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Historical Article

Early contributions of crystallography to the atomic theory of matter

GIOVANNI FERRARIS

Dipartimento di Scienze della Terra, Università di Torino, Via Valperga Caluso 35, 10125 Torino, Italy

E-mail: giovanni.ferraris@unito.it

Abstract. After briefly presenting early hypotheses on the submicroscopic origin of symmetry and polyhedral morphology in the crystals, the structural model proposed by Haüy in 1784, based on the periodic repetition of integrant molecules made up of simple molecules, is discussed. It is then highlighted how – through investigation of crystal hemihedry, isomorphism (mixed crystals) and optical activity – researches aiming at overtaking drawbacks of Haüy's model brought basic ideas to achieve the modern knowledge of the atomic structure of matter. The atomic-scale interpretation of properties of the crystalline state soundly contributed, among others, to properly define molecules and atoms, determine the atomic weights, hypothesize stereoisomerism, build the periodic table of elements and define ionic radii and bond.

Keywords. Isomorphism, stereoisomerism, integrant molecule, crystal morphology, atomic theory.

1. INTRODUCTION

The introduction of the concept of atom as indivisible constituent of the matter dates back to the Greek philosopher Democritus (~ 460 b.C. - ~ 370 b.C.), but only at the end of the nineteenth century the modern science made the atom from a debated philosophical category definitively transit to a physical certainty. Towards the end of its long and troubled history, the concepts of atom and molecule intertwined and sometimes even clashed. Only the determination of the first crystalline structures – made possible after the discovery of the X-ray diffraction by Max von Laue (1879-1960) in 1912 – convinced the entire scientific community that atoms and molecules are different entities, both necessary to model the structure of matter at atomic scale.

The contribution of crystallography to the atomic theory of matter can certainly not be limited to the irrefutable evidence acquired through the aforementioned structural determinations. In fact, for centuries the geometric regularity (symmetry) of the crystal morphology has played a stimulating role to develop hypotheses on the submicroscopic structure of the matter suitable to explain the macroscopic observations. In this article, only contri-

butions of the pre-diffraction era, inspired by morphology-related investigations, are qualified as early ones.

Following ingenious but quite approximate earlier hypotheses on the internal structure of the crystals – mostly based on close packing of particles – and Nicolas Steno's (Niels Steensen, 1638-1686) statement on the constancy of the angles between corresponding faces in all crystals of the same mineral¹ – later assumed by Jean-Baptiste Romé de L'Isle (1736-1790) as a genuine law of nature² –, in the last quarter of the eighteenth century the French crystallographer René Just Haüy (1743-1822) proposed a revolutionary model based on the periodic repetition of a submicroscopic polyhedron named integrant molecule and comparable to the unit cell of the modern structural crystallography. This model preceded the atomistic theory of John Dalton (1766-1844) for over thirty years and represented a first modern and general attempt to reasonably represent the atomic structure of the matter. Although the integrant molecule was primarily intended as a tool to explain the crystal morphology, we shall see that Haüy's structural model contributed to inspire Amedeo Avogadro (1776-1856) and André Ampère (1775-1836) to draw fundamental theoretical consequences from the results published by Jean Louis Gay-Lussac (1778-1850) on the chemical combination of gases.

Subsequently, as illustrated in this paper, researches aiming to overcome drawbacks of Haüy's model brought sound contributions in issues such as: distinct roles of atoms and molecules; determination of the atomic weights; stereoisomerism of chemical groups; building of Mendeleev table; definition of ionic radii; nature of the chemical bond.

2. EARLY HYPOTHESES

Before the second half of the eighteenth century various conjectures on the internal structure of the crystalline materials had been proposed aiming to explain features of the crystals, such as their symmetry and polyhedral morphology. Among the scientists who investigated the property-structure relationships of crystals we find famous names, usually better known for their important contributions to frontier non-crystallographic problems.

The Italian polymath Gerolamo Cardano (1501-1576), inventor of several mechanical devices, including the Cardan shaft with universal joints, in 1550³ noted the hexagonal symmetry common to the cells of the honeycombs and to the prismatic habit of quartz crystals and assumed for the latter an internal structure based on hexagonal particles.

