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Polymorphism in Cronstedtite

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Single-crystal X-ray diffraction photographs have revealed eight polymorphs of cronstedtite, and the structures of four of them, with space groups $P31m$, $P6_3cm$, $P3_1$ and $R3$, have been determined. All the structures, assumed to have the idealized composition $(Fe^{2+})_3(Fe^{3+}Si)O_4(OH)_5$, are formed from kaolin-type layers, the principal differences being in the manner in which these layers are stacked together. Distortion of the Fe, Si–O, OH tetrahedra is related to the cation–anion attraction either within a layer or between adjacent layers.

Introduction

Cronstedtite is a hydrous ferro-silicate mineral. Gossner (1935) found that its chemical composition and X-ray diffraction pattern were consistent with its having a kaolin-type structure, but the crystal he examined was too disordered to permit a structure determination to be carried out, or even the unit cell to be found with certainty. The composition, expressed as oxides, is as follows:

SiO_2	2·00 mols.
Al_2O_3	0·06
Fe_2O_3	1·36
FeO	4·26
CaO	0·17
H_2O	4·12

Two kaolin-type formulae have been proposed to correspond to this composition. Hendricks (1939) suggested the formula $(Fe^{2+}Fe^{3+}AlCa)_{2-3}(SiFe^{3+})O_4(OH)_5$, and used it in a determination of the structure, and Brindley (1951), whilst regarding the formula given by Hendricks as a possible one, suggested the ideal formula $(Fe^{2+}_2Fe^{3+})(SiFe^{3+})O_5(OH)_4$. In both formulae, it is assumed that the sites of tetrahedral coordination, which in kaolinite are occupied entirely by silicon, are shared equally between silicon and ferric iron. The reduction in tetrahedral-cation valency is balanced, in Hendricks's formula, by replacing oxygen by a hydroxyl ion at the apex of each tetrahedron occupied by ferric iron. Brindley keeps the hydroxyl content of the mineral equal to that of other kaolin-type minerals, but increases the valency of the cations in octahedral coordination to seven, against the normal six. This produces a distribution of cation valency among tetrahedral and octahedral sites identical with that found in amesite (Brindley, Oughton & Youell, 1951).

In the present work structure factors have been calculated using the formula $(Fe^{2+})_3(SiFe^{3+})O_4(OH)_5$, and the diagrams and tables given later correspond to this idealized form of Hendricks's formula, but it is not possible, on the X-ray evidence alone, to distinguish between the two possible formulae discussed above.

The X-ray analysis carried out by Hendricks confirmed that the cronstedtite layers had the kaolin-type structure proposed by Gossner, and showed that they appeared to be stacked together in a rhombohedral manner. The projection of one layer normal to the cleavage plane is shown in Fig. 1.

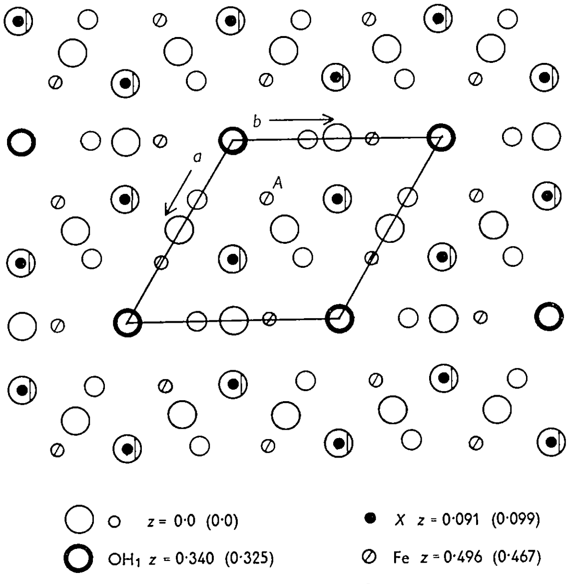

Fig. 1. Projection of cronstedtite layer along [001]. The z-coordinates given are fractions of the c-axis of the 1-layer cell, and the outlined hexagonal cell is that of the 1-layer structure. It is also the unit cell of the 2-layer structure, with the atoms then representing the lower of the two layers. X represents $\frac{1}{2}(Fe+Si)$. The coordinates in parenthesis are those given by Hendricks (1939).

During the course of the present work, eight different structures of cronstedtite have been found. Good crystals of four of these have been obtained, and their structures determined. The remaining four have been detected either as poor crystals, or twinned with one of the other forms. The structures differ principally only in the manner in which the layers are stacked together. The layer itself remains as Hendricks described it, but some changes in its dimensions have been made.

Several different polymorphs are sometimes found to exist within specimens with volumes of 1 to 2 mm.^{3}, and polymorphism may perhaps be related to variations in composition. If this is so, further chemical analysis, carried out on large specimens, would be of limited value. This uncertainty about the composition of any particular crystal, equivalent to an uncertainty in the atomic scattering factor, sets the limit of accuracy to be expected in determinations of these non-centrosymmetrical structures.

