The structure of orthoclase.

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I. Introduction.

THE structure of sanidine was described by Taylor in 1933,[1] and Taylor, Darbyshire, and Strunz[2] in 1934 extended the investigation to include the potassium-barium-felspars and albite, and presented a small amount of experimental data for potash-soda perthitic felspars and for members of the plagioclase series. X-ray work on the potash-soda perthitic felspars has recently been reported by Ito and Inuzuka,[3] by Ito,[4] and by workers in this laboratory,[5] and a preliminary report of an examination of the plagioclase felspars is given in a thesis presented by one of us (S.H.C.) in 1939 for the degree of Ph.D. in the University of Manchester.

The investigations to be described in this paper, as well as those already published from this laboratory, form part of a programme of researches dealing with various aspects of the problem of felspar structure, undertaken in an attempt to obtain a correlation between the physical and chemical properties on the one hand and the details of the structure on the other. For this purpose it is essential that the 'key-structures' of the felspar group shall be known as accurately as possible. The earlier work by Taylor and by Taylor, Darbyshire, and Strunz included the determination, by *qualitative* methods only, of the structures of a specimen of sanidine of undetermined chemical composition, and of albite. If a structure is to be used as a standard of reference it is desirable that *quantitative* X-ray methods shall be used, and that the

[1] W. H. Taylor, Zeits. Krist., 1933, vol. 85, p. 425. [M.A. 5–473.]

[2] W. H. Taylor, J. A. Darbyshire, and H. Strunz, ibid., 1934, vol. 87, p. 464. [M.A. 6–177.]

[3] T. Ito and H. Inuzuka, ibid., 1936, vol. 95, p. 404. [M.A. 7–92.]

[4] T. Ito, ibid., 1938, vol. 100, p. 297. [M.A. 7–396.]

[5] S. H. Chao, D. L. Smare, and W. H. Taylor, Min. Mag., 1939, vol. 25, p. 338. S. H. Chao and W. H. Taylor, Nature, 1939, vol. 143, p. 1024. [M.A. 7–396.] S. H. Chao and W. H. Taylor, Proc. Roy. Soc. London, Ser. A, 1940, vol. 174, p. 57.

chemical composition and physical properties of the specimen shall be known. In this paper we describe our application of quantitative X-ray methods of measurement in the determination of the structure of a typical orthoclase, containing only a small proportion of soda-felspar. The structure is, of course, similar in general features to that of sanidine, but the details of the atomic arrangement can be given with much greater accuracy and certainty, and some interesting new features are revealed.

II. EXPERIMENTAL DETAILS.

We have obtained all our experimental data from fragments of a crystal supplied by Dr. Edmondson Spencer, to whom we are indebted for much of the material which we have used in our researches. The present material was collected by him at the ruby mines of Mogok in Upper Burma, and was listed on the border-line of the moonstone and orthoclase-microperthite series with the designation 'Specimen C, Burma colourless'. The chemical composition and physical properties given below are taken from his publications.[1]

The material contains 91 % (by weight) potash-felspar, 6·5 % soda-felspar, and 2·5 % lime-felspar; it is glass-clear and optically homogeneous even under optimum illumination, and is free from schiller; the optic axial angle is 2V 44° in a plane perpendicular to the symmetry-plane and the extinction-angle on (010) is 5·3°. Spencer (1930, p. 330) gives reasons for supposing that the amount of soda-felspar (including lime-felspar) actually present in this specimen may be held in solid solution, and we assume that our material represents a typical ortho-clase having the structure of pure potash-felspar.

To obtain Weissenberg photographs suitable for the quantitative measurement of intensities of reflection, crystal specimens of suitable dimensions must be selected. The excellent (001) and (010) cleavages simplify the cutting of a needle-shaped fragment of uniform cross-section and with its length parallel to the a-axis [100], but correspond-ingly increase the difficulty of preparing a specimen of uniform section with its length parallel to b [010]. The fragments finally chosen were of dimensions 1·23 × 0·20 × 0·18 mm. (length along a [100]), and 0·6 × 0·2 × 0·2 mm. approximately (length along b [010]). The linear absorption coefficient calculated for the Mo-Kα radiation (wave-length λ 0·71 Å.) used in these experiments and for pure potash-felspar is 14, and refer-ence to Bradley's tables[2] for absorption corrections shows that for a

[1] E. Spencer, Min. Mag., 1930, vol. 22, p. 330; 1937, vol. 24, p. 465, pl. XVIII.
[2] A. J. Bradley, Proc. Phys. Soc. London, 1935, vol. 47, p. 879. [M.A. 6–164.]

cylindrical specimen of diameter 0·2 mm. the variation in absorption for the range of glancing-angles used is less than 1 %; for a specimen with *square* cross-section the maximum variation in absorption of reflections issuing in different directions in a plane normal to the needle-axis is not greater than 8 %, and for most reflections the uncertainty introduced by this factor will not exceed 4 or 5 %.

In an attempt to estimate the effect of extinction in reducing the measured intensities of the strongest reflections, a Weissenberg photograph was obtained from a fragment of crystal of dimensions 0·67 × 0·08 × 0·04 mm., with rotation about the needle-axis which is parallel to *a* [100]. The extinction correction will be discussed later.

