Lecture 5:

- Overflow from last lecture: Ewald construction and Brillouin zones
- Structure factor

Review

Consider direct lattice defined by vectors $\boldsymbol{R} = u_1\boldsymbol{a_1} + u_2\boldsymbol{a_2} + u_3\boldsymbol{a_3}$ where u_1, u_2, u_3 are integers and $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3}$ are primitive translation vectors

The reciprocal lattice is defined by (primitive) vectors $\boldsymbol{b_1}, \boldsymbol{b_2}, \boldsymbol{b_3}$ defined in the following way:

$$\boldsymbol{b_1} = 2\pi\frac{\boldsymbol{a_2} \times \boldsymbol{a_3}}{\boldsymbol{a_1} \cdot \boldsymbol{a_2} \times \boldsymbol{a_3}}$$

$$\boldsymbol{b_2} = 2\pi\frac{\boldsymbol{a_3} \times \boldsymbol{a_1}}{\boldsymbol{a_1} \cdot \boldsymbol{a_2} \times \boldsymbol{a_3}}$$

$$\boldsymbol{b_3} = 2\pi\frac{\boldsymbol{a_1} \times \boldsymbol{a_2}}{\boldsymbol{a_1} \cdot \boldsymbol{a_2} \times \boldsymbol{a_3}}$$

The reciprocal lattice is also a lattice, with all points accessed by reciprocal lattice vector

$$\boldsymbol{G} = v_1\boldsymbol{b_1} + v_2\boldsymbol{b_2} + v_3\boldsymbol{b_3}$$

Where v_1, v_2, v_3 are integers

Another important property of the reciprocal lattice is that $\boldsymbol{R} \cdot \boldsymbol{G} = 2\pi n$ where n is an integer.

One important application of the reciprocal lattice is **diffraction**—a type of experiment used to determine the repeating structure of a crystal by shining x-rays, neutrons, or electrons onto the crystal and investigating how much the beam is deflected. In previous courses, you might have seen the Bragg forula for diffraction:

$$2dsin\theta = n\lambda$$

Where n is an integer, λ is the wavelength of light (or debroglie wavelength of particles), and d is the spacing between identical crystal planes. Any crystal can be subdivided into planes (containing atoms) in several different ways.

There is another way to express this same formula using the reciprocal lattice. If a plane wave with wavevector **k** is incident on the crystal ($\sim e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$)and the outgoing wave has wavevector **k'** ($\sim e^{i\boldsymbol{k'}\cdot\boldsymbol{r}}$), a diffraction peak will be seen only if $\boldsymbol{k'} - \boldsymbol{k} = \boldsymbol{G}$

We can also use the reciprocal lattice to find spacting between identical lattice planes more easily.

If we have a plane described by miller indices (hkl)

It turns out that $d(hkl) = 2\pi/|\boldsymbol{G}|$ where $\boldsymbol{G} = h\boldsymbol{b_1} + k\boldsymbol{b_2} + l\boldsymbol{b_3}$**.** It also turns out that $\boldsymbol{G}_{hkl}$ is **normal** to the plane described by the (hkl) miller index

Ewald construction

The Ewald construction is a way of visualizing a diffraction experiment, and also illustrating that reciprocal space is an empty space.

1. Draw reciprocal lattice
2. Pick a point at the origin and draw the wavevector of the incident beam, **k**, the outgoing beam, **k’**, and their difference, Δk
3. Remember, if $\Delta k = \boldsymbol{G}$ (a reciprocal lattice vector), we will get constructed interference and a finite diffraction signal
4. The vectors **k** and **k’** define a sphere, the Ewald sphere. If this sphere intersects another point on the reciprocal lattice, the laue condition (stated in step 3) will apply. However, this is very difficult to accomplish just by chance because the reciprocal lattice is mainly empty space.
5. There are three ways to get around this difficulty

