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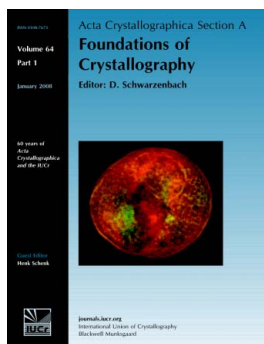
**Massimo Nespolo**

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# Does mathematical crystallography still have a role in the XXI century?

Massimo Nespolo

LCM3B UMR-CNRS 7036, Nancy Université, BP 239, F-54506 Vandœuvre-lès-Nancy CEDEX, France. Correspondence e-mail: massimo.nespolo@lcm3b.uhp-nancy.fr

Mathematical crystallography is the branch of crystallography dealing specifically with the fundamental properties of symmetry and periodicity of crystals, topological properties of crystal structures, twins, modular and modulated structures, polytypes and OD structures, as well as the symmetry aspects of phase transitions and physical properties of crystals. Mathematical crystallography has had its most evident success with the development of the theory of space groups at the end of the XIX century; since then, it has greatly enlarged its applications, but crystallographers are not always familiar with the developments that followed, partly because the applications sometimes require some additional background that the structural crystallographer does not always possess (as is the case, for example, in graph theory). The knowledge offered by mathematical crystallography is at present only partly mirrored in *International Tables for Crystallography* and is sometimes still enshrined in more specialist texts and publications. To cover this communication gap is one of the tasks of the IUCr Commission on Mathematical and Theoretical Crystallography (MaThCryst).

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## 1. Introduction

*Mathematical Crystallography* is the title of a classical textbook by Hilton (1903), which represented one of the first efforts of providing a comprehensive presentation of the theory of symmetry in crystals in the English language. Hilton's book was mainly devoted to morphological symmetry and lattice symmetry, with some excursions into the physical properties of crystals and the theories of crystal growth.

Nowadays, the field of mathematical crystallography has greatly enlarged its horizons: not only because of its development towards higher-dimensional crystallography (Yamamoto, 1996) and non-Euclidean spaces (Robins *et al.*, 2004) but also because different types of symmetry relations (such as partial symmetry acting on a subspace of the crystal space and polychromatic symmetry describing physical properties of crystals and mapping of individual orientations in twins) have been discovered which naturally fell into the field of mathematical crystallography. Symmetry, however, is far from exhausting the targets of mathematical crystallography, which also investigates the crystal-chemical problems related to the topology of crystal structures by means of mathematical tools, such as graph theory, whose relation with crystallography has been recognized relatively recently.

The basis of the theory of symmetry in crystals, and thus of crystallography itself as a modern science, is found in mineralogy. The term 'crystallography' was introduced by Capper (1723) but it was with the studies by Romé de L'Isle (1772, 1783), Bergman (1773), Haüy (starting from 1784) and

Delafosse (1840) that a new route opened towards a systematic derivation of the properties of periodicity and symmetry of crystals, developed especially in France (*e.g.* Bravais, 1850; Mallard, 1879; Friedel, 1926) and in Germany (*e.g.* Bernhardt, 1808*a,b,c*; Weiss, 1809*a,b*, 1815; Neumann, 1823; von Groth, 1895). The modern notation of lattice planes and crystal faces is due to the British school (Whevell, 1825; Miller, 1839). The theory of space groups was finally developed by Fedorov (1890), Schoenflies (1891) and Barlow (1894) (for a recent historical review, see Lalena, 2006). A systematic path through space groups was presented by Wyckoff (1930), in what can be considered the ancestor of Vol. A of *International Tables for Crystallography*. Nowadays, eight volumes of *International Tables* are published, which may give the impression that exhaustive information on all aspects of crystallography is available there. Actually, some aspects of crystallography, and especially of mathematical crystallography, are inadequately presented in *International Tables*, and several topics are still quite unknown to a large number of structural crystallographers. This partly comes from the use of concepts and language that are unfamiliar to non-specialists. Some efforts to provide the necessary introduction have been made, for example by Hahn & Wondratschek (1994) and with the production of a series of *Teaching Pamphlets* freely available from the IUCr website (<http://www.iucr.org/iucr-top/comm/cteach/pamphlets.html>) and, more recently, with the launch of the *IUCr Online Dictionary of Crystallography* ([http://reference.iucr.org/dictionary/Main\\_Page](http://reference.iucr.org/dictionary/Main_Page)). At the same time, crystallography, a victim of its own successes, is often

considered as a *diffraction technique* rather than a *multi-disciplinary science*.

The purpose of this article on *Mathematical Crystallography* for this Special Issue celebrating the 60th Anniversary of the IUCr is to present some of the topics that are often overlooked by the structural crystallographer and to give him a key to navigate the literature on the subjects, as well as to present some hot topics in mathematical crystallography which are currently under-represented in *International Tables*. Needless to say, there is no aim at compiling an exhaustive review: the topics selected for this article are among those of central interest to the MaThCryst commission.

Mathematical methods and probabilistic theories used in the solution and refinement of crystal structures from experimental data are addressed by the IUCr Commission on Computational Crystallography and are not treated in this article.

## 2. Coincidence and symmetry operations acting on a component of the crystal space

The symmetry operations of a space group are isometries operating on the whole crystal space and are also called ‘total operations’ (Dornberger-Schiff, 1964a) or ‘global operations’ (Sadanaga & Ohsumi, 1979; Sadanaga *et al.*, 1980). These are the operations that normally come to mind when one thinks of the symmetry of a crystal. The fact that they act on the whole crystal space may sound an obvious prerequisite for any coincidence operation in a crystal structure. This is not true because more generally a coincidence operation can act on just part of the crystal space, which we will call a ‘component’, and bring it to coincide with another component. As a consequence, one is led to consider a much wider category of coincidence operations, which nevertheless play an important role in some types of crystal structure.

Let us imagine subdividing the crystal space into  $N$  components  $S_1$  to  $S_N$ , and let  $\Phi(S_i) \rightarrow S_j$  be a coincidence operation transforming the component  $i$  into the component  $j$ . Such an operation in general is not a coincidence operation of the whole crystal space and therefore is not one of the operations of the space group of the crystal. It is called a *partial* operation and in general it is not required that it brings  $S_j$  back onto  $S_i$ ; more strongly,  $\Phi(S_k)$  in general is not defined for any component  $k$  different from  $i$  and therefore a partial operation is not necessarily a symmetry operation. From the mathematical viewpoint, partial operations are space-groupoid operations, in the sense of Brandt (1927).<sup>1</sup>

When  $i = j$ , *i.e.* when the operation is  $\Phi(S_i) \rightarrow S_i$  and brings a component to coincide with itself, the partial operation is of special type and is called *local* (Sadanaga & Ohsumi, 1979; Sadanaga *et al.*, 1980). A local operation is in fact a symmetry operation, which is defined only on a part of the crystal space: local operations may constitute a subperiodic group (Kopský

& Litvin, 2002), and in particular a diperiodic group (Holser, 1958) when  $S_i$  corresponds to a layer.

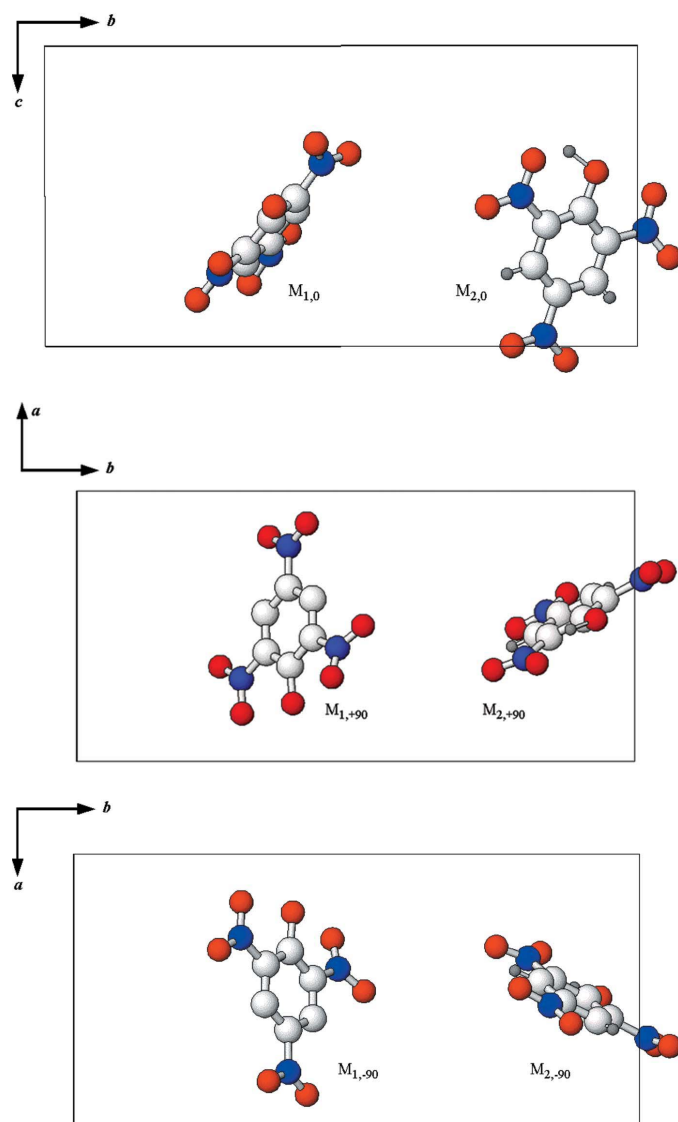
On the basis of these very general definitions, we can briefly analyse some examples that will make clear the role of partial and local operations in describing and rationalizing a crystal structure.

