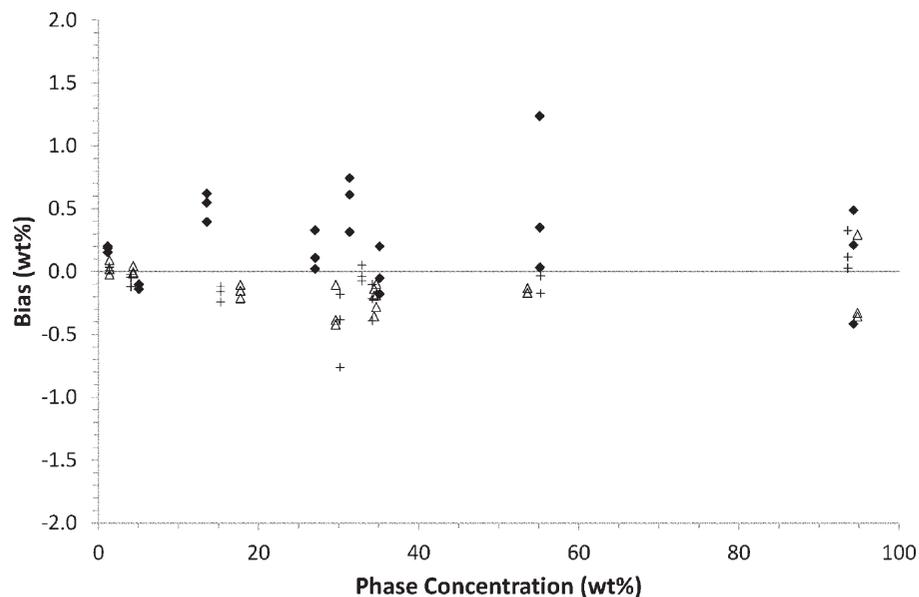
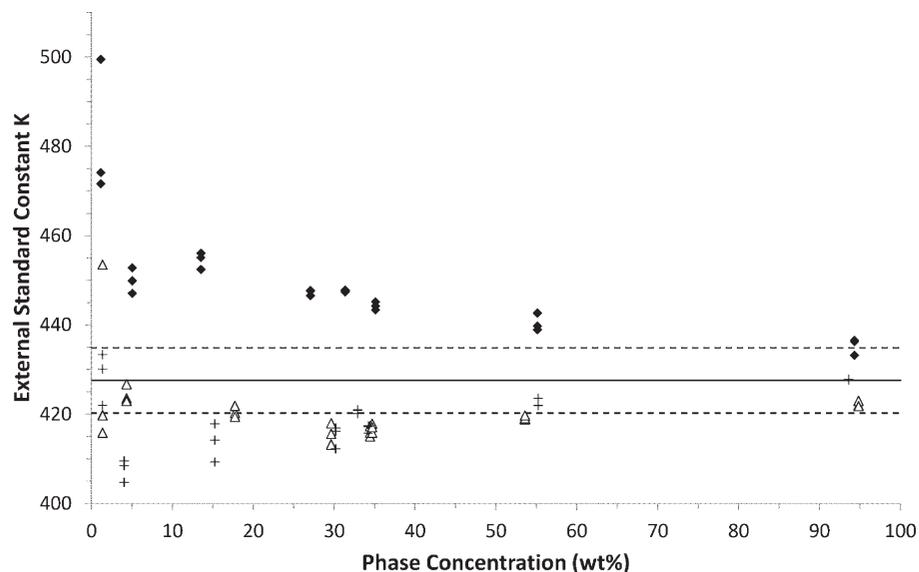


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**Figure 3.9.9**

Plot of the bias (known – determined) in the analysed phase abundances using the Zevin & Kimmel (1995) approach for corundum (black diamonds), fluorite (open triangles) and zincite (crosses). The 72 determinations derive from three replicates of eight mixtures containing three phases each.



