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PARALLEL INTERGROWTHS IN CRONSTEDTITE-1*T*: IMPLICATIONS FOR STRUCTURE REFINEMENT

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Abstract—Cronstedtite is a member of the kaolin-serpentine group. It yields a wealth of more or less disordered polytypes. The crystals of polytype 1*T* (space group *P*31*m*, *a* = 5.512, *c* = 7.106 Å) contain, within coherently scattering blocks, variable concentrations of stacking faults so that domains of the basic 3D periodic structure can be shifted by $1/3(\mathbf{a}_2 - \mathbf{a}_1)$ or $1/3(\mathbf{a}_1 - \mathbf{a}_2)$. These so-called OD parallel intergrowths have been confirmed by high-resolution transmission electron microscopy. The effect manifests itself in the diffraction pattern so that reflections with $h\text{-}k = 3n$ – the family reflections – are always sharp, whereas remaining reflections – the characteristic polytype reflections – may be smeared out parallel to **c***. The intensities of the latter are thus underestimated during diffractometer measurements. An analysis of such multiple OD intergrowths reveals that the moduli of structure factors for all characteristic (*i.e.* non-family) polytype reflections are reduced relative to those calculated for the non-intergrown basic structure, by a common factor. This fact usually leads to the appearance of ghost peaks in Fourier maps and to their erroneous interpretation. The structure of the basic model can, however, be refined much better if two scale factors are assigned to the family and non-family reflections, respectively.

Key Words—Cronstedtite, Fourier Syntheses, OD Structure, Polytype Structure Refinement, Stacking Disorder, Trioctahedral 1:1 Phyllosilicates.

INTRODUCTION

Cronstedtite is a trioctahedral 1:1 phyllosilicate with the general formula $^{VI}(Fe^{2+}_{3-x}Fe^{3+}_{x})^{IV}(Si_{2-x}Fe^{3+}_{x})O_5(OH)_4$, where x is between 0.5 and 0.8. Due to the almost ideal OD symmetry of its structure (Dornberger-Schiff and Ďurovič, 1975), cronstedtite yields many more or less disordered polytypes. Recent refinements have treated polytypes 3*T* (Smrčok *et al*., 1994), 1*T* (Hybler *et al*., 2000) and $2H_2$ (Hybler *et al*., 2002). Owing to its high Fe content, cronstedtite is resistant to beam damage during HRTEM (high-resolution transmission electron microscopy) investigations, and thus it is suitable for the determination of the actual stacking of layers in the structure (Kogure *et al*., 2001). Together with X-ray investigations, HRTEM leads to a better understanding of polytypism in cronstedite (Kogure *et al*., 2002; see also Kogure, 2002).

The refinement of different cronstedtite polytypes offers particular challenges. In the refinement of the 3*T* polytype (Smrčok *et al*., 1994), for example, residual maxima are apparent in difference Fourier maps, despite the low *R*-factor of 4.8%. These maxima appear at positions corresponding to the superposition structure (see Appendix in Smrčok *et al*., 1994) the Fourier map of which can be obtained from the family reflections ($h\text{-}k = 3n$) only. This effect was interpreted by assuming that the moduli of structure factors of the reflections with $h\text{-}k \neq 3n$ (the characteristic polytype reflections) were reduced relative to the corresponding theoretical values, so that difference Fourier maps showed the rest of the superposition structure – a phenomenon known as the Ďurovič effect (Nespolo and Ferraris, 2001). The reason for the reduction of intensities of these reflections might have been a slight disorder in the crystal investigated which causes their faint streaking whereas the intensities of the family reflections which are always sharp, are unaffected by disorder. A refinement using the same set of intensities and two scale factors leads to $R = 3.1\%$ and eliminates the residual peaks from the final difference map.

Another unexpected situation was encountered during the refinement of the 1*T* polytype (Hybler *et al*., 2000). Although the 1*T* structure is known – it is the simplest polytype containing one 1:1 layer per period – Hybler *et al*. started their investigation *ab initio* using the Patterson function (Petříček, pers. comm.; Hybler, 1997). The structure could be interpreted as a superposition of two identical structures shifted relative to one another by **b**/3 (**b** is the orthohexagonal basis vector). With an appropriately chosen origin, the structure could be refined either with two tetrahedral sheets with centers at $+b/3$ and $-b/3$, and with halved occupancies of atoms, or as a 1:1 parallel intergrowth in the subgroup *P*3. The octahedral sheet remains unaffected because of its *H* centering. For both models, the refinement of cronstedtite from Herja, Romania, converged to *R* =

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3.78% using one scale factor. The R value dropped to 3.07% when two scale factors were employed. Especially remarkable was the fact that the simple structure model derived from Bailey (1969) could be smoothly refined with two scale factors, using the same set of intensities as for the intergrown models. This refinement yielded virtually the same set of atomic coordinates and R factor, and only the final scale factor of the characteristic polytype reflections was significantly different. In the paper by Hybler *et al*. (2000), only the simple model is treated. A refinement with two scale factors was successfully applied to the structure refinement of phlogopite-2O and 1M (Ferraris *et al*., 2001), and Nespolo and Ferraris (2001) wrote a separate paper devoted to this effect. The problems related to the facts described above are the subject of this study.