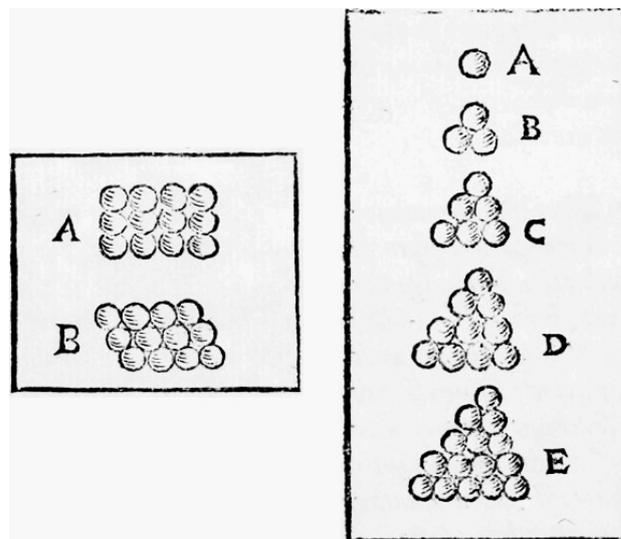


Figure 1. Close packing of spheres described by J. Kepler. (From reference 4, pp. 9-10).

Intriguing is the case of Johannes Kepler (1571-1630) – best known for his laws of planetary motion – who, in a booklet published in 1611⁴, where he questions on the origin of snow crystals morphology, derives close packings of spheres (Figure 1) but, surprisingly, he does apply this finding to the investigated morphology.

Robert Hooke (1635-1703), discoverer of the law of elasticity that bears his name, in 1665⁵ attributed the morphology of the rock alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) crystals to a compact packing of submicroscopic spheres (Figure 2).

In 1690⁶ Christiaan Huygens (1629-1695) proposed an anisotropic model of crystal structure based on a compact packing of ellipsoids (Figure 3) to explain – via his well known wave theory of light – the birefringence observed in calcite by Rasmus Bartholin (1625-1698) in 1669⁷ (Figure 4). It might be worth to recall here that birefringence has been the first physical property to be explained via an anisotropic structure of the matter, i.e. an inherent characteristic of the crystalline state.⁸

Finally, in 1749 Michail Vasil'evič Lomonosov (1711-1765) – mineralogy was among his multifaceted interests – imagined that the morphology of the niter (KNO_3) crystals was related to a submicroscopic packing of hexagonal particles.¹

¹ The original manuscript (M.V. Lomonosov, *Dissertatio de generatione et natura nitri, concinnata pro obtinendo praemio, quod illustris scientiarum Academia regia liberalitate Berolini florens proposuit ad 1-mum aprilis anni 1749*) is kept in the archives of the Berlin-Brandenburgische Akademie der Wissenschaften (Berlin, Germany). In 1934 it has been printed for the first time.⁹