**Figure 3.9.10**

Plot of the experiment constant  $K$  as a function of known phase concentration for corundum (closed diamonds), fluorite (open triangles) and zincite (crosses) using the phase-specific method. The 72 determinations derive from three replicates of eight mixtures containing each of the three phases. The solid line is the mean of 24 values determined using the whole-sample approach. The dashed lines represent  $\pm 2$  standard deviations about this mean.

overestimated relative to the fluorite and zincite. This results in an overestimation of the value of  $K$  relative to an ideal sample; the magnitude of this difference is about 5% relative. Use of these values for subsequent analysis will result in an underestimation of phase concentrations using equation (3.9.21). The converse is true if fluorite or zincite is used to determine  $K$ .

However, if the whole-sample approach embodied in equation (3.9.40) is used for the determination of  $K$ , these residual sample-related aberrations can be eliminated; the results of the determination of 24 values of  $K$  using this approach are also included in Fig. 3.9.10. The mean of all 24 determinations is 427.6 (3.7) representing a relative error of <0.8%. The important point to note here is that knowledge of the individual phase concentrations is not needed; the only assumption needed relates to the total crystallinity of each sample.

For *in situ* studies, using equation (3.9.40) to calculate  $K$  at each step  $i$  in the reaction (defined as  $K_i$ ) can be useful in deriving details of the reaction mechanism. If  $K_i$  increases as the reaction progresses, this may be indicative of increasing crystallinity in the sample. Reductions in  $K_i$  during the reaction may point to the formation of intermediate amorphous material or unidentified crystalline components, the total concentration of which can be readily calculated using

$$\text{wt\%}_{\text{amorphous}} = 100 \left( 1 - \frac{K_i}{K} \right). \quad (3.9.41)$$

Application of this can be demonstrated using sample 3 from the QPA round robin (Scarlett *et al.*, 2002), as it contains the same three crystalline phases as the sample 1 suite with the addition of 29.47 wt% amorphous silica flour. Calculation of  $K_i$  for sample 3, based only on the three crystalline phases, results in a value of 301.8. Substituting this into equation (3.9.41) along with the previously determined value of  $K$  (427.6) gives a measured amorphous content of 29.42 wt% – this is in good agreement with the known weighed amount. The important point to note here is that the data for sample 3 were collected at the same time, and under the same instrumental conditions, as for sample 1, which ensured that the true value of  $K$  was the same for all data.

### 3.9.6. Quantification of phases with partial or no known crystal structures

While the Rietveld-based methods described in Section 3.9.3.6 work for well ordered phases with known crystal structures, they are limited when published structure data do not accurately represent the phase actually present in the sample, are incomplete or do not exist. Poor agreement with published structure data is a common occurrence in mineralogical research where disorder exists and observed diffraction data deviate significantly from the ideal; this situation occurs with many of the

clay minerals. The issue of incomplete or non-existent structure data can occur in almost any area where new materials are either synthesized or discovered. The growing demand for the analysis of materials from the nanotechnology community, where phases are at the boundary of what can be considered crystalline, serves to further highlight these limitations. Recent developments in diffraction methods have sought to address these issues and have used approaches that include the development of calibrated models or, where appropriate, the extension of existing structure data to incorporate systematic disorder such as stacking faults in clay minerals.

#### 3.9.6.1. Use of calibrated models

Calibrated models are generally developed in one of two ways. The first (which uses what is referred to hereafter as an

### 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  $W_\alpha$  and  $W_s$  of the unknown and standard, respectively. Recalling equation (3.9.25), the ratio of the weight fractions is then given by

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

where  $S_\alpha$  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:

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

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

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

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

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

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

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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.

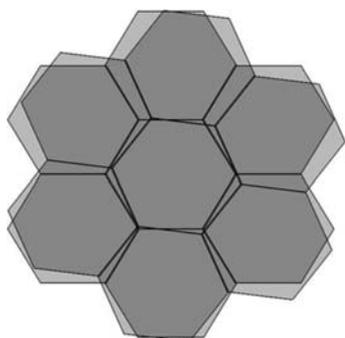
#### 3.9.6.2. Modelling of structural disorder

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



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

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

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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  $P1$  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.

