Surface Structure and Reconstruction

Classification of solids

Crystal structure

Unit cell

Bravais lattices

Surface Structure of Metals

- At the microscopic level, most materials can be considered as a collection or aggregate of single crystal crystallites. The surface chemistry of the material as a whole is therefore crucially dependent upon the nature and type of surfaces exposed on these crystallites. *In principle*, therefore, we can understand the surface properties of any material if we

- know the amount of each type of surface exposed , and

- have detailed knowledge of the properties of each and every type of surface plane.

- It is therefore vitally important that we can independently study different, well-defined surfaces. The most commonly employed technique, is to prepare macroscopic (i.e. size ~ cm) single crystals of metals and then to deliberately cut-them in a way which exposes a large area of the specific surface of interest.

Most metals only exist in one bulk structural form - the most common metallic crystal structures being :

bcc: body-centred cubic
fcc: face-centred cubic
hcp: hexagonal close packed

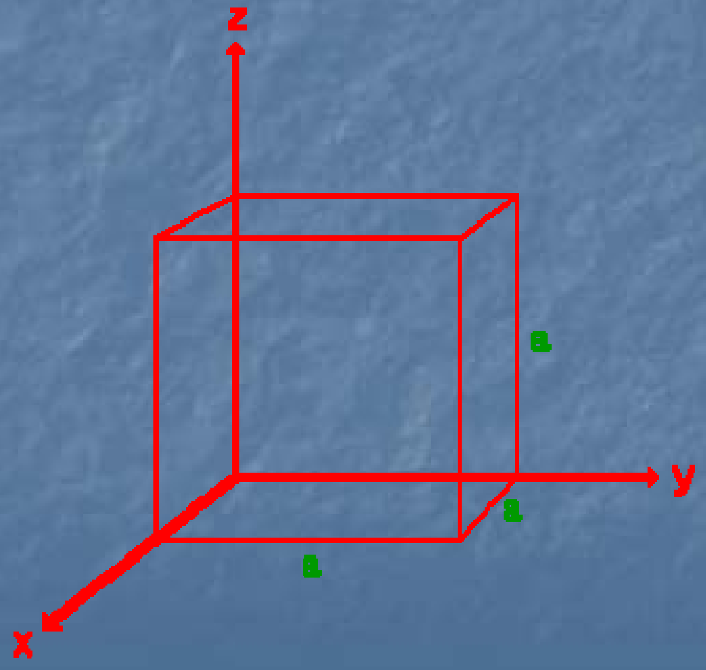
For each of these crystal systems, there are in principle an infinite number of possible surfaces which can be exposed. In practice, however, only a limited number of planes (predominantly the so-called "low-index" surfaces) are found to exist in any significant amount and we can concentrate our attention on these surfaces. Furthermore, it is possible to predict the ideal atomic arrangement at a given surface of a particular metal by considering how the bulk structure is intersected by the surface.

Miller Indexes

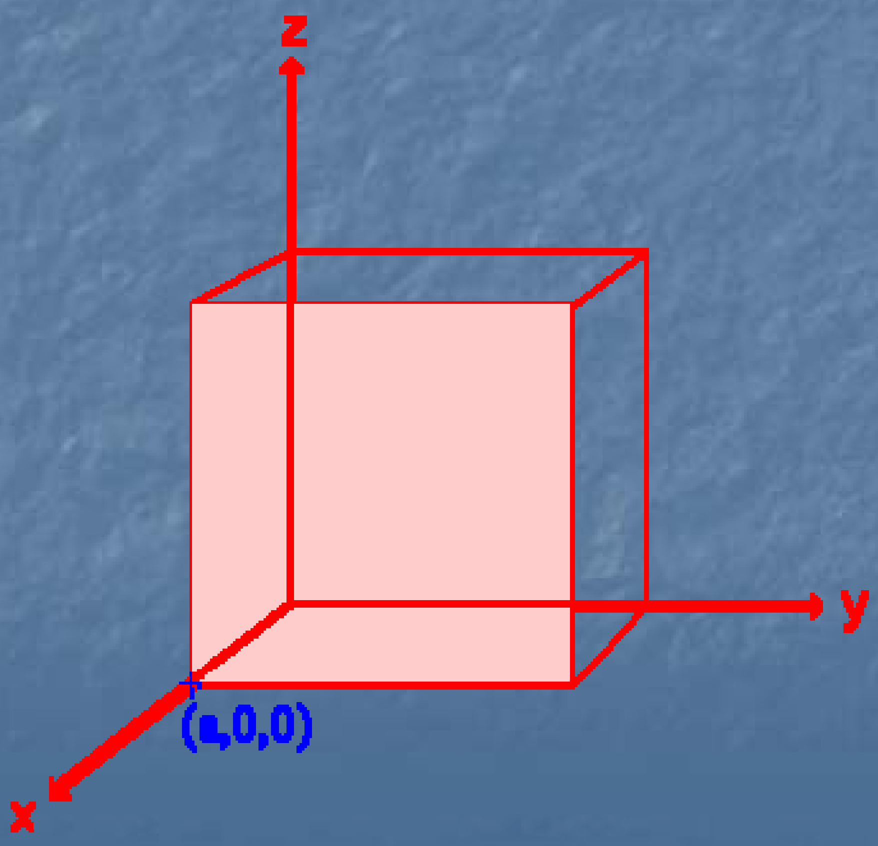
The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid.

The application of a set of rules leads to the assignment of the Miller Indexes , (*hkl*) ; a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the Miller Indexes is a simplified one and only a **cubic** crystal system (one having a cubic unit cell with dimensions *a* x *a* x *a*) will be considered.



The procedure is most easily illustrated using an example so we will first consider the following surface/plane:



Step 1 : *Identify the intercepts on the x- , y- and z- axes.*

In this case the intercept on the x-axis is at $x = a$ (at the point (a,0,0)), but the surface is parallel to the y- and z-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the x- , y- and z-axes are thus

Intercepts : a , ∞, ∞

Step 2 : Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (*x*,*y*,*z*) in a unit cell of dimensions *a* x *b* x *c* has fractional co-ordinates of (*x*/*a* , *y*/*b* , *z*/*c*). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant , *a* . This gives

Fractional Intercepts : *a/a* , ∞ */a*, ∞ */a* *i.e.* *1* , ∞, ∞

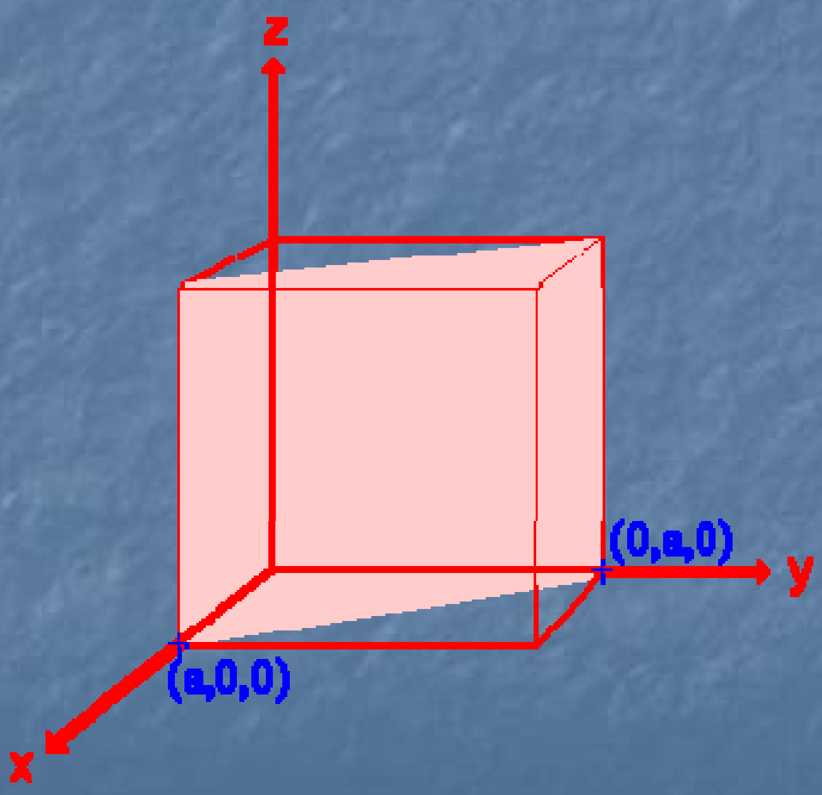
Step 3 : Take the reciprocals of the fractional intercepts

This final manipulation generates the Miller Indexes which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indexes are also enclosed within standard brackets (….) when one is specifying a unique surface such as that being considered here.