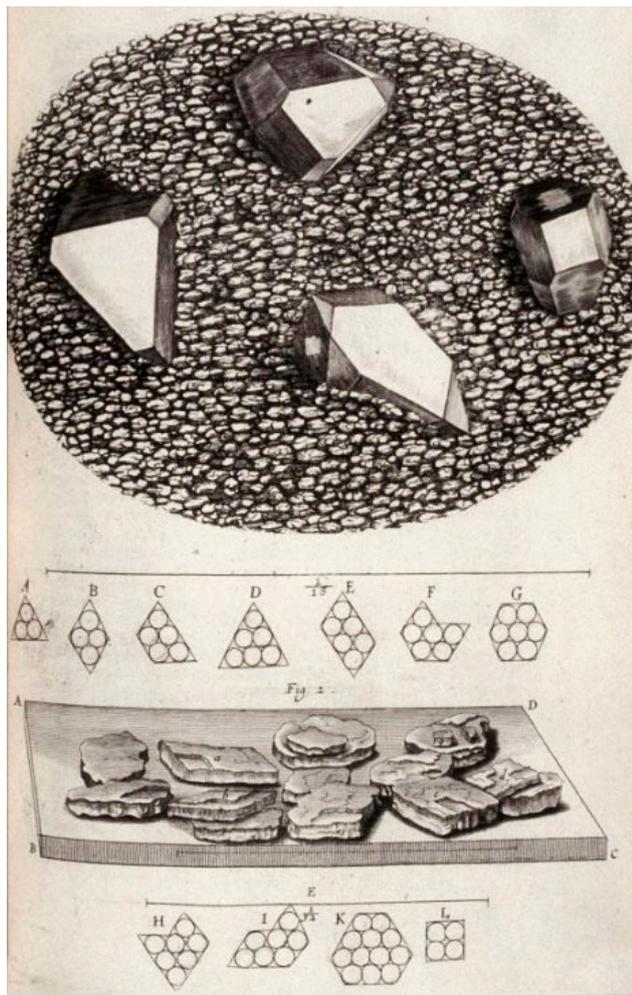


Figure 2. Morphology of the rock alum crystals related to close packing of spheres by R. Hooke. (From reference 5, opposite to page 82).

3. HAÜY AND THE INTEGRANT MOLECULE

Molecules and atoms were not yet clear and distinct concepts, when in 1766¹⁰ Pierre Joseph Macquer (1718-1784) defined the *integrant molecule* as a submicroscopic particle consisting of *simple molecules* that, as a matter of fact, correspond to the modern atoms. In 1784 Haüy adopted the integrant molecule as polyhedral building block of his general and innovative model of crystal structure aiming to explain symmetry and morphology of the crystals.¹²

Haüy's model (Figure 5)¹³ hypothesized a periodic arrangement of an integrant molecule, whose polyhe-

² Actually, in the reference 11 Haüy named constituent molecule (*molécule constituante*) the building block of his model and adopted the term integrant molecule (*molécule intégrante*) few years later.¹²

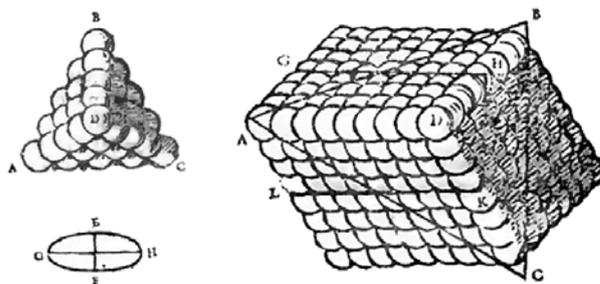


Figure 3. Anisotropic structure model based on close packing of revolution ellipsoids proposed by C. Huygens to explain the birefringence of calcite; a bidimensional section through the revolution axis of an ellipsoid is shown. (From reference 6, pp. 92-93).

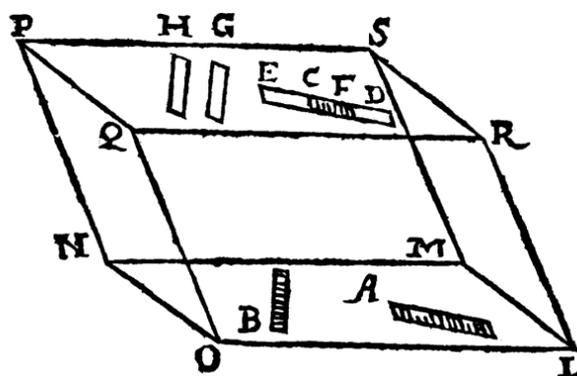


Figure 4. Birefringence in calcite observed by R. Bartholin. H and G, EC and FD are the double refracted images of B and A, in the order. (From reference 8, p. 12).

dral shape and chemical nature of the constituent simple molecules are characteristic of each mineral species and, by extension, of any crystalline material.

