**Electron – Crystal Interaction**

So we’ll be interested in describing those elements which form metals, as indicated below,

Table

Description automatically generated

And here is another useful table, indicating the (most common?) crystal structure of all the solids in the periodic table, at ambient temperature and pressure. Note that the structures referenced will often have a basis. We’ll talk more about crystal structure later.

A table of the elements

Description automatically generated

Now let’s discuss the Hamiltonian for the metallic elements in particular,

**The Model**

So if we construct an elementary model of a solid – a metal in particular – we’d have basically a sea of negative electrons floating around against a background of positive (ionic) charge. To be clear(er), the ‘floating’ electrons would be taken to be the atom’s *valence* electrons. So for instance we could write the electron configuration of Cu as

[Cu] = 1s22s22p63s13p64s13d10 = [Ar]4s13d10. And the 4s13d10 electrons would be the ‘valence’ electrons. Should also be admitted that these valence electrons may not be ‘floating’ around willy nilly. For Cu, many/all of the 3d valence electrons will be sticking pretty close to the Cu ion core, and could *probably* be treated as core electrons themselves. But that’s something we’ll get into later [tight binding model]. Point is, the valence electrons are the ones whose properties we’ll be interested in, while the other ‘core’ electrons will be presumed inert and simply part of the atomic ion core.

So we could say, roughly H = He + Hion + Hei, where He is the kinetic + potential energy of the (valence) electrons, Hion is the interaction between ions (see Quantum Mechanics/Distinct Particles/Lattice file), and Hei is the interaction between electrons and ions:



where the electron number density is:



where i is the ith electron’s position (operator). **x**(**R**) is the deviation of the ion from its equilibrium point **R**. And Vei(r) is ostensibly the potential that the ions exert on an electron. This could be just a simple Coulomb interaction. If there is a basis of atoms within the primitive cell, then Vei(r – R – x(R)) could be written as Σiλ Vei(r-R-ai-xiλ(R)), where the sum over i runs over all λ atoms in the basis. The simplest approximation, vis a vis the ions, is to presume the ions are immobile. Then we’d just have:



The last term is the potential energy between interacting ions (that simple harmonic potential (1/2)Kx(R)x(R´) above). This last term is just a constant if the ions are immobile and so we’ll ignore it. Furthermore, we’ll neglect the ee interaction, or rather just approximate it by presuming the local density of electrons never changes much from the overall density ne(**r**) = N/V. Then the middle term is just a constant. So then we’re left with:



The potential term we’ll call the crystal potential. So then we have:



So we basically just have a bunch of electrons traveling in a single particle potential.



We can also add EM fields to the mix. If a magnetic field is part of our situation, then it is prudent to add the spin-magnetic field interaction:



where (φ,**A**) is the electro-magnetic 4-vector potential, and γ = e/2m. Remember that we can represent the same EM field with different (φ,**A**) gauge choices. Also remember that it’d be the total magnetic field that enters into H.

**More on the Crystal Lattice**

The crystal potential has all the symmetries of the lattice, including translations, rotations, etc. For instance, consider some translational symmetry of the crystal whereby we can displace every atom by Δ**R** without changing the set of coordinates describing the crystal (we’ll suppose periodic boundary conditions for the crystal at its surface so that atoms on one surface so displaced will just end up at the opposite surface). In other words, we suppose {**R** + Δ**R**} = {**R**}. Then we’ll have: Vcrystal(**r**+Δ**R**) = Vcrystal(**r**) as well, as can see by changing variables in the summation index of Vcrystal(**r**). According to group theory, there are seven basic crystal lattice types. I guess a crystal lattice is the set of points which can be generated by Bravais Lattice Vectors (see below)? All of these pictures are stolen from: <https://glossary.periodni.com/glossary.php?en=body-centred+cubic+lattice>

