The structure of kaolinite.

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Introduction.

A POSSIBLE structure for kaolinite was first put forward by Pauling (1930) in a paper dealing generally with the structures of layer-type minerals, chlorites, micas, &c. He suggested that the structure consisted of a sheet of Si–O tetrahedra arranged in a hexagonal network with a superposed sheet of Al–(O,OH) octahedra, the two together forming a layer of composition $Al_2Si_2O_5(OH)_4$ (fig. 2). Ross and Kerr (1931), from a detailed microscopic study of the kaolin minerals, concluded that the symmetry of kaolinite is 'probably monoclinic'. The first attempt at a detailed structure analysis was made by Gruner (1932a) from X-ray powder photographs. The reflections, some 40 altogether, were indexed on the basis of a monoclinic cell with a 5·14, b 8·90, c 14·51Å., β 100° 12'. Gruner's work confirmed Pauling's suggestion regarding the structure of the layer. The values of the parameters a and b are determined by the dimensions of the Si–O network and the ratio of these values, $\sqrt{3}$, follows from the hexagonal arrangement of the Si–O tetrahedra. The height of the cell, $c \sin \beta$, is 14·26Å. and this requires two $Al_2Si_2O_5(OH)_4$ layers per cell. The space-group finally chosen by Gruner was $C_s^4 = Cc$; the two layers of atoms are related by the glide planes of symmetry parallel to (010). Hendricks (1936) obtained additional confirmatory data for Gruner's structure by both X-ray and electron diffraction methods; he agreed with Gruner's values for a, b, and c, but gave β 101° 30'. Lists of kaolinite reflections have also been published by Nagelschmidt (1934) and by Favejee (1939), but no further work on the structure of the mineral has been attempted.

We have recently had occasion to examine many kaolinite specimens and in a brief note (Brindley and Robinson, 1945) have reported that more reflections are obtained than Gruner recorded and that there are noteworthy differences between his and our observations. In particular, we find it impossible to index the reflections with a monoclinic cell. To account for the observed reflections it is necessary to postulate a triclinic cell having half the height of Gruner's cell, i.e. containing only one layer of atoms. The reflected intensities are in general agreement with this structure. We have so far confined our attention to a layer of ideal type, i.e. consisting of regular tetrahedra and octahedra. It is very questionable whether the structure can be determined in any greater detail from powder photographs alone, since the majority of the higher-order lines are composed of several reflections. We believe, however, that the analysis has been carried sufficiently far to show that the structure is essentially triclinic and that the unit cell contains one layer of the type suggested by Pauling.

X-ray powder diagrams of kaolinite.

Powder photographs have been taken with two types of camera: (1) A semi-focusing camera of diameter 20·05 cm. has been used for spacings greater than 2Å. The material to be examined forms a thin flat powder layer at the centre of the camera and is mounted in a dry state without adhesive. (2) A cylindrical camera of the Bradley type of diameter 12 cm. has also been used; specimens of diameters ranging 0·3–0·45 mm. were mounted either as dry powders in thin cellophane tubes or by coating them on fine glass fibres. Cu$K\alpha$ radiation filtered by nickel foil was employed.

The more outstanding differences between Gruner's observations and our own occur for spacings greater than 2Å. These reflections are also the most useful for identifying kaolinite in a mixture of minerals. We have therefore examined a variety of kaolinite specimens from widely different localities with the 20 cm. diameter camera. The results for spacings greater than 2·1Å. are set out in table I, which gives also the source of the specimens used and, for materials obtained from the British Museum, their register number. The final column lists Gruner's data. The estimated intensities, which are indicated by the numbers in small type, depend partly on the experimental arrangement, viz. the use of a flat powder layer; if these intensities are to be compared with those for cylindrical specimens (as in table II) allowance must be made for the different absorptions in the two cases. It should further be noted that the use of a flat layer tends to introduce a preferential orientation which enhances the basal reflections at 7·13, 3·57, and 2·37Å.

Kaolinites from the following sources have also been examined, but the results are less satisfactory owing to impurities, but in no case do they conflict with the data of table I.

   (i) Halle, Province of Saxony (B.M. 14402) with quartz impurity.
  (ii) Rainbow Cliff, St. Kitts, British West Indies (B.M. 1924,12,454) with cristobalite and other impurities.
 (iii) Shore Hill, Otford, Kent (B.M. 1921,119) with quartz and mica.
 (iv) Ayrshire, Scotland, with quartz and anatase.

The unit cell of kaolinite.

The full list of reflections now obtained for kaolinite is given in table II. These cannot be indexed on the basis of the monoclinic cell given by Gruner, for not only are some of the spacings different but there are also additional lines. Attempts to interpret the data in terms of a monoclinic cell of somewhat different dimensions were unsuccessful. The angle β and also the angle α were varied between 90° and 115°. The parameters a and b of Gruner's structure arise from the dimensions of the hexagonal network of Si–O tetrahedra and closely similar values are found in many layer-type minerals, such as micas and chlorites. If therefore this type of structure exists in kaolinite—and its occurrence in the other kaolin minerals, dickite and nacrite, strongly suggests that it is so—then the a and b parameters cannot differ greatly from those given by Gruner. We have examined variations of a from 5·05 to 5·2Å. and of b from 8·8 to 9·1Å. The height of the cell is obtained as a multiple of 7·13Å. from the basal reflections which are greatly enhanced by the use of orientated layers.

