Lecture 4: Crystal structures
In this lecture we cover the concepts and formalism used in the description of the structure of perfect crystals. Perfect crystals are regular, with a repeating pattern of atoms.

They break the continuous symmetry of free space, which is translationally invariant (you can displace an arbitrary distance, in any direction, and it looks the same). The consequence of translational invariance in free space is conservation of momentum. [So, you might ask, what happens to conservation of a momentum in a crystal? We'll see!].

Two dimensional crystals
Let us consider two dimensional crystals first, for simplicity and ease of visualisation. All of the ideas and concepts we introduce are then generalised later to three dimensions.

1. **Crystal = lattice + basis**
We first define a lattice of points. These points are equivalent. If you sit on any one of these points and look at where the neighbouring points are, they are always in the same orientation. [Periodic translational invariance].


The two dimensional lattice can be specified mathematically, by defining two vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$; these are called the <u>primitive vectors</u> of the lattice. Pick one of the lattice points as the origin. Then the coordinates of any lattice point are given by $\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, where n_1 and n_2 are integers (positive or negative). There are several ways of doing this eg:
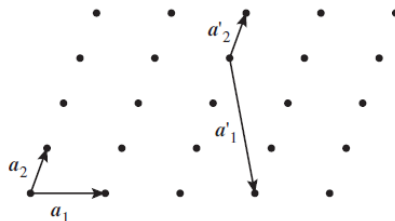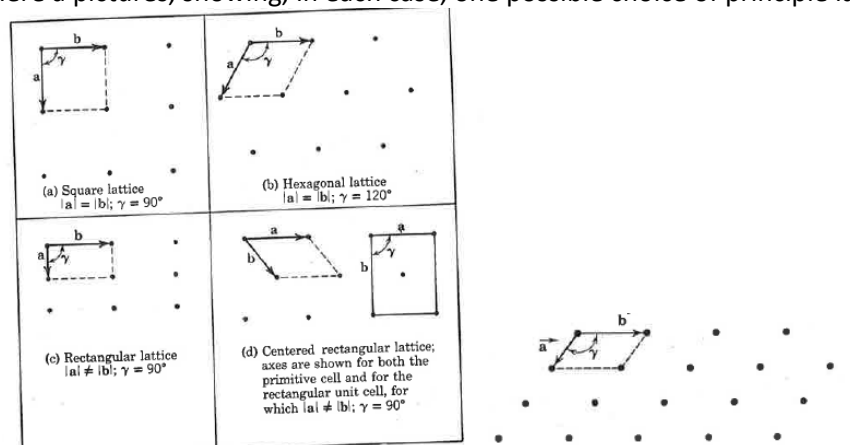

Now associate atoms with each of these points. The simplest thing is to put one atom on each point. That generates a crystal.

On the other hand you could put a group of atoms, oriented in a particular way with respect to each other and relative to the lattice point, at each lattice point. That group of atoms is called the basis. It is described by the set of vectors which specify the position of each atom with respect to a lattice point.
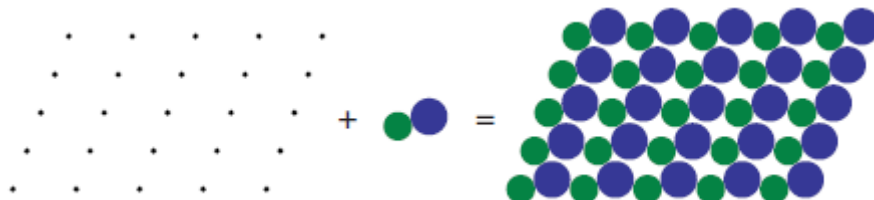
In two dimensions there are just 5 Bravais lattices: square, rectangular, hexagonal, centred rectangular and oblique. Here a pictures, showing, in each case, one possible choice of principle lattice vectors.

