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

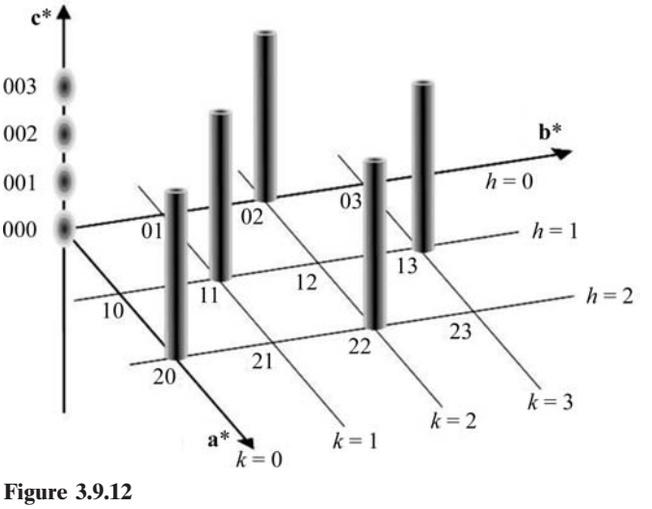

Figure 3.9.12
Section of the reciprocal lattice of a turbostratically disordered pseudo-hexagonal *C*-centred structure.