



Symmetry II: The symmetry of crystal structures and X-ray diffraction patterns

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A crystal structure and its X-ray diffraction pattern are related to each other, in both directions, by the mathematical procedure of Fourier transformation, the details of which are considered elsewhere. A diffraction pattern of a single crystal consists of a pattern of discrete spots (reflections) with a range of intensities. The pattern has a definite geometry, seen in the regular arrangement of spots, and a degree of symmetry in the positions and intensities of the individual spots.

The geometry of the diffraction pattern, usually interpreted as a **reciprocal lattice**, can be described by measuring the distances between spots and angles between rows of them. This corresponds to measuring the directions in which diffracted X-ray beams leave the irradiated crystal, relative to the incident X-ray direction and the orientation of the crystal. This diffraction pattern geometry gives information about the regular arrangement of molecules in the crystal structure; more specifically, it can be used to determine the geometry of the **crystal lattice** and define a suitable **unit cell**.

The symmetry of the diffraction pattern is related to the symmetry of the crystalline arrangement of molecules, which is expressed in terms of the **space group**. Some aspects of the space group are manifest in the observed symmetry of the diffraction pattern, and others can be deduced from **systematic absences**, which are specific subsets of reflections that are found to have zero intensity.

The intensities of the individual reflections, among which there is generally no obvious relationship except for the symmetry, hold information about the actual shapes and orientations of molecules, i.e. the positions of atoms in the crystal structure.

The symmetry of crystalline solids: space groups

Some basic concepts have already been introduced in *Symmetry I*. Here we review them briefly, and extend the understanding to a description of three-dimensional space groups and related topics.

A complete crystal structure can be specified by describing the contents of one repeat unit, together with the way in which this unit is repeated by translation symmetry. The pure translation symmetry is described by the lattice of the structure, which is uniquely defined for a particular crystal structure. The lattice is given numerical expression in the six parameters (three distances and three angles) of a unit cell, a parallelepiped constructed from eight lattice points at its vertices. Unlike the lattice, a unit cell is not uniquely determined, as its vertices may be chosen in different ways, but there are standard conventions regarding preferred choices, particularly in selecting a unit cell with a shape that displays any non-translation symmetry (rotation and/or reflection) in the structure; note that all unit cells, ignoring the detailed contents, have inversion symmetry. The presence of any rotation or reflections symmetry in a crystal structure leads to a corresponding symmetry of the lattice and of conventionally selected unit cells, the shapes of which are classified under seven **crystal systems**, each with a characteristic symmetry and a corresponding set of restrictions on some or all of the six unit cell parameters (equalities and/or special values).

For a single finite object such as a molecule or a crystal, all symmetry elements present must pass through a common central point; if there is an inversion centre, there can be only one and it is at this point. Thus the total collection of all the symmetry operations is a **point group**, with properties satisfying mathematical group theory. Each point group has its own characteristic properties and a conventional symbol. Because the only rotation axes compatible with an infinite lattice are of order 1 (trivial), 2, 3, 4, and 6, point groups relevant to crystalline solids are finite in number: there are 32, ranging from the least symmetrical 1 (no symmetry operations except the identity) to the most symmetrical $\frac{4}{m}\bar{3}\frac{2}{m}$ (abbreviated $m\bar{3}m$, the symmetry of a cube and octahedron). Point group symmetry applies to individual molecules, to the morphology of single crystals, to the shapes of unit cells, to particular sites in a crystal structure, and also to diffraction patterns, as these have a central point corresponding to the unmeasurable reflection with indices $h = k = l = 0$ (000).

Because of the presence of translation symmetry – both the pure translation of a lattice and symmetry operations that combine translation with rotation (screw axes) and reflection (glide planes) – the symmetry elements of a crystal structure do not all pass through one point. Instead they are arranged at regular intervals, consistent with the lattice, in space. The complete collection of symmetry operations is, therefore, not a point group. It is a space group. Just as in point groups, the symmetry operations in a space group can be combined only in certain consistent ways in order to satisfy group theory, and so there is only a finite number of three-dimensional space groups: 230 to be precise. The distribution of space groups across the seven crystal systems is far from uniform: for example, there are only two triclinic space groups (in which there is no rotation or reflection symmetry – $P1$ without, and $P\bar{1}$ with inversion symmetry), but there are 68 tetragonal space groups (each of which has some form of fourfold rotation axis in just one direction). The occurrence of the different space groups in real structures is also far from equally distributed, and is quite different in various fields of structural science. Some space groups are extremely rare, while others are very common. Most molecular materials crystallise in lower-symmetry crystal systems, while higher symmetries are more commonly found for inorganic ionic and network structures and minerals. Chiral compounds, including natural biopolymers such as proteins and nucleic acids, can crystallise only in space groups having no **improper rotations** (these include inversion and reflection as special cases) and are thus confined to 65 space groups.

