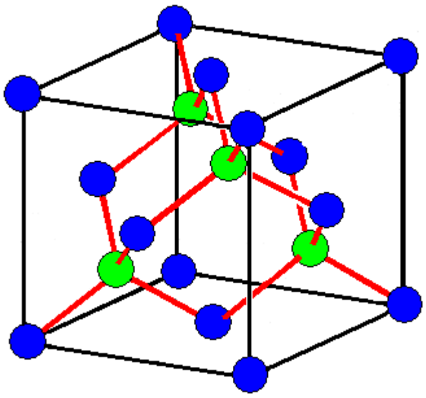
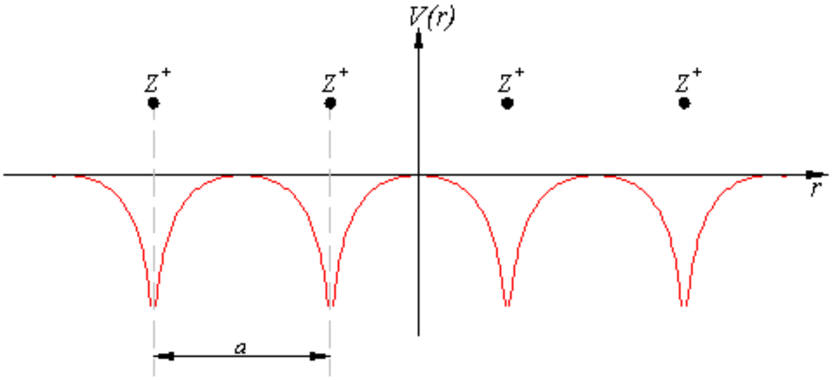
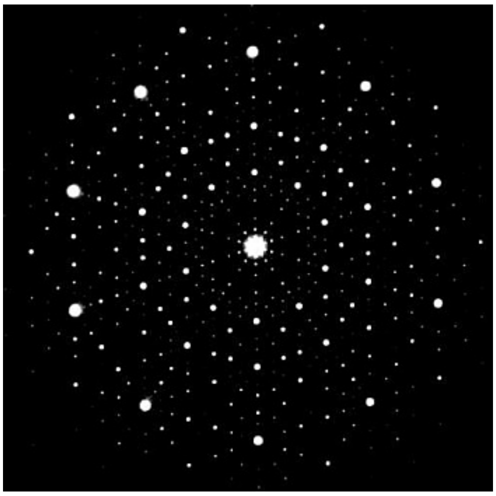






KYA322

Solid State Physics

Andrew Cole
andrew.cole@utas.edu.au

Solid State Physics

Condensed matter physics is the largest branch of modern physics because of the wide range of phenomena it encompasses and the high degree of connection to materials science and technology fields.

Before the mid-20th century, fields like *crystallography, metallurgy, magnetism, optical materials, elasticity*, etc., were considered as separate fields.

Condensed matter physics combines quantum mechanics, stat mech, and electromagnetism to understand and manipulate the properties of many-atom systems. Distinct from classical kinetic theory because forces between particles are the dominant feature of condensed systems.

Solid state physics is the largest branch of condensed matter physics. Historically developed out of the study of crystal properties and attempts to understand how long-range ordered structure could arise from interactions at the atomic level. Generalised to glasses and amorphous solids.

Textbooks

The classic textbook in the field is “Introduction to Solid State Physics”, by Charles Kittel, now in its 8th edition (2005)*.

The material is partially covered elsewhere in other sources you may have run across, e.g., Eisberg & Resnick, “Quantum Mechanics of… Solids…”, specifically Chapters 13-14 and Appendix Q. This book is also useful for the background on the physics of molecular bonds and statistical mechanics concepts.

A set of lecture notes covering many of the important concepts and including several derivations has been prepared by retired UTAS associate professor Peter Jarvis. This is available on MyLO as a supplement.

An introduction to many of the main concepts is given in the book “Modern Physics”, by Kenneth Krane (1983), which is an intermediate-level text concerned with quantum mechanics, relativity, and applications. Chapter 14 of Krane is the relevant chapter and I’ve also posted that on MyLO.

Experimental Techniques

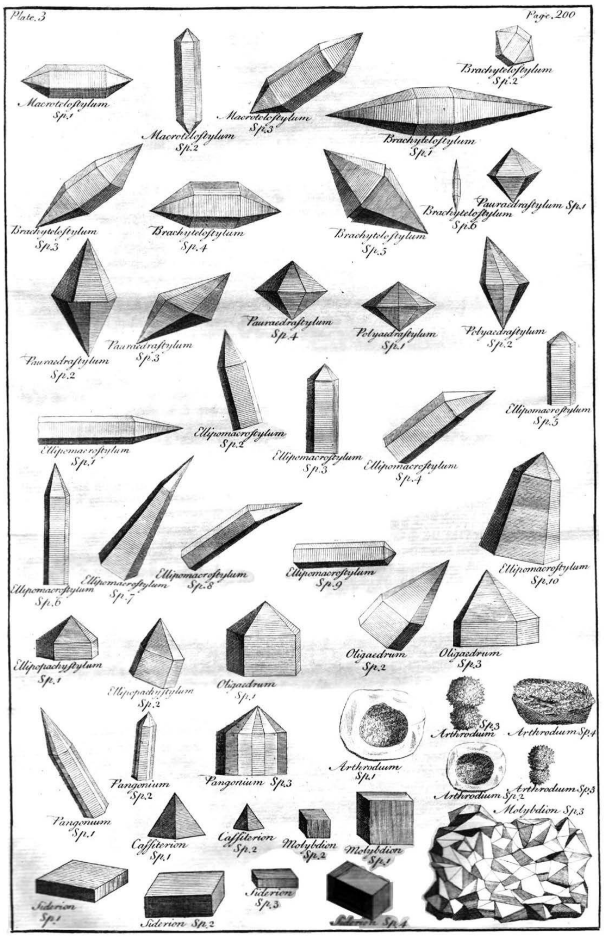
- Scattering experiments (including diffraction): x-rays, electrons, neutrons
  - Where are the electrons? What are the energy level excitations?

- Thermodynamic properties: specific heat, thermal conductivity
  - What entities carry the heat and how?

- Electronic properties: resistivity, photoemission, Hall effect
  - Metal, insulator, semiconductor? (superconductivity)
  - How does the charge move?

- Optical properties: transparency, index of refraction, wavelength depend.
  - interactions with EM waves

- Resonances: NMR, muon spin resonances
  - magnetic properties



Hill (1748), Natural History of Fossils

Types of Solids

The origins of solid state physics are in mineralogy, specifically the study of crystal.

The regularity, hardness, and optical properties of crystals led easily to the idea that they are formed from repeating patterns of a few basic building blocks.

In a modern context, a crystal is a 3-dimensional periodic array of atoms or molecules.

This was first proven by Max Laue in 1912 by experiments with the diffraction of x-rays. This almost immediately led to the determination of crystal structures (e.g., Bragg 1913).

Crystals: Introduction

Crystals are particularly good for solid state study because of their *long-range order*. The placement of one atom is directly related to the placement of an atom very far away.

The regular arrangement is called the *lattice* of the crystal.

Crystals are relatively easy to describe because of their periodicity, and relatively easy to link atom-level properties to everyday scale measurements because of their great regularity.

The ideal crystal is perfectly regular and infinitely repeatable. Real crystals always have impurities. These can be important for the electron mobility and other properties even at the level of a 1% impurity (e.g., semiconductors such as Ge doped with Sb).

Other deviations from the ideal crystal: surface effects, thermal lattice vibrations.

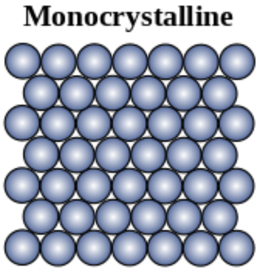
Amorphous Solids

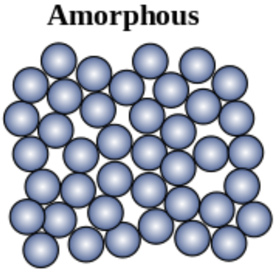
Amorphous solids have no long-range order.

We can still define basic properties like the average spacing between atoms, and work out what we expect the material strength, and other bulk properties to be.

- In amorphous solids, bulk properties depend more on the properties of the constituent atoms and their bond types than they do on the arrangement of atoms.