THE q FUNCTION

Symmetry/crystal chemistry background

In the idealized trigonal model [The trigonal model (Nespolo and Ďurovič, 2002), sometimes also called the Radoslovich model (Radoslovich, 1961), differs from the classical Pauling model by non-zero rotations of tetrahedra], the tetrahedral sheet (Tet) for all cronstedtite structures has the layer symmetry $P(3)1m$ (basis vectors $\mathbf{a}_1,\mathbf{a}_2,\mathbf{c}$). The octahedral sheet (Oc) – $H(3)1m$ is hexagonally centered with centering points at ⅓, ⅔, 0 and ⅔, ⅓, 0. The orders of these layer groups are N_{Tet} = 6 and N_{Oc} = 18, respectively, and, since the pair (*Oc*;*Tet*) has the layer group $P(3)1m$ with the order F = 6, the number Z of the possible positions of Tet relative to Oc leading to geometrically equivalent pairs (Oc;Tet) is $Z = N_{\mathrm{Oc}}/F_{(\mathrm{Oc,Tet})}$ = 3 (see *e.g.* Ďurovič, 1992). Cronstedtite-1T belongs to subfamily C (Hybler *et al*. 2000) and here any cronstedtite 1:1 layer can be shifted relative to a neighboring layer by 0 (zero vector), $1/3(\mathbf{a}_2 - \mathbf{a}_1)$ and $1/3(\mathbf{a}_1 - \mathbf{a}_2)$, which in the orthohexagonal system is 0, $+\mathbf{b}/3$ and $-\mathbf{b}/3$.

From a crystal chemical point of view this means that there are three positions of a cronstedtite layer in which its tetrahedral sheet can form equivalent systems of hydrogen bonds with the octahedral sheet of the preceding layer. In a structure of cronstedtite-1T, domains of 1T polytype shifted relative to each other by 0, $+\mathbf{b}/3$ and $-\mathbf{b}/3$ (Figure 1) can coexist. These domains are not separated by grain boundaries – a phenomenon known as the OD parallel intergrowth (Dornberger-Schiff, 1966, p. 59) – as confirmed by HRTEM investigations (Figure 2), and this has to be taken into account when discussing Fourier transforms of structures thus formed. In the following, we shall use consistently the orthohexagonal axial system, which is simpler and does not affect the general validity of the results. The shifts by $\pm\mathbf{b}/3$ correspond thus to a change of the fractional y coordinate of any point in the unit-cell by ±1/3. We shall also not consider the size of domains and concentration of stacking faults.

Furthermore, to simplify the way of expressing but also to avoid misunderstanding, we shall use the term 'basic structure' for the 3D periodic structure of cronstedtite-1T, 'double intergrowth' and 'triple intergrowth' for a parallel integrowth in which domains – no matter how many – of the basic structure appear in two and all three possible positions indicated above, respectively. The structures of such double- or triple intergrowths will be referred to as (parallel) intergrown.

Domains at 0 and +b/3

Let $F_0(hkl) = \sum_N f_j \exp\{2\pi i(hx_j + ky_j + lz_j)\}$ be the structure factor of the basic structure related to the origin at $y = 0$. Let $0 \leqslant p \leqslant 1$ be the proportion of this structure shifted by $+\mathbf{b}/3$ ($\Delta y = +1/3$) so that $1 - p$ remains at $y = 0$. The structure factor of such an intergrown structure then is

$$\begin{aligned} F(hkl) = {} & \\ & (1-p)\textstyle\sum_N f_j \exp\{2\pi i(hx_j + ky_j + lz_j)\} + \\ & p\textstyle\sum_N f_j \exp\{2\pi i[hx_j + k(y_j + 1/3) + lz_j]\} = \\ & (1-p)\,F_0(hkl) + pF_0(hkl)\,\exp\{2\pi ik/3\} = \\ & F_0(hkl)\,[(1-p) + p\,\exp\{2\pi ik/3\}] = \\ & F_0(hkl).g(p,k) \end{aligned} \qquad (1)$$

There are three possibilities for the term $g(p,k)$ depending on whether $k = 3n$, $k = 3n+1$ or $k = 3n - 1$.

Evidently

$$g(p,3n) = 1 \text{ (family reflections, independent of } p)$$
$$g(p,3n+1) = (1-p) + p/2(-1 + i\sqrt{3}) = \tfrac{1}{2}(2 - 3p + ip\sqrt{3}) \quad (2)$$
(characteristic polytype reflections)

$$g(p,3n-1) = (1-p) + p/2(-1 - i\sqrt{3}) = \tfrac{1}{2}(2 - 3p - ip\sqrt{3}) \quad (3)$$
(characteristic polytype reflections)

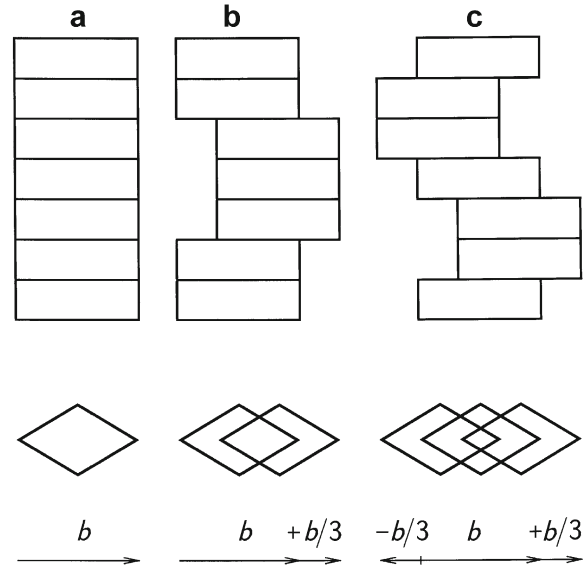


Figure 1. (a) Domains of cronstedtite-1T with origins at $y = 0$ only, (b) domains with origins at $y = 0$ and $y = +\mathbf{b}/3$, (c) domains with origins at $y = 0$, $y = +\mathbf{b}/3$ and $y = -\mathbf{b}/3$. Schematic yz (top) and xy (bottom) projections.

