

REFINEMENT OF THE CRYSTAL STRUCTURE OF CRONSTEDTITE-3T

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Abstract—The crystal structure of cronstedtite-3T from Kutná Hora (Bohemia, Czechoslovakia), space group $P3_1$, was refined to $R_w(\text{all}) = 3.1\%$ for 1336 independent diffractions. There are two and three independent tetrahedral and octahedral positions, respectively, in this structure. The tetrahedra are occupied by 0.75 Si and 0.25 Fe while the octahedra are uniformly occupied by Fe. The refinement process was hindered by two problems: a “strong” superposition structure (all atoms of the octahedral sheets, i.e., $\div 70\%$ of the total diffraction power contribute almost solely to the family diffractions with $\text{mod}(h-k, 3) = 0$), and a slight disorder of the investigated crystal. The first problem was resolved by a preliminary block-diagonal refinement procedure where the atoms coinciding in the superposition structure were separated into individual blocks. The second problem was resolved by including two scale factors into the final full-matrix refinement: one for family diffractions, the other for the remaining ones which are characteristic for this polytype.

Key Words—Cronstedtite, Order-disorder (OD), Polytypism.

INTRODUCTION

Steadman and Nuttall (1963, 1964) and Steadman (1964) determined and refined partially by Fourier methods the structures of four polytypes of cronstedtite $\text{Fe}_3[(\text{Si}, \text{Fe})_2\text{O}_5](\text{OH})_4$: 1T, 3T, 2H₁ and 6R with space groups $P31m$, $P3_1$, $P6_3cm$ and $R3$, respectively. They also detected three other polytypes: 2T ($P31c$), 2M₂ (Cc) and 1M (Cm) as small regions intergrown with other structures. They found that diffractions with $\text{mod}(h-k, 3) = 0$ (hexagonal) were always sharp, but the remaining diffractions were affected by diffuse streaks, indicating disorder. Also twinning was common.

Dornberger-Schiff and Ďurovič (1975a,b) recognized that the structures of 1:1 phyllosilicates can be interpreted as OD (order-disorder) structures of layers. Thus, not only could the symmetry relationship between polytypes be explained, but this also greatly facilitated the derivation of MDO (maximum degree of order) polytypes and also the understanding of diffraction patterns of minerals belonging to the serpentine-kaolin group (Ďurovič 1981).

An extensive study of cronstedtites from different

localities was made by Mikloš (1975). He examined 30 crystals and found all of them to be disordered.

A refinement of the structure of cronstedtite-2H₂ was published by Geiger *et al* (1983). However, due to the poor quality of the crystal, the authors were required to work with a multiple twin, thereby making the study very difficult and the results uncertain. Thus problems of stacking disorder and twinning have greatly hampered structural work on cronstedtite. The discovery of a crystal of cronstedtite which does not show diffuse streaking, was too good an opportunity to ignore.

EXPERIMENTAL

The cronstedtite crystal from Kutná Hora (Bohemia, Czechoslovakia) used for this study has the form of a black trigonal prism with size 0.3 mm and thickness 0.05 mm. An electron microprobe analysis of the crystal together with the loss on ignition determined from the bulk sample (Table 1) indicated that the crystallochemical formula was $\text{Fe}_{2.96}\text{Al}_{0.02}\text{Mg}_{0.02}[(\text{Si}_{1.26}\text{Fe}_{0.74})\text{O}_5](\text{OH})_4$. Because of a very small amount of the specimen, no distinction of Fe^{3+} and Fe^{2+} could be performed by a wet chemical analysis. All Fe deter-

Table 1. Chemical composition of cronstedtite from Kutná Hora.

Oxide	Weight percent
SiO ₂	18.52
Al ₂ O ₃	0.25
Fe ₂ O ₃	72.73
MgO	0.20
H ₂ O ⁺	8.60
Total	99.80

mined by the microprobe analysis was calculated as Fe³⁺. X-ray precession photographs showed strong diffractions only for mod($h-k, 3$) = 0. The distribution of intensities along reciprocal rows 11/ (hexagonal indexing) and 10/ lead unambiguously to the identification of this crystal as cronstedtite-3T with space group P3₁. The diffractions with mod($h-k, 3$) = 0 are referred to as family diffractions, the remaining ones as characteristic polytype diffractions, (Đurovič 1981). Data collection details are given in Table 2.

