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Crystallography from Haüy to Laue: controversies on the molecular and atomistic nature of solids[1]

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To the memory of Caroline H. MacGillavry (1904–1993)

Molecularism / Lattice theory / Isomorphism / Polymorphism / Symmetry / Projection techniques / Group theory / Crystal systems / Crystal classes / Space lattices / Discovery of X-rays

Abstract. The history of crystallography has been assessed in the context of the emergence and spread of the molecular theory. The present paper focuses on the 19th century, which saw the emancipation of crystallography as a science *sui generis*. Around 1800, Laplace's molecularism called the tune in the various sciences (physics, chemistry, biology, crystallography). In crystallography, two schools opposed each other: that of Weiss, in Berlin, and that of Haüy, in Paris. Symmetry proved essential. It will be shown how the lattice theory arose in an essentially *molecular* framework and how group theory imposed itself. The salt hydrates suggested the idea of (two or more) *superimposed* molecular lattices. Gradually it became clear that an ultimate lattice theory ought to be *atomic*. The experiments of Laue, Friedrich and Knipping confirmed that atomic basis.

1. Introduction

The term 'crystallography' was introduced, in 1723, by Moritz Anton Cappeller (1685–1769) (Lima-de-Faria, 1990). From about 1800 crystallography definitely branched off from mineralogy. It is noteworthy that René-Just Haüy's first manual, published in 1801, was entitled *Traité de Minéralogie*. It was followed, in 1822, by a *Traité de Cristallographie*. Ever since, the science of crystals – often considered as a form of applied mathematics – has been called crystallography. It not only assessed the crystalline part of Nature's minerals, but also the crystals grown in the chemical laboratory.

In the present paper we will sketch the development that led to the crucial experiment of Laue, Friedrich and Knipping, that is, the directing of a beam of X-rays, first at an arbitrary crystal of copper sulfate, next at a well defined zinc sulfide platelet. We shall, first, give an impression of the broad context by considering the concept of 'individual' in natural history in general and in crystallography in particular. Next we will see how ideas like 'isomorphism' and 'polymorphism' emerged in chemical contexts. Gradually, what came to be known as 'symmetry' imposed itself. We will follow it in the two predominating schools, that of Haüy (Fig. 1) in France and that of Weiss in Germany. In the French framework, the molecular theory reigned supreme. Those molecules were extremely small, that much was certain; their exact dimensions defied the imagination. Their particular 'symmetry', however, had to be related to that of a crystal. We will see how Haüy's pilings of polyhedra metamorphosed into Bravais' point lattices. Those lattices, then, came to be analyzed from the viewpoint of the new group theory. Laue, Friedrich and Knipping, in a way, put a final end to that development.

Fig. 1. René-Just Haüy (1743–1822). Engraving by R. H. Delvaux, from Lucas, *Tableau Méthodique des Espèces Minérales* (Lucas, 1806) (courtesy: Bibliothèque Nationale de France).

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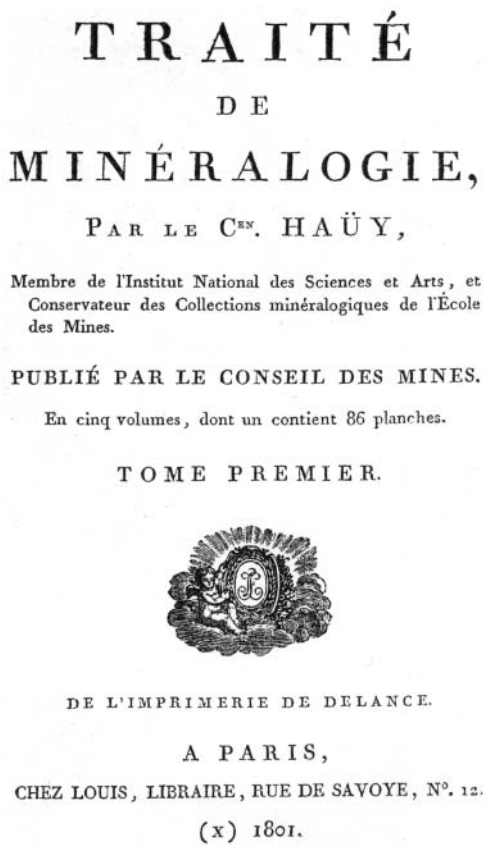
Our presentation of the facts is based on the original texts of the foremost protagonists (Kubbinga, 2009). It greatly profited from consulting John Burke's monograph *Origins of the Science of Crystals* (Burke, 1966) and the collective *Historical Atlas of Crystallography*, as edited by José Lima-de-Faria (Lima-de-Faria, 1990). In matters of symmetry we, moreover, gladly made use of Johann Jacob Burckhardt's *Die Symmetrie der Kristalle* (Burckhardt, 1988).

2. Natural history *circa* 1800: the concept of 'individual'

In various respects the *oeuvre* of Jean-Baptiste Lamarck (1744–1829) serves as a landmark in the history of science of the early 19th century. The French naturalist distinguished himself perhaps first and foremost in the domain of zoology, but his ideas on the relations between the three natural-historical realms have had nonetheless a broader influence. So it happened that one of the supplements to Lamarck's *Recherches sur l'Organisation des Corps Vivants* was devoted to the problem *De l'Espèce Parmi les Minéraux*, in other words, to that of the mineralogical species. In reaction to a claim to the contrary by Daubenton, Lamarck here defends the view that mineralogy, too, knows 'individuals'. According to the author "the individual of each and any mineral resides in its integrant molecule" (Lamarck, 1802, p. 155). The context is such that Lamarck cannot have had in mind something other than the 'integrant molecule' of Haüy, freed, it is true, from some disturbing details, about which more in the following. Haüy had just published his impressive *Traité de Minéralogie*, a textbook that was soon to become a classic in the field and whose atlas was to count among the most wonderful of the 19th century (Fig. 2).

The figures in that atlas are indeed such that the reader gets the impression of seeing, as it were, the 'integrant molecules' piling up themselves, first to constitute the 'kernel' (*noyau*) and next to form the successive indented lamellae, the packing of which upon the facets of the 'kernel' nicely fits the decrescence laws. So the cubic molecules of pyrite first constitute the equally cubic 'kernel', before forming one of the various derived forms, among which is the pentagonal dodecahedron (Fig. 3). The aesthetics, to be sure, are not a haphazard detail: the engravings simply obey the prescripts of descriptive geometry, that almost new branch of applied mathematics that had been brought to maturity by Gaspard Monge (Taton, 1951, 1986), a mathematical advisor of Napoleon. The main argument, comprehensibly, was the correspondence between theory and practice: the outcomes of Haüy's calculations of the interfacial angles of his specially made beech models indeed neatly lined up with those measured from the pyrite crystals of his collection. In his own way Haüy symbolized that alliance of space geometry, crystallography and aesthetics, or more generally, that of mathematics and physics, that was bound to determine the future. Lamarck's words, quoted above, otherwise stress the crucial role of the molecular theory in the natural sciences. Indeed, molecularism was flowering everywhere.


TRAITÉ

DE

MINÉRALOGIE,

PAR LE Cᵀᴱᴺ. HAÜY,

Membre de l'Institut National des Sciences et Arts, et Conservateur des Collections minéralogiques de l'École des Mines.

PUBLIÉ PAR LE CONSEIL DES MINES.

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TOME PREMIER.

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A PARIS,

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(x) 1801.

Fig. 2. Title page of Haüy's *Traité de Minéralogie* (Paris, 1801) (courtesy: University Library Groningen).

An interesting case in point was the doctrine of Déodat de Gratet de Dolomieu (1750–1801), as exposed in a small but insightful tract entitled *Sur la Philosophie Minéralogique et sur l'Espèce Minéralogique*, in which he assessed the basic ideas of his science (Dolomieu, 1801; *cf.* Godant, 2005). The booklet appeared in 1801 and its author is revealed as congenial to Haüy. He underscores for instance, in Haüy's spirit, a number of errors in traditional

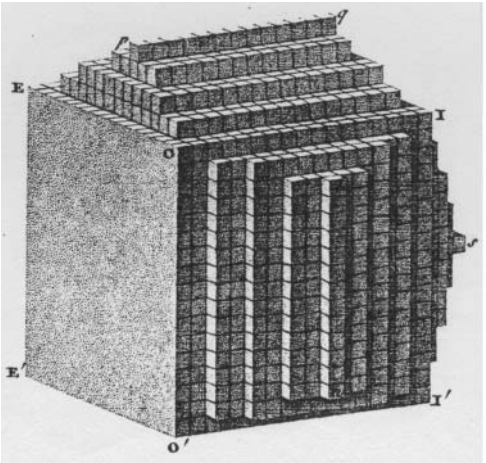


Fig. 3. The piling of the cubic 'integrant molecules' which forms the pentagonal dodecahedron of pyrite. Notice the decrescence of the molecular lamellae in the proportion of 2 : 1, which leads to an interfacial angle at *pq* of 126°52′12″, closely corresponding to that of the empirical crystal, *viz* 127°56′08″ (Haüy, 1801, Atlas).

mineralogy, especially with respect to the identification of 'species'. In a sense, Dolomieu completes the theory of his colleague. He indeed takes all his time to work out the molecular framework of inorganic nature up until the subtlest details. In nature, after all, there is not only the matter of nicely formed polyhedral crystals, but also of the formless materials of the chemists and the geologists, and the pebbles and rocks of the petrologists. In Dolomieu's view, then, the mineralogists commit two methodological errors. The first relates to their predelection to define first the 'classes' and to distinguish only afterwards the 'species' that constitute them. The second error concerns the habit of considering each sample as an 'individual'. When we may believe Dolomieu, "the species only exists in the integrant molecule" (Dolomieu, 1801, pp. 38–39), a tenuous particle that is said to be determined by a fixed chemical composition and by a characteristic geometrical form, the so-called primitive form. There are 'demarcations' between the species, in other words: the species do not imperceptibly transform into each other, but only in a saltatory way, with jumps. The implication is that one of the current classificatory schemes, that of the great 'chain of being', in which the lowest minerals gradually pass into the highest forms of life, is bound to be erroneous (Dolomieu, 1801, pp. 43–44). The 'integrant molecule' is a really 'complete individual'; the question whether or not there exists an 'aggregate' of such 'individuals' is in fact irrelevant, at least in this connection. Such an 'aggregate' is at best a 'collection of mineral individuals', comparable to a bunch of grass or cereal picked from a field by the botanist. So-called pure aggregates are similar to a sheaf of cereal, mowed from a particular field that had been sowed with one particular kind of seed. Undoubtedly one of the cereals – let's say, wheat – will predominate, but the sheaf will surely also contain ears of barley and rye and, of course, weeds. Elsewhere in his tract Dolomieu compares what we would call a 'mechanical mixture' with a mixture of grains of wheat and rye or with a piece of granite, of which the grain-like structure is directly visible to the eye. He is even conscious of the fact that many kinds of substances might remain unknown to us for the only reason that their imperceptibly small 'individuals' have not had occasion to form 'aggregates' big enough to be observed. The professional mineralogist only encounters 'aggregates' and the physical particularities of these add up with the chemical properties of their 'integrant molecules'. It is for this reason that, on the one hand, the 'chemical' existence of a material species is realized in each and every molecule, while, on the other hand, the 'physical' existence depends on the occurrence of an 'aggregate'. Only with this distinction in mind is one at liberty to consider a more or less regularly formed 'aggregate' as an 'individual'. In favorable circumstances the molecules may assemble in a symmetric way, such that the aggregate adopts the form of the separate molecule, or at least an analogous one. Such a pile, Dolomieu writes, may "by metaphoric extension" be considered as an 'individual'. This holds, for instance, for the mineral calc spar. A substance like 'Champagne chalk' (*craye de Champagne*) belongs, it is true, to the same *chemical* species, *viz* lime carbonate, but the *physical* form is principally different. Other deviations derive from lesser regularity in the piling up of the 'integrant molecules' or are due to the presence of other molecules. In the first case they concern 'varieties', in the second 'variations'. In the latter case there are either 'superfluities' or 'pollutions'. 'Superfluities' concern coloring or odoring bodies and sometimes phosphorescent components that are enclosed *inside* the 'integrant molecules' without changing the latters' nature. The transparency of the crystal does not suffer from them and neither do the other properties. Such a crystal, therefore, still is a *pure* one. 'Pollutions' are additions that, during the crystallization process, take place *between* the 'integrant molecules' bringing about important changes in transparency, color, lustre, hardness and density. The result, Dolomieu claims, is always a 'heterogenous body' or, in our words, a mechanical mixture.

Dolomieu concludes with a parallel between living beings and crystals. For crystals, too, it would be true, in a metaphysical sense, that the same produces the same. The observable 'physical individual' reproduces on a larger scale the 'chemical individual', a process in which the 'precision' (exactitude) of nature is far greater than with living beings (Dolomieu, 1801, p. 116).

In summarizing we may contend that Dolomieu provided precisely what lacked with the chemist Lavoisier and the physicist Laplace, to mention only the foremost protagonists of the molecular theory. His notion of the 'mineral individual' is such that the integrant molecule has to be considered as a 'complete' individual. Because of its wealth of details, Dolomieu's booklet is at once highly illuminating of the situation in 1801. Where Dolomieu emphasizes the *chemical* composition of the mineral and reasons from the viewpoint of its molecules as its *raison d'être*, Haüy had gone the other way around. Indeed, in Haüy's view it is only possible to establish something valuable about the integrant molecule when one begins at the level of the aggregate, a procedure implying that crystallographic considerations ought to prevail. As late as 1822, in his *Traité de Cristallographie*, the crystallographical species is defined as a 'collection' of crystals, each of which has to be regarded as an 'individual', that is to say, in the *physical* sense of Dolomieu (Haüy, 1822).

In the following, we propose to study first those aspects that concern chemical composition. Although the 'fixed composition' seemed perhaps self-evident, in view of the specific geometry of the 'integrant molecule', there were nonetheless several most disturbing cases. Dolomieu himself referred to calcareous spar and Champagne chalk, minerals that decidedly represent the same chemical substance, although they have essentially different crystalline forms. Apparently it is possible that one and the same substance may occur in *different* solid states, a fact that is hardly reconcilable with the doctrine of three states of aggregation, that is, incompatible with the very foundation of the physico-chemical molecularism of about 1800. Dolomieu could have mentioned two more forms of lime carbonate, *viz* Icelandic spar and aragonite, crystal species that had seriously worried Haüy. Another nasty question concerned the discovery, in 1819, that the opposite of what we indicated is also possible, namely that *different* substances of an otherwise comparable composition may

adopt the *same* crystalline form. For a chemist like Berzelius this amazing find had important consequences as to the magnitude of the *atoms* of different elements. The two phenomena in question, *i.e.* 'allotropy' – or, more generally, 'polymorphism' – and 'isomorphism', will be discussed in the following section. Next we will consider there the emergence of a mineral individual in the *physical* sense, more or less as envisaged by Dolomieu, that is, by starting from the 'integrant molecules'. Dolomieu had indicated that that process of crystallization proceeds under favorable circumstances "in a symmetric way", such that the growing crystal maintains the 'primitive form', that is, the one of the 'integrant molecule'. In Section 4 we intend to deal with that notion of 'symmetry', its introduction to crystallography and its irresistable advances. So we will see how considerations of symmetry were going to determine the terminology, while enabling at the same time techniques to relate faces and angles among each other, all this against a plainly molecular background. Two schools of thought came up in this context, a French one around Haüy and a German one around Weiss. It was a momentous event, in the autumn of 1895, when Wilhelm Röntgen (1845–1923) discovered a new kind of radiation. In the 1910s the specialists would succeed in finding correlations between the 'photograms' made with the new radiation and the highly abstract fruits of the theorizing in the domain of 'symmetry' by the mathematical crystallographers.

3. Mitscherlich: isomorphism and polymorphism

In Haüy's crystallography the chemical identity of a substance dwells in each and every of its integrant molecules. Such an 'integrant molecule', naturally, cannot but result from particular numbers of the atoms of the various species in question, heaped up in a particular spatial way. For a contemporary chemist like Joseph Louis Proust (1754–1826) this was a capital claim, since it supported his law of definite mass composition of compounds. About 1808, the year of the publication of the first parts of John Dalton's *New System of Chemical Philosophy*, the 'integrant molecule' came close to what might be called a 'substantial individual': it determined the species of the substance in question and was composed of atoms, the form of which was mostly thought of as spherical. Dalton himself went even farther afield and believed all kinds of atoms to be of the same magnitude. This equality was hard to accept for many colleagues who realized that it did not really fit in with the traditional view, held since Antiquity, that atoms are just fragments of one and the same prime matter. Dalton, however, had other concerns; his conviction was based upon the thermal behavior of gases, the cornerstone of his new chemical philosophy.

Dalton's hypothesis was not too bad after all, as became evident at the end of 1818 and the beginning of 1819. The newly converted chemist and crystallographer Eilhard Mitscherlich (1794–1863) – he had been a linguist before – was struck at that time by the equality in form of the crystals of two different compounds of otherwise similar composition: potassium phosphate and potassium arsenate. In Mitscherlich's train of thought, two compounds corresponding in the numbers of the various kinds of atoms could not possibly crystallize without adopting the same geometrical form. On transit in Berlin, in August 1819, while traveling home from Paris, the great chemist Jacob Berzelius (1779–1848) made Mitscherlich's acquaintance. Hearing of his host's most surprising discovery, Berzelius was excited, since it implied the confirmation of his own – and Dalton's! – hypothesis in which the equality in form and magnitude of the atoms was a fundamental idea.

