ELECTRON-DIFFRACTION DETERMINATION OF THE STRUCTURE OF KAOLINITE

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Kaolinite was the first clay mineral to be the object of a structure analysis. The history of these structural studies extends over more than 25 years; however different investigators have not been able to arrive at the same results and consequently, derived different unit cells [1-4].

To some extent this is connected with the fact that kaolinite has several modifications: monoclinic with the *c* axis corresponding to a single layer [1, 2], monoclinic with *c* corresponding to three layers and perhaps to six layers [1], and triclinic with *c* corresponding to one layer [3].

The most prevalent triclinic variety of kaolinite was established by x-ray diffraction [3]. In addition, the unit cell was determined, and, with the aid of a trial-and-error method, the most likely idealized model of the structure was found. Later this result was refined by taking into consideration the characteristics of the structure of the "two-story" layers of dickite [5,6].

A direct determination of the structure of kaolinite became possible, thanks to the electron-diffraction method [1, 7, 9, 10].

As a sample we used Turbovskii kaolinite (No. 553a from the collection of M. F. Vikulova) which was chosen from a large number of preparations studied earlier. The initial experimental data were those obtained from texture electron-diffraction photographs from the ÉM-4 apparatus [Fig. 1); these photographs contained a rich collection of reflections up to 15 ellipses $0.12.l$, $\overset{\pm}{6}\overset{\pm}{6}l$; electron-diffraction photographs from single crystals were also used and reflection electron-diffraction photographs of the $00l$ reflections obtained on Popov's [11] apparatus.

Texture electron-diffraction photographs of kaolinite (Fig. 1) are characterized by peculiar features in the arrangement of the reflections which create the impression that the mineral is monoclinic and mask the fact that it is triclinic. In order to look into this it is necessary to dwell briefly on the natural arrangement of the reflections in the case of a triclinic cell.

A Geometrical Analysis of Texture Electron-Diffraction Photographs of Triclinic Lamellar Silicates and Its Application to Kaolinite

As in the monoclinic case [1], the base plane of the texture coincides with the plane ab and the texture axis with the axis c*. For each individual crystal the axes a* and b* make with the c* axis angles β^* and α *respectively, and lie in the planes ac* and bc *, in as much as for lamellar silicates $\gamma = \pi/2$.

In the reciprocal lattice of the texture the radii of the cylinders b'_{hk} along which the circular nodes are situated, are equal to the projections of the corresponding vectors $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ onto the plane ab, i.e.,

$b'^{a}\,hk = ha^*$ in $\beta^*\mathbf{i} + kb^* \sin\alpha^*\,\mathbf{j}$ ($\mathbf{i}$, $\mathbf{j}$ — are unit vectors in the directions of the a and b axes).

In this connection, in the given case

$$a^* = \frac{bc\sin\alpha}{abc\sin\alpha\sin\beta^*} = \frac{1}{a\sin\beta^*}, \quad b^* = \frac{1}{b\sin\alpha^*}, \quad b = a\sqrt{3}, \tag{1}$$

then

$$b'_{hk} = \sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2}} = \frac{\sqrt{3h^2 + k^2}}{b}. \tag{2}$$

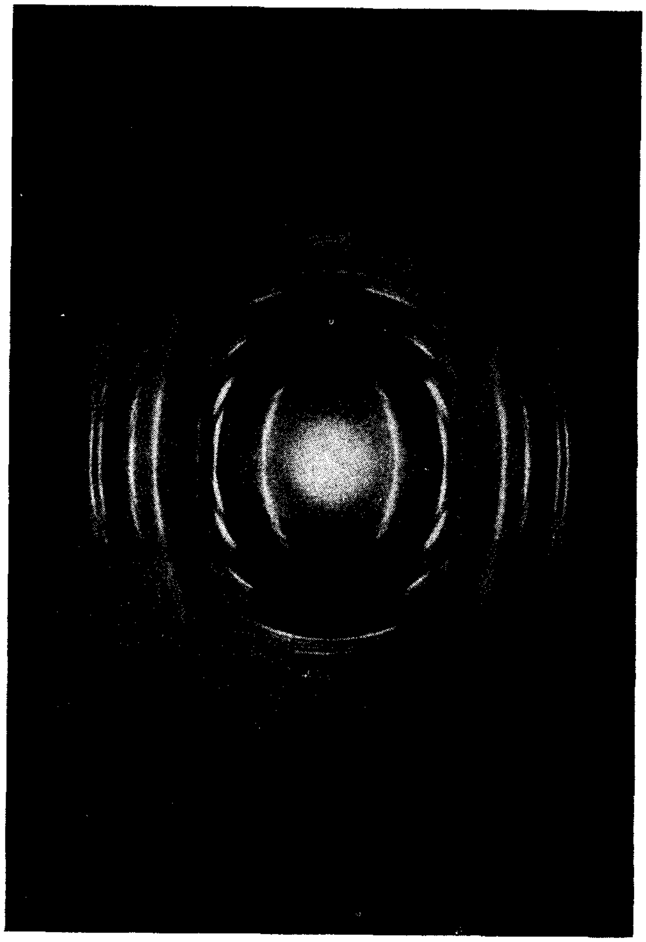

Fig. 1. Texture Electron-Diffraction Photograph of Kaolinite ($\varphi \sim 55°$).

