$

Composite data based on reinforced epoxy with 60 vol% of aligned carbon (CFRE), aramid (AFRE), or glass (GFRE) fibers.

HOT TOPIC

PHYSICAL REVIEW B 85, 144117 (2012)

Site preference and effect of alloying on elastic properties of ternary *B*2 NiAl-based alloys

A. V. Ponomareva,[1,*] E. I. Isaev,[1,2] Yu. Kh. Vekilov,[1] and I. A. Abrikosov[2]
[1]*Theoretical Physics and Quantum Technology Department, National University of Science and Technology MISIS, RU-119049 Moscow, Russia*
[2]*Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*

(Received 14 October 2011; revised manuscript received 18 March 2012; published 25 April 2012)

Using the exact muffin-tin orbitals method in conjunction with the coherent potential approximation, we study the site preference of transition metal impurities X (X = Sc, Ti, V, Cr, W, Re, Co) in *B*2 NiAl and their effect on its elastic properties. Analyzing interatomic bonding of NiAl-X alloys and elastic characteristics evaluated from the elastic constants C_{11}, C_{12}, and C_{44}, we predict that the addition of W, V, Ti, and Re atoms could yield improved ductility for *B*2 NiAl-X alloys without significant changes in the macroscopic elastic moduli.

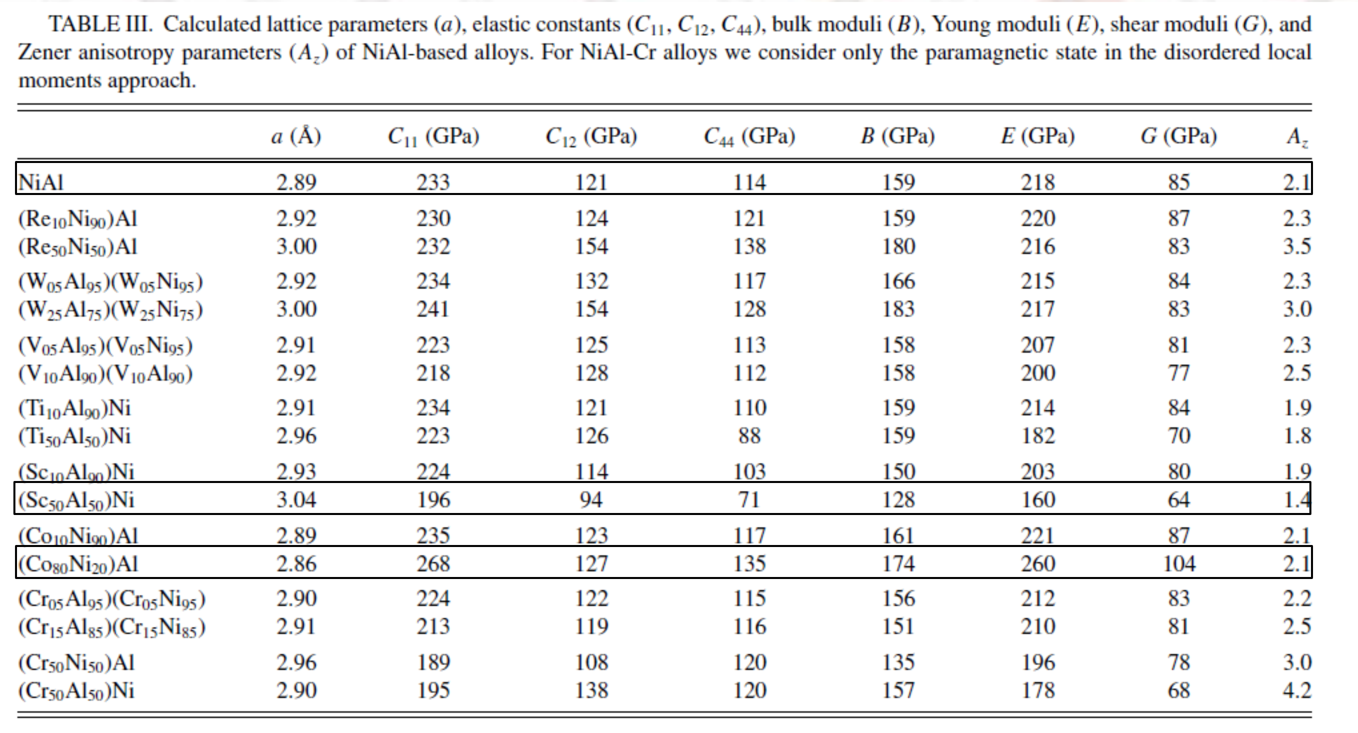
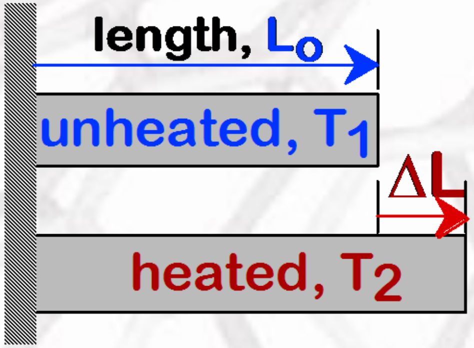