TABLE I. X-ray powder data for specimens of kaolinite (spacings greater than 2·1 Å.).

(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	(9).	(10).	Gruner's data.
7·134 10	7·15 10	7·15 10	7·14 10	7·16 10	7·15 10	7·16 10	7·15 10	7·16 9	7·15 13	7·13
4·460 4	4·446 7	4·451 6	4·453 4	4·445 6	4·453 6	4·457 6	4·451 5	4·458 6	4·455 5	—
4·354 5	4·354 5	4·352 6	4·344 6	4·352 6	4·343 5	4·357 9	4·347 6	4·346 5	4·339 5	4·39
4·176 5	4·174 6	4·169 7	4·166 7	4·162 4	4·145 4	4·170 8	4·168 4	4·155 5	4·158 3	4·21
4·128 3	—	4·119 2	4·117 3	—	—	4·120 3	4·119 2			(4·02)*
3·844 4	3·836 8	3·835 4	3·832 4	3·840 1	3·837 2	3·836 4	3·832 3	3·840 2	3·840 2	3·76
3·733 2	3·732 1	3·733 1	3·725 2	3·757 1	3·741 1	3·732 2	3·731 1	3·742 1	3·716 1	3·57
3·567 15	3·568 15	3·567 15	3·561 15	3·567 15	3·564 15	3·566 16	3·564 15	3·569 15	3·570 15	3·35
3·368 3	3·379 2	3·372 1	Quartz	—	Quartz	3·360 3	3·337 1	3·377 1	—	—
3·148 1	—	—	3·129 ½	—	—	—	—	—	—	3·08
3·094 1	—	—	3·088 ½	—	—	—	—	—	—	—
2·746 2	—	2·745 ½	2·749 5	—	2·768 ½	—	2·736 ½	—	—	—
2·556 4	2·554 5	2·555 5	2·551 4	2·553 5	2·552 5	2·553 5	2·554 4	2·552 6	2·553 4	2·556
2·529 2	2·515 3	2·523 2	2·520 2	2·520 2	2·517 1	2·521 2	2·521 2	2·520 2	2·520 1	—
2·486 4	2·488 6	2·485 6	2·482 5	2·488 6	2·482 5	2·486 6	2·486 5	2·488 6	2·486 4	2·491
2·376 2	2·372 2	2·378 1	2·371 1	2·375 1	2·373 2	2·374 1	2·375 1	2·375 2	2·373 3	2·373
2·333 6	2·332 9	2·334 10	2·329 7	2·333 11	2·329 8	2·332 11	2·331 9	2·329 10	2·329 7	2·341
2·286 4	2·286 5	2·288 6	Quartz	2·285 5	2·282 5	2·285 7	2·286 4	2·285 6	2·281 4	2·272
2·242 1	2·250 ½	2·250 ½	2·239 1	—	—	2·240 ½	—	2·244 ½	—	—
2·183 2	2·188 1	2·182 ½	2·180 ½	—	—	—	2·179 ½	2·182 1	—	2·200
2·127 1	—	—	—	—	—	—	—	—	—	—

* This may be the CuKβ reflection from 3·57 Å. spacing.

1. A purified Cornish china-clay; a very good kaolinite with a trace of mica; most of our measurements have been made on this material; results in column 1 are average values for eight determinations.
2. Röchlitz, Saxony (B.M. 1911,1113,5); a good kaolinite containing impurity not identified with certainty, but may be analcime.
3. Stahlberg, Pfalz, Rhenish Bavaria (B.M. 60088); very good kaolinite; no impurities observed.
4. Kahan hill, Mergui district, Lower Burma (B.M. 1911,634; excellent kaolinite giving very sharp lines. With appreciable amount of quartz.
5. Ambalangoda, Ceylon (B.M. 1923,1002); kaolinite lines diffuse; with coarse quartz and other impurities not identified.
6. Darling Range, Western Australia (B.M. 66161); kaolinite lines rather broad; trace of coarse quartz and other impurities.
7. Westcott, Dorking, Surrey (B.M. 1908,315); good kaolinite with trace of quartz; specimen pink coloured.
8. Kashina, Kamyshlov district, Perm, Russia (B.M. 1922,911); with trace of quartz.
9. Cook's Kitchen mine, Redruth, Cornwall (B.M. 19014), var. lithomarge. A clear photograph agreeing with kaolinite; the 4·17—4·12 Å. doublet not resolved. No observable impurities.
10. Rosemellyn china-clay works, St. Austell, Cornwall (B.M. 1910,582); a washed sample, with some mica.

