Lecture 3 — Symmetry in the solid state -

Part III: The reciprocal lattice and its symmetry.

1 Symmetry and reflection conditions in reciprocal space

1.1 Recap of the key properties of *real* and *reciprocal* space and their relations.

The following important concepts have been illustrated in the previous lectures, but are summarised again here[1].

***Real* space and real lattice**

- **Real-space points** are described by means of an **origin** and **real-space position vectors**, as $p = o + \mathbf{v}$. The choice of the origin is *arbitrary*, and gives rise to sets of related position vectors.
- **Real-space position vectors** are generally described as linear combinations of the **real or direct basis vectors** (*covariant*, dimensions: length) with **dimensionless coefficients** (*contravariant coordinates*).
- **Real lattice vectors** are linear combinations of the **primitive basis vectors** with **integral components**. For certain lattices, they can also be expressed as linear combinations of the **conventional basis vectors** with **integral or simple fractional components**. Real lattice vectors with *fractional* components are known as **centering vectors**.

***Reciprocal* space and reciprocal lattice (RL)**

- **Reciprocal-space position vectors** are described as linear combinations of the **reciprocal or dual basis vectors** (*contravariant*, dimensions: length^{-1}) with **dimensionless coefficients** (*covariant components*).
- **Reciprocal-space points** are obtained by adding the **reciprocal-space position vectors** to an **origin**, which, unlike the real-space origin, is **not arbitrary** (see below).
- **Reciprocal lattice vectors** are linear combinations of the **dual basis vectors** with **integral components**.

[1] In the remainder we will use the abbreviation RL to mean "reciprocal lattice", and RLV to mean "reciprocal lattice vector".

Dot products

- The dot product of *real* and *reciprocal* ***space*** vectors expressed in the usual coordinates is

$$\mathbf{q} \cdot \mathbf{v} = 2\pi q_i v^i \tag{1}$$

- The dot product of *real* and *reciprocal* ***lattice*** vectors is:

  - **If a *primitive* basis is used to construct the dual basis**, 2π times an integer for *all* **q** and **v** in the real and reciprocal lattice, respectively. In fact, as we just said, all the components are integral in this case.
  - **If a *conventional* basis is used to construct the dual basis**, 2π times an integer **or** a simple fraction of 2π. In fact, as we just said, *the components of the* ***centering*** *vectors are fractional*.

- Therefore, if a **conventional** real-space basis is used to construct the dual basis, **only certain reciprocal-lattice vectors will yield a $2\pi n$ dot product with *all* real-lattice vectors**. It is quite easy to show (left as an exercise) that those reciprocal-lattice vectors **are exactly those generated by the corresponding primitive basis**.

A *conventional* basis generates *more* RL vectors that a corresponding *primitive* basis. As we shall see, the "*extra*" points are not associated with any scattering intensity — we will say that they are *extinct by centering*.

1.2 Centering extinctions

As anticipated in the previous section, reciprocal space vectors generated by a conventional basis are said to be *extinct by centering* if their dot product with real-lattice vectors having fractional coordinates (known as "centering" vectors) is not an integral multiple of 2π. These vectors are therefore not part of the reciprocal lattice generated by a *primitive* basis. Based of the known form of the centering vectors for the various lattices, we can easily find the form of these vectors. Because the conditions are expressed in fractional coordinates, the **extinction conditions** are the same for the same type of centering, regardless of the symmetry. These conditions are described in some detail in Appendix I and summarised in tab. 1 for all the lattice types admitting a conventional unit cell (conventional basis vectors).

Table 1: Centering extinction and scattering conditions for the centered lattices. The "Extinction" columns lists the Miller indices of reflections that are **extinct by centering**, i.e., are "extra" RLV generated as a result of using a conventional basis instead of a primitive one. The complementary "Scattering" column corresponds to the listing in the International Tables vol. A [1], and lists the Miller indices of "allowed" reflections. "n" is any integer (positive or negative).

Lattice type	Extinction	Scattering
P	none	all
A	$k+l=2n+1$	$k+l=2n$
B	$h+l=2n+1$	$h+l=2n$
C	$h+k=2n+1$	$h+k=2n$
F	$k+l=2n+1$ *or* $h+l=2n+1$ *or* $h+k=2n+1$	$k+l=2n$ *and* $h+l=2n$ *and* $h+k=2n$
I	$h+k+l=2n+1$	$h+k+l=2n$
R	$-h+k+l=3n+1$ *or* $-h+k+l=3n+2$	$-h+k+l=3n$

2 Fourier transform of lattice functions

In this section, we will consider a generic **real** or **complex** function $f(\mathbf{r})$ defined over the real space, **r** being a position vector from an appropriately defined origin). We assume that $f(\mathbf{r})$ has the symmetry properties defined by one of the 230 space groups. We will calculate the Fourier transform of this function, $F(\mathbf{q})$, over the *whole* space. As we shall see in the next lectures, $F(\mathbf{q})$ corresponds to the diffraction ***structure factor***. We have:

$$F(\mathbf{q}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \int d\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \tag{2}$$

where the integral extends to the whole space. We now exploit the *lattice* periodicity of the function $f(\mathbf{r})$, which we can express by writing $\mathbf{r} = \mathbf{r}_0 + \mathbf{x}$ and

$$f(\mathbf{r}_0 + \mathbf{x}) = f(\mathbf{x}) \tag{3}$$

The $\mathbf{r}_0$ are the symmetry translation vectors, and **x** is a position vector **within the first unit cell**, i.e., $x, y, z < 1$. We can also decompose the integral in Eq. 2 in integrals over the unit cells:

$$
\begin{aligned}
F(\mathbf{q}) &= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{\mathbf{r}_0} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{q}\cdot(\mathbf{r}_0+\mathbf{x})} \\
&= \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{\mathbf{r}_0} e^{-i\mathbf{q}\cdot\mathbf{r}_0} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{-i\mathbf{q}\cdot\mathbf{x}}
\end{aligned} \tag{4}
$$

where the integral is now over a *single* unit cell. We now introduce a set of coordinates that are appropriate for the symmetry[2] and recall that in these coordinates the symmetry translation vectors are expressed as $[n^i]$, i.e., a set of three integers. Eq. 4 becomes:

$$
F(\mathbf{q}) = \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_{n_i} e^{-2\pi i q_i n^i} \int_{u.c.} dx^i f(x^i) e^{-2\pi i q_i x^i} \tag{5}
$$

