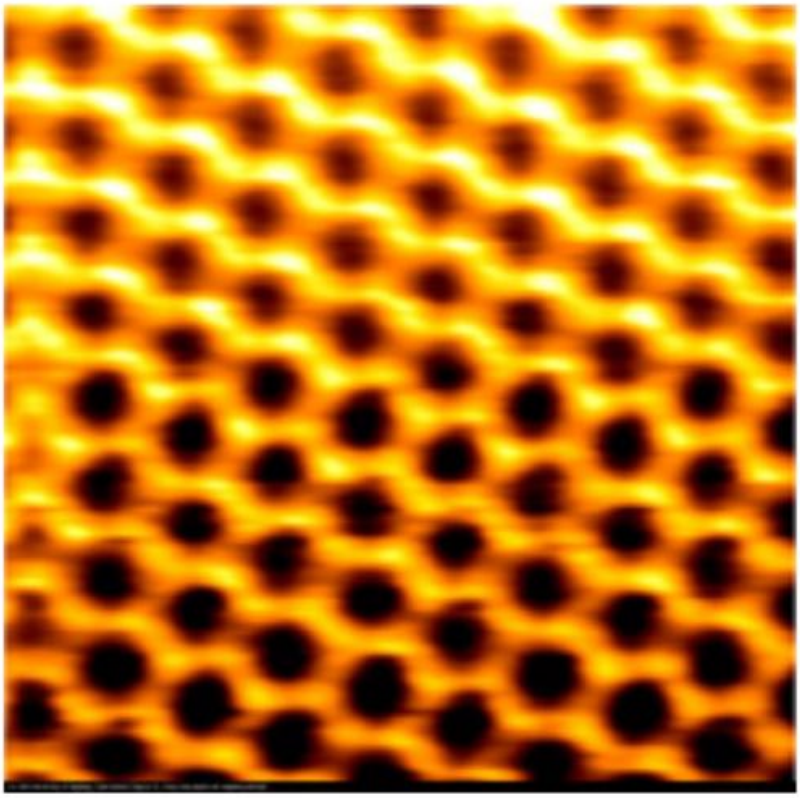
3

Crystalline Solids



AFM image (atomic force microscope) of graphene.
From https://chemistry.beloit.edu/Edetc/SlideShow/slides/scanning/graphite_AFM.html

The Bravais lattice

3.1 Rectangular lattice

Let's consider a simple rectangular lattice in 2D. Let's place type A and type B atoms respectively at the corner points and in the center of the rectangles.

1. Draw a scheme representing this lattice. Clearly indicate the motif of the Bravais lattice and draw the primitive vectors.
2. Let's consider now that A $\equiv$ B. Draw a primitive unit cell. How many primitive cells does the conventional rectangular cell contain in this case?

3.2 Cubic lattice

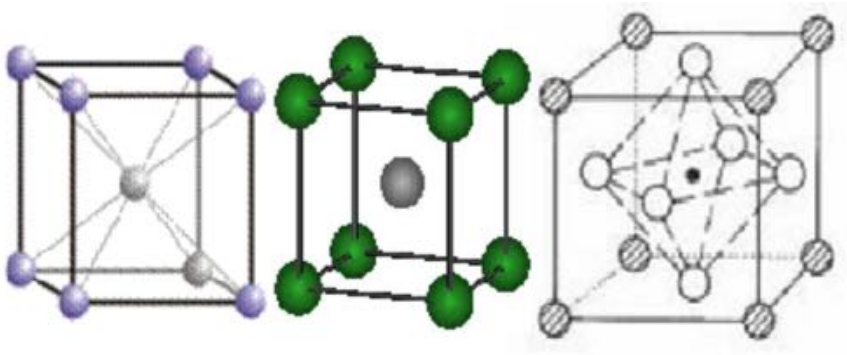


Figure 3.1: From left to right: structures of Lithium, CsCl and perovskite

For each of the following crystal cubic structures

- Lithium type: all atoms at the corner and the center of the cube are identical
- CsCl type: the atom at the center of the cube is different from the atoms at the corner points
- perovskite type: one type of atom (Ba, Ca, ...) is placed at the center of the cube, another type of atom (e.g. Ti) is placed in the corners of the cube and oxygens occupy the center of the faces

give the

1. motif and the coordinates of the atoms in the motif with respect to the cubic lattice vectors. In which case the cube is also the primitive unit cell?
2. chemical formula and the number of motifs per cube.

