AN X-RAY STUDY OF A SINGLE CRYSTAL OF KAOLINITE

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Translated from Kristallografiya Vol. 5, No. 2, pp. 224-227, March-April, 1960
Original article submitted January 8, 1960

There are several papers on x-ray studies of kaolinite [1-4], but the structure has not yet been established in that way, because in every case powder patterns have been used. The reason is, of course, that kaolinite occurs only in a very finely divided form.

Recently, the structure was established by means of electron diffraction [5]. X-ray studies on a single crystal remain of interest, though; we report here on such studies.

B. B. Zvyagin pointed out to us that a single crystal suitable for use in x-ray diffraction might be found by examining the deposit from a very dilute suspension, as has been done for another mineral [6].

In this way we found a single crystal about 0.2 × 0.2 × 0.01 mm in size. The patterns were recorded with copper radiation in a KRON-2 camera. Oscillation and rotation photographs on the a and b axes were recorded; these showed 112 spots of $h0l$ and $0kl$ types. The intensities were estimated visually. The F_0 were corrected for the Lorentz and polarization factors; absorption was neglected as the crystal was so small. We used Bragg's [7] atomic-scattering factors in the calculation.

The Laue patterns (recorded along c^*) showed that the spots did not display hexagonal symmetry (although they appeared to form a hexagonal array), because their positions and intensities were inappropriate to that symmetry; kaolinite is triclinic. The cell parameters calculated from powder patterns agree within the errors of experiment with those given in [3], namely a = 5.14, b = 8.93, c = 7.37 A, $\beta = 104.5°$ and $\alpha = 91.8°$.

The oscillation pattern gave c as about 7.4 A. This means that the unit cell contains one layer.

The oscillation and rotation patterns on a and b were found to have spots with $h + k = 2n$ only; the cell is base-centered. As our initial model we assumed one consisting of octahedral and tetrahedral grids, with the latter displaced by -b/3 relative to the former.

The agreement with the measured intensities was best for that form of the structure in which the triangles at the tops of the octahedra lie opposite the bases of the tetrahedra above them along a (if we use the regular figures proposed in [8]).

Similar deductions have been made elsewhere [3, 5] about the orientations of the layers.

The F for the ideal model bore a relation to the F_0 such that R was large, so the structure had to be revised by determining the coordinates of the atoms more precisely. Successive Fourier syntheses were used in that revision. Appropriate difference syntheses were used for overlapping atoms; the F were also calculated for various relative positions of the overlapping atoms, and those giving the best R were chosen. The structure factors were calculated from sums taken with respect to 13 independent atoms, whose coordinates were reckoned relative to an origin taken at the center of an empty octahedron. The projection along a (Fig. 1) gave us the y and z for all atoms except O_4 and O_5, which overlap in that projection. Difference syntheses were used for those atoms. It was very much more difficult to find the coordinates from the projection along b (Fig. 2), because that projection shows no isolated atoms. These coordinates were found by means of difference syntheses and by minimizing R. Table 1 gives the values finally adopted. Vainshtein's formulas [9] for the errors in the results are (in A) Si ± 0.014, Al ± 0.015, and O ± 0.020.

TABLE 1

Coordinates of the Atoms in the Structure of Kaolinite

Group	x/a	y/b	z/c	Group	x/a	y/b	z/c
OH_1	0.778	0.180	—0.140	O_4	0.612	—0.120	0.455
OH_2	0.278	0.320	—0.138	O_5	0.108	—0.058	0.455
OH_3	0.316	—0.008	—0.136	Al_1	0.502	0.172	0.003
OH_4	0.248	0.184	0.155	Al_2	0.002	0.330	0.002
O_1	0.754	0.315	0.155	Si_1	0.800	0.322	0.382
O_2	0.690	0.004	0.157	Si_2	0.800	000	0.385
O_3	0.791	0.165	0.482				