The sum is now over *all* the symmetry translations, i.e., over all the positive and negative values of the $[n^i]$. We will perform the infinite summation by summing over a finite number N real-lattice vectors first , and then letting $N \to \infty$. The following statements is now clear by inspecting Eq. 5:

$F(\mathbf{q})$ ***is non-zero only for*** **q** ***belonging to the*** **primitive *RL.***

In fact, if **q** belongs to the *primitive* reciprocal lattice, then by definition its dot product to the symmetry lattice translation is a multiple of 2π, the exponential factor is 1 and the *finite* summation yields N (i.e., the number of unit cells). Conversely, if **q** does *not* belong to the *primitive* reciprocal lattice, the exponential factor will vary over the unit circle in complex number space and will *always* average to zero. In particular, $F(\mathbf{q})$ is *zero* for the conventional *RLV* that are **extinct by centering** (as we anticipated — this explains the terminology "extinction" we just introduced). For non-extinct RL vectors, the infinite summation yields ∞. In lecture 5, we shall see that that $F(\mathbf{q})$ is actually a series of δ **functions**, centered at the RL nodes.

2.0.1 Supplementary extinction conditions due to roto-translations

When the symmetry of the crystal contains roto-translation operators, *supplementary extinction conditions are present*. Unlike centering extinctions, roto-translation extinctions only apply to certain hkl's within *planes* (glides) or *lines* (screws) in reciprocal space.

Roto-translation extinctions are listed in the International Tavles vol A [1] for each space group, and are discussed in [2].

[2] In this section, it should become absolutely clear why we do not use Cartesian coordinates.

2.1 The "weighed" reciprocal lattice and its symmetry

The previous results have been deduced in a completely general way, regardless of the specific form of the function $f(\mathbf{x})$. In fact:

It is the *periodic* nature of $f(\mathbf{x})$ that is responsible for the *discrete* nature of $F(\mathbf{q})$.

In this section, we are interested in determining the **symmetry** of the RL and of the functions obtained, given a certain lattice function $f(\mathbf{x})$, by "weighing"or "dressing" each point of the *RL* with $|F(\mathbf{q})|^2$, calculated at that particular *RL* point. As we shall see shortly, in diffraction experiments, $|F(\mathbf{q})|^2$ is **proportional to the observed scattering intensity**. We will simply state the results, without any derivations. For more details, see [2].

2.1.1 The symmetry of the reciprocal lattice

The "bare" reciprocal lattice has translational invariance, although this property is not retained by any of the "dressed" lattices. By exploiting the rotational invariance of the dot product [2], it is straightforward to prove that **the *RL* has the same point-group symmetry (holohedry) of the real lattice**. However, this is **not** to say that the *RL* is the same Bravais lattice as the real lattice. The relation between real-space and reciprocal-space Bravais lattices is sumarised in tab. 2 (more details in [2].

2.1.2 The symmetry of $|F(\mathbf{q})|^2$ and the Laue classes

Let g be a symmetry operator in *normal form* with rotational part $\mathbf{R}$ and translational part $\mathbf{t}$. One can show in a completely general way that

$$F(\mathbf{q}) = \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d(\mathbf{x}) f(\mathbf{x}) e^{-i(\mathbf{R}^{-1}\mathbf{q})\cdot\mathbf{x}} e^{-i\mathbf{q}\cdot\mathbf{t}} = F(\mathbf{R}^{-1}\mathbf{q}) e^{-i\mathbf{q}\cdot\mathbf{t}} \tag{6}$$

Eq. 6 shows that:

The reciprocal lattice weighed with $|F(\mathbf{q})|^2$ has the *full point-group symmetry of the crystal class*.

This is because the phase factor $e^{-i\mathbf{q}\cdot\mathbf{t}}$ clearly disappears when taking the modulus squared. In fact, there is more to this symmetry when f(**x**) is *real*, i.e., $f(\mathbf{x}) = f^*(\mathbf{x})$: in this case

Table 2: Reciprocal-lattice Bravais lattice for any given real-space Bravais lattice (BL).

Crystal system	Real-space BL	Reciprocal-space BL
Triclinic	P	P
Monoclinic	C	C
Orthorhombic	P	P
	A or B or C	A or B or C
	I	F
	F	I
Tetragonal	P	P
	I	I
Trigonal	P	P
	R	R
Hexagonal	P	P
Cubic	P	P
	I	F
	F	I

$$
\begin{aligned}
F^*(\mathbf{q}) &= \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d\mathbf{x} f^*(\mathbf{x}) e^{i\mathbf{q}\cdot\mathbf{x}} \\
&= \frac{N}{(2\pi)^{\frac{3}{2}}} \int_{u.c.} d\mathbf{x} f(\mathbf{x}) e^{i\mathbf{q}\cdot\mathbf{x}} = F(-\mathbf{q})
\end{aligned}
\tag{7}
$$

Consequently, $|F(\mathbf{q})|^2 = F(\mathbf{q})\,F(-\mathbf{q}) = |F(\text{-}\mathbf{q})|^2$ is *centrosymmetric*. As we shall shortly see, the lattice function used to calculate non-resonant scattering cross-sections is *real*. Consequently, the $|F(\mathbf{q})|^2$-weighed *RL* (proportional to the Bragg peak intensity) has the symmetry of the crystal class *augumented by the center of symmetry*. This is necessarily one of the 11 centrosymmetryc point groups, and is known as the *Laue class* of the crystal.

Fridel's law

For normal (non-anomalous) scattering, the reciprocal lattice weighed with $|F(\mathbf{q})|^2$ has the *full point-group symmetry of the crystal class supplemented by the inversion*. This symmetry is known as the *Laue class* of the space group.
In particular, for normal (non-anomalous) scattering, **Fridel's law holds**:

$$|F(hkl)|^2 = |F(\bar{h}\bar{k}\bar{l})|^2 \tag{8}$$

Fridel's law is violated for non-centrosymmetric crystals in anomalous conditions. Anomalous scattering enables one, for example, to determine the *orientation of a polar crystal* or the *chirality of a chiral crystal* in an absolute way.