The idea of an integrant polyhedral molecule as basic building block was suggested to Haüy by the cleavage polyhedron of crystals – originally observed in calcite – that can be reduced to microscopic dimensions by iterated cleavages. Haüy did not conceive empty spaces in the matter; therefore, both integrant and simple molecules had to be space-filling polyhedra. That clearly appears in a drawing (Figure 6), published (1822) in his treaty of crystallography¹⁴, where, also considering critical comments received in the meantime, he improved his structural model of the 1784 *Essai* by graphically showing packing of simple molecules filling an integrant molecule.

The model was widely accepted, thus contributing to the advancement of a theory of matter based on molecules and atoms. In particular, the terminology of Haüy was adopted by Avogadro in his theoretical interpretation¹⁵ of the experimental results obtained by Gay-Lus-

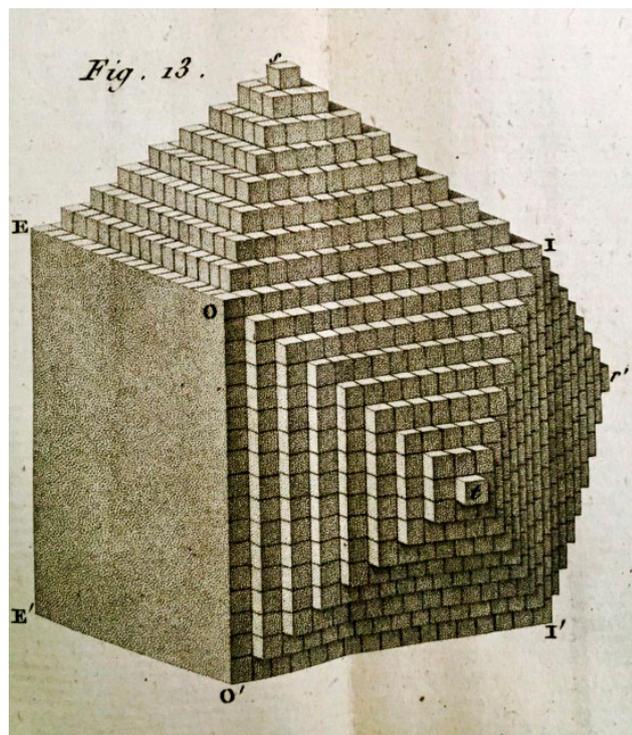


Figure 5. Haüy's model of a cubic crystal showing the periodic translation of a basic cubic building block (integrant molecule) and how different crystallographic forms can be obtained subtracting integrant molecules from an original cube. (From reference 13, vol. 5, fig. 13).

sac¹⁶, which led him to hypothesize that, under the same conditions of pressure and temperature, equal volumes of different gases contain the same number of (integrant) molecules. Precisely, the keystone to reconcile the ideas of Gay-Lussac (simple ratio between the volumes of reagent gases) with those of Dalton¹⁷ (fixed relationship between the reactant masses) was the distinction between the concept of integrant molecule (today molecule) and that of simple molecule (today atom); a step this, not made by Dalton who, instead, conceived atoms only. Independently, in 1814 André Ampère (1775-1836) proposed¹⁸ the same hypothesis of Avogadro. Whereas, the latter did not quote Haüy's model – whose influence on his work seems, however, hardly deniable¹⁹ – Ampère made explicit reference to this model with the variant of locating polyhedral atoms not inside, but at the vertices of the polyhedron representing the integrant molecule.

For long debated, but never sufficiently clarified reasons (cf., e.g., 20), the distinction between molecules and atoms affirmed by Avogadro was practically neglected for half a century. In fact, it was only at the first international congress of chemistry (Karlsruhe 1860) that Stanislao Cannizzaro (1826-1910) (cf., e.g., 21) brought