One of the structures determined was recognized by its diffraction photographs as that on which Hendricks's work was carried out. The structure he proposed accounted satisfactorily for reflexions for which, using the hexagonal cell described in this paper, $h-k=3n$, but he found that all other reflexions were affected by diffuse streaking caused by random shifts of the layers in directions parallel to the layers, and the proposed structure took no account of their existence. They would have fractional Miller indices, using Hendricks's cell. The more perfect crystals now available have made possible a complete description of the structure.

Experimental

Two mineral specimens were used, both from Truro, Cornwall, England, one being from Wheal Jane (specimen B.M. 51868) and the other from Wheal Maudlin. Oscillation photographs were taken of many crystal fragments from each specimen, in all cases about an axis perpendicular to the cleavage plane, and four crystals, each the best example of its particular structure, were selected for detailed examination. These will be referred to as 1-, 2-, 3- and 6-layer cronstedtite, these being the numbers of kaolin-type layers within the hexagonal unit cell of each type.

The 1-, 2- and 6-layer crystals were from the Wheal Maudlin specimen. Even after examination of many of these crystals, it was not possible to predict their structures from their external appearance. Crystals from the Wheal Jane specimen, however, were almost always of 3-layer type, and were truncated triangular pyramids.

For the four crystals chosen, oscillation and Weissenberg photographs were taken of two or three principal zones, using Co $K\alpha$ or Mo $K\alpha$ radiation, and these were indexed in terms of hexagonal cells with the dimensions given in Table 1. The unit-cell measurements were made on oscillation photographs taken on a 6 cm. diameter camera. The c-dimension shows immediately the number of layers in the cell, because it is known that the thickness of a kaolin-type layer is about 7 Å. Throughout this paper, reference will consistently be made to these cells, even in the case of the 6-layer type, where a smaller, rhombohedral cell could be used.

The specific gravity measured by Gossner is 3·445 g.cm.$^{-3}$, and that calculated from the composition of the layer used in this work is 3·55 g.cm.$^{-3}$.

The diffraction data are summarized in Table 1. In choosing the space groups, it was assumed that all the structures would consist of polar layers stacked together in the same sense with respect to [001]. With this condition the only space groups considered (see Table 1) were those which did not possess a centre of symmetry, or a reflexion plane or a 2-fold axis parallel to (0001). No further assumptions concerning the structures were necessary for space-group determination, except for the 1-layer crystal.

Of the four undetermined structures which were detected, two were 2-layer structures and two were 6-layer, but the space groups could not be determined because of twinning.

Structure determinations

These will be described for the four crystals individually.

Refinement was carried out on the [001] and [010] projections of the 1-layer structure. For the 3- and 6-layer types, the z-coordinates within a single cronstedtite layer were taken, without change, from these refinements, but adjustments were made to the x- and y-coordinates of the basal oxygen atoms to improve the R values.

The 2-layer type showed, by the faint streaking on reflexions with $h-k\neq 3n$, that slight disorder was present, and no refinement of this structure was undertaken. This type of disorder, common among kaolin-type minerals, is caused by stacking faults between the layers, and has been described in detail by Oughton (1957). The atomic coordinates for this

Table 1. *Cell dimensions and diffraction data*

	1-Layer	2-Layer	3-Layer	6-Layer
a (Å)	5·49 ± 0·01	5·49 ± 0·01	5·49 ± 0·01	5·49 ± 0·01
c (Å)	7·085 ± 0·01	14·17 ± 0·02	21·21 ± 0·05	42·5 ± 0·1
Laue group	$\bar{3}m$	$6/mmm$	$\bar{3}$	$\bar{3}$
Extinction symbol	P	P–c–	$P3_1$ or $P6_2$	R
Space groups considered	$\begin{pmatrix}P3m1\\P31m\end{pmatrix}$	$P6_3cm$	$\begin{Bmatrix}P3_1\\P3_2\end{Bmatrix}$	$R3$
Space group chosen	$P31m$	$P6_3cm$	$P3_1$	$R3$

type, given in Table 2, are derived from those of the 1-layer, without further adjustment.

