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

Lecture 1: Crystal Structure

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These notes are prepared based on "Introduction to Solid State Physics" by C. Kittel and "Solid State Physics" by N. W. Ashcroft and N. D. Mermin.

Since mineralogists first discovered a geometrically regular form of minerals, it has been suggested that the minerals or solids in general are consisted of repeating geometric units in a microscopic scale. Later atoms were discovered and it was evidenced that the arrangement of atoms forms a matter and makes up the macroscopic structure, whose geometric shape corresponds to the symmetry of the underlying periodic microscopic units.

In this chapter, we will learn how to describe in mathematical terms these repeating, microscopic units that form a kind of a skeleton, which we will call a lattice, for atoms. This description will be proved to be very useful later when we study scattering techniques by both neutrons and x-ray to study nuclear or magnetic structures and when we investigate dynamic behaviors of phonons and magnons and band structures of electrons.

All of the aforementioned quantities share one important aspect, that is, they all represent the response of the interest systems when disturbed by a wave where spatial and temporal parts can be described by an oscillation function $e^{-i(\vec{k}\cdot\vec{r}-\omega t)}$. The periodicity of the lattice gives strong response to the wave function with a particular wavevector $\vec{k}$, which we will describe in detail in the next chapter. Before we get to that point, let us first start by defining mathematical objects to describe the periodicity of the lattice.

1.1 Bravais lattice

In general a lattice, which is a mathematically abstract object, is a set of discrete points in space, which can be in one, two, or three dimensions. However, for a particular lattice to be physically useful and meaningful, this set of discrete point has to have extra mathematical properties, that is for one thing, its arrangement has to repeat itself or is periodic. We call this special type of lattice a **Bravais lattice**. Mathematically, the Bavais lattice in three dimensions can be described by three vectors, which we will call $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, where the first two are not co-linear and the third vector is not in the plane formed by the the first two vectors, that is, it is not co-planar with the first two vectors. From $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, one can define a **lattice translation vector**:

$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, \tag{1.1}$$

where n_1, n_2, and n_3 are integers. Note that $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are not necessarily orthogonal (an angle between any two vectors does not have to be 90°). A set of all lattice points created by $\vec{T}$ forms the Bavais lattice, which means that for any given two points on the Bravais lattice, there exists $\vec{T}$ that connects them. Some of you might notice that for a given three dimensional Bravais lattice, $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are not uniquely defined. $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are called the **primitive translation vectors**, if a parallelepiped, which we will call **cell**, formed by these vectors contains only one lattice point, that is, there is no parallelepiped of a smaller size that can build up the lattice, and we call this smallest

parallelepiped the **primitive unit cell**. The volume of the primitive unit cell (or a parallelepiped in general) with the primitive translation vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ can be written as

$$V_c = |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|. \tag{1.2}$$

Since by definition the primitive unit cell can only contain one lattice point, if n is the density of the lattice point and V_c is the primitive unit cell, then one has the relation $n \cdot V_c = 1$.

We can formally define the Bravais lattice, and in fact there are two equivalent definitions of the Bravais lattice.

1. The Bravais lattice is an infinite array of discrete points which repeat themselves and look the same from any part on the array.
2. In the Bravais lattice, every point is separated from every other point by the lattice translation operator defined in Eq. 1.1, and a set of the lattice translation operators spans the space.

As it might be clear to you by now that not all lattices are the Bravais latitice. A few examples of the non-Bravais lattice are the kagome lattice that is consisted of corner-sharing triangles and the honeycomb lattice that looks like the internal structure of a beehive. Having defined the Bravais lattice, we now have a skeleton for filling in atoms to make a crystal structure. We call a set of atoms that are put at or around the lattice point **a basis** of atoms. The basis can contain more than one atom or lattice point. Using the idea of basis, one can think of the non-Bravais lattice as the Bravais lattice with a basis. For both of the kagome and honeycomb lattice, one can describe them as the Bravais lattice with two bases. We will explore this idea in more detail when you study examples of the crystal structure. There can be many types of Bravais lattices, particularly in three dimensions, and hence to study them we first need to classify them.

How to construct the primitive cell There are two methods to construct the primitive cell.

1. **Conventional primitive cell**: This type of the primitive cell can be created by connecting the translation vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ to create a closed volume, and that volume represent your primitive cell.
2. **The Wigner-Seitz cell**: The Wigner-Seitz cell is used to represent the first Briliouin zone in the reciprocal lattice, which we will discuss more in the next chapter. To construct the Wigner-Seitz cell, one first draws lines connecting a lattice point to all of its nearest neighbors. One then draws another lines that bisect and are perpendicular to the first set of lines. The volume enclosed represents the Wigner-Seitz cell.

