SCIENCES SORBONNE UNIVERSITÉ

Crystalline Structure Workshop

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A - Bravais Lattices and Basis

1. Recall the three Bravais lattices of the cubic system.
2. Determine the number of nodes per unit cell for each cubic structure.
3. Indicate the Bravais lattice and the positions of atoms for each crystal structure in figure 1.

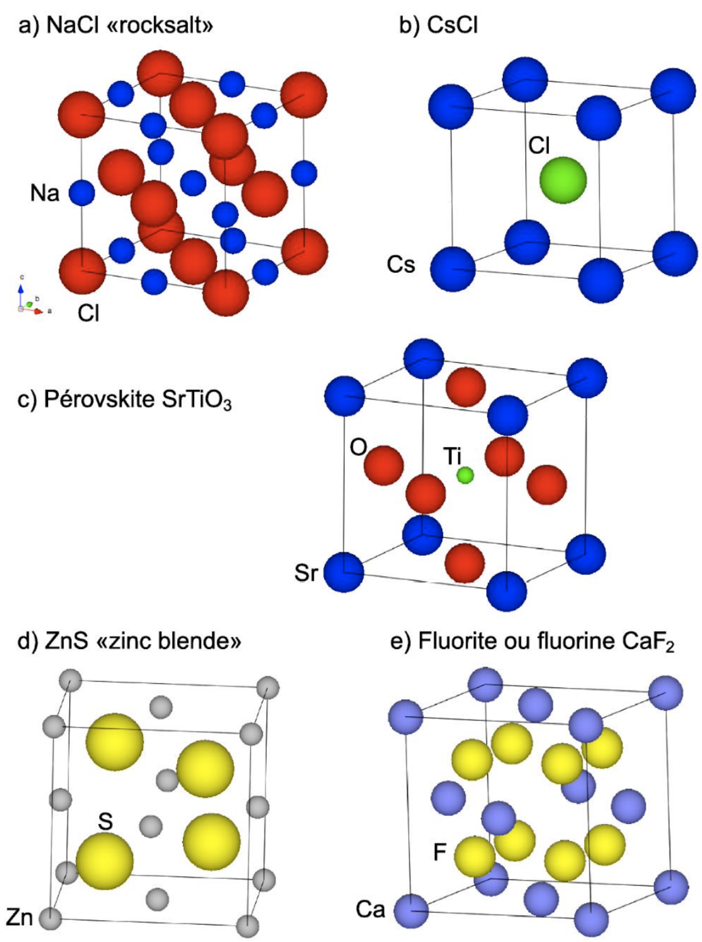

Figure 1 – Bravais lattice and basis

Let's consider a rhombohedral lattice, represented on Figure 2. Its basis vectors are $\vec{LP} = \vec{a}$, $\vec{LM} = \vec{b}$ and $\vec{LN} = \vec{c}$. The MNP plane is a (111) plane denoted Π_1. Π_0 is the (111) plane containing node L, Π_2 the one containing nodes Q, R and S and Π_3 the one containing T.

