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From patterns to space groups and the eigensymmetry of crystallographic orbits: a reinterpretation of some symmetry diagrams in IUCr Teaching Pamphlet No. 14

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The space group of a crystal pattern is the intersection group of the eigensymmetries of the crystallographic orbits corresponding to the occupied Wyckoff positions. Polar space groups without symmetry elements with glide or screw components smaller than 1/2 do not contain characteristic orbits and cannot be realized in patterns (structures) made by only one crystallographic type of object (atom). The space-group diagram of the general orbit for this type of group has an eigensymmetry that corresponds to a special orbit in a centrosymmetric supergroup of the generating group. This fact is often overlooked, as shown in the proposed solution for Plates (i)–(vi) of IUCr Teaching Pamphlet No. 14, and an alternative interpretation is given.

1. Introduction

Although crystallography is a centennial science, its presence in higher education is in jeopardy. Indeed, crystallography is very often nothing more than a chapter in introductory solid-state physics and chemistry books and in mineralogy textbooks, and therefore the treatment it receives in graduate-level courses is often only incidental. As a result of this lack of formal crystallographic education, many young crystallographers have acquired their knowledge in the field through a rather slow and sometimes tortuous self-education process, using some excellent books available on the different aspects and applications of crystallography, and attending schools and workshops covering basic and advanced aspects and new developments of crystallography at different levels. This continues to be the case nowadays, especially, but not only, in the developing world, where the lack of strong crystallographic societies or associations keeps crystallography as a very rarely taught topic at the undergraduate level and only for specific areas in graduate schools. Paradoxically, this difficulty of learning crystallography may also be at the root of its outstanding development in the past century, since modern crystallographers come from such different knowledge areas as physics, chemistry, materials science, mineralogy and biology, permanently enriching this already wide area of science.

This problem has been tackled by the IUCr at different times through different strategies, all aimed at compensating for the lack of formal education in crystallography. The creation of the IUCr Teaching Commission (IUCr-TC) in 1954 was one of these actions, and the systematic work of convincing academia to include crystallography as a separate subject in undergraduate and graduate-level courses has always been part of the work of the IUCr. Nowadays, in some universities in Europe specific graduate programmes on crystallography exist as a consequence of this push, but they are often isolated efforts by researchers in just a few universities. Being very aware of the differences in development of crystallographic teaching in different regions of the world, in the late 1970s the IUCr-TC undertook the task of providing academia with a series of short booklets or pamphlets directed at helping students to self-educate and teachers to introduce the basic concepts of crystallography to advanced undergraduate or graduate students. These so-called IUCr Teaching Pamphlets have become standard and widely used crystallographic teaching materials. Since the first series published in 1980, continued by the second series published in 1984, up to some recent additions, a total of 23 IUCr Teaching Pamphlets have been published and made available for free at the IUCr website (http://www.iucr.org/education/pamphlets). These are in general high-level teaching materials checked carefully for errors and inconsistencies. Nevertheless, some topics that should form the common background of a crystallographer are not (yet?) included and their absence results in some inconsistencies, even in this professional series. Here, we point out the concepts of orbit eigensymmetry and intersection symmetry, which are practically never presented even in

graduate courses. Without them, serious oversights may occur, and indeed have occurred, as we will show.

2. Space groups as intersection groups of the eigensymmetries of crystallographic orbits

The operations of a space group G applied to an atomic position give rise to an infinite set of equivalent atoms called a crystallographic orbit or point configuration [for details of the difference between these terms, see Koch & Fischer (1985)]. Let the eigensymmetry of the ith orbit O_i be $E(O_i)$, or E_i for brevity. The relation between E_i and G gives rise to the following subdivision, where T is the normal subgroup of translations (Engel *et al.*, 1984):

(1) $E_i = G$: the orbit is called characteristic;

(2) $E_i > G$: the orbit is called noncharacteristic; it can be further subdivided depending on whether

(2.1) $T(E_i) = T(G)$: the noncharacteristic orbit is non-extraordinary (term usually omitted);

(2.2) $T(E_i) > T(G)$: the noncharacteristic orbit is extraordinary, the latter term taking priority over the former (an extraordinary orbit is always noncharacteristic, while the opposite is not true).

A crystal structure S can be seen as the union (in the algebraic meaning) of all the crystallographic orbits O corresponding to the Wyckoff positions occupied by the atoms of the structure. The space group of the structure $G(S)$ is, instead, the intersection of the eigensymmetries of these orbits. In fact, for each orbit, only the symmetry operations that are common to the other orbits are promoted to symmetry operations of the whole structure, the others being local symmetry operations [for the meaning of a local operation, see Nespolo *et al.* (2008)];

