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A review of some elements in the history of grain boundaries, centered on Georges Friedel, the coincident 'site' lattice and the twin index

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Abstract I trace the origin of the inverse density of coincident lattice sites to Georges Friedel in 1904 (Études sur les groupements cristallins). Georges Friedel (1865–1933), son of the Chemist and Mineralogist Charles Friedel, called this parameter the twin (macle) index and defined it as the ratio of the total number of nodes of the primitive lattice to the number of coincident nodes restored by the twin operation. Friedel's 1904 'multiple lattice' is our Coincident Site Lattice. Georges Friedel introduced the Σ symbol in 1920 (Contribution à l'étude géométrique des macles) as the ratio of the volume of a (not necessarily primitive) multiple cell to the volume of the primitive cell. G. Friedel provides his reader with several formulae which, in the cubic case, give $\Sigma = h^2 + k^2 + l^2$ (h, k and l being the indices of the twin plane) and a twin index I equal to Σ if Σ is odd, equal to $\Sigma/2$ if Σ is even. All these definitions and formulae are included in the 1926 version of his celebrated textbook 'Leçons de Cristallographie'. Georges Friedel was also concerned with the 'material lattice' (the crystal structure) behind the mathematical lattice, but besides his contributions to the study of liquid crystals, Georges Friedel was mainly interested in Mineralogy and not in Metallurgy. This may explain why Walter Rosenhain apparently never knew of Friedel's work and why Kronberg and Wilson had to re-discover the importance of the density of coincidence sites, at the atomistic level, in 1949 in copper. Georges Friedel's grandson, Jacques Friedel, made the first numerical estimate of interface energies using interatomic potentials that same year but only published these results in 1953. Knowledge of these past events may help us to better understand the present theories and, hopefully, to develop our future understanding more efficiently.

Introduction

Materials scientists know that most crystals, in metals, semiconductors or ceramics, are actually polycrystalline so that the study of interfaces in crystalline materials is an important topic. Several books or monographs are entirely dedicated to this topic: [1–11], not to mention proceedings of conferences or dedicated chapters in more general books. These specialized books all introduce and discuss the geometrical concept of a possible coincidence (sub-)lattice common to the two grains at a grain boundary, together with the use of the twin index. Except for Murr, these books attribute the origin of the concept of coincidence to Kronberg and Wilson in 1949. Georges Friedel's explicit contributions will be recalled in the following, put into some historical context starting with Romé de l'Isle and Haüy. Yet, these contributions were ignored by Walter Rosenhain who developed an amorphous cement model for grain boundaries in metals. This model faded only very slowly, until 1949, despite objections occasionally but unsuccessfully raised by other metallurgists (Desch, Guertler and Lantsberry in 1912–1913, Foley in 1925, Hargreaves and Hills in 1929, see the penultimate section on Metallurgy and Rosenhain's challenge). Friedel's geometrical approach had, however, kept in being used by mineralogists. It is suggested that these independent evolutions are partly due to an unfortunate dichotomy between natural materials, usually studied by mineralogists, and man-made materials, usually studied by metallurgists or materials scientists, even when both materials are (poly-)crystalline.

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Table 1 Synoptic of Friedel's scientific lineage

Charles Friedel (1832–1899)	Georges Friedel (1865–1933)	Edmond Friedel (1895–1972)	Jacques Friedel born 1921
		Marguerite, married Louis Crussard (1876–1959)	Charles Crussard (1916–2008)

See [14] (and [97] for Charles and Louis Crussard). Edmond Friedel worked on liquid crystals [91]. Louis Crussard worked on several problems concerned with the coal mining industry and also on the thermodynamics of explosion. Charles Friedel's maternal grandfather was a Professor of zoology who eventually succeeded the famous Naturalist Georges Cuvier (1769–1832) as a Professor at the Collège de France (Among the Historical Eulogies written by G. Cuvier, one is dedicated to René-Just Haüy and another to Abraham Gottlob Werner). Charles Friedel's aunt married a member of the Peugeot family (Jules Peugeot (1811–1899)) [14]

For the sake of clarity I translated the original French texts and I gathered the most significant ones in a final Appendix G. I developed in appendices some technical points which are important and too long to be put in footnotes.

Georges Friedel, son of Charles Friedel

Georges[1] Friedel (1865–1933) [12–14] was the 4th child of Charles Friedel who was both a chemist and a mineralogist [14–17]. Charles Friedel (1832–1899, see Table 1) defended two theses in 1869, one on the ketones and aldehydes and another on pyroelectricity. In organic chemistry Charles Friedel discovered the Friedel–Crafts reactions with James Mason Crafts in 1877. In physics he kept on investigating pyroelectricity of crystals in relation to their symmetry, in the spirit of his Professor Henri de Sénarmont and as had been the fashion since Franz Neumann (see [18]). One of his students working on pyroelectricity was Jacques Curie, who extended this investigation to piezoelectricity in Friedel's laboratory at the Sorbonne with his brother Pierre Curie.

In a basement of the École des Mines, Ch. Friedel also synthesized minerals using a tubular steel pressure vessel of his own design, in which nutrient was supplied along with water raised at elevated temperature and pressure.[2] He was able to grow crystals of quartz large enough to be measured with a goniometer.[3] With his student Émile Sarasin he also synthesized several minerals until he could have his own son, Georges Friedel, work with him to grow minerals on mica in 1890 and 1891. Georges Friedel entered the École Polytechnique in 1885, 1 year after his father and Henry Le Chatelier had both been refused the chemistry professorship in that School.[4]

Major in his class, Georges Friedel was urged to continue his studies in the so-called 'corps des mines' at the École des Mines in Paris, where he perfected his knowledge of Mineralogy and Crystallography[5] and grew minerals with his father. He then worked as a mining engineer for 2 years and started a teaching career at the École des Mines in Saint-Étienne in 1893. Georges Friedel had brought his father's steel pressure tube with him to Saint-Étienne, and, in 1897, he synthesized a salt whose crystals were readily twinned and un-twinned by compression [19]. This 'toy' mineral was a hydrated calcium chloroaluminate, $Al_2O_3,3CaO,CaCl_2,6H_2O + 4H_2O$, and is now well-known as *Friedel's salt* in the cement industry, where it serves a protective role in the retention of chloride anions in cement and concrete initially rich in tri-calcium aluminate (see, for instance, [20]). Georges Friedel is also remembered for his contributions in the field of liquid crystals as he described their structures and properties in a 201 page paper, in which he identified three classes of liquid crystals which he named *nematics*, *smectics*, and *cholesterics*[6] [21].

Macles or twins: starting with Jean-Baptiste Romé de l'Isle

While recording regularities in the shapes of crystals,[7] Jean-Baptiste-Louis Romé de l'Isle (1736–1790) also

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[1] In French, Georges is spelt with a silent final *s*.

[2] A process called 'hydrothermal synthesis'. Robert Bunsen used glass vessels in 1839.

[3] In 1893, in parallel with Henri Moissan, he even thought he might have succeeded in synthesizing diamond.

[4] Charles Friedel had studied at the University and was not a 'Polytechnicien'. Conversely, the French University always refused to grant Georges Friedel a salary when he taught at Strasbourg University after 1919. This dual French school system still exists today.

[5] Having spent his youth in an apartment in the building of the School of Mines, where his parents lived since his father also was the curator of the mineralogical collection, Georges had first expressed the wish to specialize in a quite different field, namely Naval Architecture, after the École Polytechnique. Yet, being rated first, he was not free to choose.

[6] G. Friedel strongly objected to the inappropriate term 'liquid crystal' (Otto Lehmann's Fliessende Krystalle) but this appellation remained.

[7] First noted by Nicolas Steno, or Nils Stensen ['Son of Stone'], (1638–1686), an outstanding anatomist who also layed down the fundamental principles of stratigraphy, and thus of geology. Steno later ruined his health in Catholic missionary work. He was beatified in 1988. His 'preamble about solids naturally contained within solids' (De solido intra solidum naturaliter contento dissertationis prodromus, that is, an attempt to explain the formation of fossils), published in Florence in 1669, remained largely unknown. To give full support to the law of constancy of inter-facial angles for minerals of the same species, the technical invention of the contact goniometer by Arnould Carangeot, Romé de l'Isle's assistant, was essential. About goniometers, see [22].