There can be short-range order (correlations between the positions and energies of adjoining atoms and electrons).





Cohesive Energy

The structure of solids is determined by the relationships between the wavefunctions of the individual atoms and molecules that make up the solid.

This is almost entirely a function of the outermost (valence) shell of electrons, because these wavefunctions have by far the largest spatial extent and therefore the highest degree of overlap.

The relationships between wavefunctions mean that quantum statistics play a critical role in determining the energy levels of bonds between atoms and molecules. At different temperatures a solid can have very different properties depending on how the thermal energy relates to the energy levels dictated by the quantum state.

Solids are held together by electrostatic forces. The cohesive energy is typically on the order of a few electron-volts.

Ionic Solids

When two atoms approach each other to within the distance at which the wavefunctions of their outer electrons overlap, it can be the case that the total energy is minimised when one electron is transferred from one atom to the other. This forms two "closed-shell" ions.

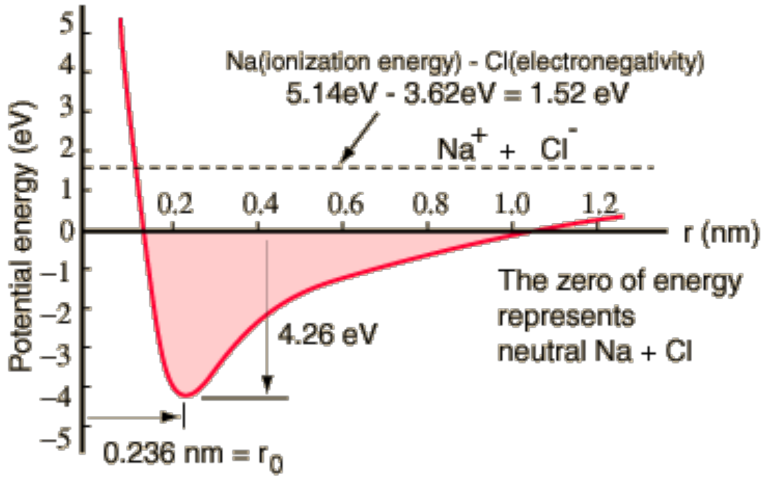


image: hyperphysics.phy-astr.gsu.edu

Electrostatic attraction between the two ions forms a stable molecule with an ionic bond.

e.g., NaCl.

In nature, many Na^+ and Cl^- ions tend to be found together and can all mutually attract one another.

Ionic Solids

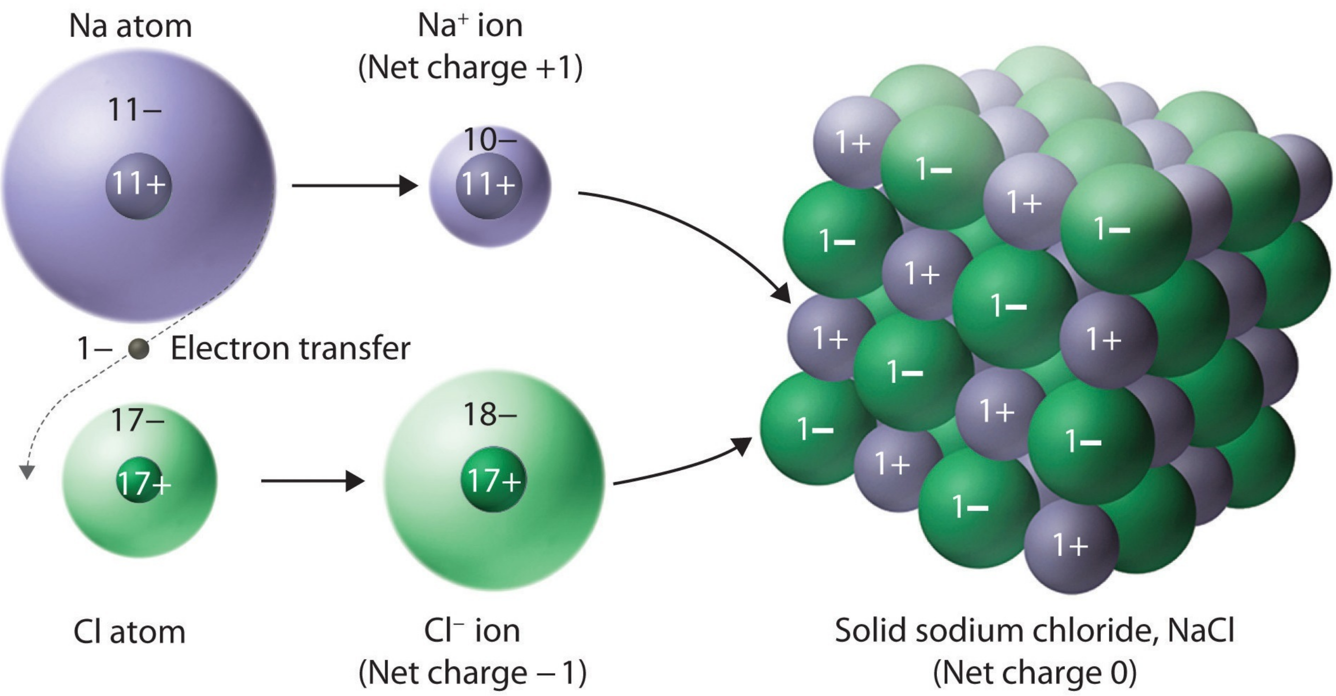
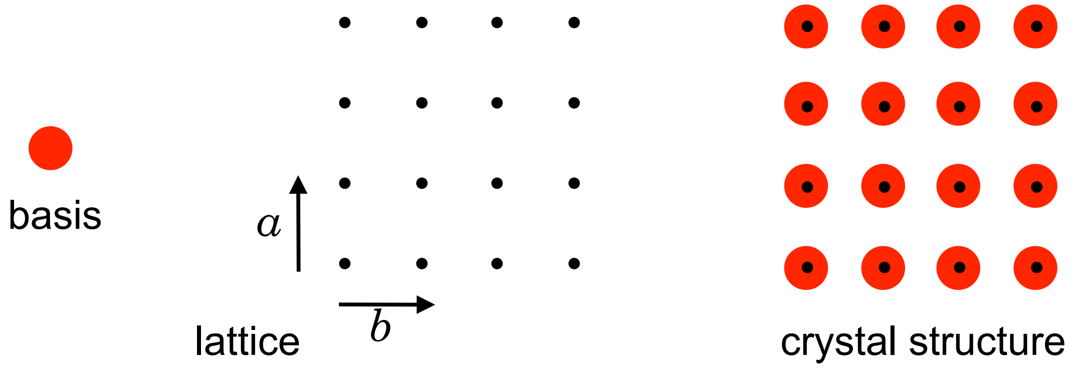


image: https://chem.libretexts.org/

Crystals: Basics

All crystals have two basic components: a *basis*, and a *lattice*.

The basis is the fundamental unit of the crystal, e.g., an NaCl molecule. The lattice is the pattern with which the basis repeats, defined by the symmetry and the spacing between points, in three dimensions



Lattice Definitions

The lattice in 3-dimensions is defined by three vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ such that the crystal appears identical from any two locations $\boldsymbol{r}$ and $\boldsymbol{r}'$ if they are separated by integer multiples of the $\boldsymbol{a}$'s:

$$r' = r + u_1 a_1 + u_2 a_2 + u_3 a_3$$

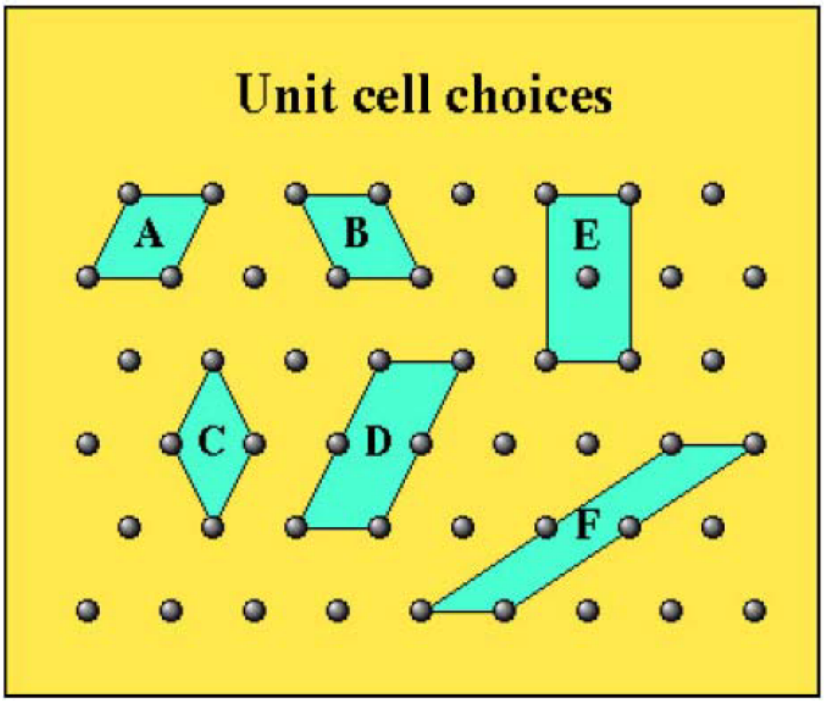
The set of points $\boldsymbol{r}'$ for all integers u defines the lattice.