### 2.1. Partial and local operations in ‘supersymmetric structures’

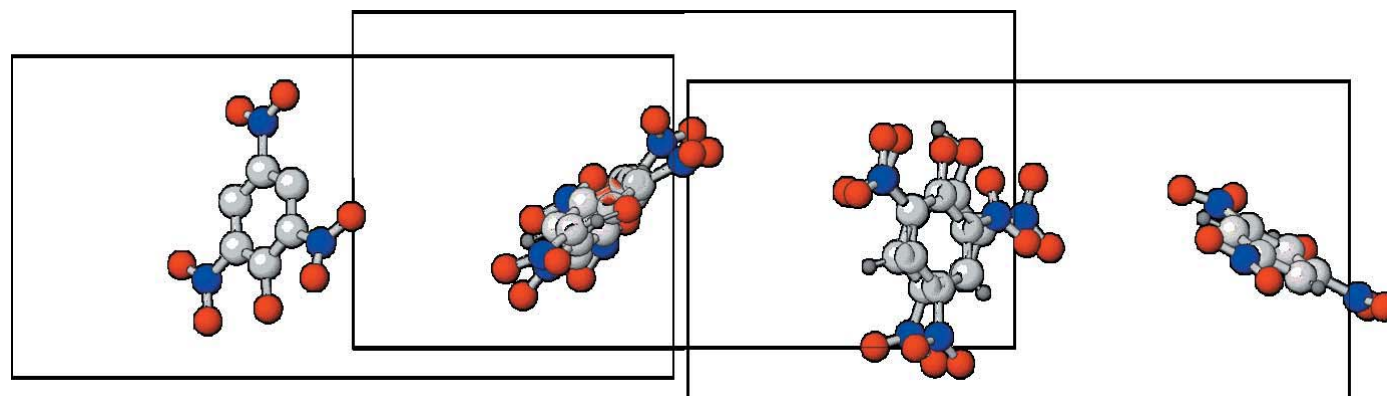
About 8% of crystal structures contain more than one formula unit in the asymmetric unit ( $Z' > 1$ ). In the case of molecular crystals, the crystallization mechanism and the structural relations among the molecules in the asymmetric unit is the subject of extensive research because of its direct applications in supramolecular chemistry and crystal engineering (see *e.g.* Steed, 2003). The role of pseudosymmetry (approximate symmetry) has been emphasized but the panorama obtained is not always fully satisfactory. As a matter of fact, the role of *partial* and *local* operations is of paramount importance.

Molecular crystals characterized by  $Z' > 1$  have been called ‘supersymmetric structures’ by Zorkii (1978) because the independent molecules in the asymmetric unit can be brought to more or less exact superposition by a screw rotation about a direction relating the molecules, and this direction has some special orientation with respect to the lattice basis. The ‘supersymmetry operations’ evidently act only on part of the crystal space and may be either local or partial, depending on whether a component is mapped to itself or to a different component. The cases of picric acid and phenol were analysed by Sadanaga *et al.* (1980). In the first case, two molecules of picric acid exist in the asymmetric unit of space group  $Pca2_1$ ,  $a = 9.254$  (2),  $b = 19.127$  (4),  $c = 9.704$  (2) Å, which has a pseudo-tetragonal mesh in (010) (Duesler *et al.*, 1978). The two molecules in the asymmetric unit are related by a pseudo-partial  $4_2$  axis parallel to the crystallographic  $b$  axis. Fig. 1 shows the two molecules in the unit cell in the original orientation (top) and after  $\pm 90^\circ$  rotation about the crystallographic  $b$  axis (centre and bottom). Let us indicate by  $M_{N,\vartheta}$  the molecule No.  $N$  ( $N = 1$  or  $2$ ) after a rotation of  $\vartheta^\circ$  ( $\vartheta = 0, +90$  or  $-90^\circ$ ).  $M_{2,+90}$  has almost the same orientation as  $M_{1,0}$ , whereas no relation can be found between  $M_{1,+90}$  and  $M_{2,0}$ . In the same way,  $M_{1,-90}$  has almost the same orientation as  $M_{2,0}$  whereas no relation can be found between  $M_{2,-90}$  and  $M_{1,0}$ . We can therefore conclude that a (pseudo) partial  $4_2$  axis exists parallel to  $\mathbf{b}$ , as shown in Fig. 2, where the three parts of Fig. 1 are overlapped. It is partial because  $4_2^+$  acts on  $M_{1,0}$  producing  $M_{2,+90}$ , but it does not act on  $M_{2,0}$ . At the same time,  $4_2^-$  acts on  $M_{2,0}$  producing  $M_{1,-90}$  but it does not act on  $M_{1,0}$ . The pseudo-character of this partial coincidence operation is shown by the imperfect overlap of the molecules in Fig. 2. Fig. 3 (modified after Sadanaga *et al.*, 1980) shows the idealized unit-cell contents, where each molecule of picric acid is represented by a paper kite, the smaller higher-angle side indicating that the corresponding part of the molecule is directed towards the observer. Corresponding molecules along the  $c$  axis in the

<sup>1</sup> The alternative meaning of ‘groupoid’ introduced by Hausmann & Ore (1937), namely a set on which binary operations act but neither the identity nor the inversion are included, is nowadays called a magma (see *e.g.* Bourbaki, 1998).



**Figure 1**  
Projection of the unit cell of picric acid, showing the two molecules in the asymmetric unit. Top: projection along the  $-a$  axis, taken as original orientation. Centre: after  $+90^\circ$  rotation about the  $b$  axis (projection along the  $-c$  axis). Bottom: after  $-90^\circ$  rotation about the  $b$  axis (projection along the  $+c$  axis).



**Figure 2**  
Superposition of the portions of Fig. 1 showing the existence of a pseudo partial  $4_2$  axis along the crystallographic  $b$  axis.

same row differ in their  $y$  coordinate by about  $\frac{3}{4}$  (row I) or  $\frac{1}{4}$  (row II). The symmetry operations of the space group map solid kites on one side and dashed kites on the other side. The pseudo partial  $[\cdot 4_2]$  rotation maps a solid kite onto a dashed kite. The combinations of these two types of operations map a solid kite to a dashed kite located in different positions in the (010) projection: these are partial pseudo- $[\cdot 4_1]$  and partial pseudo- $[\cdot 4_3]$  axes. These partial operations can be seen as space-groupoid operations or, alternatively, as cosets of the space group of the crystal (Grell, 1998) obtained by composing the  $[\cdot 4_2]$  partial operation with the operations of the space group. However, as seen above,  $[\cdot 4_2]$  and  $[\cdot 4_2^{-1}]$  do not possess the same domain and therefore they cannot be composed with themselves, as would be the case of a local operation. The crystal structure as a whole has to be described in terms of groupoids instead of groups, although each operation in itself is a group operation, namely from the group generated by the space group  $Pca2_1$  and the  $4_2$  operation.

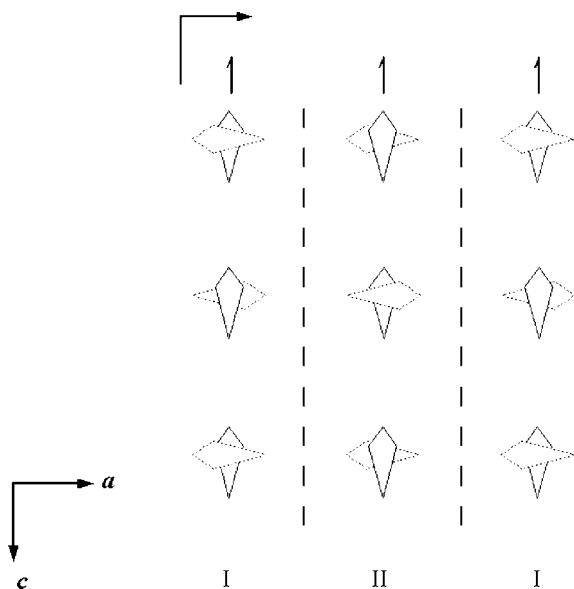
In the case of phenol (Fig. 4), three molecules exist in the asymmetric unit of the space group, which is of type  $P2_1$ . The lattice parameters ( $c$ -unique setting) are  $a = 6.050$  (1),  $b = 8.925$  (2),  $c = 14.594$  (3) Å,  $\gamma = 90.36$  (2) $^\circ$  (Zavodnik *et al.*, 1988). The structure is thus metrically pseudo-orthorhombic. The three molecules in the asymmetric unit are related by a pseudo local  $3_2$  axis parallel to the crystallographic  $a$  axis. The structure, however, is not pseudo-hexagonal because, despite the almost exact orthohexagonal relation between the  $b$  and  $c$  parameters ( $c \simeq b3^{1/2}$ ), the lattice type is primitive and not  $A$ -centred, as would be required to obtain a pseudo-hexagonal metric symmetry. In this case, the ‘supersymmetry axis’ is local because it acts on the same part of the crystal space, defined by the three phenol molecules in the asymmetric unit. Both the direct and the inverse operations are defined. The pseudo-character of the operation is shown by the  $x$  coordinates in Fig. 4, which are *slightly* displaced with respect to the ideal  $\pm a/3$  screw motion.

## 2.2. Partial and local operations in OD structures

The OD theory (Dornberger-Schiff, 1964*a*, 1966) specifically deals with structures in which partial operations act on

layer structures, although extensions to rod and block structures have been suggested too (see *e.g.* Dornberger-Schiff, 1964*b*; Belokoneva, 2005). The OD theory distinguishes two types of partial operations:  $\lambda$ , which transform a layer into itself, and  $\sigma$ , which transform a layer into an adjacent layer (Dornberger-Schiff & Grell-Niemann, 1961).  $\lambda$  operations correspond to local operations in Sadanaga *et al.* (1980);  $\sigma$  operations are partial operations as defined above.

OD structures are polytypic, namely structures built by stacking layers in different orientations/positions; the opposite may or may not be true depending on the degree of idealization one adopts in describing the layer structure (for a critical discussion, see Zvyagin, 1993). OD stands for order-disorder, has no relation with the chemical order-disorder phenomena but indicates that the stacking of layers may produce both periodic (ordered) and non-periodic (disordered) structures. The crystal chemical reason for polytypism is that adjacent layers (two-dimensionally periodic units) can be linked to each other in more than one translationally non-equivalent way, which however preserve the nearest-neighbour relationships. The operations interchanging the layers of a pair of adjacent layers are partial operations: they act on a part of the crystal space (consisting of the layer pair) and, in general, they are not the same for each layer pair. Moreover, the local  $\lambda$  operations  $\Phi$  mapping layer  $i$  onto itself –  $\Phi(S_i) \rightarrow S_i$  – and  $\Phi'$  mapping layer  $j$  onto itself are, in general, not the restriction of a common operation mapping both components. In the OD language, one says that these operations do not have a ‘continuation’ in the rest of the crystal structure:  $\Phi$  acts on  $S_i$  but not on  $S_j$ ,  $\Phi'$  acts on  $S_j$  but not on  $S_k$ , and so on.



