SCPY 371: Solid State Physics **1st Semester 2021**

Lecture 2: Reciprocal lattice and diffraction

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In the previous chapter, we have learned about the crystal structure and how to describe it using mathematical objects namely translation operators and point operators. In this chapter, we will proceed and describe how one can measure the crystal structure of an interest system. The obvious answer is, of course, to take a 'very-high resolution' picture of the system to study its microscopic-scale structure. As you might have learned in the electromagnetic class, in order to look at something small with wave one needs to use the wave with the wavelength smaller than the size of the object one wants to see. In this case, one wants to see the structure in an atomic scale, and hence one needs to use the wave with the wavelength in an order of angstrom. For light, it is in the range of x-ray or in the energy range of keV (eV stands for electron volt, which is the energy gained by an electron accelerated across 1 V of electric potential). For the particle wave such as a neutron beam, the energy of neutron is in the energy range of meV.

2.1 Reciprocal lattice

Since in order to study the crystal structure, we have to shine wave onto the system we want to study and look at the diffracted wave, we will first learn the basic theory of diffraction. Then, the first question we need to answer is how the wave interacts with the crystal. We now know that the crystal is made up of a repeating unit that can be abstractly described by the Bravais lattice with a basis of atoms. Since the wave will interact with electrons around the atoms in the case of x-ray and with nuclei in the case of neutron beam, the potential term of the total Hamiltonian of the crystal must embed the periodicity of the lattice. That means when the wave interact with the crystal through this periodic potential, the diffracted wave must also gain the information about the periodicity of the lattice. In the case of plane wave, we should get the following relation for the diffracted wave function:

$$e^{i\vec{K}\cdot\vec{r}} = e^{i\vec{K}\cdot\left(\vec{r}+\vec{R}\right)},$$

which means

$$e^{i\vec{K}\cdot\vec{R}} = 1, \tag{2.1}$$

where $\vec{R}$ is the lattice translation operator or vector (from now on we will call the Bravais lattice created by a set of $\vec{R}$ the **direct space**) that we introduced in the previous chapter (note that in the previous chapter, we used $\vec{T}$ to represent this lattice translation operator). We will call $\vec{K}$ the **reciprocal lattice vector**. We note that a set of $\vec{K}$ creates the Bravais lattice in a dual space, which we will call the **reciprocal space**. The word *reciprocal* is used because the length of the primitive vectors in the reciprocal is inversely proportional to (or reciprocal to) the length of the primitive vectors in the direct space. If we know the primitive vectors in the direct space, we can calculate the primitive vectors

in the reciprocal space. Given $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, we have

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}. \end{aligned} \tag{2.2}$$

The denominator is basically the volume of the primitive unit cell. From these relations, you can right away see that

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij},$$

where δ_{ij} is the Kronecker delta:

$$\delta_{ij} = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j. \end{cases}$$

We then can define $\vec{K}$ from $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ the same way we obtain $\vec{R}$ from $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$. That is,

$$\begin{aligned} \vec{K} &= m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3, \\ \vec{R} &= n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3. \end{aligned}$$

wherer m_i and n_i with $i = 1$, 2, and 3 are integers. Taking the dot product of $\vec{K}$ and $\vec{R}$, we get

$$\vec{K} \cdot \vec{R} = 2\pi \left(m_1 n_1 + m_2 n_2 + m_3 n_3 \right).$$

And since $m_1 n_1 + m_2 n_2 + m_3 n_3$ is an integer. $e^{i\vec{K}\cdot\vec{R}} = 1$ as required by Eq. 2.1. This is roughly the proof that the definition of $\vec{b}_1$ in Eq. 2.2 satisfies the condition required for the diffracted wave function from the periodic crystal.

Examples of reciprocal lattices In this section, we will study a few examples of the simplest reciprocal lattices in three dimensions. Given the primitive translation vectors, one can calculate the primitive reciprocal vectors using Eq. 2.2.

