Concepts of spectral analysis

1.INTRODUCTION

Discovered in 1895 by the German physicist Röntgen, X-rays are the basis of different analysis techniques such as radiography, spectroscopy and diffractometry. These electromagnetic radiations have a wavelength of the order of Ångström (1 Å = 10^{-10} m).

A crystal is an arrangement of atoms, ions or molecules, with a periodically repeating pattern in three dimensions. Interatomic distances are of the order of Ångström, of the same order of magnitude as the wavelengths of X-rays: a crystal therefore constitutes a 3D network which can diffract X-rays.

In 1913, William Lawrence Bragg and his father Sir William Henri Bragg used this radiation to determine the crystal structure of NaCl and then those of many other metal salts. They were jointly awarded the Nobel Prize in Physics in 1915 for their contributions to "the analysis of crystal structure by means of X-rays".

We present the basic theory of the interaction of X-rays with solid structures as well as the implementation of application examples: the resolution of crystal structure on single crystals and the recognition of phases in crystallized solids.

2.INTERACTION OF X-RAYS WITH MATTER

2.1. PRODUCTION OF X-RAYS FOR DIFFRACTION

The production of X-rays is generally done following the same process as that used in medical imaging. Electrons torn from an electrically heated tungsten filament are accelerated under the effect of an intense electric field (voltage of 50 kV) to bombard an anode (or anticathode) made of different materials depending on the targeted applications. X-rays are emitted by the anode according to two mechanisms detailed in the article "Radiography II. What is an x-ray? How to produce it? What mechanism allows you to obtain an x-ray? ".
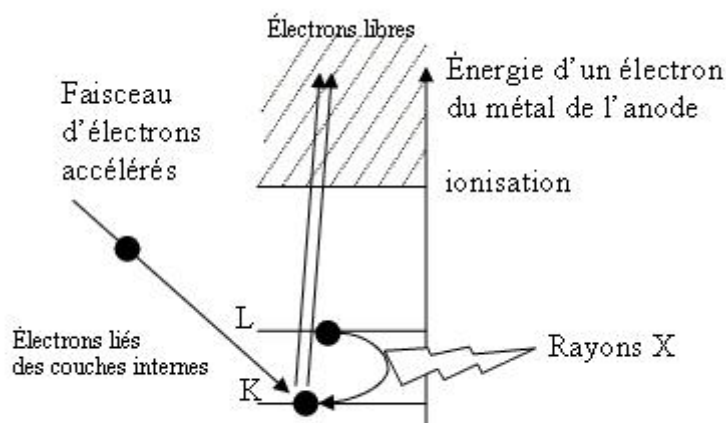
Figure 1. Electronic transitions responsible for X-ray production


Figure 2. Coolidge tube

The two metals commonly used for the anode are copper, which produces X-rays of wavelength $\lambda = 1.54$ Å, and molybdenum, $\lambda = 0.709$ Å. How to choose the material? To have optimal diffraction, it is necessary to use radiation with a wavelength of the same order of magnitude as the size of the grating, here the interatomic space. This is why molybdenum-based sources are suitable for single-crystal structure resolution of small molecules. Copper is used in the case of macromolecules (such as a protein) and for powder analyzes because it allows better separation of diffraction spots.

Another source of X-ray radiation is the synchrotron. Indeed, any charged particle in motion emits continuous electromagnetic radiation (synchrotron radiation) covering a wide frequency range from far ultraviolet to X-ray. The intensity of synchrotron radiation greatly exceeds that of other sources. The use of such an instrument is reserved for the most difficult cases, to

highlight very fine details or to characterize crystals with very small dimensions (of the order of ten micrometers).

