

# F7360 Characterization of thin films and surfaces

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2. Chapter - Structure of Condensed Matter  
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# Outline

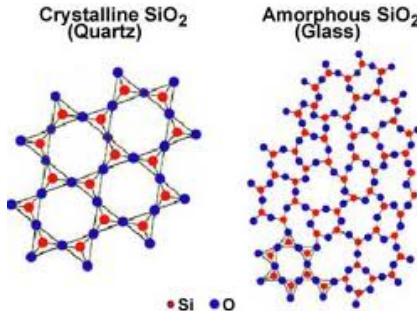
- 2. Structure of Condensed Matter
  - 2.1 Amorphous and Crystalline Materials
  - 2.2 Bonds in solids
    - 2.2.1 Ionic Bonds
    - 2.2.2 Van der Waals bonds
    - 2.2.3 Covalent bonds
    - 2.2.4 Metallic Bonds
    - 2.2.5 Summary of Bonds in Solids
  - 2.3 Types of Materials

When the temperature of a melt is lowered to a certain point, the liquid will form either a **crystalline** or **amorphous** solid.

- ▶ Crystals are periodic arrays of long-range ordered atoms. A real crystal is never perfect – contains defects (vacancies, dislocations, impurities, and other imperfections).
- ▶ Amorphous materials possess only short-range ordering.

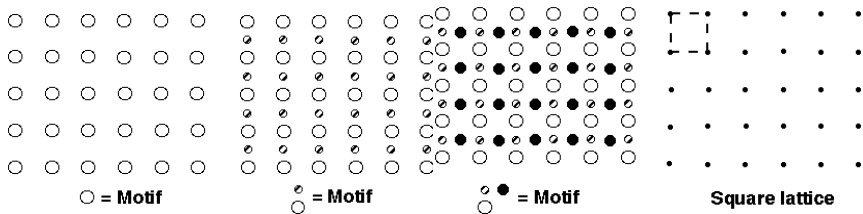
$\text{SiO}_2$  demonstrates the difference between crystalline and amorphous materials:

- ▶ Short-range ordering: silicon atoms are surrounded by three oxygen atoms.
- ▶ Long-range ordering in quartz: hexagonal structure.



An ideal crystal is constructed by the infinite repetition of identical groups of atoms (a motif):

- ▶ A group is called the **basis**.
- ▶ The set of mathematical points to which the basis is attached is called the **lattice**.



The lattice in 3D is defined by three **translation vectors**  $\vec{a}_1$ ,  $\vec{a}_2$ ,  $\vec{a}_3$   
 - the arrangement of atoms in the crystal have to look the same  
 when viewed from the points  $\vec{r}$  and  $\vec{r}'$

$$\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

where  $u_1$ ,  $u_2$  and  $u_3$  are arbitrary integers.

The lattice is **primitive** if any two points from which the atomic arrangement looks the same always satisfy

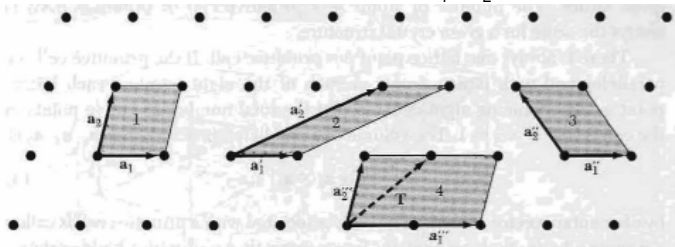
$$\vec{r}' = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

with a suitable choice of the integers  $u_1$ ,  $u_2$  and  $u_3$ .

Then, the vectors  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_3$  are **primitive translation vectors**.

Lattice points in 2D -

all pairs of  $\vec{a}_1$ ,  $\vec{a}_2$  are translational vectors but  $\vec{a}_1''$ ,  $\vec{a}_2''$  are not primitive.

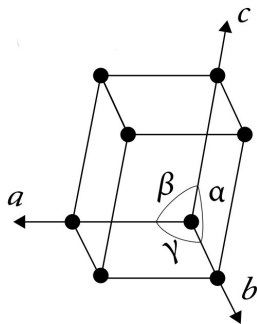


The parallelepiped defined by the primitive axes  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_3$  is a **primitive cell**.

A primitive cell is type of unit cell (or just cell).

It is the smallest cell that can serve as a building block for the crystal structure. Its volume is

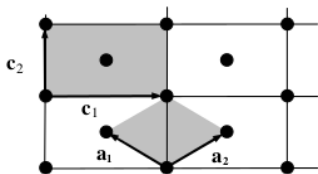
$$V = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|$$



Primitive translation vectors  $\vec{a}_i$  are often used to define the **crystal axes**

- three adjacent edges of the primitive parallelepiped.

Nonprimitive axes are used as crystal axes when they have a simple relation to the symmetry of the structure.



2D centered rectangular lattice with

- ▶ **primitive translation vectors**  $\vec{a}_1$  and  $\vec{a}_2$  and
- ▶ **nonprimitive translational vectors**  $\vec{c}_1$  and  $\vec{c}_2$ .

In order to describe the crystal structure it is necessary to answer three important questions:

1. **what lattice** we have (for a particular structure can be more than one),
2. **what translational vectors**  $\vec{a}_1, \vec{a}_2, \vec{a}_3$  are we using to describe the lattice (more sets of translational vectors can be selected for a given lattice) and
3. **what is the basis** (which is chosen after the lattice and translational vectors are selected).

Crystal lattice can be transformed into themselves by the lattice translation  $\vec{T}$

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

and by various other symmetry point operations.

A typical **symmetry point operation** -

rotation about an axis that passes through a lattice point

Lattices can be found such that one-, two-, three-, four- and six-fold rotation axes carry the lattice into itself (corresponding rotations by  $2\pi$ ,  $2\pi/2$ ,  $2\pi/3$ ,  $2\pi/4$  and  $2\pi/6$  and their integral multiples).

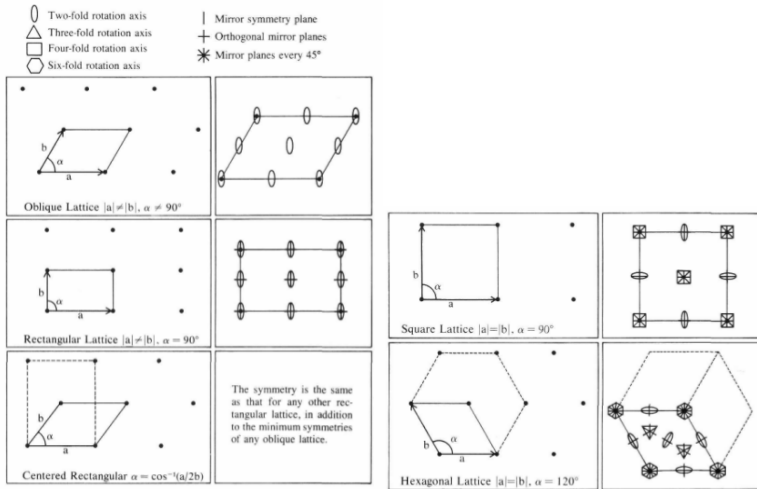
Another symmetry operations are **mirror reflections about a plane through a lattice point**.

The collection of symmetry point operations which, applied about a lattice point, carry the lattice into itself is called **lattice point group**.



## Bravais lattices in two dimensions:

- ▶ general lattice known as oblique lattice - invariant only under rotation of  $\pi$  and  $2\pi$  about any lattice point
- ▶ four special lattices (rectangular, centered rectangular or rhombic, hexagonal and square) - can be invariant under rotation  $2\pi/3$ ,  $2\pi/4$  and  $2\pi/6$  or under mirror reflection



In **3D** - 7 distinguishable point groups of unit cells (**7 crystal systems**) that can fill the space (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic).

The **Bravais lattices** are obtained by combining one of the 7 lattice systems with one of the **lattice centerings**:

- ▶ simple - lattice points on the cell corners only.
- ▶ body-centered
- ▶ face-centered
- ▶ base-centered



Simple cubic



Face-centered cubic



Body-centered cubic



Simple tetragonal



Body-centered tetragonal



Hexagonal



Simple orthorhombic



Body-centered orthorhombic



Base-centered orthorhombic



Face-centered orthorhombic



Rhombohedral



Simple Monoclinic



Base-centered monoclinic



Triclinic

in total  $7 \times 6 = 42$  combinations but from the full symmetries (point operations and translations) 14 different space groups (**14 Bravais lattices**) have been found.