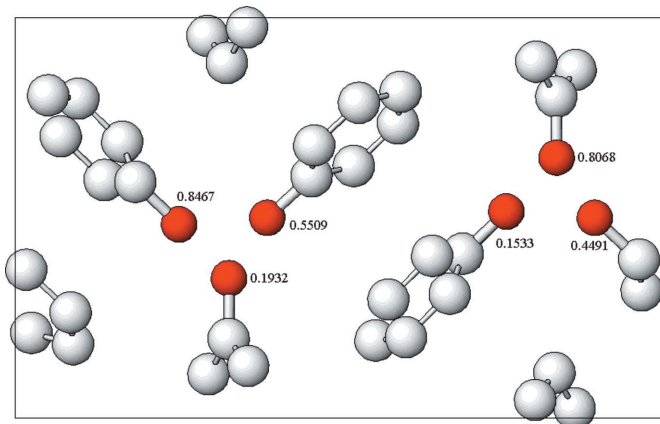
**Figure 3**  
The idealized unit-cell content of picric acid, where each molecule of picric acid is represented by a paper kite, the smaller higher-angle side indicating that the corresponding part of the molecule is directed towards the observer.

It must be emphasized that the choice of layers is made precisely to locate the components of the crystal space on which the local operations act and the layers located in this way do not necessarily coincide with the classical crystal-chemical layers defined by cleavage properties. This is why one speaks of ‘OD layers’, to emphasize the choice criterion, even in the cases when the result coincides with the crystal-chemical layers. Moreover, there may exist more than one possibility of dividing the crystal space into layers so that local operations are defined: this is why one says that the choice of OD layers is in general not unique (Grell, 1984).

Among the infinitely many possible polytypes, those in which not only the pairs but also triples, quadruples *etc.* of layers are geometrically equivalent (or, when this equivalence is not possible, the number of different triples *etc.* is minimal) are called *maximum degree of order (MDO) polytypes*. In a class of compounds, they are normally the most frequent polytypes, a fact suggesting that the geometrical equivalence of layers is actually somehow related to a thermodynamic stability, although it is hardly conceivable that long-range interactions like those existing between the second or third layer may play a fundamental role in discriminating the stability of different polytypes.

The OD interpretation of polytypic structures is not only an elegant way of rationalizing a series of structures within a general framework but also an extremely powerful way of interpreting the diffraction pattern of these structures and to model unknown structures. This becomes possible once the concept of *family* is introduced.

If one takes two or more identical copies of the same polytype, translated by a vector corresponding to a submultiple of a translation period – what is commonly called a *superposition vector* – a fictitious structure is obtained, which is termed a *superposition structure*. Among all possible superposition structures, one plays a special role: it is the one in which the superposition vectors correspond to all possible positions of each layer. It is called a *family structure* and it exists only if the shifts between adjacent layers are rational, *i.e.* if they correspond to a submultiple of lattice translations. Because it is built by superposing *all* possible positions of a



**Figure 4**  
The structure of phenol in  $P112_1$  seen along the  $[100]$  axis ( $\gamma = 90.36^\circ$ ).

layer, the family structure is common to *all* polytypes of the same family (Dornberger-Schiff, 1964a; Đurovič, 1994). From a group-theoretical viewpoint, building the family structure corresponds to transforming ('completing') all the partial symmetry operations of a space groupoid into the global symmetry operations of a space group (Fichtner, 1977, 1980). From the symmetry viewpoint, pairs of adjacent layers remain *geometrically equivalent* in all polytypes of the same family.<sup>2</sup>

The OD character of a polytype appears also in its diffraction pattern. The group of translations of the reciprocal lattice of a given polytype can be decomposed into a subgroup of translations (*family sublattice*), which corresponds to the Fourier transform of the family structure and one or more cosets. The family sublattice is again common to all polytypes of the same family. This means that all polytypes of the same family, normalized to the *same volume of scattering matter*, have a weighted reciprocal sublattice in common.<sup>3</sup> The diffractions that correspond to the family sublattice are termed *family diffractions* (or, more commonly, *family reflections*). When indexed with respect to the basis vectors of any of the polytypes of the same family, the family sublattice may show several non-space-group absences, which is a clear indication of the existence of partial symmetry (space-groupoid) operations. The family reflections are always sharp, even in the case of non-periodic (disordered) polytypes. In fact, in the family structure, *all* the layer-stacking operations are completed to global operations so that the family structure, as well as its Fourier transform, is common to both periodic and non-periodic polytypes of the same family (Đurovič & Weiss, 1986; Đurovič, 1997, 1999). The remaining diffractions, which correspond to the cosets of the weighted reciprocal lattice with respect to the family sublattice, are termed *non-family diffractions* (*non-family reflections*, *characteristic reflections*) and are instead typical of each polytype: they can be sharp or diffuse, depending on whether the polytype is ordered or not.

When inspecting the diffraction pattern of an unknown structure, the regular sequence of reciprocal-lattice rows showing and not showing non-space-group absences is a strong indication of the OD character of the structure. The disorder in the stacking sequence appears as streaking along the non-family rows; the coexistence of reciprocal-lattice rows that are not affected by streaking (family rows) suggests at a glance the OD character. Frequent twinning may also indicate an OD character. Inspection of the family rows gives information about the family structure. If one or more polytypes of this family are already known, then the structure of the layer(s) is known too and the problem of solving the structure reduces, for ordered (periodic) polytypes, to that of obtaining the stacking sequence from the non-family rows. For simple

polytypes, like those based on the symmetric packing of spheres, the task may be relatively easy. For more complex structures, special techniques have been developed (see e.g. Takeda, 1967).

### 3. Crystallographic orbits, point configurations and lattice complexes

The symmetry of an atomic structure can be seen as the intersection of the symmetries of the spatial distribution of each crystallographic type of atom. The structure of a crystal containing  $N$  crystallographically different types of atoms can be ideally decomposed into  $N$  distributions of points in space, similar to what is commonly done in the study of crystal morphology, when the external shape of a crystal is analysed in terms of its face forms. Each point, under the action of the symmetry operations of the space group  $G$  of the crystal, generates an infinite set of symmetrically equivalent points, called a *crystallographic orbit* (Matsumoto & Wondratschek, 1979, 1987). The space group  $G$  is called the *generating space group of the orbit*. Three features of each crystallographic orbit have to be considered: the *inherent symmetry* (eigen-symmetry)  $E$ , which may coincide with  $G$  or be a supergroup of it; the *site-symmetry group*  $S$ ; and the *translation subgroup*  $T$ . The intersection of the inherent symmetries  $E_i$ ,  $i = 1, N$ , of the  $N$  crystallographic orbits gives back the space group  $G$  of the crystal.

A space group  $G$  is an infinite group that can be seen as an extension of an infinite group of translations  $T$ , representing the lattice, by a point group  $P$ .  $P$  then is isomorphic to the factor group  $G/T$ <sup>4</sup> (Hahn & Wondratschek, 1994).

The *site-symmetry group*  $S$  of a Wyckoff position is the subgroup of  $G$  that maps a point of that position onto itself: in the language of abstract algebra, it is the *stabilizer* of the point. The site-symmetry group  $S_{\max}$  of the highest-symmetry lowest-multiplicity Wyckoff position is isomorphic with  $P$  for symmorphic space groups or with a subgroup of  $P$  for non-symmorphic space groups. The site-symmetry groups of the other Wyckoff positions are subgroups of  $S_{\max}$ .

The *inherent symmetry*  $E$  of a crystallographic orbit corresponding to a Wyckoff position in  $G$  is at least  $G$ . If  $G = E$ , the orbit is called a *characteristic crystallographic orbit*, otherwise it is called a *non-characteristic crystallographic orbit*.  $G$  can be a *translationengleiche* subgroup of  $E$  (same translation group  $T$ :  $G \stackrel{k}{\prec} E$ ,  $T_G = T_E$ ): the atoms sitting in the corresponding Wyckoff position contribute to the diffraction pattern a symmetry higher than that from the whole crystal.  $G$  can also be a *klassengleiche* subgroup of  $E$  (same geometric crystal class:  $G \stackrel{k}{\prec} E$ ,  $T_G < T_E$ ):  $E$  then contains translations additional to those of the generating space group  $G$  and the orbit is called an *extraordinary crystallographic orbit*.<sup>5</sup> The atoms sitting in a Wyckoff position corresponding to an extraordinary orbit do

<sup>2</sup> The geometrical equivalence must be fulfilled not necessarily by the real layers but by their archetypes, i.e. the slightly idealized layers to which the real layers can be reduced by neglecting some distortions occurring in the true structure. The notion of polytypism becomes thus unequivocal only when it is used in an abstract sense to indicate a structural type with specific geometrical properties.

<sup>3</sup> The weighted reciprocal lattice is obtained by assigning to each node of the reciprocal lattice a 'weight' that corresponds to  $F(hkl)$  (Shmueli, 2001).

<sup>4</sup> The translation subgroup  $T$  is a normal subgroup of  $G$ : the factor group or quotient group  $G/T$  is the set of all cosets of  $T$  in  $G$ .

<sup>5</sup> The role of extraordinary orbits was first addressed by Sándor (1968), who suggested extending the concept of 'special positions' to positions having translational symmetry higher than that of the general position.

not contribute to some classes of reflections: this information appears under the 'special reflection conditions' tabulated in *International Tables for Crystallography* (2002), Vol. A (ITA for short), but, as we are going to show, it is actually incomplete. The case when  $G$  is a general subgroup of  $E$  ( $G < E$ ) includes the features of both  $G \stackrel{l}{<} E$  and  $G \stackrel{k}{<} E$ .

The concept of crystallographic orbit is closely related to that of *point configuration* but differs from it by the fact that point configurations are detached from their generating space groups. As said above, from a given position in a certain space group  $G$ , a crystallographic orbit is obtained by the actions of the symmetry elements of  $G$ . The result is a spatial distribution of points with an inherent symmetry  $E$ , which is a fundamental feature of the spatial distribution of points and does not depend on the space group having generated it. This same spatial distribution may occur in space groups of different type and takes the name of *point configuration*. There exists evidently a surjection of point configurations onto crystallographic orbits because a crystallographic orbit depends on the space group  $G$  where it occurs and, consequently, corresponds to a well defined site-symmetry group, whereas point configurations do not. In other terms, a set of points is called a point configuration if there exists at least one space group that generates it as an orbit of one of its points. The relation between crystallographic orbits and point configurations in point space has a close analogy in vector space to the relation between the face form attached to the point group that has generated the form and the face form detached from its generating point group. There again, the same form may occur in different point groups. For example, the tetragonal prism has inherent symmetry  $E = 4/mmm$  and may occur in  $4/mmm$ , where it is a characteristic form, but also in all the other six tetragonal point groups, where it is a non-characteristic form.