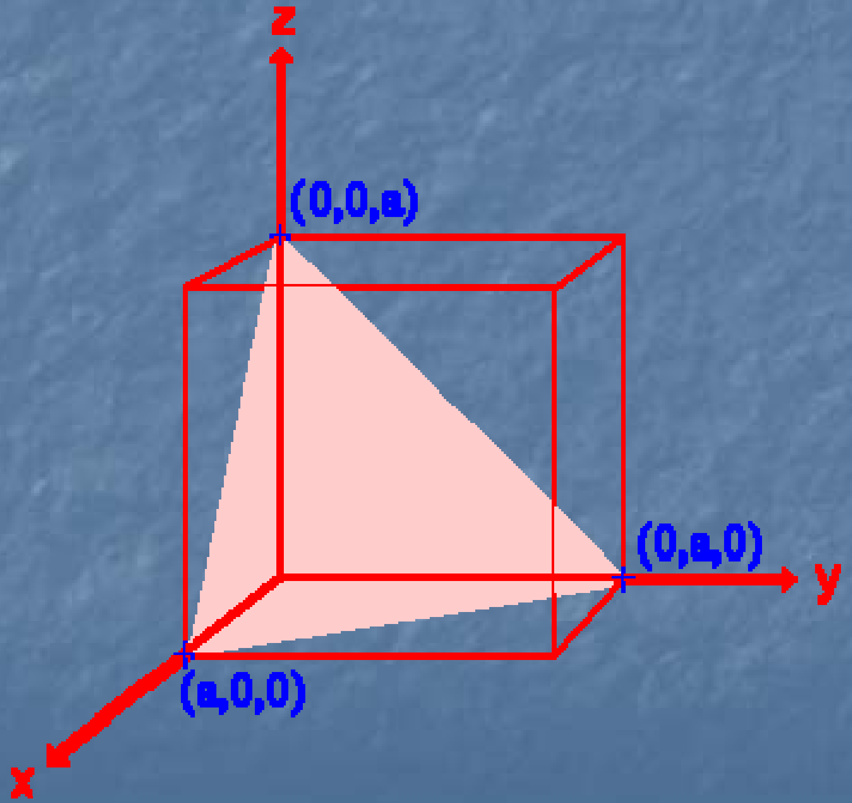
The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding Miller Indexes : (100)

So the surface/plane illustrated is the (100) plane of the cubic crystal.

The (110) surface

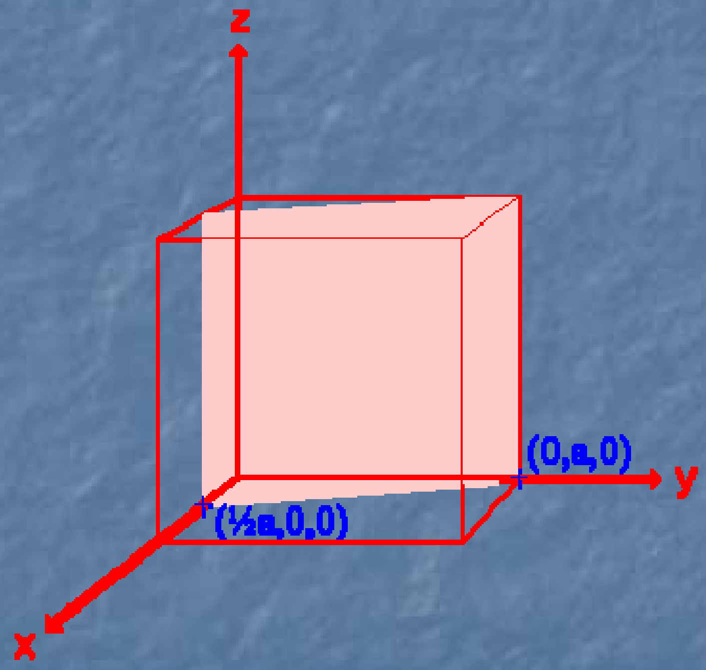


The (111) surface

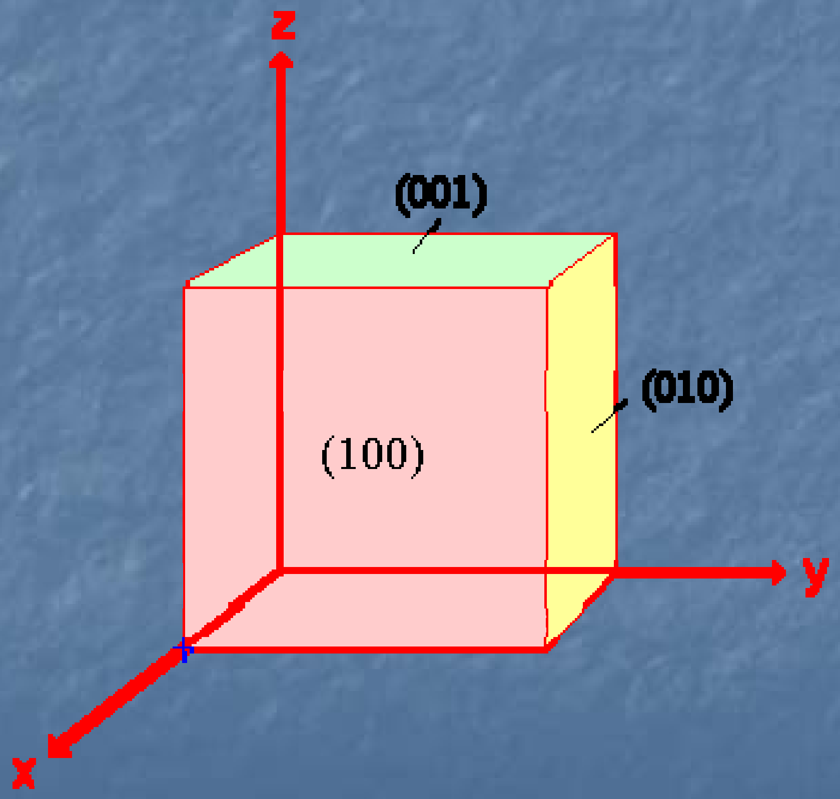


The (100), (110) and (111) surfaces considered above are the so-called low index surfaces of a cubic crystal system (the "low" refers to the Miller indexes being small numbers - 0 or 1 in this case). These surfaces have a particular importance but there an infinite number of other planes that may be defined using Miller index notation.

The (210) surface



What are symmetry-equivalent surfaces ?



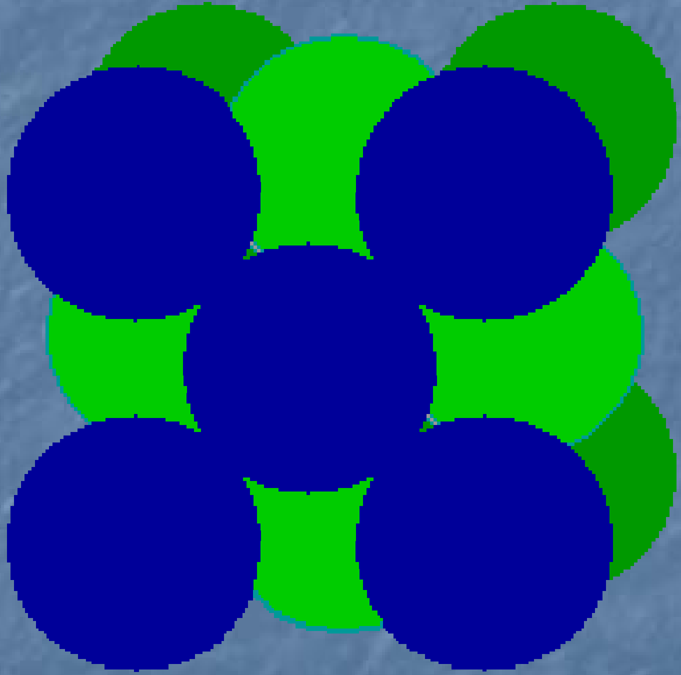
Surface Structure of fcc Metals

Many of the technologically most important metals possess the *fcc* structure : for example the catalytically important precious metals (Pt, Rh, Pd) all exhibit an *fcc* structure.