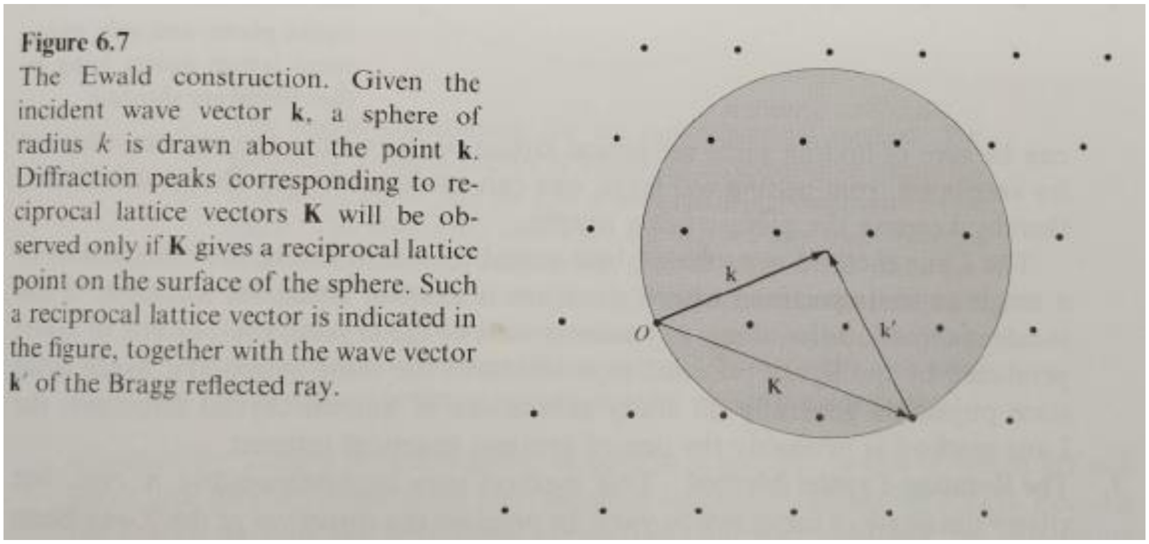


Figure 6.7
The Ewald construction. Given the incident wave vector **k**, a sphere of radius k is drawn about the point **k**. Diffraction peaks corresponding to reciprocal lattice vectors **K** will be observed only if **K** gives a reciprocal lattice point on the surface of the sphere. Such a reciprocal lattice vector is indicated in the figure, together with the wave vector **k**′ of the Bragg reflected ray.

Note: in the image above the difference between k and k’ is called K, but in the rest of these notes it is called G

Method 1: rotate the crystal

(The direct lattice is defined relative to the crystal, so when we rotate the crystal, we rotate the direct lattice, and hence we rotate the reciprocal lattice)

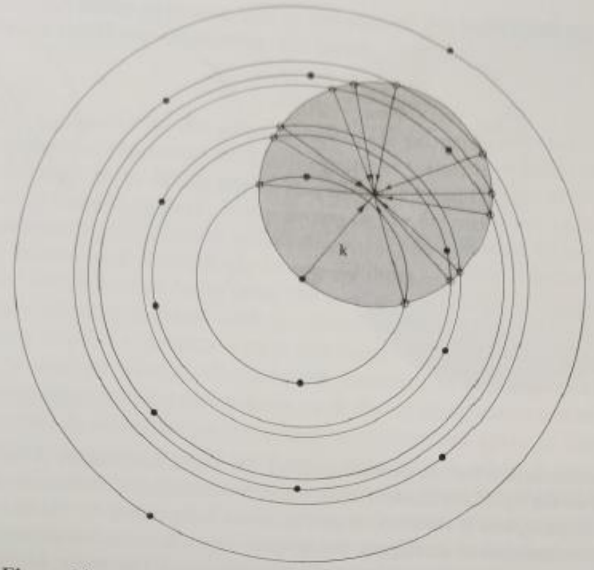
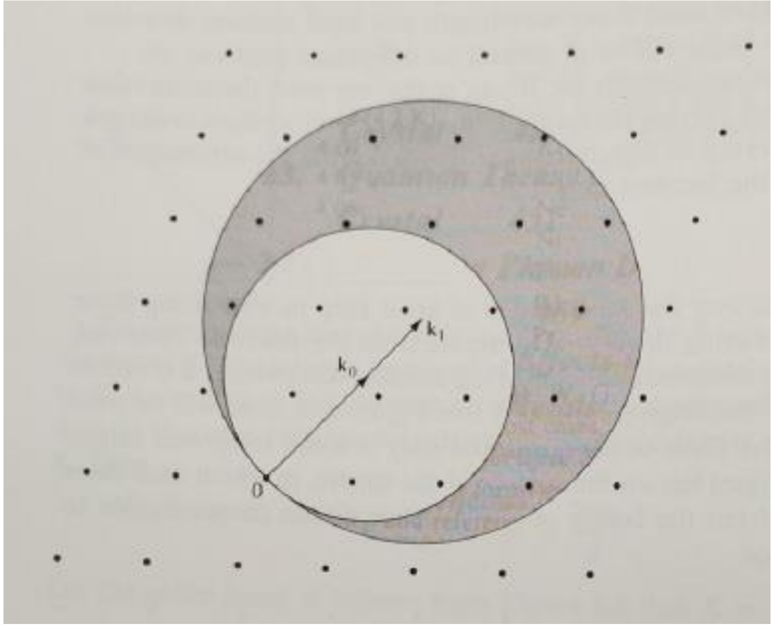