The measurements previously reported (Chao, Smare, and Taylor, 1939) show that the X-ray reflections confirm the monoclinic symmetry of the specimen and gave the following values for the axial lengths: *a* 8·60, *b* 13·02, *c* 7·22 Å. The angle β is assumed to have the value 63° 57′. If the crystal is assumed to be holohedral (a test for pyroelectric effect, using the liquid-air method, gave negative results), the space-group is $C_{2h}^3 = C2/m$. The unit cell contains four felspar molecules, the density calculated on the assumption that the crystal is a pure potash-felspar being 2·55, which compares sufficiently well with Spencer's measured density 2·563.

Reflections of the types (0*kl*) and (*h0l*) have been registered on zero layer-line Weissenberg photographs with crystal specimens (described above) rotating about the axes *a* [100] and *b* [010] respectively. The intensities of reflection have been measured by means of an integrating photometer of the Robinson-Dawton type,[1] due care being taken to obtain a reliable mean value of the integrated intensity for each reflection.

The most intense of all the reflections of the type (0*kl*) is the (002), and next in order are (040) and (060). Extinction is therefore most likely to affect (002), and we have attempted a very rough correction for this effect as follows. The smaller the fragment of crystal, the smaller is the influence of secondary extinction in reducing observed intensities below their true values. The use of a crystal of extremely small cross-section (0·08 × 0·04 mm.) should therefore result in relative enhancement of the strongest reflections if extinction is in fact effective in the larger specimen (section 0·20 × 0·18 mm.) from which the data for reflections (0*kl*) are obtained. Unfortunately, the *only* reflections of measurable intensity recorded on the film from the small crystal are (002), (040), and (060),

[1] B. W. Robinson, Journ. Sci. Instr., 1933, vol. 10, p. 233; and R. H. V. M. Dawton, ibid., 1937, vol. 14, p. 198.

so that it is impossible to make a thorough comparison of the alterations in relative intensities of very intense and of moderately weak reflections. The (002) is, however, relatively much stronger, compared with (040) and (060), when the small crystal is used, and an approximate correction has therefore been applied to this one reflection.

For the reflections of type $(h0l)$ no direct estimate of extinction effects was attempted, owing to the difficulty of obtaining suitably shaped specimens for rotation about b [010], but a correction was applied to $(20\bar{1})$, $(20\bar{2})$, $(20\bar{4})$, and (402), which are very intense reflections, the amount of the correction being similar to that for (002).

The values of '$F_{observed}$' quoted in table II include these corrections for extinction. A few of the reflections included in the list of measured F's were too weak for photometric measurement and were estimated visually; in the table these reflections are distinguished by the presence of brackets—thus reflection (602), $F_{obs.} = (20)$.

To convert the integrated intensities of reflection, which are measured on an arbitrary scale, into absolute F-values it is necessary to determine at least one integrated reflection in absolute units. This we were unable to do, and we have therefore reduced our observed F's to an absolute scale indirectly as follows. From the first synthesis of the projection along the a-axis [100] approximate values of the atomic co-ordinates θ_2 and θ_3 can be deduced, and from these the F's were calculated for all reflections $(0kl)$ which are neither very strong nor very weak. All the measured F's for reflections $(0kl)$ are now multiplied by that factor which secures the closest possible agreement between observation and calculation for these reflections of medium intensity, and it is assumed that the new values of F $(0kl)$ (observed) are now expressed in absolute units. In this comparison the very strong reflections are omitted because of the uncertainty with regard to the effect of extinction, and the very weak because of the difficulty of accurate measurement and the relatively large effect of small changes in atomic co-ordinates.

To convert to absolute units the measured F's for reflections $(h0l)$, the arbitrary scale of values is multiplied by a factor which makes the intensities of reflections $(00l)$ as measured on the film with rotation about b [010] identical with the intensities of the same reflections as measured on the film with rotation about a [100]. (The reflections $(00l)$ are, of course, the only set to appear on both films.)

It is clear that, although the measurements of F's are quantitative, the final scale is not necessarily identical with the absolute scale. That the scale of values quoted in table II is in fact identical with the absolute

scale to a very close approximation is shown, firstly, by the close agreement between observed and calculated F's for the structure as finally determined, and secondly, by the satisfactory agreement between the electron-counts in the projections obtained from the observed F-values and the known unit-cell contents (see section III).

Before the Fourier synthesis can be constructed from the measured F's it is necessary to know the sign of each F. For this purpose we have assumed that the structure of sanidine, as originally described by one of us (Taylor, 1933), provides a reasonably close approximation to the orthoclase structure now under discussion, and in the first synthesis for each axial projection the F's were given the same signs ($+$ or $-$) as for the sanidine structure. The F's were then recalculated using the atomic co-ordinates deduced from the first synthesis. Although many reflections show appreciable alterations in intensity, it is only in a very small number of the weaker reflections that there is a change of sign as compared with sanidine.

One further detail in the treatment of the experimental data must be described. The Fourier synthesis constructed from the measured F's is incomplete because no account can be taken of reflections at large glancing-angles which are too weak for measurement, which may nevertheless correspond to F's only *slightly* smaller than those which are included in the series. As a consequence, false detail may appear in the projection representing the Fourier synthesis. To remove this difficulty new syntheses were made, in which the coefficients were the F-values modified by the operation of an artificial temperature-factor of the usual form $e^{-B\sin^2\theta}$, where θ is the glancing-angle; with the value $B = 9$ the smallest coefficients are only a few units. In the resulting projections no false detail should appear.