On 9 December 1819, Mitscherlich's find was reported before the Königliche Akademie der Wissenschaften, in Berlin. It by now concerned the crystalline form of the salts of phosphoric and arsenic acid with one and the same series of metal oxides, all featuring the formula $Me + 2\,O$. The acids in question had the formulae $P + 5\,O$ and $As + 5\,O$. In order to express the proper character of the resulting salts it was enough for Mitscherlich to specify the numerical proportion between the oxygen atoms in the oxide, the acid and the crystallization water[2]. So he found for Me = Fe, Cu, Zn, Pb, Co, Ni, Ba and Ca in each case the same crystalline form. Almost in passing he wrote that he used the reflection goniometer, a new instrument deviced by Wollaston, but did not give angle measurements. Small variations in the interfacial angles – up to 2°, to be precise – had been neglected, the audience was told. What Mitscherlich had noticed for phosphates and arsenates appeared to hold also for other groups of salts. His investigations not only included mineral salts, as found in nature, but also new compounds, artificial ones, made in the laboratory, particularly a whole series of sulfates. With *artificial* salts interesting peculiarities showed up. One succeeded, for instance, in bringing them to crystallize together from a solution, the mother liquor, in which case 'double salts' resulted. It was also possible to crystallize a salt upon the crystal of another salt. In both cases there was no change in crystalline form. As such, this phenomenon was not completely new. After all, it was Haüy who had drawn attention to the coexistence of the carbonates of iron and calcium in fossilized shells. The Frenchman had been surprised to see that the iron carbonate that had taken the place of the calcium carbonate in the shell had adopted the crystalline form of the latter (Haüy, 1801, i, p. 140). This was problematic indeed since different salts, with Haüy, ought to have different crystalline forms, almost on principle. In order to save himself from the embarrassing situation, he claimed that it seemed as if the calcium carbonate had put its stamp upon the newcomer. It was a matter of 'crystallization force' (*Krystallisationskraft*), we read in Mitscherlich's paper (Mitscherlich, 1819, p. 431). In normal circumstances iron carbonate always adopts its customary crystalline form, but in the presence of calcium carbonate it subjects itself to that of the latter. In the case of the sulfates something similar was at stake, Haüy believed. A mixture of the sulfates of

[2] Mitscherlich did not use formulae; for shortness' sake we here use those of Berzelius, upon whose chemistry Mitscherlich based his own.

iron and zinc, for instance, always adopts the form of the iron salt; barely 1% suffices. The implication of his reasoning is evident: in all cases where an *impossible* crystalline form shows up, there is in fact a polluting substance in the game, one with a great 'crystallization force'. Mitscherlich, however, was not really convinced by Haüy's evident subterfuge. His own experiments on triple salts, more particularly on the double salts with crystallization water known as the alums, showed that the salts mostly adopt another form, instead of their own, *i.e.* when they are in the pure state. With the pure sulfate hydrates he distinguished otherwise three groups, depending on the quantity of crystallization water: it was a matter of either five, six or seven 'proportions' (*Proportionen*). The sulfates of copper and manganese have five 'proportions' of water, those of iron and cobalt six, those of zinc, nickel and magnesium seven. When preparing double-salt hydrates from equal amounts of the salts in question, it seemed reasonable, then, to expect a hydrate with the *summed* 'proportions' of water. In the case of the sulfates of iron and zinc, for instance, a number of $6 + 7 = 13$ 'proportions' of water could be foreseen. In practice, however, one always found only 12 of these. Similarly, in case of the double salt of iron and copper sulfate one expects 11 'proportions', but finds 12. The conclusion apparently is that in their double salts the sulfates behave differently as compared to the pure state. An appeal to the greater 'force of crystallization' of one of the components thus is in vain, the more so since the alums of copper sulfate (5× water), on the one hand, and equal amounts of either zinc or nickel sulfate (both 7× water), on the other, adopt the same rhombohedral form as the forementioned alums. In the style of Haüy's reasoning, one would feel compelled to conclude that they stick to the form of iron sulfate, even in the *absence* of that salt.

What applies for the double and triple salts of the sulfates probably also holds for the metal oxides present in them, Mitscherlich thinks, all having the formula $Me + 2\,O$. This is no more than a hypothesis on a provisional basis, since one had not yet been able to crystallize those oxides. With oxides of the type $Me + 3\,O$, at least for those of iron and aluminum, though, it is the case that they possess the same crystalline form and produce similar double and triple salts. From the oxides of the type $Me + 3\,O$ to those of the type $Me + 2\,O$, then, is but a small step.

Mitscherlich contented himself with describing his theory and with indicating that it confirms the stance of Berzelius. At the same time he avoided criticising the 'dynamic' crystallography of his colleague in Berlin, Weiss, although he consciously chose the atomic theory instead. At the end of 1819, as the prospective successor to the chemist Klaproth, he was allowed to make a trip to Stockholm on the account of the Prussian government in order to familiarize himself with both the theory and practice of his great example, Berzelius. In the latter's laboratory he was to concentrate upon the salts of phosphoric and arsenic acid. The results were first published in Swedish, later also in French, more particularly in the *Annales de Physique et de Chimie*, the flagship of contemporary natural science. In the French text he called metals 'isomorphous' when a group of similar salts adopted the same crystalline form. It is for that reason that (Mitscherlich, 1821, p. 419):

> "The same number of atoms combined in the same way [produce] the same crystalline form; and that same crystalline form is independent of the chemical nature of the atoms and is only determined by their number and relative positioning."

But there was more at issue. Some of the investigated salts suggested that one and the same substance, depending on the circumstances, could adopt essentially different crystalline forms. The oxides of the type $Me + 2\,O$, for instance, appeared to occur in two groups. One group concerned Me = Ca, Mg, Mn, Fe, Cu, Zn, Co and Ni, the other group Me = Pb, Sr and Ba. These two groups thus also formed two groups of phosphates, sulfates *etc*. and, moreover, two groups of double and triple salts. No other reason could be imagined than the two 'proportions' of oxygen, or perhaps better the two O 'atoms', occupying different positions with respect to the central Me 'atom'. Calc spar and aragonite gave the clue to the riddle: lime carbonate belonged to the first group, aragonite to the second. Calcium oxide, $Ca + 2\,O$, is part of both minerals and the only reasonable difference that could be invented was a difference in position of its three 'atoms'. This oxide in a way bridges the gap between both groups and the reader of the captivating account of Mitscherlich is by now ready to accept the conclusion that the Me 'atoms' of the type $Me + 2\,O$ have to be of the same magnitude. Interestingly, that conclusion had already provisionally been drawn by his host, Berzelius, in the latter's *Essai sur les Proportions Chimiques* (1819).

Berzelius had in fact maintained that *all* atoms, whatever the element, have the same size, in the understanding that small variations are allowed to explain the differences between crystals of comparable composition. Howsoever this may be, Mitscherlich remains silent. It seems as if he grants his host the honor of the practical application. Sure enough, he is conscious of the fact that particular substances may adopt different forms and that this phenomenon as such derives from the properties of the atoms. Before long, Mitscherlich hit upon the interesting case of two forms of the *very same* substance that can be prepared independently and, what is more, could be transformed from one into the other. It concerns sulfur. This, chemically speaking, simple substance – in the sense of Lavoisier – was known to be soluble in carbon disulfide. When such a solution is evaporated, crystals emerge that are perfectly similar to those of native sulfur. When, on the contrary, natural sulfur is melted and the resulting melt allowed to slowly cool down, a wholly new kind of crystal is obtained (Fig. 4). The case strangely resembles that of aragonite and calc spar, or perhaps that of pyrite, of which Berzelius had just found a new, white form (marcasite).

The tenor of Mitscherlich's logic is obviously firm support for the atomic and molecular theory: it is sufficient to imagine an alteration in the piling of the atoms inside the 'integrant molecule' to understand what happens during the interconversion of both kinds of sulfur. With Dalton, Berzelius, and by now also Mitscherlich, most of the theoreticians assessing the nature of matter would endorse, in

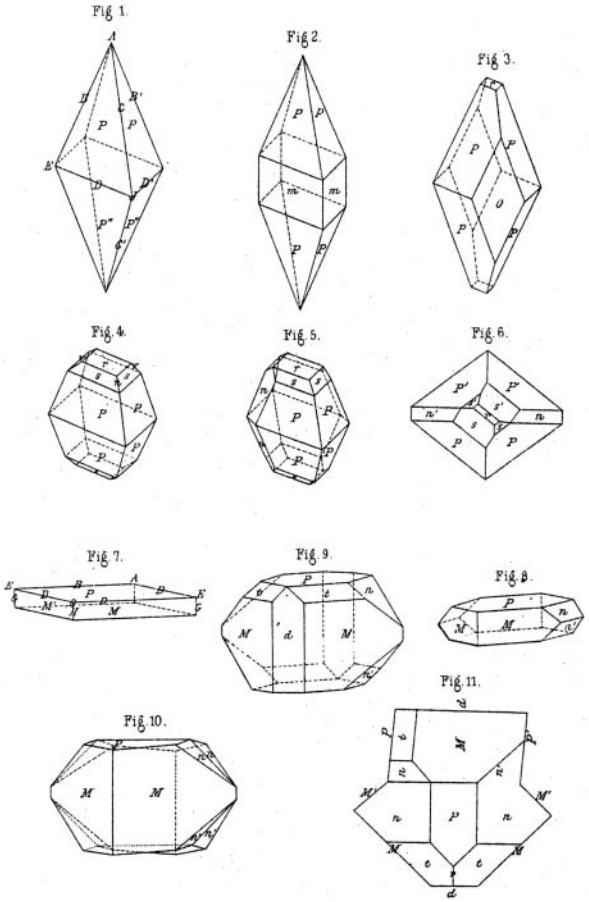


Fig. 4. The two crystalline forms of sulfur and some of their varieties according to Mitscherlich. Nos. 1–6 represent either natural crystals or crystals obtained by evaporation from dissolutions in carbon disulfide. Nos. 7–11 show crystals that emerged from melted sulfur (Mitscherlich, 1896, Table IV). Since Gadolin (1871) they have been known as the 'rhombic' and the 'monoclinic' form, respectively.

the years 1819–1840, the atomic theory and maintain that all atoms are of the same magnitude. The favorite example was the isomorphism of potassium permanganate and potassium perchlorate: where such greatly differing elements like Cl and Mn are interchangeable, there is every reason to suppose that it is a general phenomenon, or in the terminology of the time, a 'law of nature'. When one allows, with Mitscherlich, for slight variations in the magnitude of characteristic angles, from species to species, and that even within one and the same species a change in temperature may bring about small alterations, the idea of the 'integrant molecule' as a specific unit with a characteristic spatial structure seems almost obvious. It is perfectly understandable, in hindsight, that this purely crystallographic notion could contribute to the coming of age of structural chemistry.

The term 'isomorphism' may perhaps come from Mitscherlich: in the particular case of sulfur one was to speak shortly of 'dimorphism'. Carbon and phosphorus[3] appeared to be similar in this respect. Carbon even knows a third mode of existence, that of soot and coal, formless ones, that would be called therefore 'amorphous' (1833).

[3] Red phosphorus was not yet known; it was discovered in 1847 by the Austrian chemist Anton Schrötter.

In his *Jahres-Bericht* of the year 1841 Berzelius was to propose the term 'allotropy' instead of 'dimorphism', if only to indicate that both forms may be converted into each other. The difference between the classical form of pyrite and the new, white one he here attributed to both forms of sulfur: the yellow pyrite was said to contain the one form, the white pyrite the other. Since there was likewise a question of a fixed transition temperature, about 96 °C, Berzelius moreover thought that it concerns a change in the number of sulfur atoms per molecule, eventually a change in their orientation in space. From about 1859 onwards the term 'polymorphism' came into use as a general word for the phenomenon that *compounds* and *simple substances* alike may occur in different crystalline forms. From time to time one realized, with Berzelius, that the chemical phenomenon of 'isomerism', implying the same molecular formulae for different substances, could be something similar. This was the reason that 'allotropy' and, more generally, polymorphism, were sometimes considered as forms of 'physical isomerism'. Implicitly, the doctrine of three states of aggregation is under critique, the doctrine that had been proclaimed the basis of all theory of matter by Lavoisier and Laplace. That doctrine apparently had to be taken as a first approximation, that much was certain by now. The phenomenon of 'polymorphism' or 'physical isomerism' after all seemed to indicate that one and the same substance might occur in not just one, but in various solid states. Anyway, in the debate on the nature of the various solid states of the very same substance one may see the roots of a much more general theory, that of 'phases', the theory that Josiah Willard Gibbs would formulate in the 1870s.

4. The concept of *symmetry*; Haüy and Weiss

The systematic study of the geometry of crystals, launched in the last decennia of the 18th century by Romé de l'Isle, Werner and Haüy, led to considerations about their 'symmetry'. As we will see in the following, this concept stems from architecture. Above we noticed how Dolomieu described the growth of crystals: in his eyes, it was a process that proceeded "in a symmetric way", an expression meant to stress the regularity in the growth. It was not at all a current expression, neither in crystallography, nor in mineralogy. In all probability we owe its introduction to Haüy. At a particular moment the latter came to speak of a 'law'. Ever since, crystal symmetry would be of central importance. Here we will discuss its development in the two foremost schools, the one centering around Haüy, in France, the other around Weiss, in Germany. The two schools were diametrically opposed to each other, particularly as to the standing of the molecular theory; their concept of 'individual' was also different. For both schools the virgin crystal and its outward geometry were perhaps the starting point; the French tried to go back to the constitutive, imperceptibly small parallelepipeda, where the Germans stuck to the 'axes' which could be deduced from the physical and geometrical properties at our level. The French parallelepipeda were just tiny, block-like polyhedra, those of the integrant molecules. These were, it is

true, hypothetical entities but they charmed the imagination and led to interesting associations. Something similar may be said of the German 'axes'. What was called the 'decrescence law' in the one school carried the name 'zone law' or, although somewhat later, 'law of rational indices', in the other. In the course of the 19th century the German school, which was initially decidedly anti-molecular, gradually surrendered to the French crystallography on a molecular footing, the French school estranging itself from the scientific community by a rigid scepticism of a would-be positivistic inspiration. This explains why the great innovations of the years 1876–1891 were put forward if not in Germany as such, then at any rate in the germanophone literature. Before its turn to scepticism, the French school, it is true, would resolve some weak points in Haüy's theory. The English crystallographers generally followed the German example, particularly since William Whewell. As if John Dalton had not been one of theirs, they came to take their distances from the molecular theory, although – let us say, as an apology – they may be credited for having introduced interesting improvements in the German mathematical approach (Sénarmont, 1842).

4.1 The French school

In order to get an idea of what was understood in the 18th and at the beginning of the 19th century by the notion of 'symmetry' it suffices to consult the *Encyclopédie [...]* of Diderot and d'Alembert. The lemma in question is without the name of the author, but a reasonable guess would be that it is a contribution by d'Alembert. It reads as follows:

> "SYMMETRY (Architect.) is the relation, the proportion and the regularity of parts that are necessary to compose a nice whole [...]."

The author adds that the Roman Vitruvius, in antiquity, had argued that between the parts of a whole:

> "there has to be a proportion like that particularly precise one between the arms, elbows, hands, and fingers and other parts of the human body, with respect to each other and to the whole."

In 1795 this idea of 'symmetry' would be applied to the polyhedra of geometry by Adrien-Marie Legendre (1752–1833), one of the professors at the Ecole normale meetings of that year, in Paris. In his *Eléments de Géométrie* he described as 'symmetric polyhedra' (Legendre, 1794, p. 167):

> "two polyhedra that have a basic plane in common and are built in the same way, the one at the upper-side of that plane, the other at the lowerside, in such a way that the homologous solid angles are at the same distance from the basic plane and situated at the same perpendicular through that plane [...]."

Legendre was conscious of the fact that, rather often, polyhedra are 'symmetric' without being superimposable. Later, it was Alexandre Joseph Hidulphe Vincent (1797–1868) who, in his *Cours de Géométrie [...]*, argued that different forms of symmetry had to be distinguished in one and the same polyhedron, indeed not only with respect to a *plane*, as with Legendre, but also with respect to a *point* or with respect to an *axis*. Vincent's proposition implies in practice that both polyhedra of Legendre are to be taken as just one polyhedral whole which, henceforth, is the object proper whose 'symmetry' must be determined.

A first crystallographic application of the concept of 'symmetry' we found in the work of Haüy, more particularly in his course at the Ecole normale. During the first lecture he came to speak in detail about the relation between the 'kernel' of a crystal and the derivative forms that result when the layers of additional molecules are piled up correctly (Fig. 3). Those derived forms are such that they correspond to the simplest decrements, namely with one, two or three ranks of molecules, in the understanding that the decrements on corresponding faces are equal. The word 'symmetry', it is true, was used in his first publication, the *Essai d'une Théorie sur la Structure des Crystaux [...]* of 1784, but it was only in his classes at the Ecole normale that he spoke for the first time of a 'law' (*loi*) (Haüy, 1795, p. 45):

> "[...] the manner in which Nature creates crystals is always obeying to the law of the greatest possible symmetry, in the sense that oppositely situated but corresponding parts are always equal in number, arrangement, and form of their faces."

