

Description of X-ray powder pattern of turbostratically disordered layer structures with a Rietveld compatible approach

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Abstract. We address the problem of the quantitative description of X-ray powder pattern of turbostratically disordered layer compounds. The Debye formula is used, which allows the aperiodic description of any arrangement of atoms. With the extension of Yang and Frindt (1996) for the ideal turbostratic case, these calculations are used to generate reference data that are subsequently treated by the Rietveld method. We are able to show that the case of uncorrelated turbostratic disorder can be modelled equally well in a periodic supercell approach with a single layer in the supercell that is suitable for the Rietveld technique. A brief introduction of this new model was given as an oral contribution at EUROCLAY 2003 (Ufer et al., 2003). The fundamental principles are described in this article because of its complexity. The applicability of this approach to real systems is demonstrated for smectite and corundum mixtures.

Introduction

Many layer structured materials display turbostratic stacking faults, this leads to an extremely asymmetric peak broadening. This broadening effect has prevented the use of the standard Rietveld method in determining structural information or phase content. The Rietveld method, which is successfully used in powder X-ray and neutron diffraction for minerals which contain only minor disorders, has however severe problems when dealing with this kind of disorder.

Turbostratic disorder of layered structures can be explained as a random rotation and/or translation of the individual layers relative to each other (Warren, 1941; Biscoe and Warren, 1942). In the 'ideal' turbostratic case of layer stacking, no correlation between translations/rotations of

consecutive layers occurs. This effect has been demonstrated for several materials such as expandable clay minerals (Brindley, 1961), graphitic carbon (Warren and Bodenstein, 1965), BN (Hubáček et al., 1996; Andreev and Lundström, 1994) and MoS₂ (Borsella, 1998).

Clay minerals in particular tend to form various kinds of disorder with a more or less high degree of disorder. For example disordering of the octahedral vacancies (Drits and McCarty, 1996), disorder concerning the interlamellar space such as the exact position and coordination of the interlayer cations in smectites (Van der Gaast et al., 1999) or stacking faults either containing translations and/or rotations of one kind of layer or stacking of two or more different kinds of layers (mixed layer structures) (Altaner and Ylagan, 1997). Brindley (1980) gives a detailed introduction to these topics. A mathematical description is given by Drits and Tchoubar (1990).

The degree of translational or rotational disorder for the stacking of one kind of layer ranges from regular stacking with perfect regularity to completely random rotations and translations, which is regarded as the turbostratic case. Between these two extreme cases there are many different degrees of ordering. Drits and Tchoubar (1990) describe smectites with an intermediate state of ordering, Viani et al. (2002) offer a new model of disorder with random shifts of $-a/3$ and $+b/3$ for a Ca-montmorillonite. These authors discuss the still unsolved question, whether turbostratically disordered smectites are a totally random sequence without any correlations between the layers or must it be considered as a sample dependent degree of disorder. The model proposed in our paper regards turbostratic disorder as completely uncorrelated stackings. In powder patterns, this kind of disorder can be identified by the presence of extremely asymmetric peaks close to the position of the $hk0$ reflections (assumed that c^* is the stacking direction). No hkl reflections with $l \neq 0$ and h or $k \neq 0$ can be observed. The electron density projected onto the stacking direction, however, is unaffected by the rotations/translations, so that symmetric $00l$ reflections are present.

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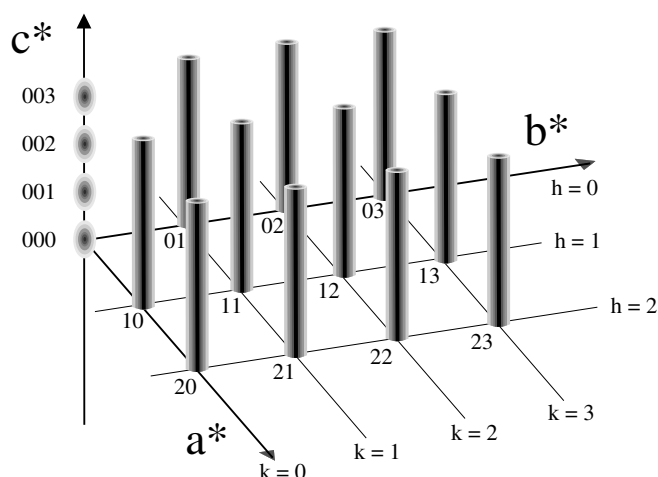


Fig. 1. Schematic representation of the reciprocal space for a turbostratically disordered crystallite.

These effects can best be visualised in reciprocal space (Fig. 1). For the above mentioned ideal turbostratic case, the scattering intensity distribution of an individual crystallite corresponds to a set of rods perpendicular to the stacking plane (here: a^*-b^*). They intersect this plane at the $hk0$ points. As the electron density projected onto the stacking direction is unaffected by the rotations/translations within the layers, the $00l$ reflections remain symmetric and relatively sharp, depending on the coherence length of the stacks along the stacking direction. This intensity distribution of a single crystallite in reciprocal space then has to be averaged over all orientations in 3-D to obtain the powder pattern.

