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X-ray studies of halloysite and metahalloysite.

Part I. The structure of metahalloysite, an example of a random layer lattice.

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METAHALLOYSITE is one of the kaolin group of minerals with a composition approximating to the formula $Al_2O_3.2SiO_2.2H_2O$, and its structure is generally considered to be built of composite layers of atoms of the kind found in other minerals of this group. It differs from them most strikingly in that it can be produced by the dehydration of the hydrated mineral halloysite, which has the approximate composition $Al_2O_3.2SiO_2.4H_2O$. Both minerals give comparatively poor X-ray diagrams showing relatively few lines and bands. The lines correspond to reflections from a basal spacing of about 7·2 Å. in metahalloysite and 10·1 Å. in halloysite. The similarity of the basal reflections from metahalloysite with those from the other kaolin minerals together with their similar chemical constitutions have provided the main evidence hitherto that metahalloysite is built from the same type of atomic layers. Hendricks (1942, p. 279) has stated that 'There is no reason at the present time for considering [meta] halloysite $Al_2O_3.2SiO_2.2H_2O$ to have types of layers different from kaolinite, nacrite, and dickite. New evidence, however, might be found that would lead to a more complete understanding of its structure. The powder-diffraction pattern of [meta] halloysite differs somewhat from that of kaolinite, but in a manner that can be accounted for by its degree of organization', and later he states that there is great lack of order in the stacking of the layers in both metahalloysite and halloysite. It is this question of the disorderliness in the stacking of the layers which will be mainly considered in the present paper.

The present writers with MacEwan (1946) have already suggested in a brief note that the layers may be assembled in so random a manner in their own planes that the diffraction effects which are observed may be produced by two-dimensional sheet-like gratings, apart from the basal reflections which arise from the stacking of the layers. The evidence for this view was that the form of the most prominent band in the diffraction pattern could be explained by a simple application of the theory developed by Warren (1941) for X-ray diffraction by two-dimensional lattices. The bands, however, are of various forms and require more detailed consideration than was possible in the previous note.

The diffraction bands (not the basal reflections) from halloysite and metahalloysite appear to be identical; no change can be observed when halloysite is dehydrated to metahalloysite. This indeed would be expected if in both cases the bands arose from the same randomly displaced layers. We have preferred to examine in detail the phenomena obtained with metahalloysite partly because the basal reflections can be sharpened by heat-treatment, which, however, does not affect the diffraction bands, and also because the smaller basal spacing gives fewer reflections of this type.

Comparatively little attention has been given to the structure of metahalloysite, probably because the diffraction pattern is poor and provides unpromising material for detailed study. Nevertheless the question is worth examining in as much detail as possible in order to obtain the clearest possible picture of the difference between kaolinite and metahalloysite and their relation to other kaolin-type minerals, such as those which commonly occur in many fireclays (*see* Brindley and Robinson 1946b, 1947) and which appear to have intermediate degrees of orderliness.

The X-ray powder diagram of metahalloysite.

X-ray diagrams of a number of metahalloysites have been taken with Cu-$K\alpha$ radiation in a camera of 20 cm. diameter of the semi-focusing type, employing a flat plate of powder; a few measurements have also been made with a camera of 12 cm. diameter using a fine rod of powder. The measurements were made on metahalloysite from Lawrence County, Missouri, U.S.A., which was the purest natural material available when this work was begun. Subsequently, however, we suspected that two lines in this diagram were spurious and further data, more particularly the photometric measurements, have been based on a natural metahalloysite from Simla, India, which does not give these two suspected lines. A number of artificial metahalloysites prepared by dehydration of halloysites from Angleur (Belgium), Northamptonshire (England), and Indiana and Utah (U.S.A.), have also been examined and these give results in agreement with the Simla material; the last two, however, contain gibbsite as an impurity. In table I we record the data for the Missouri and Simla specimens; the higher orders, which owing to their diffuseness are difficult to measure accurately, have been determined only for the Missouri material and the data in the table are mean values from a number of films. The table also contains data supplied privately

TABLE I. Lattice spacings (in Å.) for specimens of metahalloysite.