$$S = \cup_i O_i;\ G(S) = \cap_i E(O_i). \qquad (1)$$

A space group whose general orbit is noncharacteristic does not contain any characteristic orbits. This arises immediately from the consideration that the eigensymmetry of a special orbit is at least equal to that of the general orbit. Space groups without characteristic orbits cannot be realized in structures with only one crystallographic type of atom. In fact, if a structure S is composed of only one type of atom, which, under the action of G, generates one orbit O, then necessarily $G(S) = E(O)$, which requires that the orbit is characteristic. Space groups without characteristic orbits are typically pyroelectric groups without d mirrors, or screw axes with a screw component different from $\frac{1}{2}$ (*i.e.* containing only 2_1, 4_2 and 6_3 as screw axes). In these space groups, the eigensymmetry of each orbit has an additional symmetry element q perpendicular to the symmetry element defining the polar direction(s): either a mirror perpendicular to the polar axis or a twofold axis perpendicular to the polar plane (in the absence of metric specialization, space group $P1$ is an exception because the triclinic metric is not compatible with a proper or improper rotation of order higher than 1). In fact, atoms in the orbit are in one of the following four situations: (i) on planes separated by full lattice translations; (ii) on planes separated by half lattice translations; (iii) along directions separated by full lattice translations; and (iv) along directions separated by half lattice translations. These atoms have q in their eigensymmetry, and the symmetry operation $s(q)$ about q defines a coset $s(q)G$ so that $G \cup s(q)G = E$ is the eigensymmetry of the orbit. As a consequence, the general orbit in G corresponds to a special orbit in E, whose site symmetry group is precisely defined by q. For these cases, the space-group diagrams in Volume A of *International Tables for Crystallography* (2011) do not indicate any additional symmetry elements, because for structures composed of more than one orbit these are local elements, although each diagram gives only one general orbit. However, when applying the opposite reasoning, from the orbit to the space group, the implicit assumption that the orbit is general may result in the underestimation of the eigensymmetry and thus of the space group, as we will now show.

3. Missing symmetry elements in the IUCr Teaching Pamphlets

IUCr Teaching Pamphlet 14 (*Space Group Patterns*; Meier, 2001) is the continuation of IUCr Teaching Pamphlet 13 (*Symmetry*; Dent Glasser, 2001). It contains 15 plates showing groups of feet or hands (or, as we interpret them, footprints and handprints) periodically and symmetrically arranged to represent crystal patterns[1] in each of the 230 types of space group in a particular setting. Pamphlet 14 is designed to put into practice the concepts of symmetry introduced in Pamphlet 13, and starts with an explanatory introduction where the symbols and rules for the use of the plates are outlined.

In general, two types of symbol are used for the symmetry patterns. Footprints are used for space groups containing only twofold symmetry operations [Plates (i)–(vi)], while handprints are used for space groups with rotations of higher order. The feet symbols are also used to exemplify planar groups that can be obtained as a projection of a space group along the vertical axis. The difference between a hand and a foot may not be evident from examining real hands and feet, but in the plates footprints are only used to represent polar space groups, the polar direction being taken as the direction of projection, since footprints are always looked at from above. Feet differ, however, in their handedness (right or left). Handprints, instead, are shown both right and left and palm up or palm down.

The polar space groups represented by footprint patterns are precisely the types without characteristic orbits: *Pma*2 (No. 28) [Plate (i)], *Pnc*2 (No. 30) [Plate (ii)], *Pbn*2_1 (No. 33) [Plate (iii)], *Cc* (No. 9) [Plate (iv)], *Cmc*2_1 (No. 36) [Plate (v)] and *Aea*2 (former space group symbol *Aba*2) (No. 41) [Plate (vi)]. The plates represent only the general orbit of these groups, so that $G(S) = E(O)$. Because the eigensymmetry of

[1] A crystal pattern is a generalization of a crystal structure to a set of any objects or figures. A crystal structure is a special case of a crystal pattern, where the objects are atoms.

the orbit is higher than that of the generating group, the space group given in the text is systematically a subgroup of the space group corresponding to the plates. In other words, each plate shows a special orbit in a centrosymmetric space group, while the text describes it as a general orbit in a polar group.

Let us examine Plate (i), reproduced in Fig. 1. This is a crystal pattern corresponding to the general orbit of a space group of type *Pma*2. The + symbol at the top right of the picture indicates that the z coordinate of the feet is located away from $z = 0$. A footprint has eigensymmetry *m*. Because all feet are located at the same z coordinate, this mirror also occurs in the space group of the pattern, at z coordinates + and $\frac{1}{2}$+ with respect to the chosen origin. This mirror implies the existence of further symmetry elements, namely twofold screw axes parallel to [100], twofold axes parallel to [010] and inversion centres at the intersection of $2_{[001]}$ with $m_{[001]}$ (Fig. 2). The space group of the pattern shown in Plate (i) is thus *Pmam* [standard symbol *Pmma* (No. 51) obtained by an **acb** transformation]. In this type of space group the footprints are no longer in a general position but in a special position with site symmetry *..m* (*.m.* in the standard setting). A shift of the origin is necessary to obtain the standard description. Once this shift is applied, it is possible to recognize that the orbit corresponds to Wyckoff position 4*i* or 4*j*, depending on where the origin is placed with respect to the orbit. The space group of the pattern would only be of type *Pma*2 if the footprint did not possess eigensymmetry *m*, *i.e.* if the top and the bottom of the footprint were different, as is the case for the handprints, for which palm up and palm down are shown.