The expression just obtained coincides with that which was obtained earlier for a monoclinic cell (cf.[1]), but is more general.

The height D'_{hkl} of a node above the plane ab is equal, as in [1], to the projection of H onto the c * axis

$$D'_{hkl} = ha^* \cos\beta^* + kb^* \cos\alpha^* + lc^*. \qquad (3)$$

Consequently the position of a reflection on an electron-diffraction photograph is characterized by the minor axis of the corresponding ellipse

$$b_{hk} = L\lambda b'_{hk} \qquad (2')$$

and by a height (distance from the minor axis)

$$D_{hkl} = \frac{L\lambda}{\sin\varphi} D'_{hkl} = hp + ks + lq. \qquad (3')$$

With the use of equation (1), and also of the relationships

$$\cos\beta^* = -\cos\beta / \sin\alpha; \quad \cos\alpha^* = -\cos\alpha / \sin\beta;$$
$$\cos\widehat{(cc^*)} = \sqrt{1 - \cos^2\alpha - \cos^2\beta}$$

we obtain

$$\begin{aligned} p &= -\frac{L\lambda}{\sin\varphi} \cdot \frac{\cos\beta}{a\sqrt{1-\cos^2\alpha-\cos^2\beta}}, \\ s &= -\frac{L\lambda}{\sin\varphi} \cdot \frac{\cos\alpha}{b\sqrt{1-\cos^2\alpha-\cos^2\beta}}, \\ q &= \frac{L\lambda}{\sin\varphi} \cdot \frac{1}{c\sqrt{1-\cos^2\alpha-\cos^2\beta}}. \end{aligned} \qquad (4)$$

As also for monoclinic structures, the equations (2)–(2') define the indices h, k of the ellipses. On a given ellipse we find reflections for several combinations of h, k with identical values of $3h^2 + k^2$. Having available all possible combinations of pairs of numbers h, k of the same parity in order of increasing $3h^2 + k^2$, it is easy to establish the succession of ellipses and the indices h, k which correspond to them. The minor axis of any ellipse, for instance b_{02} and b_{20} (1st and 2nd ellipses), determines the a and b periods.

The positions of the reflections on a given ellipse, their l indices, and the signs of h, k, and also the values of c, α, and β, are determined by the values of p, s, and q in accordance with equations (3) – (3').

As the entire set of reflections lies in one quadrant of the texture electron-diffraction photograph, it is possible to take into account only reflections with D, p, q, s ≥ 0. Then in accordance with (4) the cell has the angles $\alpha, \beta, \geq \pi/2$.

By studying the succession of reflections on any given ellipse, the following regularities may be noted: since D ≥ 0, then for a given ellipse the index $l \geq (hp + ks)/q$ can only be positive, and for this the indices h, k may be either positive or negative. If $l \leq (hp + ks)/q$ then the indices h and k are positive but the index l is either positive or negative.

As a result, the same absolute value of the index l on a given ellipse is found for two reflections for each index h $\neq 0$ and for two reflections for each index k $\neq 0$ or for one reflection for each index h = 0 or k = 0. Whatever reflection hk$l$ is taken, successive reflections with the same indices h and k, but with the third index (l + 1) or (l -1) should be found at a height D from it at a distance $\Delta D = q$. Hence in any interval $\Delta D = q$ there are found for a given ellipse, reflections with two possible combinations of h, k, and neither of these can be encountered in the given interval more than once; otherwise the difference in heights of reflections with identical h, k and successive l would be more or less than q. Consequently q is equal to the interval of the heights taken up on a given ellipse by successive reflections the number of which is equal to the number of combinations h, k, which differ either in absolute values, or signs, or both of these simultaneously.

The absolute values h, k are determined from b_{hk} according to (2) – (2'), and for layer silicates they are well-known, and the sign may be established as a result of studying the deviation of the positions of reflections from the orthogonal relation $D = l\,q$ or, in the monoclinic case, $D = hp + l\,q$.

