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Letter

Geminography – The science of twinning applied to the early-stage derivation of non-merohedric twin laws

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Abstract. The recognition of twinning and the determination of the twin laws are nowadays often entrusted to "black-box" software packages. This approach may be both risky and uneconomical. It is risky because never a procedure should be blindly applied. It is uneconomical if procrastinates the analysis of twinning at the very late stage of structure solution and refinement, whereas in many cases this analysis can and should be applied much earlier. In this paper we present a brief survey of the working strategies to be applied to the structural study of twinned crystals, emphasizing the role of the crystallographer, rather than that of the machine.

Introduction

Nowadays the solution of the crystallographic problems is often entrusted to automatic machines and software packages, and the crystallographer sees his role shrinking towards that of a technician who pushes the appropriate buttons. In particular, structural crystallography risks to be considered simply a tool and to see overlooked and forgotten its status of interdisciplinary science. As a matter of fact, crystallography has entered a perverse cycle: space for basic crystallographic education is shrinking everywhere, non-specialists who use crystallography as a tool are increasing in number and they demand more powerful "black-box" packages, these packages offer a blind analysis, and the need for a "specialist of crystallography" is felt almost everyday weaker (Nespolo and Ferraris, 2003). The important contribution given by professional programmers to the routine structural work of the crystallographer is beyond doubt. However, these programmers not always come from a sound crystallographic background, a fact which sometimes brings in use non-standard language (thus generating a confusion which is even inherited in the literature, as discussed below) and implementation of blind solution-seeking strategies.

This problem is becoming particularly severe in case of twinning. Twins, especially in the mineralogical field, were considered an important object of investigation from the crystallographic, morphological and crystal-growth viewpoint (see, e.g., Friedel 1904, 1926; Buerger, 1945, 1954; Cahn, 1954; Hartman, 1956; Holser, 1958; Takano, 1973). Twins are so peculiar "objects" that Takeda (1975), following an idea by J. D. H. Donnay (Takeda, personal communication) introduced the term *geminography* (from the Latin "geminus" for twin) to mean a specific "science of twinning", namely the complex of notions and experience specifically addressing the treatment and solution of the structure of twinned crystal.

But when molecular crystallographers, who are interested more in the structure and conformation of the molecule rather than to the crystal structure, "discovered" the phenomenon of twinning, twins came to be considered simply an obstacle to the automatic solution and refinement of crystal structures, and were relegated to the role of "demons" (Flippen-Andersen et al., 2001), together with disorder, polytypes and modular crystallography, as shown by the homonymous microsymposium at the XIX IUCr congress (IUCr 2002). As a result, the demand of crystallographic tools capable of dealing with such "demons" increased dramatically, actually leading to the introduction of successful methods for the treatment of twinning in the programs for the solution and refinement of crystal structures (Herbst-Irmer and Sheldrick, 1998). These programs are of invaluable help, provided that the twin laws have been correctly identified by the user. In fact, an automatic software is still unable to foresee and treat *all* real cases. The skill and experience of recognizing a twin and the corresponding transformation matrices remains thus of paramount importance for the structural crystallographer.

Notwithstanding, even the identification of the twin law(s) is nowadays tentatively entrusted to black-box soft-

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ware packages (Cooper et al., 2002). Whereas the automatic analysis and treatment can be successful in common cases, daily experience shows that failure by these "black boxes" in solving the structure of a twinned crystal is not at all an exception. When it comes to more complex cases, like those of multiple individuals[1] or of twinning by metric merohedry (*i.e.* twins in which the individuals have a metric of their lattice higher than that required by their space group: Nespolo and Ferraris, 2000), the expectation of success is even lower. Besides, this automatic analysis is applied at a very late stage, during or even after the structure solution (assuming that an acceptable solution can be found when being still unaware of twinning, which generally is not the case), *i.e.* in a very uneconomical way. For all the reasons exposed above, it is worth summarizing the strategies for *early-stage* identification of non-merohedric twinning. Before that, however, it is necessary to make a bit of order in the nomenclature.

The problem of terminological imprecision

In the recent literature the adjective "merohedral" has become a sort of "hybrid" with unclear meaning. "Merohedral", in contrast to "holohedral", identifies a crystal whose point group is a subgroup of the point group of its lattice (Friedel, 1926). A merohedral crystal may undergo twinning by merohedry: the twin operation belongs to the point group of the lattice of the individual but not to the point group of the structure. But the same crystal can as well, although less frequently, undergo twinning by reticular (pseudo) merohedry, provided it possesses in the direct space, exactly or approximately, a sublattice (*i.e.* a lattice built on a supercell of the cell of the individual) of higher symmetry. This is the same kind of condition for the twinning of holohedral crystals. In this case, the twin operation belongs to the point group of the sublattice, and not to the point group of the lattice.