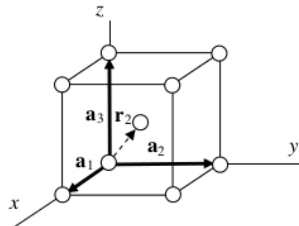
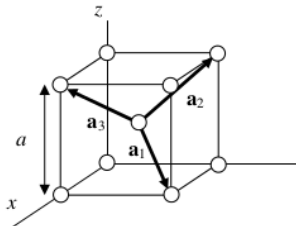
Crystal System	Centering	Axial Distances (edge lengths)	Axial Angles	Examples
Cubic	simple body-centred face-centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Zinc Blende, Cu
Tetragonal	simple body-centered	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO <sub>2</sub> , TiO <sub>2</sub> , CaSO <sub>4</sub>
Orthorhombic	simple body-centered face-centered base-centered	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Allotropes of sulfur, KNO <sub>3</sub> , BaSO <sub>4</sub>
Hexagonal	simple	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	Graphite, ZnO, CdS
Rhombohedral (trigonal)	simple	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO <sub>3</sub> , HgS
Monoclinic	simple base-centered	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	Monoclinic Sulphur, Na <sub>2</sub> SO <sub>4</sub> *10H <sub>2</sub> O
Triclinic	simple	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , CuSO <sub>4</sub> *5H <sub>2</sub> O, H <sub>3</sub> BO <sub>3</sub>

**Primitive translation vectors** of the **body-centered cubic (bcc) lattice** (in units of lattice parameter  $a$ )

- ▶  $\vec{a}_1 = (1/2, 1/2, -1/2)$ ;
- ▶  $\vec{a}_2 = (-1/2, 1/2, 1/2)$ ;
- ▶  $\vec{a}_3 = (1/2, -1/2, 1/2)$

The **primitive cell** is the rhombohedron. The **packing ratio** is 0.68, defined as the maximum volume which can be filled by touching hard spheres in atomic positions. Each atom has 8 nearest neighbors.

The **conventional unit cell** is a cube based on vectors  $\vec{a}_1 = (0, 0, 1)$ ;  $\vec{a}_2 = (0, 1, 0)$ ;  $\vec{a}_3 = (0, 0, 1)$ . It is twice big compared to the primitive unit cell and has two atoms in it with coordinates  $\vec{r}_1 = (0, 0, 0)$  and  $\vec{r}_2 = (1/2, 1/2, 1/2)$ .



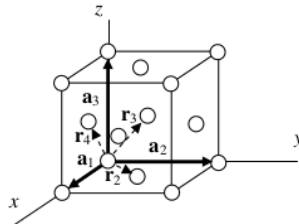
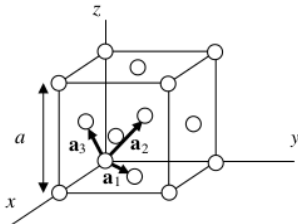
The bcc lattice have alkali metals such as Na, Li, K, Rb, Cs, magnetic metals such as Cr and Fe, and refractory metals such as Nb, W, Mo, Ta.

**Primitive translation vectors** of the **face-centered cubic (fcc)** lattice (in units of lattice parameter  $a$ )

- ▶  $\vec{a}_1 = (1/2, 1/2, 0)$ ;
- ▶  $\vec{a}_2 = (0, 1/2, 1/2)$ ;
- ▶  $\vec{a}_3 = (1/2, 0, 1/2)$ .

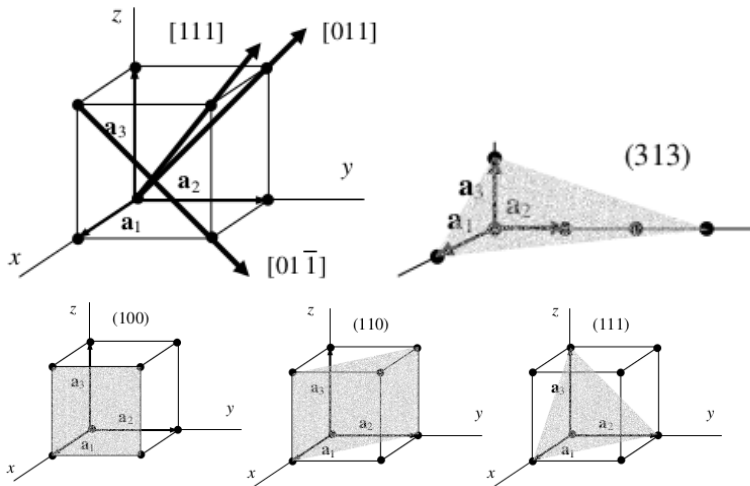
The **primitive cell** is the rhombohedron. The **packing ratio** is 0.74. Each atom has 12 nearest neighbors.

The **conventional unit cell** is a cube based on vectors  $\vec{a}_1 = (0, 0, 1)$ ;  $\vec{a}_2 = (0, 1, 0)$ ;  $\vec{a}_3 = (1, 0, 0)$ . It is 4 times bigger than the primitive unit cell and has 4 atoms in it with coordinates  $\vec{r}_1 = (0, 0, 0)$ ;  $\vec{r}_2 = (1/2, 1/2, 0)$ ;  $\vec{r}_3 = (0, 1/2, 1/2)$ ;  $\vec{r}_4 = (1/2, 0, 1/2)$ .



The fcc lattice have noble metals such as Cu, Ag, Au, common metals such as Al, Pb, Ni and inert gas solids such as Ne, Ar, Kr, Xe. NaCl is fcc with the basis consisting of two atoms (Na and Cl) - the closest neighbours are 6 atoms of different type. Diamond is fcc, the basis two same atoms at  $000, \frac{1}{4} \frac{1}{4} \frac{1}{4}$ , tetrahedral bonds (4 closest neighbours).

## Index systems for crystal directions and planes (Miller indices)

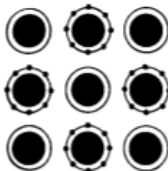


Interatomic bonds in solids are

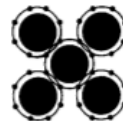
- ▶ ionic (a)
- ▶ covalent (b)
- ▶ metallic (c)
- ▶ Van der Waals (d), (e)

bond energy:

1 kJ/mol = 0.010364 eV/atom



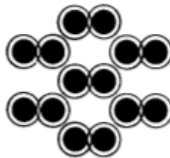
(a)



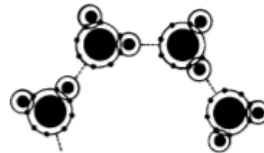
(b)



(c)



(d)



(e)

## Ionic bonds - between particles which have a net electrical charge

- ▶ positive ions - **cations**, atoms with low **ionization energy** (lose electrons easily) - alkaline metals (only 1 s electron in outer shell)
- ▶ negative ions - **anions**, atoms with high **electron affinity** (easily accept electrons) - halogens (missing 1 p electron)

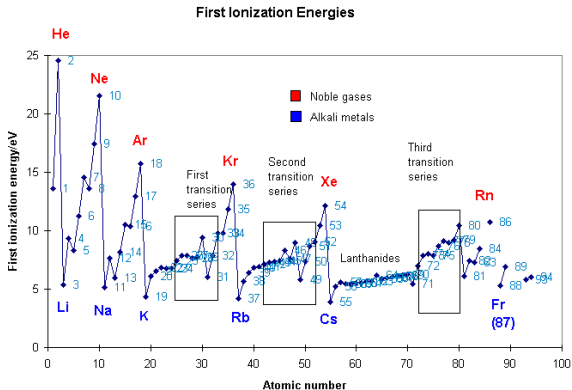
Interaction force - **Coulomb**. Repulsive forces of similarly charge ions and attractive forces of differently charged ions are equilibrated. **Pauli exclusion principle** does not allow ions to come too close.