It is this 'law' that plays in the background of all later publications and was to be proclaimed once and for all in the well known *Mémoire sur une Loi de Cristallisation, Appelée Loi de Symétrie* (Haüy, 1815). In this memoir he otherwise consciously excludes certain crystals, among others boracite and the tourmalines, a group of silicates which, when heated, charge themselves electrically, a process showing the presence of an 'axis' linking the oppositely charged parts of the crystal. Strictly speaking, the presence of such an 'axis' ought to be accounted for in the outward geometrical properties that determine the species.

Apparently it is true that with crystals, although the material distribution in the aggregate is everywhere the same, there may occur a variation in their properties, depending on the direction that one chooses to inspect. In other words: crystals are at once *homogeneous* and *anisotropic*. As early as 1677, this had been considered by Huygens in the context of his search for an explanation of the behavior of Icelandic spar, more particularly its double refraction. At the beginning of the 19th century Thomas Young took the next step; he based his new undulatory theory of light directly on Huygens' results. It gradually became clear that the combination of homogeneity and anisotropy was not at all exceptional. During the course of the 19th century more and more properties were discovered that behaved like double refraction. One may think of hardness, elasticity, thermal expansion, and the thermal and electrical conductivities (Delafosse, 1840, pp. 17–18). Generally speaking, even the cleavages that a crystal admits may be interpreted as expressions of its anisotropy. This holds particularly for those crystals in which exactly one half, one third or one quarter of the corresponding parts of the 'kernel' are at issue. The crystallographers speak of 'homohedry' when *all* faces and *all* angles of a crystal are equivalent. In the same vein, the terms 'hemi-

hedry', 'tritohedry' and 'tetartohedry' referred to cases in which only one half, one third or one quarter of the present faces and angles featured similarly.

The doctrine of crystal symmetry would evolve in France against a background of exclusively *molecular* ideas about the internal structure of crystals. Gabriel Delafosse (1796–1878), a former student and collaborator of Haüy, devoted his dissertations to this subject, dissertations that he defended in September 1840 before the Faculty of Science of the Sorbonne, Paris (Delafosse, 1840). In the principal dissertation he stressed the importance of the notion of 'crystal system', meant to represent the collection of all forms in which a crystal may occur. As such, the unlimited number of possible forms that a crystal may adopt can be reduced to a small number of so-called 'generic forms'. Here the only lead to follow in the deduction of the various forms from each other and their distribution in 'systems' is the 'symmetry law' of Haüy. In particular, the German crystallographers, urged by Weiss, had ventured to derive the first classifications in terms of 'crystal systems'. In so doing they noticed, it is true, the various gradations of symmetry, but they did not dare to present an explanation. So one reads in their works that, often, it occurs that geometrically corresponding parts are also physically equivalent, although this is not always the case. Delafosse refers to the cubic crystals of rock salt as an example: the solid angles, here, are both geometrically and physically identical, since eventual imperfections always occur at *all* eight angles. All diagonals of the faces are equivalent, just like all the edges, while at those edges, the left-hand side is equal to the right-hand side. However, in case of the cubic crystals of boracite, there are two groups of four solid angles, the diagonals being divided into two groups of six; moreover, the diagonals of the same face are not equivalent. The edges are equal, though, manifesting what Delafosse calls 'bilateral symmetry' (*cf.* Figs. 5 and 6a).

Finally, Delafosse alludes to the existence of a third kind of cubic crystals, of which those of pyrite are a good example. A cube of this type may be derived, in the mind, either from the pentagon-dodecahedron by suitable homohedral truncations – that is, on all sides – or from the cube itself by such hemihedral truncations that there results a body with parallel faces. In these instances, all solid angles, all diagonals and all edges are mutually equivalent. The only deviation concerns the edges, which lack that forementioned 'bilateral symmetry'. One glance at a pyrite cube suffices indeed to notice that deviation: on the left-hand side and on the right-hand side of each edge, sets of parallel lines – striations – show up that, although not lying in the same plane, are perpendicular to each other (Delafosse, 1840, pp. 19–20).

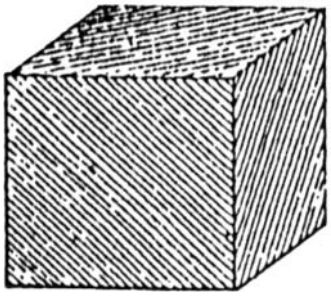


Fig. 5. Cubic crystal of boracite. The sets of parallel lines, the striations, suggest a molecular piling of lower symmetry (Delafosse, 1843).

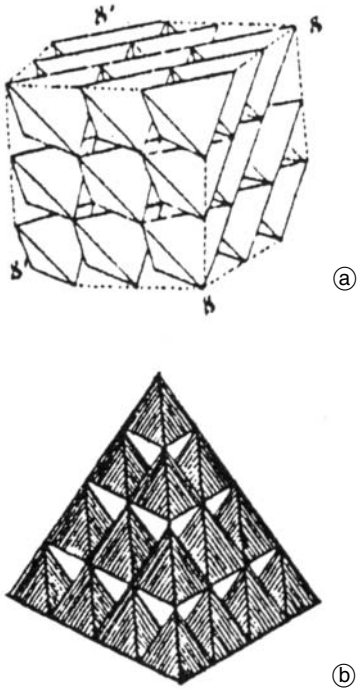


Fig. 6. The 'lattices' (*réseaux*) of the tetrahedral molecules of boracite that constitute either a cube, (**a**), or a tetrahedron, (**b**) (Delafosse, 1843). A packing such that there would result a dodecahedron of pentagons appears to be impossible.

In short, not every cubic crystal is blessed with the maximum of symmetry. More generally speaking one may claim that the same polyhedron, depending on the internal piling of the molecules, manifests different kinds of symmetry and, therefore, pertains to different crystal systems. Consequently, the external symmetry of a crystal has to be carefully distinguished from its internal symmetry, the latter having both physical and geometrical aspects reflecting the molecular structure. Delafosse complains, curiously enough, that of the mathematicians only Legendre and Vincent have taken the trouble to analyze the symmetry of space polyhedra. Howsoever this may be, he continues, the term 'symmetry' is best reserved for the mutual relations between the parts of one and the same whole, thus clearly in the spirit of Vincent (Delafosse, 1840, p. 24):

> "A whole is symmetric when it manifests a particular regular building plan which ordains the arrangement of the composing parts, a condition that implies that among those parts there are some that repeat themselves various times, maintaining in the process the same form and the same value, while occupying also similar positions with respect to a center or system of axes."

Elsewhere, in the second dissertation, he defines as follows (Delafosse, 1840, p. 51):

> "Symmetry [...] is nothing but the geometrical expression of that analogy in form and structure which is so common for natural beings and which has led to the declaration that everywhere one finds back the unity in the variety."

In crystallography this implies that all crystals of a particular mineral may be called 'iso-symmetric'. The maximum of symmetry is realized in those regular polyhedra that are named after Plato: in these, all constitutive parts are of the same kind, in other words, all edges, diagonals, faces and solid angles are identical. In contrast, the minimum of symmetry is manifested by those bodies in which there is no repetition of equal parts at all, that is, in which all parts are unique. Crystals usually position themselves between these extremes and the same holds for their 'integrant parts' and the physico-chemical molecules which compose these[4]. Definitely: as to symmetry, the crystallographer has to proceed down to the molecules. The latter are perhaps still imperceptible as to their magnitude, their 'symmetry' may be determined nonetheless exactly and expressed in a so-called 'representative form'. With rock salt, for instance, the symmetry of the molecule is maximal, *viz* that of the cube. In boracite, on the contrary, the molecular symmetry is that of a regular tetrahedron, while that of pyrite corresponds to that of a dodecahedron of pentagons. That 'representative form' in a way is the 'physical equivalent' of the real molecules.

With the foregoing in mind, the structure of crystals may be deduced in the following way. The observer acts as if he is situated at the center of gravity of one of the molecules of the crystal. Looking around, from that position, he remarks in particular directions 'rows of molecules' (*files moléculaires*), each with determinate quantitative regularities, namely the orientation in space and the mutual distance. The number of directions in which those 'rows of molecules' manifest themselves will be small, all 'rows' of the same direction being equivalent. In the same way the 'planes' may be considered that, filled with molecules, intersect at the point of observation. There thus are three distinct categories: 'molecules', 'rows of molecules' and 'planes of molecules'. Since the molecules possess a symmetry of their own, it is obvious that the two extremities of the same molecular 'row' need not necessarily be equivalent, the 'row' itself, depending on the nature of the molecules, having a 'bilateral', 'trilateral' or even higher symmetry. When the endings of the same molecular 'row' are not equivalent, one could speak of 'polarity': this could be the explanation of that curious phenomenon of thermoelectricity of boracite and the tourmalines, the phenomenon that had defied if not daunted Haüy. What applies for the 'rows' equally holds for the 'planes', that is to say the molecular monolayers: their upper and lower sides may be equivalent or not, depending on the symmetry and the orientation of the molecules.

Delafosse ends up by summarizing the conclusions of his profound reflections on the interior of crystals in seven 'propositions'. The message is unambiguous: the external geometry is insufficient to determine the crystal's species, the physical properties have to be accounted for. The 'species' thus is determined by both the geometrical and physical symmetries, which together derive from the chemical composition of the molecules. The latter we may, for want of well founded knowledge, replace, *in abstracto*, by their symmetry, as carried by their 'representative form'. With emphasis, though, Delafosse remarks that homohedry, hemihedry and tetartohedry are not to be confused. Hemihedry and tetartohedry are not, as the Germans think, imperfect cases of homohedry, but testify to principally different crystalline structures.

It will be the task of the crystallographer, then, to determine the measure of symmetry of a crystal. Delafosse discusses two procedures. The one is a succession of approximations: first one applies Haüy's purely geometrical method, before envisaging the physical properties. The choice of the 'kernel' – named 'fundamental form' in this context – is somewhat arbitrary, Delafosse concedes, but this is said to be unavoidable. The other procedure for the determination of the symmetry is that of Weiss and his school. It consists of choosing a system of axes of appropriate dimensions and angles, and indicating, subsequently, the symmetry properties. It will be a matter of establishing, on the one hand, whether those axes are 'isopolar' or 'heteropolar', and, on the other hand, their numerical laterality (bi-, tri- *etc*.). The latter procedure appears to be the most attractive to Delafosse, although he adds that, as far as he himself is concerned, those 'axes' are more than just geometrical aids that exist only in the mind of the observer: those 'axes' in reality are 'rows of molecules' that exist as such in the crystal.

Next follows a paragraph about the nomenclature of derived crystal polyhedra. The cube with six lower pyramids upon its faces, for instance, is called a hexakistetrahedron, or more simply, as with Haüy, a hexatetrahedron.

The German school had arrived at the recognition of the existence of *six* different systems of axes and thus of *six* crystal systems. Considering the various physical properties, each of these was supposed to consist of many species. Therefore Delafosse divides them into what he calls 'natural groups'. The 'hemihedral' forms of the German crystallographers, for instance, constitute such a 'natural group', along with the 'tritohedral' and the 'tetartohedral' forms. With the tritohedral derivative forms of the cube two of the three pyramidal axes are eliminated; in the tetartohedral group three of the four rhombohedral axes are lacking. The classification, then, ends up with six 'systems': in Delafosse's terminology the cubic, the hexagonal, the tetragonal, the orthorhombic, the klinorhombic and the klinohedral system, roughly in order of decreasing symmetry.

In the *Thèse Supplémentaire* – in 1840, at the Sorbonne, the *promovendus* was expected to defend *two* theses, the *Thèse Principale* and the *Thèse Supplémentaire* – Delafosse underscores the importance of symmetry in the other kingdoms of nature, that of the vegetables and that of the animals. All depends on the notion of 'individual', he deems here. Whether one looks at organic or at inorganic bodies, they always concern either 'individuals' or 'aggregates'. In mineralogy and crystallography the species is concentrated in the physico-chemical molecule which features as the 'individual'. The symmetry of those constitutive molecules therefore determines the crystal structure, of course only if that crystal adopts indeed a regular form. The physico-chemical molecule apparently determines all relevant properties. Such a molecule, in

[4] The 'integrant part' of Delafosse corresponds to the 'subtractive molecule' of Haüy.

Delafosse's sense, thus behaves just like what we called, above, a 'substantial individual'. Anyway, Delafosse next observes that similar considerations apply in zoology and botany, where it is after all also customary to discriminate 'individuals' from 'aggregates of individuals'. Some natural historians, he writes, go so far, conversely, as to conceive of the chemical molecules as living beings, that is, as the smallest possible ones. There is, all the same, an important difference between plants and crystals, he believes: with crystals a rigorous mathematical deduction of *all* possible forms is feasible, with plants this is not the case. In the reasoning of Delafosse, it seems to us, we may see the spirit of the time, since many of his colleagues have searched for an aprioristic mathematization of the science of crystals. In the following we shall indeed have to refer to some of them. Let us conclude provisionally with the remark that Delafosse considers 'fivefold' (*quinaire*) symmetry as a prerogative of the organic realms of nature.

In a tract entitled *Investigations of Crystallization from a Physical and Mathematical Point of View*, Delafosse was to work out his theory (Delafosse, 1843). Performing crystallography without considering Haüy's theory he here compares with performing astronomy in Kepler's way, that is, without making use of Newton's law, which summarizes and explains the heavenly motions. After all, crystallography is not only a mathematical science, but also a physical one. Therefore one has to include the 'integrant molecules' which constitute the 'subtractive molecules', the latter being the building blocks proper of the crystal. Now Delafosse substitutes, in the mind, the integrant molecules of Haüy by their centers of gravity. He speaks of 'material points' which, in the style of his doctoral dissertations, constitute the 'rows' and 'monolayers' that, in their turn, form the crystal. All things considered, a crystal becomes a 'continuous lattice of parallelepipeda'. Haüy's 'subtractive molecule', then, is nothing but such a parallelepipedon, whose corners are occupied by the physico-chemical molecules. Some novelty becomes evident: the small faces of Haüy's 'subtractive molecules' are at once cleavage planes, while in the new theory these planes pass *through* the parallelepipeda. The abovementioned 'law of symmetry' thus not only concerns the external geometry of the crystal but also the physical properties that come to light as soon as the geometrically equivalent parts are compared with each other. In order to be *identical* there should be both geometrical and physical equality. Once again Delafosse stresses that hemihedry, tritohedry and tetartohedry are not to be considered as more or less accidental deviations from homohedry. They represent fundamentally different things, directly related to the molecular structure. An example may illustrate this. Delafosse refers to rock salt and fluorspar which, ever since Haüy, had been attributed to the regular or cubic system, although they never occur in hemihedral forms like the tetrahedron and the pentagon-dodecahedron. Other cubic substances like boracite, panabase (a copper pyrite) and zinc blende (sphalerite), on the contrary, do indeed occur in the tetrahedral form, but not in that of the pentagon-dodecahedron (Figs. 5 and 6). Finally, iron pyrite usually adopts the cubic form, but occasionally occurs as a pentagon-dodecahedron, the tetrahedral form here being completely unknown. To understand why this is the case, one has to inspect the molecules and pay attention to their particular symmetry, which is, naturally, an expression of their physico-chemical properties.

What was perhaps lacking in Delafosse's analysis as to axiomatic rigor was brought in, between 1848 and 1850, by Auguste Bravais (1811–1863), in some conferences before the French Academy of Sciences. As a former *polytechnicien* Bravais had been involved in navy activities before being nominated, in 1845, Professor of Physics at his *alma mater*. His mathematical interest was aroused by the publications of Delafosse and the eventuality of an exhaustive deduction of all forms of point lattices. In his first conference he limited himself to point lattices in the most abstract sense; the word 'molecule' is barely mentioned, and only at the end (Bravais, 1848). In thought, Bravais imagines the emergence of such a point lattice starting from two 'generator points', situated at a certain distance from each other. Both points define a straight line, upon which he next imagines an infinite number of points, all at the same distance from each other. In this way emerges what Bravais calls a 'row', characterized by that constant distance, the so-called parameter. Two of these 'rows' define a plane that may be filled with an infinite number of similar 'rows', parallel to each other and at one and the same distance. When the first points of two 'rows' are linked by a line, then a new 'row' results, more or less inclined to the ones that already exist. When the other points, too, are linked in this way a plane 'lattice' (*réseau*) emerges. A parallel piling-up of such 'lattices' in such a way that the first 'generator point' of the first lattice will line up with the first ones of the others finally produces an 'assemblage' (Fig. 7). In such an 'assemblage' of infinite dimensions with its three 'parameters' and its characteristic angles, the environment of each point, wherever in the 'assemblage', is the same. Bravais takes his 'points' to denote the centers of gravity of the 'molecules' proper, just like Delafosse, to whom he could have referred in this context. Bravais calls them 'summits' (*sommets*).