The calculation of a correct powder average is rather involved: It can be performed geometrically by intersecting the rods in reciprocal space with a continuously increasing sphere around the origin of the reciprocal lattice (Warren, 1941; Wilson, 1949; Brindley and Méring, 1951). The radius of the sphere corresponds to the diffraction angle of the sampled intensity. Warren (1941) introduced the so called “tangent cylinder approximation” to reduce computation time (Fig. 2). A cylinder is used in-

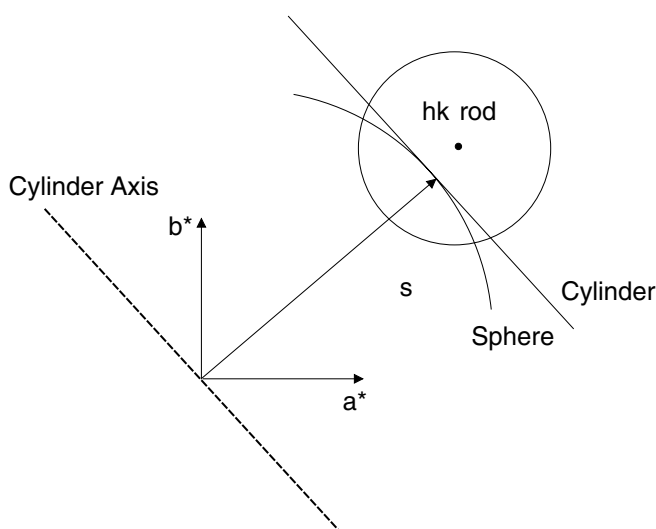


Fig. 2. The tangent cylinder approximation (Shi et al. 1993, modified).

stead of a sphere to integrate the intensity. This cylinder has the same radius as the sphere and its axis passes through the origin of the reciprocal lattice, perpendicular to the c^* direction and a line between the origin and a point of the rod which has to be integrated. In the case of large crystals this approximation is justified because the intersected plane of the rods with a sphere is close to that of a cylinder. Diamond (1957) showed that these approximations introduce quite serious errors in the case of small dimensions of the crystallites within the stacking layers because the interference function has appreciable values throughout a large region of reciprocal space. Warren and Bodenstein (1966) also recognised these deviations by comparing this method with an earlier work where they had used the Debye formula (Debye, 1915) to simulate the powder patterns.

The Debye formula is, in fact, a rather elegant way to deal with structural disorder. With this method it is possible to calculate diffraction intensities by estimating atomic distances in real space. The algorithm automatically performs the correct powder average. Jones (1949) simulated patterns of periodic linear structures, Diamond (1957) used the Debye formula to calculate patterns of single layers with different shapes. Warren and Bodenstein (1965) used it to calculate patterns of turbostratically disordered carbon. They extended Diamond's treatment of single layers to calculate the case of an arrangement of parallel layers with random orientation relative to each other. To consider the diffraction between two randomly disordered layers, they regarded the position of atoms as uniformly distributed within the layer. Yang and Frindt (1996) derived a further extension of this approach to calculate the diffraction of turbostratically disordered structures in a very effective way.

Both methods, the calculation of the single crystal intensity distribution in reciprocal space followed by an appropriate powder averaging as well as the Debye formula have been successfully used to simulate powder patterns of various kinds of disordered layer structures (Plançon, 1981; Drits and Tchoubar, 1990; Shi et al., 1993; Andreev and Lundström, 1995; Plançon, 2002).

Another widespread method to simulate powder patterns of crystals containing planar faults is the method of Treacy et al. (1991), which describes diffraction in a recursive way using the Hendricks-Teller equation (Hendricks and Teller, 1942), the Cowley equation (Cowley, 1976) and Michalski's recurrence treatment (Michalski, 1988; Michalski et al., 1988). They developed the computer program DIFFaX to study faulted layer structures (Hines et al., 1997; Braunbarth et al., 2000). This program was successfully used to describe disordered clay minerals such as talc (Gualtieri, 1999) or kaolinites (Artioli et al., 1995). Viani et al. (2002) used DIFFaX to develop a model for a high faulted (but not turbostratically disordered) smectite which was transferred to a Rietveld QPA analysis. Leoni et al. (2004) presented a highly sophisticated advancement of DIFFaX called DIFFaX+. This program allows the refinement of disorder parameters. Unfortunately this program does not yet allow a multiphase refinement and so cannot be used for determining mineral contents, which was the major goal of our research.

In the present work, the Debye formula is used to calculate model patterns. It has the disadvantage of being very time consuming but it does not use approximations which may fail in the case of small crystallites and it is the only formalism which allows the calculation of a powder pattern without the definition of a unit cell. Therefore it is suitable to introduce rotations of random degrees. These patterns are then evaluated in order to arrive at a model which still realistically describes turbostratic stacking disorder but, at the same time, is simple enough to be suitable for the Rietveld refinement technique. The transfer to a standard Rietveld program is aspired to combine it with developments in the field of planar disorders, which were made in the last years (Bergmann et al., 1998).