Table 2 Classification of Friedel twins

Type of twin	Index	Comments
1 merohedric twin	$I = 1$	The orientation of the atomic motif changes from one grain to the other
1′ pseudomerohedric twin		Idem, for structures which have quasi-symmetry elements (lattice)
2 reticular merohedric twin	$I > 1$	With respect to its 'twin lattice', it is like a merohedric twin
2′ pseudo reticular merohedric twin		Idem, for structures which have quasi-symmetry elements (lattice)

By construction, the orientation of the 'twin lattice' of a reticular merohedric twin does not change whereas the orientation of the associated super motif, which contains I primitive motifs, changes from one grain to the other, hence the analogy with the merohedric twin case (as explicited by Georges Friedel). Merohedric twins are common in minerals which have complicated atomic motifs, although staurolite is a beautiful counter example (see caption of Fig. 1). For elements with only one atom per primitive cell, like fcc and bcc metals for instance, only reticular merohedric twinning is possible. Georges Friedel explicited in 1933 a new type of twin for which there is no three-dimensional twin lattice, but just a one-dimensional, or two-dimensional, twin lattice at the boundary [110]. He died on the 11th of December of that very same year. See Nespolo and Ferraris [127] for an extended classification of twins

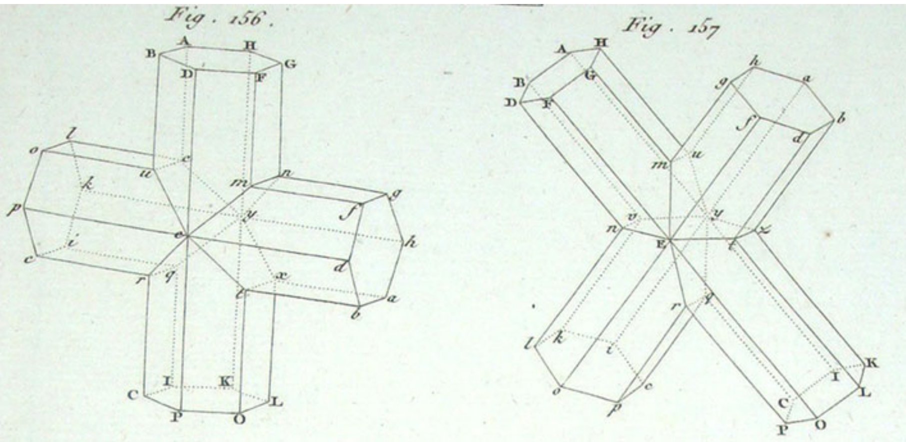

Fig. 1 Reproduction of the sketches drawn by René-Just Haüy for the two types of staurolite twins. These sketches are useful to understand Haüy's quotation given in Appendix A. They also illustrate the 'entering angles' mentioned by Jean-Baptiste-Romé de l'Isle. They are in the 21st plate in the fifth volume of Haüy's 1801 treatise on mineralogy. The picture here has been taken at the Library of the École des Mines in Paris. The (rare) Greek cross variety (on the left, 90°-variety) has a twin index equal to 6, and the (frequent) Saint Andrew's cross variety (on the right, 60°-variety) has a twin index equal to 12, see [41] and [128]. Considered as the paragon of the penetration twins, staurolite twins are actually very complicated. The chemical formula of staurolite is complex: it is a hydrated ferro-alumino-silicate which contains other metallic elements such as Mg, Zn, Ti and Mn. The 'Staurolite story' up to 1983 is given by the Donnays [129]. In Greek *stauron* means cross, and *lithos* means stone

observed the common occurrence of crystal groups with two inverted halves of similar shape, which he named 'macles' in 1783: 'When, in a given crystal, there is one or several entering angles (as in Fig. 1 for instance), one must conclude that this is not an elementary crystal but a group of two or several crystals, or even two inverted halves of a similar crystal. This crystal is then named a MACLE' [23] (see G1 in Appendix G). Abraham Gottlob Werner (1750–1817) used the word 'Zwillingskristall' more casually in 1791, and spoke of 'zwillings cristallen' when his students Johann-Pierre Vanberchem-Berthout and Henri Struve translated his lectures in French in 1795, writing 'jumeaux' (twins) and also 'groupes de crystaux'.[8] René-Just Haüy (1743–1822) proposed the term 'formes secondaires' in 1801. While German and English scientists use *Zwillingskristalle* and *twins*,[9] macle is still the word

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[8] Note the variability of the orthography: *crystaux*, *cristaux*, *cristallen*, *Krystalle*, *Kristalle*. The Greek root 'krustallos' meant

Footnote 8 continued
'solidified by cold' (kruos: see cryogenics). In ancient times quartz was believed to be a permanently solidified form of ice. Robert Boyle was the first to use the word crystal in a general sense, not restricting it to rock crystal, in The Sceptical Chymist (1661). The German word Quarz is presumed to be of Slavic origin, although its exact meaning is not known.

[9] With the common etymology of *zwei* and *two*, akin to duo, double, duplex, dyad, as well as *deux* in French. Macle was also used in English, for instance by Lord Kelvin of Largs, in a Robert Boyle Lecture delivered at the Oxford University Junior Scientific Club, on the evening of May 16, 1893 (and reproduced as Appendix H in the Baltimore Lectures): 'Coming back to quartz, we can now understand perfectly the two kinds of macling which are well known to mineralogists …'.

used in French.[10] Twins exist in a fascinating variety of secondary shapes to which Haüy gave enchanting names such as transposé, hémi-trope, sexradiée, cruciforme, or géniculée.[11] These secondary shapes also seemed to comply with some rules of regularity and Mineralogists speak of 'twin laws'.

Twins, with Charles Friedel, Ernest Mallard, and Georges Friedel

In his studies of pyroelectricity, only present in homogeneous crystals belonging to polar crystal classes, Charles Friedel noted that the possible occurrence of hidden or partially hidden twins could prevent the pyroelectric phenomenon [24]. This suggested that twins change the global symmetry of the crystal in which they occur, at least with respect to pyroelectric behaviour. Similarly, Ernest Mallard actually explained the optical properties of many crystalline materials that could not be accounted for otherwise [25]. This globally correct explanation based on twins implied phenomenological models about the internal, atomic structure of crystalline minerals and their twins. Such models were still crude and even wrong, but the symmetry principles were enthralling. Ernest Mallard wrote in 1887: 'The frequency of such groupings [the (multiple) twins] is such that we must consider them as corresponding to a very important property of inorganic matter which they show us as striving to realize the most symmetrical arrangement possible, probably because maximum symmetry is related to maximum stability'. [26]. Some of Mallard's disciples extended this idea to the point that the cautious Georges Friedel felt the need to warn explicitly, in 1926, against 'the vague and mystical idea, often expressed, that the macle is due to a natural tendency of the crystal towards a more symmetric state'.[12]

The time was not ripe for a complete understanding of twinning and, at the beginning of the last century, Georges Friedel tried mainly to improve and complete the geometric classification of mineral twins that had been started by his revered mentor Mallard (who died in 1894). He included all known twins, but excluded unjustified hypotheses about the atomistic level.[13] This task, of course, was a formidable one, as Mallard had given only the main outlines and had to be corrected on some points. This work involved the critical examination of hundreds, perhaps thousands of samples,[14] as well as the critical re-examination of tens or hundreds of papers written by mineralogists,[15] together with a prodigious capacity for geometrical abstraction. Most minerals are chemically and crystallographically complex objects. Their Bravais lattices can take any

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[10] The French also use the name 'joint de grains' = grain boundary (Korngrenze). For the etymology of macle, Webster's dictionary gives the heraldry term mascle which corresponds to an empty lozenge, from the middle-old Dutch mask and maesche, which also gave mesh (= Maesche = maille). Hence, sometimes, a circumflex on the *a*: mâcle (for instance Pierre Curie in 1900, [17]). Recent comprehensive French dictionaries like Le Grand Robert (1985) and the Trésor de la langue française (CNRS & INLF Nancy, 1985) give the same etymology. The Trésor writes both macle and mâcle (mâcler).

[11] As a Teacher of Grammar at the Cardinal Lemoine College in Paris, René-Just Haüy got acquainted with Charles Lhomond, a famous grammarian who was very keen in botany. In order to please his Friend, René-Just learned the names of hundreds of plants and this certainly later helped him name crystals and groupings of crystals. René-Just Haüy had no inherent taste for Botany, but his walks with Charles Lhomond in the Jardin du Roy, adjoining their College led him to attend the lectures of Louis-Jean-Marie Daubenton who also taught Mineralogy.

[12] But from a purely aesthetical view point, I am sure that all would have been delighted at the sight of a drawing by Albrecht Dürer in his manual on measurement of lines, areas and solids by compass and ruler [27]. This drawing looks like a (double) five-fold twin, almost quasiperiodic (a size-limited approximant in fact), see [28] and [29]. Figure 2.3, by Eric Lord, Alan Mackay and S. Ranganathan, has a perfect pentagonal shape, much akin to the characteristic hexagonal shape of multiple twinning in aragonite. It is a pity that multiple-twinning led Linus Pauling (1901–1994) to reject the discovery of quasicrystals in 1985 [30]. Yet that challenge was not illogical and certainly stimulated refinement of the arguments in favour (the pigeons pro eventually won versus the contra cat, see [31]). Linus Pauling tried to contact with Danny Shechtman but unfortunately no satisfactory agreement was reached before Pauling's death (D. Shechtman, personal communication, July 2010).

[13] Even if his father was a proponent of the existence of atoms, as was his mentor Adolphe Wurtz (1817–1884), it was clear that little was known about their actual organization within a crystal until the advent of X-ray diffraction in 1912. It is worth noting that 'Friedel's law' in X-ray crystallography was established by Georges Friedel as early as 1913. [32]. This law states that the intensities of the Laue-Bragg diffractions I(Q) and I($-Q$) are equal under normal conditions. That is, the information obtained by diffraction is centro-symmetric and cannot establish whether the real-space atomic distribution is centro-symmetric (with a point of inversion) or not. This also means that diffraction spots appear in pairs which have recently been called 'Friedel pairs': Friedel pairs are key to both the efficiency and accuracy of X-ray diffraction contrast tomography, which permits non-destructive mapping of grain shape and crystal orientation in polycrystals. [33].

[14] With the rejection of many chance crystal groupings that may look like twins at first sight but are actually aberrant twins ('macles aberrantes'). For instance, 'specimens noted I and III [in quartz] by Zyndel would be [according to Zyndel] twinned according to the La Gardette law (Japanese law). It suffices here to look at the sample with the naked eye, without any measuring and just having its faces glance, to realize that such is not the case'. [34].

