Physics of Materials

Dr. Thomas LaGrange

Masters Course PHYS-307

Fall 2024

Course Organization

Lectures

- 12 Chapters, one chapter per week
- 13h15-15h on Friday
- The last lecture is on Dec. 13th
- **No Lectures or exercises on Oct. 18th and 25th**

Exercises

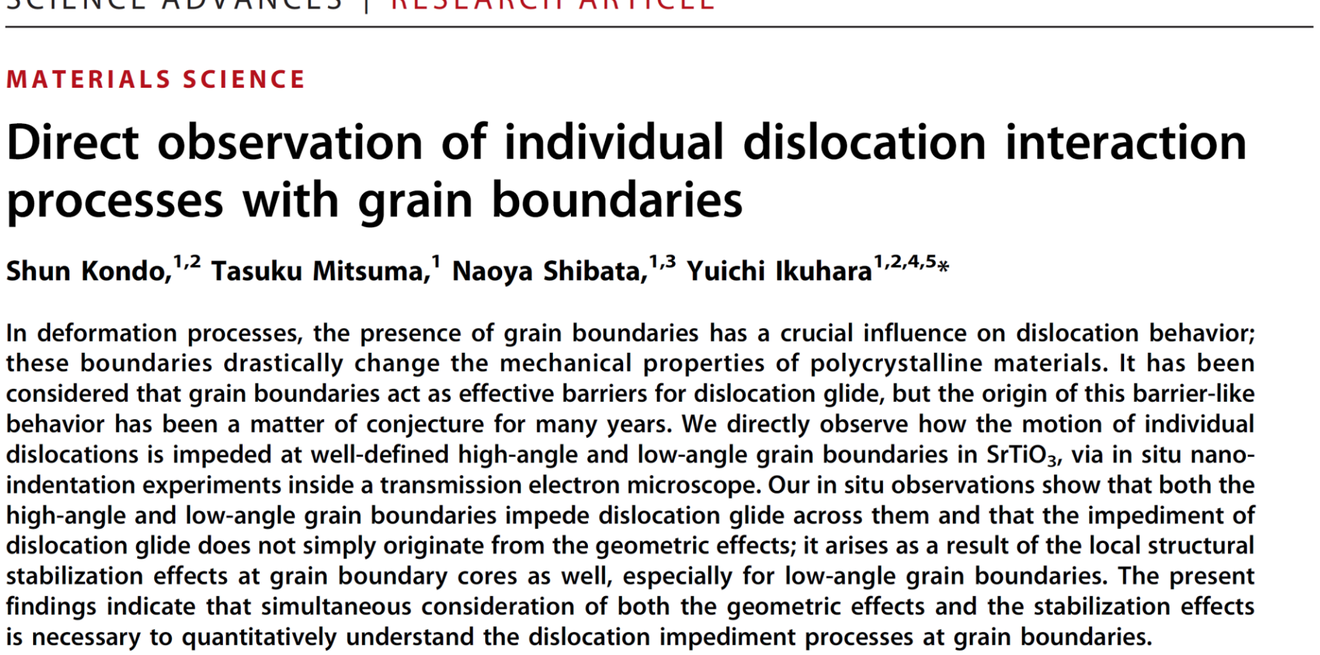
- Not mandatory but is recommended
- 15h15-17h on Friday- no lecture; the last exercise session is on Dec. 20th
- There will be **3** Electron Microscopy demonstrations/tours
  (Today-September 22nd, November 1stand the 29th)
- First part – review and questions on lectures and solutions of previous week's exercises
- Second part – is a discussion and questions on the current week's exercise

Moodle

- Schedule
- Course text and slides
- Additional reference materials for future studies and background information
- Exercises and solutions
- Group Communication- periodic emails and question forum

Course Exam Information and Format

- They will be individual Oral exams and a 5-10max page report on an article chosen for your exam
- Report due on the day of oral exam (TBA)
- Oral exams are in-person. Schedule: January, exact date TBA
- 30mins: 15-minute presentation and 15-minute questions on this article and other questions on the course
- You can choose the articles, or I can suggest one for you.
- Articles must be submitted to me by Dec. 20th (last day of exercises)
- The articles must be related to course content
- The presentation should focus on applying course theory to article data and interpretation, i.e. your slides should discuss the article's content in the context of the course materials.
- You can bring notes. The exam is an open book.
- My exam questions are still not hacked by ChatGPt



SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

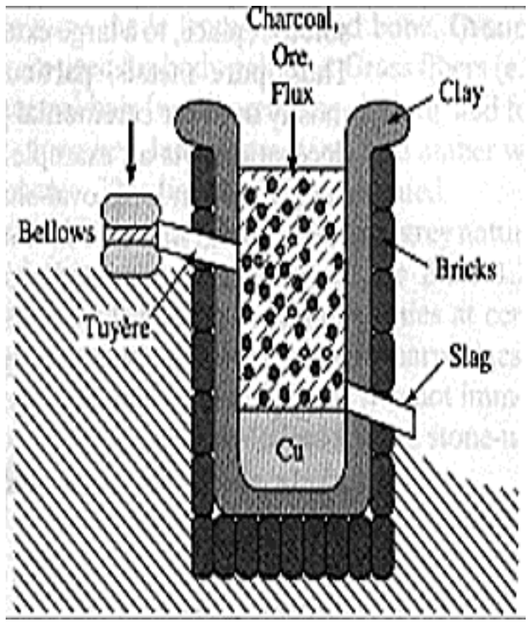
Direct observation of individual dislocation interaction processes with grain boundaries

Shun Kondo,[1,2] Tasuku Mitsuma,[1] Naoya Shibata,[1,3] Yuichi Ikuhara[1,2,4,5]*

In deformation processes, the presence of grain boundaries has a crucial influence on dislocation behavior; these boundaries drastically change the mechanical properties of polycrystalline materials. It has been considered that grain boundaries act as effective barriers for dislocation glide, but the origin of this barrier-like behavior has been a matter of conjecture for many years. We directly observe how the motion of individual dislocations is impeded at well-defined high-angle and low-angle grain boundaries in $SrTiO_3$, via in situ nano-indentation experiments inside a transmission electron microscope. Our in situ observations show that both the high-angle and low-angle grain boundaries impede dislocation glide across them and that the impediment of dislocation glide does not simply originate from the geometric effects; it arises as a result of the local structural stabilization effects at grain boundary cores as well, especially for low-angle grain boundaries. The present findings indicate that simultaneous consideration of both the geometric effects and the stabilization effects is necessary to quantitatively understand the dislocation impediment processes at grain boundaries.

Historical Influence of Materials

Stone age



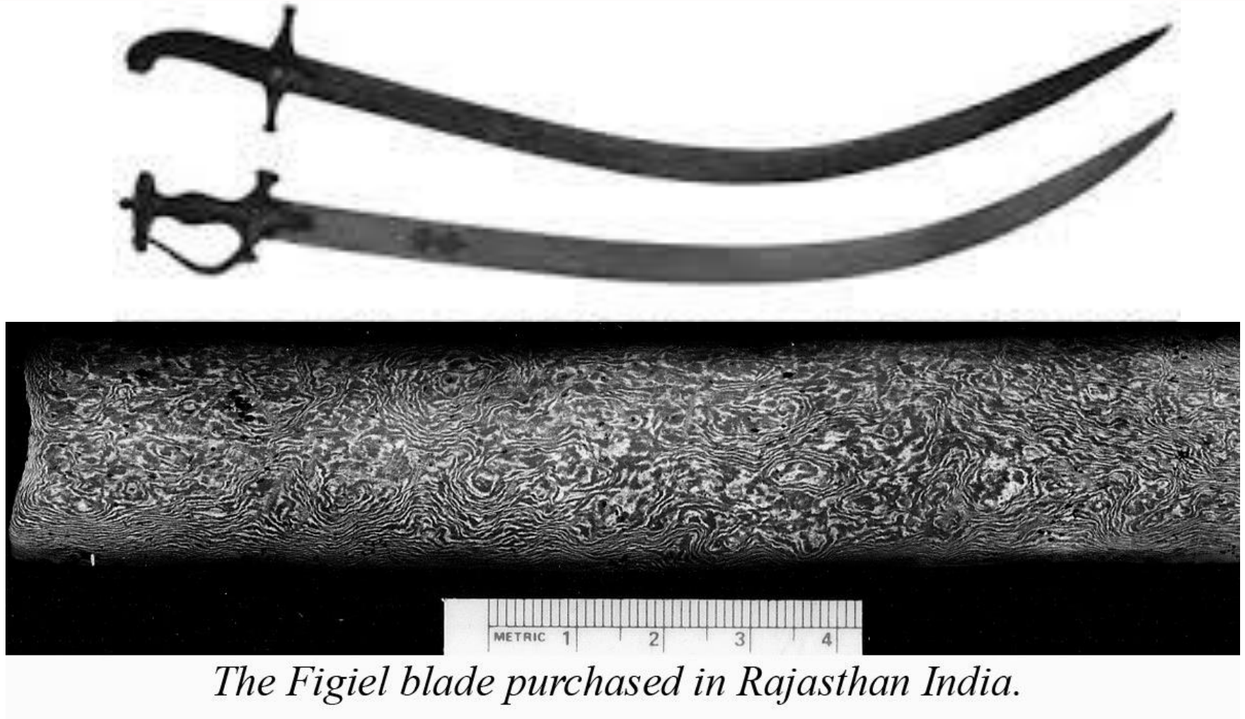
Chalcolithic (copper) age

Materials and Civilisations

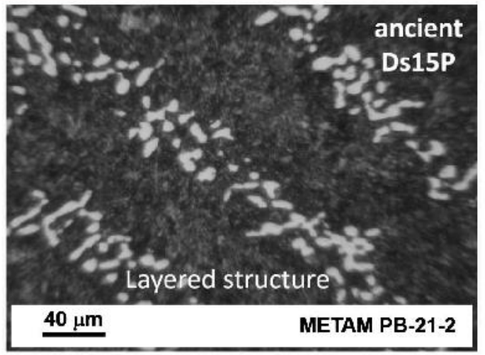
Bronze age

Iron age

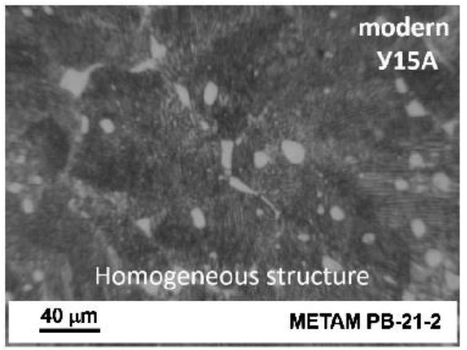
Weaponary and Warfare



The Figiel blade purchased in Rajasthan India.



(a)

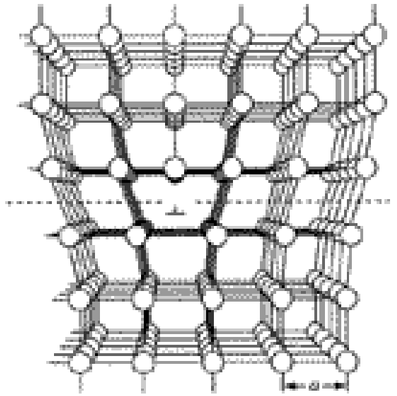


(b)

Writings found in Asia Minor said that to temper **Damascus** sword, the blade must be heated until it glows "like the sun rising in the desert. " It then should be cooled to the color of royal purple and plunged "into the body of a muscular **slave**" so that his strength would be transferred to the sword

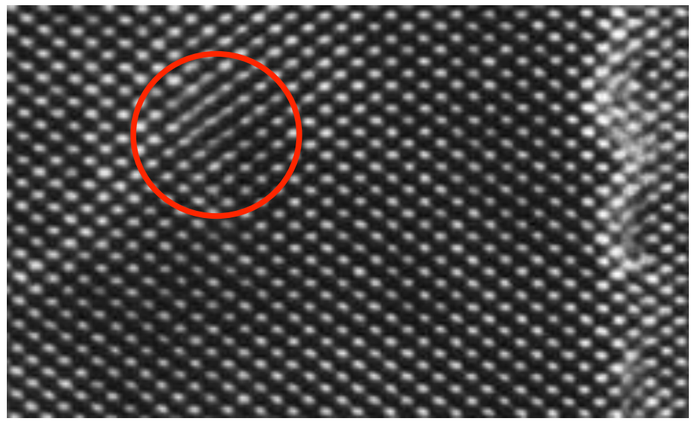
Metals and 20th-century science

dislocations



1934 Taylor, Polanyi, Orowan

1956, JP Hirsch



COMMENTARY

The science of dirt

Nature Materials(2002)

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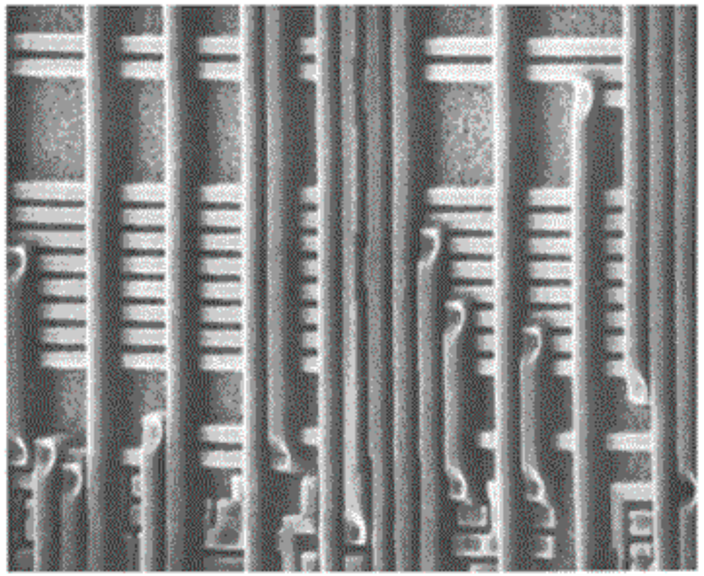
e-mail: rwc12@cam.ac.uk

Economics is often called the dismal science, but to many outsiders materials research is still the dirty science. Robert Cahn explains why materials scientists should be proud of their history.