(a) Square lattice $|a| = |b|; \gamma = 90°$

(b) Hexagonal lattice $|a| = |b|; \gamma = 120°$

(c) Rectangular lattice $|a| \neq |b|; \gamma = 90°$

(d) Centered rectangular lattice; axes are shown for both the primitive cell and for the rectangular unit cell, for which $|a| \neq |b|; \gamma = 90°$

A physically realized manifestation of a two dimensional crystal is graphene, for which the carbon atoms form a honeycomb structure. The honeycomb structure is not a Bravais lattice. It is not possible to define two primitive vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ such that $\mathbf{r} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ generates all the points of a honeycomb lattice: so a honeycomb lattice is not a Bravais lattice.

You can see this since all points on the honeycomb lattice are not equivalent: P and Q are equivalent but they are not equivalent to R. [The relative positions of the neighbouring points to P and Q are the same and different from the relative positions of the neighbouring points to R}.

The honeycomb crystal must be described/specified by a hexagonal lattice with a two atom basis. [Crystal = lattice + basis]. This structure is discussed in more detail below.
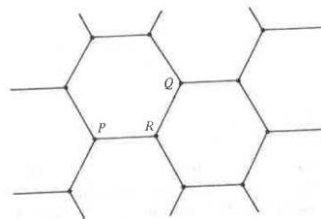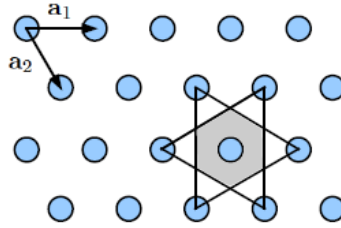

2. Primitive unit cell

Primitive lattice vectors define the primitive unit cell, a parallelogram in two dimensions. This contains one lattice point [since it has four corners and the point on each corner is shared between four unit cells, so contributes ¼].

If one of these parallelograms is repeated, by translating it through space by a lattice vector, you cover all space. There is however no unique primitive unit cell. But the primitive unit cell we have defined is most useful. The area of the primitive unit cell is $A = |\mathbf{a}_1 \times \mathbf{a}_2| = a_1 a_2 \sin\theta$, the usual expression for the area of a parallelogram.

3. Wigner Seitz cell

This is one further and useful way of defining a primitive cell. The concept of a Wigner Seitz cell will turn out to be very important in future, and of deep physical significance. You draw lines connecting a lattice point to each of its neighbours. You draw a perpendicular bisector to each of those lines, which together define a polygon. This polygon (we are still in two dimensions) is called the Wigner Seitz cell. It contains one lattice point, so it is a primitive cell. This is illustrated below for the hexagonal lattice (the lines shown are the perpendicular bisectors):
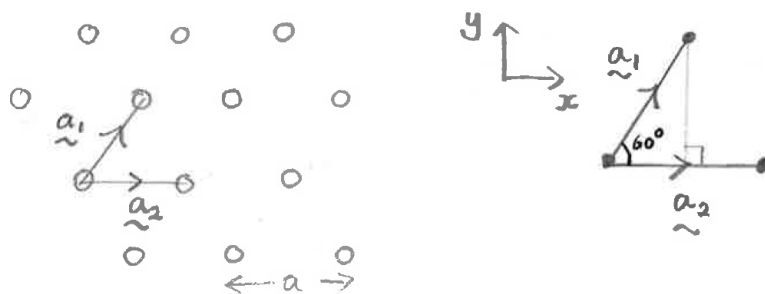
4. Unit cell

In certain lattices it is often convenient to specify a unit cell that is defined by orthogonal unit vectors, which are not primitive vectors. This cell may contain more than one lattice point. [So if the crystal is described by one atom on each lattice point, the unit cell contains more than one atom]. In the example below the rectangular unit cell contains two points, and has twice the area of the primitive unit cell.
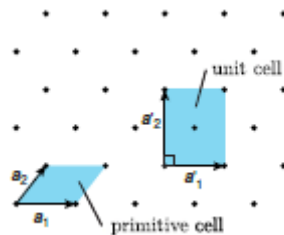
**Examples: Let us contrast the 2D hexagonal and honeycomb crystals in more detail.**

Here is a sketch of a hexagonal lattice. The nearest neighbour separation is *a.* We show a possible choice of primitive lattice vectors, and work out what they are.

$$\underset{\sim}{a_2} = a\hat{x}$$

$$\underset{\sim}{a_1} = \frac{1}{2}a\hat{x} + (a\sin 60°)\hat{y}$$

$$= \frac{1}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$$

The primitive unit cell is the parallelogram defined by the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Consider a crystal formed by placing one atom on each of these lattice points. You can see that the primitive unit cell has one atom, since each of the atoms on the four corners is shared between 4 primitive cells.