[15] Many German scientists also contributed to the descriptions and analyses of twins: Christian Samuel Weiss, Friedrich Mohs, Carl Friedrich Naumann, Gustav Rose, Friedrich Eduard Reusch, Heinrich Adolf Baumhauer, Otto Mügge, Gustav Tschermack, Victor Moritz Goldschmidt, Jakob Beckenkamp, not to name all. Georges Friedel opposed many of them, but not because France had lost in Sedan in 1870: Georges Friedel also opposed his compatriot Frédéric Wallerant [35], and criticized Ernest Mallard when their views differed.

crystallographic symmetry and usually the positions of the atoms further lower the space group symmetry. If the symmetry is not lowered, the crystal may exhibit all its main faces and is called holohedral. If the available samples of a crystal exhibit two sets of facets (both sets being clearly related), it is called hemihedral. If parts of a complex crystal group can be divided into four sets, it is a case of tetartohedry, and one can even have ogdohedral crystals. One speaks of merohedrism versus holohedrism.[16]

Many twins correspond to simple transitions, across the twin boundary, from one crystallization of a merohedry to another one, without having to change the orientation of the Bravais lattice.[17] These 'twins' are termed merohedric, or twins by merohedry. There are also numerous cases of pseudomerohedry for crystals possessing elements of quasi, or pseudo, symmetry, within an (obliquity) acceptance limit of 5° to 6°.

On the other hand, some twins may only imply a tilt of the Bravais lattice with respect to a surface which includes the tilt axis, and these twins correspond to our familiar symmetric tilt grain boundaries.

René-Just Haüy, Auguste Bravais, Georges Friedel and the 'common lattice:' the twin index

Symmetric tilt grain boundaries (GBs) were first described by René-Just Haüy and by Auguste Bravais (1811–1863)[18] as 180° twist GBs: 'half turned' crystals with respect to an axis perpendicular to the boundary surface or twins by hemitropy. Since this geometrically correct description does not correspond to any physical mechanism,[19] Mallard finally recommended avoiding this designation,[20] as did G. Friedel. Georges Friedel was the first to realize, in 1904, that for these twins, although the primitive (Bravais) lattice of one grain does not extend without change of orientation into the other grain,[21] nevertheless a sublattice of that Bravais lattice does. This sublattice may be termed a 'multiple lattice' with respect to the primitive Bravais lattice because its generative translation vectors are combinations of multiples of the primitive vectors (caveat Reader: the multiple lattice is a sublattice from a mathematical viewpoint but, because it is based on a supercell, i.e., a multiple cell, it is sometimes improperly called a superlattice). The sublattice is common to the two lattices of the twin and is the well known, although not too well named, *coincident site lattice*, and is commonly known as the *twin lattice*. Its nodes, the twin lattice nodes, are the lattice nodes (nodes, not atomic sites, see Appendix D) which are common to both crystal lattices, which are *coincident*, or, to use Friedel's language, which are restored ('rétablis') by the twin operation (a general, non-twin, transformation would not ensure any coincidence). Then, 'what is of importance', as Friedel wrote in 1904, 'is to know what is the ratio of the total number of nodes of the simple [primitive] lattice to the number of restored nodes. We shall name this ratio the twin *index*'. [39] (see G2 in Appendix G). This twin index, is our well known (inverse density of) coincidence index. G. Friedel also noted that the volume of the multiple cell is a multiple of the volume of the primitive cell and it is clear from his reasoning that this multiple number corresponds to the twin index even though Friedel did not state this last remark explicitly in 1904 (he will in 1920). With respect to the shape of the multiple (twin) cell, the primitive lattice cell is different and the positions of the primitive nodes in each grain correspond to two distinct possibilities for associating them as motifs with the twin nodes of the twin cell. This view of the lattice elements in each grain of the twin with respect to the twin lattice that does not change its orientation from one grain to the other is reminiscent of the merohedric twin definition except that it constitutes an unformal extension of it.[22] Georges Friedel called such twins 'twins by reticular [lattice] merohedry' ('macles par mériédrie réticulaire') to distinguish them from the twins by merohedry, yet suggesting the connection.

To summarize, Mallard had considered what Friedel named twins by merohedry and twins by pseudomerohe-

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[16] *Mero* means *part* in Greek, as opposed to *holo* meaning *whole*. *Hedra* means *seat*, *base* or *face*. *Hemi* means *half*, *tetartos* means *four* and *ogdoas eight*. When *hedra* comes with a prefix it usually looses the aspired *h* (a special diacritic sign on the *E* in Greek which is then pronounced by rough breathing). This explains the French and German spellings of for instance: polyèdre, holoèdre, polyeder and holoeder. Modern English spelling keeps the *h* and writes polyhedron and holohedry, etc. French writes *mériédrie*, although *méroédrie* would be slightly more correct.

[17] Only the orientation of the atomic unit (basis) within the primitive cells changes. These twins have a twin index (see below) equal to 1.

[18] Auguste Bravais first wrote with his elder brother, Louis: an Essai géométrique sur la symétrie des feuilles curvisériées et rectisériées. This was transmitted to the French Academy of Sciences before 1837, see [36].

[19] 'But it is clear that this is a purely fictional move' ('mais il est clair que c'est là un mouvement purement fictif, et que la coordination moléculaire se fait symétriquement par rapport au plan d'hémitropie'), said Auguste Bravais in 1850 [37]. For instance, the $\Sigma = 3$ $\{111\}\ \langle 110\rangle\ \theta \sim 70.53°$ twins in cubic systems can also be described as hemitropic $\Sigma = 3$ $\{111\}\ \langle 111\rangle\ (\theta = 180°)$ (as well as $\Sigma = 3$ $\{111\}\ \langle 111\rangle\ \theta = 60°$ twist grain boundaries since $\langle 111\rangle$ are threefold axes in cubic systems).

[20] In 1885 [38], not in 1876 [25].

[21] As is the case for the twins by merohedry described previously.

[22] The primitive lattice point group is not necessarily a subgroup of the coincidence lattice point group, because it may possess symmetry elements that are not shared by the coincident lattice (see [40] and [41]).

dry,[23] [25, 26, 38], while Friedel had extended this idea to cases where only a sublattice ('multiple lattice') is common to the two grains, and named theses cases twins by reticular merohedry.[24] For elementary metals with monoatomic occupancy of lattice nodes, these are the only possible twins and that is why metallurgists are so used to the idea. Friedel was working with natural twins macroscopically observable in his time, in consequence he noted that the twin index was only very low, by definition equal to 1 for (pseudo)merohedric twins, usually equal to 3 for twins by reticular merohedry, and rarely equal to 5, for cubic crystals with the (210) reflective plane.[25] Twins with higher indices were assumed to be even rarer. Besides the adequation to sheer observable data (once properly observed, see footnote 14 on the aberrant twins), and the predictive power of the concept of a low index, Friedel also argued that the smaller the index, the better the continuity from one grain to the other: 'Whatever the mechanism thanks to which the continuity of a multiple lattice suffices to ensure the cohesion between the differently oriented multiple motifs, this cause can act only if the multiple cell is not too large'. [39] (see G3 in Appendix G).

Georges Friedel published his 'Études sur les groupements cristallins' (Studies on Crystalline Groupings) in three long articles in the French Bulletin de la Société de l'Industrie Minérale, and, simultaneously, as a monograph [39]. He used them in his lectures at the École des Mines in Saint-Étienne.[26] These 1904 articles are partly integrated in his 1911 book 'Leçons de cristallographie'. [42]. In 1905 Georges Friedel almost attributed his discovery to René-Just Haüy, see Appendix A.

The twin index 'Σ' (Friedel's *I*): geometrical formulae

In 1920, in 'Contribution à l'étude géométrique des macles' [43], Georges Friedel consolidated his work on the coincident lattice and the twin index by providing explicit formulae to obtain this index. There he introduced the Σ symbol for the ratio of the volume of a multiple cell of the twin lattice to the volume of the primitive cell. Georges Friedel indicates that if p, q and r are the indices of the twin plane, and g, h and k the indices of the axis perpendicular to it, then $\Sigma = |pg + qh + rk|$ ([43, p. 290]; [44, p. 250]). The summation character of this analytical formula probably explains the choice of the 'Σ' symbol. In the cubic case, it gives $\Sigma = p^2 + q^2 + r^2$. Then if Σ is odd, the twin index I is Σ, but $I = \Sigma/2$ if Σ is even. In some other, non-cubic cases, one may even have $I = \Sigma/4$. This also implies that the multiple cell Friedel first considers is not always the minimal multiple cell. All the definitions and formulae given by Friedel in 1920 are included in the 1926 version of his celebrated book 'Leçons de Cristallographie' that he taught at the University of Strasbourg[27] [44]. A table presentation of all the possible cases is given in Table 3 where Friedel's Σ is noted S by José Donnay [45]. In today's materials science, one uses only one symbol, Σ, as the ratio of the volume of the (minimal) multiple (twin) cell to the volume of the primitive cell, this ratio being equal to the ratio of the total number of nodes to the number of nodes 'restored' by the twin operation.[28]

The material lattice: where are the atoms and what can they do?

Georges Friedel considered his laws as empirically demonstrated and thus free of any theoretical objection. That did not mean of course that all questions were settled. Already in 1904 he wrote: 'We shall find, during the study of crystal structures, reasons to believe that it is the material lattice [the crystal structure] rather than the mathematical lattice which determines twins' [39] (see G4 in Appendix G). He insisted in his 1911 book: 'Twins are like external facets: given a lattice, one can tell what are the possible options and which will be the more frequent, roughly, but not in any detail which will occur under such and such crystallisation conditions'. 'The properties of the motif intervene again, in a way yet impossible to predict and explain, to make frequent a given macle, rare or unknown another which would have seemed inevitable according to lattice conditions'. [42][29] (see G5 in Appendix G).

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[23] These twins are frequent in minerals which have a complicated atomic group associated with each primitive lattice point or node.