Special care was devoted to the correction for absorption. The data collection was carried out with Ag-radiation to reduce absorption effects. The regular crystal shape defined by natural crystal faces enabled the use of the analytical method (Templeton and Templeton 1978).⁴

Refinement

The SDS program package (Petříček and Malý 1988) was used for the refinement with neutral-atoms scattering factors of Cromer and Mann (1968). Starting coordinates were taken from Steadman and Nuttall (1963). Weights were set to $w_i = 1/\sigma_i^2$, the occupancy factors α of the tetrahedral sites were constrained so that $\alpha_{Fe} + \alpha_{Si} = 1$.

Since precession photographs did not show diffuse streaking affecting the characteristic polytype diffractions, the initial calculations used standard procedures, i.e., with the full-matrix technique and one scale factor for all diffractions. Though the overall convergence was smooth, the Fe-contribution to the tetrahedral sites was unexpectedly reduced to zero after several cycles. The removal of Fe atoms was accompanied by increasing instability of the corresponding anisotropic coefficients β_{ij} and several atoms became non-positive definite. Also the disagreement with chemical composition was serious and thus, although the $R_w(\text{all}) = 6.3\%$ was acceptable, the refinement was abandoned.

⁴ The influence of the uncertainty of the measured crystal thickness (0.05 ± 0.005 mm) which can strongly affect the crystal volume used for the calculation, was tested. The change of 0.005 mm lead after re-scaling to a maximum difference between the corrected values of structure factors to be about 1.5% and the average difference less than 1%. None of the important results in this paper were significantly affected by such a variation of the thickness.

Table 2. Crystal data and data collection.

Crystal system: trigonal
Space group: P3 ₁
$a(\text{Å}) = 5.497(2)$, $c(\text{Å}) = 21.355(7)$
$Z = 3$
$V(\text{Å}^3) = 558.6(4)$
Radiation: Pd filtered AgK α (0.56087 Å)
No. of reflection for lattice parameters: 43
θ -range for lattice parameters (deg): 10.03–24.89
Diffractometer: Hilger & Watts
Collection method: learnt profile (Clegg 1981)
Absorption correction: analytical
Absorption coefficient (mm^{-1}): 6.807
Reflections measured: 3983
No. of independent reflections: 1336 of which 1114 observed
$\theta_{\text{max}}(\text{deg}) = 25$
$R_{\text{int}} = 7.9\%$
No. of standard reflections and the interval: 3/30
Variation of the standards: <10%
Criterion for observed: $I > 3\sigma(I)$
$h_{\text{min,max}}: -7, 7$
$k_{\text{min,max}}: -7, 7$
$l_{\text{min,max}}: 0, 32$

Influence of the superposition structure. An analysis of the correlation matrix revealed strong correlations (0.90–0.98) between certain parameters. These atomic parameters correspond to atoms which repeat with the periods of a fictitious structure called superposition structure (also average structure, see Appendix). This holds in the cronstedtite structure for all atoms of the octahedral sheet, which represents 70% of the total diffraction power and causes the family diffraction to be very strong compared with the characteristic polytype diffractions so that the latter have very small influence in the refinement process.

To circumvent this problem, the refined parameters were divided into five groups (blocks). The first consisted of the scale factor and the rest was as follows (see Table 3 for atom labelling): i) O1, O2, O3; ii) O4, T2, M3, OH2; iii) M2, OH1, OH4 and finally, iv) O5, T1, M1 and OH3, respectively; i.e., the atoms repeating with the subcell periods (Appendix) were separated into separate blocks. Because the block-diagonal refinement converged slowly, many cycles were necessary to achieve a satisfactory level of convergence. Nevertheless, the parameters were stable in the course of refinement. The block-diagonal refinement ended with $R_w(\text{all}) = 4.8\%$, $R(\text{all}) = 7.3\%$ and goodness-of-fit index S was equal to 3.4. (See Table 3 for the atomic coordinates at this stage.) A few subsequent cycles with full matrix confirmed stability of the refinement. But the main trouble with the results were the occupancy factors of the octahedral Fe atoms (1.15–1.16).

Influence of disorder. A residual electron-density map at the level involving (in part) basal oxygen atoms and tetrahedral cations revealed systematic phenomena which can be explained with the help of Figure 1. A

Table 3. Atomic coordinates resulting from the final full-matrix refinement (FM), from the preliminary block-diagonal refinement (BD), their comparison with an ideal OD model, occupancy and anisotropic temperature factors. O1, O2, O3 = basal oxygen atoms, T1, T2 = tetrahedrally coordinated atoms, O4, O5 = apical oxygen atoms, M1, M2, M3 = octahedrally coordinated Fe atoms.

