Chapter 1

Crystal structure

1.1 Crystal lattices

We will concentrate as stated in the introduction, on *perfect crystals*, i.e. on arrays of atoms, where a given arrangement is repeated forming a *periodic structure*, in principle over the whole space. Although crystals have in reallity a finite extension, they posses of the order of 10^{23} atoms, such that to consider them infinite is a rather good approximation. In doing so, we will disregard those phenomena taking place close to the surface of the crytals, such that we will leave aside a big area of Solid State Physics, namely Surface Physics. However, we will develop the ideas also necessary to deal with that part of physics, so that those interested in that area, can participate later in corresponding lectures offered as elective ones.

Another restriction due to the assumption of a periodic structure is that we will not consider the effect of *impurities* and *disorder*. *Impurities* can be considered as a perturbation of an ordered system, and as such, their treatment can be seen as an extension of the lectures here, i.e. they could be the subject of a special lecture. *Disorder* on the other hand, an important area of research in statistical as well as in solid state physics, prompted the development of many new theoretical techniques like e.g. *supersymmetry*, needed to study phenomena like *localization* or *glassy behavior*. Unfortunately, we are not going to have time to deal with such interesting subjects, but elective lectures are available in our faculty.

Once we stated what we are not going to deal with, let us come back to our subject. A *perfect crystal*, that is a *periodic structure* posses a *translation symmetry*. This means, that there is some group of atoms that can build up the whole crystal by translations. The smallest of such groups is called the *elementary cell*. As shown by the examples below (Fig. 1.1), the elementary cell is not uniquely determined.

We can also give a mathematical meaning by saying that *translational symmetry means that there exist vectors $\boldsymbol{a}_i$, $i = 1, \ldots, d$, where d is the number of space dimensions, such that the structure remains invariant under translations by any*

vector which is the sum of integral multiples of these vectors. The vectors

$$\boldsymbol{R}_i \;\; = \;\; \sum_{j=1}^{d} n_{i,j} \boldsymbol{a}_j \; , \tag{1.1}$$

with $n_{i,j}$ integers are called *lattice vectors* and define a *Bravais lattice*. The vectors $\boldsymbol{a}_i$ are called *basis vectors*.
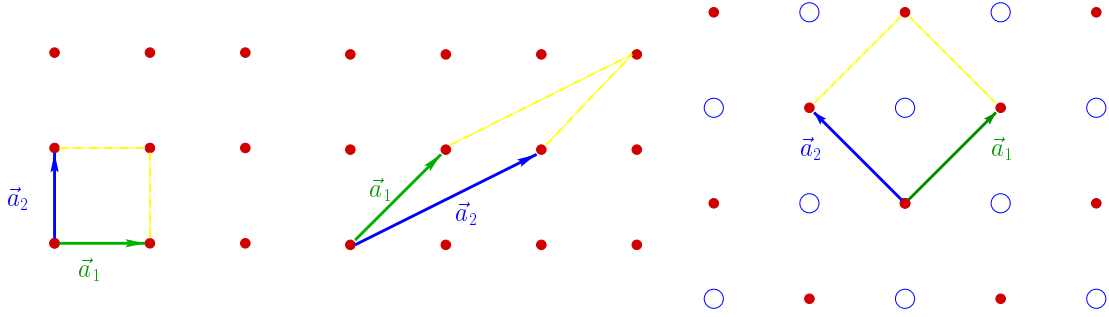

Figure 1.1: Examples of different elementary cells.

Since as we said above, the determination of an elementary cell is not unique, we can find an elementary cell by constructing a *Wigner-Seitz cell*, that is determined by drawing the perpendicular bisector planes of the translation vectors from one lattice point to its nearest neighbors (Fig. 1.2).
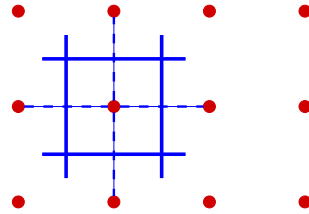

Figure 1.2: Wigner-Seitz cell.

A structure, where the atoms are sitting on the sites of a Bravais lattice, is called a *primitive lattice*. In this case we have only one atom per elementary cell. In the case, where there are several atoms per elementary cell, one speaks of a *lattice with a basis*.