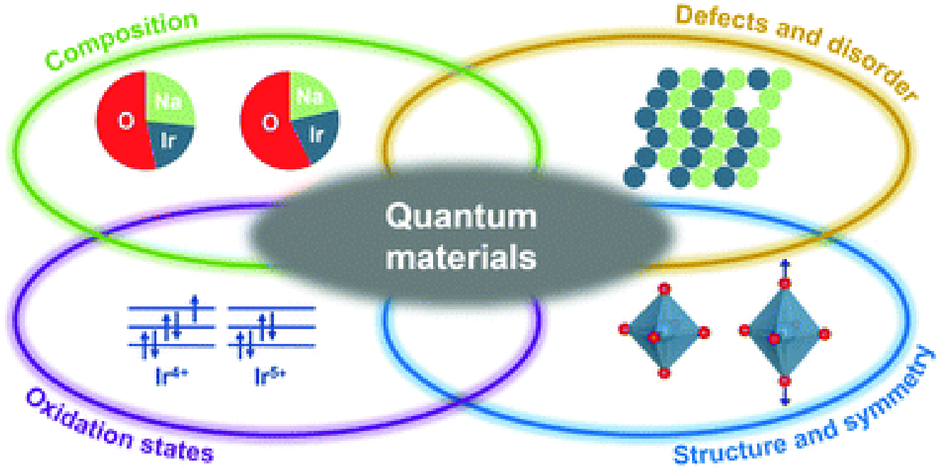
Tracing the roots of materials science is, much as for any other discipline, an undertaking fraught with pitfalls. Those who research the origins of scientific disciplines are inclined to search for the 'founders' of those disciplines, Newton as the father of physics say, or Lavoisier as the father of chemistry. Despite this tendency, in reality all disciplines have multiple founders; it is just a question of which aspects of a discipline are judged to be the most central. The historian of 'materials science' need only look back to the late 1950s, when the term first entered into common usage, to encounter Morris Fine of Northwestern University, Chicago, who fought successfully to introduce the concept into the university teaching there in 1958.

In US industry, at about the same time, a hyperactive research manager for General Electric Corporate Research Center in New York State — Herbert Hollomon — organized a brilliantly successful research group based on the broad concept of materials science. In 1958, Hollomon wrote: "Out of metallurgy, by physics, comes materials science." He was not alone. William Baker of Bell Laboratories in Murray Hill, New Jersey, another early protagonist of materials science, had learnt a valuable lesson from the development of the transistor at the institute a decade earlier — without the close collaboration of physicists,

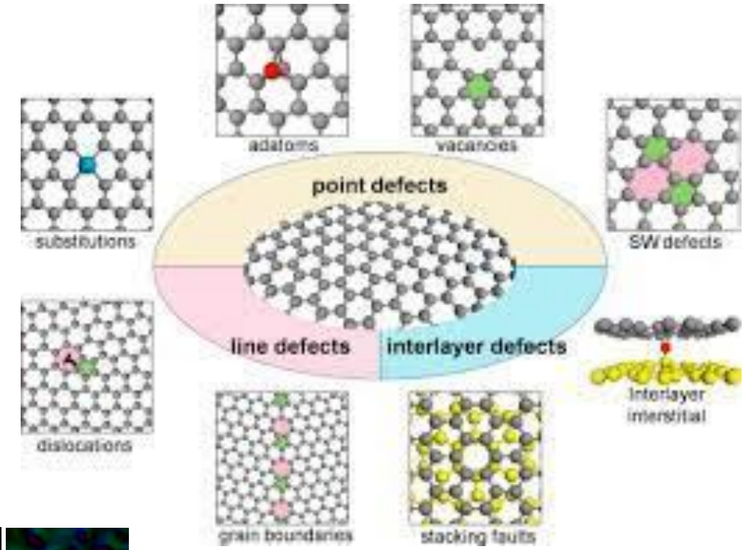


Silicon age

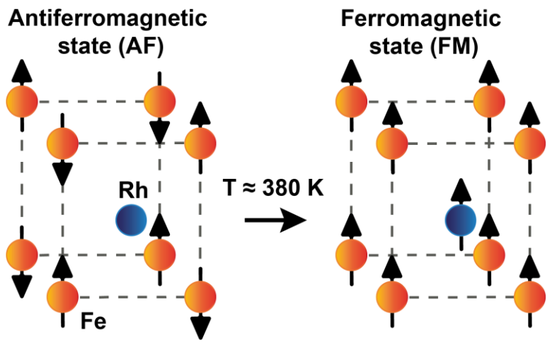
Quantum materials



Defects in 2-D materials

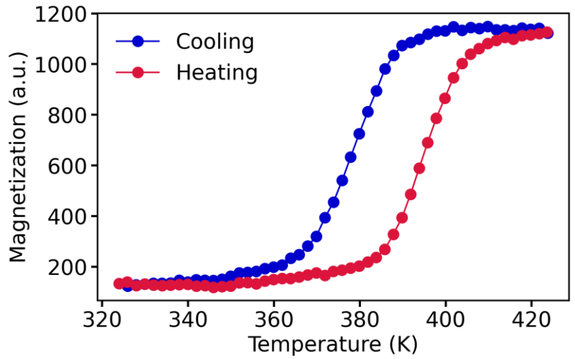


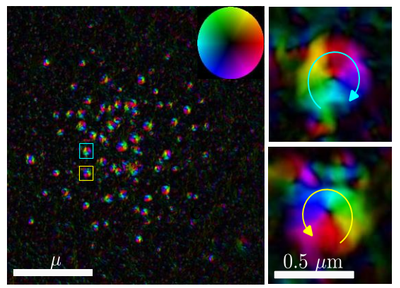
Phase transitions

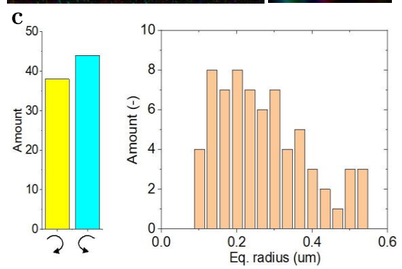


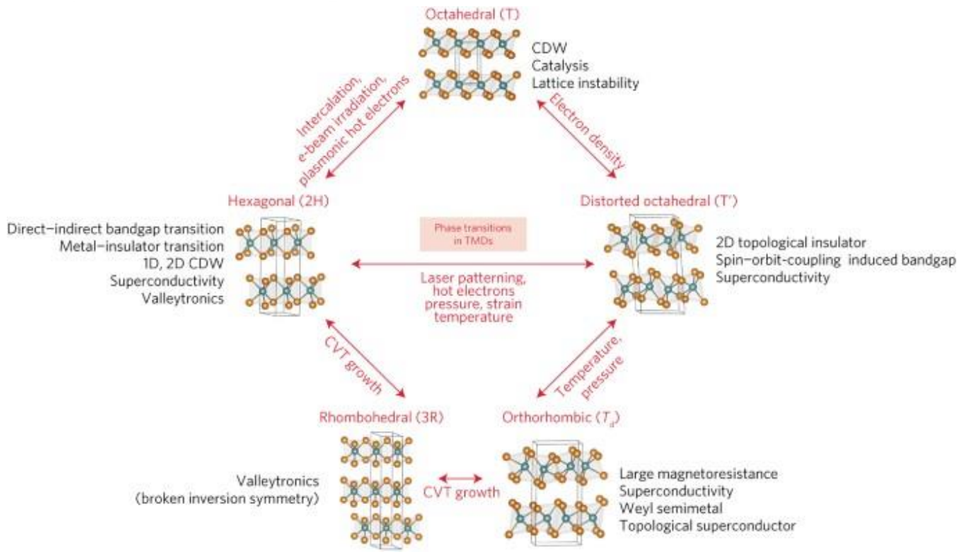
Fe_xRh_{1-x}; x $\in (0.48; 0.52)$

Coexistence of AF-FM phases

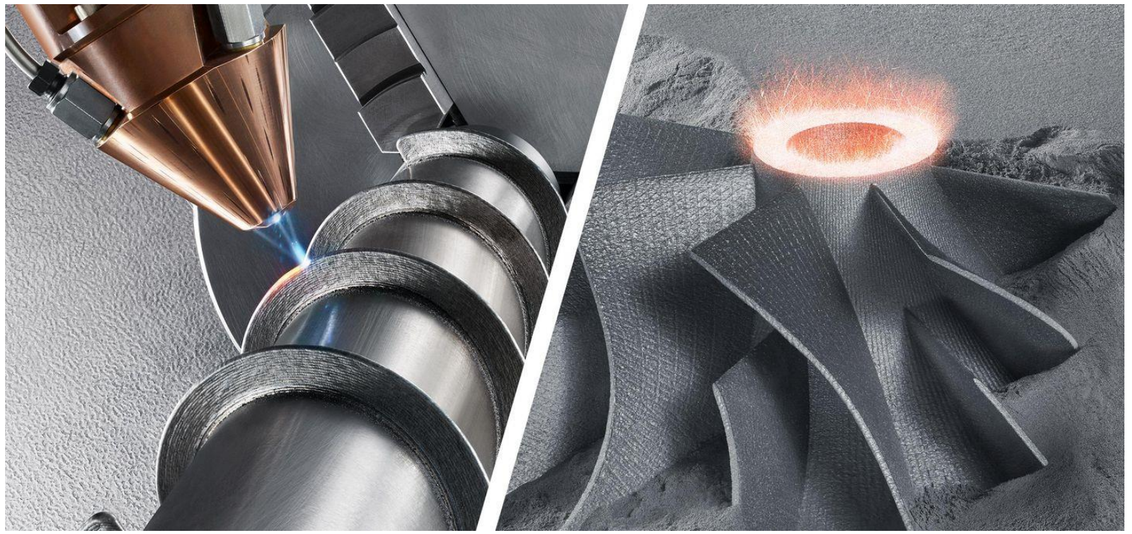




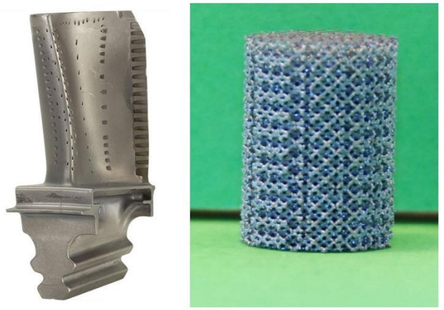


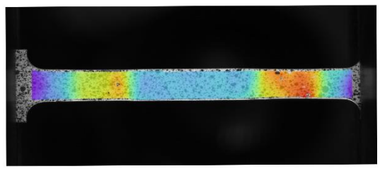


Additive Manufacturing (3-D printing)

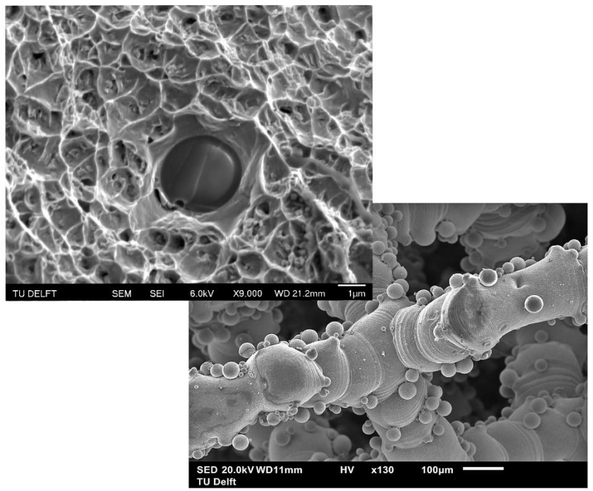


Macro Level

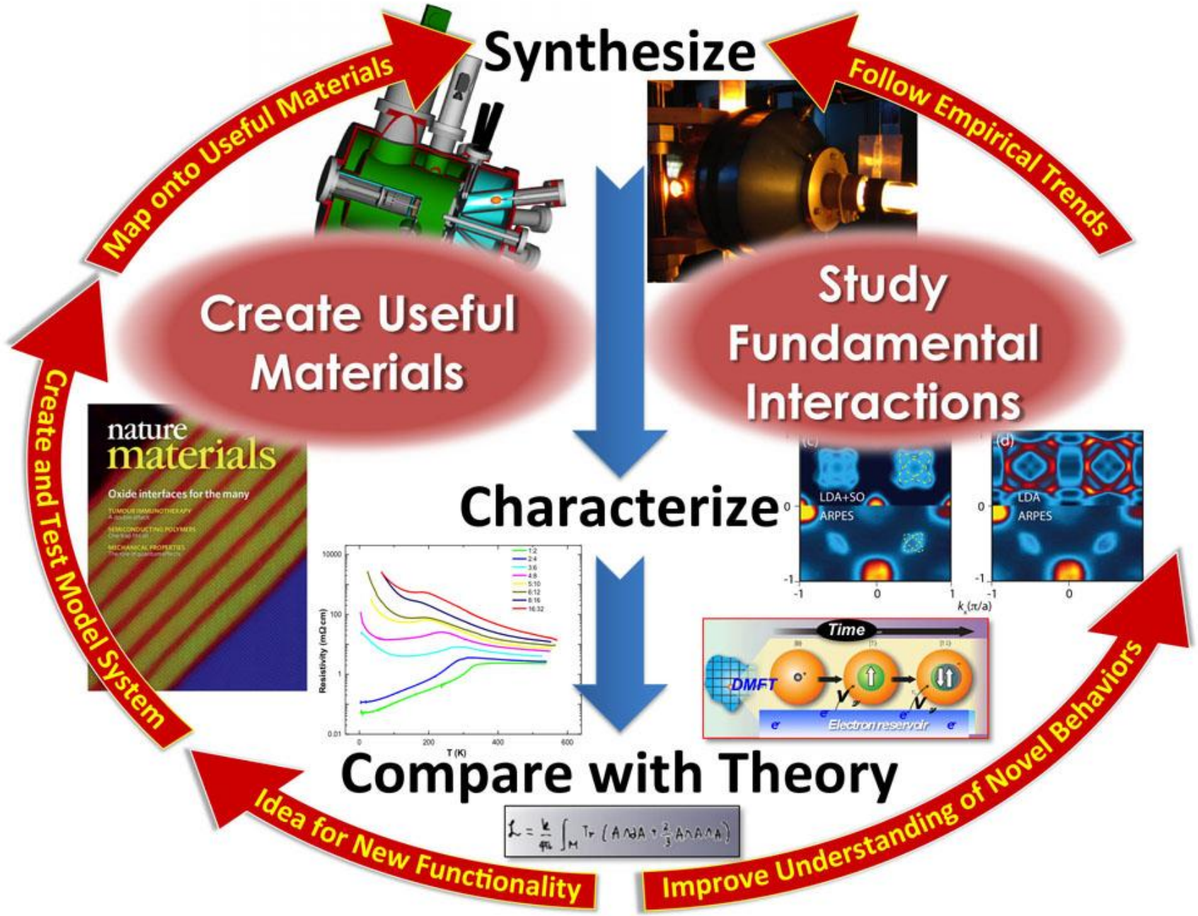




Micro Level



Materials by Design



Theoretical correlations between defects (Dislocations) and mechanical behavior

Course Outline

1. Atomic bonds and crystals
Ionic bond. Van der Waals bond. The diatomic molecule: covalent bond. Metal bond. Characterizing bonds with Electron Energy Loss Spectroscopy (EELS)

2. Refresher on crystallography
Periodic lattice, crystalline structures, coordination number

3. Theory of elasticity
Phenomenology, the thermodynamic basis of elasticity, generalized Hooke's law

4. Defects in crystals
Point, linear, bi and tri-dimensional, amorphous and quasicrystals, fractal defects, concentration of vacancies

5. Diffusion
Fick's laws, Einstein equation, Boltzman-Matano couple, Kirkendall effect

6. Dislocations' model
Introduction, Burgers vector, Orowan equation, and EM characterization of dislocations

Course Outline

7. Elastic theory of dislocations
Stress field, energy of a dislocation, force between dislocations, line tension, Frank-Reed sources