I.	II.	III.	IV.	V.
7·69	7·40	7·55	7·48	7·46
4·422	4·423	4·42	4·44	4·45 4·41
3·578	3·596	3·66	3·62	3·63
2·559	2·557	2·56	2·60	2·55
—	2·486÷	—	—	—
2·403	2·400	—	—	—
—	2·335÷	2·36	2·33	2·32
2·218	trace	2·23	—	—
—	—	2·06	—	—
—	1·801*	—	—	—
1·678	1·677	1·678	1·70 1·64	1·67
1·481	1·481	1·481	1·487	1·48
1·281	1·281	1·283	1·290	1·27
1·231	1·231	1·232	1·237	1·23
—	1·201*	—	—	—
—	1·108	1·105	—	—
—	1·021	1·021	—	—
—	0·968	0·968 0·958	—	—
—	0·856	0·855	—	—
—	0·840	0·838	—	—

* Observed only after heating for several hours at 300° C.
÷ Doubtful metahalloysite lines.

I. Specimen from Simla, India (B.M. 43087).
II. Specimens from Lawrence County, Missouri, U.S.A.
III. Data from D. M. C. MacEwan (specimen from Hungary).
IV. Data by G. Nagelschmidt (1934) (specimen from Harz, Germany).
V. Data by M. Mehmel (1935).

by Dr. MacEwan for a Hungarian halloysite together with data by Nagelschmidt (1934) and by Mehmel (1935). There is good general agreement between the results, and especially between the higher order spacings obtained by MacEwan and ourselves. The two doubtful lines in the Missouri pattern, marked + in table I, occur in a range of continuous scattering for which most previous workers have recorded only the approximate beginning and end of the band. We find for all metahalloysites evidence of two intensity maxima in this band.

Indexing of the powder diagram.

The diffraction pattern consists of lines and bands which may conveniently be considered separately. A microphotometer trace of the lower-order reflections (fig. 1) shows an almost continuous distribution of intensity across the film and the lines are distinguished from the bands only by having a more symmetrical distribution of intensity.

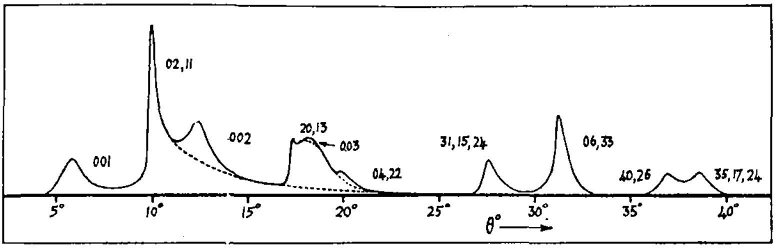

Fig. 1. Microphotometer trace of X-ray powder diagram of metahalloysite; X-ray intensity plotted against Bragg angle θ.

(*a*) *The basal reflections*, (00*l*).—These consist of lines which can be indexed as various orders of (001) with a spacing of about 7·2 Å. They are listed in table II together with the corresponding kaolinite reflections (Brindley and Robinson, 1946a). The greater breadth and more rapid diminution of intensity towards higher angles of the metahalloysite reflections indicates smaller crystals and/or less perfect parallelism of the layers; probably both causes are operative. In part III of this group of papers the effect of heat-treatment on metahalloysite is considered; heat-treatment sharpens the basal reflections and makes it possible to observe some of the higher orders which normally are not visible. Moreover, the observed spacings then agree better with submultiples of the fundamental spacing of 7·20 Å. There appears to be no doubt that the basal spacing of metahalloysite is somewhat greater than that of kaolinite.

TABLE II. Comparison of basal reflections (00l) from metahalloysite and kaolinite. d_{001} (metahalloysite) = 7·20 Å., d_{001} (kaolinite) = 7·132 Å.

	Metahalloysite (Missouri).			Kaolinite.		
00l.	d (obs.).	d (calc.).	I (obs.).	d (obs.).	d (calc.).	I (obs.).
001	7·40	7·200	vst	7·15	7·132	vvst
002	3·596	3·600	vst	3·566	3·566	vvst
003	2·400	2·400	w	2·374	2·377	mst
004	1·801*	1·800	w	1·778	1·783	m
005	—	1·440	abs.	1·426	1·426	w-m
006	1·201*	1·200	vw	1·188	1·189	w-m
007	—	1·029	abs.	1·019	1·019	w

* Observed only after heating for several hours at 300° C. Visual intensity scale: vvst, vst, st, mst, m, w-m, w, vw, abs.

