Crystal Structure

Lattices and Unit Cells

1) A lattice is an infinite set of points defined by integer sums of a set of linearly independent primitive lattice vectors.

\[ \mathbf{R} = [h_1, h_2] = h_1 \mathbf{a}_1 + h_2 \mathbf{a}_2 \]

where \( h = \ldots, 0, \pm 1, \pm 2, \ldots \) and \( h_1, h_2 \in \mathbb{Z} \)

2) A lattice is a set of points where the unit cell looks the same and eq. to any lattice point.

VESTA is an important tool for this class. Free to download and install.
**Primitive lattice vectors**

For a 3D lattice, we can find three primitive lattice vectors (primitive translation vectors), such that any translation vector can be written as

$$\vec{t} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

where $n_1$, $n_2$, and $n_3$ are three integers.

Red (shorter) vectors: $\vec{a}_1$ and $\vec{a}_2$

Blue (longer) vectors: $\vec{b}_1$ and $\vec{b}_2$

$\vec{a}_1$ and $\vec{a}_2$ are primitive lattice vectors

$\vec{b}_1$ and $\vec{b}_2$ are NOT primitive lattice vectors

$\vec{b}_1 = 2\vec{a}_1 + 0 \vec{a}_2$  

Integer coefficients

$\vec{a}_1 = \frac{1}{2} \vec{b}_1 + 0 \vec{b}_2$  

noninteger coefficients
1D crystal
3 atoms/periodicity

Choice I:

Choice II:

Choice III:
A unit cell is a region of space that has identical units stacked up and tiles are the space.

A conventionally derived unit cell is the elementary building block of the periodic structure.

Equivalent Definition 12.1.1

Equivalent Definition 12.1.2

Equivalent Definition 12.2.1

The Wigner–Seitz construction for a lattice in two dimensions. On the left is the regular (honeycomb) lattice, while on the right are two lattices which are non-orthogonal.

Definition 12.3

Definition 12.4

Given a lattice point, the set of all points in space that have the same environment. Some people (perhaps confusingly) use the term "lattice point" to refer to the set of points in space that have the same environment. Other people, however, use the term "lattice point" to refer to a single point inside a lattice point (not just its nearest neighbors). Then draw perpendicular bisectors are added between the darker point and each of its neighbors.

There is a rather simple scheme for constructing such a Wigner–Seitz cell, i.e., given a lattice point, choose a lattice point and draw lines to all of its possible near neighbors (not just its nearest neighbors). Then draw perpendicular bisectors are added between the darker point and each of its neighbors.

Fig. 12.7

The Wigner-Seitz construction for a lattice in two dimensions. On the left is the regular (honeycomb) lattice, while on the right are two lattices which are non-orthogonal.

Definition 12.4

The Wigner–Seitz cell is a primitive unit cell. (The cells on the right are exactly the same shape as the bounded area on the left!)

The choice of a unit cell is not unique. All of these unit cells can be used as "tiles" to perfectly reconstruct the infinite lattice. This is known as a Voronoi cell.

As mentioned in Section 10.1 the definition of the unit cell is never shifting the unit cell a tiny amount in almost any direction such that a single lattice point is completely inside the unit cell and the others are on the boundary of the unit cell, it should only be counted fractionally depending on what fraction of the point is actually in the cell. So for example, in this cell, it is by definition not primitive.) Similarly for the primitive unit cell containing exactly one lattice point.

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A conventional unit cell

A primitive unit cell

Wigner–Seitz unit cell

Primitiv e u.c. for a periodic crystal should contain exactly one lattice point.
5 Bravais lattices in 2D

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Description</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$</td>
<td>a_1</td>
</tr>
<tr>
<td>2</td>
<td>$</td>
<td>a_1</td>
</tr>
<tr>
<td>3</td>
<td>$</td>
<td>a_1</td>
</tr>
<tr>
<td>4</td>
<td>$</td>
<td>a_1</td>
</tr>
<tr>
<td>5</td>
<td>$</td>
<td>a_1</td>
</tr>
</tbody>
</table>

http://en.wikipedia.org/wiki/Bravais_lattice
points live at the corners (or edges) of the cells. When a lattice point is on the boundary of the unit cell, it should only be counted fractionally depending on what fraction of the point is actually in the cell. So for example in the conventional unit cell shown in Fig. 12.6, there are two lattice points within this cell. There is one point in the center, then four points at the corners—each of which is one quarter inside the cell, so we obtain $2 = 1 + 4\left(\frac{1}{4}\right)$ points in the cell. (Since there are two lattice points in this cell, it is by definition not primitive.) Similarly for the primitive cell shown in Fig. 12.6 (upper right), the two lattice points at the far left and the far right have a $60^\circ$ degree slice (which is $1/6$ of a circle) inside the cell. The other two lattice points each have $1/3$ of the lattice point inside the unit cell. Thus this unit cell contains $2\left(\frac{1}{3}\right)+2\left(\frac{1}{6}\right)=1$ point, and is thus primitive. Note however, that we can just imagine shifting the unit cell a tiny amount in almost any direction such that a single lattice point is completely inside the unit cell and the others are completely outside the unit cell. This sometimes makes counting much easier.