Methods

Calculation of powder patterns

In order to develop a practical approach for the quantitative refinement of powder patterns of turbostratically disordered substances, a careful investigation of such patterns and their characteristics is necessary. The key question is, to what extent the model of the disordered structure can be simplified without losing essential quantitative information. For that purpose numerous patterns were simulated and their characteristics with respect to their structural and disorder parameters were examined. In contrast to measurements, simulations offer the advantage that all parameters that influence the diffraction curve can be controlled. As a suitable method for the computation of such models the formalism of Debye was selected. The results of these simulations were then transferred to computations within a Rietveld program.

a) Debye formula

In 1915 Debye developed a formalism to describe the scattering effects of single atoms or of small groups of atoms (Debye, 1915). With this approach, the scattered X-ray intensity (powder average) of any arrangement of atoms can be calculated.

$$I(s) = \frac{1}{N} \sum_i \sum_j f_i \cdot f_j \cdot \frac{\sin(2\pi \cdot s \cdot r_{ij})}{2\pi \cdot s \cdot r_{ij}} \quad (1)$$

s : modulus of the scattering vector, $s = 2 \cdot \frac{\sin \theta}{\lambda}$

r_{ij} : distance between two atoms i and j

N : total number of atoms

f_i, f_j : scattering factor of the two atoms i and j at diffraction angle θ

As translational symmetry is not assumed within this formalism, it is most suitable to simulate diffraction from crystals that are not strictly periodic in one or more dimensions. Yang and Frindt (1996) developed an approach with which they achieved a formal separation of the diffraction contributions within a layer (I_{intra}) and between the individual turbostratically disordered layers (I_{inter}). For a turbostratically disordered layer system with M homogeneous layers each containing N atoms, the following equa-

tions arise:

$$I(s) = I_{\text{intra}}(s) + I_{\text{inter}}(s), \quad (2)$$

$$I_{\text{intra}}(s) = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N f_i \cdot f_j \cdot \frac{\sin(2\pi \cdot s \cdot r_{ij})}{2\pi \cdot s \cdot r_{ij}}, \quad (3)$$

$$I_{\text{inter}}(s) = \frac{1}{M \cdot D \cdot \pi \cdot s^2} \sum_{n=1}^{M-1} (M-n) \sum_{i=1}^{N_{\text{sub}}} \sum_{j=1}^{N_{\text{sub}}} D_i \cdot D_j \cdot f_i \cdot f_j \times \cos[2\pi \cdot s(n \cdot c + d_i + d_j)] \quad (4)$$

N_{sub} : number of sublayers of one layer

M : number of layers

D : number of unit cells per layer area

D_i and D_j : atomic layer densities of the sublayers i and j

d_i and d_j : relative position of the sublayers i and j in the layer package

c : lattice parameter

Equation (3) corresponds to the standard Debye formula, applied to only one layer. The separation into two contributions in equation (2) leads to a drastic speed-up of the calculations: Instead of using three-dimensional atomic positions, only atomic layer densities are considered for the computation of the I_{inter} part of the diffracted intensity. These layers have the distance $n \cdot c$. For layers containing several sublayers with different z positions their relative positions d_i and d_j in the layer package must be considered.

Expressed in reciprocal space, the I_{intra} part calculates the intensity of the hk rods, including a diffuse 00 rod. The I_{inter} part subtracts that intensity of the 00 rod and instead adds the intensity of well separated 00 l reflections.

b) Rietveld method

The principle of the Rietveld method consists of the computation of diffraction intensity profiles around distinguishable Bragg reflection positions from a given structural model. This data will be fitted to a measured pattern by a non-linear least squares minimization. In this work, the Rietveld method is primarily used to simulate powder patterns. The time needed for a complete cycle is, however, short enough to also perform adjustments of parameter values. An example will be presented at the end of this paper.

For the application of the Rietveld method, the definition of a unit cell, which represents the three-dimensional periodic structure, is essential in order to identify each reflection with the hkl indices and Bragg angle θ . In such a unit cell the simulation of random rotations is not possible because this would break the translational symmetry. However, random translations, which dominate the turbostratic effect, can be simulated by using a supercell containing several layers that are translated by random amounts relative to each other.

In the case of turbostratically disordered layer structures, the periodicity of the electron density is destroyed in one direction. In order to stay compatible with the usual structure factor calculations, the aperiodic structure along the stacking direction is modelled within a periodic supercell. It is well known (see for instance Press et al.,

1988) that the approximation of an aperiodic Fourier-transform by a periodic one requires the supercell to be at least twice as large (along the aperiodic direction) as the object that is to be transformed. The rest of the unit cell has to be filled with zero density. Otherwise, so called 'wrap-around-effects' occur, which affect the Fourier coefficients. In the case of a layer structure with stacking direction c this means that the supercell may be filled only up to $z < 0.5$. The appropriate size of the supercell depends on two factors: Firstly, it should be sufficiently large to generate smooth hk peaks by superposition of different orders of hkl reflections ($l = 1 \dots n$). Secondly, it has to be large enough to contain all relevant stacking correlations. To limit the computational burden, the superperiod should be kept as small as possible.

Extensive simulations have shown that, in the absence of such correlations, a supercell with about 10 times the size of a standard cell is suitable for practical purposes. Sufficient reflection positions are produced by the use of this supercell as sampling points for the representation of the hk peaks.

c) Structural parameters used for the calculation of powder patterns

The lattice parameters used for the computations follow those of the smectites, a group of minerals that is known to show turbostratic disorder very frequently. In contrast to monoclinic smectites, an orthogonal unit cell with a basic distance of 15.00 Å and $a = 5.21$ Å, $b = 9.00$ Å was chosen. This choice is justified in the case of turbostratic disorder, since translational symmetry perpendicular to the a – b plane is destroyed by random translations and rotations.

