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History of Physics and Related Sciences.

Crystallography before the Discovery of X-Ray Diffraction

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This paper presents a brief description of the prevailing ideas and hypothesis about the nature of matter from antiquity to the end of XIX century. It shows how gradually, since the Hauy proposal of the existence of the unit cell, the crystal lattice and symmetry and subsequent derivation of the 14 crystal classes by the French Physicist A. Bravais, the 32 point groups by the German mathematician A. Shoenfliess and the 230 space groups independently deduced by the Russian mathematician E. S. Fedorov and A. Shoenflies confirmed the atomic theory suggested by the Greek philosopher Democritus. These empirical and theoretical findings, conducted by several scientists, are one of the most brilliant theoretical predictions of all time in Science, fully confirmed after von Laue discovery of X-ray diffraction by crystals in 1912 and its application on the determination of molecular and crystalline structure by the English physicists W. H. Bragg (1862-1942) and his son W. L. Bragg (1890-1971).
Keywords: Atomic theory of matter, Democritus, Aristotle, Saint Thomas, crystallography before XRD, unity cell, crystal lattice, point groups, space groups, Haüy, Bravais, Pasteur, Shoenfliess, Fedorov.

1. Introduction

Since ancient times, the search for the understanding of natural phenomena has led to hypotheses about the Universe, from the origin and features of Earth's animate and inanimate beings to those of celestial objects. These explanations occurred involving the supernatural and, in a more objective way, by observation. The concepts and interpretations developed in Ancient Greece strongly influenced Western culture, mainly through the ideas of Socrates, Plato, Leucippus, Pythagoras, Archimedes, Democritus, and Aristotle. The very important role of Aristotle is mainly due to his notable work of registration and systematization of the ancient Greek Nature knowledge.

The Greek ideas on the constitution of matter had as exponents Leucippus (400 BC) and Democritus (360 BC) [1], who advocated the discontinuous nature of matter. Democritus coined the word *atom*, or indivisible (from Greek, "a" negation and "tome" divisible) to describe the smallest portion of matter that was responsible for its macroscopic properties. On the other hand, Aristotle (384 BC - 322 BC) [2] rejected this idea and assumed that matter was continuous, with no limit to its divisibility. The conflict between these ideas persisted until the early twentieth century, with some scientists still advocating the continuous constitution of matter.

During the Middle Age, however, the knowledge of Ancient Greek Culture had vanished in the West except in the Christian monastic schools in Ireland. The first significant renewal of learning in the West came with the Carolingian Renaissance of the early Middle Ages (the period from the 5^{th} to the 10^{th} century AD). During the 8^{th} century, the great emperor Charlemagne (742-814), advised by Peter of Pisa and Alcuin of York, attracted scholars from England and Ireland. Furthermore, by decree in 787, he established schools in every abbey in his empire. These schools, from which the name *scholasticism* derived, became centers of medieval learning. [3]

However, among the sages of the Church, there arises the uneasiness derived from the existence of two worlds: that of theology (faith) and that of philosophy (reason). St. Thomas Aquinas [4], an important thirteenth-century theologian, philosopher, and priest, in order to reconcile Christian faith with rational thought in the Christian monastic schools (especially the concepts of physics, astronomy, chemistry and biology from Greek natural philosophy) creates the Thomist School of theology accepting Aristotle's ideas, having in mind that *"both kinds of knowledge ultimately come from God"* and were therefore compatible. Not only were they compatible, according to Thomas's ideology, but they could work in collaboration: he believed that revelation could guide reason and prevent it from making mistakes, while reason could clarify and demystify faith. Unfortunately, the latter followers of Thomism adopted a rigid view and, in a way, transformed the Aristotelean ideas of the physical universe in objects of faith.

This situation prevailed until the seventeenth century when Thomist theory began to be openly contested by many religious, philosophers, and scientists who established new laws concerning the constitution of the universe and particularly of matter due to their great capacity for observation and generalization.

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Until the seventeenth century, Crystallography, like other sciences, was included in the general conception of the part of human knowledge named Natural Philosophy. New ideas and crystallographic discoveries, derived from observations, took place towards the establishment of the atomic theory of matter as advocated by Democritus, who stated that in nature there are only "*atoms et vasium*".