1.2   The reciprocal lattice

Let us suppose for definitness, that we are dealing with three dimensions, i.e. $d = 3$. Then, the *volume of the elementary cell* is

$$\Omega \;\; = \;\; \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3) \; . \tag{1.2}$$

Let us define now three new vectors as follows

$$\left.\begin{aligned} \boldsymbol{b}_1 &= (2\pi/\Omega)\,\boldsymbol{a}_2 \times \boldsymbol{a}_3 \\[2mm] \boldsymbol{b}_2 &= (2\pi/\Omega)\,\boldsymbol{a}_3 \times \boldsymbol{a}_1 \\[2mm] \boldsymbol{b}_3 &= (2\pi/\Omega)\,\boldsymbol{a}_1 \times \boldsymbol{a}_2 \end{aligned}\right\} \quad b_i^\alpha = \frac{\pi}{\Omega}\varepsilon_{ijk}\,\varepsilon^{\alpha\beta\gamma}\,a_j^\beta a_k^\gamma \left\{ \begin{aligned} i,j,k &= 1,2,3 \\ \alpha,\beta,\gamma &= x,y,z \end{aligned}\right. \tag{1.3}$$

ε_{ijk} and $\varepsilon^{\alpha\beta\gamma}$ are called Levi-Civita symbols. They are totally antisymmetric tensors with the property

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{for } i=1, j=2, k=3 \text{ or an even permutation of them} \\ -1 & \text{for } i,j,k \text{ an odd permutation of 123} \\ 0 & \text{for any two indices equal} \end{cases} \tag{1.4}$$

Using the definition of the vectors $\boldsymbol{b}_i$ and the properties of the Levi-Civita symbols, it can be shown that

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\,\delta_{ij} \;, \tag{1.5}$$

where δ_{ij} is called the Kronecker delta with the property

$$\delta_{ij} = \begin{cases} 1 & \text{for } i=j \\ 0 & \text{else} \end{cases} \tag{1.6}$$

The vectors $\boldsymbol{b}_i$ can be seen as basis vectors of the *reciprocal lattice*, i.e. they can be used to construct another Bravais lattices with vectors

$$\boldsymbol{G} = \sum_{j=1}^{3} k_j\,\boldsymbol{b}_j \;, \tag{1.7}$$

with k_j integer. These vectors are called *reciprocal lattice vectors*. Recalling (1.1), we find an important property of the reciprocal lattice vectors

$$\begin{aligned} \boldsymbol{G} \cdot \boldsymbol{R} &= \sum_{i,j} n_i\,k_j\,\boldsymbol{a}_i \cdot \boldsymbol{b}_j \\ &= 2\pi \sum_i n_i\,k_i = 2\pi M \;, \end{aligned} \tag{1.8}$$

with M some integer. This implies that

$$\exp\left(i\boldsymbol{G}\cdot\boldsymbol{R}\right) = 1 \;, \tag{1.9}$$

a fact with important consequences for the next point.

Since the reciprocal lattice vectors form a Bravais lattice, we can construct a Wigner-Seitz cell on this lattice. It is called the *Brillouin-zone*. Its volume can be obtained in the same way as in real space, namely

$$\Omega_B = \boldsymbol{b}_1 \cdot (\boldsymbol{b}_2 \times \boldsymbol{b}_3) \;. \tag{1.10}$$

Using (1.3), it can be shown that

$$\Omega_B = \frac{(2\pi)^3}{\Omega} \;. \tag{1.11}$$

1.2.1   Fourier decomposition of periodic functions

Let us recall without demonstration, what a Fourier transform is. For a mathematical rigorous discussion, see e.g. *Mathematics for Physicists* by P. Dennery and A. Krzywicki, Dover 1995, ch. III, sec. 11.

Given a function $f(x)$ defined in the interval $[-\frac{a}{2}, \frac{a}{2}]$, such that $f\left(\frac{a}{2}\right) = f\left(-\frac{a}{2}\right)$, one has the Fourier expansion

$$
\begin{aligned}
f(x) &= \frac{1}{\sqrt{a}} \sum_{-\infty}^{\infty} f_m \exp\left(im\frac{2\pi}{a}x\right) , \\
f_m &= \frac{1}{\sqrt{a}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \mathrm{d}x\, f(x) \exp\left(-im\frac{2\pi}{a}x\right) ,
\end{aligned}
\tag{1.12}
$$

where m is integer. It is here easy to see that the function $f(x)$ is a function with period a, i.e. $f(x) = f(x+a)$. At this point we could introduce a quantity

$$
g = m\frac{2\pi}{a} ,
\tag{1.13}
$$

with the obvious property $g\,na = 2\pi M$, with n and M integers, so that g is the one-dimensional version of a reciprocal lattice vector. With such a notation, the generalization to more than one dimension is straightforward.

