# CRYSTAL STRUCTURE PART II

MILLER INDICES

In Solid State Physics, it is important to be able to specify a plane or a set of planes in the crystal. This is normally done by using the Miller indices. The use and definition of these Miller indices are shown in fig. 9.

Figure 9 This plane intercepts the a, b, c axes at 3a, 2b, 2c. The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. The smallest three integers having the same ratio are 2, 3, 3, and thus the Miller indices of the plane are (233).
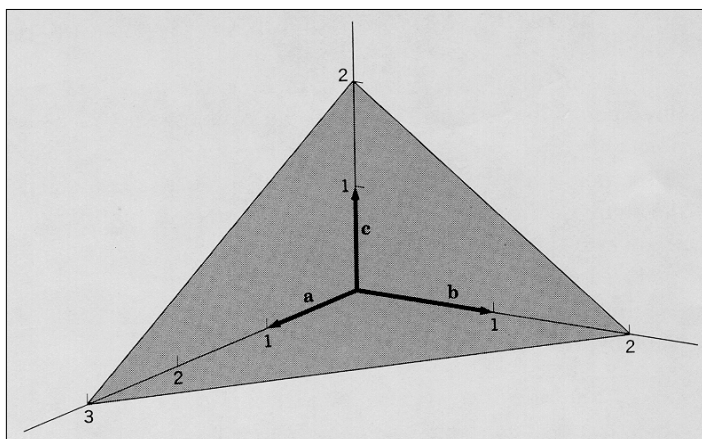
The translation vectors of the convenient unit cell, e.g. the cube edges of the fcc structure (which is not primitive) are used for the coordinate axes. The plane shown intercepts at 3, 2, 2 on the axes. As, by definition, these three points are not co-linear, therefore they can adequately define the plane. As we shall see later, the reciprocal of these numbers are more useful. First, reciprocate these numbers thus getting 1/3, 1/2, 1/2. Miller indices are the smallest integers having the same ratio as these. The Miller indices of this plane is

(hkl) = (2,3,3)

By this definition, if the plane cuts an axis at infinity, the corresponding index will be zero. By convention, if the intercept has a negative value, the corresponding index is also negative. A minus sign is normally placed above that index in the bracket.

Miller indices are also used to denote a set of planes which are parallel. For instance, the plane (200) is parallel to (100). The former cuts the x-axis at $\bar{a}/2$. Also by symmetry, many sets of planes, e.g. all the faces of a cube, may be represented by a single set of Miller indices (100). In this case the curly bracket is used, hence {100}. In other words the {100} automatically includes the planes (100), (010) and (001).

The direction of any general vector can also be expressed in terms of a set of indices h, k and l. These indices are the smallest integers that are proportional to the components of the vectors along the axes of the crystal (same as the translation vectors of the unit cell). Unlike the Miller indices above, these integers used for defining the direction of the general vector <u>are not</u> derived from the reciprocal. To distinguish from the Miller indices for planes, i.e. (hkl) or {hkl}, the direction indices are enclosed in square brackets, hence [hkl]. Also the indices [hkl] are used to denote many sets of equivalent directions similar to the plane designations above.

For a cubic system, it can be shown that the vector [hkl] is normal to the planes defined by the Miller indices {hkl}. This fact happens to be extremely useful in the analysis of x-ray diffraction.

Finally, the position of basis or atoms in the conventional cell is often expressed in terms of the axes defining the cell. For instance, the position of the body-centred atoms is 1/2, 1/2, 1/2 and the face-centred atom is 1/2, 1/2, 0.