TABLE III. Calculated lattice parameters (a), elastic constants (C_{11}, C_{12}, C_{44}), bulk moduli (B), Young moduli (E), shear moduli (G), and Zener anisotropy parameters (A_z) of NiAl-based alloys. For NiAl-Cr alloys we consider only the paramagnetic state in the disordered local moments approach.

	a (Å)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	B (GPa)	E (GPa)	G (GPa)	A_z
NiAl	2.89	233	121	114	159	218	85	2.1
$(Re_{10}Ni_{90})Al$	2.92	230	124	121	159	220	87	2.3
$(Re_{50}Ni_{50})Al$	3.00	232	154	138	180	216	83	3.5
$(W_{05}Al_{95})(W_{05}Ni_{95})$	2.92	234	132	117	166	215	84	2.3
$(W_{25}Al_{75})(W_{25}Ni_{75})$	3.00	241	154	128	183	217	83	3.0
$(V_{05}Al_{95})(V_{05}Ni_{95})$	2.91	223	125	113	158	207	81	2.3
$(V_{10}Al_{90})(V_{10}Al_{90})$	2.92	218	128	112	158	200	77	2.5
$(Ti_{10}Al_{90})Ni$	2.91	234	121	110	159	214	84	1.9
$(Ti_{50}Al_{50})Ni$	2.96	223	126	88	159	182	70	1.8
$(Sc_{10}Al_{90})Ni$	2.93	224	114	103	150	203	80	1.9
$(Sc_{50}Al_{50})Ni$	3.04	196	94	71	128	160	64	1.4
$(Co_{10}Ni_{90})Al$	2.89	235	123	117	161	221	87	2.1
$(Co_{80}Ni_{20})Al$	2.86	268	127	135	174	260	104	2.1
$(Cr_{05}Al_{95})(Cr_{05}Ni_{95})$	2.90	224	122	115	156	212	83	2.2
$(Cr_{15}Al_{85})(Cr_{15}Ni_{85})$	2.91	213	119	116	151	210	81	2.5
$(Cr_{50}Ni_{50})Al$	2.96	189	108	120	135	196	78	3.0
$(Cr_{50}Al_{50})Ni$	2.90	195	138	120	157	178	68	4.2