Chart, radar chart

Description automatically generated

Chart

Description automatically generated

A picture containing diagram

Description automatically generated

Shape, rectangle, polygon

Description automatically generated

Chart, radar chart

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Chart, radar chart

Description automatically generated

Chart, radar chart, line chart

Description automatically generated

Interesting that this means the crystal isn’t the same if we tilt it on a side. If we look at the set of coordinates/lattice points generated by repeating these structures, then we get the crystal lattice. It’s important to note that the lattice points are not themselves atoms, necessarily. If we want to generate the *atomic* structure of the crystal then we have to attach a basis of atoms to each of the lattice points. For some metals it’s easy. The basis of atoms that gets attached to each lattice point is just the atom itself. Consider these three guys,

Diagram

Description automatically generated

For others, the basis consists of two or more atoms. Consider this, stolen from (<https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/s4_2_1.html>). To construct diamond, we start with an fcc lattice, and attach to each lattice point a basis consisting of two carbons (the blue and gold). Note if the origin of our coordinate system is at the 0, and the edges of the cube have length *a*, then the coordinates of the yellow atom in that base attached to 0 would be (*a*/4)(++). This is also the structure of GaAs (a semiconductor, actually), with Ga and As taking the place of the two Carbons.

Chart, bubble chart

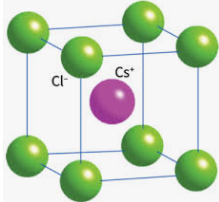
Description automatically generated

NaCl (an insulator) is similar; we start with an fcc lattice, and attach to each lattice point a basis consisting of an Na and Cl (the blue and red). Note if the origin of our coordinate system is at the 0 (the lower front left corner), and the edges of the cube have length *a*, then the coordinates of the red atom in that basis attached to 0 would be (*a*/2)(++).

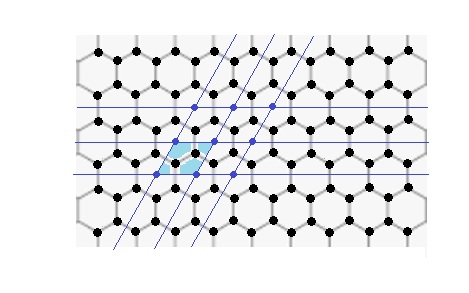
A white background with black and red symbols

Description automatically generated

Cesium Chloride is a simple cubic lattice, with a basis. The chlorides form the cubic lattice structure, and the cesium is the guy in the middle. CsCl’s structure is sometimes confused with BCC, but it would only have this structure if the Cs and Cl were identical.



And here’s an example of a Honeycomb lattice. Two-dimensional Graphene has this structure. *Technically*, it’s not a lattice itself, as it isn’t one of those guys listed above (the honeycomb lattice looks like the hexagonal lattice above, but it’s not because it’s missing the lattice point at the center). But, it *can* be considered a 2D hexagonal lattice with a *basis*. And it’s hexagonal because that obuse angle is γ = 120o.



Below’s an example of carbon/graphite. It kind of looks like a two-layer honeycomb ‘lattice’, with the two layers off center. But like we said above, a honeycomb lattice is not a *real* crystal lattice. In fact the graphite structure can be described as a hexagonal lattice with a net four-atom basis. The unit cell of the hexagonal lattice is delineated in bold below (compare to hexagonal lattice vectors below). The blue atom, two green atoms, four purple atoms, and eight red atoms each contribute one atom, respectively, to the unit cell. The basis does not provide the best way to understand the bonding though. So a given carbon atom is covalently bonded to its three nearest neighbors in the sheet, leaving one electron free to conduct along the sheet (so I guess this gives each atom an effective valence of 2p4?). And the sheets are held together via VanderWaal’s forces.

A diagram of a cube with lines and dots

Description automatically generated

And below is an example of Bismuth. It can be described as a rhombohedral lattice with a two-atom basis. The unit cell is delineated in light black. The blue atom and eight red atoms each contribute one atom respectively to the unit cell, for a total of two.

A diagram of a cube with lines and points

Description automatically generated

So yeah.