REAL CRYSTAL STRUCTURES

We have already looked at the seven major groups of lattice systems out of which the cubic and the hexagonal systems are most common in Solid State Physics. Here we shall list a number of very common structures and their variations:

SODIUM CHLORIDE

NaCl crystals are of the fcc type. The lattice is fcc. As we have already discussed, the primitive cell is a special rhombohedron four of which may be fitted into the fcc conventional cell. In terms of the fcc coordinates, the four lattice points making up the rhombohedron are the:

$$\text{site A} = 0\,0\,0, \tfrac{1}{2}\,\tfrac{1}{2}\,0, \tfrac{1}{2}\,0\,\tfrac{1}{2}, 0\,\tfrac{1}{2}\,\tfrac{1}{2} \tag{4}$$

The first point is the origin at a cube corner and the other three points are three adjacent face centres. In NaCl, each molecule has two different ions, namely the sodium and the chlorine. For any given lattice point, say the origin 000, we cannot have both the Na and the Cl ions at the same position. The Cl ion is displaced by a certain distance.

In fact, another way to look at the structure is to regard the Cl ions to have their own fcc sub-lattice. The Cl sub-lattice is displaced by one half of the body diagonal of the Na sub-lattice defined in (4). Thus here we have two <u>inter-locking</u> fcc sub-lattices. The four sub-lattice points for the Cl ions forming the primitive cell are:

$$\text{site B} = \tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}, 1\,1\,\tfrac{1}{2}, 1\,\tfrac{1}{2}\,1, \tfrac{1}{2}\,1\,1 \tag{5}$$

Thus, for the Cl sub-lattice, the reference point is no longer at the origin. Instead, it is at the body centre of the Na sub-lattice. Of course, the picture would be identical if we were to regard the Cl sub-system as the starting point with Cl at the origin. Looking at the Na fcc, we now have Cl ions also at the mid point of each cube edge as indicated in (5).

Here the nearest-neighbour distance is that between the Cl and the Na neighbours. If we take the Cl ion at the cube centre, the nearest Na ions are at the cube faces. Therefore, the number of nearest neighbours is six. Apart from NaCl, other crystals having the sodium chloride structure include KCl, KBr, LiH and PbS. Note that in practice there are very few crystals with the sc structure.

CESIUM CHLORIDE

The bravais lattice of CsCl is sc. This means that both the Cs and the Cl sub-lattices are sc. Again, like the NaCl structure, the Cl frame is displaced by one half of the body diagonal of the conventional cubic cell. Here the nearest neighbour distance is that between the Cl at the centre of the cube and the Cs ion at one of the cube corners. Thus there are eight nearest neighbours. Other compounds having the CsCl structure include CuZn (beta brass), and AgMg.

HEXAGONAL CLOSE-PACKED

Essentially, the hexagonal close-packed (hcp) structure is a form of the hexagonal lattice type. It has a six-fold symmetry. The basis contains two ions. The second ion comes from a layer between the identical layers forming the hexagon.

Fig. 10a shows how identical hard spheres may be arranged in a plane to minimise the interstitial space.
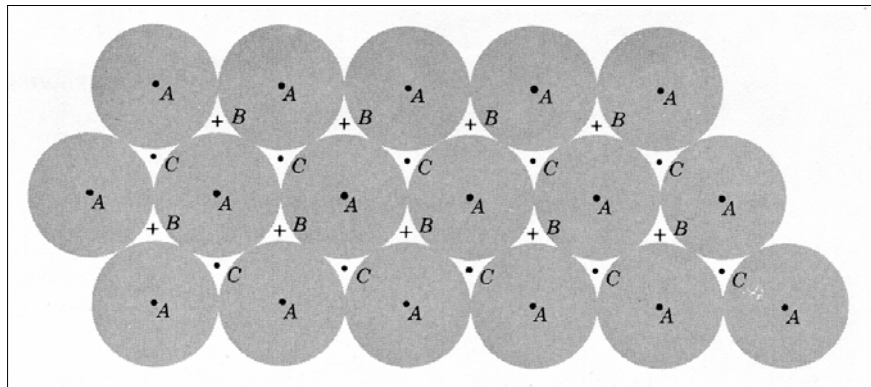

Fig. 10a A close-packed layer of spheres is shown, with centers at points marked *A*. A second and identical layer of spheres can be placed over this, with centers over the points marked *B* (or, equivalently, over the points marked *C*). If the second layer goes in over *B*, there are two nonequivalent choices for a third layer. It can go in over *A* or over *C*. If it goes in over *A* the sequence is *ABABAB…* and the structure is hexagonal close-packed. If the third layer goes in over *C* the sequence is *ABCABCABC…* and the structure is face-centered cubic; the plane is a (111) plane, as in Fig. 10b.