[24] With a natural extension to cases of twins formed by pseudo reticular merohedry. See Table 2 for a synthetic presentation of the four classes developed by Friedel.

[25] Friedel noted that the (310) case had never been observed.

[26] A School to whose development he significantly contributed. He became Head of the School from 1907 to 1919, except for the war years.

[27] The Friedels were Alsatian from Strasbourg. As a first name, Friedel is a variant for Gottfried. The German *Friede* means peace.

[28] See Appendix C for some further considerations on simple analytical properties of the twin index in cubic crystals.

[29] It is remarkable that G. Friedel immediately understood the principles of X-ray diffraction discovered in 1912, and explicited the inversion symmetry limitation (under normal conditions) known as Friedel's law ([32], see also footnote 13). Donnay and Harker were able to expand Friedel's 1911 preview for surfaces in 1937 [46]. Friedel's formalism is limited to a consideration of Bravais lattices and does not incorporate the Schönflies-Fedorov space groups. Denis Gratias, Richard Portier, Robert Pond and others further extended Friedel's formalism for twins in the 1980's, but this goes beyond the scope of this article. Also see Appendix D.

Table 3 Reproduction of the synoptic table of Friedel's twin indices drawn by José and Gabrielle Donnay in the International Tables for X-Ray Crystallography 1959 [45], with IUCr's copyright permission

Twin index in terms of $S = \|hu + kv + lw\|$ Twin plane (hkl) quasi-normal to row [uvw] or twin axis [uvw] quasi-normal to net (hkl)			Index
The crystal lattice is primitive (P):			
		S odd	S
		S even	S/2
The crystal lattice is one-face-centred (say C):			
$h + k$ odd			S
$h + k$ even	$u + v$ and w not both even	S odd	S
		S even	S/2
	$u + v$ and w both even	S/2 odd	S/2
		S/2 even	S/4
The crystal lattice is body-centred (I):			
$h + k + l$ odd			S
$h + k + l$ even	u, v, w, not all odd	S odd	S
		S even	S/2
	u, v, w all odd	S/2 odd	S/2
		S/2 even	S/4
The crystal lattice is all-face-centred (F)			
$u + v + w$ odd			S
$u + v + w$ even	h, k, l not all odd	S odd	S
		S even	S
	h, k, l all odd	S/2 odd	S/2
		S/2 even	S/4

This table expresses in modern language, for the naming of the crystal lattices, the results already given by Friedel in 1920 (pp. 293–294; idem in 1926 p. 252). Donnays' S symbol corresponds to Friedel's Σ. The 'quasi-normal' cases give rise to 'pseudo-merohedries'. Joseph Désiré Hubert Donnay (1902–1994) was born in Grandville in Belgium. Gabrielle Donnay (1920–1987) was born in Silesia. Also see [106]

For the very simple case of the {111} twin in elemental face centred cubic materials, such as copper, nickel or gold, elements of a solution had been provided by William Barlow in the second of his seminal 1883 Nature papers: 'The modification, as we see, involves *no departure from the condition that each particle is equidistant from the twelve nearest particles*'. [47]. Indeed, the modification at the twin boundary consists in a local hexagonal-like [ABA] plane stacking replacing the periodic ABC stacking which characterizes the face centred cubic (fcc) packing in the ⟨111⟩ direction. We now know that explaining the crystal structure (Friedel's material lattice) must extend beyond simple, hard-sphere packing considerations. Copper and alumin(i)um, which are both fcc elemental metals, have very different {111} twin fault energies and the proportion of {111} twin faults in polycrystalline copper is far higher than in polycrystalline aluminium. The situation gets even more complicated for the cubic diamond structures like diamond, silicon or germanium because of the two-atomic motif in the primitive, rhombohedric, cell. Consider also the Dauphiné twin in α-quartz as analysed by Friedrich Heide in 1928 [48]: there a local hexagonal β-quartz structure occurs at the twin plane of a Dauphiné twin between two (merohedral) trigonal α-quartz grains. The α-quartz is the common low temperature phase whereas β-quartz is the stable polymorph above 573 °C. An elementary description of this relationship on the twin plane was given by Clifford Frondel in 1945, [49] (also see Fig. 3.3.10.7 in volume D of the International Tables of Crystallography [41]). The β-quartz is now believed to be a dynamic structure, a temporal average between two α orientations, see for instance [50], with an obvious connection to the Dauphiné twin (Ernest Mallard would have been pleased with this symmetry consideration).[30] This discussion illustrates the Aminoff and Broomé's rules expressed in 1935 [56].[31]

George Preston, from simple atomic considerations (see [58]) argued in 1927 that the {111} twins which commonly exist in fcc metals probably cannot exist in elemental body centred cubic structures, for which the {112} twin plane seemed more acceptable [59]. Thus, the claims for {111} twins observed in α-iron most probably corresponded to {112} twins. Preston's argument was based on maximum continuity and minimum stress at the atomistic level of the interface.

Some twins appear intrinsically more frequent than they ought to be, through indirect causes, such as the geometrically necessary occurrence of nth order $\Sigma = 3^n$ twins in fcc crystals containing many $\Sigma = 3$ {111} twins, such as diamond [60], germanium [61] or copper [62].[32] These $\Sigma = 9$ and 27 twins do not occur because they have a low Σ or a low interfacial energy, but rather because there are many $\Sigma = 3$ {111} twins which cannot but meet.[33] A more complex phenomenon can occur in quartz where (merohedric) Dauphiné twins (see above) are induced easily by cooling from above 573 °C and may cut across pre-existing twins of another kind (e.g., Brazil twins), thus 'twinning the twin', as Clifford Frondel nicely expressed it [49].

Metallurgy. man-made grain boundaries. still structured? Rosenhain's challenge

In Metallurgy things seemed more difficult to handle. Natural crystals of pure metals were rare, although some existed.[34] As far as specialists were concerned,[35] there was little doubt that all metals under normal conditions, i.e., not severely deformed plastically as in Tresca's extrusion machine ([71]), were crystalline. For instance, Henry Clifton Sorby had no doubt in 1887 that the heat-prepared iron he observed with his optical microscope was made of crystalline grains: 'It seems to me nearly certain that the separate grains (seen in his Fig. 2) are separate, though imperfectly developed, crystals'. [72]. Yet there was not much to be deduced from the shapes of these grains, let alone the nature of their boundaries. In 1904/1905, Georges Friedel wrote that due to lack of sufficient data, he would restrain his (numerous) case studies to twins exhibited by natural minerals. He only has a few lines in his 1911 book concerning the 'soft metals' ('métaux doux') such as lead and copper, and not a word in his 1926 book.

With the development of the so-called Second Industrial Revolution (1870–1914), the interesting metals were not the native ('mineral') ones but the industrial products artificially prepared from the melt through various heat-treatments and purification, or alloying.[36] In developing the knowledge of steel, Floris Osmond (1849–1912) and Jean Werth (1855–1928), considered in 1885 the solidification of liquid iron containing carbon: They explained that globulites of iron precipitate within a liquid essentially made of iron carbide. These globulites grow until they almost touch one another along faces delimiting them as polyhedra. The liquid iron carbide separates them at the interfaces and eventually solidifies thus keeping the polyhedra united together so that Osmond and Werth called it the *cement*. [73] (see G6 in Appendix G).

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[30] In contrast, the French('La Gardette')-Japanese twin in quartz is much rarer and complicated, see [48, 51–54]. There are many other twin laws for quartz. One of these is also known as the Friedel-law, or Friedel-twin, having been found by Charles Friedel in artificial quartz in 1888 [55].

[31] Gregori Aminoff and (his wife) Birgit Broomé proposed several rules in 1935 about the atomic structure of twins in minerals. These rules have been reported by Robert Cahn [39]: 1. When two individuals form a contact twin either one or two layers of the structure at the interface are common to both individuals. 2. The atomic coordination in the transition layer is either (almost) identical with that in the crystal structure or closely related to it. In the latter case, the transition structure is that of a possible polymorphic modification of the structure, or else that of a modification which would be possible for that substance. British physicist by heart, R.W. Cahn was born in Germany and could speak French, see [57]. His 1954 review article is a wealth of informations about twins. .

[32] The order n of a $\Sigma = 3^n$ twin (or any $\Sigma = \Sigma_o^n$ twin) should not be confused with the twin index Σ itself. Such a confusion can arise because n has also been used as a symbol for the twin index (by G. Friedel himself, in his textbooks. In 1926 one finds n and I), and Paul Niggli (see Appendix B) translated Friedel's French word *indice* by *Ordnung* in his books in German ([63, 64]).

[33] These twins thus merit study at the atomistic level, and have been investigated by joint numerical and observational studies, see [65, 66]. These twins are called grain boundaries in these studies. See, however, Appendix E.

[34] For instance William Lawrence Bragg, Bragg junior, could derive the fcc structure of copper as soon as 1914 thanks to natural crystal specimens from the Mineral Laboratory at Cambridge [67]. Other metal samples, usually consisting of tiny crystalline grains, had to await the development of the powder diffraction technique in 1917 (Peter Debye and Paul Scherrer in Göttingen, Germany, Albert Hull in Schenectady, in the US).

[35] Compare the following with Ronald King and Bruce Chalmers [68], Chaps 1 and 2 of Donald McLean [1], Ernest Hondros' 'enquiry' in 1995 [69], and David Brandon's recent perspective [70].

[36] Typical is the first sentence of HC Sorby in his article 'On the microscopical structure of iron and steel', published in 1887: 'It is now more than 20 years since I first commenced to carefully study the microscopical structure of iron and steel, in order, if possible, to throw light on the origin of meteoric iron; but soon found that the results were of even more value in connection with practical metallurgy'. [72]. Most ceramic materials are also manufactured, but rarely from the melt and, at first glance, look more like hard minerals than like soft metals.