Indeed, if for an orthogonal lattice the reflections hkl, $\bar{h}kl$, $h\bar{k}l$, and $\bar{h}\bar{k}l$ coincide and lie at a height $D = lq$, then, for the oblique-angled cell, there occurs a splitting of the reflections that is a deviation from the level $D = l\,q$, for a change in the sign of h of magnitude $\Delta D_h = \pm hp$ or for a change in the sign of k of magnitude $\Delta D_k = \pm ks$. Such splittings are found most clearly for the reflections $h0l$ and $0kl$, particularly if p or s is small.

After this, even if it is presumably established whether or nor the values p and s differ from zero, and hence on a given ellipse the number of different reflections having the same value of l is known, q is measured as the difference in height of successive reflections of the ellipse which have the same indices h, k but differ only in the index l. These reflections, as was shown above, may be picked out without difficulty, if they are all present individually on the electron-diffraction photograph. Then, if the number of different reflections for a given l is equal to n, then whichever reflection is taken, (n - 1) reflections from it on the same ellipse should be found a reflection with the same indices h, k and with inaex l differing from it by one; and q is equal to the difference in height between each 1st and n + 1th reflection. After q is determined, the values of p and s may be found from the difference in heights of reflections on the levels $D = l\,q$.

In reality, on electron-diffraction photographs, all reflections are not found, and some of the reflections overlap one another. Hence, to obtain correct values of p, q, and s it is necessary to compare carefully the heights of reflections on different ellipses; it is necessary to try not to miss weak reflections and not to take one of several close reflections. A criterion for the correctness of the selected values of p, q, and s is the possibility of getting values of D, for all reflections with the aid of (3') for whole numbers hkl.

The relation (3'), governing the positions of reflections on the ellipses, permits, by using the simple values of p, s, and q directly connected with the cell parameters, the indexing of the electron-diffraction photograph, and thus to clarify variations of the lattice from one diffraction photograph to another. In this way we interpreted the electron-diffraction photographs of kaolinite.

The heights of all reflections on these photographs were expressable only with the aid of the "triclinic" formula (3'), althought a large number of these reflections also could be adjusted to the "monoclinic" formula. The values of p, s, and q were, within the limits of error, found to satisfy the relations

$$p = \frac{5}{14}q, \quad s = \frac{p}{15} = \frac{q}{42}. \tag{5}$$

On the first ellipse the reflections $\overset{\pm}{1}1l$ and $\overset{\pm}{1}\bar{1}l$, separated by the interval $\Delta D = 2_s$, overlap one another and appear as a single reflection. Of the reflections $0\overset{\pm}{2}l$ the reflections $0\bar{2}2$ and 023 have very weak intensities, and, hence, on insufficiently good electron-diffraction photographs they may not be noticed, and the observed re- reflections 022 and $0\bar{2}3$ may be erroneously taken as the "monoclinic" $02l$. Only the pairs of reflections $0\bar{2}1$, 021, clearly separated by the interval $\Delta D = 4s$, do not allow us to ignore the difference of α from $\pi/2$.

On the second ellipse the reflections $\overset{\pm}{2}0l$ lie on the "monoclinic" relation according to the equation $D = \pm 2p + l\,q$, whereby the reflections $\bar{2}0(l+1)$ and $20l$ are separated in height by the interval $\Delta D = 4p - q = 6q/14$. If $s = 0$, then between them because of $\Delta D = (p + l\,q) - [-2p + (l+1)q] = 3p - q = q/14$, from the lower reflection $\bar{2}0(l+1)$ would be found the reflection $13l$, and analogously at $\Delta D = q/14$ from the upper reflection $20l$ would be found the reflection $\bar{1}3(l+1)$. However, since $s \neq 0$ and $3s = q/14$, these intermediate reflections are split, whence $\bar{1}3l$ lies on $\bar{2}0(l+1)$ and $\bar{1}3(l+1)$ on $20l$, and in the space equally divided into intervals $\Delta D = 2q/14$ are the reflections $13l$ and $\overline{13}(l+1)$. Hence the four groups of reflections $\bar{2}0(l+1)$, $13l$, $\bar{1}3(l+1)$, and $20l$ may be taken as "monoclinic". But, as is easy to see, their heights cannot be obtained from the equality $D = \pm hp + l\,q$ with the aid of any integral values p, q. On the contrary, while the solution of a system of two simultaneous equations for the extreme reflections gives the a above values of p and q, solution of a system of equations for middle reflections

$$\left.\begin{array}{r} lq' + p' = lq + p + 3s \\ (l+1)\,q' - p' = (l+1)\,q - p - 3s \end{array}\right\}$$

gives

$$q' = q, \text{ но } p' = p + 3s = \frac{6}{5}\,p.$$

According to the principle of similarity, such positions of reflections are repeated also for the rest of the ellipses 2h.0.l , h.3h.l . On the 5th ellipse is found a triplet of reflections, which by analogy may be taken as monoclinic.

$$\bar{3}3\,(l+1),\ 06l,\ 33\,(l-1).$$

In reality there are three pairs of weak reflections

$$0\bar{6}l,\ \bar{3}\bar{3}\,(l+1);\ \bar{3}3\,(l+1),\ 3\bar{3}\,(l-1);\ 06l,\ 33\,(l-1),$$

which analogously indicate the numerical values of their heights.