Layer translations and rotations as well as the formfactor of the layer itself both influence the intensity distribution of the hk peaks. To study the influence of the layer stacking separately, the model calculations were performed with only two point atoms in the unit cell. One atom is located at the origin of the unit cell and the second at the position $\frac{1}{2}a, \frac{1}{2}b, 0$, in order to take into account the C -centering of the smectites and the associated systematic extinctions.

For the model calculations with the Debye formula, which does not assume periodicity in any direction, layers consisting of the above unit cell containing 19 cells in the a direction and 11 cells in the b direction were defined. This corresponds approximately to a square layer with an edge length of 100 Å. Figure 3 shows a schematic display of one layer. Ten of these layers were stacked along c . In case of pure translational disorder, random displacements of $0 < t_a < a$ along a and $0 < t_b < b$ along b were chosen, relative to the lowest layer.

For the computation of the effect of the random rotations in combination with random translations each layer was rotated by a random angle relative to the lowest layer. The centre of rotation was placed in the unit cell in the centre of the 19×11 unit cell slab. The exact position of this point within this cell was randomly selected, which corresponds to an additional translation of this rotated layer of $0 < t_a < a$ in direction a and $0 < t_b < b$ in direction b .

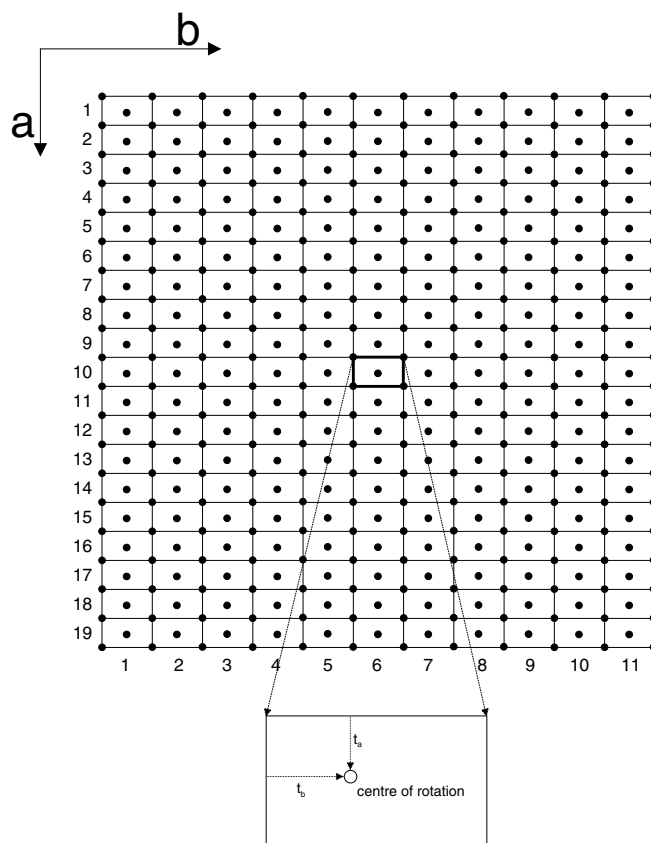


Fig. 3. Schematic display of one layer for the Debye calculations. The unit cell containing the centre of rotation is highlighted.

To calculate the pattern with the Rietveld method the same structural data were used, but the unit cell was expanded to 10 times the unit length in c direction so that a supercell with the basic distance of 150 Å results. For the simulation of the translations, this unit cell was filled with 10 layers with each layer randomly translated in the a and b direction. In the one layer case the supercell was filled with only one layer. The $00l$ reflections were computed from the subcell. All reflections were represented with a Lorentzian peak shape with a constant width. For these computations, the program BGMN (Bergmann et al., 1998) was used (assuming $\text{CuK}_{\alpha 1/2}$ radiation).

Results of the Debye calculations

a) The turbostratic case calculated according to Yang and Frindt (1996)

The typical characteristics of a pattern calculated with the Debye extension according to Yang and Frindt (1996) are shown in Fig. 4.

Sharp, symmetrical $00l$ reflections are observed together with hk peaks with a steep rise towards small s values (low 2θ angles) and a slow decay to large s values. The separate view of the I_{inter} and the I_{intra} part shows that the symmetrical $00l$ reflections are produced by the I_{inter} part. It can be understood as the diffraction contribution from stacks of layers containing the atomic density averaged over the a – b plane. The hk peaks are assigned to