Figure 6.9
The Ewald construction for the rotating-crystal method. For simplicity a case is shown in which the incident wave vector lies in a lattice plane, and the axis of rotation is perpendicular to that plane. The concentric circles are the orbits swept out under the rotation by the reciprocal lattice vectors lying in the plane perpendicular to the axis containing **k**. Each intersection of such a circle with the Ewald sphere gives the wave vector of a Bragg reflected ray. (Additional Bragg reflected wave vectors associated with reciprocal lattice vectors in other planes are not shown.)

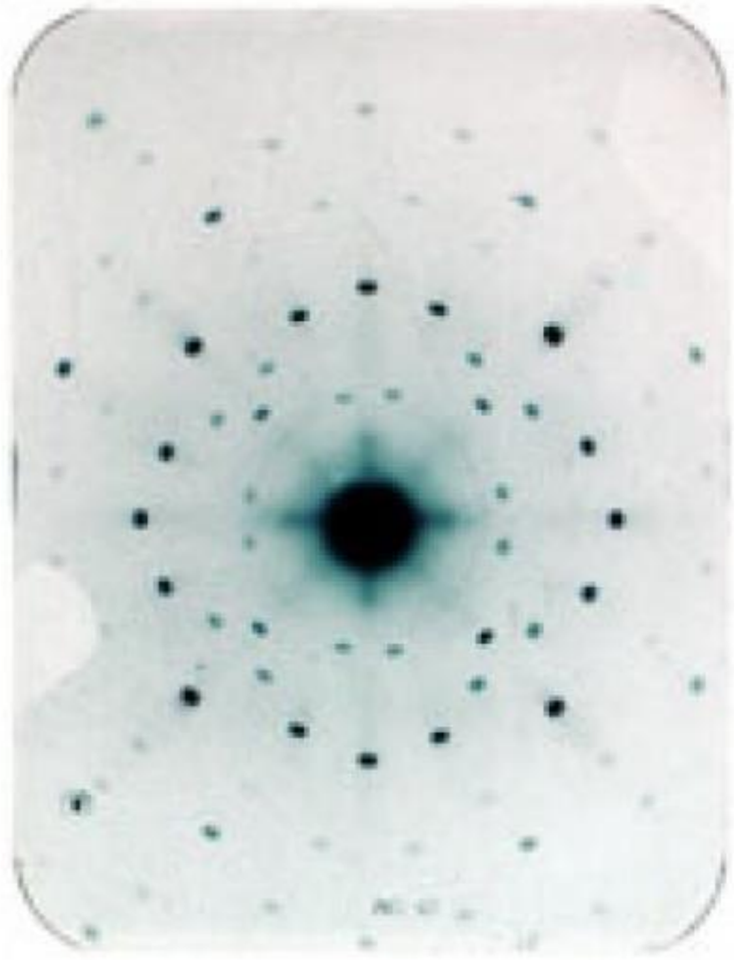
Method 2: use polychromatic x-rays (e.g. white light) so that many values of k are incorportated. This is called the Laue method, and it is frequently used to find the orientation of single crystal specimens.