Failing to find a suitable monoclinic cell, we examined the possibility that the cell might be triclinic. This seemed not unlikely because of the occurrence of a number of doublets, particularly at small angles; the closeness of the doublets suggested that one angle, either α or β, might be close to 90°. The angle γ between the a- and b-axes was kept at 90°. A cell to fit the observed reflections was eventually found with:

$$a\ 5{\cdot}14,\ b\ 8{\cdot}93,\ c\ 7{\cdot}37\text{Å.},\ \alpha\ 91{\cdot}8°,\ \beta\ 104{\cdot}5°\text{--}105{\cdot}0°,\ \gamma\ 90°.$$

The main difference between this cell and Gruner's, apart from its triclinic nature, is the c parameter which is approximately half of Gruner's value. The closeness of the agreement between the observed and the calculated planar spacings is shown in table II; the observed values down to $2{\cdot}1$Å. are mean values for the ten specimens of table I, and below $2{\cdot}1$Å. are mean values for specimens 1 and 3 only. The latter were selected for the higher-order measurements because they gave the sharpest lines and contained little or no observable impurities.

TABLE II. Comparison of observed and calculated spacings and reflected intensities for kaolinite.

$hkl.$	$d_{\text{calc}}.$	$F^2\phi(\theta)10^{-3}.$		$d_{\text{obs}}.$	Observed intensity.	$hkl.$	$d_{\text{calc}}.$	$F^2\phi(\theta)10^{-3}.$		$d_{\text{obs}}.$	Observed intensity.
001	7·132	488		7·15	vvs*	$2\bar{2}\bar{1}$	2·217	4			
020	4·460	59		4·453	m−	201	2·193	4			
$\bar{1}10$	4·361	172		4·349	m	$1\bar{3}\bar{2}$	2·191	4 } 20		2·182	w+
110	4·323	17				$2\bar{2}\bar{0}$	2·178	12 }			
$11\bar{1}$	4·164	181		4·170	m	220	2·161	1			
$1\bar{1}\bar{1}$	4·117	86		4·120	w+	$04\bar{1}$	2·150	4			
$02\bar{1}$	3·841	141		3·837	wm	$02\bar{3}$	2·126	14 } 22		2·127	w
021	3·729	73		3·734	w	041	2·110	8 }			
002	3·566	265		3·566	vvs*	$22\bar{2}$	2·083	0·0			
$1\bar{1}1$	3·416	8		—	—	023	2·071	0·4 } 9·7		2·057	vw
111	3·363	85		3·365	wm	$2\bar{2}\bar{2}$	2·059	9·3 }			
$11\bar{2}$	3·142	25		3·138	w	$20\bar{3}$	1·990	17·8 } 48·6		1·985	ms
$1\bar{1}\bar{2}$	3·092	37		3·091	w	$1\bar{3}\bar{2}$	1·985	30·8 }			
$0\bar{2}2$	2·832	3		—	—	$2\bar{2}1$	1·973	2·5			
022	2·743	34		2·748	w	221	1·945	14·0 } 43·5		1·935	wm
$1\bar{3}0$	2·561	23 }				132	1·932	29·5 }			
$20\bar{1}$	2·558	22 } 85		2·553	ms	$1\bar{1}3$	1·926	3·5			
130	2·543	40 }				$04\bar{2}$	1·920	10·4			
$13\bar{1}$	2·525	46 }				113	1·902	2·8 } 18·1		1·892	w
$1\bar{1}2$	2·515	35 } 81		2·521	wm	$1\bar{3}3$	1·893	15·3 }			
$1\bar{3}1$	2·495	57 }				042	1·865	8·4		1·865	vw
200	2·485	54 }				$1\bar{3}\bar{3}$	1·841	12·6 }			
112	2·478	13 } 124		2·486	s	202	1·832	11·7 } 38·3		1·835	wm
003	2·378	50		2·374	ms*	$2\bar{2}\bar{3}$	1·831	14·0 }			
$20\bar{2}$	2·337	159 }				$11\bar{4}$	1·806	7·9 } 12·1		1·805	vw
$1\bar{3}1$	2·336	164 } 323		2·331	vs	$2\bar{2}3$	1·804	4·2 }			
$11\bar{3}$	2·330	11		—	—	$1\bar{1}4$	1·786	0·3			
$1\bar{1}3$	2·297	24 }				004	1·783	12·7		1·778 m*	sharp
131	2·284	161 } 185		2·284	s	$2\bar{2}2$	1·708	9·4		1·704 vw	very clear back‑ground
$13\bar{2}$	2·244	6 }									
040	2·230	7 } 13		2·243	vw						
$22\bar{1}$	2·220	13									

* (00l) reflections for which the observed intensities are enhanced, owing to preferential orientation. Observed intensities estimated visually in decreasing order of strength, vvs, vs, s, ms, m, m−, wm, w+, w, w−, vw.