8. Kinetics of dislocations
Interaction of dislocations with: lattice, dislocations, other defects

9. Movement of dislocations activated thermally
Activation energy, measurements of activation parameters

10. Electron Microscopy techniques for characterizing dislocations and their dynamics
Contrast theory, methods for determining dislocation type, in-situ observation of dynamics

11. Transformations of phases I: solidification
Thermodynamics of solidification, phase diagrams

12. Transformations of phases II: solid-solid
Nucleation, precipitation, martensitic transformations

Physics of Materials

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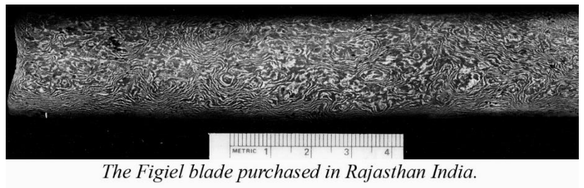
Chapter 1: Atomic bonding

Masters Course PHYS-307

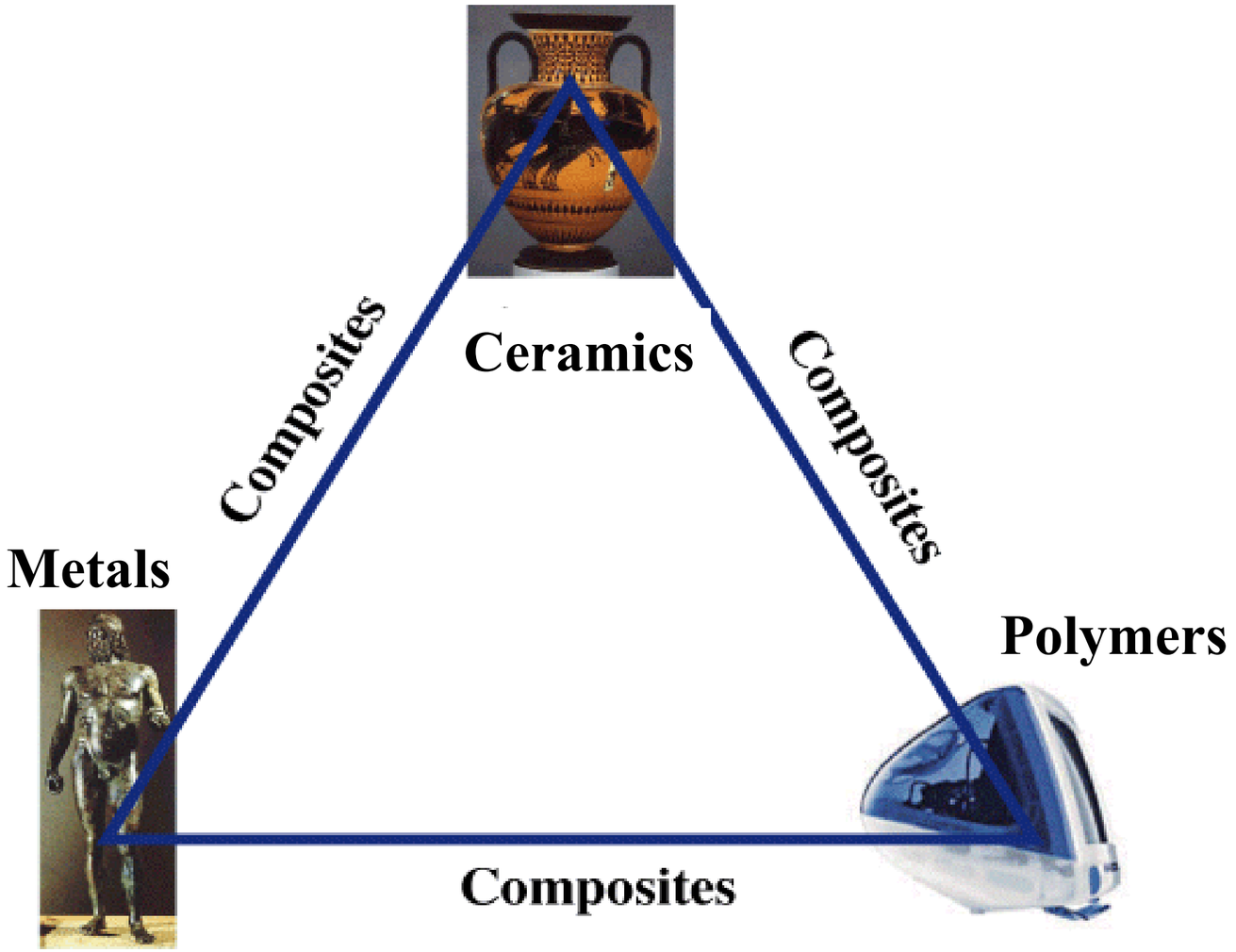
Fall 2024

Families of materials

Glasses

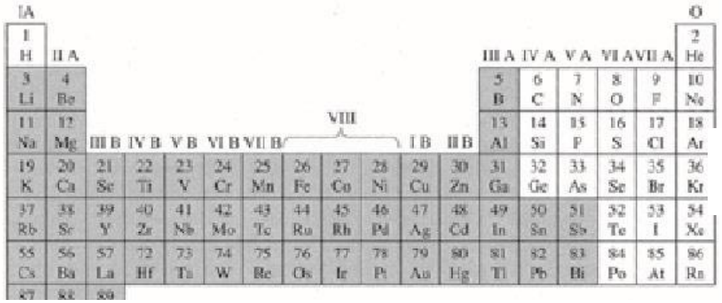


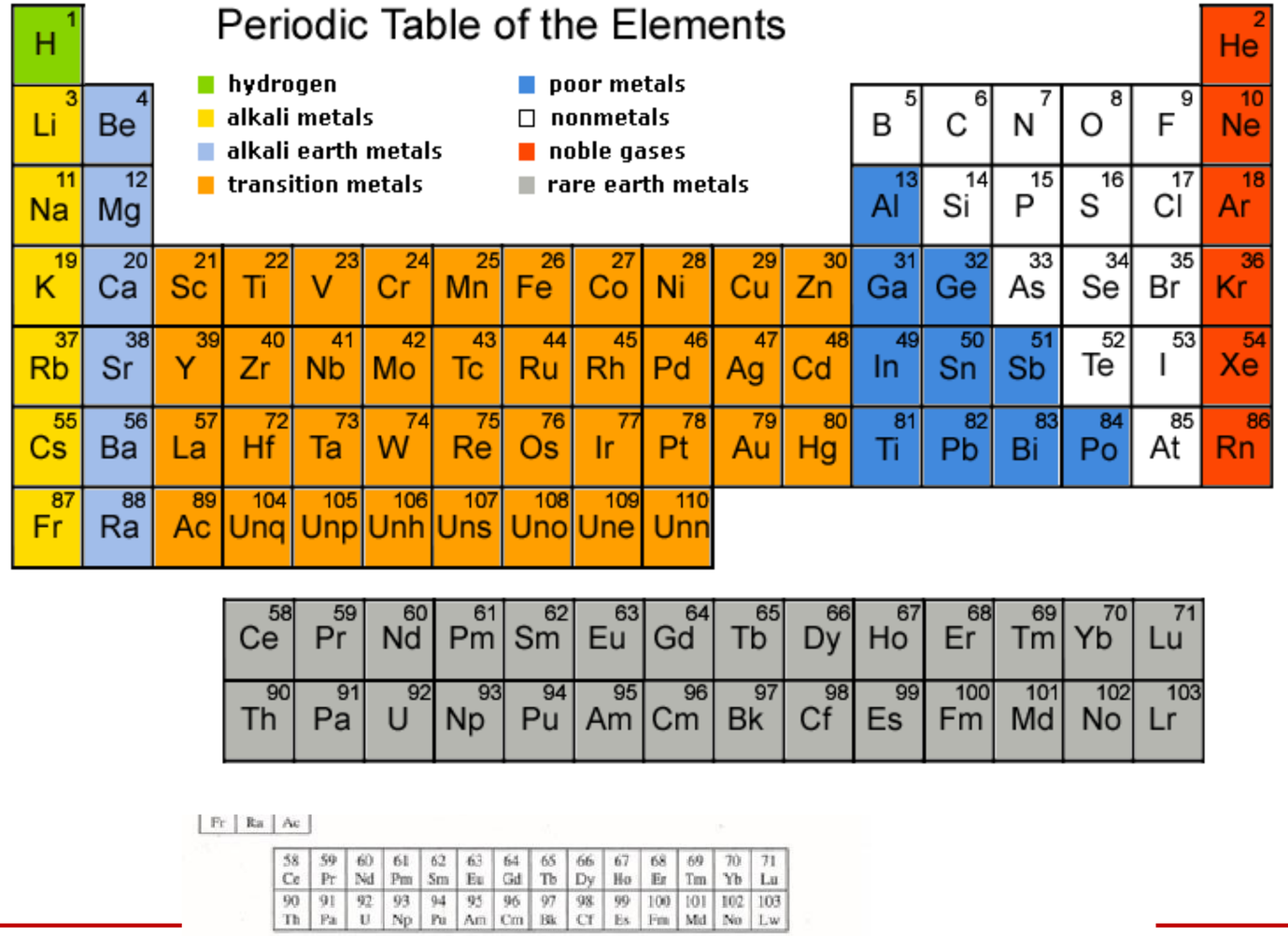
The Figiel blade purchased in Rajasthan India.



Diamond

Metals




Periodic Table of the Elements
hydrogen
alkali metals
alkali earth metals
transition metals
poor metals
nonmetals
noble gases
rare earth metals
H 1
He 2
Li 3
Be 4
B 5
C 6
N 7
O 8
F 9
Ne 10
Na 11
Mg 12
Al 13
Si 14
P 15
S 16
Cl 17
Ar 18
K 19
Ca 20
Sc 21
Ti 22
V 23
Cr 24
Mn 25
Fe 26
Co 27
Ni 28
Cu 29
Zn 30
Ga 31
Ge 32
As 33
Se 34
Br 35
Kr 36
Rb 37
Sr 38
Y 39
Zr 40
Nb 41
Mo 42
Tc 43
Ru 44
Rh 45
Pd 46
Ag 47
Cd 48
In 49
Sn 50
Sb 51
Te 52
I 53
Xe 54
Cs 55
Ba 56
La 57
Hf 72
Ta 73
W 74
Re 75
Os 76
Ir 77
Pt 78
Au 79
Hg 80
Ti 81
Pb 82
Bi 83
Po 84
At 85
Rn 86
Fr 87
Ra 88
Ac 89
Unq 104
Unp 105
Unh 106
Uns 107
Uno 108
Une 109
Unn 110
Ce 58
Pr 59
Nd 60
Pm 61
Sm 62
Eu 63
Gd 64
Tb 65
Dy 66
Ho 67
Er 68
Tm 69
Yb 70
Lu 71
Th 90
Pa 91
U 92
Np 93
Pu 94
Am 95
Cm 96
Bk 97
Cf 98
Es 99
Fm 100
Md 101
No 102
Lr 103