The following quotation found under the "Democritus" entry in Wikipedia illustrates well the atomist thinking of Democritus and followers: *The consistency of the clusters of atoms that makes something appear solid, liquid, gaseous or moody ("state of mind") would then be determined by the shape (figure) and arrangement of the atoms involved. Thus, atoms of steel have a shape that resembles hooks, which hold them solidly together; the atoms of water are smooth and slippery; the atoms of salt, as their taste shows, are harsh and pointed; the atoms of air are small and little connected, penetrating all other materials; and the atoms of the soul and of the fire are spherical and very delicate. [5]*

2. Beginnings of Crystallography in the 17th Century

Pierre Gassendi (1592-1655) [6], an important French philosopher, scientist and mathematician, played a very important role in the development of modern science by definitively reintroducing atomism. Gassendi came to atomism after studying the writings of Epicurus (born around 341 BC), who had adopted Democritus' theory. The rebirth of this theory was central to future interpretations of the nature of matter and, in particular, of crystals. He claims: *"Hence, from atoms there are formed initially certain molecules, which differ among themselves and which are the seeds of diverse substances, and then each substance is constructed or composed from its own seeds, so that nothing exists from any other things"* [7].

Johannes Kepler (1571-1630) [8], the famous German scientist and a key figure in the seventeenth-century scientific revolution, was one of the first scientists to verify, in 1611, the spontaneous symmetry presented by the particles of snow. *'Why do snowflakes always fall as flat structures with six corners?'* asked Kepler (1611) [9]. Although he could not formulate any explanation as to why this phenomenon occurred, he had tried it by considering the water crystals made of fundamental spherical particles. Nevertheless, Kepler is very famous for other works, mainly his analysis of Tycho Brahe's accurate astronomical observations, which led to the undeniable conclusion of the heliocentric movement of the planets in the solar system

Nicolas Steno (1638-1686) [10] was an illustrious Danish scientist who provided the first accurate crystal observation and described it in his 1669 book "De solido intra solidum naturaliter contento" [10] establishing the first law of crystallography, called Steno's law or law of constant dihedral angles. This law establishes that the angles between corresponding crystal faces of the same material are constant even when the development of such faces is uneven. This concept was first proposed by Steno in 1669 and was reformulated as a law by Romé de l'Isle in 1772.

3. Fundamentals of Crystallography in the XVIII Century

Steno's findings were confirmed after the invention of the contact goniometer, shown in Figure 1, by Arnold Carangeot (1742-1806) [11], a student of Romé de l'Isle, French mineralogist who is also considered one of the creators of modern crystallography. The precise novel goniometer allowed the measurement of inter-face dihedral angles of many crystalline materials confirming the Steno's law of constant dihedral angles.

The advances in the production of lenses and mirrors, as well as in the mechanical features of equipment construction during the XVIII century, enabled William Hyde Wollaston (1766-1828), an illustrious British physicist and chemist, to invent various optical instruments, among them the reflection goniometer [12]. This instrument was very precise in taking goniometric measurements around various crystallographic directions, even in small samples, making it possible to obtain accurate morphological data from a large number of crystals.

Renée Just Haüy (1743 - 1822), sometimes referred to as Abbé Haüy, was a French mineralogist pioneer in the study of crystal geometry. Haüy's interest in mineralogy awakened when he accidentally dropped a sample of calcite that belonged to a friend. While examining the fragments of the broken sample, he noticed that they had no random forms – instead, they appeared to obey a geometric law. Haüy himself [13] described this event:

> "The observation I have just noted is that which has served to develop my ideas on the structure of crystals. It presented itself in the case of a crystal that the citizen Defrance was kind enough to give me just after it had broken off from a group this enlightened amateur was showing me, and which formed part

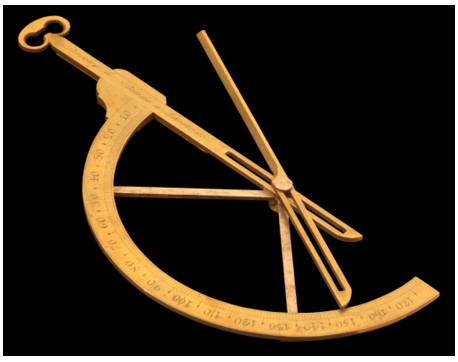

Figure 1: The contact goniometer

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of his mineralogical collection. The prism had a single fracture along one of the edges of the base, by which it had been attached to the rest of the group. Instead of placing it in the collection I was then forming, I tried to divide it in other directions, and I succeeded, after several attempts, in extracting its rhomboid nucleus. This at once surprised me, and gave me the hope that I could advance beyond this first step."

This led Haüy to propose that crystals should be formed by the juxtaposition of small identical units (which he termed *celule integrante* and which we presently call unit cells), with edges of lengths a, b, c and 90 or 60 degrees interaxial angles. Based on this model, he reproduced, as shown in Figure 2, the shape of several crystals by the tridimensional juxtaposition of their unit cells [14].