Here is a sketch of a honeycomb crystal (physically realized in graphene).
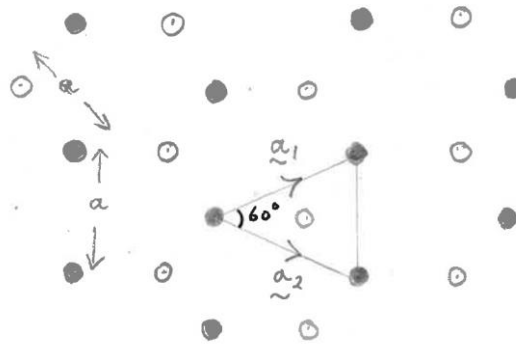
As discussed the honeycomb is not a lattice, as not all points are equivalent. We emphasize this in the crystal by giving the (carbon) atoms placed on the non-equivalent sites different symbols (open and closed circles). You can see that the equivalent sites form a hexagonal lattice; so the honeycomb may be thought of as two interpenetrating hexagonal lattices.

As we have discussed **crystal = lattice + basis**. The sketch shows one possible choice of the primitive lattice vectors. Associated with each point is a basis of two atoms. These two atoms are joined by a basis vector (not shown in sketch). There are three possible choices of basis here: choose one.

We need to do a little simple trigonometry to figure out the primitive lattice vectors. This is done below, for the vectors shown in the sketch above. (The key point is to realize that the angle shown is 60°. The starting point is that the angle between the sides of a hexagon is 120°, and the main triangle you can see here is equilateral, with angles 60°).

$$a_1 = (a + a\cos 60°)\hat{x} + a\sin 60° \hat{y}$$
$$= \frac{3}{2}a\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}$$
$$\frac{1}{2}a(3, \sqrt{3})$$
$$a_2 = \frac{3}{2}a\hat{x} - \frac{\sqrt{3}}{2}a\hat{y}$$

The primitive cell is the parallelogram formed by vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. It contains one lattice point, but two atoms (since we have a two atom basis).

Three dimensional crystals
We now generalise the above discussion to three dimensional lattices and crystals. We consider primitive lattice vectors, primitive unit cell, basis, unit cell to generate some specific common and important structures. [We will not attempt a complete discussion of all possible Bravais lattices]. The structures we consider are: simple cubic, body centred cubic, face centred cubic, hexagonal close packed, the diamond structure. Bear in mind that in all cases there are different perspectives on a given structure, which will be helpful under different circumstances.

In general we define three primitive lattice vectors. Then the position of each point of a Bravais lattice is $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ where $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the primitive lattices vectors n_1, n_2, and n_3 are integers. The volume of the **primitive cell**; $V_p = |\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3|$.

Simple cubic
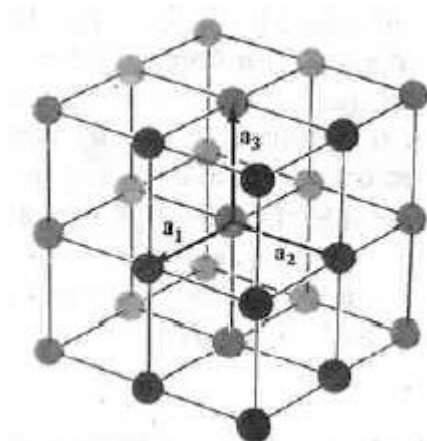
The simple cubic lattice is shown above. It has **primitive vectors** $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, $a\hat{\mathbf{z}}$. Where a is the nearest neighbour separation. The volume of the **primitive cell**; $V_p = |\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3|$. $V_p = a^3$. The primitive cell is a cube of side *a*. A simple cubic crystal is obtained by putting one atom at each lattice point. The **Wigner Seitz primitive cell** is also a cube of side *a*, with one point at the centre. The Wigner-Seitz cell is now (in 3D) constructed by drawing planes normal to the lines connecting a point to each neighbouring point. These planes intersect, and enclose a volume; that volume is Wigner-Seitz cell.