Coordinates								
Atom	x_{FM}	x_{BD}	x_{id}	y_{FM}	y_{BD}	y_{id}	z_{FM}	z_{BD}
O1	.7836(12)	.7877(18)	.7826	.1122(12)	.1121(17)	.1111	.0061(3)	.0076(4)
O2	.2242(12)	.2247(17)	.2222	.6721(12)	.6740(18)	.6715	.0069(3)	.0082(4)
O3	.6639(12)	.6612(17)	.6618	.5503(12)	.5475(19)	.5507	.0062(3)	.0076(4)
T1	.8913(5)	.8915(6)	.8889	.4447(6)	.4455(6)	.4444	.03158(7)	.03316(7)
T2	.5564(2)	.5565(3)	.5555	.7781(2)	.7782(3)	.7778	.03158(7)	.03319(7)
O4	.8913(12)	.8924(10)	.8889	.4407(12)	.4435(10)	.4444	.1139(2)	.1160(3)
O5	.5622(13)	.5624(9)	.5555	.7816(12)	.7819(10)	.7778	.1138(2)	.1159(3)
OH1	.2214(13)	.2235(10)	.2222	.1129(13)	.1143(9)	.1111	.1151(2)	.1165(3)
M1	.8909(2)	.8911(2)	.8889	.1132(5)	.1136(2)	.1111	.16500 ¹	.16620(5)
M2	.2258(2)	.2258(2)	.2222	.7784(4)	.7792(2)	.7778	.16335(6)	.16503(5)
M3	.5607(2)	.5603(2)	.5555	.4481(4)	.4482(2)	.4444	.16341(6)	.16500 ¹
OH2	.5580(14)	.5568(13)	.5555	.1124(13)	.1124(12)	.1111	.2116(2)	.2135(3)
OH3	.2225(14)	.2229(10)	.2222	.4420(13)	.4433(10)	.4444	.2116(3)	.2134(3)
OH4	.8923(13)	.8915(10)	.8889	.7814(12)	.7807(10)	.7778	.2114(2)	.2134(2)

Temperature factors						
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1	.033(2)	.034(2)	.0011(1)	.016(2)	.0011(4)	-.0000(4)
O2	.032(2)	.034(2)	.0011(1)	.017(2)	.0007(4)	.0007(4)
O3	.032(2)	.033(2)	.0011(1)	.016(2)	.0002(4)	.0003(4)
T1	.0062(8)	.0063(8)	.00070(5)	.0032(4)	.00039(7)	.00026(8)
T2	.0056(8)	.0057(8)	.00059(5)	.0028(5)	-.00087(11)	.0004(2)
O4	.008(1)	.009(1)	.0012(1)	.005(1)	.0010(4)	.0003(4)
O5	.009(2)	.010(2)	.0012(1)	.005(1)	.0011(4)	.0007(4)
Fe1	.0057(3)	.0056(2)	.00105(2)	.0027(2)	.00074(7)	.00049(9)
Fe2	.0055(3)	.0056(3)	.00104(2)	.0028(2)	.00081(7)	.00062(8)
Fe3	.0048(3)	.0050(3)	.00104(2)	.0022(2)	.00082(6)	.00057(11)
OH1	.010(2)	.007(1)	.0013(1)	.004(1)	.0006(4)	.0004(4)
OH2	.011(2)	.012(2)	.00061(9)	.006(1)	.0009(5)	.0003(5)
OH3	.014(2)	.014(2)	.00073(10)	.009(1)	.0004(4)	.0001(4)
OH4	.009(2)	.011(2)	.00077(12)	.004(1)	.0002(4)	.0001(4)

¹ The origin-fixing coordinate along z. Occupancy factors: T1: 0.75(1) Si + 0.25 Fe, T2: 0.76(1) Si + 0.24 Fe, M1: 1.048(9), M2: 1.040(9), M3: 1.033(9).

Table 4a. Tetrahedral bond lengths and angles.

Bond lengths (Å)			Bond angles (°)		
Tetrahedron T1					
T1-O1	1.704(7)	O4-O1	2.799(8)	O4-O1	107.9(3)
-O2	1.703(5)	O4-O2	2.803(7)	O4-O2	108.2(3)
-O3	1.708(8)	O4-O3	2.822(9)	O4-O3	109.0(4)
-O4	1.757(5)	Mean (apical)	2.808	Mean	108.4
Mean	1.718	O1-O2	2.808(7)	O1-O2	111.0(4)
		O2-O3	2.806(9)	O2-O3	110.7(3)
		O1-O3	2.796(11)	O1-O3	110.0(3)
		Mean (basal)	2.803	Mean	110.6
Tetrahedron T2					
T2-O1	1.713(5)	O5-O1	2.805(7)	O2-O3	107.9(3)
-O2	1.700(6)	O5-O2	2.813(8)	O5-O2	108.9(3)
-O3	1.718(8)	O5-O3	2.814(9)	O5-O3	108.2(3)
-O5	1.757(5)	Mean (apical)	2.811	Mean	111.1
Mean	1.722	O1-O2	2.803(7)	O1-O2	110.6(3)
		O2-O3	2.813(11)	O2-O3	110.8(3)
		O1-O3	2.819(9)	O1-O3	110.4(3)
		Mean (basal)	2.812	Mean	110.6

Table 4b. Octahedral bond lengths (Å).