The symmetry properties of the 230 space groups are well established, and extensive information is provided in standard references, the most comprehensive of these being *Volume A* of the *International Tables for Crystallography*, published by the International Union of Crystallography and Wiley, and available in printed and online versions. There is also a *Brief Teaching Edition (Volume A1, print only)*, covering a selected set of space groups. Related information can also be found on the *Bilbao Crystallographic Server*.

The point group symmetry of a diffraction pattern is clearly not the same as the space group symmetry of the corresponding crystal structure, but they are related in a definite way. The diffraction pattern symmetry can be uniquely derived from a known space group in simple steps, but there may be a number of possible space groups consistent with an observed diffraction pattern symmetry. Every space group has a corresponding point group. In the absence of **resonant scattering** (see diffraction theory notes for this), all diffraction patterns have a centrosymmetric appearance of intensities as well as geometry, so there are only 11 different point groups relevant to diffraction patterns (one each for the three lowest-symmetry crystal systems, and two each for the other four); these are called the 11 **Laue classes**, and recognising the correct one is one important step in determining a crystal structure by X-ray diffraction.

Additional points on the symmetry of crystal structures

While one unit cell is the basic repeat unit of a crystal structure, with its contents replicated at each lattice point, the presence of any rotation, reflection, and/or inversion symmetry means that the unique, symmetry-independent part of the structure is only a fraction of the unit cell, the fraction depending on the amount of symmetry present. This unique structural portion is called the **asymmetric unit** of the structure, and it may consist of a single molecule, a group of more than one chemically equivalent molecule, a fraction of a molecule possessing symmetry within itself, or a combination of different molecules and/or ions, for example including co-crystallised solvent molecules. Operation of all the space group symmetry generates the complete crystal structure from the asymmetric unit. The detailed contents of the asymmetric unit, together with unit cell parameters and the space group, are what need to be determined experimentally in order to describe the crystal structure.

For a crystal structure containing just one kind of molecule, the number of molecules in each unit cell, is conventionally known as Z , and the number of molecules in the asymmetric unit is Z' .

Space group determination

At some stage in the determination of a crystal structure by diffraction methods, it is necessary to decide which one is the correct space group out of the possible 230. Information about the space group is obtained from a number of sources, not all of them necessarily from the diffraction experiment. There is no single universal procedure for space group determination; the methods depend on the available information and its reliability.

At least some indication of the space group, or at least of the crystal system and preferably of the Laue class and crystal point group, is useful during the measurement of diffraction data, in order to ensure that all symmetry-unique reflections are measured. In cases of uncertainty, it is best to assume the lowest possible symmetry during data collection.

1. Prior knowledge and non-diffraction information: examples

If a compound is known to be chiral and enantiomerically pure, then the space group can contain only proper rotation axes; there are just 65 such space groups, and all others can be excluded.

Indications of the absence or presence of certain symmetry elements may come from the external morphology of well-formed crystals; from physical properties such as non-linear optical behaviour; and from optical examination of crystals with a crossed-polars rotating-stage microscope.

2. Unit cell and diffraction symmetry

While the unit cell parameters obtained from initial diffraction images will usually indicate the correct crystal system, there are not infrequent cases in which the unit cell shape approximates a higher symmetry than the true crystal system; examples include a monoclinic cell with angle close to 90° (appears orthorhombic), and an orthorhombic cell with two almost equal axis lengths (appears tetragonal). It is important to examine the intensities of reflections that would be symmetry-equivalent for the assumed crystal system. In other words, the Laue class, obtained from the reflection intensities, is a more reliable indication of true crystal symmetry than the unit cell parameters, derived only from diffraction geometry. It should be noted also that there are two Laue classes for each of the tetragonal, trigonal, hexagonal, and cubic crystal systems, and the correct one, based on intensity comparisons, needs to be chosen.