Body centre cubic (bcc)
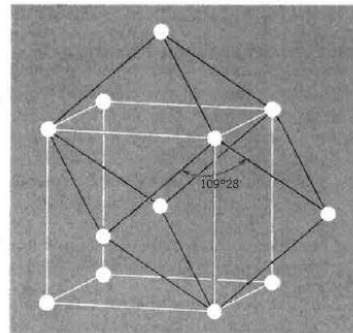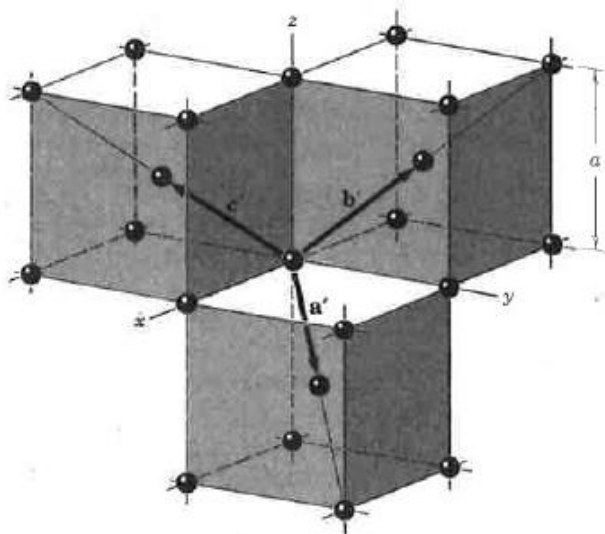
Imagine adding a point at the centre of each cube of the simple cubic lattice. This gives you a bcc lattice. One choice of **primitive lattice vectors** is shown. Take the length of the side of the cube to be a. The vectors are:

$\mathbf{a}_1 = \mathbf{a}' = \frac{a}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}-\hat{\mathbf{z}})$, $\mathbf{a}_2 = \mathbf{b}' = \frac{a}{2}(-\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$, $\mathbf{a}_3 = \mathbf{c}' = \frac{a}{2}(\hat{\mathbf{x}}-\hat{\mathbf{y}}+\hat{\mathbf{z}})$

[An example of an alternative choice would be $a\hat{\mathbf{x}}$, $a\hat{\mathbf{y}}$, $\frac{a}{2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}+\hat{\mathbf{z}})$].

The primitive lattice vectors define a rhombohedron (left picture). This is the **primitive cell**. The **volume of the primitive cell** $V_p = |\mathbf{a}_1.\mathbf{a}_2 \times \mathbf{a}_3|$ is $\frac{1}{2}a^3$ in this case.

A bcc crystal has one atom on each lattice point. The volume per atom is $\frac{1}{2}a^3$.

It is often helpful to think in terms of the cubic unit cell (apart from anything else these has orthogonal sides, unlike the primitive unit cell).

For the bcc crystal the **cubic unit cell** is the cube of side a, with an atom at the centre. It contains two atoms [one at the centre, the eight corner atoms are each shared by eight cubes so each contributes 1/8. $1 + \frac{1}{8} \times 8 = 2$]. The volume of the cube is a^3, so the volume per atom is $\frac{1}{2}a^3$, as we established just above.

