CRONSTEDTITE-1*M* AND CO-EXISTENCE OF 1*M* AND 3*M* POLYTYPES

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An individual single crystal of cronstedtite-1M has been identified in a specimen from Eisleben (Saxony). Its quality, however, does not allow for a structure refinement. If cronstedtite-1M coexists with cronstedtite 3T in the same crystal, it "monoclinizes" its single-crystal diffraction pattern. These two polytypes cannot be distinguished by powder diffraction.

INTRODUCTION

Cronstedtite-1*M* is one of the twelve MDO polytypes (called also "standard" or "regular" polytypes) existing within the homo-octahedral family of the serpentine-kaolinite group of phyllosilicates. It belongs, together with exceptionally rare 2*M*$_1$ and relatively abundant 3*T* (polytype), to subfamily **A** with the same stacking principle [1]. The general formula of cronstedtite is $Fe_3[(Si,Fe)O_5](OH)_4$. The first evidence on 1M was brought by Steadman and Nuttall [2] who found intergrowths of 3*T* and 1*M*, the latter manifesting itself by enhancing the intensities of certain characteristic polytype diffractions of 3*T* (these diffractions coincide exactly in both polytypes).

Bailey [3] reporting about his own unpublished results mentions 3*T* crystals "having an apparent monoclinic symmetry ... perhaps as a result of twinning ...". This statement is consistent with that of Steadman and Nuttall [2].

Mikloš [4] screened 30 cronstedtite crystals from various localities and labelled the crystal CR-8 from the specimen of Eisleben (Saxony) as 1*M*, however, without an intelligible X-ray documentation and without any comment.

Petrova [5] and Varček *et al.* [6] claimed to have identified all cronstedtite crystals from Rožňava (Slovakia) as 1*M*. These works, however, contain no diffraction photographs supporting this find and, moreover, two crystals from this locality, supplied for diffractometric studies, turned out to be 1*T* [Petříček: private communication].

Coey *et al.* [7] published the results of their measurements of electrical and magnetic properties of cronstedtite, by using 1*M* polytype. The trouble is, however, that they identified this polytype by indexing powder patterns of their specimens, and this is ambiguous: powder patterns of 3T, but even of disordered polytypes of the subfamily **A** might lead to the same conclusions (see below).

A re-examination of the Mikloš's CR-8 crystal by precession method revealed that it is indeed an 1*M* polytype. It is the aim of this paper to present the experimental evidence of this find, together with a structural background of the often observed common occurrence of polytypes 1*M* and 3*T*, and with a discussion of the corresponding diffraction patterns.

EXPERIMENTAL EVIDENCE

The procedure leading to the identification of an MDO polytype of a phyllosilicate from its single-crystal diffraction pattern, has been described in detail in [1] - cronstedtite being used as an example. It has been shown that the distribution of intensities along the reciprocal row 20*l* (orthogonal indexing *h*, *k*; 11*l* for hexagonal indexing *h*, *k*) enables the determination of the subfamily which, together with the distribution along the row $02l_{\mathrm{ort}}$ ($11l_{\mathrm{hex}}$) determines unambiguously the MDO polytype - simply by a visual inspection of the corresponding diffraction photograph and by using the classification table (table 1). The identification diagrams calculated for $Fe_3[Si_{0.76}Fe_{0.24}O_5](OH)_4$ are in figure 1 (for details see below).

Figure 2 shows the precession photographs of the crystal CR-8 from the specimen from Eisleben (Saxony). The distribution of intensities along the reciprocal rows $20l_{\mathrm{ort}}$ ($11l_{\mathrm{hex}}$) in figure 2a and $02l_{\mathrm{ort}}$ ($11l_{\mathrm{hex}}$) in figure 2b, compared to the identification diagrams (figure 1) indicates unambiguously the subfamily **A** and the MDO group I - thus, according to table 1, the polytype 1*M*. Let us emphasize that this is the first description of an individual single crystal of cronstedtite-1*M*. Unfortunately, the characteristic polytype diffractions $0kl_{\mathrm{ort}}$ with

$k \not\equiv 0(mod\ 3)$ (or hkl_{hex} with $-h + k \not\equiv 0(mod\ 3)$) are smeared-out into diffuse streaks so heavily that this crystal cannot be used for a refinement of its crystal structure.