Fig. 2 Sketches of a grain boundary structure at the atomic level, as given by Hargreaves and Hills in 1929 [89], with Maney Publishing copyright permission. It corresponds to an asymmetrical tilt grain boundary $(100)_1//(\bar{4}30)_2$, [001], for simple cubic lattices, with a twin index equal to 5. I circled the atoms in coincidence at the interface in the geometrical sketch on the left to emphasize the periodicity and I enclosed the 'transition zone', that is the interface-periodic cell within which the atomic positions may be considered as modified with respect to the geometric positions. It is relatively thick

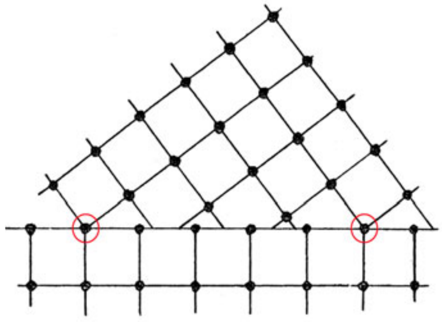

FIG. 11.—Normal Atomic Position.

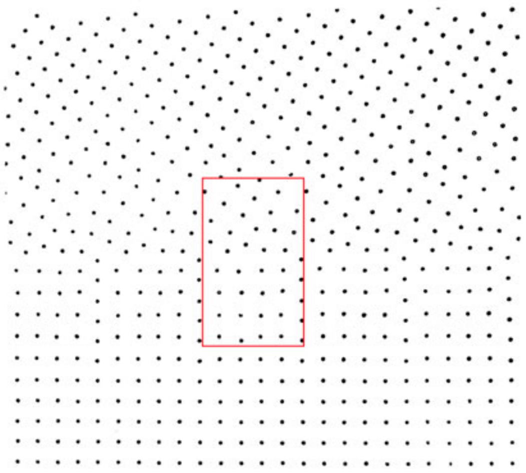

FIG. 12.—Formation of Transition Zone Patterns. To illustrate the conception and not to give the actual positions of the atoms.

Marcel Brillouin (1854–1948, Léon Brillouin's father) wrote in 1898, explicitly considering industrial metals, full of fluxes and impurities: 'Let us consider a body made of isolated crystalline grains, very small, embedded in a more or less continuous lattice of very viscous matter'. [74] (see G7 in Appendix G).

Georg Quincke (1834–1924), in a presentation made before the Royal Society of London in 1905 and summarizing 'the results of a lengthy research on the formation of ice and the grained structure of glaciers' observed that 'the "glacier grains" are foam-cells filled with pure or nearly pure ice, and separated from one another by visible or invisible walls of soily salt solutions'. [75]. The role of the eutectic separation was clear, as in the two previous quotations.

Floris Osmond, in 1911, in the written discussion of a paper by Louis Grenet, on heat transformations of steel, wrote: 'When two grains possessing different crystalline orientation touched one another, their respective reticular systems could not interlock, and there was strong reason for the belief that there existed between the two grains a sort of amorphous envelope, the average thickness of which was of the same order of thickness as the crystalline molecule'. [76]. In Osmond's discussion it appeared that although invisible under the microscope the thickness was not negligible. When Osmond writes that reticular systems of different orientations cannot interlock, he indicates an intrinsic microscopical mechanism, free from any eutectic separation consideration.

Walter Rosenhain and Donald Ewen were thus entitled to explicitly quote that suggestion in 1912 and to extend it as follows (p. 155): 'The proposed explanation depends upon the concept in Osmond's remark quoted above, viz. that of a "crystalline molecule" or unit which is large compared with what one might term the liquid molecule. This concept implies that the act of crystallization from the liquid state requires not merely the orderly arrangement of the molecule, but also a grouping together of the previous existing liquid molecules into larger molecules or groups of molecules which we may term the "crystal units"' [77, 78]. During his thesis work under the direction of Alfred Ewing some 12 years before, Walter Rosenhain had been able to explain the plasticity of metals in terms of shear between their crystalline planes: [79, 80]. He had then worked for 5 years on glasses for industry (see [81]). His statements were therefore accepted when, to explain the ductile behaviour of polycrystalline metals at elevated temperatures as opposed to their brittle behaviour at low temperatures, he suggested that grain boundaries were intrinsically amorphous like glass, invoking additionally Osmond's authority.[37] Three persons challenged the possible thickness of the amorphous envelope: C.H. Desch in

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[37] Rosenhain had been thinking about the problem for several years, presumably since 1904, as would appear from the discussion of a paper by GD Bengough [82] where Guy Bengough (1876–1945) wrote that 'the first action of a dilute reagent is to eat into the crystalline boundaries' so that 'the deduction may reasonably be drawn that the individual crystals in a pure metal are normally bound to one another by some substance stronger than the crystals themselves, but more easily attacked by etching agents. This substance must surely be no other than Beilby's amorphous material, arranged in a thin, more or less continuous layer round the crystals'. Sir George Beilby (1850–1924) never reacted positively to this hypothesis concerning the structure of grain boundaries.

1912 and Guertler and Lantsberry in 1913, in the discussion sections of Rosenhain and Ewen's two papers. Floris Osmond himself died in 1912 so we cannot know what he would have said. Georges Friedel apparently never developed a scientific relationship with metallurgists[38] but continued to teach crystallography after the war and also became involved in the understanding of the nature of liquid crystals (an oxymoron he always refused to use, see footnote 6). During the war years he was attached to the French National Armament Factory at Le Creusot in Burgundy (see [83]) and employed his spare time translating English novels just to improve his English.

It is significant that Rosenhain insisted that his metals were pure and free from any impurity that could form eutectic.

In their textbook The Science of Metals published in 1924, two American metallurgists, Zay Jeffries and Robert Archer, wrote: 'The amorphous metal cement hypothesis is at the present time the *only* satisfactory explanation of the effect of temperature and rate of loading on the strength and manner of rupture of metals'. [84]. This hypothesis was explicitly retained in preference to two alternative models: '(1) There are voids between the two crystals; (2) there is a zone in which some of the atoms are held in *both* crystal lattices, in which case the lattices would be distorted at the surface of contact'.

The following year, at a meeting of the American Institute of Mining Engineers (AIME) in New York in February 1925, Francis Foley showed, based on the growing knowledge of ordered atomic structure of metallic crystals derived from X-ray diffraction analysis, that the interface layer had no 'atomic' reason to be thick and ought really to be very thin: In the discussion of a paper by Anderson and Norton that opposed the amorphous hypothesis of Beilby for the surfaces of mechanically polished metals, on the basis of X-ray data [85], Foley drew a planar diagram of the junction of three crystals, adjusting the interfaces atom by atom, and wrote: 'Such a diagram does not show much room for an intercrystalline amorphous cement'. [86][39] Foley augmented his argument at a fall meeting in Syracuse (NY) and his hand-made drawing was then supported during the discussion by a kitchen-recipe bubble model proposed by a man named Thum, from New York, even though bubbles admittedly could not be considered true atoms. [87, 88]. It is worth quoting Thum: 'The structures shown [in the drawing proposed by Foley] can be readily made in the kitchen. Place a dishpan containing a couple of inches of water, a piece of soap and a dish mop (one that has a wooden handle, and a tuft of cotton thread at the end of a piece of twisted wire) over a gas jet. Then as the water heats, a stream of fine bubbles apparently exactly the same size, will rise to the surface from the point where the twisted steel enters the wooden handle. These bubbles collect in blocks, perfectly arranged in a geometric pattern and float around, finally attaching themselves to the edges of the pan or the floating wood. You will get a typical arrangement, such as shown, with the intercrystalline cavities shown here; but there is no suggestion of amorphous cement in such a bubble aggregate, that is to say, the geometric arrangement is apparently perfect even out to the intersection. You can shove these bubbles groups with a knife and see the development of slip planes, and you can get a close picture of many ideas that have been introduced into the literature of X-ray investigation and theoretical metallurgy. One thing to remember is that bubbles of this sort are different from atoms (…)'. These arguments went unnoticed, however, probably because Foley's model was not able to explain the phenomena Rosenhain's model was assumed to account for.[40] Hargreaves and Hill in 1929 [89] also opposed Rosenhain's theory. Their drawings, see Fig. 2, correspond to an asymmetrical tilt grain boundary $(100)_1//(\bar{4}30)_2$, [001], in a simple cubic lattice, with $\Sigma = 5$, and $\theta = \cos^{-1}(4/5) \sim 36.87° \sim 36°52'$ (they actually wrote 'approximately 36°50′'). Their model suggested that the atomic structure at a selected grain boundary, at least for a set of special misorientations, ought to be ordered with a regular, periodic, pattern associated with a coincidence of some atomic sites in the interfacial plane. This proved independent on the relative thickness of the assumed interface after what they estimated what would be the relaxed atomic positions.[41] In the written

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[38] Although he did teach ferrous metallurgy in the 1890's at the École des Mines in Saint Étienne.

[39] Speaking of Anderson and Norton, Foley wrote: 'The authors have apparently driven another spike in the coffin of the general amorphous-metal hypothesis which has been reared a weakling from its inception'.

[40] That is, the (ductile) intergranular fracture of metallic polycrystals at high temperatures versus the (brittle) transgranular fracture at low temperatures (when the amorphous interface can be assumed to be as hard as a glass below its transition temperature).