PROPERTIES FROM BONDING: α

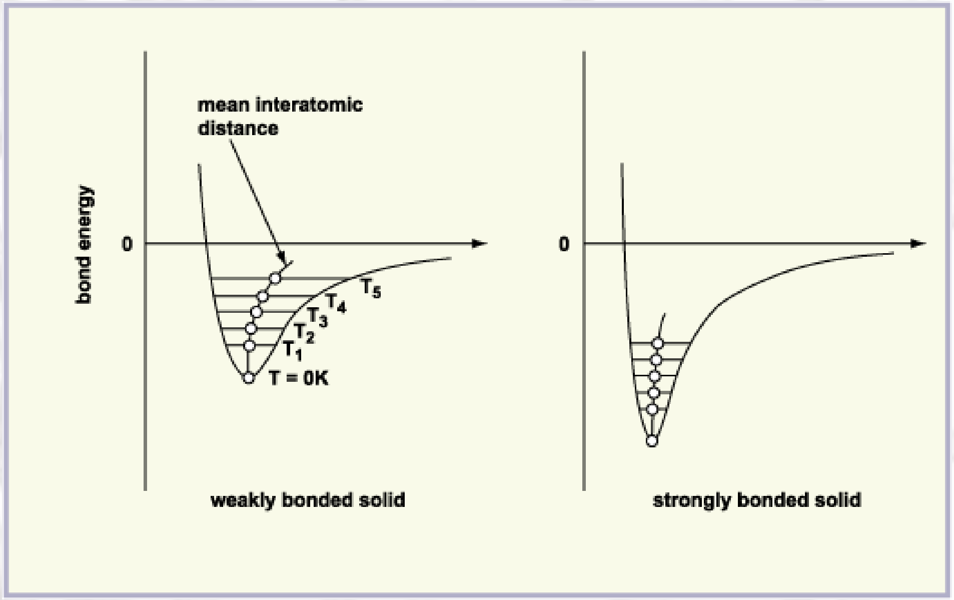
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

α is larger if U_o is smaller.