Table 2 *Fractional coordinates referred to the equivalent positions in International Tables for hexagonal cells*

The terms basal, central, apical and top can be understood by comparing the 1-layer coordinates with Fig. 1. X represents $\frac{1}{2}$(Fe + Si)

1-Layer structure

Multiplicity	Position in layer	Atom	x	y	z
3	Basal	O	0·52	0	0
1	Central	OH$_1$	0	0	0·340
2	Apical	O, OH	0·333	0·667	0·340
3	Top	OH$_2$	0·333	0	0·649
2		X	0·333	0·667	0·091
3		Fe	0·667	0	0·496

2-Layer structure

Multiplicity	Position in layer	Atom	x	y	z
6	Basal	O	0·5	0	0
2	Central	OH$_1$	0	0	0·170
4	Apical	O, OH	0·333	0·667	0·170
6	Top	OH$_2$	0·333	0	0·325
4		X	0·333	0·667	0·046
6		Fe	0·667	0	0·248

3-Layer structure

Multiplicity	Position in layer	Atom	x	y	z
3	Basal	O$_1$	0·096	0·778	0
3	Basal	O$_2$	0·556	0·318	0
3	Basal	O$_3$	0·016	0·238	0
3	Central	OH$_1$	0·556	0·778	0·113
3	Apical	(O, OH)$_1$	0·222	0·111	0·113
3	Apical	(O, OH)$_2$	0·889	0·444	0·113
3	Top	OH$_2$	0·889	0·778	0·216
3	Top	OH$_3$	0·556	0·111	0·216
3	Top	OH$_4$	0·222	0·444	0·216
3		X_1	0·222	0·111	0·030
3		X_2	0·889	0·444	0·030
3		Fe$_1$	0·222	0·778	0·165
3		Fe$_2$	0·556	0·444	0·165
3		Fe$_3$	0·889	0·111	0·165

6-Layer structure

Multiplicity	Position in layer	Atom	x	y	z
9	Basal	O$_1$	0·49	0	0
9	Basal	O$_2$	0·51	0	0·167
3	Central	OH$_1$	0	0	0·057
3	Central	OH$_2$	0	0	0·223
3	Apical	(O, OH)$_1$	0	0	0·557
3	Apical	(O, OH)$_2$	0	0	0·890
3	Apical	(O, OH)$_3$	0	0	0·390
3	Apical	(O, OH)$_4$	0	0	0·723
9	Top	OH$_3$	0·333	0	0·108
9	Top	OH$_4$	0·667	0	0·275
3		X_1	0	0	0·515
3		X_2	0	0	0·849
3		X_3	0	0	0·349
3		X_4	0	0	0·682
9		Fe$_1$	0·667	0	0·083
9		Fe$_2$	0·333	0	0·249

The final atomic coordinates for the four structures determined are collected in Table 2. The values of F_o and F_c are given in Table 3, the F_c values being obtained using the scattering factors of Bragg & West (1929), corrected for dispersion by the K electrons.

1-*Layer cronstedtite*

The c-dimension shows that the unit cell contains only one kaolin-type layer, and that the layers are stacked together with no displacement or rotation between successive layers. This stacking gives a structure with space group $P31m$, and this was adopted for refinement. (The cronstedtite layer of Fig. 1 cannot, in a cell of this size, form a structure with the other space group considered, $P3m1$)

For the [001] projection, the value of

$$R\,(=\Sigma|F_o-F_c|/\Sigma|F_o|)$$

obtained using the atomic coordinates of Fig. 1 was 0·19. These can be regarded as 'ideal' coordinates because of the high symmetry of the arrangement of tetrahedra. The tetrahedra were rotated from these positions by varying the x-coordinate of O (Table 2) between 0·45 and 0·55, and an optimum $R(hki0)$ of 0·165 was obtained when the coordinate was 0·52.

In the [010] projection, estimates of the z-coordinates to be expected in a kaolin-type structure were made from values of the atomic radii, and the refinement of this projection was carried out by difference syntheses, using the 37 independent structure factors obtained from Co $K\alpha$ radiation, until an R of 0·13 was reached. Fig. 2(a) shows the final F_o synthesis.

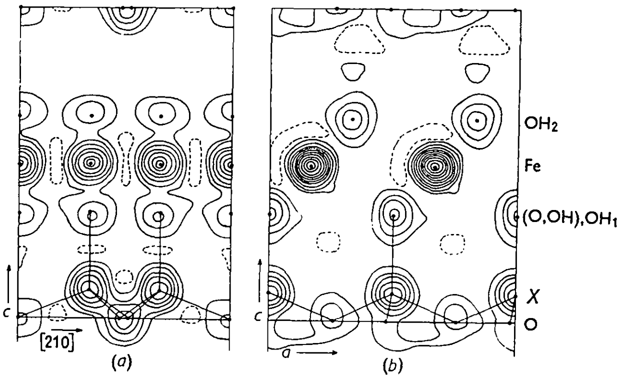

Fig. 2. F_o syntheses of 1-layer cronstedtite. (a) [010] projection. (b) [$1\bar{1}0$] projection. The contours are at intervals of 5 e.Å^{-2}, with the zero contour dashed.

Photographs taken with Mo $K\alpha$ radiation provided twice the number of $F(h0\bar{h}l)$ values given by Co $K\alpha$, but, because of a peculiarity of the structure, it was not possible to take advantage of this. The reason was that all reflexions with $h-k \neq 3n$ are very faint in comparison with the rest, since only atoms X and O (Table 2) contribute to them, and cannot be detected at high Bragg angles. The use of molybdenum in place of cobalt provides no increase in the number of these reflexions, so that the weighted reciprocal lattice has large systematic gaps in it. The corresponding synthesis contains errors which are too large to be corrected by the usual difference methods.