Table 1. Classification table for MDO polytypes of cronstedtite [1]. The polytype belonging simultaneously *e.g.* to the subfamily **C** and MDO group I. is 1*T*, *etc.*

	A	B	C	D
I.	1*M*	2*O*	1*T*	$2H_1$
II.	-	$2M_2$	3*T*	6*R*
III.	$2M_1$	-	2*T*	$2H_2$
IV.	3*T*	-	-	-
V.	-	6*H*	-	-

CO-EXISTENCE OF POLYTYPES 1*M* AND 3*T*

Structural background

The MDO polytypes 1*M*, $2M_1$ and 3*T* belong to the subfamily **A** (group A according to Bailey [8]) of the homo-octahedral (trioctahedral, with identical occupation of the three octahedral positions [9]) family within the serpentine-kaolinite mineral group. In all polytypes of this subfamily, including the non-MDO and also the disordered ones, any individual layer with symmetry $P(3)1m$ (figure 3) is shifted relative to the preceding one by $a/3$ (*i.e.* by $\boldsymbol{a}_{hex}/3$, $\boldsymbol{b}_{hex}/3$ or $-(\boldsymbol{a}_{hex}+\boldsymbol{b}_{hex})/3$) and the octahedral sheets in all layers have the same orientation, see also [10]. Figures 4*a* and 4*b* show the relative position of layers in the polytypes 1*M* and 3*T*, respectively; the layers are represented by equilateral triangles as indicated in figure 3.

Identical geometrical relation between any two adjacent cronstedtite layers in any polytype of the same