**Bravais Lattice Vectors**

So to specify the coordinates of the atoms in a lattice we need to be able to specify the positions of the lattice points, and of the atoms within the basis attached to each latttice point. Apropos the first task, the coordinate/lattice vector, **R**, of any lattice point can be written as an integer combination of basis vectors, also called primitive basis vectors,



So we can say **R**{m1,m2,m3}= m1**a**1 + m2**a**2 + m3**a**3, where m1,2,3 are any integer. And **R**{m1,m2,m3} is called a lattice vector. The **a**’s don’t have to be normal to each other. For instance, here is a basis for an orthorhombic, BCC, FCC, and hexagonal lattice, respectively,

Chart, line chart

Description automatically generated Chart, line chart

Description automatically generated Chart, radar chart

Description automatically generated A diagram of a cube with lines and dots

Description automatically generated

And in fact, they are not even unique, as the following illustration, taken from (<https://www.tf.uni-kiel.de/matwis/amat/iss/kap_4/illustr/s4_2_1.html>), shows.

Chart, scatter chart

Description automatically generated

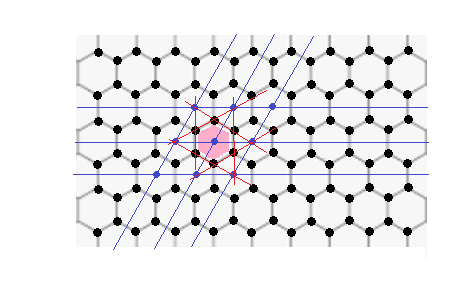
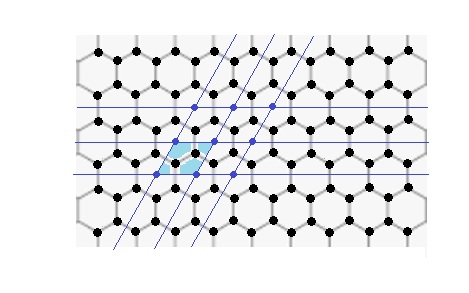
The only requirement for a primitive basis set is that all points in the lattice can be generated by integer combinations of the BLV’s. If we compare the honeycomb ‘lattice’ and the hexagonal lattice, and think about it a bit, you’ll see that while we can write down Bravais lattice vectors for the hexagonal ‘lattice’, we can’t for the honeycomb lattice. And so the honeycomb ‘lattice’ isn’t a lattice, in the technical sense.

**Bravais Lattice Unit Cell**

Even though there are different primitive bases, the volume enclosed by each is the same. This is called the primitive volume. The primitive volume as implicitly just described, is what’s called the conventional primitive volume. It is the set of points within the range Vcell = α**a**1 + β**a**2 + γ**a**3, where α, β, and γ can each range between [0,1), say (could range from [-1/2,1/2) etc., as long as range is 1).



But the main requirement for a primitive volume is that it is a region which when displaced by all lattice vectors in the BL, it will encompass the entire crystal w/o overlap. One popular primitive volume is the Wigner-Seitz cell. It is defined as the set of points closer to a given lattice point than any other lattice point. It can be constructed geometrically by drawing lines from a lattice point to all of its nearest neighbors, perpendiculary bisecting those lines with planes, and shading in the region between the lattice point and all those planes. For the honeycomb lattice, a conventional primitive volume is shown in blue, and the Wigner-Seitz primitive volume is in pink. The Wigner-Seitz primitive cell just happens to be the honeycomb itself. In general, the Wigner-Seitz primitive cell/volume has the advantage that it possesses all of the symmetries of the lattice, where as the conventional primitive volume may not.