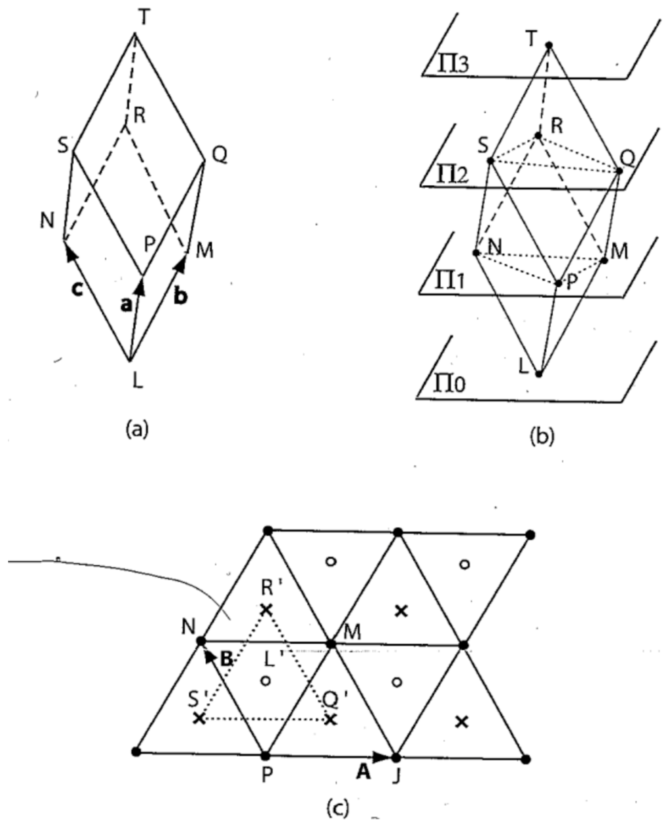

FIGURE 2 – Rhombohedral lattice : (a) Unit cell. (b) Highlighting of successive (111) planes. (c) Projection of the lattice onto plane Π_1 perpendicular to the 3-fold axis : empty circles for the nodes in Π_0 and Π_3, filled circles for the nodes in Π_1, and crosses for the nodes in Π_2. Adapted from "Symmetries and Physical Properties of Crystals", by C. Malgrange, Ch. Ricolleau, and F. Lefaucheux. EDP editions, CNRS editions 2011.

1. Show that the nodes of each (111) plane form a hexagonal planar network.
2. Figure 2-c shows that the rhombohedral lattice can be described by a hexagonal cell of basis vectors $\vec{A}$, $\vec{B}$ and $\vec{C}$. Write $\vec{A}$, $\vec{B}$ and $\vec{C}$ as a function of $\vec{a}$, $\vec{b}$ and $\vec{c}$.
3. What is the multiplicity of this new cell ?

C - The primitive cell of an fcc is rhombohedral !

We can clearly see in the figure that the fcc cell is multiple and allows us to highlight the symmetry of the network (in particular the square face of the cube).

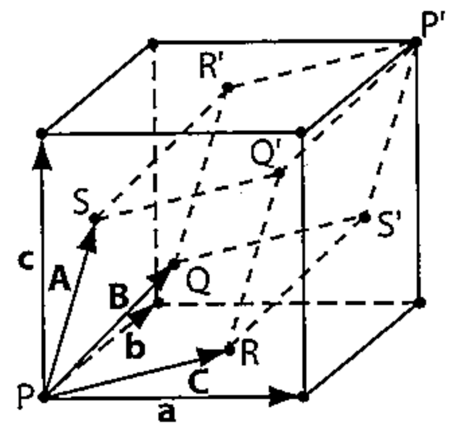

FIGURE 3 – FCC unit cell and its primitive rhombohedral cell. Adapted from "Symmetries and Physical Properties of Crystals", by C. Malgrange, Ch. Ricolleau, and F. Lefaucheux. EDP editions, CNRS editions 2011.

1. What is the multiplicity of this new cell ?
2. Show that the three angles α, β and γ (angles between $\vec{A}$ and $\vec{B}$, $\vec{B}$ and $\vec{C}$, $\vec{A}$ and $\vec{C}$) are equal to 60°.

   The cubic F structure can be described as a stack along the [111] axis of (111) type layers shifted with respect to each other. They form and ABCABC arrangement.

3. Draw the stacking of the fcc structure in the [111]. direction. Compare with Figure 2b.
4. Express vectors $\vec{A}$, $\vec{B}$ and $\vec{C}$ as a function of $\vec{a}$, $\vec{b}$ and $\vec{c}$.

   This ABCABC stacking of the face-centered cubic (FCC) lattice is the most compact possible. However, there is another stacking possibility that leads to the same packing efficiency as the FCC structure, but in this case, the resulting structure exhibits hexagonal symmetry, as seen in part A. This structure can be described as an ABABAB stacking and is called a hexagonal close-packed (HCP) structure.