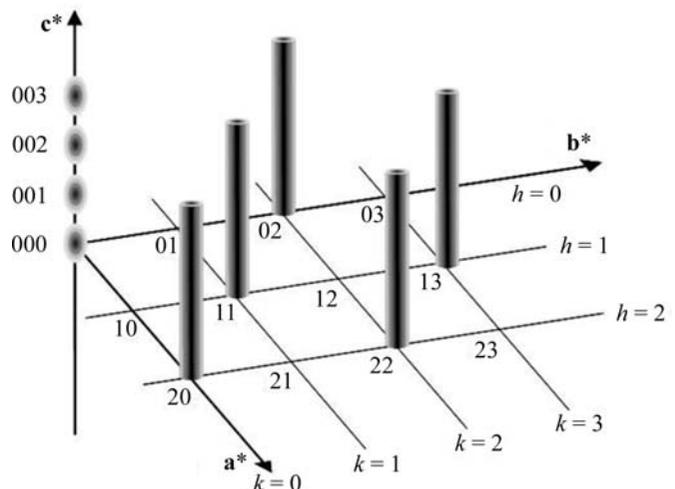
Other Rietveld-based methods attempt to approximate the diffraction features of disordered layered materials by empirical enhancement of the number of reflections. The simplest method is the splitting of the reflections of a traditional cell into two or three separate reflections that can be separately 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  $\mathbf{b}/3$  translations or multiples of  $120^\circ$  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  $00l$  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  $00l$  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.

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development of reliable structure models and enhanced computational power (Coelho *et al.*, 2016, 2015; Bette *et al.*, 2015).

#### 3.9.6.3. Quantitative determination of amorphous material

Traditionally, most activity in diffraction-based QPA has been concerned with the assessment of the crystalline components. However, all materials possess a non-diffracting surface layer with some degree of disorder or contain some surface reaction products and adsorbed species. While such a layer can easily account for  $\sim 1$  wt% of the entire sample in a finely divided solid, the fraction of this surface layer will increase as the particle size decreases (Cline *et al.*, 2011). In addition, some materials can contain separate phases that may be amorphous or at least poorly crystalline. The advent of nanotechnology has served to further blur the boundaries between what is defined by powder XRD as crystalline or amorphous.

During *in situ* studies, some phases undergo transformations *via* amorphous intermediate components; the presence of these phases has the potential to influence our understanding of reaction mechanisms. Given the potential for these amorphous components to influence bulk-material properties, the need to quantify them is an increasingly important issue for analysts using diffraction-based methods. Many of the traditional phase-quantification techniques described in this chapter fail to take into account the occurrence of amorphous material in the sample and, without careful attention by the analyst, its presence may remain undetected.

Madsen *et al.* (2011) recently reviewed a range of techniques for the determination of amorphous content and assessed their applicability for various analytical situations. The study used both single-peak and whole-pattern methodology and applied it in two distinct ways.

(1) The first method used an indirect approach; the crystalline components were quantified and put onto an absolute scale using either an internal- or external-standard method. The amorphous content was then determined by subtracting the

sum of the absolute weight fractions of the crystalline components from unity.

(2) The second method used a direct approach; it relied on being able to ‘see’ the amorphous contribution in the diffraction and being able to obtain an estimate of its intensity during analysis (Fig. 3.9.13). Intensity contributions of amorphous phases are not always evident in the diffraction pattern, especially at low concentrations. Even when their presence is apparent, it can be difficult to resolve their contribution from other components of the diffraction pattern such as pattern background. However, once an intensity estimate is obtained, and an appropriate calibration constant derived, the amorphous phase can be included in the analysis along with the crystalline components.

