

13. Diffraction from crystals

Structure factor

The structure factors are proportional to the Fourier coefficients of the crystal potential. We assumed discrete, spherically symmetric atoms. The position of atom m can be specified by a short vector \mathbf{d}_m that points to a location in the unit cell:

$$F_{\mathbf{g}} = \sum_{m \text{ atoms}} f_m \cdot e^{2\pi i \mathbf{g} \cdot \mathbf{d}_m}$$

The factor f_m is an abbreviation for the function that we previously called $f^{(m)}(s)$, where $s = g/2$ (which is how the form factors are usually tabulated). The simplest way to specify the vectors \mathbf{d}_m is in terms of the direct-lattice basis vectors

$$\mathbf{d}_m = x_m \mathbf{a}_1 + y_m \mathbf{a}_2 + z_m \mathbf{a}_3 = (x_m, y_m, z_m)$$

in which case we just need the atomic coordinates (x_m, y_m, z_m) . These are typically dimensionless fractions in the range 0 to 1, indicating any position in the unit cell.

We know that any RLV is just $\mathbf{g} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3$, so the dot product in the exponent has a simple form.

$$\mathbf{g} \cdot \mathbf{d}_m = hx_m + ky_m + \ell z_m$$

Fortunately, all of the cross terms vanish. Now we can write the structure factors in a form that is still very general using Miller indices, instead of vectors:

$$F_{hkl} = \sum_{m \text{ atoms}} f_m e^{2\pi i (hx_m + ky_m + \ell z_m)}$$

If you have been tracking signs carefully up this point, you may notice that the exponents used in the structure factor should actually have the opposite sign to that shown above. In other words, our F_{hkl} is really $(F_{hkl})^*$, depending on who you ask, but it looks a little simpler this way.

Example: Simple cubic lattice with two-atom basis

Here is an example that is somewhat general, but also easy. For a simple cubic (sc) crystal (simple implying there are lattice points only at the cube corners), we might as well align the direct lattice along the Cartesian coordinates:

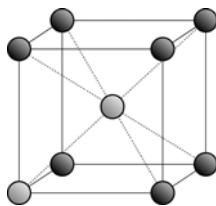
$$\mathbf{a}_1 = a\hat{x}, \mathbf{a}_2 = a\hat{y}, \mathbf{a}_3 = a\hat{z}$$

where a is the cubic lattice parameter. A word we used before has another meaning here: The "basis" of the crystal sometimes refers to all of the atoms in the unit cell and their arrangement. Let's say atom 1 is particularly heavy (large Z), so we put it at the corner site: $\mathbf{d}_1 = (0,0,0)$. A second atom may be at some arbitrary location $\mathbf{d}_2 = (x, y, z)$. If atom 1 is of type "A" and atom 2 is of type "B", the structure factor in this example is then

$$F_{hkl} = f_A e^{i0} + f_B e^{2\pi i (hx+ky+\ell z)} = f_A + f_B e^{2\pi i (hx+ky+\ell z)}$$

Example: Body-centered cubic lattice

The sc lattice is not the only one with cubic symmetry. Sometimes extra lattice points can be identified within the unit cell that have the same symmetry as those at the corners. These lattices are called "centered". The body-centered cubic (bcc) lattice occurs when there is an extra lattice point at the cube center. This often occurs when there is just one type of atom that prefers to have eight nearest neighbors of its one kind.



To describe the crystal, we just need a cubic unit cell with atom 1 at the corner position and atom 2 at the body center.

atom	form factor	site
1	f	$(0,0,0)$
2	f	$(1/2,1/2,1/2)$

The structure factor is:

$$F_{hkl} = f \cdot [1 + e^{\pi i(h+k+l)}]$$

Interesting things happen in the sum of phase factors. Notice that

$$e^{\pi i(h+k+l)} = \begin{cases} 1, & h+k+l = \text{even} \\ -1, & h+k+l = \text{odd} \end{cases}$$

Because of the centering, there is constructive interference between the corner and centered atom when $h+k+l = \text{even}$ and destructive interference when $h+k+l = \text{odd}$. So