Thus, since **crystal = lattice + basis** you can generate a bcc crystal by a simple cubic lattice and a two atom basis; one atom at a corner and the other at a body centre eg $a(0,0,0)$ and $a(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Thinking of the bcc lattice like this is often useful (eg when we introduce the idea of *structure factor* in x-ray diffraction). The bcc lattice can also be thought of as two interpenetrating simple cubic lattices, with relative displacement $a(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

Last but not least here is an image of the **Wigner Seitz primitive cell** of the bcc lattice. It is a truncated octahedron. The atom at the body centre of the cube has 8 nearest neighbours, at the 8 corners of the cube. Draw lines from the centre of the cube to the 8 corners. Drop a plane perpendicular to each line, halfway along each line. Draw lines from the body centre to the body centre of neighbouring cubes, with common faces (there are four). Drop a plane perpendicular to each line, halfway along each line. The intersection of these planes defines the **Wigner Seitz primitive cell** of the bcc lattice, which is a truncated octahedron.

[Aside: This object plays a key role in understanding how electrons behave in a metallic fcc crystal. Yes I did say fcc, not bcc!]
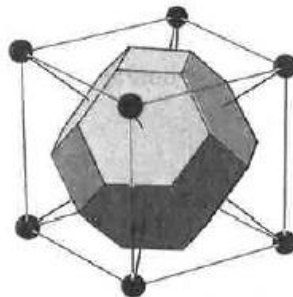
Face centred cubic (fcc)
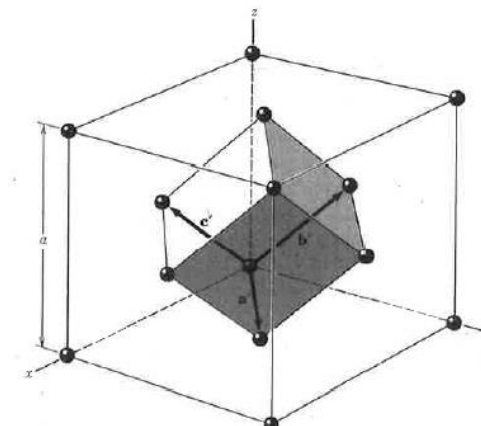
Imagine adding a point at the centre of each face of the simple cubic lattice. This gives you a fcc lattice. One choice of **primitive lattice vectors** is shown. Take the length of the side of the cube to be a. The vectors are:

$$\mathbf{a}_1 = \mathbf{a}' = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}) \ , \ \mathbf{a}_2 = \mathbf{b}' = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \ , \ \mathbf{a}_3 = \mathbf{c}' = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}})$$

The primitive lattice vectors define the rhombohedron shown. This is the **primitive cell**. The **volume of the primitive cell** $V_p = |\mathbf{a}_1 . \mathbf{a}_2 \times \mathbf{a}_3|$ is $\frac{1}{4}a^3$ in this case.

A fcc crystal has one atom on each lattice point. The volume per atom is $\frac{1}{4}a^3$.

It is often helpful to think in terms of the cubic unit cell (apart from anything else these has orthogonal sides, unlike the primitive unit cell).

For the fcc crystal the **cubic unit cell** is the cube of side *a,* with an atom at the centre of each face. It contains four atoms [the eight corner atoms are each shared by eight cubes so each contributes 1/8; the atoms on each of the six faces of the cube are shared by two cubes so each contributes 1/2. $\frac{1}{8} \times 8 + \frac{1}{2} 6 = 4$]. The volume of the cube is a^3 , so the volume per atom is $\frac{1}{4} a^3$, as we established just above.

Since **crystal = lattice + basis** you could generate a fcc crystal by a simple cubic lattice and a four atom basis; one atom at a corner and the other at a body centre eg $a(0,0,0), a(0,\frac{1}{2},\frac{1}{2}), a(\frac{1}{2},0,\frac{1}{2}),$ $a(\frac{1}{2},\frac{1}{2},0)$. Thinking of the fcc lattice like this is often useful (eg when we introduce the idea of *structure factor* in x-ray diffraction).

Last but not least here is an image of the **Wigner Seitz primitive cell** of the fcc lattice. It is a rhombic dodecahedron. [Aside: This object plays a key role in understanding how electrons behave in a metallic bcc crystal. Yes I did say bcc, not fcc!]