A subset of the lattice points defines a ***primitive cell***. The primitive cell is the smallest set of lattice points that can be arbitrarily translated by the vectors $\boldsymbol{a}$ and always have the crystal structure appear the same.

The primitive cell is the building block for the entire crystal structure. In three dimensions, its volume is $a_1 \cdot a_2 \times a_3$

There is one basis per lattice point. Remember: often, the atoms are not located on the lattice points, but displaced by some amount.

Primitive Cells



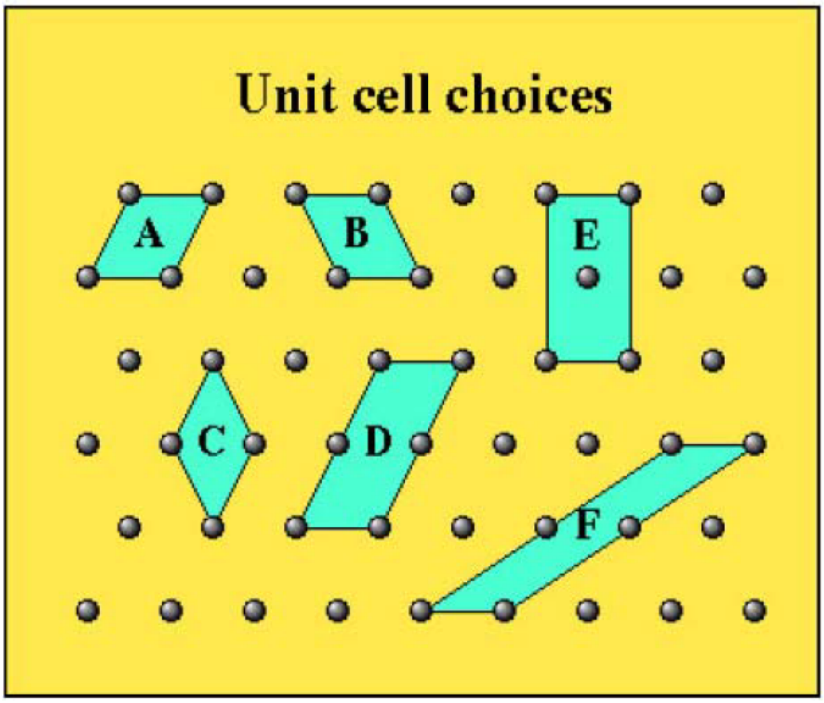
There is often freedom in the choice of primitive cell. (2-d example)

A, B, and C are equally good choices of primitive cells. The plane can be tiled completely with them, and no smaller units. They have the same volume (area).

Only the choice of coordinate system origin differs.

Note: each lattice point is at a vertex of a primitive cell. It is therefore shared with some other cells. It works out that there is one lattice point per primitive cell.

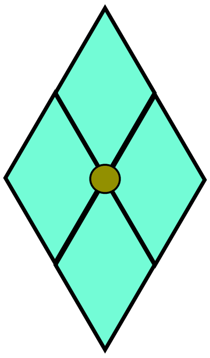
Primitive Cells



Cells D, E, & F contain 2 lattice points; they are not primitive.

Shaded areas D, E, and F are valid unit cell choices (in 2-d) because one could tile the plane completely without any gaps using only those shapes.

However, D, E, and F are NOT **primitive cells**, because they are not the smallest possible such tiles.

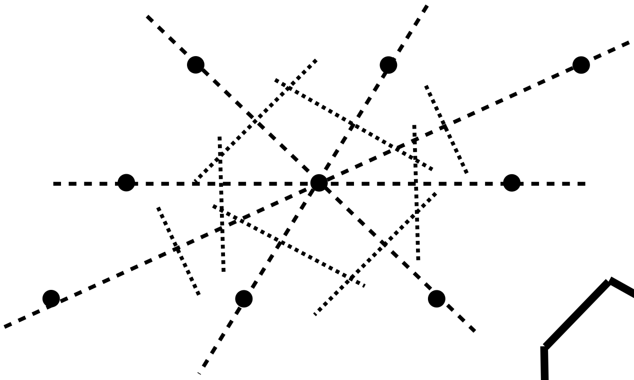


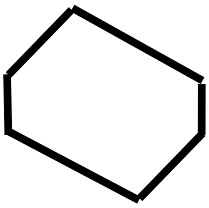
E.g., for cell C, each point is shared with 4 adjacent cells. There are 4 of these, so each cell contains 1 lattice point.

Wigner-Seitz Primitive Cell

For those who prefer a standard procedure to define the unit cell, the following steps define the *Wigner-Seitz* primitive cell.

It has the same volume as any other primitive cell and contains the same (minimum) number of basis atoms, but the vertices and edges have a more abstract relationship to the lattice points.

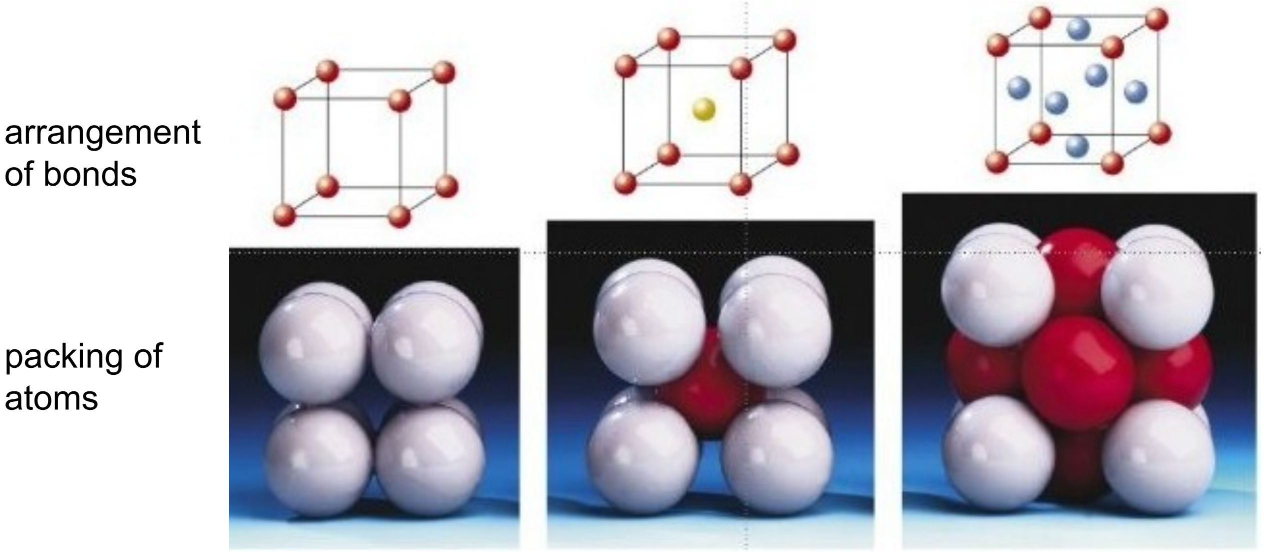




1) Connect a lattice point to all its neighbours.
2) Draw new lines perpendicular to the original lines, at the midpoint.
3) The intersection of the secondary lines define the Wigner-Seitz primitive cell. All space may be tiled uniformly with these shapes.