2.2. X-RAY DIFFRACTION

2.2.1. Bragg's law
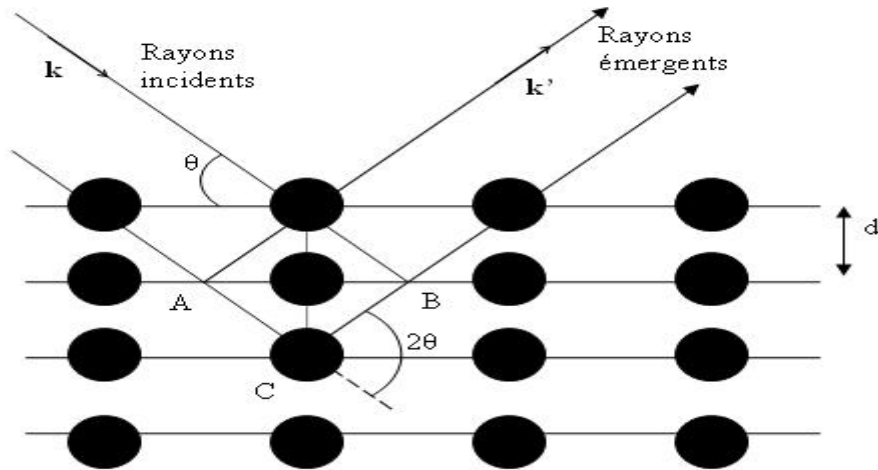
Figure 3. Reflection of X-rays by a family of reticular planes spaced by a distance d.

A crystal can be seen as the three-dimensional periodic repetition of elements (atoms or molecules), called nodes, marked by black disks in Figure 3. The diagram represents a section of reticular planes passing through the centers of these elements, spaced 'a distance d. The angle θ (Bragg angle) determines the incidence of a parallel beam of X-rays on these reticular planes. Note that θ is the complement of the angle of incidence usual in optics. The difference in optical path between the two particular light rays represented is worth AC + CB = 2 d sinθ. They interfere constructively when the path difference is equal to an integer p of wavelength. This is Bragg's law: $2d \sin \theta = p\lambda$.

2.2.2. Crystal lattice and reciprocal lattice

An elementary cell of a crystal is determined by a trihedron formed by three base vectors a, b, c, making between them the angles α, β, γ (figure 4). The tiling of nodes in space is represented by the row vectors defined by:

n = u **a** + v **b** + w **c**

(u, v and w being integers).

This direct network corresponds to a reciprocal network: the vectors a*; b* ; c* such as
a . a* = 1, **b . b*** = 1, **c . c*** = 1, **a . b*** = 0, **a . c*** = 0, **b . a*** = 0, **b . c*** = 0, **c . a*** = 0, **c . b*** = 0.

In the same way, the row vectors of the reciprocal network are: : **n*** = h **a*** + k **b*** + l **c*** (h, k
and l being integers, called Miller indices). Consequently, a row vector of the reciprocal lattice
is normal to a reticular plane of the direct lattice.
The different vectors of the two networks are represented in Figure 5 for the particular case of
a hexagonal system (a=b≠c and α=β=90° and γ=120°). We can check for example that the vector
a* is perpendicular to the reticular plane (b,c).
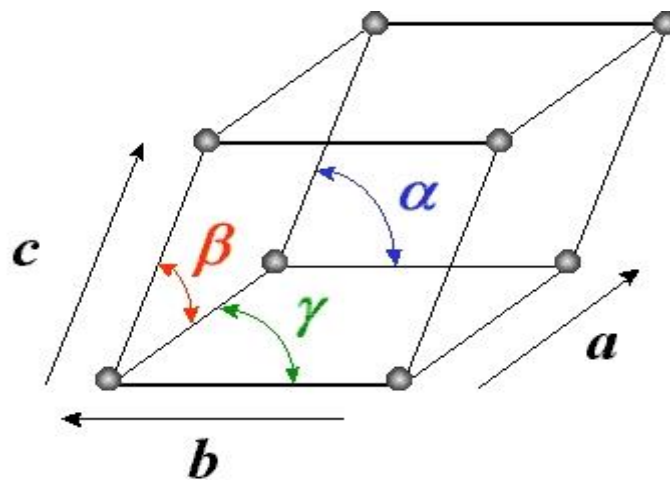