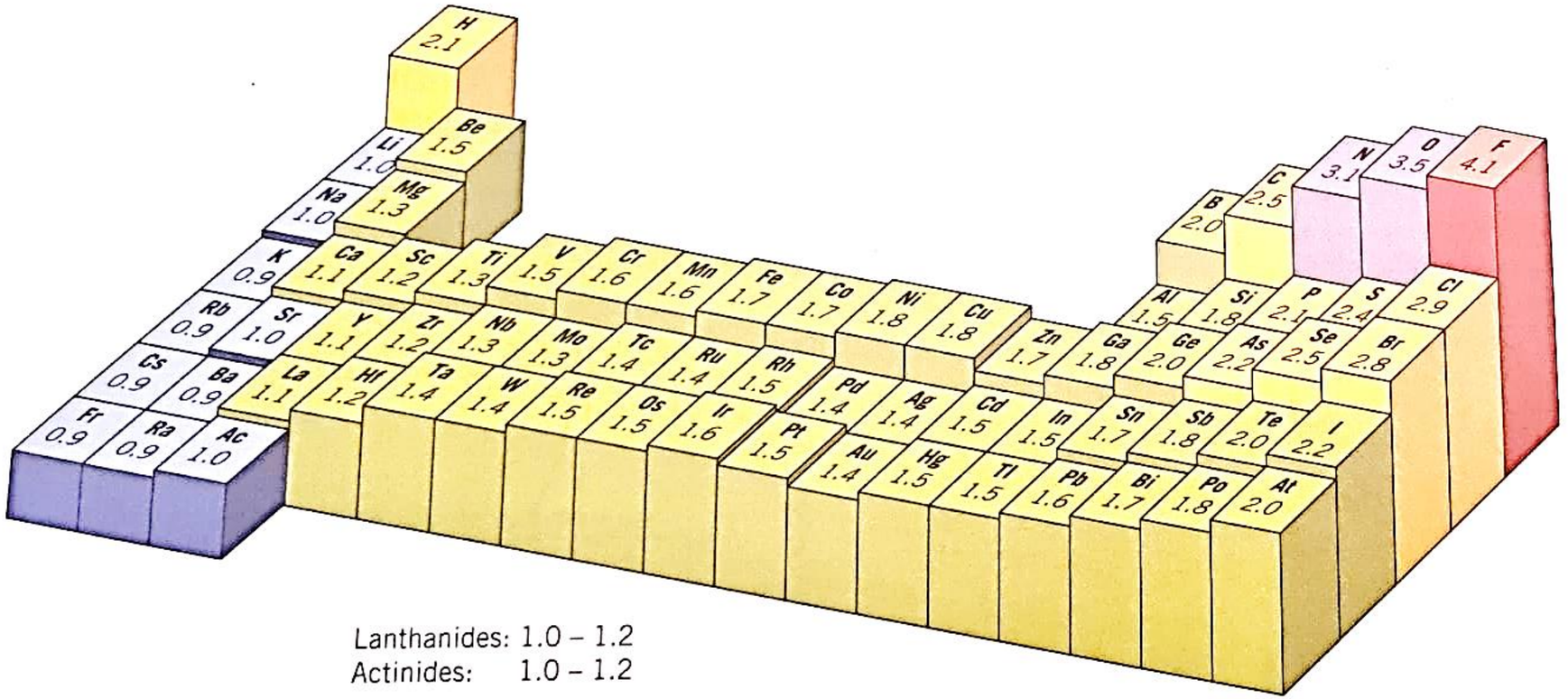
Atomic bond

$$E_C = (E_{at.free} - E_{at.bonded})$$

$$(H_0 + H_1) \cdot \psi = (E_0 + \Delta E) \cdot \psi$$

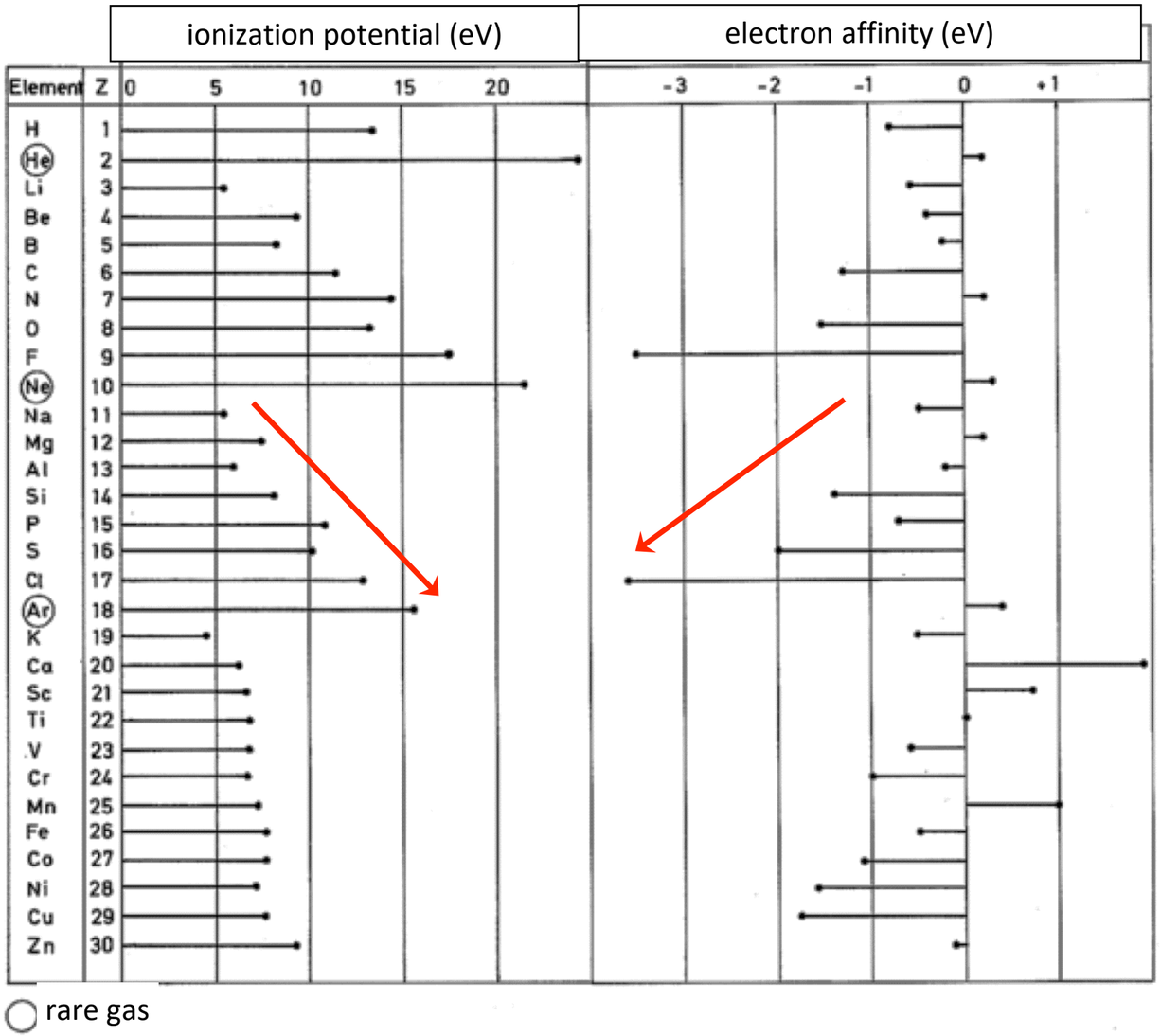
Perturbation

Ionic bond



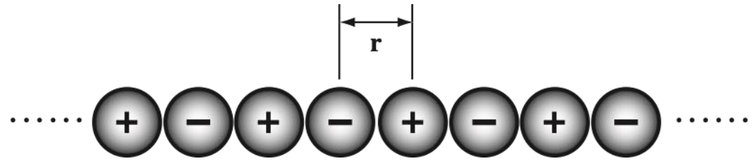
Electronegativity

Ionic bond

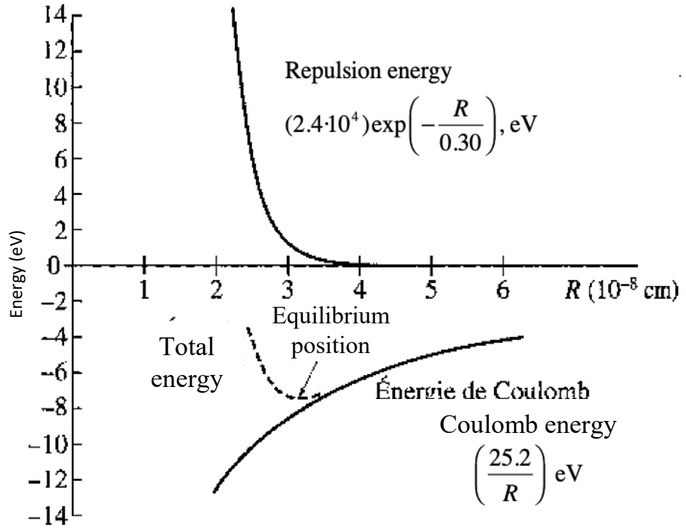


◯ rare gas

Ionic bond



$$U_i = \sum_j U_{ij} \qquad U_{ij} = \lambda \exp((-r_{ij})/\rho) \pm \frac{q^2}{4\pi\varepsilon_0 r_{ij}}$$



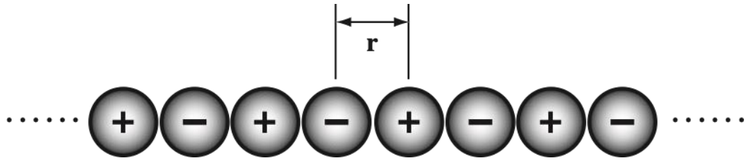
Energy (per molecule) of the KCl crystal, showing the Madelung and repulsion contributions

ρ compressibility constant
q electron charge
ϵ_o permittivity
r_{ij} distance between ions i - j
z atomic number
R average radial spacing of ions
λ is constant

$$\sum_j \lambda \exp((-r_{ij})/\rho) = \lambda z \exp(-R/\rho)$$ Repulsion term

Coulombic term $$\sum_j \pm \frac{1}{r_{ij}} = \frac{\alpha}{R}$$ α is the Madelung constant

Ionic bond



$$U_i = \left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{4\pi\varepsilon_0 R} \right) \quad N \text{ bonds}$$

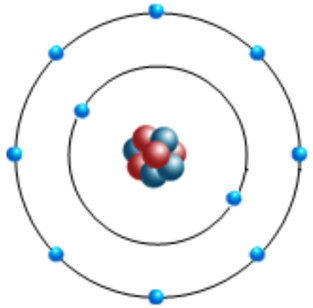
$$\frac{dU_i}{dR} = 0 \longrightarrow R_0 \quad \text{Equilibrium ion spacing}$$

$$E_c = U_{tot} = -\frac{N\alpha q^2}{4\pi\varepsilon_0 R_0}\left(1 - \frac{\rho}{R_0}\right) \qquad \frac{\rho}{R_0} \approx 0.1 \quad \text{For solids}$$

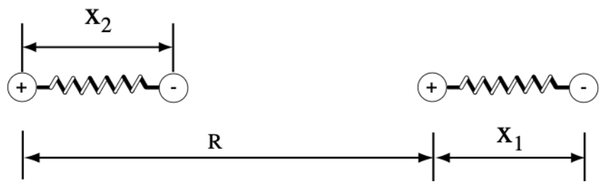
$$E_B = E_c + E_I + E_A$$

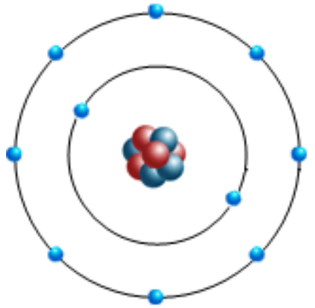
E_c=coulombic energy
E_I= ionization energy
E_A= electron affinity

Van der Waals interaction



Electron dipole interactions





$$H_0 = \frac{1}{2m}p_1^2 + \frac{1}{2}kx_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}kx_2^2$$

$$(H_0 + H_1)\cdot\psi = (E_0 + \Delta E)\cdot\psi \qquad h\omega_0 \qquad \omega_0 = \sqrt{k/m}$$

$$\Delta E = -h\omega_0 \frac{1}{32\pi^2\varepsilon_0^2}\left(\frac{e^2}{kR^3}\right)^2$$

Solve for eigenvalues

R/σ is a constant at equilibrium, i.e., $\frac{dU}{dR} = 0$

	Ne	Ar	Kr	Xe
R/σ	1.14	1.11	1.1	1.09

Lennard-Jones

$$U = \left(\frac{A}{R^{12}} - \frac{B}{R^6}\right) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right]$$

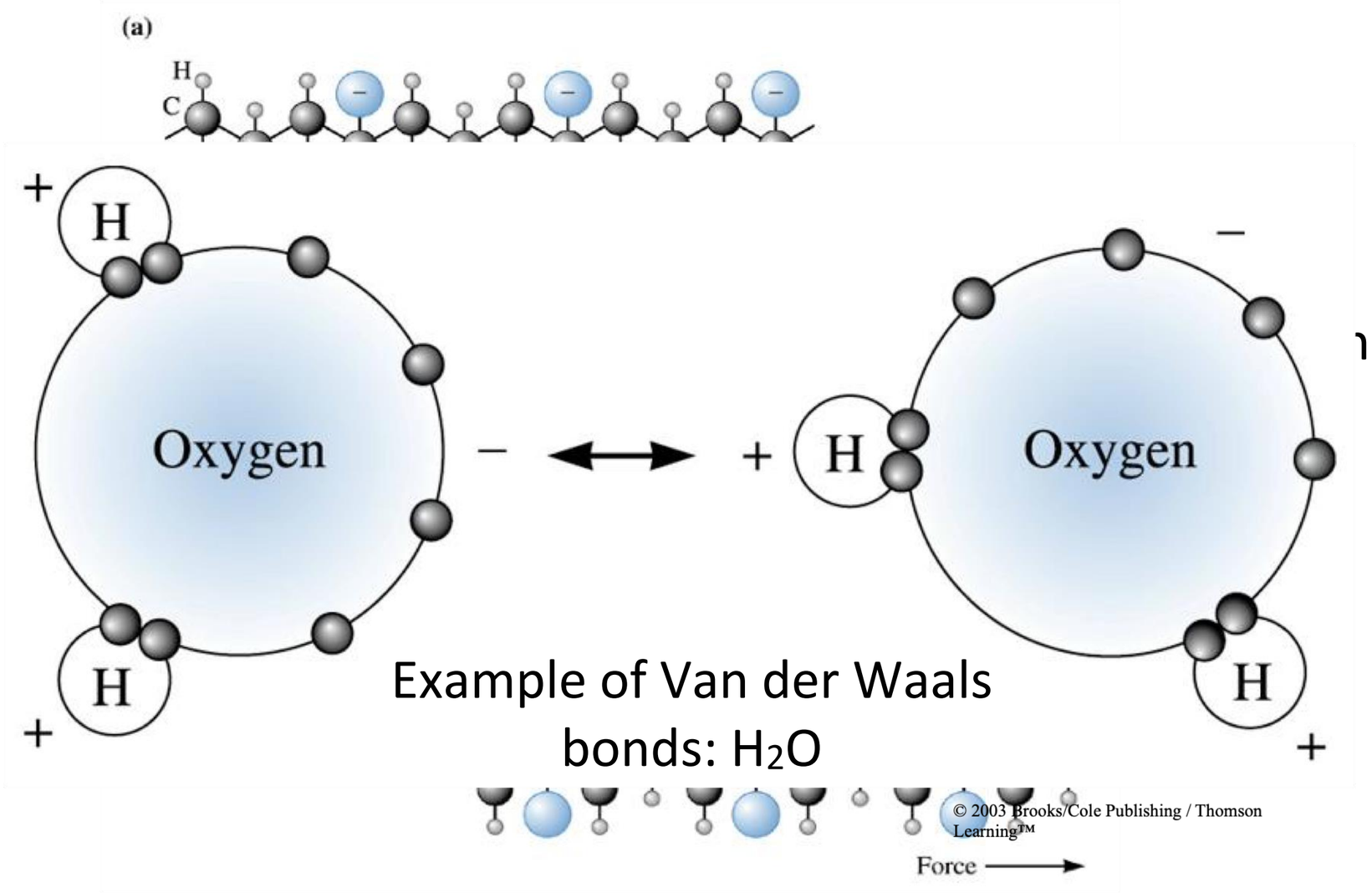
$$U_{tot} = \frac{1}{2}N(4\varepsilon)\left[\sum_{ij}\left(\frac{\sigma}{p_{ij}R}\right)^{12} - \left(\frac{\sigma}{p_{ij}R}\right)^6\right]$$

F.C.C. structure

$$\sum_{ij}\left(\frac{1}{p_{ij}}\right)^{12} = 12.13188$$

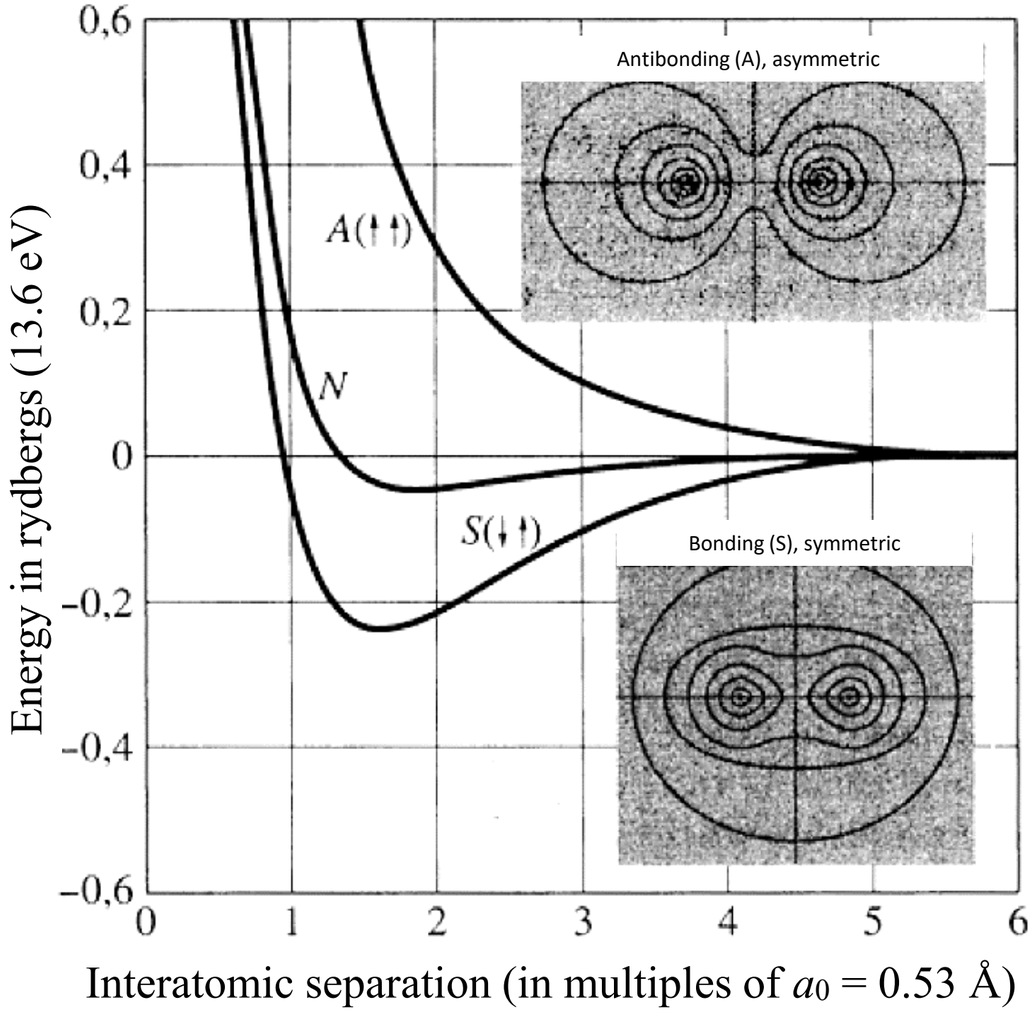
$$\sum_{ij}\left(\frac{1}{p_{ij}}\right)^{6} = 14.45392$$