1. **Simple cubic**: The reciprocal lattice of the simple cubic Bravais lattice is also simple cubic with
$$\vec{b}_1 = \frac{2\pi}{a}\hat{x}, \quad \vec{b}_2 = \frac{2\pi}{a}\hat{y}, \quad \text{and } \vec{b}_3 = \frac{2\pi}{a}\hat{z},$$
2. **Face-centered cubic**: The reciprocal lattice of the face-centered cubic Bravais lattice is body-centered cubic with
$$\vec{b}_1 = \frac{2\pi}{a}\left(-\hat{x}+\hat{y}+\hat{z}\right), \quad \vec{b}_2 = \frac{2\pi}{a}\left(\hat{x}-\hat{y}+\hat{z}\right), \quad \text{and } \vec{b}_3 = \frac{2\pi}{a}\left(-\hat{x}+\hat{y}-\hat{z}\right),$$
You should try derive these expressions of $\vec{b}_i$ yourself.
3. **Body-centered cubic**: As you have guessed, the reciprocal lattice of the body-centered cubic Bravais lattice is face-centered cubic with
$$\vec{b}_1 = \frac{2\pi}{a}\left(\hat{y}+\hat{z}\right), \quad \vec{b}_2 = \frac{2\pi}{a}\left(\hat{x}+\hat{z}\right), \quad \text{and } \vec{b}_3 = \frac{2\pi}{a}\left(\hat{x}+\hat{y}\right),$$

First Brillouin zone The primitive unit cell in the reciprocal lattice is usually represented by the Wigner-Seitz cell. We have learned how to construct the Wigner-Seitz cell given the primitive vectors in the previous chapter. The Wigner-Seitz cell in the reciprocal lattice is called the first Brillouin zone. One can represent all relevant physical quantities such as phonon or magnon dispersion relations and the band structure as a function of $\vec{K}$ in the first Brillouin zone. Therefore, knowing 'physics' inside the first Brillouin zone, one knows 'physics' of the whole crystal due to its periodic structure.

2.1.1 Lattice planes

One can create a plane of lattice points in the direct space from at least three noncolinear lattice point. The lattice plane is important because it shows the relationship between the direct space and the reciprocal space. From the relation $e^{i\vec{K}\cdot\vec{R}} = 1$, one can define a vector in the reciprocal space that is normal (perpendicular) to a plane of lattice points in the direct space. To explore this idea, we will first start with the following theorem.

Theorem: Relationship between lattice planes and reciprocal vectors Suppose there is a set of lattice planes which are equally separated by a distance d. One can find a vector in the reciprocal space that is perpendicular to these lattice planes, and the shortest length of such a vector is $2\pi/d$.

Conversely, suppose that there is a vector $\vec{K}$ in the reciprocal space. One can find a set of lattice planes in the direct space such that $\vec{K}$ is perpendicular to the lattice planes. And if the shortest length of such a vector is $|\vec{K}|$, then the separation between adjacent lattice planes is $d = \frac{2\pi}{|\vec{K}|}$.

Proof This theorem is the result of Eq. 2.1.

To prove the first part of this theorem, we will suppose that we have a set of lattice planes with the distance of separation d. We know that all points in the Bravais lattice must satisfy $e^{i\vec{K}\cdot\vec{R}} = 1$. Now given that all $\vec{R}$'s point to lattice points in the same plane, one can find $\vec{K}$ such that $\vec{K}\cdot\vec{R} = 2\pi n$, where n is an integer Since the dot product only takes the product of $\vec{K}$ and the component of $\vec{R}$ along K and it does not matter what the component of $\vec{R}$ perpendicular to $\vec{K}$ is, $\vec{K}$ must be normal to the lattice planes from by $\vec{R}'s$. To prove that the shortest length of $\vec{K}$ is $\frac{2\pi}{d}$, we suppose that a vector $\vec{K}$ is shorter than $\frac{2\pi}{d}$, then $e^{i\vec{K}\cdot\vec{R}} = 1$ cannot be satisfied for all planes in this set. Therefore, by contradiction $\vec{K}$ cannot be shorter than $\frac{2\pi}{d}$.

To prove the second part, we will start with a vector $\vec{K}$ in the reciprocal space. We will assume that $\vec{K}$ is the shortest vector in a set of all parallel vector in the reciprocal space. The same argument can be applied here. Since $e^{i\vec{K}\cdot\vec{R}} = 1$, given $\vec{K}$ one can obtain a set of $\vec{R}$ that satisfies this condition. This set of $\vec{R}$ forms a family of planes with the separation distance $d = \frac{2\pi}{|\vec{K}|}$.