**Periodic Table of the Elements**

																13	14	15	16	17	18	
																IIIA	IVA	VA	VIA	VIIA	VIIIA	
																3A	4A	5A	6A	7A	8A	
1																			2			
1A																			8A			
11A																			8A			
1	2											10			18							
H	He											B	C	N	O	F	Ne					
Hydrogen	Helium											Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon					
1.00794	4.002602											10.811	12.0107	14.00644	15.999	18.9984032	20.1797					
3	4															10						
Li	Be															Ne						
Lithium	Beryllium															Neon						
6.941	9.012182															20.1797						
11	12	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18					
Na	Mg	III	IV	V	VI	VII	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA					
Sodium	Magnesium	3B	4B	5B	6B	7B	8	9	10	11B	12B	3A	4A	5A	6A	7A	8A					
22.98976928	24.30409	26.9815386	28.0855286	28.96	30.973762	31.9988	35.45	36.96657	39.0983	40.078	48.958264	50.9415	51.9961	54.938	55.93494	58.9332	69.923					
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton					
39.0983	40.078	44.955912	47.88	50.9415	51.9988	54.938	55.93494	58.9332	58.9332	63.546	65.38	69.723	72.6305	74.9216	78.96	79.904	83.80					
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine	Xenon					
85.4678	87.62	88.90584	91.224	92.90638	95.94	98.90625	101.07	102.9055	106.9055	107.8682	112.411	114.818	117.259	121.757	127.46	126.90547	131.29					
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86					
Cs	Ba	Lanthanide Series	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
Cesium	Barium	Lanthanide Series	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon					
132.90545196	137.327		178.49	180.9479	183.84	186.207	187.02	188.9054	195.084	196.966569	200.59	204.3833	207.2	208.9804	208.9824	210	222.01758					
87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118					
Fr	Ra	Actinide Series	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Uuq	Uup	Uuh	Uus	Uuo					
Francium	Radium	Actinide Series	Rutherfordium	Dubnium	Seaborgium	Berkelium	Hassium	Mtnerium	Darmstadtium	Roggenbergium	Copernicium	Nihonium	Unbinilium	Untrium	Unquadium	Unseptilium	Unoctilium					
223.01851	226.0254		261.101	262.1098	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109	263.109					
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71								
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
Lanthanum	Cerium	Praseodymium	Niodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium								
138.90547	140.12	140.90766	144.24	144.9127	150.36	151.964	157.25	158.92534	172.043	174.96706	175.053	178.49	173.054	174.967								
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103								
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								
Actinium	Thorium	Protactinium	Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lrutherfordium								
227.027721	232.0377248	231.036888	238.02891	237.048173	244.06422	247.07125	251.076269	264.10154	267.10352	271.103691	277.10361	283.1034864	287.1034	260.103298								
Alkali Metal	Alkaline Earth	Transition Metal	Transition Metal	Transition Metal	Transition Metal	Transition Metal	Transition Metal	Transition Metal	Transition Metal	Noble Gas	Lanthanides	Lanthanides	Lanthanides	Lanthanides	Actinides	Actinides						



**Ionization energy** (energy necessary to release electron) is periodic function of atomic number, large atoms or molecules have lower ionization energy.



**Electron affinity** (energy released if electron is added):

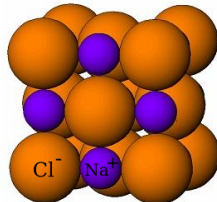
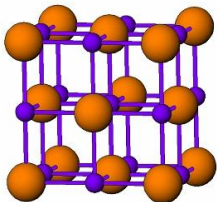
Fluorine	3.45 eV
Chlorine	3.61 eV
Bromine	3.36 eV
Iodine	3.06 eV

**Directionality of ionic bond** is low - electron configuration of ions resemble filled shells of inert gases, i. e. electron density is spherically symmetric.

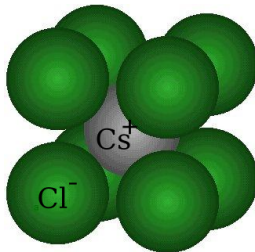
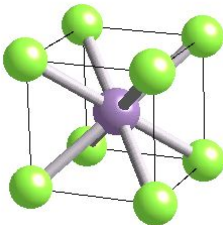
**High coordination** - cation (anion) is surrounded by as many anions (cations) as possible.

Relative size of cations and anions determines the lattice type. The most frequent types

- ▶ fcc - typical example NaCl (6 neighbors of different type)



- ▶ bcc - typical example CsCl (8 neighbors of different type)



**Cohesive energy** of the crystal - energy released if ionic crystal is formed. The most important contribution - **Coulomb interactions** between ions, long range interaction

Consider  $\text{Na}^+$  in NaCl. It is surrounded by six  $\text{Cl}^-$  at the distance  $r$ :

$$V_1 = -\frac{6e^2}{4\pi\epsilon_0 r}$$

Another neighbors are 12  $\text{Na}^+$  each at the distance  $\sqrt{2}r$ :

$$V_2 = +\frac{12e^2}{4\pi\epsilon_0\sqrt{2}r}$$

Summed for the entire crystal:

$$\begin{aligned} V_{Coulomb} &= -\frac{e^2}{4\pi\epsilon_0 r} \left( 6 - \frac{12}{\sqrt{2}} + \dots \right) \\ &= -1.748 \frac{e^2}{4\pi\epsilon_0 r} \\ &= -\alpha \frac{e^2}{4\pi\epsilon_0 r}. \end{aligned} \tag{1}$$

The constant  $\alpha$  is called **Madelung crystal constant**, values 1.6–1.8 for simple crystals.

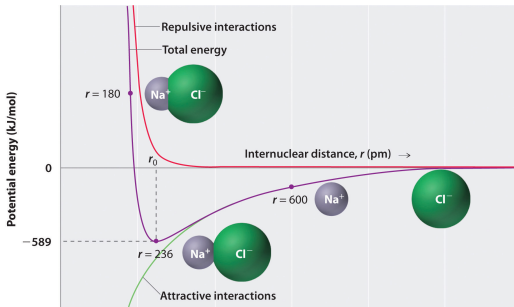
The contribution of the **quantum-mechanical repulsive force** to the total potential energy can be written as:

$$V_{\text{repulsive}} = \frac{B}{r^n}.$$

Total potential energy in the crystal is:

$$V = V_{\text{Coulomb}} + V_{\text{repulsive}} = -\frac{\alpha e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}$$

where  $n$  is about 9.



In the steady case the separation of ions at a distance  $r_0$  must have minimum:

$$\left(\frac{dV}{dr}\right)_r = r_0 = 0,$$

SO

$$B = \frac{\alpha e^2}{4\pi\epsilon_0 n} r_0^{n-1}$$

**Total potential energy:**

$$V = -\frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

**Total potential energy** (from previous slide):

$$V = -\frac{\alpha e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

**In case of NaCl**

- ▶  $r_0 = 2.81$ , thus  $V = -1.27 \times 10^{-18} \text{ J} = -7.97 \text{ eV}$
- ▶ we have take into account energy for electron transfer between Na and Cl, i. e. the difference between the ionization energy 5.14 eV for Na and the electron affinity of -3.61 eV for Cl  $\rightarrow 1.53 \text{ eV}$
- ▶ each atom is contributing with half of the value, so the overall cohesive energy per atom  $E_{\text{cohesive}} = (-3.99 + 0.77) \text{ eV/atom} = -3.22 \text{ eV/atom}$ .

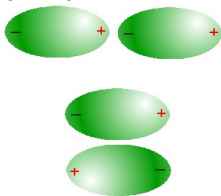
$\Rightarrow$  Ionic crystals are hard and they have high melting point.

They conduct electricity when molten or in solution, but not as a solid.

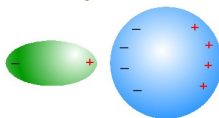
They tend to be soluble in water.

All atoms and molecules, even inert-gas atoms, exhibit weak, short-range attractions for one another (proportional to  $r^{-7}$ ) due to **van der Waals forces** (0.01–0.1 eV/molecule).

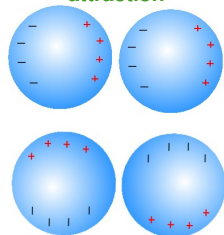
### polar-polar attraction



### polar-nonpolar attraction



### nonpolar-nonpolar attraction



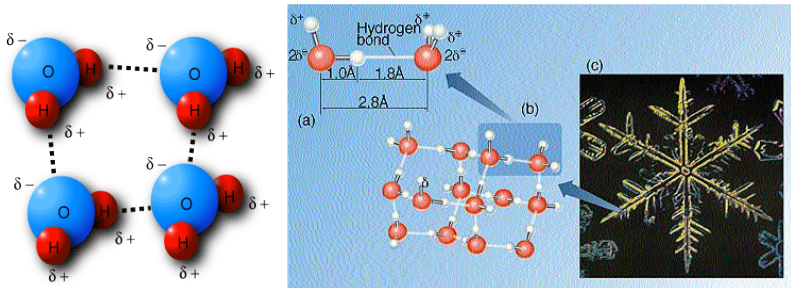
The different types of van der Waals forces were first explained by different people at different times  $\Rightarrow$  different names

- ▶ **London dispersion forces** between **non-polar** atoms or molecules were described by Fritz London in 1930. He suggested that the motion of electrons within an atom or non-polar molecule can result in a transient dipole moment. Dispersion forces are the weakest of the van der Waals forces. They are stronger for larger atoms and molecules (higher polarizability).
- ▶ **dipole-dipole interactions** explained by Keesom in 1912 as interaction between permanent electrical dipole moments of molecules (depends on the value of electrical dipole).