III. DISCUSSION OF RESULTS.

The orthoclase structure is very similar to that of sanidine, and reference should be made to the account (Taylor, 1933) of that structure for a description of its general features and for details of the space-group symmetry.

The results of our present measurements are summarized in the contoured graphs of electron-density reproduced in figs. 1A, 1B, 2A, 2B, which we now consider in turn.

Fig. 1A represents electron-densities projected along the b-axis [010] on the plane (010). The whole unit-cell area is included because otherwise it is difficult to see how the peaks lie in the cell. The quantity

which is plotted is $S(xoz)$, the density per unit area being $S(xoz)/ac \sin \beta$, and the contours drawn are $S = 0$ (dotted), 400, 1200, 2000, and at intervals of 800. Fig. 1B represents the corresponding projection, modified by the application of the temperature-factor, as described in the previous section. The zero contour is again dotted, but contours are now drawn, at uniform intervals of 400, for $S = 0$, 400, 800, &c.

Fig. 2A represents the projection, along the a-axis [100], of one-eighth of the unit cell. The projection of the whole unit cell may be obtained by the operation of the symmetry elements, and the portion reproduced is sufficient to enable the atomic peaks to be seen clearly. The quantity plotted is $S(oyz)$, the density per unit area being $S(oyz)/bc \sin \beta$, and contours are drawn at intervals of 400, the zero contour being dotted. Fig. 2B is the corresponding projection when the artificial temperature-factor is applied: the contours are 0 (chain-dotted), 200 (dotted), 400, 800, 1200 . . ., these being selected to give maximum clarity.

If all atoms were clearly resolved in both projections, it would be possible to write down for each atom the co-ordinates θ_2 and θ_3 from the a-axis projection, and the co-ordinates θ_1 and θ_3 from the b-axis projection; the two sets of values of θ_3 should be identical, and the agreement actually found would be a measure of the accuracy with which θ_1, θ_2, and θ_3 have been determined for each atom.

In practice, as will be clear from figs. 1 and 2, there is serious overlapping of atomic peaks in many cases, and it is only by the use of both projections that any approach to a complete list of co-ordinates can be obtained. The limits within which the atomic co-ordinates must lie, and their most probable values, have been deduced from the projections: in some cases the range of possible values is small, in others it is rather large; in many of the latter it has been possible to narrow the range by direct comparison of observed and calculated F's for some reflection which happens to be specially sensitive to a change in the particular co-ordinate under consideration. Proceeding in this way 16 of the 20 variable parameters (co-ordinates) can be determined with considerable accuracy, the remaining 4 being located within limits which correspond to distances 0·1 Å., 0·2 Å. (for co-ordinates θ_3 of atoms O_B and O_C) and 0·2 Å., 0·3 Å. (for co-ordinates θ_1 of the same atoms). The final values of these four atomic co-ordinates were selected in such a way as to make the tetrahedral $(Si,Al)O_4$ groups as regular in shape as possible: in doing this we are, of course, departing from the strictly impartial procedure which was applied to determine the other 16 parameters, but we believe that we are justified, *firstly*, because there is a unique pair of positions
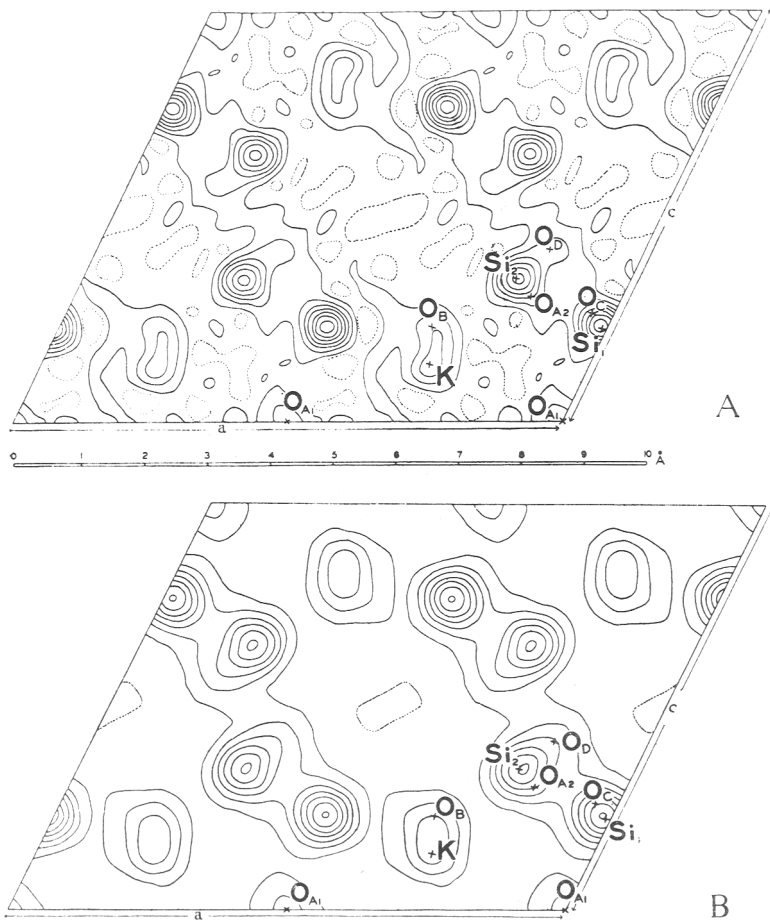
Fig. 1A. The electron-density projected along the b-axis [010]. The zero contour is dotted, and encloses regions of small negative density. The positions finally selected for the atoms are marked by crosses, which correspond to the co-ordinates quoted in table 1.