Octahedron M1			
	M1-O4		2.105(7)
	-O5		2.119(5)
	-OH1		2.107(8)
	-OH2		2.082(8)
	-OH3		2.070(5)
	-OH4		2.079(8)
	Mean		2.094
O5-OH2	2.777(9)	O5-O4	3.138(9)
O4-OH2	2.769(7)	O5-OH1	3.138(8)
O4-OH3	2.767(9)	O4-OH1	3.132(9)
OH1-OH3	2.741(9)	OH4-OH2	3.167(10)
OH1-OH4	2.744(7)	OH2-OH3	3.164(8)
O5-OH4	2.763(9)	OH3-OH4	3.145(9)
Mean (shared)	2.760	Mean (unshared)	3.147
Octahedron M2			
	M2-O4		2.128(5)
	-O5		2.123(7)
	-OH1		2.118(8)
	-OH2		2.102(8)
	-OH3		2.109(8)
	-OH4		2.108(8)
	Mean		2.115
O4-OH4	2.800(9)	O4-OH1	3.200(10)
OH4-OH1	2.744(7)	O4-O5	3.194(9)
OH1-OH2	2.771(10)	O5-OH1	3.200(8)
O5-OH2	2.777(9)	OH4-OH2	3.169(10)
O5-OH3	2.800(7)	OH2-OH3	3.191(9)
O4-OH3	2.767(9)	OH3-OH4	3.188(9)
Mean (shared)	2.777	Mean (unshared)	3.190
Octahedron M3			
	M3-O4		2.121(7)
	-O5		2.113(7)
	-OH1		2.122(5)
	-OH2		2.107(8)
	-OH3		2.110(8)
	-OH4		2.095(5)
	Mean		2.111
OH1-OH3	2.741(9)	OH1-O5	3.184(8)
OH3-O5	2.800(7)	O4-O5	3.190(9)
O5-OH4	2.763(9)	O4-OH1	3.190(10)
O4-OH4	2.800(9)	OH2-OH3	3.166(8)
OH2-O4	2.769(7)	OH3-OH4	3.188(9)
OH1-OH2	2.771(10)	OH2-OH4	3.185(10)
Mean (shared)	2.774	Mean (unshared)	3.184

unit slab containing these two types of atoms is shown at the top. The corresponding superposition structure is at the centre. Here, the tetrahedral cations generate additional "atoms" at the origins whereas the basal oxygen atoms generate characteristic triples of "atoms" located at corners of equilateral triangles. The size of these triangles depends on the deviations of the actual structural model from the idealized Pauling model: the greater is the ditrigonalization, the smaller become these triangles. A comparison with the difference Fourier map (a section which involves, in part, basal O atoms as well as tetrahedral cations) at the bottom of Figure

1 shows a nice coincidence of residual maxima with the superposition structure. This effect can be explained by an assumption that the family diffractions were at a higher scale than the characteristic polytype diffractions so that the difference Fourier map shows simply the rest of the superposition structure. The reason for different scales of the two types of diffractions might be a slight disorder of the investigated crystal which causes streaking of the characteristic polytype diffractions and reducing thus their intensities relative to the family diffractions when measured together in a single diffractometer run.