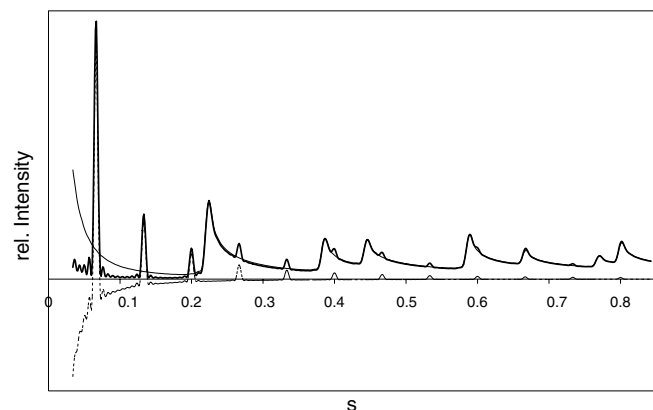


Fig. 4. Reference pattern calculated with the extension of the Debye formula for the ideal turbostratic case. Dotted line: I_{inter} part. Solid line: I_{intra} part. Bold line: sum of I_{inter} part and I_{intra} part.

the I_{intra} part and thus can be regarded as the diffraction from a single layer. The I_{intra} part also shows a strong rise towards small s values. This increasing intensity derives from the diffuse 00 rod which is still present. To compensate for this extra intensity at low angles, the I_{inter} part contributes not only sharp 00 l reflections, but also exhibits (nonphysical) negative scattering contributions. The sum of both contributions is, of course, again a physically reasonable quantity without negative values.

b) Random translations

With the help of the standard Debye formula, random translations in the a and b direction were simulated. An individual computation, however, simulates only the case of a powder with crystallites with exactly the same random translations. A pattern computed in such a way still shows clear deviations from the turbostratic case (Fig. 5b). For the reproduction of a pattern of a turbostratically disordered sample it is necessary to sum over several statistically equivalent but different random values for the translations. The average over 50 different simulations results in a pattern (Fig. 5c) that closely resembles the one obtained from the Yang and Frindt calculation and shows the typical characteristics of a real measurement of a turbostratically disordered sample (see below).

For the calculation with the extension by Yang and Frindt (1996) this averaging procedure is not necessary because the averaging effect is already accounted for by the uniformly distributed atomic density.

c) Combination of translations and rotations

Simulations were carried out with layer stacks whose layers were randomly rotated and translated relative to each other. Figure 5d shows the result of such a computation. Also, these computations were done several times with different random rotation and translation values. The use of additional random rotations produces, already with a single computation, a pattern that strongly resembles that of the ideal turbostratic case (Fig. 5d). The deviations of the individual computations among each other are also much smaller than in the case of mere translations. Qualitatively, this is due to the fact that translations plus rota-

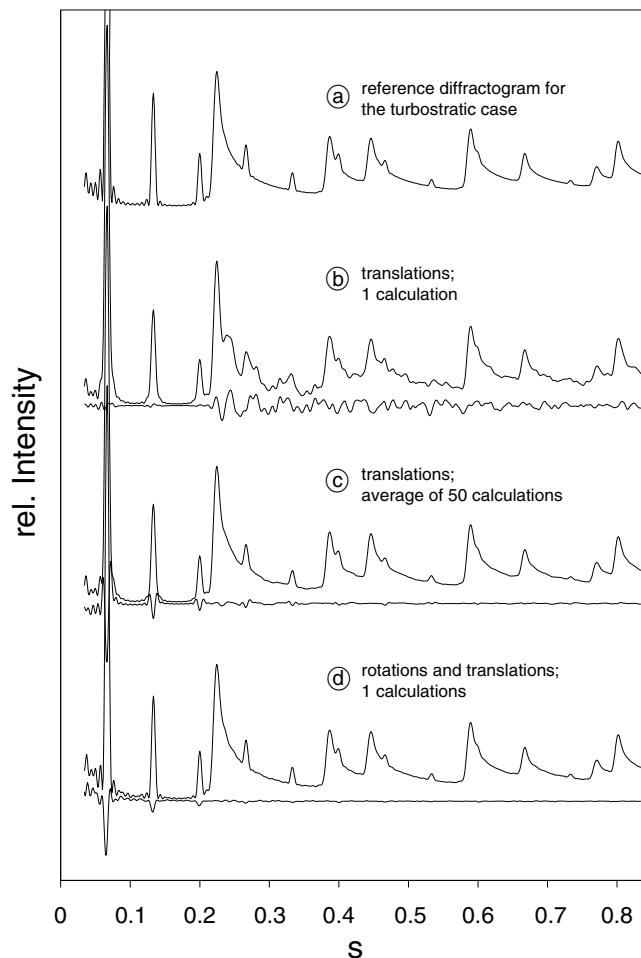


Fig. 5. Results of the Debye calculations; (a) reference pattern calculated with the extension for the ideal turbostratic case according to Yang and Frindt (1996); (b) simulation of a layer package with 10 layers randomly translated relative to each other and difference line with reference pattern; (c) averaged result of 50 simulations of a layer package with 10 layers randomly translated relative to each other and difference line with reference pattern; (d) simulation of a layer package with 10 layers randomly translated and rotated relative to each other and difference line with reference pattern.

tions introduce a much larger degree of disorder than pure translations.

Results of the Rietveld pattern calculation

a) Translations within a supercell

Similar to the computations of the random translations with the Debye formula, translations were simulated by filling a supercell with several layers and shifting these layers randomly relative to each other (Fig. 6).