3 Symmetry in Reciprocal Space — the Wigner-Seitz construction and the Brillouin zones

Up to this point, we have only considered the symmetry of the RL *nodes*, showing that this is in fact completely adequate when dealing with the Fourier transform of *periodic* functions. In essence, crystallography is only interested in the very sharp "spikes" of scattering at the RL nodes, ignoring completely the vast regions of reciprocal space outside these nodes. For a well-ordered crystal, scattering outside the RL is weak by comparison but by no means zero, and contains a wealth of information about *intrinsic static disorder* (elastic scattering) and *dynamics* (inelastic scattering from phonons, spin waves etc.) General (non-RL) reciprocal-space vectors are also essential in describing phenomena such as lattice electrons, phonons, etc. In short,

Non-periodic phenomena in the crystal (elastic or inelastic) are described in terms of generic (non-RL) reciprocal-space vectors and give rise to scattering outside the RL nodes.

Although the individual excitations may break every crystal symmetry, the crystal maintains its symmetry **on average** (either temporal average or average over different regions of a large crystal). One therefore usually deals with a reciprocal space that retains the full crystal class symmetry at the very least or sometimes the Laue symmetry. In describing these phenomena, however, one encounters a problem: as one moves away from the RL origin, symmetry-related "portions" of reciprocal space will become very distant from each other. In order to take full advantage of the reciprocal-space symmetry, it is therefore advantageous to **bring symmetry-related parts of the reciprocal space together in a compact form**. This is exactly what the Wigner-Seitz construction and the Brillouin zone scheme accomplish very cleverly. A very good description of the Wigner-Seitz and Brillouin constructions can be found in [3].

3.1 The Wigner-Seitz construction

The Wigner-Seitz construction is essentially **a** method to construct, for every Bravais lattice, a **fully-symmetric** unit cell that has **the same volume of a *primitive* cell**. As such, it can be applied to both real and reciprocal spaces, but it is essentially employed only for the latter.

For a given lattice node τ, the Wigner-Seitz unit cell containing τ is the set of points that are *closer* to τ than to any other lattice node.

It is quite apparent that:

- Each Wigner-Seitz unit cell contains one and only one lattice node.
- Every point in space belongs to at least one Wigner-Seitz unit cell. Points belonging to more than one cell are *boundary* points between cells.
- From the previous two points, it is clear that the Wigner-Seitz unit cell has the same volume of a primitive unit cell. In fact, it "tiles" the whole space completely with identical cells, each containing only one lattice node.
- The Wigner-Seitz unit cell **containing the origin** has the full **point-group symmetry of the lattice** (holohedry). In **real space**, the origin is arbitrary, and all the Wigner-Seitz unit cells are the same. In **the "weighed" reciprocal space the Wigner-Seitz at $\mathbf{q} = 0$ is *unique* in having the full point-group symmetry**. As we shall see shortly, the Brillouin zone scheme is used to project fully-symmetric portions of reciprocal space away from the origin into the first Wigner-Seitz unit cell.

A dummies' guide to the Wigner-Seitz construction (fig. 1)

- Draw segments connecting the origin with the neighbouring points. The first "ring" of points (marked with "1" in fig. 1 **A**) should be sufficient, although these points may not all be symmetry-equivalent.
- Draw orthogonal lines bisecting the segments you just drew. These lines define a polygon containing the origin (fig. 1 **B**)— this is the Wigner-Seitz unit cell. In 3D, one would need to draw **orthogonal bisecting planes**, yielding Wigner-Seitz **polyhedra**.
- Fig. 1 **C** shows an extended construction (to be used later) including lines bisecting the segments to the second and third "rings". As you can see, the new lines do not intersect the original Wigner-Seitz unit cell.
- The whole space can be "tiled" with Wigner-Seitz cells (fig. 2).

