



MINERALOGY AND GEOLOGY: THE ROLE OF CRYSTALLOGRAPHY SINCE THE DISCOVERY OF X-RAY DIFFRACTION IN 1912

Mineralogía y Geología: el papel de la Cristalografía desde el descubrimiento de la difracción de Rayos X en 1912

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Abstract: Minerals are geological resources of major economic importance. Most of them are crystalline which explains the important role played by crystallography in their study. Minerals may occur either massive or forming characteristic geometric forms known as crystals. In 1912, Max von Laue discovered the diffraction of X-rays by crystals and almost immediately diffraction methods were applied to the structural characterization of minerals. One early success of X-ray crystallography was the structural classification of silicate minerals. However, application of X-ray diffraction was not limited to minerals. It was soon used for the structural characterization of molecular crystals as well and, later on, even of proteins. Nowadays, crystallography is commonly employed in many branches of experimental sciences such as physics, chemistry, biochemistry, and geology among others.

Key words: Mineralogy, crystallography, historical relationship, X-ray crystallography, structural determination.

Resumen: Los minerales son recursos geológicos de gran importancia económica. La mayoría de ellos son cristalinos lo que explica el importante papel desempeñado por la cristalografía en su estudio. Pueden presentarse en forma masiva o como formas geométricas características, conocidas como cristales. En 1912, Max von Laue descubrió la difracción de los rayos X por los cristales y casi de inmediato los métodos de difracción se aplicaron a la caracterización y determinación estructural de los minerales. Uno de los primeros éxitos de la cristalografía de rayos X fue la clasificación estructural de los silicatos minerales. Sin embargo la aplicación de la difracción de rayos X no se limitó a los minerales. Pronto se utilizó también para la caracterización estructural de cristales moleculares, y más tarde, incluso de proteínas. Actualmente la cristalografía es utilizada por muchas ramas de las ciencias experimentales, tales como física, química, bioquímica y geología entre otras.

Palabras clave: Mineralogía, cristalografía, relación histórica, cristalografía de rayos X, determinación estructural.

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Mineralogy is the part of geology that studies the physical and chemical properties of minerals, mineral classification, mineral processes and formation, deposit types, uses, applications and environmental impact. Since the late XX century the International Mineralogical Association (IMA) has somewhat relaxed the definition of mineral, not discrediting the work done by mineralogists in the past, but currently accepting some amorphous substances or of very low crystallinity as minerals. Today a mineral is an element or chemical compound that is normally crystalline and has been formed as a result of geological processes (Nickel, 1995; Nickel and Grice, 1998). Some naturally occurring non-crystalline substances (e.g., georgeite, calciouranoite) have been accepted as minerals by the IMA in spite of being amorphous. Some mineralogists are reluctant to accept amorphous substances as minerals since lack of a complete crystal structure analysis renders it difficult to establish if the substance is a true chemical compound or a mixture; some prefer to call such substances *mineraloids*. The necessity of a complete chemical analysis is more stringent with amorphous materials. A special case of non-crystalline naturally occurring substances are those that are liquid under ambient conditions. The solid quality excludes gases and liquids. Thus H₂O as ice from a glacier is a mineral, but liquid water is not. An exception could be the drops of liquid mercury found on the surface of cinnabar (HgS).

The limiting condition '*natural processes*' exclude materials synthesized in the laboratory. Frequently, industrial and research laboratories produce synthetic equivalents of many valuable natural products (gems, raw materials of chemical industry...). These materials produced by laboratory techniques should be designated by the name of the *mineral* followed by the adjective *synthetic*. Notice that natural processes may have an organic or biological origin. The most notable example is the formation of calcium carbonate in the shells of molluscs; these usually consist of aragonite which is identical to the mineral formed by geological processes. Not only the various forms of CaCO₃ (calcite, aragonite...) may have bio-organic origin. There are many other minerals being precipitated by organisms e.g. opal (an amorphous form of SiO₂) or pyrite (FeS₂). In the case of extraterrestrial substances (meteorites, moon rocks, etc) produced by processes similar to those on Earth the naturally occurring components of extraterrestrial rocks and cosmic dusts are now accepted as minerals.

According to their definition, minerals must have a *definite chemical composition*. This means that a mineral can be represented by a specific chemical formula e.g. quartz only contains silicon and oxygen and has the fixed formula, SiO₂. However, most minerals have a certain compositional variability; that is, the chemical composition varies between certain limits.

Aim of this paper is to show the status of mineralogy and crystallography before and after Laue and his collaborators Friedrich and Knipping demonstrated at the University of Munich in May 1912 that crystals diffract X-rays. This result verified for the first time the hypothesis that crystalline matter corresponds to a periodic arrangement of atoms. Until 1912, crystallography was used almost exclu-

sively by mineralogists for the description of minerals. Laue's discovery promoted the development of new crystallographic characterization techniques, so that crystal structure determination extended from mineralogy to other experimental sciences, principally chemistry, for the characterization of non-mineral inorganic materials and also organic compounds. In spite of the increasing automation, a few fundamentals on crystallography are still required for successfully applying current crystallographic methods to single crystals and polycrystalline materials. Sadly, these fundamentals have not been included in some of the new experimental science degrees recently implemented in Spain. In this contribution, the basis of some important crystallographic diffraction methods will be briefly introduced.

Today, crystallographic diffraction methods are essential not only for studying minerals, but in many other experimental fields. X-ray diffraction techniques have revealed the structure of organic and biological compounds like vitamins and proteins. Crystallographic methods also played an essential role in the elucidation of the double helix of DNA.

Brief history of mineralogy from its beginnings until the discovery of X-ray diffraction

In spite of the fact that minerals and rocks were the first materials used by humans, the development of mineralogy as science is relatively recent (~XVI century). Minerals were used as tools, weapons and ornamental objects during the Stone Age e.g. silex and variscite, and ancient civilizations employed them to colour paintings and sculptures e.g. the Egyptian artisans (Fig. 1). As the properties of minerals became better understood, metals could be extracted from the respective ores, giving rise to the so called Copper, Bronze and Iron Ages.