[41] 'such positions as will balance the atomic forces'. This over estimation of the amplitude of atomic relaxations probably allowed them to consider that, under stress the interface would become amorphous so that 'the material will behave in the manner described by Rosenhain in connection with the amorphous cement theory'. Yet, even in the unstressed condition, Rosenhain wrote in the discussion that he could not accept their illustration: 'I think that it implies an arrangement of atoms in a condition which I think is not one of possible stable equilibrium. It implies atoms being brought in some places too close together and in others too far apart to fulfil what we believe is known of the conditions of atomic linkage that exist in solid metals. Such an arrangement of atoms is certainly improbable and would require proof before one could accept it as a fact'. Recent observations *and* simulations of asymmetrical grain boundaries in copper show that atomic disorder exists only locally [65, 66]. A true $(100)_1//(\bar{4}30)_2$ tilt GB has recently been grown, observed and simulated, in a ceramic material: $SrTiO_3$ [90].

discussion we find: 'It is to be regretted that neither Dr. Rosenhain nor Dr. Gough made any reference to the very definite point raised in the paper respecting the facility with which boundary movement [: crystal growth] takes place, and the objection on this score to both the amorphous cement theory and Dr. Gough's suggestion [viz that crystal boundaries consist of a layer of very small crystals]. The phenomenon indicates a very intimate connection between the lattices'. No doubt Georges Friedel would have been happy to read this last sentence (see the last quotation given in the next to last paragraph in the fifth section, labelled as G3 in Appendix G).

It was one thing to dismiss Rosenhain's model on theoretical atomistic grounds, but quite another thing was to replace it with a theory capable of explaining in a unified fashion the impressive series of observed phenomena that Rosenhain convincingly claimed he could explain. A dramatic change of paradigm occurred around 1934 with the official advent of a viable model of atomic dislocations.[42] But Rosenhain died in 1934. Georges Friedel had developed a related concept for liquid crystals[43] but was apparently not interested in metallurgy, and had died the year before.

In the second of his 1934 papers, Geoffrey Taylor gave a schematic figure of the 'boundary of two crystals at slightly different orientations' and he commented in writing that there are regions where: 'the disturbance of the lattice in passing from one block to the other is small', whereas, in the intermediate regions: 'the disturbance is a maximum'[44] [95]. Taylor's model, of course, explicitly includes dislocations and naturally was also used by Johannes (Jan) Burgers in 1939 (reprinted in 1940, with additional comments exchanged between J.M. Burgers and W. Lawrence Bragg). This model, which considers low angle GBs ('two crystals at slightly different orientations') allows for the derivation of an analytic formula for interfacial energy, since one can consider the dislocations as sufficiently deparated to be modelled as isolated lattice dislocations, as demonstrated by Read and Shockley in 1950.[45] This approximation is, of course, not valid for large angle twins where only an atomistic model can be applied. As recently noted [97], such a model had been applied by two of Georges Friedel's grandsons, Jacques Friedel and Charles Crussard (see Table 1), to complement an experimental study of grain boundaries observed in aluminium sheet prepared previously by Barney Cullity (the work was done in 1948–1949 but published only in 1953, [98]). Their model involved a crude interatomic potential taken from the 1936 book 'Metals and Alloys' by Mott and Jones.[46] The calculation involved almost no relaxation of the atomic positions other than the possible removal of an atom when two atoms either side of the boundary were found to 'overlap' at the interface (accompanied by the possible centring of the remaining atom). Although crude, this model could reproduce the main features derived experimentally for the relative variations in boundary energy. In retrospect, this agreement can be interpreted as an argument for a periodic and ordered structure of the grain boundary, even in metals. David Brandon and his coo-workers, Brian Ralph, Srinivasa Ranganathan and Mike Wald, were to demonstrate this directly on the basis of experimental observation with field ion microscopy in 1964 [100]. From an epistemological point of view, the visual evidence, provided by an imaging technique capable of resolving interatomic spacings, gave this latter study considerable impact.

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[42] Thum saw the development of slip planes but he unfortunately failed to recognize dislocations (which were probably present) because he had not been expecting to see them. Bubble soap models were rediscovered by Sir W. Lawrence Bragg and John F. Nye in 1947. With respect to Rosenhain's model, dislocations did not help to simplify the considerations of deformation mechanisms in polycrystalline metals, but they are necessary to explain in details what is observed because they correspond to reality. At about the same time, the early thirties, the neutrino was postulated, not to simplify the existing theories, but to explain the riddle of the observed continuous energy spectrum of nuclear beta electrons.

[43] G. Friedel proposed the term *nematics*, from the Greek *nema* meaning thread, 'because of the linear discontinuities, which are twisted like threads', ('à cause des discontinuités, contournées comme des fils' [21]). These topological defects correspond to *disclinations*. For discontinuities in smectics, G. Friedel and his son Edmond (see Table 1) noted in 1931 that they must have 'the form of groups of *focal conics*' ('les discontinuités n'y peuvent apparaître que sous la forme d'un groupe de coniques focales' [91], See also G. Friedel and François Grandjean in 1910/1911 [92, 93]). François Grandjean (1882-1975) later became a specialist of acarians.

[44] This idea was generalized by Nevill Mott in 1948: 'If two crystal planes are in contact, but cannot fit owing to different indices of orientation, one may suppose that the surface of contact is divided into islands where the fit is reasonably good, separated by lines near which fit is bad'. [94].

[45] The same reasoning applies for twin orientations near the special {111} twin in elemental fcc crystals, and as well as for the contribution of widely spaced secondary dislocations, so, as noted by Thornton Read and William Shockley, misorientations near energetically favoured twins may have the characteristic $|\delta\theta| \ln|\delta\theta|$ additional cusp contribution [96]. This does not work near the structurally favoured {122} twin, the energy of which does not correspond to a cusp.

[46] Jacques Friedel went to Bristol (1949–1952) to work with Nevill Mott and learn more about the electronic interactions in metals. Some of Jacques Friedel's later contributions in that field eventually led, with François Ducastelle, to the development of the Finnis–Sinclair potentials for transition and noble metals (see [99]). His stay in Bristol also led Jacques Friedel meeting his future wife, a younger sister of Nevill Mott's wife. He also met there with Charles Frank, who thus learnt of Georges Friedel's Leçons.

Conclusion: interfacing past, present and future and interfacing scientific communities

The year he died, Georges Friedel was in the process of extending his own classification of twins to incorporate some twins which formed by chance contacts between crystals in solutions probably followed by orientational accommodation at the two crystalline surfaces so as to reach a common periodicity along only one direction [40].[47] This pointed to the importance of the contact interface itself, its topology and atomic morphology. By learning both from the past and from contemporary observations, Georges Friedel kept an open mind right to the end of his life. His teaching on twins is still well-known by crystallographers in the 'mineralogical' community where it has been further extended and formalized. Scientists with a metallurgical background have largely forgotten his books and articles, and still seem to have as few contacts with crystallographers as Georges Friedel himself seemed to have had with metallurgists. In either case this is a pity, since both communities could only gain by learning more from each other and, by absorbing past teachings, perhaps more consciously and efficiently go beyond them.

Acknowledgements I thank Professor Jacques Friedel for uncounted mail exchanges. I thank my two anonymous referees for their valuable suggestions. I thank David Brandon for his encouragements and several email exchanges, and Hans Grimmer and Massimo Nespolo for several interesting discussions. I also thank the library department of the École Polytechnique, and the 'fonds patrimoniaux' of the École des Mines in Paris.

Appendix A

Georges Friedel and René-Just Haüy and the common lattice

Just after he had published his conceptual discovery of the existence of 'common lattices' in twins, Georges Friedel found [101] a preliminary indication of this phenomenon in Haüy's first Treatise on Mineralogy (1801) when Haüy discusses what he intends to prove by examination of the staurolite twins: 'In the examination (…) we shall mainly apply ourselves to show: 1°. That each hexagon junction [that is, each mathematical interface which can be drawn at the junction of the branches of the cross in the two varieties of staurolite, see Fig. 1: 90° (Greek cross staurolite) and 60° (Saint Andrews cross staurolite)] is, with respect to one or other of the prisms [that is, the grains], as would be a surface produced by the 'decrement'-law [that is, the boundary plane is a lattice plane of simple indices with respect to both grains]. 2°. That if one supposes the planes of each prism to be extended into the other prism, these extensions will have positions which can similarly be understood according to a 'decrement'-law [and this, together with 1° and the fact that this is the same lattice plane for a symmetrical twin, will give the common lattice]' [102] (see G8 in Appendix G).

Georges Friedel was correct of course. He could have added that Haüy's statement 2° is only preliminary. In fact Haüy failed to repeat it in his 1822 Treatise of Mineralogy (nor in the accompanying 1822 Treatise of Crystallography).

Only Georges Friedel could have found that preliminary indication, and only he would have written that this was *a clear statement* ('exprimé avec la plus grande clareté') of his own discovery.

In 1905 Georges Friedel gave the precise reference to Haüy: 1801, vol. 2, p. 88. He was not to give it again in his 1926 book (p. 425), where he only referred to 'Haüy (1801)', a treatise which comprises four volumes of written text.

Appendix B

The transmission of G. Friedel's teaching about twins: both ups and downs

The Swiss crystallographer Paul Niggli (1888–1953) was the first to integrate Friedel's classification of twins into his German textbooks in 1919 and 1924 [63, 64]. With a smaller impact, G. Friedel's approach appears also in published studies by some German scientists: Ernst Schiebold in 1919 [103] and Friedrich Heide in 1928 [48]. Jakob Beckenkamp in 1923 [104] and Margarette Löffler in 1934 [105] mentioned this approach in their review articles. In English, Joseph Désiré Hubert (José) Donnay, a Belgian born crystallographer and mineralogist, wrote an obituary of G. Friedel in 1934 [13] and used his approach in 1940 [106]. Charles Crussard referenced Friedel's basic idea in 1945 in a metallurgical study of zinc (hexagonal), containing 'obliquity' (pseudo reticular merohedric twins) [107].

