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Abstract

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ELECTRON-DIFFRACTION DETERMINATION OF THE STRUCTURE OF KAOLINITE

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One of the most important advantages of electron diffraction in its application to the study of clay minerals is the possibility of their deep structural analysis, despite their high dispersion and low symmetry ([3,6,7,9]). Such a possibility was realized in the structural determination of celadonite-glauconite ([6]). Determination of the structure of kaolinite, because of its triclinic symmetry, presented a considerably more complicated problem. Over the last 25 years a considerable number of both X-ray and electron-diffraction studies have been devoted to the study of this mineral ([4,10–13] and others), which, however, did not lead to the determination of its structure.

In the work presented here, the most widespread structurally perfect triclinic variety of kaolinite was investigated (sample of Turbov kaolinite 553a from the collection of M. F. Vikulova). The initial experimental material consisted of electron diffraction patterns from textures (Fig. 1), obtained on an EM-4 instrument, containing a rich set of sufficiently well separated and indexable reflections, electron diffraction patterns from single crystals, and reflection electron diffraction patterns with 001 reflections, obtained on N. M. Popov' s instrument ([8]).

Fig. 2. Projection of the structure of kaolinite onto the *xoz* plane

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Electron diffraction patterns from kaolinite textures (Fig. 1) are characterized by very distinctive features in the arrangement of reflections, which at first glance created the impression of monoclinicity of this mineral and masked its triclinicity. Although most of the reflection heights D could be fitted to the "monoclinic" formula $D = hp + lq$ ([5]), the heights of all reflections could be expressed only with the aid of the "triclinic" formula ([7])

$$D = hp + ks + lq, \tag{1}$$

where

$$p = -\frac{L\lambda}{\sin\varphi}\,\frac{\cos\beta}{a\sqrt{1-\cos^2\alpha-\cos^2\beta}}, \qquad s = -\frac{L\lambda}{\sin\varphi}\,\frac{\cos\alpha}{b\sqrt{1-\cos^2\alpha-\cos^2\beta}},$$

$$q = \frac{L\lambda}{\sin\varphi}\,\frac{1}{c\sqrt{1-\cos^2\alpha-\cos^2\beta}}. \qquad (2)$$

The impression of monoclinicity was created by coincidences of reflections characteristic of the electron diffraction patterns of kaolinite, in particular on the 2nd ellipse: reflections $\bar{2}0(l+1)$ and $\bar{1}3l$, $20l$ and $\bar{1}3(l+1)$; and on the 5th ellipse: reflections $0\bar{6}l$ and $\bar{3}3(l+1)$; $33(l+1)$ and $33(l-1)$; $06l$ and $33(l-1)$. After all features of the arrangement of the reflections had been clarified with the aid of equalities (2), the unit cell of kaolinite was determined: $a = 5.13$ kX; $b = 8.89$ kX; $c = 7.25$ kX; $\alpha = 91°40'$; $\beta = 104°40'$; $\gamma = 90°$; with some difference in b, c, it agrees in its main features with that found by the X-ray method ([12]).

The estimation of intensities was carried out visually from series of photographs with multiple exposures. Many coincidences of reflections naturally proved to be a substantial difficulty here. Coincidences of reflections $h0l$ and $0kl$ could be taken into account by using the known relationship between the structure factors of layered silicates for those reflections which in this case coincide, which made it possible to study the structure of kaolinite by two-dimensional syntheses of projections of Φ^2- and Φ-series on the planes xoz and oyz.

The values of Φ, calculated from I according to the formulas of B. K. Vainshtein (3), for the reflections $h0l$ and $0kl$ recorded in electron diffraction patterns from kaolinite textures, are given in Table 1. For constructing the initial model of the structure as a definite combination of structural polyhedra (1,2,6), some features (the orientation of the octahedral network) were established from syntheses of the Φ^2-series in projection on the planes xoz and oyz; others (the orientation of the tetrahedral network and the form of its linkage with the octahedral one) were established as a result of comparison of experimental and calculated intensities for various variants. The structural model thus created was then refined more and more as a result of successive construction of syntheses of projections of the Φ-series on the planes xoz, oyz with coefficients formed from experimental $|\Phi|$ and phases, corresponding first to the initial model and then to the results of the preceding syntheses. In this process the projections onto the plane oyz proved to be the most expressive, since in them most of the maxima are isolated. In particular, the configurations of ditrigonal motifs formed by the bases of tetrahedra and octahedra ([2],[6],[14]) appear directly in them, since the characteristic parameter s ([6],[7]) can be measured from the deviations of the coordinates of the oxygen maxima from the positions of closest packing (Fig. 4).