Figure 4. Crystal mesh (a, b, c, α, β, γ)
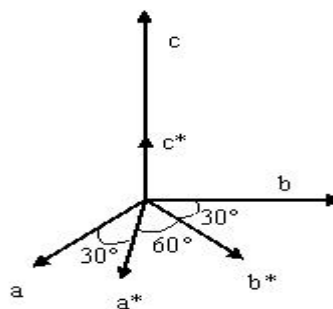
**Figure 5.** Vectors of direct and reciprocal networks of a hexagonal system

3. X-RAY DIFFRACTION TECHNIQUES

3.1. NATURE OF THE SAMPLE

We have just put in place the theoretical tools for describing a crystal and its interactions with X-rays. We will now show in detail the experimental implementation using two different methods, depending on the nature of the sample to be analyzed: either a single crystal (dimension of the order of 0.1 mm), or a crystalline powder (set of microscopic crystals). Exposing a single crystal to an X-ray beam produces an image consisting of well-defined diffraction spots (fig. 6). The numerous orientations of the small crystals of a powder produce a very large number of spots grouped in concentric circles around the point $\theta = 0$, due to the symmetry of revolution around the direction of the incident beam (fig. 7).
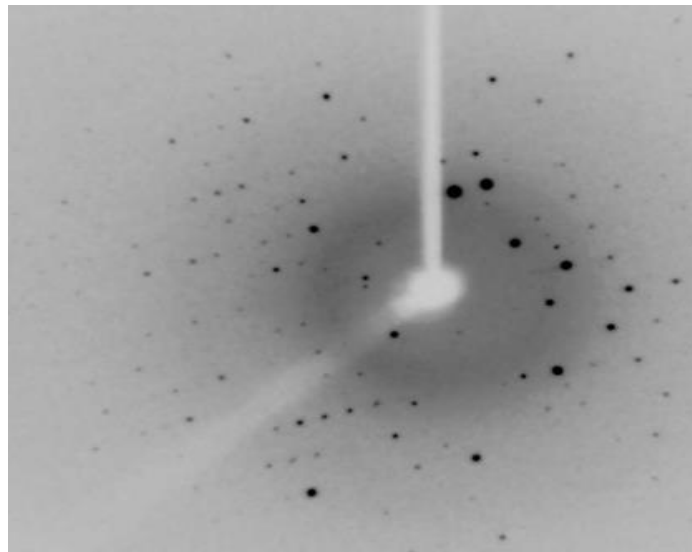
Figure 6. Image obtained during exposure of a single crystal to an X-ray beam
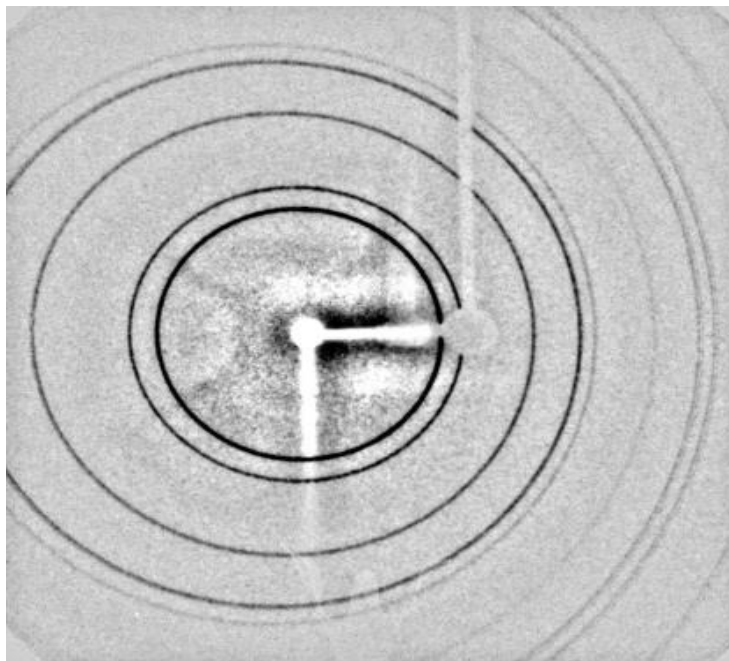
Figure 7. Image obtained when exposing a crystalline powder to an X-ray beam