To my knowledge, Whitwham, Mouflard & Lacombe were the first to restate Friedel's Σ with its explicit formula for the case of cubic crystals such as germanium and

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[47] Friedel wrote that what mostly prompted this extention was a 'beautiful work' by M. Schaskolsky and A. Schubnikow using in 1933 crystals of alum in an experiment very much akin to the later MgO smoke experiments. This Schubnikow is no one else that Alekseï Vasil'evich Shubnikov (1887–1970) who is famous for the Shubnikov groups, or antisymmetry groups, magnetic groups, coloured groups, which have been used in many fields, including the study of Grain Boundaries (for instance by Yves Le Corre and Hubert Curien in 1958, and by Denis Gratias and Richard Portier, and Demosthenes Vlachavas and Robert Pond in the 1970s and 1980s). Shubnikov had also been a pioneer in the formation and growth of crystals, in Leningrad (St Petersburg) and in Moscow.

copper: $\Sigma = h^2 + k^2 + l^2$ or $\{h^2 + k^2 + l^2\}/2$, in 1951 [62].

At the same time, Jacques Friedel, attending Charles Frank's lectures in Bristol (see footnote 46), commented on Frank's description of twins and led him to discover his grandfather's 'Leçons de Cristallographie'. The 'Leçons' fitted Frank's own sense of geometry (Jacques Friedel, personal communication, June 2010).

Jacques Friedel and Charles Crussard did not mention the twin index in their 1953 paper [98] because it was unnecessary.

JDH Donnay and his wife Gabrielle Donnay presented Friedel's possible twin indices in terms of $S = |hu + kv + lw|$ (Friedel's original Σ) in a synoptic table in the International Tables for X-Ray Crystallography in 1959 [45], see Table 3.

Besides to his own grandsons, Charles Crussard and Jacques Friedel, Georges Friedel's book was familiar to all French Metallurgists. These included Paul Lacombe and Claude Goux. The latter, after completing a PhD on grain boundaries thanks to bicrystals of pure aluminium specially prepared in Georges Chaudron's laboratory at Vitry near Paris [108], established an important research group for both experimental and theoretical work on grain boundaries at the École des Mines in Saint Étienne in the sixties. Srinivasa Ranganathan learned about Friedel's book through Claude Goux at Saint Étienne (see [109]).

It seems that this memory of Georges Friedel's work faded in the international metallurgical community. In his 1957 milestone monograph 'Grain boundaries in Metals', Donald McLean mentioned the work of Jacques Friedel and Charles Crussard, but not that of Georges Friedel [1]. In contrast the memory of Georges Friedel is very much alive in the mineralogy community (see Appendix F for a tentative explanation of this contrast), with Hans Grimmer, Theo Hahn, Helmut Klapper, Giovanni Ferraris and Massimo Nespolo, for instance ([41, 110–112], being selective). It is interesting to read in volume D of the International Tables of Crystallography that the 'Σ' symbol is specially used by metallurgists: 'The degree of three-dimensional lattice coincidence is defined by the *coincidence-site lattice index*, *twin lattice index*, or *sublattice index* [*j*], for short: *lattice index*. This index is often called Σ, especially in metallurgy. It is the volume ratio of the primitive cells of the twin lattice and of the (original) crystal lattice (i.e., $1/j$ is the 'degree of dilution' of the twin lattice with respect to the crystal lattice)'. [41].

A new term has been proposed to designate a specific 'science of twins': geminography [111, 112]. This comes from the Latin 'geminus' for twin. Gemini: twins, e.g., Castor and Pollux. The term should not be confused with gemology or gemmology, which is the science of gems and comes from the Latin 'gemma' meaning either a bud or precious stone. The term geminography appears for the first time in an article in Japanese by Hiroshi Takeda [113]. It has been proposed by José Donnay in a personal communication to Hiroshi Takeda who followed his lectures at the Johns Hopkins University in 1963 (see [112]). Donnay and Takeda published several articles together, including one on Compound tessellations in crystal structures (Acta Cryst. 1965 19:474–476), following Harold Coxeter's idea of a 'compound tessellation' (Configurations and Maps, Rep. Math. Colloquium, 1948/1949 8:18–38). Formulae in this same 1949 report inspired Srinivasa Ranganathan to derive his generative function during his PhD work in Cambridge. This was shortly before David Brandon left Cambridge for the Battelle Memorial Institute in Geneva, Switzerland, to work with Walter Bollmann (1920–2009) [100, 109].

Appendix C

Ranganathan's generating formula versus Friedel's approach, for cubic crystals

Friedel's approach: (hkl) $[hkl]$ 180° (hemitropy)

$$\Sigma = \left(h^2 + k^2 + l^2\right)/\beta$$

h, k and l are the (Miller) indices of the boundary plane: three relatively prime integers and β is 1 or 2 according to parity (in order to have Σ odd as it ought to be for cubic crystals)

Comments

One may then want to look for the minimal $(\langle uvw\rangle, \theta)$ mathematical representation (among the 24 equivalent representations in cubic crystals), or for a representation more suitable for a given purpose (for instance, the fcc twin $\Sigma = 3$ (111) [111] 180° is also (111) [111] 60° (the $\langle 111\rangle$ axes are threefold axes in cubic crystals) but is better visualized along a $\langle 110\rangle$ direction if one wants to see the traces of the ABC planes and the ABA fault in the …ABCABACBA… mirror structure. It is then described as a tilt (111) $[1\bar{1}0]$ $2\mathrm{tg}^{-1}(1/\sqrt{2})$ (~70.53°).

Ranganathan also noted in 1966 that 'this approach leaves the question of finding the possible Σ for a given axis undecided', without the help of a computer.

Ranganathan's formula [109]: considering a rotation axis $\langle uvw\rangle$

$$\Sigma = \left(x^2 + R^2y^2\right)/\alpha R = \sqrt{u^2 + v^2 + w^2}$$
$$= \mathrm{Norm}(<uvw>)\ \mathrm{tg}(\theta/2) = Ry/x$$

x and y are the two relatively prime integers (with no common divisors except 1) and α is a multiple of 2 so as to get Σ odd (as it ought to be for cubic crystals)

Comments

It is then not too difficult to find three relatively prime integers h, k and l which will fit Friedel's equation and $hu + kv + lw = 0$ (because the plane contains the rotation axis). The solution may not be unique (thanks to the possible division by α). Ranganathan's formula is concerned with coincidence, not with the choice of a GB. Now, for a symmetrical tilt GB, what matters most is the knowledge of its (hkl) Miller indices: one needs to know the interfacial plane, just as one needs to know the Miller indices of a surface plane. Σ is a non univocal associated number, and θ is also ambiguous when the rotation axis is a symmetry axis of the structure. One may also be concerned with asymmetrical tilt GBs, best defined as $(h_1 h_1 l_1)//(h_2 h_2 l_2)$ which may have a coincidence index or not (see for instance [65, 66, 114]), or with twist GBs or mixed tilt/twist GBs.

If one has a computer program, one can use Friedel's approach and the search for the minimal $(\langle uvw \rangle, \theta)$ rotation matrix in a systematic way. That approach can also be generalized to non cubic crystals in a brute force way with computers, and tolerance limits in cases of reticular pseudomerohedry (as it is most often the case in non cubic crystals, see Hans Grimmer, David Warrington, Roland Bonnet, George Bleris, Pierre Delavignette, Gérard Nouet, Serge Hagège, Theodoros Karakostas, not to name them all).

One can mention another property of Σ for cubic crystals: considering coincidence rotations, Warrington and Bufalini showed in 1971 that Σ^2 is a sum of three squared integers: $\Sigma^2 = R_{i1}^2 + R_{i2}^2 + R_{i3}^2$, $i = 1, 2, 3$ where R_{ij} are the nine integer elements of the $\frac{1}{\Sigma}(R_{ij})$ rotation [115]. Grimmer, Bollmann and Warrington later provided a nice demonstration that Σ is odd for cubic crystals [116]: Let us express $R_{i1}^2 + R_{i2}^2 + R_{i3}^2$ in the form $4n + k_i$ where n is an integer and $k_i = 0, 1, 2$, or 3, i.e., k_i is the number of odd integers among R_{i1}, R_{i2}, R_{i3}, $i = 1, 2, 3$. If Σ is even, then Σ^2 is a multiple of 4 and $k_1 = k_2 = k_3 = 0$, so that all R_{ij} and Σ are even, which contradicts the convention that there is no integral factor common to Σ and the nine R_{ij}. Thus, for cubic crystals, Σ is odd.

Appendix D

'Lattice sites:' atomic sites or mathematical lattice sites

This is an important question. Unfortunately, common usage has imposed a confusing terminology. The 'sites' of the coincident site lattices (CSLs) are mathematical nodes of Bravais lattices. Yet 'lattice sites' correspond to atomic sites (occupied or empty) in many papers, and matter is made of atoms, not mathematical nodes.[48]

Initially, people who believed in the existence of atoms did not know what they look like: neither their size nor how they could be distributed in crystalline matter. For instance physicists thought of salt (NaCl, halite as the mineral, common salt otherwise) as made of tiny 'molecules' (NaCl) regularly spaced, so that compression of a crystal of halite would decrease the lattice spacing but not necessarily the size of the 'molecule'. Georges Friedel strongly opposed such ideas and considered it better, in a first approach, not to include the atoms in his description of twins, although he believed in their existence and knew that the atomic motif played a role in crystal structure: see the 1904 and 1911 quotations reproduced in the section on the material lattice. In consequence, he only considered Bravais lattices, for the sake of simplicity. Friedel did mention Fedorov's work quite respectfully but wrote he was unsure how it might add to the Bravais' description. In his 1926 book, he of course acknowledged the Schönflies-Fedorov work.