The low index faces of this system are the most commonly studied of surfaces : as we shall see they exhibit a range of

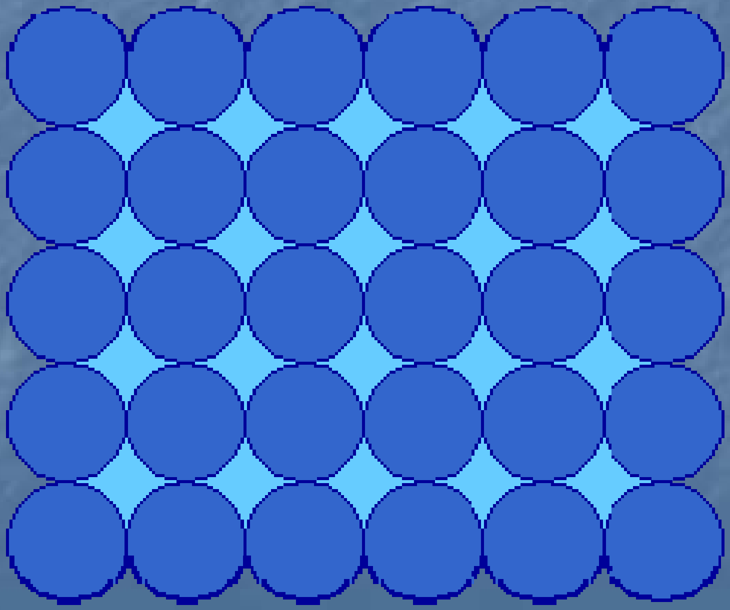
Surface symmetry
Surface atom coordination
Surface reactivity

The fcc (100) surface



The diagram below shows the conventional birds-eye view of the (100) surface - this is obtained by rotating the preceding diagram through 45° to give a view which emphasises the 4-fold (rotational) symmetry of the surface

layer atom

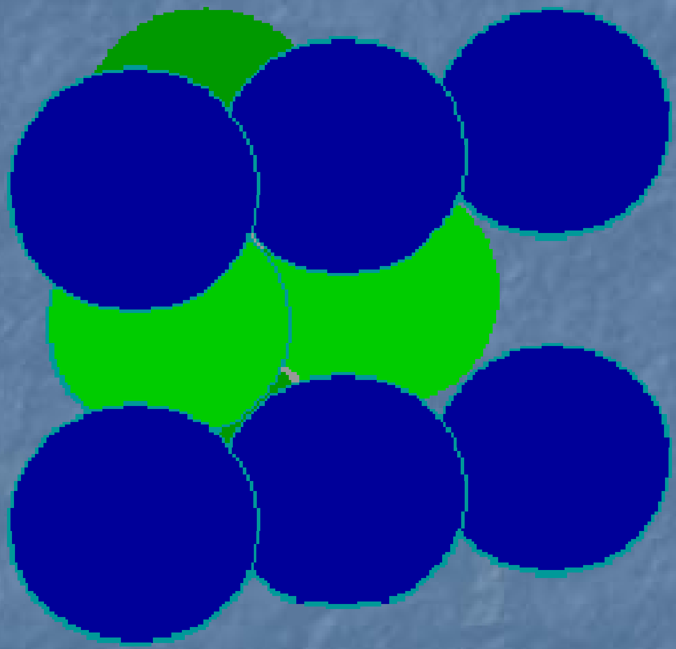


All the surface atoms are equivalent
The surface is relatively smooth at the atomic scale
The surface offers various adsorption sites for molecules which have different local symmetries and lead to different coordination geometries - specifically there are :

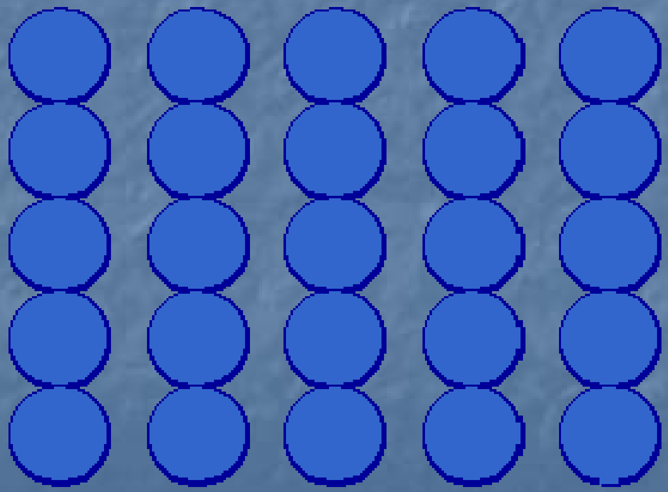
On-top sites (above a single metal atom)
Bridging sites, between two atoms
Hollow sites, between four atoms

Depending upon the site occupied, an adsorbate species (with a single point of attachments to the surface) is therefore likely to be bonded to either one, two or four metal atoms.

The fcc(110) surface

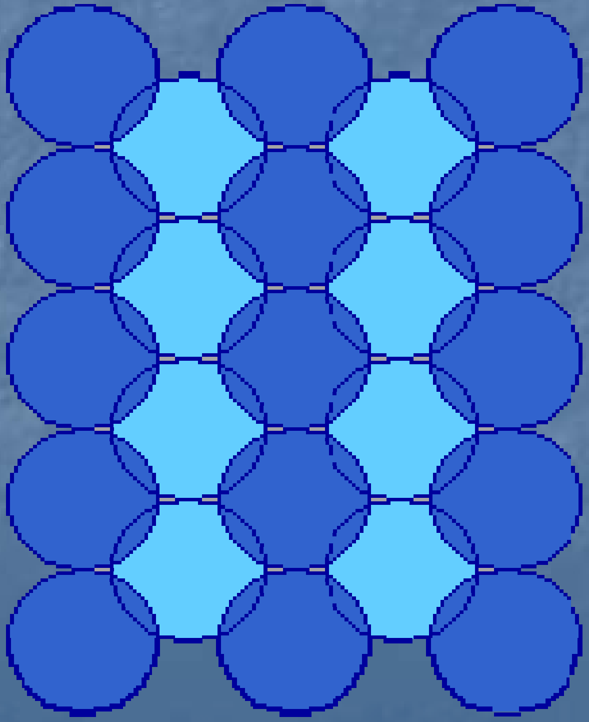


The diagram below shows the conventional birds-eye view of the (110) surface - emphasising the rectangular symmetry of the surface layer atoms. The diagram has been rotated such that the rows of atoms in the first atomic layer now run vertically, rather than horizontally as in the previous diagram.



It is clear from this view that the atoms of the topmost layer are much less closely packed than on the (100) surface - in one direction (along the rows) the atoms are in contact i.e. the distance between atoms is equal to twice the metallic(atomic) radius, but in the orthogonal direction there is a substantial gap between the rows.

This means that the atoms in the underlying second layer are also, to some extent, exposed at the surface



All first layer surface atoms are equivalent, but second layer atoms are also exposed

The surface is atomically rough, and highly anisotropic

The surface offers a wide variety of possible adsorption sites, including :

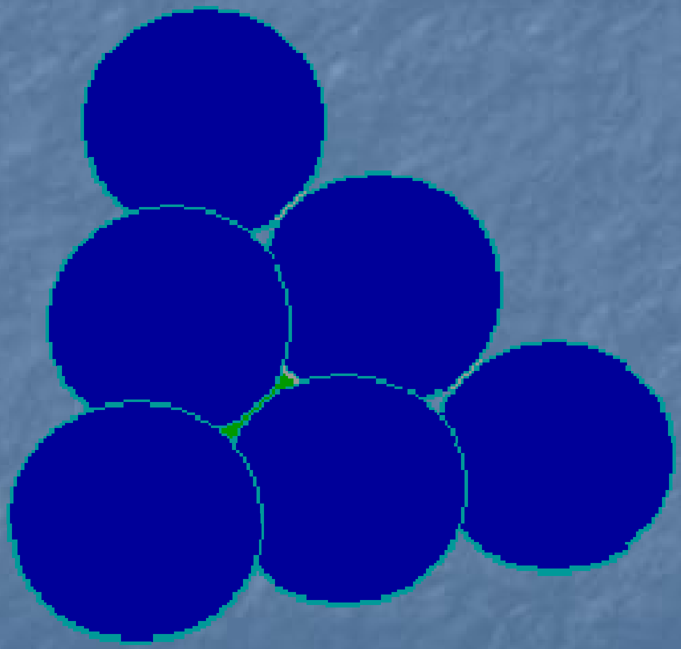
On-top sites

Short bridging sites between two atoms in a single row

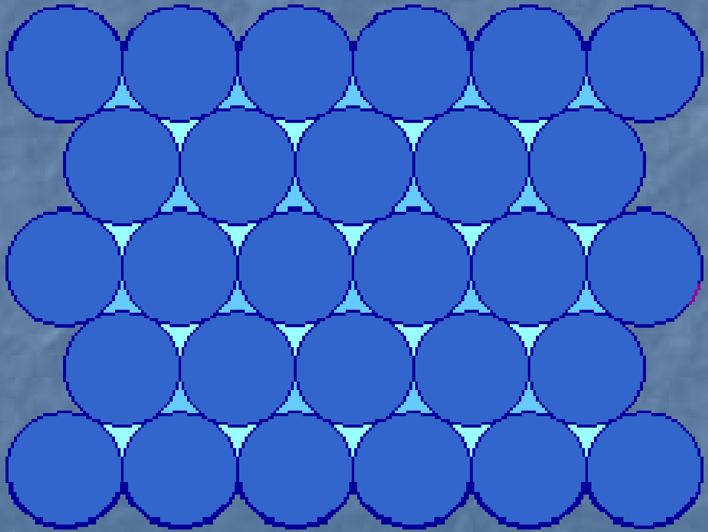
Long bridging sites between two atoms in adjacent rows

Higher coordination sites (in the troughs)

The fcc (111) surface



The diagram below shows the conventional birds-eye view of the (111) surface - emphasising the hexagonal packing of the surface layer atoms. Since this is the most efficient way of packing atoms within a single layer, they are said to be "close-packed".