**Hydrogen bonds** - a special type of attractive dipole-dipole interaction between an electronegative atom and a hydrogen atom bonded to another electronegative atom (e. g. for H-F, H-O or H-N).

- ▶ It is strong type of van der Waals forces (0.04–0.26 eV/molecule) because H atom has only 1 electron that is “donated” almost whole to the electronegative atom, leaving the small effective size of proton unshielded (electric forces vary as  $r^{-2}$ ).
- ▶ Hydrogen bonds can occur between molecules or within parts of a single molecule.

Typical example of molecules with permanent electric dipole moments is  $\text{H}_2\text{O}$ :



Characteristics of attractive force between **polar and nonpolar molecules**:

The electric field  $\vec{E}$  at a distance  $r$  from a polar molecule having **dipole moment  $\vec{p}$**

$$\vec{E} = \frac{1}{4\pi\epsilon_0} \left[ \frac{\vec{p}}{r^3} - \frac{3(\vec{p}\vec{r})}{r^5} \vec{r} \right]$$

$\vec{p}\vec{r} = pr \cos \theta$  ( $\theta$  is angle between  $\vec{p}$  and  $\vec{r}$ ).

**induced electric dipole moment  $\vec{p}'$**  in the other, normally nonpolar molecule,

$$\vec{p}' = \alpha \vec{E}$$

where  $\alpha$  is a constant called **polarizability** of the molecule.

The energy of the induced dipole in the electrical field  $\vec{E}$  is

$$\mathcal{E} = -\vec{p}' \vec{E} = -\frac{\alpha}{(4\pi\epsilon_0)^2} (1 + \cos^2 \theta) \frac{p^2}{r^6}$$

The mutual energy of the molecules that arises from their interaction is thus negative, signifying that the force between them is attractive, and is proportional to  $r^{-6}$ .

The **force** itself is equal to  $d\mathcal{E}/dr$  and so **proportional to  $r^{-7}$** , which means that it drops rapidly with increasing separation. Doubling the distance between two molecules reduces the attractive force between them to only 0.8 % of its original value.

http:

[//chemwiki.ucdavis.edu/Physical\\_Chemistry/Physical\\_Properties\\_of\\_Matter/Atomic\\_and\\_Molecular\\_Properties/Intermolecular\\_Forces/Intermolecular\\_Forces](http://chemwiki.ucdavis.edu/Physical_Chemistry/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Intermolecular_Forces/Intermolecular_Forces)

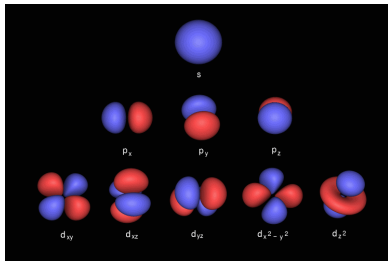


Explanation of **covalent bonds** - quantum mechanics is necessary. Two theories

- ▶ **valence bond (VB) theory** or local electron model: chemical bonds are formed by overlapping of atomic orbitals. This overlap of orbitals causes localization of the electrons in the bond region.
- ▶ **molecular orbital (MO) theory**: construction of new orbitals called molecular orbitals, electrons are redistributed throughout the molecules.

VB theory provides an excellent agreement with observed molecular geometries (bond angles and bond lengths) but physical properties cannot be explained  $\Rightarrow$  MO theory.

In discussing chemical bonds it is helpful to visualize the various atomic orbitals qualitatively resembling those of hydrogen:



Schrödinger's equation for hydrogen atom:

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r}) \quad \text{and} \quad \hat{V} = -\frac{e^2}{4\pi\epsilon_0 r}$$

Solution for  $\lim_{r \rightarrow \infty} \psi = 0$  is

$$\psi_{n,l,m}(\vec{r}) = R_{nl}(r)P_l^m(\cos\theta)e^{im\phi}$$

$$E_n = -\frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} \frac{1}{n^2}$$

$n = 1, 2, 3, \dots$

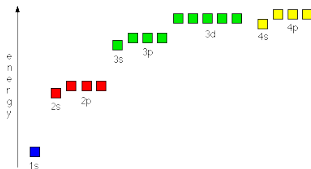
$l = 0, 1, 2, \dots, n-1$

$m = -l, \dots, 0, \dots, l$

principal quantum number

orbital quantum number

magnetic quantum number



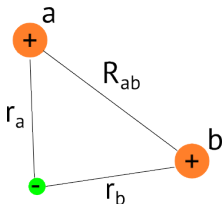
- ▶ Carbon, C -  $1s^2 2s^2 2p^2$
- ▶ Nitrogen, N -  $1s^2 2s^2 2p^3$
- ▶ Oxygen, O -  $1s^2 2s^2 2p^4$
- ▶ Fluorine, F -  $1s^2 2s^2 2p^5$
- ▶ Titanium, Ti -  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

<http://www.docbrown.info/page07/ASA?table?a.htm>

Electron Configurations in the Periodic Table

1 H 1s																	2 He 1s
3 Li 2s	4 Be 2s											5 B 2p	6 C 2p	7 N 2p	8 O 2p	9 F 2p	10 Ne 2p
11 Na 3s	12 Mg 3s											13 Al 3p	14 Si 3p	15 P 3p	16 S 3p	17 Cl 3p	18 Ar 3p
19 K 4s	20 Ca 4s	21 Sc 3d	22 Ti 3d	23 V 3d	24 Cr 3d	25 Mn 3d	26 Fe 3d	27 Co 3d	28 Ni 3d	29 Cu 3d	30 Zn 3d	31 Ga 4p	32 Ge 4p	33 As 4p	34 Se 4p	35 Br 4p	36 Kr 4p
37 Rb 5s	38 Sr 5s	39 Y 4d	40 Zr 4d	41 Nb 4d	42 Mo 4d	43 Tc 4d	44 Ru 4d	45 Rh 4d	46 Pd 4d	47 Ag 4d	48 Cd 4d	49 In 5p	50 Sn 5p	51 Sb 5p	52 Te 5p	53 I 5p	54 Xe 5p
55 Cs 6s	56 Ba 6s	57 La 5d	72 Hf 5d	73 Ta 5d	74 W 5d	75 Re 5d	76 Os 5d	77 Ir 5d	78 Pt 5d	79 Au 5d	80 Hg 5d	81 Tl 6p	82 Pb 6p	83 Bi 6p	84 Po 6p	85 At 6p	86 Rn 6p
87 Fr 7s	88 Ra 7s	89 Ac 6d	104 Rf 6d	105 Db 6d	106 Sg 6d	107 Bh 6d	108 Hs 6d	109 Mt 6d	110	111	112	113	114				
		58 Ce 4f	59 Pr 4f	60 Nd 4f	61 Pm 4f	62 Sm 4f	63 Eu 4f	64 Gd 4f	65 Tb 4f	66 Dy 4f	67 Ho 4f	68 Er 4f	69 Tm 4f	70 Yb 4f	71 Lu 4f		
		90 Th 5f	91 Pa 5f	92 U 5f	93 Np 5f	94 Pu 5f	95 Am 5f	96 Cm 5f	97 Bk 5f	98 Cf 5f	99 Es 5f	100 Fm 5f	101 Md 5f	102 No 5f	103 Lr 5f		

# H<sub>2</sub><sup>+</sup> molecule - the easiest quantum mechanical calculation



For separated cores

$$\hat{H}_a \phi_a(r_a) = \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} \right) \phi_a(r_a) = E_a^0 \phi_a(r_a)$$

and similarly for  $\phi_b$ ;  $E_a^0 = E_b^0 = E^0$ .

