

Table 4. *The relations between colour and interatomic distance Tl-X in halogeno-thallium complexes*

Substance	$\text{K}_3\text{TlCl}_6 \cdot 2\text{H}_2\text{O}^*$	$\text{Cs}_2\text{TlCl}_6 \cdot \text{H}_2\text{O}^\dagger$	$\text{Co}(\text{NH}_3)_6\text{TlCl}_6$	$r(\text{Tl}^{+3}) + r(\text{Cl}^-)^\ddagger$	
Tl-Cl	2.55 kX.	2.53 kX.	2.48 kX.	2.86 kX. (P) 2.76 kX. (G)	
Colour	Colourless	Colourless	Orange red	—	
Substance	$\text{KTlBr}_4 \cdot 2\text{H}_2\text{O}^\S$	$\text{Rb}_3\text{TlBr}_6 \cdot \frac{8}{7}\text{H}_2\text{O}^*$	CsTlBr_4^\S	$\text{Co}(\text{NH}_3)_6\text{TlBr}_6$	$r(\text{Tl}^{+3}) + r(\text{Br}^-)^\ddagger$
Tl-Br	2.75 kX.	2.70 kX.	2.65 kX.	2.58 kX.	3.01 kX. (P) 2.91 (G)
Colour	Pale yellow	Gold yellow	Yellow	Reddish brown	—

* Hoard & Goldstein (1935).
† (P) after Pauling; (G) after Goldschmidt.
‡ Watanabé & Atoji (1950).
§ Watanabé *et al.* (1950).

halogen atoms, and the large size and low polarizing power of the complex $\text{Co}(\text{NH}_3)_6^{+3}$ must be responsible for these short distances. The latter effect would be considerable in halogeno-thallium complexes, as both thallium and halogen atoms have large polarizabilities. In fact, this effect is clearly shown in Table 4. In caesium tetra-bromothalliate, CsTlBr_4 , thallium and bromine atoms form a co-planar square, while in potassium tetrabromodiaquothalliate, $\text{KTlBr}_4(\text{H}_2\text{O})_2$, two water molecules are, in addition, in contact with the central thallium atom, forming an octahedral complex (Watanabé *et al.* 1950). As the octahedral and square bonds differ little in character, we may compare these complexes in the same scheme.

Though not sufficient and conclusive, we can see in the examples given in Table 4 the change of colour which may well accord with the Pitzer-Hildebrand rule concerning the colour of compounds in relation to bond character. The cleavage observed parallel to the cube faces would naturally be expected from the structure.

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Polymorphism of the Chlorites. I. Ordered Structures

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A variety of polymorphic forms has been found among single crystals of chlorites, consisting of ordered, partially ordered and disordered structures. Four different ordered structures have been analysed in detail. The reflexions are of two types: those with $k=3n$ are similar for all chlorites and confirm Pauling's structure of the chlorite layer and the ac projection of McMurchy's structure. Reflexions with $k \neq 3n$ show marked variations for the different ordered structures and degenerate into two-dimensional streaks for completely disordered structures. Four ordered structures are analysed in terms of three types of layer with displacements along the a and b axes, but a simpler description is given in terms of layers of a single type which are displaced along one of the three 'hexagonal' a axes by $-\frac{1}{3}a$, together, in some structures, with regularly occurring rotations of $\pm 120^\circ$ about the normal to the basal cleavage plane, which is the plane of the layers.

1. Introduction

The chlorites are a group of layer-lattice silicates of very variable composition (Orcel, 1927; Hallimond, 1939)

which may be expressed approximately by the formula $X_m Y_4 O_{10}(\text{OH})_8$, where m lies between 4 and 6, and X and Y stand for positive ions in octahedral and tetra-

hedral positions, respectively; usually X represents Mg with substitution by some Al, Fe, Cr or Mn, and Y represents Si and Al. These minerals are all built from the same type of layer unit, which will be called the chlorite layer and which is illustrated in Fig. 1 (a); this consists of a talc- or mica-type layer of composition $X_m Y_4 O_{10}(\text{OH})_2$ together with a brucite-type layer of composition $X_{\frac{1}{2}m}(\text{OH})_6$. The unit cell was first correctly deduced by Mauguin (1928, 1930), whilst Pauling (1930) first suggested the correct sequence of planes of atoms in the layer structure and gave the monoclinic cell dimensions,

$$a_0 = 5.2-5.3, b_0 = 9.2-9.3, c_0 = 14.3-14.4 \text{ kX.}; \beta = 96^\circ 56'.$$

This cell contains two 'molecules' of composition $X_m Y_4 O_{10}(\text{OH})_8$ and is centred on the c face. The height of the cell, $c_0 \sin \beta$, is about 14.2 kX., which is the thickness of one chlorite layer.

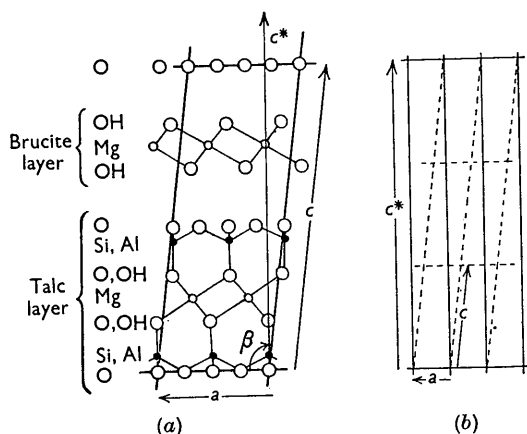


Fig. 1. (a) Projection of the chlorite layer on the ac plane. (b) Diagram showing the equivalence of a one-layer monoclinic cell and a three-layer orthorhombic cell.

McMurphy (1934), using X-ray powder analysis, confirmed Pauling's structure for the individual layers. He examined systematically the various ways in which the tetrahedral and octahedral sheets may be arranged relative to one another, and from a consideration of the ($h0l$) reflexions was able to select, out of eight possible arrangements of the atoms in the ac projection, one arrangement, Fig. 1 (a), giving good agreement with the observed reflexions. As regards the (hkl) reflexions, McMurphy observed only those corresponding to $k=3n$, where n is integral. These suffice to determine the b parameters of atoms in the octahedral layers which repeat at intervals of $\frac{1}{3}b_0$, but the exact location of the Si-O hexagonal networks can be uniquely determined only from a consideration of reflexions with $k \neq 3n$ which McMurphy was unable to observe. His final conclusion, namely, that the whole structure was based on a two-layer unit cell of height 28.4 kX. and monoclinic symmetry $C2/c$, or possibly a single-layer unit cell of height 14.2 kX. and symmetry $C2/m$, was therefore not fully justified, for these are only two of a number

of structures which would equally well explain his experimental observations.

2. The present experiments

These have been carried out mainly with single crystals, but some powder photographs have also been taken using a 20 cm. diameter semi-focusing type of camera.

The powder diagrams confirm McMurphy's findings, and in addition they show quite clearly a diffraction band having a sharp, low-angle termination corresponding to the (110) or (020) reflexion which McMurphy also considered might exist. The nature of this band, its similarity to bands commonly found with other finely divided layer silicate minerals such as clays (see, for example, Brindley & Robinson, 1947), and more particularly the observations obtained with single crystals, all indicate that it arises from random displacements between the layers. The fact that reflexions with $k=3n$ are apparently unaffected by these displacements indicates that they are parallel to the b axis and of integral multiples of $\frac{1}{3}b_0$. In consequence, when k is not equal to $3n$, incoherent scattering occurs, and only two-dimensional diffraction bands, with indices (hk), are then possible. Apart from the (02), (11) band, these reflexions are too weak to be observed on powder photographs, and this accounts for McMurphy not obtaining reflexions for $k \neq 3n$. It is evident that finely powdered materials containing (presumably) many random layer displacements are not suitable for detailed structure analyses of these minerals.

The majority of the single crystals we have examined give photographs similar to that of Fig. 3 (b). This is a rotation photograph taken about the normal to the cleavage plane, i.e. the plane of the chlorite layers, the (001) plane. Reflexions from planes with $k=3n$ are recorded as sharp spots, while planes with $k \neq 3n$ give continuous lines of scattering which follow the row lines of the photograph. The occurrence of both the sharp spots for $k=3n$ and the continuous lines for $k \neq 3n$ can be explained by random layer displacements parallel to b of multiples of $\frac{1}{3}b_0$.

We have, however, obtained single crystals of peninitite (or pennine), a magnesium chlorite, showing sharp spots for all reflexions and which therefore possess a high degree of order in the arrangement of the layers. While reflexions with $k=3n$ appear to be constant for all chlorites, those with $k \neq 3n$ show considerable diversity, indicating a multiplicity of structural types. This evidence for the polymorphism of the chlorites recalls the work of Hendricks & Jefferson (1939) on the micas, where a similar problem arose. We have also found a few specimens of an intermediate type showing evidence of partial order or disorder; Garrido (1949) has reported similar results for k ammererite, a chromium-bearing chlorite.

The present paper deals mainly with the well-ordered polymorphic forms. They are all based on the

same fundamental type of layer, as is shown by the identity of the reflexions with $k=3n$, of which the $(00l)$ reflexions form a particular group. The unit cells have approximately the same a_0 and b_0 parameters, but the stacking of successive layers varies from one crystal to another. The main problem therefore lies in determining the sequence of layers for each of the crystals we have examined.

3. The general approach to the problem

As already stated, McMurchy determined completely the atomic arrangement in the ac projection, and our own observations with both powders and single crystals

arrangements, designated L , M and N respectively, are illustrated in plan and elevation in Fig. 2. Arrangement L alone has monoclinic symmetry, $C2/m$. In M and N , the relative positions of the Si-O networks destroy both the twofold axis and the reflexion plane normal to it; a monoclinic-shaped cell containing only one M - or one N -type layer can have no higher symmetry than $C1$.

It will subsequently be shown (§ 6) that the relative movements of layers and the arrangement of the Si-O sheets can be considered in terms of rotations of layers. The actual analyses, however, have been carried out in terms of linear displacements, and it is probably simpler to approach the problem from this standpoint.

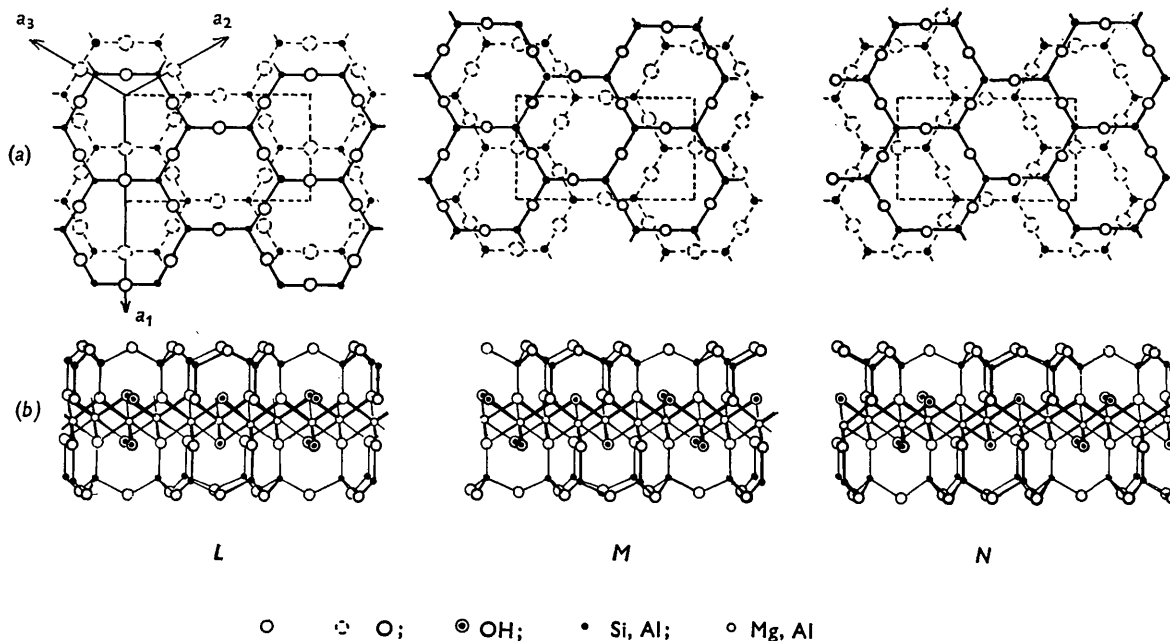


Fig. 2. Diagrams showing three arrangements, L , M and N , of the Si-O networks in projection on (a) the ab plane, (b) the bc^* plane. The unit cells are outlined in the ab projections and in one case the axes a_1 , a_2 and a_3 are indicated.

fully confirm this part of his work. He assumed a β angle of $97^\circ 8' 40''$, corresponding to a regular displacement of successive chlorite layers in the a direction by $-\frac{1}{3}a_0$. In a preliminary report (Robinson & Brindley, 1948) two of us have already shown that for one particular ordered crystal of penninite this displacement must be *exactly* $-\frac{1}{3}a_0$ because there exists a larger *orthorhombic* cell of height $3 \times c_0 \sin \beta$ (see Fig. 1 (b)). The similarity of the $(h0l)$ reflexions from all chlorites suggests that this displacement of successive layers by exactly $-\frac{1}{3}a_0$ is a constant feature of these structures.

Two sources of variation remain to account for the polymorphic forms: (i) regular displacements of successive layers by multiples of $\frac{1}{3}b_0$ along the b axis, and (ii) various possible arrangements of the two Si-O networks relative to each other within the individual layers. There are, in fact, three possible positions for the upper Si-O network relative to the lower one, all of which contribute equally to the reflexions with $k=3n$. These

The discovery that a larger orthorhombic cell existed for one penninite crystal has been found generally true for all the ordered structures. Experimentally it is advantageous to work in terms of this larger cell, because of the ease and certainty with which the orthorhombic c axis may be found. From the spacing of the layer lines, the number of chlorite layers in the larger orthorhombic cell can be found immediately. In this way, we have discovered orthorhombic cells containing 3, 6 and 9 chlorite layers. This approach to the problem gives at once a measure of the structural complexity of any particular chlorite specimen.

4. A survey of the chlorite structures so far analysed

Fig. 3 shows some of the X-ray diagrams which have been obtained by rotation of various crystals about the c^* axis. Attention should be directed principally to the fine structure of the first row line which corresponds

to (11*l*) and (02*l*) reflexions and which differs markedly from one crystal to another. The second row line with much stronger reflexions having indices (13*l*), (20*l*) is the same for all crystals. Similarly, all the reflexions with $k=3n$ remain constant, but those with $k\neq 3n$ show marked variations. The fine details of some of the higher-order row lines are not easily reproduced, but are clearly visible in the original negatives. These photographs illustrate the progression from completely ordered to completely disordered structures.

Table 1 summarizes the principal data for these crystals.

Table 1. *Summary of data for six chlorite crystals*

Crystal	A	B	C	D	E	F
No. of layers in orthorhombic cell	3	3	6	9	Partially disordered	Extensively disordered
No. of layers in smallest monoclinic cell	1	1	2	3	—	—
Symmetry of atomic arrangement	<i>C1</i>	<i>C2/m</i>	<i>C1</i>	<i>C1</i>	—	—
Monoclinic cell dimensions (kX.)	a_0 5.3 b_0 9.2 c_0 14.3	5.3 9.2 14.3	5.3 9.2 28.6	5.3 9.2 42.6	5.3 9.2 —	5.3 9.2 —
Monoclinic angle	$\beta=97^\circ 6'$	$\beta=97^\circ 6'$	$\beta=97^\circ 6'$	$\alpha=86^\circ$	—	—
No. of examples so far discovered	2	2	1	1	1	Many

5. Details of the ordered structures

All the crystals with ordered structures come from a single sample of penninite supplied by Monsieur G. Vigneron, of the University of Louvain. All other samples so far examined revealed disordered or only partially ordered structures. The details of the ordered structures are set out below.

(i) *Crystal A, a 'single-layer' structure*

Since the atomic arrangement in chlorites tends towards hexagonal symmetry, it is not easy to select the true *a* and *b* axes of the monoclinic cell. Photographs were taken about each of the three possible *a* axes and the corresponding *b* axes, but only one pair permits all the reflexions to be indexed in terms of a monoclinic cell. This cell has a β angle of $97^\circ 6'$ in accordance with the earlier results of Pauling and McMurchy, and a height of 14.2 kX., i.e. it contains only one chlorite layer.

To decide which type of layer, *L*, *M* or *N*, is present in this structure requires consideration only of reflexions with $k\neq 3n$. The *L*-type structure, which alone has monoclinic symmetry, should give equal intensities for (*hkl*) and (*h $\bar{k}l$*) pairs of reflexions, but experimentally these are found to be unequal for this crystal, so that the *L*-type structure is ruled out. The *M* and *N* types have a mirror-image relation to each other, (*hkl*) of one being (*h $\bar{k}l$*) of the other, so that only one of them needs to be considered. These pairs of reflexions should therefore be recorded separately by oscillation or other methods, but unfortunately the crystal was lost before this work was complete. The intensities were obtained, however,

from available photographs taken by rotation about a pseudo-*b* axis, on which the majority of the desired reflexions are separated. The observed intensities were obtained from films taken in triplicate by visual comparison with a scale 0–25; F_{obs}^2 values derived by systematic correction for Lorentz, polarization and Cox–Shaw factors, were suitably scaled for comparison with the F^2 values calculated for the *M*- (or *N*-) type structure. The observed and calculated values corresponding to one 'molecule' of $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ are set out in Table 2. The close agreement shows that the structure is in fact composed of *M*- (or *N*-) type layers

and has one such layer per unit cell; the cell is of monoclinic shape, but the space group is *C1*.

(ii) *Crystal B, a 'single-layer' structure*

The analysis of this crystal was similar to that for crystal A. Rotation photographs about the *c* and c^* axes prove the crystal to be another example of a single-layer structure, but the intensities of reflexions with $k\neq 3n$ differ from those of crystal A. Oscillation photographs prove the identity of (*hkl*) and (*h $\bar{k}l$*) reflexions, and the F^2 values deduced from the observed intensities agree with those calculated for the *L*-type structure (see Table 3). The atomic arrangement for this crystal corresponds to the space group *C2/m*.

(iii) *Crystal D, a 'three-layer' structure*

(a) *Determination of the unit cell.* Rotation about the c^* axis shows that the orthorhombic cell contains nine chlorite layers. As it seemed likely that a smaller cell might exist, rotation photographs were taken systematically about a series of axes passing through lattice points in the zero and ninth layers. These axes are shown in Fig. 4, which depicts the zero and ninth layers of the structure with lattice points at the corners and centres of the *c* faces. Point *O'* is vertically above *O*, and *OO'* is the c^* axis.

Rotation about each of three axes corresponding to successive $-\frac{1}{3}a$ displacements between layers, e.g. *OC* in Fig. 4, also gave a 'nine-layer' spacing; each of these is equivalent to Pauling's monoclinic *c* axis. By systematic investigation, the axes *OC*₁, *OC*₂ and *OC*₃ were found which gave 'three-layer' spacings. These

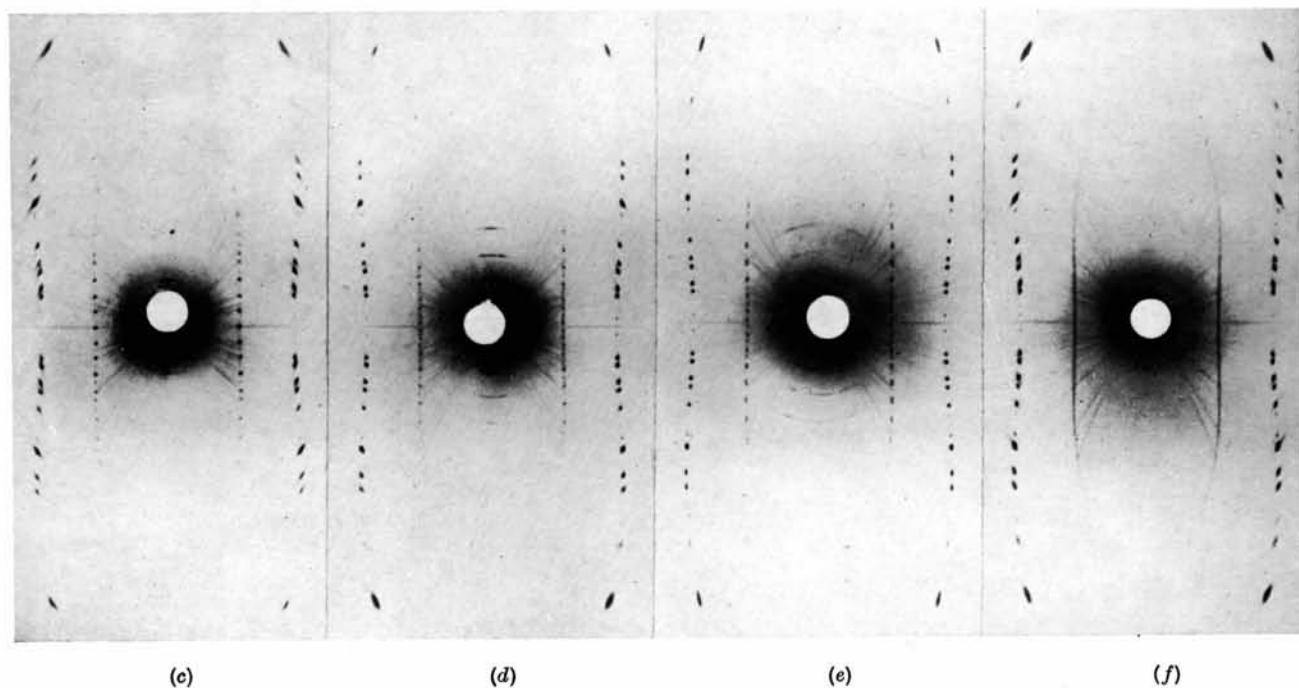
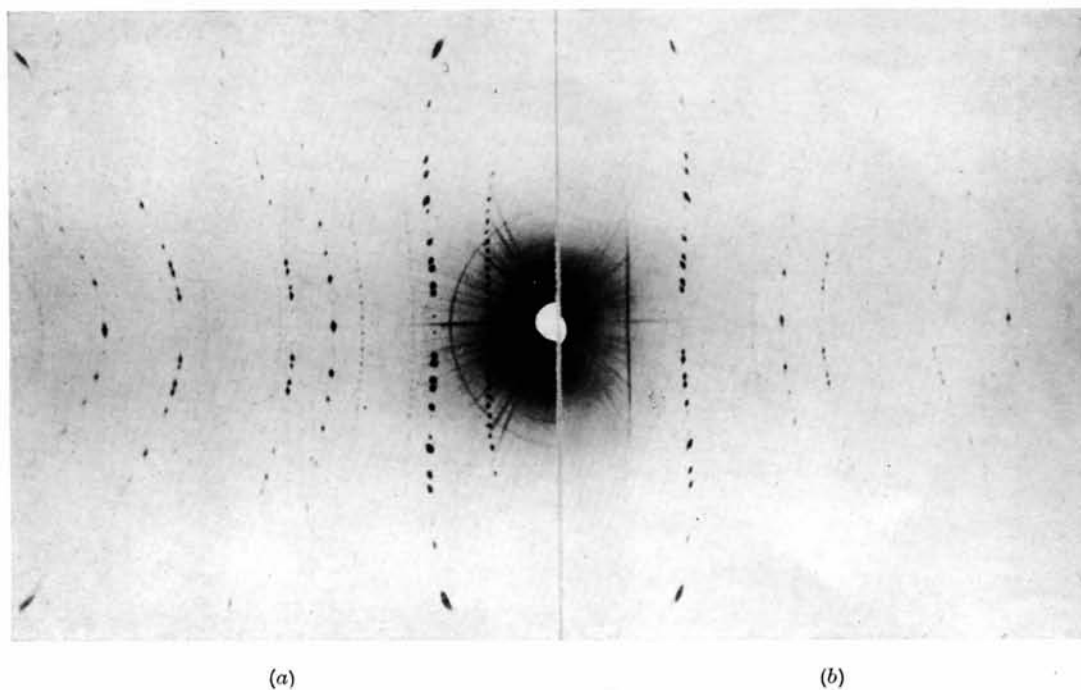


Fig. 3. Rotation diagrams of chlorites about c^* . (a) Fully ordered structures: 3×14 kX. orthorhombic spacing (crystal A). (b) Fully disordered structure with random stacking of layers (crystal F). (c)–(f) Central portions of rotation photographs. (c) 3×14 kX. spacing: crystal B. (d) 6×14 kX. spacing: crystal C. (e) 9×14 kX. spacing: crystal D. (f) partially ordered structure: crystal E.

Table 2. Comparison of observed and calculated F^2 values for crystal A

(Indices are based on a three-layer orthorhombic cell; groups of overlapping reflexions are indicated by brackets.)

(11l) reflexions			(1l) reflexions			(2l) reflexions		
(hkl)	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	(hkl)	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	(hkl)	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$
111	115	—†	111	95	92	221	15	22
112	56	43	112	18	0	222	7	
114	5	5	114	75	42	224	3	0
115	46	34	115	135	103	225	12	21
117	117	103	117	25	15	1.1.17	9	
118	96	81	118	2	0	227	30	37
1.1.10	9	10	1.1.10	93	91	228	19	21
1.1.11	2	0	1.1.11	74	68	2.2.10	2	3
1.1.13	55	47	1.1.13	0	0	2.2.11	21	24
1.1.14	70	71	1.1.14	27	40	2.2.13	48	93
1.1.16	33	66	1.1.16	52	49	2.2.14	24	24
1.1.17	9	21	1.1.17	7	12	2.2.16	9	14
225	12		20	1.1.19	16	19	2.2.17	42
1.1.19	7	4	1.1.20	34	35	2.2.19	50	52
1.1.20	21	0	1.1.22	10	10	1.1.25	2	
0.4.12†	34/2	45				2.2.20	13	9
0.4.12†	14/2					2.2.22	28	37
1.1.22	30					2.2.23	63	72
0.4.15†	72/2	111				1.1.28	9	
0.4.15†	90/2					2.2.25	28	39
1.1.23	21	16				2.2.26	1	9
1.1.25	2	52				1.1.31	8	
2.2.19	50	0						
1.1.26	0	0						
1.1.28	9	72						
2.2.23	63	121						
1.1.29	12							
0.4.24†	13/2	46						
0.4.24†	54/2							
1.1.31	8	9						
2.2.26	1	6						

† Not recorded on film.

‡ The multiplicity factor is 2 for (11l) reflexions but only 1 for (04l) and (04l) reflexions. $F^2(04l)$ and $F^2(04l)$ must be halved to obtain a correct comparison.Table 3. Comparison of observed and calculated F^2 values for crystal B

(Indices based on a three-layer orthorhombic cell.)

(11l) and (1l) reflexions			(02l) and (02l) reflexions		
l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$
1	1	0	0	144	125
2	137	169	3	17	11
4	120	131	6	95	80
5	20	15	9	48	39
7	35	46	12	24	13
8	70	67	15	59	42
10	45	43	18	0	0
11	62	64	21	30	31
13	61	62			
14	10	5			
16	2	0			
17	53	37			
19	42	29			
20	2	0			
22	5	0			

Table 4. Transformations of (11l), (02l) indices for monoclinic and orthorhombic axes, l having all positive and negative values

Monoclinic axes			Orthorhombic axes		
a_1, b_1, c_1	a_2, b_2, c_2	a_3, b_3, c_3	a_1, b_1, c^*	a_2, b_2, c^*	a_3, b_3, c^*
11l	0.2.l-1	11l	1.1.3l-1	0.2.3l-1	1.1.3l-1
11l	11l	0.2.l-1	1.1.3l-1	1.1.3l-1	0.2.3l-1
0.2.l-1	11l	11l	0.2.3l-1	1.1.3l-1	1.1.3l-1

three axes are related by the pseudo-hexagonal symmetry of the individual layers, each of them corresponding to an overall displacement of b_0 after nine layers. The similarity of reflexions with $k=3n$ with those of the other crystals shows that the $-\frac{1}{3}a_0$ displacements between successive layers are still present,

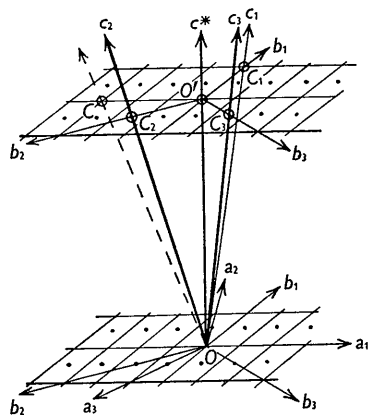


Fig. 4. Possible c axes for crystal D.

but for layer sequences which occur in multiples of three they may be neglected when considering the *simplest unit cell* (but not, of course, when considering the atomic arrangement). This cell therefore contains three chlorite layers and has the c axis inclined along b , giving a net $\frac{1}{3}b_0$ displacement. Thus the cell dimensions are:

$$a_0 = 5.3, \quad b_0 = 9.2, \quad c_0 \sin \alpha = 42.6 \text{ kX.};$$

$$\alpha = 86^\circ, \quad \beta = \gamma = 90^\circ.$$

These dimensions have not been determined with high accuracy, since the main interest lies in the structure.

There are then three equally probable monoclinic cells having these dimensions and corresponding to the three sets of axes (a_1, b_1, c_1) , (a_2, b_2, c_2) and (a_3, b_3, c_3) shown in Fig. 4. The relationships between the three sets of indices of the $(11l)$, $(02l)$ group of reflexions are set out in Table 4, in which are also given the corresponding orthorhombic indices. Photographs taken about the 'monoclinic' axes c_1 , c_2 and c_3 have different distributions of spots along rows with $k \neq 3n$, showing that the atomic arrangement is different with respect to each of these c axes and that c^* is not a truly hexagonal or trigonal axis of symmetry. The threefold ambiguity in the indexing can only be resolved by a consideration of the intensities of the reflexions.

(b) *The atomic arrangement within the three-layer cell.* The resultant displacement of the layers by $\frac{1}{3}b_0$ every three layers can be obtained in three ways, each involving a different sequence of interlayer displacements, namely:

I. $0, 0, +\frac{1}{3}b_0$ displacements.

II. $-\frac{1}{3}b_0, -\frac{1}{3}b_0, 0$ displacements.

III. $+\frac{1}{3}b_0, +\frac{1}{3}b_0, -\frac{1}{3}b_0$ displacements.

At first sight there appear to be 81 possible structures since there are 27 ways of filling three layers with the three types of layers, L , M and N , and for each of these 27 ways there are the three stacking sequences given above. It is found, however, that these three stacking sequences are related to each other by rotations of 120°

Table 5. Comparison of observed and calculated F^2 values for crystal D

(Indices based on a nine-layer orthorhombic cell.)

(02l) reflexions			(11l) reflexions			(1l) reflexions		
l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$	l	$F^2_{\text{calc.}}$	$F^2_{\text{obs.}}$
2	2×10^2	2×10^2	2	19×10^2	15×10^2	2	1×10^2	1×10^2
5	9	11	5	23	15	5	77	111
8	8	7	8	1	0	8	3	5
11	24	33	11	82	74	11	10	10
14	0	0	14	0	0	14	2	2
17	80	102	17	10	9	17	23	25
20	0	0	20	0	0	20	0	0
23	9	7	23	20	23	23	71	102
26	$2\frac{1}{2}$	3	26	0	0	26	0	0
29	17	13	29	60	59	29	7	6
32	1	0	32	2	2	32	8	9
35	45	44	35	4	4	35	18	9
38	2	3	38	14	16	38	2	2
41	4	4	41	9	6	41	30	25
$\bar{1}$	66×10^2	57×10^2	$\bar{1}$	8×10^2	4×10^2	$\bar{1}$	19×10^2	24×10^2
$\bar{4}$	4	2	$\bar{4}$	9	9	$\bar{4}$	32	37
$\bar{7}$	13	8	$\bar{7}$	51	59	$\bar{7}$	6	8
$\bar{10}$	45	56	$\bar{10}$	4	6	$\bar{10}$	13	9
$\bar{13}$	4	1	$\bar{13}$	10	11	$\bar{13}$	35	44
$\bar{16}$	15	20	$\bar{16}$	55	62	$\bar{16}$	7	5
$\bar{19}$	20	22	$\bar{19}$	2	1	$\bar{19}$	3	4
$\bar{22}$	7	7	$\bar{22}$	17	13	$\bar{22}$	60	79
$\bar{25}$	$2\frac{1}{2}$	2	$\bar{25}$	8	5	$\bar{25}$	1	0
$\bar{28}$	61	70	$\bar{28}$	7	6	$\bar{28}$	17	13
$\bar{31}$	0	0	$\bar{31}$	1	0	$\bar{31}$	2	0
$\bar{34}$	14	16	$\bar{34}$	57	62	$\bar{34}$	8	6
$\bar{37}$	0	0	$\bar{37}$	0	0	$\bar{37}$	0	0
$\bar{40}$	6	4	$\bar{40}$	10	11	$\bar{40}$	62	41

in the ab plane, as are also the L -, M - and N -type layers. It is only necessary, therefore, to consider the 27 structures arising from a single stacking sequence, since these cover all the possible arrangements of the atoms within the three-layer cell. There remains the indeterminacy of the true crystallographic axes, which means that the 27 possible structures must be considered for the three orientations of the axes.

By choosing a small number of reflexions with markedly differing intensities it has been possible to show that only one of the 27 arrangements for one of the three sets of axes gives satisfactory agreement between observed and calculated values. In Table 5 a comparison is made between the observed and calculated F^2 values for all the reflexions in the (02 l), (11 l) group, and it is clear that the agreement is very close. The F^2 values in the table correspond to three 'molecules' of $Mg_6Si_4O_{10}(OH)_8$.

(c) *Discussion.* The structure is composed of a sequence of layers $LMMLMM\dots$ with a displacement of $\frac{1}{3}b_0$ on passing from an M - to an L -type layer. Alternatively, the structure may be described in terms of the other two stacking arrangements if the corresponding axes and layer sequences are used, as indicated in Table 6.

Table 6. *Equivalent layer sequences and interlayer displacements along a and b axes in crystal D*

Succession of layers along c^*	Sequence I LMM type	Sequence II MNN type	Sequence III NLL type
3	L	M	N
2	M	N	L
1	M	N	L
0	L	M	M

	$\left. \begin{array}{l} -\frac{1}{3}a_1 + \frac{1}{3}b_1 \\ -\frac{1}{3}a_1 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_2 \\ -\frac{1}{3}a_2 - \frac{1}{3}b_2 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_3 - \frac{1}{3}b_3 \\ -\frac{1}{3}a_3 + \frac{1}{3}b_3 \end{array} \right\}$
	$\left. \begin{array}{l} -\frac{1}{3}a_1 \\ -\frac{1}{3}a_1 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_2 - \frac{1}{3}b_2 \\ -\frac{1}{3}a_2 - \frac{1}{3}b_2 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_3 + \frac{1}{3}b_3 \\ -\frac{1}{3}a_3 + \frac{1}{3}b_3 \end{array} \right\}$

The atomic arrangement in the structure has only triclinic symmetry, though the cell itself has a monoclinic shape.

(iv) *Crystal C, a 'two-layer' structure*

Rotation about c^* shows a six-layer orthorhombic spacing, indicating either a six-layer or a two-layer structure. The effect of the regular $-\frac{1}{3}a_0$ displacements rules out any other possibilities. A full structural analysis could doubtless have been made along the same lines as for crystal D, but unfortunately the crystal was lost at a very early stage and a second example has still not been found from the material at our disposal.

From the available c^* rotation photographs, however, we have been able to arrive at the structure in the following way. c^* oscillation 'setting' photographs show that the six components of the (11 l), (02 l) group of reflexions overlap in pairs, one pair on $l=3n$ layers, another on $l=3n+1$ layers and the third on $l=3n-1$

layers, an arrangement of the reflexions which can only arise from a two-layer structure.

We have now to examine systematically all the possible two-layer sequences. As regards the succession of *displacements* parallel to b , these may be of any of the following types:

- I. $0, \frac{1}{3}b_0$. II. $-\frac{1}{3}b_0, 0$. III. $\frac{1}{3}b_0, -\frac{1}{3}b_0$.
 IV. $-\frac{1}{3}b_0, -\frac{1}{3}b_0$. V. $\frac{1}{3}b_0, \frac{1}{3}b_0$. VI. $0, 0$.

With three types of layer, L, M, N , there are $3^2=9$ ways of filling the two-layer cell. Since both the layer types and the stacking sequences are related by 120° rotations, the nine structures corresponding to case I cover also cases II and III. For sequences IV, V and VI, it is only necessary to consider one sequence for *dissimilar* layers, giving three structures only for consideration. Twelve structures in all had therefore to be considered. The F^2 values of the six components of the (11 l), (02 l) group of reflexions were calculated for each of these structures for l values from 0 to 31. The sums of the calculated F^2 values for the overlapping pairs of reflexions on the c^* rotation photograph were compared with the visually estimated intensities. One structure alone gave good agreement, the other eleven giving no agreement whatsoever. We consider, therefore, that we are justified in accepting this one structure as the correct atomic arrangement. We are not giving a table of numerical values for this crystal as we are unable to give the observed values for the individual reflexions, but the agreement found for the pairs of reflexions compares favourably with those given for the other three crystals.

The structure consists of alternating L - and M -type layers with a $+\frac{1}{3}b_0$ displacement on passing from an M - to an L -type layer in the positive direction of c , but with no b displacement in passing from an L - to an M -type layer in the same direction. Equivalent layer sequences and displacements are set out in Table 7.

Table 7. *Equivalent layer sequences and interlayer displacements along a and b axes in crystal C*

Succession of layers along c^*	Sequence I LM type	Sequence II MN type	Sequence III NL type
2	L	M	N
1	M	N	L
0	L	M	N

	$\left. \begin{array}{l} -\frac{1}{3}a_1 + \frac{1}{3}b_1 \\ -\frac{1}{3}a_1 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_2 \\ -\frac{1}{3}a_2 - \frac{1}{3}b_2 \end{array} \right\}$	$\left. \begin{array}{l} -\frac{1}{3}a_3 - \frac{1}{3}b_3 \\ -\frac{1}{3}a_3 + \frac{1}{3}b_3 \end{array} \right\}$
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For the NL sequence the unit cell is of monoclinic shape with the following dimensions:

$$a_0=5.3, \quad b_0=9.2, \quad c_0=28.6 \text{ kX.}; \quad \beta=97^\circ 6'.$$

The LM and MN sequences give triclinic-shaped cells. The symmetry of the atomic arrangement is no higher than $C1$. This structure is not the same as that suggested by McMurchy which contains alternating M - and N -type layers with $-\frac{1}{3}b_0$ displacements on changing from an N - to an M -type layer and $+\frac{1}{3}b_0$ displacements on changing from an M - to an N -type layer.

6. Discussion of the chlorite structures

The four chlorite structures described above have been considered in terms of fixed a and b axes together with sequences of three types of layer, L , M and N , and inter-layer displacements parallel to the a and b directions. A simpler description of these results can be given in terms of a single kind of layer (which need not be specifically labelled L , M or N) which may be rotated by multiples of 120° and displaced *only along the a axes* (a_1 , a_2 or a_3) of the layer itself. The a_1 axis will be taken parallel to the symmetry plane with a_2 and a_3 at 120° to a_1 as shown in Fig. 2.

Having analysed these structures in terms of fixed a and b axes, we have found it difficult to dispel the idea that the a_1 axis parallel to the symmetry plane is in some way more fundamental than the a_2 and a_3 axes, but in what follows we shall endeavour to treat them as being of equal importance.

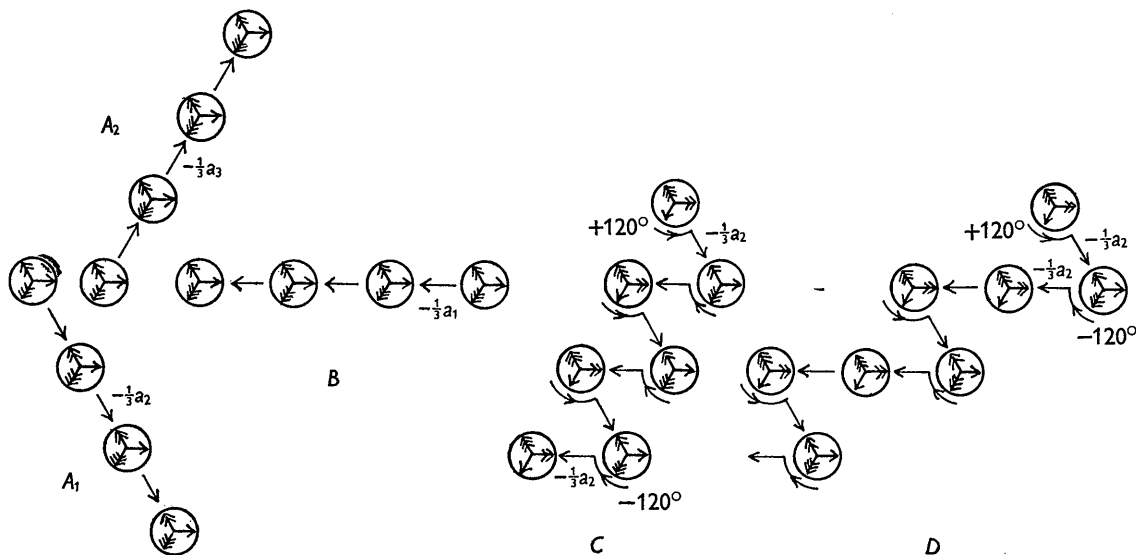


Fig. 6. Diagrammatic representation of the displacements and rotations of successive layers. Each circle represents one chlorite layer projected on to the ab plane and the single, double and triple arrow-heads represent the a_1 , a_2 and a_3 axes of the layer. The arrows between circles indicate the rotations and displacements which occur on passing from one layer to the next. Diagrams A , B , C and D correspond to the four ordered structures analysed.

