

The Structure of Orthoclase

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A new structural study of orthoclase has confirmed that this feldspar shows a partially ordered Si, Al distribution. No final decision is reached on the true symmetry of orthoclase—whether monoclinic or an intimate intergrowth of triclinic units, but any departure from monoclinic symmetry is probably very small. The details of the structure are discussed in relation to those of sanidine and microcline, with special reference to the configuration of the tetrahedral groups, the environment of the potassium atom, and the application of the charge-balance hypothesis concerning the stability of the alkali feldspars.

1. Introduction

The material studied is a colourless orthoclase from Mogok, Upper Burma, obtained from Dr E. Spencer and designated by him (1930, 1937) as Specimen C. Its structure has already been examined by Chao, Hargreaves & Taylor (1940). The present authors, while accepting full responsibility for the conclusions reached in this re-examination of the structure, wish to emphasize their indebtedness first to Dr J. V. Smith (Department of Mineralogy, Pennsylvania State University, University Park, Pennsylvania, U.S.A.) who took the X-ray photographs for axes [100], [010] and [001], and afterwards to Miss A. Vos† (Laboratorium voor Anorganische en Fysische Chemie, Rijksuniversiteit, Groningen, The Netherlands) and Miss J. Unwin (of this Laboratory) who measured the intensities of reflexions on these photographs and carried out the first stages of refinement of the structure. We are also indebted to Dr P. Gay and Mr K. Rickson (Department of Mineralogy and Petrology, Cambridge) for preparing X-ray photographs for the axis $[\bar{1}10]$ for our use.

The original structure-analysis of this material (Chao *et al.*, 1940) showed a marked difference in the sizes of the two crystallographically distinguishable tetrahedra in the monoclinic unit cell, and this was interpreted as corresponding to partial ordering of the Si and Al atoms—8 Si atoms in the tetrahedral groups at sites 'Si₂', and 4 Si + 4 Al atoms randomly distributed over the somewhat larger tetrahedra at sites 'Si₁'. Later Cole, Sörum & Kennard (1949) demonstrated that the accuracy of the earlier work was insufficient to establish with certainty this partially-ordered Si, Al distribution. Laves and his co-workers (see, for example, Laves, 1952) consider that microcline and sanidine are the only stable forms of $KAlSi_3O_8$,

regard monoclinic orthoclase as an unstable form, and believe that most apparently monoclinic low-temperature potassium feldspars correspond to submicroscopically twinned (triclinic) microcline domains. Finally Ferguson, Traill & Taylor (1958) have suggested that if local balance of charge controls the stability of alkali feldspar structures then for potassium feldspar maximum stability would correspond to partial ordering in a monoclinic structure with (0.36 Al + 0.64 Si) in site Si₁ and (0.14 Al + 0.86 Si) in site Si₂. The new analysis of Spencer's orthoclase C, described in the present paper, confirms that tetrahedra Si₁ are larger than tetrahedra Si₂, though the difference in size is much less than was previously suggested and corresponds to a smaller degree of ordering (0.3 Al + 0.7 Si) in Si₁ and (0.2 Al + 0.8 Si) in Si₂. The meaning of these findings is discussed fully in Section 5.

General accounts of the potassium feldspar structure are available in Cole *et al.* (1949) and in Bailey & Taylor (1955), and the former authors quote accurate values of unit-cell dimensions and physical properties for Spencer's Specimen C.

2. Experimental

The crystal used for a set of X-ray photographs around [100], [010] and [001] axes was very nearly cubic in shape, with edge 0.4 mm. Additional [100] photographs were obtained from another crystal 0.14 × 0.14 × 0.42 mm., with length along [100]. Reflexions $0kl$ of medium intensity were measured on both sets of [100] photographs, and the average values used in the structure-analysis; weak reflexions were measured on the first set (large crystal), strong reflexions on the second set (small crystal). A two-dimensional correction for absorption computed for the [010] photographs proved to be much smaller than the expected experimental error of measurement, and so no absorption corrections were applied to the [100] and [001] photographs.

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A set of photographs around $[\bar{1}10]$ was obtained from a crystal in the form of an irregular rectangular parallelepiped $0.32 \times 0.26 \times 0.35$ mm. The accuracy of measurement of the intensities justified the application of a three-dimensional procedure for correction of absorption errors, developed for use on Edsac II by M. Wells.