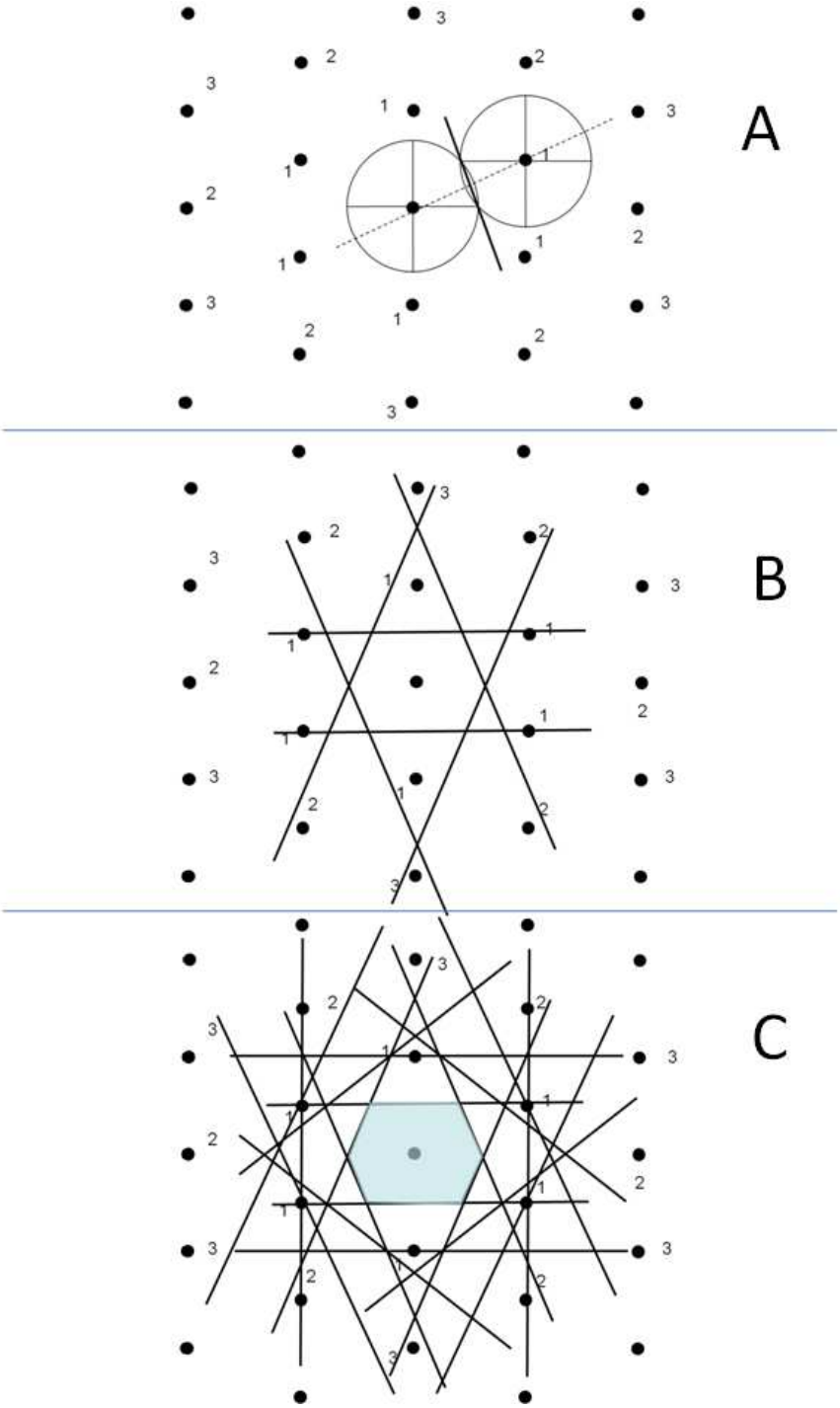

Figure 1: Construction of the Wigner-Seitz unit cell for the case of a C-centered rectangular lattice in 2D. **A**: bisecting lines are drawn to the segments connecting the origin with the neighbouring points (marked "1". **B**: these lines define a polygon — the Wigner-Seitz unit cell. **C**: the Wigner-Seitz unit cell is shown together with lines bisecting segments to more distant lattice points.

3.1.1 "Reduction" to the first Wigner-Seitz unit cell (first Brillouin zone).

As anticipated, the main use of the Wigner-Seitz unit cell is in reciprocal space:

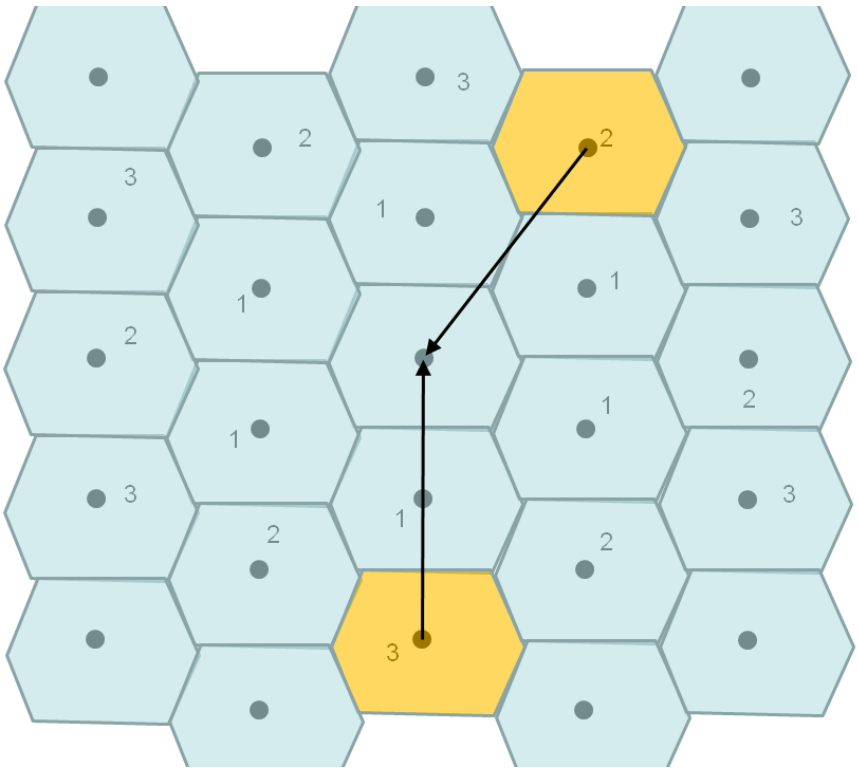

Figure 2: Extended Wigner-Seitz cell scheme, showing how the entire space can be tiled with these cells. Each cell can be "reduced" to the first Wigner-Seitz cell with a *single* RL vector.

Every vector **q** in reciprocal space can be written as

$$\mathbf{q} = \mathbf{k} + \boldsymbol{\tau} \tag{9}$$

where $\boldsymbol{\tau}$ **is a** RL **vector and k is within the *first* Wigner-Seitz unit cell**. (i.e., the one containing the origin). We more often say that **k** is the "equivalent" of **q reduced to the first Brillouin zone** (see here below).
The **extended Wigner-Seitz scheme** shown in fig. 2 is used to determine **which $\boldsymbol{\tau}$ should be used for a given q** — clearly, the one corresponding to the lattice node *closer* to it.

3.2 The Brillouin zones construction

We have just learned how to "reduce" every reciprocal-space point to the first Wigner-Seitz unit cell (or first Brillouin zone). But the question is: which "bits" of reciprocal space should be "reduced" together? One may be tempted to think that an entire Wigner-Seitz unit cell should be "reduced" together — after all, one would only need a *single* RL vector to accomplish this. It is readily seen, however, that this is not a good idea. As we mentioned before, higher Wigner-Seitz unit cells (i.e., other than the first) do not possess any symmetry, and we are specifically interested in "reducing" together symmetry-related parts of reciprocal space. Therefore, **a different construction, known as the Brillouin-zone construction-is required to reduce symmetry-**