# 4.STRUCTURAL DETERMINATION IN THE CASE OF A SINGLE CRYSTAL

4.1. SINGLE CRYSTALS

A single crystal is composed of a single periodic arrangement of the same pattern. Usual crystals are made up of an irregular accumulation of numerous single crystals.

Since crystals are anisotropic systems given their different mesh parameters (except in the case of cubic), they have a preferred direction for the propagation of light; this is what causes the phenomenon of birefringence. For example, Figures 8 and 9 show that polarized light is modified as it passes through a birefringent crystal.

**Figure 8**. Transmission of natural light by a single crystal
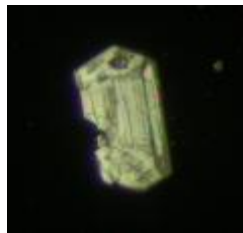
Figure 9. Transmission of polarized light by the same single crystal placed between two crossed polarizers

We use the phenomenon of double refraction to make an initial selection between complex crystals and optically identify the single crystals most suitable for measurement.

Technology

The selected crystal is mounted on the diffractometer, either using a lasso (Figure 10), or using modeling clay for larger single crystals (of the order of cm). The assembly is mounted on an angle measuring head, which will make it possible to rotate the crystal in 3 dimensions and thus modify the angle θ. If the crystal is sensitive to air, it is inserted into a capillary tube filled with its stock solution. This avoids contact with oxygen and humidity in the air. We can also send a

flow of liquid nitrogen using a cooling rod to work at low temperature and in an inert atmosphere (Figure 11).
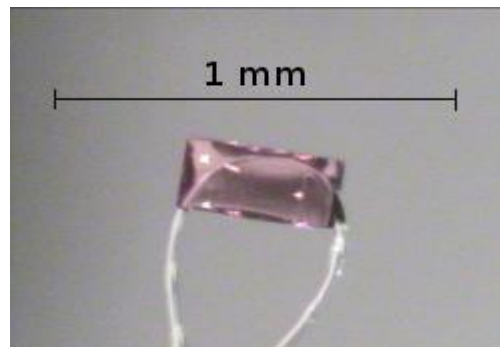
Figure 10. Single crystal mounted on a lasso
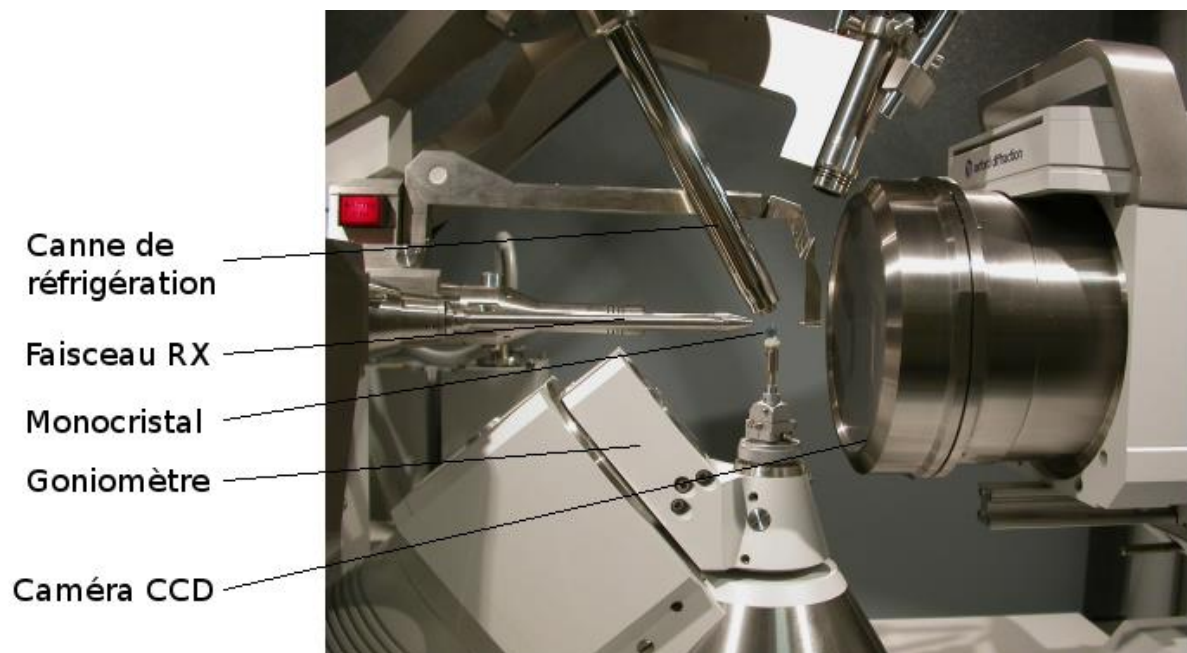
**Figure 11.** Single crystal mounted on plasticine on the diffractometer