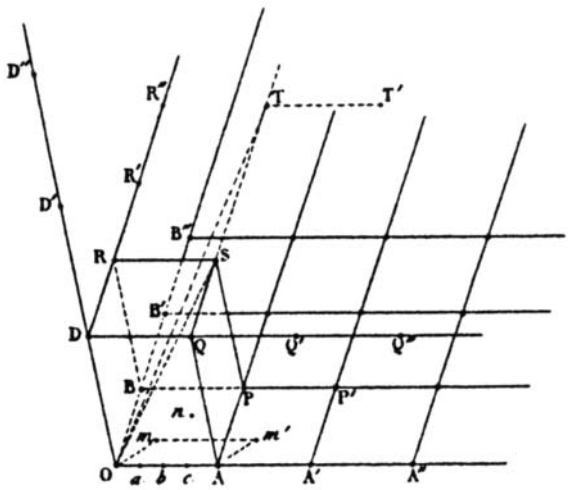


Fig. 7. The emergence of an 'assemblage' of 'integrant points' according to Bravais. The 'rows' $OAA'A''\ldots$, $ABB'B''\ldots$, with 'parameter' OA first constitute a plane 'lattice'. A stacking of such 'lattices' following $ODD'D''\ldots$ produces the 'assemblage' which models the crystal (Bravais, 1848).

Not unlike any other macroscopic object, an 'assemblage' may be moved, either parallel to itself, or by turning it around an axis. When it is shifted in the direction of one of the 'rows' over a distance corresponding to the 'parameter' in question, then each 'summit' will take the place just left by another, such that its environment does not change in the least.

The nature of one and the same 'assemblage' may be further defined by an infinite number of different 'lattices', three of which are to be selected: this troika defines the 'generator parallelepipedon' and at the same time the 'kernel' of the 'assemblage', the 'kernel' taken in the sense of Haüy. When those parallelepipeda are ranked together, the 'assemblage' will be the result.

Generally speaking, within a 'lattice', the choice of a 'generator parallelogram' is completely arbitrary (*OAPB*, *OAP′P* in Fig. 7), although its surface will ever be the same. The 'parallelogram' with the smallest edges, however, is to be preferred. The mean distance of the 'summits' of a 'lattice' will be equal to the square root of the surface of that 'generator parallelogram'. In this connection Bravais refers to Siméon-Denis Poisson, the foremost follower of Laplace, who had introduced the notion of the 'mean distance of the molecules' of a substance: that distance would be the cube root of the volume occupied by one molecule. The experimental determination of that 'mean distance' is perhaps as yet impossible, Bravais argues, but that is at this stage irrelevant. Bravais' innovations hide in the evaluation of the symmetry aspects of the 'lattices' and 'assemblages', successively. To begin with the plane 'lattices', he defines, in Section III, 'axes of symmetry' lying in the 'lattice' plane and of such a nature that a rotation over 180° leads to a coincidence of all 'summits' of both halves, the one upon the other.

Two 'axes' are called of the same kind when their environments are the same and a translation of the one 'axis' with its environment suffices to make it coincide with the other. Therefore, in practice, all 'rows' are at the same time 'axes of symmetry', at least in 'lattices' in which the generator parallelogram is a rectangle.

When one introduces new 'points' at the centers of the right-angled meshes of such a lattice plane, a new 'lattice' is produced with lozenge-like units. Bravais speaks of 'centering'. Conversely, the centering of a lattice with lozenge-shaped meshes produces a right-angled lattice. It concerns the superposition of two 'lattices', of which the one has smaller 'parameters' than the other. The lattice that results from their superposition, therefore, may represent two different kinds of crystals.

When we just simplify slightly Bravais' argument, we may maintain that in case of a square generator parallelogram the lattice plane features four axes of symmetry which, in sets of two, are perpendicular to each other. In case of a regular lozenge generator parallelogram, there are six axes of symmetry: three axes coincide with the sides of the triangles that constitute the lozenge, three others are perpendicular to these.

Reasoning in this way, Bravais arrives at the conclusion that there are, all in all, four 'symmetric lattices', depending on the form of the generator parallelogram:

(1) that of the regular lozenge (six axes, in groups of three equivalent);
(2) that of the square (four axes, in groups of two equivalent and perpendicular to each other);
(3) that of either the lozenge-like or rectangularly shaped parallelogram or its centered version (two mutually perpendicular, but dissimilar axes); and
(4) that of the irregular parallelogram (without any axis).

Bravais continues with propositions about the number of and the relations between the various 'point rows' of one and the same lattice: these concern axes of fourfold or sixfold symmetry, which constitute a bunch of parallel straight lines through the 'summits', and pointing perpendicular to the lattice.

What Bravais first derives for the *two* dimensions of the lattices is next applied to the *three* dimensions of the assemblages. Such an assemblage is presented as a surface of distinct, closed 'carpets' which have zero values in their 'summits'. Bravais next introduces the notation (*hkl*) to characterize a whole of parallel planes within the system of axes *xyz*[5]. For these reasons it holds that if $h = \xi/a = 0$ *etc*. the symbol (001) represents a plane that is parallel to the plane *xy* and situated at a distance $\zeta = +1c$ from it; at the same time it symbolizes all planes parallel to it. If $\zeta = -1c$, one writes $(00\bar{1})$ *etc*.

For a particular assemblage all generator parallelepipeda will have the same volume and it will therefore be important to choose the one with the smallest parameters. The 'mean distance between two summits', then, may be defined, in the spirit of Poisson, as the edge of a cube equal to the unit volume divided by the number of summits per unit volume.

In order to obtain the various so-called symmetry elements in the assemblages, Bravais imagines two mutually identical assemblages, one of which remains at rest while the other may be moved to see in which ways it may be brought to coincide with the first one. The Frenchman considers two possible motions: translation and rotation. Next he distinguishes 'axes' of two-, three-, four- and sixfold symmetry, which reproduce the resting assemblage after rotations over 180, 120, 90 and 60°, respectively. There are said to be just *four* such axes, not more.

Two equilateral axes, of which one is situated in the stationary assemblage and the other in the mobile, are of the same kind if a translation suffices to make the movable axis coincide with the resting one. Finally, there will also be 'planes of symmetry', so-called mirror planes that split the assemblage in two halves, such that each summit on the one side will have a homologous point on the other.

Next follows an analysis of the different forms of what Bravais calls the binary, the ternary, the quaternary, the senary and the terquaternary symmetries, which leads to the following classification of assemblages, more or less in order of decreasing symmetry of the generator parallelepipedon (see Fig. 8):

[5] Bravais, it is true, writes (*ghk*), but since it concerns evidently the 'indices' that Miller had proposed in 1839, we stick to the latter's notation.

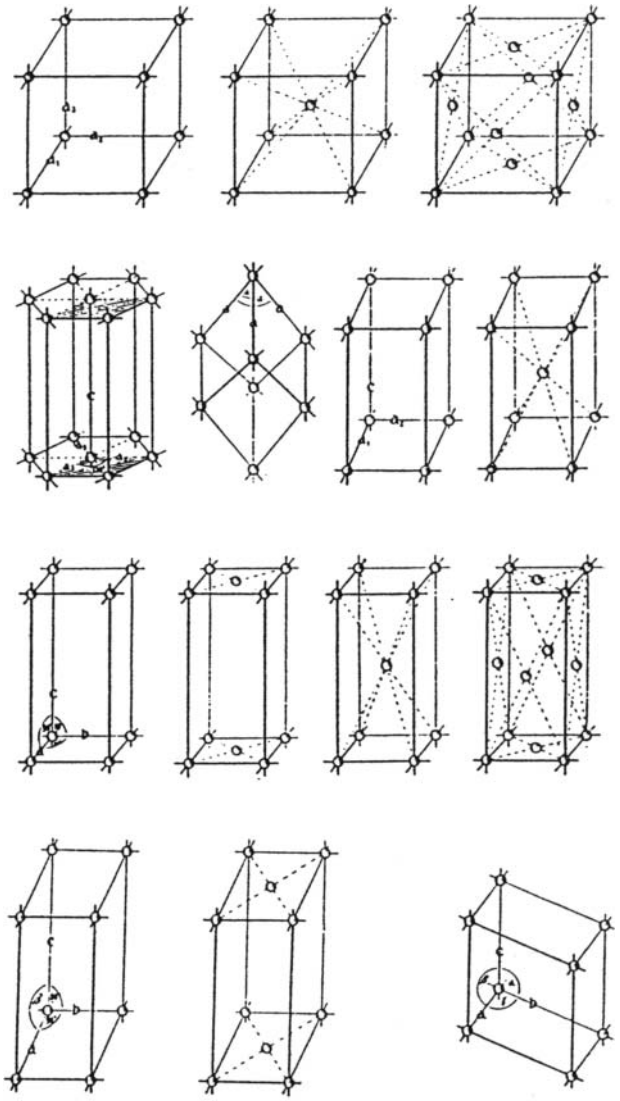


Fig. 8. One of the first graphic representations of the seven crystal 'systems' with their derived 'centered' forms (to be read, from the upper left, in alphabetical order: *a*, *b etc*.). Together they constitute the 14 'space lattices'. When the various 'axes of symmetry' and 'mirror planes' are applied to them, there result 32 crystal 'classes' (source: Niggli, 1920; the order has been adapted to Bravais' deduction).

(1) the terquaternary symmetry (right-angled prism, 8*a*; body-centered cube, 8*b*, and face-centered cube, 8*c*);
(2) the senary symmetry (right-angled prism with an equilateral triangle as base, 8*d*);
(3) the quaternary symmetry (right-angled prism with a square base, centered, 8*g*, or not, 8*f*);
(4) the ternary symmetry (rhombohedron, 8*e*);
(5) the terbinary symmetry (right-angled prism with a rectangle as base, centered, 8*i*, or not, 8*h*; right-angled prism with a lozenge as base, centered, 8*k*, or not, 8*j*);
(6) the binary symmetry (right-angled prism with a parallelogram as base, centered, 8*m*, or not, 8*l*);
(7) without symmetry (inclined prism with a parallelogram as base, 8*n*).

On reaching the end of his considerations, Bravais emphasizes that the new doctrine is not just a geometrical speculation, but nothing other than the true foundation of crystallography. Ever since Haüy, he writes, one has implicitly or explicitly deemed that the centers of gravity of the molecules in crystallized materials are distributed like the 'summits' in the assemblages of points. His aprioristic theory is confirmed retroactively by an inspection of all available crystals, of which it is known that there are six different classes of symmetry and one class without any. At last, we read, all derives from "the polyhedral or, if you please, polyatomic form" of the molecule proper, which determines the symmetry of the assemblage. It is also that form which determines, ultimately, some peculiar phenomena, such as for instance that of isomorphism as discovered by Mitscherlich, and moreover some cases advanced by Delafosse in which the physical properties co-determine the symmetry (hemihedry, tritohedry and tetartohedry). 'Twin crystals' (*macles*), too, are important. These are very meaningful deviations, like those dovetailed crystals of gypsum or the cross-like crystals of sodium thiosulfate. Although the 'polyatomic form' does not directly make clear how the dimorphism of, for instance, sulfur, ought to be understood, it shows nonetheless that it is something fundamentally else when compared with the chemists' isomerism.

Bravais would publish three follow-up articles in 1851. The first of these treats the crystal as an assemblage of points. The second is somewhat more concrete in the sense that the crystal is now presented as an assemblage of polyatomic molecules. The third one, to conclude, deals with some peculiar cases, *viz* 'twin crystals' in general and their hemitropic forms in particular. It suffices here, for our purpose, to observe that the titles of these three publications bear testimony to the fact that the 'points' of the new crystallography are indeed meant as the classical molecules of physics and chemistry. The elegant deductions of Bravais would be crowned by a systematic investigation of the precise nature of the phenomenon of symmetry and of all thinkable 'symmetry elements', of which we have mentioned already the axes and the mirror plane. Somewhat later, one realized that a combination of particular 'symmetry elements' sometimes has the same effect as just *one* other. In the event it thus became an interesting challenge to find out, conversely, which combinations apply. In 1868, such combinations of determinate 'symmetry elements' were baptized 'symmetry groups' by the French mathematician Camille Jordan (1838–1921). According to the theory of Jordan, which was proposed as an exhaustive analysis of Bravais' crystallography, the number of such 'groups' had to be, from a mathematical point of view, essentially limited. The crystallographic consequences of this 'group theory' would be elaborated by some theoreticians, a development that came to an end in the 1890s. We shall come back to this below in Section 5.

The moment has come to leave France and to cross the Rhine to the other focus of crystallographic and mineralogical interest in the notion of 'symmetry'. Let us conclude therefore by putting on record the fact that, at the end of the 19th century, French crystallography began renouncing the molecular theory. One of the latest great theoreticians of 'symmetry', Pierre Curie (1859–1906), had to note this, much to his regret, in some *Remarques sur la Cristallographie [...]*, an article published in 1893. On that occa-

sion he argued that the molecular hypothesis, which had been so fruitful in the physical gas theory and in stereochemistry, enabled one moreover to work out the most general and complete analysis of crystalline structure in the context of the crystallography of Bravais and Jordan, and so in such a way that it was possible to account *afterwards* for the geometrical exterior (Curie, 1893). The reader, then, expects Curie to conclude that only to his own disadvantage the crystallographer could deny himself the practice of such a useful tool. Curie, however, does not go that far, although he appears familiar with the recent work of the principal theoreticians (Sohncke, Fyodorov and Schoenflies). He could perhaps have been somewhat more spirited in his defense of the molecular approach, in our opinion. Curie's aloofness seems at any rate supplementary evidence for the existence of an atmosphere of scientific arbitrariness in France, an atmosphere that was maintained by Marcelin Berthelot, the mighty chemist who had made a speedy career in politics and who, once minister of national education, would abuse his term to enforce his own scientific ideas upon the French high-school and university curricula. Some of Berthelot's scientific contemporaries, however, were courageous enough to publicly oppose his ideas. In particular, the organic chemist Charles Friedel (1832–1899) may respectfully be mentioned in this connection.

4.2 The German school

Generally speaking, the concept of symmetry has been very fruitful in the German mineralogical and crystallographical tradition, although in quite another way than in the French one. The Germans more particularly assessed the outward geometrical appearance of the crystal, just as it presents itself to the observer. From 1815 to 1830 various attempts aiming at an exhaustive classification of the crystalline forms using this key concept had already been reported. The great inspirator was Christian Samuel Weiss (1780–1856), although his personal contribution was a rather limited one. It was Moritz Ludwig Frankenheim (1801–1869) and Johann Friedrich Christian Hessel (1796–1872) who first realized that, notwithstanding the seemingly endless disparity, there are limits as to the geometry of crystals, and that a rigorously strict deduction of the distinct possibilities in terms of symmetry was a feasible enterprise. This concerned here deductions wholly different from those of Haüy. The latter had focused, it will be recalled, upon the number of secondary forms within the same species, a number that he calculated on the hypothesis that the number of allowed decrescences was itself limited. So we know, for instance, of detailed calculations on calcareous spar. However, according to his successor Delafosse – as an acknowledged authority endowed with a subtle feeling for historical justice – the German crystallographers promulgated a generalized doctrine and a complete classification at a moment when his boss, Haüy, busied himself with adapting the facts to his theory and lost himself at last in ever more detailed distinctions.

We here propose to give a general account of the crystallography of Weiss and his school, a crystallography that was based on the notions of 'axis', 'zone' and 'symmetry'. Weiss had studied medicine, chemistry and physics under Klaproth, in Berlin. There, in Berlin, he had made the acquaintance of Dietrich Karsten, the Director of the Royal Mineralogical Cabinet, who suggested him to translate Haüy's *Traité de Minéralogie* that had just appeared from the press. Weiss was enchanted and aquitted himself with full honors of the task. He not only made a faithful German rendering of the text, but added an extensive commentary, more particularly an assessment of the precise nature of the crystallization process. In that commentary he rather sharply criticized Haüy's views, proposing instead a theory of his own, in which the 'idealism' of what we named *Naturphilosophie* in the foregoing prevailed. Weiss even visited Haüy in imperial Napoleonic Paris; that was in 1806. In the French capital he also made the acquaintance of Claude Louis Berthollet, the leading French chemist, and of Jean-François-Marie Brochant de Villiers (1772–1840), a mineralogist who, later, was to translate Weiss' doctoral dissertation into French. That thesis was entitled *De Indaganda Formarum Crystallinarum Charactere Geometrico Principale*, which we may translate here as *On the Principal Geometrical Character of Crystal Forms that Ought to be Studied.*

In this dissertation, read in 1809 on the occasion of his nomination as Professor of Physics at Leipzig, Weiss first acclaims the work of Haüy and Romé de l'Isle before exposing the headlines of the theory of the integrant molecules (Weiss, 1809). Next he deals with the geometry of the various polyhedra: there is a section on the regular sexangular prism, others are devoted to parallelepipeda in general and the rhombohedral one in particular. In the second part of the dissertation, about the physical aspects of the crystallization process, Weiss introduces the notion 'axis' (Weiss, 1809, p. 42):

> "An axis [...] is a line that dominates the whole of the crystal form and around which all parts are uniformly arranged."

The emergence of a rhombohedron, an octahedron or another of the fundamental forms, then, may be explained as the consequence of the differences with respect to such an 'axis' between upper and lower parts, on the one hand, and between lateral parts, on the other. In practice there appear to exist different 'axes' which characterize those fundamental forms. In Weiss' words they refer to (Weiss, 1809, p. 44):

> "the directions in which the forces principally work that impose themselves when [it is time that] a form is produced [during the crystallization proper]."

