Modulated crystal structures – periodicity in more than three dimensions

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Abstract: The initial definition of a crystal was that it is an object with flat faces. When diffraction studies were developed it turned out that crystal consists of a highly ordered particles and it is possible to isolate a small unique part of their structure – a unit cell – and the definition has been changed to rely on this fact. Nowadays by a crystal we mean *any solid having an essentially discrete diffraction diagram*. It is because in recent years scientists found that there are some solids with discrete diffraction pattern, but there is no possibility to choose any unit cell. This is the case of quasicrystals discovered by Shechtman (Chemistry Nobel Prize 2011), polytypes and incommensurately modulated crystals – these all are called aperiodic crystals. However modulated crystals are not exactly aperiodic – their structures can be described as periodic, but in more than three (up to six) dimensions…

1. INTRODUCTION

There are four fundamental states of matter – solid, liquid, gas and plasma. Most commonly used as a construction material is the first one. For example we have buildings, vehicles, furniture, toys and electronic devices made of metals, salts, polymers, semiconductors etc.

Two main classes of solids can be distinguished: crystalline and amorphous. Both found wide range of applications, but the first one is especially interesting. Crystals may have many unique, highly predictable and adjustable properties.

Crystal engineering is “the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties” [1].

1.1. Periodicity in crystal structures

Initially it was believed that a crystal is an object with flat faces. When diffraction studies were developed it turned out that crystals consist of a highly ordered particles and it is possible to isolate a small unique part of their structure – a unit cell.

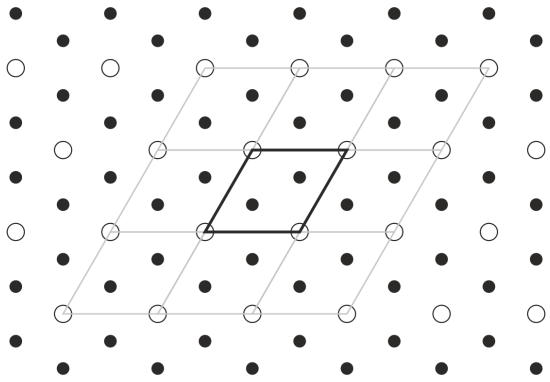

Figure 1: Two-dimensional structure with one of the possible unit cells selected (black parallelogram).

A unit cell is a parallelepiped through the translation of which the original structure will be reproduced (see model in Figure 1). We say therefore that crystals have translational symmetry. In the ideal conditions each unit cell should have exactly the same arrangement of atoms inside. In fact in real crystals there are some defects but their contribution to the statistical diffraction image is often negligible.

1.2. Symmetry and space groups

In addition to the translational symmetry there can be more symmetry operations present in a crystal structure: inversion centers, proper, screw and rotoinversion axes (2-, 3-, 4- and 6-fold) as well as mirror and glide planes. There is 230 possible combinations of all these operations, which are called space groups. They are numbered in order of increasing symmetry, but also named in a specific way to be easily recognized by a crystallographer.

If there is only translational symmetry in a crystal then it belongs to triclinic $P\,1$ space group. *P* stands for 'primitive', meaning that this is simple unit cell without centering. Usually if a crystal consists of achiral compounds then there are some centers of inversion and it is $P\,\bar{1}$ space group at least. There are of course space groups with higher symmetry and more sophisticated names such as: $P\,2_1/c$, *F ddd*, $I\,m\bar{3}m$, etc.

Why 2-, 3-, 4- and 6-fold axes
are allowed while 5-fold is not?

If we consider regular *n*-sided polygons then only these with $n = 3$, 4 and 6 can fill the plane without gaps. For $n = 2$ we can think of line segments, which can fill the plane as well. On the other hand points can also fill the plane without gaps, hence we have the limit groups with ∞-fold axes. It can be easily proved that regular *n*-sided polygons with $n > 6$ cannot fill the plane.

1.3. Single-crystal X-ray diffraction

Crystalline solids are characterized by a high internal arrangement of particles, so they can be considered as a three-dimensional grid of atoms. A beam of X-rays is scattered when it strikes a crystal. At each point with high electron density a flat wave is diffracted and a spherical wave is formed. Resulting waves interfere and characteristic diffraction pattern can be observed using appropriate detector (see model in Figure 2).

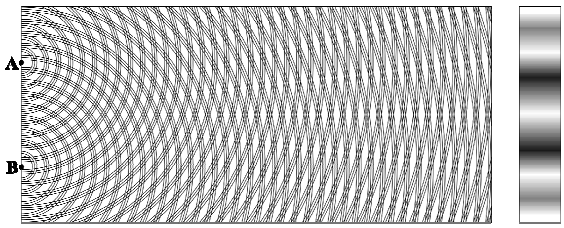

Figure 2: Double-slit (Young) experiment. Flat wave is diffracted at **A** and **B**, and spherical waves are created. Resulting waves interfere and the diffraction pattern is formed on the screen (right side of figure).

Modern (after 1991) definition of a crystal relies on this phenomenon [2]:

*A material is a **crystal** if it has essentially a sharp diffraction pattern.*

When there is no long-range ordering in a solid (such as in amorphous materials) then there is no discrete diffraction pattern.

Diffraction pattern is an image of so-called reciprocal lattice (with a unit vectors **g**) related to direct lattice (with a unit vectors **a**) with the mathematical equation: $e^{i\mathbf{ga}} = 1$.