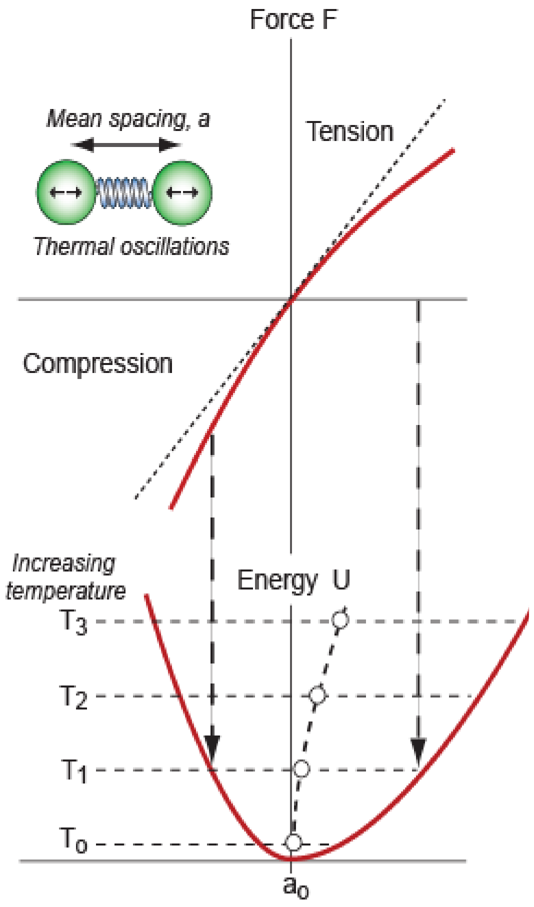


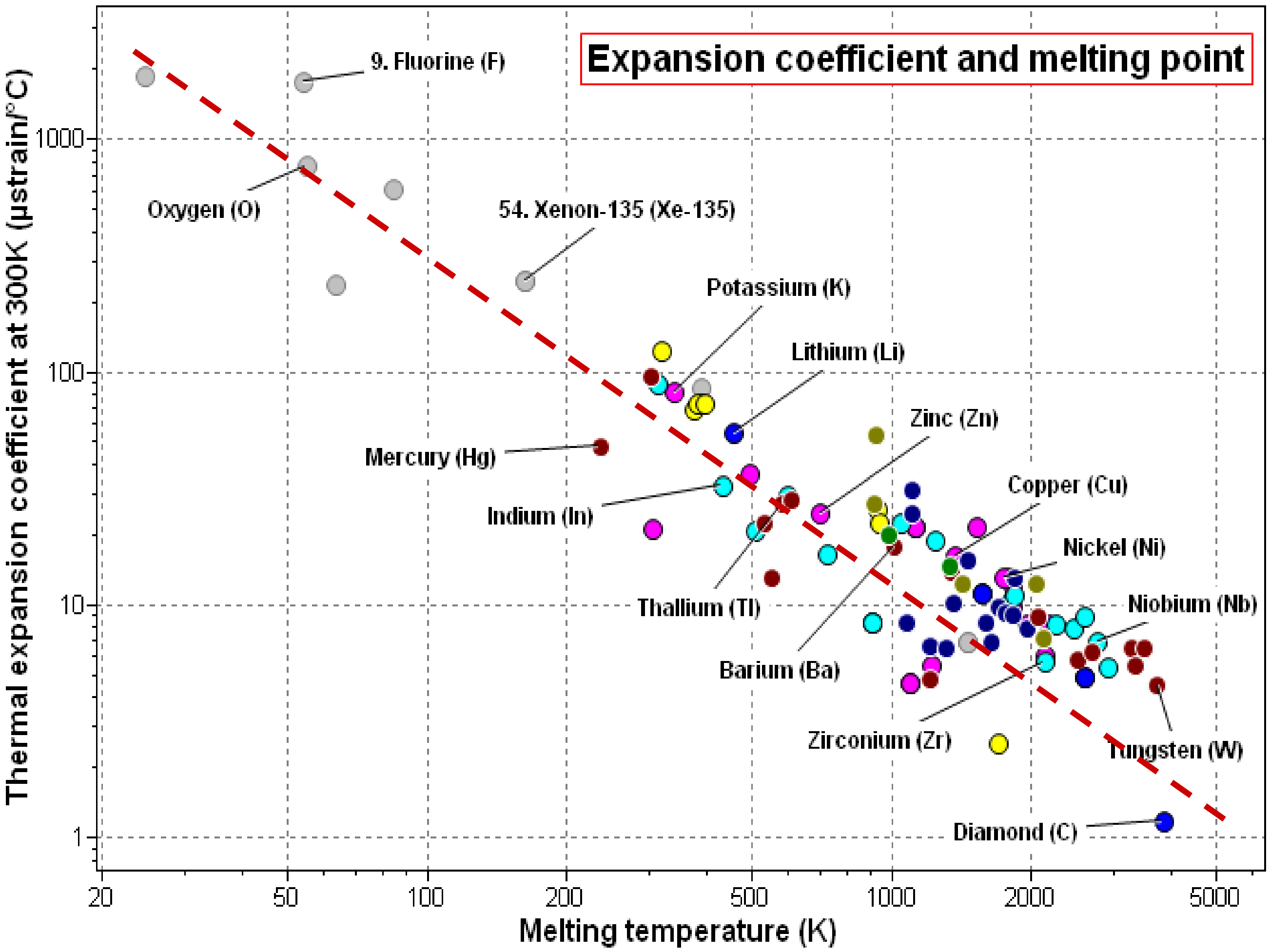
- α ~ symmetry at r_o

material	CTE (ppm/°C)
silicon	3.2
alumina	6–7
copper	16.7
tin-lead solder	27
E-glass	54
S-glass	16
epoxy resins	15–100
silicone resins	30–300