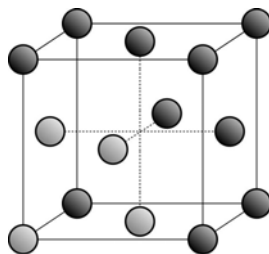
$$F_{hkl} = \begin{cases} 2f, & h+k+l = \text{even} \\ 0, & h+k+l = \text{odd} \end{cases}$$

The Miller indices with non-zero structure factor correspond to "allowed reflections". The rest are called "systematic absences". A list of these by Miller indices would be infinitely long, but we can write out a partial list of the first few:

$\{110\}$
 $\{200\}$
 $\{202\}$
 $\{222\}$
 $\{400\}$
 \vdots
 \vdots
 \vdots

Example: Face-centered-cubic lattice

The face-centered-cubic (fcc) lattice is very common in metals, for reasons we will examine later. An fcc crystal with only one atom per lattice site has four atoms in the cubic unit cell, with one on the corner and one on each face:



atom	form factor	site
1	f	$(0,0,0)$
2	f	$(0,1/2,1/2)$
3	f	$(1/2,0,1/2)$
4	f	$(1/2,1/2,0)$

The structure factors for fcc are:

$$F_{hkl} = f \cdot [1 + e^{\pi i(k+\ell)} + e^{\pi i(h+\ell)} + e^{\pi i(h+k)}]$$

We can again divide this into allowed reflections and systematic absences.

$$F_{hkl} = \begin{cases} 4f, & h, k, \ell \text{ all even or all odd} \\ 0, & h, k, \ell \text{ mixed even/odd} \end{cases}$$

A partial list of allowed indices begins as follows:

$\{200\}$
 $\{111\}$
 $\{220\}$
 $\{311\}$
 $\{400\}$
 \vdots
 \vdots
 \vdots

Crystal potential and structure factors

The choice of unit cell is not unique, so that means we may get different value for $F_{\mathbf{g}}$ if we pick a different unit cell. Say we picked a unit cell that was twice as big, with twice as many atoms. I'm claiming that, when you calculate the diffracted amplitude (and intensity), you will get the same number. Let's see how that works.

The crystal potential is the Fourier series:

$$\Phi(\mathbf{r}) = \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}$$

The Fourier components are $\Phi_{\mathbf{g}} = \phi(\mathbf{g}) \cdot X_{\mathbf{g}}$. We saw that $X_{\mathbf{g}} = 1/v$ whenever \mathbf{g} is an RLV. The unit-cell potential is

$$\phi(\mathbf{g}) = \sum_{m \text{ atoms}} \phi_m e^{2\pi i \mathbf{g} \cdot \mathbf{d}_m}$$

which is linked to the atomic form factors by

$$f_m = \frac{2\pi m e}{h^2} \phi_m$$

We were just looking at the structure factors:

$$F_{\mathbf{g}} = \sum_{m \text{ atoms}} f_m e^{2\pi i \mathbf{g} \cdot \mathbf{d}_m}$$

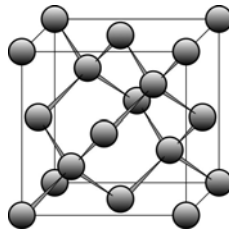
But what really showed up in dynamical-diffraction theory are the extinction distances, which involve the Fourier components of the structure function:

$$U_{\mathbf{g}} = \frac{2me}{h^2} \Phi_{\mathbf{g}} = \frac{F_{\mathbf{g}}}{\pi v}$$

The whole point of this discussion was to show that if we change the unit-cell volume, we will be summing over more atoms, but then we will need to divide by a bigger volume, so the $U_{\mathbf{g}}$ stay the same, and all is well.

Diamond structure

We are systematically going through some common, simple crystal structures. The next one up is diamond, which is built on the fcc structure, but instead of just one fcc lattice, we have two identical fcc lattices, with one offset from the other by $\frac{1}{4}[111]$.