$$
\begin{aligned}
f(\boldsymbol{x}) &= \frac{1}{\sqrt{\Omega}} \sum_{-\infty}^{\infty} f_{\boldsymbol{g}} \exp\left(i\boldsymbol{g}\cdot\boldsymbol{x}\right) , \\
f_{\boldsymbol{g}} &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} \mathrm{d}\boldsymbol{x}\, f(\boldsymbol{x}) \exp\left(-i\boldsymbol{g}\cdot\boldsymbol{x}\right) ,
\end{aligned}
\tag{1.14}
$$

where we have to require now that $f(\boldsymbol{x}) = f(\boldsymbol{x}+\boldsymbol{R})$. But this is equivalent to require that $\exp(i\boldsymbol{g}\cdot\boldsymbol{R}) = 1$. Recalling (1.9), we see that $\boldsymbol{g} = \boldsymbol{G}$, as we already expected.

A special periodic function that will be usefull later is the following

$$
f(\boldsymbol{x}) = \sum_{\boldsymbol{R}} \delta(\boldsymbol{x}+\boldsymbol{R}) ,
\tag{1.15}
$$

where $\delta(\boldsymbol{x})$ is the Dirac delta-function (recall that this is actually a generalized function, or distribution) with the following properties:

$$
\begin{aligned}
\int \mathrm{d}^3x\, \delta(\boldsymbol{x}) &= 1 , \\
\int \mathrm{d}^3x\, f(\boldsymbol{x})\, \delta(\boldsymbol{x}-\boldsymbol{x}_0) &= f(\boldsymbol{x}_0) .
\end{aligned}
\tag{1.16}
$$

The function (1.15) is obviously translational invariant since it contains all lattice vectors, and therefore, it will not be affected by a translation by any $\boldsymbol{R}$. Using

(1.14), we can now calculate the coefficients of the Fourier expansion

$$
\begin{aligned}
f_{\boldsymbol{G}} &= \frac{1}{\sqrt{\Omega}} \int_{\Omega} \mathrm{d}^3x \, f(\boldsymbol{x}) \exp(-i\boldsymbol{G} \cdot \boldsymbol{x}) \\
&= \frac{1}{\sqrt{\Omega}} \sum_{\boldsymbol{R}} \int_{\Omega} \mathrm{d}^3x \, \delta(\boldsymbol{x} + \boldsymbol{R}) \exp(-i\boldsymbol{G} \cdot \boldsymbol{x}) \\
&= \frac{1}{\sqrt{\Omega}} \; .
\end{aligned}
\tag{1.17}
$$

Inserting this result in the Fourier expansion as shown in (1.14), we finally have

$$
\Omega \sum_{\boldsymbol{R}} \delta(\boldsymbol{x} + \boldsymbol{R}) = \sum_{\boldsymbol{G}} \exp(i\boldsymbol{G} \cdot \boldsymbol{x}) \; .
\tag{1.18}
$$

This equality will be useful in the next section.

1.2.2   Periodic boundary conditions

Although the fact that we are dealing with a periodic crystal will imply for many quantities that they have the same period as the crystal, like e.g. the electronic density, there may be other quantities that will not have this periodicity. One could imagine departures from the equilibrium electronic density caused by the interaction with an electromagnetic wave, or departures of the atoms from their equilibrium position due to the excitation with an acoustic wave. In these cases, the waves induced in the solid by the external perturbation should essentially have a wavelength of the order of those of the perturbation. For electromagnetic waves (light) this will be of the order of several thousand Angstroms and for acoustic wave even much longer. This means that we have to treat the solid as a whole and in the spirit we mentioned at the beginning of this chapter, the infinite solid. However, dealing with infinities have to be made with care. We therefore introduce *periodic boundary conditions*.

