3.4. Classification and use of modulated and composite structures data

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3.4.1. Introduction

Aperiodic structures do not have lattice periodicity, but do show long-range order. Their diffraction patterns exhibit sharp Bragg peaks that have to be indexed using more than three Miller indices. All aperiodic structures can be classified into one of three groups: incommensurately modulated structures, incommensurate composite structures and quasicrystals. It is the purpose of the modulated and composite structures CIF dictionary (msCIF dictionary), presented in Chapter 4.3, to provide machine-readable descriptions of the first two of these groups.

Modulated structures represent the simplest case and are described by periodic distortions of an underlying (reference) crystal structure. The distortions involve one or several atomic parameters – positions, occupation probability or thermal parameters (the term *displacement parameters* is ambiguous in this context) – and their periodicity may be commensurate or incommensurate with the lattice of the reference structure. The first case corresponds to a three-dimensionally periodic crystalline phase, whereas the second case defines an incommensurate structure. In both cases, the diffracted intensities can be divided into two groups: the prominent main reflections, which are located in a three-dimensional reciprocal lattice (that of the reference structure), and additional (generally) weaker satellite reflections situated at points determined by the wave vectors of the modulations. Strictly speaking, the number of parameters needed to describe the atomic modulations of an incommensurate structure is infinite. In practice, however, the number of structural parameters is often drastically reduced owing to the strong hierarchy (demonstrated by the discreteness of the diffraction diagrams) that exists among them.

Composite structures can be thought of as being built of two or more periodic subsystems whose lattices are mutually incommensurate. Therefore, the set of main reflections no longer defines a unique three-dimensional reciprocal lattice. Moreover, the interaction between the different subsystems provokes modulations and, as a consequence, the presence of satellite reflections in the diffraction diagram.

Quasicrystals not only lack three-dimensional lattice periodicity but also show noncrystallographic symmetry.

The methodology for solving aperiodic crystal structures has been well developed since the introduction of the concept of superspace (de Wolff, 1974; de Wolff *et al.*, 1981). Superspace allows the recovery of the periodicity and a simple description of the symmetry of quasicrystalline structures in a higher-dimensional space. The real aperiodic structure is recovered from the superspace through appropriate three-dimensional sections. The dimension of the superspace $(3 + d)$ is equal to the number of reciprocal vectors needed to index the whole diffraction pattern of the quasicrystalline structure. More information on the superspace approach can be found, for example, in van Smaalen (1995) and Janssen *et al.* (2004).

The success of this concept relies above all on the systematic description of the symmetry of the aperiodic materials using superspace groups. Superspace groups for the simplest (but most common) case of one-dimensional modulated structures are tabulated in Janssen *et al.* (2004).

Within the superspace approach, all the aperiodic atom positions are embedded in dense sets (atomic domains) in the $(3 + d)$-dimensional unit cell of the associated periodic structure in superspace. They are parallel on average to the 'internal' (or 'perpendicular') space, which is a d-dimensional subspace chosen to be orthogonal to the real (physical or parallel) space. The three-dimensional structure is then a section of the $(3+d)$-dimensional structure parallel to the real space. The atomic domains are distorted along the internal space by the modulation functions. In many incommensurate structures and composites, the atomic domains are continuous periodic functions along the internal subspace and are parameterized by Fourier series. Some compounds, however, need to be described using discrete atomic domains whose parameterization is more complicated and will be discussed in Section 3.4.2. Note that commensurate structures can also be included within the superspace approach. The difference between incommensurate and commensurate modulations is that for commensurate modulations only a finite number of values of the atomic modulation functions are relevant.

The number of modulated and composite structures solved with software that uses the superspace formalism has grown rapidly and in many cases the determination of the structures of such systems is now almost routine. A standard for the description of incommensurate modulated structures has been established by the Commission on Aperiodic Crystals of the International Union of Crystallography (Chapuis *et al.*, 1997) using a checklist that is easily extensible to composite crystals. However, there was until recently no standard way to represent these structures electronically. Structural databases tend to contain only a brief reference to the modulated character of the structure and it has not been possible to transmit, archive and retrieve information about modulated and composite structures as efficiently as for normal crystal structures. Extending the core CIF dictionary to form a modulated and composite structures CIF (msCIF) dictionary seemed the appropriate way to deal with these problems, and has the additional benefits derived from the use of a well tested standard for which several tools have been developed.

In the case of quasicrystals, however, although the theoretical foundations seem to be well established, the determination of accurate models requires a combination of different strategies and techniques. The parameterization of the atomic domains with physical meaning is far from being an automated procedure (Cervellino *et al.*, 2002) and some of the existing models are now disputed. Major problems arise from sample quality, intrinsic disorder and rather low data-to-parameter ratios (Haibach *et al.*, 2000). Quasicrystals are not covered by the msCIF dictionary detailed in Chapter 4.3.

3.4.2. Dictionary design considerations

The CIF dictionary for modulated and composite structures (msCIF dictionary) is an extension of the core CIF dictionary

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