Figure 12. Device overview.

5. THE STRUCTURAL RESOLUTION

The observed diffraction spots correspond to the set of directions of the vectors k' satisfying Laue's conditions (see the first part). We define in the space of the reciprocal lattice, a sphere of radius $1/\lambda$ centered on the crystal, called the Ewald sphere. Depending on the direction of diffraction relative to the crystal lattice, the Ewald sphere intercepts different nodes of the reciprocal lattice. At each coincidence, the diffusion vector K is equal to a vector n* of the reciprocal lattice and a diffraction spot is then formed in the corresponding direction (fig. 13).

This is illustrated by the following animation. We observe the successive appearance of diffraction spots. For the six spots observed at increasing diffraction angles, we can note their order of appearance (1,3,5,2,4,6) and identify the corresponding n* vectors (b*, a*+b*, 2b *, a*+2b*, 3b*, a*+3b*).
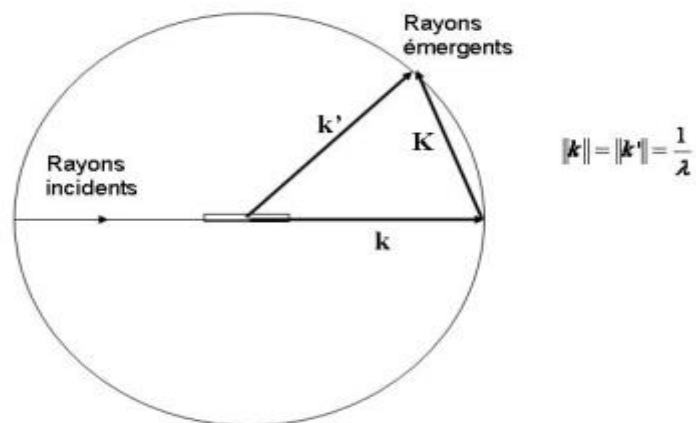
Figure 13. Ewald sphere and diffusion vector K

The single crystal is represented by the rectangle in the center.
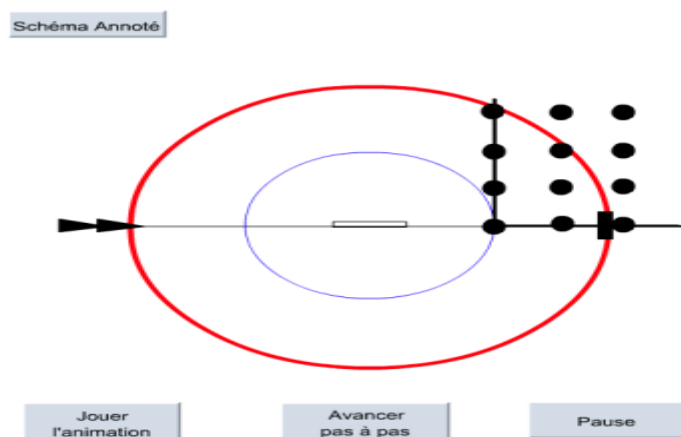
Figure 14. Formation of diffraction spots during rotation of the single crystal