It is generally accepted that the first written work on minerals was by the Greek philosopher Theophrastus (372-287 b. C.). Approximately 400 years later, Plinius compiled the existing mineralogical knowledge. The birth of mineralogy as an independent discipline is due to the German physician Georgius Agricola who in the year 1556 published the book "*De Re Metallica*". This book describes all the known mining and metallurgical practices of that time including a first compilation of minerals.

The Danish Niels Stensen (Nicolas Steno) was besides a medical anatomist, an example of multidisciplinary scientist. He is considered the father of geology by his paleontological work entitled "*De naturaliter solid content dissertationis intra solidum prodromus*" published in 1669. Until that time the Earth had practically no history. Since then the estimated age of the Earth gradually increased to reach the present 4500 millions years. In this work, three important stratigraphic principles were introduced: *the overlapping layers or strata, their original horizontality and their lateral continuity*. In addition to this important geological contribution, the *constancy of the dihedral angles between faces* in the crystals of quartz and hematite was also established. It took more than 100 years until in 1783

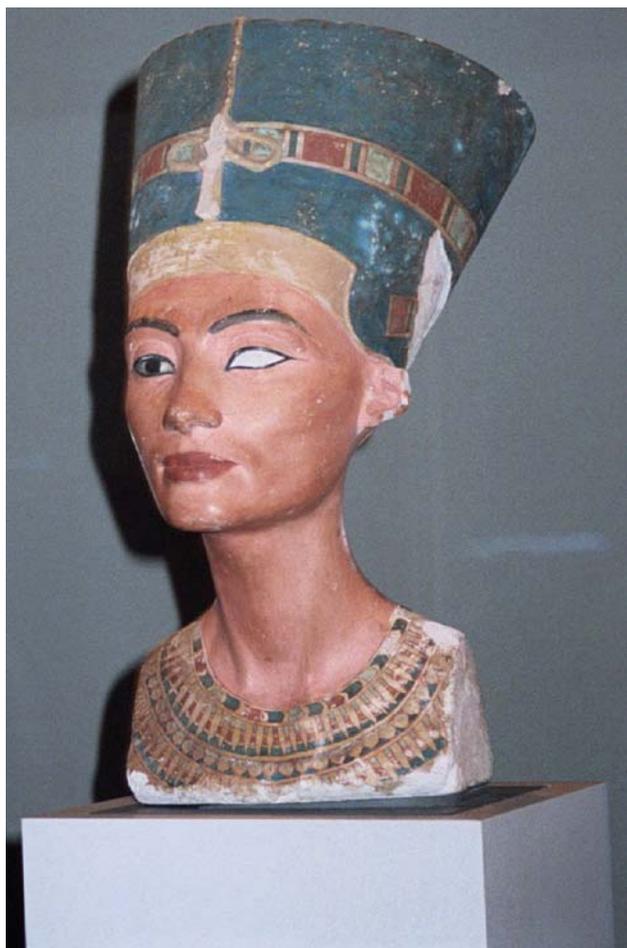


Fig. 1.- Egyptian Museum of Berlin. Egyptian artists used the turquoise mineral, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, to produce the blue and blue-green colours of queen's Nefertiti bust.

the French mineralogist Romé de l'Isle carried out goniometric measurements between crystal faces which confirmed the initial observations of Steno. These results led to a reformulation of the law, also called *Steno-Romé de l'Isle law*, in the following terms: “*In different crystals of one substance, the size and shape of faces, and the distance between them can change, but the dihedral angles formed by homologous faces remain constant*”. Based on this and later works, most of them supported on goniometric observations, crystallography evolved to a science. In 1784, René Just Haüy, a French mineralogist who is considered the founder of crystallography, suggested that *the crystals are formed by the regular repetition of a basic unit* originally called ‘molécule intégrante’ (Fig. 2).

The ‘molécule intégrante’ concept is related to the *unit cell* concept used today in crystallography. Based on his experiments Haüy formulated in 1801 the *theory of the rational indices* of the faces of a crystal which is important for crystallographic calculations. According to this theory, “*the intercepts of a crystal face with the crystallographic axes can be expressed as a/h , b/k and c/l , where $1/h$, $1/k$, $1/l$ are three simple rational numbers*”. Later on, in 1839, the British mineralogist William H. Miller used the reciprocal quantities i.e. the integer numbers h , k , l , to describe the crystal faces e.g. (111) identifies the crystal face that cuts

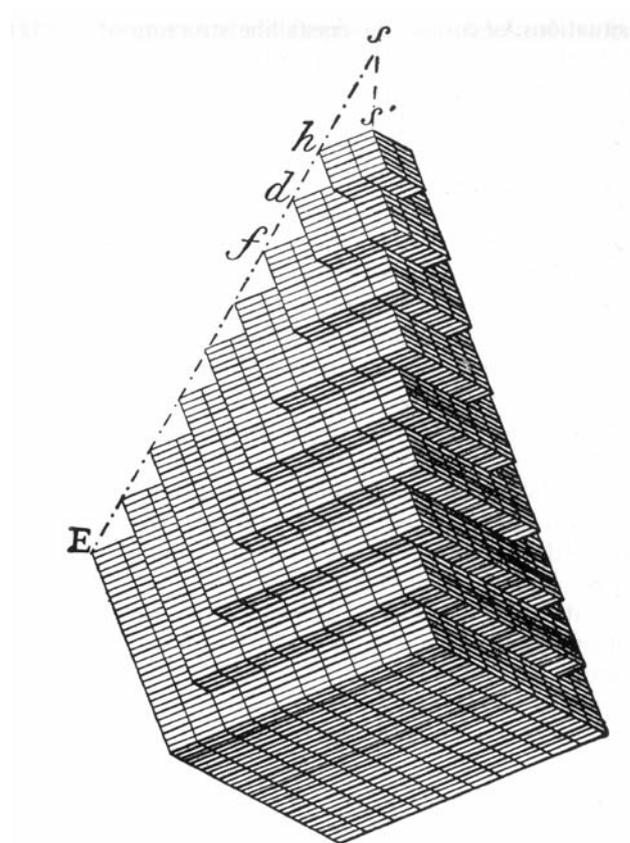


Fig. 2.- In 1784 Haüy showed how calcite crystals are composed of many little rhombs which he called “molécules intégrantes” (Hammond, 1997).

the crystallographic axes at distances a , b and c (which are proportional to the unit cell dimensions).