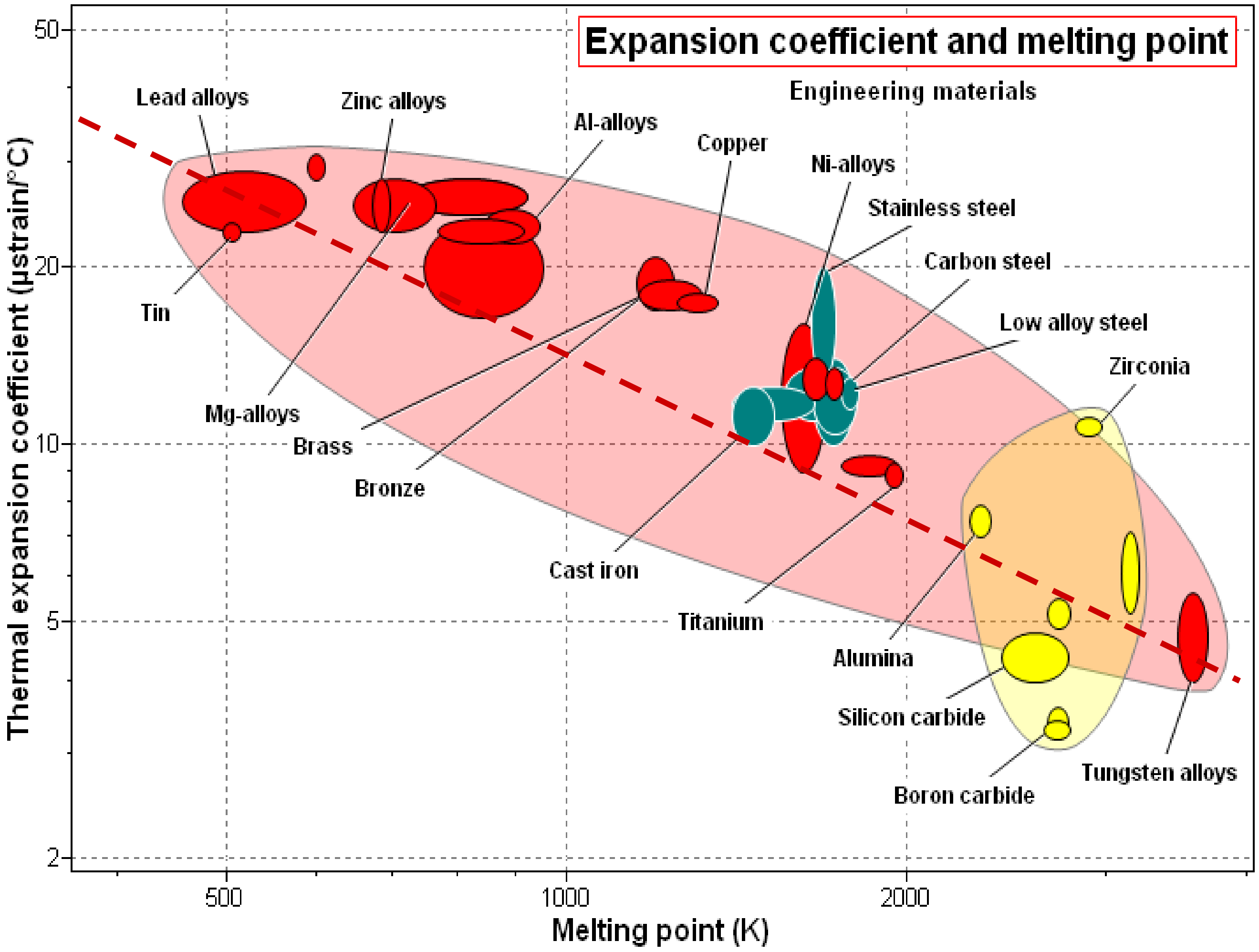
Relationships between properties

- Expansion coefficient and melting point



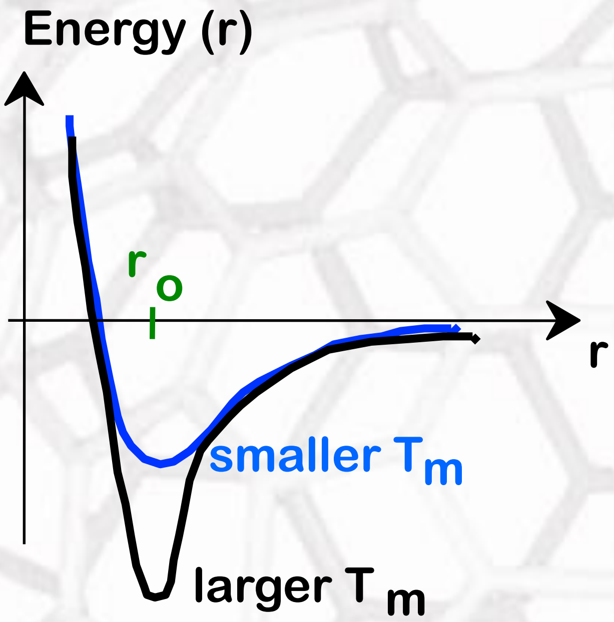


Engineering materials – the same dependence



PROPERTIES FROM BONDING: T_M

- **Melting Temperature**, T_m



T_m is larger if U_o is larger

The **melting point** of a solid is the temperature at which it **changes state from solid to liquid** at atmospheric pressure.
At the melting point the solid and liquid phase exist ***in equilibrium***.

The **Lindemann criterion** states that melting is expected when the root mean square vibration amplitude exceeds a threshold value.