In each individual space group and in all space groups of that type, there exist infinitely many point configurations. They can however be grouped into *types*, which are called *lattice complexes*. The concept of lattice complex is actually older than that of crystallographic orbit, having been introduced by Niggli (1919) and fixed by Hermann (1935). A rigorous definition, however, was provided much later by Fischer & Koch (1974) and by Zimmermann & Burzlaff (1974). The same lattice complex may occur in different types of space groups of the same crystal family. For example, the set of six points  $\pm x, 0, 0; 0, \pm x, 0; 0, 0, \pm x$  in  $Pm\bar{3}$  corresponds to the Wyckoff position  $6e$  of site-symmetry group  $mm2..$  but it occurs also in  $Pm\bar{3}m$  where it corresponds again to the Wyckoff position  $6e$ , which now has site-symmetry group  $4m.m$ . The inherent symmetry  $E$  of this set of points, which forms the vertices of an octahedron around the sites of a cubic primitive lattice, is  $Pm\bar{3}m$  independently of the space group  $G$  where it occurs. Taken as such, it defines a point configuration and  $Pm\bar{3}m$  is the characteristic space-group type of the point configuration ( $G = E$ ). When instead it is considered together with the space group  $G$  from which it has been generated, it is a crystallographic orbit. Evidently,  $6e$  in  $Pm\bar{3}m$  is a characteristic orbit because the inherent symmetry  $E$  coincides with the generating group  $G$ . Instead, in  $Pm\bar{3}$ ,  $6e$  is a non-

characteristic orbit because the inherent symmetry ( $Pm\bar{3}m$ ) is higher than the generating group ( $Pm\bar{3}$ ). It is not an extraordinary orbit, however, because  $Pm\bar{3}m$  contains no additional translations. In the lattice-complex approach, the phenomenon of extraordinary orbits is treated in analogy to the concept of limiting forms in crystal morphology: a lattice complex  $L_1$  is called a *limiting complex* of another lattice complex  $L_2$  if the set of its point configurations forms a (true) subset of the set of point configurations of  $L_2$ . In this sense, the lattice complex of all cubic primitive lattices is a limiting complex of the set of all tetragonal primitive lattices.

The contribution of atoms in a primitive cubic lattice complex to the diffraction pattern of the crystal corresponds always to that of  $Pm\bar{3}m$ . Besides, when this lattice complex defines a superlattice with respect to the axial setting of the space group – in other words, it forms an extraordinary orbit in  $G$  – special reflection conditions occur too. This becomes clear when the example of the primitive cubic lattice complex is worked out.

The primitive cubic lattice complex occurs, quite obviously, in  $Pm\bar{3}m$ , which is the characteristic space group of this lattice complex. It occurs in the Wyckoff positions  $1a$  and  $1b$ , which differ by a shift of  $\frac{111}{222}$ . In this space-group type, it does not define any superlattice and no special reflection conditions are observed. The contribution to the diffraction symmetry is that of  $Pm\bar{3}m$ . In the language of the crystallographic orbits, this lattice complex corresponds to two characteristic orbits.

The primitive cubic lattice complex occurs also in  $P\bar{4}3m$ ,  $P432$ ,  $Pm\bar{3}$  and  $P23$ , again corresponding to the Wyckoff positions  $1a$  and  $1b$ . The situation is essentially the same as in  $Pm\bar{3}m$  but, because the inherent symmetry is higher than the space group, the diffraction symmetry from atoms in this lattice complex is higher than that from the whole crystal. In the language of the crystallographic orbits, this lattice complex corresponds here to two non-characteristic ( $G < E$ ), non-extraordinary (same translation lattice:  $T_G = T_E$ ) orbits.

The primitive cubic lattice complex occurs also in  $Im\bar{3}m$ ,  $Fm\bar{3}m$ ,  $I432$ ,  $Im\bar{3}$  (Wyckoff position  $8c$ ),  $Fm\bar{3}c$ ,  $F\bar{4}3c$  and  $Ia\bar{3}$  (Wyckoff positions  $8a$  and  $8b$ ). In all these space-group types, the primitive cubic lattice complex corresponds to a primitive superlattice with halved translations along each of the three translation directions: for this reason, the symbol  $P_2$  is used (cf. Chapter 14 in ITA). As a consequence, atoms in this lattice complex only contribute to diffractions with even values of  $h$ ,  $k$  or  $l$ . In the language of the crystallographic orbits, this lattice complex corresponds here to extraordinary orbits ( $G < E$ ,  $T_G < T_E$ ).

Although the above example seems well representative of how lattice complexes can occur in different space groups and of the consequences on the diffraction symmetry, there is another, even more specialized, category, which is not explicitly taken into account in ITA. Wyckoff positions with one or more free coordinates can be specialized by making these free coordinates take a rational value. This specialization may result in switching to another Wyckoff position, which therefore has a different inherent symmetry and a different site-symmetry group. If, however, the result remains in the same

Wyckoff position but the inherent symmetry  $E$  of the orbit is enhanced, two cases have to be distinguished: (i) the orbit is extraordinary because it defines a (different) superlattice with respect to  $G$ , to which additional special reflection conditions necessarily correspond; (ii) the orbit shows no additional translations, *i.e.* it is non-extraordinary. Then it nevertheless may give rise to additional reflection conditions, although not necessarily. These additional conditions can be obtained, *e.g.* with the aid of the list in Engel *et al.* (1984). Two examples will make the situation clear.

(I) The space-group type  $P\bar{4}3m$  contains nine special positions, none of which corresponds to special reflection conditions. This is no longer true when one assigns particular values to one or more free coordinates, as we are now going to show.

The position  $12h\ x\frac{1}{2}0$  can be specialized by making  $x$  take the value  $\frac{1}{4}$ . The coordinates  $\frac{1}{4}\frac{1}{2}0$  still correspond to the Wyckoff position  $12h$  but now the inherent symmetry is  $E = Im\bar{3}m$ . Atoms in this extraordinary orbit do not contribute to diffractions with odd values of  $h + k + l$ : these special reflection conditions do not appear in ITA.

The position  $4e\ xxx$  can be specialized by making  $x$  take the value  $\frac{1}{4}$  or  $\frac{3}{4}$ . This results in two non-equivalent (in this space-group type) occurrences of a lattice complex with inherent symmetry  $E = Fm\bar{3}m$ . Atoms in these extraordinary orbits do not contribute to diffractions with odd values of  $h + k$ ,  $h + l$  or  $k + l$ : these special reflection conditions do not appear in ITA.

(II) In the space-group type  $I2_13$ , position  $8a\ xxx$ , the parameter  $x$  may be specialized to  $x = 1/8$ . The resulting orbit is non-characteristic and non-extraordinary. It has the inherent symmetry  $E = I4_132$  with the additional conditions  $hkl$ :  $h = 2n + 1$  or  $h, k, l = 4n + 2$  or  $h, k, l = 4n$ .

The symmetry of the diffraction pattern from a crystal is finally the intersection symmetry of the diffraction symmetry from each lattice complex (the effect of Friedel's law, when respected, can be taken into account as the union of an inversion centre and the diffraction symmetry of the crystal). This makes a close parallel with the situation in the direct space, where the space group of the crystal corresponds to the intersection of the inherent symmetries of the lattice complexes occupied by the atoms in the crystal.

The occurrence of limiting-complex relations between space groups of different crystal families depends on the realization of special metric conditions and may be coupled with special coordinates. This means that only part of the space groups within one type contains such non-characteristic orbits. A striking example is given by space groups of type  $P2_12_12_1$ , position  $4a\ xyz$ . Here, simultaneous specialization of the lattice parameters to  $a = b = c$  and of the coordinates to  $x = y = z = 1/8$  result in a non-characteristic (non-extraordinary) orbit with inherent symmetry  $E = P4_332$  and the complicated addition reflection conditions for  $h, k, l$  (permutable):  $h, k = 2n + 1$  or  $h = 2n + 1, k = 4n$  and  $l = 4n + 2$  or  $h, k, l = 4n + 2$  or  $h, k, l = 4n$ . So far such relations have been systematically worked out only for the cubic limiting complexes of tetragonal and trigonal lattice complexes (Koch & Fischer, 2003; Koch & Sowa, 2005). It must be noticed that these additional reflection conditions are valid for all space groups of type  $P2_12_12_1$  only if

$x = y = z = 1/8$ . This is because structure factors are independent of the cell metric.

When heavy atoms occupy non-characteristic orbits and light atoms are in characteristic orbits, the symmetry of the diffraction pattern is closer to that of a higher-space-group type and this pseudosymmetry makes the refinement more complex. Furthermore, when the positions occupied by heavy atoms correspond to extraordinary orbits, some classes of diffractions receive contributions only from light atoms, and in the diffraction pattern one can see strong diffractions, contributed by all atoms, and weak diffractions, contributed by light atoms only.

The literature on the subject is huge. Fundamental texts on crystallographic orbits are: Wondratschek (1976), Lawrenson & Wondratschek (1976), Matsumoto & Wondratschek (1979, 1987) and Engel *et al.* (1984). Chapter 8 in ITA introduces the concept of crystallographic orbits, without making a detailed analysis, however. An extension to polychromatic orbits has been introduced by Roth (1988). About point configurations and lattice complexes, besides the literature quoted above, the book by Fischer *et al.* (1973) and Chapter 14 in ITA cover the subject with full details. An exhaustive discussion on the difference between crystallographic orbits and point configurations can be found in Koch & Fischer (1985). The application of lattice complexes to the classification of crystal structures is treated in several articles, for example Hellner (1965).

#### 4. Normalizers

Normalizers are a mathematical concept extensively used in the solution of crystallographic problems, such as the choice of the origin and of the absolute structure in direct methods, the comparison of equivalent descriptions of crystal structures, the choice of a setting for indexing a diffraction pattern, the choice for indexing morphological faces of a crystal, the interchangeability of Wyckoff positions, and the definition of lattice complexes. Chapter 15 in ITA gives an extensive presentation of the application of normalizers.

To understand what a normalizer is and how it works, the concepts of conjugacy and of normal subgroup have to be recalled first.

