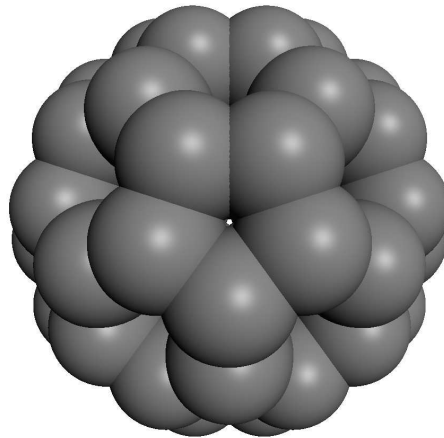


MATTER, MATERIALS, CRYSTAL STRUCTURE AND BONDING

Chris J. Pickard



WHY SHOULD A THEORIST CARE?

Where the atoms are determines what they do

Where the atoms can be determines what *we* can do

OVERVIEW OF STRUCTURE AND BONDING

Atoms and Elements

Non-crystalline materials

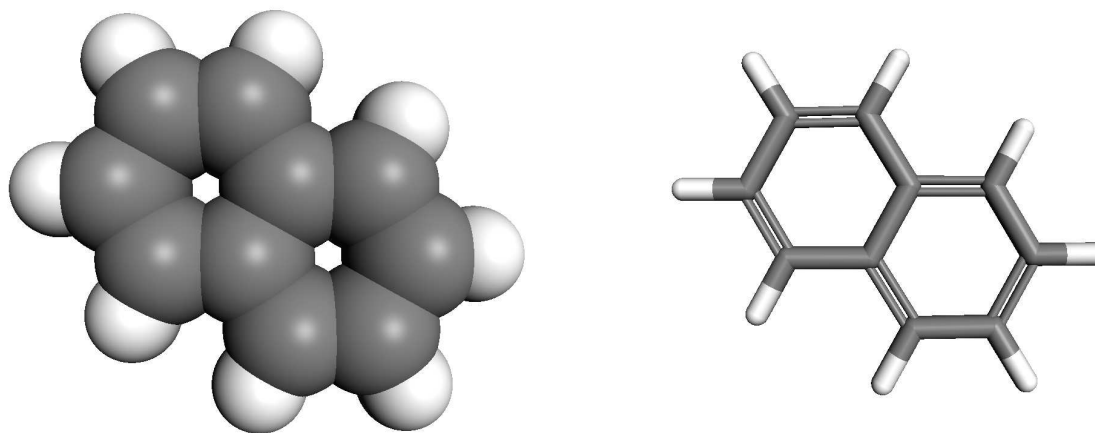
Crystalline materials

Bonding and cohesion

ATOMS AND ELEMENTS

1																	18
1 H 1.0079	2																2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71 *	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 #	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)				
* Lanthanide series			57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
# Actinide series			89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

MOLECULES

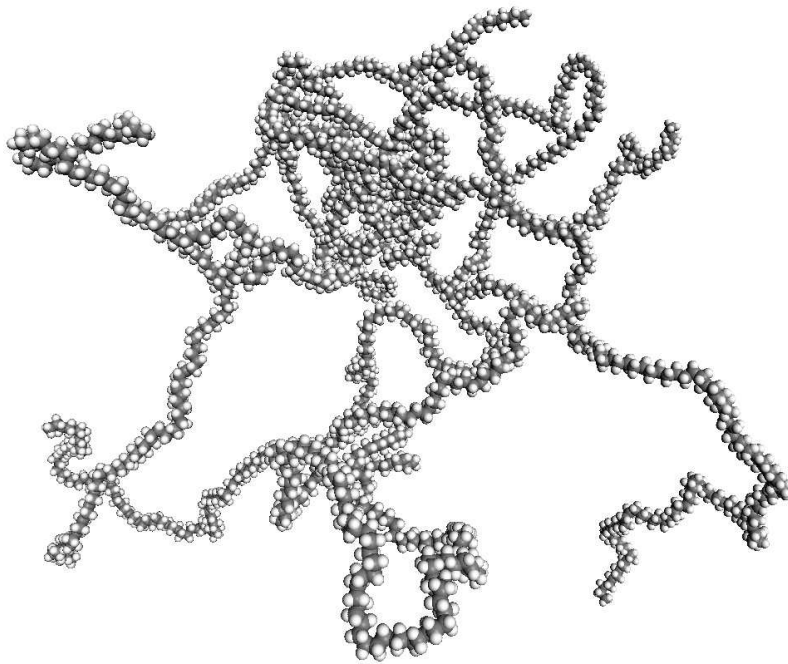


Naphalene

Molecules are finite collections of covalently bonded atoms

They vary from diatomic molecules, to massive proteins

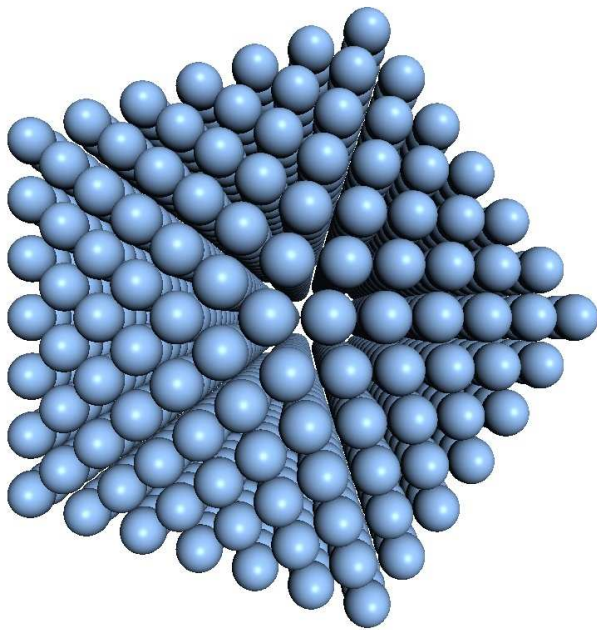
POLYMERS



Polyethylene (or polythene)