The contribution of Haüy in the development of crystallography was decisive. However, the *theory of ‘molécules intégrantes’* (each chemical substance has a corresponding specific and a characteristic external form) did not consider the existence of certain exceptions which were intuited by the Swedish chemist Jöns Jacob von Berzelius. He recognized that the aragonite and calcite minerals have identical chemical composition (CaCO_3), an idea that was not accepted by Haüy. The polemic was solved a century later by the German chemist and crystallographer Eilhard Mitscherlich (Berlín, 1819). He suggested that both minerals have identical chemical composition but different crystal morphology. Mitscherlich introduced two concepts of great relevance for the progress of mineralogy and other experimental sciences: (i) **isomorphism** = *property of some substances which have different chemical composition but crystallize with a similar external shape because of their similar crystal structure*; (ii) **polymorphism** = *property of certain substances which have same chemical composition but different external shapes because they can crystallize with more than one crystal structure*.

In the last part of the nineteenth century, Hessel, Bravais, Fedorov, Schönflies and Barlow, working independently, almost simultaneously developed the mathematics and the physical basis of geometric crystallography, i.e. that part which deals with the *internal symmetry* and the *ordered*

structure of the particles that constitute the crystalline material.

In 1830, Johann Friedrich Christian Hessel, a German physicist and mineralogist, proved that, as a consequence of Haüy's law of rational intercepts, morphological forms can combine to give exactly 32 types of crystal classes, since only two-, three-, four-, and six-fold rotation axes occur (Lalena 2006). Unfortunately, his work was recognized by the scientific community only after his death.

Auguste Bravais, a French physicist and crystallographer, is well known for having demonstrated in 1848 the existence of the 14 three-dimensional lattices (Fig. 3). Bravais's work corrected the small error of the German physicist and crystallographer Moritz Ludwig Frankenheim who previously proposed 15 three-dimensional lattices. The Bravais lattices can be either primitive or centred. In primitive lattices (*P*) the nodes are the only points that are equivalent, i.e. equal and with identical surrounding. In centred lattices, there are additional points (*centrings*) that are equivalent to the nodes. Centred lattices with only one centring in the middle of one face and are called *A*, *B* or *C* depending on the centred face. If all three faces are centred, the lattice is named *F*. In body-centred lattices (*I*) the centring is in the middle of one cell. The triclinic, monoclinic, orthorhombic, tetragonal and cubic crystal systems derive directly from the corresponding Bravais lattices. The rhombohedral lattice *R* implies the existence of a three-fold axes and hence always belong to the trigonal system. The hexagonal lattice *P* is compatible with the hexagonal system (presence of a six-fold axis) or with the trigonal one (presence of three-fold axis). In total there are 7 crystal systems.

A primitive unit cell is the smallest repeating portion of the lattice and is normally specified by the three *a*, *b* and *c* vectors. (Notice that the lattice is unique but not the choice of the unit cell). The set of all symmetry operations of the crystal form the *space group* (including lattice translations). Normally, for simplicity, only the space group symmetry operations in the unit cell volume are listed. Space groups derive from the combination of the 14 Bravais lattices with the symmetry operations of the crystal point group coupled to fractional translations (*screw axes* and *glide planes*). As a result of this combination the 230 different space groups follow (Fig. 4). The first to find them was the Russian geologist E.S. Fedorov (1891). Independently from Fedorov, the German mathematician Arthur Moritz Schönflies (1891), and the English geologist and amateur crystallographer William Barlow (1894) also deduced the existence of the crystallographic space groups (Amorós, 1978).

X-ray diffraction

X-rays are electromagnetic radiation of undulatory and corpuscular nature discovered in 1895 by the German physicist Wilhelm Conrad Röntgen who was honoured with the first Nobel Prize in Physics in 1901. This discovery, somewhat imprudent because it ignored the potential danger of X-rays, opened a new field in medicine (medical radiology).

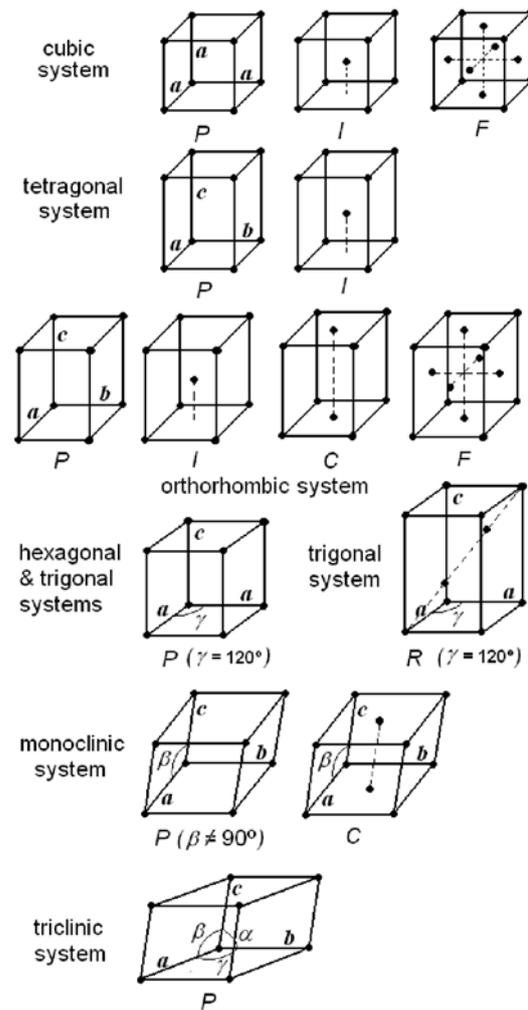


Fig. 3.- The 14 Bravais lattices. The rhombohedral lattice *R* can be expressed either as a primitive unit cell with $a = b = c$ and $\alpha = \beta = \gamma$ or, alternatively, as a multiple unit cell ($a = b \neq c$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) with centrings at $(2/3, 1/3, 1/3)$ and $(1/3, 2/3, 2/3)$.