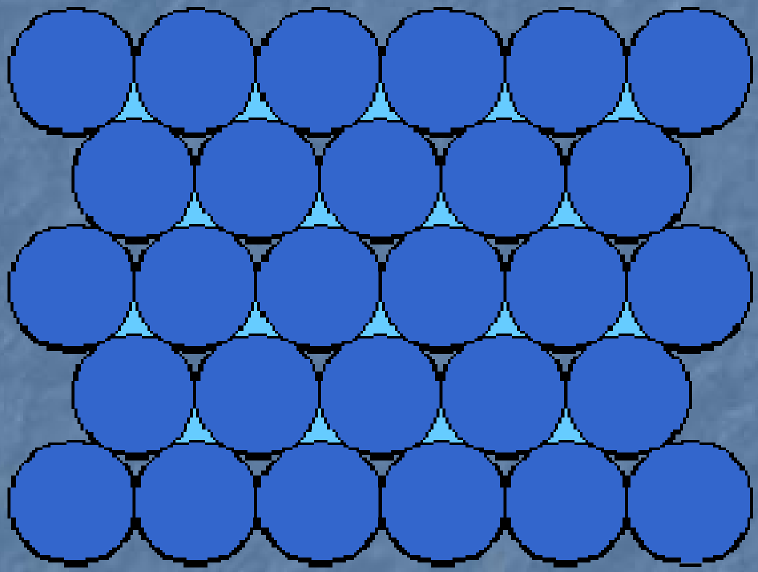
Surface Structure of hcp Metals

This important class of metallic structures includes metals such as Co, Zn, Ti & Ru.

The Miller Index notation used to describe the orientation of surface planes for all crystallographic systems is slightly more complex in this case since the crystal structure does not lend itself to description using a standard cartesian set of axes- instead the notation is based upon three axes at 120 degrees in the close-packed plane, and one axis (the *c*-axis) perpendicular to these planes.

This leads to a four-digit index structure ; however, since the third of these is redundant it is sometimes left out !

The hcp (0001) surface



This is the most straightforward of the *hcp* surfaces since it corresponds to a surface plane which intersects only the *c*-axis, being coplanar with the other 3 axes i.e. it corresponds to the close packed planes of hexagonally arranged atoms that form the basis of the structure. It is also sometimes referred to as the (001) surface.

All the surface atoms are equivalent and have CN=9
The surface is almost smooth at the atomic scale
The surface offers the following adsorption sites :

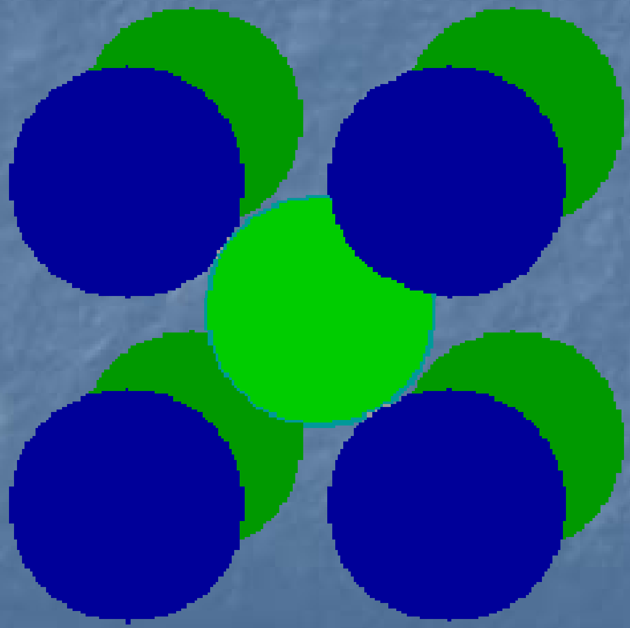
On-top sites
Bridging sites, between two atoms
Hollow sites, between three atoms

Surface Structure of bcc Metals

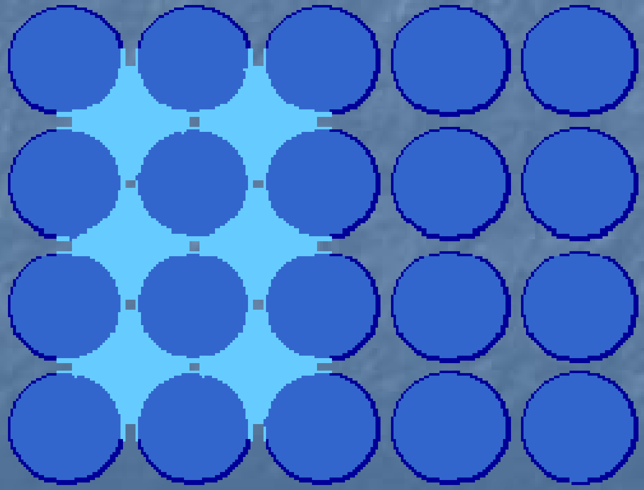
A number of important metals (e.g. Fe, W, Mo) have the bcc structure. As a result of the low packing density of the bulk structure, the surfaces also tend to be of a rather open nature with surface atoms often exhibiting rather low coordination numbers.

The bcc (100) surface

The (100) surface is obtained by cutting the metal parallel to the front surface of the bcc cubic unit cell - this exposes a relatively open surface with an atomic arrangement of 4-fold symmetry.

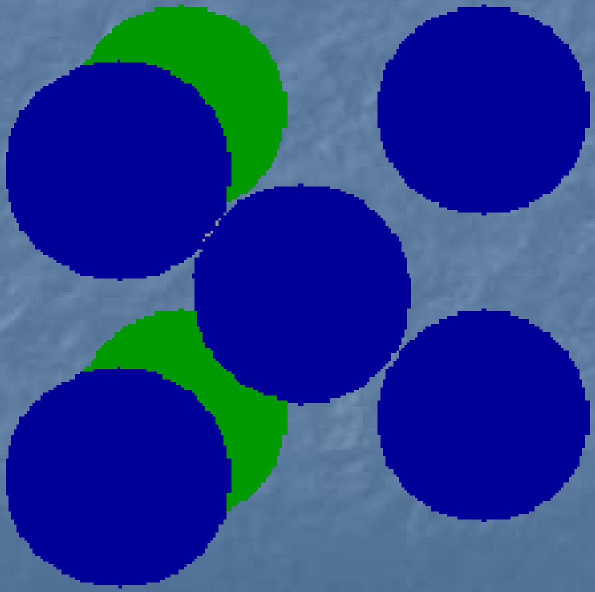


The diagram below shows a plan view of this (100) surface - the atoms of the second layer (shown on left) are clearly visible, although probably inaccessible to any gas phase molecules.

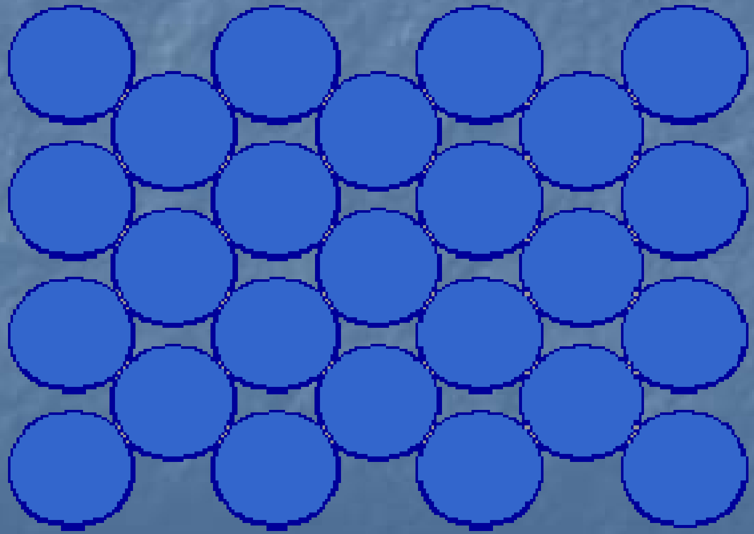


The bcc (110) surface

The (110) surface is obtained by cutting the metal in a manner that intersects the x and y axes but creates a surface parallel to the z-axis - this exposes a surface which has a higher atom density than the (100) surface.