hkl	d_{calc}	$F^2\phi(\theta)10^{-3}$	d_{obs}	Observed intensity.
1̄50	1·686	1·0		
24̄1	1·684	10·4		
31̄1	1·682	3·3	1·682	w ↓ (17·5)
3̄1̄1	1·682	1·8		
222	1·681	1·0		
2̄41	1·679	0·5		
150	1·676	7·4		
15̄1	1·676	6·8		
02̄4	1·675	3·7		
2̄40	1·666	9·8		
20̄4	1·663	44·7	108·5 1·659	s
15̄1	1·660	9·9		
1̄33	1·659	44·1		
04̄3	1·654	6·2		
240	1·654	3·9		
31̄2	1·649	3·3		
3̄1̄2	1·644	9·2		
024	1·638	4·9		
3̄10	1·631	4·8		
24̄2	1·627	0·4		
310	1·627	8·1		
1̄51	1·619	6·4	62·0 1·616	ms
133	1·614	40·0		
2̄4̄2	1·604	7·1		
043	1·601	3·8		
151	1·591	0·8		
15̄2	1·590	1·1	11·6 1·581	wm
13̄4	1·583	10·5		
2̄41	1·574	2·5		
22̄4	1·572	1·9		
1̄5̄2	1·557	1·4		
241	1·546	2·8		
22̄4	1·546	9·2		
1̄1̄4	1·542	0·8	52·2 1·539	m (very broad)
13̄4	1·539	15·9		
31̄3	1·538	6·2		
203	1·534	17·3		
3̄1̄3	1·531	0·4		
114	1·525	3·8		
3̄1̄1	1·511	4·9		
311	1·505	0·1		
24̄3	1·500	4·7		
15̄2	1·491	3·4		
060	1·487	41·5		
33̄1	1·484	42·5	125·4 1·486	vs (sharp)
33̄1	1·483	41·4		
24̄3	1·470	0·3		
06̄1	1·466	13·4		
33̄2	1·463	13·6	31·8 1·464	w
2̄2̄3	1·462	4·8		
11̄5	1·462	0·2		

hkl	d_{calc}	$F^2\phi(\theta)10^{-3}$	d_{obs}	Observed intensity.
3̄3̄2	1·455	8·2		
15̄3	1·454	4·8		
152	1·453	4·7		
3̄30	1·452	7·8	44·0 1·449	wm(broad)
061	1·447	4·2		
1̄1̄5	1·447	1·8		
223	1·439	8·4		
330	1·439	4·1		
2̄4̄2	1·435	1·6		
005	1·427	8·2	1·426	wm*(sharp)
04̄4	1·418	3·2		
1̄5̄3	1·412	2·1		
205	1·401	6·8		
242	1·400	3·5	16·5 1·400	w
1̄34	1·398	6·2		
31̄4	1·392	0·0		
06̄2	1·390	2·4	4·7 1·387	w
3̄3̄3	1·388	2·3		
3̄1̄4	1·384	1·2		
3̄3̄3	1·373	3·0		
02̄5	1·372	0·1		
044	1·372	6·7		
3̄3̄1	1·369	2·8	10·5 1·368	w
3̄1̄2	1·363	0·0		
134	1·362	0·9		
062	1·357	3·6		
312	1·355	2·8		
331	1·352	3·7		
24̄4	1·349	1·6		
22̄5	1·348	5·2		
025	1·346	1·1		
1̄53	1·339	0·3		
135	1·338	34·2	1·335	m↑ (very clear background)
2̄2̄5	1·326	0·9		
2̄4̄4	1·318	0·5		
1̄3̄5	1·305	28·6		
204	1·300	30·0	59·3 1·302	ms(broadened line)
153	1·300	0·3		
15̄4	1·299	0·4		
06̄3	1·291	2·2		
26̄1	1·288	6·8	20·5 1·289	w
2̄6̄1	1·284	11·5		
40̄1	1·280	11·8		
2̄60	1·280	7·4		
24̄3	1·280	2·3		
33̄4	1·280	2·1	32·4 1·280	m (sharp)
1̄1̄5	1·279	1·6		
40̄2	1·279	7·2		
260	1·271	7·5		
115	1·268	0·4		

* (00*l*) reflections for which the observed intensities are enhanced, owing to preferential orientation. Observed intensities estimated visually in decreasing order of strength, vvs, vs, s, ms, m, m−, wm, w+, w, w−, vw.