We can see that there are six spheres surrounding any given sphere. The centres are marked by A. This will immediately give us the six-fold hexagonal symmetry. There are now holes in the plane defining the space that cannot be occupied by any sphere in the same plane. The separation of these holes is smaller than the diameter of the hard spheres. If we are to pack another layer of spheres in a new plane above the first, we can only put spheres in half of these holes. These holes belong to the groups B or C. Thus, there are now two ways of forming the second layer. This layer is identical with the first but with the sphere centres displaced. By symmetry, the choice of either B or C will not change the structure as B and C for this purpose are equivalent.

Suppose that we have chosen the holes at B. The next step is to form a third layer of such close-packed spheres. Here we either pack the spheres over the holes C that did not get filled by the second layer or we can put the spheres directly over A, the centres of the spheres in the first layer.

The first choice will give us the packing sequence <u>ABCABC...</u> It can be shown that these sphere layers are corresponding to the {111} planes of the fcc structure. The second packing technique will give us the sequence <u>ABABAB…</u> This arrangement gives us the hcp. Both of these structures give a very high packing volume. The proportion of volume occupied by the spheres is 0.74. The structures of the fcc and the hcp as viewed from the close packing pictures are shown respectively in fig. 10b and 10c.
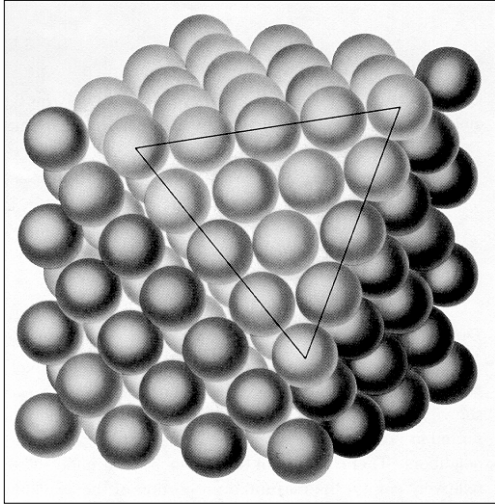
Fig. 10b The fcc structure with one corner sliced off to expose a (111) plane. The (111) planes are close-packed layers of spheres. (After W. G. Moffatt, G. W. Pearsall, and J. Wulff, *Structure,* Vol. 1 of *Structure and properties of materials*, Wiley, 1964.)

Fig. 10c The hexagonal close-packed structure. The atom positions in this structure do not constitute a space lattice. The space lattice is simple hexagonal with a basis of two identical atoms associated with each lattice point.
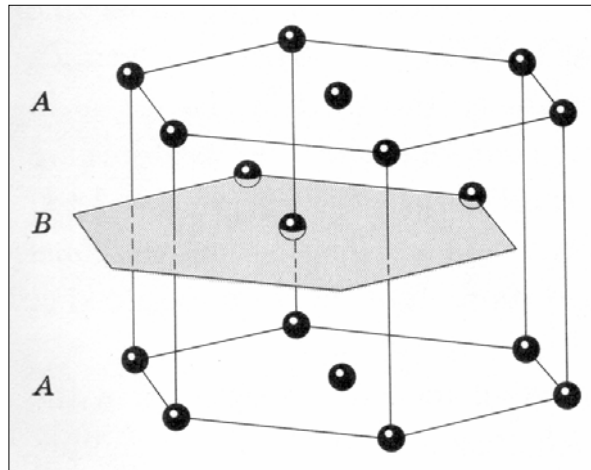
Looking at the hexagon, the primitive cell concerned occupies one-third of the figure, i.e. it takes two of the six outside edges as shown in fig. 10d.
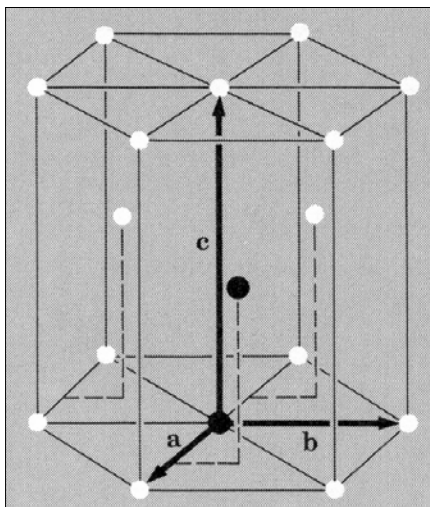