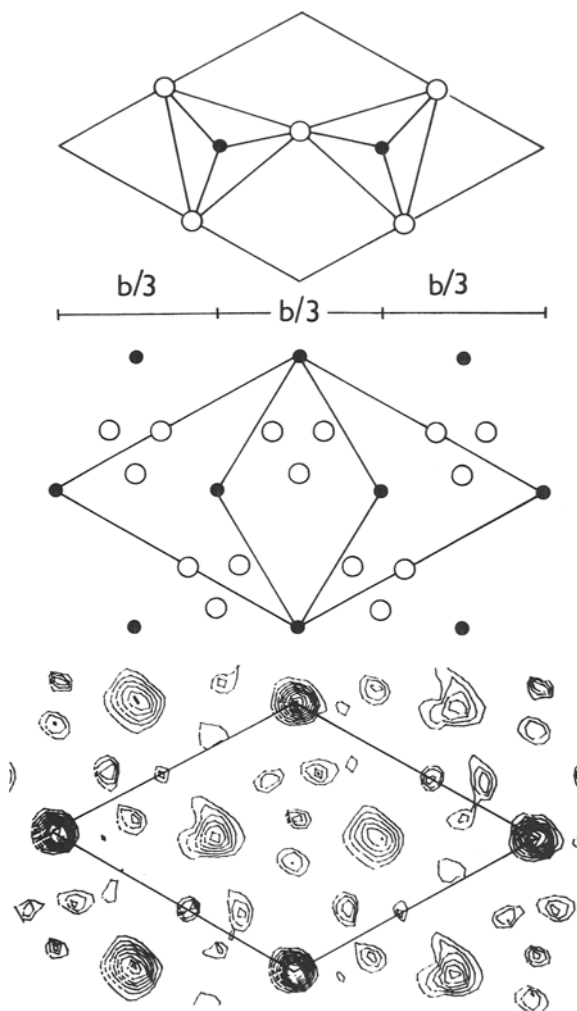


Figure 1. A slab within the cronstedtite structure containing basal oxygen atoms (open circles) and the nearest tetrahedral cations (full circles) is shown at the top. The corresponding part of the superposition structure and of the residual electron-density map for the structure refinement when all diffractions were treated with the same scale factor, are shown at the center and bottom, respectively, $b = a\sqrt{3}$.

Additional precession photographs were taken. Strong overexposure revealed faint streaks on the characteristic polytype diffractions (Figure 2), which was not obvious previously. An additional attempt to refine the cronstedtite structure involved full matrix technique but with two scale factors, the first for the family diffractions (i.e., with h, k such that $\text{mod}(h-k, 3) = 0$) whereas the second scaled the characteristic polytype diffractions. The refinement converged smoothly to $R_w(\text{all}) = 3.1\%$, $R(\text{all}) = 5.0\%$ and $S = 2.32$; the scale factors refined to significantly different values of 3.97(3) and 4.79(3), respectively. For this refinement, the origin of the structure was shifted to the screw triad which is closer to the origins of individual packets than in

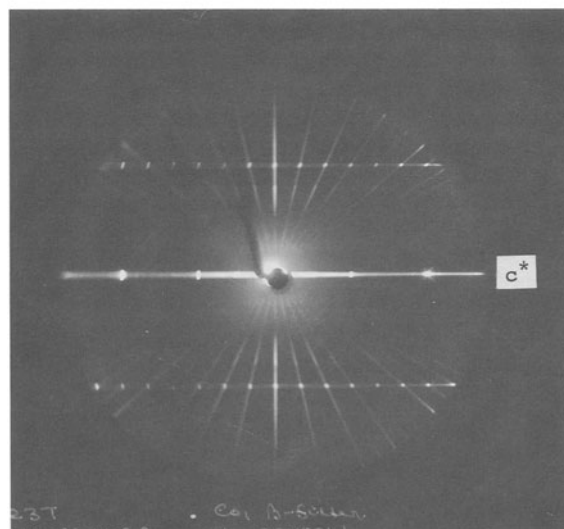
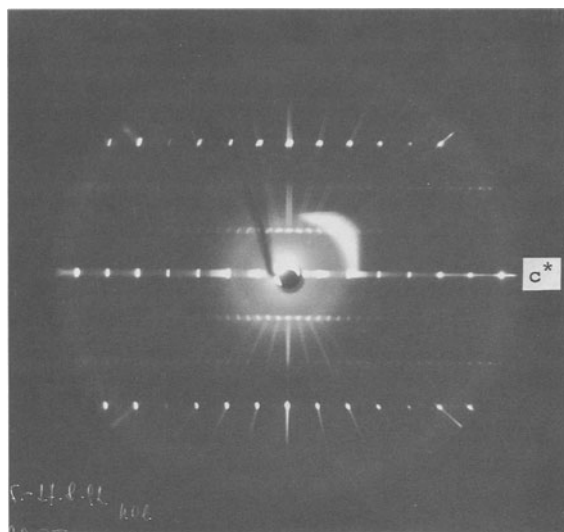


Figure 2. $[h0l]$ precession photographs of cronstedtite-3T: (a) taken with $\text{MoK}\alpha$ radiation; note the difference in intensity of family and characteristic polytype diffractions; (b) taken with $\text{CoK}\alpha$ radiation; note the diffuse streaks along the $10l$ row.

the model of Steadman and Nuttall (1963), in accordance with Bailey (1969).

RESULTS AND DISCUSSION

Final atomic coordinates together with coefficients of anisotropic thermal vibrations are in Table 3. Selected interatomic distances and bond angles are in Table 4. The table of observed and calculated structure factors can be obtained from the third author (V.P.) on request. Figure 3 shows a schematic representation of this polytype following the symbolism of Dornberger-Schiff and Đurovič (1975a, 1975b).