In 1912 Max von Laue at the University of Munich in collaboration with Friedrich and Knipping irradiated a crystal with X-rays. The observed diffraction pattern verified the undulatory nature of X-rays and indirectly demonstrated, for the first time, the periodic arrangement of crystalline matter (thus clarifying the '*molécule intégrante*' concept of Haüy which should be replaced by the modern unit cell concept).

Laue's interpretation of X-ray diffraction

The unit cell outlines the smallest portion of crystalline matter that when repeated in all three directions generate the whole crystal content. As already indicated the unit cell is defined by the fundamental *a*, *b* and *c* vectors. A crystalline material diffracts when the waves scattered by the contents of all unit cells interfere constructively, i.e. the difference of λ paths travelled by the individual waves are multiples of λ . Diffraction is a three dimensional phenomenon and, therefore, constructive interference must be satisfied simultaneously in all three directions.

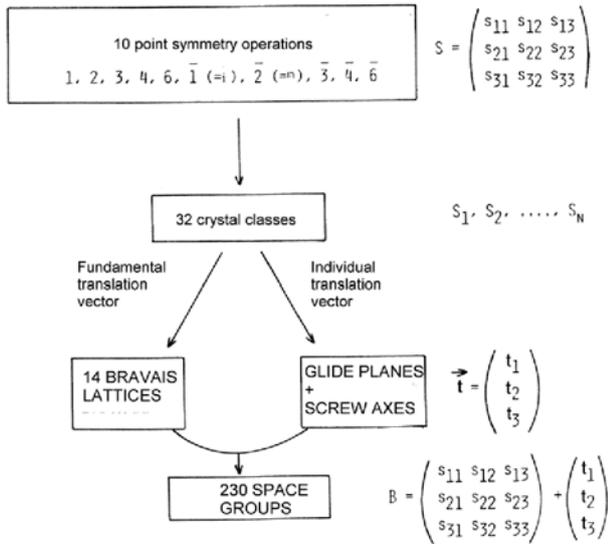


Fig. 4.- Schematic derivation of the 230 space groups (Luger, 1980). These groups result from the combination of the 14 Bravais lattices and the 32 point groups (including *screw axes* and *glide planes*). *S* represents the matrix expression of the point group symmetry operation, *t* is the resulting translational component and *B* the space group symmetry operation in matrix form.

Let us first consider the situation were an incoming beam with direction parallel to the unit vector S_0 is scattered by one row of atoms whose period is given by the translation vector a . These row of atoms will scatter in phase, when the path difference between the waves reemitted by consecutive atoms is equal to an integer number of λ . If S is the unit vector defining the direction of the diffracted beam, this condition can be expressed as $a \cdot S - a \cdot S_0 = a \cdot (S - S_0) = h\lambda$, or also

$$a \cdot \cos \varphi - a \cdot \cos \varphi_0 = a (\cos \varphi - \cos \varphi_0) = h\lambda$$

where h is an integer, φ_0 is the angle between incoming beam (S_0) and lattice vector a , and φ is the angle between diffracted beam (S) and lattice vector a . Since a crystal is a three dimensional object, the necessary condition for observing the diffraction phenomenon is that three (*Laue*) equations are satisfied simultaneously

$$\begin{aligned} a \cdot (S - S_0) &= a (\cos \varphi - \cos \varphi_0) = h\lambda \\ b \cdot (S - S_0) &= b (\cos \chi - \cos \chi_0) = k\lambda \\ c \cdot (S - S_0) &= c (\cos \omega - \cos \omega_0) = l\lambda \end{aligned}$$

in all a , b and c directions (The meaning of χ , χ_0 , ω , ω_0 can be deduced by comparison with the one-dimensional case).

Treatment of X-ray diffraction by the Bragg

Somewhat later, in 1914, the British physicist and crystallographer William Henry Bragg (father), and William Lawrence Bragg (son), physicist, chemist and mathematician, demonstrated that X-rays diffracted by crystals could be considered as reflected by lattice planes, i.e. planes made of lattice nodes. For a given $\{hkl\}$ family of planes, diffraction will occur when the waves “reflected” by consec-

utive planes are in phase (*constructive interference*). The diffraction angle θ at which constructive interference takes place is given by Bragg’s equation

$$n\lambda = 2d_{\{hkl\}} \sin \theta$$

where $d_{\{hkl\}}$ is the spacing between the $\{hkl\}$ lattice planes, λ is the wavelength of the radiation used, and n is the order of the reflection (Fig. 5). To simplify the equation, it is normal practice to divide d by n and to denote the harmonics of the $\{hkl\}$ family of planes by $(n \cdot h, n \cdot k, n \cdot l)$, so that by re-naming h, k and l if follows

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

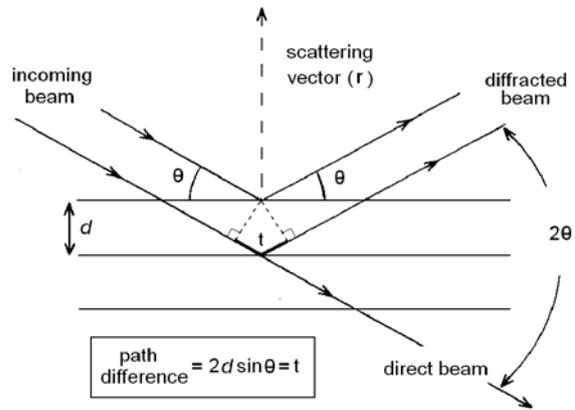


Fig. 5.- Bragg equation: Interference of waves reflected in a crystal by a given family of lattice planes with d spacing. Constructive interference only occurs for $2d \sin \theta = n\lambda$ with n an integer, since only then the outgoing waves will be in phase.