3.3 Hexagonal lattice

Let's consider an hexagonal lattice in 2D, like the one displayed in the Fig. 3.2. The angles formed in each direction are 60°.

1. Sketch different possible primitive unit cells. We shall use in the following the one generated by the primitive translation vectors $\vec{a}$ and $\vec{b}$ displayed in the figure.

2. Sketch a conventional centered rectangular cell. How many primitive cells are there in this cell? Determine the length of the primitive vectors of this conventional cell as a function of $a = \|\vec{a}\|$.

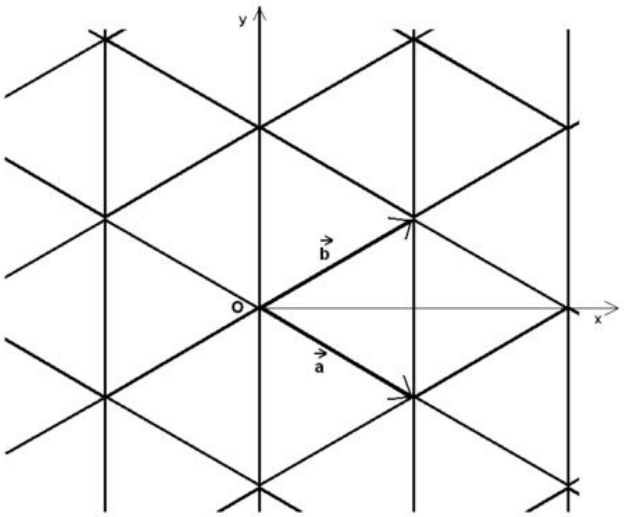


Figure 3.2: Hexagonal lattice in 2D

3.4 Honeycomb lattice

Graphene is a 2D monolayer of graphite, formed by carbon atoms at the corner points of regular hexagons of side ℓ.

1. Find the Bravais lattice and the associate motif of the honeycomb lattice.
2. Sketch the primitive unit cell which has primitive vectors forming an angle of 60°. Mark these vectors on the drawing as $\vec{a}$ and $\vec{b}$.
3. Find the norm of $\vec{a}$ and $\vec{b}$ as a function of ℓ. Give then the coordinates of the atoms of the motif according to $\{\vec{a}, \vec{b}\}$.
4. Sketch different families of crystal rows. For one of these families give the distance between two rows.

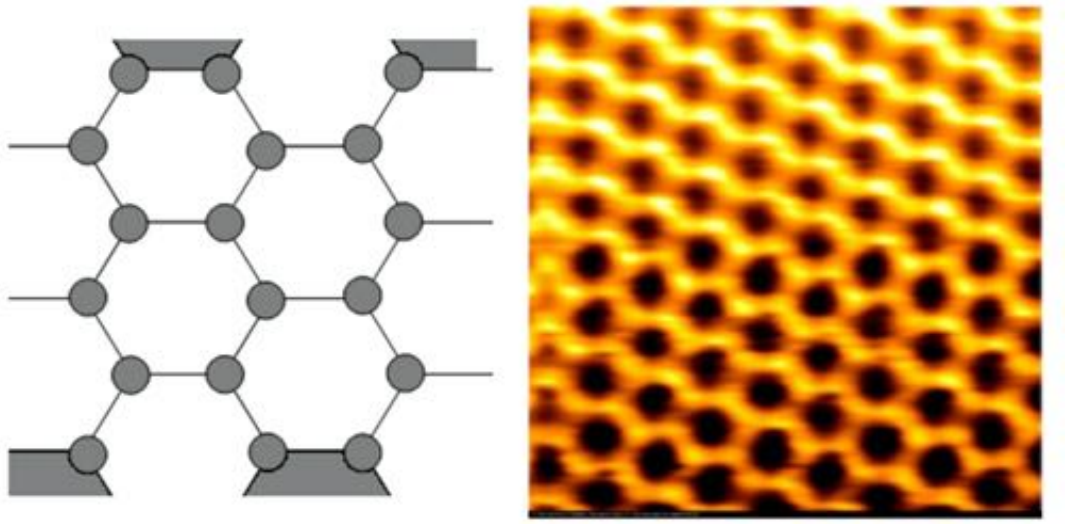


Figure 3.3: Left: honeycomb lattice. Right: AFM (atomic force microscope) image of graphene.