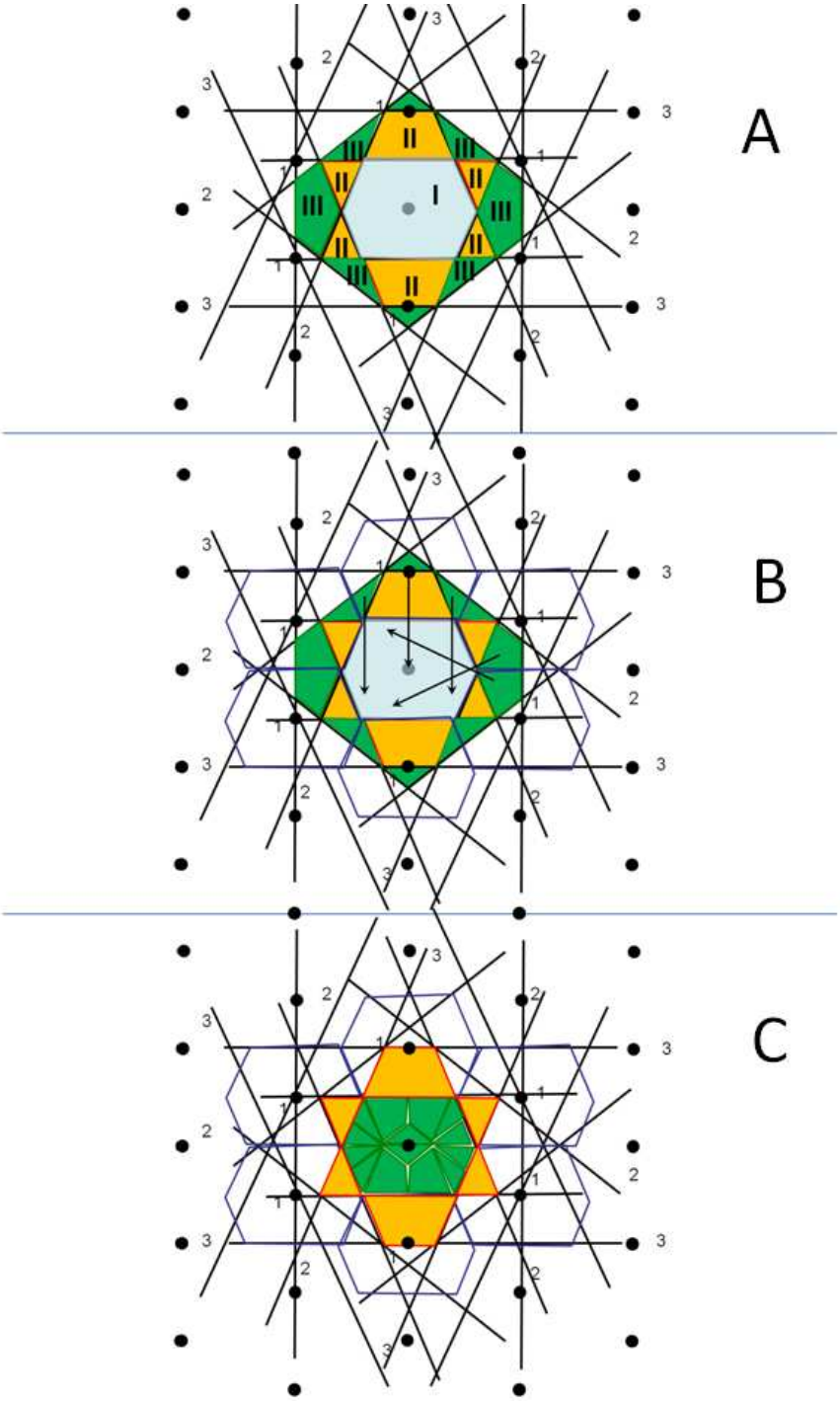

Figure 3: Procedure to construct Brillouin zones. The starting point is fig. 1 **C**. **A** A number is given to each polygon, according to how many lines are crossed to reach the origin. Polygons with the same number belong to the same Brillouin zone. The figure shows the scheme for the first **three** Brillouin zones. **B** Portions of a higher Brillouin zone can be reduced to the first Brillouin zone in the normal way, i.e., by using the extended Wigner-Seitz construction (here, the reduction procedure is shown for the third zone). **C** When reduced, higher zones "tile" perfectly within the first Brillouin zone.

related portions of reciprocal space simultaneously.

The first Brillouin zone coincides with the first Wigner-Seitz unit cell. Higher Wigner-Seitz unit cells are *emphatically not* Brilloun zones.

A dummies' guide to the Brillouin-zones construction (fig. 3)

- Start off in the same way as for the Wigner-Seitz construction, but with lines bisecting the segments to higher-order "rings" of points, as per fig. 1 **C**.
- Many polygons of different shapes (polyhedra in 3D) will be obtained. Each of these will be given a **number according to how many lines (planes in 3D) are crossed to reach the origin with a straight path**. If m lines (planes) are crossed, the **order of the Brillouin zone will be** $m + 1$.
- A Brillouin zone is formed by polygons (polyhedra) having the same number (fig. 3 **A**).
- As anticipated, **the first Brillouin zone is also the first Wigner-Seitz cell** (no line is crossed).
- The different portions of a Brillouin zone are "reduced" to the first Brillouin zone in the normal way, i.e., using the extended Wigner-Seitz construction (fig. 3 **B**).
- All the portions of a higher Brillouin zone will **tile perfectly within the first Brillouin zone** (fig. 3 **C**).

4 "Real" crystal structures

Having discussed at length the symmetries of periodic "patterns" in 2 and 3 dimensions, we will devote the last part of this lecture to looking at "real" crystal structures. This is in itself a vast subject that cannot be exhausted in such a short space. An interesting set of lectures devoted to the subject can be found in [5]. It is also worth pointing out to the interested student the existence of several very useful Crystal Structure Databases. The Inorganic Crystal Structures Database (ICSD), freely accessible on-line from the UK [4], can be searched for names, chemical formulas, crystallographic data and more, to display the resulting crystal structures in 3D and even to plot their powder diffraction patterns. The Cambridge Structural Database is the corresponding source for small-molecule structures. Here, we will outline a few basic principles that should provide a starting point to understand "real" crystal structures.

4.1 Cohesive forces in crystals — atomic radii

A number of different forces contribute to the cohesion of crystals, including:

- The **Coulomb interaction** between charged ions.
- **Chemical bonding** and **metallic bonding**.
- The **Van der Waals** (dipole-dipole) interaction.
- **Hydrogen bonding**.