For a single calculation (Fig. 6a) the hk peaks show strong modulations and still deviate substantially from the ideal turbostratic case. Similar to the Debye computations with random translations, several computations with different translation values were performed and the results were averaged (Fig. 6b). This averaging also leads to a pattern with the typical turbostratic characteristics. Notably, the oscillations on the high angle side of the hk peaks do not average out. These oscillations are caused by the finite

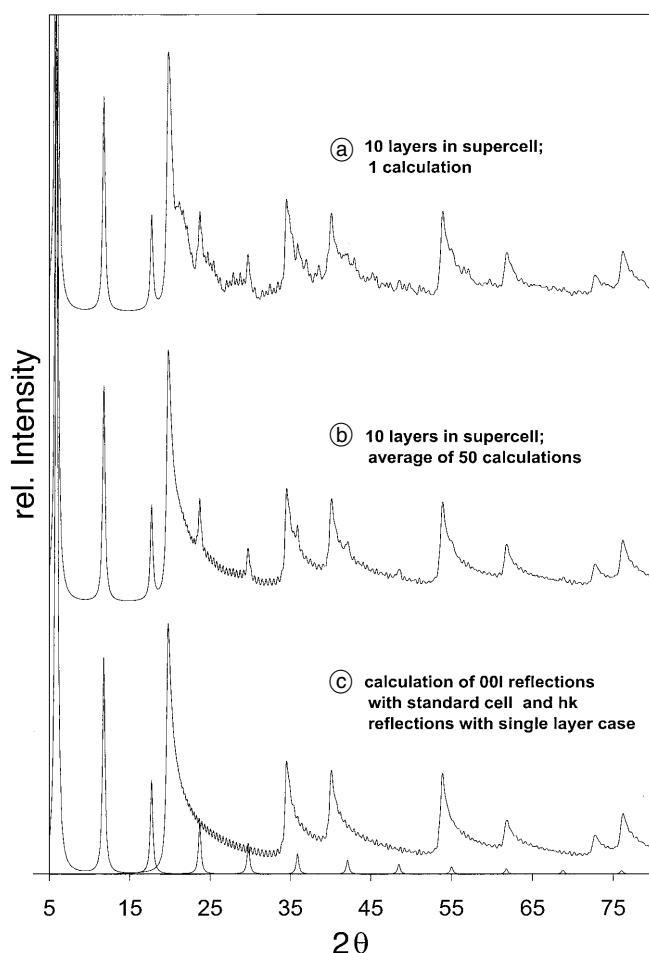


Fig. 6. Results of the Rietveld pattern calculations; (a) simulation of a layer package with 10 layers randomly translated with respect to each other in a supercell; (b) averaged line of 50 simulations of a layer package with 10 layers randomly translated relative to each other in a supercell; (c) calculation of the hk peaks with the single layer case and of the $00l$ reflections with the subcell.

superperiod and become more pronounced with increasing l for a given hk peak. The effect could be reduced by choosing a larger supercell or by increasing the reflection width. In more sophisticated program codes, like BGMN, functions can be used, which widen the reflection profile with rising l indices systematically.

b) One layer case

Figure 6c shows the result of the simulation of the one layer case in the 10-fold supercell. The computation of the hkl reflections were performed with a supercell that contains only one layer and thus represents the aperiodic case of diffraction from a single layer. Again, the $00l$ reflections were calculated from the subcell. The sum of the two curves which are shown separately in Fig. 6c shows only very small deviations from the line in Fig. 6b, which, however, needed much more CPU time.

Discussion

The Debye computations showed that the case of turbostratic disorder can be modelled in a multilayer approach

by allowing translations only. Several statistically equivalent models have to be averaged. Depending on the model size, correlated displacements of adjacent layers with a short correlation length could in principle be incorporated. The same results can also be obtained with the help of a supercell in a Rietveld program. However, this procedure is rather time consuming, since many reflections and atomic positions must be taken into account. The computation must be repeated several times to get a pattern with clear turbostratic features. The resulting computational burden is much too large to be acceptable for the purpose of a Rietveld refinement.

If one ignores possible stacking correlations, however, the 'ideal turbostratic case' can be very effectively transferred to the Rietveld-method: The idea is analogous to the computation with the extended Debye formula: The procedure starts with the calculation of the diffraction intensity of a single layer in a partly filled supercell, which contributes the hk peaks. The diffuse 00 rod has to be subtracted and is replaced by sharp $00l$ reflections calculated from the subcell. This combined periodic/pseudo-aperiodic calculation offers a fast and simple way to produce a pattern of a turbostratically disordered layer structure. Comparison of Figs 5a or 5c with 6c demonstrates this close resemblance. The method has the advantage (over the multi layer approach) that fewer atom positions must be considered and the computation must only be made once. The time needed for the one layer case for one cycle of pattern calculation is in the order of minutes even for rather complex structures like smectites with roughly 40 atoms per unit layer. Such cycle times are also acceptable for a standard Rietveld refinement.

Application to a real system

To prove the applicability of this approach to real systems we show the results of Rietveld refinements for patterns with mixtures of 40, 60 and 80 wt% smectite with NIST SRM 676 corundum powder.

Two remaining issues need to be addressed in order to present a practical and workable approach:

- 1) Is the hypothesis of completely uncorrelated stacking that allows us to use the single layer approach, a reasonable approximation for natural systems?
- 2) Are the current structural models available sufficiently accurate in order to allow quantitative phase analysis?