Fig. 2(*b*) shows also the F_o synthesis of the $[1\bar{1}0]$ projection, for which R is 0·17.

3-*Layer cronstedtite*

This is the structure which was examined by Hendricks.

One or two crystals with this structure were found which, amongst reflexions with $h-k \neq 3n$, gave exceptionally high intensities whenever $l=3n+1$ or $l=3n+2$, depending on h and k. These crystals were not used in this structure determination, because the intense reflexions appeared to be caused by some unusual stacking sequence occurring in part of the crystal.

The unit cell contains three layers related by a 3_1 or 3_2 axis. There are no geometrical limitations on the choice of position at which the axis passes through the layer, except that the layer must not have 3-fold symmetry about that point, but the physical limitation is that the basal oxygen atoms of each layer are expected to be located relative to the hydroxyl ions of the adjacent layer in a manner found in all minerals of this type, and described by Hendricks (1938) and Brindley (1951).

Positions for the axis which will produce this O–OH relationship are marked with crosses in Fig. 3(*a*), (*b*), in which the outlined cells correspond, in relation to the cronstedtite layer, to the cell in Fig. 1. But the points in Fig. 3(*a*) are unsuitable, since a 3_1 or 3_2 axis through them would produce a structure with

Table 3. *Observed and calculated structure factors*

1-Layer

hki	*l*	F_o	$\lvert F_c \rvert$
[010] projection			
000	1	37	41
	2	60	72
	3	29	23
	4	27	21
	5	40	39
	6	34	31
	7	29	32
$10\bar{1}$	0	22	23
	1	20	20
	2	19	16
	3	13	11
	4	9	8
	5	4	5
$20\bar{2}$	0	4	4
	1	7	8
	2	13	13
	3	12	17
	4	17	16
	5	12	15
	6	11	12
	7	5	8
$30\bar{3}$	0	67	69
	1	36	32
	2	33	30
	3	22	22
	4	12	10
	5	33	37
	6	17	16
$40\bar{4}$	0	5	1
	1	7	4
	2	8	7
	3	8	9
	4	8	10
	5	8	9
$50\bar{5}$	0	6	7
	1	7	6
	2	7	6
[001] projection			
$10\bar{1}$	0	20	23
$20\bar{2}$	0	2	4
$30\bar{3}$	0	58	69
$40\bar{4}$	0	3	1
$50\bar{5}$	0	6	7
$11\bar{2}$	0	26	20
$12\bar{3}$	0	15	14
$13\bar{4}$	0	12	11
$14\bar{5}$	0	15	11
$22\bar{4}$	0	24	20
$23\bar{5}$	0	8	8
$33\bar{6}$	0	34	36
$[1\bar{1}0]$ projection			
000	1	33	41
	2	56	72
	3	29	23
	4	25	21
	5	36	39
	6	32	31
	7	30	32
$11\bar{2}$	0	22	20
	1	72	68
	2	55	46
	3	58	59
	4	37	30
	5	22	15
	6	26	26
	7	9	5
	$\bar{1}$	23	23
	$\bar{2}$	33	35
	$\bar{3}$	28	16
	$\bar{4}$	48	64
	$\bar{5}$	46	26
	$\bar{6}$	24	27
	$\bar{7}$	21	17
$22\bar{4}$	0	21	20
	1	24	26
	2	29	27
	3	19	18
	4	36	41
	5	22	20
	6	13	17
	$\bar{1}$	48	51
	$\bar{2}$	24	20
	$\bar{3}$	45	45
	$\bar{4}$	21	15
	$\bar{5}$	12	11
	$\bar{6}$	11	17
$33\bar{6}$	0	22	36
	1	10	16
	$\bar{1}$	10	17