Expressions like "merohedral twins" or "non-merohedral twins", so often employed today, are confusing in the fact that they refer to the twin a feature of the individual, without a 1 : 1 correspondence between them. Rigorously speaking, "merohedral twin" should indicate a twin of a merohedral crystal, which not necessarily is a twin by merohedry. Authors who find too cumbersome the use of the original locution "twinning by merohedry" and absolutely need an adjective to label the type of twinning, should employ the adjective "merohedric", introduced long ago with specific reference to the twin, precisely to avoid any confusion with the characteristics of the individual (Catti and Ferraris, 1976).

Optical analysis at the pre-data collection stage

The first indication of possible twinning can be obtained from a morphological observation, at least when the forms of the crystal are sufficiently developed. Among the morphological features of twinning, the presence of re-entrant corners is most typical (Kitamura *et al.*, 1979). Besides, several morphologies are so typical of twins that, with some rare exceptions (Pabst, 1971), they should be considered as strong signals (Shafranovskii, 1973).

The observation under polarized light can also reveal the presence of twinning, at least in case of non-merohedric twins. Non-merohedric twins in fact, as well as twins by metric merohedry, are composed by individuals related by a twin operation which belongs to a holohedry higher than that of the crystal. In other words, the twinned individuals have orientations that are not equivalent under the symmetry operations of their holohedry. Consequently, the principal axes of their optical ellipsoids in general do not coincide (Nye, 1987). The observation under the polarizing microscope reveals the presence of twinning through the different position of extinction shown by different individuals.

Pre-structure solution analysis I. The geometry of the diffraction pattern

The second step in the "search for twinning" consists in the analysis of the geometry of the diffraction pattern, which can reveal two distinctive features of twins: 1) splitting of reflections; 2) non-space group absences. The splitting appears at glance if the investigator records the diffraction pattern with a bidimensional detector like CCD camera, image plate and film. When only a point-detector is used in the diffraction study, attention must be paid to the shape of the peaks.

In the following, the term "twin lattice" is used without specific reference to its derivative nature. However, it is implicitly understood that in case of non-merohedric twins, the twin lattice is a *sublattice* of the crystal lattice in direct space (the group of translation is a subgroup, *i.e.* the unit cell is larger), whereas it is a superlattice in reciprocal space (the group of translation is a supergroup, *i.e.* the unit cell is smaller). The diffraction pattern of the twin derives from the superposition of the diffraction patterns of the individuals and it corresponds to a lattice only when a univocal correspondence between *reflections* and *nodes* does exist.

1) When the obliquity (Friedel, 1926) of the twin is sufficiently large to show split reflections contributed by the different individuals, the presence of twinning by (reticular) pseudo-merohedry is easily recognized. This splitting, however, may appear for some classes of reflections only: it is thus necessary to observe the diffraction pattern of some reciprocal planes. Besides, the splitting increases with the diffraction angle, and should thus be looked for in the regions of the reciprocal space farther from the origin, when it does not appear at low angles. This type of twinning is easier to recognize, but more difficult to treat, because the intensities from different individuals are not (exactly) superposed. For low (quasi-superposition) and high (clear splitting) obliquity, the treatment is relatively easier, whereas for intermediate values the partial superposition of the intensities requires a correction which is

[1] The term "individual" is here used to indicate one crystal of a twin.

function of *hkl* and of the actual shape of the peak, and can be rather complex, limiting the quality of the structure refinement which can be obtained. On the other hand, the relative intensity of split reflections permits to obtain the volume ratio of the individuals.

2) Twins by reticular merohedry usually produce a diffraction pattern containing systematic non-space group absences, which are an alert signal for the presence of twinning. Let n be the twin index[2]; n' the ratio between the order of the twin lattice point-group and the order of the individual point-group; and n'' the number of individuals. To each *node* of the twin reciprocal lattice, a *reflection* may or may not correspond, depending on whether reflections from one or more individuals appear or not on that node. The nodes of the reciprocal lattice common to all the individuals (*i.e*. the nodes overlapped in both the reciprocal lattice of the individuals and the reciprocal twin lattice) always correspond to reflections: these are the reflections (one out of n) which are always overlapped for all the individuals. Other $n'' - 1$ reflections come from each individual but are not overlapped, because they correspond to nodes of each individual reciprocal lattice which do not overlap in the reciprocal twin lattice. The result is that, in general, in the diffraction pattern we observe systematic non-space group absences coming from the incomplete correspondence between the *nodes* of the twin reciprocal lattice, and the *reflections* coming from the n'' individuals.