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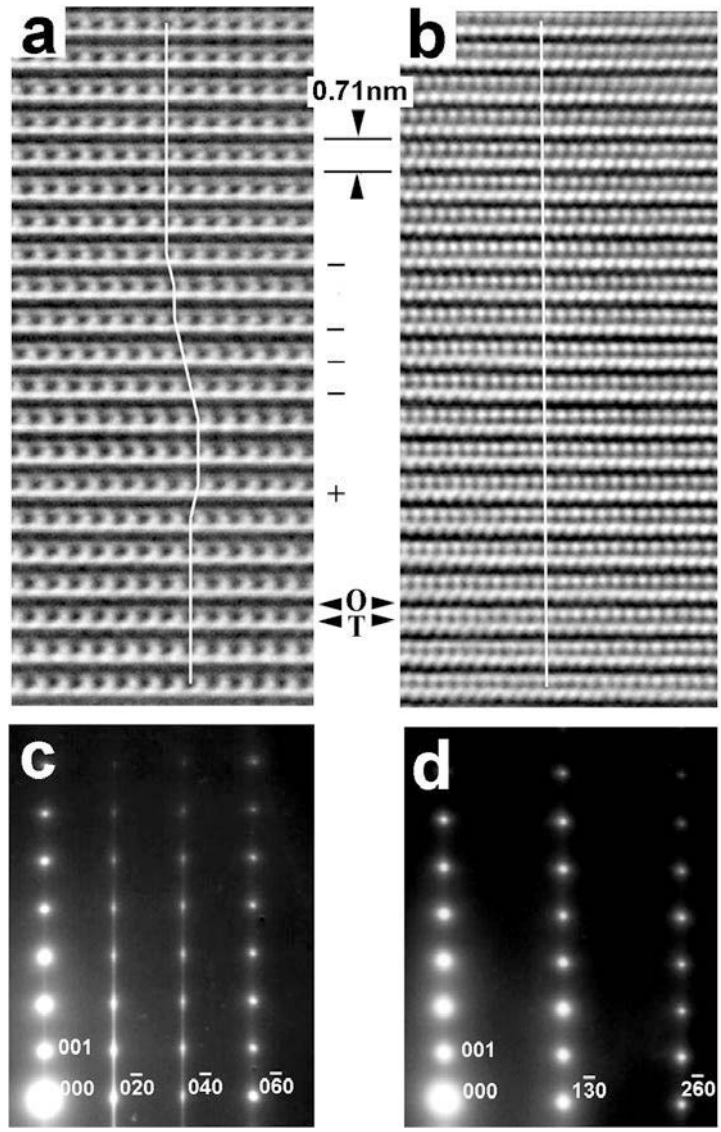


Figure 2. HRTEM images and SAED patterns from partially disordered 1*T*-cronstedtite. The specimen is the apical part of a pyramidal crystal from Lostwithiel, England (Kogure *et al*., 2002). Orthogonal indexing is used throughout. (a) HRTEM image along [100]. (b) HRTEM image along [310] recorded in almost the same area as in (a) but the specimen was rotated by 30º in the TEM. (c) SAED pattern along [100] from the same area as in (a). (d) SAED pattern along [310] from the same area as in (c). O and T indicate the positions of octahedral and tetrahedral sheets, respectively, in a unit layer (see Kogure *et al*., 2001 for interpretation of the HRTEM images). The white line connecting equivalent positions in each layer, shows the lateral stagger between adjacent layers at the interlayer positions indicated with '+' or '−' in (a) whereas there is no stagger in (b). Streaks that are a consequence of stacking disorder are apparent along $0kl$ ($k \neq 3n$) reciprocal lattice rows in (c) whereas no streaks are observed in (d). All images and patterns were recorded using a JEOL JEM-2010 operated at 200 kV. The point resolution is ~0.2 nm

Note that $g(p,3n + 1)$ and $g(p,3n - 1)$ are complex conjugate numbers and thus their absolute values are the same. For the square of g we obtain

$$g^2(p,3n \pm 1) = 3p^2 - 3p + 1 = q \qquad (4)$$

The plot of this quadratic function appears in Figure 3. The parabola has its minimum $q = 1/4$ for $p = 1/2$, *i.e.* when equal proportions of the basic structure are in both positions: a double intergrowth 1:1. Since $|g| = \sqrt{q}$, the moduli of structure factors of the characteristic polytype reflections are halved in comparison with those calculated for the non-intergrown basic structure, *i.e.* for $p = 0$. For $p = 1$, $q = 1$ which corresponds to the basic structure at $+b/3$ but related to the origin at $y = 0$.

Domains at −b/3, 0 and +b/3

We can now extend the previous model for triple intergrowths so that $(1 - p)$ of the basic structure remains at $y = 0$ and a new parameter $0 \leqslant x \leqslant 1$

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indicates how the remaining part p is distributed between the positions at $-b/3$ and $+b/3$ ($\Delta y = -1/3$ and $+1/3$, respectively), so that equation 1 changes to

$$F_0(hkl)[xp \exp\{-2\pi ik/3\} + (1-p) + (1-x)\, p \exp\{+2\pi ik/3\}] = F_0(hkl)\, g(p,x,k) \quad (5)$$

(at $-b/3$) (at 0) (at $+b/3$)

In an analogy to equations 2 and 3

$$g(p,x,3n) = 1$$

(family reflections, independent of both p and x)

$$g(p,x,3n+1) = \tfrac{1}{2}[(2-3p) - ip\sqrt{3}(2x-1)] \quad (6)$$

(characteristic polytype reflections)

$$g(p,x,3n-1) = \tfrac{1}{2}[(2-3p) + ip\sqrt{3}(2x-1)] \quad (7)$$

(characteristic polytype reflections)

Again, the expressions 6 and 7 are complex conjugate and for their absolute value we obtain

$$g^2(p,x,3n \pm 1) = 3(x^2 - x + 1)\, p^2 - 3p + 1 = q \quad (8)$$

This function will be called the q function.