- Polymers are long chain molecules, often with a carbon backbone (sometimes silicon)
- The repeat unit, or monomer, is repeated and joined together many times
- The chemical formula for polyethylene is $(\text{CH}_2)_N$
- Many properties depend simply on N

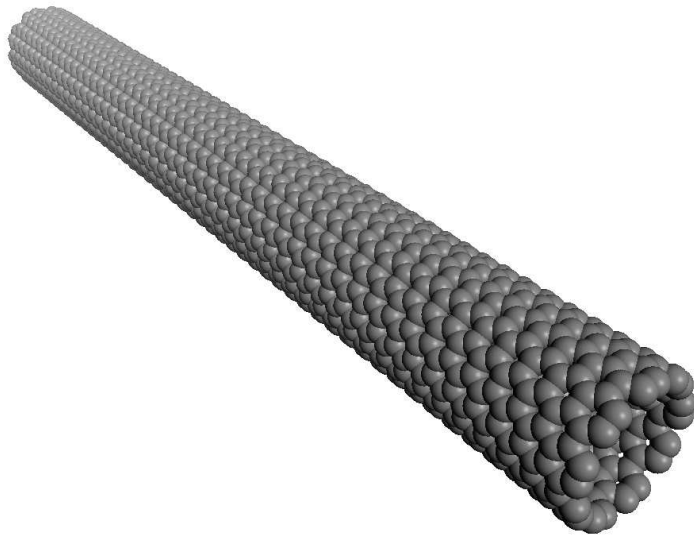
NANOPARTICLES



Silver Nanoparticle

- Nanoparticles range in size from 1 – 100 nm and can contain from 10 to 100,000 atoms
- Their properties are not necessarily the same as the bulk material
- The physical, mechanical, electronic, magnetic, optical and chemical properties can all differ

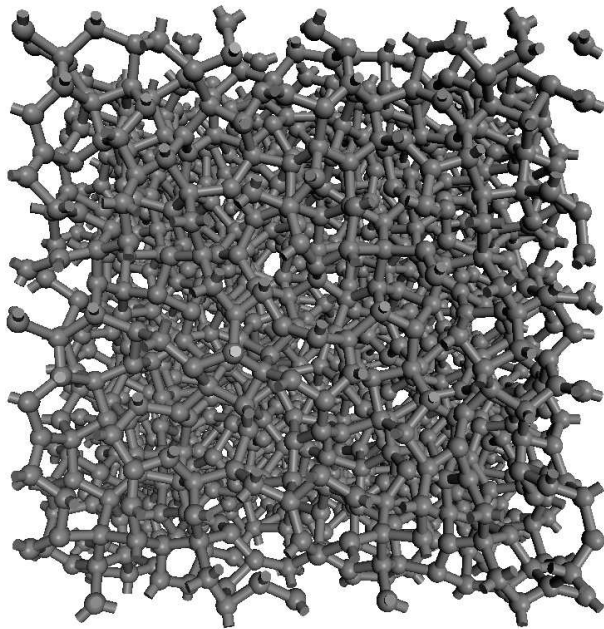
NANOSTRUCTURES



(9,9) armchair nanotube

- More complex structure than nanoparticles
- Might be designed, and often self assembled
- Nanotechnology is a very hot topic, with strong technological promises for nanoelectronics etc.

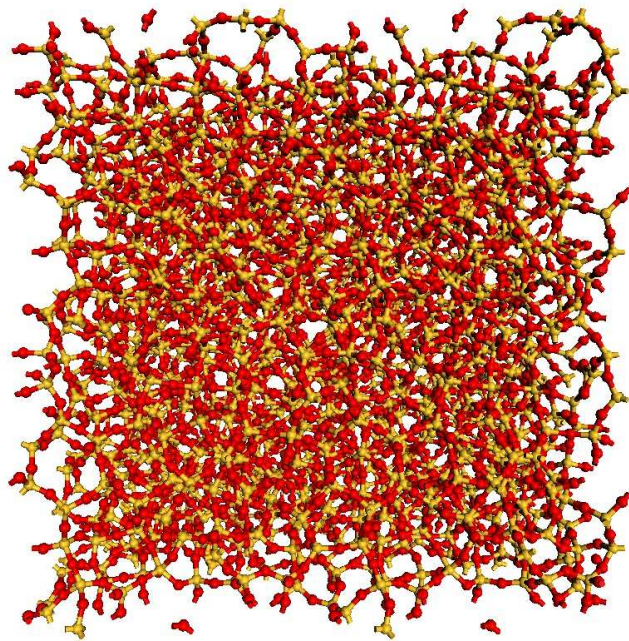
AMORPHOUS SOLIDS



Amorphous Carbon

- Amorphous solids have no *long range* order
- They are disordered, and the kind of disorder is *structural* as opposed to *compositional*
- In this example both sp^3 and sp^2 bonding is found
- Can have a variety of electronic and mechanical properties