The reciprocal lattice and Ewald’s construction

The Laue equations define the diffraction conditions but are difficult to manage. To simplify the mathematical treatment of diffraction, the German mathematician and physicist Peter Paul Ewald introduced in 1913 the *reciprocal lattice* concept. For each triplet of a, b, c unit cell vectors spanning the crystal lattice, there is a triplet of vectors a^*, b^*, c^* , directly calculable from a, b, c and fulfilling the scalar products

$$\begin{aligned} a \cdot a^* &= b \cdot b^* = c \cdot c^* = 1 \\ a \cdot b^* &= a \cdot c^* = b \cdot a^* = b \cdot c^* = c \cdot a^* = c \cdot b^* = 0 \end{aligned}$$

that generate the reciprocal lattice. By taking the three Laue equations and multiplying both sides of the first equation by a^* , the second by b^* and the third one by c^*

$$\begin{aligned} a \cdot a^* (S - S_0) &= h a^* \lambda \\ b \cdot b^* (S - S_0) &= k b^* \lambda \\ c \cdot c^* (S - S_0) &= l c^* \lambda \end{aligned}$$

then addition of the three resulting equations followed by division of both sides by λ yields

$$(\mathbf{S}-\mathbf{S}_0)/\lambda = h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^* = \mathbf{r}_{hkl}$$

i.e. the Laue conditions are fulfilled when the coordinates of the reciprocal space vector \mathbf{r} are integers (hkl). This corresponds to the nodes of the reciprocal lattice. If 2θ is the angle subtended by \mathbf{S} and \mathbf{S}_0 , it can be shown by trigonometry that the modulus of \mathbf{r}_{hkl} is

$$r_{hkl} = \frac{S-S_0}{\lambda} = \frac{2 \sin\theta}{\lambda}$$

Comparison of this result with Bragg's equation evidences the inverse relationship between the modulus of \mathbf{r}_{hkl} and the interplanar spacing d_{hkl} :

$$d_{hkl} = 1 / r_{hkl}$$

The Ewald's construction (Fig. 6) is useful for visualizing the diffraction conditions and consists on plotting a sphere (*reflection sphere*) of radius $1/\lambda$ with its centre on an arbitrary node of the reciprocal lattice which will be considered as the origin of the reciprocal lattice. Each time a vector of type \mathbf{r}_{hkl} (i.e. a node of reciprocal lattice) crosses the reflection sphere, diffraction will occur, since then and only then Bragg's equation is fulfilled, i.e. $r_{hkl} = 2 \cdot \sin(\theta_{hkl}/\lambda) = 1/d_{hkl}$.

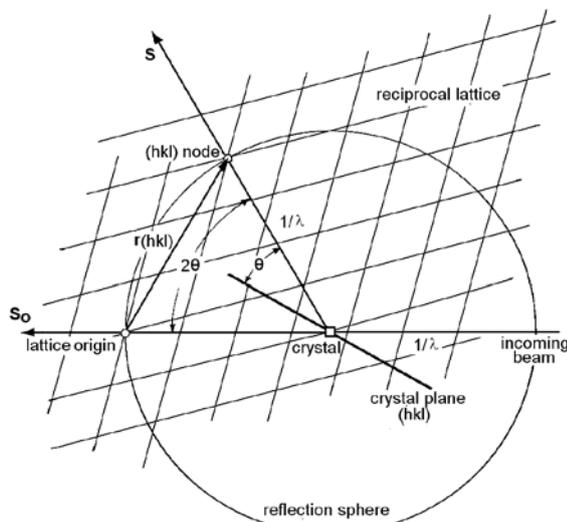


Fig. 6.- Ewald's construction: Plot of a section of the reflection sphere showing the relation between reciprocal lattice and diffraction condition. Diffraction only occurs when a reciprocal lattice node cuts the surface of the sphere.

Introduction to crystal structure determination methods

In the course of the 100 years after the discovery of X-ray diffraction by crystals, a number of experimental techniques summarized in Table I have been developed for characterizing and solving crystal structures of single-crys-

tals and polycrystalline materials. From the positions of the reflections on the diffraction patterns, the crystal system and the unit cell dimensions can be found which allows the assignment of the Miller indices to each reflection (*indexing*).

By analysing the presence or absence of specific reflection groups, the lattice type and the extinction symbol of the crystal can be determined. Once the space group and the unit cell parameters known, the electron density distribution in the crystal can be calculated by means of the Fourier synthesis

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l \mathbf{F}_{hkl} e^{-i2\pi(hx + ky + lz)}$$

where V = unit cell volume

h,k,l = Miller indices specifying a given reflection

\mathbf{F}_{hkl} = structure factor of the hkl reflection.

The structure factor $\mathbf{F}_{hkl} = F \exp i\phi = A + iB$ is a complex number, whose modulus F is directly derivable from the diffracted intensities through the $I = F^2$ equality. For a given hkl reflection, the relationship between reduced intensity (I) and measured one (I_{meas}) is

$$I = \frac{I_{meas}}{K \cdot L \cdot P \cdot A}$$

where K , scaling factor that depends on the crystal size and beam intensity

L and P are, respectively, the Lorentz factor (it depends on the measurement geometry) and the polarisation factor,

A , the absorption factor that depends on the linear absorption coefficient of the sample and on the crystal form

The passage from I_{meas} to I is called *data reduction*. According to Friedel's law, the intensities of the pair of reflections hkl and $-h-k-l$ are equal, $I(hkl) = I(-h-k-l)$. This means that the **diffraction pattern is always centrosymmetric**, whether or not the crystal has a centre of symmetry. The symmetry of the diffraction pattern corresponds to one of the 11 Laue groups which result from adding a symmetry centre to the point group symmetry of the crystal.

Unfortunately, the remaining part of \mathbf{F}_{hkl} , i.e. the associated phase angle, ϕ , is not accessible from experiment and its calculation requires the previous knowledge of the atomic positions. If the phase values were known, computation of the Fourier synthesis would allow the straightforward location of the atoms or molecules in the unit cell by simply selecting those regions displaying the highest electron density. In other words, the solution of a crystal structure is equivalent to finding the ϕ values (*phase problem*). In general ϕ can take any value between 0 and 2π . However, there are some groups of reflections with possess restricted phase values. For example, for centrosymmetric crystal structures with the symmetry centre placed at the origin, the structure factors are real numbers with ϕ being either 0 or π .