All intensities were measured by eye-comparison of the photographs with a standard intensity-scale. Lorentz and polarization corrections were calculated in the usual way or (later) on Edsac II.

3. Special features of the structure-analysis

The unit-cell dimensions for this material quoted by Cole *et al.* (1949) have been used throughout. With the fairly accurate structure of Chao *et al.* (1940) as a starting-point, successive refinements have been obtained from difference-syntheses. The following special points require discussion.

(i) Symmetry and space group

All previous X-ray measurements on this material have been in conformity with monoclinic holohedral symmetry and space group $C2/m$ (using the conventional axes). (Chao, Smare & Taylor, 1939; Chao *et al.*, 1940; Cole *et al.*, 1949; Bailey, Ferguson & Taylor, 1951.) In view of the suggestion due to Laves (1952) that monoclinic orthoclase is really built up from triclinic microcline, the evidence for a truly monoclinic structure must be scrutinized with care.

The positions of the reflexions in our X-ray photographs correspond to a unit cell showing no significant departure from monoclinic geometry with

$$\beta = 116.015, \alpha = 90, \gamma = 90^\circ.$$

Our measurements of intensities of reflexion, more accurate than those hitherto available for this material, have been used to test pairs of reflexions such as $hk0$ and $h\bar{k}0$ which are identical for monoclinic symmetry. The overall comparison is good ($\sim 7\%$, corresponding to the expected accuracy of measurement); but some reflexions of medium intensity show differences up to $\sim 30\%$ (considerably above the expected maximum difference arising from experimental error $\sim 10\text{--}15\%$), and some very strong and some very weak reflexions show even bigger differences. Although these observations suggest at first sight that the structural symmetry must be triclinic, further consideration indicates that the differences may be explicable, while retaining monoclinic symmetry, as arising from variations in absorption and extinction. For most of the refinement process, therefore, the space-group $C2/m$ has been retained: the effect of a change of symmetry to triclinic was also examined directly at a late stage in the refinement (see Section 5, (vi)).

The above discussion refers to the possibility that the structure is based on a true unit cell which is very

accurately monoclinic dimensionally but in which the atomic arrangement departs significantly from this symmetry. Alternatively, in Laves' view, the monoclinic cell is only an average derived from intergrowth of truly triclinic microcline units, and such an intergrowth, on a sufficiently fine scale, should be revealed by diffuse streaks adjacent to the Bragg reflexions. In heavily exposed photographs of orthoclase C, it is possible to detect traces of such streaks; their peak intensities are small, in relation to the weakest of the measured reflexions, and it appears that they may be ignored without invalidating our conclusions. It must be emphasized that we do *not* assert that other so-called 'orthoclases' are necessarily structurally identical with our Specimen C. The question of intergrowth of triclinic individuals is further discussed below (Section 5, (vi)).

(ii) Resolution in projections

In all three axial projections along $[100]$, $[010]$ and $[001]$ there is a considerable degree of overlapping of atoms even in difference syntheses, so that refinement becomes progressively more difficult and less certain. For this reason a fourth projection, along $[\bar{1}10]$, was prepared: in this there is no overlap except for two oxygen atoms, one of which is well resolved in two of the other projections. Moreover, in this projection most of the atoms appear twice, giving two independent values of the z -coordinate, as well as values of the x and y coordinates, for each atom. The need for the application of an absorption correction (Section 2, above) was indicated by the appearance of certain characteristic features (Jellinek, 1958) in the difference syntheses prepared from uncorrected F -values. (Section 5, (vi) below.)

(iii) Absolute scale of F 's

The measured F_o 's are on a relative scale. The use of the difference synthesis for structure refinement requires the F_o 's to be placed on an absolute scale for comparison with the calculated F_c 's. The initial scaling of F_o 's was from comparison with F_c 's calculated for the structure of Chao *et al.* (1940), and the scaling operation was repeated after each cycle of refinement using the new set of atomic coordinates to obtain F_c 's. The curve of $\log F_o/F_c$ against $\sin^2 \theta/\lambda$ or $\sin^2 \theta$ gives a direct evaluation of the overall temperature factor to be applied to the atomic scattering factors; once derived, it was not varied, although considerable adjustments of the temperature factors on individual atom types were required. To avoid difficulties arising from extinction, which become more obvious as refinement proceeds, after the stage represented by $R = 12\%$ only reflexions with $\sin \theta > 0.3$ were included in the sequence of operations refinement-scaling-temperature factor determination; this excludes the strong low-angle reflexions most likely to be affected by extinction (cf. Jellinek, 1958).