2.1.2 Miller indices of lattice planes

The above theorem implies that one can use a vector in the reciprocal space to represent a family of lattice planes in the direct space. Given a vector $\vec{K}$ in the reciprocal space where

$$\vec{K} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3,$$

one can write the **Miller indices** (h,k,l) to represent this vector. From $e^{i\vec{K}\cdot\vec{R}} = 1$, we know that $\vec{K}\cdot\vec{R} = A$ where A is a constant if $\vec{R}$ represents a lattice point in the same lattice plane. Now let us choose the point x_1, x_2, and x_3 such that the plane intersect the $\vec{a}_1$ axis at x_1, the $\vec{a}_2$ axis at x_2, and the $\vec{a}_3$ axis at x_3. Since all x_i are in the same plane, we have

$$\vec{K}\cdot x_i\vec{a}_i = A,$$

that is,

$$x_1 = \frac{A}{2\pi h}, \quad x_2 = \frac{A}{2\pi K}, \quad x_2 = \frac{A}{2\pi l}.$$

One can rewrite this relations as:

$$x_1 : x_2 : x_3 = \frac{1}{h} : \frac{1}{k} : \frac{1}{l}.$$

For example, $\vec{K} = (1,0,0)$ is normal to the plane that intersect $\vec{a}_1$ at 1, $\vec{a}_2$ at infinity, and $\vec{a}_1$ at infinity.

2.2 Diffraction of wave by crystals

The lattice planes of crystals discussed in the previous section can reflect the wave of x-ray, electrons, and neutrons just like a mirror reflects light. The wave reflected off different parallel lattice planes can then interfere with each other creating a interference pattern of bright and dark spots. The interference is due to the path difference for wave reflected from adjacent planes. Therefore, in order to be able to study the structure of the crystal, in which the separation between atoms is in an order of 10^{-8} cm, the wavelength of the incident wave has to be of the same order, which means for x-ray it has to be:

$$\hbar\omega = \frac{hc}{\lambda} = \frac{hc}{10^{-10}\text{ m}} \approx 10\text{ keV}.$$

However, for neutron beam, the energy of the incident neutrons is in the range of meV.

2.2.1 Diffraction laws

There are two ways to describe diffraction by the crystals.

1. **Bragg's law**: W. H. and W. L. Bragg shone x-ray on a crystal and discovered that the scattered x-ray from a pattern of bright spots, which we now call Bragg peaks. They then came up with the explanation by assuming that atoms in the crystal arrange themselves into parallel planes off which x-ray reflects.

   If the incident angle, which is defined as the angle between the incident wave and the plane, is θ, then this path difference is equal to $2d\sin\theta$. The constructive interference occurs when the path difference is equal to the wavelength of the wave, giving the relation between the separation distance d of the planes, θ, and the wavelength λ of the incident ray, which is called **Bragg's law**:

   $$2d\sin\theta = n\lambda, \tag{2.3}$$

   where n is an integer.

2. **von Laue's law**: This method does not first assume that atoms form parallel planes. Instead, this approach treats crystals as a periodic group of microscopic objects, which in this case are atoms or nucleus, at a position vector $\vec{R}$. These microscopic objects then act as scattering centers that scatters off the incident wave. To achieve the constructive interference, the phase of the scattered wave must be in phase, that is, the phase difference must be an integer multiple of 2π. Therefore, the path difference of the scattered wave from any two scattering centers can be described by:

   $$\vec{R}\cdot\left(\vec{k}-\vec{k}'\right) = 2\pi m.$$

   where $\vec{R}$ is the translation vector in the direct space, $\vec{k}$ is the wave vector of the incident beam, and $\vec{k}'$ is the wave vector of the diffracted beam. This expression also implies that $e^{i\vec{R}\cdot\vec{k}-\vec{k}'} = 1$. One can relate the difference between $\vec{k}$ and $\vec{k}'$ with the reciprocal lattice vector $\vec{K}$, that is, $\vec{K} = \vec{k}-\vec{k}'$. In the diffraction, we know that the energy of the incident beam is equal to the energy of the scattered beam, that is, $|\vec{k}| = |\vec{k}'|$. Therefore, we have

   $$\begin{aligned}
   \vec{k}' &= \vec{k}-\vec{K} \\
   |\vec{k}'|^2 &= |\vec{k}-\vec{K}|^2 \\
   |\vec{k}|^2 &= |\vec{k}|^2 - 2\vec{k}\cdot\vec{K} + |\vec{K}|^2 \\
   \Rightarrow \vec{k}\cdot\vec{K} &= \frac{|\vec{K}|^2}{2} \\
   \Rightarrow \vec{k}\cdot\hat{\vec{K}} &= \frac{|\vec{K}|}{2}.
   \end{aligned} \tag{2.4}$$

The last equation implies that the length of the wave vector $\vec{k}$ along the reciprocal lattice vector $\hat{\vec{K}}$ is equal to the length of the reciprocal lattice vector $|\vec{K}|$ divided by 2. It is sometimes much easier to visualize this statements by drawing a diagram.