If the cores come closer electron from the core  $a$  will be influenced by the core  $b$ . Additionally, Coulomb repulsive force occurs (shifts energies by constant value up, i. e. omitted for now)

$$\left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi = E \psi$$

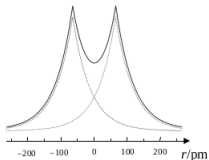
Solution by **Linear Combination of Atomic Orbitals** (LCAO)

$$\psi = c_1 \phi_a + c_2 \phi_b$$

results in equation

$$\left( E^0 - E - \frac{e^2}{4\pi\epsilon_0 r_b} \right) c_1 \phi_a + \left( E^0 - E - \frac{e^2}{4\pi\epsilon_0 r_a} \right) c_2 \phi_b = 0$$

that will be multiplied by  $\phi_a^*$  or  $\phi_b^*$  (but  $\phi_a, \phi_b$  are real - ground state of H)



Wave functions are normalized  $\int \phi_{a,b} \phi_{a,b} dV = 1$

Wave functions are not orthogonal  $\Rightarrow$  **overlap integral**

Interaction of  $e^-$  with separated cores (charge density  $-e\phi_a^2$  with core  $b$  or  $-e\phi_b^2$  with core  $a$ )

Interaction of electron exchanged density  $-e\phi_a\phi_b$  with core - **exchange integral**

$$S \equiv \int \phi_a \phi_b dV$$

$$C \equiv \int -e\phi_{a,b}^2 \frac{e^2}{4\pi\epsilon_0 r_{b,a}} dV$$

$$D \equiv \int -e\phi_a \phi_b \frac{e^2}{4\pi\epsilon_0 r_{a,b}} dV$$

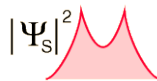
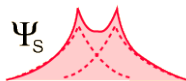
It gives algebraic set of equations

$$(\Delta E + C)c_1 + (\Delta E.S + D)c_2 = 0 \quad (\Delta E.S + D)c_1 + (\Delta E + C)c_2 = 0$$

which determinant has to be equal to zero  $\Rightarrow c \equiv c_2 = \pm c_1$  i. e.

**bonding state** (symmetric wave functions)  $\psi_S = c(\phi_a + \phi_b)$

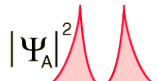
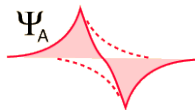
$$E_{\text{binding}} = \frac{C + D}{1 + S} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$



Bonding

**antibonding state** (antisymmetric wave function)  $\psi_A = c(\phi_a - \phi_b)$

$$E_{\text{binding}} = \frac{C - D}{1 - S} + \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$



Anti-bonding

# Valence Bond Theory

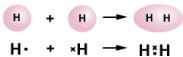
Valence bond theory concentrates on direction of bonds given by the overlap of atomic orbitals (s, p) - pairing of unpaired electrons from valence shell atomic orbitals.

In VB we name the bond according to its direction:

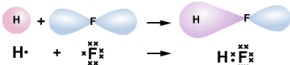
- ▶  $\sigma$  bond - cylindrical symmetry, no nodal plane on the internuclear axis.
- ▶  $\pi$  bond - a single nodal plane along the internuclear axis

**Sigma bond** head on overlap, can form between differently shaped orbitals:

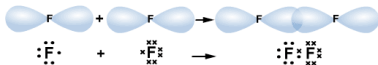
## A. s orbital + s orbital



## B. s orbital + p orbital

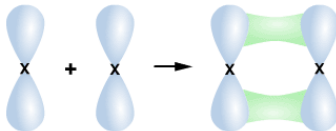


## C. p orbital + p orbital ('head-on' overlap)



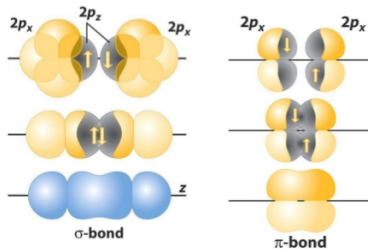
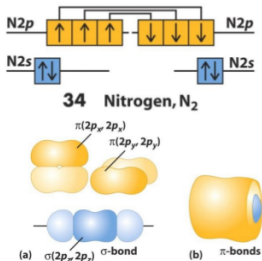
**Pi bonds** form as a side on overlap when p-orbitals are parallel  $\Rightarrow$  overlap in two places, below and above the line connecting the two atoms nuclei.

## p orbital + p orbital ('side-on' overlap)



**Pi bond** only occurs in molecules with **double or triple bonds**:

- ▶ the first bond is always a sigma bond
- ▶ the second and the third bond are pi bonds.

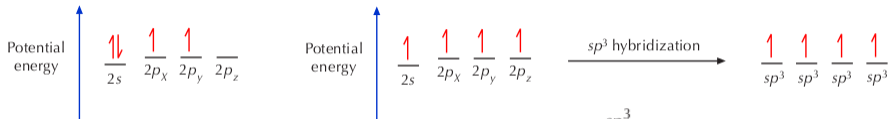


However, this is oversimplified sketch because so called **hybridization of orbitals** takes place.

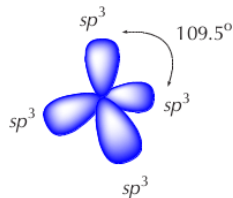
**Hybrid orbitals** - mixtures of atomic (s, p, d) orbitals. Hybrid orbitals do not exist in an isolated atom, even when it is in excited state but arise while the atom is interacting with others to form molecule.

## Theory of hybridization is necessary to explain bonding in CH<sub>4</sub>

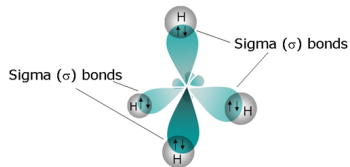
- ▶ One 2s electron of carbon atom is **promoted** to higher state, i. e. 2p and
- ▶ 4 equivalent **sp<sup>3</sup> hybrid orbitals** are formed:



Four sp<sup>3</sup> hybrid orbitals may be considered as combination of 1/4s and 3/4p - tetrahedral bonding directions



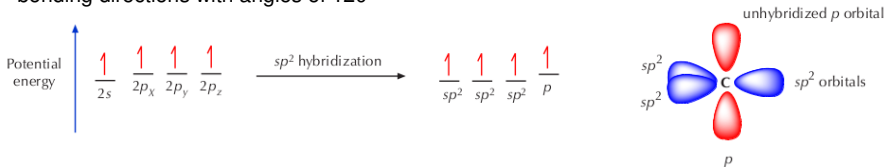
In CH<sub>4</sub>, 4 sp<sup>3</sup> hybrid orbitals create 4 σ bonds in combination with 4 hydrogen atoms (1s orbitals)



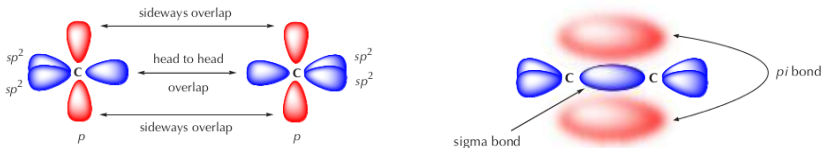
Two other types of hybrid orbital can occur in C atoms:

- ▶ in **sp<sup>2</sup> hybridization**, one valence electron is in pure p state and the other three are in hybrid orbitals
- ▶ in **sp hybridization**, two valence electrons are in pure p state and the other two are in hybrid orbitals

**Formation of 3 sp<sup>2</sup> hybrid orbitals:** combination of 1/3s and 2/3p - trigonal planar bonding directions with angles of 120°

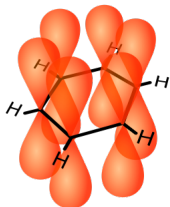
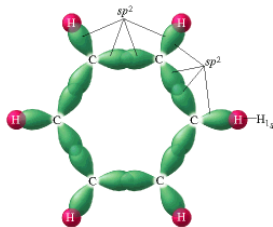


In ethylene, C<sub>2</sub>H<sub>4</sub>, two C atoms are joined by two bonds, 1 σ bond formed by sp<sup>2</sup> hybrid orbitals and 1 π bond created by p orbitals. Four H atoms create σ bonds with sp<sup>2</sup> hybrid orbitals of C atoms:

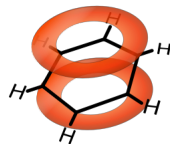




In benzene,  $C_6H_6$ , the six C atoms are arranged in a flat hexagonal ring, bond angle  $120^\circ$   
 $\Rightarrow sp^2$  hybrid orbitals forming the  $\sigma$  bonds between C atoms and hydrogen.