(iv) *Extinction*

As expected, in view of the large size of the crystals used (Section 2), effects arising from extinction have been observed in all projections; thus, at any stage in the refinement, a graph of F_o against F_c shows increasing deviations from the 45° line of $F_o = F_c$ as F becomes larger. As refinement proceeds, the graph becomes smoother and it is possible to detect the effect of extinction in more and more reflexions: to enable refinement to be continued, ($F_o - F_c$): for these reflexions was set equal to zero—i.e. these reflexions were excluded from the further refinement process.

This procedure enables refinement to continue, but it is nevertheless desirable to obtain a set of F_o 's corrected for the effect of extinction; a method suggested by Vand (1955) was therefore attempted. This depends upon an (approximate) relation

$$-\log (F_o/F_c)^2 = a + b(F_c)^2 + cLp(F_c)^2,$$

where the constants a , b , c depend upon absorption, primary extinction, secondary extinction, respectively. If either primary or secondary extinction is dominant, values for a and either b or c may be derived from the nearly linear relation between $-\log (F_o/F_c)^2$ and $(F_c)^2$. If both extinctions are operative, it may nevertheless be possible to derive an approximate value of a from one of the graphs, thence b and c from a graph of $\{-\log (F_o/F_c)^2 - a\}/(F_c)^2$ against Lp .

An attempt to treat the measurements for our orthoclase in this way failed. A least-squares procedure was therefore tried, using (instead of Vand's weighting factor proportional to F) a weighting factor given by the quotient obtained on dividing the maximum percentage error permitted by the intensity scale used in estimation, by the standard deviation of all the measurements of this reflexion. On treating two projections [010] and [001] in this way, apparently reasonable values of the constants b and c were obtained, but negative values of a . On selecting for use only those reflexions with F values near or above the region where the effect of extinction becomes obvious in the graph of F_o against F_c , new values of b and c , but with nearly the same ratio b/c , were obtained, and a positive value of a . On applying the two sets of values of b and c to low-angle reflexions (which include those with large F), and re-scaling, the final (corrected) F_o values are almost identical. It appears that the Vand relation takes account of other than pure extinction effects, by adjusting the value of a , but that the ratio b/c remains approximately constant irrespective of the assumptions made as to the weighting factor in the least-squares treatment.

In view of the uncertainty about the significance of this attempted correction for extinction, it was finally decided to use a completely empirical procedure—the comparison of the smooth curve of F_o against F_c with the straight line which would represent $F_o = F_c$: the corrected F_o values thus obtained were

almost identical with those derived by the complicated Vand method.

These corrected F_o values are given in Table 4, but it should be emphasized that they were not used in the course of the refinement.

4. Final parameters: accuracy

The final atomic coordinates, referred to the monoclinic unit cell with space group $C2/m$, are set out in Table 1; they should be compared with those of sanidine—i.e. the same material, orthoclase Spencer C, after heat treatment resulting in sanidinization (Cole *et al.*, 1949), and with those of an intermediate microcline Spencer U (Bailey & Taylor, 1955). The interatomic distances and angles calculated from these atomic coordinates are given in Table 2: comparable figures are given for sanidine by Cole *et al.* (their Tables 4 and 5) and for microcline by Bailey & Taylor (their Table 8).

Table 1. Atomic parameters for orthoclase (Spencer C)

Atom	x	y	z
OA ₁	0	0.1461	0
OA ₂	0.6335	0	0.2840
OB	0.8276	0.1465	0.2271
OC	0.0347	0.3104	0.2631
OD	0.1801	0.1256	0.4051
Si ₁	0.0101	0.1848	0.2237
Si ₂	0.7084	0.1175	0.3437
K	0.2843	0	0.1361

The standard deviations of electron density and atomic coordinates have been calculated from relations given by Lipson & Cochran (1953)

$$\sigma(\rho_0) = \{\overline{D^2}\}^{\frac{1}{2}} \quad \text{and} \quad \sigma(x_n) = \{(\partial D/\partial x)^2\}^{\frac{1}{2}}/C_n.$$