5. Represent the hexagonal close-packed structure and give the number of atoms per cell.
6. Propose atomic positions to perfectly define the structure.
7. Calcule the c/a ratio for the hexagonal compact structure.

D - The complex case of SiC

One of the major features of SiC is its polytypism. It crystallizes in different forms characterized by a unique sequence of stacking of Si-C bilayers. The best-known polytypes are illustrated in Figure 5. More than 200 polytypes have been identified to date!

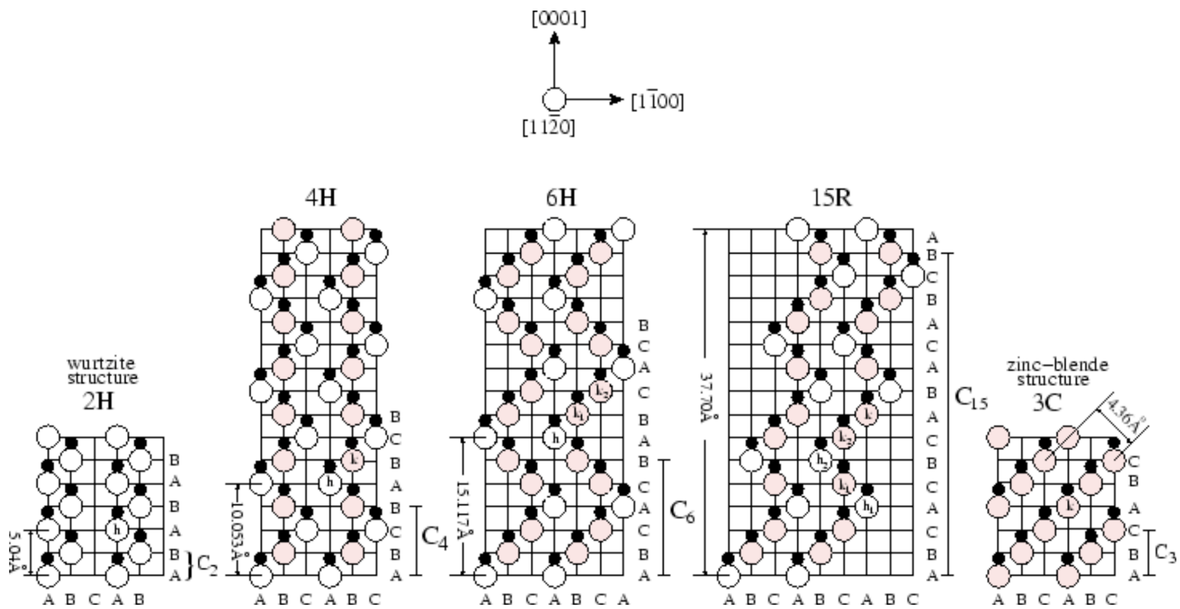

FIGURE 4 – The principal SiC polytypes.

1. Show that the 4H polytype contains one cubic and one hexagonal site, and that the 6H polytype contains two cubic and one hexagonal sites.
2. What is the type of sites in polytype 3C?

E - Scanning Tunneling Microscopy of Graphene on 6H-SiC

The structure of graphite consists of hexagonal honeycomb-like sheets. Within each sheet, carbon atoms are strongly connected by covalent bonds. Between the sheets, the interactions are weak, of the van der Waals type, which explains the cleavage and low hardness. The crystal structure of graphite is shown in Figure 5.

1. Express the crystalline structure of graphite in the form of a Bravais lattice + basis (atoms).
2. Figure 6 shows an STM image (atomic scale!) of a graphene sheet on 6H-SiC, obtained by a method described in the article by A. Ouerghi *et al.*., ACS Nano 6, 6075 (2012).The 2ML graphene (2 monolayers = 2 sheets) exhibits a triangular lattice, while the 1ML (1 monolayer) exhibits a hexagonal lattice. Based on Figure 5 (crystal structure of graphite), provide a possible interpretation of the STM image.
3. In 2013, theoreticians (Kopnin *et al.* Phys. Rev. B 87, 140503(R) (2013)) predicted that rhombohedral graphite would be superconducting at 250K. Suggest a good SiC substrate to stabilize this phase.