Fig. 10d The primitive cell has $a = b$, with an included angle of 120°. The c axis is normal to the plane of a and b. In ideal hcp we have $c = 1.633\,a$. The two atoms of one basis are shown as solid in the figure. One atom of the basis is at the origin 000; the other atom is at $\dfrac{2}{3}\ \dfrac{1}{3}\ \dfrac{1}{2}$, which means at

$$\vec{r} = \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{2}\vec{c} \ .$$

The primitive vectors $\vec{a}$ and $\vec{b}$ are equal and the angle between them is 120 degrees. We have already dealt with this earlier. The $\vec{c}$ axis is normal to the $\vec{a}\ \vec{b}$ plane. In the

ideal hcp, i.e. when the spheres are hard and touching the ratio of c/a is 1.633. There are two atoms for the primitive basis. One is at the origin 000 and the second at 2/3, 1/3, 1/2, see fig. 10 d. It should be noted that many so-called hcp crystals do not have the ideal c/a value. Many values are smaller than 1.633 but some are larger. By convention, these crystals are still referred to as hcp. Note also that both the fcc and the hcp structures have the same number of nearest neighbours, namely twelve.

DIAMOND

This is a very interesting structure and is commonly found in covalent bonding material such as Si and Ge. The building block of diamond is a tetrahedron which is made up of four equilateral triangles. The reference atom is at the centre of the tetrahedron and this atom has four equal 109 degree 26 minute angle covalent bonds connecting it to each of the four atoms at the apices of the figure.

These tetrahedral building blocks can be arranged in two ways. The first is the fcc cubic structure and the second is the hexagonal structure. The stacking variations of these two types are similar to those discussed in the fcc/hcp structures in the previous section. In some substances such as ZnS, the two forms exist and the phase transition occurs at a very high temperature. The former is the most common form of diamond and we shall confine our discussions to the fcc structure here.

In terms of the fcc cube, the primitive vectors connect the origin to the adjacent face centres as defined in the caption of fig. 7. These three vectors define the 60 degree special rhombohedron. This is the fcc diamond primitive cell. It may be proved that the volume of this cell is 1/4 of the cubic volume a^3. The tetrahedral volume containing the four covalent bonds is at one end of this primitive rhombohedron and is defined by the same set of equal primitive vectors in fig. 7. Therefore, the tetrahedron is not the primitive cell. It can be proved that the body diagonal of the rhombohedral primitive cell is the same as that of the fcc. Thus, apart from the carbon atom at the origin of the rhombohedron, the only other atom belonging to the same basis is at 1/4 of the body diagonal. In other words, the primitive cell is empty at the far end of the body diagonal. It is left to the student to show that the volume of the tetrahedron is 1/6 of that of the primitive rhombohedron. Referring to the fcc frame, the basis has two atoms, one at 000 and the second at 1/4 1/4 1/4. Thus the second atom is at a quarter of the way along the body diagonal of the fcc. The situation is very similar to the NaCl structure. Here the second atom is of the same species and the displacement of the second sub-lattice is only one quarter of the body diagonal as opposed to one half of the body diagonal in the NaCl structure. In this fcc form there are four primitive cells packed in the fcc cube. According to this picture, only 0.34 of the total volume is occupied by hard spheres and thus the diamond lattice is relatively empty.