Fig. 3. Combined pattern of Fourier syntheses for the O_{tetr} and Si atoms

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Table 1

Theoretical, experimental (initial and reduced to a common normalization) moduli $|\Phi|$ for reflections $0kl, h0l$ recorded in electron diffraction patterns from textures

			Renormalized				Renormalized				Renormalized
hkl	$\lvert\Phi_r\rvert$	$\lvert\Phi_e\rvert$	$\lvert\Phi_e\rvert$	hkl	$\lvert\Phi_r\rvert$	$\lvert\Phi_e\rvert$	$\lvert\Phi_e\rvert$	hkl	$\lvert\Phi_r\rvert$	$\lvert\Phi_e\rvert$	$\lvert\Phi_e\rvert$
020	10.7	23.7	11.8	0$\bar{6}$10	3.2	2.95	3.95	$\bar{2}$06	8.25	7.0	
022	11.5	9.2	12.2	0$\bar{6}$1	8.75	9.2	7.75	$\bar{2}$08	3.1	2.2	
02$\bar{4}$	4.3	2.35	3.15	0$\bar{6}$3	1.9	1.3	3.9	$\bar{2}$01	11.9	29.5	14.0
021	12.6	11.8	15.8	0$\bar{6}$5	3.45	3.65	4.9	$\bar{2}$03	16.9	18.0	
023	3.1	1.1	1.45	0$\bar{6}$7	4.8	1.95	2.6	$\bar{2}$05	5.25	5.0	
02$\bar{2}$	2.7	1.65	2.2	080	3.35	6.7	3.35	$\bar{2}$07	3.7	2.75	
02$\bar{4}$	3.1	2.35	3.15	082	2.35	1.5	2.0	$\bar{2}$09	6.3	2.75	
0$\bar{2}$1	18.8	15.0	20.0	08$\bar{4}$	2.25	1.1	1.45	400	10.2	13.9	10.1
0$\bar{2}$3	8.75	5.25	7.0	081	2.15	1.5	2.0	402	9.5	8.8	
040	1.4	6.7	3.35	083	2.1	1.1	1.45	404	2.6	3.1	
042	5.75	4.2	5.6	085	1.15	1.85	2.45	401	9.2	7.65	
044	8.3	4.75	6.35	08$\bar{2}$	1.75	1.85	2.45	403	1.5	0.75	
041	7.95	3.0	4.0	08$\bar{4}$	1.15	0.85	1.15	405	1.0	0.75	
043	5.2	2.4	3.2	08$\bar{1}$	3.6	4.75	4.0	$\bar{4}$02	9.95	19.8	9.3
04$\bar{2}$	6.55	5.25	7.0	08$\bar{3}$	2.1	1.5	2.0	$\bar{4}$04	4.35	5.4	
04$\bar{4}$	4.75	3.0	4.0	08$\bar{5}$	1.5	1.1	1.45	$\bar{4}$06	10.05	6.95	
04$\bar{1}$	1.15	1.85	1.55	0.10.0	2.55	6.5	3.25	$\bar{4}$08	3.5	1.0	
04$\bar{3}$	6.1	5.25	7.0	0.10.2	2.1	1.2	1.6	$\bar{4}$01	8.75	19.8	9.9
04$\bar{5}$	4.85	1.1	1.45	0.10.1	2.35	1.2	1.6	$\bar{4}$03	3.35	4.4	
060	19.8	39.0	19.5	0.10.3	2.6	1.65	2.2	$\bar{4}$05	7.2	7.65	
062	5.7	4.1	5.5	0.$\bar{1}$0.2	1.75	2.35	3.15	$\bar{4}$07	3.25	3.1	
064	5.75	4.1	5.5	0.$\bar{1}$0.1	0.9	2.35	2.0	600	4.85	2.4	
066	5.5	5.0	6.7	0.$\bar{1}$0.3	3.7	2.35	3.15	602	4.95	1.7	
068	5.35	3.65	4.9	0.12.0	6.1	6.1	3.1	601	2.85	3.8	
0610	2.85	1.3	1.75	200	14.8	27.8	13.1	603	6.05	2.95	
061	4.5	6.5	5.5	202	7.05	8.5		$\bar{6}$02	8.9	10.1	7.3
063	3.45	1.3	1.75	204	17.5	18.4		$\bar{6}$04	3.1	1.7	
065	4.55	4.5	6.0	206	5.1	3.15		$\bar{6}$06	1.35	2.4	
067	5.0	0.85	1.15	201	6.8	11.0	8.0	$\bar{6}$01	3.9	2.95	
06$\bar{2}$	7.1	6.5	8.7	203	11.6	14.0		$\bar{6}$03	3.05	1.7	
06$\bar{4}$	7.0	5.0	6.7	205	2.35	3.15		$\bar{6}$05	1.1	1.7	
06$\bar{6}$	5.35	4.1	5.5	$\bar{2}$02	19.0	27.0	19.4	$\bar{6}$07	1.9	1.7	
06$\bar{8}$	6.2	3.65	4.9	$\bar{2}$04	13.8	17.2					