Fig. 1B. The electron-density projected along the b-axis [010] as in fig. 1A, the coefficients of the Fourier series being modified by the application of an artificial temperature-factor.

for O_B and O_C which results in almost perfectly regular tetrahedra about *both* atoms of types Si_1 and Si_2 (the co-ordinates θ_2 for both atoms being fixed in advance from consideration of the projections), and *secondly*, because the four co-ordinates finally chosen in this way (θ_1 and θ_3 for

O_B and O_C) all lie within the permissible limits previously established from the projections.

The atomic co-ordinates finally selected are shown in table I, which also contains the co-ordinates given in the sanidine paper (Taylor, 1933, p. 430.)
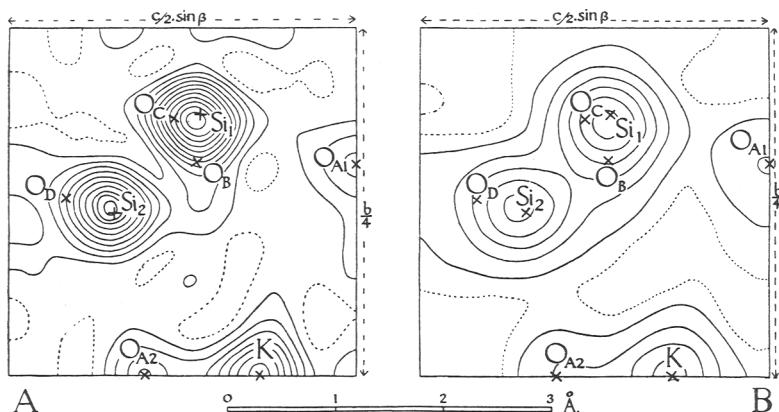

Fig. 2A. The electron-density projected along the a-axis [100]. The zero contour is dotted, and only one-eighth of the unit cell is shown in the diagram. Atomic positions represented by the co-ordinates quoted in table I are marked by crosses.

Fig. 2B. The electron-density projected as in fig. 2A, an artificial temperature-factor being included in the calculations. The zero contour is chain-dotted, and the 200 contour is dotted.

The accuracy of the structure represented by these atomic co-ordinates is confirmed if there is close agreement between the measured F's and F's calculated from the structure for a large number of reflections of all types. Table II contains observed and calculated F's for reflections of types $(0kl)$ and $(h0l)$, and it is clear that there is very close agreement, with perhaps a slight tendency for $F_{calc.}$ to fall numerically below $F_{obs.}$. The weak reflections for which the intensity was estimated are marked by brackets in the column $F_{obs.}$, and the uncertainty as to the influence of extinction of the strongest reflections, and the accuracy of our corrections, must not be forgotten. Reflections are arranged in two sets, the $(00l)$ being included in both, corresponding to the photographs obtained by rotation about a and b axes respectively; in each set the reflections are in order of increasing glancing-angle. Fig. 3 presents the same figures in convenient graphical form. Since we are concerned to obtain high accuracy for a structure, the main features of which are
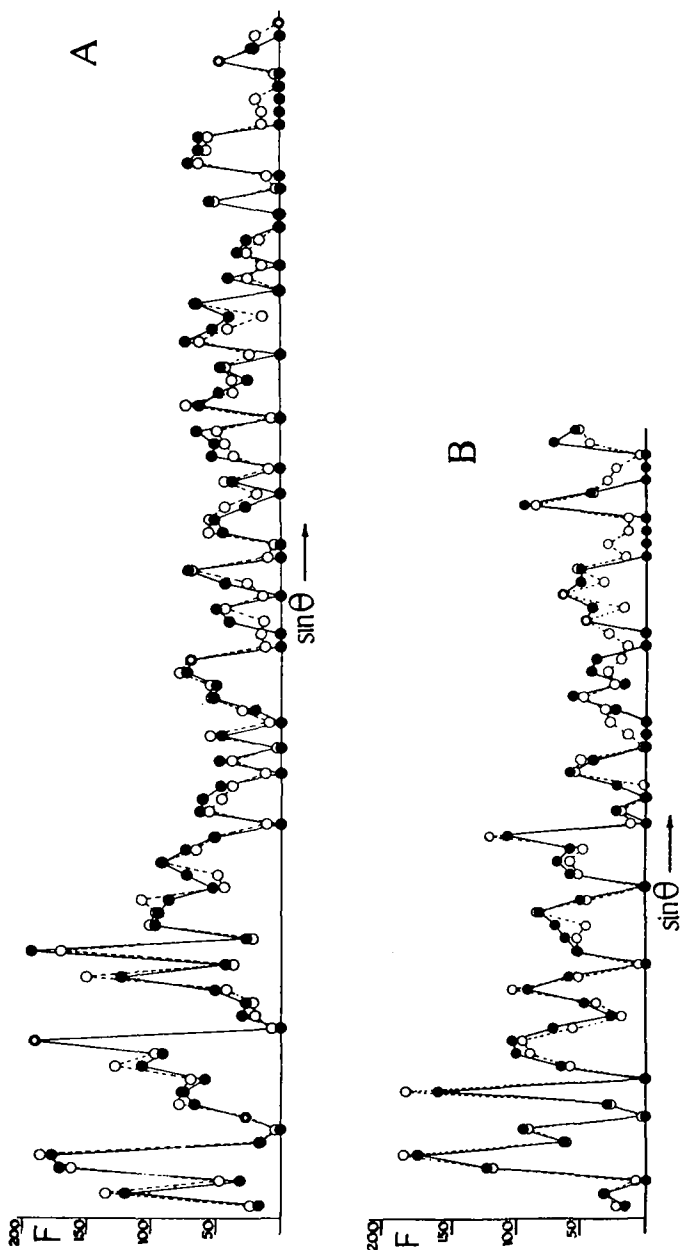
FIG. 3. Comparison of observed and calculated F's for reflections of the types $(h0l)$ (fig. 3A), and $(0kl)$ (fig. 3B). The reflections in each diagram are arranged in order of increasing glancing-angle, as in table II. Observed F's are represented by black circles connected by full lines, calculated F's by open circles connected by dotted lines.