As a first and tentative answer to these questions, a natural white bentonite product (Marocco) was separated of pure montmorillonitic smectite. The Na saturated bentonite was dispersed and the fraction $< 0.2 \mu\text{m}$ was separated by centrifugation. After Ca saturation and washing in distilled water, the salt-free solid was dried at 25°C and equilibrated to 42% relative humidity. The solid was investigated by XRD, XRF and thermal analysis (TG/DTA). No crystalline impurity could be detected by X-ray powder diffraction. The exact chemical composition (determined by XRF) for the TOT layer is $[\text{Si}_{7.50}\text{Al}_{0.50}]^{\text{IV}}[\text{Al}_{3.34}\text{Fe}_{0.25}\text{Mg}_{0.40}]^{\text{VI}}\text{O}_{20}(\text{OH})_2$. This leads to a layer charge of 0.46 charges per half unit cell,

which is compensated by an interlayer cation occupancy of 0.23 Ca per half unit cell.

The smectite material was mixed with 20, 40 and 60 wt% of corundum powder (NIST SRM 676). Two grams of each powder mixture have been ground with 10 ml ethanol in a McCrone micronising mill for 5 minutes. The slurry was filtered and air dried, and the material was disaggregated by careful grinding in an agate mortar. Random powder sample mounts were prepared using a side-loading technique (Srodon et al., 2001) in a 27 mm diameter sample holder. The XRD data were collected on a Seifert XRD 3000 TT Θ – Θ diffractometer equipped with an automatic divergence slit, a 0.02 radians primary beam Soller collimator, a diffracted beam graphite monochromator, a 0.2 mm receiving slit and a scintillation counter. A copper long-fine focus tube was operated at 40 kV and 40 mA. The scans were performed in the range of 4–80° 2θ at 15 s per 0.02° 2θ step and a constant irradiated sample length of 10 mm.

The structural data for the smectite was taken from the model for a cisvacant dehydrated and K-saturated smectite by Tshipurski and Drits (1984). The interlayer space was increased to a basal distance of 15 Å in order to represent a hydrated Ca-saturated smectite. The interlayer cation is octahedrally coordinated by 6 water molecules in such a way that three molecules form a triangle parallel to the layer surface. This is in good agreement with a study by Van der Gaast et al. (1999), who investigated the hydration structure of Ca intercalated in montmorillonite. For the present calculations, the water molecules are represented only by oxygen. The position and orientation parameters were refined.

The Rietveld code BMGN (Bergmann et al., 1998) was used for the calculations. The instrumental part of the diffraction profiles was calculated by a Monte-Carlo simulation and introduced in the fundamental parameter peak profile model. Refined parameters were lattice parameters for both corundum and smectite, the cation distribution over the cis- and trans-octahedra and orientation parameters of the hydrated interlayer cation complex for smectite. Firstly, we refined size and microstrain broadening parameters for corundum. Because the microstrain broadening was found to be not significantly different from zero, the final refinements were done only with an isotropic size broadening model for corundum.

No attempts were made to refine the total interlayer content and the mean octahedral occupation. These values were set according to the results of the chemical analysis. Additional non-structural parameters to be refined were the zero point and the sample displacement error and a 7th degree polynomial for background modelling.

The single layer approach was implemented by defining a supercell with the lattice parameters $a = 5.19$ Å, $b = 8.98$ Å and $c = 150.0$ Å. The monoclinic angle beta is 101.4°. This corresponds to a 10 fold elongation of the unit cell in the c direction. The factor of this elongation does not correspond to a crystallite size and is rather arbitrary. It has to be at least twice as large as one layer thickness to approximate the aperiodic Fourier-transform and it must be large enough to produce enough peak positions to generate a smooth decay of the hk reflection. On the other

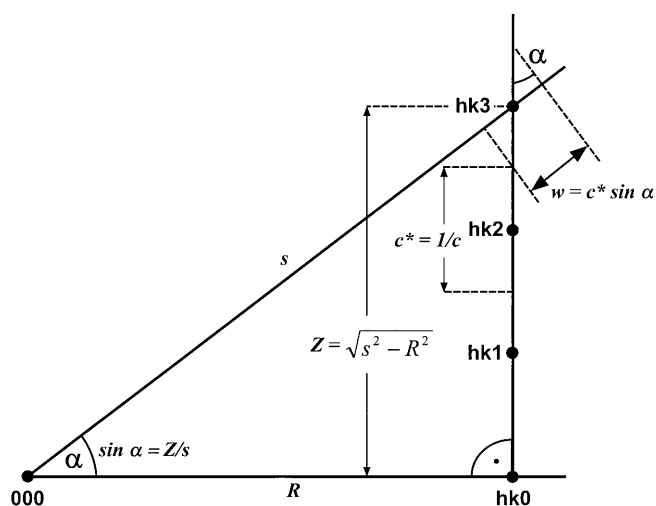


Fig. 7. Dependency of the peak width from the l -value.

hand a factor that is too large increases the computation time, producing too many reflections. The factor of 10 emerged to be suitable. To destroy the coherence perpendicular to the a – b plane, this supercell was only filled to one tenth. The hkl reflections with $l \neq 0$ and h or $k \neq 0$ are very close to each other and produce the asymmetric pseudo-two-dimensional hk reflections. With increasing l indices the distance between two neighbouring peaks becomes bigger and for large l -values “ripples” are visible. This effect can be noticed in fig. 6b and c.