1.1.1 Classification of Bravais lattices

In two dimensions (2D) (note that we have only two translation vectors in this case) there are five distinct Bravais lattices.

1. Square lattice: $|\vec{a}_1| = |\vec{a}_2|$ and the angle between $\vec{a}_1$ and $\vec{a}_2$ that we will call γ is 90°.
2. Hexagonal lattice: $|\vec{a}_1| = |\vec{a}_2|$ and $\gamma = 120^\circ$.
3. Rectangular lattice: $|\vec{a}_1| \neq |\vec{a}_2|$ and $\gamma = 90^\circ$.
4. Centered rectangular lattice: $|\vec{a}_1| = |\vec{a}_2|$ and $\gamma \neq 90^\circ$ or $|\vec{a}_1| \neq |\vec{a}_2|$ and $\gamma = 90^\circ$ (the same as the the rectangular lattice cell) with an extra lattice point in the middle of the cell.
5. Oblique lattice: $|\vec{a}_1| \neq |\vec{a}_2|$ and $\gamma \neq 90^\circ$.

However, since all real crystal structures are crystallized in three dimensional lattices, we will only focus our interest in the three dimensional Bravais lattices, which was first characterized correctly by A. Bravais. There are 14 types of Bravais lattices in three dimensions, which can be characterized into seven groups or crystal systems according to the shape of unit cells (see Table 1.1).

Table 1.1: Seven systems and fourteen Bravais lattice in three dimensions. α is the angle between $\vec{a}_2$ and $\vec{a}_3$, β between $\vec{a}_1$ and $\vec{a}_3$, and γ between $\vec{a}_1$ and $\vec{a}_2$.

System	Number of Bravais lattices (centering types)	Restrictions
Triclinic	1 (P)	$\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2 (P, B)	$\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4 (P, I, C, F)	$\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2 (P, I)	$\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3 (P, I, F)	$\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1 (P)	$\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1 (P)	$\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$

The characterization of the Bravais lattice into 14 types is based the second type of operators, which we call a **point operator**. The point operator is an operator that takes the lattice into itself but leaves a point or a set of points unchanged as in contrast to the translation operator where there is no fixed point. A few examples of the point operators are:

1. **Identity**: This point symmetry leaves the lattice unchange, that is, it does nothing to the lattice.
2. **Rotations**: Rotation by $2\pi/n$ where $n = 1, 2, 3, 4$, and 6 about an axis can be represented by $n(\mathrm{C}_n)$ in the International (Schoenflies) notation. For example, $2(\mathrm{C}_2)$ is the rotation by 180° and $6(\mathrm{C}_6)$ is the rotation by 60°. Note that n cannot be 5, that is, there is no Bravais lattice with the five-fold symmetry.
3. **Inversion**: This point symmetry takes (x, y, z) to $(-x, -y, -z)$, which is usually written as $(\bar{x}, \bar{y}, \bar{z})$. Note that the inversion changes the handedness of the lattice namely from the right hand to left hand and vice versa while the rotation leaves the handedness the same.
4. **Reflection across a plane**: This point symmetry is sometimes called a mirror reflection since it basically takes the lattice and converts it to its mirror image.
5. **Rotation-inversion/reflection**: One sometimes refers to this type of a point operator as an improper rotations, since it is a combination of the rotations and either inversion or reflection.

In general, all of these point operators can be written in a form of matrices. However, we will not go into detail on how to deal with these operators. If you would like to learn more about point operators, I would suggest that you read *Space Group for Solid State Scientists* by Burns and Glazer [1].

Table 1.2: Space groups in three dimensional Bravais lattice without the screw axis and the glide plane.

System	Number of Bravais Lattices	Number of Point Groups	Product
Triclinic	1	2	2
Monoclinic	2	3	6
Orthorhombic	4	3	12
Tetragonal	2	7	14
Cubic	3	5	15
Trigonal	1	5	5
Hexagonal	1	7	7
–	–	–	–
Totals	14	32	61

Centering of Lattices In some case more lattice points can be added to the Bravais lattice, which does not alter the crystal system. The Bravais lattice that does not have extra lattice points added are called primitive, which we will abbreviate as **P**. One can add extra points at the following positions.