These forces, which often coexist within the *same* crystal structure, are of very different strength. Another crucial difference is the **directionality** of these forces. **Chemical bonding** (both ionic and covalent) **is usually strongly directional**, and leads to the formation of specific **coordination polyhedra** (e.g., octahedra, tetrahedra) within the crystals. Conversely, most other interactions are poorly directional.

One useful way to understand many crystal structures, particularly those of inorganic compounds of greater interest for physicists, is that of considering them as **packings of spheres of different sizes**. Within this very simplistic picture, each ion is characterised by a **radius**. Atomic radii are not completely unique to each species, but vary depending on several factors:

- The **valence** state of the ion.
- The **spin** state of the ion.
- The number of neighbours (**coordination number**).
- Whether the bonding is **ionic** or **covalent**.

The standard reference for covalent and ionic radii was compiled by R.D. Shannon and can be found in [6]. Several versions of this table can be found on line.

Over most of the periodic tables, ionic and covalent radii vary between 0.5 Åand 2 Å. Typical interatomic distances are therefore of the order of 1.5–2.5 Å. This sets the lengthscale of the probes (X-rays, neutrons, electrons) that can be most profitably used to study these structures.

4.2 Close-packed structures

When all the "spheres" are of equal size and the interactions between them are not strongly directional, the most common arrangement is one of the **close packed structures** (fig. 4):

CCP i.e., **Cubic Close-Packed**, which has a face-centered cubic (**FCC**) lattice (space group $Fm\bar{3}m$). Many metals, including all those of the Cu and Ni groups, adopt this structure.

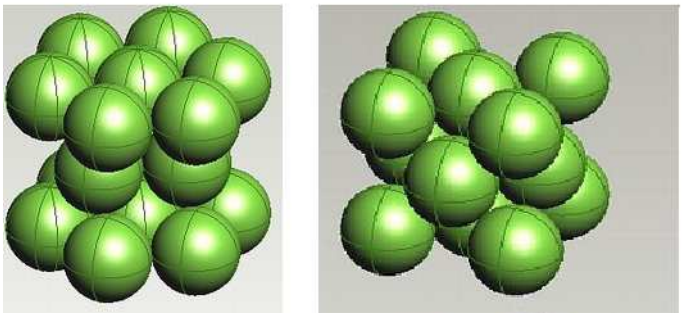

Figure 4: The close-packed structures of rigid spheres: HCP (**left**) and CCP (**right**).

HCP Hexagonal Close-Packed, which has a hexagonal lattice with two atoms per unit cell (space group $P6_3/mmc$). Metals such as Co, Zn, Cd, Hg, Mg and others adopt this structure.

Several metals, including Fe, Cr and its group, V and its group and all the alkaline metals adopt the **BCC (Body Centered Cubic) structure** — space group $Im\bar{3}m$, which is **not close-packed**.

Close-packed and BCC structures are also adopted by much more complex systems — for instance C_{60} ("Buckyballs") and even viruses (fig. 5) — clearly with much larger inter-sphere distances. Here we have roughly spherical objects with strong internal bonding, which are weakly bonded among themselves.

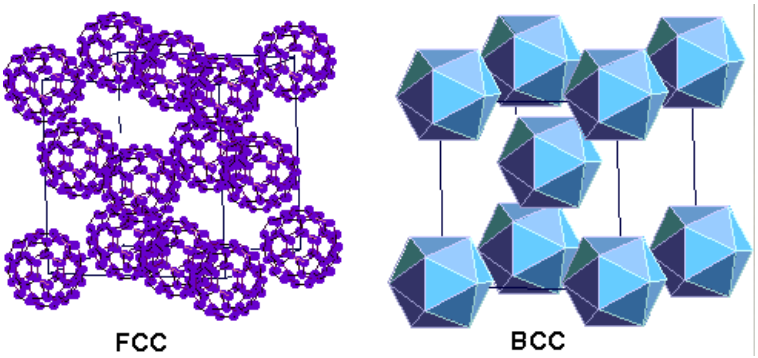

Figure 5: Simple arrangements of complex objects: (**left**) the CCP structure of C_{60} ("Buckyballs") and (**right**) the BCC structure of the foot-and-mouth virus.

4.3 Packing spheres of different radii

Many simple binary or ternary compounds are made of ionic species with different radii. In these cases, their crystal structures can often be thought of as being close-packed arrangements of the *larger* spheres, with the *smaller* spheres located in the "interstices" or "vacancies" between the larger spheres. Both CCP and HCP structures have vacancies of this type, surrounded by four

spheres (**tetrahedral vacancies**) or six spheres (**octahedral vacancies**). Because of the geometry of the vacancies, this structural arrangement is suitable for ions with **strongly directional bonding**. When strong directional bonding is present, compounds with ions with similar radii and even mono-atomic compounds can adopt these structure. Among the structures that can be described in this way are:

The NaCl structure (space group $Fm\bar{3}m$) where Na fills *all* the octahedral holes of the CCP structure.

The fluorite structure (prototype compound CaF_2, space group $Fm\bar{3}m$), where the F atoms fill *all* the tetrahedral holes of the CCP structure (fig. 6).

The zinc blende structure (prototype compound ZnS, space group $F4\bar{3}m$), where the Zn ions fill *half* of the tetrahedral holes of the CCP structure.

The perovskite structure (prototype compound $CaTiO_3$, space group $Pm\bar{3}m$). In this interesting ternary example, the CCP array is formed by *both* Ca^{2+} (positively charged) *and* O^{2-} (negatively charged). The smaller Ti ion fills *a quarter* of the octahedral vacancies.

The corundum structure (Al_2O_3, space group $R\bar{3}c$). Here, the oxygen ions form a HCP structure, and the much smaller Al ions fit into 2/3 of the the octahedral vacancies (1/3 of the vacancies are empty). The **ilmenite** ($FeTiO_3$, space group $R\bar{3}$) is a variant with two metal ions instead of one.

The diamond structure is adopted, among others, by C and Si. It is identical to the zinc blende structure but with two identical, strongly-bonded atoms.

