

Travaux Pratiques Matériaux Cristallisés

X-ray Diffraction Methods

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Abstract

The methods of radio-crystallography are to determine the structural properties of materials at the atomic scale. The lattice space group and crystal structure can be characterised, but the nature and precision of the information obtained will depend very much on the material (solid, pasty pulverulent, polycrystalline, mono-crystalline) and adapted methods implemented. Therefore, through this experiment we explore the atomic properties of FeS_2 by firstly challenged to be creative and determine how to mount a mineral crystal in a powder XRD system and then practice critical thinking in order to determine the pyrite crystal structure by its diffraction pattern. This experiment may also be generalized to crystals other than pyrite.

Keywords: Pyrite; X-ray Crystallography; Solid State Chemistry

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1. Introduction

Pyrite (FeS_2), also known as “fool’s gold”, is a mineral with pale brass-yellow appearance and metallic luster. Although it commonly forms cubes, octahedral and pentagonal dodecahedra forms can also be found. XRD experiments on pyrite samples are typically done using the powdered mineral; however, in this paper, we will demonstrate how large pyrite cubes found in nature can be probed using a powder XRD system. We will also try to determine the crystal structure of pyrite by the knowledge we learned in crystallography. Other minerals or single crystals could be studied using powder XRD systems.

As shown in Figure 1, each black dot stands for a family of planes in the crystal lattice. Any particular lattice has multiple sets of planes, which have different d-spacing. Each d-spacing will lead to a particular diffraction peak later we will see in the XRD.

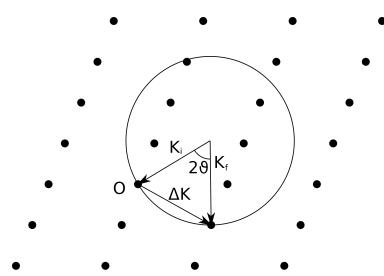


Figure 1. Ewald Sphere

A set of planes with miller index (hkl) is in diffraction position if the end of a reciprocal vector is perpendicular to these planes on the sphere. Therefore, we have equation 1:

$$\vec{q} = \vec{r}_{HKL}^* \quad (1)$$

with $H = n * h$; $K = n * k$; $L = n * l$, in which n is integer and h, k, l are prime integers.

Bragg’s law is satisfied when a reciprocal lattice

point sits on the Ewald sphere.

$$2d_{HKL} \sin\theta = \lambda \quad \text{or} \quad 2d_{hkl} \sin\theta = n\lambda \quad (2)$$

Here, we have further interpretation. As shown in Figure 2, a) and b) just show the direction of X-ray beam in the XRD; c) and d) show the exact schematic diagram when Bragg's law is satisfied on the reciprocal lattice point of (3 2 0) and (2 3 0) after a rotation of a certain angle of crystal. It's worth to mention that here for one point, it stands for one particular set of planes. At different crystal orientations, different planes satisfy

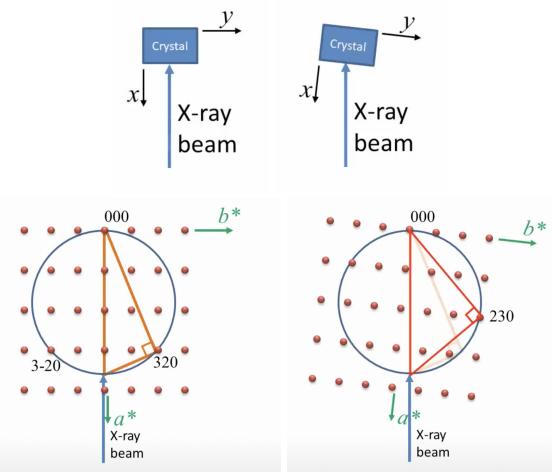


Figure 2. a)Direction of the First X-ray beam 1.
b)Direction of the First X-ray beam 2. c)Bragg's law is satisfied for the reciprocal lattice point (3 2 0).
d)Bragg's law is satisfied for the reciprocal lattice point (2 3 0).

Bragg's law. Certainly, there will be a difference in 2θ angles for the XRD in different d-spacing. Every dot in the reciprocal lattice is a 2D projection of a 3D lattice. Thence, for the 3D environment, a circle becomes a sphere and it follows all the same laws and rules.