For the article by B. B. Zvyagin, p. 1023

Fig. 1. Electron diffraction pattern from a kaolinite texture ($\varphi = 55°$)

For the article by F. A. Margolina, p. 1124

Fig. 1. Tracheal cartilage. Vessels in transverse section. Celloidin section. Hematoxylin and eosin. Ap. obj. 20, comp. approx. 5×

Fig. 2. Tracheal cartilage. Vessel in longitudinal section. Frozen section. Hematoxylin and eosin. Ap. obj. 10, comp. approx. 5×.

Fig. 3. Thyroid cartilage. Capillary-type vessels. Celloidin section. Hematoxylin and picroindigocarmine. Ap. obj. 20, comp. approx. 5×

Fig. 4. Costal cartilage. Group of capillary-type vessels. Celloidin section. Hematoxylin and eosin. Ap. obj. 10, comp. approx. 10×.

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In the process of approaching the true structure, peculiar anomalies became apparent in the distribution of intensities, expressed in an additional weakening of reflections remote from the minor axes of the ellipses in comparison with nearby reflections, and still more with those directly adjacent to them; moreover, this proved to be different for the reflections $h0l$ and $0kl$. Within each of these zones it was possible roughly to distinguish three groups of reflections, differing in the normalization of their experimental $|\Phi_e|^2$ to the calculated $|\Phi_t|^2$. The corresponding modified $|\Phi_e|$ are given in Table 1.

The noted anomalies in the intensity distribution are, in all probability, connected with the fact that the two-dimensional ordering of the structure—the ordering of each plane net of atoms or of an individual layer—is higher than in the structure as a whole; and this applies to a greater degree to the features expressed by projections onto oyz, whose ordering is less than in the projection onto xoz.

Figure 2 gives the final projections of the syntheses of the Φ-series onto the plane xoz, and Fig. 3 gives the combined picture of subtraction syntheses, in which the coincident Si and O_{tetr} peaks in the projection onto oyz are shown separately. From these projections the coordinates of atoms in the kaolinite structure were determined, and from them—the interatomic distances. Based on these data, the scheme of the kaolinite structure in its normal projection onto the plane xoy is shown in Fig. 4 in the form of a combined motif of the lower and upper bases of octahedra and the upper bases of tetrahedra, with the Si and Al atoms indicated inside these polyhedra.

The numerical values of the atomic coordinates and interatomic distances, in accordance with the numbering of the atoms in Fig. 4, are given in Tables 2 and 3. The accuracy of determining the coordinates, calculated by Weinstein' s formulas ([3]), is 0.015 kX for Al and Si atoms and 0.025 kX for O atoms.

Table 2

Atomic coordinates

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

Table 3

Interatomic distances (in kX)

$O_1 – O_3$	2.88	$O_6 – O_8$	2.64	$Al_1 – O_1$	1.88	$O_{17} – Al_2$	1.96
$O_1 – O_4$	2.88	$O_6 – O_9$	2.50	$Al_1 – O_3$	1.94	$O_{18} – Al_2$	2.02
$O_2 – O_6$	2.84	$O_6 – O_7$	2.62	$Al_1 – O_2$	1.86	$Si_1 – O_5$	1.58
$O_3 – O_4$	2.84	$O_5 – O_9$	2.58	$O_4 – Al_1$	1.92	$O_7 – Si_1$	1.56
$O_5 – O_3$	2.52	$O_8 – O_4$	2.63	$O_5 – Al_1$	2.00	$O_8 – Si_1$	1.68
$O_4 – O_1$	2.42	$O_{13} – O_4$	2.58	$O_6 – Al_1$	1.95	$O_9 – Si_1$	1.58
$O_7 – O_6$	2.68	$O_{14} – O_5$	2.65	$Al_2 – O_1$	1.87	$Si_2 – O_3$	1.64
$O_9 – O_1$	2.71	$O_{10} – O_7$	3.04	$Al_2 – O_{15}$	1.92	$O_8 – Si_2$	1.63
$O_8 – O_3$	2.75	$O_{11} – O_8$	2.90	$Al_2 – O_{16}$	1.88	$O_{13} – Si_2$	1.54
$O_9 – O_5$	2.66	$O_{12} – O_8$	2.92	$O_4 – Al_2$	1.96	$O_{14} – Si_2$	1.60