On other ellipses are found isolated reflections which, like the reflections $0\overset{\pm}{2}l$, are directly connected with a triclinic cell, as well as coincident ones.

After elucidating all of these peculiarities it is not difficult with the aid of relations (2) – (4), to determine the unit cell of kaolinite to be a = 5.13, b = 8.89, c = 7.25 A; α = 91°40'; β = 104°40'; γ = 90°, which agrees in general features with the cell determined by the x-ray method [3].

Analysis of the Intensities of the Reflections

Intensities were estimated visually from a series of photographs with multiple exposures. As was shown above, coincidence of reflections brought about unavoidable errors in the estimation of intensities.

Because of this, one can predict that only two-dimensional projections of Φ^2 and Φ series for the kaolinite structure onto the coordinate planes will be correct.

The presence of coincidences even for the reflections used in the construction of these projections: 2n.0.l and $\bar{n}$.3n.(l + 1), 0.6n.l and 3n.3n.(l – 1) (n=± 1,± 2,...),can be taken into account, using the interdependence among structure factors of layer silicates for such reflections.

The values of |Φ| , calculated from I according to Vainshtein's formula [7], for the reflections h0l and 0kl are given in Table 1.

With the object of obtaining the preliminary data necessary for constructing an initial model of the kaolinite structure, projections of Φ^2 series onto the planes x0z and 0yz were first computed. However because the distribution of I showed the influence of the imperfections in the structure peculiar to kaolinite, these syntheses were not very useful, and from them we were able to obtain information only concerning the orientation of the octahedral nets. Other important features, such as the orientation of the tetrahedral nets and how they are coupled to the octahedral nets could be established only upon comparison of the experimental intensities with those calculated from the corresponding ideal models; although these models led to reliability factors R of about 50%, they deviated greatly from the real structure. In addition, the ratios of the intensities of some reflections show very great sensitivity to the structural features being elucidated. Thus, as shown above, the ratio of the intensities of the reflections $0\overset{\pm}{2}2$, $0\overset{\pm}{2}3$ is correct only for a displacement of the tetrahedral nets relative to the octahedral nets by $\Delta = b/3$ from positions coinciding with symmetry planes. For $\Delta = b/3$ they change in the opposite way and reflections 022 and $0\bar{2}3$ become considerably weaker than $0\bar{2}2$ and 023. For Δ=0 the intensities of the reflections of each pair do not differ appreciably.

After establishing these features, which conform to the general principles of the formation of two-storied layers, for the case of kaolinite [8, 12, 13], and using the dimensions of the structural polyhedra which follow from the dimensions of the unit cell, we constructed an initial model of the structure of kaolinite consisting, in accordance with the triclinic unit cell, of polar layers without centers or planes of symmetry. This model was refined as a result of successive Fourier projections of the potential onto the x0z and 0yz planes. Of these the most effective was the projection onto the 0yz plane, as on it the majority of the maxima are isolated. In particular, on this projection the configuration of the ditrigonal motif formed by the bases of the tetrahedra and octahedra [6, 8, 13], is observed directly; as a characterization of this motif the parameter s (cf.[8,9]) can be measured from the deviation of the coordinates of the oxygen maxima from the positions of closest packing (cf. Fig. 4, 6) $\Delta y = s/3$, or from the corresponding change, expressed in the y coordinates, of the projection of the edge of the base (e.g.,O_4–O_6) $\Delta y = 2s/3$.

TABLE 1

Theoretical and Experimental (initial and normalized) Amplitudes $|\Phi|$ Recorded on Electron-Diffraction Texture Photographs for 0k*l* and h0*l*