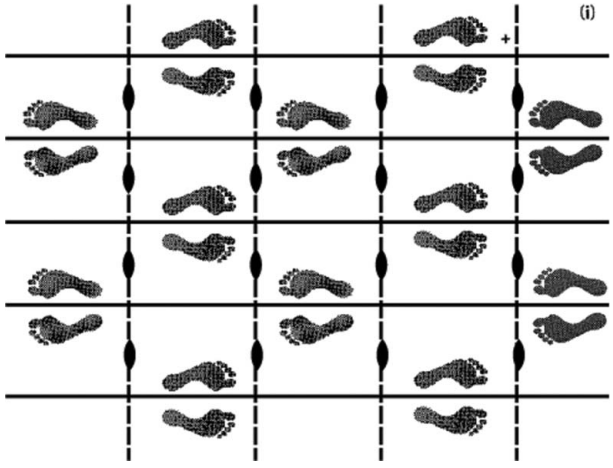

Figure 1
Plate (i) of IUCr Teaching Pamphlet 14, with the symmetry elements of the space group that has generated the orbit represented by the set of footprints. Axes, not shown in the original plate but described in the text, are oriented as in the first projection of each orthorhombic group, *i.e.* *c* is the projection direction, *a* is directed vertically down and *b* is directed horizontally right.

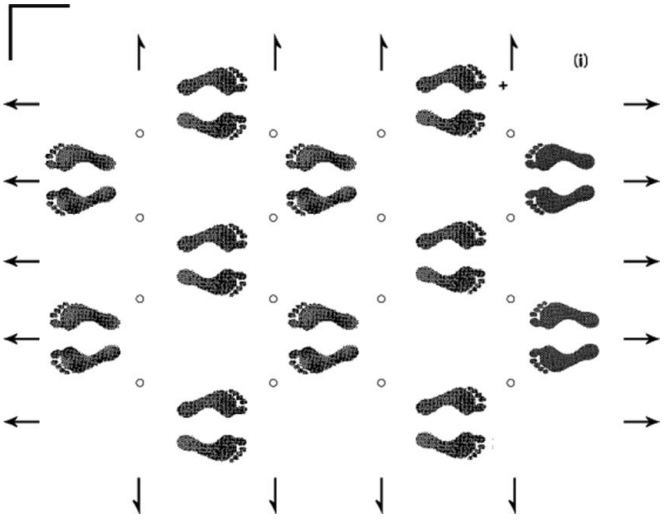

Figure 2
Plate (i) of IUCr Teaching Pamphlet 14, with the symmetry elements missing in Fig. 1. The eigensymmetry of this orbit is *Pmam* [standard symbol *Pmma* (No. 51)], which is also the space-group type of a crystal pattern composed of this orbit alone.

The same argument applies to Plates (ii)–(vi), where the supposedly polar arrangements of footprints correspond not to a general orbit in *G* (polar) but to a special orbit in the centrosymmetric supergroup *E*. The correct space-group types are then *Pncm* [Plate (ii); standard symbol *Pmna* (No. 53)], *Pbnm* [Plate (iii); standard symbol *Pnma* (No. 62)], *C*2/*c* (No. 15) [Plate (iv)], *Cmcm* (No. 63) [Plate (v)] and *Aeam* (No. 64) (former space group symbol *Abam*) [Plate (vi); standard symbol *Cmce*].

4. Discussion

The usual way of introducing space groups in crystallography courses is *via* the application of space-group operations to objects in a general position to generate a crystal pattern. The opposite approach, from pattern to space group, is didactically more interesting, not only because a space group is indeed the *a posteriori* interpretation of a crystal pattern in terms of its symmetry, but also because it underlines several features that normally go unnoticed, namely (i) the eigensymmetry of each orbit, (ii) the nature of a space group as the intersection group of these eigensymmetries, and (iii) the presence of local symmetry operations, which are part of the eigensymmetry of an orbit but not common to the other orbits. Adopting this approach in parallel with the more common way of introducing space-group symmetry avoids oversights like those present in Teaching Pamphlet No. 14 discussed in this article. This pamphlet is frequently downloaded from the IUCr web site, suggesting it is still in widespread use, making our reinterpretation and this discussion of some didactic value for teachers who use it.

LS thanks the anonymous student who first solved Plate (i) 'incorrectly' by placing a mirror plane in the plane of the feet, drawing our attention to the possible misinterpretation that the use of footprints may lead to in the first six plates of pamphlet No. 14. The authors are also indebted to Brian McMahon from the Chester office of the IUCr for providing information on the download of IUCr Teaching Pamphlet No. 14 from http://www.iucr.org/education/pamphlets/14. The

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