3. METHODOLOGY

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.
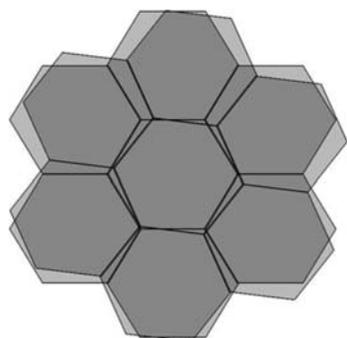
3.9.6.2. *Modelling of structural disorder*

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 (turbostatic 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.

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

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