(i) Conjugacy is an equivalence relation that partitions a space group into equivalence classes. If  $g_1$  and  $g_2$  are two elements of a space group  $G$ , they are called *conjugate* if there exists an element  $g_3$  in  $G$  such that  $g_3g_1g_3^{-1} = g_2$ . The *equivalence class* that contains the element  $g_1$  in  $G$  is formed by all elements of  $G$  obtained by  $g_3g_1g_3^{-1}$  for all  $g_3$  belonging to  $G$ .

(ii) In general, the structure of a group is not commutative: if  $g_1$  and  $g_2$  are two elements of a group  $G$ ,  $g_1g_2 \neq g_2g_1$ . One can however always choose a subgroup  $H$  of  $G$  such that, for any element  $g$  of  $G$  and for all elements  $h$  of  $H$ ,  $gh = hg$  holds. The subgroup  $H$  is called a *normal subgroup* of  $G$  (in symbols,  $H \leftrightarrow G$ ) and the above condition is synthetically written as  $gH = Hg$  or  $gHg^{-1} = H$ . That such a group always exists is evident if one considers that *at least* the trivial subgroup composed of the identity only is a normal subgroup of any

group. For space groups, a group of type  $P1$  containing all translations of  $G$  is a normal subgroup of  $G$ .

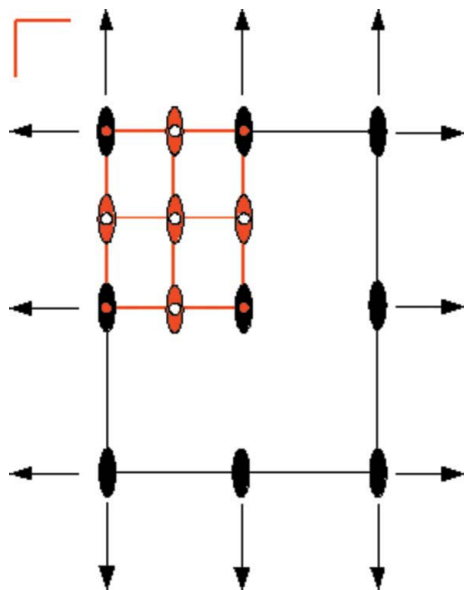
A group  $G$  and one of its supergroups  $S$  are uniquely related to a third, intermediate, group  $N_S(G)$ , called the *normalizer of  $G$  with respect to  $S$* .  $N_S(G)$  is defined as the set of all elements  $s$  of  $S$  that map  $G$  onto itself by conjugation, *i.e.* all the elements  $s$  of  $S$  such that  $sgs^{-1} = g'$ , for all  $g$  and  $g'$  belonging to  $G$ ; this condition is synthetically written as  $sGs^{-1} = G$ . Two limiting cases may exist, namely: (i) the normalizer  $N_S(G)$  coincides with  $G$ , *i.e.* the elements of  $S$  that map  $G$  onto itself are just the elements of  $G$ ; (ii) the normalizer  $N_S(G)$  coincides with  $S$ , *i.e.* all elements of  $S$  map  $G$  onto itself. Evidently,  $G$  is always a normal subgroup of its normalizer, a fact that explains the name 'normalizer' itself.

Two types of normalizers are useful in crystallographic problems: *Euclidean normalizers* (also initially known as *Cheshire groups*) and *affine normalizers*. The difference between them is easily understood after recalling the corresponding types of mappings (transformations or functions).

(i) An *affine mapping* is any mapping that preserves collinearity and ratios of distances, while *angles and lengths in general are not kept constant*. Geometric contraction, expansion, dilation, reflection, rotation, shear, similarity transformations, spiral similarities and translation are all affine transformations, as are their combinations.

(ii) A *Euclidean mapping* is a special case of affine mapping that also keeps distances and angles.

The Euclidean and affine normalizers of a space group  $G$  are the normalizers obtained by taking as supergroup  $S$  the



**Figure 5**

Symmetry elements of a space group  $G$  of type  $P222$  with the unit cell shown in (001) projection (black). Depending on whether the metric of  $G$  is general or specialized, the Euclidean normalizer is of type  $Pmmm$ ,  $P4/mmm$  or  $Pm\bar{3}m$ , with translations halved along the three axes. The unit cell common to these three Euclidean normalizers is shown in red. The symmetry elements of  $N_E(G) = Pmmm$  are also shown in red. The extension to the other two normalizers is obvious.

group of all Euclidean or affine mappings,  $E$  or  $A$ , respectively. They are the set of all elements  $e$  of  $E$  or  $a$  of  $A$  that map  $G$  onto itself by conjugation.

Each operation of the Euclidean normalizer  $N_E(G)$  maps the group  $G$  onto itself, and thus also the symmetry elements of  $G$ : it represents the *symmetry of the symmetry pattern*. Fig. 5 shows the symmetry elements of a space group  $G$  of type  $P222$  as well as the unit cell, in (001) projection. If we think of the symmetry of the distribution of these symmetry elements, it is easily shown that they repeat with symmetry  $N_E(G) = Pmmm$ . Moreover, the lattice translations in  $N_E(G)$  are all halved with respect to  $G$ . The Euclidean normalizer becomes however more symmetric in the case of the specialized metric. If two of the lattice parameters of  $G$  are equal (for example,  $a = b$ ), then a fourfold axis arises in  $N_E(G)$  that relates the symmetry elements of  $G$ :  $N_E(G)$  is now of type  $P4/mmm$ . Finally, if  $a = b = c$ ,  $N_E(G)$  becomes of type  $Pm\bar{3}m$ . The existence of more than one type of Euclidean normalizer for the same type of space group, depending on the metric, concerns the triclinic and monoclinic space groups as well as 38 types of orthorhombic groups, where two or three lattice directions may interchange if the corresponding lattice parameters become equal.

The affine normalizer  $N_A(G)$ , being defined by the group of affine mappings, never depends on the metric and, when more than one type of Euclidean normalizer  $N_E(G)$  exists for the groups of type  $G$ , the affine normalizer  $N_A(G)$  always corresponds to the highest-symmetry  $N_E(G)$ . In the above example,  $N_A(P222) = Pm\bar{3}m$ ,  $a/2, b/2, c/2$ . One could say that the symmetry of the symmetry elements of  $P222$  for a general metric becomes more symmetric under geometric contraction, expansion, dilation, rotation . . . , *i.e.* under an affine mapping that corresponds to modifying the lattice parameters towards a specialized metric. This process is repeated until the highest symmetry is obtained and the result is the affine normalizer. Evidently, when only one Euclidean normalizer exists for a space-group type, it coincides with the affine normalizer.

For monoclinic and triclinic space groups, the affine normalizers are not symmetry groups and have to be described by a matrix-column pair and the corresponding restrictions on the coefficients.

Crystals belonging to space groups  $G$  whose factor group  $G/T$  is isomorphic to a pyroelectric point group cannot have their origin fixed with respect to some appropriate symmetry element. The origin may be chosen at any point along one direction (for space groups of crystal classes 2, 3, 4, 6,  $mm2$ ,  $3m$ ,  $4mm$  and  $6mm$ ), in a plane (crystal class  $m$ ) or anywhere in space (crystal class 1). The Euclidean normalizers for these space groups are not space groups themselves but contain continuous translations in one, two or three independent directions.

As an example of the use of normalizers and of their relation with the lattice complexes described in the previous section, we consider the position  $12h\ x, \frac{1}{2}, 0$  in  $P43m$ , already discussed in dealing with lattice complexes. The point configurations corresponding to this position, which has inherent symmetry  $Pm\bar{3}m$ , form cube-octahedra around the sites of a

cubic primitive lattice. The Euclidean normalizer (which in this case coincides with the affine normalizer) is  $N_E(P\bar{4}3m) = Im\bar{3}m$  with identical translation subgroups. The additional generator  $t(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  of  $N_E(G)$  with respect to  $G$  generates a second point configuration in the same Wyckoff position, and the two are said to be Euclidean-equivalent (they are evidently also affine-equivalent). There exist therefore two point configurations by which the same atomic distribution can be described, and only the other atoms in different Wyckoff positions define which of the two is actually occupied in the structure under investigation or, if both are occupied, by which atoms they are occupied. If however  $x$  takes the value  $\frac{1}{4}$ , the two point configurations coalesce in one, with inherent symmetry  $Im\bar{3}m$ , *i.e.* the symmetry of the normalizer.

When, for each crystallographically independent type of atom there exist two or more Euclidean-equivalent point configurations, the same crystal structure can be described differently. To verify whether two apparently different crystal structures actually simply differ in their description, it is sufficient to verify whether the corresponding point configurations are Euclidean-equivalent or not. The case of crystals composed of only one type of atom is the simplest example: when the only independent atom occupies one Wyckoff position out of a Wyckoff set, *i.e.* a set of Wyckoff positions having a site-symmetry group that is conjugate under the Euclidean normalizer, then there are  $N - 1$  alternate equivalent descriptions, where  $N$  is the number of Wyckoff positions in the Wyckoff set. Evidently, in the case of crystals composed of only one type of atom, the Wyckoff position that it occupies must correspond to a characteristic orbit ( $E = G$ ).

An exhaustive presentation of normalizers, with several examples, is given in Chapter 15 of ITA and references therein. A didactic text has been published by Koch & Fischer (2006).

## 5. Derivative structures and symmetry relations

A *derivative structure* is any structure derived from another structure (*basic structure*) by the suppression of one or more sets of operations of the space group (Buerger, 1947). Basic structures are also known as *aristotypes* and derivative structures as *hettotypes* (Megaw, 1973). Two important kinds of derivative structures exist: *substitution structures* and *distortion structures*. In the former, two or more different kinds of atoms replace one kind of atom in the basic structure and consequently the space-group symmetry decreases; furthermore, some atomic sites that were equivalent in the basic structure may be divided into two or more different sites in the derivative structure. Distortion structures correspond to displacive phase transitions: the space-group type of the derivative structure, often called *daughter phase*, is a subgroup of the space-group type of the basic structure, often called *parent phase*.