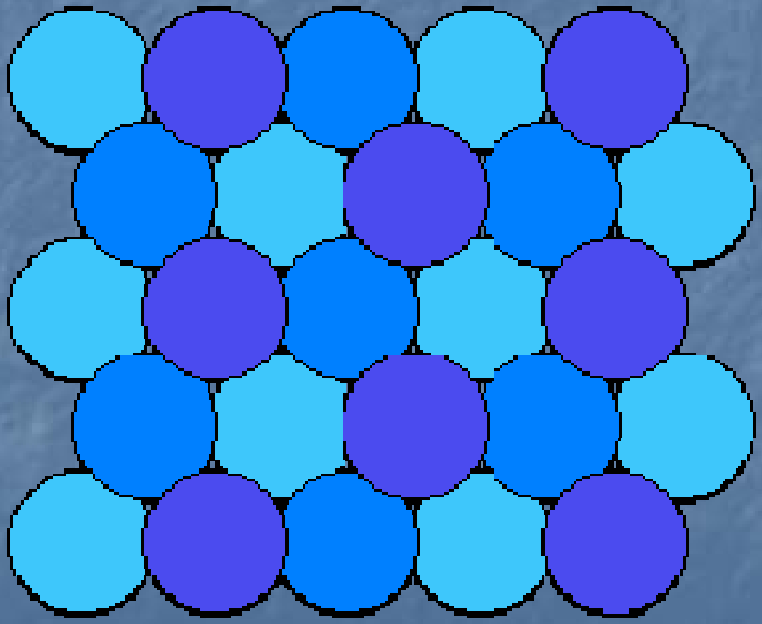


The following diagram shows a plan view of the (110) surface - the atoms in the surface layer strictly form an array of rectangular symmetry, but the surface layer coordination of an individual atom is quite close to hexagonal.

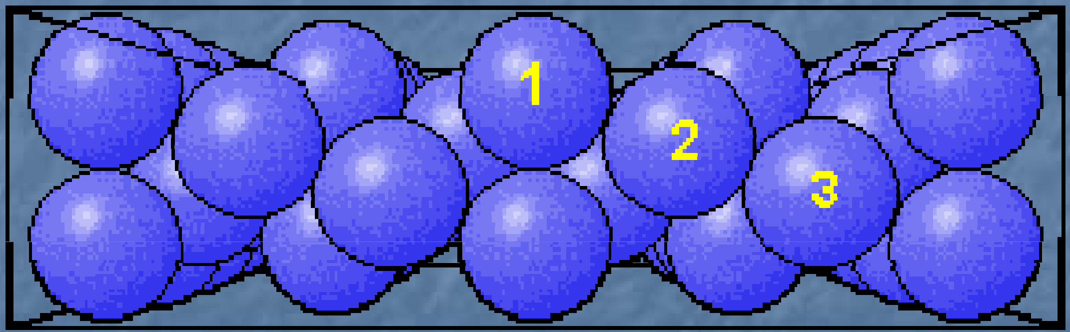


The bcc (111) surface

The (111) surface of bcc metals is similar to the (111) face of fcc metals only in that it exhibits a surface atomic arrangement exhibiting 3-fold symmetry - in other respects it is very different



In particular it is a very much more open surface with atoms in both the second and third layers clearly visible when the surface is viewed from above. This open structure is also clearly evident when the surface is viewed in cross-section as shown in the diagram below in which atoms of the various layers have been annotated.



Energetics of Solid Surfaces

All surfaces are energetically unfavourable in that they have a positive free energy of formation. A simple rationalisation for why this must be the case comes from considering the formation of new surfaces by cleavage of a solid and recognizing that bonds have to be broken between atoms on either side of the cleavage plane in order to split the solid and create the surfaces. Breaking bonds requires work to be done on the system, so the surface free energy (surface tension) contribution to the total free energy of a system must therefore be positive.

Minimize the free energy

- By reducing the amount of surface area exposed
- By predominantly exposing surface planes which have a low surface free energy
- By altering the local surface atomic geometry in a way which reduces the surface free energy

the most stable solid surfaces are those with :
a high surface atom density

surface atoms of high coordination number

(Note - the two factors are obviously not independent, but are inevitably strongly correlated).

Consequently, for example, if we consider the individual surface planes of an fcc metal, then we would expect the stability to decrease in the order

fcc (111) > fcc (100) > fcc (110)

Classification of Overlayer Structures

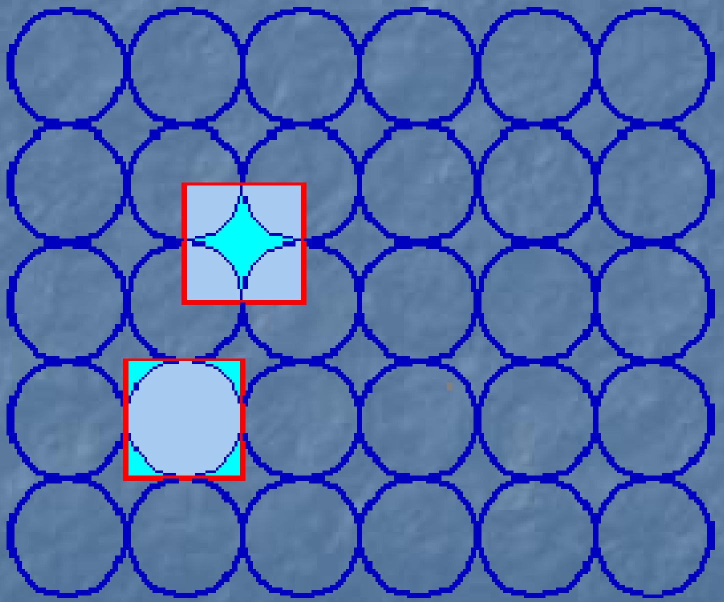
Adsorbed species on single crystal surfaces are frequently found to exhibit long-range ordering ; that is to say that the adsorbed species form a well-defined overlayer structure. Each particular structure may only exist over a limited coverage range of the adsorbate, and in some adsorbate/substrate systems a whole progression of adsorbate structures are formed as the surface coverage is gradually increased.

The Concept of the Surface Unit Cell

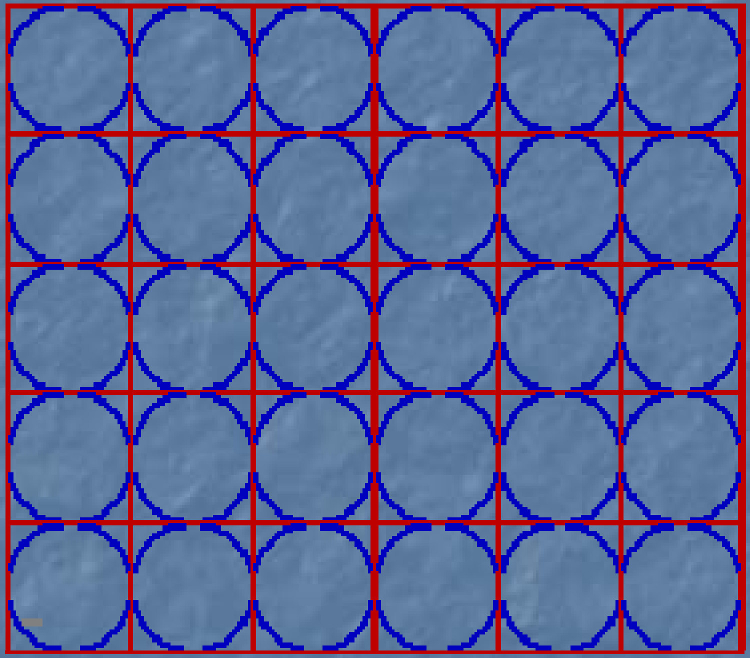
The primitive unit cell is the simplest periodically repeating unit which can be identified in an ordered array - the array in this instance being the ordered arrangement of surface atoms. By repeated translation of a unit cell, the whole array can be constructed.