2.2 Powder Method

The ideal sample for powder method is a small-scale polycrystalline material (crystals of the mm or much smaller) or a powder obtained by synthesis or by wrapping the material.

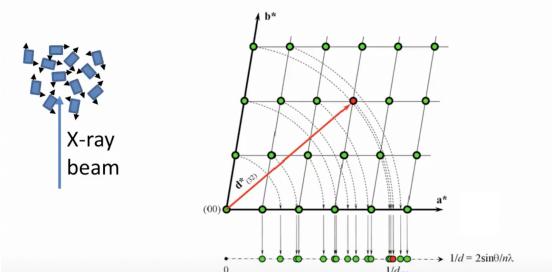


Figure 3. Powder Method

As shown in Figure 3, in the left, powder sample or polycrystalline sample consists of many crystals

in different orientations; in the right, it is the reciprocal lattice. Again, each point represents a particular family of planes. If we pin the lattice at the origin, and rotate every single point downwards and intersects with a single vector. And this single vector basically collects the d-spacing for all of the different potential families of planes that could diffract. This just gives us a relationship between the overall d-spacing from the origin to the diffraction point which is just called inverse distance ($1/d$) and Bragg's law.

Therefore, powder diffraction, one way to think about it, it is equivalent to mapping out all of the reciprocal lattice points and rotate them so that every single reciprocal lattice point at some point gets projected down on to a single vector.

2.3 Precession Method

The precession or Buerger method allows the obtaining of an undistorted image of the different planes of the reciprocal network. This method uses monochromatic radiation applied to a small single crystal (dimension from 0.1 to 1 mm). The goal of this method is to obtain a homothety of a reciprocal plane on a film plane.

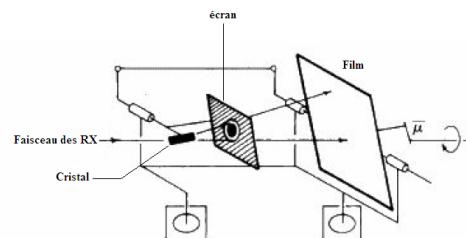


Figure 4. Composition of Burger's room

As shown in Figure 4, the single crystal no longer rotates around a direct axis, but around an inverse axis. The monochromatic X-ray beam is perpendicular to the reverse axis (axis of rotation). For each reciprocal axis, there is a direct plane that is perpendicular to it and therefore parallel to the X-ray beam. Buerger's method consists in directing a direct axis in the X-ray beam around which it will precess (describe a cone), as a result of precession of the reciprocal axis around the perpendicular axis. A photographic film is kept parallel to the plane of the reciprocal network to be recorded. This plane cuts the sphere of reflection according to a circle (circle of reflection). If this plane is oscillated by a precession movement, the reflection circle will sweep part of the reciprocal plane and encounter nodes that, located at this time on the Ewald sphere, will correspond to diffracted beams.

In our experiment set up, the homothety ratio is $X_{film}/|r_{hkl}^*| = 60\lambda$, which will be useful in the later section.

3. Material: FeS₂

Natural pyrite single crystals often occur as cubes of a few millimeters to several centimeters aside, whose faces have golden metal reflections.

The cubic crystalline system of this sulfide can be easily checked by Laue diagrams. Therefore, in order to study the lattice structure of pyrite, we should start from the very beginning by constructing its reciprocal lattice.

3.1 Reciprocal Lattice

We assume the reciprocal lattice vector can be written as $(\vec{a}^*, \vec{b}^*, \vec{c}^*)$, so its reciprocal lattice can be determined by generating its three reciprocal primitive vectors, through equation 3:

$$\vec{r}_{hkl}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \quad (3)$$

And the d-spacing between planes can be written as equation 4:

$$d_{hkl} = \frac{1}{|\vec{r}_{hkl}^*|} \quad (4)$$

Then the lengths of the basic reciprocal vectors are obtained by precise measurements on the film, corrected from the homothety factor:

$$|\vec{r}_{hkl}^*|(\text{\AA}^{-1}) = \frac{X_{film}}{60\lambda}(\text{\AA}) \quad (5)$$

with $\lambda = 0.70926 \text{\AA}$. They correspond to simple interrecticular distances ($d_{hkl}(\text{\AA}) = 1/|\vec{r}_{hkl}^*|$) of FeS₂.