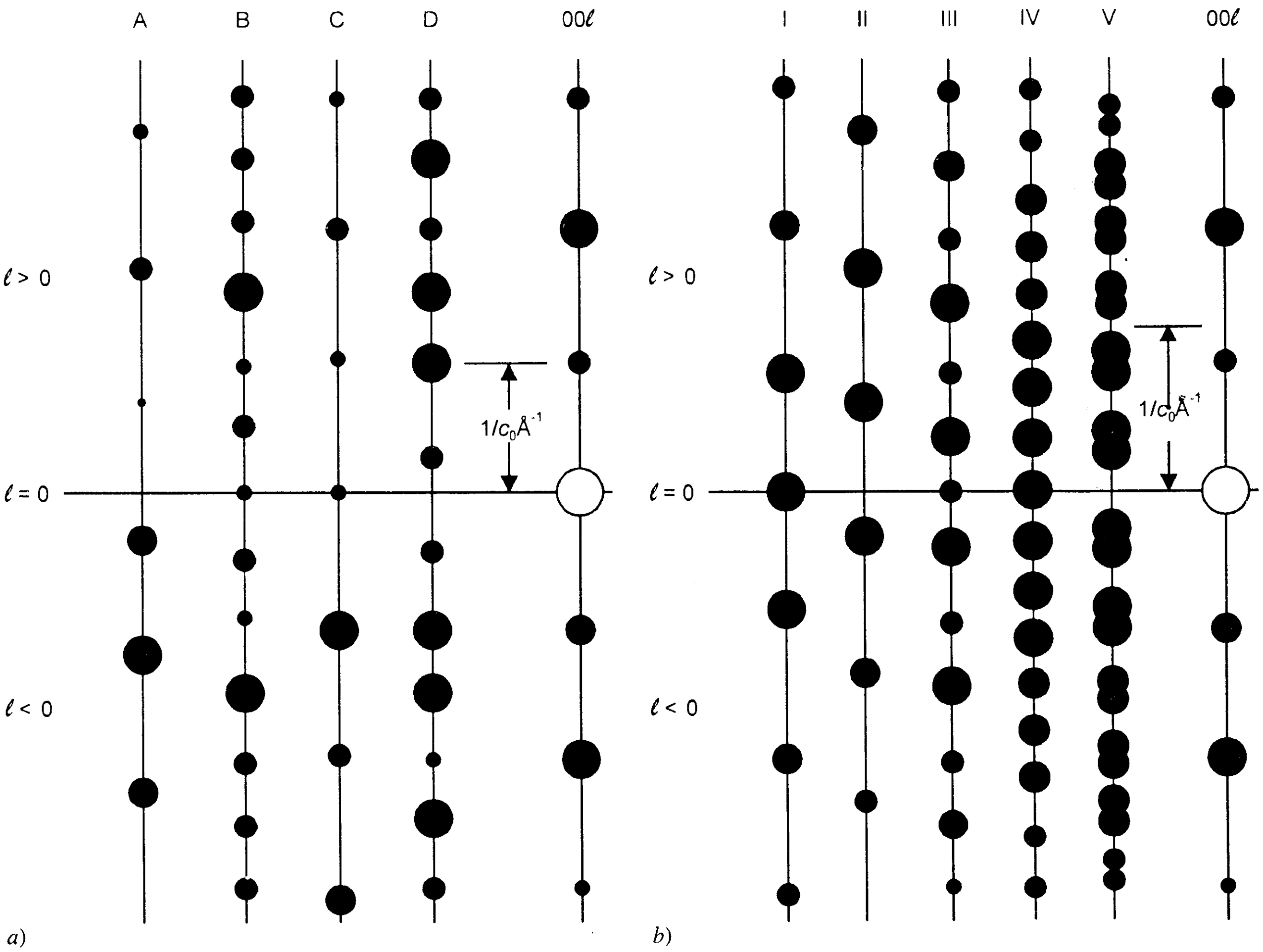

Figure 1. Identification diagrams for MDO polytypes of cronstedtite.
a) distribution of intensities along the reciprocal row $20l_{ort}$ ($11l_{hex}$) in the subfamilies **A** to **D**;
b) The same for $02l_{ort}$ ($11l_{hex}$) in the MDO groups I to V. The sizes of full circles, proportional to $|F(hkl)|^2$, are normalized to the largest $|F(hkl)|^2$ value within the respective reciprocal row (the largest circle). For an orientation, the reciprocal row $00l$ is also shown: the intensity distribution along this row is the same for all cronstedtite polytypes.

subfamily can be formulated so that these pairs are geometrically equivalent. As a consequence, the pairs are energetically equivalent, the individual polytypes differ only by the interactions between next-but-one layers, and these are small in comparison with the interactions between adjacent layers. Thus, a regular stacking of layers characteristic for a given periodic polytype can easily be disrupted by stacking faults and even a stacking, characteristic for a different periodic polytype of the same subfamily can set on. This phenomenon when two or even more polytypes co-exist within one single crystal, or, at least, when a polytype is disordered, is in cronstedtite a commonplace [2, 4], because the structures of its polytypes deviate only very slightly from the corresponding ideal OD models [11, also Hybler, in preparation]. As a matter of fact, it is a rare event to find an ordered cronstedtite crystal.