In fig. 11, the carbon atoms in an fcc conventional cell are projected onto one cube face in the plane of the paper.
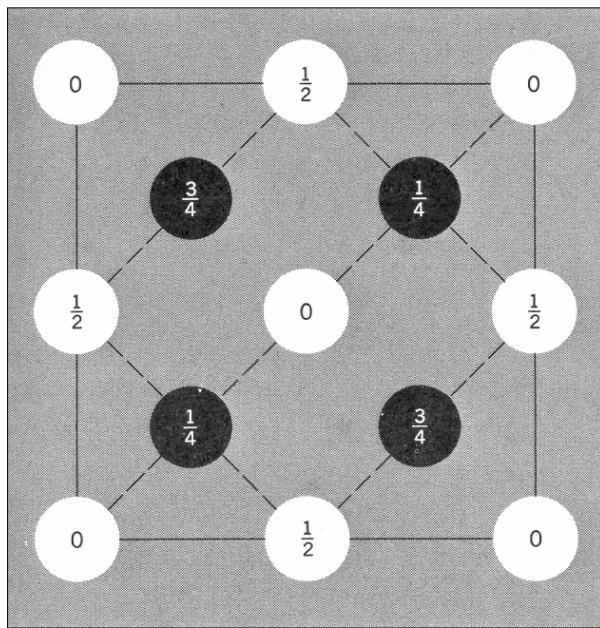
Figure 11 Atomic positions in the cubic cell of the diamond structure projected on a cube face; fractions denote height above the base in units of a cube edge. The points at 0 and $\frac{1}{2}$ are on the fcc lattice; those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced among the body diagonal by one-fourth of its length. With a fcc space lattice, the basis consists of two identical atoms at 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

Taking unity as the cube edge, the numbers denote the distances above the projected face. The 0 and 1/2 numbers are for the cube corner and face centre atoms of the first sub-lattice while the numbers 1/4 and 3/4 are those from the second sub-lattice. This will give you a good idea of the atom distribution in such a structure. To just see how empty the lattice actually is, you can see that the packing sequence along the body diagonal is C C v v C C v v C C..., where C and v denote the carbon atom and the vacancy respectively. Fig. 12 shows the actual tetrahedral bonds in diamond.
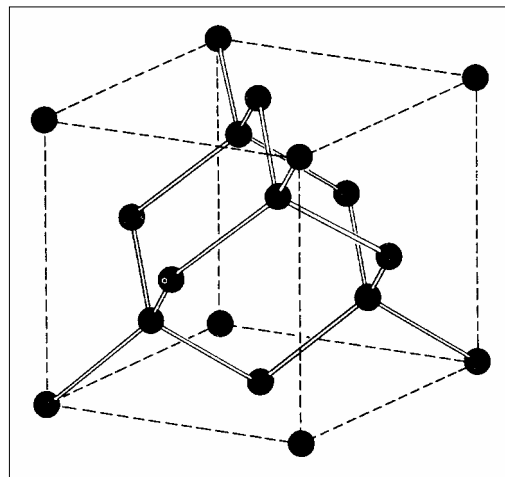

Figure 12 Crystal structure of diamond, showing the tetrahedral bond arrangement.

At first sight, one might tend to think that it might be possible to find a cell containing only one atom but this is not possible. The diatomic rhombohedral cell is definitely the primitive cell. Thus the primitive basis has two atoms. This is most interesting. As we shall see in the analysis of phonons a diatomic basis involves extra vibrational modes.