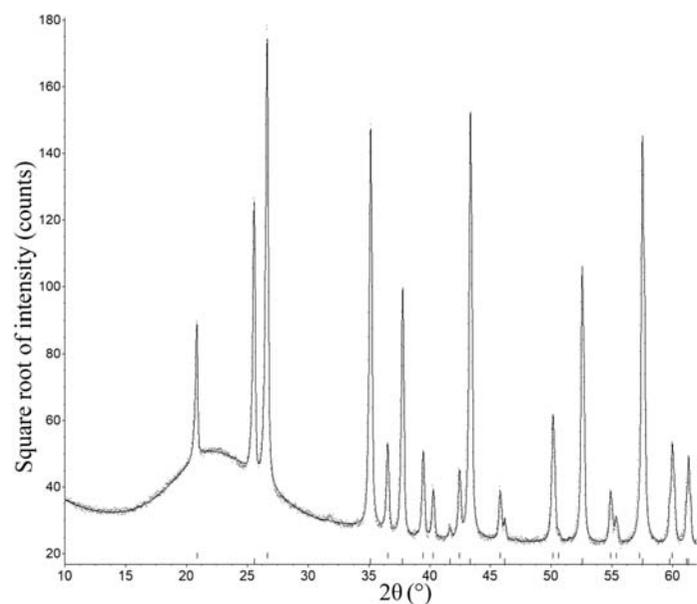
In general, for the determination of amorphous material the problem will dictate the method(s) used. All methods discussed in the study of Madsen *et al.* (2011) are, in principle, capable of determining the concentration of amorphous material in mixtures with similar levels of accuracy and precision as is possible for crystalline phases (down to  $\sim 1\%$  absolute or better). The limitations are similar to those for the QPA of crystalline phases, and are dictated by sample properties and the analytical techniques used.

A summary of the recommendations resulting from the study include:

- (1) Where the intensity contribution of the amorphous content to the diffraction pattern is not evident, one of the indirect methods (internal or external standard) should be used. For indirect methods, any errors in the analysis of the crystalline phases will decrease the overall accuracy attainable since the amorphous phase abundance is determined by difference.
- (2) Where intensity contributions of amorphous phases are evident in the diffraction pattern, any method based on the direct modelling of the amorphous component provides improved accuracy relative to the indirect methods.
- (3) Calibration-based methods usually have the potential to achieve the highest accuracy, as residual aberrations in the data, such as microabsorption, are included in the calibration function. Caution is advised here as the magnitudes of these residual errors may change with different sample suites, and so a calibration function derived for one sample suite may not be generally applicable.
- (4) A sample of pure amorphous material, or a sample where the amorphous content is high and its concentration known, is normally required to establish an accurate model for the direct methods.

Some materials contain more than one amorphous phase and there may be a desire to quantify these separately rather than as a group. This provides a significant challenge since their broad diffraction patterns will be highly overlapped, thus leading to a high degree of correlation during analysis. However, Williams *et al.* (2011) have demonstrated that, with careful experimentation and data analysis, it is possible to provide QPA for two poorly crystalline components in geopolymers.

Phase abundances reported in the literature are often provided in a manner that suggests they are absolute values. Where no specific allowance for amorphous content has been made and reported, it is better to assume that the reported phase abundances are correct relative to one another, but may be over-estimated in an absolute sense. Therefore, standard practice in QPA should be to use methodology which produces *absolute* rather than *relative* phase abundances. Any positive difference between unity and the sum of the absolute weight fractions will



**Figure 3.9.13**

Output of Rietveld refinement of XRD data (Cu  $K\alpha$  radiation) for a synthetic sample containing a mixture crystalline and amorphous phases. The observed data are represented as grey dots and the calculated pattern as the solid black line overlaying them. The broad peak centred at  $\sim 22^\circ 2\theta$  is due to amorphous silica flour. The rows of tick marks at the bottom represent the positions of the Bragg reflections for quartz (upper) and corundum (lower).