The structure factor can be found by summing the two. Say the first lattice is just the fcc lattice we discussed before, with a lattice point at the cube corner.

$$F_{hkl}^{(1)} = f \cdot [1 + e^{\pi i(k+\ell)} + e^{\pi i(h+\ell)} + e^{\pi i(h+k)}]$$

The second is offset by

$$\mathbf{d} = a(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})/4 = (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/4 = (1/4, 1/4, 1/4)$$

This amounts to just multiplying by an extra phase factor:

$$F_{hkl}^{(2)} = f \cdot [1 + e^{\pi i(k+\ell)} + e^{\pi i(h+\ell)} + e^{\pi i(h+k)}] \cdot e^{\pi i(h+k+\ell)/2}$$

We have to add them together:

$$F_{hkl} = F_{hkl}^{(1)} + F_{hkl}^{(2)} = f \cdot [1 + e^{\pi i(k+\ell)} + e^{\pi i(h+\ell)} + e^{\pi i(h+k)}] \cdot [1 + e^{\pi i(h+k+\ell)/2}]$$

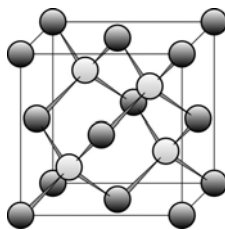
As before, the first factor in square brackets is either 4 or 0. The second factor can be 2, $1 \pm i$, or 0. From the first factor, we again know that hkl for allowed reflections must be all even or all odd. (The rest are systematically absent.) Among that subset of allowed reflections, we have:

$$F_{hkl} = \begin{cases} 8f, & h+k+\ell = 4N \\ 4(1 \pm i)f, & h+k+\ell = 2N+1 \\ 0, & h+k+\ell = 4N+2 \end{cases}$$

Reflections in the last category, with zero structure factor, are called "kinematically forbidden". It is not that we never see them, just that they only appear when dynamical effects are strong.

Zincblende structure

Zincblende is a variation on the diamond structure. Instead of two identical fcc sublattices, one contains a different element than the other (ZnS, for example.)



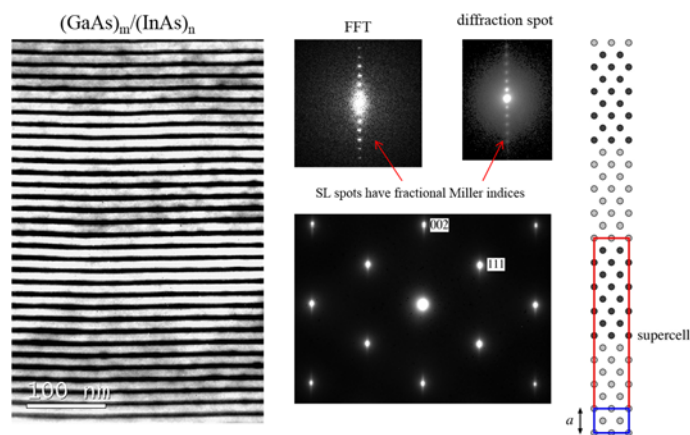
We still know that allowed reflections have hkl all even or all odd. But within that set, we now get

$$F_{hkl} = F_{hkl}^{(1)} + F_{hkl}^{(2)} = \begin{cases} 4(f_A + f_B), & h + k + \ell = 4N \\ 4(f_A \pm if_B), & h + k + \ell = 2N + 1 \\ 4(f_A - f_B), & h + k + \ell = 4N + 2 \end{cases}$$

We no longer have kinematically forbidden reflections, but there may be very weak reflections if dynamical effects are not present and $h + k + \ell = 4N + 2$, such, as for example $\{200\}$ and $\{420\}$.

Superlattices

One way we can start with simple crystals and build up more complex, periodic (or quasi-periodic) crystals is by forming superlattices. Sometimes these occur spontaneously; other times they are synthesized by nanofabrication techniques in the lab. A common type of synthetic superlattice consists of alternating layers of two compatible materials, such as GaAs and InAs semiconductors. TEM is a great tool to characterize these, because the length scale is easily accessible at typical TEM resolutions. To be a superlattice, there must be some quantity that is being alternated periodically; in this case it is a periodic substitution of In for Ga.