3.5 Reciprocal lattice and diffraction on crystals

3.5.1 2D Rectangular lattice

1. Build the reciprocal lattice of a rectangular Bravais lattice $(\mathbf{a}, \mathbf{b})$.
2. Let's consider now a centered rectangular lattice, whose conventional unit cell is the rectangular Bravais lattice $(\mathbf{a}, \mathbf{b})$. Identify the translation vectors $\mathbf{a_0}$ and $\mathbf{b_0}$ of the primitive unit cell. Determine then the primitive translation vectors $\mathbf{A_0}$ and $\mathbf{B_0}$ of the reciprocal lattice using two different methods:
   - by geometrical construction;
   - relating first $(\mathbf{a_0}, \mathbf{b_0})$ to $(\mathbf{a}, \mathbf{b})$ of the conventional rectangular unit cell and then relating in the corresponding reciprocal space $(\mathbf{A}, \mathbf{B})$ to $(\mathbf{A_0}, \mathbf{B_0})$.

3.5.2 Diffraction on the honeycomb lattice

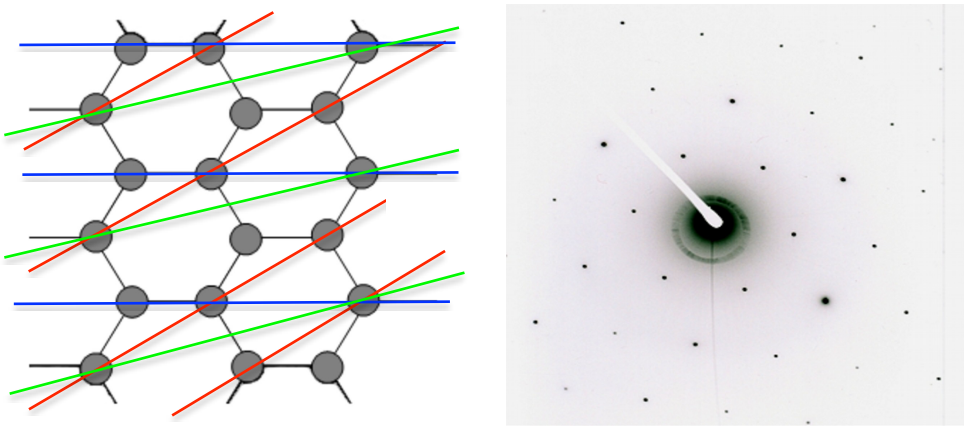


Figure 3.4: Left: honeycomb lattice. Right: diffraction pattern of the graphite surface obtained by diffraction of slow-electron beams.

By cutting the graphite along a proper crystal plane, we observe that the carbon atoms form regular hexagons (see Fig. 3.4). This structure is the *honeycomb lattice*, which we have already encountered in 3.3.

1. Identify a motif and the type of Bravais lattice of the honeycomb lattice. Write down the primitive vectors $\vec{a}$ and $\vec{b}$, expressing their coordinates in the (x, y) orthogonal reference system. We shall call the norm of these vectors a. Calculate then the reciprocal primitive vectors, and identify the reciprocal lattice.

2. Calculate the structure factor $S(h, k)$. Show that $|S|$ can have two different values. Is the diffraction pattern that you find consistent with the experimental one shown in Fig. 3.4?

Magnetic crystal structures

3.6 Reciprocal lattice and diffraction

Let's consider a simple tetragonal structure ($a = b \neq c$).

1. Specify the nature of the reciprocal lattice and determine the primitive vectors as a function of a an c.

2. Using Bragg law, relate the angle 2θ, between the incident and scattered beams, with the beam wavelength λ, the lattice parameters a, a/c and the Miller's indices h, k, l.

3. We want to use as scattering particles neutrons, which are thermalized at 440 K in a neutron reactor. At this temperature the kinetic energy of the neutrons may be consider as the the one of classical particles. Show that in this case the neutron wavelength $\lambda = 1.2$ Å.