This model building procedure and the use the contact goniometer for the measurement of the dihedral angles between the crystal faces led Haüy to recognize, in many crystals, the existence of rotational symmetry axis and mirror planes m. The axis consisted of rotations through 180, 90, and 60 degrees around some well-defined directions, such as edges or normal to faces, A_2, A_4, or A_6 correlating respectively 2, 4, or 6 faces and mirror planes (dashed lines). Figure 3 displays some of these symmetry elements for the case of a tetragonal crystal [15].

The results of Haüy's speculations led him to classify the crystals into four morphological crystallographic systems, according to the relative type, dimensions and symmetry of the unit cells as cubic (four mutually threefold axis), tetragonal (one fourfold axis), orthorhombic (thee mutually perpendicular twofold axis) and hexagonal (one sixfold interaxial axis) with the interaxial angles of the unit cells as 90 and 60 degrees.

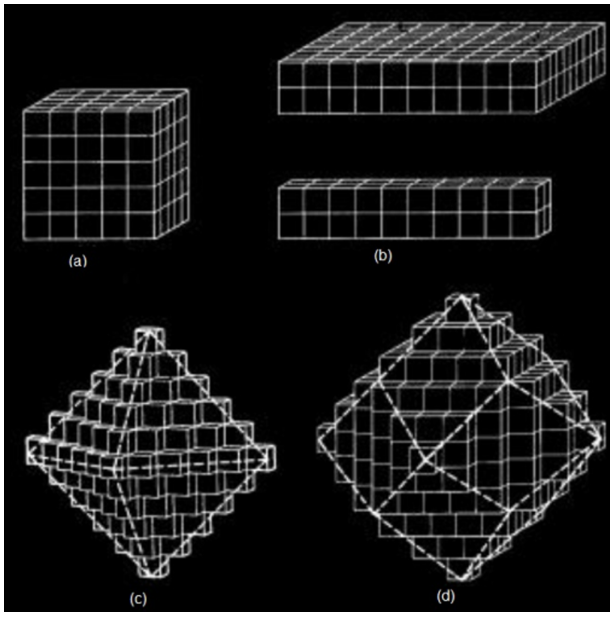

Figure 2: Hauy crystal models based on the unit cell concept.

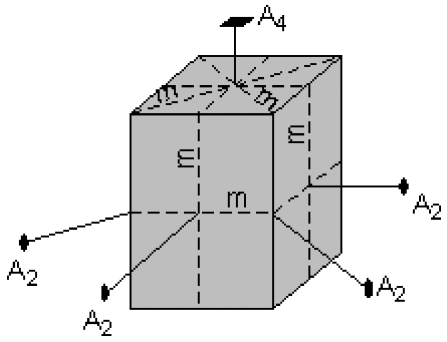

Figure 3: Tetragonal crystal's symmetry elements.

Based on his observations and crystal models, Haüy also established that the intercepts of the natural faces of a crystal on the unit-cell axes X, Y, Z shown in Figure 4 [16] are constant and expressed by rational numbers. This finding constitutes the *Law of Rational Intercepts*

We can say that the concepts of the unit cell and crystal symmetry were decisive for the establishment of crystallography and, for this reason; Renée Just Haüy (Abbé Haüy) is considered the Founder of Crystallography (Figure 5).

4. Development of Crystallography in the 19th Century

4.1. Invention of the reflection goniometer and the polarimeter

During the eighteenth century, the advance in the production of lenses and mirrors and the good quality of the mechanical construction led to the invention of the reflection goniometer and the polarimeter.

William Hyde Wollaston (1766-1828), an illustrious British physicist and chemist, invented various optical instruments, among them, the reflection goniometer. Wollaston had the ingenious idea of using crystal faces as

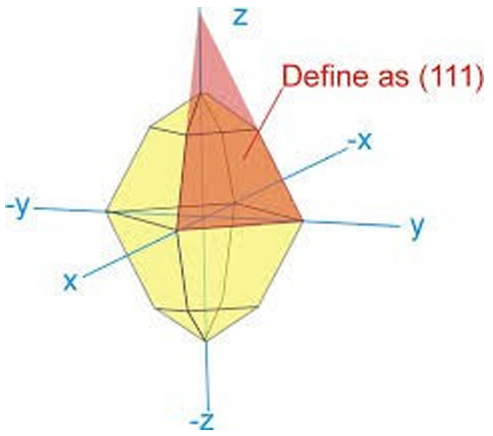

Figure 4: Lattice plane intercepts.