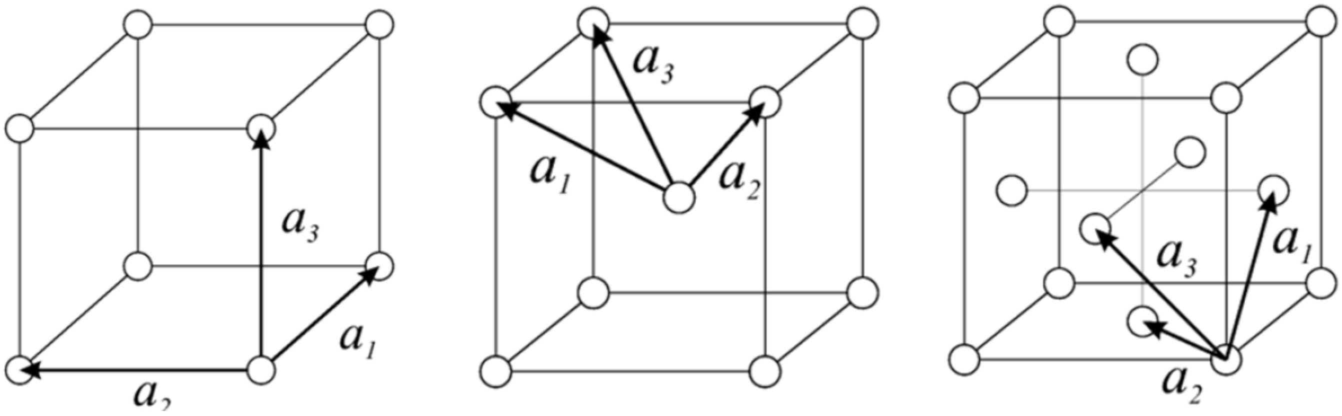
Crystal Lattices

Ionic bonds are non-directional because the positive and negative ions are spherically symmetric and the forces between them are radial. This leads to ionic solids forming densely packed crystalline structures that are uniform in all directions. The **cubic lattices** fill space uniformly.



simple cubic body-centred cubic face-centred cubic

Cubic Primitive Cells



sc bcc fcc

In this quite simple case it’s easy to see that all the primitive translation vectors and the angles that orient them are equal. This in general won’t be true for every lattice type.

fcc and bcc structures

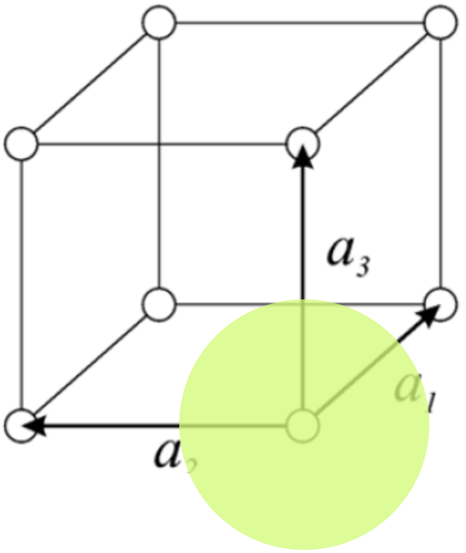
Because every + ion is surrounded by several – ions (e.g., 6 of them for face-centred cubic), it is a mistake to consider the wavefunction of the crystal as a simple sum of atomic or molecular wavefunctions. The crystal properties will depend on the lattice spacing and symmetry and the cohesive energy of the crystal more than the individual molecular properties.

The simple cubic structure is a very inefficiently packed structure, since there is a large empty volume in the centre, as well as along each face.

The face-centred cubic (*fcc*) achieves the highest number of ions/atoms per unit volume, so it tends to be the most energetically favourable. NaCl is an extremely common *fcc* crystal

The body-centred cubic (*bcc*) is also commonly encountered. It is sometimes called the CsCl structure. Its packing fraction is slightly less, but it may be more energetically favourable depending on relative atom sizes or thermal energy.

Lattice Properties



Packing fraction is the ratio of the atomic volume to the volume of the primitive cell.

Example: the *sc* lattice:

$a_1 = a_2 = a_3$. $V = a^3$.

$$V_{\text{atom}} = \frac{4}{3}\pi(a/2)^3$$

packing fraction = $\pi/6$

The nearest-neighbour distance to another atom in the *sc* lattice is a. There are 6 nearest neighbours.

There are 12 next-nearest neighbours, and their distance is $\sqrt{2}a$

Cohesive Energy: Madelung Constant

In an ionic solid, the attractive forces holding the crystal together are simply electrostatic. Each positive ion has 6 neighbours, so the strongest contribution to the energy (for the simple cubic structure) will be

$$U = -6\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

The next-nearest neighbours have the same charge as the original ion, so they exert a *repulsive* force. Then there is another group of opposite charged ions at a slightly farther distance,...

The net effect is that $U = -\alpha\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$ where α is known as the Madelung constant.

The Madelung constant depends on the lattice structure, but *not* on the specific type of atoms. The mean separation *r* will depend on the type of atom as well.

Cohesive Energy continued

fcc (NaCl structure): α = 1.7476
bcc (CsCl structure): α = 1.7627

The potential is not completely attractive: the Pauli exclusion principle prevents the electron wavefunctions (especially for filled subshells) from complete overlap. This contributes a repulsive term to the potential, setting the minimum separation between atoms.

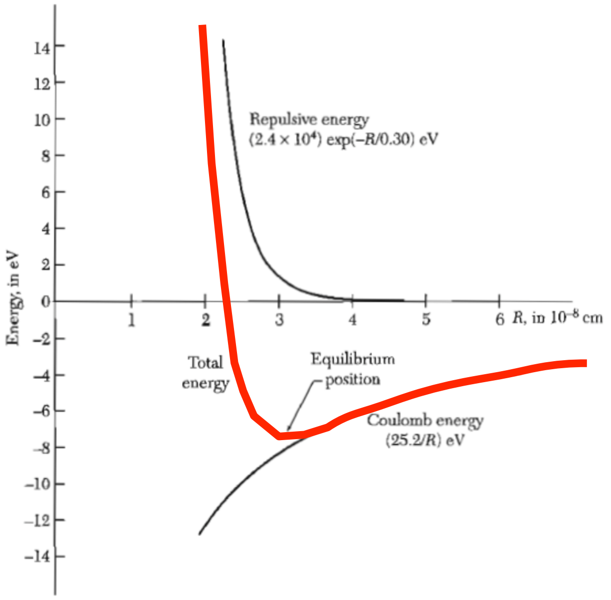


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

Equilibrium Separation r_0

The exclusion principle force is very hard to compute exactly, but it can be approximated as: $U_{\text{repulsive}} = Ar^{-n}$
where A is the strength of the exclusion interaction and *n* gives the decrease with distance. (Approximate, OK as long as *r* not too small).

The total potential is then $U_{\text{total}} = -\alpha \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r} + \frac{A}{r^n}$

Find r_0 by differentiating and solving where dU/dr = 0.

This gives a relationship between *A*, r_0, and *n*: $A = \frac{\alpha e^2 r_0^{n-1}}{4\pi\varepsilon_0 n}$

So by substitution the potential energy at r = r_0 is $U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$

The energy $-U_0$ is the *ionic cohesive energy* of the solid.

Ionic Cohesive Energy

$$U_0 = -\frac{\alpha e^2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

This is the energy needed to take the solid apart into positive and negative ions, *not* into neutral atoms. And in this form, it is measured per ion pair.

The value of n for many ionic solids is in the range from about 8-10, or more broadly from 6-12. Calculation shows that the exact value of n does not make much difference to U_0.

Nearest neighbour separations for ionic solids may be around 0.2-0.4 nm, and the resulting cohesive energies are in the range of ~5-10 eV per ion pair.

Cohesive Energy Example: NaCl

From a standard reference work we find $r_0 = 0.281$ nm, and $n = 8$, for a face-centred cubic crystal structure.

The equation of ionic cohesive energy gives

$$U_0 = -(1.7476)\frac{1.44\ \text{eV}\cdot\text{nm}}{0.281\ \text{nm}}\left(1-\frac{1}{8}\right) = -7.84\ \text{e}V$$

which is the energy required to pull Na^+ and Cl^- ions from the crystal.