For each relation the electron density was evaluated over the entire final $[\bar{1}10]$ difference map; according to Lipson & Cochran this may lead to a value of the standard deviation slightly too large. The central curvature was derived from the final $[\bar{1}10]F_o$ synthesis. Peak heights of electron density, and data relating to standard deviations and significance levels (Cruikshank, 1949) are listed in Table 3. In considering the accuracy achieved, it is probably unwise to rely blindly on a strictly arithmetical assessment; in the present case, some weight must be given to the outcome of a comparison between independent values for a given parameter obtained in two different axial projections and also in the $[\bar{1}10]$ projection. Detailed reproduction of the figures would be unwieldy here: the general conclusion reached is that the Cruikshank procedure provides unduly cautious estimates of the final accuracy of each atomic position in the present case. This view receives support from certain features of the structure discussed in the next Section. Our experience tends to suggest that in this structure little improvement would be likely even with a three-

dimensional synthesis so long as photographic methods are used for intensity measurements.

Table 2. *Interatomic distances and angles for orthoclase*

Interatomic distances (Å)						
	Si ₁ (OA ₁)	Si ₂ (OA ₂)		Si ₁	Si ₂	K
OA	1.651	1.639	OA-OB	2.639	2.674	OA ₁ 2.898
OB	1.650	1.624	OA-OC	2.781	2.588	OA ₂ 2.698
OC	1.654	1.634	OA-OD	2.645	2.661	OB 3.029
OD	1.651	1.635	OB-OC	2.710	2.690	OC 3.135
Mean	1.652	1.633	OB-OD	2.726	2.689	OD 3.111
			OC-OD	2.692	2.690	
			Mean	2.699	2.665	

Interatomic angles						
	Si ₁	Si ₂				
OA-Si-OB	106° 6'	110° 7'	Si ₁ -OA ₁ -Si ₁	144° 12'		
OA-Si-OC	114° 38'	104° 32'	Si ₂ -OA ₂ -Si ₂	138° 50'		
OA-Si-OD	106° 9'	108° 43'	Si ₁ -OB-Si ₂	153° 3'		
OB-Si-OC	110° 12'	111° 20'	Si ₁ -OC-Si ₂	130° 54'		
OB-Si-OD	110° 0'	111° 9'	Si ₁ -OD-Si ₂	141° 44'		
OC-Si-OD	108° 45'	110° 49'				
Mean	109° 28'	109° 27'				

Table 3. *Analysis of accuracy of orthoclase structure*

	O	Si	K	Si-O	K-O
Curvatures $-C_n$ (e.Å ⁻⁴)	453	1560	1285		
Errors $\sigma(x)$ (Å)	0.013	0.004	0.005	0.014	0.014 ₅

For Si₁-O and Si₂-O $\delta l/\sigma = 0.019/(0.014 \times 2\frac{1}{2}) = 0.96$ corresponding to a probability P 17%, figures which may be compared with Cruickshank's limit for a 'possibly significant' difference at 1.645, P 5%.

	O	Si ₁	Si ₂	K
Peak heights ρ_0 (e.Å ⁻²)	21.4	51.2	54.1 ₅	53.6
Error $\sigma(\rho_0)$ (e.Å ⁻²)	0.64			

For Si₁ and Si₂ $\delta \rho_0/\sigma = 2.95/(0.64 \times 2\frac{1}{2}) = 3.26$ which lies within Cruickshank's 'highly significant' range.

Table 4 contains lists of observed F_o values, corrected for extinction, and F_c values calculated for the atomic coordinates of Table 1. The final R -value, 7.2%, does not include $F(000)$ nor reflexions which were unobserved (see also, notes to Table 4).

5. Discussion

In the following paragraphs we assess the significance of the factual information set out above, bearing in mind certain special features observed in F_o and $F_o - F_c$ syntheses at various stages in the refinement of the structure. For most of the discussion we ignore the possibility that the structure as described represents only an average of well-defined triclinic domains of microcline type, basing our treatment on the assumption of a monoclinic unit cell with space group $C2/m$. The problem of the true structural symmetry of orthoclase is considered at the end—paragraph (vi).