1. **Body centering (I)**: In this case, one lattice point is added at the middle of the cell, i.e., $\vec{a}_1/2+\vec{a}_2/2+\vec{a}_3/2$, and the original unit cell now contains two lattice points, one at 0 and the other at $\vec{a}_1/2+\vec{a}_2/2+\vec{a}_3/2$. Note that the primitive unit cell is smaller than the original unit cell but the crystal system of the original lattice does not change.
2. **Face centering (F)**: In this case, three extra points are placed at the middle of the faces of the unit cell at the positions $\vec{a}_1/2+\vec{a}_2/2$, $\vec{a}_1/2+\vec{a}_3/2$, and $\vec{a}_2/2+\vec{a}_3/2$. The original unit cell now contains four lattice points.
3. **One-face centering (A, B, or C)**: In this case, one lattice is added at the middle of only one of the faces. We call

$$\begin{aligned} &\text{A centering if the point is placed at } \vec{a}_2/2 + \vec{a}_3/2, \\ &\text{B centering if the point is placed at } \vec{a}_1/2 + \vec{a}_3/2, \\ &\text{C centering if the point is placed at } \vec{a}_1/2 + \vec{a}_2/2. \end{aligned}$$

   Note that if we place the lattice point at the middle of the bottom face, then there must be a lattice point at the middle of the top face (the bottom face of the next unit cell) as well. This is also true for the side faces. There are two lattice points in the original unit cell.

1.1.2 14 Bravais lattice in three dimensions

With little knowledge about the point operators and centering of lattices, we are now equipped with an essential tool and ready to reconsider the crystal systems, which is categorized according to their point symmetries. The following list of crystal systems is numbered so that their symmetry is progressively higher. The number in the parentheses indicates a number of the *unique* Bravais lattices in that crystal system.

1. **Triclinic (1)**: The triclinic crystal system has the lowest symmetry. It has no rotational symmetry and there is no restriction on a unit cell. This crystal system has only two point group, one is identity (1) and the other is inversion ($\bar{1}$).

2. **Monoclinic (2)**: The monoclinic crystal system has the 2-fold rotational symmetry 2(C_2) and/or reflection symmetry. It can be created by distorting the orthorhombic lattice so that one of the angle is no longer 90°. The restrictions on the unit cell are $\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ and $\alpha = \gamma = 90^\circ \neq \beta$. The two Bravais lattices are simple monoclinic (P) and side-face-centered monoclinic (B).

3. **Orthorhombic (4)**: The orthorhombic crystal system has three 2-fold rotational axes along $\vec{a}1_1$, $\vec{a}_2$, and $\vec{a}_3$ instead of one in the monoclinic case and reflection symmetry. It can be created by deforming the square faces of the tetragonal one. The restrictions on the unit cell are $\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ and $\alpha = \beta = \gamma = 90^\circ$. The four Bravais lattices are simple orthorhombic (P), based-centered orthorhombic (C for base-centered), body-centered orthorhombic (I), and face-centered orthorhombic (F).

4. **Tetragonal (2)**: The tetragonal crystal system has the 4-fold rotational symmetry 4(C_4). It can be created from the cube by stretching any opposite two faces of the cube. The restrictions on the unit cell are $\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ and $\alpha = \beta = \gamma = 90^\circ$. The two Bravais lattices are simple tetragonal (P) and body-centered tetragonal (I).

5. **Cubic (3)**: The cubic crystal system has the highest symmetry. The restrictions on the unit cell are $\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ and $\alpha = \beta = \gamma = 90^\circ$. The three Bravais lattices are simple cubic (P), boody-centered cubic (I), and face-centered cubic (F).

6. **Trigonal (1)**: The trigonal crystal system has the 3-fold rotational symmetry 3(C_3). It can be thought of as a stretched cube along a body diagonal. We list it after the cubic case but its symmetry is in fact lower than that of the cube. The restrictions on the unit cell are $\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ and $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$.

7. **Hexagonal (1)**: The hexagonal crystal system has the 6-fold rotational symmetry 6(C_6). It cannot be constructed from the cube. The restrictions on the unit cell are $\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ and $\alpha = \beta = 90^\circ; \gamma = 120^\circ$.

For each crystal system, one can place a basis of atoms to form a crystal structure according to their respective point group or operator. Note that each crystal system has different number of point groups depending on their symmetry. As you can see from Table 1.2, one can create 61 space group from 14 Bravais lattices and 32 point groups. However, in general a number of space groups is 230, which is much larger. It turns out the majority of the space groups are non-symmorphic, which can be constructed if one adds two more types of operators not included in the aforementioned point operators and translation operators. These operators are a combination of point operators and translation operators.

1. **Screw Axes**: It is a combination of translation and rotation operators.

2. **Glide Planes**: It is a combination of translation and reflection operators.

One example of the crystal structure that requires one of these new type of operators is the hexagonal closed-packed, which we will consider in detail later.