Van der Waals interaction

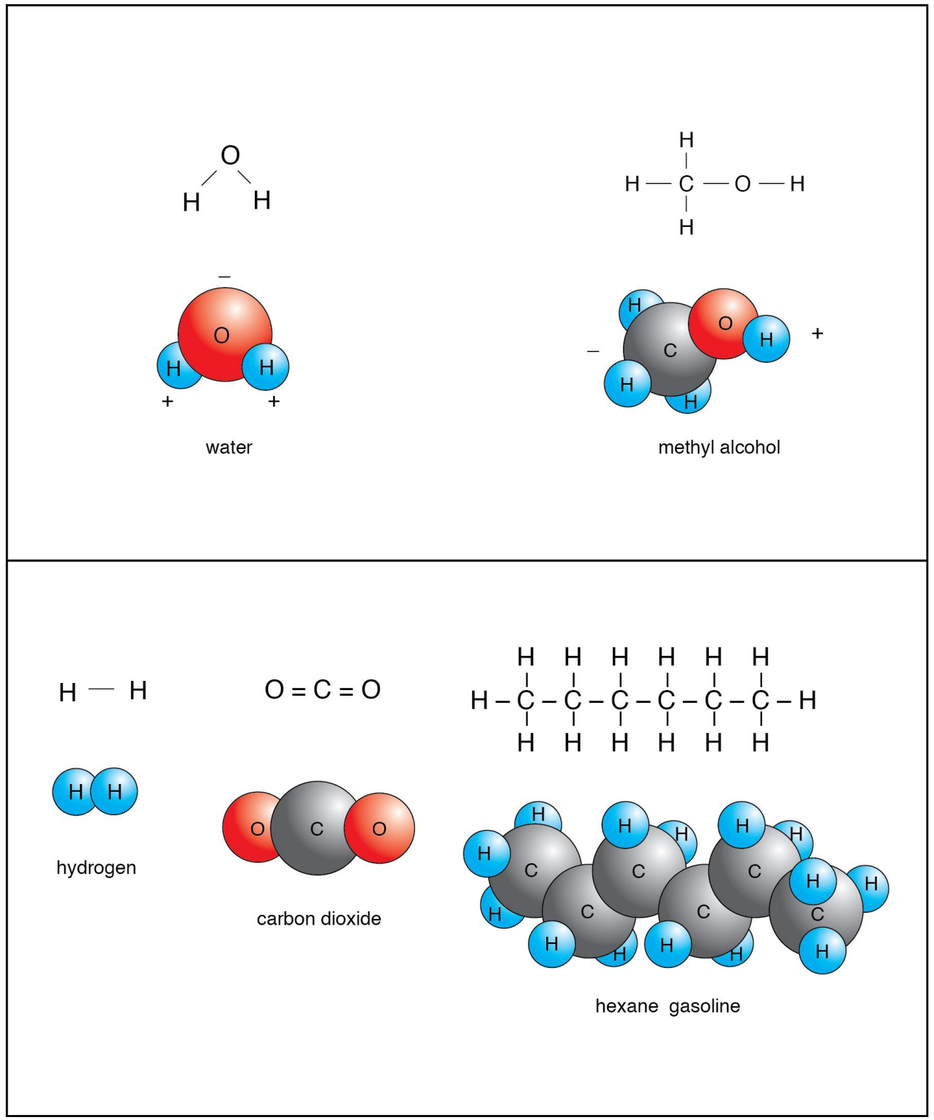


Example of Van der Waals bonds: H_2O

Covalent bond



Why do covalently bonded compounds tend to have low densities?

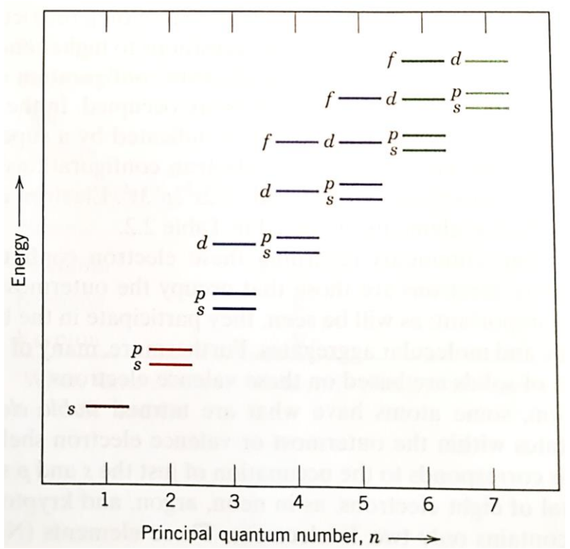


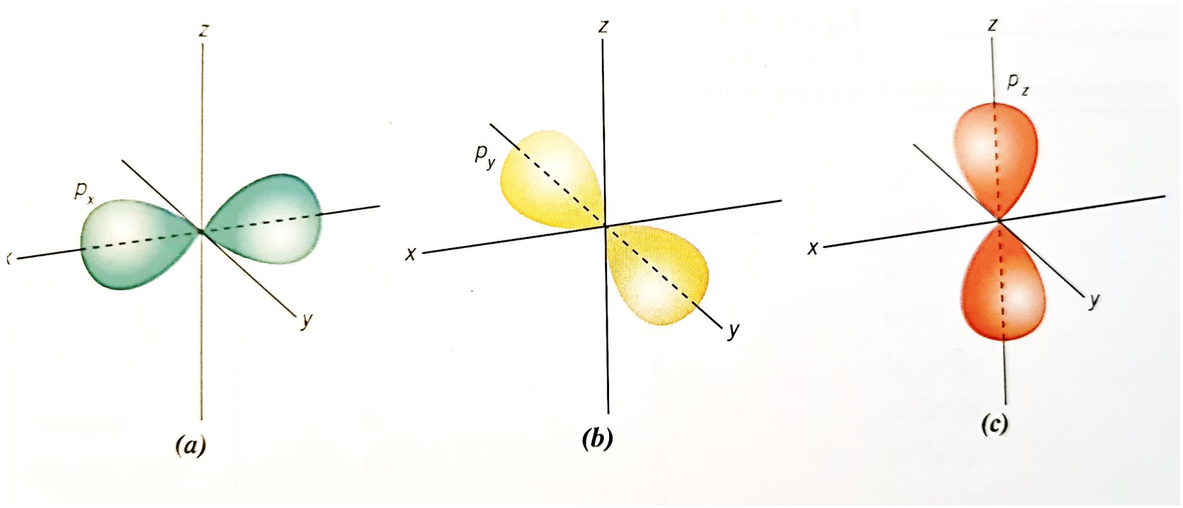
- Atomic packing is low due to directional bonding
- Unit cell dimensions are larger
- Thus, densities tend to be lower

Molecule	Bond Type	Molecular Shape	Molecular Type
Water	Polar Covalent	Bent	Polar
Methane	Non-Polar Covalent	Tetrahedral	Non-Polar
Carbon Dioxide	Polar Covalent	Linear	Non-Polar

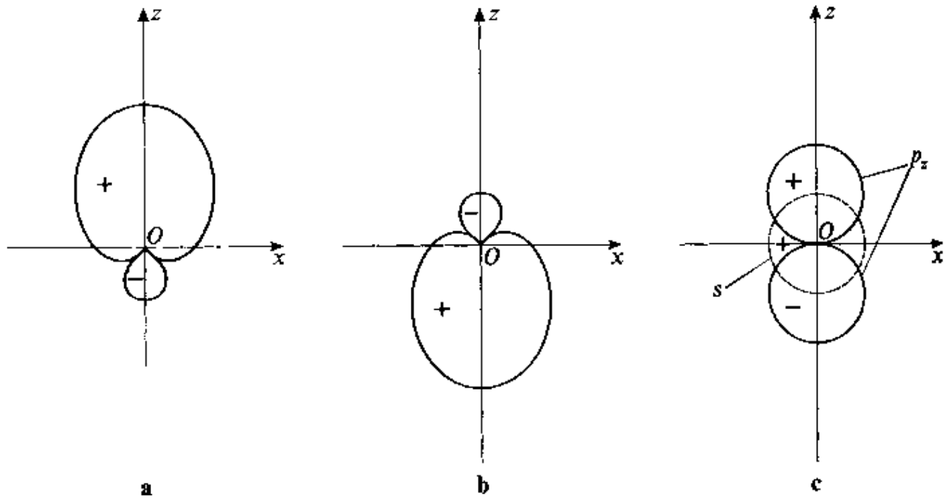
Covalent bond

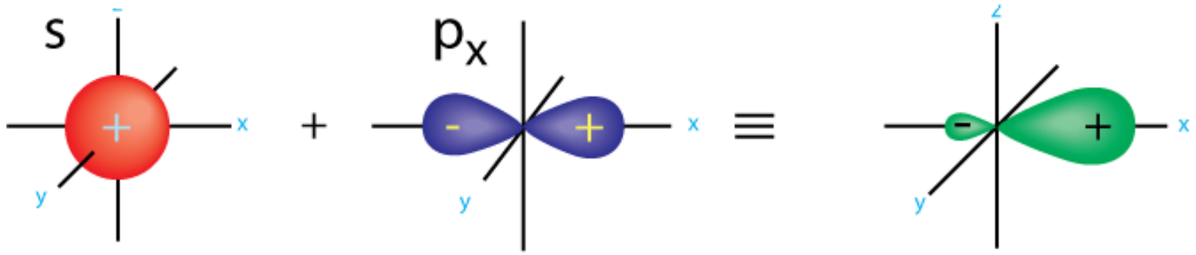
Value of n	Value of l	Values of m_l	Subshell	Number of Orbitals	Number of Electrons
1	0	0	1s	1	2
2	0	0	2s	1	2
	1	-1,0,+1	2p	3	6
3	0	0	3s	1	2
	1	-1,0,+1	3p	3	6
	2	-2,-1,0,+1,+2	3d	5	10
4	0	0	4s	1	2
	1	-1,0,+1	4p	3	6
	2	-2,-1,0,+1,+2	4d	5	10
	3	-3,-2,-1,0,+1,+2,+3	4f	7	14