Definition 12.4
Given a lattice point, the set of all points in space which are closer to that given lattice point than to any other lattice point constitute the Wigner–Seitz cell of the given lattice point.

A construction analogous to Wigner–Seitz can be performed on an irregular collection of points as well as on a periodic lattice. For such an irregular set of points the region closer to one particular point than to any other of the points is known as a Voronoi cell.

There is a rather simple scheme for constructing such a Wigner–Seitz cell: choose a lattice point and draw lines to all of its possible near neighbors (not just its nearest neighbors). Then draw perpendicular bisectors of all of these lines. The perpendicular bisectors bound the Wigner–Seitz cell. It is always true that the Wigner–Seitz construction for a lattice gives a primitive unit cell. In Fig. 12.7 we show another example of the Wigner–Seitz construction for a two-dimensional lattice.

Fig. 12.7
The Wigner–Seitz construction for a lattice in two dimensions. On the left perpendicular bisectors are added between the darker point and each of its neighbors. The area bounded defines the Wigner–Seitz cell. On the right it is shown that the Wigner–Seitz cell is a primitive unit cell. (The cells on the right are exactly the same shape as the bounded area on the left!)
He passed away in 2007.

Fredrick Seitz was far less famous, but gained notoriety in his later years by being a consultant for the tobacco industry.

Perhaps as important to physics was the fact that his sister, Margit, married a physicist.

In other words, we think of reconstructing the entire crystal by associating the positions of the atoms in the crystal with respect to the reference lattice point in the unit cell.

Crystal Structure

With respect to the reference point in the unit cell, the coordinates of the objects in the unit cell are given with different shades. The unit cell is outlined with dashed lines.

The simplest lattice in three dimensions is the simple cubic lattice shown in Fig. 12.11. The orthorhombic unit cell has three different lengths of lattice vectors, whereas the tetragonal and cubic lattices have two different lengths.

The same honeycomb is shown in Fig. 12.8 (top) with the lattice and the basis explicitly shown. Here, the reference points (small black dots) form a honeycomb, and the large light gray atoms have positions marked by the outlying corners of unit cells.

In this way you can say that the positions of the atoms in the crystal are "the lattice plus the basis". Therefore, we can describe the basis of this crystal as follows:

In Fig. 12.8 (bottom) we show a primitive unit cell of two types of atoms. On the bottom we show a primitive unit cell with the coordinates of the two larger circles with respect to the lower left-hand corner. The basis is marked with a dotted line that coincides with the lower left-hand corner.

We can describe the basis of the crystal as follows:

\[
\begin{align*}
[a/2, a/2] & \quad [3a/4, 3a/4] \\
[0, 0] & \quad \left[\frac{a}{4}, \frac{a}{4}\right] \quad \left[\frac{3a}{4}, \frac{a}{4}\right] \\
\end{align*}
\]

Basis and location of atoms in unit cell

To remember: CRYSTAL = LATTICE + BASIS
Crystalline Structure

the spheres than packing the spheres in a simple cubic lattice (see also Exercise 12.4). Correspondingly, bcc and fcc lattices are realized much more frequently in nature than simple cubic (at least in the case of a single atom basis). For example, the elements Al, Ca, Au, Pb, Ni, Cu, Ag (and many others) are fcc whereas the elements Li, Na, K, Fe, Mo, Cs (and many others) are bcc.

In fact it is impossible to pack spheres more densely than you would get by placing the spheres at the vertices of an fcc lattice. This result (known empirically to people who have tried to pack oranges in a crate) was first officially conjectured by Johannes Kepler in 1611, but was not mathematically proven until 1998! Note however that there is another lattice, the hexagonal close packed lattice which achieves precisely the same packing density for spheres as the fcc lattice.

12.2.4 Other Lattices in Three Dimensions

Fig. 12.19

Conventional unit cells for the fourteen Bravais lattice types. Note that if you tried to construct a “face-centered tetragonal” lattice, you would find that by turning the axes at 45 degrees it would actually be equivalent to a body-centered tetragonal lattice. Hence face-centered tetragonal is not listed as a Bravais lattice type (nor is base-centered tetragonal for a similar reason, etc.).

In addition to the simple cubic, orthorhombic, tetragonal, fcc, and bcc lattices, there are nine other types of lattices in three dimensions. These are known as the fourteen Bravais lattice types. Although the study of all of these lattice types is beyond the scope of this book, it is probably a good idea to know that they exist.

Figure 12.19 shows the full variety of Bravais lattice types in three dimensions.
The primitive unit cell in this case can most conveniently be taken to be a single cube—which includes 1/8 of each of its eight corners (see Fig. 12.10, sometimes known as cubic "P" or cubic-primitive lattice). The simplest lattice in three dimensions is the simple cubic lattice shown in Fig. 12.10.