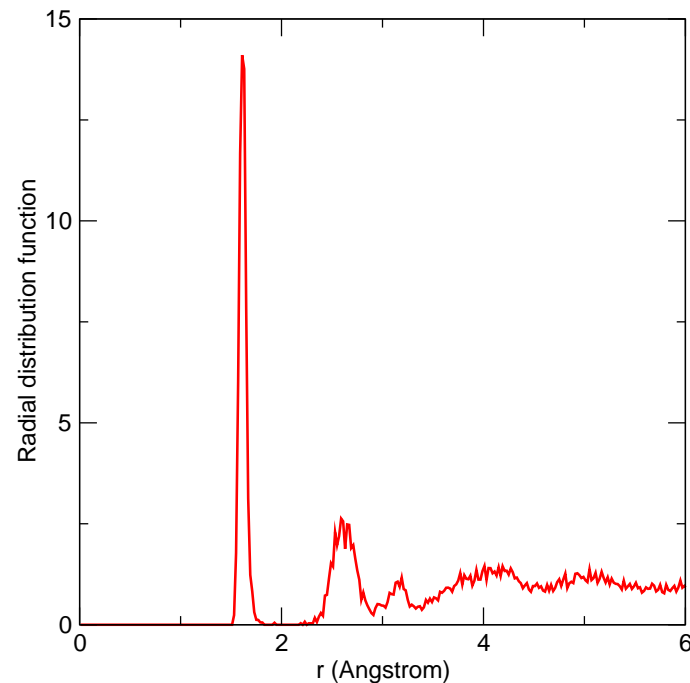
ORDER IN RANDOMNESS



A silica glass

- The atomic positions are rarely entirely random
- The structural constraints impose some order on the randomness
- The result is *short range* order, without long range order
- This order can be probed experimentally

THE RADIAL DISTRIBUTION FUNCTION



- The RDF is the probability density of finding particle i at a given distance from particle j :

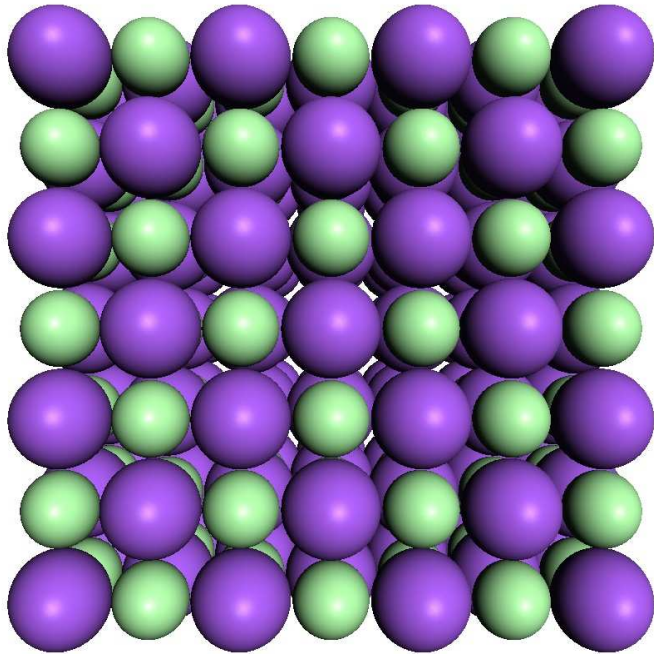
$$G_{i,j} = \sum_{i \neq j}^N \delta(r - |\mathbf{r}_i - \mathbf{r}_j|)$$

- Can be measured in scattering experiments (X-ray, neutron)
- For a crystalline solid this would just be a set of delta spikes . . .

CRYSTALLINE SOLIDS

- A crystal is a homogeneous solid with a regularly repeating atomic arrangement
- The majority of the solid state physicists theoretical tools have been developed for dealing with crystals
- Most current scientific questions concern non ideal crystals (or structures that are simply not crystalline)
- Our tools are still useful . . .

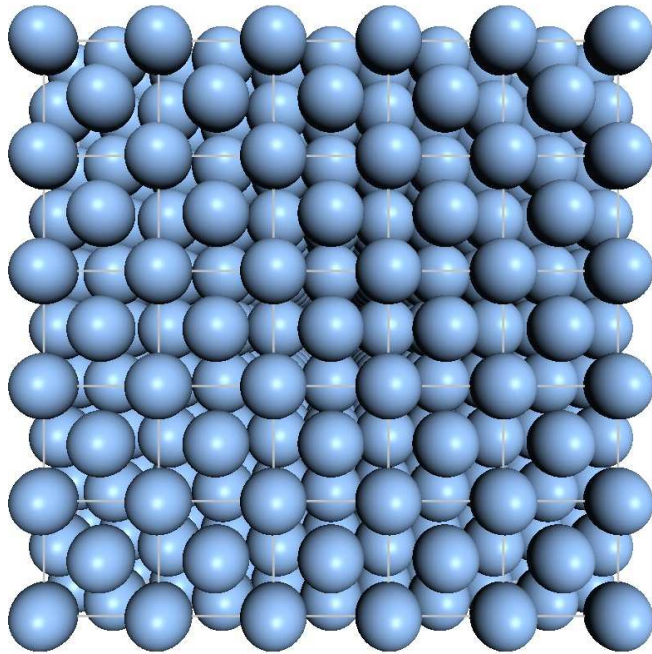
IONIC CRYSTALS



Halite (NaCl)

- The Alkali Halides are typical ionic crystals
- Can only exist for compounds (different elements)
- Are electronic wide band gap insulators
- Are of technological importance for their optical properties