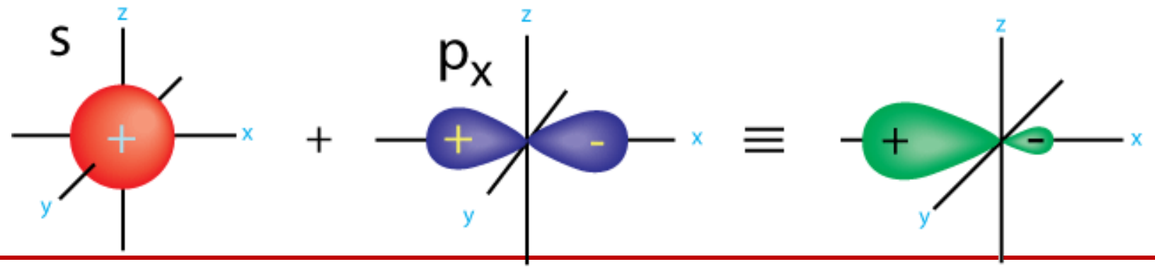




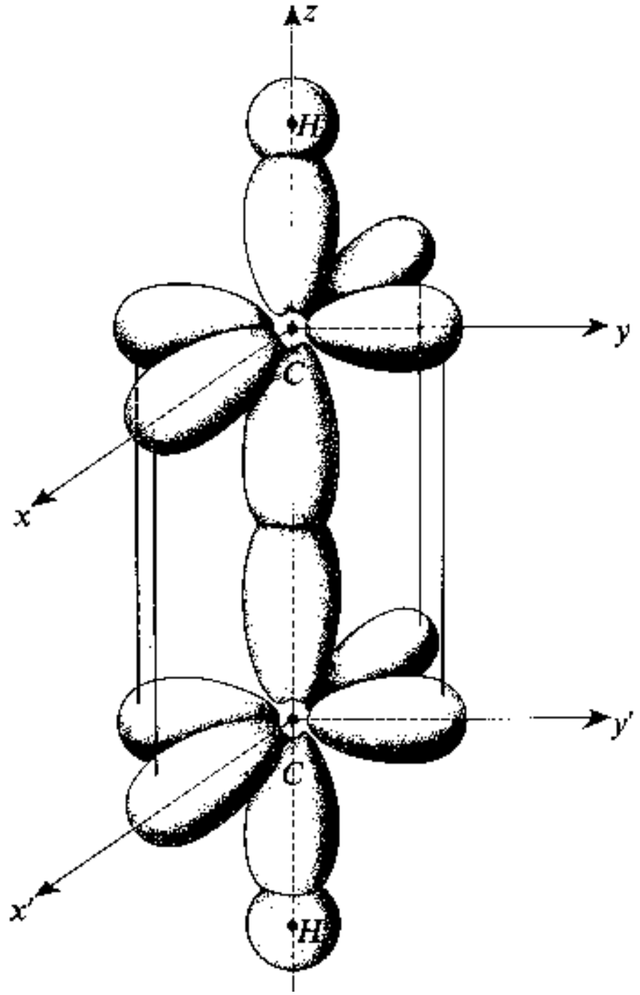
Covalent bond : *sp* hybridization



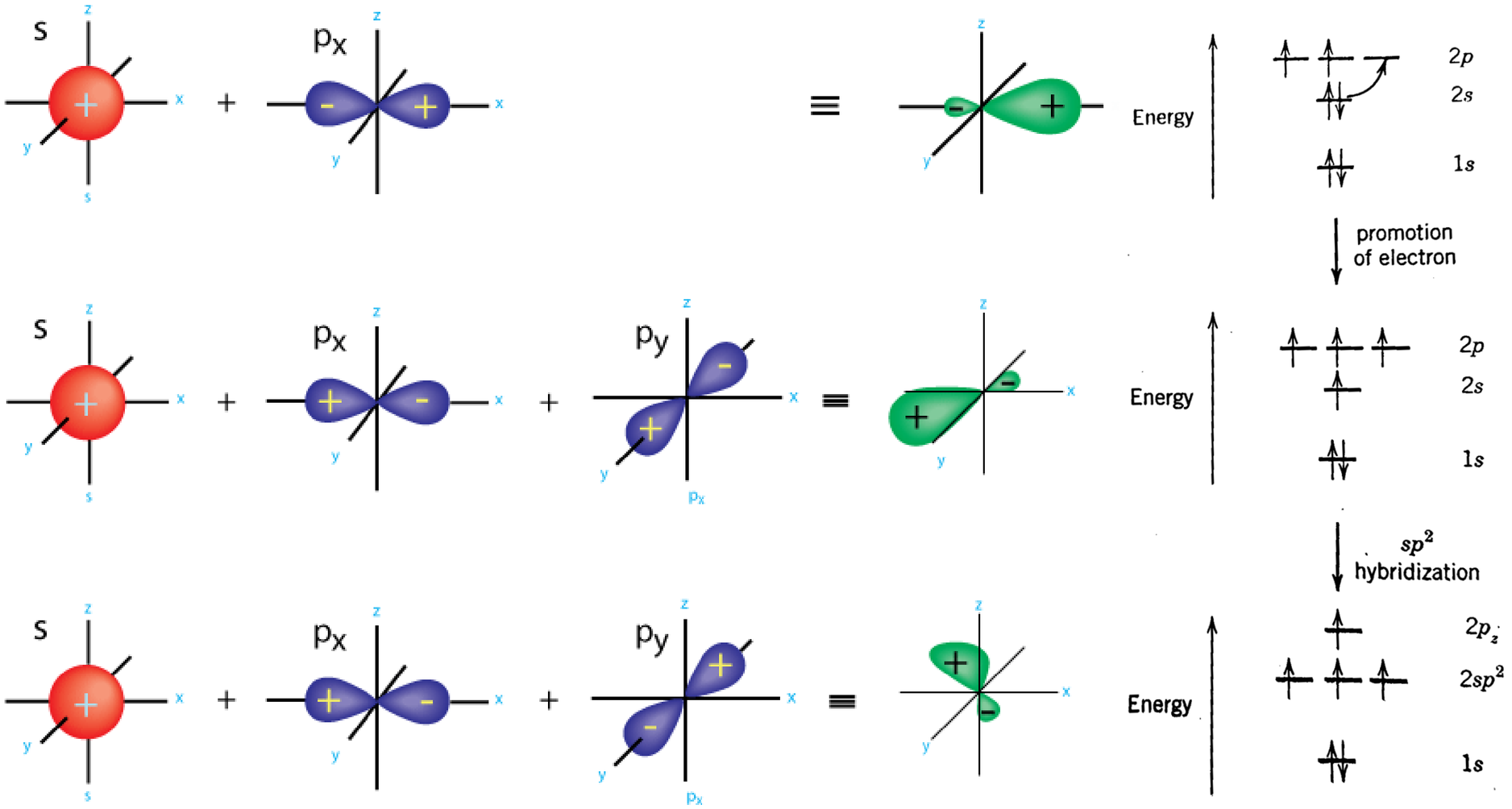




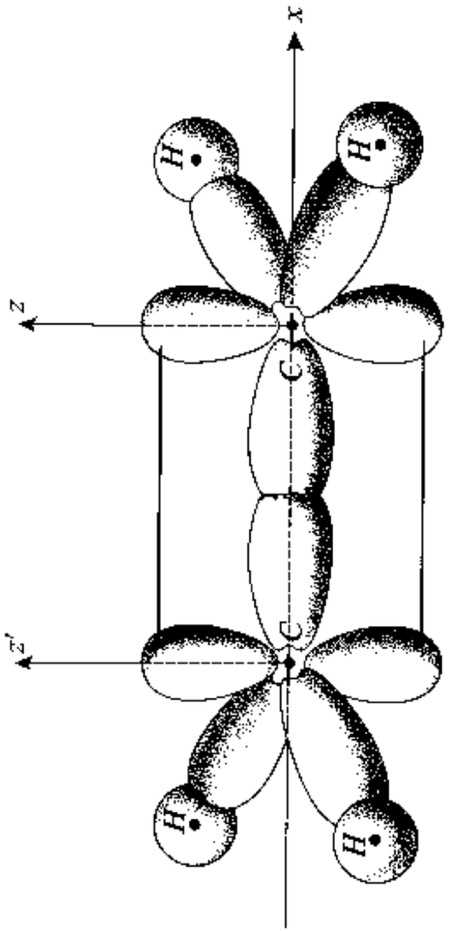
acetylene



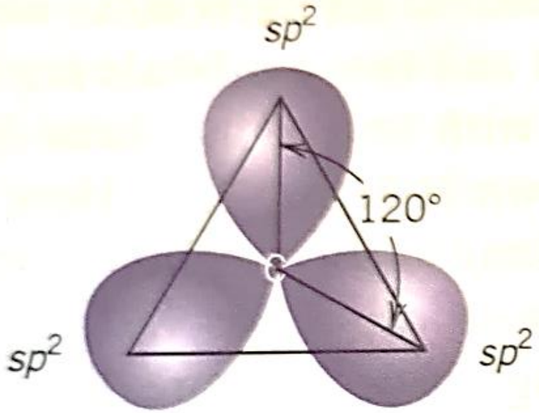
Covalent bond: *sp2* hybridization

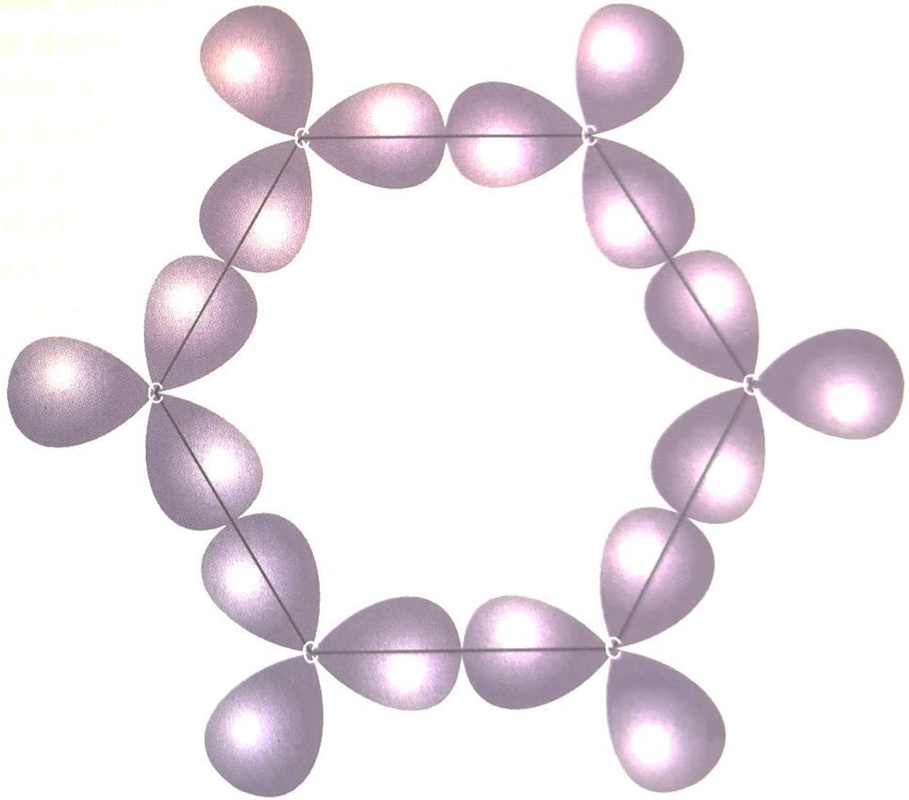


ethylene

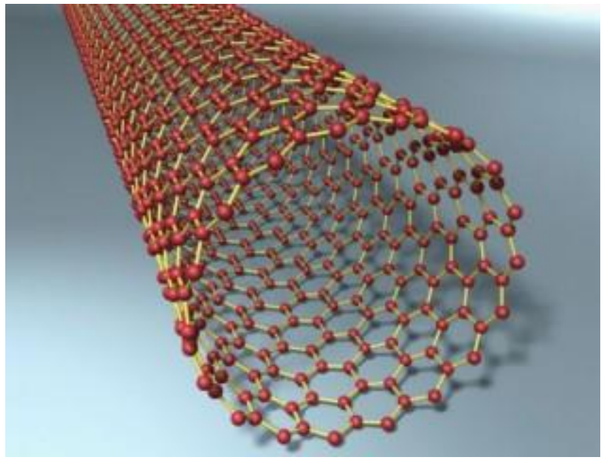


Covalent bond: *sp2* hybridization Graphite



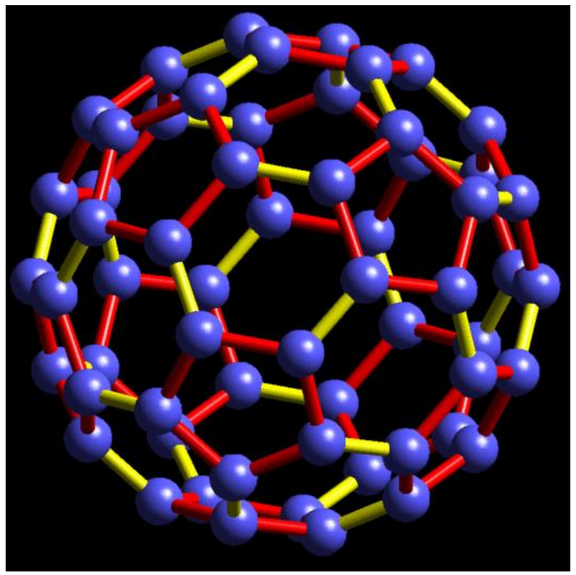


Covalent bond: examples



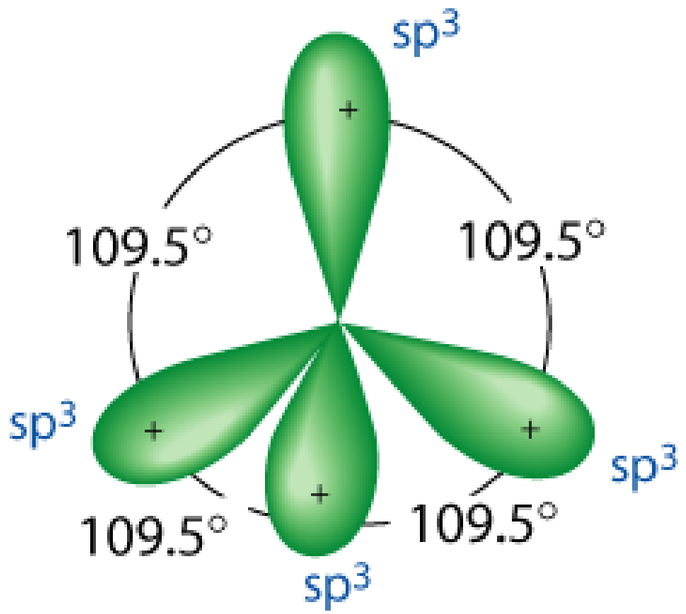
Carbon nanotube

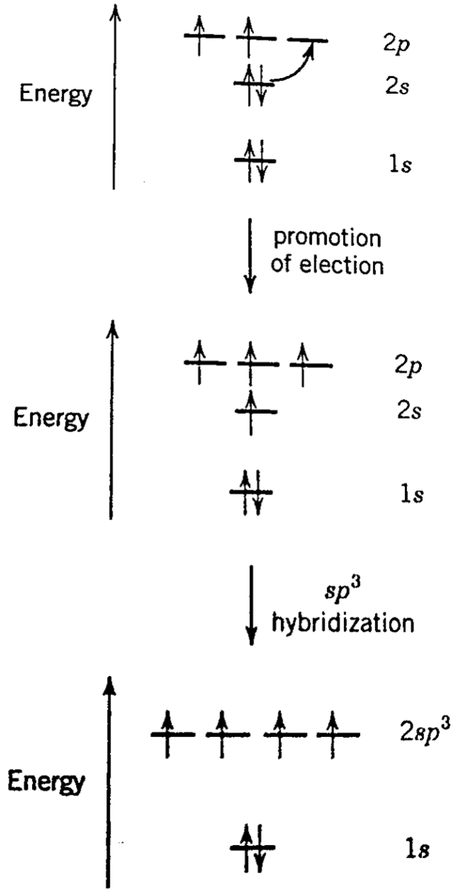
sp^2

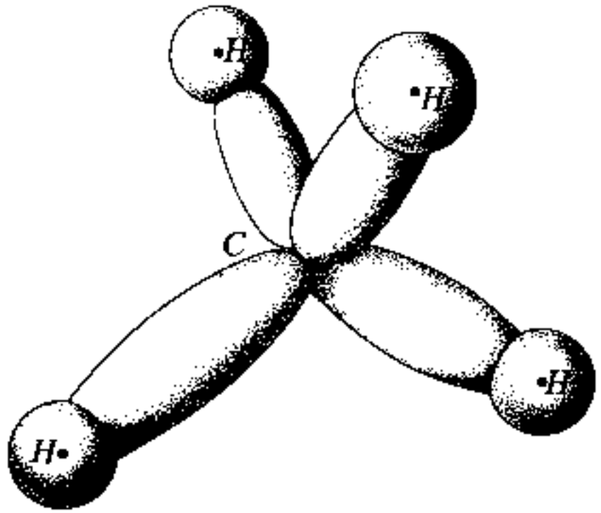


Bucky balls

Covalent bond: *sp3* hybridization

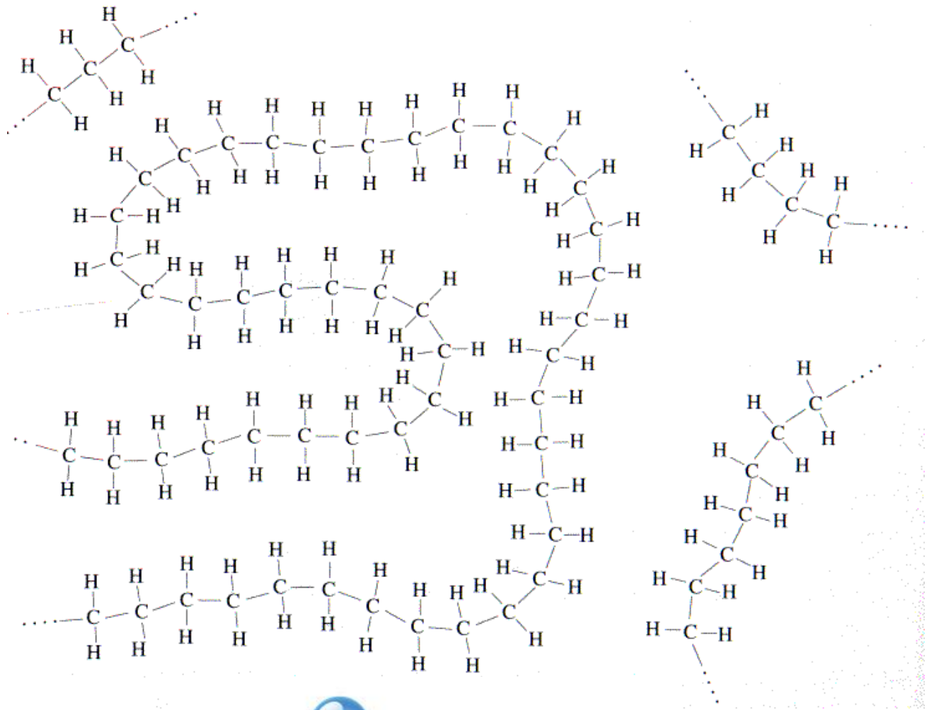






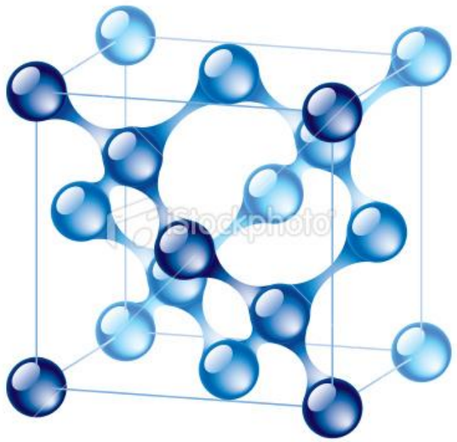
Methane