Experimentally, we typically end up measuring the *atomic* cohesive energy, which is related to the *ionic* cohesive energy by the energy needed to form neutral atoms from the ions.

E.g., it takes 5.14 eV to ionize Na, and Cl releases 3.61 eV when it acquires an electron, so the atomic cohesive energy would be
$-7.84 - 3.61 + 5.14 = -6.31$ eV. Agrees well with the measured value of 6.39 eV. Often expressed in kJ/mole: 6.39 eV/ion pair = 615 kJ/mol

Ionic Solids Summary

The bond strengths of several eV mean that room temperature thermal energies are completely insignificant (remember Boltzmann's constant $k = 8.617\times10^{-5}$ eV/K means that a thermal energy of 1 eV corresponds to a temperature of 11,600 K.)

★ Expect ionic solids to be quite stable and have high melting points.

★ The competition between the Madelung and Pauli forces means they are quite rigid - stable, hard crystals are expected.

★ From the bond properties, we see that there are *no free electrons available.* Every electron is associated with a single molecule and the position is localised in space. Therefore we expect ionic solids to be poor electrical conductors.

★ Ionic solids are often transparent to visible light. We will show this explicitly in discussing the band theory of solids, but for now just remember that the energy differences between, e.g., the 3*s* and 4*s* shells are more than a few eV.

★Ionic solids may also be very strong infrared absorbers (consider forces on atoms).

Infrared Absorption in Ionic Solids

In classical mechanics the force is given by $F = -\nabla U$.

In one-dimension, $F = -\dfrac{dU}{dr} = -\dfrac{\alpha e^2}{4\pi\varepsilon_0 r^2}\left(1 - \dfrac{r_0^{n-1}}{r^{n-1}}\right)$

For a small displacement x away from r_0, expand using $(x/r_0) << 1$, to get:

$$F \approx -\frac{\alpha e^2}{4\pi\varepsilon_0 r^2}\left(1 - \frac{2x}{r_0}\right)(n-1)\frac{x}{r_0}$$

Because x/r_0 is small, ignore second order terms and see that $F \approx -kx$, with

$$k \approx \frac{\alpha e^2}{4\pi\varepsilon_0 r_0^3}(n-1)$$

For the NaCl molecule described above, this has the numerical value of around 795 eV/nm^2

Infrared Absorption in Ionic Solids

Treating the system as a harmonic oscillator, the frequency $\nu = \frac{1}{2\pi}(k/m)^{1/2}$

To be correct the mass used should be the *reduced mass* of the system.
E.g., for NaCl, m = $(m_{Na}m_{Cl})/(m_{Na}+m_{Cl})$ = (23)(35.5)/(23+35.5) ≈ 14 *u*.

This will only be a rough estimate. For NaCl the answer is ~ 10^{13} Hz. This is a wavelength of ~30 microns, in the mid-infrared part of the spectrum.

We should expect sodium crystals to absorb strongly when exposed to mid-infrared radiation, and that IR radiation will set the ions into oscillatory motion.

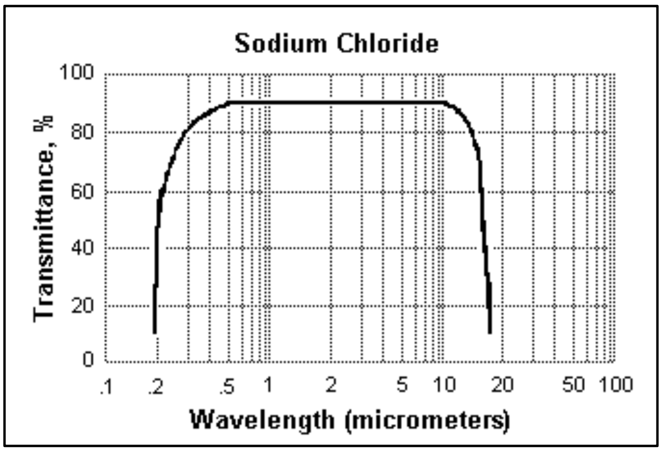
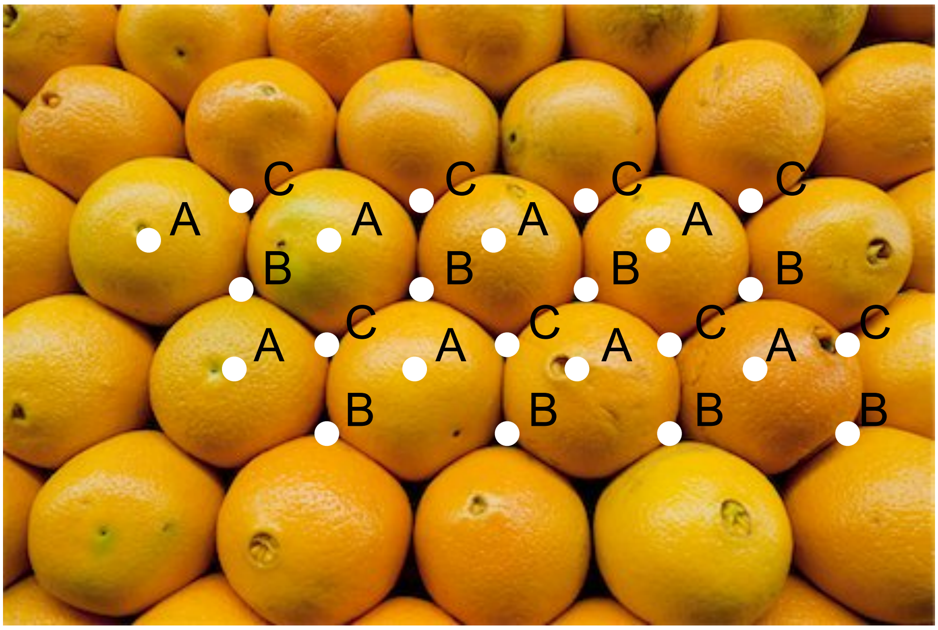


image: http://www.alkor.net, "Crystal Optics"

Close-Packed Structures



To maximise the packing fraction of spheres in a 3D structure, we have several different choices.

Label the positions of the atoms in a layer A.

The next layer of atoms can have centres at B or C.

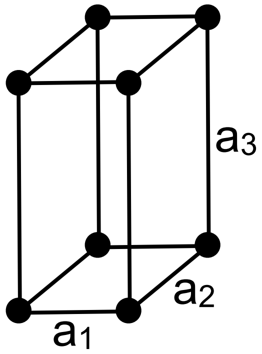
Then the third layer can be directly above A, or further offset to the third choice.

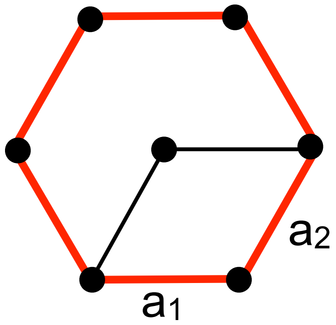
The face-centred cubic (fcc) structure is close-packed, with pattern ABCABCABC…

Hexagonal Close-Packed Crystals

Another type of close-packed configuration is hexagonal (*hcp*). The packing repeats with pattern ABABAB…

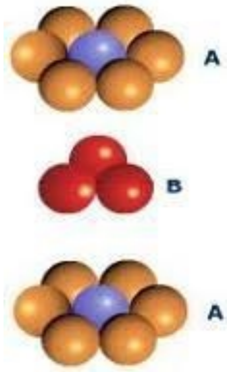
Its usual primitive cell is a parallelipiped with rhomboidal ends, with included angle 120°.

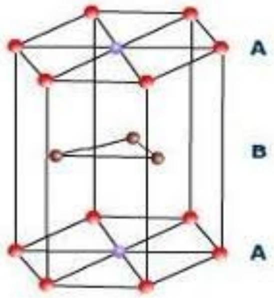




$a_1 = a_2 \neq a_3$

The hcp structure



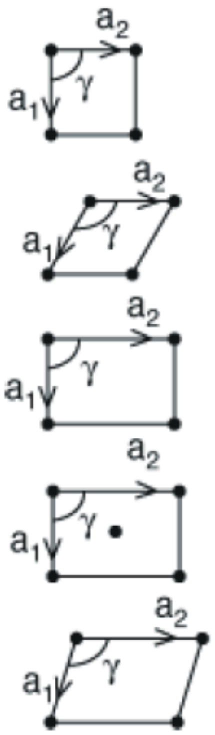


The basis is typically two identical atoms/ions, one of them located at a lattice point and the other at an intermediate point.