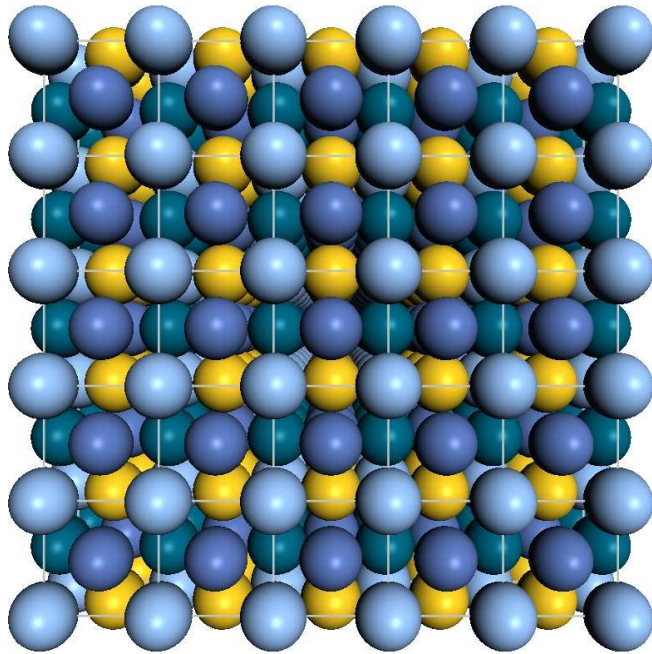
PURE METAL



Aluminium

- The pure form of the majority of the elements in the periodic table are metallic
- Metals conduct electricity freely, and reflect light
- Many pure metals are soft, but transition metals are harder

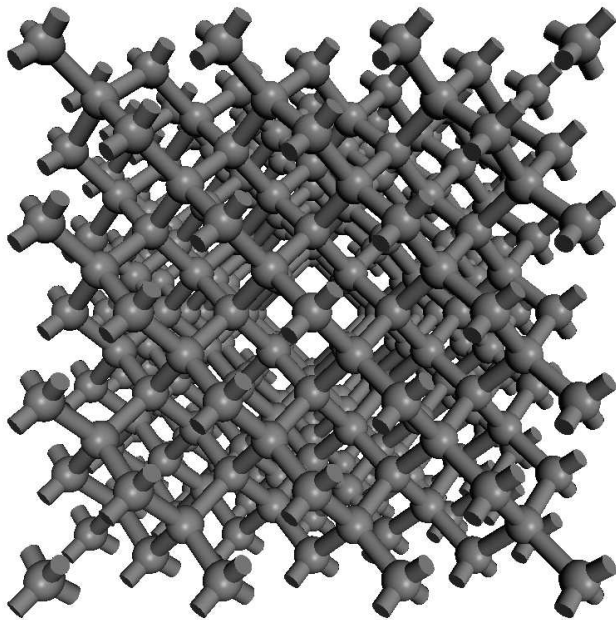
ALLOYS



Ordered metallic alloy

- Alloys are mixtures of elements, not exclusively metallic and can be either ordered or disordered
- The properties depend dramatically on the composition, and history of the alloy
- Understanding alloying is of immense economic and technological importance

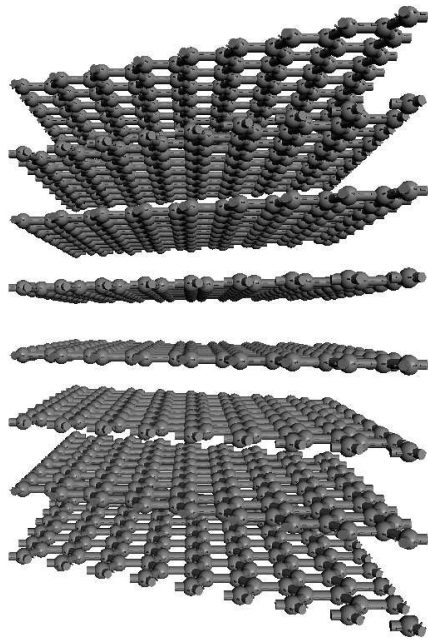
COVALENT CRYSTALS



Diamond

- The strong directional covalent bonds lead to mechanically strong crystals
- Covalent crystals are less well insulating than ionic crystal
- Carbon can form a range of different covalent bonds, in this case sp^3

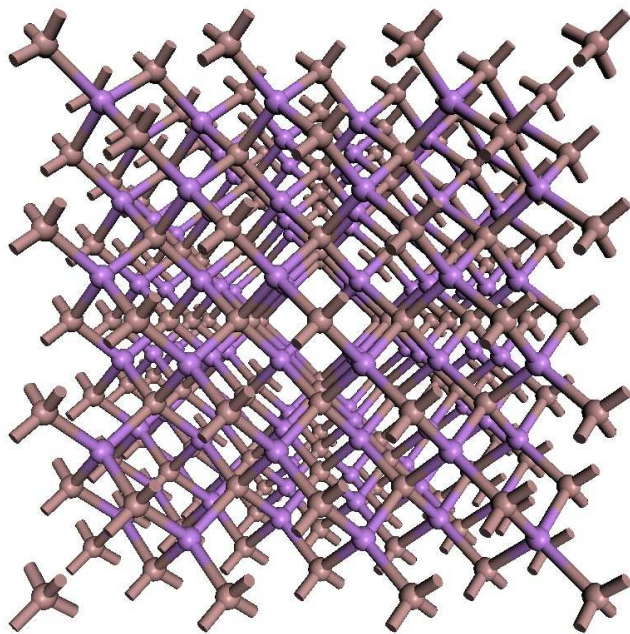
GRAPHITE



Bernal Graphite

- The graphene sheets are purely sp^2 covalently bonded
- Graphite can exist in different phases, according to the stacking
- Bernal graphite (structure found by J. D. Bernal in 1924) has an . . . ABABABA . . . stacking
- Graphite is a semi-metal (a non-zero DOS at the Fermi level)

