its importance in low-grade nickel laterite ores (Scarlett *et al.*, 2008; Wang *et al.*, 2011).

A calibration-based method such as PONKCS may also find increasing application with phases that have a known crystal structure. It has the greatest potential for accuracy, as the calibration process may obviate residual aberrations in the data such as microabsorption. Assuming that the sample suite has the same absorption characteristics as that used for calibration, such aberrations will be included in the calibration function and require no further correction during the sample analysis. This is a realistic scenario for routine analyses in industries as diverse as mineral processing, cement production and pharmaceutical production.

3.9.6.2. *Modelling of structural disorder*

One major challenge for QPA is the treatment of stacking disorder. An alternative to the use of calibrated models is to develop extended structure models that more effectively represent the phases present in the sample than the simple structure models. Stacking disorder occurs in layered structures where long-range order is present within the layers but there is only partial or even no relationship from one layer to another. It is a commonly occurring type of microstructure and is of great interest in various fields including mineralogy and material science.

The most common types of stacking faults in lamellar structures are:

(i) translational stacking faults, characterized by well defined translation vectors between successive layers;

(ii) rotational stacking faults, characterized by irregular but well defined rotation of adjacent layers in a stack; and

(iii) random stacking faults (turbostratic stacking), where there is no registry from one layer to another. This can be readily visualized as a stack of playing cards lying flat on top of each other but with no alignment between the edges (Fig. 3.9.11).

Mixed-layer (interstratified) systems contain different types of layers in a single stack, hence it is necessary to distinguish these from the types above. In this case, the layer types have different basal spacings and atomic coordinates (for example, illite–smectite interstratifications; Reynolds & Hower, 1970). Combinations of several of these types of disorder frequently occur in natural clay minerals. Intricate structural analysis using modelling techniques can give a reliable picture of the disorder of selected pure clay minerals, but such information is difficult to obtain from multiphase samples. Therefore, the type and degree of disorder of the components in natural rocks is one of the major unknowns when starting a quantitative analysis of such samples. The field of clay mineralogy represents a discipline where QPA has a long tradition, but has struggled with issues arising from a wide variety of disorder types. This complexity has led practitioners away from the use of crystallographic models and encouraged modification of the classical methods of quantitative analysis to incorporate empirical, calibration-based techniques such as those described earlier in this section.

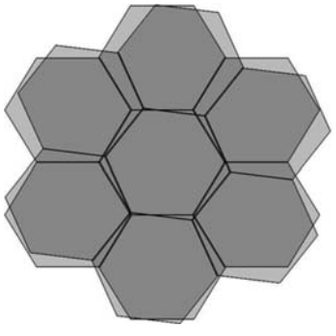

Figure 3.9.11
Turbostratic disorder, illustrated by the stacking of two hexagonal layers rotated by 7°.

An alternative approach is the application of a robust mathematical description of the observed features in the diffraction pattern, thus minimizing their impact on the QPA. In QPA, the existence of disorder contributes to inaccuracy through line broadening and shifting, which results in difficulties in the extraction of integral intensities or scale factors. A range of tools for the modelling of diffraction patterns of disordered layer structures has existed since the middle of the last century (Hendricks & Teller, 1942; Warren, 1941); these have been summarized by Drits & Tchoubar (1990).

In clay mineralogy, highly oriented samples are used for phase identification and characterization. One-dimensional diffraction patterns are collected initially from these, commonly air-dried, oriented samples and contain the information along **c*** that is characteristic of the type, composition and sequence of the layers comprising the clay. Based on this information, the clay minerals are classified into layer types, a classification which is a precursor to more precise identification of mineral species. Diffraction patterns are often collected again following various treatments of the oriented samples (*e.g.* solvation with ethylene glycol, heating to predetermined temperatures for specified times, wetting and drying cycles). Changes in peak positions, shapes and intensities between treatments are also diagnostic for identification of the clay mineral type present.