TABLE I. Co-ordinates of atoms in the unit cell of orthoclase.

Atom.	Number in cell.	Orthoclase			Sanidine		
		θ_1.	θ_2.	θ_3.	θ_1.	θ_2.	θ_3.
O_{A1}	4	0°	55°	0°	0°	50°	0°
O_{A2}	4	240	0	109	237	0	85
O_B	8	295	55	82	295	55	85
O_C	8	15	114	94	0	115	90
O_D	8	62	46	150	55	45	150
Si_1	8	3½	67½	81	0	67	78
Si_2	8	255½	42	125	253	40	125
K	4	105	0	50	106	0	50

In the above table θ_1, θ_2, θ_3 are the angular co-ordinates defined by the expressions $\theta_1 = 360\frac{x}{a}°$, $\theta_2 = 360\frac{y}{b}°$, $\theta_3 = 360\frac{z}{c}°$, where x, y, z are the atomic co-ordinates in Å., and a, b, c are the axial lengths in Å.

For orthoclase the unit cell dimensions are a 8·60, b 13·02, c 7·22 Å., and the monoclinic angle β 63° 57'.

Silicon and aluminium are not distinguished in the above table. Reasons are given in section IV of the text for supposing that in orthoclase the group $8Si_1$ includes four silicon and four aluminium atoms, the group $8Si_2$ containing only silicon atoms.

The co-ordinates of the actual atoms marked by crosses in figs. 1 and 2 are all less than 180°. In some of the type-atoms included in the table the co-ordinate θ_1 is greater than 180°. In these cases the particular atom chosen as representing the group of 8 or 4 per unit cell, as the case may be, is selected to correspond with the atomic co-ordinates given in the original description (Taylor, 1933) of the sanidine structure, which are quoted alongside the orthoclase co-ordinates to facilitate comparison.

already known, it is not necessary to test reflections of the general type (hkl); this test was, of course, applied to the sanidine structure.

A further check on the accuracy of the work, and especially on the correct choice of the absolute scale of F-values, is obtained by counting electrons in the regions which represent atoms in the projections. In an ideal projection the background between atoms would correspond to zero electron-density, and the electrons could be counted for each of the clearly resolved atoms. In our projections there is much overlapping of atoms, and the background does not correspond to zero density; nevertheless, useful confirmation of the accuracy of the structure is obtained. For in *both* projections the total number of electrons per unit cell (including background) corresponds with the number of electrons in four molecules of $KAlSi_3O_8$, thus confirming that the scale of absolute units is correctly chosen (see section II). And the counts for separate peaks correspond approximately to the electrons in the atoms included in the peaks, as is shown in table III.

TABLE II. Comparison of observed and calculated F's for orthoclase.

(1) Reflections of the type $(h0l)$.