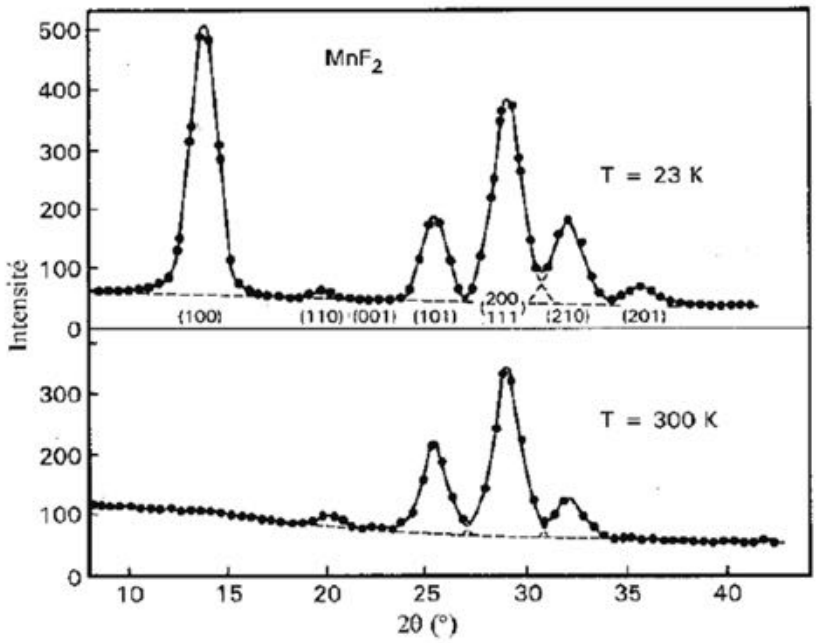


Figure 3.5: Neutron scattering intensity of MnF_2 above (top panel) and under the magnetic transition temperature

4. Certain bivalent transition metal oxides based on florine (AF_2, A= Mn, Fe, Co, Ni, Zn) present a rutile structure (the same as TiO_2), which is simply a tetragonal structure. Here we consider specifically the case of MnF_2, for which $a = b = 4.8734$ Å and $c = 3.3103$ Å. Can you explain the peaks which appear in the diffraction-intensity pattern displayed on Fig. 3.5 for $T = 300$ K? You may just focus on the lines (1,1,0) and (2,1,0).

3.7 Bravais lattice and structure factor of MnF_2

Let's now describe the crystal structure of MnF_2 as a tetragonal lattice with a motif given by:
A^{2+} (0,0,0); (1/2,1/2,1/2)
F^- (u, u, 0); (1-u, 1-u, 0); (1/2+u, 1/2-u, 1/2); (1/2-u, 1/2+u, 1/2)
where $u \simeq 0.3$.

1. Draw a schema of the conventional tetragonal unit cell of the crystal structure of MnF_2.

2. How many formulas MnF_2 are there in the conventional tetragonal unit cell?

3. By denoting f_A and f_F the atomic form factors respectively of the ions A^{2+} and F^-, calculate the structure factor $S(h,k,l)$ associated with the above motif. Write it in the form:

$$S(h,k,l) = f_A[1 + g(h+k+l)] + 2f_F[\cos 2\pi(h+k)u + g(h+k+l)\cos 2\pi(h-k)u]$$

where g is a function to be determined.

4. For the case $h + k + l$ odd, explain why the scattering intensity goes to zero if h (or k) is zero.

5. Which is the Bragg peak that should appear at the smallest angle θ? Is this in agreement with the diffraction intensity displayed on Fig. 3.5 for $T = 300$ K?