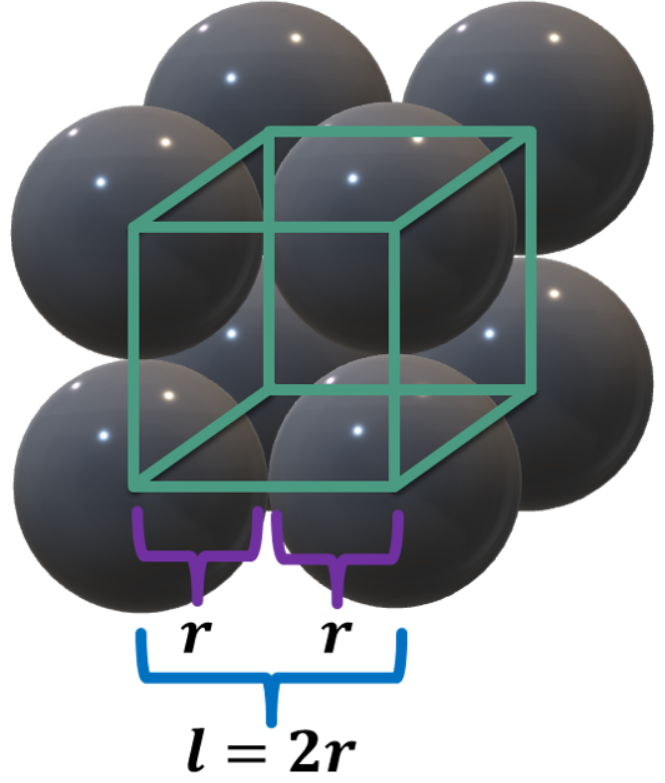
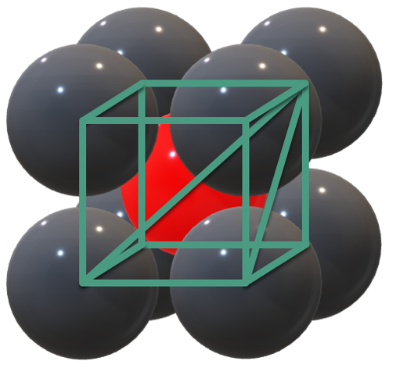
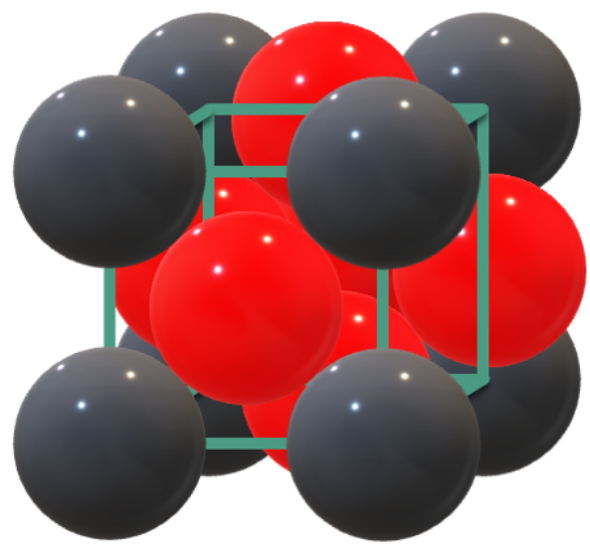


As you can see in the picture, the pink Wigner-Seitz cell has the symmetries of the lattice. For instance, you can flip it 180o about the vertical. But the blue conventional cell does not have this symmetry. And we’ll note that for both unit cells/volumes, displacing them by the two primitive lattice vectors, we can cover the entire crystal w/o overlap.

Also note that either way, there are two full atoms per unit cell. In the blue guy, both atoms ly complettely within the cell; in the pink one, there are six atoms partially within the cell. But each atom is equally shared amongst three cells. So there are in a sense two whole atoms per pink unit cell as well.

**Atomic Radii**

The effective atomic radii are estimated by assuming these cells are close-packed. Went to chemlibre.org to steal some nice pictures:

The first on the left is a simple cubic cell. If it’s close-packed, then the atomic radius is just r = ℓ/2, where ℓ is the length of the cell. The middle one is a BCC. If it’s close packed, then the corner atoms won’t actually touch, but they will touch with the central atom. You can sort of make out that the central diagonal, running through the cube comprises 1 + 2 + 1 atomic radii. So we have √(3ℓ2) = 4r -> r = (√3/4)ℓ. And the FCC guy on the right, we can see that the atoms on the faces are touching each other. So we have √(2ℓ2) = 4r -> r = (√2/4)ℓ. So altogether:



and the website works out more structures too.

**Example**

A metallic crystal adopts a body-centered (BCC) structure, where atoms are located at all eight corners and at the center of the unit cell. Give that the atomic radius of the element is r = 0.142nm (atomic radius in this context is half the length of the edge of the unit cell), calculate the density of the metal in g/cm3, assuming its atomic mass is 52.01 g/mol.