Digital processing of the observed positions of the diffraction spots and their intensities makes it possible to trace the complete structure of the molecule. It is therefore necessary to record a large number of spots to cover all the diffraction directions as much as possible.

6.CRYSTALLINE POWDERS

A powder is made up of microcrystals ideally presenting all possible crystal orientations. As a result, the reciprocal space observed for a single crystal is projected along a single dimension. The diffraction image of a powder formed from a crystalline phase is made up of phase-specific

circles. A diffractogram (examples fig. 15 and 16) can therefore be considered as a fingerprint of a crystalline phase.
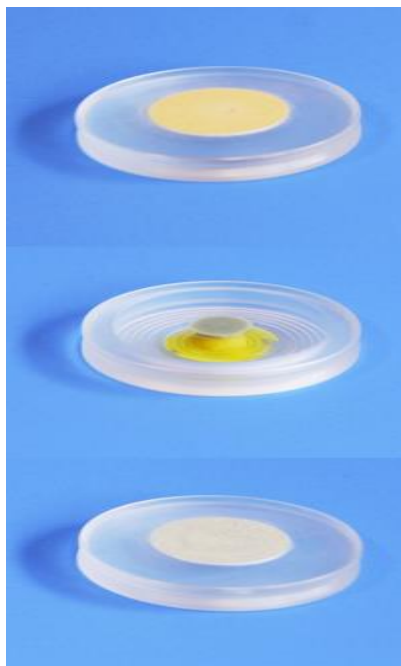
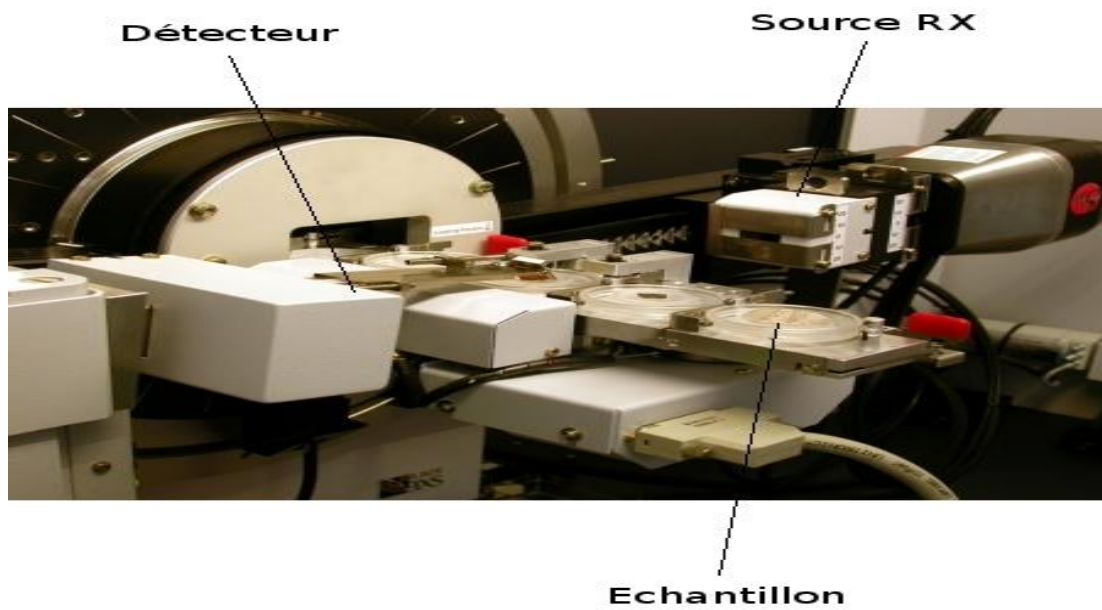**Figure 15.** Powder samples on different supports
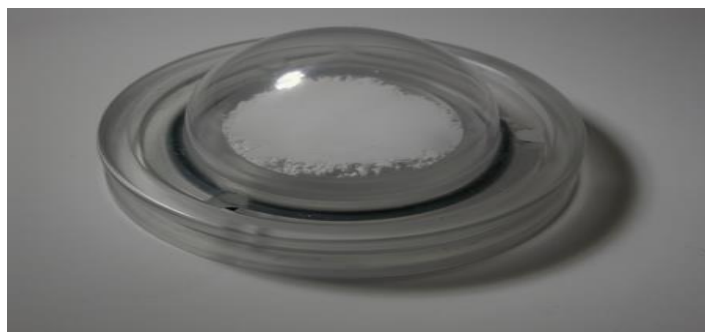
Figure 16. Samples under inert atmosphere