Figure 4 shows the plot of this function for $0 \leqslant p \leqslant 1$ and $0 \leqslant x \leqslant 1/2$. The other portion for which $1/2 \leqslant x \leqslant 1$ is not shown for the sake of clarity as it is a mirror image of the first half (symmetry plane at $x = 1/2$) because $q(p,x) = q(p,1-x)$. The section at $x = 0$ is the same parabola as in Figure 3. Sections at $x > 0$ are parabolas too but their respective minima are gradually shifted with increasing x towards $p > 1/2$ until the absolute minimum $q = 0$ is reached at $p = 2/3$ and $x = 1/2$, which means that all the three positions are equally occupied by 1/3 of the basic structure, *i.e.* the superposition structure for which all characteristic polytype reflections disappear.

The parabola at $x = 1/2$ (triple intergrowths with equal occupancy of the positions at $-b/3$ and $+b/3$) deserves special attention. The imaginary terms in equations 6 and 7 vanish and a simple linear function $g(p,\tfrac{1}{2},3n\pm1) = \tfrac{1}{2}(2-3p)$ results. It follows that for all the triple intergrowths with $0 < p < 2/3$, the phase angles of the structure factors of the basic structure remain unchanged whereas for $2/3 < p \leqslant 1$, all these angles are changed by $\pm 180^\circ$.

From Figure 4 it can also be seen that the same set of $F^2(hkl)$ values for any $q < 1$ can be obtained by a whole series of double-/triple intergrowths with p and x satisfying equation 8 for q = const. Some situations for $q = 1/4$, *i.e.* $\sqrt{q} = 1/2$ are illustrated by inserted bar graphs. It is evident that all structures with q = const <1 yield the same Patterson function.

From the above it also follows that whereas $|F(hkl)|$ with $k = 3n$ (the family reflections) are unaffected by intergrowth, $|F(hkl)|$ with $k = 3n+1$ and $|F(hkl)|$ with $k = 3n-1$ (the characteristic polytype reflections) are reduced by the same coefficient $\sqrt{q} < 1$. The latter reflections will be referred to as non-family reflections in the following.

FOURIER SYNTHESES

Let us now investigate separately the role of family and non-family reflections in the formation of Fourier images.

Family reflections

A Fourier series calculated with a three-dimensional subset of coefficients with $k = 3n$ corresponds to a 3-fold superposition structure (known also as average structure)

$$\hat{\rho}(xyz) = (1/3)[\rho(xyz) + \rho(x,y+1/3,z) + \rho(x,y-1/3,z)] \quad (9)$$

Although this expression is known, let us derive it to facilitate analogous considerations for non-family reflections. Let

$$\rho(xyz) = (1/V)\textstyle\sum_{hkl} F(hkl) \exp\{-2\pi i(hx+ky+lz)\} \quad (10)$$

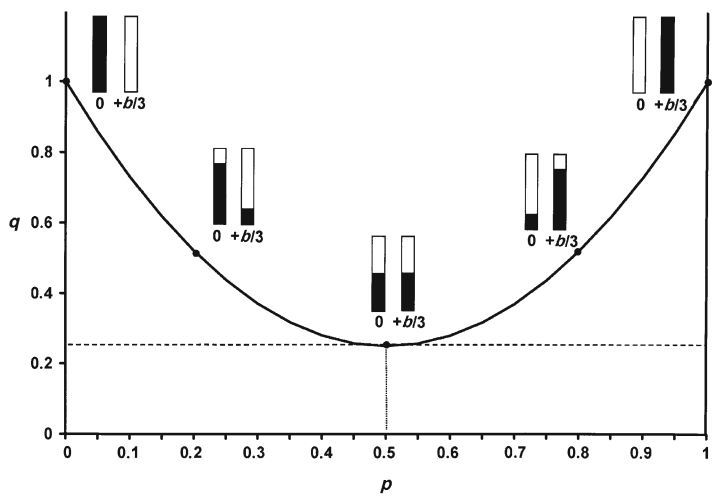


Figure 3. Plot of the function $q = 3p^2 - 3p + 1$. The bar graphs correspond to some selected distributions of the basic structure between the positions with origins at $y = 0$ and $y = +1/3$.

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be the electron-density distribution in the basic structure. Then

$$\rho(x,y + 1/3,z) = (1/V)\sum_{hkl}F(hkl) \exp\{-2\pi i(hx + ky + lz)\}\exp\{-2\pi ik/3\} \quad (11)$$

$$\rho(x,y - 1/3,z) = (1/V)\sum_{hkl}F(hkl) \exp\{-2\pi i(hx + ky + lz)\}\exp\{+2\pi ik/3\} \quad (12)$$

are the electron-density distributions of the basic structure shifted by +**b**/3 and −**b**/3 or, in fractional coordinates, $\Delta y = +1/3$ and $-1/3$, respectively. The three equations 10−12 can be written as partial sums for reflections with $k = 3n$, $k = 3n + 1$ and $k = 3n - 1$, respectively. For the sake of clarity, these sums will be abbreviated as $\sum_{k=3n}$, $\sum_{k=3n+1}$ and $\sum_{k=3n-1}$, respectively, in the following. Also realizing that $\exp\{-2\pi ik/3\}$ is equal to 1, $\exp\{-2\pi i/3\}$, and $\exp\{+2\pi i/3\}$ for $k = 3n$, $k = 3n + 1$ and $k = 3n - 1$, respectively, we obtain

$$\rho(xyz) = \sum_{k=3n} + \sum_{k=3n+1} + \sum_{k=3n-1} \quad (13)$$

$$\rho(x,y + 1/3,z) = \sum_{k=3n} + \exp\{-2\pi i/3\}\sum_{k=3n+1} + \exp\{+2\pi i/3\}\sum_{k=3n-1} \quad (14)$$

$$\rho(x,y - 1/3,z) = \sum_{k=3n} + \exp\{+2\pi i/3\}\sum_{k=3n+1} + \exp\{-2\pi i/3\}\sum_{k=3n-1} \quad (15)$$