As it follows from the mean bond lengths in Table

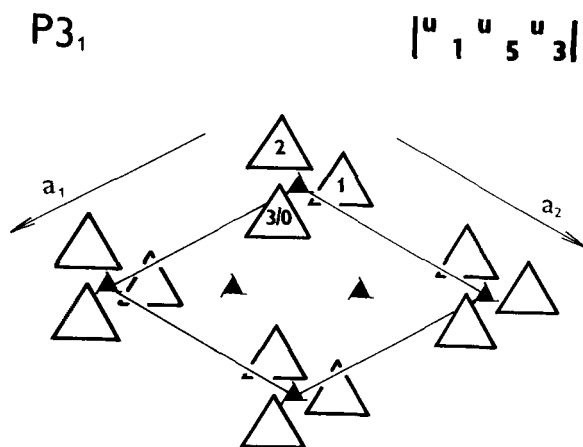


Figure 3. Pictorial representation of the arrangement of OD packets in the present structure of cronstedtite-3T. The individual packets corresponding roughly to 1:1 cronstedtite layers with origins at the centers of ditrigons formed by basal oxygen atoms, are represented by equilateral triangles and they are numbered according to their sequence in the structure. The origin of the 0-th packet is at $\frac{2}{3}$, $\frac{1}{3}$ relative to the nearest three-fold screw axis. The space group and the descriptive symbol of this polytype, are also given.

4, octahedral sheet of the cronstedtite 3T is geometrically meso-octahedral with M2 and M3 octahedra significantly larger than M1 although all octahedra are occupied by Fe. To explain this, the distribution of Fe^{3+} and Fe^{2+} has been investigated using partial octahedral bond lengths according to Weiss *et al* (1992): $\text{Fe}^{3+} - \text{A} = 2.047 \text{ \AA}$ and $\text{Fe}^{2+} - \text{A} = 2.110 \text{ \AA}$ (A is defined as an "average" anion $(2\text{O} + 4\text{OH})/6$). The proportion of Fe^{2+} in an octahedral position can be calculated by the equation

$$x_{\text{Fe}^{2+}} = [d(\text{M}-\text{A}) - 2.047]/0.06.$$

If a small amount of Mg and Al in the octahedra (determined by microprobe analysis) is neglected, the following distribution results: M1: $\text{Fe}_{0.73}^{2+}\text{Fe}_{0.27}^{3+}$, M2: Fe^{2+} , M3: Fe^{2+} . Partial cation-anion bond lengths for octahedral Al and Mg (1.920 and 2.076 \AA , respectively) are shorter than 2.11 \AA and, therefore, the small amount of Al and Mg can occupy only the M1 position. The observed bond lengths $d(\text{M2}-\text{A})$ and $d(\text{M3}-\text{A})$ are just in agreement with the partial bond lengths derived for Fe^{2+} . The distribution of cations in the octahedral sheet of cronstedtite 3T assumed under these circumstances is given in Table 5.

The degree of distortion of the octahedral sheet can be evaluated from the characteristics of the three octahedra (Table 7). They are flattened (for an ideal octahedron $\Psi = 54.74^\circ$) with a small counter-rotation angle δ . Differences between individual octahedra are small and the entire octahedral sheet is only slightly distorted.

The distribution of Fe^{3+} and Si in the tetrahedra T1

Table 5. Cations in octahedral positions.

Position	Al	Mg	Fe^{3+}	Fe^{2+}	$d(\text{M}-\text{A})$ ref.	[\AA] pred.
M1	0.02	0.02	0.23	0.73	2.094	2.091
M2	—	—	—	1.00	2.115	2.110
M3	—	—	—	1.00	2.111	2.110
M ¹	0.02	0.02	0.23	2.73	—	—
M ²	0.02	0.02	—	2.96	—	—

¹ M1 + M2 + M3.

² Coefficients in the crystallochemical formula unit; all Fe was calculated as Fe^{3+} .

ref. = $d(\text{M}-\text{A})$ for individual octahedra based on refined atomic coordinates; pred. = $d(\text{M}-\text{A})$ predicted from the chemical composition of individual octahedra according to Weiss *et al* (1992).

and T2 was also calculated by using partial bond lengths (Weiss 1992) derived for phyllosilicate structures (Table 6). The agreement of the calculated amounts of Fe and Si with that, based on the crystallochemical formula is fair.