hkl	Φ_{theor}	Φ_{exp}	Normalized Φ_{exp}	1	2	3	4	1	2	3	4	1	2	3	4
1	2	3	4												
020	10.7	23.7	11.8	$0\bar{6}2$	7.1	6.5	8.7	200	14.8	27.8	13.1	$\bar{4}01$	8.75	19.8	9.3
022	11.5	9.2	12.2	$0\bar{6}4$	7.0	5.0	6.7	202	7.05	8.5		$\bar{4}03$	3.35	4.4	
024	4.3	2.35	3.15	$0\bar{6}6$	5 35	4.1	5.5	204	17.5	18 4		$\bar{4}05$	7.2	7.65	
021	12.6	11.8	15.8	$0\bar{6}8$	6.2	3.65	4.9	206	5.1	3.15		$\bar{4}07$	3.25	3.1	
023	3.1	1.1	1.45	$0\bar{6}10$	3.2	2.95	3.95	201	6.8	11.0	8.0	600	4.85	2.4	
$0\bar{2}2$	2.7	1.65	2.2	$0\bar{6}1$	8.75	9.2	7.75	203	11.6	14.0		602	4.95	1.7	
$0\bar{2}4$	3.1	2.35	3.15	$0\bar{6}3$	1 9	1.3	3.9	205	2.35	3.15		601	2.85	3.8	
$0\bar{2}1$	18.8	15.0	20.0	$0\bar{6}5$	3.45	3.65	4.9	$\bar{2}02$	19.0	27.0	19.4	603	6.05	2.95	
$0\bar{2}3$	8.75	5.25	7.0	$0\bar{6}7$	4.8	1.95	2.6	$\bar{2}04$	13.8	17.2		$\bar{6}02$	8.9	10.1	7.3
040	1.4	6.7	3.35	080	3.35	6.7	3.35	$\bar{2}06$	8.25	7.0		$\bar{6}04$	3.1	1.7	
042	5.75	4.2	5.6	082	2.35	1.5	2.0	$\bar{2}08$	3.1	2.2		$\bar{6}06$	1.35	2.4	
044	8.3	4.75	6.35	084	2.25	1.1	1.45	$\bar{2}01$	11.9	29.5	14.0	$\bar{6}01$	3.9	2.95	
041	7.95	3.0	4.0	081	2.15	1.5	2.0	$\bar{2}03$	16.9	18.0		$\bar{6}03$	3.05	1.7	
043	5.2	2.4	3.2	083	2.1	1.1	1.45	$\bar{2}05$	5.25	5.0		$\bar{6}05$	1.1	1.7	
$0\bar{4}2$	6.55	5.25	7.0	085	1.15	1.85	2.45	$\bar{2}07$	3.7	2.75		$\bar{6}07$	1.9	1.7	
$0\overline{44}$	4.75	3.0	4.0	$0\bar{8}2$	1.75	1.85	2.45	$\bar{2}09$	6.3	2.75					
$0\bar{4}1$	1.15	1.85	1.55	$0\bar{8}4$	1.15	0.85	1.15	400	10.2	13.9	10.1				
$0\bar{4}3$	6.1	5.25	7.0	$0\bar{8}1$	3.6	4.75	4.0	402	9.5	8.8					
$0\bar{4}5$	4.85	1.1	1.45	$0\bar{8}3$	2.1	1.5	2.0	404	2 6	3.1					
060	19.8	39.0	19.5	$0\bar{8}5$	1.5	1.1	1.45	401	9.2	7.65					
062	5.7	4.1	5.5	0.10.0	2.55	6.5	3.25	403	1.5	0.75					
064	5.75	4.1	5.5	0.10.2	2.1	1.2	1.6	405	1.0	0.75					
066	5.5	5.0	6.7	0.10.1	2.35	1.2	1.6	$\bar{4}02$	9.95	19.8	9.3				
068	5.35	3.65	4.9	0.10.3	2.6	1.65	2.2	$\bar{4}04$	4.35	5.4					
0610	2.85	1.3	1.75	$0.\overline{10}.2$	1.75	2.35	3.15	$\bar{4}06$	10.05	6.95					
061	4.5	6.5	5.5	$0.\overline{10}.1$	0.9	2.35	2.0	$\bar{4}08$	3.5	1.0					
063	3.45	1.3	1.75	$0.\overline{10}.3$	3.7	2.35	3.15								
065	4.55	4.5	6.0	0.12.0	6.1	6.1	3.1								
067	5.0	0.85	1.15												

The parameter s, equal to the projection of the edge of the base expressed in the x coordinates (e.g., O_4–O_6,Fig.6) may be expressed in terms of the angle of rotation of the base of the tetraedra or octahedra. If ψ is measured from the position corresponding to closest packing ($s = 0.1$), and if ψ is measured from the other limiting motif with a hexagonal mesh ($s = 1/4$), then $\varphi = 30° - \varphi$ and it is not difficult to show (Fig. 2) that

$$\operatorname{tg}\varphi = \frac{s\sqrt{3}}{1-s}, \quad \operatorname{tg}\psi = \frac{1-4s}{\sqrt{3}}. \tag{6}$$

For the determination of the positions of the maxima which are overlapped in projection on the 0yz plane (O_{tetr}, Si) the corresponding difference syntheses were computed.