Simple examples of Bravais lattices in three-dimensions There are a total of 14 Bravais lattice in three dimensions as shown in Table 1.1. We will only consider three examples of the most common Bravais lattices with the cubic crystal system. Remember that we just learned that there are three Bravais lattices with the cubic crystal system. We will assume that the distance between the nearest lattice points is a.

1. **Simple cubic (SC)**: The lattice points are at the corners of the cube. The primitive translation vectors for SC are

$$\vec{a}_1 = a\hat{x}, \tag{1.3}$$
$$\vec{a}_2 = a\hat{y}, \tag{1.4}$$
$$\vec{a}_3 = a\hat{z}. \tag{1.5}$$

2. **Body-centered cubic (BCC)**: The first set of lattice points are the same as SC, but there is an extra lattice point at the middle of the cube. The primitive translation vectors for BCC are $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, and $\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$. However, one can define a more symmetric set of the translation vector as

$$\vec{a}_1 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z}), \tag{1.6}$$
$$\vec{a}_2 = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z}), \tag{1.7}$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z}). \tag{1.8}$$

   In this case, the vectors point to the lattice point located in the middle of three of the nearest cubes.

3. **Face-centered cubic (FCC)**: The first set of lattice points are also the same as SC, but there are extra lattice point at the middle of all of its six faces of the cube. The symmetric primitive translation vectors are

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}), \tag{1.9}$$
$$\vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z}), \tag{1.10}$$
$$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}). \tag{1.11}$$

   All three vectors point to the lattice points located at the middle of the adjacent faces of the cube.

One can construct other lattices, which can be either Bravais or non-Bravais lattices, from the Bravais with a basis of lattice points. For example, we often describe BCC and FCC in terms of the simple cubic space group with a basis. For BCC, if we use the SC space group with $\vec{a}_1 = a\hat{x}$, $\vec{a}_2 = a\hat{y}$, and $\vec{a}_3 = a\hat{z}$, then the basis will have two lattice points, one at 0 and the other at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$. For FCC, the basis have 4 lattice points at 0, $\frac{a}{2}(\hat{x}+\hat{y})$, $\frac{a}{2}(\hat{y}+\hat{z})$, and $\frac{a}{2}(\hat{x}+\hat{z})$.

1.2 Example of crystal structures

As previously mentioned, the crystal structure is the Bravais lattice with a basis of atoms. In this section, I will give you examples of some of the most common crystal structures.

1. **Sodium chloride (NaCl) structure**: This structure is the FCC lattice with two bases of two different elements, where one element is at 0 (Na ion) and the other is at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ (Cl ion).

2. **Cesium chloride (CsCl) structure**: This structure is the SC lattice with two bases of two different elements, where one element is at 0 (Cs ion) and the other is at $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$ (Cl ion).

3. **Diamond structure**: The diamond structure is consisted of two interpenetrating FCC lattices, where the origin of one FCC lattice is located at 0 and and that of the other FCC lattice is at $\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$. One can think of the diamond lattice as the FCC lattice with two bases of the same element. Elements that can form the diamond structure are all in Group IV of the periodic table such as C, Si, Ge, $\alpha-$Sn (grey).

4. **Zincblende structure**: Its crystal structure is the same as the diamond structure but with two bases (at 0 and $\frac{a}{4}(\hat{x}+\hat{y}+\hat{z})$) of two different elements.

5. **Hexagonal closed-packed structure** (hcp): The hcp structure is not the Bravais lattice, but is consisted of two interpenetrating simple hexagonal lattices. The origin of the first lattice is located at 0 and that of the other at $\vec{a}_1/3+\vec{a}_2/3+\vec{a}_3/2$, where

$$\vec{a}_1 = a\hat{x},\ \vec{a}_2 = \frac{a}{2}\hat{x}+\frac{\sqrt{3}a}{2}\hat{y},\ \vec{a}_3 = c\hat{z}.$$

We can think of *hcp* as the stacking of triangular lattices, where the second layer of the triangular lattice is placed at the depressions formed by three atoms of the first layer of every other positions, and the third layer is placed at the depressions formed by atoms on the second layer that is aligned with the first layer. If we will the arrangement of the first and second layers *A* and *B*, then this type of stacking is called ...*ABABAB*....

Alternatively, one can place the third layer at the depressions that are not aligned with the first layer. In this type of closed-packed structure, since the third layer is different from the first and second layers, we will call the arrangement of the third layer *C*. This type of stacking is called ...*ABCABC*.... This structure is in fact the same as the FCC structure. The other type of closed-packed structure are ...**ABAC***ABAC***ABAC**..., which is most common in rare earths, and random close-packed structure.

References

[1] Burns, G. and Glazer, A. M.: Space Group for Solid State Scientists 2nd Edition, Academic Press, Inc. (1990).