When one observes, to be more concrete, an oversaturated solution that is cooling down, initially nothing occurs. At a particular moment, however, a first little crystal shows up, Weiss continues, and the observer witnesses a growth process in different directions. These directions are straight lines that indicate where the planes will appear that together will constitute the fundamental crystal polyhedron. Mostly, the numerical ratio between such 'axes', and therefore, Weiss believes, between the 'forces' involved, are not expressed in integral numbers, but seems to concern square roots. The author, enraptured with his

own train of thought, next asks himself more or less rhetorically whom of his readers, in this context, would not directly think of Kepler's laws. This reference is not elaborated, but probably concerns only Kepler's third law, the one that stipulates that the ratio of the square of the time of revolution of a planet to the cube of its mean distance is a constant. It might be indeed, Weiss continues, that one of the forces obeys a square-root law, the other following a cubic root. "Why not, indeed?" the reader might ask the author. The necessary measurements and calculations remain in the dark, however. Weiss carefully avoids entering into such nasty details, but nonetheless does not refrain from triumphantically claiming (Weiss, 1809, p. 46):

> "What would one say when it becomes evident that the same forces that regulate the distances and the motions of the planets henceforth also determine the formation of terrestrial matter?"

All things taken together, the benevolent reader understands the despair of Delafosse before such texts full of question marks and overflowing with "idle subtleties" and "vague and obscure explanations" (Delafosse, 1843).

In 1814 Weiss was perhaps still a supporter of 'dynamism', the doctrine of forces current in *Naturphilosophie*, rejecting in the same mood Haüy's molecular theory; his style and outlook, though, had greatly changed. In his *Surveyable Presentation of the Various Natural Divisions of the Crystallization Systems*, a lecture dated 14 December of that year, before the Royal Academy of Sciences of Berlin, he only gives a new principle of classification, that of the crystal 'axes' (Weiss, 1814). The simplest case is that of three identical and mutually perpendicular axes, Weiss begins; the 'system' in question is called the 'spherohedral'. The basic forms are the octahedron, the cube and the lozenge-dodecahedron. When upon the faces of these forms pyramids are placed, derivative polyhedra are obtained composed of equal facets. Generally speaking, the number of facets of a convex polyhedron will not exceed 48. Enlarging the number of facets produces polyhedra that come closer and closer to the circumscribed 'sphere'; hence the name 'spherohedral' for the 'system' as a whole. Mostly, all faces are equally well developed, but there are also crystals which feature only half of the expected number. When all faces are similarly present, the crystal is called 'homospheroidal'; when only half of them are there, the crystal is named 'hemispheroidal'. The latter group may be further divided into tetrahedral and pentagon-dodecahedral forms.

In the other 'systems' at best two of the three axes are the same, one of the 'systems' being characterized by four axes. In the latter case, three of the axes are situated in the same plane and cut each other at one point, making angles of 60°; the fourth axis passes through that point and stands perpendicular upon the plane of the other three.

Weiss' classification is at once semi-empirical and rigorous in the sense that it takes into account what is found in nature before deducing which 'systems' correspond to those data. In the long run it was to take the place of Haüy's more intuitive division. In fact, Weiss' classification is essentially still the current one. It concerns the simplest cases of Fig. 8, more precisely the uncentered forms. When the three axes are equal and mutually perpendicular, we have the 'regular' system (Fig. 8*a*–*c*). When two are equal and the third deviates, we have the 'tetragonal' system (Fig. 8*f* and *g*). When all three axes are different, but nonetheless mutually perpendicular, the system is called 'orthorhombic'. Inspection of the angles teaches the following. One of the angles may be unequal to 90°, but also all three of them: this applies for the 'monoclinic' and the 'triclinic' system, Fig. 8(*l*) and (*m*), respectively, and 8(*n*). In the case of four axes, the fourth, perpendicular one is the foremost: when it is equal to the three others, then we have the 'rhombohedral' system, if it is unequal the system in question is called 'hexagonal' (Fig. 8*d*). For clarity, we use modern nomenclature (which stems from Axel Gadolin; see below), although the derivation was that of Weiss.

Later, in 1817, Weiss would attempt to denote more exactly the faces of a crystal. Haüy had related them to the 'kernel'. A new face, for instance, was always defined in terms of its decrescences with respect to the 'kernel' face in question. Weiss objects to this view, maintaining that one and the same facet sometimes may result from different decrescences, while the converse, *viz* that different faces are defined by the same decrescences, may also occur. In his view it is better to define faces with respect to a system of axes and to completely abandon the notion of 'primitive form' or 'kernel', since then it suffices to indicate the ratio of the segments cut from those axes in a rectangular system by the faces. In a system of three axes a facet of an arbitrary octahedron may be symbolized by the ratio $a:b:c$. When two axes are equal we get $a:a:c$ for the octahedron with a square as cross section. In the very same way $a:a:a$ symbolizes a plane of a regular octahedron. Each arbitrary plane may be summarized as such. So $a:b:\infty c$ symbolizes an arbitrary plane parallel to the c axis, while $a:\infty b:\infty c$ stands for a plane perpendicular to the a axis. To indicate the various octants of an orthogonal system of axes Weiss proposes the use of primes: a', then, is situated opposite to a and the plane symbolized by $a':b':\infty c$ thus is opposite and parallel to the plane $a:b:\infty c$. In this way, a group of planes parallel to one and the same axis and cutting each other in parallel lines may be recognized, on paper, by the proportions that hold for them. Such a group of planes has a particular status in the context of Weiss' approach. He speaks of a 'zone'; the common axis is called the 'zone axis'. In a particular crystal 'system', then, the wholly determined 'zones' of the primitive form define, together, the in principle possible secondary facets and in so doing the secondary 'zones'. Each and every polyhedron now can be characterized by a combination of such proportions. In the 'regular' or 'cubic system' it suffices to specify just *one* face; the proportion $a:a:a$, for instance, symbolizes not only one face of the regular octahedron, but at the same time that octahedron as a whole. This new approach of crystallographic polyhedra presumed that there ought to be a geometry in which the interfacial angles are brought in relation with the characteristic proportions of the faces. Weiss himself hinted at this possibility in an arti-

cle of 1820. His student Franz Ernst Neumann (1798–1895) would expand the idea. In 1823, Neumann's *Beiträge zur Krystallonomie* had appeared. Three years later he passed the PhD under Weiss on a dissertation entitled *De Lege zonarum [...]* or *On the Zone Law [...]*. Neumann not only proposed some improvements in the calculations of his supervisor, but seized the opportunity to derive from them two graphical methods, so-called projections, to summarize the spatial relations of the facets of a crystal species in one single characteristic scheme. We will discuss his procedure using vesuvianite, $Ca_{10}(Mg,Fe)_2Al_4[(OH)_4(SiO_4)_5(Si_2O_7)_2]$, as an example (Fig. 9).

Such a crystal may be conceived of as a polyhedron that emerges when families of planes of well defined 'zones' happen to intersect: each facet of such a crystal, then, is determined by the intersection lines of the families to which it belongs. The idea is now to represent the polyhedron as a whole in a projection scheme. Therefore we imagine ourselves in the middle of the crystal that is to be characterized, at a point upon the principal axis. Then, we displace all the planes of the facets of the crystal in a parallel way such that they pass through that point. These planes will intersect a so-called projection plane, above the crystal and perpendicular to the principal axis, in straight lines. So the group of facets parallel to the principal axis, which constitute a 'zone', will become visible upon the projection plane as a fan of lines through the center of the projection. Other 'zones' show up as arrays of parallel lines. In the scheme that results (Fig. 10) the intersection points of two 'zone lines', indicated by small circles, symbolize a plane that belongs to both 'zones' at the same time.

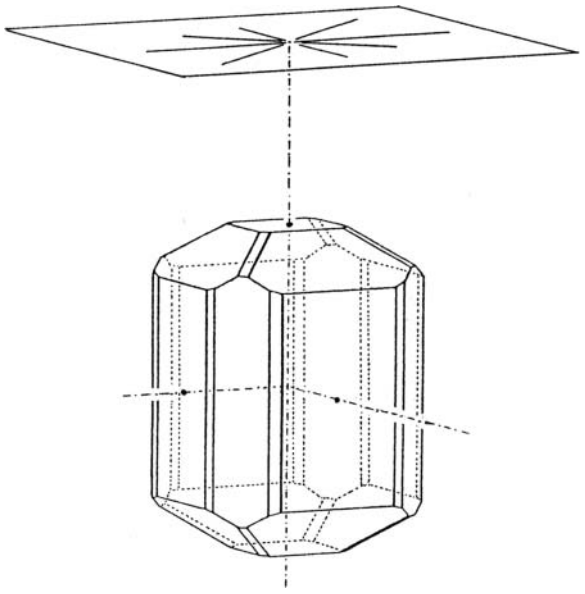


Fig. 9. The technique of the 'linear' projection of Neumann illustrated using a vesuvianite crystal as an example. We choose a system of axes including the principal one, such that the origin coincides with the center. The principal axis is simultaneously the 'zone axis'. Then we move all the facets parallel to it – facets that together constitute the 'zone' – such that they pass through that 'zone axis'. Obviously, parallel facets will coincide. The displaced planes cut the horizontal projection plane above the crystal in the form of a fan-shaped star through the intersection point of the 'zone axis'. The other 'zones' that determine the nature of the crystal manifest themselves as groups of parallel lines. Since, in our case, the a and b axes are equivalent, given the geometry of the vesuvianite crystal, we use two a's in characterizing the proportions. In the indicated fan we therefore find back the intersection lines of the following facets: $a:\infty a:\infty c$, $a':\infty a:\infty c$, $\infty a:a:\infty c$, $\infty a:a':\infty c$, $a:a:\infty c$, $a':a':c$, $a:a':\infty c$ and $a':a:\infty c$.

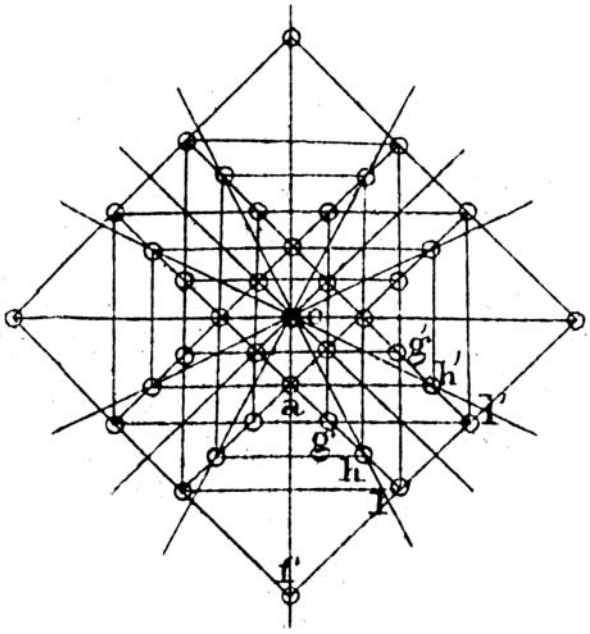


Fig. 10. The 'linear' projection of a vesuvianite crystal made by Neumann (Neumann, 1823, Table IV).

The distances between the lines of a particular 'zone' naturally reflect the magnitude of the corresponding interfacial angles *etc*. This graphical technique for representing the proper nature of a crystal species was called 'linear projection' by Neumann. He merely outlined it in his treatise of 1823. Later it was elaborated by Friedrich Quenstedt (1809–1899).

Neumann's second method for characterizing a crystal species was named the 'spheric' or 'stereographic' projection. The crystal in question is imagined at the center of a great sphere, such that both centers coincide. Then perpendiculars are drawn from that center upon the facets of the crystal; they are extended until they cut the sphere (Fig. 11). Next, the intersection points at the sphere are connected with the sphere's south pole. The connecting lines will pass through the equatorial plane, which is to be used as the new projection plane. The facets of one and the same 'zone' will feature on the sphere as dots upon a great circle, a circle that, in the projection plane, will narrow down to an ellipse around the center.

The ellipse in question, then, will be more flattened the closer the 'zone axis' approaches to the horizontal plane, and more circular the closer the 'zone axis' is to the principal axis (Fig. 12). This 'spheric' or 'stereographic projection' has the advantage that all crystal facets appear finally as dots within the equatorial circle; in a 'linear projection', by contrast, some facets may in particular cases escape from the paper surface as used for the diagram. It is worth mentioning, finally, that each triangle formed by three projection dots is related to a spherical triangle on the enveloping sphere, which, in its turn, refers to crystal

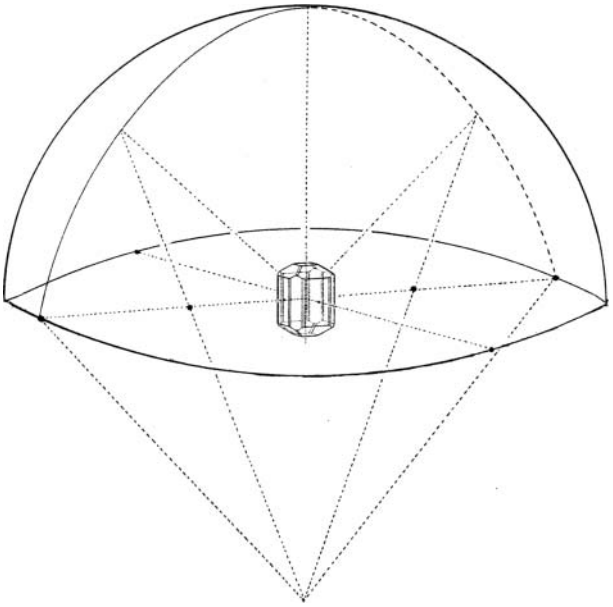


Fig. 11. The 'spheric' or 'stereographic' projection technique of Neumann applied to a vesuvianite crystal. The perpendicular drawn from the center upon a facet (or upon the plane in which it is situated) meets the circumscribed sphere at a point, which is, subsequently, linked to the south pole of the sphere. This produces a dot in the circular projection plane defined by the sphere's equator.

facets that come together in a trihedral angle. It is hardly necessary to say that Neumann's ingenious examination markedly simplified both research and education in crystallography. The experienced crystallographer got a handy new tool at his disposal to characterize known crystal species and to wholly identify newly discovered ones, while the student had fewer problems in bridging the gap between mostly familiar, classical stereometry and the new world of crystalline polyhedra. It is important, then, that the crystal-specific scheme be determined as accurately as possible, such that, during practical fieldwork, it could be used for the identification of either disformed or incomplete specimens. After all, on expedition in the field, the measurement of a limited number of interfacial angles suffices to see whether there are one or more zones and next to calculate the direction of the 'zone axis' or 'axes', which at once provides the numerical proportion between the crystal axes. In practice this implies that the geometrical nature of a crystal and the 'system' to which it pertains may be easily established. An investigation of the physical properties, then, makes up the last step in the identification of a crystal.

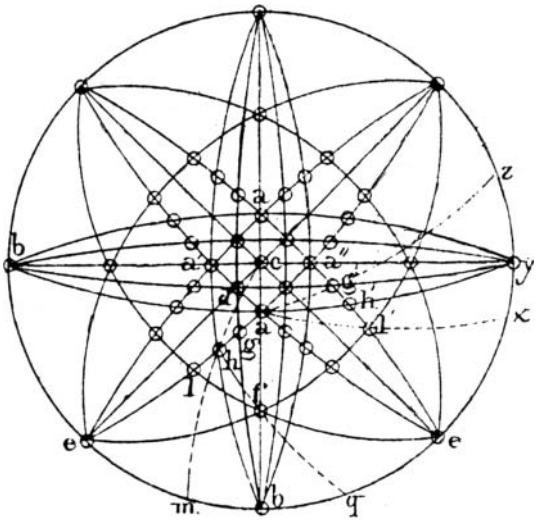


Fig. 12. The 'spheric' or 'stereographic' projection of a vesuvianite crystal according to Neumann (Neumann, 1823, Table IV). Each crystal facet is symbolized by a tiny roundel – the dots of Fig. 11 – either upon or inside the projection circle. The roundels of one and the same 'zone' all lie either upon that circle, or upon an ellipse of varying width. For simplicity's sake these ellipses are represented by cutting arcs of a circle.

For the most part, the identification of a mineral hardly posed a problem, but there remained some difficult cases. Above we have already mentioned the reticence of Gabriel Delafosse before what was called 'hemihedry'. The Frenchman had felt obliged to explain this phenomenon in terms of molecular symmetry; others had tried to interpret it by elaborating the concept of symmetry on the macroscopic level, that of the outward appearance of the crystals. History has handed over to us a number of successful attempts, but most unfortunately these passed unnoticed and were largely forgotten long before they could bear fruit. We mean the attempts of Frankenheim (1826) and Hessel (1830). These crystallographers deduced, more than twenty years before Bravais, the different crystal 'systems' and their principal subdivisions on the basis of macroscopic considerations. They arrived, indeed, at seven 'systems' as the heading under which the 32 crystal 'classes' could be summarized. In order to give an impression of such a deductive approach we would like to reproduce here the main line of that of Hessel. Hessel's technique is the more interesting because he, unlike the adherents of the 'dynamism' in the spirit of Weiss, was not in principle opposed to the molecular theory. To this adds the fact that he chose Haüy's 1815 article on the role of symmetry as his starting point: he himself had taken care of a German translation. For that reason, he, Hessel, could have been useful as some kind of *trait d'union* between the German and French crystallographic communities, if not between France and the rest of the world. On this point, too, Delafosse appears an equally trustful and righteous witness where he maintains that the molecular theory, as if it were a French monopoly, divided the crystallographic world into two camps. It is indeed remarkable to notice that Great Britain which, at the beginning of the 19th century, had had in Dalton a most impressive partisan of the molecular theory, was to join the German school. William Whewell (1794–1866) and his successor, since 1832, in the Chair of Mineralogy at Cambridge, William Hallowes Miller (1801–1880), for instance, profiled themselves preferably in the German tradition, that of Weiss, Neumann and Mohs. Hessel thus could have brought about, when we may again believe Delafosse, the long expected synthesis (Delafosse, 1840). However, in Delafosse's eyes, the notation that Hessel used to express his ideas was so bizarre and his language so abounding with neologisms that but few people were able to follow him.