So each of the corner atoms are shared by 8 different unit cells (4 for bottom half, and 4 for top half). So corner atoms contribute 1 net atom per cell. The mass of these two atoms is:



And there is another atom wholly contained within the cell, so that’s 2 atoms/cell. Let’s work out the length of the cell,



So the volume of the cell is:



So the density is:



**The Reciprocal Lattice**

So if the potential has the periodicity of the lattice, then it should be periodic over every primitive cell/volume. Given this, we can make a Fourier expansion of the crystal potential, or any function periodic over the basis, in a set of plane waves with special wavevectors **G** which make waves with such wavevectors periodic over the lattice. This set of special wavevectors is called the reciprocal lattice. The primitive reciprocol lattice vectors are denoted,



in terms of which we can say **G**{n1,n2,n3}= n1**b**1 + n2**b**2 + n3**b**3. We can solve for **G**primitive in terms of **R**primitive as follows. The defining condition of the **b**’s is that they form such a basis that any linear combination of them, i.e. any **G**, will satisfy the following equation:



This equation requires,



where p is any integer. I guess we can take it as the definition of sorts. And physically, the ni (in equation above) would be the number of times the wave repeats itself within the cell, in the ith direction. Now this equation must hold for any of the **R**primative’s. So let’s say **R**primative = **a**1. Then we need,



(again, p can be any integer and it certainly depends on the value of nj) And this equation must hold for any n1, n2, and n3. Set n2, n3 = 0. Then we must have **a**1·**b**1 = 2π (say). But if so, then we cannot guarantee that **a**1·**b**2 and **a**1·**b**3 will also be proportional to 2π and thus preserve the required **G**·**R**primative relation. Thus, we’d have to say **a**1·**b**2 and **a**1·**b**3 = 0. We can argue similarly with **R**primative = **a**2 and **R**primative = **a**3. So in general we can say,



So for instance, **b**1 must be perpendicular to **a**2 and **a**3. From this, and analogous considerations on the other guys, we can conclude that:



To find the normalization, we explicitly invoke the **a**i·**b**j = 2πδij condition. So for instance,



And making similar arguments on the other guys, we get:



Better to switch order of cross-products in second guy,



Then, by the cyclic identity **a**·(**b**×**c**) = **b**·(**c**×**a**) = **c**·(**a**×**b**), and that fact that these are the volume of the primitive cell, we can say:



So **b**1 is perpendicular to the plane defined by **a**2×**a**3, **b**2 is perpendicular to the plane defined by **a**3×**a**1, and **b**3 is perpendicular to the plane defined by **a**1×**a**2. Might observe that the volume of k-space taken up by a RLV cell is:



It’s interesting to note that the RLV basis **b**1,2,3 is, aside from the normalization, the same as the contravariant basis associated with associated with any coordinate system with rectilinear covariant basis **a**1,2,3. Well, we can use the previous stuff to expand any function periodic over the primitive basis in a Fourier series of reciprocal lattice vectors – in particular the crystal lattice potential.



To motivate this result, just suppose that the left equation is true. Then the right equation will be true, if it is the case that:



To see that it is, let’s change variables to a coordinate system consisting of the basis vectors **a**1, **a**2, **a**3. And let 1,2,3 stand for the original, say Cartesian, basis vectors. We can express a position in the unit cell in either basis:



And now we’ll take our integral implicitly expressed in the **e**i basis,



and change coordinates to the **a**i basis, so as to decouple the coordinates so that the 3D integration just turns into a product of three 1D integrals. The transformation is:



The Jacobian of transformation is:



now changing variables in the integrand,



That was simple. So now we have:



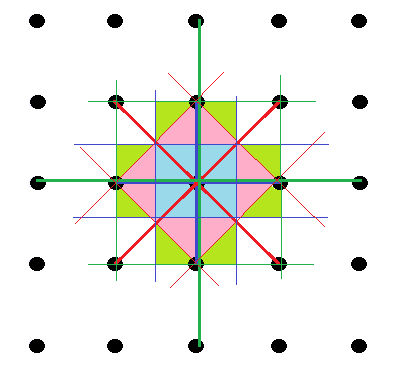
So there we go.