We assume that the system we are dealing with consists of a periodic repetition of what happens in a cell of linear size $N_i \, \boldsymbol{a}_i$, $i = 1, 2, 3$, with $N_i \gg 1$. We set the condition that *all* physical quantities fulfill the condition

$$
f(\boldsymbol{R} + N_i \boldsymbol{a}_i) = f(\boldsymbol{R}) \; ,
\tag{1.19}
$$

for $i = 1, 2, 3$. At the end of the calculation we take the limit $N_i \to \infty$, in order to reach the thermodynamic limit. Since again we are dealing with a periodic function, we can perform a Fourier transformation as in (1.14). Let us call the corresponding wavevector $\boldsymbol{k}$. The condition (1.19) will imply now

$$
\exp(i\boldsymbol{k} \cdot N_i \, \boldsymbol{a}_i) = 1 \; .
\tag{1.20}
$$

As in Sec. 1.2.1, we can set $\boldsymbol{k}$ equal to a reciprocal lattice vector, however we have now many more vectors also satisfying the condition above, namely

$$
\boldsymbol{k} = \frac{n_1}{N_1} \boldsymbol{b}_1 + \frac{n_2}{N_2} \boldsymbol{b}_2 + \frac{n_3}{N_3} \boldsymbol{b}_3 \; .
\tag{1.21}
$$

Wavevectors with $n_i = 0, \pm 1, \ldots, \pm \left(\frac{N_i}{2} - 1 \right), \frac{N_i}{2}$, belong to the *first Brillouin zone.* As we pass to the thermodynamic limit, we will increase the density of wavevectors inside the first Brillouin zone, and since the number of states inside it is equal to the number of degrees of freedom in the system, it will contain all the relevant physical information as long as the orginal periodicity is preserved.

At this point we can consider again a Fourier decomposition of a function $f(\boldsymbol{x})$, as prescribed in (1.14),

$$f(\boldsymbol{x}) \;=\; \frac{1}{\sqrt{V}} \sum_{\text{all } \boldsymbol{q}} f_{\boldsymbol{q}} \exp(i\boldsymbol{q} \cdot \boldsymbol{x}) \;, \tag{1.22}$$

where by 'all $\boldsymbol{q}$' we mean all the q-vectors compatible with the periodic boundary conditions, and V is the volume of the system with $V = \Omega N$, and $N = N_1 N_2 N_3$. This sum can be splitted as follows

$$\sum_{\text{all } \boldsymbol{q}} \;=\; \sum_{\boldsymbol{G}} \sum_{\boldsymbol{q} \in \text{BZ}} \;, \tag{1.23}$$

such that (1.22) can be written as

$$(1.22) \;=\; \frac{1}{\sqrt{V}} \sum_{\boldsymbol{q} \in \text{BZ}} \exp(i\boldsymbol{q} \cdot \boldsymbol{x}) \sum_{\boldsymbol{G}} f_{\boldsymbol{q}+\boldsymbol{G}} \exp(i\boldsymbol{G} \cdot \boldsymbol{x}) \;. \tag{1.24}$$

Let us assume that the Fourier coefficients do not depend on the reciprocal lattice vectors and see which are the consequences of that. In this case we have

$$(1.24) \;=\; \frac{1}{\sqrt{V}} \sum_{\boldsymbol{q} \in \text{BZ}} f_{\boldsymbol{q}} \exp(i\boldsymbol{q} \cdot \boldsymbol{x}) \sum_{\boldsymbol{G}} \exp(i\boldsymbol{G} \cdot \boldsymbol{x}) \;. \tag{1.25}$$

Next recall the formula (1.18), that leads to

$$(1.25) \;=\; \frac{\Omega}{\sqrt{V}} \sum_{\boldsymbol{R}} \delta(\boldsymbol{x} + \boldsymbol{R}) \sum_{\boldsymbol{q} \in \text{BZ}} f_{\boldsymbol{q}} \exp(i\boldsymbol{q} \cdot \boldsymbol{x}) \;. \tag{1.26}$$

This tells us, that the assumption we made implies that $f(\boldsymbol{x})$ is a function only defined on the lattice sites:

$$f(\boldsymbol{x}) \;=\; \sqrt{\Omega} \sum_{\boldsymbol{R}} f(\boldsymbol{R}) \delta(\boldsymbol{x} + \boldsymbol{R}) \;, \tag{1.27}$$

with

$$f(\boldsymbol{R}) \;=\; \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q} \in \text{BZ}} f_{\boldsymbol{q}} \exp(-i\boldsymbol{q} \cdot \boldsymbol{R}) \;. \tag{1.28}$$

We can understand this fact physically, since a wavevector $\boldsymbol{G}$ corresponds to a wavelength shorter than a, the lattice constant. Then, if we find that the Fourier coefficients do not depend on $\boldsymbol{G}$'s, this means that we have no information on distances

shorter than a. Functions defined only on lattice sites are commonly encountered in models in solid state physics, as we will see in the course of the lecture (*tight binding electrons*). Using (1.28), we can obtain also the coefficients of the Fourier expansion.