Assuming that all atoms in a crystal vibrate with the same frequency *v*,
the average thermal energy can be estimated using the equipartition theorem:

$$E = 4\pi^2 m\nu^2\ u^2 = k_B T$$

where *m* is the atomic mass, *v* is the frequency, *u* is the average vibration amplitude, k_B is the Boltzmann constant, and *T* is the absolute temperature
If the threshold value of u^2 is c^2a^2 where *c* is the **Lindemann** constant and ***a* is the atomic spacing**, then the melting point is estimated as

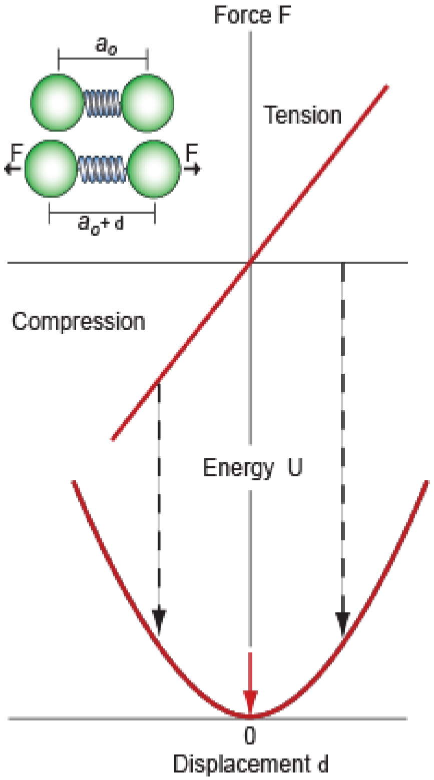
$$T_m = \frac{4\pi^2 m\nu^2 c^2 a^2}{k_B}.$$