Using the diagram (see Figure 6.5 in Ashcroft & Mermin), which is not drawn here, one can immediately see that the von Laue's and Bragg's laws are equivalent. Starting from the von Laue's law, we can rewrite the left hand side of Eq. 2.4 as:

$$\vec{k}\cdot\hat{\vec{K}} = |\vec{k}|\cos\psi = |\vec{k}|\sin\theta = \frac{2\pi}{\lambda}\sin\theta,$$

where ψ is the angle between $\vec{k}$ and $\hat{\vec{K}}$ while θ is the angle between the lattice plane and $\vec{k}$. On the other hand, for the right side of Eq. 2.4,

$$\frac{|\vec{K}|}{2} = \frac{2n\pi}{d}\frac{1}{2} = \frac{n\pi}{d},$$

where d is the separation of the lattice planes. Therefore, one can rewrite Eq. 2.4 as:

$$2d\sin\theta = n\lambda,$$

which is the Bragg's law. Similarly, one can also start from the Bragg's law and derive the von Laue's law.

Using the Bragg's or von Laue's law, we can now describe the diffraction from the lattice planes. However, we know that atoms, which is a basis in the lattice, also form the planes of atoms, and in fact the wave scatters off those planes giving rise to the interference pattern. So far, we know at which $\vec{K}$ in the reciprocal lattice we expect to observe a peak in the scattering intensity. In the next section, we will calculate this scattering intensity.

2.2.2 Diffraction from the monatomic crystal

We will first start with the simplest case where we have only one type of atoms in the unit cell. From the von Laue's method, we have learned that the wave scattered from two scattering centers will have a phase difference of $\vec{K}\cdot\left(\vec{d}_i - \vec{d}_j\right)$, that is, the amplitude of the two scattered wave will be different by a factor of $e^{i\vec{K}\cdot\left(\vec{d}_i-\vec{d}_j\right)}$. In the other words, each scattered wave from the scattered center at a position $\vec{d}_i$ will have a phase factor of $e^{i\vec{K}\cdot\vec{d}_i}$. By summing up all of the phase factors from each atoms, we obtain the diffracted wave with the total amplitude, which we call the **structure factor**, equal to:

$$S_K = \sum_{j=1}^{n} f_j e^{i\vec{K}\cdot\vec{d}_j},$$

where the sum is over all n atoms in the unit cell, f_j is an atomic cross section ($f_j = f$ is all the same for the monatomic crystal), and d_j is the distance of each of the atoms from the origin of the cell. One can get the scattering intensity from $I = |S_K|^2$. Note that S_K is a complex number. Next we will see a few simple examples of how one can apply the above equation to a real system.

Examples

1. **Based-centered cubic** (*bcc*): We will think of *bcc* in a cubic system with two bases, one at 0 and the other at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ ($n = 2$), that is,

   $$\vec{d}_1 = 0 \quad \text{and} \quad \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z}).$$

   Therefore, we have,

   $$S_K = f\left(1 + e^{i\vec{K}\cdot\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})}\right).$$

If $\vec{K} = \frac{2\pi}{a}(h\hat{x}+k\hat{y}+l\hat{z})$, then

$$\begin{aligned} S_K &= f\left(1+e^{i\pi(h+k+l)}\right) \\ &= f\left(1+(-1)^{h+k+l}\right), \end{aligned}$$

which means

$$S_K = \begin{cases} 2f & \text{if } h+k+l \text{ is even} \\ 0 & \text{if } h+k+l \text{ is odd.} \end{cases}$$

Therefore, we can get scattering peaks at $\vec{K}$ such that $h+k+l$ is even.