Hessel developed his views in an article entitled *Krystal* that was to be published in the multivolume *Physikalische Wörterbuch*, edited by Johann Gehler (Hessel,

1830). The article opens by mentioning that the abstract study of space figures is but a young science, whose foundations have not yet been fully explored. Then Hessel discusses the peculiarities of plane figures with respect to a line perpendicular to the plane under consideration. If the situation is such that a particular figure p may adopt different positions with respect to such an axis, the result is a "plane system of rays of p members," p being 1, 2, 3, 4 or 6. To this one can add that a figure with p members may be identical, or not, to its mirror image. The relation between three-dimensional objects may also be described with respect to such an axis, which is in practice a 'rotation axis' (*Umdrehungsnormale*).

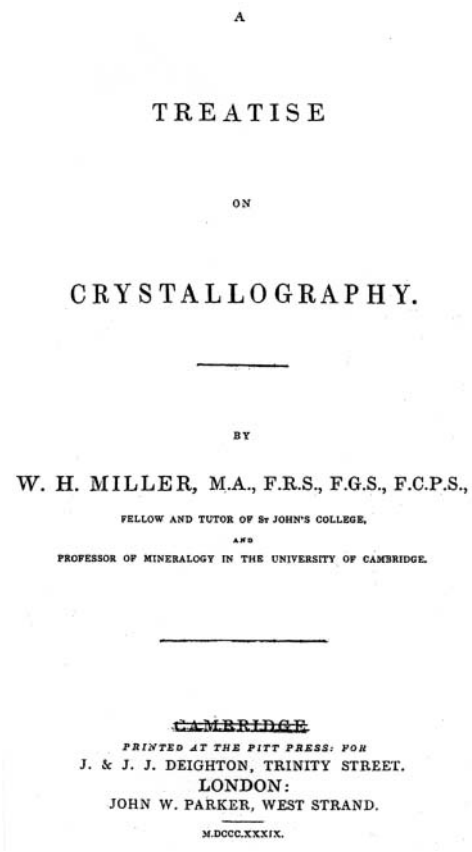
When the two extremities of an axis of order p are equal, but not each other's mirror image, then such an axis is called 'bifinal and conformal' (*ebenbildlich 2endig*). In the first case it may be either 'equipositional' (*gleichstellig*), or not. When such an axis happens to be 'equipositional', then both endings are not only 'conformal' but also each other's mirror image, or only each other's mirror image without being 'conformal'. When, on the contrary, the axis is not 'equipositional', then there are three possibilities for both extremities, namely:

(1) they are only each other's mirror image;
(2) they are both each other's mirror image *and* conformal; or
(3) they are only conformal.

Finally, if such an axis of order p is 'bifinal and conformal', both endings may be exchanged or not.

The subdivision of the space polyhedra that results embraces, to a first approximation, *two* groups, of which one is characterized by four axes of order 3 and the other by ten axes of order 3. The first group has five subgroups, of which No. 1, for instance, corresponds to the so-called 'spherohedral' or regular crystals of Weiss. The other group, with its ten axes of order 3, has two subgroups. All in all, we thus have *seven* subgroups, neatly corresponding to the crystal 'systems' of Weiss, and superimposed – because of the rationality of the axis' order, p – a further subdivision in 'classes', making a total of 32.

The considerations of Hessel concern first of all the space polyhedra in general. It is only in a second approximation that they focus upon the natural, that is, the crystalline, polyhedra. The symmetry elements made use of are the mirror plane, the inversion point, and the rotation axes of order 1, 2, 3, 4 and 6, just like in Bravais' later approach. The successors of Bravais will, still later, try out all possible combinations of symmetry elements, a development that would culminate, in the 1890s, in a complete solution. In the interim, one of the projection methods of Neumann, the 'stereographic' one to be precise, was to be expanded by Whewell's successor at Cambridge, Miller, in the latter's *Treatise on Crystallography* (Fig. 13). Miller understood that Neumann's techniques enabled the application of spherical trigonometry to indicate the relative positions of the crystal facets and to relate these with the interfacial angles in question (Miller, 1839). For reasons of simplicity he substituted those interfacial angles for the angles between the perpendiculars on the facets involved; the two angles are complementary, so there is no problem. What counts in this mode of projection are just those perpendiculars and


A

TREATISE

ON

CRYSTALLOGRAPHY.

BY

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Fig. 13. Title page of William H. Miller's *A Treatise on Crystallography* (1839) (courtesy: University Library, Leiden).

their intersection points on the enveloping sphere, the latter determining the dots in the plane of projection.

Miller also introduces a new system to indicate the particularities of crystal facets in a suitably chosen system of coordinates *xyz* in an equally short and practical way. That system of coordinates simply concerns the three intersection lines of three groups of either mutually parallel crystal faces or potential cleavage planes. The relation between two facets, the cleavage planes included, then, may be expressed in proportions such that a plane parallel to one of the groups of planes of the system of coordinates gets the 'index' 0 for the third axis instead of ∞ (Fig. 14). In this way, for example, a Weiss or Neumann proportion could be transformed into a triplet of *indices*.

A plane that, with Neumann, would be indicated as $1a:1b:\infty c$ is converted by Miller into $a/1:b/1:c/\infty$ before being abbreviated and written down between brackets as (110). In the same way $2a:1b:\infty c$ first becomes $a/2:b/1:c/\infty$, before being multiplied by 2 – giving $1a:2b:0c$ – and at last abbreviated to (120). Miller's technique allows one to fix the forementioned perpendicular on the facets: its direction is after all determined by the angle it makes with the axes of the system of coordinates. The ratio of the cosines of those angles happens to be equal to that of the converted values of the axes' segments cut off by the plane under consideration. It further provides a simple way to calculate the direction of the intersection line of two crystal facets and that of the zone axis. Throughout his booklet Miller only gives the axiomatic and highly technical part of his crystallography wholly in

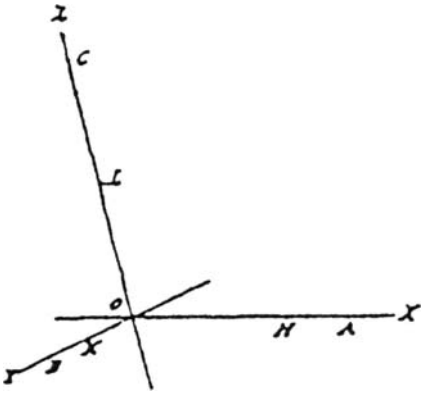

Fig. 14. Three intersecting lines *OX*, *OY* and *OZ* of three groups of parallel facets or cleavage planes. An arbitrary plane, be it a real or perhaps an only possible one, meets these axes at *A*, *B* and *C*, another at *H*, *K* and *L*, respectively. The fundamental law of crystallography, then, implies that the ratio $AO/HO : BO/KO : CO/LO$ shall be such that small integer values may be found, the so-called *indices* *h*, *k* and *l*, which satisfy the relation $(1/h)(AO/HO) : (1/k)(BO/KO) : (1/l)(CO/LO)$. In Miller's view these 'indices' are never greater that 6. Posterity was to speak of the 'law of rational indices', a law that would take the place of Haüy's 'decrescence law' (Miller, 1839, Table I).

terms of 'indices'. He is conscious, naturally, that the decrescence law of Haüy may also be expressed in his 'indices'. As indicated above, his version of that law would be known by posterity as the 'law of rational indices'. Later the 'stereographic projection' of Neumann would be used by the Finnish crystallographer Axel Gadolin (1828–1892) in view of a shorthand characterization of the 32 different crystal 'classes' (Fig. 15).

Originally composed in Russian, in 1869, his tract was translated into French and appeared as such in 1871, in the proceedings of the Academy of Sciences of Helsinki. This detail is of importance since it was Gadolin's francophone nomenclature for the seven by now classical crystal 'systems' that would become ours. Leonhard Sohncke, a

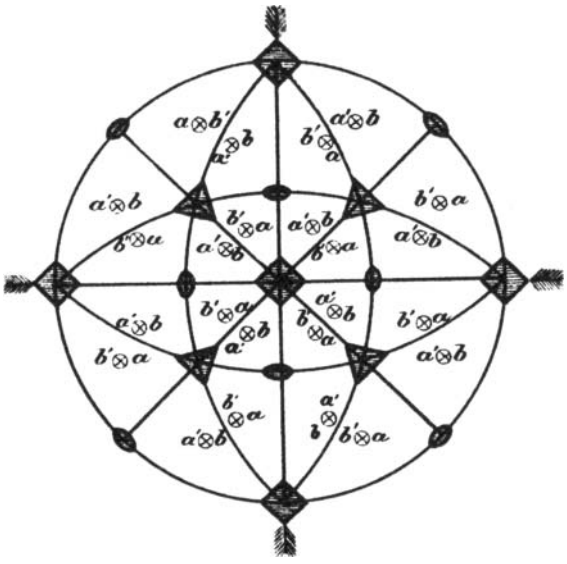

Fig. 15. The simplified 'stereographic projection' of Gadolin for the homohedral forms of the cubic system: the small triangles and quadrangles symbolize rotation axes of order 3 and 4, respectively, the ellipses mirror planes (source: Gadolin, 1871). Each of the 32 crystal 'classes' has such a specific 'stereogram' of its own to characterize its outward symmetry.

former student of Neumann and one of the most influential crystallographers of the second half of the 19th century, played an instrumental role in all this. It was Gadolin's projection format and his nomenclature together with Miller's notation for the crystal faces that later determined the outlook of descriptive crystallography.

5. Group theory and symmetry; from Jordan to Schoenflies

In the introduction to his work *The Unlimited Regular Systems of Points [...]* Leonhard Sohncke (1842–1897), Professor of Physics at Karlsruhe, reconsiders, in 1876, the idea of the space lattice as it had been outlined by Delafosse and Bravais. His main argument in its favor is that the classification of those lattices, or properly speaking 'assemblages', in terms of symmetry exactly corresponds with the empirically found crystal systems: in both cases there are just seven. Sohncke is conscious of the fact that 'hemihedry' is only accounted for in hindsight, that is, in a second approximation; it is as it were masked by the point molecules in the lattices. Delafosse in his days had imagined, supported by persuasive figures, that in the case of boracite the molecules of the 'tetrahedral' type pile up in such a way that either a tetrahedral crystal or a cubic one results (Fig. 5). Bravais did not even ask himself the question whether molecules of a particular symmetry could eventually give rise to crystals of *higher* symmetry. This does not alter the fact, Sohncke esteems, that from a methodological point of view his approach seems correct, for the simple reason that he begins where he ought to begin, that is, with point lattices. As early as 1862, therefore, Sohncke takes over Bravais' theory. Initially he supposes that the 'crystal elements', that is, the chemical molecules proper or comparatively small congruent aggregates, are parallel. Subsequently, he abandons that condition as being too restrictive. Exchanging the 'crystal elements' for their centers of gravity, Sohncke articulates the following hypothesis (Sohncke, 1876, p. 3):

> "Crystals are, when they are conceived of as unlimited regular point systems of infinite dimensions, of such a nature that in the environment of each point the arrangement of the other points is equal to that in the environment of any other point."

The task of the theoretician, then, is "to search for all regular point systems that are infinitely large in all directions". For plane lattices the problem is a simple one, according to Sohncke: there it is just pure geometry. For the space lattices – Haüy and Bravais' 'assemblages' – that geometrical approach does not work, unfortunately, and a better one has to be developed. It concerns what Sohncke calls the "geometry of motion", of which Bravais gets the honor of having sketched-in the seminal idea. The observer here imagines two space lattices, one mobile, the other stationary, and next evaluates which motions are such that they make the first lattice coincide in all its points with the resting one. As possible 'coincidence motions' (*Deckbewegungen*) Sohncke not only envisages simple 'translations' and 'rotations', but also their combination in helicoidal ones. What is striking is that the succession of mo-

tions in such a combination does not make a difference and, moreover, that combinations like this, the screw for instance, represent a specific kind of motion on its own. This means that those 'coincidence motions' are not completely independent from each other and that they may be reduced to some elementary motions. In this connection each regular system of points may be characterized by a limited number of elementary displacements.

Sohncke next defines 'groups of motions' as particular combinations of elementary motions. The total number of such 'groups' is doubtless infinitely great, but this does not preclude its being reducible to a limited number of kinds. The question, then, is to find that set of different kinds of 'groups of motions'. With this set in mind, the characterization of a particular 'lattice' implies the determination of the 'groups of motions' that, together, are able to generate the whole lattice with all its peculiarities starting from just one lattice point.

This was approximately the situation in about 1875, when Sohncke suddenly discovered that the problem under consideration had already been described, analysed and solved almost completely by the French mathematician Camille Jordan (1838–1921), in two articles of 1868 and 1869, published in an otherwise barely known journal. Sohncke immediately recognized the priority of his French colleague, but argued that the latter's treatment had been too abstract to be practical in crystallography. His own task in the following thus was to deduce such a crystallographically useful application. Where Bravais had only considered translations to make the mobile lattice coincide with the stationary one, Sohncke – following Jordan – introduced the rotation and, moreover, the helicoidal motion as a combination of a translation and a rotation. Using these three types of motion Jordan had derived 174 'groups' of simple and composed motions, corresponding to as many 'space point groups'. The first nine of these 174 'groups' concern all kinds of translations, both simple and composed; 'groups' 10–17 are the 'rotations'; and 'groups' 18–174 are all possible combinations of the previous two, subdivided into six 'categories'. An evaluation of Jordan's division showed Sohncke that some hundred of these 'groups' were redundant, since they played no role in crystallography. All 'groups' implying infinitesimal motions, for instance, could be discarded, just like those in which lattices featured that were not infinitely extended in space. A dozen of the remaining 'groups' dropped out for the simple reason that they had been counted twice. To the rest of Jordan's 174 'groups' new, crystallographically relevant 'groups' implying helicoidal motions had to be added, that is to say screw motions that cover integral numbers of parts of a translation. Taken all in all, the German crystallographer ends up with 54 "infinite, regular point systems" (Sohncke, 1876, p. 70), which are supposed to represent from the geometrical point of view all forms deemed possible for crystalline bodies. Since the "molecules' law of action" is not yet known, Sohncke argues, the crystallographer unfortunately is incapable, for the time being, of indicating which forms may actually exist, but this is another question. It is clear at any rate that the seven empirically found 'systems' correspond completely with the theoretically derived ones. The subdivisions of the 'systems', both the practical and the theoretical ones, allow one to foresee that, in the near future, it will be possible to indicate for each type of crystal the corresponding point lattice. At this stage it is already obvious that for cases of hemihedry no accessory hypothesis on the molecular level is needed, let us say, a hypothesis similar to those of Delafosse and Bravais. Indeed, there simply is a particular 'class' for those assemblies of points corresponding to the hemihedral forms of the regular or cubic 'system'. Sohncke is otherwise conscious that some kinds of crystals, *e.g.* the tourmalines, only manifest half of the prescribed number of facets. Earlier Delafosse had stressed the 'polarity' of the main axis of the tourmalines, a 'polarity' that shows up on heating the crystal, when opposed electrical charges appear that concentrate on opposite extremities. In fact it concerns a particular instance of hemihedry, known as 'hemimorphism', a phenomenon only occurring with crystals having just one axis.

Broadly speaking, the anisotropy of crystals is satisfactorily explained in the new theory, since a difference in geometrical direction has immediate consequences for the mechanical properties. In this connection one could think of cleavage, hardness, elasticity, thermal conductivity and solubility. The optical activity of crystals, here, is of course of particular importance. Sohncke believes that this is caused by a helicoidal piling of the molecules in the crystalline aggregate. Recently, he relates, one had noticed that thin mica sheets, when they are stacked like the steps of a spiral staircase, produce a whole that is optically active: the plane of polarization of polarized light appears to turn depending on the stacking direction of the sheets. It is essential, here, that the optical activity emerges from *inactive* parts, since the normal parallel deck of mica sheets, as in native mica, has not the slightest influence upon plane-polarized light. Sohncke does not exclude for that matter that either in solution or in the gaseous state optically active compounds exist in the form of spiralized molecular groupings (see also below, Section 6). In some of those cases, too, one had after all noticed an influence upon the plane of polarization, the angle of rotation being proportional to the concentration of the active substance and the length of the light path. Sohncke even knows of the existence of substances that are optically active in solution, although losing their activity on crystallization. The phenomenon ultimately has to be reduced to the 'nature of the molecule' (*Beschaffenheit des Moleküls*). That molecular nature after all determines whether or not one can form tiny spiralized groupings (dissolutions, gaseous state) and, at a higher level, the crystal structure of the solid state. Sohncke appears persuaded that his approach will make it possible to directly relate the structure of a particular kind of molecule with the way of aggregation in the corresponding crystal form.