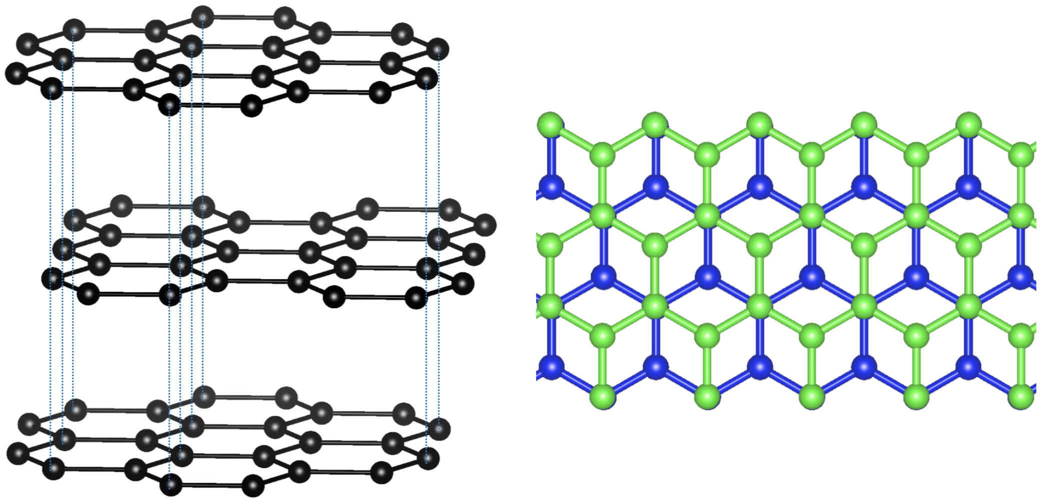

FIGURE 5 – Crystal structure of graphite. Left : side view of graphite composed of three sheets. Right : top view of two sheets.

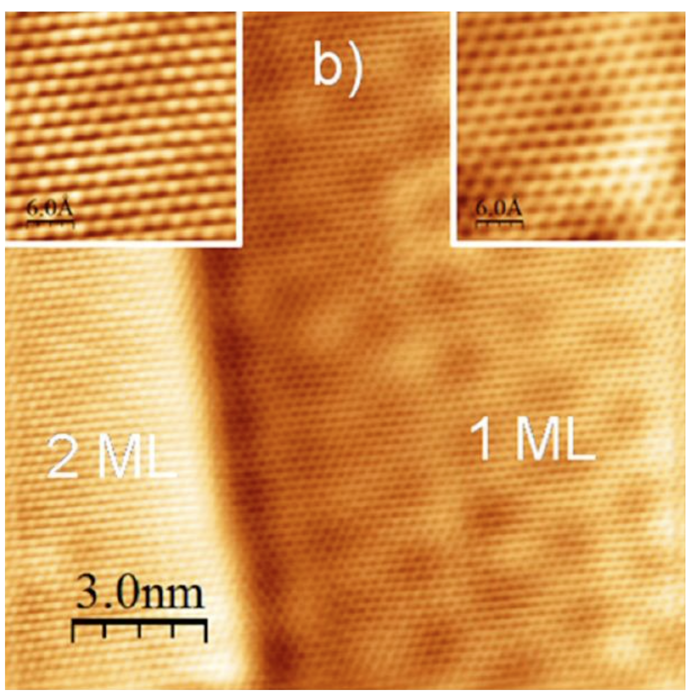

FIGURE 6 – STM of graphene on 6H SiC (adapted from Ouerghi *et al.* ACS Nano 6 6075 (2012)).