3.2 XRD

As shown in Figure 5, it is the diagram showing the relationship among incident beam \vec{k}_0 , diffraction beam \vec{k} and diffusion vector \vec{q} .

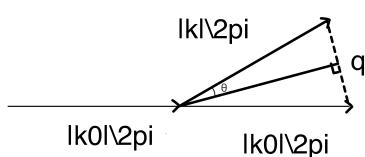


Figure 5. Diagram of beam relationship in XRD

From Figure 5, we can mathematically get the value of diffusion vector \vec{q} , as is shown in equation 6.

$$\vec{q} = \frac{\vec{k} - \vec{k}_0}{2\pi} \quad (6)$$

Therefore, we can calculate the value of diffusion vector and wavelength of X-ray beam by the equations

following:

$$\begin{aligned} \frac{q}{2} &= \frac{|\vec{k}|}{2\pi} \sin\theta \\ q &= \frac{2}{\lambda} \sin\theta \\ \lambda &= \frac{2}{q} \sin\theta \end{aligned} \quad (7)$$

For the XRD, due to the experiment set up, we used copper whose $\lambda \simeq 1.54 \text{\AA}$. Moreover, when the condition of Laue is satisfied in this case, we can get equation 8:

$$\vec{q} = \frac{1}{d_{hkl}} \quad \text{or} \quad \vec{q} = \vec{r}_{hkl}^* \quad (8)$$

Then by applying the theory of Ewald sphere we have discussed in Section 2. We know at some points, Bragg's law is satisfied. Therefore, X-ray diffraction can be observed. Furthermore, as the implementation of experimental procedures goes, a Laue diagram film will be obtained at last, for which we will have further exploration in the next section.

4. Result and Discussion

As a result of XRD, 2 XRD films of state 0 and 1 in pyrite crystal can be obtained, as is shown in Figure 6. However, to make a further analyse of this figure,

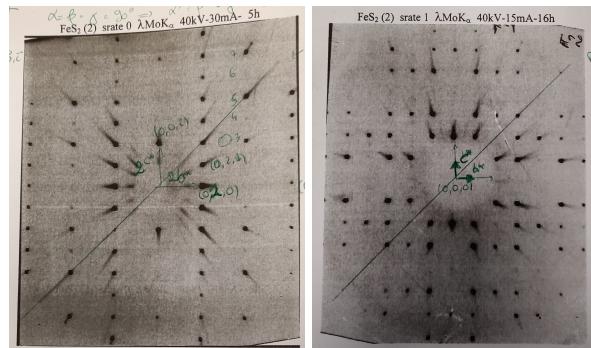


Figure 6. XRD Pattern

firstly, we should make a brief summary of the pyrite lattice, as followed by Table 1.

Table 1. Lattice Information Table of Pyrite crystal

Name	Property
Crystal system	Cubic
Patterson symmetry	$m\bar{3}$
Atom distance	$a = 5.45 \text{\AA} \pm 0.02$
Bravais lattice	P
Glide	$\vec{b}/2$

As we know for a cubic system, $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. So, we can have $a^* = 1/a$ and

$\alpha^* = \beta^* = \gamma^* = 90^\circ$. For point group, by observing carefully of the two XRD patterns in Figure 6 and comparing in details in the symmetry, rotation and etc, we can determine its Patterson symmetry is $Pm\bar{3}$.

Then as shown by the pattern of reciprocal lattice, we can set the origin at the center and set the direction of b^* to right and c^* to up and map out miller index of each point. By comparing the regular pattern with the table of characteristics of reflections related to networks and symmetry elements, we can find that when in the case of $0kl$ and $k = 2n$, for the plane of $(1\ 0\ 0)$, there is a glide of $\vec{b}/2$. Here we have conducted all the information for Table 1. We can now determine its point group is $Pa\bar{3}$.

Then suppose we have one Bravais lattice of Pyrite, there are 4 Fe atoms and 8 S atoms. we know for the position of Fe atoms it can be either on $4\ b\ \bar{3}$ or $4\ b\ \bar{3}$. Then we know the Wyckoff position is $(4a)$ for Fe atoms. And for the S atom, we know it's $8\ c\ 3$. Then we know the Wyckoff position is $(8c)$ for S atoms. So, we can take their coordinates and calculate the diffraction factor similarly.