Figure 5: Haüy with the contact goniometer

mirrors to measure the angles between them. A crystal was stuck with wax to a cradle mounted on a vertical spindle. This spindle was in turn, attached to the horizontal axle of a much larger circle, graduated in degrees and equipped with a Vernier scale, as shown in Figure 6 [17]. After adjusting the orientation of the crystal with the vertical wheel to ensure that the light was reflected from each crystal face, the main circle was set to zero with one surface bright and then rotated until the second face shone. The new goniometer made possible the measurement of smaller and less perfect crystals, and by changing the crystal rotation axis, measure the interfacial angles along other directions.

The invention of the optical goniometry allowed the realization of very precise goniometric measurements around various crystallographic directions, even using small crystals. In this way, it was possible to obtain accurate data concerning the morphology and symmetry of a large number of crystals.

The polarimeter is a scientific instrument (scheme shown in Figure 7) used to measure the angle of rotation of polarized light caused by passing a beam of polarized light through an optically active substance [18]. This phenomenon is typical of noncentric crystals.

Figure 6: Mitscherlich's optical goniometers for use in crystallography, c. 1900

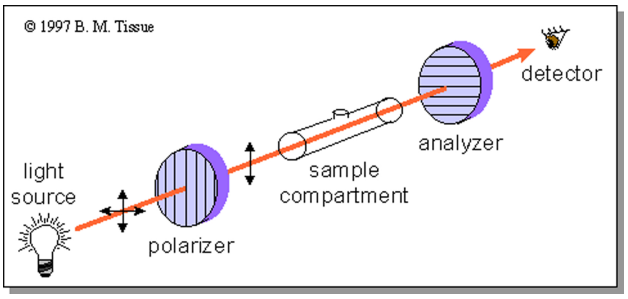

Figure 7: Scheme of an optical polarimeter.

The morphology of a crystal may be displayed by plotting the directions of every face normal on the surface of a sphere, as shown in Figure 8 [19]. As the projection on the surface of the sphere is not practical, a new projection is obtained by the intersection on the equatorial plane of every point situated on the northern hemisphere, projected from the south pole, and the contrary done with the normal intersections of the southern hemisphere. These projected points are called "poles" of the crystal face and yield the stereographic projection of all crystal faces. From the analysis of this projection, we may devise its symmetry, as shown in Figure 9 [20].

4.2. The possible lattice symmetries

Auguste Bravais (1811-1863) was an important French physicist who, based on the concept of infinite crystalline lattice proposed by Haüy, studied which unit cell symmetries could generate a crystalline lattice formed by the vertices of the juxtaposed unit cell. Bravais mathematically concluded that there were only 14 possible arrays

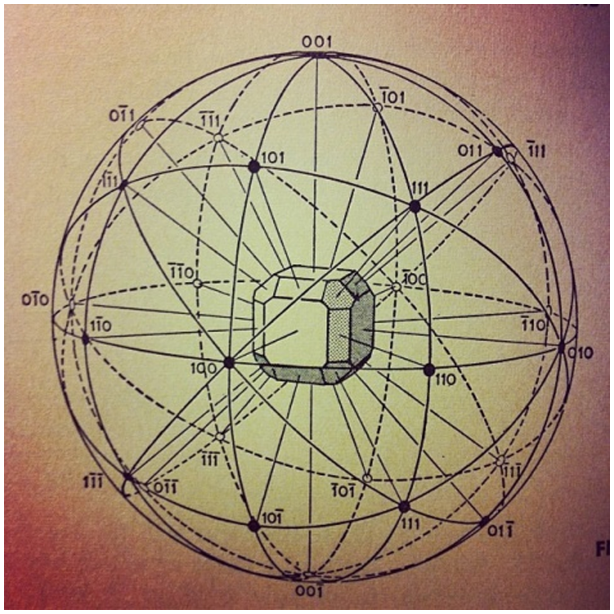

Figure 8: Stereographic representation of the faces normal's of a cubic crystal.

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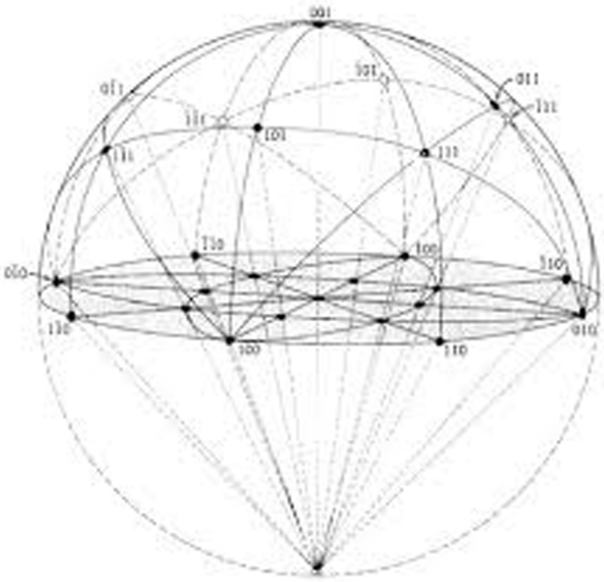

Figure 9: Stereographic projection of the poles of each face normal on the equatorial plane.

in three-dimensional space and 5 in two dimensions. In homage to their discoverer, they were named Bravais lattices and nets [20].