$$
\begin{aligned}
f_{\boldsymbol{q}+\boldsymbol{G}} &= \sqrt{\frac{\Omega}{V}} \sum_{\boldsymbol{R}} f(\boldsymbol{R}) \int_V \mathrm{d}\boldsymbol{x}\, \delta(\boldsymbol{x}+\boldsymbol{R}) \exp\left[-i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{x}\right] \\
\hookrightarrow f_{\boldsymbol{q}} &= \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} f(\boldsymbol{R}) \exp(i\boldsymbol{q}\cdot\boldsymbol{R}) \ .
\end{aligned} \tag{1.29}
$$

We see that in fact, the coefficients do not depend on the reciprocal lattice vectors. The last formula together with (1.28) give the transformation laws for functions on the lattice with periodic boundary conditions.

Let us close this section by discussing several formulae that are usefull in dealing with periodic systems:

$$
\int_\Omega \mathrm{d}^3 x\, \exp\left[i(\boldsymbol{G}-\boldsymbol{G}')\cdot\boldsymbol{x}\right] = \Omega\, \delta_{\boldsymbol{G},\boldsymbol{G}'} \ , \tag{1.30}
$$

$$
\int_{\Omega_B} \mathrm{d}^3 k\, \exp\left[i(\boldsymbol{R}-\boldsymbol{R}')\cdot\boldsymbol{k}\right] = \Omega_B\, \delta_{\boldsymbol{R},\boldsymbol{R}'} \ , \tag{1.31}
$$

$$
\Omega_B \sum_{\boldsymbol{G}} \delta(\boldsymbol{k}+\boldsymbol{G}) = \sum_{\boldsymbol{R}} \exp(i\,\boldsymbol{k}\cdot\boldsymbol{R}) \ . \tag{1.32}
$$

It is easy to see that (1.30) is fulfilled in one dimension, and after seeing this, the generalization to higher dimensions is straightforward. Once (1.30) is understood, (1.31) results obvious, since its evaluation requires the same steps. Of course, the integral in (1.31) is understood in the thermodynamic limit, where there is a dense set of points inside the Brillouin zone. Finally, (1.32) can be obtained in the same way as (1.18) by exchanging the roles of $\boldsymbol{k} \to \boldsymbol{x}$ and of $\boldsymbol{R} \leftrightarrow \boldsymbol{G}$.

1.3   Symmetries and types of Bravais lattices

Apart from translational symmetry there are other structural symmetries that transform a crystal into itself. As for the translation, it is said that these symmetry transformations build a *group*. A group is defined as follows:

A set $\mathcal{G}$ is a group if

a) there is an operation ('product') that for any two elements $T, T' \in \mathcal{G}$, assigns another element $T'' \in \mathcal{G}$,

b) $\forall\, T, T'$, and $T'' \in \mathcal{G}$, it holds

$$
(TT')\, T'' = T\, (T'T'')
$$

c) $\exists\, E \in \mathcal{G}$, such that

$$TE = ET = T$$

d) $\forall\, T \in \mathcal{G}$, $\exists\, T^{-1} \in \mathcal{G}$, such that

$$TT^{-1} = T^{-1}T = E$$

The kind of symmetries that can appear in a crystal are:

- *Point group*: all operations that transform the lattice into itself and leave a given point invariant. These operations are rotations, reflections, inversions (no translations).
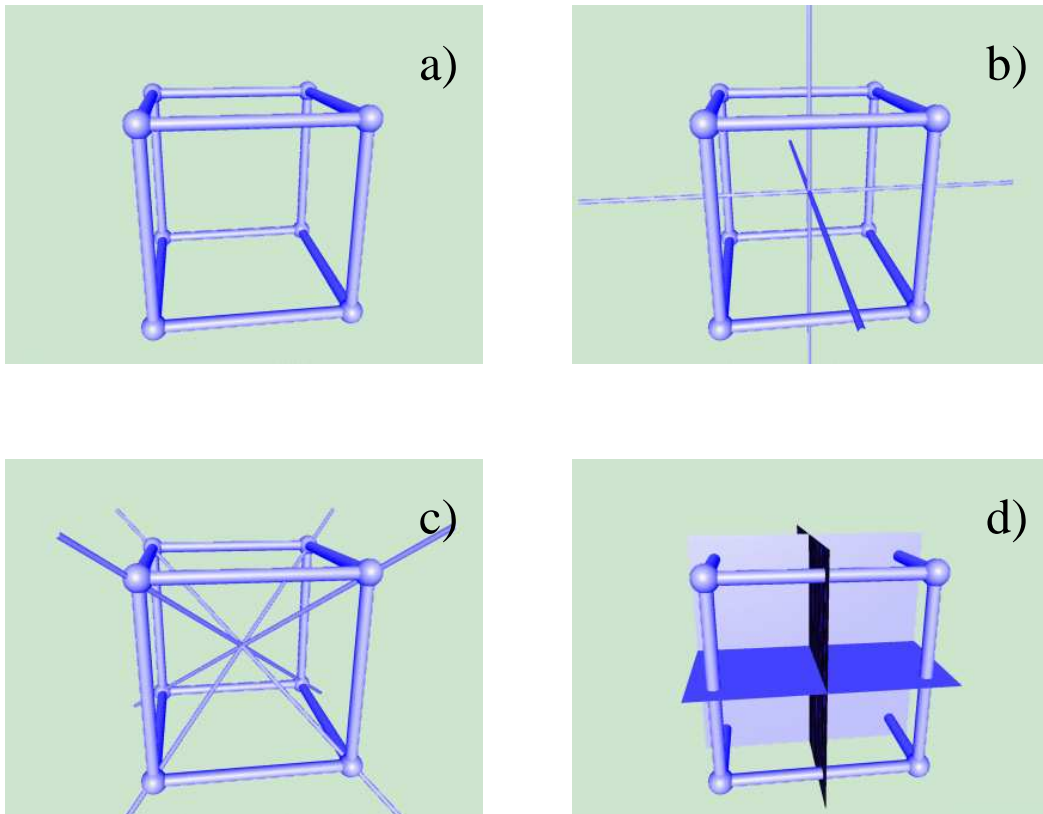

Figure 1.3: Examples of point symmetry operations on a cube a): b) Rotations by 90°, c) rotations by 120°, d) reflexion planes.

- *Space group*: all operations that transform the lattice into itself (point group operations + translations).

There are seven possible point groups and fourteen Bravais lattices that are enumerated in the following.

1. <u>*Cubic*</u>: here belong all lattices with the symmetry group of a cube. There are **3** Bravais lattices with non-equivalent space groups: *simple cubic* (sc), body-centered cubic (bcc), and *face-centered cubic* (fcc).
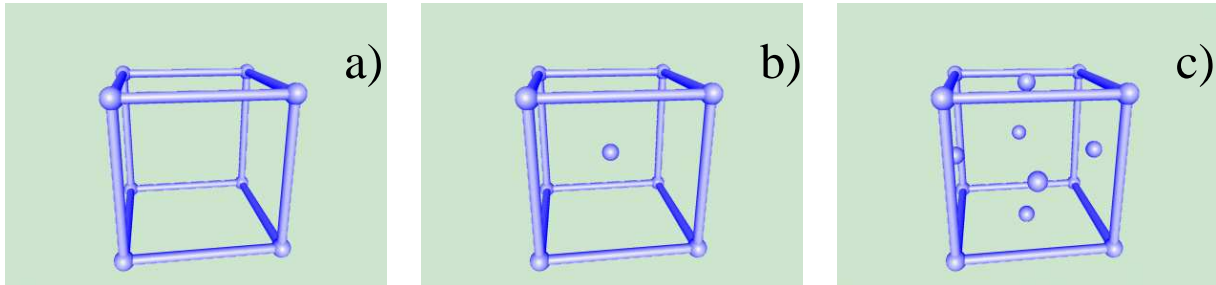
Figure 1.4: Cubic Bravais lattices: a) simple cubic, b) body centered cubic, c) face-centered cubic.