In 1879 Sohncke was to conclude his innovations and brought them together in a general theory on the structure of crystals. All in all, it concerned 65 'point systems'. In comparing his results with those of Bravais, Sohncke sees the following advantages. In the first place, it is the simplicity and the persuasive character of the hypothesis of 'crystal elements' which enervate all reproaches of arbitrariness. The correspondence between theory and practice

is a second argument, at least as to the 'crystal systems': both lead to seven of them, the seven by now classical ones of Hessel and Bravais. The new theory, moreover, is more complete than that of Bravais, which had only reckoned with translations; indeed it also accounts for rotations and screw-like motions. As to the phenomenon of hemihedry, it is more or less presupposed in the new theory, so that no auxiliary hypothesis is needed. As a last advantage, Sohncke adduces the phenomenon of optical activity, upon which a new light is shed.

Posterity would acknowledge Sohncke's nicely abstract handling, but recognize at the same time that there are still two more symmetry elements to be taken into account. Rotations, after all, may not only be combined with a translation, as with Jordan and Sohncke, but also with a mirror plane and an inversion. These latter combinations were suggested by substances with asymmetric molecules, known since Van't Hoff and Le Bel's 1874 publications. At the beginning of the 1890s, the mathematical crystallographers arrived at 230 so-called space groups. The first who fully succeeded was the crystallographically oriented mathematician Evgrav Stefanovich Fyodorov (1853–1919). In 1890, he published his almost complete deduction, which was based upon the aforementioned article by Gadolin. Unfortunately, though, it was composed in Russian and that was the reason why it remained unnoticed. When, at the end of 1891, the work *Krystallsysteme und Krystallstructur* of the German mathematician Arthur Moritz Schoenflies (1853–1928) came out, Fyodorov was quick to make a German summary of his original text. This summary appeared as late as 1895 in *Zeitschrift für Krystallographie [...]*, the leading journal in the field. In the interim even a third approach had been published in that journal, one elaborated by the English scholar William Barlow (1845–1934). Barlow had not worked completely independently, it is true; he had used Sohncke's work and knew Schoenflies' book. Evidently, the idea of a strictly deductive crystallography, as a kind of applied mathematics, had won the interest of the scientific community. What remained as a subject of debate was the exact number of 'space groups' and the nature of the constitutive 'points'; the 'theory of groups' as such was by now a completely accepted branch of mathematics. In the next section we will see how the notion of 'point' evolved following its introduction into crystallography.

6. The status of the *points*; molecules and/or atoms

With Gabriel Delafosse we noticed how sensible it is to substitute the physico-chemical molecules in thought by their centers of gravity. Those molecules are supposed to be situated at the 'summits' of the 'meshes' of the 'lattice' that is projected in the crystal. In that substitution, the influence of contemporary mathematical physics in the style of Laplace may be seen. In this physics, each material object – either a molecule, or an aggregate – is conceived of as a point-like center of force, allowing one to concentrate upon its *mass* and its *gravitation*. This is the 'mechanics of the material point'. One of the great challenges of that mathematical physics was the problem of elasticity. The wave theory of light, originating with Huygens but actualized by Young and Fresnel, was based on the assumption of a light-carrying medium in which the postulated 'transversal' waves propagated. One of the indispensable properties of that medium was an extreme elasticity. Elasticity as such was already an age-old problem, also in the molecular tradition. The interest of someone like Poisson, for instance, is well documented. For a review of the debate about the nature and the analysis of elasticity we gladly refer to the classical and still valuable monograph of Isaac Todhunter, entitled *A History of the Theory of Elasticity [...]* (Todhunter, 1886). We learned from it that the debate in question continued until the end of the 19th century, when it became clear that a stationary, light-carrying ether, even in its simplified form, failed to account for the phenomena.

By 1840, the crystallographer Delafosse was conscious of the fact that one had to begin at the molecular level in order to explain certain deviations within the seven 'crystal systems'. To explain the demanded *physical* symmetry he had felt compelled to exchange the molecules proper for their 'representative form'. Within the 'regular system' this concerns the cube, the tetrahedron and the octahedron. With boracite, it is recalled, there arises, as a consequence of the particular *physical* symmetry, a certain polarity in the crystal. The molecular centers of gravity, the points of the lattice, are ultimately no more than abstract carriers of physical properties of a particular symmetry. This is, in our view, almost Bravais' conception where he attributed the physical aspects of the observed crystal symmetry to the 'polyhedral form' or, preferably, to the 'polyatomic form' of the molecules. For the rest, he, Bravais, left the molecules out of consideration and focused upon the 'points'. One of the first manuals in which both the geometrical and the physical aspects would be assessed on the same footing was the work *Physikalische Krystallographie [...]* by Paul Heinrich von Groth (1843–1927), the first edition of which appeared from the press in 1876. We will deal with it in the following.

With Camille Jordan and Leonhard Sohncke, who both proceeded in the direction indicated by Bravais, the lattice 'points' were still the centers of gravity of the 'crystal elements'. The latter could be imagined either as the chemical molecules proper, or as minute aggregates of these. Those aggregates were otherwise well defined packings and therefore mutually 'congruent', as Sohncke put it.

As far as Sohncke is concerned, it is interesting to notice that his utterances are among the very first manifestations in the German crystallographic community of a turning away from a consciously anti-molecular attitude. Given the versatility of Weiss' earlier crystallography, that of the 'zones', we should perhaps excuse his obstinacy in rejecting the molecular theory, the more so since the new generation of crystallographers would succeed in reconciling the theory of 'zones' with the latest edition of the molecular theory of physicists and chemists. Among the physicists there were men like Clausius, Maxwell and Boltzmann, who investigated the various aspects of the molecular theory in the context of the kinetic theory of gases. The chemists, for their part, had never renounced

the molecular theory and ever since the famous congress of Karlsruhe (1860) it was central in chemical thinking, particularly in Germany, where chemistry lived triumph after triumph. What is striking, then, is that at a time when French natural science went through an epistemological crisis as to the status of the molecular and/or atomic theory, that very same theory finally and almost completely seduced German physics and chemistry. For all these reasons, the new mathematical crystallography of 'point lattices' and 'groups of motions', as accepted and elaborated by successively Sohncke, Fyodorov and Schoenflies, was a thoroughly molecular science. In Paris it was the symmetry theoretician and crystallography expert Pierre Curie who, crippled by the reigning politico-scientific cohabitation of positivistic inspiration, followed the German approach, although without publicly taking position.

Apart from the established authorities Schoenflies and Fyodorov, there was a third specialist, namely the independent scholar William Barlow (1845–1934). Barlow liked to profile himself as a model builder, more or less like his fellow countryman William Hyde Wollaston, long ago. Barlow, too, arrived at 230 'space groups' and published in 1894 an exhaustive deduction of them; in the previous section we referred to this. The approach of the Englishman was peculiar to the extent that, in contrast to the other proposals, he commenced at the lowest possible level, that of the atoms. His leading idea was the following. If it is true that the chemical molecules consist of groupings of atoms, then crystals arise by the piling up of such groupings, such that a crystal is basically more an aggregate of *atoms* than an aggregate of *molecules*. In the supposition that all atoms have the same magnitude, Barlow next deduces among other things three kinds of cubic packings, packings in which the crystallographers of his time doubtless immediately recognized the three types of lattice of Bravais' regular system (Fig. 16). His model was supported by the empirical fact that the majority of the compounds *XY* (*X*, metal; *Y*, non-metal) crystallize in a cubic form, with a symmetry corresponding to either the first or the second of the three acknowledged lattices types. Apart from those three cubic types there are still two other forms of internal symmetry, *viz* that in which the base plane is occupied by a sphere surrounded by six other spheres; in both cases there arise packings of a hexagonal symmetry (*cf.* Fig. 16d). According to Barlow, these two types are particularly suited for compounds of the general formula XY_2; he mentions H_2O and SiO_2 as examples. As to silicon dioxide, Barlow continues, it is most rewarding to see that one of those hexagonal pilings may have a helicoidal ordering, either to the left, or to the right. The phenomenon of the so-called circular polarization, that is, the optical activity of quartz, may be directly attributed to it. Rather oddly, Barlow develops his ideas without the slightest allusion to the historical context or to the ongoing debate about point lattices and it is, therefore, easy to imagine the irritation of an otherwise-generous specialist like Leonhard Sohncke, whose almost complete deduction had appeared in 1879. Above we saw indeed that Sohncke had envisaged a helicoidal ordering of the molecules – in the crystalline state, in solution or in the gaseous state – in order to explain the phenomenon of optical activity.

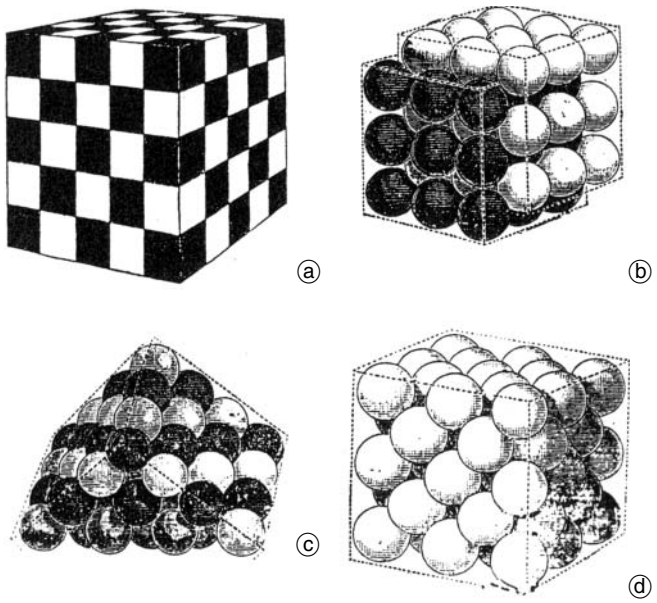

Fig. 16. The deduction of the three cubic kinds of lattice according to William Barlow. The packing of white and black spaces, (**a**), is used in thought as a rack for white and black atoms. Barlow first fills the black spaces of the first, the third and fifth rows of the first layer of the rack, the front layer, and then the second and fourth rows of the white spaces of the second layer. The third layer is filled like the front one, the fourth like the second *etc*. This results in (**b**). In a second approach, he fills all the spaces of (**a**) with atoms of the corresponding color; this leads to (**c**). He concludes by filling only one kind of the spaces of (**a**), which gives (**d**) (Barlow, 1883a, b). Packing (**b**) represents the body-centered cubic lattice (an envelope of 8 black atoms surrounds 1 white atom), (**c**) the normal cubic lattice (envelope 6) and (**d**) the face-centered cubic lattice (envelope 12).

Generally speaking, the spherical atomic model also appears attractive for explaining the occurrence of twin crystals: in an aggregate of spheres it is very easy to rotate two halves of a crystal over a particular angle without changing the number of atoms in the immediate environment of each of them. Isomorphism is not a problem either: $CaCO_3$ and $FeCO_3$ will adopt the same crystalline form and the minute differences in interfacial angles that are noticed may be attributed to an unequal shrinking of C and O atoms. As to the dimorphism of $CaCO_3$, this stems, according to Barlow, from very small alterations in the arrangement of the spheres: such alterations would suffice to convert the one symmetry into the other.

In Barlow's model, free atoms all have one and the same diameter, while they shrink or expand on crystallization depending on the atomic species. This explains why the octahedra of substances from the same cubic system show slight differences in their angles. Later, Barlow called upon different laws for the attraction and repulsion forces to explain these data. A dead-end road, unfortunately, and therefore we do not follow him. From a crystallographic point of view, it was only the spherical form of the atoms, their variable diameter and their eventual aggregation that remained of Barlow's meddlings.

Compared to earlier attempts of Wollaston, in 1812–1813, the results of Barlow are even more impressive when one realizes that, with him, the numerical proportion between the atoms is essential. Where the particles of Wollaston had been mere abstractions endowed with a spheri-

cal, a spheroidal or an elliptical symmetry, the spheres of Barlow represent concrete atoms, although he had to renounce going into much detail as to the precise atomic species. The hypothesis of the similar if not identical diameter of each and every atom, interesting perhaps in the days of Dalton, Berzelius and Laurent, was, however, much too adventurous. Indeed, in the 1880s the determination of the relative magnitude of atoms had become a standard procedure, especially since the elucidation of the Periodic System of the elements by Mendeleev. The German chemist Hermann Kopp, early in the 1840s, calculated such properties of compounds, with sustained attention for the so-called specific volume, that is, the ratio between the molecular weight and the density, the latter measured at the boiling point, at atmospheric pressure. In the 1860s Julius Lothar Meyer would attempt such calculations for the elements, an investigation which brought to light a periodicity that came very close to that recently found by Mendeleev. Barlow unfortunately has missed all this; even for the contemporaneous crystallographers, headed by the great Leonhard Sohncke, he had remained an outsider. The German crystallographer nonetheless had been fair enough to react upon Barlow's publications. In his commentary he showed that the five kinds of internal symmetry as proposed by the Englishman correspond to some groups of particular cases of the 65 recognized 'point lattices' (Sohncke, 1884). This was not all. The scientific statures of the Professor of Physics and Crystallography of the University of Karlsruhe and the solitary independent scholar were perhaps unequal, the issue at stake was a fundamental one all the same, particularly from the molecular point of view. Sohncke argued, for instance, that the atomic spheres' approach lost sight of the interatomic bond relations and, in so doing, overlooked the presence of secondary specific particles, the chemical molecules. Since the notions of 'valence' and 'molecule' have proved their utility elsewhere in chemistry and physics, Barlow should have explained why they are irrelevant in the solid state. Another complicating factor is that Barlow's atoms may change their volume, a hypothesis which badly needs complementary hypotheses to make plausible the fact that $CaCO_3$ and $FeCO_3$ are isomorphic: why, after all, would the shrinking of atoms be limited to the atoms of the carbonate group? In his answer to Sohncke's objections Barlow is at pains to hide the lack of generality of his theory. As to the interatomic relations, he refers to the phenomena of electrolysis, which show, in his view, that particles of an opposite nature may react at the electrodes without something happening in the rest of the liquid. Apparently, a particle can change atomic partner without the chemical bonding relations between the atoms of the molecule being affected (Barlow, 1884). In hindsight, the discussion between Barlow and Sohncke at all events manifests the weak points of current theoretical crystallography: when the atoms are indeed the ultimate building blocks of the molecules and, hence, of the aggregates, in one way or another their volume and packing have to be accounted for. From this point of view the crystal lattice of a chemical compound may be considered as the superposition of a number of partial lattices, namely of those of the various atomic species present. The salt hydrates come close to this model: here two partial lattices may be imagined, that is, that of the centers of gravity of the salt molecules and that of those of the water molecules. This interpretation is supported by the easy way in which salt hydrates split into salt and water and may be recomposed from these. Seen in this light, the salt hydrates are no more than a particular case of the so-called molecular compounds, substances which in complexity lie one level above that of the normal atomic compounds. In 1888 Sohncke would draw the ultimate consequence from this insight and proclaim that each and every crystal of a chemical compound has to be considered essentially as a superposition of as many partial lattices as there are atomic species. In the case of variously linked atoms of the same species, there are as many partial lattices.

In the exchange of ideas between Sohncke and Barlow there are also resonances of the old debate about the nature of isomorphism and polymorphism. In the foregoing we saw, in Section 3, that in the case of isomorphism one esteemed that all atoms are of an equal or almost equal magnitude and if perhaps this does not apply for all atoms, it holds at least for the metals in a series of isomorphic salts. On the other hand, the polymorphism of one and the same substance had suggested that there are particles of a higher level, the 'crystal molecules'; the chemist Kekulé had weighed this idea. In a more remote past, Haüy had considered the occurrence of 'subtractive molecules'. The hydrates and, for instance, the polyhalides, too, may be imagined in a similar way. Hence the regular appearance of the notion of 'physical isomerism', the molecular analog of the now well established chemical isomerism, where it is a matter of atomic arrangements alone. In case of 'physical isomerism' the arrangement of the chemical molecules, be they equal or not, determines the nature of the 'crystal molecule'. One could find occasion in all this to distinguish 'chemical' from 'physical molecules', a step, though, that would put at risk the doctrine of the three states of aggregation[6]. Indeed, as soon as two such kinds of molecules are postulated, as by Kekulé, the doctrine of three states of aggregation collapses and there is no place left for the notion of 'substantial individual'.

Arthur Schoenflies, the new Professor of Applied Mathematics at Göttingen, seems to us a model of logical consistence and profoundness in the sense that, between the lines of his *chef-d'oeuvre Krystallsysteme und Krystallstruktur*, he appears fully aware of the exact range of his 'point' concept. According to Schoenflies, a crystal may be defined as a (Schoenflies, 1891, p. 5):

> "[. . .] solid homogeneous substance, of which the properties are generally dependent on the direction and vary depending on such direction following fixed laws of symmetry."

It is these laws of symmetry which, taken together, constitute a real 'law of nature' (*Naturgesetz*) of such a character that in a mathematical way all possible cases may be deduced in advance. All the same, the crystal is always a molecular aggregate, Schoenflies claims, in the first place regarding its physical properties and in the sec-

[6] Sohncke considered a similar distinction. His dilemma concerned the gaseous state, particularly that of sulfur.

ond place, more or less implicitly, regarding the geometry ar our level. Indeed, he writes, its is the physical behavior that mirrors "the essential and indestructible character of the crystalline substance". In comparison to Delafosse the emphasis is clearly relocated: where the Frenchman focused upon the geometry before inspecting the physical properties, the German radically opted for physics and, in consequence, for the carriers and ultimate causes of the corresponding properties.