When such systematic non-space-group absences appear, the search for the twin law should proceed while taking into account the following criteria:

1. the reciprocal cell of the individual is n-times larger than that of the twin (the reciprocal lattice of the individual is a sublattice of the twin reciprocal lattice);
2. the reciprocal lattice of the individual should not contain systematic non-space-group absences;
3. the twin operation must be found among those operations which are symmetry operations for the twin lattice but not for the lattice of the individual; the twin lattice must be re-obtained by applying this operation to the lattice of the individual.

These non-space-group absences do not appear in the diffraction pattern of a non-merohedric twin when *each* node of the twin reciprocal lattice is occupied by a *reflection* from one or more individuals. Such a diffraction pattern may appear when $n'' = n' \geq n$. This is the only case when a non-merohedric twin cannot be identified by the geometry of its diffraction pattern.

[2] The twin index corresponds to the ratio of the number of nodes in the twin cell and in the individual cell. It coincides also with the ratio between the order of the group of translation of the individual lattice and that of the twin lattice (both definitions apply in the direct space).

Pre-structure solution analysis II. The diffraction intensity

When the diffraction pattern does not show non-space-group absences, the presence of twinning can still be investigated on the basis of the symmetry of the diffraction intensities and of their statistic (Giacovazzo, 2002), keeping into account the effect of the relative volume of the individuals and of the relative orientation of the individuals.

1. The twin operation appears as symmetry element for the measured intensities only if the volume of the individuals related by that element is similar (ideally identical). Otherwise, the twin elements appear only in the geometry of the diffraction pattern.
2. Symmetry elements of the individuals which are not parallel in the twin do not appear in the diffraction pattern (Buerger, 1954).

If L is the Laue point group as obtained from the diffraction pattern, H the holohedry which corresponds to L, and G the point group derived from the geometry of diffraction pattern, the following cases can thus be recognized:

1. $H \subset G$ (ex. $L = 4/m$, $H = 4/mmm$, $G = m\bar{3}m$). Such a diffraction pattern can be produced by: a) a twin by reticular merohedry in which the individuals have different volume; or b) a crystal with a specialized metric of the lattice (the Bravais class of the lattice is a *t*-supergroup of the Bravais class of the space group[3]), untwinned or twinned by metric merohedry (Nespolo and Ferraris, 2000).
2. $H = G$. The presence of twinning can be recognized only at the stage of structure solution. This situation can correspond to a non-merohedric twin only when all the individuals of the twin have the same volume.

Structure solution stage analysis

As seen above, the sole case of non-merohedric twinning which can be recognized, from its diffraction pattern, only at such a late stage is the rare case in which the diffraction pattern does not present non-space-group absences and the symmetry of the intensities is consistent with the geometrical symmetry of the diffraction pattern because of the identical volume of the individuals. In the unfortunate case the investigator has also failed to recognize the presence of twinning by the observation under polarized light, the situation becomes parallel to the case of class IIA merohedric twins (Nespolo and Ferraris, 2000). Here, the twin operation overlaps reflections which are not equivalent under the Friedel law and an acceptable structure solution cannot be obtained, unless the twin operation(s) are very close to symmetry operation(s) for the structure (case of marked pseudo-symmetry), in which case it is the refinement which shows anomalies. Several

[3] The *t*-supergroup (translationengleiche supergroup) of a space group has higher point symmetry but the same translational symmetry (Wondratschek, 2002).

tests on the intensities can be applied to reveal this type of twinning (Kahlenberg, 1999).

In the case of class I, the twin operation overlaps reflections which are equivalent under the Friedel law (Catti and Ferraris, 1976). The structure can be solved and even refined to an acceptable degree. However, warning signals, although weaker than in all the previous cases, remain, in particular a distribution of intensities midway between centric and acentric (Viterbo, 2002), unusual displacement parameters or, if the group chosen is acentric, the impossibility of fixing the polarity of the crystal. These signals require critical analysis by the investigator and cannot be entrusted to a "black-box" software package.

Conclusions

The on-going trend towards automatization of crystallographic investigation is transforming the crystallographer into a technician often unaware of what the machines and software packages he uses are doing. The example of entrusting the non-merohedric twin inspection to the late stage of automatic computer analysis of the collected diffraction pattern has been presented, showing that, in most cases, such an analysis can be performed in the early-stage. The choice is, once again, between a black-box tool whose answers are accepted uncritically, and a human evaluation based on crystallographic education and working experience.

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