The ditrigonalization angle (Radoslovich 1961) is relatively high ($\alpha = 11.77^\circ$, Table 7) and this polytype belongs to the Franzini type A (Franzini 1969). Steadman and Nuttall (1963) obtained for the 3T polytype $\alpha = 8^\circ$. The two tetrahedra are relatively regular (cf. the tetrahedral edge-lengths in Table 4a), however, both of them exhibit larger apical $d(\text{T}-\text{O})$ than the basal ones.

Table 3 gives also x and y coordinates in an ideal OD model constructed so that any individual 1:1 layer has the symmetry $P(3)1m$ with all atoms in special positions: O_{bas} , T, O, OH1, M and OH2-OH4 at (Wyckoff) $3c$ ($x = \frac{1}{2} + \Delta x$), $2b$, $2b$, $1a$, $3c$ ($x = \frac{2}{3}$) and $3c$ ($x = \frac{1}{3}$), respectively. The only variable parameter is Δx of O_{bas} which determines the ditrigonalization angle; for the Table 3 it has been chosen as the mean value (0.0604) determined from the refined coordinates (see also Figure 3 for the choice of the origin of the entire polytype). The z coordinates are irrelevant for the symmetry of this polar group provided that O_{bas} , T, O_{ap} , M and OH2-OH4 are at the same z-levels, respectively. A comparison with the atomic coordinates in the refined structure shows that the deviations are in the range 0.002–0.040 \AA . This very low desym-

Table 6. Cations in tetrahedral positions.

Position	$d(\text{T}-\text{O})$ (\AA)	Distribution calculated according to Weiss <i>et al</i> (1992) ¹	
		Fe^{3+}	Si
T1	1.718	0.31	0.63
T2	1.722	0.39	0.61
T1 + T2		0.76	1.24
T ²		0.74	1.26

¹ Calculated as $x_{\text{Fe}^{3+}} = (d(\text{T}-\text{O}) - 1.616)/0.274$.

² Coefficients from half-cell crystallochemical formula.

Table 7. Characteristics of tetrahedral and octahedral sheets in 3T cronstedtite.¹

Tetrahedra		
	$\alpha = 11.77$	
$d(T1-O) = 1.718$		$d(T2-O) = 1.722$
$\Delta z = 0.02$		$\Delta z = 0.02$
$e(T1) = 2.806$		$e(T2) = 2.811$
Octahedra		
$d(M1-A) = 2.094$	$d(M2-A) = 2.115$	$d(M3-A) = 2.111$
$\psi(M1) = 60.3$	$\psi(M2) = 60.6$	$\psi(M3) = 60.5$
$\delta(M1) = 0.14$	$\delta(M2) = 0.75$	$\delta(M3) = 0.89$
$e(M1) = 2.954$	$e(M2) = 2.983$	$e(M3) = 2.979$

¹ $d(T-O)$ = mean cation–oxygen bond length (Å); Δz = tetrahedral tilt (Å); $e(T)$ = mean edge length (Å); α = tetrahedral rotation angle (°); $d(M-A)$ = mean cation–anion bond length (Å); $\psi(M)$ = flattening angle (°); $\delta(M)$ = counter-rotation angle (°) (see Weiss *et al* 1985); $e(M)$ = mean octahedral edge (Å).

metrization might explain the strong tendency of cronstedtites to form twins and disordered polytypes, because the partial symmetry typical for OD structures, which ensures the geometrical (and thus also energetic) equivalence of pairs of adjacent OD layers in all their possible positions (see e.g., Dornberger-Schiff and Ďurovič 1975a; Appendix), is then nearly perfect.

Especially interesting is the fact that the Fe cation at M1 lies by 0.035 Å higher than the remaining two Fe cations at M2 and M3. A possible explanation might be the stacking mode in the subfamily A which is such that the two tetrahedral cations within the layer above the given one exactly superimpose (in the projection along z) with the two octahedral cations at M2 and M3. There is an empty center of the ditrigonal ring above M1 so that no repulsive forces are exercised upon a cation at M1. This effect cannot be observed in the subfamilies C and D (Bailey 1969).

CONCLUDING REMARKS

Refinement of a polytypic structure with a “strong” superposition structure is still a problem which deserves more attention in the future. Routine measurement of intensities by a single-crystal diffractometer may lead to incorrect values for weak diffractions which are diffuse in the reciprocal space, and that these should be measured so that the streaks will cut the Ewald sphere in an equal and appropriate way.

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APPENDIX

Any family of OD structures of layers with rational shifts of adjacent layers, can be assigned a *superposition structure* which can be obtained if all possible positions of any OD layer are realized simultaneously (Dornberger-Schiff 1964). It

is a fictitious structure whose symmetry is obtained by completing any of the family groupoids to a group (Fichtner 1977). A superposition structure is by definition three-dimensionally periodic and common to all, even disordered structures belonging to the family. The corresponding diffractions (the *family diffractions*) are thus always sharp, common and characteristic for the family (Ďurovič 1992).