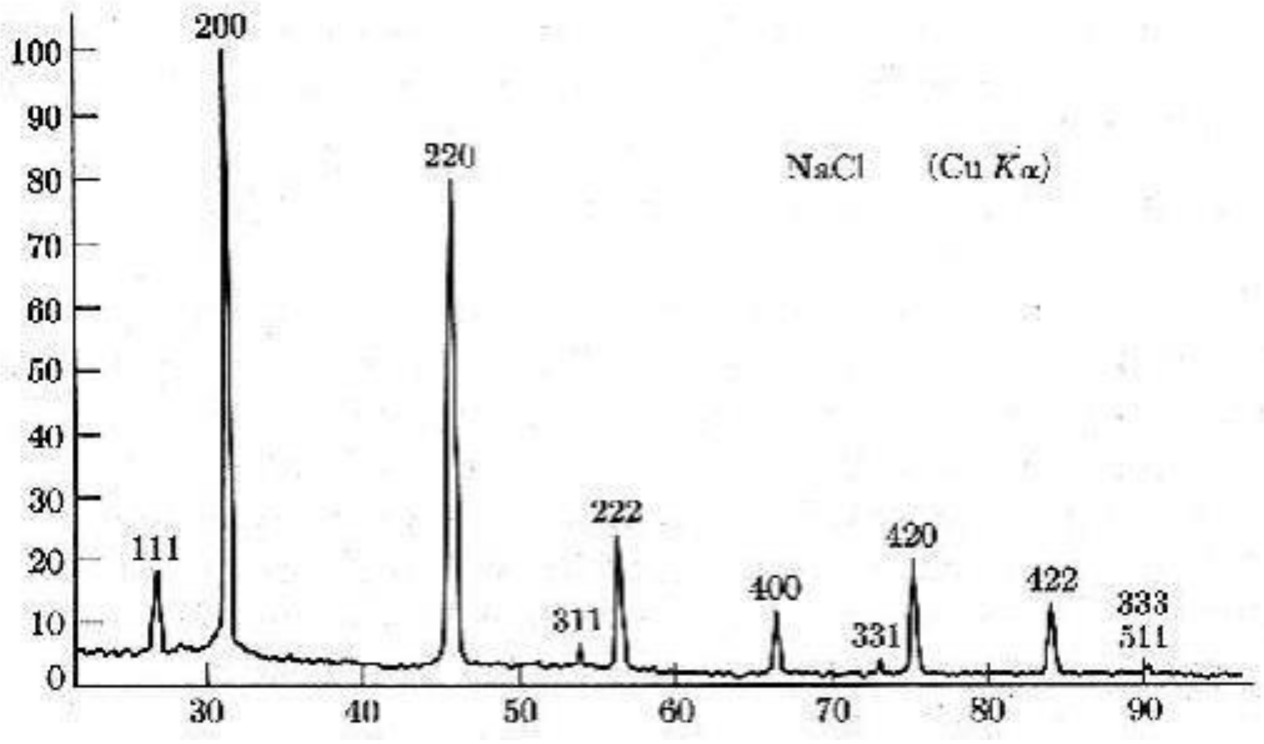
Method 3: powder diffraction. This method uses monochromatic x-rays, but instead of studying a large single crystal it studies a powder—a collection of many many microscopic crystals oriented in random directions. From the standpoint of solid state physics, a microscopic crystal is effectively infinite because

it has so many unit cells that the boundaries do not change the properties much. For a given incidence angle on this powder, θ, there might be a crystallite that has the correct orientation of crystal planes to produce a diffraction signal. As θ is varied, one picks up all of the possible crystal-plane spacings (d) in that crystal. The series of peaks from a powder diffraction experiment gives the 'fingerprint' of a material.