3-Layer

hki	*l*	F_o	$\lvert F_c \rvert$
[010] projection			
000	3	100	122
	6	178	217
	9	88	69
	12	79	64
	15	121	116
	18	84	92
	21	84	96
$10\bar{1}$	0	36	39
	1	34	38
	2	42	37
	3	34	35
	4	33	33
	5	37	31
	6	29	27
	7	24	25
	8	29	22
	9	26	20
	10	23	17
	11	20	15
	12	< 14	13
	13	23	12
$20\bar{2}$	0	< 10	6
	1	< 11	7
	2	< 11	10
	3	< 11	14
	4	17	17
	5	12	19
	6	21	22
	7	25	24
	8	14	26
	9	19	28
	10	27	28
	11	15	27
	12	20	27
	13	27	26
	14	24	25
$30\bar{3}$	0	183	200
	3	108	85
	6	122	84
	9	76	63
	12	34	26
	15	85	105
$[1\bar{1}0]$ projection			
000	3	103	122
	6	160	217
	9	79	69
	12	76	64
	15	105	116
	18	75	92
	21	73	96
$11\bar{2}$	1	149	126
	4	182	194
	7	154	137
	10	159	164
	13	67	41
	16	63	63
	19	60	66
	$\bar{2}$	33	54
	$\bar{5}$	146	102
	$\bar{8}$	95	57
	$\overline{11}$	153	168
	$\overline{14}$	144	135
	$\overline{17}$	59	60
	$\overline{20}$	62	72
$22\bar{4}$	2	45	52
	5	106	90
	8	47	21
	11	101	119
	14	86	89
	17	37	44
	20	39	56
	$\bar{1}$	129	105
	$\bar{4}$	138	126
	$\bar{7}$	97	94
	$\overline{10}$	111	117
	$\overline{13}$	33	18
	$\overline{16}$	40	44
$33\bar{6}$	0	103	106
	3	41	47
	$\bar{3}$	42	53

Table 3 (*cont.*)

6-Layer

[010] projection

hki	*l*	F_o	$\|F_c\|$
000	6	210	245
	12	338	434
	18	188	138
	24	161	127
	30	250	232
	36	165	185
	42	155	192
$10\bar{1}$	1	73	118
	4	91	65
	7	95	104
	10	90	54
	13	79	78
	16	83	39
	19	65	55
	22	59	26
	$\bar{2}$	73	67
	$\bar{5}$	83	110
	$\bar{8}$	87	58
	$\overline{11}$	79	88
	$\overline{14}$	75	44
	$\overline{17}$	62	63
	$\overline{20}$	60	30
$30\bar{3}$	0	370	412
	6	194	192
	12	201	180
	18	132	133
	24	63	61
	30	161	224
	36	111	94

[$1\bar{1}0$] projection

hki	*l*	F_o	$\|F_c\|$
000	6	234	245
	12	339	434
	18	195	138
	24	170	127
	30	242	232
	36	155	185
	42	148	192
$11\bar{2}$	0	<20	33
	3	150	144
	6	232	272
	9	189	216
	12	151	113
	15	254	237
	18	176	163
	21	207	219
	24	220	237
	27	186	166
	30	92	60
	33	102	108
	36	92	132
	39	73	78
$22\bar{4}$	0	30	88
	3	157	104
	6	219	223
	9	169	137
	12	77	26
	15	176	156
	18	121	148
	21	151	148
	24	141	135
	27	129	120
	30	28	28
	33	86	87

General reflections

hki	*l*	F_o	$\|F_c\|$
$12\bar{3}$	2	60	46
	5	61	65
	8	47	41
	11	42	57
	14	32	33
	$\bar{1}$	61	68
	$\bar{4}$	54	44
	$\bar{7}$	54	63
	$\overline{10}$	46	39
$13\bar{4}$	1	43	51
	4	40	37
	7	38	48
	10	33	33
	$\bar{2}$	44	38
	$\bar{5}$	38	49
	$\bar{8}$	35	34
	$\overline{11}$	40	45
$21\bar{3}$	1	71	74
	4	48	35
	7	60	68
	10	41	32
	13	45	56
	$\bar{2}$	47	36
	$\bar{5}$	58	71
	$\bar{8}$	41	33
	$\overline{11}$	47	61
	$\overline{14}$	36	29
$23\bar{5}$	2	33	28
	5	37	41
	8	28	26
	11	32	37
	$\bar{1}$	35	43
	$\bar{4}$	30	27
	$\bar{7}$	36	40
	$\overline{10}$	31	24
$31\bar{4}$	2	46	25
	5	52	56
	8	36	24
	11	43	50
	$\bar{1}$	49	59
	$\bar{4}$	43	24
	$\bar{7}$	47	54
	$\overline{10}$	30	23
	$\overline{13}$	42	47
$32\bar{5}$	1	38	46
	4	28	23
	7	42	43
	$\bar{2}$	27	23
	$\bar{5}$	40	44
	$\bar{8}$	28	22

space group $R3$. The correct structure is obtained using the points in Fig. 3(*b*). A 3_1 axis may pass through a cross in a shaded triangle, giving space group $P3_1$, or, alternatively, a 3_2 axis may pass through a cross in an unshaded one, giving space group $P3_2$. The origin of the cell in the complete structure is then on the 3-fold screw axis, and the cell to which the coordinates in Table 2 refer has its origin on a 3_1 axis through the encircled cross in Fig. 3(*b*). Fig. 4 shows the lowest layer in this unit cell.