3. Unit cell contents

From the unit cell parameters and the assumed chemical composition of the sample, the number of atoms and molecules per unit cell can be calculated. Measurement of crystal density gives the most reliable results, but this is rarely performed and is often not feasible. An estimate can instead be made based on the observation that, for a wide range of organic, organometallic, and coordination compounds, each non-hydrogen atom in the unit cell requires an average volume of about 18 \AA^3 . Thus it is a simple calculation to find the approximate number of atoms, and hence of molecules, in the unit cell. The answer should be a whole number appropriate to the symmetry of the crystal system. If it is not, then the assumed value of the molecular mass is wrong, which may be due to the presence of solvent of crystallisation, or it could indicate that the compound is not as expected. The value obtained may help in the choice among possible space groups, which have different expected values because of different symmetry, and it may sometimes indicate that a molecule must lie in a **special position** on a crystallographic symmetry element rather than in a **general position** with no imposed symmetry.

4. Systematic absences

The pure translation symmetry of a crystal lattice gives rise to discrete diffracted beams (reflections) – the intensity of X-ray scattering is zero in all other directions because of destructive interference. Symmetry elements combining translation with rotation or reflection also lead to additional destructive interference effects, such that the intensities of some subsets of reflections are necessarily zero. The result is a regular pattern of missing reflections in certain rows or sheets of reflections in the observed diffraction pattern.

Further systematic absences appear to arise when a crystal system convention dictates that a **centred** unit cell (one with lattice points in extra locations in addition to the cell corners) is selected instead of a **primitive** unit cell: the unit cell volume is greater by a factor of 2, 3, or 4, but the diffraction pattern does not contain a correspondingly higher proportion of reflections. In reality, of course, neither the crystal lattice nor the diffraction pattern (described geometrically on the reciprocal lattice) changes at all when a different unit cell (and reciprocal unit cell) is chosen, but the mathematical description in terms of cell parameters and reflection indices does change.

Each type of unit cell centring, glide plane, and screw axis has an associated pattern of systematic absences from which it can be identified. Some space groups, including the very common $P2_1/c$ and $P2_12_12_1$, can be uniquely determined from the Laue class and systematic absences. In other cases two or more space groups give the same effects and other information is needed in order to choose among them.

5. Statistical distribution of intensities

Although symmetry elements without a translation component do not cause systematic absences, they do have an effect on the distribution of intensities about their mean value. Symmetry means that pairs (or larger sets) of equivalent atoms tend to give stronger constructive and destructive interference than would unrelated atoms, in directions with specific relationships to the symmetry element orientation. There is therefore a greater proportion of relatively strong and weak reflections, so that intensities show more variation overall. The theoretical probability of a reflection having a particular relative intensity is rather different in the presence and absence of symmetry.

Statistical tests are not actually made with the intensities themselves, but with **normalised amplitudes** (so-called *E*-values, defined elsewhere in connection with direct methods for solving the phase problem); they are based on a number of assumptions, and may be unreliable or inconclusive, particularly when structures deviate strongly from a relatively uniform random distribution of electron density (e.g. with large planar groups, or heavy atoms). *E*-value tests can be made in a number of ways, and they are mostly used to indicate whether a structure is likely to be centrosymmetric or not.

Crystallographic symmetry tables and resources

As mentioned earlier, the principal reference for space group (and other crystallographic) symmetry is *Volume A of International Tables for Crystallography*. Presentations at ECS will include a brief conducted tour of some example entries from *Volume A*, to explain the content and layout of the information and how it can be used. Further useful resources, to be demonstrated if time permits, include the *Bilbao Crystallographic Server*, both the free and licensed versions of the CCDC graphics program *Mercury*, and a collection of tutorial material at Otterbein University, USA. Features available include **supergroup** and **subgroup** relationships, which are important when related but different structures are compared: useful applications are structures in which a chemical substitution necessarily changes the symmetry, and temperature- or pressured-induced phase transitions in which single-crystal character is maintained but the space group changes.

References

International Tables for Crystallography: <http://it.iucr.org>

Bilbao Crystallographic Server: <http://www.cryst.ehu.es>

CCDC Mercury: <http://www.ccdc.cam.ac.uk/mercury>

Otterbein crystallographic symmetry tutorials: <http://crystals.otterbein.edu/>