Only slightly more complicated than the simple cubic lattice are the tetragonal lattices where the axes remain perpendicular, whereas the tetragonal unit cell has three different lengths (shown in Fig. 12.11). In terms of the reference points of the lattice, the basis for the primitive cell has two lengths the same and one different.

Cubic unit cell

Tetragonal unit cell

Orthorhombic unit cell

$$a \neq a$$

$$a, b, c$$

all different

$$c \neq a$$
The Body-Centered Cubic (bcc) Lattice

Body-centered cubic unit cell

Lattice sites: \(a(l \hat{\mathbf{x}} + m \hat{\mathbf{y}} + n \hat{\mathbf{z}})\)

Lattice point per conventional cell: \(1 = 8 \times \frac{1}{8}\)

Volume (conventional cell): \(a^3\)

Volume (primitive cell): \(a^3\)

Number of nearest neighbors: 6

Nearest neighbor distance: \(a\)

Number of second neighbors: 12

Second neighbor distance: \(\sqrt{2}a\)

Coordinates of the sites: \((l, n, m)\)

For the site \((0,0,0)\),

6 nearest neighbors: \((\pm 1,0,0), (0,\pm 1,0)\) and \((0,0,\pm 1)\)

12 next nearest neighbors: \((\pm 1,\pm 1,0), (0,\pm 1,\pm 1)\) and \((\pm 1,0,\pm 1)\)
Packing fraction

Packing fraction:
We try to pack $N$ spheres (hard, cannot deform).

The total volume of the spheres is $N4 \pi \frac{R^3}{3}$

The volume these spheres occupy $V > N4 \pi \frac{R^3}{3}$ (there are spacing)

Packing fraction=$\frac{\text{total volume of the spheres}}{\text{total volume these spheres occupy}}$

\[
\text{Packing fraction} = \frac{N4 \pi \frac{R^3}{3}}{V} = \frac{4 \pi \frac{R^3}{3}}{V/N} = \frac{4 \pi \frac{R^3}{3}}{\text{Volume per site}}
\]

\[
= \frac{4 \pi \frac{R^3}{3}}{\text{Volume of a primitive cell}}
\]

High packing fraction means the space is used more efficiently
Packing fraction of simple cubic

\[
Packing fraction = \frac{4\pi \frac{R^3}{3}}{Volume\ of\ a\ primitive\ cell}
\]

\[
= \frac{4\pi \frac{R^3}{3}}{a^3} = \frac{4\pi}{3} \left(\frac{R}{a}\right)^3 = \frac{4\pi}{3} \left(\frac{a/2}{a}\right)^3 = \frac{\pi}{6} \approx 0.524
\]

- Nearest distance = 2R
  R = Nearest distance / 2 = a / 2

- About half (0.524 = 52.4%) of the space is really used by the sphere.
- The other half (0.476 = 47.6%) is empty.
The Face-Centered Cubic (fcc) Lattice

Face-centered cubic unit cell

Plan view

Fig. 12.16
Some Real Crystals

Sodium (Na)
Lattice = Cubic-I (bcc)
Basis = Na at [000]

Caesium chloride (CsCl)
Lattice = Cubic-P
Basis = Cs at [000] and Cl at \([\frac{1}{2} \frac{1}{2} \frac{1}{2}]\)

Plan view
unlabeled points at \(z = 0, 1\)

Plan view
unlabeled points at \(z = 0, 1\)

We can mark any unit cell by three integers: \(lmn\)
\[
\vec{t} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3
\]

Coordinates of an atom:
We can mark any atom in a unit cell by three real numbers: \(xyz\).
The location of this atom: \(x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3\)
Notice that \(0 \leq x < 1\) and \(0 \leq y < 1\) and \(0 \leq z < 1\)

Q: Why \(x\) cannot be 1?
A: Due to the periodic structure. 1 is just 0 in the next unit cell
Sodium Chloride

Face-centered cubic lattice
Na⁺ ions form a face-centered cubic lattice
Cl⁻ ions are located between each two neighboring Na⁺ ions

Equivalently, we can say that
Cl⁻ ions form a face-centered cubic lattice
Na⁺ ions are located between each two neighboring Na⁺ ions
Cesium Chloride

Simple cubic lattice
Cs+ ions form a cubic lattice
Cl- ions are located at the center of each cube

Equivalently, we can say that
Cl- ions form a cubic lattice
Cs+ ions are located at the center of each cube

Coordinates:
Cs: 000
Cl: \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \)

Notice that this is a simple cubic lattice
NOT a body centered cubic lattice

- For a bcc lattice, the center site is the same as the corner sites
- Here, center sites and corner sites are different
Diamond is not a Bravais lattice

Same story as in graphene:
We can distinguish two different type of carbon sites (marked by different color)
We need to combine two carbon sites (one black and one white) together as a (primitive) unit cell
If we only look at the black (or white) sites, we found the Bravais lattice: fcc