The volume for this extra periodicity is called the "supercell". Ideally, it matches with an integer number of the basis, or "matrix", unit cell from which it was built (i.e., it is commensurate), but that is not always true. We still expect to see diffraction from the matrix crystal structure, and the conventional Miller indices can be assigned to those reflections. But the superlattice also generates reflections, and these can be associated with either fractional Miller indices or, sometimes, systematically absent or kinematically forbidden reflections. For a long-period superlattice, these so-called "superlattice reflections" may appear very close to the matrix reflections. Often, there is a close correspondence between the reflections observed in an actual selected-area pattern and the Fourier components that appear in an FFT of an image

taken in the same orientation. This is not a coincidence, but the FFT should not be mistaken for a diffraction pattern, nor vice versa.

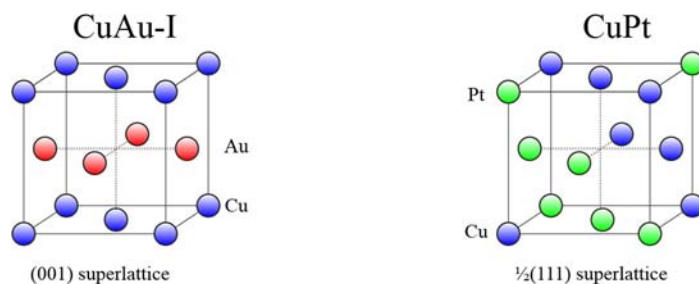
In short, we can say that a superlattice is a large unit cell built by ordering a smaller unit cell.

Atomic ordering in metal alloys

Alloys can be thought of as crystals with random substitutions of the different alloy components on the lattice sites. Atomic ordering usually refers to very short-period superlattice formation in these alloys, and it usually implies that the superlattice formed spontaneously. For the common crystal structures, there are a few types of ordered arrangements that show up often. Most of these were observed in metallurgical work of the early 20th century, so we just refer to the ordered structures by the names of the metal alloys they are known to occur in. Here are some examples:

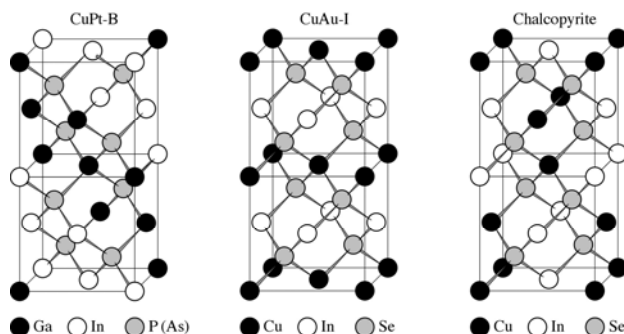
Near 1:1 atomic ratio of Cu/Au, the CuAu alloy orders with Cu and Au occupying alternating (002) planes of its fcc lattice. This generates a (001) periodicity that would otherwise be absent. (Normally, the structure factors for an fcc lattice require hkl all even/all odd.) The corresponding superlattice spots appear in the diffraction pattern.

Under some conditions, the CuPt alloy orders with Cu and Pt occupying alternating {111} planes of its fcc lattice. When the lattice spacing is doubled in direct space, diffraction spots appear at $\frac{1}{2}$ positions in the diffraction pattern.



Atomic ordering in semiconductors

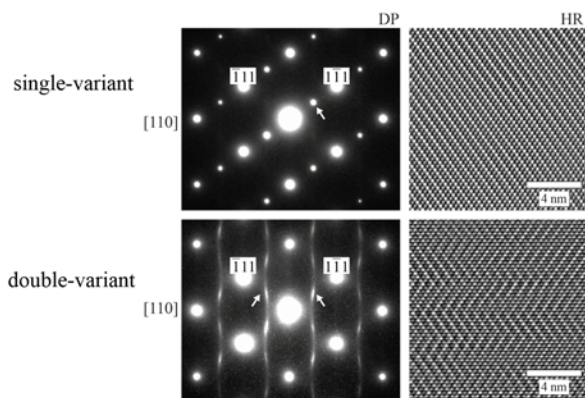
Ordering can show up in either sublattice of zincblende crystals. There are four possible {111} directions w.r.t. the surface. Ordering along two of these are called the CuPt-A “variants”; the other two are CuPt-B variants.