The point group symmetry elements are reflected in a symmetry of a diffraction pattern, while the symmetry elements with the translational components cause some characteristic systematic extinctions. If the Friedel law is fulfilled the diffraction pattern is centrosymmetric regardless of whether the structure is centrosymmetric or not, hence we have only 11 so-called Laue classes.

The exemplary diffraction diagram is presented in Figure 3.

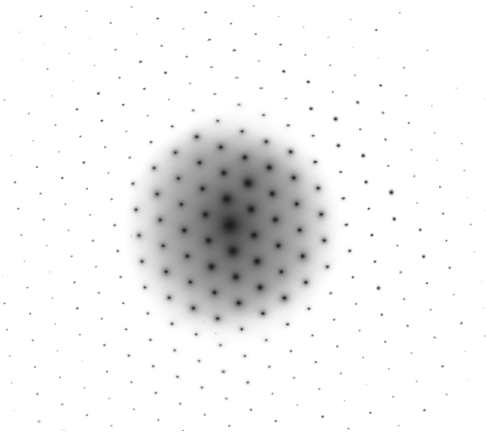

Figure 3: Example of diffraction pattern. Source: Internet Microscope for Schools, The University of Manchester.

2. MODULATED CRYSTAL STRUCTURES

Over the last years it turned out that there are crystals, where there is no possibility to choose a unit cell or it is very big. It is the case of quasicrystals discovered by Dan Shechtman in 1982 [3] (Chemistry Nobel Prize 2011), polytypes and modulated crystals [4]. This group of solids is called aperiodic crystals [5]:

> *In the following by **crystal** we mean any solid having an essentially discrete diffraction diagram, and by **aperiodic crystal** we mean any crystal in which three-dimensional lattice periodicity can be considered to be absent.*

However mentioned systems are not exactly aperiodic. Structures of the modulated crystals can be described as periodic, but in more than three dimensions.

2.1. Disorders and modulations

Usually if some atoms are found in the one fraction of unit cells in different positions than in the other we call it disorder. If there are some fixed atomic positions regardless of temperature then it is static disorder, when atoms can move feely then it is dynamic disorder. Sometimes disorders are somewhat periodic and something interesting happens to the diffraction image – additional diffraction spots accompany the main ones (Figure 4).

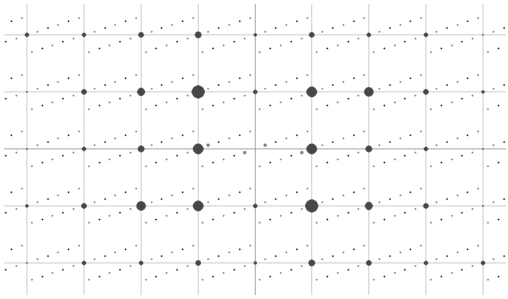

Figure 4: Reconstruction of the diffraction pattern of some occupationally modulated structure with satellite diffraction spots visible. Source: V. Petříček, M. Dušek, Institute of Physics ASCR, Prague, Czech Republic.

2.2. Simple commensurate displacive modulation in one direction

To illustrate what the modulation is let's look at the simple example. Imagine that there is two-dimensional crystal structure with the square unit cell and two objects inside (Figure 5). Position of the gray rectangle is modulated in the *a* direction. The modulation function is sinusoidal and has a period of 6 lengths of the unit cell. If a ratio of a modulation period to a unit cell length is rational then the modulation is commensurate.

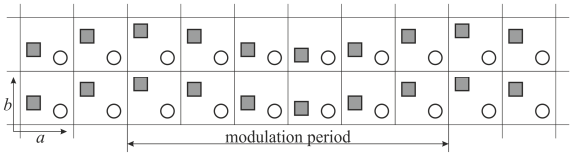

Figure 5: The one-dimensional commensurate displacive modulation with period of 6 lengths of the unit cell.

A real-world example of such a modulation type is one of the thiourea polymorphs [6].

2.3. Other types of modulations

Except already described displacive modulations there are also occupational ones. In such case different atoms can be found in the same positions in the subsequent unit cells. Both modulation types can be present in a structure simultaneously, even one atom can be modulated in both ways. Furthermore periodic distortions are sometimes incommensurable with the translation periods of the basic lattice – in such case a ratio of a modulation period to a unit cell length is irrational (not a fraction number).

2.4. Structure solution and description of modulations

It is not trivial task to solve a crystal structure and it is even harder to do it in the case of the modulated crystals. Charge flipping method invented in 2004 [7] was found to be excellent tool for solving modulated structures [8]. In 2007 the computer program Superflip that performs necessary calculations was written [9]. Now Superflip is also a part of Jana2006 – a great package for solution and refinement of normal and modulated structures both from single-crystal and powder experiments using X-ray or neutron radiation [10].

There are three common ways to describe modulated structures: 1. As an average structure with modeled disorder. This often gives poor quality solutions. 2. In the case of commensurately modulated structures it is possible to describe them in some supercell consisting of several adjacent unit cells. 3. It is common practice to describe modulated crystals in a single three-dimensional unit cell with a modulation in additional dimension. If there are modulations in all three directions then crystal has to be described in a six-dimensional superspace. Quasicrystals are usually described this way too.

3. SUMMARY

The modulated structures often relate to compounds that are in the interest of materials sciences, so it is important to understand them and to have tools for their analysis and description.

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