From the spherical geometry, the ideal ratio $a_3/a_1 = (8/3)^{1/2}$.

The number of nearest neighbours (coordination number) is 12.

2-D Lattices



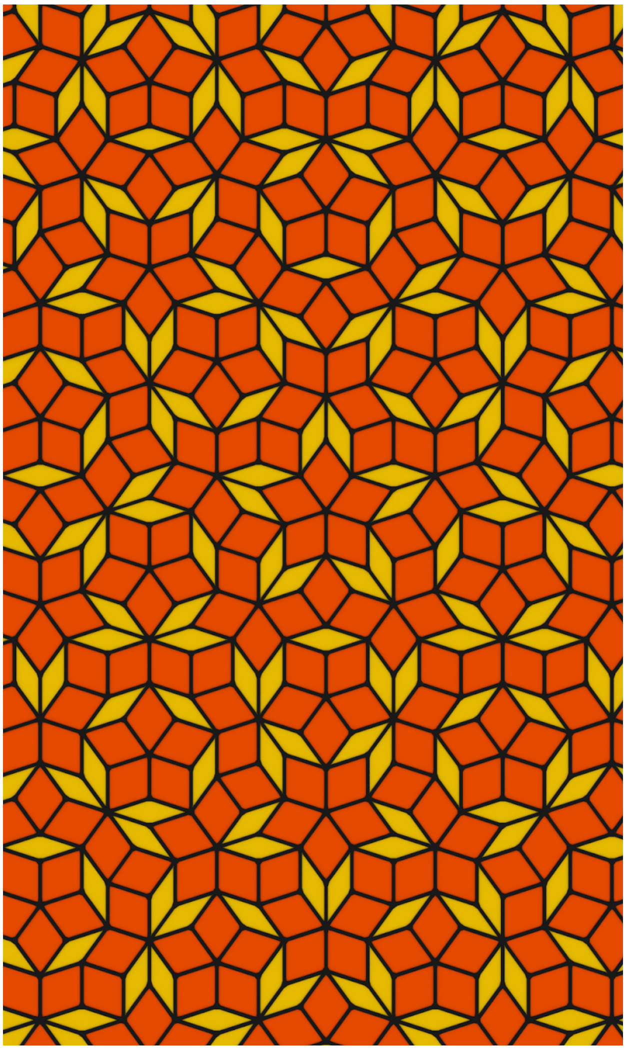
square	$a_1 = a_2$	$\gamma = 90°$
hexagonal	$a_1 = a_2$	$\gamma = 120°$
rectangular	$a_1 \neq a_2$	$\gamma = 90°$
centred rectangular	$a_1 \neq a_2$	$\gamma = 90°$
oblique	$a_1 \neq a_2$	$\gamma \neq 90°$ $\gamma \neq 120°$

The fundamental lattice shapes are referred to as a *Bravais lattice*. In 2-D there are five lattices.

Crystal lattices can be transformed by translations, but also by rotations.

Lattices can be found such that rotations by $2\pi/n$ reproduce the original, with n = 1, 2, 3, 4, and 6 (and no other values).

Penrose Tiling & Quasicrystals



No lattice can be found that tiles space with fivefold or sevenfold rotational symmetry (e.g., rotation by $2\pi/5$ radians).

Penrose tiling is a mathematical way to fill a space with two types of tiles in a non-repeating, almost periodic way.

This is not a Bravais lattice, because two basic structures are required.

This has application to *quasicrystals*, a form of matter that can be useful in technological applications

Bravais Lattices in 3D

System	lattice type	axes and angles
Triclinic	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
Monoclinic	P, C	$a \neq b \neq c$ $\alpha = \gamma = 90° \neq \beta$
Orthorhombic	P, C, I, F	$a \neq b \neq c$ $\alpha=\beta=\gamma = 90°$
Tetragonal	P, I	$a = b \neq c$ $\alpha=\beta=\gamma = 90°$
Cubic	P (sc), I (bcc), F (fcc)	$a = b = c$ $\alpha=\beta=\gamma = 90°$
Trigonal	R	$a = b = c$ $\alpha=\beta=\gamma \neq 90°, <120°$
Hexagonal	P	$a = b \neq c$ $\alpha=\beta=90°, \gamma = 120°$

There are five different types of lattices in two dimensions. In 3D there are 14 different lattice types, which are conventionally divided into seven systems, according to the type of unit cell.

The lattice types are:

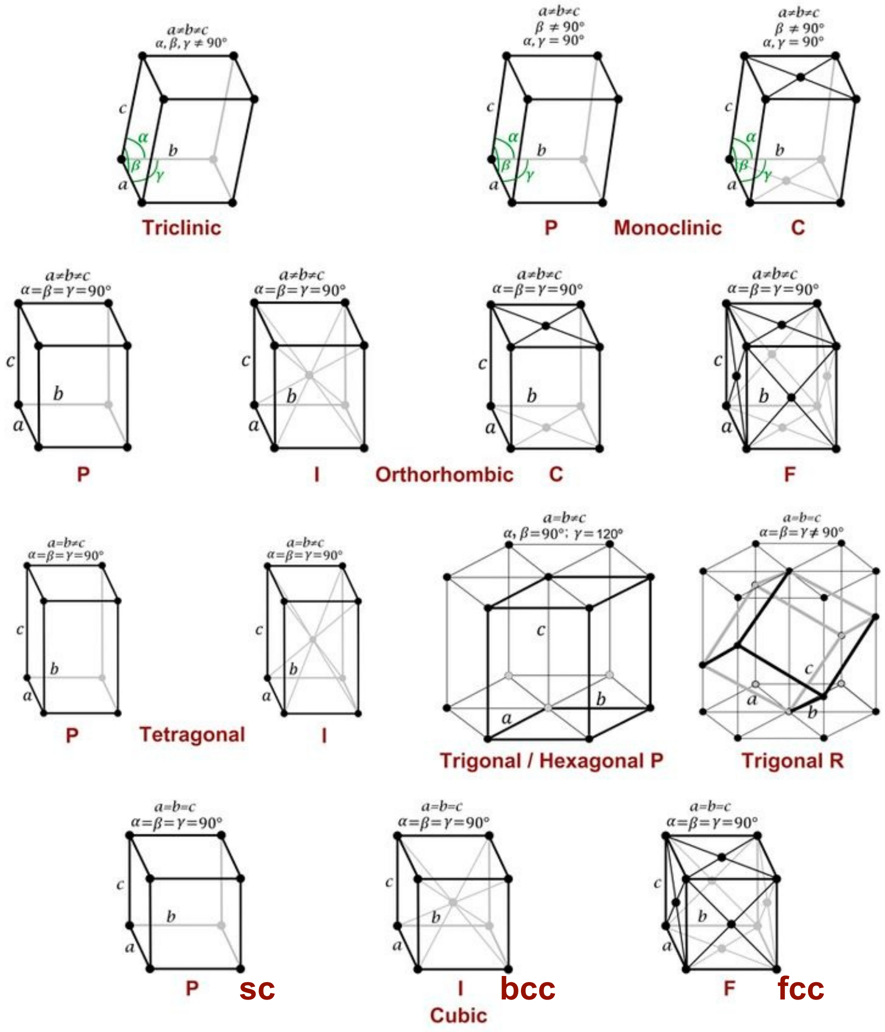
***Primitive* (P):** lattice points at the vertices of a unit cell.

***base-Centred* (C):** primitive + two extra points on opposite faces.

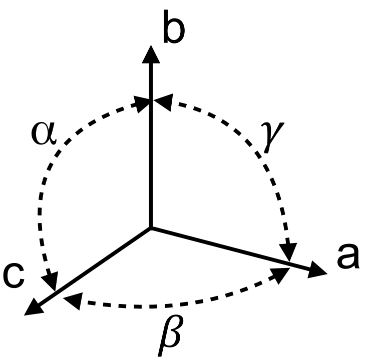
***body-centred* (I)**: primitive plus an Interior lattice point at the centre.