As previously discussed in lecture 3, the fcc lattice is close packed. The highest density plane is (111).
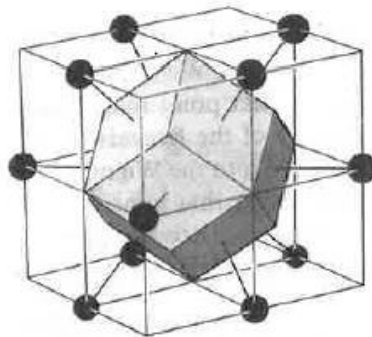

Hexagonal closed packed (hcp)

The hcp lattice is not a Bravais lattice. Let us introduce it by first considering the **simple hexagonal lattice**, shown immediately below.
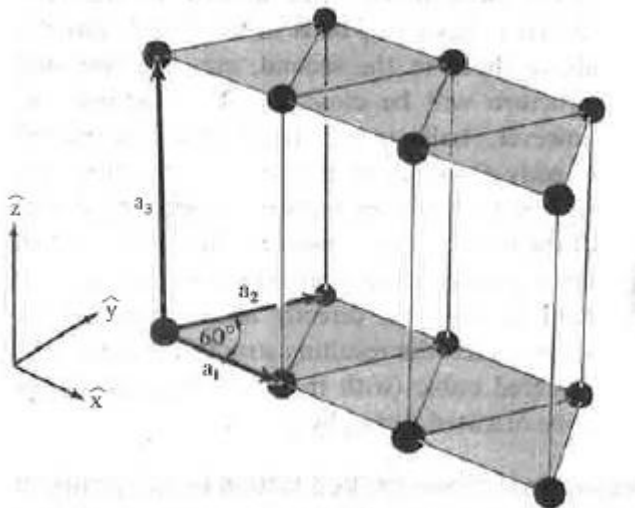
This lattice is generated by placing two dimensional hexagonal lattices vertically above each other. So the in-plane primitive lattice vectors are as discussed previously. In the notation of the picture above the primitive lattice vectors are: $\mathbf{a}_1 = a\hat{\mathbf{x}}$ $\mathbf{a}_2 = \frac{a}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}a}{2}\hat{\mathbf{y}}$ $\mathbf{a}_3 = c\hat{\mathbf{z}}$, where *a* is the nearest neighbour separation in plane and *c* is the distance between planes.

The hexagonal close packed structure, discussed in lecture 3, is shown below.
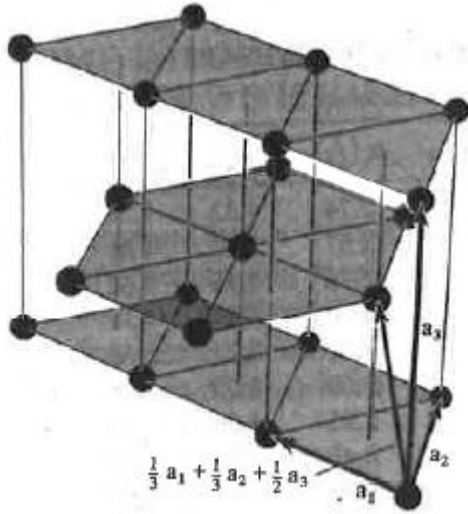
$$\tfrac{1}{3}\mathbf{a}_1 + \tfrac{1}{3}\mathbf{a}_2 + \tfrac{1}{2}\mathbf{a}_3$$

2D hexagonal layers are stacked in an ABABA…..sequence.

Since **crystal = lattice + basis** the **hcp structure it is formed of a simple hexagonal lattice with a two atom basis.** A possible basis vector $\tfrac{1}{3}\mathbf{a}_1 + \tfrac{1}{3}\mathbf{a}_2 + \tfrac{1}{2}\mathbf{a}_3$ is shown, with the upper atom situated vertically above the centre of the triangle below.

Hcp can be thought of as two interpenetrating simple hexagonal lattices. Hcp is the second closed packed lattice (the other being fcc which has 2D hexagonal layers packed in an ABCABCA…..sequence.