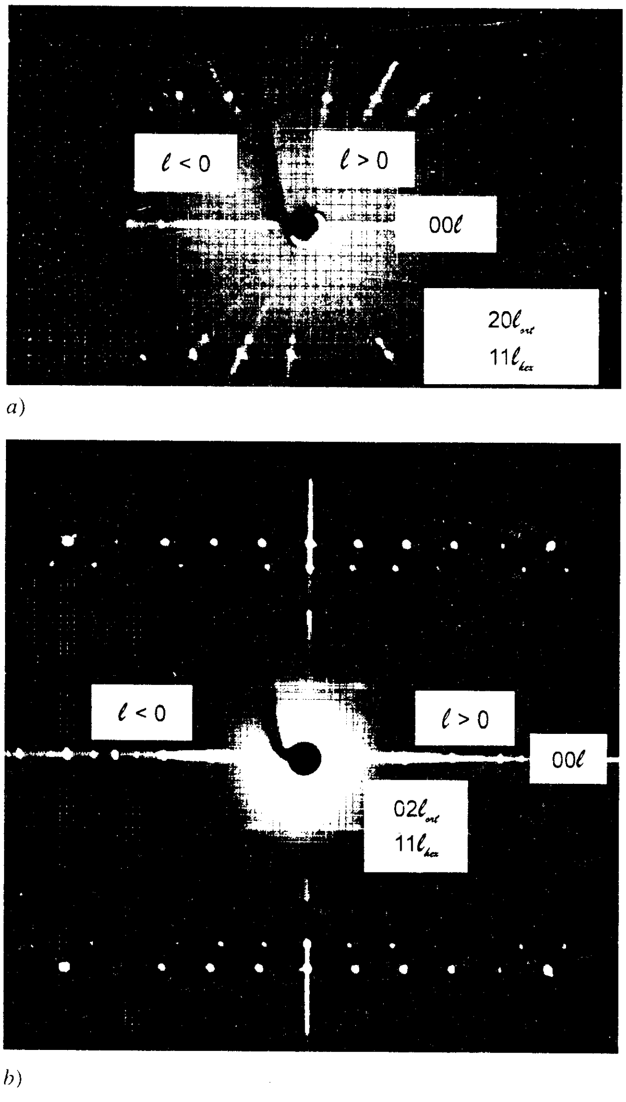

Figure 2. Precession photographs of the crystal CR-8.
a) the section $h0l_{\mathrm{ort}}$ $(hhl)_{\mathrm{hex}}$; *b)* the section $0kl_{\mathrm{ort}}$ $(\bar{h}hl)_{\mathrm{hex}}$. MoK$_{\alpha}$ radiation.

Consequences for diffraction patterns

The conventional unit cell for cronstedtite 1*M* (figure 4*a*) is monoclinic, *C*-centred, with basis vectors $\mathbf{a}_{\mathrm{mon}}$, $\mathbf{b}_{\mathrm{mon}}$, $\mathbf{c}_0$-$\mathbf{a}_{\mathrm{mon}}/3$ (*cf.* figure 3), where $\mathbf{c}_0$ is the vector perpendicular to the layer plane while $|\mathbf{c}_0|$ is the "width" of the layer. Any layer is thus shifted relative to its predecessor by $-\mathbf{a}_{\mathrm{mon}}/3$. For our further consideration we shall take the advantage of the fact that in this structure a *triply primitive cell* with hexagonal geometry and basis vectors $\mathbf{a}_{\mathrm{hex}}$, $\mathbf{b}_{\mathrm{hex}}$, $3\mathbf{c}_0$ can be chosen, identical with that of the polytype 3*T*. The advantage is that there is a simple relation between atomic coordinates in the structures of both polytypes when related to this common cell (no transformation respecting the monoclinic geometry) and, because of the same lattice geometry, the same reciprocal lattice can be used for characterization of the diffraction patterns of both polytypes. Whereas the positions of the individual diffractions coincide, the difference shows up in the symmetry and extinction rules: the Laue group for

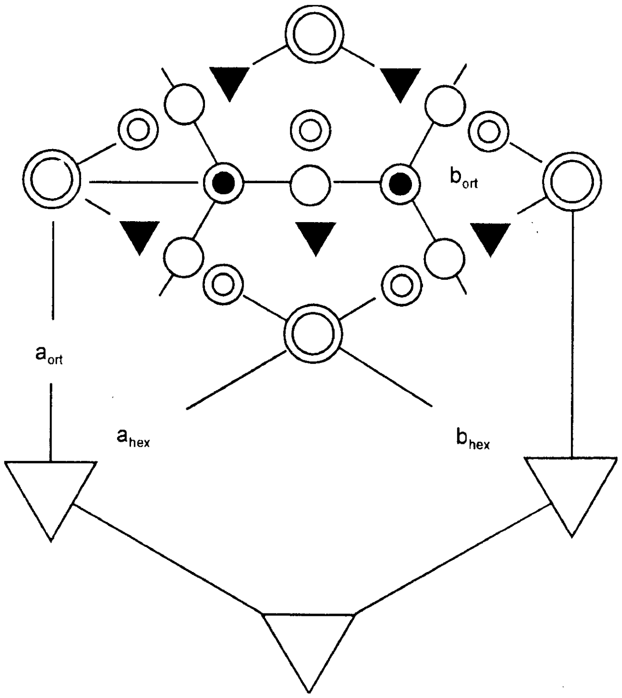

Figure 3. Projection of a cronstedtite layer with symmetry $P(3)1m$ onto the plane a_{hex} b_{hex} (top) and its pictorial representation by equilateral triangles with the same symmetry (bottom). ○ - basal O atoms, ⊙ - tetrahedral cations with apical O atoms above them, ◎ - OH groups at the level of the apical O atoms, ▾ - octahedral cations (Fe), ◎ - OH groups closing the octahedral sheet.