***Face-centred* (F)**: primitive plus points on all faces.

***primitive Rhombohedron* (R):** self-explanatory.

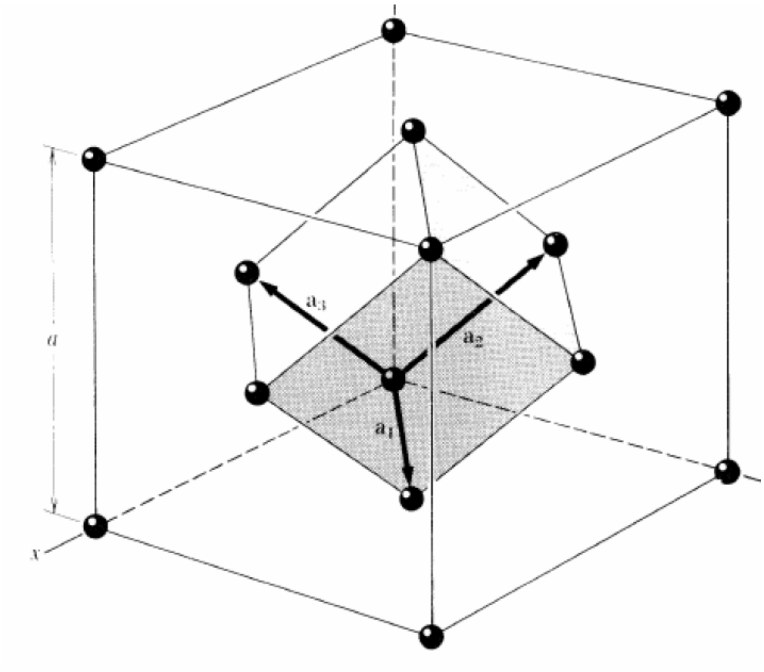


Not all the conventional cells are primitive, but drawing them this way can be useful for interpreting the symmetries of the groups.



Conventional vs. Primitive Cells

An example of the difference between the conventional cells defined by point symmetries, and the primitive cells is the face-centred cubic.



The primitive cell for the fcc lattice is a rhombohedron with axes offset by 60° from the axes of the cube.

Starting at one corner of the cube, the edges of the primitive cell are defined by the vectors connecting to the points at three adjoining faces:

$$a_1 = \frac{a}{2}(\hat{x} + \hat{y})$$
$$a_2 = \frac{a}{2}(\hat{y} + \hat{z})$$
$$a_3 = \frac{a}{2}(\hat{z} + \hat{x})$$

Location of Atoms in the Cell

The positions of points within a cell are specified by vectors in the coordinate system *x, y, z*, where each coordinate is a fraction of the cell length (*a, b*, or *c*).

The origin is usually taken to be the corner of a cell.

In this convention the cell centre is at (½, ½, ½).

The face centres are at, e.g., (½, ½, 0), (½, 0, ½), (0, ½, ½), …

For cubic cells, the atomic positions are usually given in terms of the conventional cubic cell, not the rhombohedral primitive cell.

In crystallography, it is sometimes said that the basis of atoms *decorates* the lattice points. A complete description of crystal structure specifies the type and size of the cell, and then gives the coordinates x_i, y_i, z_i for each of the atoms in the basis.

Simple Structures: NaCl

(fcc Bravais lattice type). The basis is one Na ion and one Cl ion separated by one-half the body diagonal of the unit cube. Each ion has 6 neighbours, of the opposite type. Taking an Na ion to be the origin, the atom positions are

$$\text{Na}: \quad 000 \quad \tfrac{1}{2}\tfrac{1}{2}0 \quad \tfrac{1}{2}0\tfrac{1}{2} \quad 0\tfrac{1}{2}\tfrac{1}{2}$$

$$\text{Cl}: \quad \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2} \quad 00\tfrac{1}{2} \quad 0\tfrac{1}{2}0 \quad \tfrac{1}{2}00$$

the lengths are referred to the conventional cell size, for NaCl $a = 5.63$ Å.

Some other crystals with this structure include LiH, PbS, AgBr, KBr, KCl

---

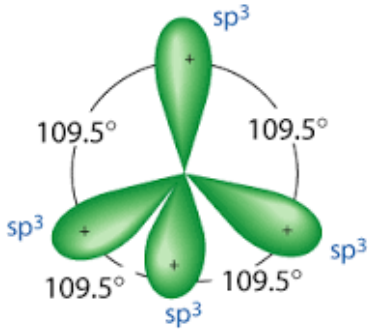
Covalent Solids

Many atoms form molecules by sharing electrons between their valence subshells rather than trading them to become ions.

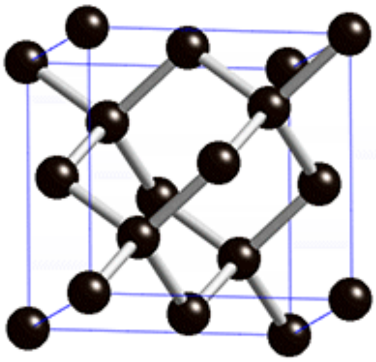
The shape of the electron probability density distributions then controls the shape of the combined probability density distribution. The charge distribution is unlikely to be spherically symmetric, and there may be preferred bond angles.

The preferred bond angles come about because of the competition between the Pauli exclusion principle, the requirement that the total energy of the molecule be minimised in a stable configuration, and the electrons' mutual electrostatic repulsion.

In carbon, this results in distortion of the orbitals so that there are no longer distinct 2*s* and 2*p* subshells, but rather a hybrid "sp^3" subshell. The electrons bond covalently with a preferred angle of 109.5°.



Covalent Solids



The diamond tetrahedral structure is also known as the zinc sulfide structure; it is shared by many covalent solids.

The material properties of covalent solids depend strongly on the type of bonds that build the molecules, so they do not have the same regularity of predictable properties as ionic solids.

E.g., carbon (in the form of diamond) has a large bond energy and is therefore very hard, and transparent to visible light. Tin has a very similar structure, but is metallic in appearance and melts at a much much lower temperature.

At room temperature, silicon and germanium both take the carbon structure (and both are semiconductors).

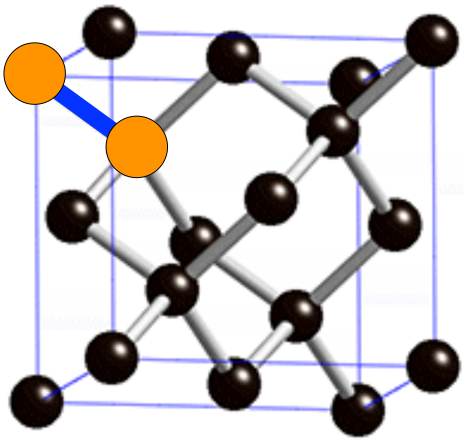
Diamond Structure

The primitive basis for the diamond crystal is two identical C atoms.

Either one of the atoms can be taken to sit on a lattice point in a face-centred cubic. The second atom then sits at distance equal to (1/4) of the cube body diagonal.

In other words, there are two identical fcc lattices, offset from each other by 1/4 of a diagonal.

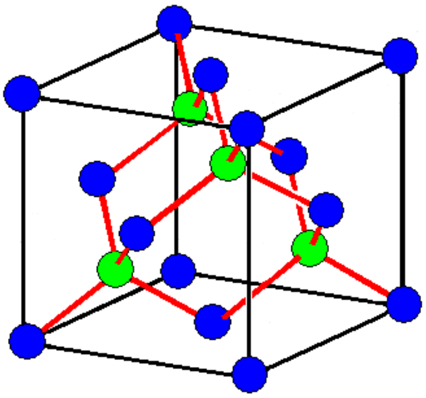
Each atom has 4 nearest neighbours and 12 next-nearest neighbours; the structure is relatively empty with only 8 atoms in a unit cube.



animation: wikimedia commons

Diamond (zinc sulfide) Structure

The fcc crystal with a two-atom basis, located at 000 and 1/4 1/4 1/4.