Covalent bond: examples



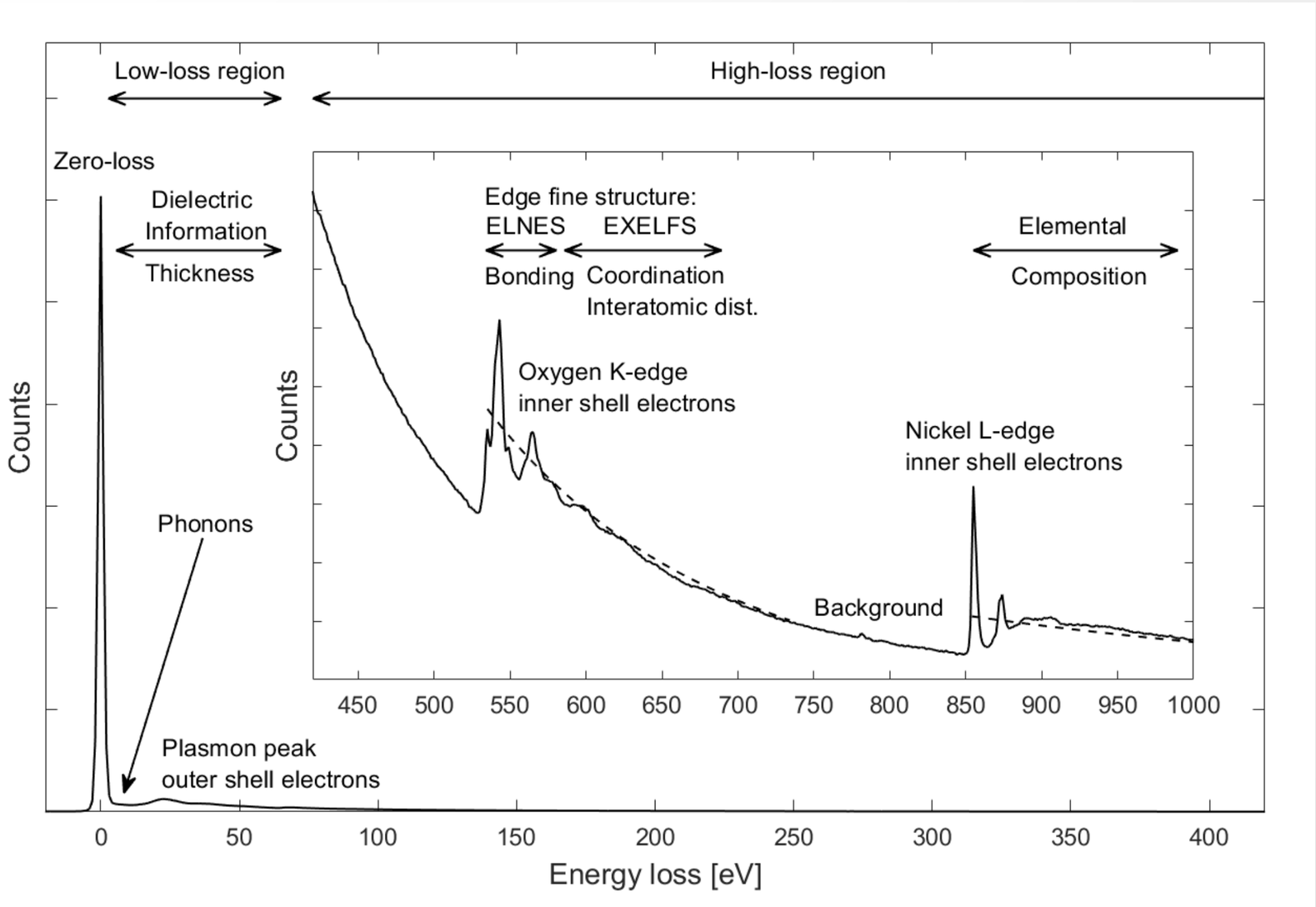
Poly-ethylene

sp^3



diamond sp^3

Electron Energy Loss Spectroscopy (EELS)



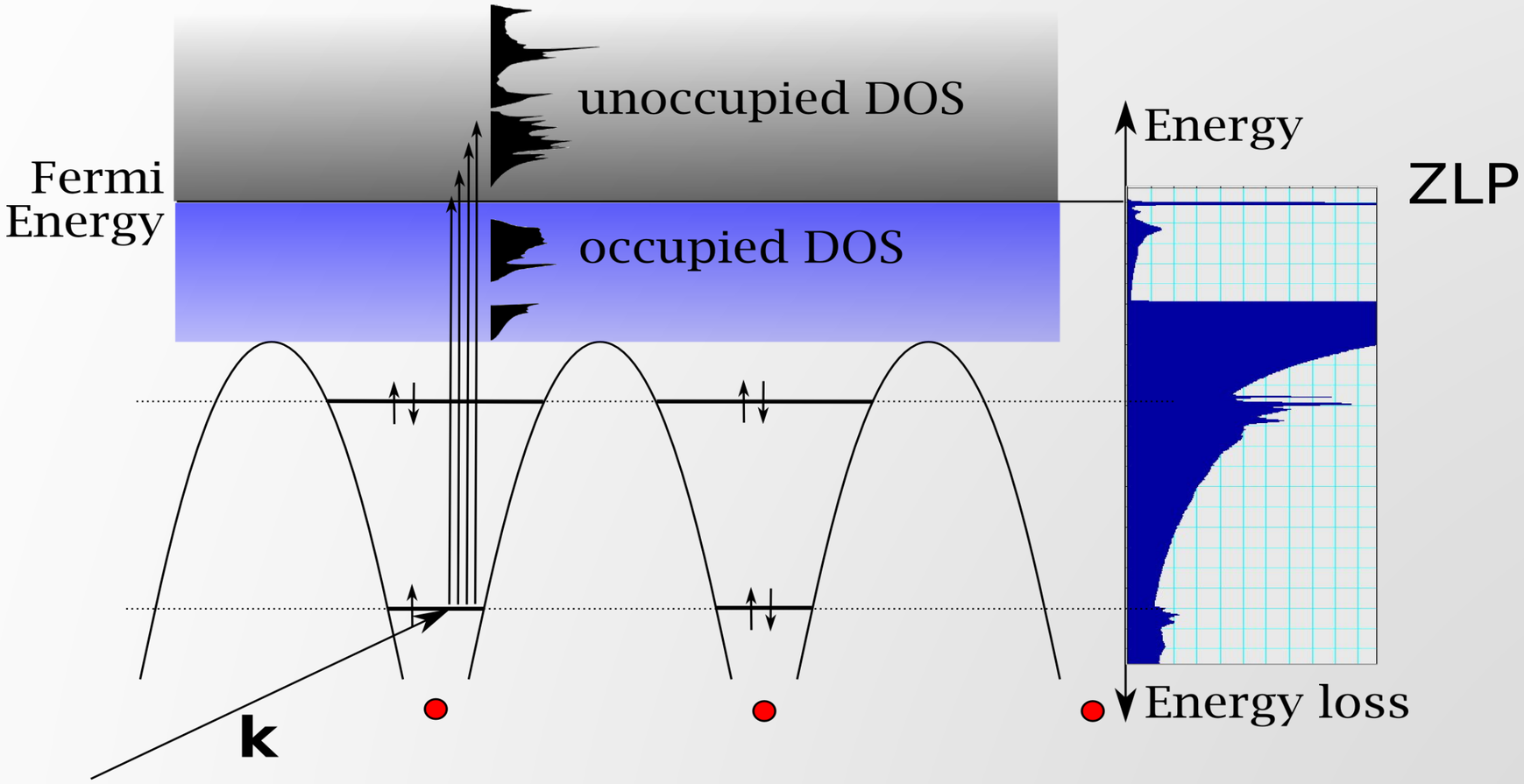
Low loss spectrum: plasmon and interband transitions

- Optical properties
- Band gap (semiconductors
- Angular resolved: plasmon dispersions
- <1eV: phonons – vibrational spectroscopy

High Loss spectrum:

- Chemical composition
- Electronic structure (DOS)
- Magnetic properties- angle resolved core loss
- Nearest neighbor bonding correlations

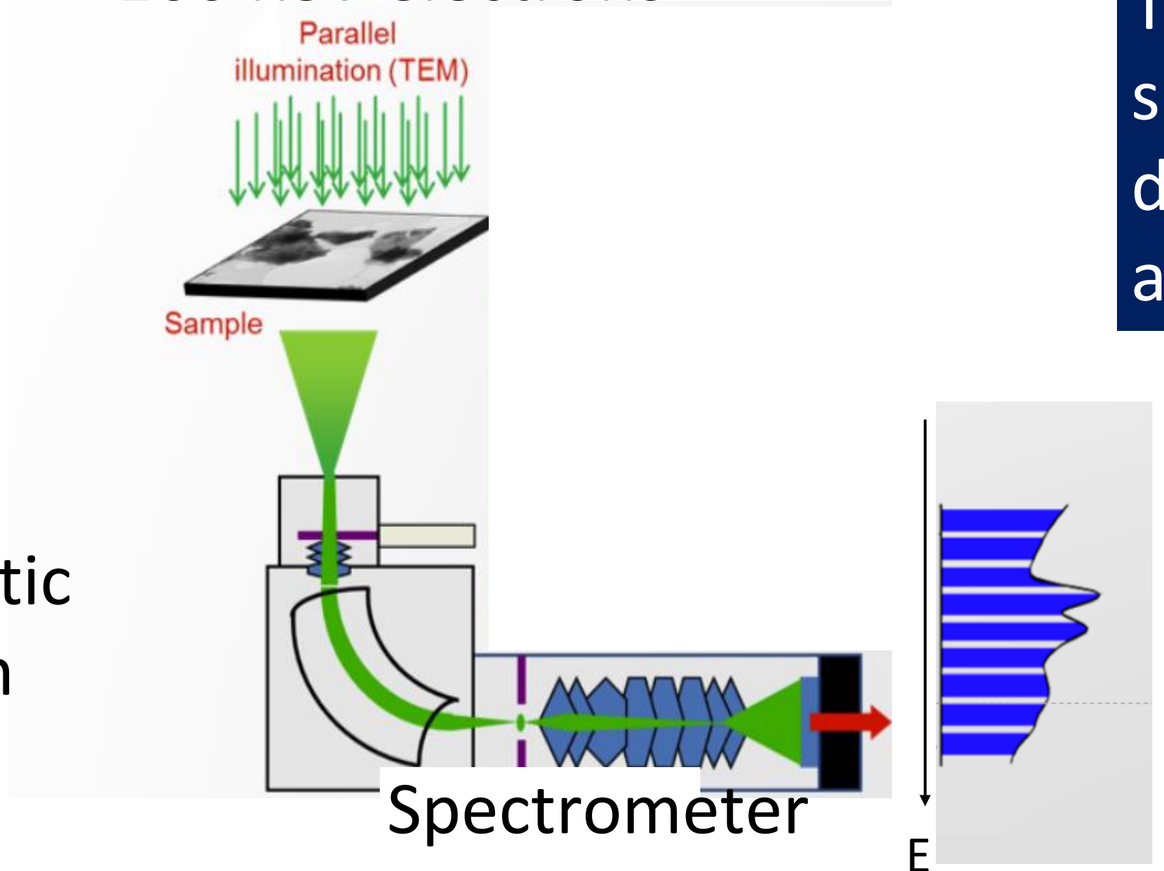
Electron Energy Loss Spectroscopy (EELS)



Core electron transitions from a localized core state to an unoccupied state. An onset energy is needed to reach the Fermi level, and transitions above the onset energy are possible.