POWDER DIFFRACTOMETER
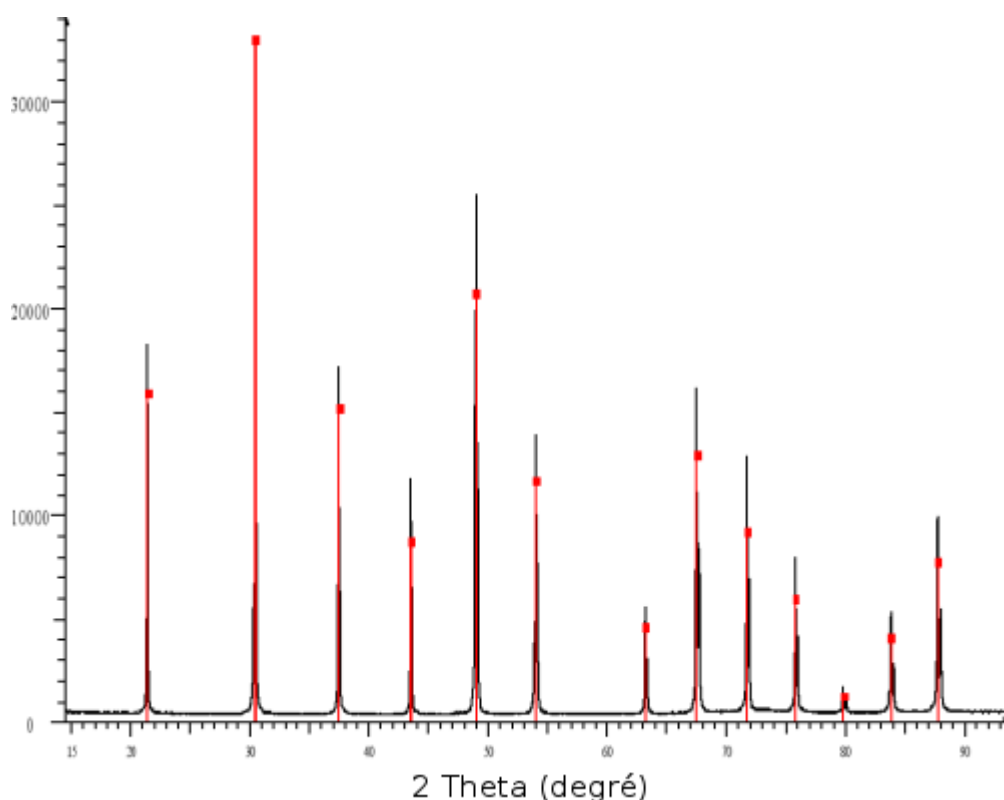

Figure 17. Powder diffractometer

Figure 18. Zoom around the detector

In this case, the sample remains fixed and the scanning angle θ is carried out thanks to the movements of the source and the detector around the sample.