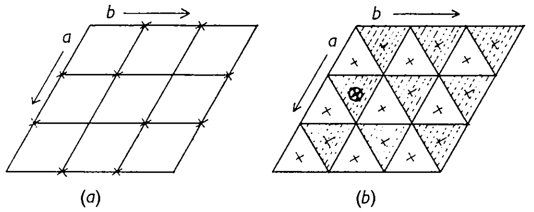

Fig. 3. Positions for a 3_1 or 3_2 axis in 3-layer cronstedtite. (*a*) The unsuitable positions. (*b*) Correct positions. The encircled cross shows the position chosen for the 3_1 axis.

This structure, composed of ideal cronstedtite layers, gave R values of 0·18 for both the $h0\bar{h}l$ and $hh\bar{2}\bar{h}l$ zones. To improve this value, the basal tetrahedra were rotated in the two possible directions, and the R found for various positions. The value of $R(hh\bar{2}\bar{h}l)$ fell to a minimum of 0·16 when the x-parameter of the atom O_1 was 0·096 corresponding to a rotation of 8° clockwise about X_2. The value of $R(h0\bar{h}l)$ was unchanged by these adjustments until the parameter of O_1 became greater than 0·116, when it began to increase.

The values of F_o and F_c in Table 3 refer to this structure with tetrahedra rotated 8° from the ideal position, and Fig. 4 shows the direction of the rotations.

The cronstedtite layer of point symmetry $3m$ is, in this structure, in a position appropriate to an

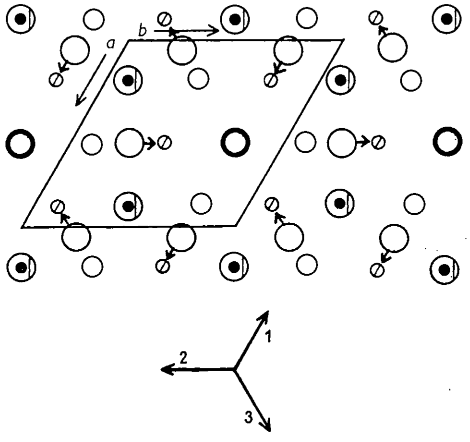

Fig. 4. The [001] projection of the lowest layer in the cell of 3-layer cronstedtite, and the directions of the shifts of magnitude $a/3$ to be made between successive layers.

asymmetrical unit, and absences, other than space group absences, are caused among reflexions with $h-k=3n$, and, in addition, $|F(h0\bar{h}l)|=|F(h0\overline{hl})|$.

The structure, though determined as described above, is more easily visualized in terms of shifts between successive layers, with no rotation of the layers taking place. The arrows in Fig. 4 show the shifts of magnitude $a/3$ which, made successively between the layers, create the complete structure. Each shift shown is relative to the layer immediately below, and not, except in the case of the first shift, to the fixed layer shown in Fig. 4.

6-*Layer cronstedtite*

The unit cell contains six cronstedtite layers. The sequence of displacements and rotations between successive layers is the same as in one form of amesite, described by Steadman & Nuttall (1962), and the reasoning leading to its elucidation will not be repeated here.

The structure is formed by placing above the cronstedtite layer of Fig. 1 another layer which has been rotated 60° or 180° about the oxygen atom at the origin of the outlined cell. This 2-layer unit is then operated upon by a 3_1 axis which passes through the atom marked A, and this creates the complete 6-layer structure.

A structure of ideal layers gave R values of 0·20 and 0·16 for the $h0\bar{h}l$ and $hh\overline{2h}l$ reflexions respectively, but, for a group of general reflexions $12\bar{3}l$, $13\bar{4}l$, $23\bar{5}l$, the R value was 0·23, the F_c values showing a marked alternation in magnitude as l varied which was not present in the series of F_o. This alternation was reduced by rotating the tetrahedra 2° about the X atoms so that this R value became 0·15, the other R values being unchanged. (Rotation in the opposite sense to that adopted here caused the disagreement to become greater). The final atomic coordinates are given in Table 2.

2-*Layer cronstedtite*

The unit cell contains 2 cronstedtite layers. The 6_3 axis which relates the layers to one another, and which will pass through the origin of the unit cell, must pass through a point in each layer about which the point symmetry is $3m$. The only such point in the layer shown in Fig. 1 is that at the origin of the hexagonal cell which is outlined. This, consequently, is also the origin of the 2-layer cell.

The complete 2-layer structure consists of the layer in Fig. 1 surmounted by another layer rotated through 60° (or 180°) about the origin of the cell. The hexagonal cell to which the ideal coordinates in Table 2 refer is shown in outline in Fig. 1.

The [010] projection of the structure is identical with that of 1-layer cronstedtite, and the [$1\bar{1}0$] projection with that of 6-layer cronstedtite. A direct comparison of the corresponding Weissenberg photographs confirms this.