For the calculation of the structure amplitudes corresponding to different models of the structure the origin of coordinates was chosen in a more symmetric point, i.e., at the center of an empty octahedron. The absence of planes of symmetry in the layers and $\alpha \neq \pi/2$ compels the use of the most primitive form of the structure

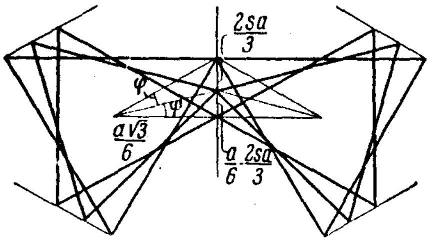

Fig. 2. Angular deviation of the bases of the octahedra and tetrahedra as a function of the displacement of their vertices.

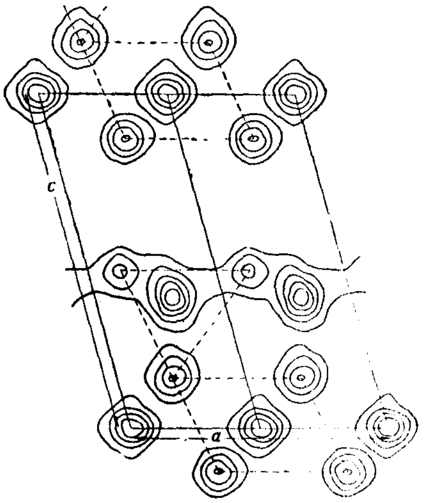

Fig. 3. Projection of the kaolinite structure onto the x0z plane.

factor for the group C_1-P_1, and to carry out the summation over the 13 independent atoms in the formula of kaolinite $Al_2Si_2O_5(OH)_4$. However, as long as in the approximate models the bases of the octahedra and tetrahedra may be taken as truly trigonal, lying in one plane, and the Al and Si atoms located on the plane of the acentric hexagonal motif, for the calculation of Φ it is possible to take advantage of this internal symmetry (C^3_{1v}) which is characteristic of the atoms lying on a single plane parallel to xy0. In the system of coordinates of each such planar net, its structure factor has the form

$$\begin{aligned} A &= 4\cos^2 2\pi \frac{(h+k)}{4}\cdot\cos 2\pi hx\cdot\cos 2\pi ky,\\ B &= 4\cos^2 2\pi \frac{(h+k)}{4}\cdot\sin 2\pi hx\cdot\cos 2\pi ky. \end{aligned} \tag{7}$$

In the system of coordinates of the complete layer, the atoms acquire a coordinate $\underline{z}$, but the coordinates $\underline{x}$, $\underline{y}$ undergo changes caused by the oblique-angled cell

$$\Delta x = g_1 z; \quad \Delta y = g_2 z,$$

where

$$g_1 = -\frac{c}{a}\cdot\frac{\cos\beta}{\sin\alpha}; \quad g_2 = -\frac{c}{b}\cdot\frac{\cos\alpha}{\sin\beta}, \tag{8}$$

and it is also possible, with the above-mentioned displacements of the tetrahedral net, to have $\Delta y = \pm 1/3$. These changes lead to additive terms to the argument hx, which now takes the form

$$h(x + g_1 z) + k(g_2 z \pm n/3) + lz.$$

In this way, we are able to reduce the number of terms in the structure factor to seven or even five.

In the process of approximation to the true structure, individual anomalies in the distribution of intensities were noted, which manifest themselves in an additional weakening of reflections distant from the minor axis of the ellipse, in comparison with neighboring ones, especially directly adjoining ones; in addition, this weakening was different for the reflections h0*l* and 0k*l*. Within the limits of each of these zones, it is possible to separate roughly three groups of reflections, differing in the normalization of their experimental $|\Phi_{exp}|^2$ to the calculated $|\Phi_{theor}|^2$. Thus, if one takes the normalized reflections h0*l* with the largest D as a basis, then for the reduction of the rest of the reflections to this same normal it is necessary to reduce the values of the $|\Phi_{exp}|^2$ reflections with small D and with D near to zero, so as to diminish by 1.95 and 4.5 times, respectively, the reflections h0*l*, and by 1.4 and 4 times, respectively, the reflections 0k*l*, while reflections 0k*l* with large D, on the contrary, must be increased by 1.78 times. These changes are shown in the third column of Table 1.

The anomalies noted in the intensities, in all probability, are connected with two-dimensional order in the structure, i.e., the order of each planar net of atoms, or of the separate layers, is greater than the order of the structure as a whole.

The Structure of Kaolinite

In Figures 3 and 4 we show the final Fourier projections of the potential onto the planes x0z and 0yz, and in Figure 5 we give a combined picture of the difference syntheses in which are shown separately the peaks of

Si and O_{tetr} which coincide on the Oyz projection. From these projections we obtained the atomic coordinates for the kaolinite structure, and from these coordinates the interatomic distances.