2. **Face-centered cubic** (fcc): Similarly, we will think of fcc in a cubic system with 4 bases (in this case $n=4$):

$$\vec{d}_1 = 0 \quad , \quad \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{y}) \quad , \quad \vec{d}_2 = \frac{a}{2}(\hat{x}+\hat{z}) \quad \text{and} \quad \vec{d}_2 = \frac{a}{2}(\hat{y}+\hat{z}).$$

We can now write the scattering amplitude as:

$$\begin{aligned} S_K &= f\left(1+e^{i\pi(h+k)}+e^{i\pi(h+l)}+e^{i\pi(k+l)}\right) \\ &= f\left(1+(-1)^{h+k}+(-1)^{h+l}+(-1)^{k+l}\right). \end{aligned}$$

We can see that if the indices h, k, and l are all odd or even then $S = 4f$. However, if only one of the indices is odd or even then S vanishes. The relationship is now more complicated than the bcc case, but we could in fact figure out whether or not there is a scattering intensity at any given $\vec{K}$ point knowing the values of h, k, and l.

3. **Diamond structure**: For the diamond structure, it would be easier if we use the primitive unit cell of fcc instead of a simple cubic unit cell as we have done in the previous two cases. We can think of the diamond structure as the fcc structure with two bases, one at 0 and the other at $\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$. Given the fact that the direct space is fcc and the reciprocal lattice is bcc, we have

$$S_K = f\left(1+e^{\frac{i\pi}{2}(h+k+l)}\right),$$

which means

$$S_K = \begin{cases} 2f & \text{if } h+k+l = 4n, \text{ where } n \in \mathbb{Z} \\ (1\pm i)f & \text{if } h+k+l \text{ is odd} \\ 0 & \text{if } h+k+l = 2(2n+1), \text{ where } n \in \mathbb{Z}. \end{cases}$$

We can see that the formula for S_K is getting more complicated when a number of atoms in the unit cell increases and when we have more than one type of atoms in the unit cell (different f_j). However, the use of the computer program has been very useful to calculate S_K.

2.2.3 Experimental set-up to measure Bragg peaks

Let us again consider the result of the von Laue condition for Bragg peaks, which states that $\vec{K} = \vec{k} - \vec{k'}$. From this equation, one can see that Bragg peaks occur when the difference (in direction) between the incident and scattered wave vectors is equal to the a reciprocal lattice vector. One can therefore construct a geometric diagram to describe the condition for Bragg peaks. This construction is called **the Ewald construction**.

Ewald Sphere Construction

1. Draw a reciprocal lattice, that is, an array of reciprocal lattice points in two dimensions.
2. Draw an incident wave function $\vec{k}$ whose origin is at one of the lattice point.
3. Use the vector drawn in (2) as a radius of a circle (sphere in three-dimensional space), which is called the **Ewald sphere** and draw a circle whose center is at the end of $\vec{k}$. From this construction, the origin of the vector is on the circumference of the circle.
4. Identify other points on the circumference besides the origin of $\vec{k}$ and draw a vector $\vec{k}'$ from the center of the circle to those points. The triangle created from $\vec{k}$ and $\vec{k}'$ illustrates the von Laue condition, that is, $\vec{K} = \vec{k} - \vec{k}'$ and $\vec{K}$ indicates a vector in the reciprocal lattice where one observes the diffraction (Bragg) peak.

For a general $\vec{k}$, one normally does not observe any other reciprocal lattice point on the circumference of the circle besides the origin. However, there are several ways which one can use to search for Bragg peaks.

Methods to search for Bragg peaks

- **Laue method**: The first method to search for Bragg peaks is to use non-monochromatic x-ray beam, which is sometimes called **white beam**. For the white beam, the wave vector can have any values within a range between a minimum wave vector $\vec{k}_1$ and maximum wave vector $\vec{k}_2$. Therefore, one can observe any Bragg peaks that lie within the area between the smaller circle with the radius $|\vec{k}_1|$ and the larger circle with the radius $|\vec{k}_2|$.
- **Rotating-crystal method**: In this method, one shines monochromatic x-ray beam with fixed $\vec{k}$ on a single crystal sample. One then search for Bragg peaks by rotating the crystal. When the crystal is rotated, the reciprocal lattice also rotates in the same direction. Under this rotation, some reciprocal lattice points will fall on the circumference of the Ewald sphere satisfying the condition $\vec{K} = \vec{k} - \vec{k}'$.
- **Powder or Debye-Sherrer method**: A powder sample can be thought of as a lot of small crystallites whose orientations are random. That is equivalent to having a crystal simultaneously rotated in all directions. Therefore, the lattice points, which is now rotated around 360° in the plane, will form a ring, which is called the **powder ring** in two dimensions or **powder sphere** in three dimensions. Bragg peaks in this case are located where the powder circle (sphere) intersects the Ewald sphere with a fixed incident $\vec{k}$ in two dimensions (three dimensions).