Under some conditions, CuAu-I ordering shows up on the Cu-In sublattice of CuInSe_2 . Chalcopyrite is another type of ordering observed in CuInSe_2 . The name comes from the CuFeSe_2 mineral the structure is associated with.

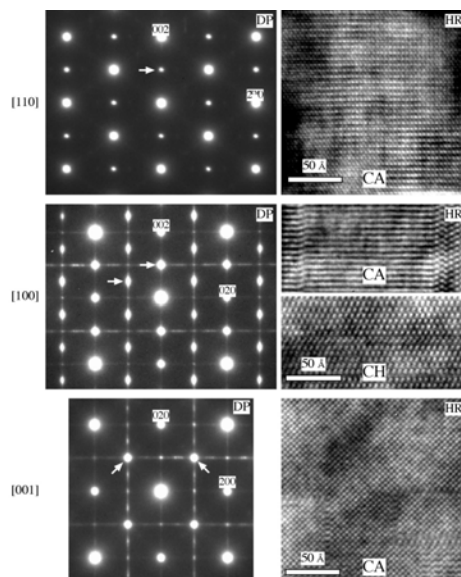
CuPt-ordered GaInP₂

The extra periodicity associated with ordering leads to many possibilities. For one thing, ordering can occur along different symmetry-equivalent directions. The CuPt-B ordered phase occurs in two possible subvariants (sometimes just called variants). Slight differences in surface orientation will allow one variant to dominate over the other. A single-variant film can show large domains, usually separated by antiphase boundaries (discussed later). Double-variant films show tiny lamellar domains that also form a quasi-periodic superlattice. The $1/2(111)$ planes are easily resolved in TEM lattice images, if we know where to look. The best place is along the $[110]_A$ zone axis, which is perpendicular to both $\{111\}_B$ directions. In this orientation, we see not only the ordered periodicity, but the underlying zincblende structure, as well. The type of ordering present is clearly evident from the superstructure intensity in selected-area diffraction patterns. These tiny domains in double-variant samples cause broadening of the ordered diffraction patterns.



Ordering in CuInSe₂

CuInSe₂ is considered a useful material for photovoltaics. Unlike Ga and In in GaInP₂, Cu and In are not from the same columns on the periodic table, so the substitution of one for another is more unusual. But at the 1:1:2 composition ratio, they can assume various structural arrangements, depending on the synthesis method. The CuAu-I and chalcopyrite structures are two possible outcomes.

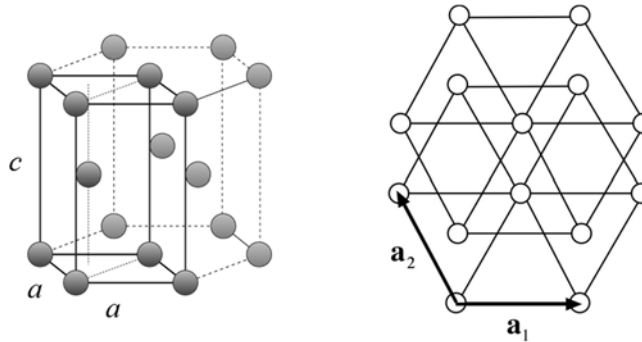


It is usually more convenient to index the patterns based on the “sphalerite” structure, in which Cu and In are randomly distributed. This is equivalent to a disordered zincblende structure. By picking this reference structure, it makes it easier to convey alterations, such as ordering, and the orientations of domains of these ordered phases with respect to one another.