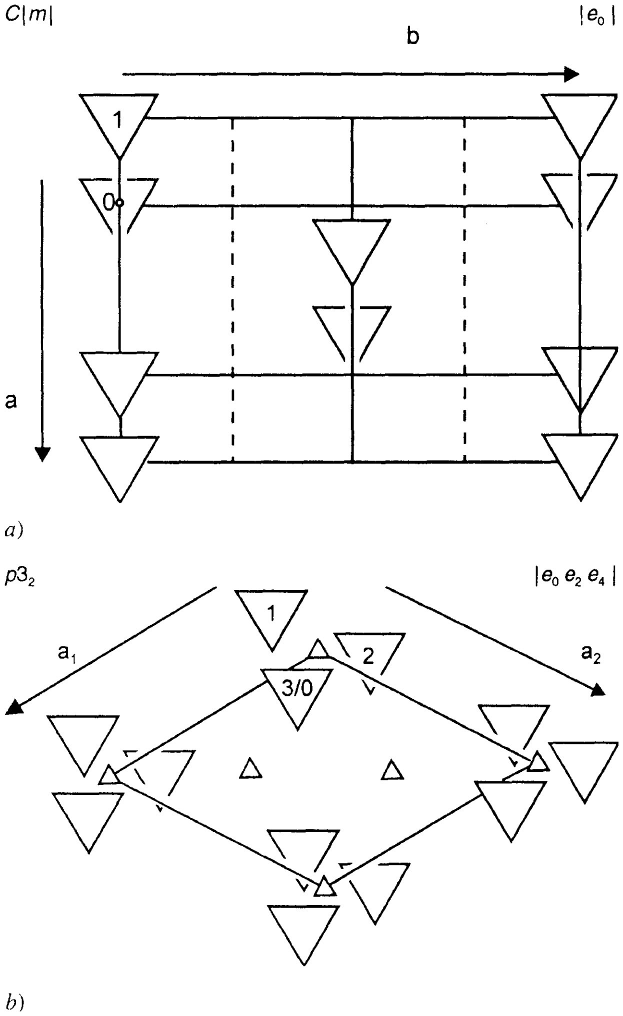

Figure 4. Pictorial representation of two cronstedtite polytypes 1*M* (*a*) and 3*T* (*b*); their space-group symmetry and descriptive symbols according to [10] are also given. The layers are numbered according to their sequence: 3/0 means a coincidence of the 3rd and the 0th layer in the normal projection.

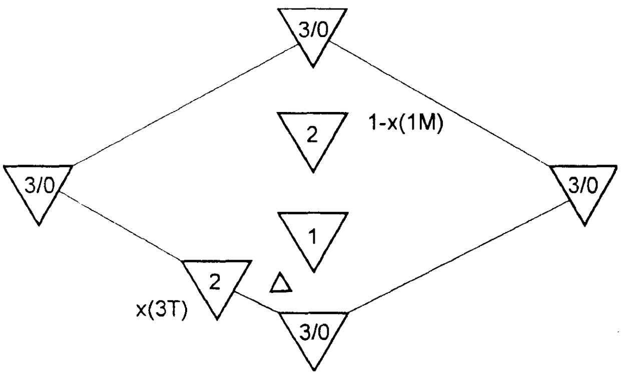

Figure 5. The positions of cronstedtite layers in the polytypes 3*T* and 1*M* related to a common cell with hexagonal geometry. The pictorial representation of individual layers and their numbering is as in figure 4. The expressions *x*(3*T*) and 1-*x*(1*M*) refer to the calculations simulating the diffraction patterns of OD intergrowths of both polytypes in different proportions.

the monoclinic polytype is 2/*m* and the diffractions are present only for $(-h-k+l) \equiv 0(mod\ 3)$; the Laue group for the trigonal polytype is 3 with no systematic absences[1].