The extraordinary work of Schoenflies is composed of two parts. The first assesses the theory of the crystal systems, their subdivisions and the geometry in the background. The author here discusses the different ways to make lattices coincide, the 'coincidence operations' (*Deckoperationen*), and a way to 'calculate' the effects of their combinations in terms of 'products' and 'powers'. The concept of group, conceived of in Jordan's sense, is here of crucial importance: the group defines the limited number of 'coincidence operations' and their combinations, the latter being related by the requirement that each newly invented combination, in terms of its effect, ought to be identical or at least equivalent to an already acknowledged combination. Using his peculiar algorithm Schoenflies thus arrives at the 32 traditional 'crystal classes'.

In the second part of his work Schoenflies develops his theory of crystal structure. This theory appears to be based upon the 'generally accepted' hypothesis, *viz* that of the molecular constitution of matter, and envisages establishing which crystal structures are compatible with it. In this context the concept of molecule is of the utmost importance, since it depends on the theory that is adopted. Chapter I of this part therefore deals with the various hypotheses that are in the game. A 'solid homogeneous substance' is described here as a mass of 'similar individuals' (*gleichartige Individuen*), in other words, of molecules. Somewhat farther, Schoenflies speaks of 'substantial individuals' (*substantielle Individuen*; Schoenflies, 1891, p. 237). All things taken together, there are two kinds of homogeneous substances, that is, amorphous and crystalline. The structure of crystalline bodies varies depending on the 'laws of nature' that direct the packing of the 'substantial individuals'. Amorphous substances, on the contrary, have no regularity whatsoever in their molecular packings. During the process of crystallization the piling that emerges will be the simplest possible and adopt a form characterized by the 'highest degree of regularity'. Each resulting 'crystal molecule' (*Krystallmolekel*), wherever in the crystal, is always surrounded in the same way by the neighboring molecules. This condition is satisfied when it holds for all the molecules in the 'sphere of action', that is to say for those molecules that co-determine the physical behavior. From a mathematical point of view one abstracts from the real dimensions of the crystal and considers it as a "regular mass of molecules of unlimited extension," which is defined as follows (Schoenflies, 1891, p. 239):

> "a packing of molecules such that it is in all directions infinitely extended, composed exclusively from similar molecules, and possessing the property that every molecule [wherever in the crystal] is surrounded in the same way by the totality of all the other molecules."

The point is that, according to the common hypothesis of most modern theories, a homogeneous crystal in each and every one of its points carries the character of a regular molecular packing of infinite dimensions. That equality of environment may be described in terms of distances and angles, and thus also comprises arrangements that are related as object and mirror image.

The aim of a structure theory therefore will be to explain the geometrical regularity in the physical behavior, more particularly the homogeneity and the symmetry. Given the 32 'classes of symmetry', deduced in the first part of Schoenflies' work, the task will be to find for all known or provisionally hypothetical crystals the infinite packings of molecules endowed with the same homogeneity and the same symmetry. The two leading theories, that of Bravais and that of Sohncke, agree in this respect. Bravais had started from parallel congruent molecules, of which the centers of gravity constitute the space lattice. In such a lattice the homogeneity not only concerns random points, but also parallel straight lines. Formally speaking, this requirement is not fulfilled at the level of the atoms and molecules, since those points and lines are necessarily parts of the lattice. Nonetheless it is true, at our level, that the differences in physical properties that may be expected at the atomic and molecular level are unmeasurably small. For the very same reason one may abstract from the constitutive parts of the molecules and, as with Bravais, only reckon with their centers of gravity. When, moreover, the condition of the parallelism of the molecules is dispensed with, the theory can be generalized. In order to express conveniently the symmetry in the physical behaviour, the regular molecular packing is to be deduced for each of the 32 classes of geometrical symmetry. After all, Schoenflies argues, there is no simpler way to visualize crystal structures than by ordered aggregates of molecules. This is, in our view, another way to say that, according to Schoenflies, the molecular model itself is the simplest possible and hence exclusively suited to express the physico-chemical character of a substance (Schoenflies, 1891, p. 247).

Having arrived at the final pages of his monograph, Schoenflies evaluates the relative merits of the theories of Bravais and Sohncke, the first of which is characterized as primarily a lattice theory of crystallographical origin, and the second as a structure theory of a mathematical imprint (Schoenflies, 1891, p. 612ff.). Sohncke's approach, at this stage, seems much more general than that of Bravais. The latter, however, is far more simple and easy to imagine, since it is of an exclusively molecular nature and enables the crystallographer to account for all physical and chemical properties of the substance in question. To this one adds that the crystallization proper as a time-dependent process can only be visualized in terms of molecules. This *mechanical* problem is left out of consideration by Sohncke and his followers, but it constitutes a real problem all the same. Therefore it would be interesting to know, Schoenflies continues, how precisely a physicist like Sohncke views those molecules. Whatever Sohncke's details, it surely is insufficient to merely construct a geometrical image of the molecular nature of crystals. We also stand in need of an exact analysis of the symmetry

relations in order to appreciate the intrinsic value of a theory. In practice this means that the space lattice has to be determined of some crystal species of which it is easy to see in advance to what crystal 'class' it belongs. In order to succeed, the physical properties have to be studied. Schoenflies gives the example of quartz, which without doubt belongs indeed to one of the 'classes' of the hexagonal 'system'. With the purpose of rendering plausible the influence of this crystal species upon plane-polarized light (circular polarization), Sohncke had proposed, in 1879, a helicoidal ordering of the molecules, either to the left or to the right, a presentation that nicely squares with the outcome of Schoenflies' own analysis. The advantage of a structure theory like that of Sohncke is, according to Schoenflies, that it also accounts for the existence of the two known kinds of quartz crystals, called 'enantiomorphic' forms because of their interrelation as mirror images. Sohncke's approach, moreover, has no problems with the latest novelty, the 'asymmetric' molecules of Pasteur, Le Bel and Van't Hoff.

At the beginning of the 20th century, then, any crystallographer who took himself seriously had a collection of 230 models at hand to classify the polyhedral specimens of his crystals or, better, the 'point lattices' of these. From the molecular point of view these 'points' were the centers of gravity of the 'substantial individuals' in the sense of Schoenflies. For those who, like Barlow, Sohncke and Groth, preferred to start at the level of the atoms, it was important to distinguish as many equivalent partial lattices as there were atoms in the molecules in question. In the daily practice of crystallography this implied that one had to content oneself with the 32 classes of external symmetry. There simply was no way to go farther, even though one knew that there was more. Very soon a new technique came up which gave an almost direct access to the building blocks of the crystals, that is, the atoms, an invention which, all of a sudden, made an exhaustive verification of the 230 space lattices a daring but realistic task.

7. Röntgen's radiation and the breakthrough of lattice theory; Laue and co-workers

In 1912, Max von Laue (1879–1960), a former student of Max Planck, who had been nominated Professor of Theoretical Physics at the University of Munich, had the lucky inspiration to direct a beam of Röntgen's radiation at a crystal. The guiding idea was that the wavelength of the new radiation in all probability had to be extremely small, to judge from its huge penetration and ionization power. That it could perhaps also be a stream of particles was otherwise not excluded at all, at least for the time being. A preliminary calculation showed that, in the undulatory hypothesis, the wavelength had to be of the same order of magnitude as the diameter of the physico-chemical molecules. Laue had reasoned in the following way. For an arbitrary substance having at 0 °C and 1 atm a density of ϱ g cm^{-3} and a molar weight of M g, the molar volume will be equal to M/ϱ cm^3. Since the number of molecules per mole, N_A, is known[7], $M/\varrho N_A$ will be the volume of one molecule. For a substance crystallizing in the cubic system like zinc sulfide, the mesh of the lattice will be equal to a molecule of cubic form, whose edge thus is $(M/\varrho N_A)^{1/3}$. In this way Laue obtained for ZnS with $\varrho = 4.06$ g cm^{-3}, $M = 97.4$ g and $N_A = 6.20 \times 10^{23}$ for the edge of its cubic molecule $\{97.4/[4.06 \times (6.20 \times 10^{23})]\}^{1/3} = 3.4 \times 10^{-8}$ cm. On the other hand, the wavelength of Röntgen's radiation, if its wave character was taken for granted, had been estimated on spectral grounds at about 10^{-8} cm. That molecular cube's edge was just the distance between the centers of gravity of two neighboring molecules when they are neatly piled up in the crystal. Such a piling reminded Laue of a three-dimensional analog of the flat line gratings of classical optics. Since the revival of the wave theory of light, through the efforts of Young and Fresnel, the most spectacular experiment, that of interference, had been studied in a great variety of ways, most of all with the help of glass diffraction gratings of parallel lines. Because of the extraordinary precision that had appeared attainable in the production of such gratings, the wavelengths, too, had been measured with extreme precision. The main argument of Laue, then, was the fact that double gratings had been tried out, gratings, that is, with mutually perpendicular series of lines. He himself had just finished an exhaustive review article on wave optics, meant for the duly famous *Encyclopaedie der mathematischen Wissenschaften [...]*, that magisterial overview of the physical and mathematical sciences of the years 1898–1926. With crossed gratings, one had established, the interference did not show up in the form of parallel light and dark fringes, but in the form of tiny quadrangular spots, distinctly ordered in rank and file in the two dimensions of the plane. In the spring of 1912, Laue was struck by the idea that a similar phenomenon could manifest itself when a beam of Röntgen's rays was directed at a crystal from a well crystallizing substance. Convinced as he was of the wave-like nature of those rays – in 1912, as said above, still fully hypothetical – and, besides, that crystals are three-dimensional lattices of molecules, Laue had every reason to expect something interesting at a photographic plate placed behind the crystal, exactly like the screen behind the grating in optics.

There was also every reason to speak of a great conjunction, there in Munich, in the Faculty of Science. Wilhelm Conrad Röntgen (1845–1923) himself, the discoverer of the radiation and, in 1901, the first Nobel laureate for physics, was still fully active as Professor of Experimental Physics. There was also Arnold Sommerfeld (1868–1951) as Professor of Theoretical Physics since 1906 and Editor-in-Chief of the forementioned *Encyclopaedie [...]*. To conclude, the name of Paul Heinrich von Groth may be mentioned, the mineralogist of worldwide renown, who, as a former colleague of Sohncke, was an

[7] The mole concept had been introduced by Wilhelm Ostwald (1893) and propagated through the chemistry textbooks of Arnold F. Holleman in their countless editions (1898–). The number of molecules involved had been established by Jean Perrin (1908), who called it after Amedeo Avogadro. For the context, see Kubbinga (2009), volume ii, pp. 520–527.

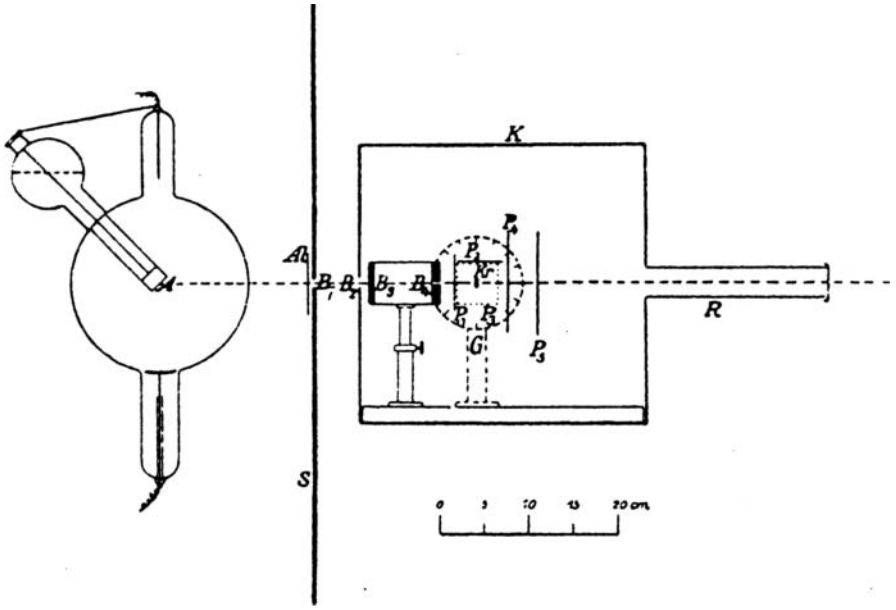

Fig. 17. Setup of Laue, Friedrich and Knipping. The source of Röntgen's radiation is separated from the crystal under investigation by a lead screen, *S*, pierced at B_1, and a series of ever-finer lead diaphragms B_2 (in the lead chamber *K*), B_3 and B_4. Around the crystal *Kr* photographic plates may be placed at various positions P_{1-5}. The extension *R* is added to trap the straightforwardly passing rays and obviate disturbing secondary rays of the wall. For precision measurements there is a diaphragm *Ab* for the pinhole B_1 in screen *S* (Friedrich *et al.*, 1912).

addict of the lattice theory. The memory of Sohncke was otherwise still alive: his models for the various point lattices were used daily in classes by Groth.

In the intervening time it had become clear that Röntgen's radiation, also known as X-rays, on hitting the surface of particular crystals released an instantaneous secondary radiation. In case of normal light, it could have been an example of 'fluorescence'. Therefore, Laue was ready to expect that such eventual secondary radiation, too, could give rise to interference.

His colleagues Walther Friedrich (1883–1968) and Paul Knipping (1883–1935), both former students of Röntgen, were easily persuaded and went on to test Laue's idea with the aid of a thin plate of crystalline copper sulfate ($CuSO_4 \cdot 5\,H_2O$) (for fascinating details, see Eckert 2012). This salt crystallizes easily and contains a metal of sufficiently high atomic weight [$Z(Cu) = 29$] to expect an intense secondary radiation at a rather limited wavelength interval. Expecting indeed interference of the secondary radiation, they placed photographic plates before and beside the crystal (P_{1-3} in Fig. 17). Later they also placed a plate *behind* the crystal (first at P_3, then at P_4) and noticed after 20 hours of uninterrupted radiation the emergence of perfectly distinct spots precisely on this photographic plate. With a subtle feeling for what was happening they replaced the triclinic crystal of copper sulfate by a nicely cubic crystal of zinc sulfide. First a ZnS platelet perpendicular to the *z* axis – that is, parallel to Miller's (001) plane – and measuring $10 \times 10 \times 0.5$ mm was used. The 'photogram' indeed showed a comparable increase in the regularity of the distribution of the spots (Fig. 18). What was more, Laue found in the 'photogram' the same symmetry elements in the distribution of the spots as could be expected from a deduction in the spirit of Gadolin for the (001) face of a homohedral crystal of the regular system, *viz* one fourfold rotation axis and four twofold axes (or four planes of symmetry). In the eyes of Laue, Friedrich and Knipping, the correspondence in symmetry elements could be considered as an equally simple and direct proof of the correctness of the lattice theory. They also noticed that there was no difference between the straightforward passing beam and the secondary beams that were responsible for the spots: if a platelet of aluminum of 3 mm thickness was placed in the beams then equal fractions of the radiation were absorbed. That is to say that the secondary beams do not differ at all from the entering beam and that there is no question of a phenomenon resembling fluorescence. Indeed, if it had been a matter of fluorescence then the wavelength of the secondary rays ought to be appreciably greater, while the major part of it should have been trapped by the aluminum.

The amazing discovery of Laue, Friedrich and Knipping happened at a time when so many theoretical and practical breakthroughs were being reported in the domain of the structure of matter. Kamerlingh Onnes, for instance, had just revealed the superconductivity of metals at low temperatures. Further, there was the new atomic model of Nobel Prize laureate Rutherford, in which a very small 'nucleus' featured prominently, a model that gradually won adherents in physics. The young Dane Niels Bohr busied himself with the elaboration of a model in which the spectral lines were brought in relation with the trajectories of

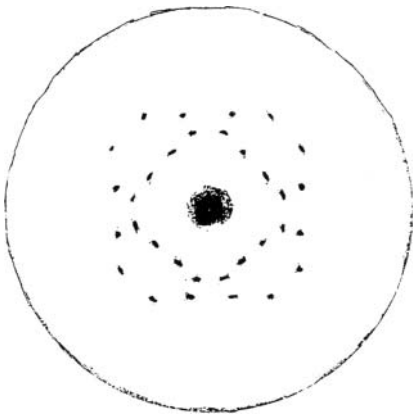

Fig. 18. The 'photogram' found for a (001) platelet of zinc sulfide (sphalerite). The symmetry elements are self-evident: the main axis is fourfold, while there are four twofold rotation axes (four planes of symmetry) (Friedrich *et al.*, 1912).

the electrons around Rutherford's 'nucleus'. This thrilling context notwithstanding, the news of the crystal-caused interference phenomena came like a flash of lightning out of the blue. The lattice theory of crystals was promoted overnight from a handy aid in classification to the unshakable cornerstone of all theory of matter. On the other hand, the atomic and molecular theory, with its already generally acknowledged aureole of undeniable experimental fact, was corroborated once more.

8. Concluding remarks

At the centenary of the epochal achievements of Laue, Friedrich and Knipping, it is interesting to see how their experiments stressed the essentially *atomic* structure of crystals. As such, this was the culmination point of a development within the framework of crystallography itself. Indeed, the new branch of natural science had seen the rise of a *molecular* lattice theory (Haüy, Delafosse, Bravais), which gradually transformed into an *atomic* lattice theory (Sohncke).

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