2. <u>*Tetragonal*</u>: here belong all lattices with the symmetry group of a rectangular prism. There are **2** Bravais lattices with non-equivalent space groups: *simple tetragonal*, and *centered tetragonal*
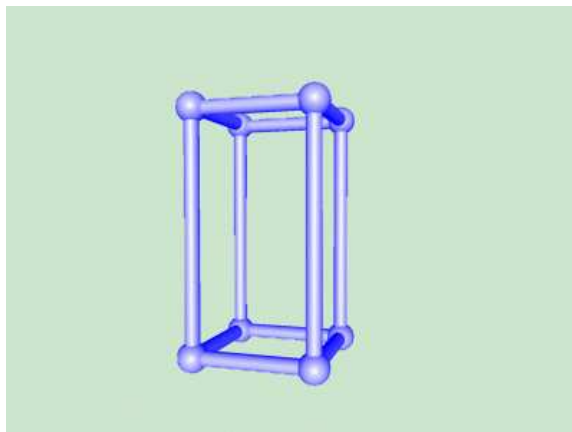
Figure 1.5: Simple tetragonal Bravais lattices.

3. <u>*Orthorombic*</u>: here belong all lattices with the symmetry group of an object with perpendicular faces and with all three perpendicular sides with unequal length. There are **4** Bravais lattices with non-equivalent space groups: *simple othorombic*, *base-centered orthorombic*, *body centered orthorombic*, and *face-*
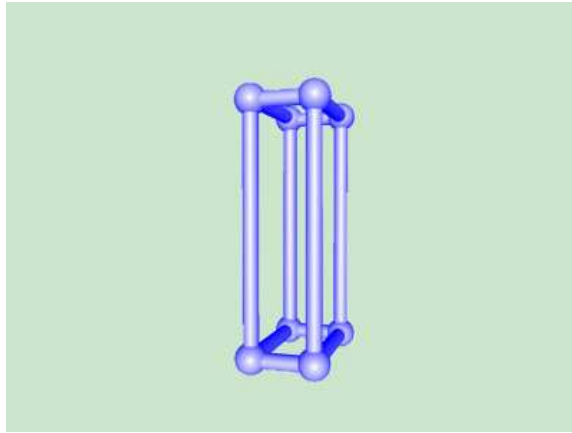
centered orthorombic.

Figure 1.6: Orthorombic Bravais lattices.

4. *Monoclinic*: here belong all lattices with the symmetry group of an object with a base made of a parallelogram and two faces perpendicular to it. There are **2** Bravais lattices with non-equivalent space groups: *simple monoclinic* and *centered monoclinic.*
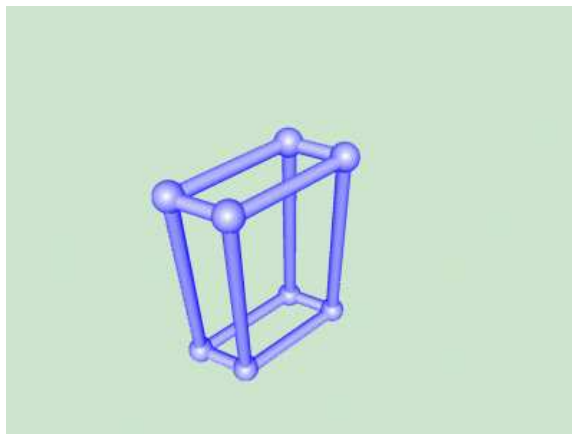

Figure 1.7: Monoclinic Bravais lattices.

5. *Triclinic*: here belong all lattices with the symmetry group of an object with all three faces forming a parallelogram with sides of unequal length. This is the Bravais lattice with minimum symmetry, so that there is only **1** type of
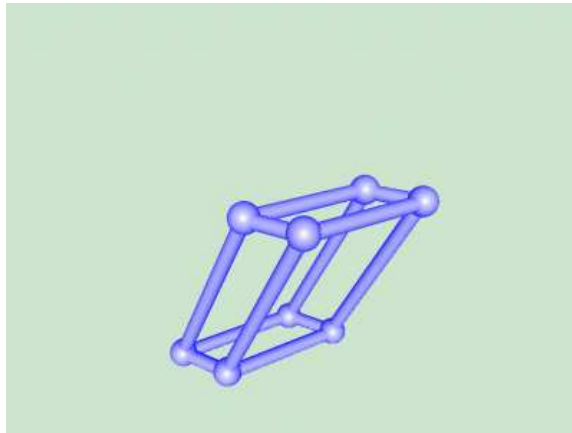
this kind.

Figure 1.8: Triclinic Bravais lattices.