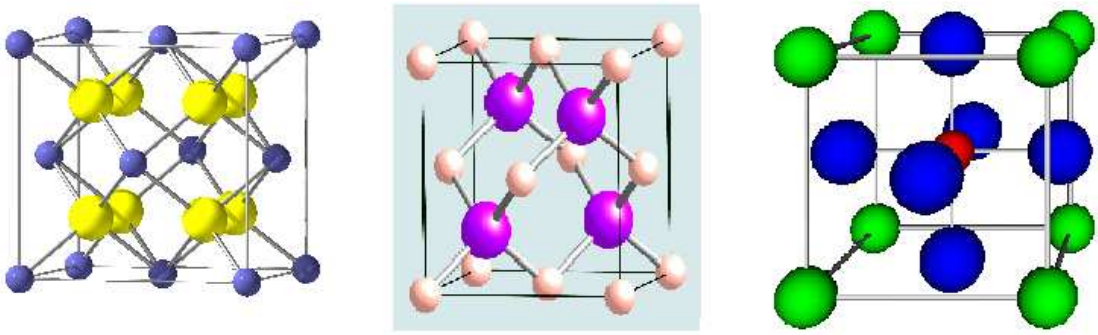

Figure 6: Three cubic structures obtaining by inserting ions in the "interstices" of the CCP structure. **Left** the fluorite structure ; **center** the zinc blende structure; **right** the perovskite structure.

4.4 Framework structures

Many crystal structures cannot be simply thought of in terms of close packing. One notable example is given by **framework structures** — structures built out of very rigid polyhedra (most often tetrahedra) with rather "flexible" connections to each other. Framework structures are low-density structures, and can often collapse rather easily to higher-density forms upon application of pressure.

The structure of **quartz** (SiO_2) consists of corner-sharing SiO_4 tetrahedra so that each Si is bonded to four oxygens, and each oxygen is bonded to two silicon atoms. The resulting structure forms an open three-dimensional framework, and it is quite flexible, so that different crystal variants exist (α- and β-quartz, crystobalite, trydimite etc.) When cooled rapidly, the quartz structure is unable to "choose" between these variants and forms a **glass**. An even more extreme example of silicate framework structure is provided by **zeolite** (SiO_2, fig. 7), where the tetrahedral framework encompasses large cavities. Zeolite is the prototype of a large family of silicates and alumino-silicates, collectively known as "zeolites", which have wide-ranging applications in catalysis.

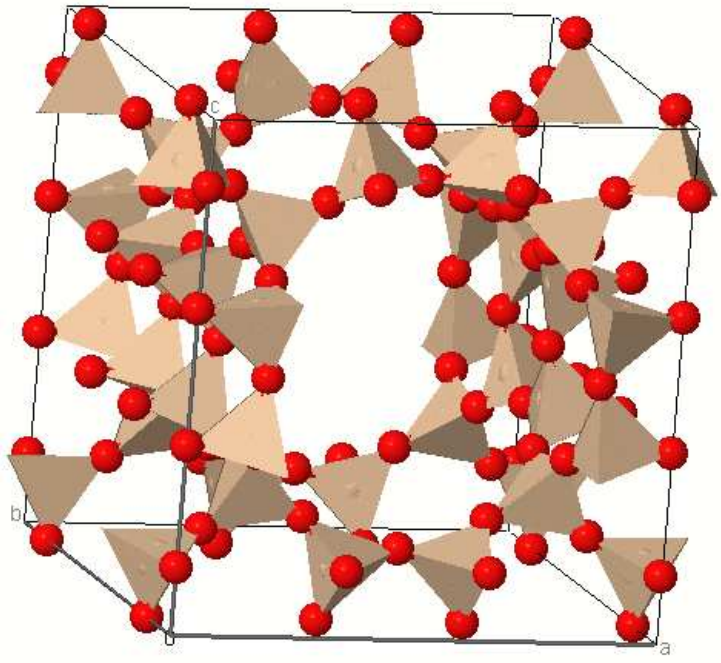

Figure 7: The structure of zeolite β (space group $P4_2/mmc$). Note the complex framework of SiO_4 tetrahedra, defining a large cavity in the middle of the unit cell. Many silicate and alumino-silicate zeolites exist, both natural and synthetic.

4.5 Layered structures

Many crystal structures have a pronounced 2-dimensional character, with strong covalent or ionic bonding in 2 dimensions and weaker (typically Van der Waals) bonding in the third. A well known example of this is **graphite** (space group $P6_3/mmc$ with two atoms per unit cell). Due to the weak inter-layer forces, the layers can "slip" onto each other, so that structures of this types are often employed as lubricants. Other examples of this kind are provided by the **clays**, such as vermiculite (fig. 8), and by the delafossite family (prototype $CuFeO_2$, space group $R\bar{3}m$ or $P6_3/mmc$). Less extreme examples of 2D structures are provided by the **high- T_c superconducting cuprates** (fig 9).

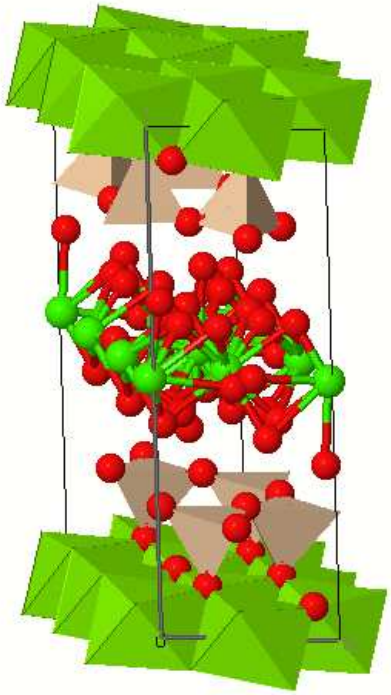

Figure 8: The structure of the vermiculite clay (chemical formula $A_3B_4O_{10} \cdot (H_2O)_n$, with A=Mg, Fe, Al, B=Al, Si; space group $C2/m$) is highly 2-dimensional. The A site forms triangular layers with formula AO_2, connected to "rings" of BO_2 tetrahedra. These layers are widely separated and weakly interacting, and, as typical of clays, can accommodate large amounts of rather disordered water molecules.