The search for possible lattices was based on the fact that any point of the lattice must be symmetrically equivalent by translation to any other point. This requirement gave rise to the discovery of multiple unit cells, i.e., unit cells that contain more than one lattice point located at either the center or the faces of the unit cell. They are respectively P (primitive, containing only one reticular point), A, B, C (face centered, with one reticular point in one of the faces of the unit cell A, B, or C), F (all faces centered) and I (centered at the center of the unit cell). The deduction of the 14 Bravais lattices [21], shown in Figure 10, also took into account the possibility of the interaxial angles of the unit cells be different from 90 degrees, thus adding two more systems to the ones proposed by Hauy: monoclinic and triclinic.

4.3. Crystallographic planes and their notation

Assuming the existence of the crystalline lattice, we have the definition of a lattice plane as any plane that passes through points of the lattice, forming families of parallel planes with fixed interplanar distances. The faces presented by the crystals correspond to one of these families of planes and result from crystallization conditions. According to Haüy's law, all faces of the crystals present intercepts given by rational numbers and so we can choose one of the prominent faces of the crystal as its parametral plane as shown in Figure 4. The intercepts of the parametral plane on a set of Cartesian coordinate axes located in the center of the crystal define in this way the direction and relative size in arbitrary units of the unit cell dimensions a, b, c. As the intercepts are relative values, they were normalized by the value of the smallest intercept In this way each face is identified by the size of

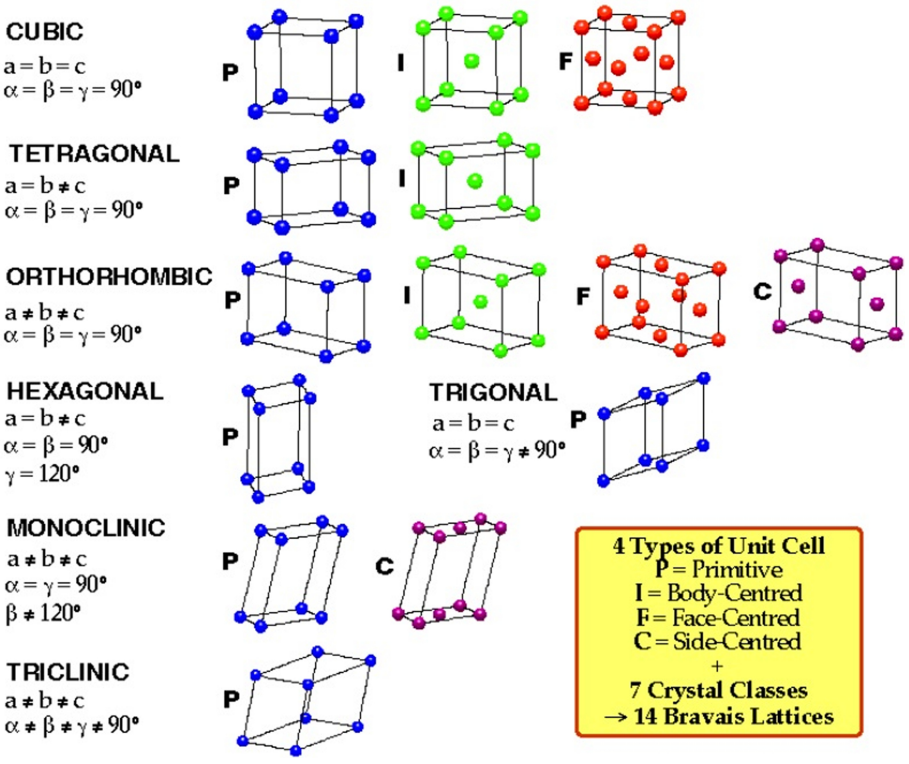

Figure 10: Bravais Lattices

its intercepts relative to the normalized intercepts of the parametral plane on that coordinate axes. If we consider three faces respectively parallel to two of the x, y, z-axes, their intercepts will be (1 ∞ ∞), (∞ 1 ∞), and (∞ ∞ 1). To avoid the infinite values of the axial intercepts the British physicist W. H. Miller (1801-1880) proposed that the inverse of each intercept be adopted, and thus these values become respectively (100), (010), (001). This notation accurately characterizes each possible face of the crystal and all the subjacent lattice planes.