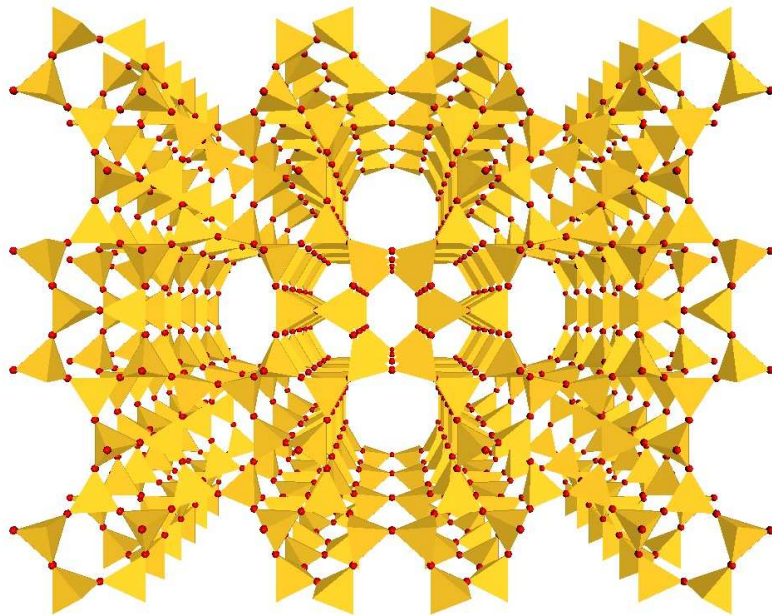
SEMICONDUCTORS



Gallium Arsenide (GaAs)

- Semiconductors are still less insulating than ionic crystals
- Band-gaps range from a fraction of an electron volt, to several
- They can be doped to control the electronic properties
- They are the basis of the “semiconductor” industry

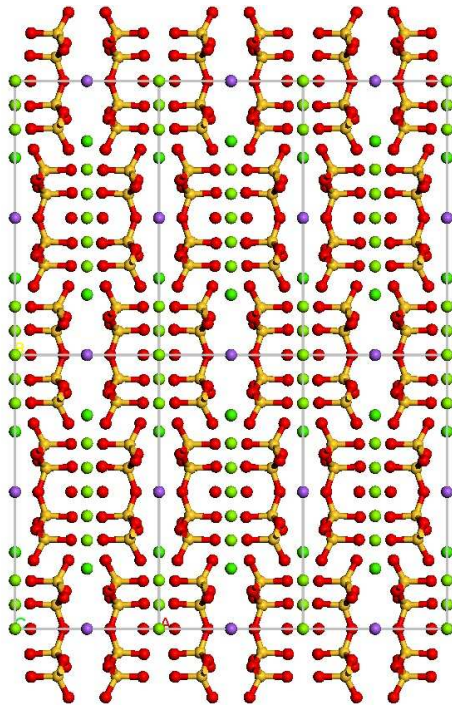
ZEOLITES



Ferrierite

- Built up from SiO_4 tetrahedral units
- Like the flexible hybridisation of carbon, these units allow many structural possibilities
- Zeolites are open silicates
- They are industrially important as catalysts

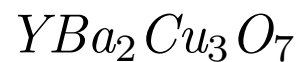
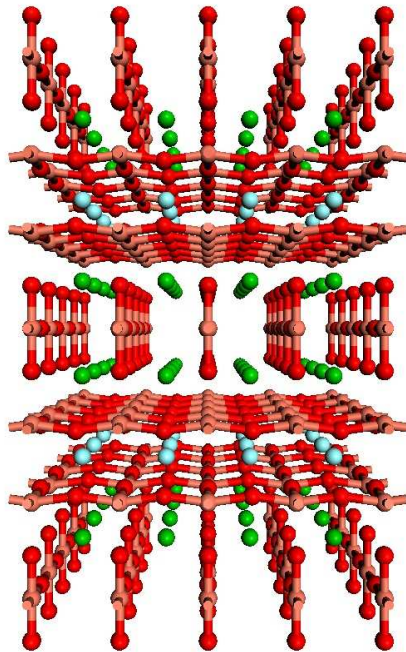
MINERALS



Amphibole

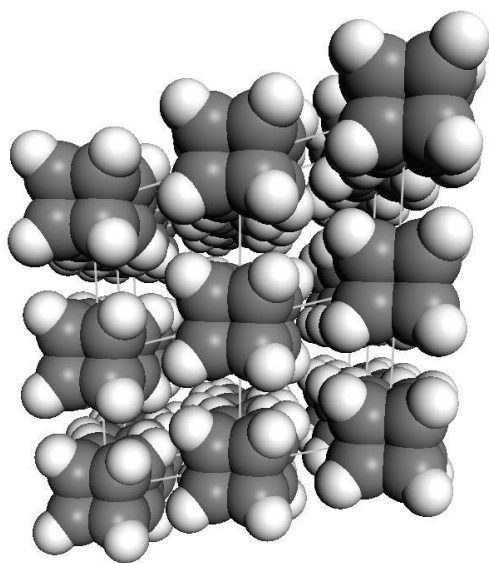
- Minerals are materials found naturally in the earth
- Many are silicate based (again, on the SiO_4 tetrahedra)
- The structures can be very complex, contain many atomic species, and depend on the geological history of the sample
- A wide range of properties