Laue pattern of NaCl (table salt) single crystal along 4-fold symmetric axis



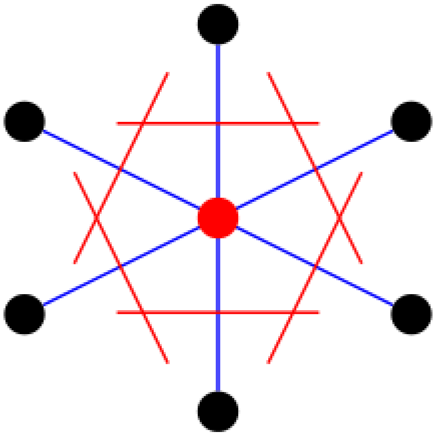
Powder x-ray diffraction pattern of NaCl



Brillouin zones

For a direct primitive lattice, there is often more than one way to define a primitive cell (the parallelogram defined by vectors which can be used to access every point in the lattice). One way to do this (this is a HW question) is the Wigner-Seitz cell, which is defined by the following procedure:

1. Pick one lattice point and draw lines to connect this to all nearby lattice points
2. Draw perpendicular bisectors through all of these lines
3. The shape formed from the intersection of the perpendicular bisectors is the Wigner-Seitz cell



When this same procedure is done for the **reciprocal lattice** the name of the cell is the first **Brillouin zone**. This concept will become important in later chapters when we add electrons into the picture. The Brillouin zone contains all of the wavevectors which can be Bragg reflected by the crystal.

Structure factor

The final piece for using what we have learned about the reciprocal lattice and diffraction to learn about the repeating periodic structure of crystalline solids is including the basis. Thus far, we have only been considering the lattice, but as we learned in chapter 1, a unit cell in a crystal consists of a lattice and a basis.

Consider a crystal of identical unit cells, each with electron density **inside** them given by n(**r**), which is a function of position inside the cell (later we will substitute atomic positions in there).

We are shining an x-ray plane wave at this crystal with wavefunction $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$and measuring a diffracted beam with wavefunction $e^{i\boldsymbol{k\prime}\cdot\boldsymbol{r}}$, where |k|=|k'|. Also, we are getting a diffraction signal, so $\boldsymbol{k}-\boldsymbol{k}'=\boldsymbol{G}$ where G is a vector of the reciprocal lattice.

The diffraction amplitude for N unit cells may be given by N multiplied by the diffraction amplitude for a single cell:

$$F_{\boldsymbol{G}} = N\int_{cell} dV\, n(\boldsymbol{r})e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} = NS_{\boldsymbol{G}}$$

What this integral physically does is it considers every position **r** inside the unit cell and introduces a phase delay from that infinitesimal volume element. We are considering a specific G, so the sum over all possible G's (last lecture) is omitted.

$S_{\boldsymbol{G}}$ is the structure factor.

n(**r**) can be decomposed into contributions from every atom inside the unit cell. For convenience, we always put one of the atoms at the origin.

$n(\boldsymbol{r}) = \sum_{j=1}^{s} n_j(\boldsymbol{r}-\boldsymbol{r_j})$, where there are s atoms in the basis

Plug this into the expression for the structure factor above

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s}\int dVn_j(\boldsymbol{r}-\boldsymbol{r_j})e^{-i\boldsymbol{G}\cdot\boldsymbol{r}}$$

$$= \sum_{j=1}^{s}\int dVn_j(\boldsymbol{r}-\boldsymbol{r_j})e^{-i\boldsymbol{G}\cdot(\boldsymbol{r}-\boldsymbol{r}_j)}e^{-i\boldsymbol{G}\cdot\boldsymbol{r}_j}$$

Define a new variable $\boldsymbol{\rho} = \boldsymbol{r}-\boldsymbol{r_j}$

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}_j}\int dVn_j(\boldsymbol{r}-\boldsymbol{r_j})e^{-i\boldsymbol{G}\cdot(\boldsymbol{r}-\boldsymbol{r}_j)}$$

$$\sum_{j=1}^{s} e^{-i\boldsymbol{G}\cdot\boldsymbol{r_j}} \int dV n_j(\boldsymbol{\rho}) e^{-i\boldsymbol{G}\cdot\boldsymbol{\rho}}$$