We shall now add the three equations 13−15 and substitute $\exp\{-2\pi i/3\}$ and $\exp\{+2\pi i/3\}$ by $\frac{1}{2}(-1 - i\sqrt{3})$ and $\frac{1}{2}(-1 + i\sqrt{3})$, respectively. The terms containing sums for $k = 3n + 1$ and $k = 3n - 1$ mutually cancel and the result becomes

$$\sum_{k=3n} = (1/3)[\rho(xyz) + \rho(x,y + 1/3,z) + \rho(x,y - 1/3,z)] \quad (16)$$

which is identical to equation 9. This function is real which also follows from the fact that the coefficients with $k = 3n$ correspond to a subgroup with index [3] of translations in the reciprocal lattice. The superposition structure thus contains one third of the basic structure, each at $y = 0$, $y = +1/3$ and $y = -1/3$: the basic structure is thus superimposed onto itself with shifts by +**b**/3 and −**b**/3 (or 2**b**/3), and normalized to the original number of electrons. It should be realized that this is a fictitious structure and it may lead to partial or complete overlapping of atoms and thus unrealistic interatomic distances.

The 3-fold superposition structure $\hat{\rho}(xyz)$ is of special importance also for the family of cronstedtite polytypes belonging to subfamily C (Hybler *et al*., 2000) which includes the 1*T* polytype. This structure is identical to a structure which can be derived by simultaneous realization of all possible positions of any OD layer (in the 1*T* polytypes corresponding to tetrahedral sheets and octahedral sheets), as postulated for a general case by Dornberger-Schiff (1964), and whose symmetry can be derived by completing any of the family groupoids to a group (Fichtner, 1977). The structure derived in this way is by definition 3D periodic and common to all, even disordered structures belonging to the family. The corresponding reflections (the family reflections) are thus always sharp, common and characteristic for the family. This is why such a structure has been called family structure $\rho(xyz)_{fam}$ (K. Fichtner, pers. comm.; see also Ďurovič, 1994). Thus $\hat{\rho}(xyz) = \rho(xyz)_{fam}$. It is evident that other conceivable superposition structures the Fourier series for which are calculated with coefficients with $k = 2n$, $4n$, $5n$, *etc*., do not possess these properties and thus we shall henceforth use the

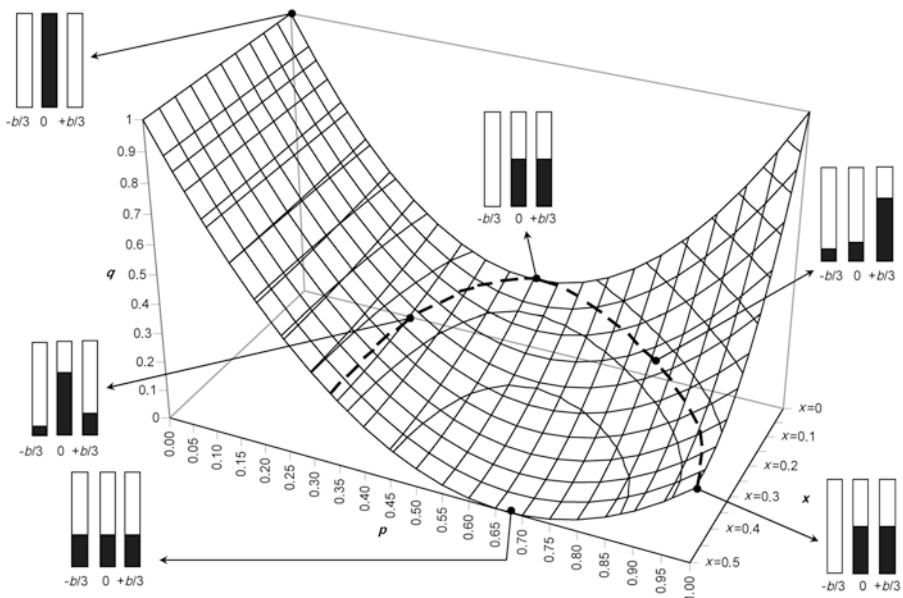


Figure 4. Plot of the function $q = 3(x^2 - x + 1)\,p^2 - 3p + 1$. The bar graphs correspond to some selected distributions of the basic structure between the positions with origins at $y = -1/3$, $y = 0$ and $y = +1/3$.

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special term family structure instead of the previously used general term superposition structure.