(*b*) *Diffraction bands, with indices* (*hk*).—These bands are of considerable interest for their intensity distribution varies noticeably from one to another. The lowest-order band is the most prominent feature of the whole powder diagram; it has a sharp low-angle termination with a maximum of intensity corresponding to a spacing of 4·42 Å. while on the high-angle side the diffracted intensity spreads well beyond the (002) reflection with d = 3·60 Å. The present writers with MacEwan (1946) have already shown that the variation of intensity in this band agrees well with the theories of diffraction by two-dimensional crystal lattices developed by Laue (1932) and Warren (1941). This preliminary study assumed the lattice-structure factor was constant over the range of angles covered by a band; in the present paper it will be shown that, while the assumption was valid for this particular band, it is not generally valid. A more searching test of the supposition that the bands are produced by two-dimensional diffraction requires that both the forms and the relative intensities of all the bands in the powder diagram should be explained on this basis.

Consideration will first be given to the *positions* of the bands and their indices. The intensity maxima would be expected to occur approximately in directions θ_0 corresponding to Bragg reflections from 'planes' (*hk*) having a spacing given by

$$d_{hk} = [(h/a)^2+(k/b)^2]^{-\frac{1}{2}}, \tag{1}$$

where a and b are the lattice parameters of the layer structure. The extension of Laue's theory by Warren (1941) takes account of the finite size of the sheets. When the linear extension L of the crystallites is small, e.g. of the order of 100 Å., the intensity maxima are displaced from θ_0 towards higher angles and the apparent spacings d' derived from the observed maxima are less than the true spacings d_{hk} by a correction term Δd given approximately by

$$\Delta d = d_{hk} - d' = 0{\cdot}32 d_{hk}^2/L. \qquad (2)$$

Such displacements have been observed by Biscoe and Warren (1942) and by A. Taylor (1942) for carbon black, and by Aruja (1944) for chrysotile, a mineral structurally similar to the kaolin group but containing magnesium in the octahedral positions.

TABLE III. Two-dimensional X-ray diffraction maxima from metahalloysite (Missouri).

d_{hk} calculated with $a = 5{\cdot}14$ Å., $b = 8{\cdot}90$ Å., $b/a = \sqrt{3}$.
Δd calculated from equation (2) with $L = 200$ Å.

(hk).	d' observed.	Δd.	$d_{hk} = d' + \Delta d$.	d_{hk} calc.	Intensity observed.
11,02	4·423	0·031	4·454	4·451	vvs
20,13	2·557	0·011	2·568	2·570	s
04,22	(2·218)*	0·008	2·226	2·225	vw
24,31,15	1·677	0·004	1·681	1·682	s
33,06	1·481	0·003	1·484	1·484	vs
40,26	1·281	0·002	1·283	1·285	ms
42,35,17	1·231	0·002	1·233	1·234	ms
08,44	1·108	0·002	1·110	1·112	w
51,28,37	1·021	0·002	1·023	1·021	vw
53,46,19	0·968	0·002	0·970	0·971	vw
55,0 10	**	—	—	0·890	—
60,39	0·856	0·001	0·857	0·857	w
62,2 10,48	0·840	0·001	0·841	0·841	vw

* Observed, but not accurately measured from Missouri halloysite. The value 2·218 obtained with a specimen from Simla, India.

** Not observed.

Visual intensity scale: vvs, vs, s, ms, m, wm, w, vw.

As table III shows, we also find evidence for measurable displacements of the intensity maxima of metahalloysite from the positions calculated by means of equation (1). In this table, d' is the directly observed spacing, Δd the correction term calculated for a crystallite size $L = 200$ Å. (see later for the determination of L), and $(d' + \Delta d)$ is the 'experimental' value of d_{hk}. The latter may be compared with d_{hk} calculated by means of equation (1) with the following lattice constants:

$$a = 5{\cdot}14 \text{ Å.}, \quad b = 8{\cdot}90 \text{ Å.}$$

These parameters are practically the same as for kaolinite, viz., $a = 5{\cdot}14$ Å., $b = 8{\cdot}93$ Å., but whereas in kaolinite a is unquestionably less than $b/\sqrt{3} = 5{\cdot}155$ Å., in metahalloysite the reflections are not sufficiently well defined or numerous to decide whether this is the case or not. We have therefore taken $a = b/\sqrt{3}$. The table shows close agreement between the experimental and calculated values of d_{hk} only when the correction term Δd is incorporated.