Example: Hexagonal close-packed structure

Another important crystal structure is hexagonal close packed (hcp). Hexagonal refers to the type of lattice, with lattice points arranged in 2-D sheets of regular hexagons (or triangles, if you prefer), which are stacked in a layered structure. We need two lattice parameters, a and c , to specify the unit cell. a is the nearest neighbor distance; $c/2$ is the interlayer spacing. The unit-cell volume is $v = \sqrt{3}a^2c/2$. We can define a unit cell as:

$$\mathbf{a}_1 = a\hat{x}, \quad \mathbf{a}_2 = -\frac{a}{2}\hat{x} + \frac{\sqrt{3}}{2}a\hat{y}, \quad \text{and} \quad \mathbf{c} = c\hat{z}$$



The hcp structure usually refers to a compound containing only one element. We need two atoms of this element to generate the unit cell.

atom	form factor	site
1	f	$(0,0,0)$
2	f	$(1/3, 2/3, 1/2)$

The structure factors turn out to be

$$F_{hkl} = f \cdot \left[1 + e^{2\pi i \left(\frac{h}{3} + \frac{2k}{3} + \frac{\ell}{2} \right)} \right]$$

Notice that the extra layer of atoms at $c/2$ causes $F_{00\ell} = 0$ for ℓ odd.

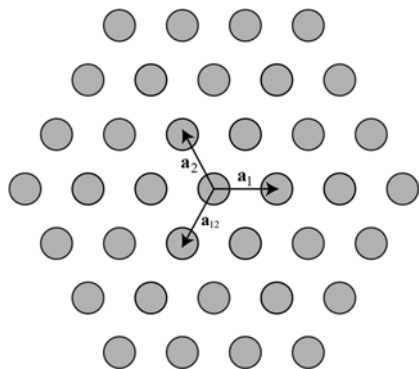
Indexing hexagonal crystals (I)

We made a choice when defining the hexagonal unit cell that \mathbf{a}_2 would be oriented 120° clockwise about \mathbf{a}_3 from \mathbf{a}_1 . A direct-lattice vector could be written:

$$\mathbf{r}_{UVW} = U \cdot \mathbf{a}_1 + V \cdot \mathbf{a}_2 + W \cdot \mathbf{a}_3$$

There is a symmetry-equivalent direction at 120° counter-clockwise about \mathbf{a}_3 from \mathbf{a}_1 :

$$\mathbf{a}_{12} = -(\mathbf{a}_1 + \mathbf{a}_2)$$



Indexing hexagonal crystals (I)

Let's rewrite the direct-lattice vector as

$$\begin{aligned}\mathbf{r}_{uvw} &= u \cdot \mathbf{a}_1 + v \cdot \mathbf{a}_2 + t \cdot \mathbf{a}_{12} + w \cdot \mathbf{a}_3 \\ &= u \cdot \mathbf{a}_1 + v \cdot \mathbf{a}_2 - t \cdot (\mathbf{a}_1 + \mathbf{a}_2) + w \cdot \mathbf{a}_3 \\ \mathbf{r}_{uvw} &= (u - t) \cdot \mathbf{a}_1 + (v - t) \cdot \mathbf{a}_2 + w \cdot \mathbf{a}_3 = \mathbf{r}_{UVW}\end{aligned}$$

We can relate the indices by:

$$U = u - t$$

$$V = v - t$$

$$W = w$$

There is an extra degree of freedom here. Let's pick $t = -(u + v)$. Now we can specify:

$$u = (2U - V)/3$$

$$v = (2V - U)/3$$

$$t = -(U + V)/3$$

$$w = W$$

The four indices $[uv tw]$ highlight the hexagonal symmetry of the crystal. For example, with three indices, it is obvious that $[100]$ and $[010]$ are symmetry equivalent: these are \mathbf{a}_1 and \mathbf{a}_2 . But $[\bar{1}\bar{1}0]$, corresponding to \mathbf{a}_{12} , is symmetry equivalent to both of these. In our new basis, the equivalence is obvious:

$$[100] \rightarrow \frac{1}{3}[2\bar{1}\bar{1}0], [010] \rightarrow \frac{1}{3}[\bar{1}2\bar{1}0], [\bar{1}\bar{1}0] \rightarrow \frac{1}{3}[\bar{1}\bar{1}20]$$

Comparing close-packed structures: fcc and hcp

There is a reason we call hcp "hcp". First, we can think of atoms as hard spheres in this context. The closest they can be packed together in a 2-D layer is like the hexagonal sheets (called the basal planes) in the hcp structure. Another sheet can be stacked on the first in one of two equivalent positions, with each atom of the top layer touching three atoms in the layer below.