hkl.	$d_{calc.}$	$F^2\phi(\theta)10^{-3}$.	$d_{obs.}$	Observed intensity.
$26\bar{2}$	1·262	20·2		
$3\bar{3}4$	1·262	1·8 } 23·8	1·262	w +
$1\bar{5}4$	1·260	1·8		
$2\bar{2}4$	1·257	2·1		
$3\bar{3}2$	1·257	2·0		
243	1·251	0·0		
$2\bar{6}2$	1·247	13·4		
063	1·243	2·6 } 30·8	1·244	wm
400	1·243	13·3		
$31\bar{5}$	1·242	1·5		
224	1·239	1·3		
332	1·239	2·1		
$2\bar{6}1$	1·239	4·3 } 15·5	1·233	wm
$40\bar{3}$	1·238	4·1		
$1\bar{7}0$	1·237	3·0		
$3\bar{5}1$	1·236	0·7		
$35\bar{1}$	1·235	0·4		
$17\bar{1}$	1·234	2·5		
$3\bar{1}5$	1·233	2·5		
170	1·232	0·1		
$4\bar{2}1$	1·231	0·1		
$42\bar{2}$	1·230	2·0		
$42\bar{1}$	1·230	2·1		
$4\bar{2}2$	1·228	2·6		
$17\bar{1}$	1·226	0·9		
$35\bar{2}$	1·225	3·0		
$11\bar{6}$	1·224	0·8		
$3\bar{5}0$	1·221	2·8		
045	1·220	4·5 } 13·3	1·215	vw
261	1·219	4·6		
$35\bar{2}$	1·217	1·4		
$3\bar{1}3$	1·215	1·5		
$11\bar{6}$	1·213	1·2		
$17\bar{1}$	1·212	0·1		
350	1·210	1·8		
$26\bar{3}$	1·203	1·2		
$24\bar{5}$	1·202	0·1		
313	1·201	0·9		
$17\bar{2}$	1·201	1·3		
$4\bar{2}0$	1·199	2·3 } 14·4	1·198	wm
$20\bar{6}$	1·197	3·4		
$42\bar{3}$	1·196	0·2		
171	1·195	2·4		
$1\bar{3}5$	1·195	2·6		
420	1·194	0·3		
$1\bar{5}4$	1·192	1·6		
$4\bar{2}3$	1·191	0·9		
006	1·188	7·1	1·188	wm*
045	1·184	0·7		(sharp)
$35\bar{3}$	1·182	0·4		
$1\bar{7}2$	1·181	0·9		
$26\bar{3}$	1·180	4·6		
401	1·174	4·6		

| hkl.	$d_{calc.}$	$F^2\phi(\theta)10^{-3}$.	$d_{obs.}$	Observed intensity.
$2\bar{4}5$	1·172	1·4		
$35\bar{1}$	1·170	0·1		
$40\bar{4}$	1·169	1·9		
$2\bar{6}2$	1·168	1·9		
135	1·168	3·0 } 16·3	1·166	w
$35\bar{3}$	1·166	1·9		
$22\bar{6}$	1·165	2·5		
$33\bar{5}$	1·162	2·5		
$06\bar{4}$	1·161	2·5		
$1\bar{7}2$	1·158	1·8		
$02\bar{6}$	1·158	1·0		
154	1·156	0·5		
155	1·155	0·6		
351	1·154	1·5		
136	1·151	1·5		
$2\bar{2}6$	1·149	4·2		
$33\bar{5}$	1·143	2·2		
262	1·142	0·2		
026	1·139	0·1		
$17\bar{3}$	1·139	0·4		
$4\bar{2}1$	1·139	1·0		
$3\bar{3}3$	1·139	2·1		
$2\bar{4}4$	1·137	0·1		
$42\bar{4}$	1·134	1·9		
421	1·132	1·9		
172	1·132	0·6		
$4\bar{2}4$	1·126	0·6		
064	1·124	1·8		
$1\bar{3}6$	1·124	0·6		
$26\bar{4}$	1·122	11·3 } 15·7	1·122	vw
333	1·120	1·7		
205	1·120	0·3		
$1\bar{5}5$	1·120	0·0		
080	1·115	0·5		
$35\bar{4}$	1·114	0·9		
$17\bar{3}$	1·112	1·6		
$44\bar{1}$	1·111	0·4		
$44\bar{2}$	1·111	0·2		
$44\bar{1}$	1·109	0·3		
$44\bar{2}$	1·108	0·7		
$08\bar{1}$	1·108	0·4		
244	1·104	0·8		
$31\bar{6}$	1·104	0·8		
352	1·099	1·2		
$3\bar{1}6$	1·097	0·1		
081	1·097	0·1		
$2\bar{6}4$	1·095	9·2		
$35\bar{4}$	1·094	0·0		
$2\bar{2}5$	1·094	3·3 } 21·9	1·092	w +
$1\bar{1}6$	1·091	0·3		
402	1·090	9·1		
$4\bar{4}0$	1·089	0·3		
$44\bar{3}$	1·087	1·1		

* (00l) reflections for which the observed intensities are enhanced, owing to preferential orientation. Observed intensities estimated visually in decreasing order of strength, vvs, vs, s, ms, m, m−, wm, w+, w, w−, vw.