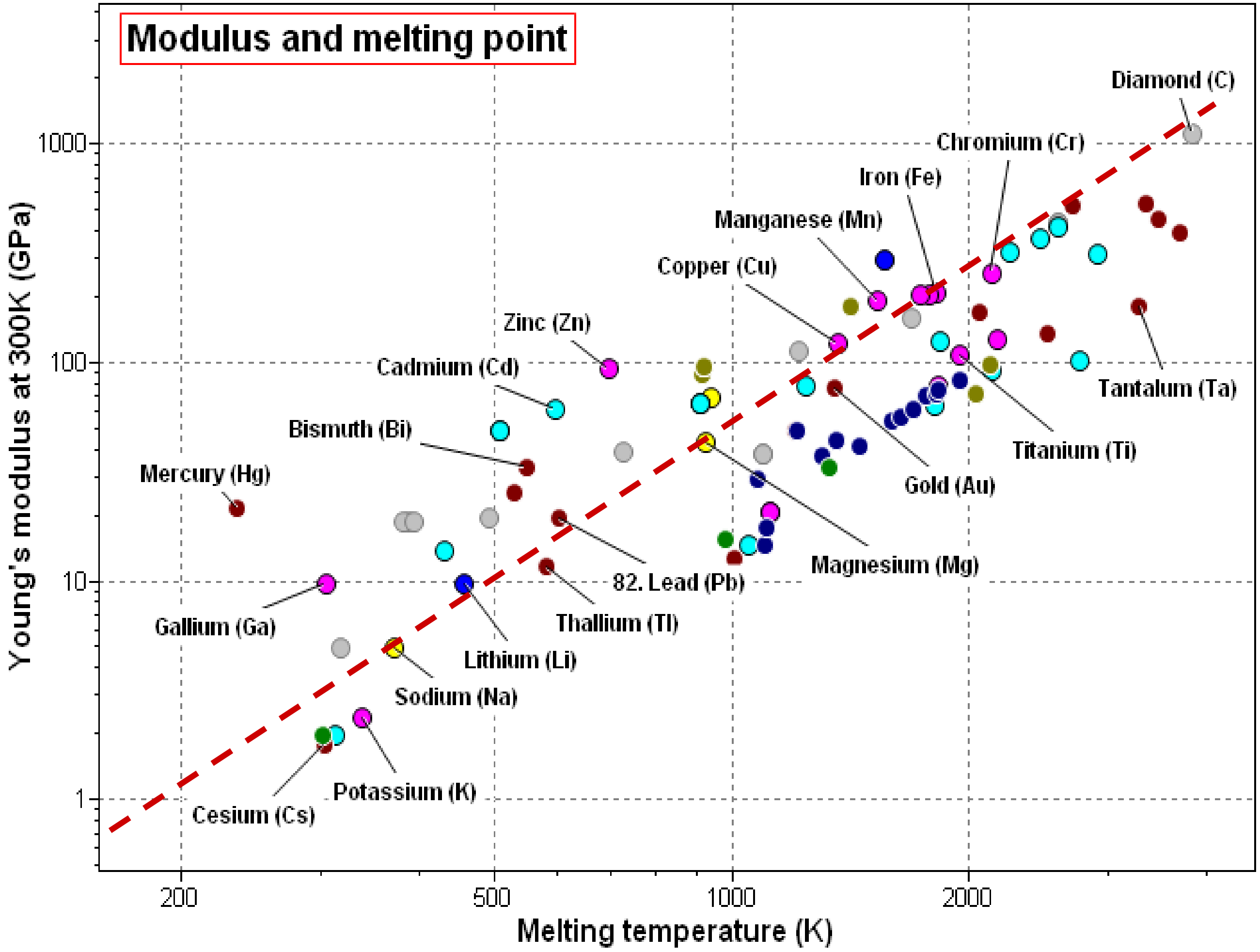
***DNA melting temperature**

The T_m is defined as the temperature in degrees Celsius, at which 50% of all molecules of a given DNA sequence are hybridized into a double strand and 50% are present as single strands.
Note that ‘melting’ in this sense is not a change of aggregate state, but simply the dissociation of the two molecules of the DNA double helix.