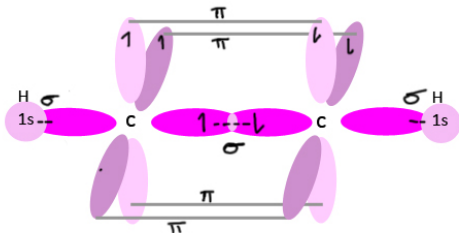


6 p-orbitals



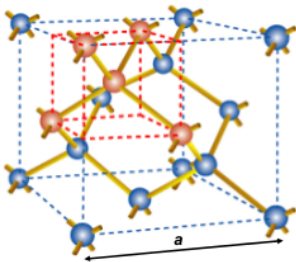
delocalized

In acetylene,  $C_2H_2$ , two C atoms are joint by three bonds, 1  $\sigma$  bond formed by  $sp$  hybrid orbitals and 2  $\pi$  bond created by p orbitals. Two H atoms create  $\sigma$  bonds with  $sp$  hybrid orbitals of C atoms:

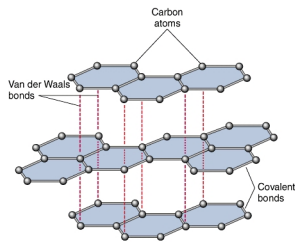


Natural solid carbon materials:

► **diamond**,  $sp^3$  bonded C



► **graphite**,  $sp^2$  bonded C



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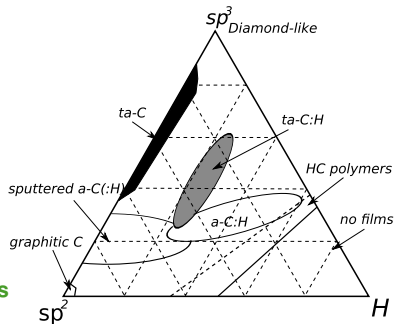
# Classification of Carbon Films

Carbon thin films can be

- ▶ crystalline or amorphous
- ▶ pure, hydrogenated or modified with other elements
- ▶ part of (nano)composite structure

Necessity of carbon film classification:

- ▶ ternary phase diagram ( $sp^3C$ ,  $sp^2C$  and H) for amorphous films (Jacob and Moller 1993, Robertson 2002)
- ▶ classification of a-C:H films into **four categories** by Cambridge University group (2005):



- ▶ **polymer-like a-C:H (PLCH)**: high H content (40–60 at. %); up to 70 %  $sp^3$  but most  $sp^3C$  are H terminated  $\Rightarrow$  soft, low density, optical band gap 2–4 eV
- ▶ **diamond-like a-C:H (DLCH)**: intermediate H content (20–40 at. %); lower overall  $sp^3$  content but more C-C  $sp^3$  bonds than PLCH  $\Rightarrow$  better mechanical properties, optical gap 1–2 eV.
- ▶ **hydrogenated tetrahedral amorphous carbon films (ta-C:H)**: increased C-C  $sp^3$  content whilst keeping a H content low (25–30 at. %)  $\Rightarrow$  higher density (up to 2.4 g/cm<sup>3</sup>) and Young's modulus (up to 300 GPa)
- ▶ **graphite-like a-C:H (GLCH)**: low H content (< 20 at. %); high  $sp^2$  content and  $sp^2$  clustering  $\Rightarrow$  gap under 1 eV

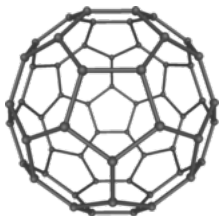
- ▶ classification of carbon films by Fraunhofer Institute for Surface Engineering and Thin Films (IST) 2009
- ▶ activities on international standardization, e.g. workshop at 12th International Conference on Plasma Surface Engineering (PSE) in 2010

		Carbon films													
Designation	1 Plasma-polymer films	2 Amorphous carbon films (diamond-like-carbon films / DLC)								3 Crystalline carbon films					
										Diamond films				Graphite films	
Thin film / thick film	Thin film	Thin film								Thin film			Thick film (free standing)		Thin film
		hydrogen-free				hydrogenated				undoped	doped	undoped	doped	undoped	
Doping, additional elements				modified				modified							
				with metal				with metal		with non-metal					
Crystal size on the growth side	/.	(amorphous)								1 to 500 nm, nano-crystalline	0.5 to 10 µm, micro-crystalline	0.1 to 5 µm	(5 µm to) 80 to 500 µm	80 to 500 µm	
		sp <sup>2</sup> or sp <sup>3</sup> , linear bond	sp <sup>2</sup>	sp <sup>3</sup>	sp <sup>2</sup>	sp <sup>2</sup> or sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>2</sup>	sp <sup>2</sup>	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>3</sup>	sp <sup>2</sup>
Film No.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6	
Designation	Plasma-polymer film	Hydrogen-free amorphous carbon film	Tetrahedral hydrogen-free amorphous carbon film	Metal-containing hydrogen-free amorphous carbon film	Hydrogenated amorphous carbon film	Tetrahedral hydrogenated amorphous carbon film	Metal-containing hydrogenated amorphous carbon film	Modified hydrogenated amorphous carbon film	nano-crystalline CVD diamond film	micro-crystalline CVD diamond film	doped CVD diamond film	CVD diamond	doped CVD diamond	graphite film	
Recommended abbreviation	/.	a-C	ta-C	a-C:Me	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti, ...)	a-C:H:X (X = Si, O, N, F, B, ...)	/.	/.	/.	/.	/.	/.	

<http://www.ist.fraunhofer.de/english/c-products/tab/complete.html>

# Carbon nanostructured materials - formed by $sp^2C$

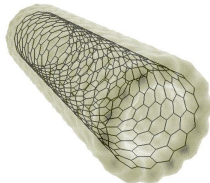
**Fullerene** - hollow sphere, ellipsoid *etc.*  
**Buckyballs** - spherical fullerenes.



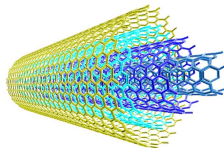
C60 -  
Buckminsterfulleren

prepared in 1985 at  
Rice University

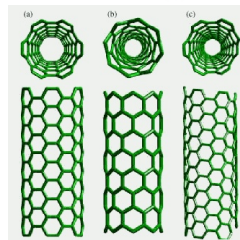
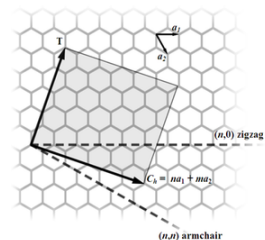
**Single-walled carbon nanotube (SWCNT)**



**Multi-walled carbon nanotube (MWCNT)**



- prepared 1991 by Iijima



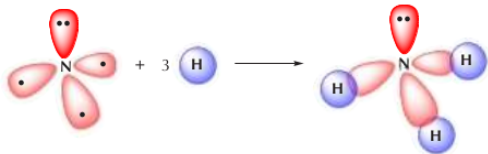
Different chirality of SWCNT:

- (a) armchair
- (b) zigzag
- (c) chiral (n,m)

## Hybridization in nitrogen

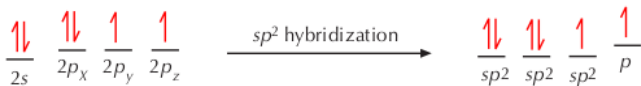


Nitrogen: 5 valence electrons

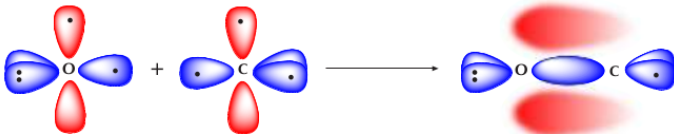


3-D representation of the ammonia molecule

## Hybridization in oxygen



Oxygen: 6 valence electrons

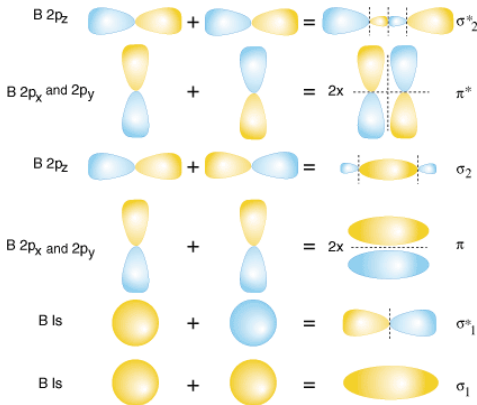


# Molecular orbital theory

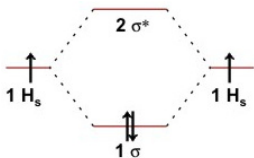
In **molecular orbital theory**, bonding atoms produce entirely new orbitals. Theory predicts energies of bonding and anti-bonding states and shape of orbitals. It depends on