6. *Trigonal*: here belong all lattices with the symmetry group of an object obtained from a cube by stretching it along a body diagonal, generating a body with sides of equal length making equal angles with one another. This type is also called *rhombohedral* and there is only **1** such type of Bravais lattice.
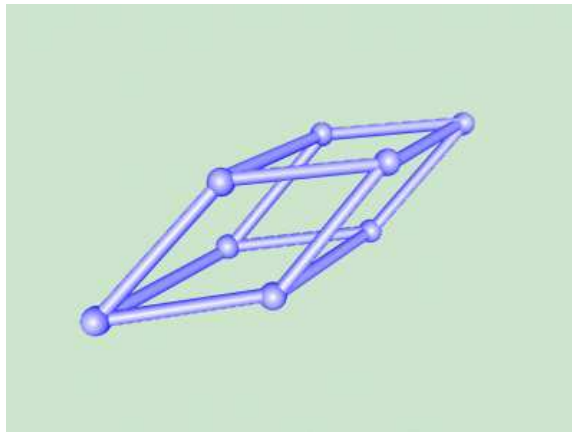

Figure 1.9: Trigonal Bravais lattices.

7. *Hexagonal*: here belong all lattices with the symmetry group of a right prism

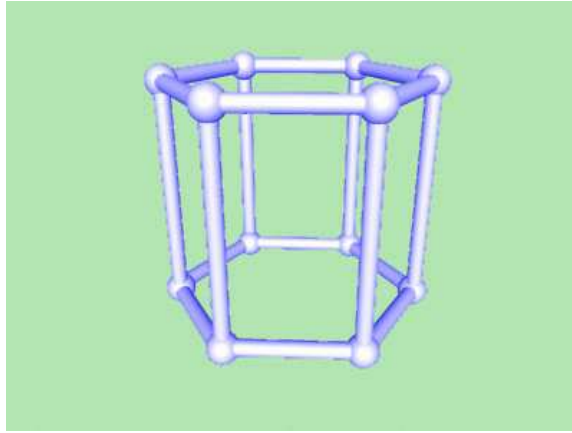with a regular hexagon as base. There is only **1** such type of Bravais lattice.

Figure 1.10: Hexagonal Bravais lattices.

This is an enumeration that should illustrate the different types of lattices but we will not go further into more details, since this is a well established topic and further lectures on crystallography may be attended by those interested in them. An interesting topic related to structure and still a subject of research is concerned with the fact that, no crystal structures are possible with n-fold rotational symmetry for $n \neq 2, 3, 4$, and 6. The first point to notice is that, given an n-fold rotation axis, there is always a set of planes where atoms form a lattice. This can be seen case by case in each of the Bravais latices discussed above. In general we can argue that given the rotation axis, we can always find a plane with at least one atom. However, if translational symmetry is present, it should be possible to translate the axis by some amount to an equivalent position, and the same should happen to the atom found. Therefore, there should be in general a two-dimensional lattice associated with a rotation axis. Next, we assume that we found two nearest neighbor atoms, and choose units of length such that this distance is unity (Fig. 1.11). We perform
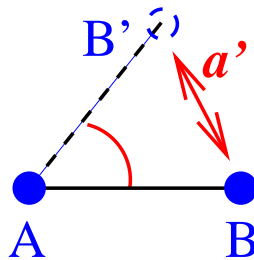

Figure 1.11: Atoms A and B are assumed nearest neighbors. a' gives the distance between B and B' after a rotation by $2\pi/n$.

now a rotation by $2\pi/n$, from the line joining both atoms around an axis passing

through one of them. Then, the distance between the new position and the atom
nearest neighbor to the one where the axis rotation was passing through is

$$a' = \sqrt{\left(1 - \cos\frac{2\pi}{n}\right)^2 + \sin^2\frac{2\pi}{n}} \ . \tag{1.33}$$

Since by assumption, $a' \geq 1$, we obtain a contradiction for $n \geq 7$. This can be easily
seen by noticing that

$$a'^2 = 2\left(1 - \cos\frac{2\pi}{n}\right) \ , \tag{1.34}$$

and $\cos\frac{2\pi}{n} > \frac{1}{2}$ for $n \geq 7$. On the other hand, for $n = 5$, we can perform the rotation
around one point in one direction and around the other point in the other direction,
such that the distance between the new points is

$$a'' = 1 - 2\cos\frac{2\pi}{5} \ , \tag{1.35}$$

reaching again a contradition. Or put in other words, it is not possible to make
a perfect covering of the plane with regular figures other than triangles, squares,
or hexagones. Experiments show that there are ordered systems (although not
perfectly periodic) with 5- and 12-fold rotation symmetry. These systems are known
as *quasicrystals*.