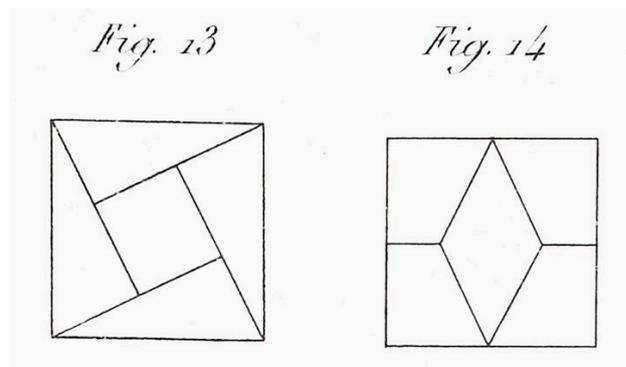


Figure 6. Two sections of a cubic integrant molecule filled with simple molecules. (From the *Atlas* of reference 14, pl. 69, figs. 13 and 14).

to general attention the paper that Avogadro had published since 1811 in a well known international journal (reference 15). Consequent to this revival, the majority of chemists and physicists accepted the idea of molecule as aggregation of chemically bound atoms.

4. ISOMORPHISM VS. ATOMS

Haüy's model was unable to explain hemihedral symmetries, polymorphism and isomorphism. Efforts to overtake these drawbacks, not only led to discover Bravais lattices, point and space groups, but also to reach agreement on the definition of molecule and atom.

Among early post-Haüy structure models able to explain hemihedral symmetries it is worth to quote the contribution by William Hyde Wollaston (1766-1828) who, in 1813, proposed mixed compact packages of spheres and ellipsoids, even of different color (nature), to explain relations between structure, morphology and chemical-physical properties of the crystals.²² Hemihedral boracite, $Mg_3B_7O_{13}Cl$ (space group $mm2$, but pseudo-cubic $-43m$), was one of the minerals debated at that time for its puzzling morphology. It was investigated by Wollaston and again, a quarter of century later, by Gabriel Delafosse (1796-1878) who proposed a structure model based on a network of tetrahedra (Figure 7).²³ As pioneering models quoted in paragraph 2, at variance with Haüy's space-filling model, Wollaston's and Delafosse's models contain "empty" space between building blocks, thus prefiguring a situation shown by modern diffractometric and microscopic methods.

Research on the crystallization of compounds from water solutions with variable composition lead to discover mixed crystals (solid solutions), i.e. the co-crystallization of two (or more) compounds whose crystals bear

Fig. 4.

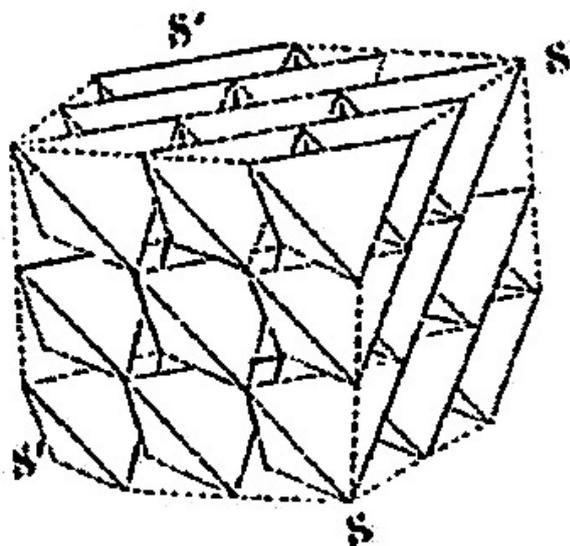


Figure 7. Model of boracite structure based on a framework of tetrahedra as proposed by G. Delafosse. (From reference 23).

the same morphology and chemical formulas differ only in the chemical nature of one element (isomorphism). In this field, pioneer results were published by Nicolas Leblanc (1742-1806)²⁴ and François Sulpice Beudant (1787-1850)²⁵ without reaching sound conclusions on the nature of the crystals showing mixed composition: either double salts or solid solutions? Beudant named crystalline mixtures (*mélanges cristallines*) these crystals that instead Wollaston considered to be solid solutions.²⁶

Continuing the research of Beudant, Eilhard Mitscherlich (1794-1863) studied crystallization from water solutions of mixed salts with analogous chemical compositions. On the basis of chemical analyses and crystallographic measurements on the precipitated crystals, Mitscherlich definitively established what the above-mentioned authors had only glimpsed: compounds with similar chemical formula that display the same morphology can co-crystallize two by two and in some cases three by three (for example, ammonium and potassium salts with iron salts).²⁷ In a subsequent article²⁸ Mitscherlich, likely influenced by the morphology of the crystals, introduced the term isomorph (= same form) referring to the chemical elements that, substituting each other, give rise to a group of co-crystallizing compounds. He wrote: "The same number of atoms combined in the same way produces the same crystalline

form. The latter is independent of the chemical nature of the atoms and is determined only by their number and arrangement"³.