1. energies of orbitals interacting
2. shape/symmetry of orbitals interacting

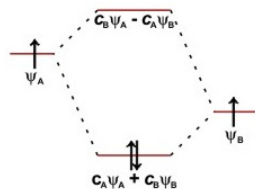
formation of **bonding** and **anti-bonding** molecular orbitals



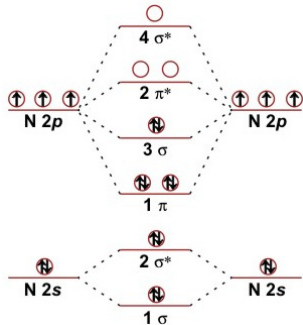
H<sub>2</sub> molecule  
(homonuclear)



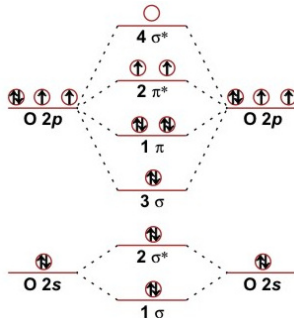
heteronuclear  
molecule



Li<sub>2</sub> to N<sub>2</sub> molecules

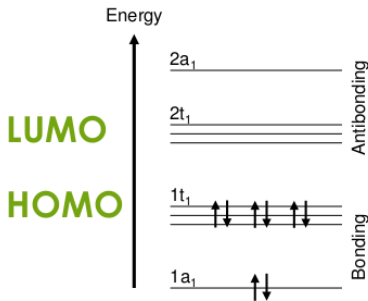


O<sub>2</sub> and F<sub>2</sub>





Molecules with more atoms, e. g.  $\text{CH}_4$



- ▶ **Highest Occupied Molecular Orbital (HOMO):**  
The highest-energy molecular orbital in the energy ground state of a molecule occupied by at least one electron.
- ▶ **Lowest Unoccupied Molecular Orbital (LUMO):**  
The lowest-energy molecular orbital that is unoccupied in the ground state.

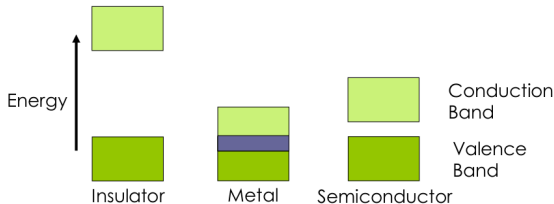
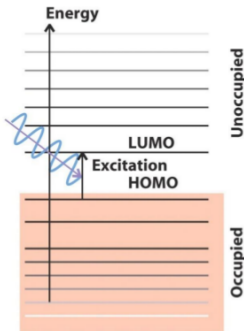
$H_2$  molecule - two 1s electrons with opposite spins (maximum electrons in K shell)

⇒ **saturated covalent bonds**

$Li_2$  (6 unfilled 2p states with energy similar to 2s):  $Li + Li_2 \rightarrow Li_3$  (without violating exclusion principle - all valence electrons remain in L shells)

⇒ **unsaturated covalent bonds**

- ▶ Li forms bcc crystals (8 nearest neighbors, i. e. each bond = 1/4 of electron instead 2 for covalent bond) - electrons participating in unsaturated bonds are **not localized**.
- ▶ Cloud of **free electrons** - atoms “lose” outermost, s or p, electrons while the positively charged ions are left over. In transition metals (partially filled d-shells under the outermost shell) further electrons may participate in metallic bonding.



# Electrons in metals

Quantum mechanically solved by the **one electron approximation** (precise only if electrons do not interact) and

- ▶ **approximation of free electrons** - can correctly explain many properties of metals, such as specific heat, thermal conductivity, electrical conductance.
- ▶ **approximation of weakly bound electrons** - explain other important phenomena such as the difference between metals, insulators and metalloid, the relationship between conductivity and valence electrons in the metal

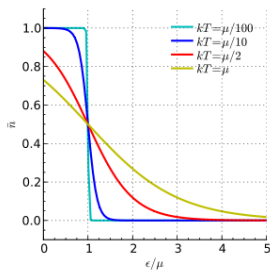
System of electrons - **ideal gas of fermions** (max 1 particle in a given state).

distribution function  $n(\epsilon)$

$$n(\epsilon)d\epsilon = f_{\text{FD}} g(\epsilon)d\epsilon$$

Fermi-Dirac distribution function  $f_{\text{FD}}$   
(for  $T = 0$  step-wise Heavyside function)

$$f_{\text{FD}} = \frac{1}{\exp\left(\frac{\epsilon - \mu}{kT}\right) + 1}$$



electrochemical  
potential

$$\mu(T)$$

Fermi energy

$$\epsilon_{\text{F}} = \mu(T = 0)$$

energy distribution  
of states  $g(\epsilon)$

$$g(\epsilon)d\epsilon = \frac{4\pi L^3}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

## Electrons in metals (contin.)

electrochemical potential is given by the normalization condition ( $N$  electrons)

$$N = \int_0^{\infty} f_{\text{FD}} g(\epsilon) d\epsilon$$

For highly degenerated gas (low  $T$ ) its temperature dependence can be approximated as

$$\mu = \epsilon_{\text{F}} \left( 1 - \frac{\pi^2}{12} \left( \frac{kT}{\epsilon_{\text{F}}} \right)^2 \dots \right),$$

The solution for Schrödinger equation in electric field for periodic ionic crystals shows the existence of a separate area of the energy bands - forbidden band (**band gap**).

The position of **Fermi level (electrochemical potential)** with respect to band gap is important for behaviour of materials.

Property	Ionic	Covalent	Metallic	Van der Waals
	Non-directional; Structures of high coordination	Direcional; Structures of low coordination and low density	Non-directional; Structures of high coordination and high density	Analogous to metallic bonds
Mechanical	Strong, hard crystals	Strong, hard crystals	Variable crystals	Weak, soft crystals
Thermal	High melting point, low expansion coefficient	High melting point, low expansion coefficient	Range of melting points extended liquidus range	Low melting point large expansion coefficient
Electrical	Weak insulator, conduction by ion transport when liquid	Insulator in solid and liquid state	Conduction by electron transport	Insulator
Optical	Absorption and other properties mainly of the individual ions	High refractive index, absorption different in solid and gas	Opaque, with similar properties in liquid state	Properties of individual molecules

Classification of materials based on **nature** and **applications** by Bever (1986):

- ▶ by nature: ceramics, glasses, metals and alloys, other inorganic materials, polymers, elastomers, fibres, composite materials, wood, paper and paperboard, other biological materials
- ▶ by application: electrical materials, electronic materials, superconductors, magnetic materials, materials for nuclear applications, materials for other energetic applications, optical materials, biomaterials, building materials, materials for textile and packaging industry (*modified*)

*M. B. Bever (ed.): Encyclopedia of Materials, Science and Engineering, 1986, sv. 1 ed. R. W. Cahn (Oxford: Pergamon)*

other references - **material science conferences**

- ▶ Spring and Fall Meetings of Material Research Society (MRS) in U.S.
- ▶ Spring and Fall Meeting of European Material Research Society (EMRS)
- ▶ TechCon of Society of Vacuum Coaters (SVC)

# Ceramic Materials

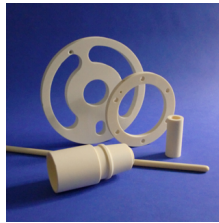
- ▶ A combination of **one or more metals** with a **non-metallic element** (usually oxygen but others include nitrogen, carbon . . .).
- ▶ May be crystalline or partially crystalline.
- ▶ The atoms are linked by ionic/covalent bonds - ionic bond character occurs especially for oxygen that effectively borrows two electrons from the neighbouring metal atoms

## Types of ceramics

- ▶ traditional ceramic materials: natural stone, clay minerals such as kaolinite
- ▶ modern ceramic materials, classified as advanced ceramics: aluminium oxide (alumina), silicon carbide, tungsten carbide, . . .



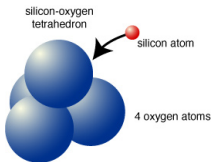
Ceramic  $\text{Si}_3\text{N}_4$  bearing parts



Fine ceramic components from alumina

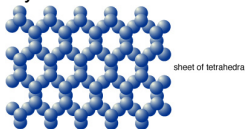
# Ceramic Materials (contin.)