(c) *The full powder diagram.*—All the observed reflections from metahalloysite can be indexed as basal (00*l*) reflections or as (*hk*) bands. In particular there are no reflections of type (*hkl*). This result is fully in accord with the general view of the metahalloysite structure described in the opening paragraphs. Absence of (*hkl*) reflections implies complete lack of order in the stacking of the layers, or such a high degree of disorder that (*hkl*) reflections are of negligible intensity. The two doubtful reflections from the Missouri metahalloysite at spacings of 2·486 and 2·355 Å. may be briefly considered; they agree closely with two prominent lines in the kaolinite diagram, viz., a strong reflection at 2·486 Å. and a very strong reflection at 2·331 Å. No trace, however, is found of an equally strong kaolinite line at 2·284 Å., or of other kaolinite lines which might have been expected if the two doubtful lines arose either from kaolinite impurity or from a partial ordering of the layers which was producing effectively regions of kaolinite within a metahalloysite matrix. If partial orderliness should occur, then the type found in many fireclays (cf. Brindley and Robinson, 1947) corresponding to random displacements of layers parallel to the *b*-axis only might have been expected. There is no evidence, however, for such ordering of the layers, for the fireclay type of kaolin mineral gives a medium-strong line at 2·50 Å. rather than a line at 2·486 Å., while there is a strong and rather broad line at 2·325 Å. as compared with 2·331 Å. in kaolinite and 2·335 Å. for the doubtful line in the Missouri metahalloysite. The origin of the two extra lines in the Missouri metahalloysite pattern must therefore be left open for the present; they are unlikely to arise from kaolinite impurity or from a partial ordering of the 'fireclay type' and there is insufficient evidence that they arise from an ordering of the kaolinite type. This uncertainty, however, is concerned only with the Missouri material, and the other metahalloysites we have examined fully support the statement that the only reflections are of types (00*l*) and (*hk*).

Distribution of intensity in the (hk) bands.

(a) *Theoretical calculation.*—Warren's treatment of the problem of diffraction by two-dimensional lattices involves certain simplifying assumptions which appear to be justified, at least to a first approximation.[1] He shows that the intensity $I_{2\theta}$ diffracted in an (*hk*)

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[1] Further work by A. J. C. Wilson and by G. W. Bradley and J. Méring (Nature, London, 1948, vol. 161, pp. 773–775 [M.A. 10-363]) tends to confirm the approximations used by Warren, but certain features, such as the structure of the 20,13 band in fig. 3, may not be given correctly by the approximate treatment.

band in direction 2θ with respect to the incident beam is given by

$$I_{2\theta} = C\Phi(\theta) \sum F^2, \tag{3}$$

where C is a constant, F is the structure factor for the unit cell of the layer and the summation extends over all reflections contributing to a band, and $\Phi(\theta)$ is given by the following expression:

$$\Phi(\theta) = 2\left(\frac{L}{\sqrt{\pi}\lambda}\right)^{\frac{1}{2}} \frac{1+\cos^2 2\theta}{(\sin\theta)^{\frac{3}{2}}} f(a), \tag{4}$$

where $f(a)$ is an integral evaluated numerically by Warren and

$$a = 2\sqrt{\pi}.\ L(\sin\theta - \sin\theta_0)/\lambda.$$

For $a > 3$, the following approximation is useful:

$$\Phi(\theta)_{a>3} \doteqdot \frac{1+\cos^2 2\theta}{\sin\theta(\sin^2\theta - \sin^2\theta_0)^{\frac{1}{2}}}.$$

The variation of F with angle θ is most conveniently calculated in terms of an artificial third index l' given by

$$l' = \frac{2c}{\lambda}(\sin^2\theta - \sin^2\theta_0)^{\frac{1}{2}}, \tag{5}$$

where c can be taken as the basal spacing, 7·20 Å. It must be emphasized that this amounts to no more than a convenient method of calculating the continuous variation of F with θ and it does not imply the usual three-dimensional diffraction process; in this equation l' can have non-integral values corresponding to any chosen values of $\sin\theta$.