Method	Radiation	Diffracting element	Detection element	Use
Laue	polychromatic	crystal or plate (fixed)	flat film (fixed)	symmetry, crystal grain orientation in a matrix, crystal defects, texture studies in alloys
Rotation (360°) Oscillation (±15°)	monochromatic	moving crystal	stationary film	symmetry, unit cell parameters
Weissenberg	monochromatic	moving crystal	mobile cylindrical film	symmetry, unit cell parameters intensity data collection
Buerger Precession	monochromatic	moving crystal	flat film perpendicular to X-ray beam	symmetry, unit cell parameters, intensity data collection
Debye-Scherrer	monochromatic	rotating capillary with specimen inside	photographic film	unit cell parameters, identification
θ - 2θ diffractometer	monochromatic	powder on flat holder	moving linear scintillation detector	unit cell parameters, identification, powder pattern measurement
4-circle diffractometer: Eulerian / Kappa geometry	Monochromatic (use of crystal monochromator is necessary)	moving single-crystal	moving point scintillation detector	symmetry, indexing, full intensity data set, structural information

Table I.- Some characteristics of conventional X-ray diffraction techniques.

One important step in the structure solution process is the choice of the correct space group from the 230 existing ones. Combination of the lattice system with the extinctions due to lattice centring and to translational symmetry elements help reducing the number of possibilities (Table II). In part, due to the centrosymmetry of the diffraction pattern, **only 122 diffraction symbols can be determined univocally** (International Tables for Crystallography, 1987), and from these, only 58 symbols define a unique space group. For the remaining 64, some ambiguities persist which normally reduce to a small set of choices (no more than 4 or 5). If necessary, the uncertainty about the presence or absence of a symmetry centre can be solved by morphological studies or by physical methods.

In the solution of the phase problem, two methods should be mentioned because of their relevance: *Patterson methods* and *direct methods*.

In 1934 the New Zealander-Canadian mathematician and crystallographer Arthur Lindo Patterson introduced the so-called **Patterson synthesis**

$$P(u,v,w) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl}^2 \cos 2\pi (hu + kv + lw)$$

differing from the electron density synthesis in the Fourier coefficients, i.e. the structure factors \mathbf{F} are replaced by the squared moduli F^2 (the latter are proportional to the observed intensities and are obtained from experiment). Patterson maps are characterized by displaying a peak at the end of each interatomic vector e.g. if (x_1, y_1, z_1) and (x_2, y_2, z_2) are the positions of two atoms in the unit cell, there will be one peak located at $u = x_2 - x_1$, $v = y_2 - y_1$, $w = z_2 -$

z_1 . The peak height is proportional to the product of the atomic numbers of the two atoms involved. It is clear that Patterson peaks between heavy atoms (i.e. those with many electrons) are easily identified if the rest of atoms of the structure are light ones; on the contrary, interpretation of Patterson maps by direct analysis of interatomic peaks is less effective for complex equal-atom crystal structures.

The phase problem for equal-atom crystal structures (small- and medium-sized ones) was solved by using *direct methods*. The development of direct methods was the result of the continued effort of many crystallographers during the twentieth century (Woolfson, 1969). The contributions of the North-American crystallographers Jerome Karle and Herbert Hauptman deserved the Nobel Prize in Chemistry in 1985. Direct methods estimate the φ phases of the strong reflections (hereafter generically called Φ) directly from the measured intensities. After data reduction, intensities are further corrected for atomic scattering factor fall-off and thermal vibration decay yielding the so-called normalized structure factor moduli E_{hkl} . Calculation of a Fourier synthesis with normalized moduli and known Φ produces a sharpened electron density map (*E map*) where atomic peaks can easily be identified.

Conventional direct methods take advantage of two general properties of electron density: peakness (atomicity) and positivity. To take advantage of the first property, the resolution of the data must be high enough to produce separated atomic peaks in the E map. The second property implies the proportionality between squared structure ρ^2 and true one ρ , i.e. $\rho^2 \approx k \cdot \rho$. If the structure factor of ρ^2 is $\mathbf{G} = G \exp i\psi$, then the magnitude of G is derivable from E , i.e.

Symmetry element	Affected reflection	Condition for systematic absence of reflection
Screw axes		
2_1 } along $\begin{cases} a \\ b \\ c \end{cases}$	$h00$	$h = 2n + 1 = \text{odd}$
4_2 } along $\begin{cases} b \\ c \end{cases}$	$0k0$	$k = 2n + 1$
6_3 } along $\begin{cases} c \\ *c \end{cases}$	$00l$	$l = 2n + 1$
$(3_1, 3_2)$ } along $*c$	$00l$	$l = 3n + 1, 3n + 2, \text{ i.e., not evenly divisible by } 3$
$(6_2, 6_4)$ } along a	$h00$	$h = 4n + 1, 2 \text{ or } 3$
$(4_1, 4_2)$ } along b	$0k0$	$k = 4n + 1, 2 \text{ or } 3$
	$00l$	$l = 4n + 1, 2 \text{ or } 3$
$(6_1, 6_5)$ } along $*c$	$00l$	$l = 6n + 1, 2, 3, 4 \text{ or } 5$
Glide plane \perp to a		
translation $b/2$ b glide	$0kl$	$k = 2n + 1$
$c/2$ c glide		$l = 2n + 1$
$b/2 + c/2$ n glide		$k + l = 2n + 1$
$b/4 + c/4$ d glide		$k + l = 4n + 1, 2 \text{ or } 3$
Glide plane \perp to b		
translation $a/2$ a glide	$h0l$	$h = 2n + 1$
$c/2$ c glide		$l = 2n + 1$
$a/2 + c/2$ n glide		$h + l = 2n + 1$
$a/4 + c/4$ d glide		$h + l = 4n + 1, 2 \text{ or } 3$
Glide plane \perp to c		
translation $a/2$ a glide	$hk0$	$h = 2n + 1$
$b/2$ c glide		$k = 2n + 1$
$a/2 + b/2$ n glide		$h + k = 2n + 1$
$a/4 + b/4$ d glide		$h + k = 4n + 1, 2 \text{ or } 3$
Centred lattices		
A	hkl	$k + l = 2n + 1$
B		$h + l = 2n + 1$
C		$h + k = 2n + 1$
I		$h + k + l = 2n + 1$
F		$h + k = 2n + 1$ } i.e., h, k, l $h + l = 2n + 1$ } not all even $k + l = 2n + 1$ } or all odd