The relation between atomic coordinates in both polytypes is (figure 5):

	1*M*	3*T*
0th layer	x,y,z	
common layer pair		
1st layer	$x-1/3,y-1/3,z+1/3$	
2nd layer	$x-2/3,\ y-2/3,\ z+2/3$	$x,\ y-1/3,\ z+2/3$

This model has been used to simulate single-crystal diffraction patterns of OD intergrowths of both 1*M* and 3*T* polytypes. The term "OD intergrowth" means that both polytypes whose constituting layers are stacked according to the scheme described in the previous paragraph (a consequence of the OD character of croustedtite structures) appear in one, *coherently scattering* crystal block. The different proportions of these polytypes have been respected by assigning corresponding occupancies x and $1-x$ to the atoms in the 2nd layer as indicated in figure 5. The results for x = 1.0, 0.7, 0.3 and 0.0 and for the six reciprocal rows closest to c^* are shown in figure 6. It turned out that *already the presence of* 20-30 % *of* 1*M "monoclinizes" significantly the diffraction pattern.* This explains the observations reported by Steadman and Nuttall [2] as well as by Bailey [3].

Figure 7 shows the precession photograph of the crystal CR-8: the section $0kl_{hex}$. The shift of diffuse maxima of the row $01l$ by $1/3|c_0^*|$ confirms the monoclinic symmetry determined by identification diagrams (*cf.* the same row in figure 6*d*).

Results of a considerable didactic value have been obtained by calculating theoretical powder diffraction patterns of the structures mentioned above. Figure 8 shows the patterns of pure 3*T* and 1*M* polytypes as well as of their intergrowth 1:1. The three patterns are *exactly the same*. This is in agreement with Bailey's results [8] that the polytypes 1*M* and 3*T* cannot be distinguished by their powder diffraction patterns. Our results, moreover, show that also powder patterns of OD intergrowths of

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[1] The transformation matrices [12] between basis vectors (and diffraction indices) of the monoclinic cell of 1*M* and the corresponding triply primitive cell with hexagonal geometry are:
MON to HEX (1/2,-1/2,0 / 1/2,1/2,0 / 1,0,3)
HEX to MON (1,1,0 / -1,1,0 / -1/3,-1/3,1/3)
with determinants 3/2 and 2/3, respectively.