hkl	$d_{calc.}$	$F^2\phi(\theta)10^{-3}$	$d_{obs.}$	Observed intensity.	hkl	$d_{calc.}$	$F^2\phi(\theta)10^{-3}$	$d_{obs.}$	Observed intensity.
$1\bar{7}3$	1·084	0·8 ⎫			$\bar{4}4\bar{4}$	1·030	1·4		
$40\bar{5}$	1·084	5·2 ⎪			155	1·029	0·9		
$2\bar{6}3$	1·082	5·2 ⎬ 11·5	1·080	w	$15\bar{6}$	1·029	0·9		
116	1·082	0·3 ⎭			$33\bar{4}$	1·026	4·6		
440	1·081	0·5			$51\bar{2}$	1·023	1·6		
$3\bar{1}4$	1·079	0·5			$37\bar{1}$	1·023	0·6		
$44\bar{3}$	1·079	1·2			$5\bar{1}2$	1·023	0·3		
225	1·079	2·4			$08\bar{3}$	1·023	0·2		
$08\bar{2}$	1·075	1·0			371	1·022	1·0		
314	1·072	0·1			$28\bar{1}$	1·022	0·3		
$24\bar{6}$	1·068	1·0			$2\bar{8}1$	1·021	1·2		
$04\bar{6}$	1·063	0·5			$2\bar{8}0$	1·021	1·1 ⎫		
$4\bar{2}2$	1·063	1·2			353	1·019	0·8 ⎪		
$17\bar{4}$	1·062	0·4			007	1·019	1·9 ⎬ 6·7	1·019	w*
$1\bar{5}5$	1·060	0·3			$37\bar{2}$	1·018	0·3 ⎪		
$42\bar{5}$	1·057	0·3			136	1·017	2·6 ⎭		
422	1·055	0·8 ⎫			$5\bar{1}1$	1·016	1·7		
082	1·055	1·5 ⎪			$51\bar{1}$	1·016	0·4		
263	1·054	8·2 ⎬ 10·9	1·055	vw	280	1·015	1·6		
173	1·054	0·4 ⎭			$37\bar{0}$	1·015	0·6		
$11\bar{7}$	1·049	0·9			065	1·013	5·8 ⎫		
$4\bar{2}5$	1·049	1·2			$2\bar{4}5$	1·013	0·5 ⎪		
$33\bar{6}$	1·047	3·3 ⎫ 6·7	1·047	w −	$28\bar{2}$	1·012	0·9 ⎪		
$06\bar{5}$	1·047	3·4 ⎭			$37\bar{2}$	1·010	1·5 ⎬ 15·5	1·011	w
$44\bar{1}$	1·045	0·6			334	1·010	5·9 ⎪		
$1\bar{1}7$	1·042	0·0			$51\bar{3}$	1·010	0·1 ⎪		
$2\bar{4}6$	1·042	0·3			$5\bar{1}3$	1·009	0·8 ⎭		
$44\bar{4}$	1·041	0·1			370	1·006	1·3		
$13\bar{6}$	1·038	2·4 ⎫			$1\bar{7}4$	1·002	0·1		
$20\bar{7}$	1·038	2·4 ⎪			$2\bar{8}2$	1·002	0·1		
046	1·035	2·9 ⎬ 9·3	1·037	w −	403	1·001	0·3		
441	1·034	1·6 ⎭			$02\bar{7}$	1·000	0·6		
$17\bar{4}$	1·032	0·0			$2\bar{8}1$	1·000	0·2		
$33\bar{6}$	1·031	4·5							

* (00*l*) reflections for which the observed intensities are enhanced, owing to preferential orientation. Observed intensities estimated visually in decreasing order of strength, vvs, vs, s, ms, m, m −, wm, w +, w, w −, vw.

The structure of kaolinite.

As regards the detailed crystal structure we have limited our considerations to the question whether a layer structure of the type suggested by Pauling (1930), and subsequently found in dickite and nacrite, will explain the observed intensities of the reflections, assuming the lattice to be triclinic with the dimensions given above.

A projection of the layer structure on (001), the basal cleavage plane, is shown in fig. 1 ; the heights of the atoms above the basal plane are indicated in the key. The oxygen atoms at heights 0 and 2·19Å. are assumed to form regular tetrahedra about the silicon atoms at height 0·60Å., and the (OH)s and oxygen atoms at heights 2·19 and 4·31Å. to form regular octahedra about the aluminium atoms at height 3·25Å. The base of the unit cell can be fitted into this structure in three different ways inclined at 120° to each other in the manner indicated. Since the height of the cell is 7·13Å., there is one layer of atoms per cell as compared with