Table II.- Translational symmetry elements and their extinctions (Stout and Jensen, 1968).

from experiment, due to the existing equality $G = k \cdot E$. The proportionality of p^2 and p also implies that φ and ψ must be equal for strong reflections (\mathbf{h}). For this subset of reflections, G can be computed in terms of Φ by means of

$$G_{\mathbf{h}}(\Phi) = \frac{1}{V} \sum_{\mathbf{h}'} E_{\mathbf{h}} E_{\mathbf{h}-\mathbf{h}'} \exp i(\varphi_{-\mathbf{h}} + \varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})$$

The degree of coincidence between observed and calculated G can be measured with the sum function

$$Z = \sum G_{\mathbf{h}} \cdot G_{\mathbf{h}}(\Phi) = \frac{1}{V} \sum_{\mathbf{h}'} E_{\mathbf{h}} E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'} \exp i(\varphi_{-\mathbf{h}} + \varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})$$

Z is characterized by the presence of the triple-phase sums (*triplets*). Each triplet constitutes a phase invariant, i.e. unlike individual phases the triple-phase sum does not depend on the position of the unit cell origin with respect to the space group symmetry elements. Physically, Z represents the product of the observed and calculated (Patterson-type) modulus functions and, logically, will be a large positive maximum for the true φ . Z can be maximized with the tangent formula

$$\varphi_{\mathbf{h}}^{new} = \sum_{\mathbf{h}'} E_{\mathbf{h}} E_{\mathbf{h}-\mathbf{h}'} \exp i(\varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})$$

Structure solution begins by assigning random values to the Φ set of phases and then these are refined by the iterative application of the tangent formula until convergence is attained. The solution is first checked by calculating some fast figures of merit. Only for the best solutions, the E maps are computed. During the last thirty years, this basic procedure has been considerably improved so that nowadays crystal structures with less than 500 atoms in the asymmetrical unit can be solved by direct methods provided that data are good enough.

Final verification of the structure model is done with the calculation of the residual

$$R = \frac{\sum |F_o - F_c|}{\sum F_o}$$

which measures the discrepancy between observed and calculated structure factor amplitudes. R values higher than 0.40 indicate wrong structure models. Values around 0.30 very often suggest partially correct models e.g. missing atoms. For high quality single-crystal data and crystal structures without disorder, R values must be less than 0.10.

Mineralogical applications of X-ray diffraction

The first applications of experimental X-ray diffraction techniques were carried out on minerals. Before the discovery of X-ray diffraction, mineralogists were limited to examine the external form of minerals, their optical properties and their chemical composition. After the discovery in 1912, the crystal structures of a large number of minerals were determined which was of great help for their classification e.g. interpretation of the diffraction pattern of quartz showed that although an oxide (SiO_2), its crystal structure clearly corresponded to a silicate.

Also with the help of X-ray diffraction, W.H. Bragg and W.L. Bragg (1913) determined the structure of halite, sphalerite and diamond. In 1930, W.L. Bragg and others established the basic structural criteria which led to the current classification of silicates in the following subclasses: **neosilicates** (composed of isolated tetrahedra [SiO_4^{-4}]), **sorosilicates** (double tetrahedral groups [$\text{Si}_2\text{O}_7^{-6}$]), **cyclusilicates** (closed structures of 3, 4 or 6 tetrahedra, giving rise to clusters of the type [$\text{Si}_n\text{O}_{3n-2n}$]), **inosilicates** (are single [$\text{Si}_2\text{O}_6^{-4}$] or double [$\text{Si}_4\text{O}_{11}^{-6}$] chains with an indefinite number of tetrahedra), **phyllosilicates** (each tetrahedron shares 3 vertices with the same number of tetrahedra, forming flat sheets of "infinite" extension of unitary composition [$\text{Si}_2\text{O}_5^{-2}$]) and **tectosilicates** (frameworks in which tetrahedra share all four vertices with other tetrahedra).

In the early years of X-ray crystallography, the determination of crystal structures of minerals required them to be available in the form of single-crystals. As most mineralogists know, this is not always possible because many minerals appear as powders. An important contribution to the identification of materials of industrial interest (minerals, ceramics,...) was achieved in the 30's by Hanawalt and colleagues (Warren, 1941; Amigó, 2002) who devised a rel-

atively easy method to identify the polycrystalline phases in a powder diffraction pattern. In 1941, the Joint Committee on Powder Diffraction Standards (JCPDS) expanded the objectives and marketed a database of powder diffraction patterns classified in 3 main files (inorganic, mineralogical and organic). The cards of these powder diffraction patterns were identified by the initials ASTM or PDF (Powder Diffraction File) followed by an index number which is still being used since 1941.

This initial effort of the JCPDS was supported by a Committee of the American Society for Testing and Materials (ASTM). In 1978, the name of the organization changed to the current International Centre for Diffraction Data (ICDD). The current database, accessible through computer, exceeds 300.000 entries. Since 2006, it also includes calculated powder patterns.