Sin θ.	Indices.	$F_{obs.}$	$F_{calc.}$	Sin θ.	Indices.	$F_{obs.}$	$F_{calc.}$
0·055	(00$\bar{1}$)	16	$\overline{24}$	0·370	(80$\bar{6}$)	50	$\overline{43}$
0·083	(20$\bar{1}$)	121	136	0·373	(603)	0	14
0·090	(200)	32	$\overline{48}$	0·382	(007)	43	$\overline{28}$
0·107	(20$\bar{2}$)	172	$\overline{163}$	0·383	(206)	72	$\overline{69}$
0·110	(002)	178	$\overline{187}$	0·388	(405)	0	$\overline{10}$
0·122	(201)	17	16	0·390	(801)	0	$\bar{5}$
0·147	(20$\bar{3}$)	0	$\bar{4}$	0·395	(40$\bar{8}$)	45	56
0·164	(003)	27	27	0·400	(80$\bar{7}$)	51	$\overline{55}$
0·166	(40$\bar{1}$)	67	79	0·404	(60$\bar{8}$)	27	$\overline{43}$
0·167	(40$\bar{2}$)	75	77	0·411	(10.0.$\bar{4}$)	0	$\overline{18}$
0·169	(202)	59	70	0·412	(10.0.$\bar{3}$)	37	$\overline{43}$
0·182	(400)	108	129	0·417	(604)	0	9
0·184	(40$\bar{3}$)	92	$\overline{98}$	0·418	(10.0.$\bar{5}$)	53	36
0·196	(20$\bar{4}$)	191	191	0·419	(10.0.$\bar{2}$)	51	$\overline{43}$
0·213	(401)	0	$\bar{7}$	0·420	(802)	65	$\overline{49}$
0·216	(40$\bar{4}$)	30	$\overline{20}$	0·428	(207)	0	$\bar{7}$
0·219	(004)	27	21	0·431	(10.0.$\bar{6}$)	63	73
0·219	(203)	51	$\overline{42}$	0·432	(80$\bar{8}$)	47	36
0·247	(60$\bar{2}$)	124	$\overline{151}$	0·434	(10.0.$\bar{1}$)	25	37
0·247	(205)	43	37	0·438	(008)	44	42
0·250	(402)	194	$\overline{171}$	0·439	(406)	0	24
0·250	(603)	27	$\overline{22}$	0·445	(40$\bar{9}$)	74	63
0·266	(60$\bar{4}$)	98	102	0·448	(60$\bar{9}$)	53	41
0·269	(204)	95	97	0·451	(10.0.$\bar{7}$)	40	$\overline{14}$
0·273	(600)	87	108	0·454	(10.0.0)	65	66
0·274	(005)	52	44	0·458	(803)	0	$\bar{1}$
0·279	(60$\bar{1}$)	73	49	0·462	(605)	40	25
0·279	(40$\bar{5}$)	92	93	0·470	(80$\bar{9}$)	0	14
0·290	(60$\bar{5}$)	74	66	0·476	(10.0.$\bar{8}$)	33	$\overline{26}$
0·292	(403)	51	52	0·480	(10.0.1)	26	$\overline{16}$
0·299	(40$\bar{6}$)	0	$\overline{11}$	0·483	(208)	0	1
0·301	(20$\bar{6}$)	63	$\overline{56}$	0·489	(407)	0	$\bar{1}$
0·301	(601)	61	$\overline{46}$	0·493	(009)	55	51
0·323	(205)	47	38	0·495	(6.0.$\overline{10}$)	0	3
0·325	(60$\bar{6}$)	0	12	0·496	(4.0.$\overline{10}$)	0	$\overline{10}$
0·327	(80$\bar{3}$)	48	$\overline{38}$	0·498	(804)	71	63
0·328	(006)	0	$\bar{3}$	0·506	(10.0.$\bar{9}$)	63	57
0·331	(80$\bar{2}$)	46	55	0·509	(606)	63	$\overline{56}$
0·333	(80$\bar{4}$)	0	9	0·510	(10.0.2)	0	$\overline{14}$
0·335	(602)	(20)	30	0·536	(209)	0	$\overline{14}$
0·341	(404)	52	54	0·539	(10.0.$\overline{10}$)	0	$\overline{19}$
0·343	(80$\bar{1}$)	50	55	0·539	(805)	0	$\bar{1}$
0·346	(40$\bar{7}$)	73	$\overline{79}$	0·542	(408)	0	4
0·348	(80$\bar{5}$)	70	70	0·544	(6.0.$\overline{11}$)	47	$\overline{47}$
0·353	(20$\bar{7}$)	0	$\overline{12}$	0·545	(10.0.3)	(20)	22
0·362	(800)	0	$\overline{15}$	0·556	(607)	0	$\overline{19}$
0·362	(60$\bar{7}$)	40	$\overline{13}$	0·585	(806)	0	0

(2) Reflections of the type (0kl).