To avoid this disturbing effect all hkl reflections with $l \neq 0$ and h or $k \neq 0$ are provided with an additional broadening parameter which results in an increasing peak width with increasing l value. Figure 7 makes clear the dependency of the peak width from the l -value. Each reflection on a reciprocal rod represents a segment with the length $c^* = 1/c$. The projection w of this segment on the scattering vector s depends on the distance R of the rod from the origin, the distance c^* of two points and the index l . The length w can be regarded as an additional broadening factor. This additional parameter is introduced in the structure model to avoid the “ripples”.

Because of the fact that the whole pattern is still built peak by peak with reasonable three-dimensional information of the hkl indices, this approach can be combined with standard models for the crystallite size or preferred orientation. In the case shown here the texture effect was considered as minimized by the preparation and a texture model was not applied. The 00 l reflections are generated from a standard subcell. These reflections have to be broadened by an additional factor that is only used for this class of reflections. To compensate the reduced X-ray density, the scale factor has to be corrected for quantitative evaluation.

For the refinement, a range from 10° 2θ to 80° 2θ was used, disregarding the 001 reflection of the smectite. Therefore, test calculations have shown that considering the entire range from 4° 2θ to 80° 2θ leads to unsatisfying results. A possible reason is the strong increase of the LP factor towards small 2θ values. Because of the large width of the 001 reflection the LP factor cannot be considered as constant over the region affected by this peak. Besides this the trend of the background line in this region is

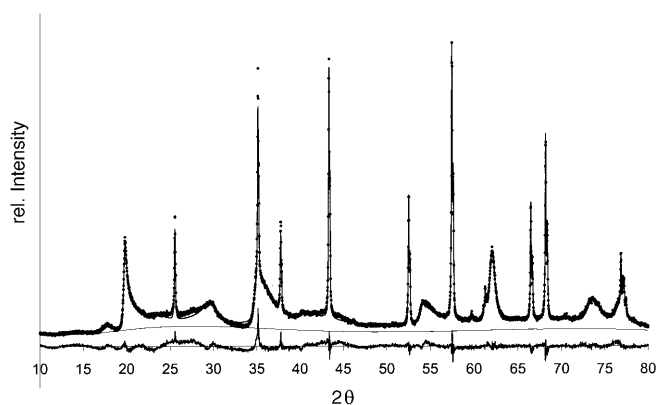


Fig. 8. Rietveld refinement of a mixture of 80 wt-% smectite and 20 wt-% corundum.

Table 1. Results of the Rietveld refinement of three mixtures of smectite and corundum. The error is given as 3 sigma.

| ratio smectite : corundum (nominal) | 80:20 | 60:40 | 40:60 |
|--|-----------------|-----------------|-----------------|
| wt-% smectite (calculated) | 79.3 +/- 0.5 | 57.3 +/- 0.7 | 38.5 +/- 0.8 |
| wt-% corundum (calculated) | 20.7 +/- 0.5 | 42.8 +/- 0.8 | 61.5 +/- 0.8 |
| R_{wp} | 6.79 | 6.52 | 6.25 |

difficult to divide from peak intensity. Moreover, smectites tend to form mixed layering of 1 and 2 water layers of Ca smectite because of not controlled relative humidity. This leads to displacements of the 00 l reflections that are difficult to describe.

The results, including the quantitative smectite content, are quite satisfactory regarding the description of the experimental profiles by the single layer approach (Fig. 8, Table 1).

However, the somewhat enhanced background in the range 20–35° 2 θ in comparison to other smectite fractions indicates the presence of some amorphous material. The content of this material was estimated by TG/DTA. The percentage of hydroxyl groups was calculated from the structural formula. From the relation of this value to the thermogravimetric mass loss between 250 and 750 °C, the amorphous content was estimated to 4–6 wt%. This impurity explains the systematic over determination of the corundum content.

Remarkable is the stability of the one layer approach model against correlation problems to the background polynomial: The “amorphous hump” could be reproduced by the polynomial without any user intervention.

Conclusions

The approach described above is fast enough to be applicable to a complete Rietveld refinement and we believe that this method has potential for the quantitative description of turbostratically disordered layer structures. In combination with a highly developed Rietveld program such as BGMN the model can be used for exact quantitative phase

analysis. The applicability of this method to quantify natural samples will be proved by the analysis of a large number of bentonites and by checking the results with an independent method. The results of this investigation will be presented in a separate paper.

It seems to be possible too with this method to refine some structural parameters for the disordered smectite phase.

Apparently, the assumption of a complete absence of stacking correlations is met at least by the smectite used in this study. It remains to be seen, in how far existing correlations in other layered materials will affect the results. This question will also be addressed in a forthcoming paper.

Beyond this application, the aperiodic Fourier transform – approximated by the partially filled supercell approach – could also be of use for the description of other types of disorder. With the ever increasing computational power of modern PCs, cases with two dimensional disorder or systems with non negligible correlations will come into reach of this method.

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