The application field of powder diffraction considerably broadened with the advent of computers, the discovery of the Rietveld method at the end of the 60's and its subsequent adaptation from neutron to X-ray data. The Rietveld method rendered possible complex crystal structure refinements from powder data. Also important was the introduction of the easy-to-implement Le Bail intensity extraction procedure that enabled the application of automated methods to structure solution from powders (Le Bail *et al.*, 1988; Rius *et al.*, 1996). Significant contributions of this period were the first application of Patterson search methods to molecular compounds (Rius and Miravittles, 1988), the first application of direct methods to powder data of zeolites at moderate resolution (Rius *et al.*, 1995; Rius, 1993) or to powder data with systematic overlap (Rius *et al.*, 1999). To take advantage of the huge computing power already available at the laboratory, direct methods have been reformulated in terms of Fourier transforms instead of triple-phase invariants (Rius *et al.*, 2007). One recent significant advance has been the so-called Patterson-function direct methods, i.e. direct methods that directly work with the extracted and equi-distributed intensities (Rius, 2011). In this way, the effective resolution of the data set is extended. Nowadays, powder diffraction techniques allow structural studies of relatively complex minerals which are only available in polycrystalline form. Modifications of the Rietveld method are also used for studying the structure of interstratified phyllosilicates and disordered zeolites from powder data (DIFFaX program), e.g. it has been used to characterize the order-disorder as well as the microstructure of *vermiculites* (Argüelles, 2009, 2010).

A new method which is acquiring increasing importance for the characterization of minerals is the combination of automated electron diffraction with the precession technique (Kolb *et al.*, 2007; Mugnaioli *et al.*, 2009). One recent impressive achievement has been the crystal structure determination of *charoite*, an asbestos-like fibrous silicate (diameter $\approx 0.2\mu\text{m}$). Electron microscopy and electron diffraction studies showed that there are two different monoclinic *charoite* phases with almost parallel fibre axes and laterally separated by an amorphous phase. The respective crystal structures were solved by applying direct methods to electron diffraction data (Rozhdestvenskaya *et al.*, 2010).

Polished thin sections of rocks with thicknesses up to 30 μm are commonly used in mineralogical and petrological studies. Recently, it has been demonstrated the capability of the through-the-substrate microdiffraction technique to produce diffraction data of selected regions of the thin section (Rius *et al.*, 2011). These data can then be used to solve the crystal structure by applying direct methods. This procedure does not destroy the sample but requires synchrotron radiation. This diffraction technique is particularly useful for studying intermediate phases e.g. phases formed at grain borders. Usual lateral resolutions go from 15 to 100 μm .

In the last years, some Spanish mineralogists have contributed to the determination of new minerals by diffraction methods. Among them, *teruelite* (Arriortua *et al.*, 1981), a ferroan variety of dolomite typical mineralogical curiosity of the Iberian Mountain Range; *wermlandite* (Rius & Allmann, 1984) and *motukoreaite* (Rius & Plana, 1986), two double layer minerals similar to pyroaurite and sjögrenite; *villamaninite*, an optically anisotropic pyrite-type disulphide whose structure was refined in the true (not cubic) symmetry (Marcos *et al.*, 1996); *stanekite*, a phosphate mineral (Keller *et al.*, 1997); *tennantite* (Ochando *et al.*, 1998), an hydrothermal copper sulphosalt, located at Vilaherrosa del Río (Castellón); *aerinite*, a fibrous aluminosilicate used in the middle-age as blue pigment (Rius *et al.*, 2004, 2009) (Fig. 7); *tinticite*, a partially disordered triclinic hydrated Fe-phosphate being the first 'direct methods' application where the intensities of the reflections in overlapped peaks were updated during the phasing process (Rius *et al.*, 2000); *cobaltoarthurite*, a new Co-arsenate (Jambor *et al.*, 2002); *calderonite*, a new lead-iron-vanadate of the brackebuschite group (González del Tánago *et al.*, 2003); *garutiite*, a new hexagonal polymorph of native Ni formed at low temperatures during post magmatic processes (McDonald *et al.*, 2010); *metarauchite*, a new

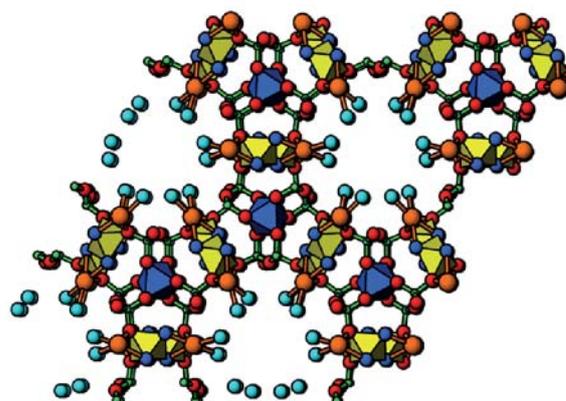


Fig. 7.- Perspective view along *c* (the fibre axis) of the trigonal crystal structure of *aerinite* showing the pyroxene-type chains, the two symmetry-independent columns of face-sharing octahedra (Fe and Al) and the brucite-type slabs of Al and Ca octahedra. Carbonate and sulphate anions (not reproduced) are allocated in the middle of the channels surrounded by the water molecules bound to Ca. This mineral was used as blue pigment by painters during the Catalan Romanesque period.

mineral of the autunite group (Plasil *et al.*, 2010); *barahonaite*, a new Ca-Cu arsenate (Viñals *et al.*, 2010); *sanzjuanite*, an aluminium phosphate-sulfate consisting of chains of tetrahedra and octahedra determined from laboratory powder data by the newly developed Patterson-function direct methods (Colombo *et al.*, 2011).

Conclusions

In 2012 we celebrate the centenary of the diffraction experiments performed by Laue and the Braggs on crystals. These experiments represented the beginning of X-ray crystallography. Also an early significant contribution of diffraction to experimental sciences was the development in 1916 of the Debye-Scherrer method by the Dutch physicist Peter Debye and the Swiss physicist Paul Scherrer which allowed the crystallographic study of polycrystalline materials when no single-crystals were available. Due to the sample preparation simplicity and also to the steady progress in computing facilities, in detector efficiency and in X-ray flux, variants of this method are still now decisive for the characterization and structural study of minerals.

Although crystallography is since 1912 no longer a part of mineralogy, it is still of fundamental importance in many experimental sciences, so that a basic crystallographic knowledge is still necessary for today's mineralogists.

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