Define the **atomic form factor** $f_j = \int dV n_j(\boldsymbol{\rho}) e^{-i\boldsymbol{G}\cdot\boldsymbol{\rho}}$. This number represents the scattering power of the j-th atom in the cell. It will be equal for two atoms of the same type (e.g. two sodium atoms at two different positions in a unit cell). It will also depend on what exactly is being scattered—x-rays, neutrons, or electrons.

$$S_{\boldsymbol{G}} = \sum_{j=1}^{s} f_j e^{-i\boldsymbol{G}\cdot\boldsymbol{r_j}}$$

The scattering intensity is proportional to $|S_{\boldsymbol{G}}|^2$ so it is ok if S_G is not real.

In terms of primitive lattice vectors, the positions of each of the atoms in the basis is given by:

$\boldsymbol{r_j} = x_j\boldsymbol{a_1} + y_j\boldsymbol{a_2} + z_j\boldsymbol{a_3}$ where x_j, y_j, z_j are fractional

$$\boldsymbol{G}\cdot\boldsymbol{r_j} = (v_1\boldsymbol{b_1} + v_2\boldsymbol{b_2} + v_3\boldsymbol{b_3})\cdot(x_j\boldsymbol{a_1} + y_j\boldsymbol{a_2} + z_j\boldsymbol{a_3})$$

$$= 2\pi(v_1x_j + v_2y_j + v_3z_j)$$

$$S_{\boldsymbol{G}}(v_1v_2v_3) = \sum_{j=1}^{s} f_j e^{-2\pi i(v_1x_j+v_2y_j+v_3z_j)}$$

Practice—Structure factor of BCC lattice.

For this exercise, we will use the **conventional** cubic unit cell of the BCC lattice, which as **2** atoms per basis.

Atom 1: $\boldsymbol{r_1} = \boldsymbol{0}$

Atom 2: $\boldsymbol{r_2} = \frac{1}{2}a\hat{\boldsymbol{x}} + \frac{1}{2}a\hat{\boldsymbol{y}} + \frac{1}{2}a\hat{\boldsymbol{z}}$

$$S_{\boldsymbol{G}}(v_1v_2v_3) = \sum_{j=1}^{s} f_j e^{-2\pi i(v_1x_j+v_2y_j+v_3z_j)}$$

$$= fe^0 + fe^{i\pi(v_1+v_2+v_3)}$$

The subscript has been dropped on the f because two identical atoms are used in this exercise, meaning they have the same form factor. The second term can be +f or –f, depending if the integers in the exponent add up to a positive or negative number

$$S_{G,BCC}(v_1v_2v_3) = \begin{cases} 0 \text{ if } v_1 + v_2 + v_3 \text{ is odd} \\ 2f \text{ if } 0 \text{ if } v_1 + v_2 + v_3 \text{ is even} \end{cases}$$

According to this calculation, the Bragg peaks from some planes will be missing. For example, the (100) and (111) peaks will be missing (odd sum of 3 miller indices), while (110) and (200) will be present (even sum).

We can try to understand this by considering the **primitive lattice** of the BCC structure.

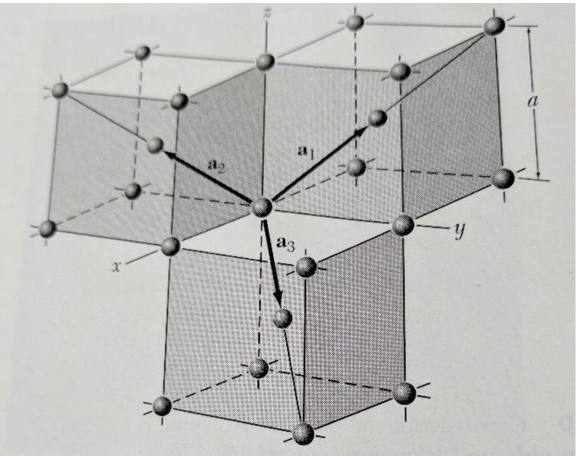


Figure 12 Primitive basis vectors of the body-centered cubic lattice.