So what about the next (third) sheet? It could either be aligned with the first sheet, or placed in alignment with the position we didn't use for the second sheet. Say the first sheet is in position A and the second is in position B. If we put the third sheet in position A, and keep repeating this sequence, we get an hcp structure, following the sequence AB/AB/AB... If we put the third sheet in the unused position - position C - we get an fcc structure, also called a "cubic close-packed" structure, following the sequence ABC/ABC/ABC...

We can make the connection even more precise by relating the interlayer spacing to the nearest-neighbor distance d_{n-n} . Consider hcp, with $d_{n-n} = a^{(hcp)}$. In general, for an hcp structure, the interlayer spacing is

$$d_{002} = c/2.$$

Now consider fcc, with $d_{n-n} = a^{(fcc)}/\sqrt{2}$. The layers here extend along $[111]$, and have spacing

$$d_{111} = a^{(fcc)}/\sqrt{3} = \sqrt{\frac{2}{3}}d_{n-n}$$

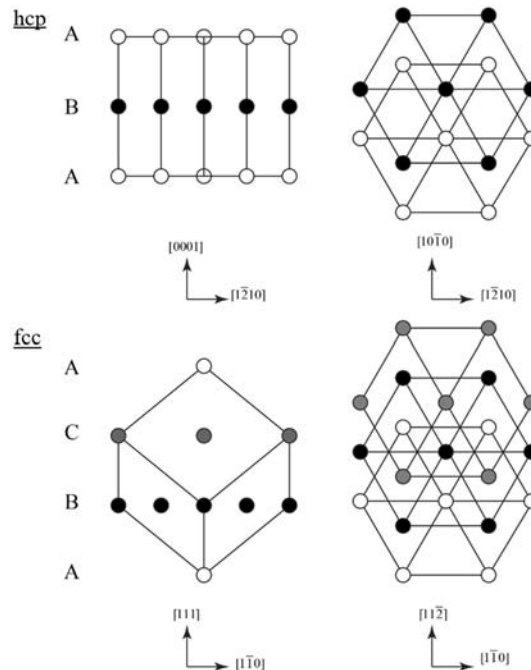
In the “ideal” hcp structure, the interlayer spacing is also related to the nearest-neighbor spacing. We would have

$$c^{(ideal)}/2 = \sqrt{\frac{2}{3}}d_{n-n}$$

So the ideal hcp structure has a c lattice parameter of

$$c^{(ideal)} = 2\sqrt{\frac{2}{3}}d_{n-n} = \sqrt{\frac{8}{3}}a^{(hcp)}$$

To summarize, the hcp and fcc structures are both close-packed structures. They differ only the sequence by which we stack the hexagonal 2-D close-packed sheets. This is at least one reason the fcc is such a common crystal structure among single element materials.



Example: CdSe on (111) GaAs

There is often only a small energy difference between fcc and hcp structures in materials with a particular composition. For example, CdSe can form either the fcc, zincblende phase, or the hcp, wurtzite phase, depending on slight differences in synthesis procedure. If we start with a cubic GaAs substrate in an (001) orientation, epitaxial CdSe crystal likely to maintain the zincblende structure, because the planes have an oblique orientation with respect to the surface. But when grown on a (111) GaAs substrate, the difference is practically negligible, because each 2-D sheet can pick one of the two available close-packed

alignments freely. So we may get patches of hcp in one area, and patches of fcc in another. these look different in TEM lattice images, and we can confirm the structures with FFTs of the images. (Double diffraction in hcp CdSe gives rise to 0001 spots, but no equivalent spot is observed for fcc.)