5. The point groups of crystallographic symmetry

Until then, crystal analyses revealed the presence of a limited number of symmetry elements, namely: the identity element, the inversion center, the reflection plane designated by the letter m (mirror), the axes of rotation of order n (rotations of 360 degrees / n where n is an integer equal to 2, 3, 4, and 6 respectively), improper axes of rotation (360 /n rotation symmetry operation followed by an inversion center operation or a mirror operation generating the corresponding roto-inversion and roto-reflection improper symmetry axes. The analysis of the improper axes reveals that several are equivalent to other symmetry operations and so it is necessary to keep only a few unique ones. Usually, only the roto-reflexion axes of order 2, 4, and 6, are kept.

The establishment, during the 19th century, of group theory, with the matrix representation of the crystallographic symmetry operations and their algebraic interactions, was of great importance to the deduction of possible combinations of crystallographic point symmetries elements. Considering systematically all observed crystallographic symmetry operations observed in crystals concurrent at the center of the crystal, the German mathematician A. Shoenflies showed that there are only 32 possible unique combinations and that they constitute the 32 Point Groups of Crystallographic Symmetry. The symmetry of the 32 Point Groups can be displayed using the stereographic representation of the symmetry elements and the symmetrically related poles of a general face normal, as shown in Figura 11 a and b, extracted from the Vol. I of the International Tables for X-ray Crystallography [22][23 p. 25]

Of the 32 symmetry point groups, 21 have no center of symmetry, and frequently its crystals crystallize in two mirroring forms of each other and, for this reason, they are called chiral forms. Figure 6 presents two types of point group notations: Shoenflies, with letters that indicate the main character of the point group,

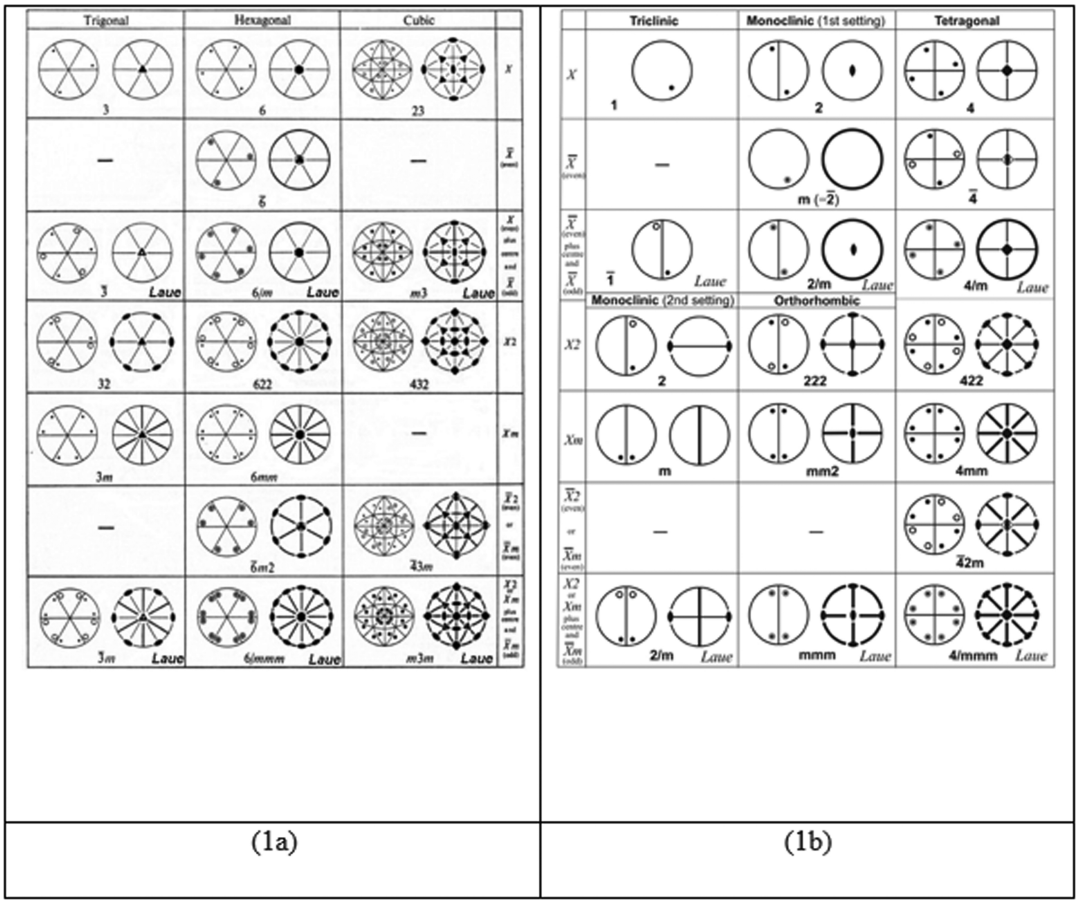

Figure 11: 1a and 1b The 32 crystallographic point groups.