The calculation of F as a function of θ for each diffracted band requires a knowledge of the structure of the layer. This has been taken to be the same as in kaolinite (Brindley and Robinson, 1946a). Although the cell has ortho-hexagonal shape, the atomic distribution does not possess hexagonal symmetry. In consequence, F^2 must be calculated for each index pair (hk) contributing to a band and this is indicated in equation (3) by the summation sign.

In order to evaluate I as a function of θ by means of equations (3), (4), and (5), the linear dimension L, the extension of the crystal layer, must be known. L may in fact be different for different reflections depending on the habit of growth of the crystalline sheets. There are various ways of obtaining an approximate value of L, but ultimately the best procedure in order to avoid unnecessary and rather doubtful approximations is to calculate I as a function of θ for a range of L values and then make comparison with the observed diffraction bands. This procedure is long and tedious, but since the Laue–Warren theory has not yet been tested by detailed comparison with experimental results, it seems worth while to make such a comparison in at least one case.

Warren shows that if F can be treated as effectively constant in equation (3) so that I depends only on $\Phi(\theta)$, then L is related to the half-breadth B of the band by the approximate relation

$$L = 1{\cdot}84\lambda/B\cos\theta, \tag{6}$$

an equation closely resembling Scherrer's equation for three-dimensional crystals. When this equation is applied to the observed half-breadths of the diffraction bands from metahalloysite after systematic correction for $K\alpha_1\alpha_2$ separation and for the focusing properties of the X-ray camera, values of L are obtained ranging from about 100–250 Å. This range of values arises, at least in part, from the quite considerable variation of F with θ for some of the bands, and it is only for those bands with approximately constant F values that L can be reliably obtained. L can also be estimated by applying equation (2); if the lattice constants a and b are determined from high-order reflections for which Δd in any case is small, then the difference between d_{hk} calculated for low-order reflections and d' observed experimentally enables L to be found. The method is again approximate and is also inaccurate because $(d_{hk}-d')$ is always fairly small.

Despite the inaccuracies and approximations of these methods, they suffice to give the order of magnitude of L, which is found to be about 100–300 Å. We have therefore calculated fully by means of equations (3), (4), and (5) the variation of I with θ for the six most prominent bands in the diffraction pattern, taking $L = 100$, 200, and 300 Å.

(*b*) *Comparison of observed and calculated intensity curves.*—The results of the calculations and their comparison with experimental data are shown in figs. 2 and 3. In the first place fig. 2*a* shows the variation of the angular function $\Phi(\theta)$ with θ for the 02,11 reflection and $L = 200$ Å.; this curve corresponds to the intensity distribution, I plotted against θ, which results when ΣF^2 is constant or nearly constant over the angular range of a band. Figs. 2*b*–2*g* show ΣF^2 plotted against θ and against the artificial third index l' of equation (5). In Warren's treatment of the problem, the calculated I,θ curves are obtained for each band and for each value of L by multiplying the appropriate $\Phi(\theta)$ curve of the type shown in fig. 2*a* by the ΣF^2 curve. The resulting intensity curves, scaled to the same peak intensity for each reflection, are shown in fig. 3*a*–3*e*.