The structure relationship between two structures whose space groups  $G$  and  $H$  are group-subgroup related ( $G \supset H$ ) can be analysed in terms of maximal subgroups.  $H$  is called a

*maximal subgroup* of  $G$  if one cannot find an intermediate group  $K$  that is a subgroup of  $G$  and a supergroup of  $H$ . The relations between  $G$  and  $H$  can be classified in the following way:

1.  $H$  is a *translationengleiche* subgroup of  $G$  ( $t$  subgroup);
2.  $H$  is a *klassengleiche* subgroup of  $G$  ( $k$  subgroup),

2.1 a special case of  $k$  subgroup is when  $H$  belongs to the same type as  $G$ : it is called an *isomorphic* subgroup of  $G$  and is sometimes indicated as an  $i$  subgroup;<sup>6</sup>

3.  $H$  can finally be a general subgroup of  $G$ , *i.e.* its translation subgroup is a subgroup of the translation subgroup of  $G$  and it also belongs to a crystal class that corresponds to a subgroup of the crystal class of  $G$ . In this case, Hermann's (1929) theorem shows that there exists a unique intermediate group  $M$ , which is a  $t$ -subgroup of  $G$  such that  $H$  is a  $k$ -subgroup of  $M$ , and suggests a privileged path from  $G$  to  $H$ .

The relation between  $G$  and  $H$  can eventually be subdivided into a number of steps  $G \rightarrow H_1 \rightarrow H_2 \rightarrow \dots \rightarrow H$ , each step involving either a  $k$ -subgroup or a  $t$ -subgroup. At each step, a Wyckoff position can either split into several symmetry-independent positions, which keep the original site symmetry, or have its site symmetry reduced; both changes may also happen simultaneously (Wondratschek, 1993). In a substitution structure, the Wyckoff position may split, whereas, in a distortion structure, the site symmetry in general is reduced when going from  $H_j$  to  $H_{j+1}$ , unless it is already low enough (Müller, 2005). Vol. A of *International Tables for Crystallography* gives part of the information necessary to build the relation, namely the maximal non-isomorphic subgroups and the isomorphic subgroups of lowest index. *International Tables for Crystallography* (2004), Vol. A1, which was published recently, gives the complete information: besides the above subgroups, it also gives the series of isomorphic subgroups, the origin shift relating the axial settings of  $G$  and  $H$  and the transformation of each Wyckoff position.

The structural relation is best represented in the form of a tree, introduced by Bärnighausen (1980), where each node consists of a group and the Wyckoff letter of the occupied positions, with the numerical values of the general coordinates, and the branches are arrows relating pairs of groups, labelled by the type of subgroup ( $t$ ,  $k$ ,  $i$ ), the order of the subgroup, followed – when these are not trivial – by the basis vectors of the subgroup in terms of those of the supergroup and by the origin shift.

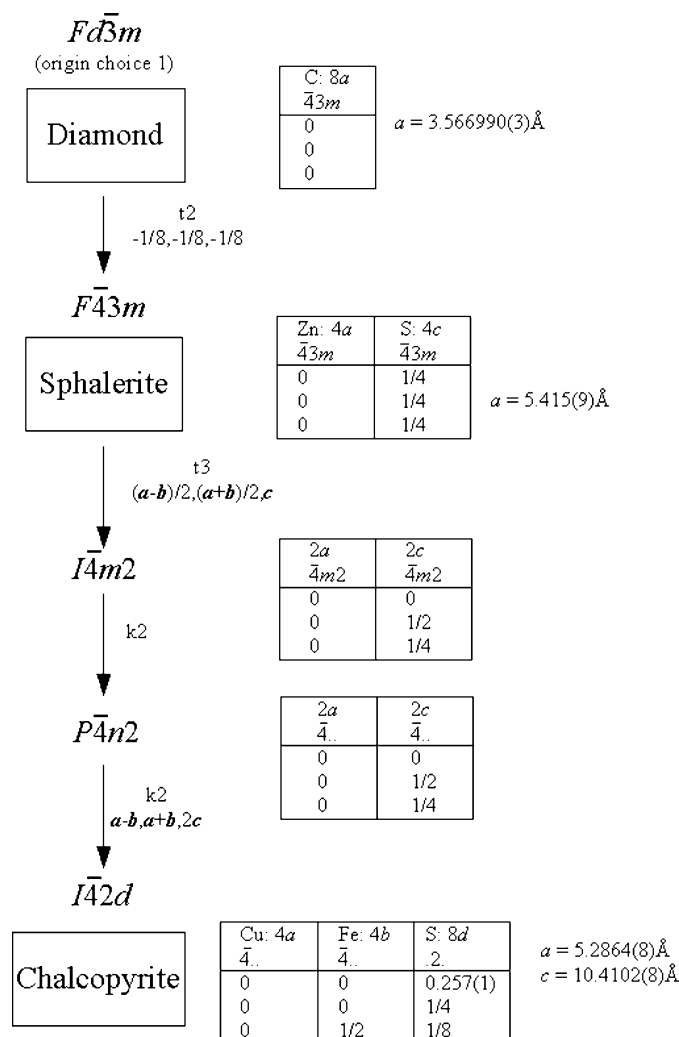
The information necessary to build a Bärnighausen tree can be obtained either from Vol. A1 of *International Tables for Crystallography* or by means of the Bilbao Crystallographic Server at <http://www.cryst.ehu.es/cryst/> (Aroyo, Perez-Mato *et al.*, 2006; Aroyo, Kirov *et al.*, 2006), in particular, using the routines *SUBGROUPGRAPH*, *HERMANN* and *WYCKSPLIT*.

<sup>6</sup> The group isomorphism as described here is limited to crystallographic equivalence. Two space groups of type  $P6_1$  and  $P6_5$  are not considered isomorphic, although they are affine equivalent.

### 5.1. The example of the diamond–sphalerite–chalcopyrite substitution derivative structure

From the space group of diamond ( $Fd\bar{3}m$ ) to that of chalcopyrite ( $I\bar{4}2d$ ), two shortest paths exist,  $Fd\bar{3}m \rightarrow F\bar{4}3m \rightarrow I\bar{4}m2 \rightarrow P\bar{4}n2 \rightarrow I\bar{4}2d$  and  $Fd\bar{3}m \rightarrow I4_1/amd \rightarrow I\bar{4}m2 \rightarrow P\bar{4}n2 \rightarrow I\bar{4}2d$ . The first one passes through the space group of sphalerite ( $F\bar{4}3m$ ). As a matter of fact, the structural relation can be separated into two steps: first, by replacing half of the C atoms by Zn atoms and the other half by S atoms, one obtains the structure of sphalerite; then, by further ordered replacement of Zn by Fe and Cu atoms, one gets the structure of chalcopyrite.

The first passage is straightforward, involving just a  $t$ -subgroup of order 2. Diamond has lattice parameter  $a = 3.566990(3) \text{ \AA}$  (Hom *et al.*, 1975). With respect to ‘origin choice 1’, the C atoms occupy the position  $8a(0, 0, 0)$ , whose site-symmetry group is  $\bar{4}3m$ . The transformation to  $F\bar{4}3m$  needs an origin shift by  $(-1/8, -1/8, -1/8)$ . The position  $8a$  of  $F\bar{4}3m$  splits to  $4a(0, 0, 0)$  and  $4c(1/4, 1/4, 1/4)$  of  $F\bar{4}3m$ , but keeps the site-symmetry group,  $\bar{4}3m$ . The lattice parameter of



**Figure 6**  
Bärnighausen tree for the diamond–sphalerite–chalcopyrite pathway.

sphalerite is  $5.415(9) \text{ \AA}$  (Jumpertz, 1955); the large difference in the lattice parameters comes evidently from the size difference between the C atom on one side and the Zn and S atoms on the other side.

To obtain the chalcopyrite structure, a three-step pathway is needed.

I.  $F\bar{4}3m \rightarrow I\bar{4}m2$ .  $I\bar{4}m2$  is a  $t$ -subgroup of order 3 of  $F\bar{4}3m$ . The transformation can be done in three different ways, which correspond to three conjugate subgroups, depending on which of the three fourfold axes of the parent group is left in the subgroup. If we keep the one along the  $c$  axis, the transformation is obtained by  $\frac{1}{2}(a-b), \frac{1}{2}(a+b), c$ , the origin being in common: the calculated lattice parameters become  $a = 3.829$  and  $c = 5.415 \text{ \AA}$ . The Wyckoff positions occupied in  $F\bar{4}3m$  do not split, keep the same Wyckoff letter, but reduce their site symmetry to  $\bar{4}m2$  and their multiplicity from 4 to 2:  $2a(0, 0, 0)$  and  $2c(0, \frac{1}{4}, \frac{1}{4})$ .

II.  $I\bar{4}m2 \rightarrow P\bar{4}n2$ . The second group is a  $k$ -subgroup of order 2 of the parent group. Computed lattice parameters and Wyckoff positions remain the same but the site symmetry is reduced to  $\bar{4}$ .; the centring vector  $I$  is lost.

III.  $P\bar{4}n2 \rightarrow I\bar{4}2d$ . The second group is a  $k$ -subgroup of order 2 of the parent group. The transformation is obtained by  $(a-b), (a+b), 2c$  and the origin is in common; the computed lattice parameters become  $a = 5.415$ ,  $c = 10.830 \text{ \AA}$ . Wyckoff positions  $2a(000)$  and  $2c(0, \frac{1}{4}, \frac{1}{4})$  of  $P\bar{4}n2$  become  $4a(000)$  and  $8d(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . Moreover, because the lattice parameter along  $c$  has doubled, a second set of atomic positions must be added, obtained from the first set by addition of  $(0, 0, \frac{1}{2})$ . From  $4a(000)$ , position  $4b(0, 0, \frac{1}{2})$  is thus obtained; from  $2c(0, \frac{1}{4}, \frac{1}{4})$ , position  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{8})$  is obtained, which corresponds again to  $8d$ .

The chalcopyrite lattice parameters are  $a = 5.2864(8)$  and  $c = 10.4102(8) \text{ \AA}$  (Kratz & Fuess, 1989), close to those calculated by the group–subgroup transformation; the difference comes obviously from the different size of the atoms which substitute in the derived structure. The atomic coordinates are Cu:  $0, 0, 0(4a)$ , Fe:  $0, 0, \frac{1}{2}(4b)$  and S:  $0.257(1), \frac{1}{4}, \frac{1}{8}(8d)$ . The generic coordinate  $x$  in position  $8d$  is fairly close to the value  $\frac{1}{4}$  obtained *via* the transition pathway. The Bärnighausen tree for the complete group–subgroup is shown in Fig. 6.

Detailed examples of applications of Bärnighausen trees are given in Müller (2004, 2005). Application to molecular crystals can be found in Gruber & Müller (1997) and Müller (1978, 1980). Rutherford (2001) presented the first application to organic crystals.