Let us consider the clean surface structures of the low index surface planes of fcc metals .

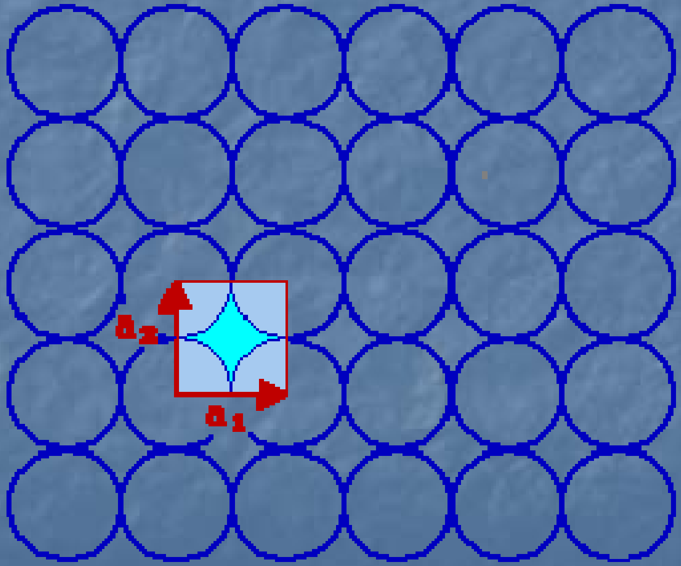
The *fcc*(100) surface has 4-fold rotational symmetry ("square symmetry") - perhaps it should not surprise us therefore to find that the primitive unit cell for this surface is square in shape



Whichever we choose then it is clear that we can indeed generate the whole surface structure by repeated translation of the unit cell



We now need to think how to define the unit cell shape, size and symmetry - this is best done using two vectors which have a common origin and define two sides of the unit cell



For this *fcc*(100) surface the two vectors which define the unit cell, conventionally called $\mathbf{a_1}$ & $\mathbf{a_2}$, are :

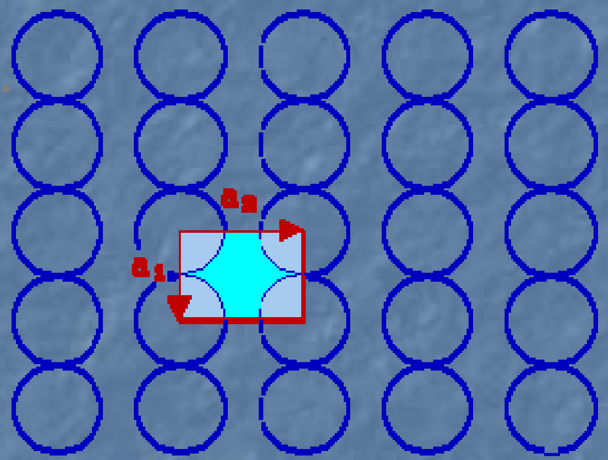
the same length i.e. $|\mathbf{a_1}| = |\mathbf{a_2}|$
mutually perpendicular

By convention , one also selects the vectors such that you go anticlockwise from $\mathbf{a_1}$ to get to $\mathbf{a_2}$ **.**

[Note : the length of the vectors $\mathbf{a_1}$ & $\mathbf{a_2}$ is related to the bulk unit cell parameter, *a* , by
$|\mathbf{a_1}| = |\mathbf{a_2}| = a / \sqrt{2}$]

The fcc(110) surface

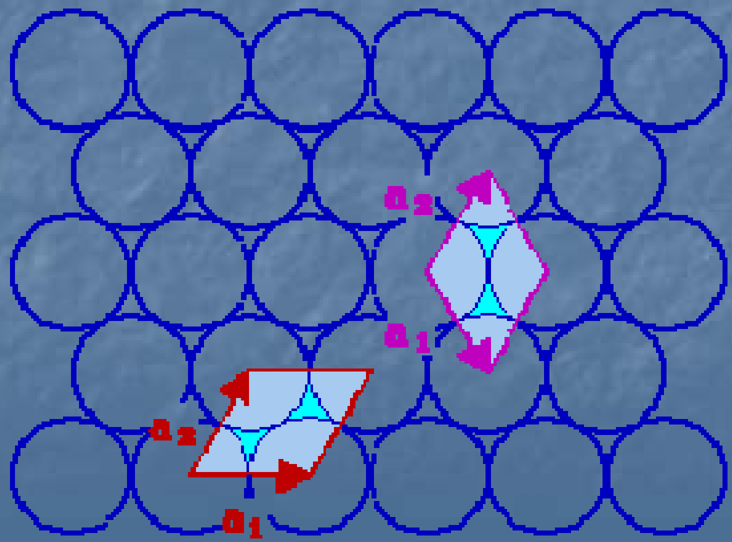
In the case of the *fcc*(110) surface, which has 2-fold rotational symmetry, the unit cell is rectangular



By convention, **$|a_2| > |a_1|$** -
if we also recall the convention that one goes anticlockwise to get from a1 to a2 , then this leads to the choice of vectors shown.

The fcc(111) surface

With the *fcc*(111) surface we again have a situation where the length of the two vectors are the same i.e. $| a_1| = | a_2|$. We can either keep the angle between the vectors less than 90 degrees or let it be greater than 90 degrees. The normal convention is to choose the latter, i.e. the right hand cell of the two illustrated with an angle of 120 degrees between the two vectors.



Overlayer Structures

If we have an ordered overlayer of adsorbed species (atoms or molecules), then we can use the same basic ideas as outlined in the previous section to define the structure.

The adsorbate unit cell is usually defined by the two vectors b_1 and b_2 . To avoid ambiguities, it again helps if we stick to a set of conventions in choosing the unit cell vectors. In this case :

b_2 is again selected to be anticlockwise from b_1 .

if possible, b_1 is chosen to be parallel to a_1 and b_2 parallel to a_2 . Once the unit cell vectors for substrate and adsorbate have been selected then it is a relatively simple matter to work out how to denote the structure.

Ordered surface structures may be described by defining the adsorbate unit cell in terms of that of the underlying substrate using :

Wood's Notation : in which the lengths of $\mathbf{b}_1$ and $\mathbf{b}_2$ are given as simple multiples of $\mathbf{a}_1$ and $\mathbf{a}_2$ respectively, and this is followed by the angle of rotation of $\mathbf{b}_1$ from $\mathbf{a}_1$ (if this is non-zero).

Matrix Notation : in which $\mathbf{b}_1$ and $\mathbf{b}_2$ are independently defined as linear combinations of $\mathbf{a}_1$ and $\mathbf{a}_2$ and these relationships are expressed in a matrix format.

Wood's Notation

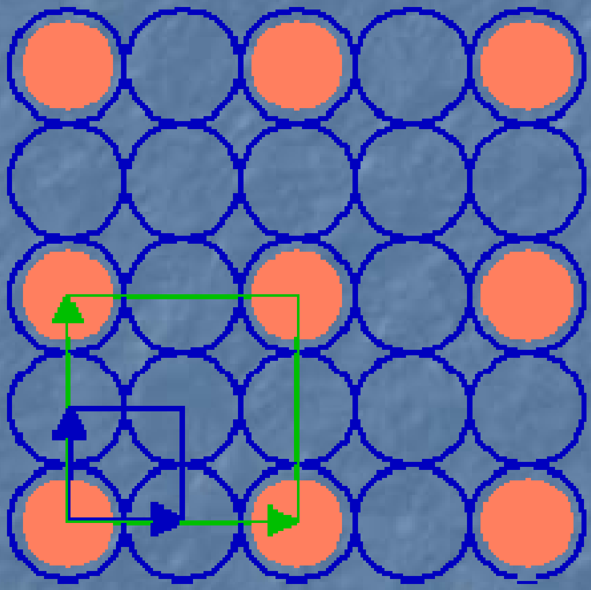
- Wood's notation is the simplest and most frequently used method for describing a surface structure - it only works, however, if the two unit cells are of the same symmetry or closely-related symmetries (more specifically, the angle between $\mathbf{b}_1$ & $\mathbf{b}_2$ must be the same as that between $\mathbf{a}_1$ & $\mathbf{a}_2$).

- In essence, Wood's notation first involves specifying the lengths of the two overlayer vectors, $\mathbf{b}_1$ **&** $\mathbf{b}_2$, in terms of $\mathbf{a}_1$ & $\mathbf{a}_2$ respectively - this is then written in the format :
- $(|\mathbf{b}_1| / |\mathbf{a}_1| \times |\mathbf{b}_2| / |\mathbf{a}_2|)$

- i.e. a (2 x 2) structure has $|\mathbf{b}_1| = 2|\mathbf{a}_1|$ and $|\mathbf{b}_2| = 2|\mathbf{a}_2|$.