$$\boldsymbol{a_1} = \frac{a}{2}(-\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$$

$$\boldsymbol{a_2} = \frac{a}{2}(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$$

$$\boldsymbol{a_3} = \frac{a}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} - \hat{\boldsymbol{z}})$$

Consider the (100) plane, referenced to the **conventional** unit cell. In terms of the **primitive** vectors, the miller indices would be:

Intersection coordinates along $\boldsymbol{a_1}, \boldsymbol{a_2}, \boldsymbol{a_3}$=(-2, 2, 2)

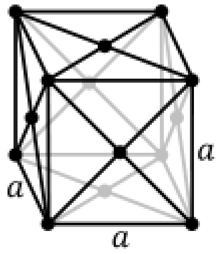
Inverses: $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Miller indices of $(100)_{cubic}$ in terms of primitive translation vectors: (-111)

But this is equivalent to the (-111) plane which is parallel to the one we were originally considering, but located a/2 along the x direction towards the origin. Thus, when we go to the primitive lattice vectors of BCC, we can see that there are no missing Bragg peaks, we just double counted some of them initially by using a cell with 2 atoms inside it when 1 would have sufficed.

Example 2: Structure factor of the face centered cubic lattice

Again, we consider the **conventional** unit cell.



Putting the origin at the back left corner and having z point up and y to the right, we have atoms at the following fractional coordinates (factor of a is omitted):

$$(0,0,0);\left(\frac{1}{2},0,\frac{1}{2}\right);\left(0,\frac{1}{2},\frac{1}{2}\right);(\frac{1}{2},\frac{1}{2},0)$$

(When atoms are shared with adjacent cells we count only enough of those atoms to get the total number contained in one cell. For example, we counted all of the back corner atom (0,0,0) and left the other 7 to other unit cells because there are 8*1/8=1 corner atoms; ditto for the face-centered atoms which are each shared with 2 other cells, only count 3 of them)

The structure factor for the conventional FCC cell is given by:

$$S_G(\nu_1\nu_2\nu_3)=\sum_{j=1}^{s} f_j e^{-2\pi i\left(\nu_1 x_j+\nu_2 y_j+\nu_3 z_j\right)}$$

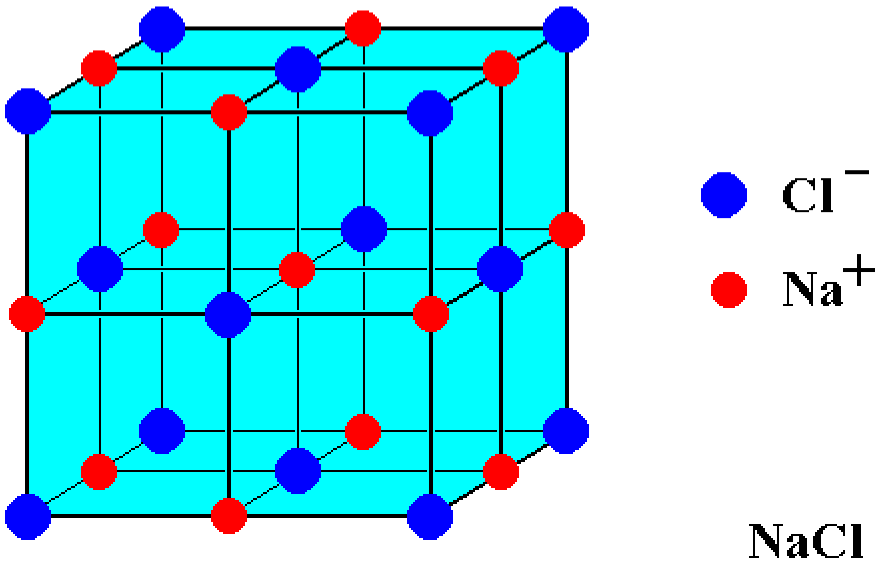
$$=f[1+e^{-i\pi(\nu_1+\nu_3)}+e^{-i\pi(\nu_2+\nu_3)}+e^{-i\pi(\nu_1+\nu_2)}$$

$$=\begin{cases} 0 \text{ if one index is odd and other two even or if two are odd and one is even} \\ 4f \text{ if all indices are odd or all are even} \end{cases}$$