3.7.1 X-ray diffraction and measure of the lattice parameter

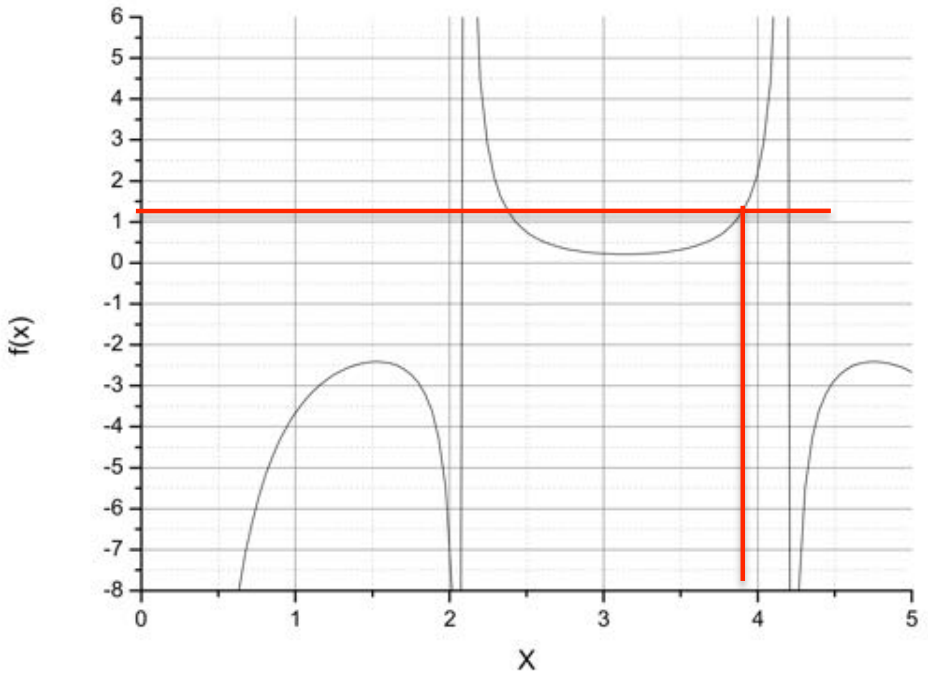


Figure 3.6: Graphical representation of the function $f(x) = (2.42 + 2\cos x)/(\cos 2x - \cos x)$

In order to determine the lattice parameter u of MnF_2, we can use a X-ray diffraction. You'll be able to appreciate the precision of this method.

1. Determine the ratio between the structure factors for the lines (2,0,2) and (3,1,1) as a function of f_{Mn}, f_F and u.

2. The ratio above can be measured experimentally, its value is 1.22. Infer the numerical value of u (consider the highest) and show that a 1% error on u induces more than 30% error on the intensity ratio. You may use Fig. 3.6 and the value $f_{Mn}/f_F = 2.42$

3.7.2 Neutron scattering and magnetic structure

In MnF_2, the ions Mn^{2+} carry a magnetic moment. Because of the magnetic next-neighbor interaction, magnetic moments order antiferromagnetically under $T = 67$ K, as displayed on Fig. 3.7. As neutrons too carry a spin (and an associated magnetic moment), their interaction with the Mn^{2+} ions depends whether the Mn^{2+} magnetic moment points up or down. It is therefore necessary to distinguish the atomic form factors for the magnetic moments pointing upwards $f_{Mn\uparrow}$ or downwards $f_{Mn\downarrow}$. The new basis is then: $Mn^{2+}_{\uparrow}$ (0,0,0); $Mn^{2+}_{\downarrow}$ (1/2,1/2,1/2) F^- (u, u, 0); (1-u, 1-u, 0); (1/2+u, 1/2-u, 1/2); (1/2-u, 1/2+u, 1/2).

1. Give the expression of the structure factor $S_m(h, k, l)$ in the magnetic phase.

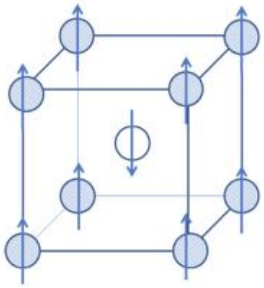


Figure 3.7: Magnetically ordered structure of MnF_2. For clarity sake, only Mn^{2+} ions are displayed.

2. For $h + k + l$ odd, is the scattering intensity still zero for $h = 0$ or $k = 0$?

3. Explain the difference between the diffraction-pattern at $T = 300$ K and $T = 23$ K, as displayed in Fig. 3.5.

4. The magnetic interaction between neutrons and Mn^{2+} is such that there is no difference between $f_{Mn\uparrow}$ and $f_{Mn\downarrow}$ if the scattering vector $\mathbf{K} = (h, k, l)$ is parallel to the Mn^{2+} magnetic moments. Explain why the scattering intensity displayed in Fig. 3.5 is in agreement with the orientation of the magnetic moments displayed in Fig. 3.7.