The set of polytypes of the serpentine-kaolin group splits into four groups (A, B, C, D) depending on the kind of the interlayer shifts. This has been recognized by Zvyagin (1967) and Bailey (1969) on the basis of calculated diffraction patterns for all trioctahedral standard (MDO) polytypes; those belonging to the same group have the same set of diffractions with $\text{mod}(h-k, 3) = 0$ (hexagonal) or $\text{mod}(k, 3) = 0$ (orthogonal). In a latter study (Mikloš and Ďurovič 1978) it has been shown that each of these groups has its characteristic superposition structure; the groups themselves are referred to as *subfamilies*. The rows of the family diffractions $11l$ (hex) or $20l$ (ort) are important for identification purposes (Ďurovič 1981).

The structure of cronstedtite-3T belongs to the subfamily A with interlayer shifts $a/3$, its superposition structure has the space group $H_R 31m$ and basis vectors $A_1, A_2, 3C_0$, where C_0 is the “width” of one layer. The subscript R indicates the possibility of selecting a smaller rhombohedral subcell (hexagonal axes) with basis vectors $A_1 = \frac{1}{2}(A_1 + 2A_2)$, $A_2 = \frac{1}{2}(2A_1 + A_2)$, $C = 3C_0$. This structure can be derived schematically with the help of Figure 3, by adding to any equilateral triangle representing an OD packet with symmetry $P(3)1m$ and position xyz , two additional triangles at $x + \frac{1}{3}, y + \frac{2}{3}, z$ and $x + \frac{2}{3}, y + \frac{1}{3}, z$, at every level z , i.e., $z = 0, \frac{1}{3}$ and $\frac{2}{3}$. In this way all possible positions are occupied, all partial triads as well as all partial mirror planes become total, so that this set of symmetry operations becomes a group. The structure is H centered (see *International Tables for Crystallography* (1992), Vol. A, p. 5). The unit cell of this superposition structure, related to hexagonal basis vectors $A_1, A_2, 3C_0$ is 9-fold, centered with points $(0, 0, 0; \frac{2}{3}, \frac{1}{3}, 0; \frac{1}{3}, \frac{2}{3}, 0) + [(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}), (\frac{2}{3}, \frac{2}{3}, \frac{2}{3})]$ which implies that only the diffractions with $\text{mod}(h-k, 3) = 0 \wedge \text{mod}(h+k+1, 3)$ are present as family diffractions.

A simple calculation shows that the electron density distribution within the superposition structure

$$\begin{aligned} \hat{\rho}(xyz) &= \frac{1}{3}[\rho(x, y, z) + \rho(x + \frac{1}{3}, y + \frac{2}{3}, z) \\ &\quad + \rho(x + \frac{2}{3}, y + \frac{1}{3}, z)] \\ &= \frac{1}{V} \sum_{h-k=3n} F(hkl) \exp[2\pi i(hx + ky + lz)] \end{aligned}$$

i.e., a Fourier synthesis calculated with family diffractions only, describes the superposition structure assigned to the

actual structure $\rho(xyz)$. Evidently, all atoms repeating in the actual structure with the periods of the superposition structure, contribute solely to the family diffractions: the greater is the diffraction power of these atoms, relative to the remaining ones, the stronger are the family diffractions, and the influence of the weaker remaining diffractions, in the full-matrix least-squares refinement process, decreases. Increasing correlation coefficients between parameters of atoms repeating with the periods of the superposition structure is the consequence.

The extinction rules mentioned above hold only for an ideal OD structure with symmetry of individual OD packets exactly $P(3)1m$ and interlayer shifts exactly $a/3$. Experience shows that the structures of real polytypes deviate almost always from the ideal OD model, desymmetrization of OD structures (Đurovič 1979). The periods of the superposition structure for some atoms may become only *pseudoperiods* and these atoms contribute then partially to all diffractions, reducing thus the intensities of the family diffractions and enhancing the intensities of the remaining ones. This improves the conditions for a full-matrix least-squares refinement. The structure of the cronstedtite-3T deviate only slightly from the ideal OD model (Table 3) but this shows up already by the presence of very weak (but measurable) diffractions on the reciprocal rows with $\text{mod}(h-k, 3) = 0$ at the points for which $\text{mod}(h+k+1, 3)$.

The homo-octahedral polytypes are closer to the ideal OD model than the meso- or hetero-octahedral ones, because the symmetry of their octahedral sheets is closer to $H(3)1m$ since these are less distorted.

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