Sin θ.	Indices.	$F_{obs.}$	$F_{calc.}$	Sin θ.	Indices.	$F_{obs.}$	$F_{calc.}$
0·055	(001)	16	$\overline{24}$	0·319	(065)	(23)	19
0·055	(020)	32	$\overline{33}$	0·328	(006)	0	$\overline{3}$
0·077	(021)	0	8	0·328	(0.12.0)	(23)	2
0·109	(040)	124	$\overline{119}$	0·332	(0.12.1)	59	55
0·110	(002)	178	$\overline{187}$	0·333	(026)	(41)	51
0·122	(022)	64	62	0·343	(046)	0	$\overline{2}$
0·122	(041)	95	91	0·346	(0.12.2)	0	$\overline{14}$
0·155	(042)	0	$\overline{3}$	0·348	(0.10.4)	0	$\overline{28}$
0·164	(003)	27	27	0·350	(085)	(24)	$\overline{32}$
0·164	(060)	162	187	0·366	(0.12.3)	57	$\overline{49}$
0·171	(023)	0	$\overline{1}$	0·367	(066)	(17)	$\overline{25}$
0·173	(061)	66	59	0·382	(007)	43	$\overline{28}$
0·197	(043)	101	$\overline{90}$	0·382	(0.14.0)	(39)	$\overline{20}$
0·197	(062)	104	$\overline{96}$	0·385	(0.10.5)	0	$\overline{14}$
0·218	(080)	72	57	0·385	(0.14.1)	0	29
0·219	(004)	27	21	0·387	(027)	(47)	47
0·225	(081)	48	$\overline{39}$	0·393	(0.12.4)	(42)	17
0·226	(024)	92	$\overline{104}$	0·395	(086)	65	65
0·232	(063)	60	$\overline{53}$	0·397	(0.14.2)	(51)	33
0·244	(044)	0	$\overline{6}$	0·398	(047)	(51)	54
0·244	(082)	53	54	0·413	(067)	0	16
0·273	(064)	63	54	0·413	(0.14.3)	0	$\overline{30}$
0·273	(083)	71	47	0·425	(0.10.6)	0	14
0·273	(0.10.0)	83	85	0·425	(0.12.5)	0	$\overline{13}$
0·274	(005)	52	44	0·436	(0.16.0)	95	86
0·277	(0.10.1)	0	$\overline{1}$	0·438	(008)	44	42
0·279	(025)	59	$\overline{53}$	0·438	(087)	0	30
0·294	(0.10.2)	69	$\overline{59}$	0·438	(0.14.4)	0	$\overline{23}$
0·295	(045)	59	$\overline{49}$	0·438	(0.16.1)	0	$\overline{5}$
0·309	(084)	108	$\overline{122}$	0·449	(0.16.2)	(62)	$\overline{44}$
0·317	(0.10.3)	0	$\overline{12}$	0·493	(009)	55	51

The values of sin θ are for Mo-Kα radiation of wave-length λ 0·71 Å.

The reflections tabulated fall into two groups, with indices (referred to the crystallographic unit cell) of types (h0l) and (0kl) respectively; reflections (00l) occur in both groups, and are therefore included in both groups in the table. All reflections up to sin θ = 0·4 are included, but for larger glancing-angles only a selection of the possible reflections have been measured or been found definitely absent.

The column headed '$F_{obs.}$' contains *numerical* values of F in absolute units, the absolute scale being fixed indirectly as described in section II of the text. Values based on *estimated* intensities, where the reflections were too weak for photometric measurement, are enclosed in brackets (   ). The tabulated values for the reflections (20$\overline{1}$), (20$\overline{2}$), (002), (20$\overline{4}$), (402), are corrected for extinction as described in section II of the text. The value *zero* in this column indicates a reflection too weak for detection; the true value of the corresponding F is therefore appreciably smaller than the smallest value measured at glancing-angles of the same order of magnitude, but is not necessarily zero.

The calculated F's are for the structure represented by the atomic co-ordinates in table I. The atomic f-curves of W. L. Bragg and J. West (Zeits. Krist., 1928, vol. 69, p. 118. [M.A. 4–17.]) are used in the calculation.

TABLE III. Electron-counts from projections reproduced in figs. 1 and 2.

(1) Projection along a [100].

Atoms included in peak.				Number of electrons counted		Theoretical number of electrons	
				Fig. 2A.	Fig. 2B.	Neutral.	Ionized.
$Si_1+O_B+O_C$	...	...	...	25	27	29½	30
Si_2+O_D	...	...	...	20	24	22	20
O_{A1}	...	...	...	9	10	8	10
O_{A2}	...	...	...	7	7	8	10
K	...	...	...	17½	18	19	18
Total per unit cell		...	...	494	548	552	552

(2) Projection along b [010].

Atoms included in peak.				Number of electrons counted		Theoretical number of electrons	
				Fig. 1A.	Fig. 1B.	Neutral.	Ionized.
$2Si_1+2O_C$ ...	...	...	...	40	40	43	40
$2Si_2+O_{A2}+2O_D$	...	...	...	46	49	52	50
$K+2O_B$	...	...	...	37	38	35	38
O_{A1}	...	...	...	10	10	8	10
Total per unit cell		...	...	532	548	552	552

In calculating the theoretical number of electrons for each peak, it is assumed that an atom Si_1 is equivalent to $\frac{1}{2}(Si+Al)$, for reasons given in section IV of the text. In the column headed 'Neutral' the atoms contribute the full number of electrons corresponding to the neutral atoms; in the column headed 'Ionized' it is assumed that the atoms are present in the form of the ions Si^{+4}, Al^{+3}, K^{+1}, O^{-2}.

If a count is made of the total number of electrons included in the background between the atomic peaks, the total number of electrons per unit cell, *including background*, is within a few units of the theoretical value 552. This indicates that the absolute scale of F's is correctly chosen, as described in section III of the text.

In the projection along a [100] there is difficulty in drawing a distinct boundary between the first two groups of atoms, in both figs. (2A and 2B). In figs. 1B and 2B, which correspond to the introduction of an artificial temperature-factor, the outlines of the peaks are very indefinite, and too much emphasis should not be laid on the very close agreement between the observed and calculated totals for the unit cell.

We may conclude that the details of the structure are correctly determined, and that the atomic co-ordinates quoted in table I are accurate within limits corresponding to shifts not exceeding ± 0.1 Å., and probably smaller than this.