Firstly, we need to calculate the density (d) of pyrite lattice, or the volume mass of the crystal lattice. And We computed the value of d thanks to the technique of the Archimedes thrust with the scale. And for the pyrite FeS_2 , a lattice contains 4 FeS_2 , in a volume a^3 , because the lattice is a cube with a side length a . Therefore, we can get equation 9.

$$d = \frac{\text{Number of atoms}}{\text{Volume}} = \frac{\frac{4(M_{Fe}+2M_S)}{N_a}}{a^3} \quad (9)$$

We know for the structure factor in a lattice can be written by the equations 10 and 11.

$$F_{hkl} = \sum_{j=\text{atoms}}^{\text{lattice}} f_i e^{-2i\pi(hx_j + ky_j + lz_j)} \quad (10)$$

$$f_i = \int_{\text{lattice}} \rho(\vec{r}) e^{-i2\pi\vec{q}\cdot\vec{r}} d^3\vec{r} \quad (11)$$

For S atoms, by taking all the coordinates we have looked up, we can get the diffraction factor for different family of planes $(1\ 1\ 2)$ and $(1\ 2\ 2)$:

$$F_{112} = 2f^s[\cos(8n\pi) - 1] \quad (12)$$

$$F_{122} = 2f^s[\cos(10n\pi) - \cos(6n\pi)] \quad (13)$$

As shown in equation 14, it shows that the intensity of diffraction is proportional to the square of absolute value of the diffraction factor.

$$I_{hkl} \propto |F_{hkl}|^2 \quad (14)$$

Then by taking the diffraction factor F_{112} and F_{122} in to equation 14, we can get a relative diffraction intensity and we draw them in Figure 7.

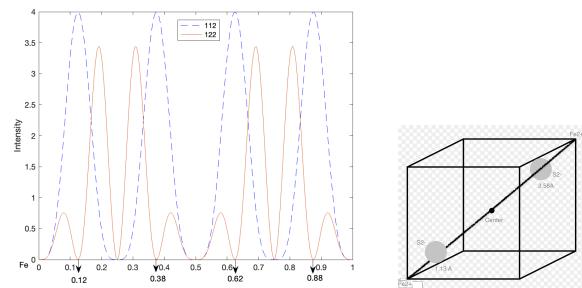


Figure 7. a)Relative diffraction intensity distribution along the diagonal axis of Pyrite lattice. b)Schematic diagram of the position of S atom in the lattice

As shown in Figure 7 a), the curves between 0 - 0.5 is symmetry with ones between 0.5. Hence, we just need to observe one side of this image. In the image, the relative intensity for 112 is strong while for 122, it is weak. At the same time, the distributions of the two curves show complementary trends, or in other words, completely opposite.

Furthermore, if we set a Fe atom at the origin, because two S atoms can not be so close as they are on the peaks of 122, the distance between which are smaller than the diameter of S atom. Therefore, the mode of 122 is impossible in this case. And we can determine that the position for S atoms can only be at $0.12a\sqrt{3}$ or $0.38a\sqrt{3}$ along the diagonal axis of Pyrite lattice, as is shown in Figure 7 b).

Moreover, the distance between Fe - S atoms can be calculated by $0.12 \times a \times \sqrt{3} = 1.13\text{\AA}$.

5. Conclusion

All in all, pyrite lattice is a cubic system with the point group of $Pa\bar{3}$, whose lattice is shown in Figure 8. It's very similar to FCC system of NaCl crystal if we view a pair of S atoms around Fe atom as an entirety. In the

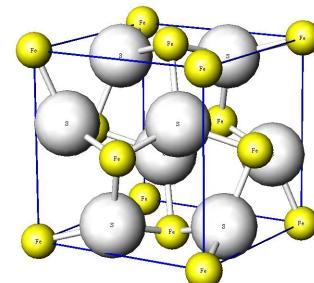


Figure 8. Lattice structure of FeS_2

meantime, it's worthwhile to mention that, in this lab, we solved the structure of pyrite crystal on by a few data. It's exceptional for a few atomic variables but sets a very typical example for future material study.