### 5.2. Structural relationships between structures with no group–subgroup relations

In the case of structures with no group–subgroup relations, the structure of one phase can still be related to that of the other phase *via* a common supergroup (see *e.g.* Bärnighausen, 1980; Hoffmann & Pöttgen, 2001), without necessarily implying the existence of a transition pathway. The possibility of using a common subgroup instead has been suggested too (see *e.g.* Capillas *et al.*, 2007). The group–subgroup relation

would then concern  $G1$  and  $H1$ , as well as  $G2$  and  $H2$ , where  $H1$  and  $H2$  are space groups of the same type as  $H$ . Finally, an affine transformation relating  $H1$  and  $H$  on one side, and  $H2$  and  $H$  on the other side, closes the structural relation.

## 6. Reticular theory of twinning

A twin is a modular structure at the crystal level (Ferraris *et al.*, 2004), *i.e.* a heterogeneous edifice consisting of the oriented association of two or more homogeneous crystals (individuals). The operation mapping the orientation of an individual onto that of another individual is called a *twin operation* and the lattice element about which this operation is performed is called a *twin element*. Mallard's law (Friedel, 1926) states that a twin element is always a direct-lattice element, although it may sometimes be useful to use a reciprocal-lattice element instead, especially when unravelling the diffraction pattern of a twin.

Twinning is often simply regarded as a problem in the process of structure solution and refinement because the measured intensities no longer come from a single crystal but from a heterogeneous edifice built by two or more crystals. Twinning represents however a most interesting subject of investigation, also for the light that twinned crystals may shed on crystal growth mechanisms. The subject is extremely wide and some recent reviews have been published (see *e.g.* Hahn & Klapper, 2003 and Grimmer & Nespolo, 2006). Here we give just a brief summary of the aspects that from the viewpoint of mathematical crystallography are more directly related to the above problems.

### 6.1. The reticular theory of twinning and the occurrence frequency of twins

In order for two individuals of the same compound to form a twin, the structure at the interface between them should fit as well as possible. Holser (1958) proposed to describe this interface by means of the 80 di-periodic (layer) groups: the intersection of the space groups of the individuals in the respective orientations should be a di-periodic group realized in the thin interface between them. This approach requires the knowledge of a thin section of the structure for the given orientation and a way to judge the goodness of fit, almost reducing the study of twins to a case-by-case analysis.

The reticular theory of twins, originally developed by the so-called 'French school' (Friedel, 1926) takes the lattice as basic criterion to judge the goodness of fit and, consequently, to evaluate the probability of occurrence of a twin. Clearly, the use of the lattice instead of the complete structure results in a certain degree of idealization; on the other hand, it has the advantage of a much greater generality, while keeping the specificity of the individuals, through their lattice parameters. Concretely, the reticular theory of twins affirms that the probability of occurrence of a twin is directly related to the goodness of fit of the lattices of the individuals in the respective orientations (see also Hahn & Klapper, 2003). Because the structure of a crystal is a periodic repetition of the

unit-cell content with the periodicity of the lattice, a good fit of the latter implies a good structural fit. The lattice nodes that are common, exactly or approximately, to the individuals in their respective orientations define a sublattice of the individual, which is called *twin lattice*. As 'goodness of fit' is taken the degree of lattice overlap in the twin lattice, as measured by two parameters:

1. the ratio of the volume of the primitive cells of the twin and of the individual, which corresponds to the *twin index*  $n$ ; for twofold twin operations, it is easily computed from the indices of the lattice elements defining the twin lattice; in the other cases, the calculation may be less straightforward (Nespolo & Ferraris, 2007);

2. the divergence from the exact overlap of the lattices of the individuals, which is related to the pseudosymmetry of the twin lattice; this is usually measured by the *obliquity*  $\omega$ , *i.e.* (a) for reflection twins, the angle between the normal to the twin plane (which, in general, is an irrational direction) and the lattice direction closest to it, (b) for rotation twins, the angle between the twin axis and the direction, in general irrational, that is normal to the lattice plane that is quasi-normal to the twin axis. When the twin operation is of order higher than 2, a pseudosymmetry of the twin lattice may no longer result in  $\omega > 0$ ; a more general parameter, called *twin misfit*  $\delta$ , has thus been introduced as a measure of this pseudosymmetry, which is defined as the distance between the first nodes along the two shortest directions in the plane of the twin lattice (quasi-)perpendicular to the twin axis, which are quasi-restored by the twin operation (Nespolo & Ferraris, 2007).

On the basis of these parameters, twins are classified in the following categories, where  $\delta$  replaces  $\omega$  in older classifications:

1.  $n = 1, \delta = 0$ : twins by merohedry
2.  $n > 1, \delta = 0$ : twins by reticular merohedry
3.  $n = 1, \delta > 0$ : twins by pseudo-merohedry
4.  $n > 1, \delta > 0$ : twins by reticular pseudo-merohedry.

Twins by merohedry are also often called 'merohedric twins'.<sup>7</sup>

The occurrence of twins with twin index  $> 1$  shows that for a twin to occur a *complete* overlap of the lattices is not necessary: a *partial* overlap is sufficient. The occurrence of twins with obliquity  $\omega > 0$  (and thus  $\delta > 0$ ) shows that for a twin to occur an *exact* overlap of the lattices is not necessary: an *approximate* overlap is sufficient. Nevertheless, in general, the probability of occurrence of a twin is inversely related to the twin index and to the obliquity, and empirical limits were also given, based on a large number of study cases: a twin index of 6 and an obliquity of  $6^\circ$  were taken as borderline between 'normal' ('Friedelian') twins and 'exceptional' ('non-Friedelian') twins (Friedel, 1926).

That the above criteria are not absolute is shown by the existence of non-Friedelian twins that, although far less frequent than low-index low-obliquity ones, are nevertheless

<sup>7</sup> It is emphasized that the expression 'merohedral twins' often appearing in the literature is inappropriate: 'merohedral' indicates the symmetry of an individual, not that of a twin (Catti & Ferraris, 1976).

well represented. The reticular theory seemed unable to explain their occurrence in the same framework as Friedelian twins. An extension of this theory has however been proposed that rationalizes a number of non-Friedelian twins as *hybrid twins*. For  $n > 1$  twins, the twin lattice is a sublattice of the lattice of the individual whose cell is defined by the twin element (axis, plane) and the lattice element (plane, direction) quasi-perpendicular to it, where 'quasi' means within an acceptable obliquity, usually taken as the Friedelian value of  $6^\circ$ . For large twin index, there may exist more than one lattice element satisfying this criterion, and therefore more than one sublattice that may be chosen as twin lattice. The overall degree of lattice overlap should therefore take into account the lattice nodes defining *all* these sublattices because the twin operation restores all these nodes, although within a different degree of approximation, measured by the obliquity of each sublattice. The ratio of the lattice nodes contained in the cell of the lowest-obliquity largest-index sublattice and the number of lattice nodes corresponding to all the sublattices defined in this way is a better estimation of the degree of lattice overlap and is termed *effective twin index*. By means of this approach, several high-index twins whose existence was previously difficult to explain on the basis of the reticular theory can now be rationalized as well (Nespolo & Ferraris, 2006).

## 6.2. Twin point groups and the polychromatic symmetry of twins

The symmetry of twins is in vector space, exactly like the morphological symmetry of crystals or the symmetry of their physical properties. Therefore, the symmetry of a twin is described by a (vector) point group, which however is not just one of the 32 crystallographic point groups but rather an extension of them.

The symmetry of a twin is the group formed by the intersection of the *oriented* point groups of the individuals augmented by the twin element(s). In the intersection group, only those symmetry elements are retained that, in the respective orientations of the individuals, are parallel. This gives a subgroup, proper or trivial, of the group of the individual. The twin element(s), as well as those produced by the combination of the latter(s) with the symmetry elements of the intersection group, are then added and the complete symmetry of the twin is obtained. In this group, the operations no longer have the same nature: part of them map an individual onto itself, the others map an individual onto another one. This behaviour has an evident parallel in the polychromatic point groups, where some operations ('achromatic') exchange only parts of the object characterized by the same colour; others ('chromatic') exchange instead parts that have different colours; finally, a third type of operation ('partially chromatic') may exist, which exchanges a subset of the colours, leaving unchanged the others. The theory of polychromatic point groups can therefore be directly applied to twinned crystals; a polychromatic point group applied to a twin takes the name 'twin point group' (Nespolo, 2004).

In the case of merohedric twins, the twin point group is evidently isomorphic to a supergroup of the crystal point group<sup>8</sup> because all the symmetry elements of the individual are retained in the intersection group. In the general case, however, this is no longer true, the twin point group often being isomorphic to a *subgroup* of the crystal point group or even to a point group that is not in group–subgroup relation with it. In fact, depending on the orientation of the individuals, few or none of the symmetry elements of the individual may be retained, and the twin element may be of a type not present in the point group of the individual. For example, the Japan/Verespatak twin of quartz,  $\{11\bar{2}2\}$ , has twin point group  $m'$ : none of the symmetry elements of the 321/622 point group of quartz is retained, and there are no mirror planes in it. A further specialized case is that when the twin element is of the same type as the symmetry element lost in the intersection group. In this case, the twin point group is isomorphic to the crystal point group, the two groups being however differently oriented. For such a special case, the term of *twinning by reticular polyhohedry* was introduced (Nespolo & Ferraris, 2004).

## 6.3. The effect of twinning on the diffraction pattern

The diffraction pattern from a twinned crystal is typically the superposition of the diffraction patterns of the individuals. In other words, the intensities from each individual sum up without any phase relation. This of course depends on the crystal size and the wavelength used, and the diffraction behaviour cannot be used as an absolute criterion to distinguish between a twin and a modular structure (see the discussion in Nespolo *et al.*, 2004). Nevertheless, in a large majority of cases, non-interfering diffraction from the individuals is what one observes from a twinned crystal. This means that, in order to solve and refine the structure of a twinned crystal, the diffraction pattern must first of all be unravelled for its components.

Twins by merohedry have their direct and reciprocal lattices completely overlapped. They are classified into three classes (Catti & Ferraris, 1976; Nespolo & Ferraris, 2000).