From a mathematical point of view, the one-dimensional calculation of intensities is much less laborious than a three-dimensional one, because only z coordinates are used and a–b translations and rotations are not considered. In 1985 Reynolds introduced the software package *NEWMOD* for the simulation of one-dimensional diffraction patterns for the study of interstratified systems of two clay minerals (Reynolds, 1985). This simulation was based upon a suite of parameters including instrumental, chemical and structural factors, and has been widely applied to the QPA of interstratified clays *via* the 'pattern-mixing' approach. An updated version (*NEWMOD+*; Yuan & Bish, 2010) has since been developed that incorporates improvements in clay-structure modelling, an improved GUI and the calculation of various fitting parameters that improve the operator's ability to estimate the quality of the profile fit.

The principal drawback of one-dimensional pattern approaches to QPA is that they are limited to the quantification of the ratio of layered structures only. Other minerals within the sample cannot be quantified at the same time. The degree of preferred orientation achieved in the oriented specimens may also differ between the mineral species present depending upon the method of sample preparation (Lippmann, 1970; Taylor & Norrish, 1966; Zevin & Viaene, 1990). This will affect the intensities of the observed peaks, which in turn affects the modelling of the relative proportions of the constituent minerals (Dohrmann *et al.*, 2009; Reynolds, 1989). Therefore, the quantification of minerals from severely oriented samples such as these is frequently inaccurate, as existing correction models are unable to describe the intensity aberrations adequately (Reynolds, 1989).

Quantification of clay minerals within multiphase specimens requires the modelling of the three-dimensional pattern of the randomly ordered clay. There are a number of approaches

incorporated in various software packages for the calculation of these three-dimensional diffraction patterns of disordered structures. *WILDFIRE* (Reynolds, 1994) calculates three-dimensional diffraction patterns of randomly oriented illite and illite–smectite powders with various types and quantities of rotational disorder. This is limited, however, to specific mineral types (the procedure has provided much information about the structural disorder of illite, for example) and is computationally demanding. Another approach is the general recursive method of Treacy *et al.* (1991), which simulates diffraction effects from any crystal with stacking disorder. This uses the intensity calculations of Hendricks & Teller (1942) and Cowley (1976) along with Michalski's recurrence relations describing disorder (Michalski, 1988; Michalski *et al.*, 1988). The calculation process for this method is less time consuming than that of *WILDFIRE*, but has the drawback of requiring the user to define the complete stacking sequence including stacking-transition probabilities and interlayer vectors. The original software for this method, *DIFFAX* (Treacy *et al.*, 1991), was extended by a refinement algorithm to *DIFFAX+* (Leoni *et al.*, 2004) and *FAULTS* (Casas-Cabanas *et al.*, 2006), but multiphase analysis is not possible within either package.

The application of Rietveld-based methods is widespread with many industrial applications, but their application to samples containing disordered materials is not yet routine. As the classical Rietveld method is based on the calculation of intensity for discrete reflections, the question of how the diffraction patterns of disordered phases may be modelled arises.

In principle, every atomic arrangement can be described in the space group *P*1 if the cell parameters are sufficiently large and a reflection-intensity calculation using the Rietveld method could then be performed. But the absence of symmetry in such 'large cell' models makes them inflexible, and parameters describing probabilities of translational and rotational stacking faults and layer-type stacking may not be directly included and refined. Nevertheless, some applications of such externally generated, large-cell structures in Rietveld phase analysis have been published; for example the phase analysis of montmorillonite (Gualtieri *et al.*, 2001).

The use of small, ideal cells in a traditional Rietveld approach for the calculation of diffraction patterns is hampered by the fact that the number of reflections generated by such models is insufficient to fit the asymmetric peak shapes of disordered layer structures. Standard anisotropic line-broadening models exist, such as ellipsoids (Le Bail & Jouanneaux, 1997), spherical harmonics (Popa, 1998) or the distribution of lattice metric parameters (Stephens, 1999), but these are typically unable to fit the patterns of disordered layered structures. They may also become unstable when physically unrealistic parameters are introduced, such as higher-order spherical harmonics. The application of such standard broadening models to clay minerals has therefore not proved successful.