In the field of crystallography, a 'node' is a mathematical point of a Bravais lattice with which an atomic motif is to be associated. The word 'site' is normally restricted to the explicit atomic distribution: either a site actually occupied by an atom, or which could be occupied by an atom. It is unfortunately not the case in the CSL where it means a 'node'.

The word 'basis' can be used in its mathematical sense of a (minimal) set of basic elements or vectors which can generate a group or lattice, viz the set of periodically spaced Bravais nodal points. The use of the word 'basis' in English in the field of solid state physics, can also mean the atomic motif associated with each Bravais node,[49] and is therefore unfortunately at odds with the other usage, despite the phonetical resemblance.

In the metallurgical community, when Kronberg and Wilson re-discovered, in 1949 the concept of coincidence sites in grain boundaries, in their study of secondary recrystallization in copper [119], they drew a 'coincidence plot showing relation between positions of atoms'. Their 'density of coincidence sites' was the density of coincident atomic sites, for instance: 'It is seen that 1/7 of the atoms of

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[48] Denis Gratias and Richard Portier already complained in 1982 that 'the terminology to day in common use in grain boundary community is often unfortunate and confuses, for example, lattice *nodes* and crystal *sites*'. [117].

[49] E.g. Charles Kittel, Introduction to Solid State Physics, pp. 4–5, Neil Ashcroft and David Mermin, Solid State Physics (1976) p. 75. It was introduced, in German, by Max Born in 1922 [118]. At the Göttingen University Born served as an assistant to David Hilbert, his mentor, who was famous for his 'basis theorem' so that Born was certainly aware of the first usage of the term basis.

the new orientation are in coincidence with atoms of the old orientation, and the positions of these coincidence atoms define a unique equilateral net which is a multiple of the primitive net'. When Ellis and Treuting further considered the atomic relationships in the cubic twinned state, and introduced the 'Coincidence Site Superlattice'[50] phrasing as the title of one section in their article [120], they were also explicitly considering atomic lattices. Ellis and Treuting were working on germanium, a semiconductor, their work is rarely cited in the metallurgical literature. At this same time, Jacques Friedel was attending Frank's lectures in Bristol, and began his discussions with Charles Frank (see Appendix B). It later became apparent that CSLs were dealing with Bravais nodes, not with atomic sites. It is important to keep in mind these semantic difficulties.

At the atomistic level, the atoms at the interface relax in such a way as to minimize stresses (and, more generally, the free energy, see [121]). Their positions and their electronic structures may change. It can be compared to surface reconstruction cases. This relaxation will move the atoms away from their positions expected from a purely geometrical model, often in a non negligible way except in some simple cases such as the coherent $\Sigma = 3$ (111) twin in fcc metals. This atomic relaxation may also involve a non negligible global translation of the grains with respect to each other. Such 'rigid body translations' were first suspected via atomistic calculations by Michael Weins and coll. [122, 123] and experimentally confirmed in 1974 using displacement fringes by Bob Pond, David Smith and William Clark [124, 125].

Appendix E

'Twins' versus 'grain boundaries'?

This may sound like a decadent scholastic question, but it still provokes lively discussions every now and then. There is no definitive answer. As for notations, it is probably best to define carefully the distinction that one wants to make.

In the first instance, a macle, or a twin, was a grouping of mineral crystals whose macroscopic shapes obviously exhibited some special orientation relationship (that is, they presumably obeyed a physical law, even if the exact nature of that law was difficult to determine). Nothing was known about the internal nature of the interface that separated the two grains. It might be planar or it might be thought of as a random interface so that the two grains seem to penetrate one another and the twin could be designated a 'penetration [inter-penetrating] twin' ('macle par pénétration'). In practice, Mallard distinguished between 'groupements par pénétration' (grouping by merohedry or pseudomerohedry), for which he thought the interface could be 'shapeless', with full interpenetration, and 'macles' for which the interface was planar, as in the Bravais reticular hemitropy, picture. Wallerant objected to this and thought the interface was necessarily shapeless. While Friedel thought the interface was essentially shapeless, but necessarily planar for some pseudo-merohedric twins. He also wrote that the situation was the same for the two reticular cases. Thus, the common assertion that twins, or twin boundaries, are simple (symmetric, even locally, at the atomic level) whereas grain boundaries are more complicated has no historical basis.

A further distinction might be that twins are 'natural' and occur in natural minerals, due to 'natural' growth mechanisms. Such twin boundaries should presumably, but not necessarily, be simple and of low energy. Industrial processes and intentional experimental growth could generate artificial, and more complex, grain boundaries. This distinction, difficult to maintain in practice, could yet sound reasonable, since it points to the true historical evolution: scientists first started by observations of the available natural specimens before they could master the production and observation of artificial materials.

Appendix F

Mineralogy versus metallurgy, or natural materials versus man-made materials

Aristotle, in his Meteorology, divided the mineral world in two groups: stones and metals (see Eichholz [126]). Stones cannot be melted whereas metals are fusible and malleable (like iron, gold and copper). Aristotle's physics is common sense physics and has some truth. Metals are rarely found in nature as recognizable crystals, as it is the case for quartz, calcite, fluorite, halite (rock salt), not to mention gemstones like topaz, sapphire, ruby and diamond. In spite of its fooling gold lustre, pyrite is not a metal (it is a semiconductor with a bandgap equal to 0.95 eV. In not that old physics textbooks, semiconductors as silicon or germanium did not exist as such and were simply considered as non metals). Even if metals are minerals, in principle, see for instance books III and IV of Albertus Magnus' De Mineralibus Libri, respectively, entitled Metals in General and The Metals Individually (see also, of course, Romé de l'Isle and Haüy's treatises), common sense clearly 'feels', still today, the distinction between Mineralogy and Metallurgy. This seems to be true in Occident as well as in Orient: Metal and Earth are two of the five *distinct*

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[50] Although, as we have seen, it is a sublattice from a mathematical point of view.

elements of the traditional Chinese system. We of course ought to be faithful to the scientific spirit of Aristotle, viz. observation and interpretation, rather than to his letter, which has been written more than two thousand years ago. Man-made metals and native minerals are nowadays equally available and observable.

Appendix G

Original french texts

G1: ‘Quand dans un criſtal quelconque, il se trouve un ou pluſieurs angles rentrans, on doit en conclure que ce n’eſt point un criſtal simple, mais un groupe de deux ou de pluſieurs criſtaux, ou même de deux moitiés retournées d’un même criſtal. Ce criſtal prend alors le nom de MACLE’ [23].

G2: ‘Ce qui importe (…), c’est de savoir quel est (…) le rapport du nombre total des nœuds du réseau simple au nombre des nœuds rétablis. Nous donnerons à ce rapport le nom d’*indice* de la macle. Il est de 1 pour les macles par mériédrie ou par pseudo-mériédrie’ [39, p. 1090].

G3: ‘quel que soit le mécanisme en vertu duquel la continuation d’un réseau multiple suffit à assurer la cohésion entre les motifs multiples diversement orientés, cette cause ne peut agir que si la maille multiple n’est pas trop grande’ [39, p. 1072].

G4: ‘Nous trouverons, au cours de l’étude des espèces, des raisons de croire que c’est le réseau matériel plutôt que le réseau cristallin des points analogues qui détermine les macles’ [39, p. 1089].

G5: ‘Il en est des macles comme des faces extérieures : étant donné un réseau, nous pouvons prévoir quelles sont les macles possibles et en gros quelles seront les plus fréquentes, mais non dans le détail quelles sont celles qui se produiront dans telles ou telles conditions de cristallisation’. ‘Les propriétés du motif interviennent de nouveau, et cela d’une manière jusqu’ici impossible à prévoir et à expliquer, pour rendre fréquente telle macle, rare ou inconnue telle autre qui semblerait, d’après les conditions réticulaires, devoir se produire’ [42, pp. 260–261].

G6: ‘Comment se fait cette solidification? (…) C’est là un fait très général que l’expérience montre vrai pour l’acier. Dans ce cas particulier, ce sont des globulites de fer qui vont se précipiter au sein d’un liquide mère formé essentiellement de carbure de fer et contenant en outre diverses combinaisons du fer avec les métalloïdes; (…) ils se serrent les uns contre les autres (…) et se limitent par des faces de polyèdres. Mais (…) les granulations restent mouillées par leur *eau-mère* qui se distribue en couches minces dans leurs intervalles capillaires. (…) Finalement, il reste à l’état fluide un mélange plus ou moins complexe, où domine ordinairement le fer carburé, qui se solidifie à son tour dans les joints des globulites polyédrisés et les unit en un seul bloc : c’est le *ciment*’ [73].

G7: ‘Considérons un corps formé de grains cristallins isolés, très petits, empâtés dans un réseau à peu près continu de matière très visqueuse’ [74].

G8: ‘Dans l’examen que nous allons faire (…) nous nous attacherons principalement à prouver : 1°. que chacun des hexagones de jonction est situé, par rapport à l’un ou l’autre des prismes, comme le seroit une face produite par une loi de décroissement; 2°. que si l’on suppose les pans de chaque prisme prolongés dans l’intérieur de l’autre prisme, les prolongements auront de même des positions que l’on pourra rapporter à des lois de décroissement’ [102].

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