IV. FEATURES OF THE STRUCTURE.

The first question which arises in discussing the structure is its relationship with sanidine as described by one of us. The two structures are, of course, very similar—in fact, the sanidine structure was the starting-point for the present determination. Since the sanidine structure was determined by purely qualitative methods, there is no point in com-

paring the precise details of the interatomic distances in the two structures: such a comparison will be of great interest when an accurate investigation of a sanidine is available, and this we hope to be able to provide in due course.

The dimensions of the tetrahedral groups in the orthoclase structure are as follows. In the tetrahedral group around atom Si_1 the silicon–oxygen distances are (in Å.) 1·66 to O_{A1}, 1·67 to O_D, 1·69 to O_C, 1·70 to O_B; and the oxygen–oxygen distances are 2·72 (O_{A1} to O_B), 2·72 (O_{A1} to O_D), 2·73 (O_C to O_D), 2·74 (O_B to O_D), 2·77 (O_{A1} to O_C), and 2·79 (O_B to O_C). In the group around Si_2, the silicon–oxygen distances are 1·57 to atoms O_{A2}, O_C, and O_D, and 1·60 to O_B; and the oxygen–oxygen distances are 2·51 (O_{A2} to O_D), 2·54 (O_B to O_C), 2·55 (O_B to O_D), 2·59 (O_{A2} to O_B), 2·59 (O_{A2} to O_C), and 2·65 (O_C to O_D). The difference between the two tetrahedra is very striking: the group around Si_1 is definitely, though of course only slightly, larger than the group around Si_2, with silicon–oxygen and oxygen–oxygen distances lying within the limits 1·66–1·70, 2·72–2·79 (for Si_1), and 1·57–1·60, 2·51–2·65 (for Si_2). Now the two groups of atoms '$8Si_1$' and '$8Si_2$' actually comprise 12 silicon and 4 aluminium atoms per unit cell (corresponding to 4 molecules of composition $KAlSi_3O_8$), and the obvious interpretation of the difference in the sizes of the two tetrahedral groups is that '$8Si_2$' includes only silicon atoms, whereas '$8Si_1$' includes 4 silicon and 4 aluminium atoms. The average size of the tetrahedron around Si_1 is increased because the (AlO_4) group is slightly larger than the (SiO_4) group, the four-co-ordinated aluminium ion being larger than silicon. It must be assumed that the distribution of aluminium atoms among the sites of the group '$8Si_1$' is random, since there is no evidence of any reduction of the symmetry from holohedry.

It will be extremely interesting to compare these tetrahedron dimensions with those of the corresponding groups in a specimen of the same material which has been heated for a long period at a temperature of about 1100° C., and so has suffered the structural change revealed by the permanent reduction of optic axial angle and its reversal into the symmetry-plane (Spencer, 1937, p. 476). It may be that the distribution of the aluminium ions among the tetrahedral groups is of primary importance in the process of 'sanidinization' revealed by the irreversible change in optic axial angle. We hope to investigate this problem.

The angles between bonds linking any given oxygen atom to two silicon (or aluminium) atoms are 147° (O_{A1} to Si_1 and Si_1), 152° (O_{A2} to Si_2 and Si_2), 152° (O_B to Si_1 and Si_2), 133° (O_C to Si_1 and Si_2), and 148°

(O_D to Si_1 and Si_2); these angles are probably accurate to within $\pm 5°$, and lie within the range of values usually observed in silicates.

The environment of the potassium atom is important for the comparison which will be made in the future with other structures containing sodium. The nearest neighbours are O_{A2} at 2·90, two O_{A1} at 3·00, two O_C at 3·09, two O_D at 3·11, and two O_B at 3·12 (all distances in Å.); the next nearest is another atom O_{A2} at 3·37 Å., but this is probably sufficiently distant to be excluded from the group of atoms which can properly be considered as in contact with the potassium ion. The potassium atom is thus surrounded by eight oxygen atoms at distances between 3·0 and 3·1 Å. (approximately), with a ninth atom (O_{A2}) at 2·9 Å., a group of the rather irregular type usually found around the larger cations in complex silicate structures.

One curious feature may be noted, though we are not sure whether it is of special significance. If our allocation of the aluminium atoms to the group Si_1 is correct, the oxygen atom O_{A2} is the *only* one to be linked to *two* silicon atoms (Si_2 and Si_2); for O_{A1} is linked to Si_1 and Si_1, and O_B, O_C, O_D to Si_1 and Si_2 (see preceding paragraph on bond-angles). The valency of the atom O_{A2} is therefore completely satisfied by its two silicon bonds, and we should expect to find no bond from O_{A2} to K. It is surprising to find that it is the nearest neighbour of the potassium atom, and it would appear that considerations of packing tetrahedra must outweigh the influence of the feeble bonds uniting monovalent potassium to the irregular group of oxygens around it.

The orthoclase structure described above is of value chiefly as a standard of comparison with structures of other felspars which we hope to be able to determine with comparable accuracy. In the meantime it is satisfactory to find that it fully confirms the essential accuracy of the felspar structures previously determined by qualitative methods.

V. CONCLUSION AND SUMMARY.

We have applied quantitative X-ray methods to the determination of the structure of a typical orthoclase containing nearly pure potash-felspar. The experimental procedure and the accuracy of the work are discussed, and the details of the structure are described.