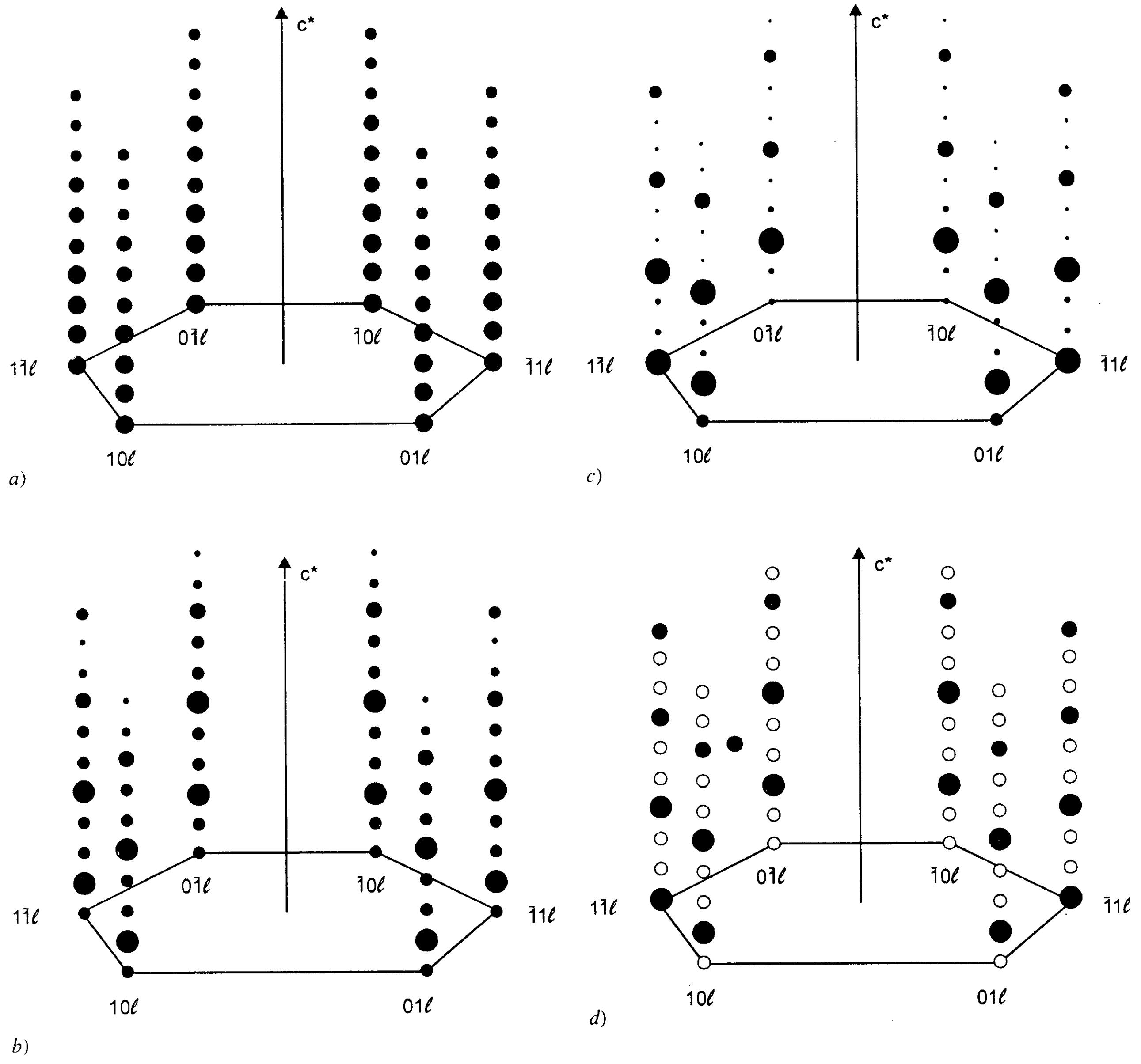

Figure 6. The distribution of intensities along six reciprocal rows closest to c^* for:
a) pure cronstedtite-3*T*; *b)* 0.7x3*T*+0.3x1*M*; *c)* 0.3x3*T*+0.7x1*M*; *d)* pure cronstedtite-1*M*.
The sizes of the full circles, proportional to $|F(hkl)|^2$ are normalized to the largest $|F(hkl)|^2$ value which appear in *d)*. Empty circles indicate here systematically absent diffractions.

both polytypes *in any proportions* (neglecting in this approximation the concentration of stacking faults and the distribution of block sizes, existing in real crystals) are the same. Thus, the identification of the 1*M* polytype by a powder diffraction as stated in [7] is by no means justified.

This phenomenon can be explained by inspecting figures 6*a* and 6*d*. Take *e.g.* the six reciprocal vectors 100, 010, $\bar{1}10$, $\bar{1}00$, $0\bar{1}0$ and $1\bar{1}0$ in the reciprocal lattice of pure 3*T*. They all contribute to the same peak in the powder diffraction pattern with equal $|F(hkl)|^2$ values. On the other hand, there are only two reciprocal vectors with the same length, namely $\bar{1}10$ and $1\bar{1}0$, in the reciprocal lattice of pure 1*M*, but, as the calculations indicate, the $|F(hkl)|^2$ value for each of them is three times as big as the corresponding $|F(hkl)|^2$ values for 3*T*. In this way, two reciprocal vectors in 1*M* "carry" the same intensity as six reciprocal vectors in 3*T*. This consideration holds, in general, for four reciprocal vectors (*l* non-zero) in 1*M* versus twelve reciprocal vectors in 3*T*.

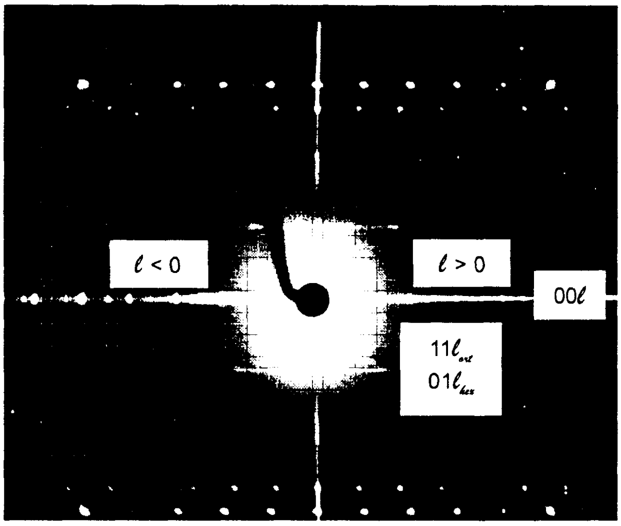

Figure 7. Precession photograph of the crystal CR-8, the section hhl_{ort} $(0kl)_{hex}$. Note the shift of the diffuse maxima on the row $(01l)_{hex}$ by 1/3|c_0| compared with figure 2*b*. MoKα radiation.

