

The Structure of Chrysotile. II. Clino-Chrysotile

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(Received 21 March 1956)

Clino-chrysotile is based on a cylindrical lattice of type c_2 . In the case of the specimen studied in most detail the lattice is monoclinic of the 3rd kind with lattice parameters $a = 14.65$, $b \approx 9.25$, $c = 5.34$ Å, $\beta = 93^\circ 16'$. The atomic positions have been refined by trial and error, and by Fourier methods. It is confirmed that the structure is based on kaolin-like layers which are stacked in a manner consistent with a cylindrical structure.

1. Introduction

Chrysotile is a fibrous silicate of magnesium, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, which constitutes approximately 90% of the asbestos of commerce. The determination of its structure has been beset by unusual difficulties, as a result of the peculiarities of its diffraction pattern. Thus, no single crystals of the mineral are available, and the finest fibre specimen which can be examined gives a diffraction pattern with the full symmetry of a rotation photograph. On all layer lines of the photograph there occur diffuse reflexions (many of which are markedly unsymmetrical) which can be approximately indexed as $0kl$ reflexions. On the even-order layer lines only there are also moderately sharp reflexions which can be indexed as $h0l$ reflexions, but there are no $hk0$ or hkl reflexions which can be distinguished with any degree of certainty from the 'tails' of the diffuse $0kl$ reflexions. Anderson & Clark (1929) published the first description of the phenomena of X-ray diffraction by chrysotile, and suggested a structural significance for the similarity between its fibre repeat period and that of diopside, but their unit-cell assignment has never found acceptance. Warren & Bragg (1930) proposed a structure based on amphibole-like silicate chains. This provides an explanation of the fibrous character of the material, and gives reasonable agreement between the calculated and observed intensities of the sharp reflexions on the zero layer line. But it demands a doubled b axis for which there is no diffraction evidence, and it does not explain the peculiar features of the diffraction pattern.

Warren & Hering (1941) and Aruja (1943) pointed out that the diffuse reflexions of chrysotile are similar to cross-grating reflexions (Warren, 1941), and therefore suggested that the mineral has a disordered layer structure. Aruja showed that, of the various layer structures compatible with the chemical composition, only a kaolin-like structure is compatible with the intensities of the sharp reflexions on the zero layer line, and that such a structure gives better agreement than Warren & Bragg's structure between the calculated and observed intensities of these reflexions. Aruja also obtained some success in associating the

varying shapes and displacements of the diffuse reflexions with particular types of step-wise random displacements of the layers, but his structure did not account quantitatively for the displacements of the diffuse reflexions, nor for the remarkable limitation on the indices of the observed reflexions which has been noted above.

The most obvious disadvantage of the layer structure of chrysotile when it was proposed was the difficulty of reconciling it with the highly perfect fibrous character of the material. Pauling (1930) had suggested much earlier that if the magnesium analogue of kaolin existed it would have curved layers, owing to the misfit between the two halves of the layer, and Aruja used this hypothesis to suggest that such curvature might limit the growth of the structure to narrow ribbons. However, electron micrographs of chrysotile published by Bates, Sand & Mink (1950) and Noll & Kircher (1951) showed the fibres to have a hollow cylindrical form, and suggested a much more satisfactory correlation between the form of the material and the postulated structure based on curved layers.

The structural results to be described here were obtained at a time when the electron microscope results appeared well established but before the theory of diffraction by cylindrically curved layers had been worked out. It was assumed at this stage that the intensities of the sharp $h0l$ reflexions would be related to the structure factors for a projection of the structure on the ac plane in the same way as would apply to a rotation photograph of a normal crystal. The general features of the structure derived in this way have already been published (Whittaker, 1953*d*, here called I), and the above assumption has been shown to be theoretically justifiable (Whittaker, 1954). The types of structures which can be formed by cylindrically curved layers have been classified (Whittaker, 1955*c*) and their diffraction effects have been discussed systematically (Whittaker, 1955*a, b, d*). It is therefore now possible to describe unambiguously the structure of chrysotile and its determination in terms of defined concepts, and the detailed results summarised in I are reported in this and subsequent papers.

Jagodzinski & Kunze (1954*a, b, c*) have also discussed the diffraction from the cylindrically curved layer structure of chrysotile and have arrived at similar theoretical conclusions, although there are some differences in the structural conclusions reached. An unfortunate misunderstanding arose with these authors, who criticised (1954*c*) the application of the Fourier method (Whittaker, 1953*d*) on the grounds that the wrong correction factors must have been applied to the intensities. As the results obtained by Whittaker (1954) showed that the correction factors used were correct, it was concluded (Whittaker, 1955*a*) that the comparisons of observed and calculated intensities given by Jagodzinski & Kunze (1954*b*) must conversely be based on inadequate corrections. It is therefore a pleasure to record that it has now been established (by private correspondence) that these strictures were incorrect on both sides. The method used by Jagodzinski & Kunze gives correct intensity distributions, while that used by the present author gives correct results when applied to the integrated intensities.

A further contribution to the theory of diffraction by cylindrically curved layer structures has also been made by Waser (1955).

The present paper is confined to a discussion of the structure of clino-chrysotile, which is identical with the material investigated by Warren & Bragg, Warren & Hering, and Aruja. The structures of the other forms of chrysotile, ortho-chrysotile (Whittaker, 1951) and para-chrysotile (Whittaker & Zussman, 1956), will be discussed in subsequent papers.

2. Experimental

The specimen studied was a fibre pencil (17 mm. long and 0.14×0.07 mm. in cross-section) from Bell's Mine, Thetford, Quebec.

Equi-inclination rotation photographs (Whittaker, 1953*a*) were taken in the equi-inclination positions for all layer lines up to the 10th, and in a near equi-inclination position for the 11th. Filtered Mo $K\alpha$ radiation was used for photographs in all these positions and filtered Cu $K\alpha$ radiation was also used for photographs in equi-inclination positions up to that for the 6th layer line. The intensity data for the zero to 4th layer lines, inclusive, were obtained as far as possible by microdensitometry of semi-integrating rotation photographs (Whittaker, 1953*a*) in the equi-inclination positions for the zero and 3rd layer lines. These photographs were taken with Cu $K\alpha$ radiation reflected from the (111) face of fluorite, and the multiple-film technique was used. A few reflexions on the 2nd and 4th layer lines cannot be recorded on photographs in the equi-inclination positions for the zero and 3rd layer lines. In order to avoid the long exposures (of the order of 200 hr.) required for further semi-integrating photographs with crystal-reflected radiation, the intensities of these reflexions were

estimated visually from equi-inclination photographs taken with a stationary film and with filtered radiation. The intensities of reflexions observable only with Mo $K\alpha$ radiation were also estimated visually, but these data were found not to be useful for reasons discussed below. The integrated intensities of the $h0l$ reflexions were corrected for the appropriate Cox & Shaw factor (Whittaker, 1953*b*), polarization factor (Whittaker, 1953*c*), Lorentz, and absorption factors. The profiles of the diffuse $0kl$ reflexions were also corrected for these factors, with the exception of the Lorentz factor.

The equi-inclination photograph for the 6th layer line with Cu $K\alpha$ radiation requires an inclination of about 60° between the fibre axis and the X-ray beam. This is beyond the normal range of a Weissenberg goniometer, but was achieved (with a stationary specimen) by combining the maximum inclination setting of the camera axis (about 40°) and a further inclination of the specimen obtained with one of the setting arcs. The central region of the 6th layer line was then photographed on a flat film parallel to the X-ray beam. Such a photograph is shown in Fig. 1.

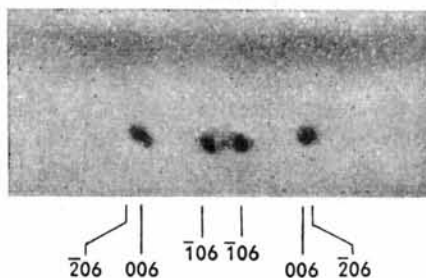


Fig. 1. Equi-inclination rotation photograph of the central region of the 6th layer line from a specimen of clino-chrysotile from Thetford, Quebec.

Although it is very restricted in range it is useful because it shows this important region of the layer line under conditions of high resolution and without the white radiation streaks associated with Mo $K\alpha$ photographs.

3. Lattice parameters and symmetry

With the minor exceptions noted below, all the reflexions from the specimen of Thetford chrysotile used are in the positions to be expected for a monoclinic cylindrical lattice of the 1st or 3rd kind (Whittaker, 1955*c*) with parameters†:

$$a = 14.65 \pm 0.01, \quad b \approx 9.2, \quad c = 5.34 \pm 0.01 \text{ \AA}, \\ \beta = 93^\circ 16' \pm 1'.$$

These two possible lattices consist of sets of co-axial cylindrical layers, each layer of which if unrolled would consist of a two-dimensional rectangular lattice, and

† The axial convention adopted here is that with c parallel to the fibre axis.

each successive layer of which is displaced by a distance $a \cos \beta$ in the direction of the cylinder axis. The difference between them lies in the fact that in the lattice of the 1st kind each cylindrical layer may be regarded as having been derived by rolling the plane lattice into a cylinder in such a way that the two ends of every line parallel to the b axis are joined together; whereas in the lattice of the 3rd kind the end of every such line is joined to the opposite end of a similar line N unit cells away from it. Thus in the lattice of the 1st kind the b axis lies on a circle whereas in the lattice of the 3rd kind it lies on a helix of order N . The value of N must be integral, unless the lattice is centred (which is true for chrysotile), when it may also adopt half-integral values. The difference between the diffraction patterns of the two possible lattices arises from the fact that the intensity distribution in the $h0l$ reflexions from a lattice of the 1st kind depends on a summation of terms containing $J_0((2\pi/\lambda)\xi\rho_m \sin \beta)$ (Whittaker, 1954), whereas that for a lattice of the 3rd kind involves terms containing $J_{Nl}((2\pi/\lambda)\xi\rho_m \sin \beta)$ (Whittaker, 1955*d*), where $\rho_m \sin \beta$ is the radius of a layer of the lattice. The difference between the positions of the $h0l$ reflexions is negligible except near $\xi = 0$, and for reasonable values of N it is small unless l is fairly large. The choice between the two possible lattice types is therefore most conveniently made by consideration of the central region of the 6th layer line, since here we have the maximum value of l which can be recorded with the high resolution possible with Cu $K\alpha$ radiation.

The matter is complicated by the fact that the value of β is such that reflexions of the type $\overline{h+1}, 0, 6$ and $h-1, 0, 6$ are almost superimposed at the position $\xi = ha^*$. Indeed, these reflexions are not resolved on

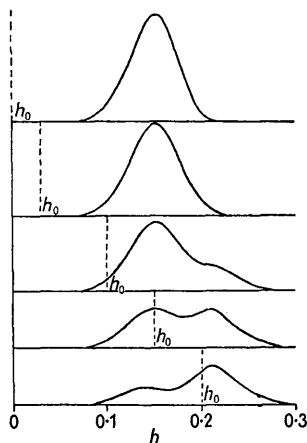


Fig. 2. Calculated profiles of the first reflexions on the 6th layer lines of the diffraction patterns of helical cylindrical lattices of unit order having various values of β . The vertical broken lines indicate the positions of the first reflexions from the corresponding regular cylindrical lattices. The profile is calculated in each case for a lattice having inner and outer radii 11 and 18 times the layer spacing respectively.

photographs taken with Mo $K\alpha$ radiation. However, on Fig. 1 the reflexions $\overline{206}$ and 006 are just resolved, and if the lattice were of the 1st kind it would be expected that two $\overline{106}$ reflexions would form an equally close pair bracketing the position $\xi = 0$. In fact this pair is much more widely separated and this displacement of the innermost reflexion is characteristic of a lattice of the 3rd kind.

Fig. 2 shows the calculated intensity distributions in the region of the meridian of the 6th layer line from a helical lattice of unit order and of internal and external radii $11 \times a/2$ and $18 \times a/2$ respectively, in which various values of β are assumed. These values of β are chosen so that the reflexion nearest to the meridian would occur at $\xi = h_0 a^*$ if the lattice were of the 1st kind. It is therefore seen that the position h_1 of the first reflexion is almost independent of h_0 provided that h_0 is not appreciably greater than h_1 . It may also be shown that h_1 is dependent on the product Nl and on the mean radius of the fibre.

Data obtained from Fig. 1 show that if N is assumed to be unity the mean of the inner and outer radii of the fibres must be 84 \AA . If any other of the permitted values of N (half-integral or integral) were assumed the radius obtained would be changed approximately inversely as N . Since the value of 84 \AA is in good accordance with other evidence, the unit value of N is assumed to be correct. It must therefore be concluded that this specimen of clino-chrysotile consists predominantly of material with a monoclinic cylindrical lattice of the 3rd kind.

It is not possible to derive an exact value of b from the positions of the diffuse $0kl$ reflexions because of the displacement of their peak positions from the reciprocal-lattice points. In fact each such reflexion leads to a different apparent value of b ranging from about 8.4 \AA to 9.3 \AA .

Such values obtained from reflexions from a cylindrical lattice (with scattering matter concentrated at the lattice points) would be linearly related to k^{-2} , whereas if the layers were flat they would be linearly related to k^{-1} . Owing to the distribution of scattering matter throughout the unit cell such a relationship cannot be expected to be exact, and is in fact found to be far from perfect, though the relationship to k^{-2} is more linear than that to k^{-1} . The best value of b should be obtained by extrapolating such relationships to an infinite value of k , and this process suggests a value of about 9.2_6 \AA .

The value of c given above agrees within experimental error with that reported by Warren & Bragg (1930) and Aruja (1943). The value of a also agrees with Aruja's value (if allowance is made for the fact that his value of 14.62 was really in kX. units and not \AA) but is 0.04 \AA smaller than Warren & Bragg's result (14.66 kX.). The value of β agrees exactly with that given by Warren & Bragg and is $4'$ larger than that given by Aruja. The value of $93^\circ 7'$ reported earlier (Whittaker, 1952) is now found to have been subject

to a systematic error because it was derived from photographs of a specimen which consisted of a mixture of ortho- and clino-chrysotile. The presence of the ortho-chrysotile reflexions results in an apparent displacement of the clino-chrysotile reflexions in this sense.

The following absences occur among the reflexions permitted by a primitive cylindrical lattice: $h00$ with $h \neq 2n$, $h0l$ with $l \neq 2n$, and $0kl$ with $k+l \neq 2n$. It is therefore concluded that the lattice is of type c_2 , and that the radial projection of (100) is centred. The possible two-dimensional space groups associated with the structure are $p111$ for the projection down [010] and $a1m1$, $a11m$, or $a2mm$ for the projection on (100).

The only reflexions on the photographs of the Thetford chrysotile which do not conform with the above scheme are as follows:

- (1) Diffuse intensity maxima not lying close to $0kl$ reciprocal-lattice points. It will be shown in a subsequent paper that these are not separate reflexions but modulations of the 'tails' of $0kl$ reflexions.
- (2) Very weak reflexions on layer lines indicative of a fibre axis repeat of 9.24 Å. These are due to the presence of a separate phase, para-chrysotile (Whittaker & Zussman, 1956), and are therefore not relevant to the structure of clino-chrysotile.
- (3) A very weak reflexion near the centre of the 2nd layer line. This is in the position of the strongest reflexion (202) of ortho-chrysotile, and is taken to indicate the presence of a small quantity, of the order of 2%, of this material in the specimen.
- (4) A weak meridional reflexion on the 6th layer line which appears on Fig. 1. This shows that a small proportion of the fibres in the specimen must possess a regular cylindrical lattice, but it is not known whether these fibres are to be identified with the small proportion of ortho-chrysotile present, or whether they are monoclinic of the 1st kind.

4. Trial-and-error analysis of the structure

Aruja (1943) has pointed out that if the two layers in the unit cell† of chrysotile are identical in structure, then the intensities of $h0l$ reflexions can most conveniently be calculated from the formula

$$|F|^2 = 8|F_1|^2 \{1 + \cos 2\pi(\frac{1}{2}h + lZ)\}$$

where F_1 is the structure factor for a single layer and Z is the relative displacement of the two layers parallel to the z axis. It is therefore possible to compare observed and calculated values of $|F|^2$ in the absence of any information as to the value of Z ,

† Strictly there is no unit cell in a cylindrical lattice, but the same result applies to the two-dimensional unit cell in the cylindrical projection down [010].

provided that different scaling factors are accepted for reflexions with different values of l and with odd and even values of h . From the ratios of the scaling factors for odd and even values of h it is possible to obtain directly an estimate of the value of Z .

The initial calculations were made from the atomic x co-ordinates derived by Aruja to fit the $h00$ reflexions, and from the y and z co-ordinates corresponding to regular hexagonal networks of atoms in the kaolin-type layer. The notation for the atoms is shown in Fig. 3, and the co-ordinates are shown in Table 1. Two pos-

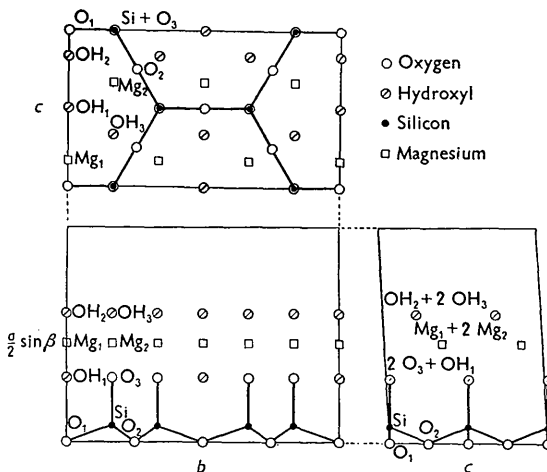


Fig. 3. Notation for the atomic positions in one layer of the chrysotile structure. The arrangement corresponds to possibility *B* of Table 1 if the origin of the c axis is taken at the top left-hand corner of the plan of the layer (upper part of the figure) and at the bottom left-hand corner of the appropriate elevation.

Possibility *A* would be obtained if the direction of the c axis were reversed and if the inclination of the a axis were also reversed so as to keep the oblique angle β between the positive directions of the axes.

Table 1. Co-ordinates

	x	y	z_A	z_B
O_1	0	0		0
O_2	0	0.250		0.250
Si	0.038	0.167		0.006
O_3	0.150	0.167		0.023
OH_1	0.150	0		0.523
Mg_1	0.225	0	0.201	0.867
Mg_2	0.225	0.167	0.701	0.367
OH_2	0.292	0	0.876	0.210
OH_3	0.292	0.167	0.376	0.710

sibilities (*A* and *B*) exist for the z co-ordinates of each of the Mg atoms and the hydroxyl groups OH_2 and OH_3 . These alternative positions exist because the layer of $O_3 + OH_1$ is approximately hexagonally close packed, and so presents two alternative sets of three positions in which the next layer of atoms (the magnesium atoms) can lie and achieve octahedral coordination when combined with a suitable disposition of the further layer of OH_2 and OH_3 groups.

The calculated values of $|F|^2$ (based on the empirical

Table 2. Values of the residue $\Sigma|F_o|^2 - |F_c|^2 \div \Sigma|F_o|^2$ at different stages of refinement

Reflexion group	Number of reflexions in group	1st trial	After trial-and-error refinement	After Fourier refinement
<i>h</i> 00	9	0.18	0.13	0.11
<i>h</i> 02 (<i>h</i> even)	12	0.10	0.19	0.14
<i>h</i> 02 (<i>h</i> odd)	3	0.16	—	0.19
<i>h</i> 04 (<i>h</i> even)	10	0.13	—	0.13
<i>h</i> 04 (<i>h</i> odd)	6	0.27	—	0.16
All observable reflexions with independent scaling factors for each group	40	0.15	—	0.12
All observable reflexions with a single scaling factor after allowing for the value of <i>Z</i>	40	0.17	—	0.14

f values of Bragg & West (1928)) were used to derive values of the residue $\Sigma|F_o|^2 - |F_c|^2 \div \Sigma|F_o|^2$. The values of this residue for the different groups of reflexions (when possibility *B* is assumed) are shown in the third column of Table 2. This residue (which is of course approximately twice as great as the more conventional one involving only the first power of $|F|$) was used because the method of calculation gives $|F_c|^2$ directly. The value of *Z* deduced in the way described above, both from the *h*02 and from the *h*04 reflexions, is 0.025.

When possibility *A* is assumed no agreement at all can be obtained with the observed intensities of the *h*02 reflexions with *h* even, and the possibility has not been considered further. The possibility that alternate layers might be of types *A* and *B* has also been considered briefly. However, it appears unlikely that such a structure could lead to consistently low intensities for all the *h*02 and *h*04 reflexions with *h* odd, and it is found that the maximum ratio of $|F_{c602}|^2/|F_{c602}|^2$, whatever the value of *Z*, would be ~ 2 for this structure, whereas the observed ratio is ~ 10 . This structure is therefore also considered to have been eliminated.

The value of *Z* found above shows that the layers are stacked with *O*₂ over rows of hydroxyl groups, and *O*₁ over grooves between these rows, in the layer below, as has already been discussed in paper I. It therefore seems likely that *O*₁ should have a lower *x* parameter than *O*₂, if its lying in these grooves is to have the locating influence which it appears to have. A series of ten trial-and-error adjustments of these and other atomic *x* co-ordinates was made in which the intensities of the *h*00 reflexions, and the corresponding residues, were calculated at each stage. As a result of this work a number of possible adjustments were shown to be undesirable, and a combination of those considered most probable, both as a result of packing considerations and of their effect on the residue, gave an improvement of the latter from 0.18 to 0.13.

The intensities of the *h*02 reflexions (*h* even) were recalculated from the adjusted *x* parameters, but gave a worsening of the corresponding residue from 0.10 to 0.19. This was not changed when the *z* parameters of *O*₁ and *O*₂ were adjusted so as to position them exactly over the ridges and grooves formed by the hydroxyl groups.

5. Fourier refinement

In order to break the impasse reached in the trial-and-error refinement a Fourier synthesis has been performed, notwithstanding the difficulty that there are several *h*0*l* reflexions whose intensities cannot be measured unambiguously because they are superimposed on diffuse *Ok**l* reflexions. It was therefore necessary to use the corresponding values of *F*_{*c*} in the synthesis in place of these undetermined values of *F*_{*o*}. The proportions of calculated and observed data used in the synthesis were therefore a little more unfavourable than in a normal Fourier synthesis of a structure without a symmetry centre, but nevertheless an appreciable degree of refinement was obtained, as shown in the last column of Table 2. The co-ordinates assumed were those of Table 1 (position *B*) combined with the directly determined value of *Z* = 0.025. The co-ordinates found were therefore entirely independent of the trial-and-error refinement. The electron-density map obtained was shown in paper I. The atomic co-ordinates deduced are shown in Table 3, and the

Table 3. Atomic co-ordinates deduced from the Fourier synthesis

	<i>x</i>	<i>z</i>
<i>O</i> ₁	~ -0.013	?
<i>O</i> ₂	0	0.250
Si	0.033	0.006
<i>O</i> ₃ + <i>OH</i> ₁	0.150	0.023
Mg	0.227	0.373
<i>OH</i> ₂ + <i>OH</i> ₃	0.292	0.217

The co-ordinates of atoms in the second layer are related to these by the shift $\frac{1}{2}Z$, where *Z* = 0.019.

Table 4. Comparison of $|F_o|^2$ with $|F_c|^2$ calculated from the results of the Fourier synthesis

hkl	$ F_o ^2$	$ F_c ^2$	hkl	$ F_o ^2$	$ F_c ^2$	hkl	$ F_o ^2$	$ F_c ^2$
200	154	146	$\overline{10},0,2$?	130	804	60	59
400	434	399	$\overline{12},0,2$	≤ 20	5	10,0,4	13	8
600	57	66	$\overline{14},0,2$	19	34	$\overline{12},0,4$	0	11
800	68	75	$\overline{16},0,2$	≤ 6	4	$\overline{20},4$	88	79
10,0,0	77	92				$\overline{40},4$	(14-51)	31
12,0,0	82	62	102	2.1	2.9	$\overline{60},4$	61	58
14,0,0	55	62	302	≤ 10	4.4	$\overline{80},4$	35	44
16,0,0	81	79	502	0	2.3	$\overline{10},0,4$	≤ 4	1
18,0,0	8	1	702	~ 4	2.9	$\overline{12},0,4$	≤ 4	7
			902	0	0			
002	16	22	11,0,2	0	0.7	104	2	1
202	195	203	$\overline{102}$	0	0.3	304	≤ 6	3
402	92	104	$\overline{302}$	0	0.4	504	≤ 0	0
602	125	151	$\overline{502}$	0	0.5	704	5	6
802	40	37	$\overline{702}$	0	0.5	904	≤ 35	3
10,0,2	≤ 20	16	$\overline{902}$	~ 4	4.0	11,0,4	≤ 0	1
12,0,2	23	21	$\overline{11},0,2$	0	1.0	$\overline{104}$	2	3
14,0,2	≤ 6	2				$\overline{304}$	9	9
16,0,2	16	25	004	17	14	$\overline{504}$	1	1
202	29	26	204	26	29	704	≤ 7	9
402	18	9	404	15	13	$\overline{904}$	1	1
602	12	10	604	15	20	$\overline{11},0,4$	≤ 7	1
802	88	89						

The values of $|F_c|^2$ given in this table are calculated from the positions of the atoms in a single layer and then scaled to the values of $|F_o|^2$ by the mean ratio in each group, i.e. separately for each value of l and for even and odd values of h .

values of $|F_c|^2$ re-calculated from them are compared with $|F_o|^2$ in Table 4.

There is some evidence in the electron-density map of ridges of spurious density running parallel to the z axis. Also, the value of the scaling factor $|F_c|^2/|F_o|^2$ is 4% higher for the even $h02$ reflexions than for the $h00$ reflexions, and 26% higher for the even $h04$ reflexions. Taken together, these facts suggest a systematic error in the F_o values of the higher layer lines. This may be due in part to the presence of small amounts of ortho-chrysotile and para-chrysotile, which contribute to the $h00$ reflexions but not to the others. It may also be due in part to the crowding of the reflexions on the 4th layer line, which may lead to the assumption of too high a 'background intensity' on the layer line. It gives some justification for the use of independent scaling factors for the different groups of reflexions, but even with a single scaling factor the residue of 0.14 may be considered satisfactory, corresponding as it does to a value of only about 0.07 for the usual residue based on $|F|$.

6. Discussion of the structure

The O_1 and O_2 atoms and the layer stacking

The packing considerations discussed in paper I, trial-and-error calculations, and the Fourier synthesis all indicate that O_1 should have a lower x co-ordinate than O_2 . Unfortunately, O_1 is poorly resolved from the silicon atom so that its position cannot be very precisely determined, but the indicated difference in x co-ordinates of O_1 and O_2 amounts to about 0.2 Å.

The z co-ordinate of O_2 is displaced by 0.1 Å from the position vertically over the row of hydroxyl groups in the adjacent layer below. If O_1 had the z co-

ordinate corresponding to that in the idealized hexagonal net shown in Fig. 3 it would be displaced by an equal amount from the position vertically over the groove between the hydroxyl groups. Since in fact the position of O_1 in this groove must provide the positioning mechanism which controls the stacking arrangement of the layers, it is assumed that O_1 has a z co-ordinate different by Z ($= \pm 0.019c$) from that in the idealized net. Unfortunately, this conclusion cannot be verified from the electron-density map because of the poor resolution of O_1 , but the assumed co-ordinate is within a range consistent with the map.

Mathieson & Walker (1952) have found a similar distortion of about the same extent in the silicate net of vermiculite, and have suggested that it is due to the attraction of O_1 by the magnesium atoms, which are disposed unsymmetrically with respect to O_1 in the z direction. This explanation cannot be invoked here, however, since the distortion must be in opposite directions in alternate layers of the structure, in order to explain the very well attested two-layer character of clino-chrysotile (Whittaker & Zussman, 1956). If the distortion did not occur, or if it were similarly directed in every layer, then one would obtain one-layer structures with slightly different values of β . It is suggested that the distortion arises from the need for lower Si-O-Si bond angles than those which would occur in the idealized structure, but no explanation is offered for its opposite direction in alternate layers.

The Si-O₃ bond

The length obtained for this bond is 1.71 Å, whereas 1.64 Å was assumed in the 1st trial co-ordinates. This is not an impossible value considering probable errors

in the structure, and it might be shortened if the observed position of O_3 is a mean position of $2O_3+OH_1$ and if these two types of atom are not exactly superimposed. Some evidence for this is discussed below.

The co-ordination of the magnesium

The position of the magnesium is anomalous in as much as it is not centrally disposed between the two sheets of co-ordinating oxygen and hydroxyl groups. This anomaly has previously been found by Aruja (1943); the present trial-and-error calculations have confirmed that it is unavoidable, and the Fourier synthesis has actually increased it slightly. The mean planes of the O_3+OH_1 and the OH_2+OH_3 groups are separated by 2.08 Å, and the magnesium atoms are 1.13 Å from the former plane and 0.95 Å from the latter.

The cause of this unsymmetrical arrangement is unknown. It is tempting to suppose that the x co-ordinate of OH_1 should be increased so as to diminish or remove the anomaly in respect of the hydroxyl groups considered separately. This would involve the assumption of a still smaller x co-ordinate for O_3 in order to conform with the result found from the electron-density map, which gives the weighted mean position of $2O_3+OH_1$. This would, however, have the desirable effect of reducing the length of the Si-O₃ bond. Evidence that such a modification of the co-ordinates has a beneficial effect on the agreement of the observed and calculated intensities of the $h00$ reflexions has also been obtained in the trial-and-error investigation. It is therefore probable that the co-ordinate of $2O_3+OH_1$ given in Table 3 is the resultant of $2O_3$ atoms lying at $x \approx 0.145$ and OH_1 lying at $x \approx 0.160$. A similar displacement of a similarly situated hydroxyl group, relative to the oxygen atoms that are bonded to silicon, has been found in crocidolite (Whittaker, 1949) and in actinolite (Zussman, 1955).

7. Conclusion

The conclusions reached by Aruja on the x co-ordinates of the atoms in clino-chrysotile have been confirmed with only minor modifications. The z co-ordinates of the atoms and the relationship between successive layers have also been established. The stacking of the layers is such as to suggest that there is complete translational disorder between the layers in the b direction, although the structure is ordered in the c direction. This circumstance provides confirmatory evidence that the layers have a cylindrical curvature about the fibre axis. This is also evidenced by the restrictions on the indices of the observed reflexions and by the displacements of the diffuse $0kl$ reflexions. The displacement of the 106 reflexion further indicates that the structure is based on a helical cylindrical lattice. All these facts accord well with the electron microscope evidence that the fibres consist of hollow tubes.

The agreement between the observed and calculated intensities of the reflexions obtainable with Cu $K\alpha$ radiation is satisfactory, although it is not claimed that the ultimate degree of refinement has been attained. An attempt has been made to refine the structure further and to improve the resolution of the atoms by including the intensity data obtainable with Mo $K\alpha$. The inclusion of these data only raises the overall disagreement residue used to 0.16 (corresponding to about 0.08 for the more usual residue) even without the assumption of different scaling factors for the different layer lines. This is quite satisfactory, but the Fourier synthesis calculated with these data was markedly worse than the previous one as regards the regularity of the atoms and the presence of spurious detail, and it could not be used to continue the refinement process. This may have resulted from excessive errors in either the calculated phases or the observed intensities of the high-order reflexions. A further possible source of error is the variation of the Fourier transform of the structure within the limits of the rather broad reflexions. It therefore appears that further refinement of the structure is unlikely without a radical re-examination of the problem.

A complete X-ray analysis of the structure of chrysotile requires that the various peculiar features of the diffuse $0kl$ reflexions should be accounted for. This has been done, but as the work involved is more closely associated with the texture of the fibres than with the atomic arrangement in clino-chrysotile it will be reported in a separate paper.

I wish to thank the Directors of Ferodo Ltd for permission to publish this paper.

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The Structure of Chrysotile. III. Ortho-Chrysotile

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(Received 21 March 1956)

Ortho-chrysotile, like clino-chrysotile, is based on a cylindrical lattice of type c_2 . The specimen studied in most detail is orthorhombic of the 1st kind with lattice parameters $a = 14.63$, $b \simeq 9.2$, $c = 5.34$ Å. The structure has been determined by trial-and-error and by Fourier methods. It is shown that the structure of the individual layers is almost identical with that of the layers in clino-chrysotile, but alternate layers are inverted end to end. This leads to a different stacking arrangement, which is still consistent with a cylindrical structure.

1. Introduction and experimental

Ortho-chrysotile (Whittaker, 1951) occurs in intimate admixture with the better known clino-chrysotile in specimens from many sources, but specimens rich in ortho-chrysotile are very rare. The variety is almost absent from the much-studied Quebec deposits. Methods for the analysis of mixed specimens by X-ray diffraction, and a survey of the distribution of ortho-chrysotile, have been published elsewhere (Whittaker & Zussman, 1956).

Ortho-chrysotile exhibits the same diffraction peculiarities which have led to difficulties in the determination of the structure of clino-chrysotile and which have been described in Part II (Whittaker, 1956). The close relationship of the two varieties is shown by the fact that the positions and intensities of their $h00$ reflexions are identical within the experimental error, and their diffuse $0kl$ reflexions show no greater differences than do those from specimens of clino-chrysotile from different sources. These differences are probably due to differences of texture rather than of atomic arrangement.

The specimen used in the present work was from Cuddapah, Madras, India. It was in the form of a fibre pencil measuring 11 mm. in length and 0.15×0.10 mm. in cross-section. The experimental methods and corrections were as described in Part II. Comparison of the intensities of the $h00$ reflexions and the $h0l$ clino-chrysotile reflexions from this specimen with those from the specimen studied in Part II showed the specimen to contain 22% of clino-chrysotile. The

intensities of the $h0l$ ortho-chrysotile reflexions were therefore multiplied by a factor 100/78 to put them on to the same scale as the $h00$ intensities.

2. Lattice parameters and symmetry

The specimen studied has an orthorhombic cylindrical lattice with parameters

$$a = 14.63 \pm 0.01, \quad b \simeq 9.2, \quad c = 5.34 \pm 0.01 \text{ Å}.$$

The values of a for ortho- and clino-chrysotile are such that the perpendicular spacing of the layers is identical.

An equi-inclination photograph of the central region of the 6th layer line with Cu $K\alpha$ radiation shows a strong meridional reflexion bracketed by very weak and rather diffuse helical reflexions. The specimen therefore consists predominantly of material with an orthorhombic cylindrical lattice of the 1st kind. Since the specimen of clino-chrysotile studied in Part II had a helical lattice it is tempting to associate the weak helical reflexions with the clino-chrysotile present. However, extensive surveys of many specimens from different sources will be necessary before a correlation can be established between ortho- and clino-structure on the one hand and regular and helical cylindrical lattices on the other.

Determination of the value of b is subject to the same difficulty as in the case of clino-chrysotile.

Absent reflexions are the same as for clino-chrysotile, so that the lattice is of type c_2 , and the radial projec-