The atomistic interpretation of isomorphism was soon successfully tested by Mitscherlich and his master Jöns Jacob Berzelius (1779-1848), who determined atomic weights via a procedure suggested by the following reasoning. If the co-crystallizing AR and BR compounds differ in their chemical composition for the substitution of A for B atoms only, one can derive the ratio between the atomic weights of A and B from the following equality:

$$\frac{(\text{atomic wt of A}) \quad (\text{wt of A combined to R})}{(\text{atomic wt of B}) \quad (\text{wt of B combined to R})} = \dots$$

The resulting first list of correct atomic weights was published by Berzelius in 1828.³⁰

As further keystone of the atomistic theory of isomorphism, one can here recall that Dmitrij Ivanovič Mendeleev (1834-1907) fruitfully exploited it to build his periodic table of elements. He was particularly interested in relating macroscopic properties to microscopic properties and, in this context, he used suggestions from the crystal morphology to fill various boxes of the table with elements whose yet unknown chemical properties were hypothesized via isomorphism between their compounds and those of already well characterized elements.³¹

5. OPTICAL ACTIVITY VS. STEREOCHEMISTRY

The rotatory polarization (optical activity) discovered in quartz crystals by Jean Baptiste Biot (1874-1862)³² was one of the properties not explainable by Haüy's structure model because it does not admit acentric crystals. The explanation, still essentially valid today, was given in 1824 by Augustin J. Fresnel (1788-1827) who, although adopting the term integrant molecule, went well beyond Haüy's model, which includes only periodic translations as repetition operations. Here are the words of Fresnel: "We conceive that this [optical activity] may result from a particular constitution of the refractive medium or of its integrant molecules, which establishes a difference between right-to-left and left-to-right. Such would be, for example, a helicoidal arrangement of the molecules of the medium, which offers inverse properties according to whether these helices are either dextrorsum or sinistrorsum".³³

³ A recent analysis of the background of Mitscherlich's work can be found in reference 29.

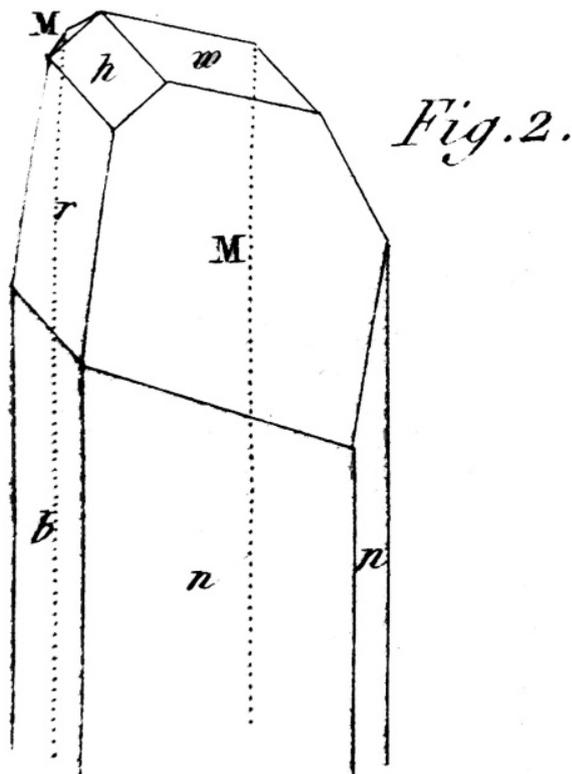


Figure 8. Hemihedral crystal of tartaric acid from the article of H. de la Provostaye (reference 36, pl. 1, fig. 2) that inspired the research of L. Pasteur on the optical activity (reference 34).