HIGH TEMPERATURE SUPERCONDUCTORS



- YBCO is a complex layered metal oxide
- It is in the Perovskite structure
- YBCO superconducts at 92K
- Oxidation state of CuO planes and chains control superconducting properties

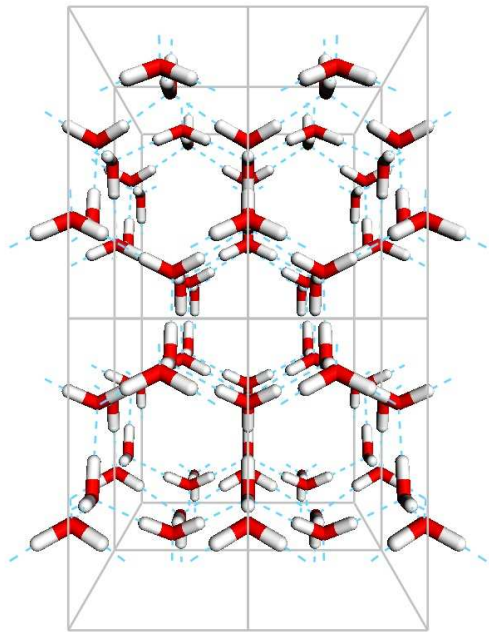
MOLECULAR CRYSTALS



Solid cubane

- Molecules play the role of atoms to form molecular crystals
- At non-zero temperature, the molecules will be in often complex motion
- Molecular crystals can be organic non-linear optical materials, and other electronic properties are of technological interest

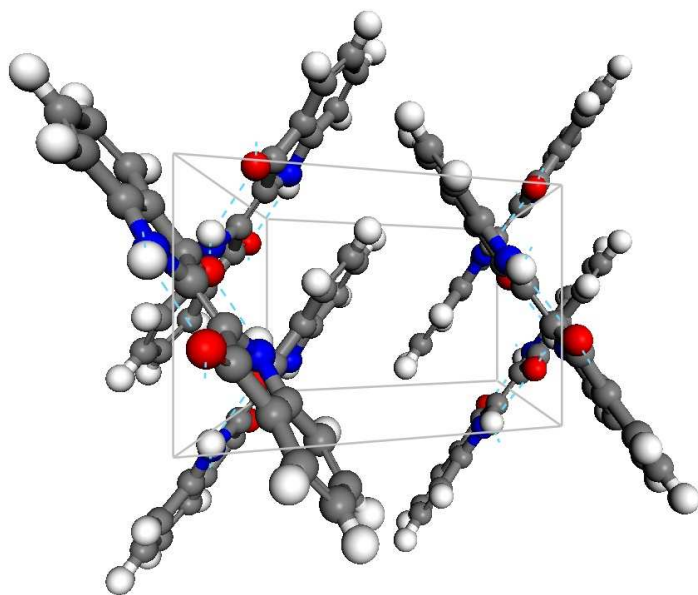
CUBIC ICE



Cubic water ice (H_2O)

- Water ice is another form of molecular crystal
- Held together by directional, but weak, hydrogen bonds
- The H_2O molecule can vibrate, but have less freedom to rotate

MOLECULAR CRYSTAL WITH HYDROGEN BONDS



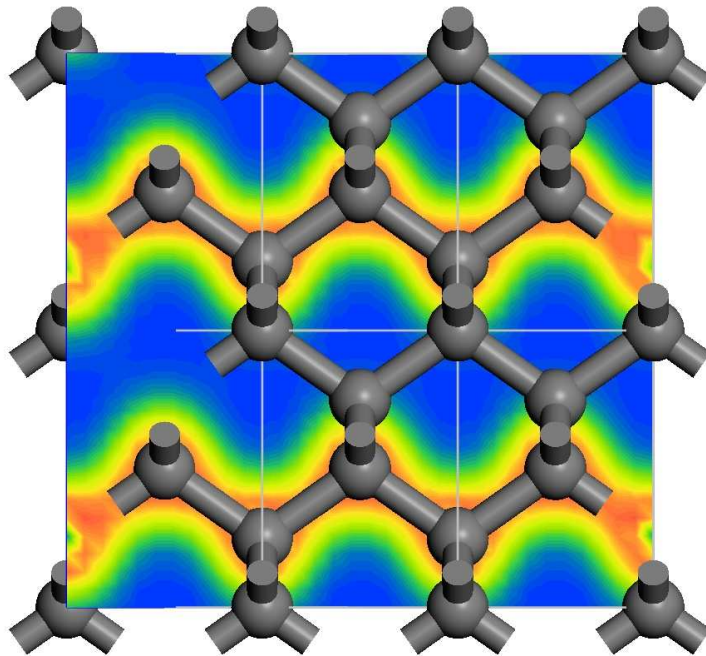
Indigo

- Many organic molecules (pigments like Indigo, or drug molecules) are held together by both hydrogen bonds, and even weaker van der Waals bonds
- There can be very many possible polymorphs
- The physical properties of the crystal will depend on the exact polymorph present

BONDING

- The energy of a collection of atoms is often lower if they are close
- The atoms stick together
- In specific ways, depending on the nature of the atoms and their neighbours
- This bonding can be classified as Covalent, Ionic, Mixed, Metallic, Molecular and Hydrogen Bonding
- Of course, in reality there is a continuum