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and the Hermann Mauguin, later adopted by the International Union of Crystallography, uses only symbols of the unique symmetry elements. The symbols used to display the poles are dots and circles to represent poles, respectively, above and below the equator. Darker lines designate mirror planes, and the symbols for the proper and improper rotation axes are quite intuitive distinguished by a bar above de order of rotation for the roto-reflection symmetry operators.

At this point, we cannot fail to mention the remarkable verification made by the French chemist Louis Pasteur (1822-1895) on chirality while studying the wine lint composition when attending the Ecole Normale Supérieure in Paris, under supervision of Gabriel Delafosse (1795–1878), a former student of Haüy, from whom he learned crystallography. Pasteur noticed that crystals of sodium and ammonium double tartrate present in wine lint occurred in two non-centrosymmetric forms, one being the mirror image of the other, as shown in Figure 12. He then carefully separated the identical crystals, dissolved them in water, and analyzed the solution using a polarimeter. The polarimeter measurements showed that the polarized light had its plane of polarization deviated in opposite directions by the solution of each mirror image crystal. Pasteur repeated the experiment with the two crystal forms he had separated and verified the same optical activity signal for each crystal form he used for the solution. He concluded that the optical activity was due to the spatial molecular structure of the salts, thus establishing a relationship between the external morphology of the crystal and the 3-dimensional structure of its constituent molecules. The existence of molecular chirality was, in this way, recognized. In May 1848, at age 25, Pasteur presented his findings to the Académie des Sciences. He is considered, for this reason, the Founder of Stereochemistry [24].

6. The Space Groups of Crystallographic Symmetry

A great stride was then made possible: the association of each of the symmetry point groups with the Bravais lattices translation operations. Although at the time the experimental verification of the result of this theoretical analysis was not possible, two mathematicians, E. S. Fedorov (1853-1919) and A. Schoenflies (1853-1928) analyzed all possible symmetry combinations of the Bravais Lattices with the 32 Point Groups and working independently, Fedorov in Russia and Shoenflies in Germany, they deduced the existence of only 230 possible space groups of crystallographic symmetry. Schoenflies published his results in the book *Kristallsysteme und Kristallstructur* (Leipzig, 1891), which immediately became a classic of crystallographic literature. Fedorov chose to publish his results in Russian in his article *Simmetriia Pravil'nykh Sistem Figure* (The Symmetry of Regular Systems of Figures, St. Petersburg, 1890), which made it more difficult to spread in the countries of Western Europe.

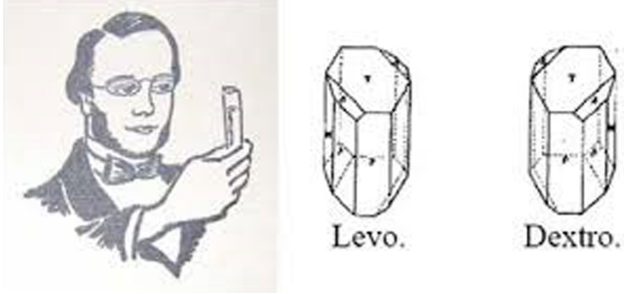

Figure 12: Pasteur and chiral crystals

One consequence of these theoretical studies was the rise of new symmetry elements due to the interactions among the known symmetry elements of the 32 point groups and the operation that generates the lattice from the unit cell: the translation symmetry. The combination of rotational axes with translations, with appropriate pitch and rotation directions, generated new elements of symmetry: the helical axes or screw axis that assign to each rotation of order n translations along the axis of rotation with fractional steps of the same order as the rotation. Figure 13 shows the representation of the rotation translation axes of fourth order with a translation of 1/4, 2/4, and 3/4. Note that the translations of 1/4 and 3/4 correspond to helices which rotate in opposite directions and are, therefore, enantiomorphic. However, the pitch equal to 2/4 also generates four objects but without rotational asymmetry.

Similarly, new reflection symmetries associated with the mirror plane m were deduced: the translation reflection mirrors corresponding to the association of a reflection followed by a translation along directions parallel to the crystallographic axes or the cell diagonals, as shown in Figure 14.