Discussion

Bond lengths

Table 4 gives the bond lengths in 1-layer cronstedtite, together with the O–OH distances in 3-layer and 6-layer. The X–O bonds are shorter than the X–O, OH bonds perpendicular to the basal plane. Other kaolin-type minerals cannot strictly be compared with cronstedtite in this respect because of the latter's unique O, OH distribution. The nearest comparison is with amesite, which has trivalent aluminium in half the tetrahedral sites, and the same relation between the bond lengths was found in that mineral by Steinfink & Brunton (1956).

Table 4. *Bond lengths*

1-Layer	
X–O, OH	1·76 Å
X–O	1·72
Fe–OH_2	2·13
Fe–(O, OH), OH_1	2·14
O–OH_2	2·69
3-Layer	
O_1–OH_4	2·58
6-Layer	
O_2–OH_3	2·67

Ordering of cations

In 1- and 2-layer cronstedtite, ordering of cations is not crystallographically permissible either in octahedral or tetrahedral positions.

Ordering may occur in either of the positions in 3- and 6-layer, but no evidence of ordering, either of substitutional Al and Ca in octahedral sites or of Fe and Si in tetrahedral sites, has been found which would justify a detailed investigation. Ordering of the Fe and Si, which seems the more likely possibility, is perhaps not to be expected because of the open arrangement of tetrahedra.

Stacking of layers

In all the polymorphs of cronstedtite, the dispositions of the basal oxygen atoms with respect to the hydroxyl ions in the neighbouring layer are as described by Hendricks (1938), but it may be misleading to interpret the O–OH pairing as an indication that the interlayer bonding is solely or even mainly maintained by O–OH bonds. Newnham (1961) states that successive layers of dickite are held to each other only by van der Waals forces and long hydrogen bonds. It does not seem possible that such bonds alone produce the hard, brittle crystals of cronstedtite. An interlayer bonding solely dependent on hydrogen bonds and van der Waals forces would require that the ionic bonds be completely satisfied within each kaolin-type layer. This is not likely to be so, and ionic attraction will exist, for instance, between the octahedral cations and the oxygen atoms of the tetrahedra in the next layer. It seems more reasonable that the O–OH relationship described by Hendricks is merely a geometrical consequence of packing a layer of oxygen atoms of one face of a cronstedtite layer, as shown in Fig. 5(*b*) against the hydroxyl ions of the next (Fig. 5(*a*)). Evidence for the ionic nature of the interlayer bonding is provided by consideration of the distortion occurring in the polymorphs, as shown later.

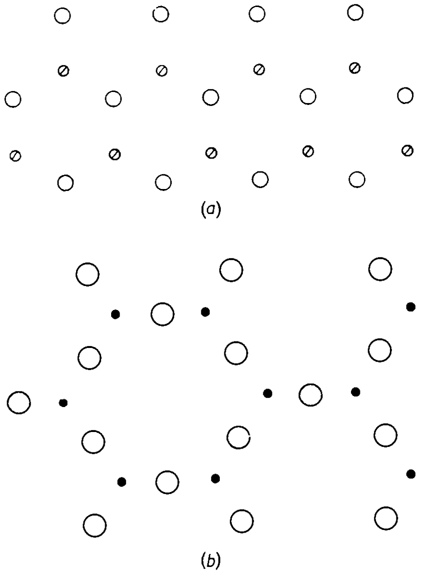

Fig. 5. (*a*) The layer of OH ions of a cronstedtite layer with the Fe ions below them. (*b*) Oxygen atoms (with X ions also shown) to be stacked against the OH layer. The same symbols are used as in Fig. 1.

But a simple argument based only on minimizing the potential energy of electrostatic cation–anion and cation–cation interaction cannot account for the existence of the cronstedtite polymorphs which are found and the non-existence of others. Half of the triangles of OH ions in Fig. 5(*a*) have, beneath them, an Fe ion, and the rest do not. In placing the layer of basal oxygen atoms of Fig. 5(*b*) on this OH layer, the position of minimum potential energy would appear to be one which fits each oxygen atom over a triangle containing an Fe ion, provided that this does not at the same time bring the X ions, to which the oxygens are bound tetrahedrally, too close to the Fe ion. The oxygens are placed in such positions in all the polymorphs of cronstedtite except one, the 3-layer. In this polymorph, which is quite common, the oxygen atoms are not placed above Fe ions, and the X and Fe ions in adjacent layers are as close together as possible.

An explanation of the existence of these polymorphs would have to take into account not the minimum potential energy of the structure, but the minimum free energy under the conditions of temperature and pressure prevailing at their formation. They may be metastable under normal conditions.

Distortion within the kaolin-type layer

As suggested by Mathieson & Walker (1954), the sense of rotation of the tetrahedra appears to be determined by the attraction between the octahedral cations and the basal oxygens. The magnitude of the rotation is dependent on the degree of misfit between the octahedral and tetrahedral parts of the layer, but, even in a hypothetical, isolated, trioctahedral layer in which no misfit existed, the energy of the layer would be reduced by rotation of the tetrahedra. The rotation is to be regarded as an integral feature of the kaolin-type layer, and the term 'ideal' is to be understood in a geometrical, and not a physical, sense. The rotation is modified by the presence of neighbouring layers, but is not created by it.