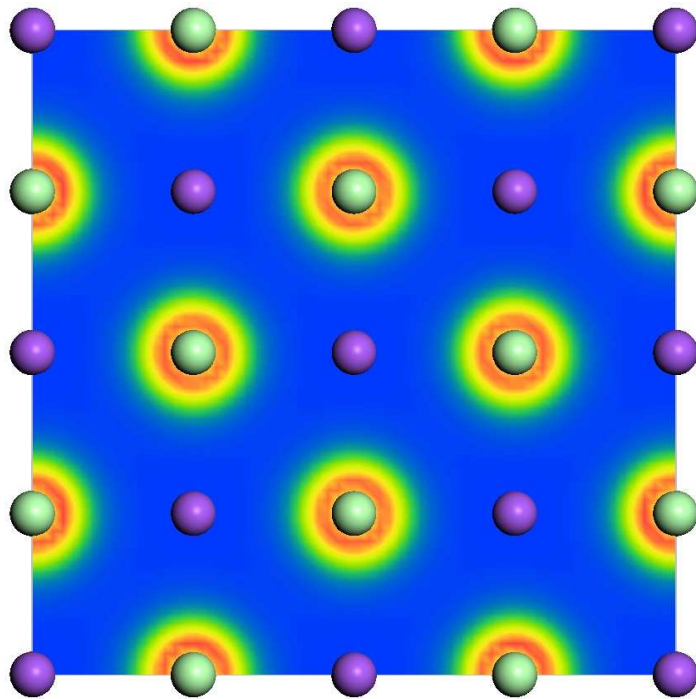
COVALENT BONDING



Diamond

- The atoms involved in a covalent bond can be said to be sharing *valence* electrons so as to attain a “magical octet”
- Visually, this expresses itself as a significant charge density between the atoms
- Covalent bonds are strong, getting stronger (and shorter) the more electrons that are shared

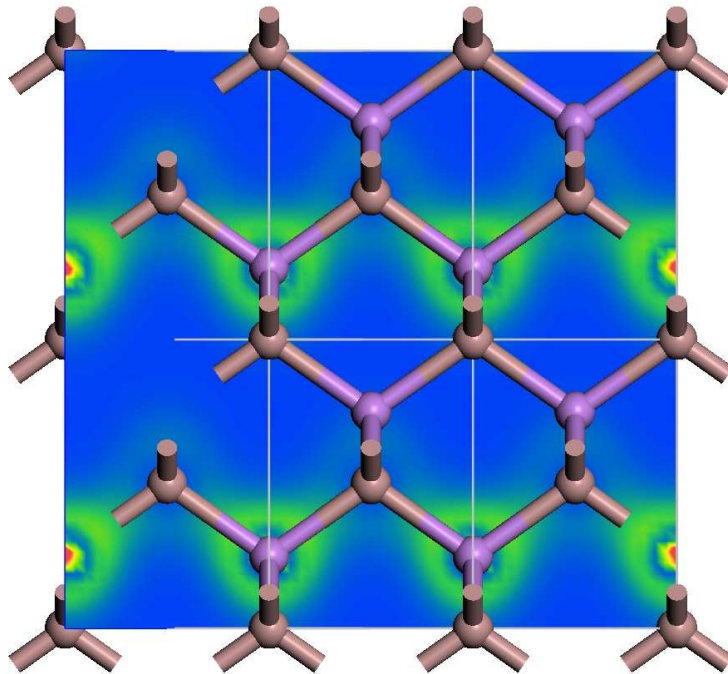
IONIC BONDING



Halite (NaCl)

- The electrons are not shared and there is a concentration of charge density on the more electronegative ion
- The ion that donates electrons becomes positively charged (*cations*), and the receiving electron negatively charged (*anions*)
- The bond is due to the electrostatic interaction between the oppositely charged ions, and non-directional

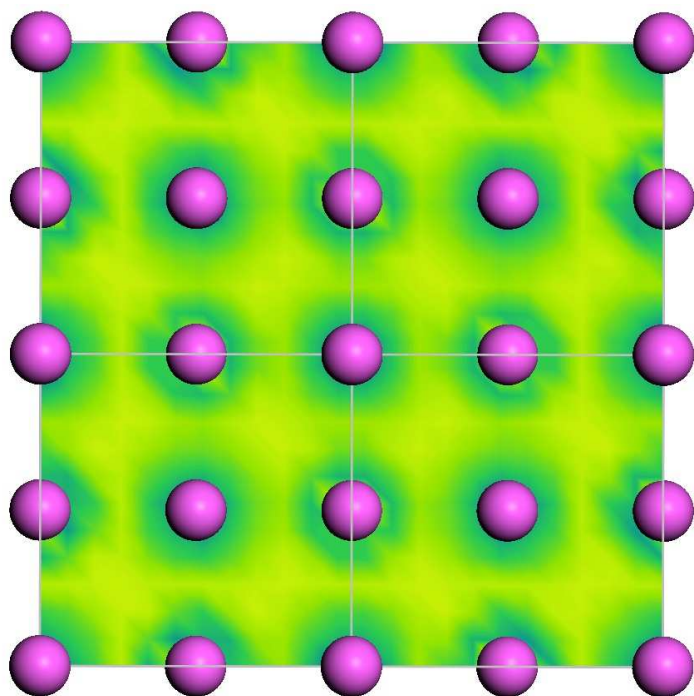
MIXED IONIC COVALENT BONDING



III-V Semiconductor (GaAs)