The space group notation was first done based on the Schoenflies symbols of the Point Groups by adding a superscript referring to the order that Schoenflies originally listed the corresponding space group. Later, at the

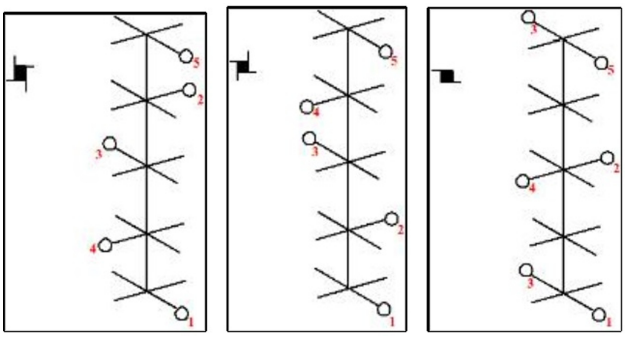

Figure 13: Representation of the possible fourfold rotation translation symmetry operations, acting on an object contained in the unit cell.

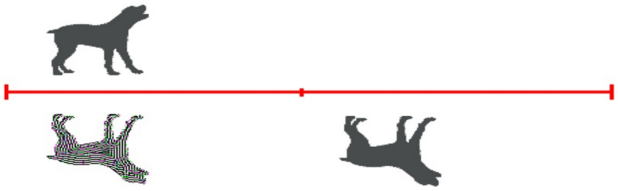

Figure 14: Representation of the mirror reflection translation symmetry.

beginning of the XX century, a new type of notation was proposed by Hermann and Mauguin (HM).

As an example, we give below in Figure 15 the representation of the characteristics of the space group number 35 which specifies the HM symbol for the space group Cmm2 (Orthorhombic crystal system, multiple unit cell type C and two reflection planes m respectively perpendicular to a and b unit cell axes and a rotation axis 2 along the c axis) [23 p. 121]. Next to it is the Shoenflies notation, which indicates that this is the eleventh space group obtained from the point group C_{2v} (full symbol C_{2v}^{11}). Figure 14 shows the projection of the unit cell with its elements of symmetry and the projection of all the objects (represented by a small circle) generated successively by each operator of symmetry. A + or – sign indicates the relative position of an object above or below the projection plane, and the distinction between the enantiomorphic pairs generated by the mirror operations is given by adding a comma inside the object symbol of the symmetrically generated object. Finally, we have a list of the coordinates of the eight objects generated by symmetry.

7. Conclusion

As we see, by the end of the nineteenth century Crystallography had become an important interdisciplinary branch of science. Its objective was, and partially still is, the study of crystal's properties based on physical measurements of their geometry and point symmetry and, theoretically, of the distribution of matter in the unit cell according to its space group. If we remember that, at the beginning of the twentieth century, there were still discussions about whether or not matter would be discontinuous, we can consider the whole development of Crystallography as a comprehensive theoretical formulation of the discontinuous nature of matter, based on a series of observations and theoretical conceptual ideas that led, from Hauy unit cell hypothesis, to the formulation of the crystallographic space groups, as one of the most brilliant theoretical predictions of all time in Science, fully confirmed after Von Laue discovery of X-ray diffraction by crystals. Moreover, Hauy's hypothesis of the crystal lattice with the definition of spatially oriented crystallographic lattice planes, some related to the crystal faces but many others underlying into the lattice space, was fundamental to the understanding of X-ray diffraction phenomenon and extremely important for its application by the English physicists W.H. Bragg (1862 – 1942) and his son W. L. Bragg (1890- 1971) to the determination of the structure of several crystalline substances.

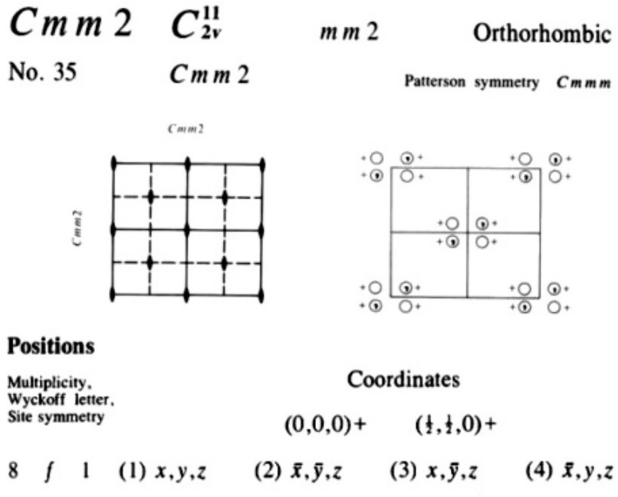

Figure 15: Graphic representation of space group symmetry Cmm2

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