Non-family reflections

In order to find a meaning of the partial Fourier series calculated with coefficients with $k = 3n + 1$, it is necessary to eliminate the exponential terms accompanying $\sum_{k=3n+1}$ in equations 14 and 15. This can be done by multiplying these two equations by the corresponding complex conjugate terms (for a general approach see Dornberger-Schiff, 1966, p. 90 ff), thus

$$\rho(xyz) = \sum_{k=3n} + \sum_{k=3n+1} + \sum_{k=3n-1} \quad (13)$$

$$\exp\{+2\pi i/3\}\rho(x,y + 1/3,z) = \exp\{+2\pi i/3\} \sum_{k=3n} + \sum_{k=3n+1} + \exp\{-2\pi i/3\}\sum_{k=3n-1} \quad (17)$$

$$\exp\{-2\pi i/3\}\rho(x,y - 1/3,z) = \exp\{-2\pi i/3\}\sum_{k=3n} + \sum_{k=3n+1} + \exp\{+2\pi i/3\}\sum_{k=3n-1} \quad (18)$$

After adding these equations and substitutions as in the case of family reflections, we obtain

$$\sum_{k=3n+1} = (1/3)[\rho(xyz) + \exp\{+2\pi i/3\}\rho(x,y + 1/3,z) + \exp\{-2\pi i/3\}\ \rho(x,y - 1/3,z)] \quad (19)$$

and likewise

$$\sum_{k=3n-1} = (1/3)[\rho(xyz) + \exp\{-2\pi i/3\}\rho(x,y + 1/3,z) + \exp\{+2\pi i/3\}\rho(x,y - 1/3,z)] \quad (20)$$

Both functions 19 and 20 are complex but their sum must be real inasmuch as it represents the complementary structure which, together with the (real) family structure yields the basic structure, thus

$$\sum_{k=3n+1} + \sum_{k=3n-1} = (1/3)[2\rho(xyz) - \rho(x,y + 1/3,z) - \rho(x,y - 1/3,z)] = \rho(xyz)_{compl} \quad (21)$$

The complementary structure contains two thirds of the basic structure at $y = 0$, and minus one third of it, each at $y = +1/3$ and $y = -1/3$. It is a fictitious structure too, even with negative electron densities. The sum of equations 16 and 21 evidently yields $\rho(xyz)$.

CONSEQUENCES

Theoretical considerations given in the previous paragraphs have consequences for two dominant steps in a structure analysis: calculation/analysis of Fourier maps and structure refinement. These considerations refer, strictly speaking, to the structure of cronstedtite-1*T* but it turns out that the approach has a more general validity.

Fourier maps

A Fourier map reflects the basic structure faithfully only if the intensities of the non-family reflections are not affected by crystal intergrowth which, in turn, can be quantified by the value of q, see equations 4 and 8. Otherwise $\rho(xyz) = \rho(xyz)_{fam} + \sqrt{q}.\rho(xyz)_{compl}$ with $\sqrt{q} < 1$, and the situation becomes more complicated. As equations 16 and 21 hold for any point in the unit-cell, they also hold for any peak in the Fourier map. To identify the consequences for the Fourier maps of the family structure, of the complementary structure and of the resulting structure as a function of $\sqrt{q}$, let us consider an isolated peak at $y = 0$ with its height defined as equal to 1. This corresponds formally to a structure containing one atom in the unit-cell and this model structure will be referred to as original structure within this paragraph including Figure 5.

Family structure. According to equation 16, the family structure exhibits three peaks with heights 1/3 each, at $y = 0$, $y = +1/3$ and $y = -1/3$. It is shown schematically in Figure 5a by columns filled up to one third. And, since the intensities of the family reflections are not affected by intergrowth, this pattern remains unchanged for all cases discussed below.

$q(p,x,3n\pm1) = 1$. In this case both sets of reflections are on absolute scale and the sum of equations 16 and 21 gives $\rho(xyz)$, the electron-density distribution in the original one-atom structure. The situation is shown schematically in Figure 5b where full columns with height 1 and partially filled columns represent the original structure and its parts, respectively. It is evident that the 2/3 of the complementary structure at $y = 0$ is added to 1/3 of the family structure to the complete original structure, whereas the negative 1/3s of the complementary structure and the positive 1/3s of the family structure at $y = \pm1/3$ mutually cancel. A look at equation 8 and Figure 4 reveals that the condition $q = 1$ can be achieved for $p = 0$ (x irrelevant), but also for $p = 1$ and $x = 0$ as well as for $p = 1$ and $x = 1$ which means that the origin of the original structure lies then at $y = 0$, at $y = +1/3$, and at $y = -1/3$.

It is commonly known that such a shift of origin is accompanied by changes of phases of structure factors without changing their moduli. In our case, however, the phases for the family structure remain unchanged (see equation 1 where $g(p,3n)$ is independent of p) and only the phases for the complementary structure are variable. With respect to the positions at $y = 0$, $y = +1/3$ and $y = -1/3$, these structures can be labeled as (1:0:0), (0:1:0) and (0:0:1).

$1 > q(p,x,3\pm1) \geqslant 1/4$. Whereas the moduli of structure factors of family reflections remain unchanged, those of all non-family reflections are reduced by $1 > \sqrt{q} \geqslant 1/2$ and the contribution of the complementary structure is reduced by the same coefficient (Figure 5c). The result is the original structure at $y = 0$ but with reduced electron density, and the rest of it at $y = \pm1/3$ because the minima of the complementary structure do not cancel the corresponding maxima of the family structure completely, leading thus to residual (ghost) peaks in the Fourier map (Figure 5c, see also Figure 1 in Smrčok *et al.*,

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1994). Therefore, the Patterson function indicates the presence of an intergrowth.