7.DIFFRACTOGRAMS, PHASES IDENTIFICATION AND OTHER APPLICATIONS

7.1. Phase identification

This is the most common application of X-ray powder diffraction. Once the diagram is obtained, we compare the positions and intensities of the peaks observed with those in the PDF (Powder Diffraction File) database of the ICDD (International Center for Diffraction Data) which contains more than 600,000 reference diagrams. We can thus quickly verify a synthesis result (good crystalline phase, presence of impurities, etc.) or confirm that we have obtained a new compound.

Figure 19. Powder diffractograms: (a) of a pure compound and (b) of a mixture (a) In black the measurement and in red the indexing by the reference compound LaB6 which makes it possible to identify all the peaks
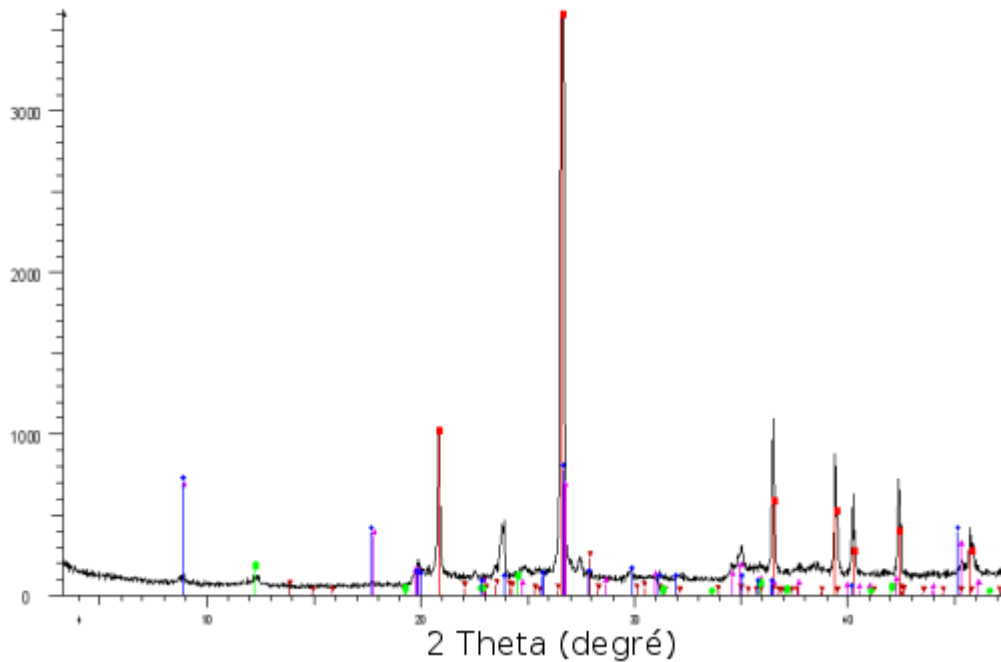
Figure 20. Powder diffractograms: (a) of a pure compound and (b) of a mixture(b) In black the measurement and in color the association of several reference diagrams (red: quartz SiO_2; purple: Muscovite$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})_{10}(OH)_2$; blue: Illite$(K,H_3O)Al_2Si_2Al_{10}(OH)_2$; brown: albite $NaAlSi_3O_8$; green: lizardite $(Al,Mg)_3((Si,Fe)_2O_5(OH)_4)$

8.CONCLUSION

X-ray diffraction is a very powerful technique because it allows the positions of atoms in a crystal to be determined, but it requires obtaining single crystals. Currently, the Riedvelt technique is being developed to solve structures from crystalline powders. It is not yet usable for the resolution of large structures (more than ten atoms). However, all of this only applies to crystalline compounds. Also, resolution techniques using amorphous powder by nuclear magnetic resonance (NMR) are the subject of research.