4.6 Molecular structures

All the structures we have defined up to this point are built of infinite "networks" of atoms, either in 3D or in 2D. By contrast, molecular structures are built out of well defined "molecules", with

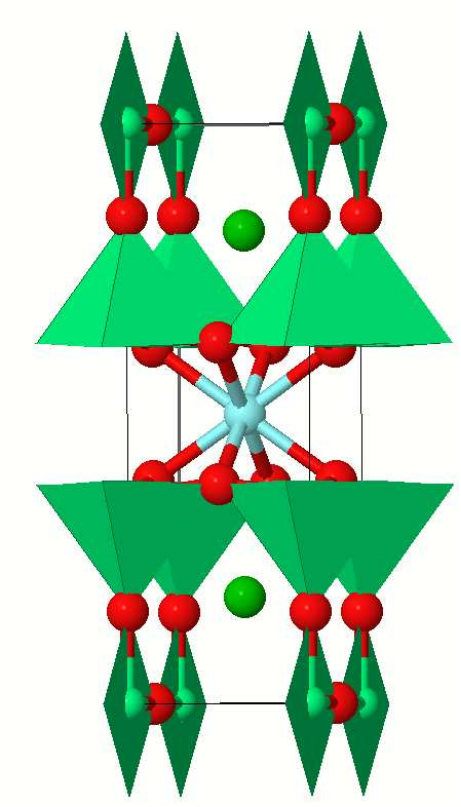

Figure 9: The structure of the 90 K-high-T_c superconductor $YBa_2Cu_3O_7$ or YBCO is also 2-dimensional, but with a less pronounced 2D *structural* character compared to clays. The central ion, Y, is ionically bonded to oxygen, so the structure does not exfoliate like that of graphite. Nevertheless, the electronic structure is highly 2D. Note that Cu exists both in square-pyramidal ("planes") and in square-planar ("chains") coordinations.

strong internal covalent bonding but weakly interacting with each other. A simple example is the structure of **ice**, with covalent bonding within the H_2O molecule and weak hydrogen bonding between molecules. Orinary ice is known as "ice 1h", and has space group $P6_3/mmc$. However, due to the particular geometry of the molecules, ice is **highly polymorphic** as a function of temperature and pressure, with 15 known different crystallographic structures being known to date. Molecular structures are adopted by most small molecules (such as drugs) and macromolecules (such as proteins). The molecule itself has rigid components (such as benzene rings) connected to each other by "joints" having some degree of flexibility. Therefore, the same molecule can often adopt different crystal structures (polymorphism), having different molecular configurations and packing of different molecules within the unit cell.

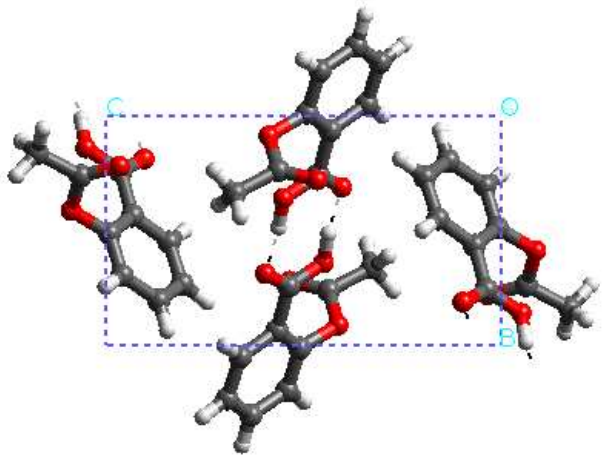

Figure 10: The molecular crystal structure of aspirin. The individual molecules are easily identifiable, and are linked to each other by hydrogen bonds (dotted lines).

5 Appendix I: centering extinction conditions

A, B or C-centered lattices The centering vectors in conventional coordinates are $0\,\frac{1}{2}\,\frac{1}{2}$, $\frac{1}{2}\,0\,\frac{1}{2}$ and $\frac{1}{2}\,\frac{1}{2}\,0$, respectively for the three types of lattice, modulo integral numbers. The dot product of a conventional *RLV* $\mathbf{q}$ with covariant coordinated h, k and l with these centering vectors is therefore $2\pi\frac{1}{2}(k+l)$, $2\pi\frac{1}{2}(h+l)$ and $2\pi\frac{1}{2}(h+k)$. We conclude that conventional *RLV* with $k+l \neq 2n$ etc., where n is any positive or negative integer, are extinct by centering.

F-centered lattices Here, all the faces are centered, so any condition $k+l \neq 2n$, $h+l \neq 2n$ and $h+k \neq 2n$ will lead to extinction. Conversely, $k+l = 2n$, $h+l = 2n$ and $h+k = 2n$ must be simultaneously true for a conventional *RLV* to be part of the primitive reciprocal lattice.

I-centered lattices Here, the centering translations are of the type $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, and their dot product with a conventional *RLV* $\mathbf{q}$ is $2\pi\frac{1}{2}(h+k+l)$. Conventional *RLV* with $h+k+l \neq 2n$ are therefore extinct by centering.

R-centered lattice in hexagonal coordinates We recall that the rhombohedral cell is *primitive*, so it does not give rise to extinctions by centering. In the hexagonal setting, there are two centering translations - $\frac{2}{3}\,\frac{1}{3}\,\frac{1}{3}$ and $\frac{1}{3}\,\frac{2}{3}\,\frac{2}{3}$. The dot products $\mathbf{q}\cdot\mathbf{v}$ are $2\pi\frac{1}{3}(2h+k+l)$ and $2\pi\frac{1}{3}(h+2k+2l)$, and both must be integral multiples of 2π for $\mathbf{q}$ to belong to the primitive *RL*. This is equivalent to $2h+k+l = 3n$, $h+2k+2l = 3n$. We now note that if the first condition is satisfied, so is the second. In fact, $h+2k+2l = 3h+3k+3l-(2h+k+l)$, and both terms on the right side are three times an integer if $2h+k+l = 3n$. The only condition for belonging to the primitive reciprocal lattice is therefore $2h+k+l = 3n$, or also $-h+k+l = 3n$, since $3h$ is three times an integer.

6 Bibliography

Ashcroft & Mermin [3] is now a rather old book, but, sadly, it is probably still the best solid-state physics book around. It is a graduate-level book, but it is accessible to the interested undergraduate.

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