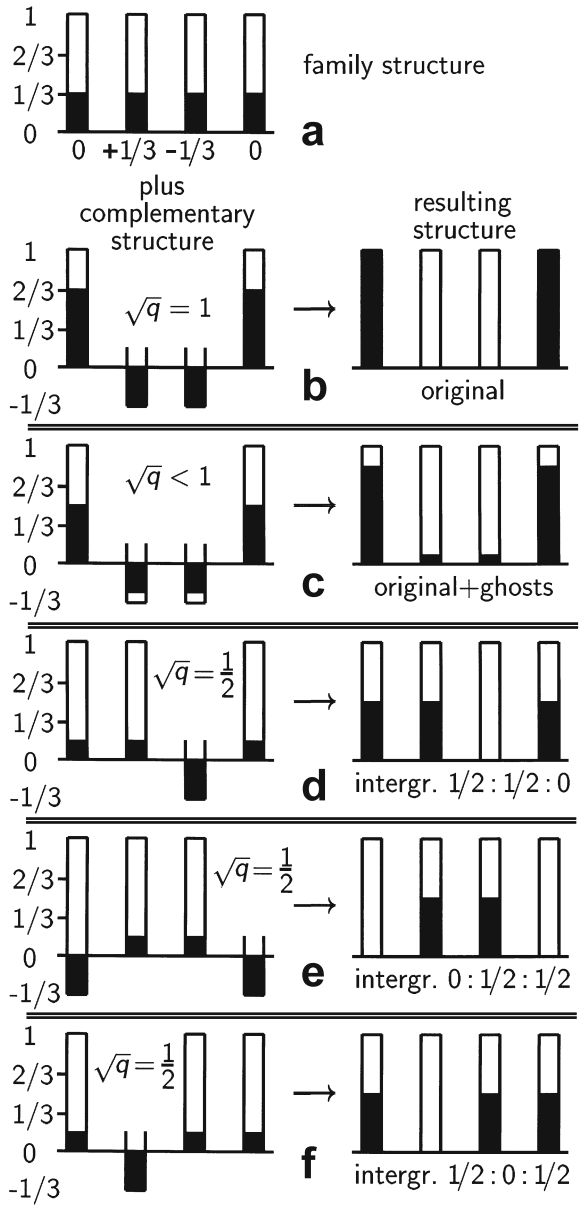


Figure 5. An illustration of how a single peak in a Fourier map at $y = 0$ represented by a full column with unit height, appears in the Fourier map of the family structure (a) and in the Fourier maps of some selected complementary and resulting structures (b–f). Partly filled columns represent reduced peak heights in fractions of 1 as indicated along the vertical axis. Entries on the horizontal axis give fractional y coordinates 0, +1/3 and −1/3 = 2/3 as indicated in (a). (b) $\sqrt{q} = 1$: resulting structure is the original one, (c) $1/2 < \sqrt{q} < 1$: phases of the complementary structure correspond to the original structure with origin at $y = 0$. (d–f) $\sqrt{q} = 1/2$: phases of the complementary structures correspond to double intergrowths ½:½:0 (d), 0:½:½ (e) and ½:0:½ (f). Entries in the symbols for double intergrowths refer to the positions $y = 0$, $y = +1/3$ and $y = -1/3$, respectively.

1/4 > q(p,x,3n±1) ⩾ 0. This situation can be handled with triple intergrowths only. A special case is the triple intergrowth (1/3:1/3:1/3), which is identical to the family structure. It corresponds to the absolute minimum of the q function for $p = 2/3$ and $x = 1/2$ (Figure 4).

Residual peaks and structure refinement

In an actual structure, the above considerations hold for all peaks in the Fourier map and thus a peak at $y = y_0$ may be accompanied by two residual (ghost) peaks at $y = y_0 \pm 1/3$, *etc*.

The fact that the residual peaks are equal in height follows from equation 21. It is also a consequence of the circumstance that these peaks correspond to $x = 1/2$ in equation 8 and, as mentioned in the discussion of the q function and Figure 4, the phase angles for these structure models for $0 < p < 2/3$ are the same as for the basic structure. Thus, if one calculates the Fourier synthesis of the basic structure without being aware of reduced intensities of the non-family reflections, the synthesis automatically produces residual (ghost) peaks. This situation occurs frequently and the residual peaks are usually interpreted as domains that really exist. The problem can be treated in two, essentially different ways:

(i) A part of the basic structure is set into positions indicated by the residual peaks and one scale factor is used, common for all reflections. The chosen model determines the phases of non-family reflections and adjusts the values of the corresponding $|F_{calc}|$ according to equation 8. As is evident from Figure 4, this can be achieved by various triple intergrowths for constant q but also by pairs of equivalent double intergrowths: for $x = 0$, $x = 1$ and $p = 1$. The parameters to be adjusted in the refinement process are, in addition to the atomic parameters, the occupancies of individual atoms; in cronstedtite-1*T*, however, it is occupancies only of atoms belonging to the tetrahedral sheet because atoms of the octahedral sheet repeat with periodicity $b/3$ and thus do not contribute to the non-family reflections. As a special case, the situation for $q = 1/4$ deserves attention because the six general double intergrowths mentioned above reduce here to three equivalent double intergrowths (1/2:1/2:0), (0:1/2:1/2) and (1/2:0:1/2). The corresponding relations between the family structure, the complementary structures and the resulting structures are shown in Figure 5d,e,f. It is evident that the complementary structures are the same, just phased differently.

(ii) The basic structure only is used as the starting model and two scale factors for the two sets of reflections are refined, together with the atomic parameters. In this way, phases of the non-family reflections are fixed, and the values of $|F_{calc}|$ for non-family reflections are adjusted to those of $|F_{obs}|$ just by the corresponding scale factor. However, for the subsequent calculation of Fourier syntheses, all reflections are re-scaled so as to bring them to the absolute scale,

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including $F(000)$. In this way the Fourier coefficients correspond to the (not intergrown) basic structure and the residual peaks disappear from the final Fourier maps. This procedure is not only evidently simpler than that described in (1), but it also eliminates overlapping of some atoms, thus avoiding incorrect electron densities and/or atomic parameters. It should, however, be kept in mind that neither of these two approaches reflects reliably the distribution of domains in the investigated crystal and the actual situation can be revealed at present only by HRTEM investigations.