For close packing $c = \sqrt{\dfrac{8}{3}} a$.

Diamond structure

$$\frac{a}{4}(\hat{x} + \hat{y} + \hat{z})$$
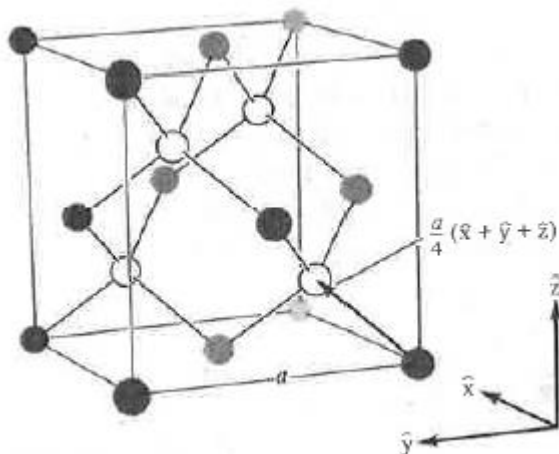
This structure is important, as discussed in lecture 3. The drawing above emphasizes the tetrahedral covalent bonds that are responsible for it.

Since **crystal = lattice + basis** we see that it is a fcc lattice with a two atom basis. A possible basis vector is shown. Equivalently it can be thought of as two interpenetrating fcc lattices displaced by this vector. You can see that the shaded atoms form an fcc structure.

Carbon, silicon and germanium have this structure.

Diamond is one crystalline form (allotrope) of carbon. Another is graphite. Graphite consists of graphene sheets (each with a honeycomb structure) stacked in an ABABA…. sequence as shown.
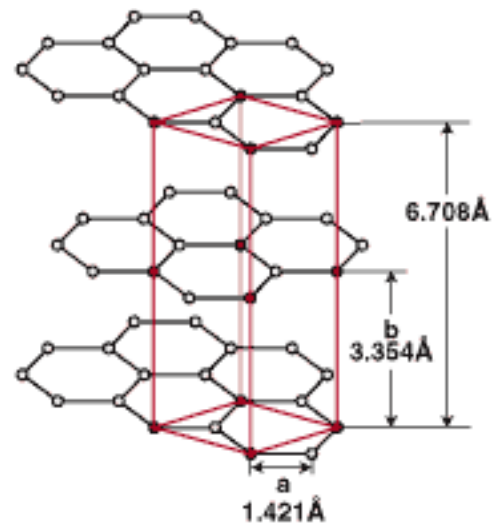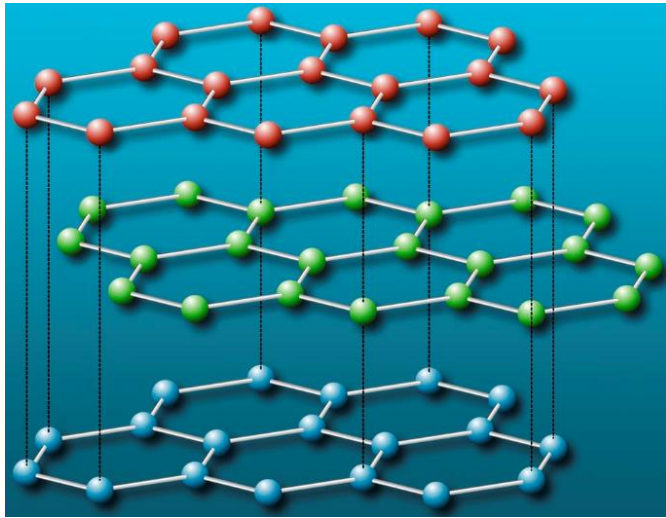
Diamond is hard and strong, because of the covalent bonding. In graphite the bonding is strong within the graphene sheets, but weak between the graphene sheets. This allows a single graphene sheet to be peeled off (exfoliated) from bulk graphite (as first demonstrated by Novoselov and Geim, Nobel Prize 2010).