As a result, the structure of kaolinite appears as follows. The two-story kaolinite layers composing the structure are formed from one octahedral net and a tetrahedral net adjoining it from above, in such a way that the upper bases of the octahedra are oriented with their apices in the negative direction, and the bases of the tetrahedra in the positive direction of the d axis; the anions in the layer are packed according to a cubic law, although not in the closest manner. The tetrahedral net is displaced relative to the octahedral net from the position in which their symmetry planes coincide by an amount $-b/3$, which eliminates symmetry planes for the layer as a whole. From the positions corresponding to closest packing of the anions, the lower and upper bases of the octahedra are rotated by angles of 3 and 5°, respectively, and the bases of the tetrahedra by an average of 20°, since their vertices are displaced by different amounts. The common edges of the octahedra are shortened; the octahedra as a whole are somewhat flattened. The Al atoms are displaced toward the lower OH bases, and the Si atoms toward the bases of their tetrahedra; moreover, the atoms of the bases of the polyhedra do not lie in one plane and have somewhat different z coordinates. The nearest atoms of successive layers are grouped into O—OH pairs, which, however, differ somewhat in their length.

The structural data thus obtained for kaolinite agree qualitatively with those that follow from the X-ray structural study of dickite ([11,14]), but quantitatively they differ somewhat. These differences mainly concern the z coordinates of the O atoms and the configuration of the motif of the bases of the tetrahedra. The electron-diffraction data correspond, for the reflections $h0l$, $0kl$ (without $00l$), to a computed factor $\bar{R} = 21\%$; those following from the X-ray study of dickite correspond to $R = 23.5\%$.

In view of the above-noted anomalies in the distribution of reflection intensities, the established features are not maintained exactly throughout the whole structure because strict spatial repeatability is not observed in it. It may be assumed that the violations of spatial repeatability of the structure are to a considerable degree associated with variation in the construction of the layers, which may differ both in coarse features (for example, the form of linkage of the nets) and in slight deviations of atoms from their most probable positions. Differences between layers, and not only their positions, apparently underlie the polymorphism of kaolin minerals and, in general, of layered silicates.

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CITED LITERATURE

1. N. V. Belov, *Structure of Ionic Crystals and Metallic Phases*, 1947.
2. N. V. Belov, *Mineralog. sborn. L' vovsk. geol. obshch.*, No. 3, 29 (1949).
3. B. K. Vainshtein, *Structural Electronography*, 1956.
4. B. B. Zvyagin, DAN, 96, No. 4, 809 (1954).
5. B. B. Zvyagin, *Tr. Inst. kristallogr. AN SSSR*, 11, 86 (1955).
6. B. B. Zvyagin, *Kristallografiya*, 2, issue 3, 393 (1957).
7. B. B. Zvyagin, *Dokl. na Mezhdunarodn. soveshch. po glinam v Bryussele v 1958 g.*, Izd. AN SSSR, 1958.
8. N. M. Popov, *Tezisy Fedorovsk. sessii po kristallogr. v Leningrade v 1959 g.*, Izd. AN SSSR, 1959.
9. Z. G. Pinsker, *Diffraction of Electrons*, 1949.
10. Z. G. Pinsker, DAN, 73, No. 1, 107 (1950).
11. G. W. Brindley, M. Nakahira, *Min. Mag.*, 31, No. 240, 781 (1958).
12. G. W. Brindley, K. Robinson, *Min. Mag.*, 27, 242 (1946).
13. J. W. Gruner, *Zs. Krist.*, 85, 75 (1932).
14. R. F. Newnham, G. W. Brindley, *Acta Cryst.*, 9, No. 9, 759 (1956).

Note: Figure translations are in progress. See original paper for figures.