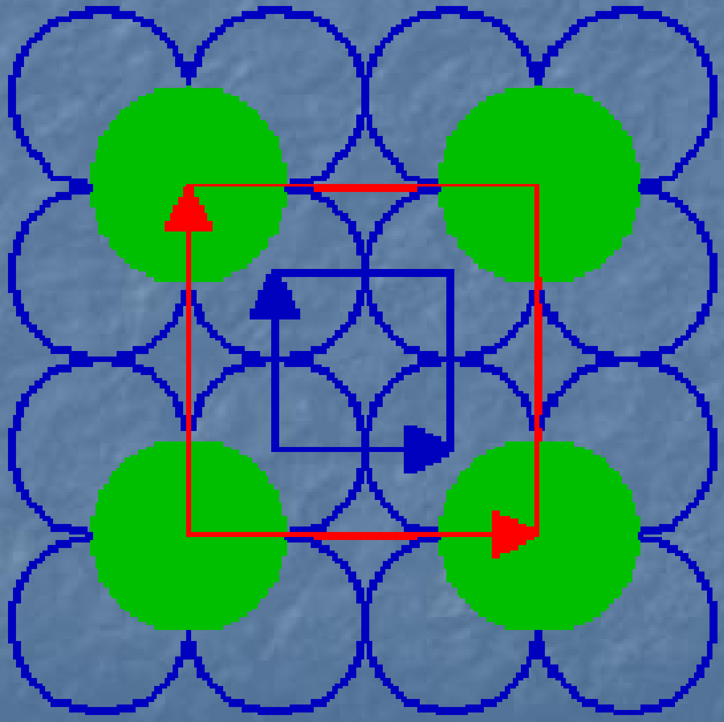
The following diagram shows a (2 x 2) adsorbate overlayer on an *fcc*(100) surface in which the adsorbate is bonded terminally on-top of individual atoms of the

substrate.



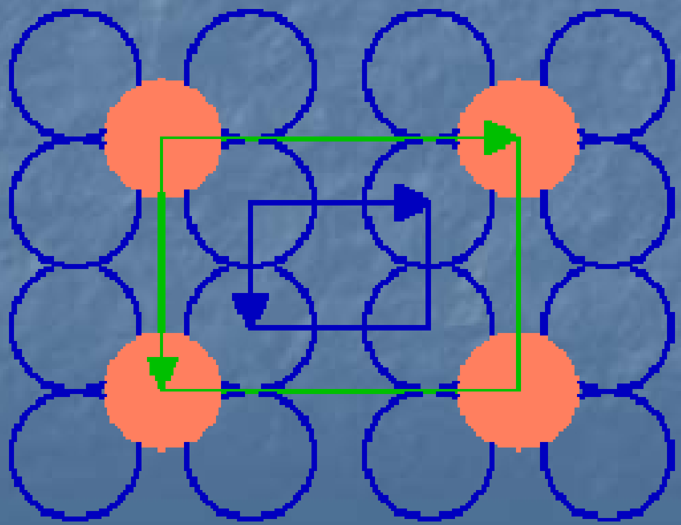
The unit cells of the (100) substrate and the (2 x 2) overlayer are both highlighted.

The next diagram shows another (2 x 2) structure , but in this case the adsorbate species is bonded in the four-fold hollows of the substrate surface. The unit cell shown would repeat to give a complete overlayer structure extending across the substrate surface.

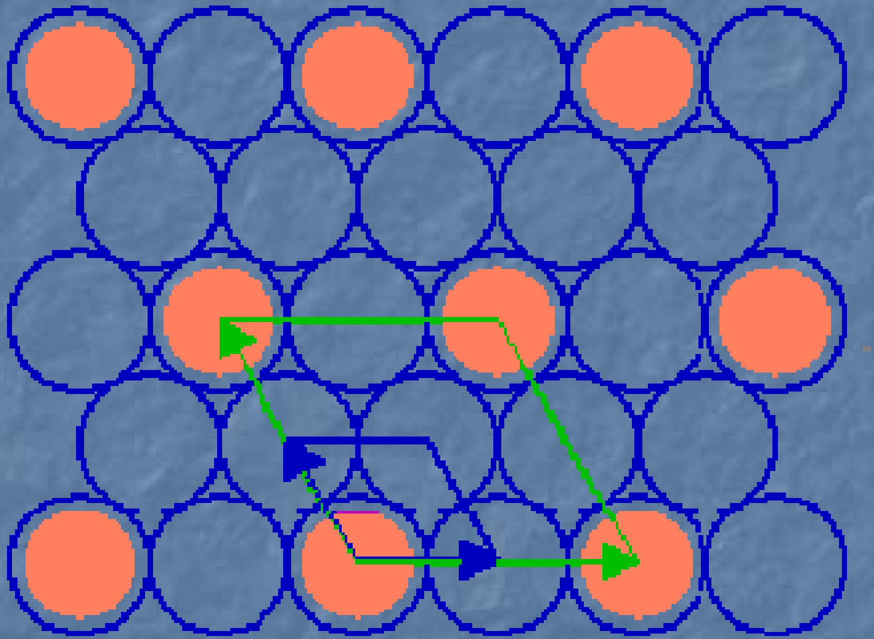


Both this and the previous structure are examples of *primitive* (2 x 2), or p(2 x 2) , structures. That is to say that they are indeed the simplest unit cells that may be used to describe the overlayer structure, and contain only one "repeat unit".

Such (2 x 2) structures are also found on other surfaces, but they may differ markedly in superficial appearance from the structure on the *fcc*(100) surface. The following diagram, for example, shows a (2 x 2) structure on a *fcc*(110) surface

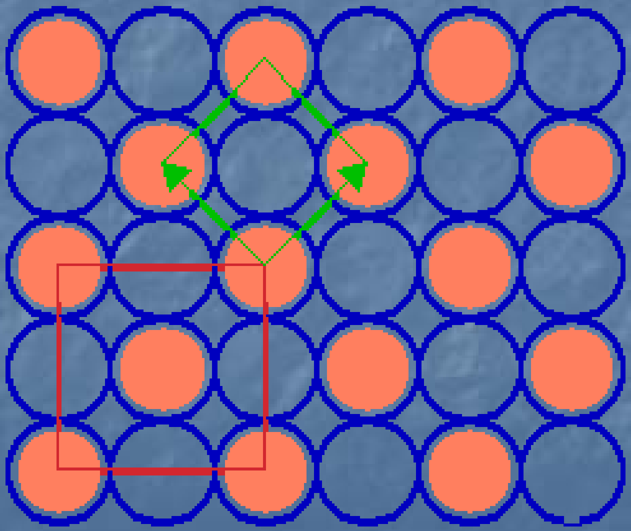


The following diagram shows yet another (2 x 2) structure, in this case on the fcc(111) surface



The next example is a surface structure which is closely related to the (2 x 2) structure : it differs in that there is an additional atom in the middle/centre of the (2 x 2) adsorbate unit cell.

Since the middle atom is "crystallographically equivalent" to those at the corners (i.e. it is not distinguishable by means of different coordination to the underlying substrate or any other structural feature), then this is no longer a primitive (2 x 2) structure.



Instead it may be classified in one of two ways :

(i) As a *centered* (2 x 2) structure i.e. c(2 x 2)
[where we are using a non-primitive unit cell containing 2 repeat units]

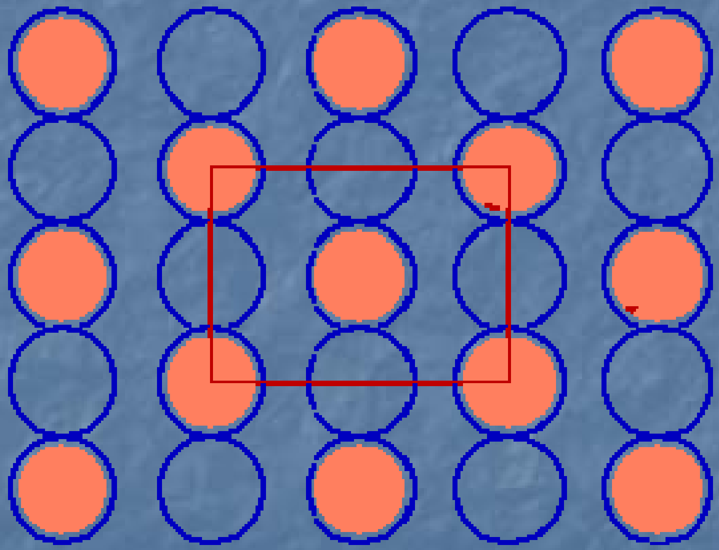
(ii) As a " ($\sqrt{2}$ x $\sqrt{2}$) R45 " structure , where we are specifying the true primitive unit cell .