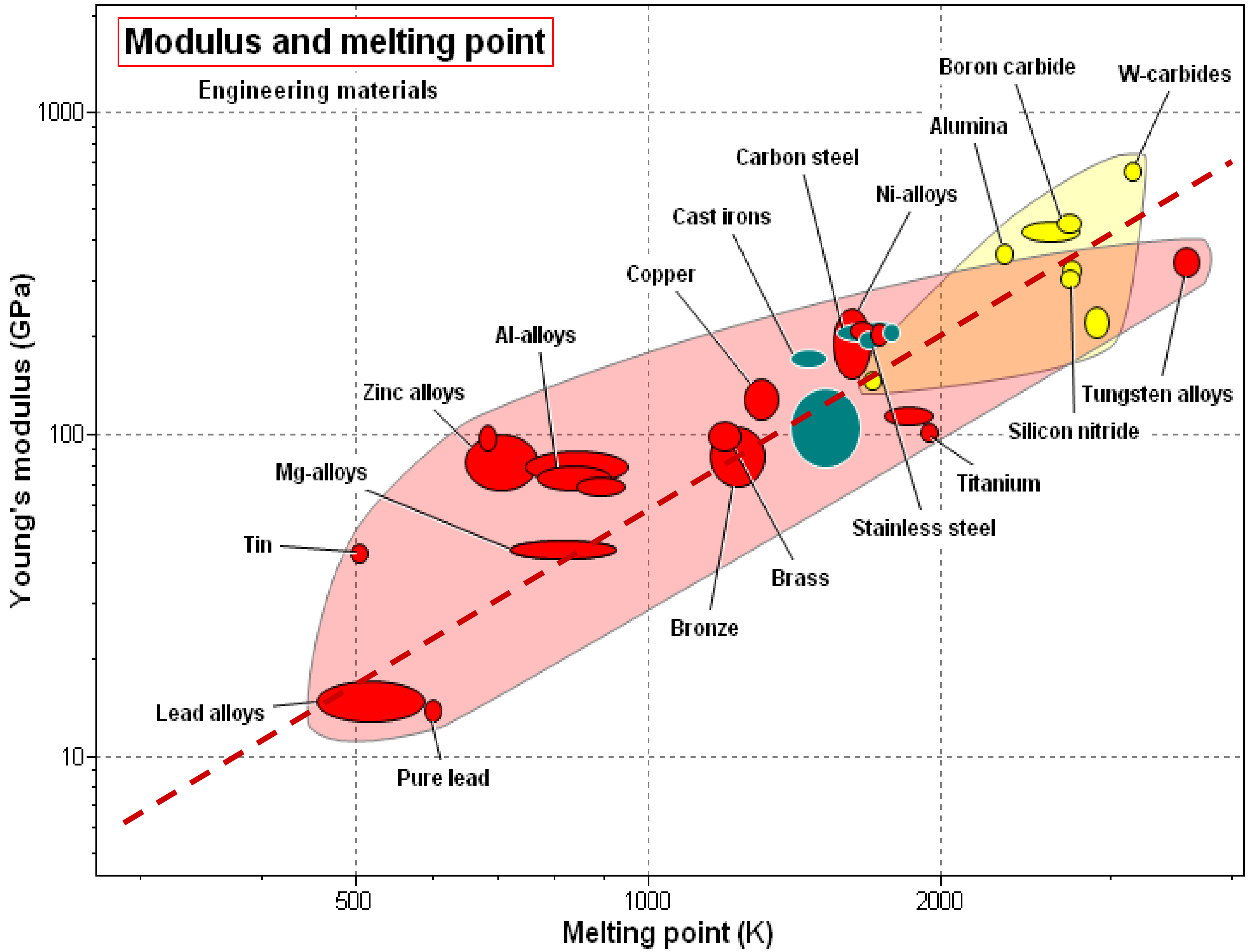
Relationships between properties

- Modulus and melting point





Engineering materials – the same dependence



SUMMARY: PRIMARY BONDS

Ceramics

(Ionic & covalent bonding):

Large bond energy
large T_m
large E
small α

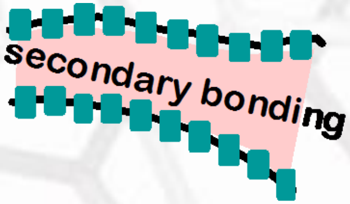
Metals

(Metallic bonding):

Variable bond energy
moderate T_m
moderate E
moderate α

Polymers

(Covalent & Secondary):



Directional Properties
Secondary bonding dominates
small T
small E
large α

SUMMARY: BONDING

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular