Acta Cryst. (1953). **6**, 747

The structure of chrysotile.

By E. J. W. Whittaker, *Technical Division, Ferodo Ltd, Chapel-en-le-Frith, Stockport, England*

(*Received* 15 *April* 1953)

It has been shown in a previous communication (Whittaker, 1951) that there exist two varieties of chrysotile, of which the better known form is monoclinic and the other is orthorhombic. Preliminary structure analyses of both these varieties have now been made, based on the $h0l$ reflexions. The intensity data were obtained from semi-integrating equi-inclination rotation photographs (Whittaker, 1953) taken with crystal reflected Cu $K\alpha$ radiation. The multiple-film technique was used, and the photographic densities were measured with a microdensitometer. Analysis of the intensities of the $h00$ reflexions confirms the type of structure proposed by Aruja (1943) for clino-chrysotile, and shows that the structure of ortho-chrysotile is based on the same layer sequence. Some further refinement of both structures has been carried out by trial-and-error methods and by Fourier methods using the $h00$, $h02$ and $h04$ reflexions. (The convention adopted is that with the c-axis as the fibre axis.) In this way it has been shown that the relationship between successive layers is the same (so far as nearest neighbours are concerned) in the two varieties of chrysotile, but differs from that found in other minerals with the kaolin-type structure. The present communication describes only the general features of the two structures. It is hoped to refine them further by taking into account the intensities of the $h06$, $h08$ and $h,0,10$ reflexions observable on equi-inclination photographs taken with Mo $K\alpha$ radiation, and the details of the structure determination will therefore be published later.

It is well known that in a kaolin-type layer there exist two alternative sets of three positions per formula unit which can be occupied by cations. In chrysotile, $Mg_3Si_2O_5(OH)_4$, one or other of these sets must be fully occupied in every layer, but there appears no *prima facie* reason for expecting one set of positions to be occupied in preference to the other. Indeed, Aruja (1943) suggested that the occupation of these alternative positions might vary randomly from layer to layer, and that such disorder might be a contributory factor in producing the diffusion which is evident in all chrysotile diffraction patterns. However, the present work makes it unlikely that this can be generally true in more than a minor degree. It is found that the intensities of the $h0l$ reflexions of clino-chrysotile demand that the layers should be all of one type, having the magnesium atoms in one only of the two possible sets of positions, while the intensities of the $h0l$ reflexions of ortho-chrysotile demand that alternate layers of the structure should be of opposite types. Thus if a layer with the magnesium atoms in one set of positions is denoted by A and a layer with magnesium atoms in the alternative set of positions is denoted by B, then we may denote the structure of the two chrysotile varieties by the sequences

clino-chrysotile: $A\,A\,A\,A\,A\,A\ldots$
ortho-chrysotile: $A\,B\,A\,B\,A\,B\ldots$

This naturally suggests the possibility of further types of polymorphism in chrysotile corresponding to more elaborate regular sequences of A and B layers such as have been observed in other materials. Such polymorphs would obviously have larger unit cells than the known varieties, and they have not so far been found among the specimens examined by the author, which number well over a hundred from a variety of sources. There have been observed, however, several specimens in which abnormal diffuseness of the $h0l$ reflexions with non-zero l provides evidence of a high degree of randomness in the sequence. Such a situation may be equally well described in terms of a finite probability of transition at each layer between the clino- and ortho-chrysotile structures. These disordered layer sequences are being subjected to further study.

It is to be noted in connection with the above discussion that the sequence $B\,B\,B\,B\,B\,B\ldots$ does not constitute a distinct arrangement. Provided that the nearest-neighbour relationship described below is maintained, it differs from the sequence $A\,A\,A\,A\,A\,A\ldots$ only by an opposite choice of the positive direction of the fibre axis.

Fourier projections down the [010] axes of the two varieties of chrysotile are shown in Fig. 1. It may be seen that in both structures the hydroxyl groups of one layer lie in the same relation to the oxygen atoms of the layer above. The change of symmetry is due to the maintenance of this relationship when the positions of the hydroxyl groups of alternate layers are changed to

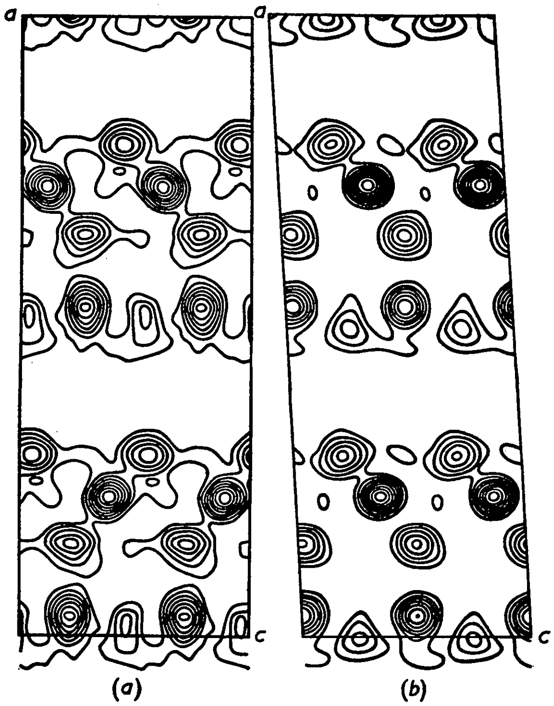


Fig. 1. Fourier syntheses of chrysotile down [010]: (*a*) ortho-chrysotile, (*b*) clino-chrysotile. Contours at equal arbitrary intervals, omitting the first.

conform with the alternative position of the magnesium atoms.

It is to be noted that in both varieties in this projection one set of oxygen atoms at the base of the silicate layer lies almost exactly over the hydroxyl groups of the layer below, while the other set of oxygen atoms at the base of the silicate layer lies almost exactly over points half way between the hydroxyl groups of the layer below. How exactly this relationship is obeyed cannot be stated with certainty until the further refinement of the structures has been completed. In the projection down [010] one of the oxygen atoms involved is not resolved from the adjacent silicon atom, but the other oxygen atom in both varieties is at present determined to be 0·1 Å from the point exactly opposite the hydroxyl group of the next layer. In other minerals of the kaolin-type whose detailed structure is known this distance exceeds 0·4 Å. The difference is presumably associated with the inter-layer disorder along [010] which must result from the cylindrical structure revealed by the electron microscope (Noll & Kircher, 1951). On account of their different radii, successive layers must be completely out of register in the [010] direction, and the basal oxygen atoms of one layer will therefore be unable to take up the two-dimensionally most favourable positions with respect to the hydroxyl groups of the layer below. Rather, they will be constrained to take up appropriate positions with respect to the rows of hydroxyl groups which, considered statistically, will have the same effect as corrugations running round the circumference of the cylinder. Then, if the two sets of basal oxygen atoms have slightly different elevations in a direction perpendicular to the layers, one will lie over the 'grooves' between the hydroxyl groups and the other will lie over the 'ridges' of hydroxyl groups. Just such a difference in the elevations of the oxygen atoms is in fact indicated by the Fourier projections.

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

References

Aruja, E. (1943). Ph.D. Thesis, Cambridge.
Noll, W. & Kircher, H. (1951). *N. Jb. Min.* **10**, 219.
Whittaker, E. J. W. (1951). *Acta Cryst.* **4**, 187.
Whittaker, E. J. W. (1953). *Acta Cryst.* **6**, 93.

Acta Cryst. (1953). **6**, 748

A contribution to the vector-algebraic method for the interpretation of the Patterson synthesis.

By A. Bezjak, *Laboratory for General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Yugoslavia*

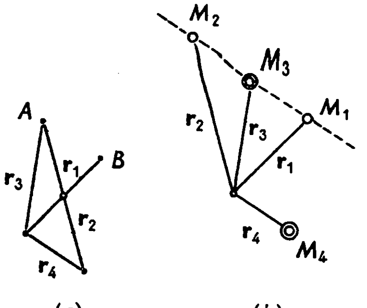
(*Received* 11 *May* 1953)

Recently Lindqvist (1952) described and successfully applied a new 'vector-algebraic method' for the interpretation of the Patterson synthesis in the case of centrosymmetrical structures. In this note a modification and further development of his method is described.

If in the centrosymmetrical lattice two atoms are chosen at the points $A(x_i, y_i, z_i)$ and $B(x_j, y_j, z_j)$, then in the Patterson function the maxima with the coordinates

$$M_1(2x_i, 2y_i, 2z_i);\ M_2(2x_j, 2y_j, 2z_j);$$
$$M_3(x_i+x_j, y_i+y_j, z_i+z_j);\ M_4(x_i-x_j, y_i-y_j, z_i-z_j)$$

are to be found. These maxima belong to the interatomic vectors $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ and $\mathbf{r}_4$, respectively (Fig. 1). If the atoms are of the same scattering power the maxima M_3 and M_4 are twice as large as the maxima M_1 and M_2.



(*a*) (*b*)

Fig. 1.

The vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ are the diagonals and the vectors $\mathbf{r}_3$ and $\mathbf{r}_4$ are the sides of a parallelogram; they are therefore related by the equations

$$\mathbf{r}_1 = \mathbf{r}_3+\mathbf{r}_4,\ \mathbf{r}_2 = \mathbf{r}_3-\mathbf{r}_4\ ,$$

upon which Lindqvist based his method.

Evidently, the maxima M_1, M_2 and M_3 are located on a straight line with M_3 exactly at the mid point of the length M_1M_2 (Fig. 1(*b*)). Moreover, the maximum M_4 is to be found on the terminal of the vector $\mathbf{r}_4$, the length of which is equal to the length M_2M_3 (or M_3M_1) and is in the same direction.

If, therefore, the positions of two atoms are to be determined from a Patterson projection, three maxima (1, 2, 1) located on a straight line must be found with a doubly-weighted maximum (2) at the mid point. On the straight line parallel to the first but passing through the origin a doubly-weighted maximum at a distance 1–2 from the origin must also be found. Consequently, the real positions of the atoms in the projection are at the mid points of the lines joining the origin to the singly-weighted maxima.

If the positions of three atoms are to be found from the Patterson projection, then the singly-weighted maxima would be located on the corners of a triangle with the doubly-weighted maxima at the mid points of its sides. On the straight lines parallel to each side of this triangle and passing through the origin the corresponding doubly-weighted maxima would also appear (Fig. 2).

It follows that for *n* atoms (of the same scattering power) the singly-weighted maxima would make in the