- The ionicity is weaker, due to the closer electro-negativity of the atoms, but still present
- There is an increase in charge density between bonded atoms
- The bond has both covalent and ionic character, and the bonding is directional

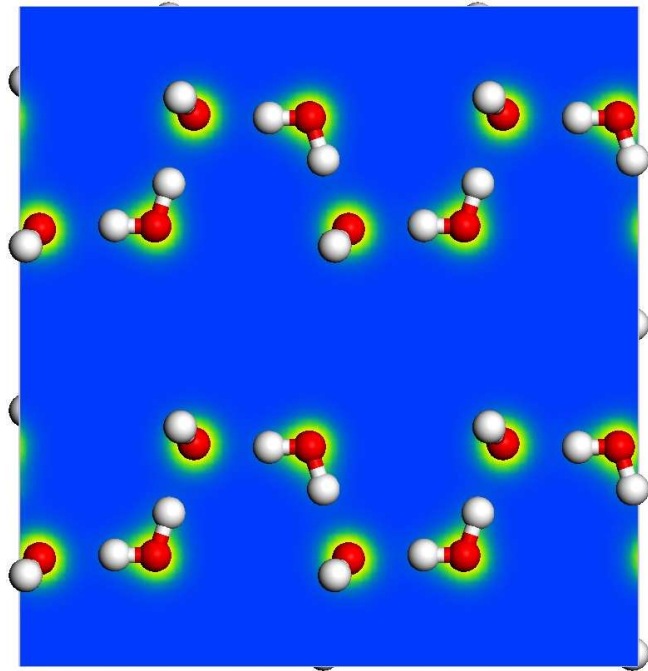
METALLIC BONDING



Aluminium

- The electrons are shared across the entire solid, and are *delocalised*: an extreme version of covalent bonding
- The more electrons shared, the stronger the metallic bonding: Mg has a higher melting point than Na
- The bonding is non directional, can have a covalent character, and results in close packed solids

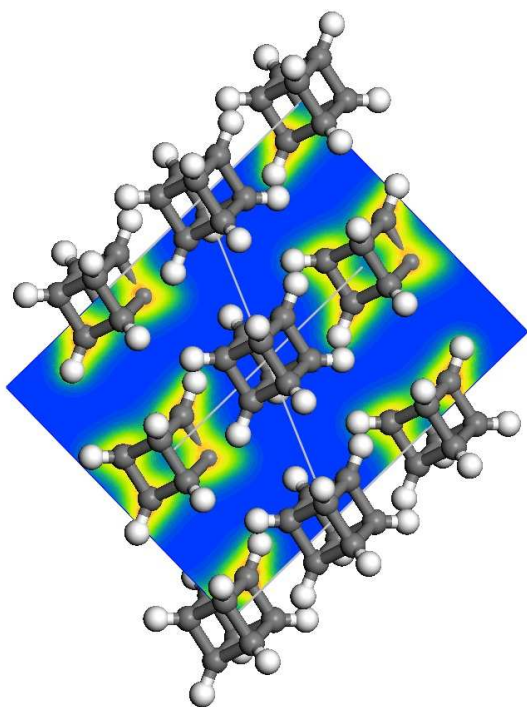
HYDROGEN BONDING



Cubic water ice (H_2O)

- Weak directional bonds due to the electrostatic attraction of polar molecules (or permanent dipoles within molecules)
- These permanent dipoles are due to differences in electronegativity
- Hydrogen is unusual: it cannot fully ionise (first ionisation potential too high), but also can form only one covalent bond

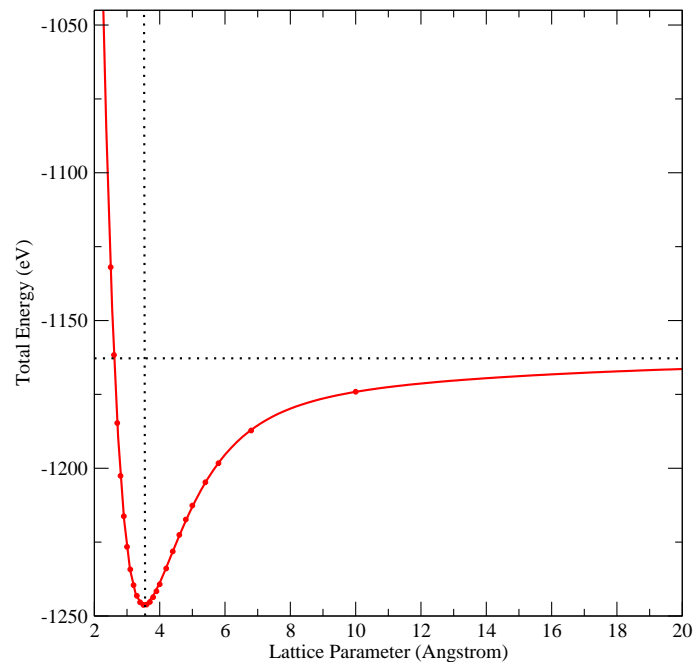
VAN DER WAALS BONDING



Solid cubane

- Weak non-directional bonds due to the electrostatic attraction between *fluctuating* dipoles
- Always present, but only dominates if all other bonds are saturated or impossible
- The charge density between van der Waals bonded “elements” is very small

COHESIVE ENERGY



*The total energy of diamond with
lattice parameter*

- See Chapter 20 of Ashcroft and Mermin for a more (slightly more ...) quantitative approach
- To do a proper job, you really need to use a first principles QM based approach
- See the lecture courses of Drs. Molteni and Towler next term