Electron Energy Loss Spectroscopy (EELS)

Parallel illumination (TEM)
200 KeV electrons



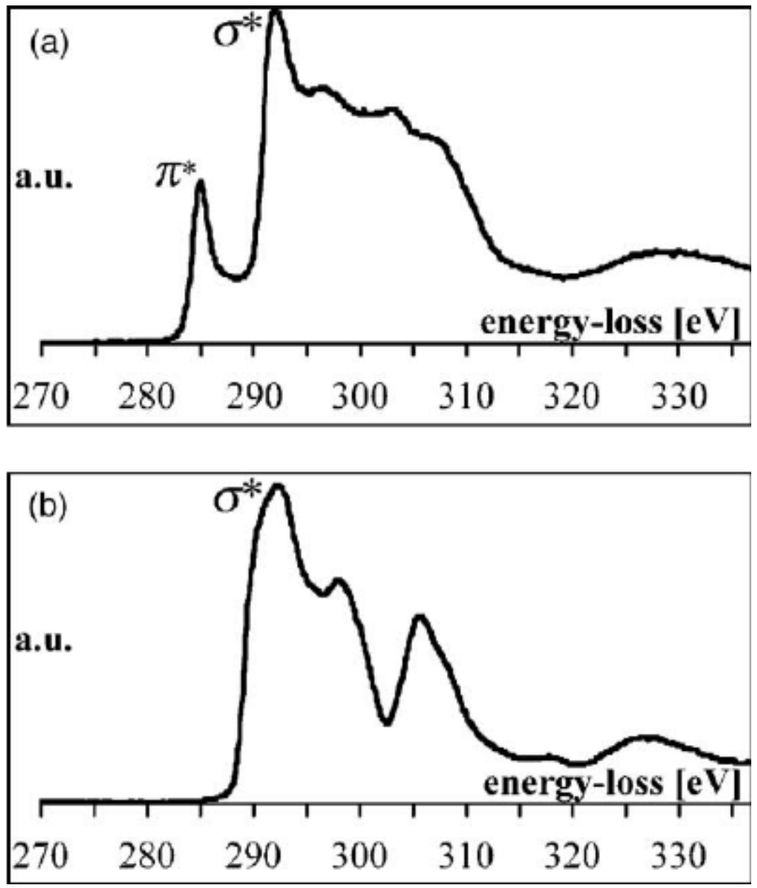
Magnetic prism

Spectrometer electron optics

The post-column electron spectrometer in the TEM disperses the electrons according to their energy

Spectra captured on CMOS/CCD detector

Covalent bond: EELS



Graphite sp^2

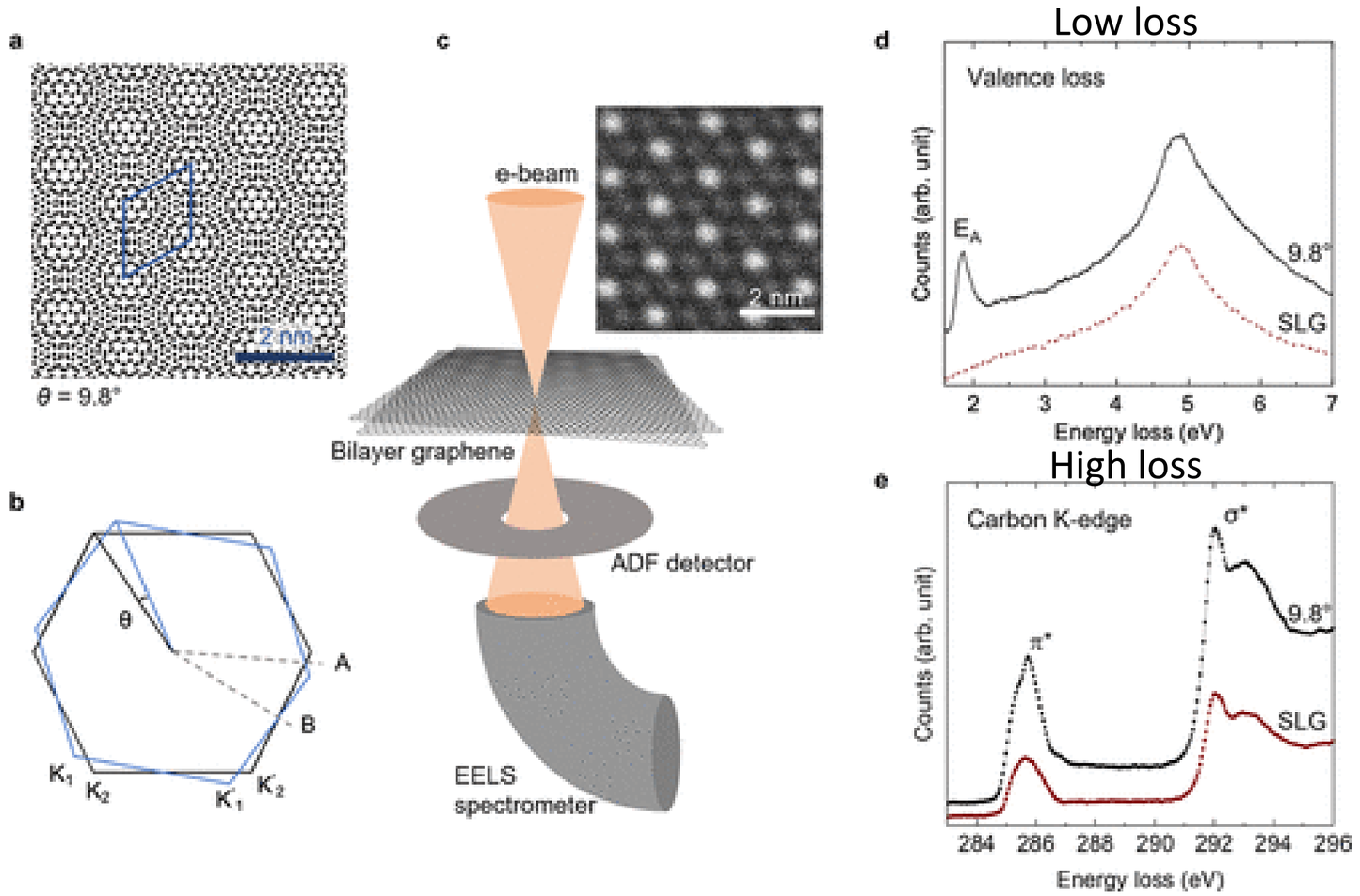
1 π bonds
3 σ bonds

Diamond sp^3

No π bonds
4 σ bonds

Electron Energy Loss Spectroscopy can measure the bond energy and ratios of π and σ bonds on ionization edges

EELS of twisted graphene bilayers



E_a peak observed in twisted bilayer

2x the counts observed in the bilayer as expected

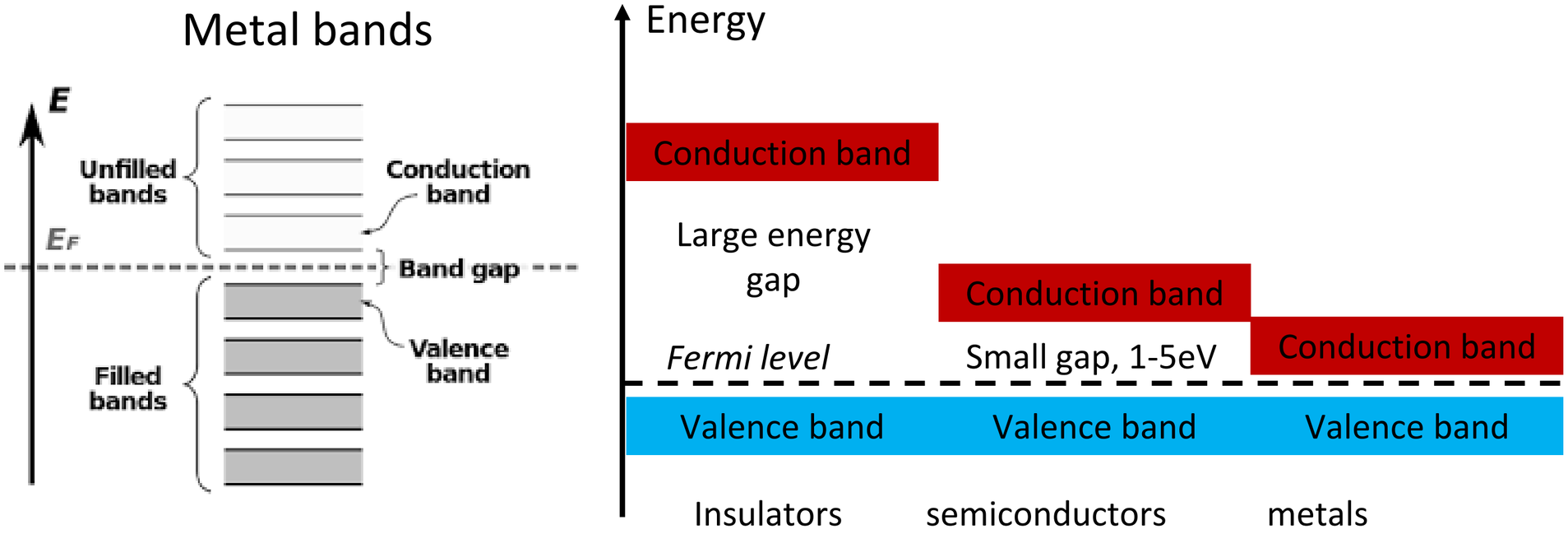
Only Low loss Spectrum shows difference between single layer graphene (SLG) and 9.8 degree twisted bilayer graphene

Exercise: DEMO on EELS Today!

Chemistry Building CH H0 604

2 groups of 6-7 people

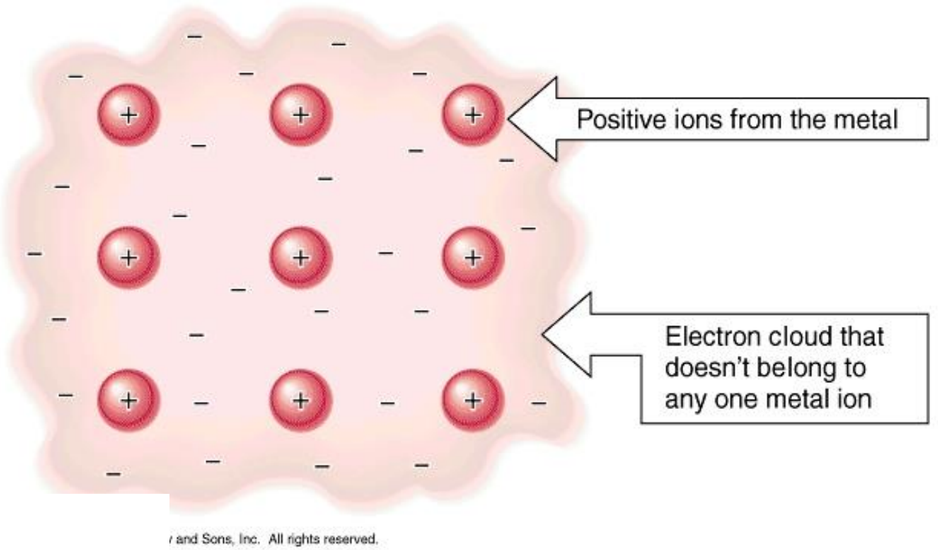
Metallic bonds



Metals have incomplete bands

Metallic bond

- Metal bonds have available states (incomplete valance band) with wave vector k.
- The momentum of the electrons can be changed.
- Electrons in metal bonds have a net velocity component along the electric field directions, i.e., why metals are good conductors.



$$\psi_k(x) = u_k(x)e^{ikx}$$ Bloch wave functions

$$\psi_k(x+L) = \psi_k(x)$$ Boundary conditions L- the size of the crystal

$$\psi(x) = \sum_k C(k)e^{ikx}$$ Fourier decomposition

Wave equation in a periodic potential

$$U(x) = U(x+a) \qquad U(x) \text{ is real}$$

Fourier (periodic potential) $$U(x) = \sum_G U_G e^{iGx} \qquad U(x) = \sum_{G>0} U_G (e^{iGx} + e^{-iGx}) = 2\sum_{G>0} U_G \cos Gx$$

$$(H_0 + H_1)\cdot\psi = (E_0 + \Delta E)\cdot\psi \qquad \left(\frac{1}{2m}p^2 + U(x)\right)\psi(x) = \left(\frac{1}{2m}p^2 + \sum_G U_G e^{iGx}\right)\psi(x) = E\psi(x)$$

Fourier (wave function) $$\psi(x) = \sum_k C(k) e^{ikx}$$

Time-independent
Schrödinger equation

Kinetic energy $$\frac{1}{2m}p^2\psi(x) = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m}\sum_k k^2 C(k) e^{ikx}$$

Potential energy $$\left(\sum_G U_G e^{iGx}\right)\psi(x) = \sum_G\sum_k U_G e^{iGx} C(k) e^{ikx}$$

Central equation

Eigenvalue Solution to Schrödinger's equation

$$(\lambda_k - E)C(k) + \sum_G U_G C(k-G) = 0 \qquad C(k)?$$

Lets suppose $U_G = U_{-G} = U$ and $U_{\pm nG} = 0 \quad n > 1$

$$U(x) = Ue^{ikx} + Ue^{-ikx} = 2U\cos(kx)$$

$$\lambda_k = \hbar^2 k^2 / 2m$$

$$\begin{vmatrix} \lambda_{k-2G} - E & U & 0 & 0 & 0 \\ U & \lambda_{k-G} - E & U & 0 & 0 \\ 0 & U & \lambda_k - E & U & 0 \\ 0 & 0 & U & \lambda_{k+G} - E & U \\ 0 & 0 & 0 & U & \lambda_{k-2G} - E \end{vmatrix} = 0$$

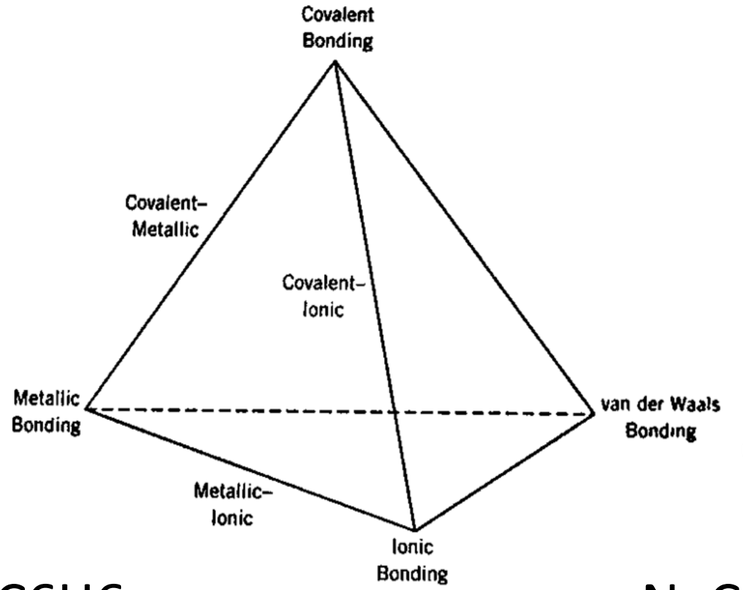
$$\uparrow \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow$$

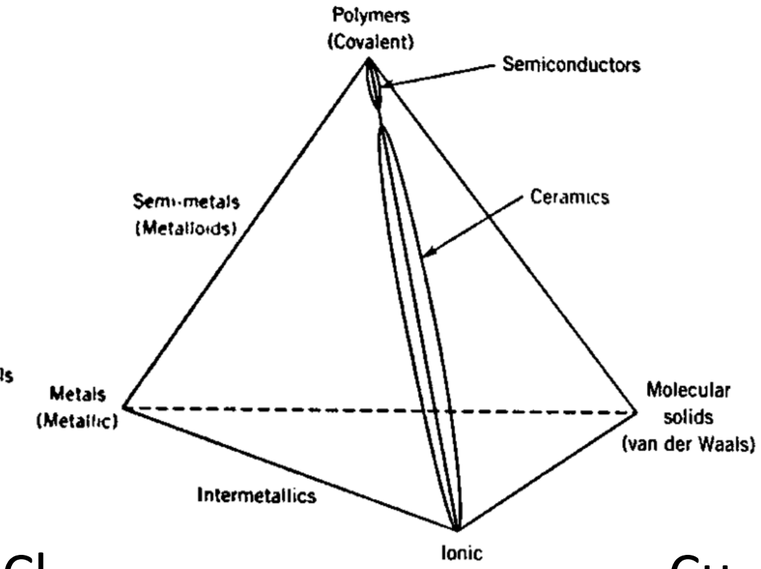
$$C(k-2G) \quad C(k-G) \quad C(k) \quad C(k+G) \quad C(k+2G)$$

solutions

$$E(k)$$

Chemical bonds and materials





C6H6

NaCl

Cu