STRUCTURE REFINEMENTS OF CRONSTEDTITE-1*T*

Our refinement of cronstedtite-1*T* as described in Hybler *et al*. (2000) was not so straightforward as it might seem; some peculiarities encountered during its early stages have already been mentioned. The two refined models (basic and intergrown) yielded reasonable inter-atomic distances with R factors of ~3−4%. Two issues raised suspicion and eventually led to the theoretical analyses given above.

(1) The Fourier syntheses reflected the basic as well as the intergrown structure equally well. Keeping in mind that the cronstedtite structures are very close to their ideal OD models (Smrčok *et al*., 1994) and thus the shifts of adjacent domains by $+\mathbf{b}/3$ and $-\mathbf{b}/3$ are equally probable, a question arose as to why double intergrowths should be preferred to triple intergrowths containing domains in both possible positions.

(2) It is known that the O atom belonging to the inner OH group in all refined structures of the kaolin-serpentine group and those of the micas, always lies closer to the atomic plane of octahedrally coordinated atoms than the apical O atoms common to both the tetrahedral and the octahedral sheet. However, the 1:1 double-intergrowth model for the Herja specimen refined to R = 3.21% with one scale factor only, indicated a different result. On the contrary the refinement of the basic model only, with two scale factors, gave a more reasonable value with R = 3.07%.

Although the latter refinement strategy leads to a better R value, this result cannot *a priori* be considered more reliable. In a cronstedtite structure, 70% of the total diffraction power is represented by atoms in the octahedral sheet that repeat with the periods of the family structure. The influence of the strong family reflections on the R factor is much greater than that of the much weaker non-family reflections which, however, are decisive for the structure of the actual polytype.

The 'opportunistic' behavior of Fourier syntheses has been dealt with in the preceding paragraphs, but the influence of the refinement strategy on fine details of the structure necessitated further investigations. We therefore decided to compare the following four refinement strategies: (1) basic structure only, with one scale factor; (2) basic structure only, with two scale factors; (3) 1:1 double intergrowth with one scale factor; (4) 1:1 double intergrowth with two scale factors. These refinements were based on the data for crystals from Herja, Romania, from Lostwithiel, Cornwall, UK (Hybler *et al*., 2000) and from Rožňava, Slovakia (Varček *et al*., 1990). A more detailed treatment of the results will be given elsewhere (J. Hybler, in prep.), so only a brief summary follows.

The refinements for intergrown structures yielded results inferior to those for crystals without intergrowths. The main reason is overlapping of atoms in the most sensitive part of the structure that encompasses the apical O atoms, O atom belonging to the inner OH group, and the tetrahedral atoms (O4, OH1 and T1 in Table 3 from Hybler *et al*., 2000). In particular, OH1 partly overlaps with O4 and, since the difference in their z coordinates is ~0.02−0.04 Å, they were refined as a single atom. Tetrahedral atoms appear in two independent positions which have to be refined separately, and the resulting Si:Fe ratios are not only significantly different from one another but sometimes they appear outside the limits derived from the chemical analyses. Moreover, correlations >0.9 are not exceptional and also the matrix of displacement coefficients is not always positive-definite. The only positive outcome was the fact that the scale factor for non-family reflections nearly doubled compared to that obtained in the refinement of the basic structure, in agreement with equation 8. The results obtained with two scale factors were better than those obtained with one scale factor.

The refinement of the basic, non-intergrown structures with one scale factor gave acceptable results only for the Lostwithiel specimen. Worse results for the two other crystals can be explained by the fact that these crystals are more disordered than the Lostwithiel crystal which is nearly perfect . The refinement with two scale factors is not only the simplest but also yields results which we consider most reliable. The results of the refinements are thus in favor of alternative (ii) discussed at the end of the preceding section.

CONCLUSIONS

The results obtained in the present study can be generalized also for other sheet silicates showing polytypism in which the family structure is represented by a translation subgroup of reflections with $k = 3n$ (or, in hexagonal indices $h\text{-}k = 3n$) and the moduli of structure factors of the two cosets of non-family reflections with $k = 3n\pm1$ (or $h\text{-}k = 3n\pm1$) are on the same scale. The recommended procedure is to refine the basic structure with two scale factors. No harm is done if these scale factors converge to the same value. But some caution is necessary if the intensities of the non-family reflections are reduced. The set of all intensities can then be interpreted by means of a wide variety of models that

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may be completely artificial since the Fourier syntheses do not 'know' the concrete stacking of layers in the crystal studied and they accept – with some restrictions – the input model. Most ghost peaks appearing in positions shifted by ±**b**/3 are mathematical artefacts. Let us consider two extremes leading to the same reduction of intensities of non-family reflections: (i) the structure within coherently scattering blocks is disturbed by numerous stacking faults but it always returns to the same axis – the result is diffuse streaks accompanying non-family reflections; (ii) there exist (also within coherently scattering blocks) large domains shifted by ±**b**/3 and the concentration of stacking faults is low – all reflections become virtually sharp. Both identical sets of intensities can be interpreted in the same way but a real existence of shifted domains can be assumed only in case (ii). The final decision can only be made on the basis of HRTEM investigations.

The frequent practice of assigning a part of the structure to ghost peaks can lead to reasonable results without destroying sensible details of the structure only if this proportion is small, *e.g*. 0.01–0.02 in the structure of Cs-ferriannite (Mellini *et al*., 1996).

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