**Reciprocal Lattice Unit Cell**

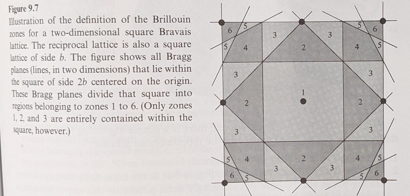
Just as the Bravais lattice has a unit cell, which, when displaced by every Bravais lattice vector, will cover the entire lattice, the reciprocal lattice also has an associated unit cell. The conventional unit cell would be (other choices possible, but α, β, γ’s should span width 1):



Like with the Bravais lattice, the most common unit cell is the Wigner-Seitz unit cell, defined in the same way here as it was there. So yeah, consider a 2D cubic RL, and we’ll draw blue thick lines to the nearest neighbors in k-space, and red thick lines to the next nearest neighbors, and then green lines to the next-next nearest neighbors.



Then draw the Bragg planes (which from our top-down perspective look like skinny lines) which bisect these thick lines. Then the 1st BZ is the set of k-points (blue region) which are closer to the origin than the nearest neighbors. Another way to say it is that it’s the set of points for which the origin is their nearest neighbor. These are also the set of points that don’t require us to cross any Bragg plane to get to. It’s also the Wigner-Seitz cell. The 2nd BZ would be the set of k-points (pink region) for which the origin is their next nearest neighbor. And these would also be the set of points that only require us to cross a single Bragg plane to get too. The 3rd BZ would be the set of k-points (green region) for which the origin is their next next nearest neighbor. And these would also be the set of points that only require us to cross two Bragg planes to get to. And so on. Note the volume in k-space of the 1st BZ is the same as that of the 2nd BZ is the same as that of the 3rd BZ, etc. Here’s a picture from the Ashcroft-Mermin book showing more BZ’s:



**Example. Primitive basis and reciprocal basis of orthorhombic lattice**

So consider an orthorhombic lattice, with given side lengths,

Chart, line chart

Description automatically generated

Starting at the origin, as labelled, we can posit the primitive basis vectors displayed above (there are others, many others).



And we see that the volume of the primitive cell would be:



What is the reciprocal lattice? Well, we have:



The volume of the primitive cell in reciprocal space is:



So that checks out. Can see that the reciprocal of an orthorhombic lattice is also an orthorhombic lattice with a → 2π/a, b → 2π/b, and c → 2π/c.

**Example. Primitive basis and reciprocal basis of BCC lattice**

So consider, the body centered cubic lattice.

Chart, line chart

Description automatically generated

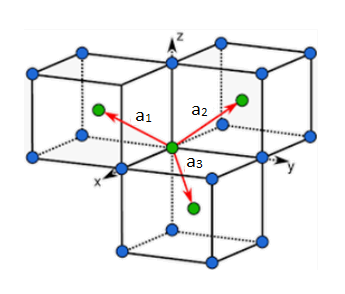
Starting at the origin, as labelled, we can posit the primitive basis vectors displayed above (there are others, many others). For the BCC guy, we have,



Another basis, would be:



illustrated here.



Using the first basis for convenience, we see that the volume of the primitive cell would be:



What is the reciprocal lattice? For the BCC we have:



The volume of the primitive cell in reciprocal space is:



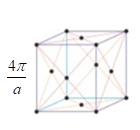
Let’s work it out again using the other basis. So,



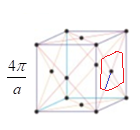
And the volume of the primitive reciprocal cell is:



And so we get the same result as before. So what does the reciprocal lattice look like? Well if we compare these b’s to the a’s in the next example, we’ll see that our reciprocal lattice is an FCC structure, where the length of the sides is 4π/a.