TABLE 2

Values of F and F_0

hkl	F	F_0	hkl	F	F_0	hkl	F	F_0	hkl	F	F_0	hkl	F	F_0
001	25.2	27.2	$0\bar{2}7$	3.2	5.2	064	7.8	9.4	0101	6.3	6.3	$\bar{2}09$	18.9	16.9
002	42.7	46.1	$0\bar{2}8$	5.2	4.3	065	17.4	15.1	0102	5.6	5.8	*400	29.4	31.8
003	25.0	30.2	*040	3.1	6.8	066	18.7	15.1	*0103	8.5	7.3	401	11.5	15.4
004	21.8	29.2	041	8.6	10.8	067	7.8	5.1	$01\bar{0}1$	7.3	7.2	402	26.1	22.0
005	21.4	22.5	042	13.9	13.6	$0\bar{6}1$	13.7	20.8	$01\bar{0}2$	8.3	8.2	403	3.0	3.9
006	21.1	21.0	043	12.8	13.2	$0\bar{6}2$	20.6	27.2	$01\bar{0}3$	1.7	3.8	404	9.9	11.3
007	15.0	15.1	044	20.9	18.5	$0\bar{6}3$	9.7	13.2	*200	32.1	30.7	405	9.3	7.7
008	19.3	15.4	045	8.6	9.2	$0\bar{6}4$	11.1	13.0	201	17.3	20.2	406	7.5	5.8
*020	17.3	15.3	046	12.7	12.1	$0\bar{6}5$	19.2	15.4	202	18.2	22.9	*$\bar{4}01$	25.2	27.0
021	18.2	16.4	047	7.9	8.1	$0\bar{6}6$	15.1	12.2	203	28.1	26.0	*$\bar{4}02$	15.4	21.0
022	22.4	22.5	048	7.5	6.9	$0\bar{6}7$	12.2	10.8	204	42.2	34.2	$\bar{4}03$	17.1	19.4
023	5.2	5.1	$04\bar{1}$	4.4	5.1	*080	11.5	14.7	205	2.9	3.9	$\bar{4}04$	14.3	13.4
024	14.7	11.7	$04\bar{2}$	17.1	14.2	081	8.9	6.9	206	18.4	15.0	$\bar{4}05$	18.9	16.5
025	6.3	7.1	$04\bar{3}$	10.4	10.7	082	9.7	8.8	207	7.5	6.2	$\bar{4}06$	27.9	19.2
026	8.2	7.7	$04\bar{4}$	17.9	12.8	083	3.1	5.4	208	10.8	7.6	$\bar{4}07$	4.6	6.0
027	8.3	9.4	$04\bar{5}$	15.2	14.9	084	5.1	5.2	*$\bar{2}01$	26.2	26.1	$\bar{4}08$	14.2	9.2
028	4.2	4.5	$04\bar{6}$	9.8	10.8	085	5.5	6.1	*$\bar{2}02$	39.4	34.8	600	15.4	11.1
$0\bar{2}1$	27.8	25.9	$04\bar{7}$	10.6	9.9	$0\bar{8}1$	11.1	7.7	$\bar{2}03$	35.7	33.0	601	12.2	8.1
$0\bar{2}2$	7.5	7.9	$04\bar{8}$	4.0	3.8	$0\bar{8}2$	5.0	5.4	$\bar{2}04$	34.9	37.0	$\bar{6}01$	8.0	12.8
$0\bar{2}3$	16.1	12.3	*060	45.3	46.2	$0\bar{8}3$	4.6	5.4	$\bar{2}05$	16.3	15.2	*$\bar{6}02$	21.7	19.5
$0\bar{2}4$	10.9	10.5	061	17.0	13.4	$0\bar{8}4$	7.2	7.5	$\bar{2}06$	15.0	17.8	$\bar{6}03$	5.5	5.8
$0\bar{2}5$	7.9	7.9	062	13.6	15.7	$0\bar{8}5$	5.4	5.8	$\bar{2}07$	15.3	14.5	$\bar{6}04$	10.9	9.6
$0\bar{2}6$	12.3	13.2	063	10.9	14.8	*0.10.0	6.9	9.3	$\bar{2}08$	7.8	3.3			

TABLE 3

Interatomic Distances (A) for Kaolinite

$Si_1 - O_1$	1.63	$Al_1 - OH_3$	1.99	$OH_1 - OH_2$	2.90	$OH_2 - O_1$	2.83
$Si_1 - O_3$	1.61	$Al_1 - OH_4$	1.92	$OH_1 - OH_3$	2.95	$OH_3 - O_3$	2.51
$Si_1 - O_4$	1.63	$Al_1 - O_1$	1.91	$OH_2 - OH_3$	2.93	$OH_3 - OH_4$	2.80
$Si_1 - O_5$	1.63	$Al_1 - O_2$	2.00	$OH_4 - O_1$	2.85	$O_2 - O_3$	2.69
$Si_2 - O_2$	1.63	$Al_2 - OH_1$	1.88	$OH_4 - O_2$	2.78	$O_2 - O_4$	2.62
$Si_2 - O_3$	1.62	$Al_2 - OH_2$	1.95	$O_1 - O_2$	2.80	$O_3 - O_5$	2.73
$Si_2 - O_4$	1.63	$Al_2 - OH_3$	1.91	$OH_1 - O_1$	2.50	$O_3 - O_4$	2.68
$Si_2 - O_5$	1.62	$Al_2 - OH_4$	1.99	$OH_1 - O_2$	2.88	$O_3 - O_5$	2.60
$Al_1 - OH_1$	1.97	$Al_2 - O_1$	1.91	$OH_2 - OH_4$	2.56	$O_4 - O_5$	2.61
$Al_1 - OH_2$	1.91	$Al_2 - O_2$	1.97				