However, it has been necessary to wait for a further quarter of a century before, again by investigating optical activity, Louis Pasteur (1822-1895) proposed a mechanism able to explain the existence of substances showing rotatory polarization both in the crystalline state and in solution, while others display this property only in the solid state. For his results Pasteur is indebted to the theory of isomorphism too, and, as reported in his article³⁴, to observations by Mitscherlich on the optical activity of tartrates that Biot had published in 1844.³⁵ Precisely, Pasteur discovered that the racemes of tartrates are not solid solutions (mixed crystals), but fifty-fifty mechanical mixtures of left- and right-handed crystals. Having in mind the drawings of tartrate crystals published in 1841 by Hervé de la Provostaye (1812-1863)³⁶⁴ (Figure 8), Pasteur identified in racemes the two types of opposite handed crystals via their specular morphologies and, patiently, under the microscope, separated them from one another.⁵

⁴ This turns out to be the only article in which de la Provostaye describes tartrates, but for some unknown reason the reference made by Pasteur to the figures of this article does not match the numbering shown therein.

⁵ For a recent analysis of Pasteur's work see references 37 and 38.

Pasteur's explanation at the atomic scale was that, as Fresnel had supposed in 1824, optical activity of a crystalline compound is determined by helical arrangement of groups of atoms / molecules in the structure. Considering that Biot had published since 1839 his observations on the absence of rotatory polarization in fused quartz and opal (i.e., in amorphous silica)³⁹, Pasteur concluded that a crystalline optically active compound preserves this property in solution only if it is due to the spatial arrangement of its atoms (stereoisomerism) in a group (molecule) which survives the structure collapsing. Thus, as a matter of fact, a distinction between molecular and non-molecular compounds was proposed; actually, this hypothesis will be fully accepted by the scientific community only after the evidence brought by experimental determination – via X-ray diffraction – of the crystal structure of NaCl and diamond in 1913.

6. FINAL REMARKS

The excursus through a selection of results achieved by crystallography between the second half of the eighteenth century and the first half of the following century, clearly highlights how – mainly thanks to the then leading French school⁶ – the search for relationships between macroscopic (morphology) and submicroscopic features (structure) of crystals has contributed substantially to clarify the atomic structure of matter. In particular, the science, through the analysis of properties such as isomorphism (mixed crystals) and optical activity, moved from unspecified submicroscopic particles to a clear distinction between atoms and molecules.

Although this article is limited to the pre-diffraction period, it is worth to remember the influence that – via diffraction results – isomorphism had in establishing concepts such as ionic radius and its consequences in terms of definition of chemical bond and of relationships between structure and properties. In fact, the resolution of crystal structures, especially of minerals, followed to the discovery of X-ray diffraction in 1912, made available experimental data to define the radius of the sphere of influence of the elements linked by chemical bonding. Among several pioneers on this matter, one has to remember at least William Lawrence Bragg (1890-1971)⁴⁴ and Victor Moritz Goldschmidt (1888-1847)⁴⁵ who in 1920 and 1926, respectively, published detailed tables of ionic radii obtained via analysis of the interatomic distances.

The concept of radius connected with the length of predominantly ionic chemical bonds was success-

⁶ Cf. references 40, 41, 42 and 43; in particular, reference 43 is fully dedicated to the nineteenth century French crystallography

ful, such that it was extended to other types of chemical bonds, defining atomic, metallic, covalent and van der Waals radii. Besides, Goldschmidt correlated the size of the cation ionic radii with the geometry of their coordination polyhedra, laying the groundwork for the five rules later established by Linus Pauling (1901-1994);⁴⁶ rules that are still useful tools for the validation and description of non-molecular crystalline structures. Finally, in 1921 Lars Vegard (1880-1963)⁴⁷ discovered that the cell parameters and the volume of the members of an isomorphous series are normally a linear function of the chemical composition.

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