Let’s look at the Wigner-Seitz cell of the reciprocal lattice. If we draw the Wigner-Seitz cell of the reciprocal lattice (only tried to draw it in that single plane; more 3D picture to right), we get:

 A picture containing handcart

Description automatically generated

Next,

**Example. Primitive basis and reciprocal basis of FCC lattice**

And for the FCC guy,

Chart, radar chart

Description automatically generated

we could say,



And the volume of its primitive cell would be:



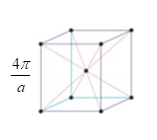
Its reciprocal lattice would be:



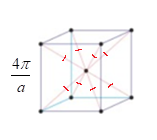
And the volume of the cell is:



which is what we expect, magnitude-wise. If we compare our FCC reciprocal lattice basis here to the second proferred BCC Bravais lattice basis above, we can see that they’re negatives of each other, and so really the same. So the FCC reciprocal lattice is a BCC lattice, with side length 4π/a, just as we likewise found in the previous example.



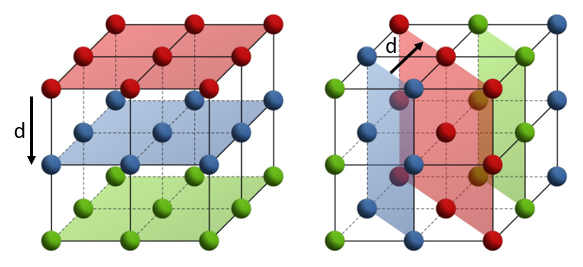
And let’s look at the Wigner-Seitz cell. This is:The Wigner-Seitz cell is not something I’m going to try to draw, but the intersections of it with those lines to the nearest neighbors is displayed in red. Well it looks like that structure on the right.

 Chart, radar chart

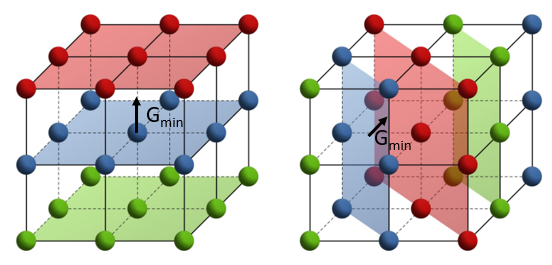
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**Lattice Planes and Miller Indices**

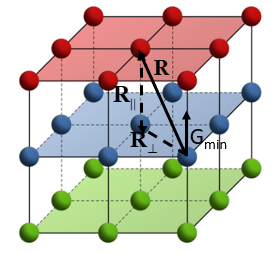
We can take any Bravais lattice, take three non-colinar points, and put a plane through them. This plane will naturally encompass many more points than just these three. This is called a lattice plane. We can encompass all the points in the crystal by interspersing these lattice planes a distance d apart (whatever d is). Two cases are illustrated below.



(d’s won’t be the same) Interestingly, there are reciprocal lattice vector pointing perpendicular to the lattice planes. The smallest one is **G**min = (2π/d), where is the unit vector normal to the planes.



We can see by looking at ei**G**\_min∙**R**. So let **R** = 0 be a point in the lattice, and decompose **R** = **R**⊥ + **R**∥.



So we have:



Now let’s include any plane by setting **R**⊥ = md, where m is any integer. Then we have:



So this shows that **G**min is a reciprocal lattice vector. Moreover, it is the smallest one perpendicular to those lattice planes since we can also see that if we went back to the top line in the equation set just above, and divided **G**min by anything, we wouldn’t be guaranteed to get 1 in the end. So,



Other RLV in the same direction can be found by multiplying by an integer n. We can go the other way too. For every reciprocal lattice vector **G** = n1**b**1 + n2**b**2 + n3**b**3, there is a smallest vector, **G**min, pointing in the same direction (basically have to find all common factors of n1, n2, n3, and take them out). Or another way to think about it is that the set of these, {**G**min}, is the set of {**G** = n1**b**1 + n2**b**2 + n3**b**3} where the n1,2,3 have no common factors. This **G**min is usually written as: **G**min = h**b**1 + k**b**2 + ℓ**b**3, or just (h,k,ℓ) for short, where h, k, ℓ are called the *Miller Indices*, and, as just discussed, h, k, and ℓ must have no common factors. And, for each such **G**min, there is a set of lattice planes spanning the entire crystal which are normal to **G**min and are spaced a distance d = 2π/Gmin apart.