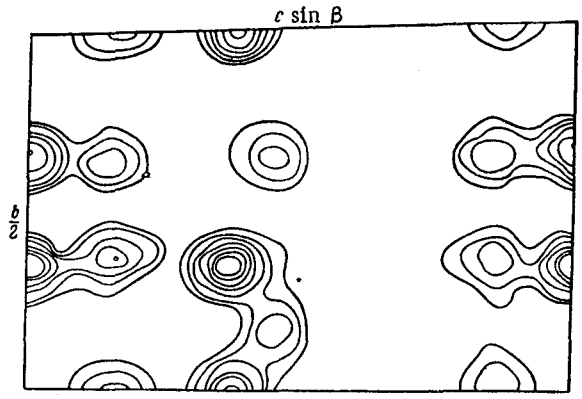

Fig. 1. The σ(yz) projection of the electron-density (only half of the projection is shown, because the other half is translationally the same).

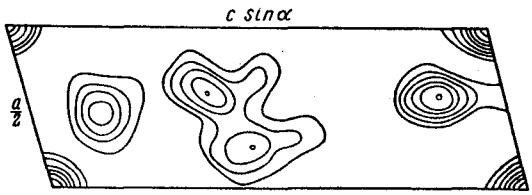

Fig. 2. The σ(xz) projection (half is shown).

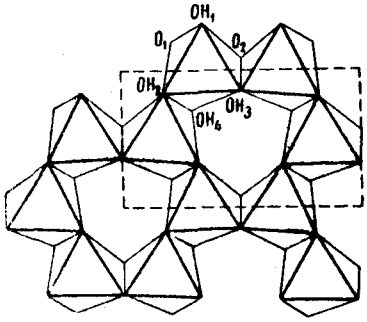

Fig. 4. Octahedral grid in kaolinite.

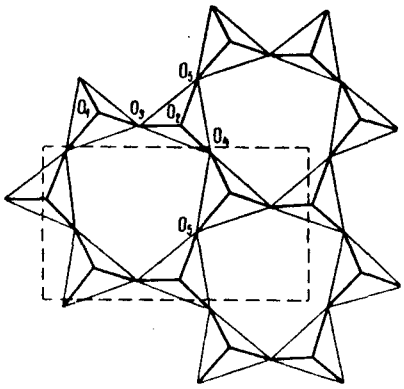

Fig. 3. Tetrahedral grid in kaolinite.

Table 2 gives the F and F_0. These have been compiled by means of two normalizations (as in [5]); the reflections were divided into two groups, to each of which we assigned a distinct factor to convert the F_0 to absolute values. One group differed from the other in that those in the first (those values indicated by* in Table 2) are single, whereas those in the other appear as doublets. Those latter are much weaker, which accounts for the need for two normalizations. The implication is that the sequence of atoms in a single layer does not apply strictly to the whole crystal [5]. Here R takes the value 15.4%.

The strengths of those reflections not visible on the films were taken as being half the strength of the weakest reflection.

The atoms are displaced from the positions corresponding to ideal cubic packing of the anions, which deviate from their ideal positions in a tetrahedral grid [10]. The tetrahedra are rotated in such a way that their bases form a ditrigonal pattern (Fig. 3). The average angle of that rotation is 21°. The top and bottom ends of the octahedra also form a ditrigonal array, but here the angles are much smaller (Fig. 4), being 6.5 and 4°, respectively. The interatomic distances (Table 3) agree well with the standard values. The common edges of the octahedra are shorter than the others. The successive layers are stacked in a way such that the oxygen atoms and OH groups in adjacent layers come together in pairs; the distances vary somewhat, the mean being 2.93 A.

These results do not differ essentially from those obtained by means of electron diffraction [5], although the coordinates and distances are by no means always in exact agreement.

The distortions resemble very closely those found in dickite, a polymorphic form of kaolinite [7].

We wish to thank B. B. Zvyagin for valuable advice and assistance in this work.

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