The layer sequences and displacements previously given may now be described as follows:

I. Changes of layer type unaccompanied by b -axis displacements are equivalent to rotations of the layer by $\pm 120^\circ$ in its own plane.

II. Displacements of a layer by $\frac{1}{3}nb_0$ when combined with the (always present) $-\frac{1}{3}a_0$ displacements are equivalent to a single displacement of $-\frac{1}{3}a$ along one of the alternative a axes. Thus

$$-\frac{1}{3}a_1 + \frac{1}{3}b_1 \equiv -\frac{1}{3}a_2,$$

and

$$-\frac{1}{3}a_1 - \frac{1}{3}b_1 \equiv -\frac{1}{3}a_3.$$

This is illustrated in Fig. 5.

III. A change of layer type accompanied by a b -axis displacement is a combination of I and II.

IV. In the four structures so far examined the direction in which a layer is displaced *relative to its own system of axes* remains constant throughout the structure. This is an aspect of the structures which is not apparent when the displacements are described in relation to *fixed* axes.

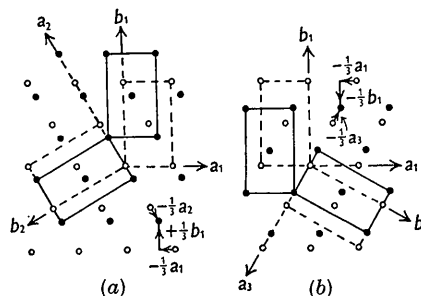


Fig. 5. Illustrating the equivalence of displacements: (a) $-\frac{1}{3}a_1 + \frac{1}{3}b_1 \equiv -\frac{1}{3}a_2$. (b) $-\frac{1}{3}a_1 - \frac{1}{3}b_1 \equiv -\frac{1}{3}a_3$.

The four structures can now be described as follows: *Crystal A*. Successive layers are displaced a distance $-\frac{1}{3}a_2$ (or $-\frac{1}{3}a_3$) along the a_2 (or a_3) axis; this ambiguity has already been discussed.

Crystal B. Successive layers are displaced $-\frac{1}{3}a_1$ along the a_1 axis. The structure is therefore truly monoclinic.

Rotations of layers do not occur in A and B .

Crystal C. The layers alternate between two orientations at 120° to each other and each layer suffers a displacement of $-\frac{1}{3}a_2$ relative to its own system of axes.

Crystal D. The sequence in this crystal consists of a rotation of $+120^\circ$ with $-\frac{1}{3}a_2$ displacement, a rotation of -120° with $-\frac{1}{3}a_2$ displacement, followed by a layer displaced by $-\frac{1}{3}a_2$ without rotation, i.e. every third

layer is rotated through -120° relative to the other layers.

These arrangements are shown diagrammatically in Fig. 6, where each circle represents a layer and the single, double and triple arrow-heads denote the a_1 , a_2 and a_3 axes. The arrows between the circles indicate the sequence of rotations and displacements. These results suggest that displacements along the a_2 axis are more common than those along the a_1 axis. The evidence is perhaps too slender to justify drawing a general conclusion that the layer displacements tend to avoid the direction of the symmetry plane, but it certainly is a feature of the results so far obtained. It may also be significant that the two crystals of type B which were examined showed some streaking along Debye-Scherrer lines indicating misalignment of mosaic fragments; such streaking was not obtained with crystals of types A, C and D.

A strong point in favour of the idea of rotations comes from the disordered structures (cf. Fig. 3 (b) and (f)), which, when described in terms of fixed axes, are disordered with respect to b but ordered with respect to a , a state of affairs which scarcely seems natural. In terms of rotations, however, it can be said that the layers are randomly rotated by multiples of 120° , with accompanying $-\frac{1}{3}a$ displacements. By analogy with the ordered structures, the displacements may, in any one crystal, be along a particular a axis of the layer. Whether or not this is the case cannot yet be stated,

but further work is in progress on the disordered structures.

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The Crystal Structure of Potassium Sodium *dl*-Tartrate Tetrahydrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$

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The crystal structure of potassium sodium *dl*-tartrate tetrahydrate has been studied by X-rays, using the Weissenberg and rotation method ($\text{MoK}\alpha$, $\lambda = 0.710 \text{ \AA}$). The lattice has the dimensions:

$$a_0 = 9.80 \text{ \AA}, \quad b_0 = 9.66 \text{ \AA}, \quad c_0 = 8.21 \text{ \AA}, \\ \alpha = 110^\circ 52', \quad \beta = 101^\circ 28', \quad \gamma = 119^\circ 44'.$$

There are two molecules of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in the unit cell. The space group is $C_2^1 - P1$. The tartrate molecules are like those in Rochelle salt, with the difference that a *d*- and an *l*-molecule form a pair, probably linked by a hydrogen bond between oxygen atoms belonging to the carboxyl groups. The potassium atom has a six co-ordination, being surrounded by one oxygen atom and one hydroxyl group from the tartrate groups and by four water molecules. The sodium atom also has a six co-ordination consisting of two oxygen atoms and one hydroxyl group from the tartrate groups and three water molecules. Water molecules themselves are in the middles of tetrahedra or of triangles formed of other atoms or atom groups. The structural relation between Rochelle salt and *dl*-tartrate is such that the two structures may be thought of as derived by different principles from the ideal building units whose features are common to them.

$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, potassium sodium *dl*-tartrate tetrahydrate, is a racemoid, its optically active counterpart

being the well-known Rochelle salt. Though known since Mitscherlich (1842) (*Gmelins Handbuch* . . . , 1938,