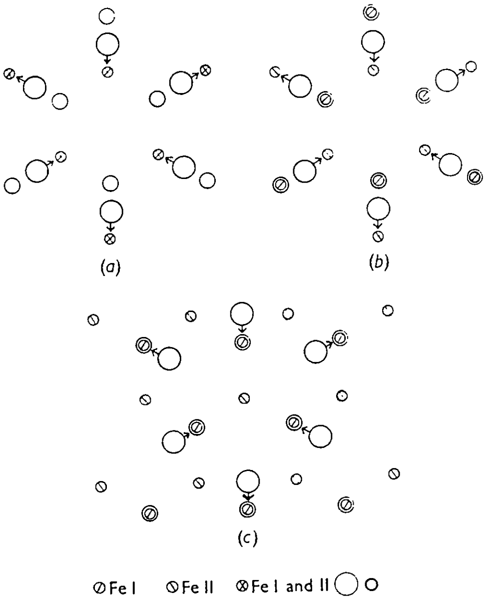

Fig. 6. The positions of basal oxygen atoms and FeI and FeII in three forms of cronstedtite. The arrows show the direction of displacement of the oxygens. (*a*) 1-layer. (*b*) 6-layer. (*c*) 3-layer.

Fig. 6 shows, for three of the cronstedtite structures determined, the positions of the basal oxygens, the hydroxyl ions of the adjacent layer, and the octahedral cations of the same and adjacent layers (referred to as Fe I and Fe II respectively). In 1-layer cronstedtite Fe I and Fe II coincide in this projection, and the movement of basal oxygens is towards the line joining them. In 6-layer cronstedtite the attractions are in opposite directions, and the shift of the oxygens is towards Fe II. This is to be expected, since the oxygen is closer to it than to Fe I. In 3-layer cronstedtite the Fe II ions are symmetrically disposed about each basal oxygen atom and exert no resultant force, and the shift is towards Fe I.

The effect on the O–OH distance is to increase it in 1-layer and 6-layer cronstedtite, and to decrease it in 3-layer. This variability of O–OH distance may be interpreted as showing that the O–OH bonds are of minor importance in the interlayer bonding, and in determining the stacking sequence of the layers.

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Determination of the Dilation Parameters in Martensitic Transformations*

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For the face centered cubic (f.c.c.: a_0) to the body centered tetragonal (b.c.t.: a, c) martensitic (or diffusionless phase) transformations, such as may occur in certain alloys of iron, for example, it is shown that if the correct variants of the habit, or interface plane and orientation relationship are known completely, then the elements of the lattice invariant (slip or twinning) shear can be calculated without knowing the lattice parameters involved or even their ratios, a/a_0, c/a_0. If in addition the ratios are known, then a maximum of two dilatation parameters can be determined. This dilatation strain is assumed to have the same principal axes as the Bain distortion, and may be considered as being imposed on the tetragonal martensite lattice at the interface.

Introduction

The crystallographic theory of martensitic transformations is now well developed and several reviews have appeared, the most recent ones being by Mackenzie (1960) and by Bilby & Christian (1961). Agreement with observed measurements is on the whole reasonable good and small discrepancies can generally be attributed to experimental error. However, this may not be altogether justified. By introducing the lattice invariant shear† and the isotropic dilatation, δ (Bowles & Mackenzie, 1954), as disposable parameters the observations can be accounted for more satisfactorily (Bowles & Mackenzie, 1954; Wechsler *et al.*, 1960; Otte, 1960*a*; Crocker & Bilby, 1961). Exact agreement is possible if two dilatation parameters are used. A best fit with observations using a suitable choice of the parameters as input data becomes rather tedious when several choices of these parameters are available. However, the problem can be worked backwards with the observations as input data (Lieberman, 1958), but if $\delta=1$, the system is usually over determined (i.e., more data are available than necessary). The possibility of using two dilatation parameters δ_1, and δ_2 (both close to unity) will be considered here in dealing with the cubic to tetragonal transformation.

The introduction of a δ parameter may be justified on several grounds in the case of the martensite transformation in iron alloys and possibly also in other systems. The habit plane, which in the theory is assumed to be planar, does, in fact, frequently exhibit measurable curvature. The constraints imposed by this and by the surrounding matrix could reasonably be accommodated elastically at the interface by a small dilatation. This has been discussed by Bowles & Mackenzie (1954), Eshelby (1957), Christian (1958, 1959) and Kaufman (1959). In addition to any possible physical origins, the dilatation parameter permits more exact agreement with experimental results of a theory that is essentially phenomenological.

A method will be presented for calculating the lattice

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† A shear by slip (or twinning) that leaves the lattice unchanged.