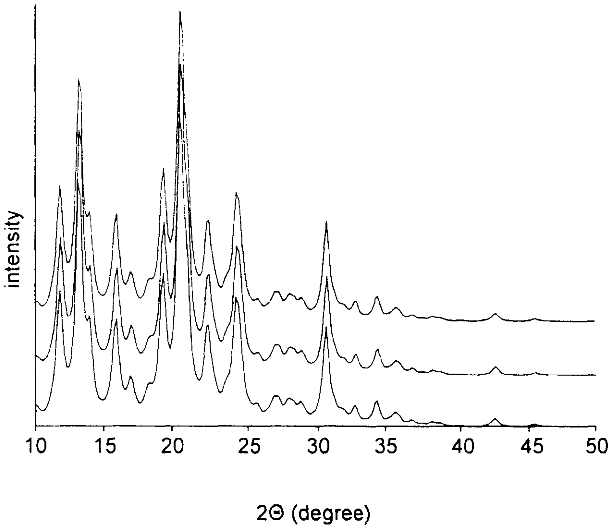

Figure 8. Calculated powder diffraction patterns of pure cronstedtite-3*T* (top), pure cronstedtite-1*M* (bottom) and of their OD intergrowth 1:1 (centre), assuming AgKα_1 radiation.

All calculations have been made by using the program DIFK [13][2] and the ideal Pauling model of a cronstedtite layer shown in figure 3, with *z*-coordinates for a three-layer polytype given in [14]. The character of the problem necessitated the formal usage of the space-group-symmetry *P*1 (all atoms in the unit cell had to be given in the input data) and hexagonal cell with a = 5.497 Å and c = 21.335 Å. Let us emphasize here that this simplification (no ditrigonalization of tetrahedral sheets, neglecting stacking faults as mentioned above) does not influence the general validity of the results thus obtained.

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Submitted in English by the author.

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[2] This program can be obtained free of charge from Dr. Ľ. Smrčok, CSc., Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava, Slovakia; e-mail: uachsmrk@savba.sk.

CRONSTEDTIT-1*M* A KOEXISTENCIA POLYTYPOV 1*M* A 3*M*

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Monokryštál cronstedtitu-1*M* bol identifikovaný vo vzorke z Eisleben (Sasko). Ide o prvý opis individuálneho kryštálu tohoto polytypu, ktorý bol doteraz identifikovaný [2,3] iba v zrastoch s polytypom 3*T*. Kryštál je však natoľko neusporiadaný, že spresnenie jeho štruktúry nie je možné. Neusporiadanosť sa na difrakčných snímkach prejavuje "rozmazaním" difrakčných stôp, charakteristických pre polytyp, v podobe difúznych chvostov v smere c^*.

Zrasty polytypov 1*M* a 3*T* sú dôsledkom toho, že obidva patria do tej istej subfamílie (A) polytypov cronstedtitu, pričom páry všetkých susediacich cronstedtitových vrstiev sú geometricky ekvivalentné, takže zmena kladu vrstiev, charakteristického pre jeden alebo druhý polytyp nastáva aj v rámci koherentne difraktujúcich blokov v kryštáli (OD zrasty).

Pre modelovanie difrakčných obrazov OD zrastov sa využila skutočnosť, že v štruktúre 1*M* možno vybrať bunku s hexagonálnou geometriou, totožnú so základnou bunkou polytypu 3*T*. Výpočty ukázali, že už prítomnosť 20-30 % polytypu 1*M* výrazne "monoklinizuje" monokryštálový difrakčný obraz polytypu 3*T*. Práškové difrakčné obrazy obidvoch polytypov sú identické, ale identické s nimi sú aj práškové difrakčné obrazy OD zrastov s ich ľubovoľným pomerom. Polytypy 1*M* a 3*T* teda nemožno identifikovať pomocou práškovej difrakcie.