On the basis of these data, we present in Fig.6 a schematic normal projection of the structure of kaolinite onto the xy0 plane in the form of a combined motif of the lower and upper bases of the octahedra and the upper bases of the tetrahedra with a designation of the Si and Al atoms inside these polyhedra.

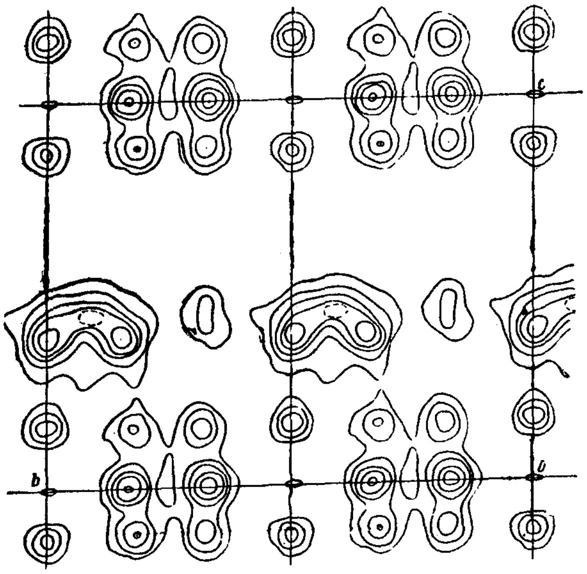

Fig. 4. Projection of the kaolinite structure onto the Oyz plane.

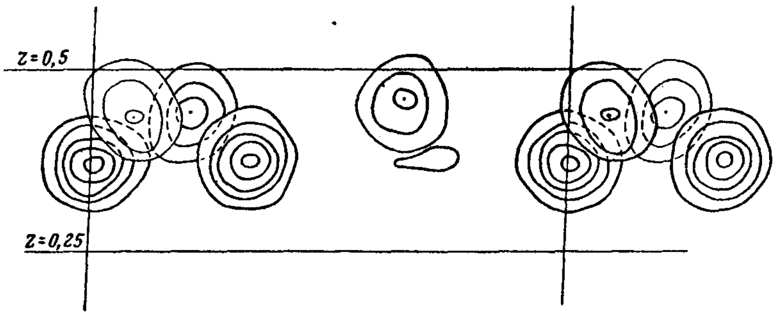

Fig. 5. Combined picture of the difference syntheses for O_{tetr} and Si atoms.

Numerical values of the atomic coordinates and interatomic distances corresponding to the numbering of the atoms in Fig. 6 are given in Tables 2 and 3. The accuracy of the determination of the coordinates, computed according to a formula of Vainshtein's [7], is 0.02 A for Al and Si, and 0.03 A for O.

As a result, the structure of kaolinite may be described in the following way.

Forming the structure are two-storied kaolinite layers which consist of an octahedral net and a tetrahedral net joined to it from above, so that the upper bases of the octahedra are oriented with their vertices in the negative, and the bases of the tetrahedra in the positive directions of the $\underline{a}$ axis; the anions in the layers are packed according to a cubic law, although not in closest packing. Nets of tetrahedra are displaced relative to nets of octahedra from the positions corresponding to symmetry planes by an amount $- b/3$, so that the symmetry planes of layers in the cell are eliminated. Relative to the positions which correspond to closest packing of anions, the lower and upper bases of the octahedra are rotated through angles corresponding to 3° and 5°, and the bases of the tetrahedra on the average through 20°, as their vertices are displaced by different amounts. The common edges of the octahedra are shortened and the octahedra as a whole are somewhat flattened. The Al atoms are displaced toward the lower OH bases the Si atoms toward the bases of the tetrahedra, whence the atoms of the bases of the polyhedra do not lie in one plane and have several different $\underline{z}$ coordinates. The closest atoms in successive layers are grouped in pairs O-OH, which, however, differ somewhat in their lengths.