Physical and mechanical properties are controlled by the crystal structure and chemical composition. It can be demonstrated for  $\text{SiO}_2$

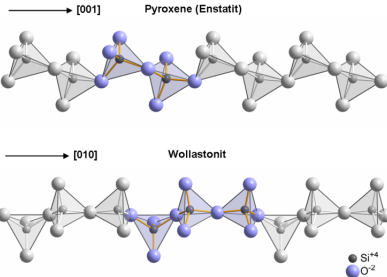
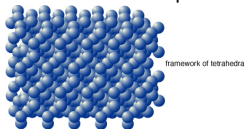


fibrous asbestos

layered minerals as mica



3D structure of quartz





## Ceramic Materials (contin.)

### Ceramic materials

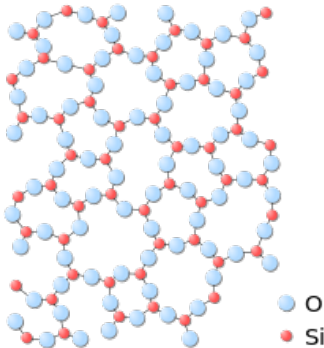
- ▶ are brittle, hard, strong in compression, weak in shearing and tension.
- ▶ withstand, in many cases, erosion that occurs in an acidic or basic environment.
- ▶ withstand very high temperatures such as temperatures that range from 1000 °C to 1600 °C, exceptions include inorganic materials that do not have oxygen such as silicon carbide.

**Crystal lattice imperfections** (vacancies, dislocations) and **microstructural defects** (inclusions, pores, voids and distribution of irregular size grain) influence the properties

- ▶ mechanical failure occurs from pre-existing flaws - high mechanical stresses which exceed the local tensile strength effect crack propagation from flaws followed by rupture
- ▶ defect is weak point for electrical load and aggressive environment

# Glasses

- ▶ Class of materials that does not crystallise when cooled from the molten state, no long range periodicity
- ▶ The major constituents of glasses are in two separated regions of the periodic table
  - ▶ Group VI (O, Si, Se and Te) plus some neighbouring elements (B) and
  - ▶ Groups I and II that are used primarily as fluxes. The addition of fluxing atoms such as sodium reduces the number of bond cross links.



The structure of soda-lime-silica float glass



# Metals and Alloys

Properties of metal and alloys are a consequence of the metallic bonds. They

- ▶ have good mechanical strength, high thermal and electrical conductivity,
- ▶ are opaque, lustrous and relatively heavy,
- ▶ are easily fabricated and shaped.

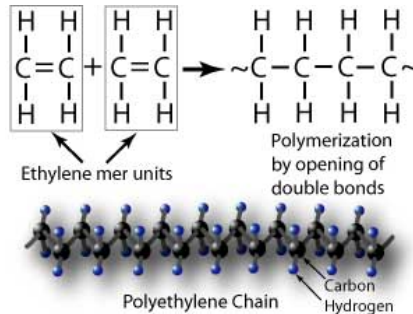
In general, they form one of the face centred cubic (fcc), body centred cubic (bcc) or hexagonal close packed (hcp) structures.

Changes in the strength of metallic bond cause differences in optical, electrical, thermal and mechanical properties.

The overall mechanical properties of metals and alloys are controlled by the crystal lattice defects, such as dislocations and vacancies. Mechanical and chemical properties can be modified by the addition of alloying elements in varying proportion.

# Polymers

Polymers are by definition materials composed of long-chain molecules, typically 10 to 20 nm, that have been developed as a consequence of the linking of many smaller molecules, monomers.

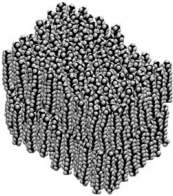


The combination of tensile strength and flexibility make these materials attractive.



⇒ polymer cross-linking

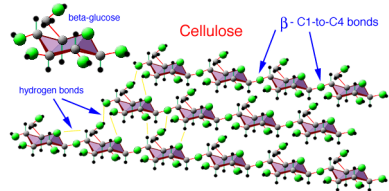
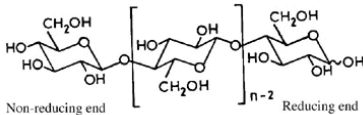
## Polymers (contin.)



If the molecular chains are packed side by side, the molecules form an array with a **crystalline structure**.

Natural polymers have complex microstructure comprising a mixture of crystalline and amorphous material.

The interatomic bonds between molecular chains are the weak van der Waals forces, but in the crystalline structures, the chains are closer  $\Rightarrow$  more rigid material.



To develop stronger, more rigid, polymers:

1. production of a crystalline structure (polyethylene, nylon),
2. formation of a strong covalent bond between the molecular chains by cross linking (vulcanising raw rubber by heating with the controlled addition of sulphur atoms).

# Composites

A composite material

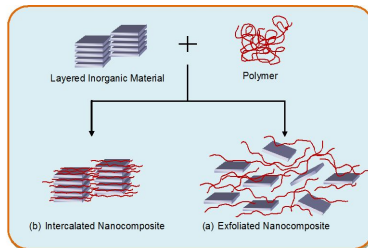
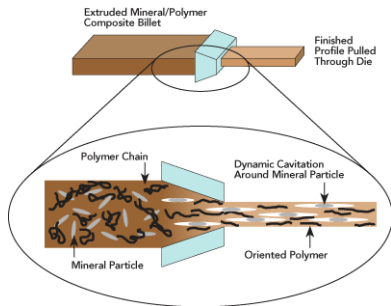
- ▶ was originally considered to be a combination of two materials
- ▶ now it is regarded as any combination of various materials or their polymorphs.

Composites have particular physical, mechanical and other properties that are not found in their constituents:

- ▶ natural composites: wood - cellulose fibres provide tensile strength and flexibility and lignin provides the matrix for binding and adds the property of stiffness; bone - strong, but soft, protein collagen and the hard, brittle mineral apatite,
- ▶ synthetic composites: combining individual properties such as strong fibres of a material (for example carbon) in a soft matrix (such as an epoxy resin).

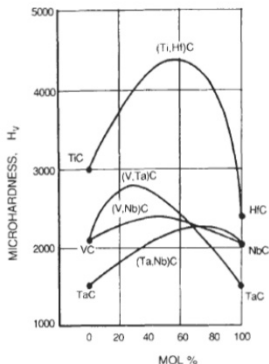
The concept of composite materials has led to the design and manufacture of a new range of structural materials that are generally lighter, stiffer and stronger than anything previously manufactured.

# Composites (contin.)



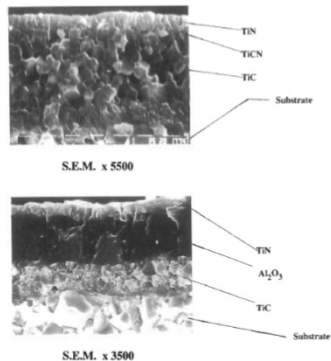
## Composites (contin.)

Alloys can have properties superior to each component



**Figure 12-5.** Microhardness of mixed carbides due to solid solution and precipitation hardening (From Ref. 3).

Multilayer structures can combine properties of different compounds



**Figure 12-6.** SEM images of CVD multilayer coatings for cutting tool inserts. (a) Carbide substrate/TiC/TiCN/TiN (5500 ×). (b) Carbide substrate-TiC-Al<sub>2</sub>O<sub>3</sub>-TiN (3500 ×). (Courtesy of S. Wertheimer, ISCAR Ltd.)

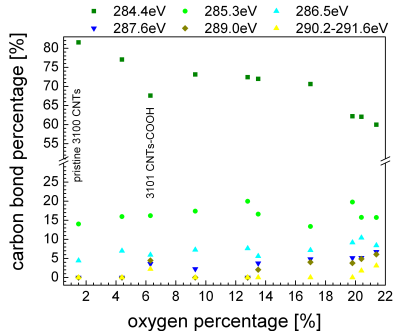
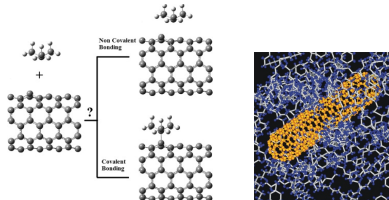
M. Ohring, The Materials Science of Thin Films



## Composites (contin.)

**Question of properties of filling material,**  
example of polymer filled with CNTs -  
necessity of CNTs functionalization:

- ▶ improves CNTs dispersion in matrix  
⇒ shorter preparation time, better uniformity
- ▶ strengthens fiber-matrix interface  
⇒ high composite stiffness and strength together with high toughness (thanks to nanotubes flexibility)



Changes of carbon bonding (by XPS) after plasma funct. in low pressure RF discharges

⇒ **significantly improved hardness and elastic modulus of polyurethane/CNTs composites** for optimum plasma conditions (Ar/H<sub>2</sub>O, O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub>O)