**Class I:** the twin operation is an inversion centre (or any other operation that is equivalent to an inversion centre under the point group of the individual). Within the limits of the validity of Friedel's law, the diffraction pattern from the twin cannot be distinguished from that of a single untwinned individual and the structure can be solved without taking twinning into account, *provided that the correct space group has been chosen*; assignment of a crystal to a centrosymmetric space group when instead it lacks the centre of symmetry probably results only in apparent disorder or abnormal displacement parameters if the structure is to some extent pseudosymmetric. When the volume ratio of the individuals is sufficiently different from 1, the presence of inversion twin-

<sup>8</sup> We say that the twin point group is isomorphic with a given crystallographic point group, not that it coincides with it because, although it has the same type of symmetry elements, some of these are chromatic. Only by neglecting the chromatic nature of its elements would a twin point group 'coincide' with a crystallographic point group.

ning can be investigated by means of the Bijouvet intensity ratio (Flack & Shmueli, 2007).

**Class IIA:** the twin operation does not belong to the Laue class of the crystal. The presence of twinning may hinder a correct derivation of the symmetry from the diffraction pattern. In particular, when the number of individuals coincides with the order of the twin operation and the volumes of the individuals are equal, the symmetry of the diffraction pattern is higher than the Laue symmetry of the individual. A wrong space group can thus be assumed in the initial stage of the structure solution. The presence of twinning can be investigated by statistical analysis of the intensities (Rees, 1980).

**Class IIB:** the situation is similar to that of class IIA but now the crystal has a specialized metric and the twin operation belongs to symmetry operations of the lattice corresponding to this specialized metric, not to that of the crystal holohedry. For example, in a monoclinic crystal with  $\beta = 90^\circ$ , the twin element is a twofold axis parallel to [100] or [001] or a mirror plane normal to one of these directions. This type of twinning has been called ‘metric merohedry’ (Nespolo & Ferraris, 2000) or ‘higher-order merohedry’ (Friedel, 1926).

Common to these three classes is that, following the perfect overlap of reciprocal lattices, the diffraction pattern from twins does not show special reflection conditions, with the exception of crystals with space group of type  $Pa\bar{3}$  (Koch, 1999).

Twins by reticular merohedry are characterized by partial overlap of the lattices of the individuals. As a consequence, special reflection conditions, corresponding to non-space-group absences, are commonly observed in the diffraction pattern. This is among the strongest alerts for the presence of twinning, although it does not uniquely come from twinning: OD structures, for example, also give non-space-group absences, typically along family rows indexed in the polytype axial setting.

Twins by (reticular) pseudo-merohedry show diffraction splitting, which is more pronounced at high angles. The degree of splitting depends on the twin misfit and for very low values it may not be observable, resulting at most in a slight enlargement of the diffractions.

## 7. Topology of crystal structures

The term *topology* is used with different meanings in crystal chemistry. For example, an affine transformation connecting the structure of two polymorphs related by a displacive transformation can be described in topological terms, although the connectivity is modified because the number of bonds is not necessarily the same in the two structures. Here we use the term topology in a narrower sense, with reference to the connectivity of a crystal structure, *i.e.* the way in which the atoms are connected to each other. The latter, reduced to its minimal terms, is a set of atoms joined in a more or less complex way along privileged directions that we call chemical bonds. In the case of completely ionic structures, the bond itself is not directional but the packing of ions determines

directions of minimal distances between ions of opposite charge, and these can be taken as ‘privileged directions’. A crystal structure can therefore be seen as a set of vertices (atoms) and edges (bonds) and is describable as an infinite undirected<sup>9</sup> graph embedded into the three-dimensional point Euclidean space: it is called a *crystal structure graph*. There exists an isomorphism between the elements of the space group of the crystal structure (isometries) and the group of automorphisms of the crystal structure graph.<sup>10</sup> Graph theory is commonly applied in chemistry to molecules. Its powerfulness in the analysis, description and foresight of crystal structures was realized only later.

The famous study of the Seven Bridges of Königsberg is regarded as the first paper in the history of graph theory (Euler, 1736). Euler’s formula relating the number of edges, vertices and faces of a convex polyhedron was studied and generalized by Cauchy (1813) and L’Huillier (1861) and is at the origin of topology. Cayley (1875) developed the study of trees and linked his results with the contemporary studies of chemical composition. The fusion of the ideas coming from mathematics with those coming from chemistry is at the origin of a part of the standard terminology of graph theory. In particular, the term *graph* was introduced by the chemist Sylvester (1878*a,b*).

An instructive example of the application of graph theory to the analysis of crystal structures is the determination of isostructural compounds. As mentioned in the section about normalizers, the same crystal structure may sometimes be described in different ways, and to verify whether two apparently different crystal structures actually simply differ in their description it is sufficient to verify whether the corresponding point configurations are Euclidean-equivalent or not. We can generalize this concept to the case of different compounds whose crystal structures have the same topology. To reveal this relation, one has first of all to establish a mapping between atoms or groups of atoms, then verify whether the corresponding point configurations are affine-equivalent or not. One of the structures compared may turn out to be a derivative of the other, as is the case of the diamond–sphalerite–chalcopyrite described in the previous section. Graph theory is a powerful tool in such a task: once the mapping of atoms has been established, the bond pattern of the structures under consideration is translated into the corresponding crystal-structure graph. It is therefore the mapping of a graph onto another graph that can reveal whether two structures are isomorphic, derivative or unrelated. Two types of mappings between graphs should be considered:

1. *homeomorphism*, which is an isomorphism between spaces that respects topological properties; in particular, it maps neighbour points and distant points in one space on neighbour points and distant points, respectively, in the other

<sup>9</sup> A graph can be undirected (a line from point *A* to point *B* is considered to be the same as a line from point *B* to point *A*) or directed, also called a digraph (the two directions are counted as being distinct arcs or directed edges).

<sup>10</sup> An automorphism is an isomorphism (bijective mapping) from a mathematical object to itself.

space; in other words, homeomorphism is a continuous invertible bijective deformation between two topological spaces;

2. *homomorphism*, which is a relation between graphs preserving the operations; the special case of isomorphism, or bijective homomorphism, is of particular interest here.

Through homeomorphism, it can be shown that crystal graphs are topologically equivalent to a potentially enumerable set of fundamental nets (see *e.g.* Delgado-Friedrichs & O'Keeffe, 2003). Then, the search for isostructurality reduces to establishing a graph isomorphism, which can be obtained by finding some graph invariants. A typical example of such an invariant is the *quotient graph*. A *finite* quotient graph is obtained from an *infinite* structure graph by finding translationally equivalent points (atoms) and lines (bonds) and preserving their incidence relations. The result is called a quotient graph because it is analogous to the quotient (factor) group  $G/T$  between a space group and its translation subgroup. The quotient graph retains the whole connectivity of the structure graph, namely the information about which point lattices are connected to each other by how many lines; however, the information about which individual point of a given lattice is joined to which individual point of another lattice is lost. As a consequence, different non-isomorphic graphs may have the same quotient graph (Klee, 1987). A system of labels can however be assigned to the edges in such a way that it uniquely determines the infinite structure up to isomorphism *via* the so-called *vector method* (Chung *et al.*, 1984). This opens the possibility of an algebraic representation of the quotient graph, which makes it possible to translate the process of comparing crystal structures into a symbolic computer language.

A graph can be represented by its *adjacency matrix*, which is a real square symmetric matrix with a row and a column for each vertex of the graph. The element corresponding to the  $i$ th row and the  $j$ th column gives the number of edges by which the two corresponding vertices are joined. Because the numbering of vertices is not unique, the adjacency matrix can be written in different ways, which differ by permutation of rows and/or columns, but do not affect the invariants of the matrix, such as determinant, trace and its eigenvalues. The latter are said to form the *spectrum of the graph*. The adjacency matrix is however not uniquely determined by the spectrum of its eigenvalues and, as a consequence, non-isomorphic graphs with the same spectral values may be found, which are called *cospectral* (Klee, 1987). The comparison of the spectra of the graph of two crystal structures is, alone, in general not sufficient to state that the two structures are isomorphic but it is sufficient to exclude that they are: a number of examples can be found in Eon (1998). Other graph invariants as possible means to establish isomorphism are presented in Eon (2002).

It must be emphasized that, in order to build a structure graph, the coordination number of each atom in the structure must be uniquely defined and known. This is not always the case, especially when a clear division between the first and second coordination spheres does not exist. The concept of

coordination number itself has been the object of critical considerations (Hoppe, 1970) and generalizations (Hoppe, 1979; O'Keeffe, 1979). To judge up to what distance an atom still coordinates with its neighbours, or the closely related question of accounting for the bond-length distribution in irregular coordination polyhedra, different methods have been proposed, such as bond valence (see a review in Urusov, 1995), resonance bond number (Boisen *et al.*, 1988; Rutherford, 1991, 1998*a*) and charge distribution (Hoppe *et al.*, 1989; Nespolo *et al.*, 1999, 2001).

Several applications of graph theory to crystal-chemical problems can be mentioned, like the analysis of possible polymorphs by means of Schlegel diagrams (Hoppe & Köhler, 1988) and the problem of finding atomic configurations satisfying neighbour-avoidance rules. The aluminium-avoidance rules in tetrahedra of aluminosilicates (Löwenstein, 1954) is an empirical rule subject to exceptions (Depmeier & Peters, 2004). Although far from being a general law of Nature, it is respected in a large number of structures. A graph-theoretical approach to the study of the distribution of Al and Si in a given structure according to this empirical rule was presented by Klee (1974*a,b*). A similar problem was addressed by Rutherford (1998*b*) to show that, in the one-dimensional ionic conductor  $[(\text{CH}_3)_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]\text{Ag}_4\text{I}_5$ , the energy of the system is minimized when Ag ions do not occupy neighbouring tetrahedra.

An exhaustive presentation of the applications of graph theory to crystallography and crystal chemistry will soon be available (Eon *et al.*, 2008).

## 8. Conclusions

Mathematical crystallography, far from having exhausted its task with the development of the space-group theory, not only represents one of the foundations of crystallography but is still a very active field of research, which nowadays extends its interests to cover several branches that were previously seldom considered in their interactions with crystallographic and crystal-chemical problems. This brief survey was limited to only some of the main topics of mathematical crystallography, but quite a few others, mentioned only *en passant*, like higher-dimensional crystallography and topology of non-Euclidean spaces, would have deserved a presentation as well. The reader is encouraged to follow the activities of the IUCr Commissions like MaThCryst and the Commission on Aperiodic Crystals to obtain a wider view of current and future developments in mathematical crystallography.

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