In using the latter Wood's notation we are stating that the adsorbate unit cell is a factor of $\sqrt{2}$ larger than the substrate unit cell in both directions and is also rotated by 45 degrees with respect to the substrate unit cell.

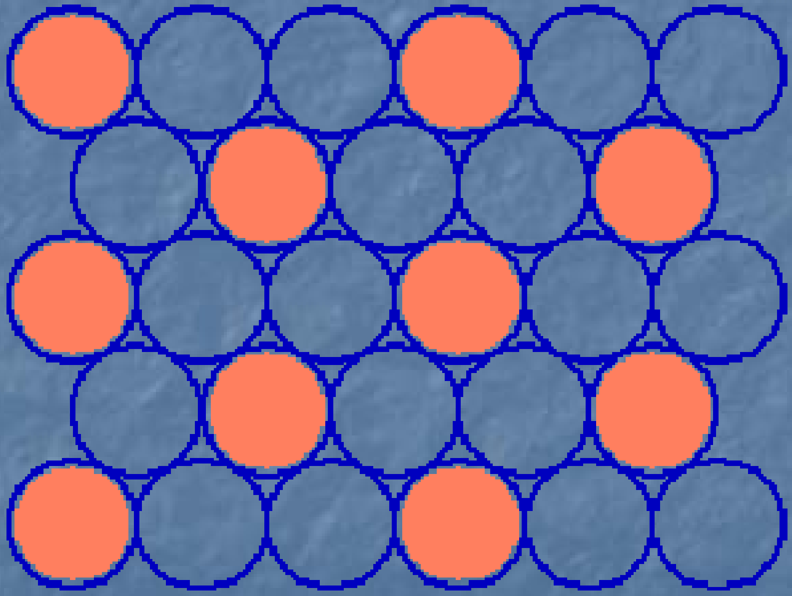
Note : if the "central" atom is not completely crystallographically equivalent, then the structure formally remains a p(2x2) unit cell but now has a basis of two adsorbate atoms per unit cell.

In some instances it is possible to use a centered unit cell description for a structure for which the primitive unit cell cannot be described using Wood's notation - for example, the c(2 x 2) structure on the *fcc*(110) surface shown

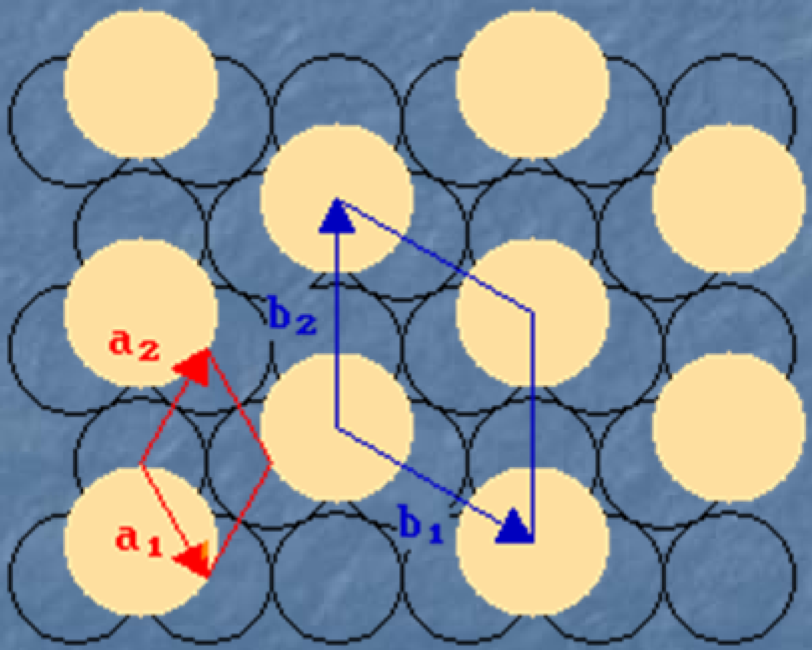
below.



The next diagram illustrates a commonly-observed structure on *fcc*(111) surfaces which can be readily described using Wood's notation.

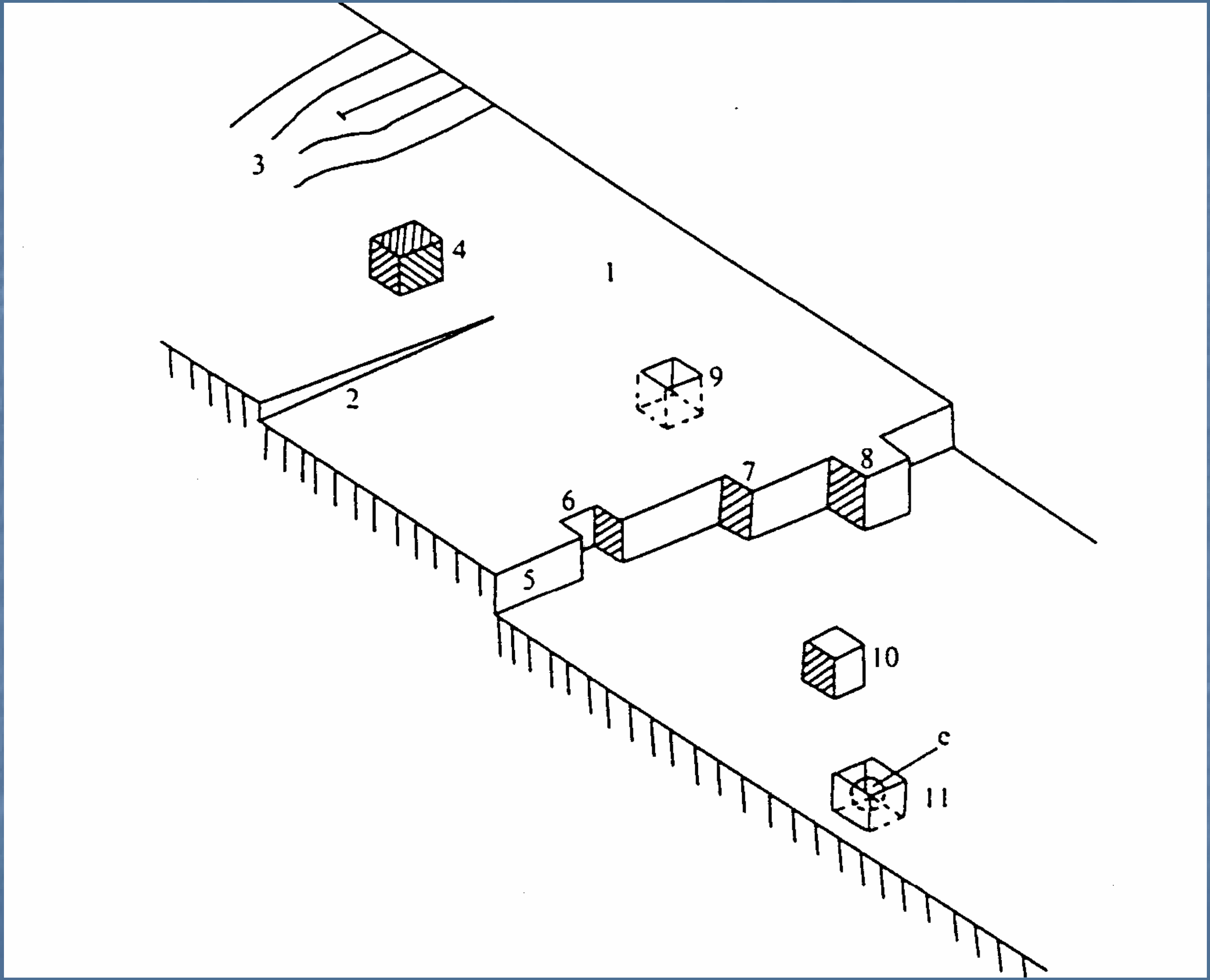


Substrate : fcc(111) (√3 x √3)R30



Surface defects

- A defect is a break in periodicity (lattice or basis)
- All real surfaces show *defects*
- Surfaces may show *domain structure* - often observed for ordered monolayers
- A well-prepared low-index metal surface contains 0.1-1 % defects
- Defects are sites of high reactivity - may dominate surface chemistry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