ZINC BLENDE STRUCTURE

This structure is also known as the cubic zinc sulphide structure. It is essentially the same as the fcc diamond structure except that the atoms at the second

sub-lattice are now of a different species. For ZnS for instance, the Zn ion is at 000 and the S ion at 1/4 1/4 1/4. This is shown in fig. 13. Many compound semiconductors such as InSb and InP have this zinc blende structure.
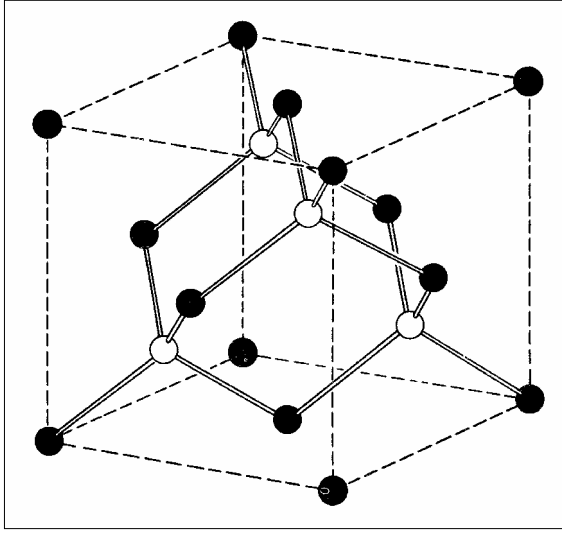

Figure 13 Crystal structure of cubic zinc sulfide.

RECIPROCAL LATTICE

We are going to introduce the concept of the reciprocal lattice. For the time being we can take this to be a mathematical formulation. We shall show in the diffraction theory how useful the reciprocal lattice is in the study of crystal structure. In a diffraction experiment, e.g. x-ray scattering, the results obtained give direct information on the reciprocal lattice rather than the "real" lattice that we studied earlier. Naturally, if we know the reciprocal lattice, it is a trivial matter to work out the "real" lattice.

In (1), we introduced the concept of the "real" primitive vector. In fact each point in the "real" lattice is corresponding to another point in the reciprocal lattice $\vec{G}$. Thus in a similar manner, we can express $\vec{G}$ in terms of its primitive components, thus:

$$\vec{G} = h\vec{A} + k\vec{B} + l\vec{C} \tag{6}$$

where h, k and l are integers. The relationship of $\vec{A}$ and $\vec{a}$ etc. is as follows:

$$\vec{A} = (2\pi)\vec{b} \times \vec{c} / [\vec{a}\vec{b}\vec{c}] \tag{7}$$

$$\vec{B} = (2\pi)\vec{c} \times \vec{a} / [\vec{a}\vec{b}\vec{c}] \tag{8}$$

$$\vec{C} = (2\pi)\vec{a} \times \vec{b} / [\vec{a}\vec{b}\vec{c}] \tag{9}$$

where the denominator in each equation is the dot scalar product of the three real primitive vectors. Note that this defines the volume of the real parallelepiped. There is a one-to-one correspondence between the real lattice $\vec{r}$ and the reciprocal lattice $\vec{G}$. From these equations we observe the following properties:

1. The vector $\vec{A}$ is normal to both $\vec{b}$ and $\vec{c}$. This is particularly simple for a cubic system in which case we can see that the reciprocal lattice is also a cubic system.

2. For any component, say $\vec{A}$, we have the relations:

$$\vec{a} \cdot \vec{A} = 2\pi \qquad\qquad\qquad\qquad\qquad\qquad (10)$$
$$\vec{b} \cdot \vec{A} = \vec{c} \cdot \vec{A} = 0 \qquad\qquad\qquad\qquad\qquad (11)$$

In fact, (10) and (11) are sometimes used to define the primitive reciprocal lattice vectors.

THE BRILLOUIN ZONE

We have already learnt how the Wigner Seitz cell is defined in the real lattice. The volume of this is equal to that of the primitive parallelepiped. In fact such a construction is also adopted in the reciprocal lattice space and the space so defined is called the first Brillouin zone. The physical significance of this will be apparent in x-ray diffraction and phonons.

Definition: The first Brillouin zone is the Wigner Seitz cell in the reciprocal lattice space. It is formed by constructing perpendicular bisectors for all the reciprocal vectors radiating from the centre of the cell.