Other Rietveld-based methods attempt to approximate the diffraction features of disordered layered materials by empirical enhancement of the number of reflections. The simplest method is the splitting of the reflections of a traditional cell into two or three separate reflections that can be separately broadened and shifted, following prescribed rules (Bergmann & Kleeberg, 1998). In this way, the broadening of special classes of peaks, for example reflections with $k \neq 3n$, can be modelled. This method is particularly suitable for structures showing well defined stacking faults, such as **b**/3 translations or multiples of 120° rotations. However, when structures show more complex disorder, such as turbostratic stacking, simple geometric dependencies of broadening and shifting are not sufficient to approximate their diffraction patterns.

Turbostratically disordered structures can be depicted in reciprocal space as infinite rods perpendicular to the *ab* plane and parallel to $\mathbf{c}^*$; see Fig. 3.9.12 (Ufer *et al.*, 2004). The diffraction features from such disordered materials consist of two-dimensional asymmetric bands, as can be observed typically for smectites and some other clay minerals (Brindley, 1980). One method for approximating the diffraction effects along the reciprocal-lattice rods within the Rietveld method is *via* the 'single-layer' approach (Ufer *et al.*, 2004). Here, a single layer is placed in a cell elongated along $\mathbf{c}^*$, which is effectively a 'supercell'. In doing this, an enhanced number of discrete lattice points are generated along the rods, according to the factor of elongation of the cell. This elongation generates a continuous distribution of additional *hkl* positions on the reciprocal rods. The inclusion of only a single layer in the supercell destroys periodicity, which is lacking in turbostratically disordered structures. By treating the pseudo-peaks of the supercell in the same manner as other structures within the Rietveld method (*i.e.*, introducing additional broadening, scaling the intensity) and separately calculating the peaks of the 00*l* series, the patterns of turbostratic structures like smectites can be reliably fitted. The model generated in this fashion can be used directly in phase quantification (Ufer, Kleeberg *et al.*, 2008; Ufer, Stanjek *et al.*, 2008).

However, this approach is limited to the turbostratic case. Moreover, the basal 00*l* series points are conventionally calculated, assuming rational diffraction from constant basal spacings in the stack. So the method cannot be applied to mixed-layered structures.

In order to overcome this limitation, Ufer *et al.* (Ufer, Kleeberg *et al.*, 2008; Ufer *et al.*, 2012) combined the recursive calculation method of Treacy *et al.* (1991) and the supercell approach in the structure-description code of the Rietveld software *BGMN* (Bergmann *et al.*, 1998). In this method a supercell is used to generate numerous discrete *hkl* spots along $\mathbf{c}^*$, but the partial structure factors are calculated by the recursive algorithm. This allows the refinement of structural parameters of mixed-layered structures and simultaneous Rietveld QPA to be performed (Ufer *et al.*, 2012). A broader introduction of such models in Rietveld phase analysis can be expected with the

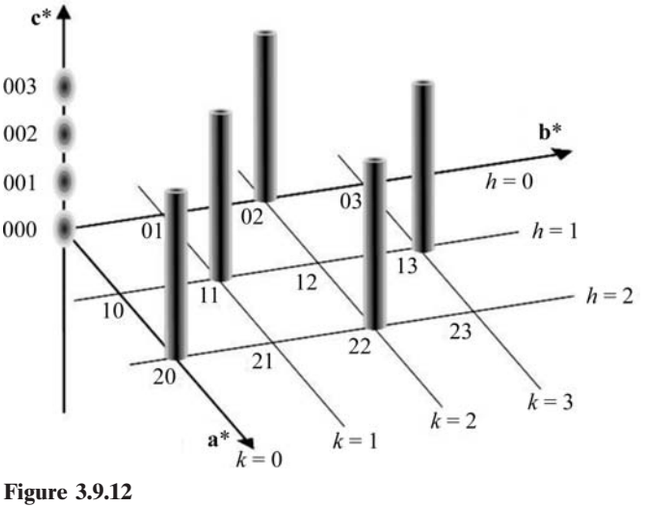

Figure 3.9.12
Section of the reciprocal lattice of a turbostratically disordered pseudo-hexagonal *C*-centred structure.

references