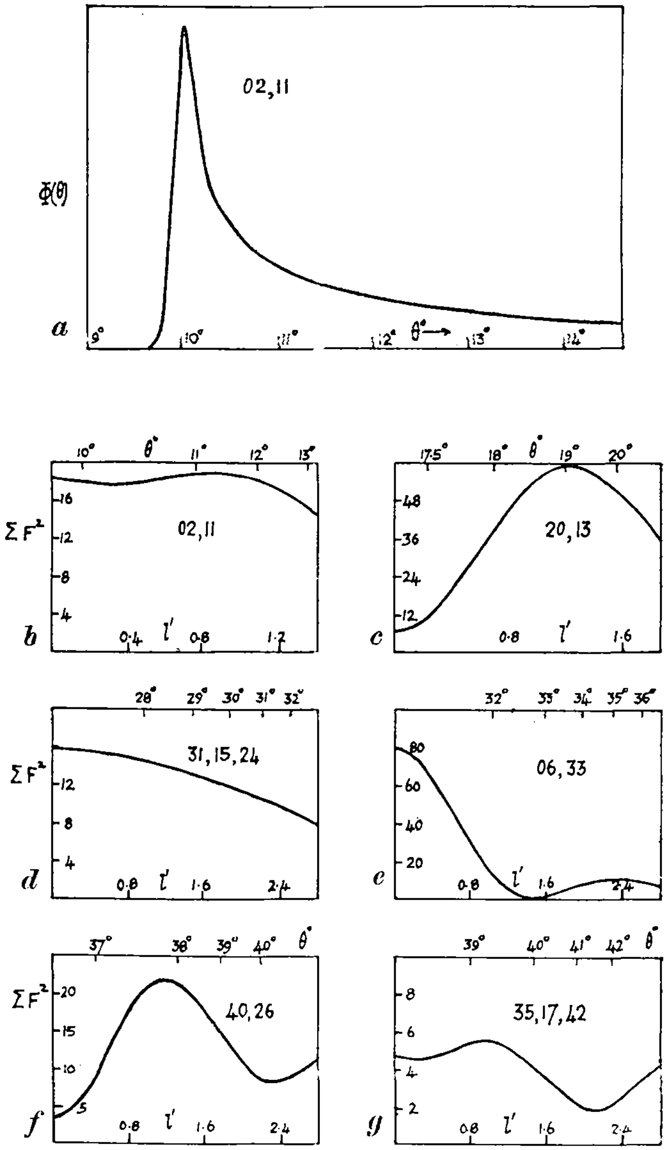

Fig. 2. Calculated data for two dimensional diffraction bands from metahalloysite.

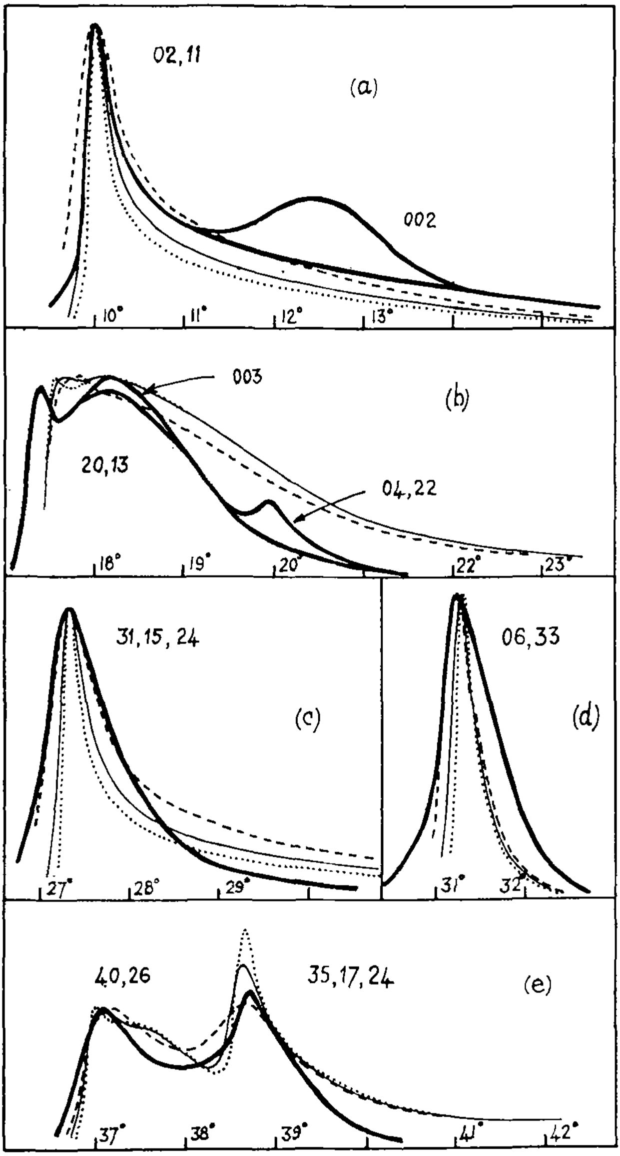

FIG. 3. Comparison of observed and calculated diffraction bands from metahalloysite. Heavy curves show experimental results. Light curves show calculated results for different crystal sizes, L; --- for $L = 100$ Å.; —— for $L = 200$ Å.; .... for $L = 300$ Å.

The experimental curves obtained by careful microphotometry of the X-ray diagrams are shown in fig. 3*a*–3*e* by heavy curves. Where reflections are superimposed, as in figs. 3*a* and 3*b*, we have endeavoured to reconstruct the separate peaks, but in the case of the overlapping bands (40,26) and (35,17,24) we have preferred to treat the two as a composite group.

