3.9. QUANTITATIVE PHASE ANALYSIS

hkl_phase) is obtained *via* the use of partial structure information. Here the peak positions are constrained by a unit cell and space group but the relative intensities, in the absence of atom types and locations in the unit cell, are determined empirically from a pure sample or one where the phase is present in a mixture at a known concentration. The second method involves the use of a discrete set of peaks whose positions, intensities, width and shape are all determined empirically. Once determined using a standard sample, this group of peaks may then be scaled as a single unit and is referred to hereafter as a peaks_phase.

The software *SIROQUANT* (Taylor & Rui, 1992) employs the simultaneous use of observed and calculated standard profiles within the framework of the Rietveld method. It draws on a library of structures that are stored as lists of reflections and intensities (hkl files). These are calculated on a cycle-by-cycle basis for well described crystalline materials but are read directly from the hkl files for poorly defined materials such as clay minerals. This method still requires some knowledge of the crystal chemistry of all phases involved and that they be included within the programme's database. By the inclusion of reflection information in this way some aberrations such as preferred orientation may be allowed for. This approach to clay mineralogy also provides for the refinement of two sets of halfwidth parameters in order to model the co-existing sharp and broad reflections generated by such minerals.

A subsequent development of the whole-pattern approach is the 'partial or no known crystal structure' (PONKCS) method (Scarlett & Madsen, 2006). This method operates within the framework of the Rietveld method but replaces the traditional crystal structure of the phases in question with an empirical set of peaks (either as an hkl_phase or a peaks_phase). These can then be scaled as a single unit in the course of refinement in similar fashion to the set of structure factors derived from a crystal structure. Since the full structure information is not available, it is not possible to calculate the *ZMV* phase constant normally required for quantification *via* equation (3.9.26) (Hill & Howard, 1987); hence, an empirical value must be derived through calibration.

3.9.6.1.1. *Generation of calibrated PONKCS models*

The generation of a suitable PONKCS model requires that:
(1) The unknown phase is available as either a pure specimen or as a component of a mixture where its abundance is known (in some instances, this may be achieved by other means, such as the measurement of bulk and/or microchemical composition.)
(2) The unknown phase does not vary considerably from the material used to derive the relative intensities of the model. Preferred orientation and other sample-related effects may be compensated for based upon an indexed diffraction pattern.

The initial step in the generation of a PONKCS model is to describe the contribution to the diffraction pattern of the phase with a series of peaks. If the phase of interest has been indexed, the Le Bail or Pawley methods (see Chapter 3.5) can be used to constrain peak positions to the space group and unit-cell parameters while the individual reflection intensities are allowed to vary to best match the observed peaks (*i.e.* an hkl_phase). If the phase has not been indexed, a series of unrelated peaks can be refined using a standard material and scaled as a group during analysis (*i.e.* a peaks_phase). While this approach is effective in most cases, it restricts the refinable parameters that may be used

in the treatment of systematic errors such as preferred orientation.

The next step is to calibrate the hkl_phase or peaks_phase and derive a 'phase constant' that is equivalent to the *ZMV* value in crystal-structure-based quantification. This is achieved by the preparation of a mixture in which there are known amounts W_α and W_s of the unknown and standard, respectively. Recalling equation (3.9.25), the ratio of the weight fractions is then given by

$$\frac{W_\alpha}{W_s} = \frac{S_\alpha (ZMV)_\alpha}{S_s (ZMV)_s}, \qquad (3.9.42)$$

where S_α and S_s are the refined scale factors for the unknown and standard, respectively.

Rearrangement of equation (3.9.42) then provides the means for determining an empirical value of $(ZMV)_\alpha$, which is required for the calibration of a peaks_phase:

$$(ZMV)_\alpha = \frac{W_\alpha}{W_s} \frac{S_s}{S_\alpha} (ZMV)_s. \qquad (3.9.43)$$

For an hkl_phase the value of V can be determined from the refined unit-cell parameters and hence can be removed from the phase constant resulting in

$$(ZM)_\alpha = \frac{W_\alpha}{W_s} \frac{S_s}{S_\alpha} \frac{(ZMV)_s}{V_\alpha}. \qquad (3.9.44)$$

Unlike the *ZMV* value derived from the unit-cell contents of a crystal structure, the phase constants derived using equations (3.9.43) and (3.9.44) have no physical meaning, since they have been derived by empirical measurement. For an hkl_phase, a more physically meaningful value of *ZM* can be obtained by deriving the true unit-cell mass from the measured phase density according to

$$(ZM)_{\alpha(\text{true})} = \frac{\rho_\alpha V_\alpha}{1.6604}. \qquad (3.9.45)$$

The empirical 'structure factor' values in the hkl_phase could then be scaled according to the relation $ZM_{\alpha(\text{true})}/ZM_\alpha$, making them approximate 'real' structure factors for the material. Note that this final step is not necessary for quantification, but may make the method more generally applicable.

3.9.6.1.2. *Application of the model*

The PONKCS method is applicable to any mixture in which there are one or more phases that are not fully characterized crystallographically, including essentially amorphous material, provided appropriate calibration samples can be obtained. In the mineralogical context, it may not be possible to obtain pure phase specimens typical of those found in the bulk mixtures, but it may be possible to concentrate them to a point where they can be used. Methods of achieving this may include gravity or magnetic separation, or selective chemical dissolution.

The original paper describing this method (Scarlett & Madsen, 2006) gives a detailed example based upon sample 1 from the IUCr CPD round robin on QPA (Madsen *et al.*, 2001; Scarlett *et al.*, 2002). There, corundum was regarded as the unknown phase, fluorite as an impurity of known crystal structure and zincite a standard material added at known weight fraction. In the same paper, there is a more realistic example regarding the poorly ordered clay mineral nontronite, which is of commercial significance but difficult to quantify *via* traditional structure-based Rietveld methodology. Further details regarding quantification of this mineral *via* the PONKCS method is given in articles detailing

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
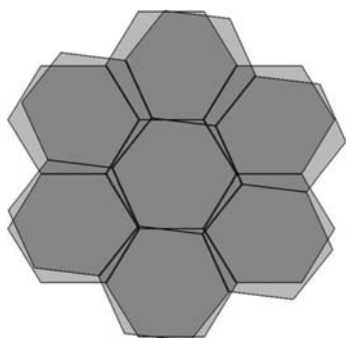
tradition, but has struggled with issues arising from a wide variety of disorder types. This complexity has led practitioners away from the use of crystallographic models and encouraged modification of the classical methods of quantitative analysis to incorporate empirical, calibration-based techniques 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°.