two layers in Gruner's cell. It remains to find how successive layers of atoms are stacked with respect to each other, i.e. to find the direction of the c-axis. For each cell base in fig. 1 there are four possible directions of this axis corresponding to the four ways of combining relative displacements of adjacent layers parallel to the a- and b-axes. It would therefore appear that there are $4 \times 3 = 12$ possi-
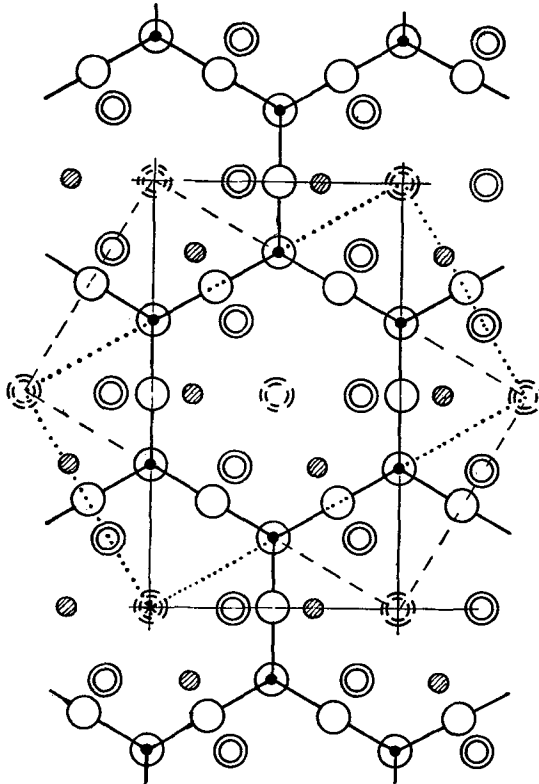
Heights of atoms above (001)

Oxygen at 0   ◎ OH at 4·31   ⊘ Al at 3·25 Å.
⬤ ,, at 2·19   ,, at 2·19   ● Si at 0·60

FIG. 1. Projection of the kaolinite layer on (001) showing the three possible bases for the unit cell; the cell adopted is shown in full lines.

bilities to be considered, but on determining the atomic co-ordinates we find actually only six different sets of co-ordinates; of these, only one set leads to calculated intensities which are at all closely related to the observed values.

The outline of the unit cell finally selected is shown by the full lines in fig. 1; the origin of the cell is at the point marked *. The atomic co-ordinates expressed in degrees with respect to these axes are given in table III. A projection of the structure on a plane perpendicular to the a-axis is given in fig. 2, which shows also the direction of the c-axis relative to the structure.

T

In calculating the reflected intensities, the f-values of Bragg and West (1928) have been used. The third column of table II gives the calculated values of $F^2\phi(\theta)$, where $\phi(\theta) = (1+\cos^2 2\theta)/\sin^2\theta \cos \theta$ and θ is the Bragg reflection angle. We agree with Gruner in finding no reflections with $(h+k)$ odd, a result which follows directly from the fact that for the ideal layer structure the c-face is centred. Although the triclinic axes could be changed to give a cell of half the volume, it
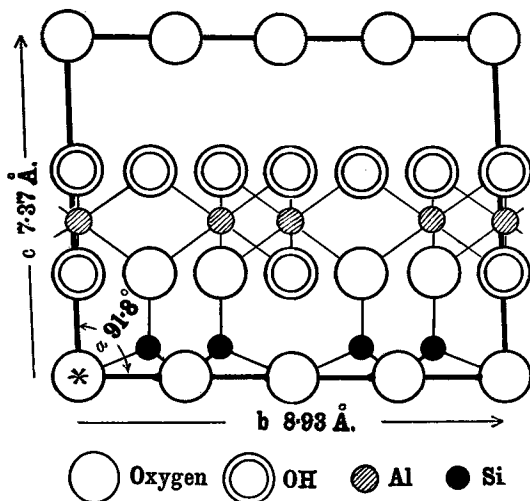
FIG. 2. Projection of the kaolinite structure on a plane perpendicular to the a-axis.

TABLE III. Atomic co-ordinates in degrees for $2Al_2Si_2O_5(OH)_4$. Two equivalent atoms for each position arising from centring of the c-face.

Oxygen　...　$(0, 180, 0)$, $(90, 90, 0)$, $(90, 270, 0)$, $(39\frac{1}{2}, 123, 110\frac{1}{2})$, $(39\frac{1}{2}, 243, 110\frac{1}{2})$.
OH　...　...　$(39\frac{1}{2}, 3, 110\frac{1}{2})$, $(18, 65\frac{1}{2}, 218)$, $(18, 185\frac{1}{2}, 218)$, $(18, 305\frac{1}{2}, 218)$.
Aluminium　$(119, 184, 164)$, $(119, 304, 164)$.
Silicon　...　$(11, 121, 30\frac{1}{2})$, $(11, 241, 30\frac{1}{2})$.

seems better to retain the a- and b-axes at right angles and parallel to the ortho-hexagonal axes of the layer itself, for this brings out the pseudo-monoclinic shape of the cell. In presenting the results, no allowance has been made for absorption of the radiation in the specimen, which has the effect of diminishing the lower-order reflections as compared with the higher orders. The observed intensities given in table II are estimated visually from photographs taken with the powder coated on thin glass fibres.