It is seen at a glance that the calculations reproduce the main features of the observed curves and furthermore it is evident that the variety of bands which are observed arises from the variety of ΣF^2 curves. Thus the (02,11) band and the (31,15,24) band closely resemble the $\Phi(\theta)$ curve of fig. 2*a* because in both cases ΣF^2 is largely constant. On the other hand, the third-order band (06,33) is comparatively sharp because ΣF^2 shows a very rapid diminution as θ increases. Conversely the broad, almost flat-topped (20,13) band is produced by a rapidly rising ΣF^2 curve. As regards the combined (40,26), (35,17,24) band, the second peak is the sharper as a consequence of the approximate constancy of ΣF^2 for this peak, while the rapid increase of ΣF^2 for the (40,26) band tends to produce a broad band of the (20,13) type.

While the Laue–Warren theory clearly goes a long way towards explaining the observed results, we have not succeeded in explaining the finer details of the observed results. There is, for example, no single value of L which will account quantitatively for the observed widths of the bands. Some differences between L values for different bands might be expected owing to the shape of the crystalline units, but no satisfactory explanation of the observed results has been obtained along these lines. In particular we see that the (02,11) and (06,33) bands are not consistent with a single L value. The observed (06,33) band appears to be broad compared with the (02,11), a result which may arise from some separation of the components bands, (06) and (33), which would occur if the b parameter were not exactly $\sqrt{3}.a$. The experimental data, however, scarcely justify detailed discussion of this point.

The observed peaks in fig. 3 owe their widths partly to separation of the $K\alpha_1\alpha_2$ components—a small effect—and to the focusing properties of the X-ray camera. Both these questions have been examined in detail. They do not affect materially the general conclusions drawn above, but when allowance is systematically made for them, we find that the observed widths of the bands indicate a crystal size L of the order of 150–200 Å.

(*c*) *Comparison of observed and calculated peak intensities.*—Owing to the broadness of the bands, it is more convenient to compare peak intensities than integrated intensities. The calculated values depend on the crystal size L and the detailed numerical work shows that the dependence of peak height on L varies with the type of band. The main interest in considering the relative peak intensities is the evidence it may provide for or against the kaolinite type of structure for the layers in metahalloysite. Further evidence regarding L may also be obtained. Table IV compares the observed and calculated peak intensities expressed relative to 100 for the 20,13 band, for L = 100, 200, and 300 Å. The effect of absorption in the powder specimen has been taken fully into account.

TABLE IV. Comparison of observed and calculated peak intensities in diffraction bands.

(*hk*).	Calculated peak intensities for			Observed peak intensities.
	L = 100 Å.	L = 200 Å.	L = 300 Å.	
02,11	147	228	274	337
20,13	100	100	100	100
04,22	15	24	32	20
31,15,24	51	77	95	72
06,33	140	223	274	157
40,26	22	29	22	46
35,17,24	22	39	35	47

Consideration of the data in the table shows that an L value of the order of 150–200 Å. gives general agreement between the observed and calculated values. This not only confirms the previous value of L, but shows that the layer structure is almost certainly the same as in kaolinite.

Summary and conclusions.

The paper provides a more extensive range of powder data for metahalloysite than has previously been published. The reflections are divided into basal reflections of type (00*l*) and bands of type (*hk*). The latter arise from X-ray diffraction by the two-dimensional regularity within the kaolin-type layers. No reflections of type (*hkl*) are observed. The lattice dimensions are $b = 8\cdot90$ and $a = b/\sqrt{3} = 5\cdot14$ Å. Possible evidence is considered that a may not be exactly equal to $b/\sqrt{3}$; while a and b are practically the same as for kaolinite, the layer spacing is 7·20 Å. which is slightly greater than 7·132 Å. for kaolinite.

Quantitative data based on the Laue–Warren theory of diffraction by two-dimensional lattices are given supporting the view that there are random displacements between successive kaolin layers. The band widths and the peak intensities are generally accounted for by assuming

(i) a layer structure of the type found in kaolinite, and (ii) a crystal size for the layer units of 150–200 Å. in the plane of the layer. The importance of taking account of the variation of structure factor F with angle θ within the range covered by a single band is specially emphasized and the variety of band types exhibited by metahalloysite is shown to arise directly from the manner in which ΣF^2 varies with θ (cf. figs. 2 and 3).

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