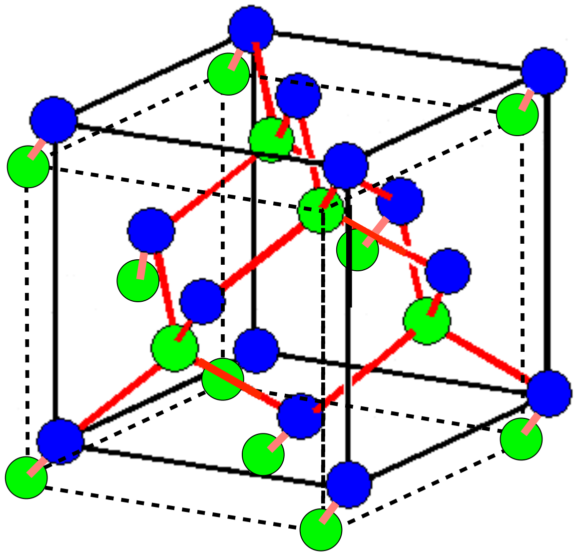
This fits the atoms into cubic structure, while accommodating the tetrahedral bond arrangement that comes from the covalent bond structure of the atoms.

However, this is a loosely-packed structure: the nearest atoms are relatively far apart. Compared to a bcc or hcp lattice, this has a low packing fraction, so solids with the diamond structure are relatively low density.

This is the same structure as for carbon, but with non-identical atoms in the offset lattices. For example, the blue atoms might be gallium, and the green atoms arsenic. Gallium arsenide (GaAs) is an essential component of many modern optical detectors.

Diamond (zinc sulfide) Structure

Try visualising the two-atom basis, and the two offset lattices. Fewer green atoms than blue are shown here, because the other green atoms fall outside the cube delineated by the black lines, but this is arbitrary.



The green atoms sit on the corner and 3 faces of the offset lattice.
The additional green atoms to complete that lattice have exactly the same relationship to the blue atoms as those shown.

Drawing in the additional points is unnecessary for specifying the structure, and complicates the visuals, although of course they are present since all of the molecules are identical and arranged in a repeating pattern.

Metallic Bonds

Because the valence electrons in metals are only very loosely bound to their atoms, they don't form very strong covalent bonds.

The basic structure of a metallic solid is a lattice of positive ions, immersed in a "gas" or "sea" of almost but not quite free electrons. The metal is bound together by the attraction between the lattice and the electron gas.

The most common metallic crystal structures are fcc, bcc, and hcp (hexagonal close-packed). Nearest-neighbour distances are on the order of 2-4 Å, and the cohesive energies are on the order of around 1-4 eV.

As a result, metals interact strongly with visible light: they are not transparent. Because the electrons can respond collectively to the perturbation by an electromagnetic wave, they are highly reflective.

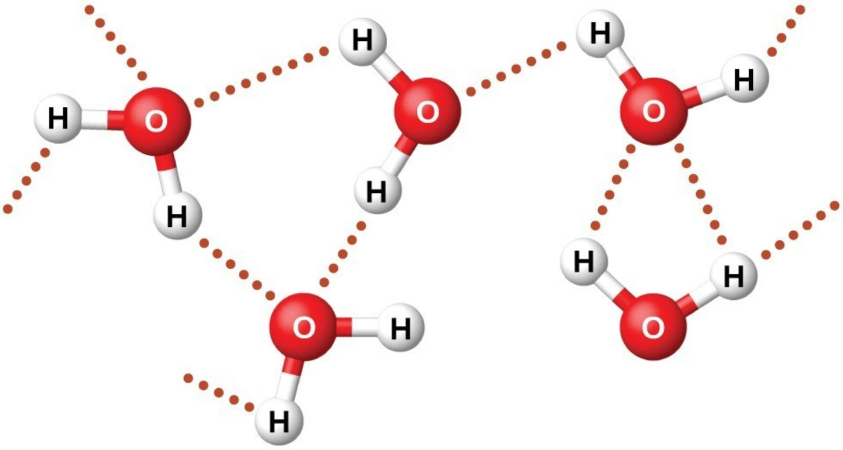
Because many of the properties are determined by the electron gas, metals tend to share characteristics in common, mostly independent of the specific element involved (alloys are easy to make).

Molecular Solids

Ionic, covalent, and metallic solids can *not* be accurately considered to be formed of individual molecules- the wavefunctions can only be accurately calculated if they are considered as a group based on the replication of the primitive cell of the crystal.

Some molecules may be very strongly bound, yet still have an interaction with other molecules to bind them into a solid (or liquid). Because the molecules are electrically neutral, the bonds rely on the existence of dipole moments in the molecules.

Example: H_2O. The O attracts the electrons and then looks like the negative end of a dipole, which can attract the positive end of other nearby dipoles.



Molecular Solids

The type of bonding between dipoles is much weaker than the direct attraction of the $1/r^2$ force law that holds together ionic, covalent, and metallic solids. The dipole force on the other hand goes like $1/r^3$.

Molecular solids have lower melting points than other solids, because the bond energy is smaller.

Molecules with a *permanent* electric dipole, e.g., H_2O, can readily make molecular solids (this is sometimes known as hydrogen bonding).

Other molecules can form similar bonds even if their permanent dipole moment is zero, because the instantaneous dipole moment fluctuates at random. In quantum mechanical language, the expectation value of the dipole moment $<d>$ is zero, but the expectation value of $(d^2 - \langle d \rangle^2)^{1/2}$ is nonzero because of the uncertainty principle.

Induced Dipole Moments

Because the dipole moments of atoms fluctuate about their expectation value, nearby molecules influence one another by inducing temporary dipole moments. Analogy: a magnet can attract an unmagnetised piece of iron.

The attractions between molecules that have no permanent electric dipole moment are known as van der Waals forces. This creates surface effects like surface tension, friction, and the cohesion of solids made from nonpolar molecules.

van der Waals forces are quite weak and fall off like approx. $1/r^7$.

Examples: H_2, O_2, CH_4, $GeCl_4$.

Because molecular solids (polar or nonpolar) have a dipole moment that depends on the number of electrons and their separation, the bond energy depends roughly on the total number of electrons per molecule.

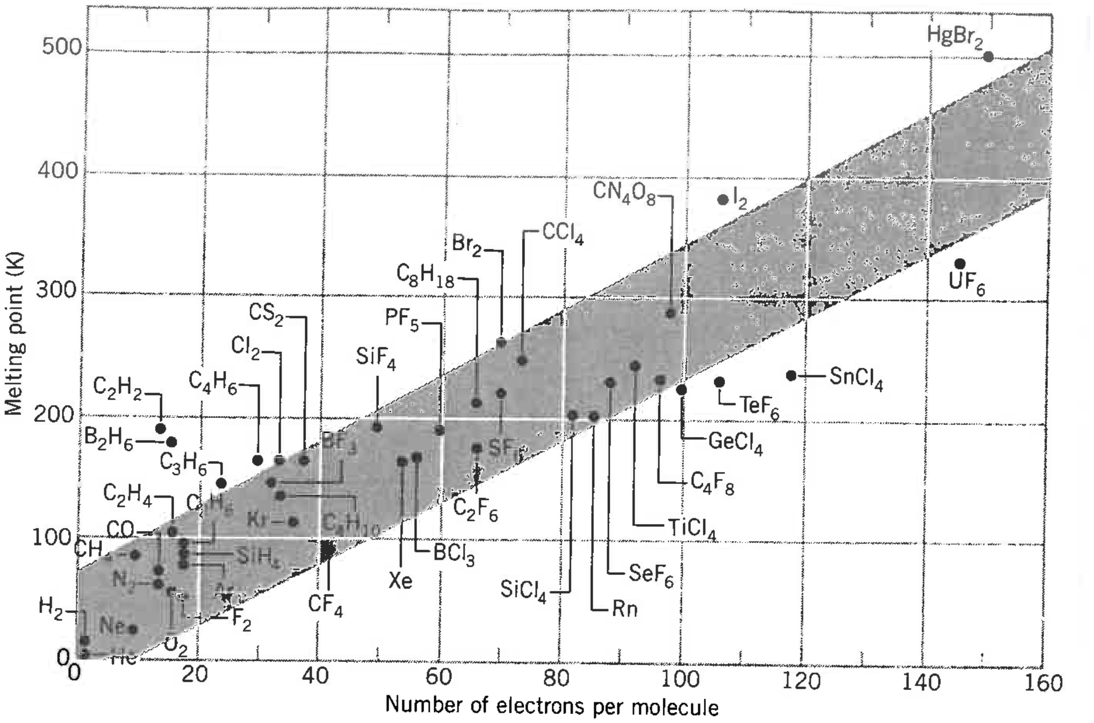


FIGURE 14.15 The melting points of molecular solids depend approximately on the number of electrons per molecule.