The measure of the agreement found between the observed and calculated intensities indicates that the layer type of structure suggested by Pauling, combined with the triclinic axes, is essentially correct. The fact that the observed intensities depend to some extent on the preferential orientation of the crystallites renders a precise comparison with the calculated values rather difficult. Specimens formed by coating thin glass fibres show enhancement of $(00l)$ reflections, while specimens prepared by packing the powder into cellophane tubes give increased intensities from planes making angles approaching $90°$ with $(00l)$.

Among the lower order reflections the following may be specially noted. The very close doublet (11$\bar{1}$) and (1$\bar{1}\bar{1}$) at d 4·170 and 4·120Å. is found with all kaolinites giving sufficiently sharp reflections, and their relative intensities agree well with the calculated ratio. The absence of the (1$\bar{1}$1) reflection is particularly noteworthy, because out of the six possible orientations of the *triclinic* axes discussed above, only two indicate a negligible intensity for this reflection, and one of these gives hopelessly incorrect values for many other reflections. There is therefore no ambiguity as to which of the six orientations to choose. The (111) reflection at d 3·365Å. has an observed intensity in good agreement with the calculated value. That kaolinite gives a reflection with this d value is important in mineralogical analysis because it may easily be mistaken for the strongest quartz line at d 3·336Å. The doublet (1$\bar{1}$0) and (110) is too close to be separated with our largest camera, but (1$\bar{1}$0) is very much stronger than (110) and the observed value lies much nearer the stronger line. The doublets (02$\bar{1}$), (021), and (11$\bar{2}$), (1$\bar{1}$2) show satisfactory agreement between observed and calculated intensities, and the very weak line (0$\bar{2}$2) has not been observed. Among the lower-order reflections the (020) alone is somewhat unsatisfactory, for the observed intensity is distinctly greater than the $F^2\phi(\theta)$ value would lead one to expect.

For the higher-order reflections it is unnecessary to discuss in detail the data set out in table II, but it may be remarked that the calculated values explain, for the most part, not only the observed intensities but also the widths of the observed composite reflections. For example, the broad lines at d 1·539, 1·449, and 1·302Å. are seen to arise from a combination of reflections spread over a range of angles. Furthermore, between the lines at d 1·778 and 1·682Å., and again between d 1·335 and 1·302Å., we find particularly clear stretches of background which are in agreement with the calculations.

Discussion.

It has been shown by Hendricks (1939) that in dickite and nacrite there is a symmetrical relationship between the oxygen atoms in the base of one layer and the (OH)s in the adjacent layer; the relative displacement of successive layers is such that each (OH) ion is at the same distance, 2·91Å. (Gruner 1932b, p. 403), from its nearest O neighbour in the next layer. In Gruner's structure for kaolinite, two-thirds of the (OH)–O distances are 2·9Å. and one-third are 2·82Å. In the present structure for kaolinite we find a similar result, namely, two-thirds of the (OH)–O distances are 2·99Å. and the remaining third 2·87Å. Our distances are slightly greater than Gruner's owing to a small difference in our c-co-ordinates. A comparison of our diagram in fig. 3, with the corresponding diagram for Gruner's structure (see Hendricks, 1939, p. 517), shows that the shorter (OH)–O distance occurs between different pairs of atoms in the two cases.

The shape of the triclinic cell suggests a closer relation to monoclinic symmetry than is really the case, for even if the angle α were 90° instead of 91·8°, a single layer structure on the base chosen would not have monoclinic symmetry owing to the arrangement of the aluminium atoms. Gruner showed that a single-layer structure with monoclinic symmetry could only be based on the cell with the dashed outline in fig. 1, corresponding to the space-group $C_s^3 = Cm$. A structure with monoclinic symmetry on the base that we have chosen would require two

layers per cell with the space-group $C_s^4 = Cc$; this in fact was Gruner's solution of the problem. The absence of monoclinic symmetry for a single-layer structure on this base perhaps indicates why the actual cell is found to be triclinic.
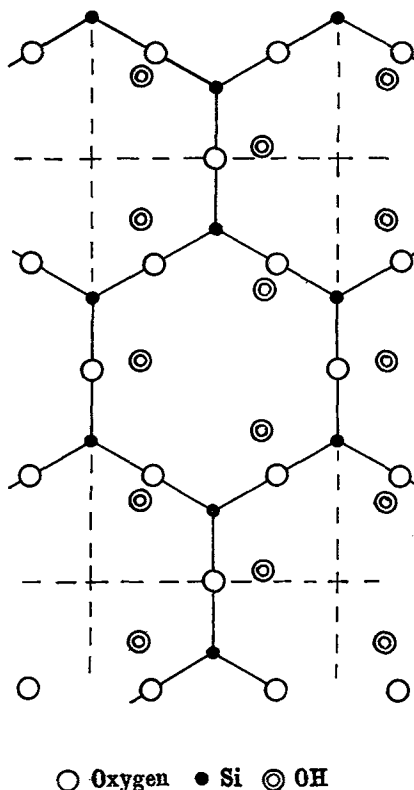

○ Oxygen   ● Si   ◎ OH

FIG. 3. Projection of adjacent oxygen and (OH) atoms on (001).

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