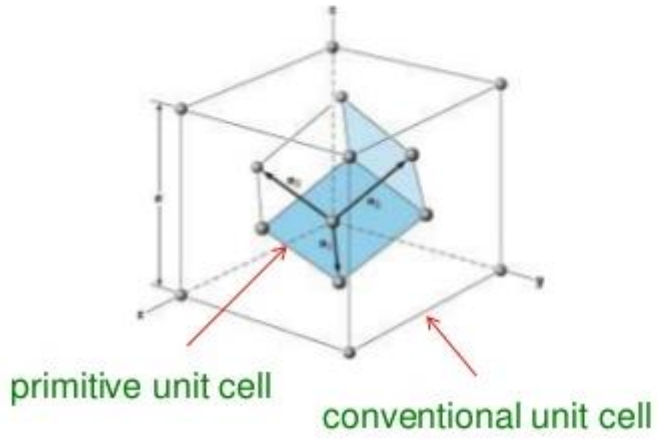
Again, the atomic form factor is the same for all terms in our summation because all atoms are identical. Similar to what we saw in the BCC lattice, only ¼ of the miller indices in FCC lattices will yield Bragg peaks (there are 2 ways to select all odd or all even indices, but 6 ways to select a mixture of odds and evens) because the conventional unit cell contains 4 atoms.

Example 3: NaCl structure

The NaCl structure can be thought of as two interweaving FCC lattices (one for Na, one for Cl)



To avoid having to write a sum over 8 different terms, let’s express the coordinates in terms of the **primitive** lattice vectors.



Primitive vectors

$$\vec{a}_1 = \frac{a}{2}(\hat{x}+\hat{y}),$$

$$\vec{a}_2 = \frac{a}{2}(\hat{y}+\hat{z}),$$

$$\vec{a}_3 = \frac{a}{2}(\hat{z}+\hat{x}).$$

Set the origin at the Cl atom in the back left corner (000)

The fractional coordinate of the Na atom next to it can be expressed as: $\frac{1}{2}(\boldsymbol{a_1} + \boldsymbol{a_3} - \boldsymbol{a_2})$

$$\boldsymbol{G} \cdot \boldsymbol{r_j} = (v_1\boldsymbol{b_1} + v_2\boldsymbol{b_2} + v_3\boldsymbol{b_3}) \cdot \left(x_j\boldsymbol{a_1} + y_j\boldsymbol{a_2} + z_j\boldsymbol{a_3}\right) = 2\pi(v_1x_j + v_2y_j + v_3z_j)$$

Thus,

$$S_{\boldsymbol{G},NaCl} = f_{Cl} + f_{Na}e^{-i\pi(v_1 - v_2 + v_3)}$$

We cannot make the same simplification as before because the atomic form factors are different, but we can make general statements:

- If indices are all even or two odd and one even, the 2nd term will give a positive contribution to the sum
- If indices are all odd or two even and one off, the 2nd term will give a negative contribution to the sum, likely making $|S_G|^2$ (which we measure) smaller.

Comparing to the powder x-ray diffraction image we can see that the 111 peak is very small compared to the nearby 200 and ditto for the 311 vs 222. In general, we expect peaks to get smaller as we move to higher angle because higher-index planes contain fewer atoms, but the analysis we did above allows us to gain further insight into why some Bragg peaks are larger than others nearby.

If we are using x-rays to do our diffraction experiments, the form factor is proportional to Z (the atomic number). This is derived sketchily in your textbook, but we will take it as a given for this lecture. To be more specific, it is electrons which do the scattering so the number of electrons on each species of atoms is what matters. This might not be the same as the atomic number for **ionic solids** like NaCl, where the crystal structure is made up of charged species.

To summarize:

$$Z_{Na} = 11$$

$$Z_{Cl} = 17$$

$$\text{Electrons on Na}^{+} = 10$$

$$\text{Electrons on Cl}^{-} = 18$$