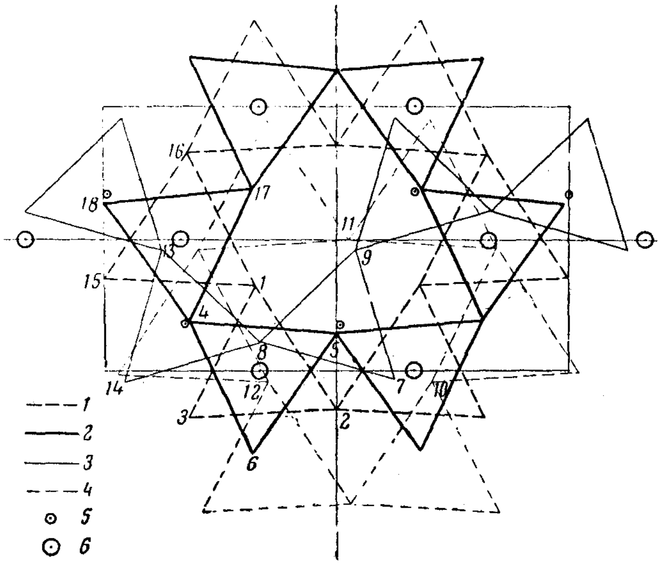

Fig. 6. Scheme of the structure of kaolinite in a normal projection onto the xy0 plane. 1) lower bases. 2) upper bases of the octahedra. 3) bases of the tetrahedra. 4) lower bases of the octahedra in the next layer. 5) Si. 6) Al.

The structure given by us for kaolinite compares qualitatively with that obtained from x-ray studies of dickite [5, 6], but quantitatively there are some differences. These differences principally are connected with the $\underline{z}$ coordinates of the O atoms and the configuration of the motif of the bases of the tetrahedra.

The electron-diffraction data when compared with those calculated for the reflections $h0l$ and $0kl$ (without $00l$) lead to an R factor of 21 %, those from the x-ray study of dickite to an R of 23.5%. In view of the anomalies in the intensities of the reflections noted above the established features cannot be carried over precisely to all structures because of nonobservance of strict repetition in space. This is reflected to some extent also in the projections obtained. Thus, from the residual maximum of Si at $y \approx 1/3$ and from the distribution of the heights of other peaks it is possible to judge that, in the sample studied, besides layers with a displacement of tetrahedral nets $\Delta = -b/3$, there were present layers with $\Delta = 0$ and $+ b/3$. Hence, it is possible to conclude that disruption of the repetition in space of the structure is connected to a considerable degree with variations in the structure of the layers, which may be distinguished both by their coarse features, for example, by the form of the coupling of the nets, and also by insignificant deviations of atoms from their most probable positions. The differences between layers and their positions apparently, is the basis of polymorphism in kaolinite minerals and layer silicates generally

The author wishes to thank N.V. Belov for consultations on the principles of constructing models of the structing models of the structures of layer silicates, and to thank B.K.Vainshtein for aid in overcoming the many difficulties which attended the execution of this work.

TABLE 2

Atomic Coordinates for the Kaolinite Structure

ATOM	x	y	z	ATOM	x	y	z	ATOM	x	y	z
$O_1(H)$	—0.223	0.175	—0.128	O_5	—0.304	0.004	0.157	Al_1	—0.500	0.171	0.002
$O_2(H)$	—0.696	—0.003	—0.136	$O_6(H)$	—0.763	0.186	0.155	Al_2	0.000	0.333	0.000
$O_3(H)$	—0.723	0.321	—0.128	O_7	—0.385	—0.105	0.455	Si_1	—0.195	0.002	0.384
O_4	—0.263	0.322	0.155	O_8	—0.209	0.177	0.475	Si_2	—0.195	0.339	0.386
				O_9	0.112	—0.041	0.454				

TABLE 3

Interatomic Distances in the Kaolinite Structure (A)

$O_1 — O_2$	2,88	$Al_1 — O_1$	1.88	$O_5 — O_1$	2.71	$Al_2 — O_{15}$	1.92	$O_8 — O_7$	2.66	$O_8 — Si_1$	1.68
$O_1 — O_3$	2,88	$Al_1 — O_2$	1.94	$O_6 — O_2$	2.75	$Al_2 — O_{16}$	1,88	$O_8 — O_4$	2.63	$O_9 — Si_1$	1,58
$O_4 — O_6$	2.84	$Al_1 — O_3$	1,86	$O_8 — O_5$	2.66	$O_4 — Al_2$	1,96	$O_{13} — O_4$	2,58	$Si_2 — O_4$	1.64
$O_5 — O_4$	2,84	$O_4 — Al_1$	1,92	$O_9 — O_5$	2.64	$O_{17} — Al_2$	1.96	$O_{14} — O_4$	2.65	$O_8 — Si_2$	1.63
$O_5 — O_2$	2.52	$O_5 — Al_1$	2.00	$O_7 — O_5$	2.50	$O_{18} — Al_2$	2,02	$O_{10} — O_7$	3,04	$O_{13} — Si_2$	1.54
$O_4 — O_1$	2.42	$O_6 — Al_1$	1.95	$O_9 — O_7$	2.62	$Si_1 — O_5$	1,58	$O_{11} — O_9$	2.90	$O_{14} — Si_2$	1.60
$O_4 — O_3$	2.68	$Al_2 — O_1$	1,87	$O_8 — O_9$	2.58	$O_7 — Si_1$	1.56	$O_{12} — O_8$	2,92		

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