(i) Evidence for Si, Al ordering

The Si-O and O-O distances listed in Table 2 show that the tetrahedron at site Si₁ is slightly larger than that at site Si₂; Smith's (1954) relation then indicates a degree of Si, Al ordering represented by (0.30 Al + 0.70 Si) at site Si₁ and (0.19 Al + 0.81 Si) at site Si₂. This departure from the random distribution of sanidine, with (0.25 Al + 0.75 Si) in all tetrahedra, is much smaller than, though in the same direction as, that proposed by Chao *et al.* (1940) with (0.5 Al + 0.5 Si) at Si₁ and (1.0 Si) at Si₂. This earlier proposed distribution was the simplest suggestion to conform with the small dimensions then found for the tetrahedron at Si₂; Cole *et al.* (1949) pointed to quantitative difficulties in accepting these numerical values. It is still true that even if the tetrahedron dimensions found in the present study are perfectly accurate, the interpretation above in terms of partial Si, Al ordering depends upon the validity of Smith's relation; we remark that its use for microcline and albite has not revealed any internal inconsistencies and that for orthoclase the size-difference is so small that serious inaccuracies in the degree of ordering deduced seem improbable.

The very small difference in size between the two types of tetrahedra cannot be accepted as real without further discussion; thus a straightforward application of the Cruickshank test (Table 3) shows that the difference in size falls below the value which would be 'possible significant'. Nevertheless, we consider that the following lines of argument provide rather strong evidence in favour of accepting that the difference in size though very small is real:

(a) Tetrahedron bond lengths were first calculated after the 5th refinement cycle: thereafter, the difference between the mean Si₁-O and Si₂-O bond lengths remained constant (at 0.020–0.025 Å), the refinement process merely resulting in a progressively closer approach of individual bond lengths in each tetrahedron to the (unchanged) mean value for that tetrahedron.

(b) The refinement process for orthoclase began from the structure proposed by Chao *et al.* (1940): the structure as finally determined copies faithfully all the detailed features of the *sanidine* structure—e.g. variations in length as between the four bonds from centre to corners of a tetrahedron, variations in the magnitudes of Si-O-Si bond angles—*except that* in orthoclase every bond (Si-O or O-O) in the Si₁ tetrahedron is slightly larger, every bond in the Si₂ tetrahedron slightly smaller,* than in sanidine (cf. Table 2 with Tables 4, 5 of Cole *et al.*, 1949). This is as expected for the Si, Al ordering proposed. The very close similarity of the two structures was demonstrated in general terms by Cole *et al.*, 1949; the present work

* The bond OB-OC excepted—this is larger by 0.004 Å, a quantity much smaller than the probable error.

Table 4. *Observed and calculated F-values for orthoclase*

1. The F_o values are corrected for extinction as described in Section (3) (iv) of the text.
2. The F_c values are calculated for the atomic parameters of Table 1, using the atomic f -curves of Tomiie & Stam (1958) modified by application of a temperature factor as described in the text.
3. Reflexions not observed owing to low intensity are marked—in the F_o column.
4. Reflexions not observed owing to mechanical obstruction, etc. are marked (—).
5. Reflexions corrected for extinction are marked *.
6. The R -value 7.2% does not include $F(000)$ nor reflexions which were not observed for any reason.

h	k	l	F_c	F_o	h	k	l	F_c	F_o	h	k	l	F_c	F_o	h	k	l	F_c	F_o
0	0	0	550	—	0	6	4	57	56	0	14	8	2	—	2	0	0	36	38
	2		27	32		8		102	104*		16		8	10	4	0	0	129	130*
	4		116	113*		10		14	14		18		4	—	6			98	99*
	6		164	166*		12		26	27		20		3	—	8			2	—
	8		63	64*		14		9	12		22		4	—	10			55	54
	10		76	76*		16		2	—		24		4	—	12			10	15
	12		20	21		18		32	28						14			19	19
	14		27	27		20		10	9	0	0	9	46	43	16			2	—
	16		79	83*		22		20	18		2		16	16					
	18		4	14		24		21	20		4		28	23	16	0	1	17	17
	20		8	11		26		1	—		6		15	15	14			5	—
	22		10	12							8		2	—	12			32	26
	24		8	—	0	0	5	44	44		10		7	8	10			34	31
	26		19	19		2		48	46		12		6	6	8			48	46
0	0	1	16	25		4		47	46		14		14	15	6			56	54*
	2		14	14		6		24	24		16		12	12	4			68	64*
	4		83	82*		8		26	26		18		0	—	2			124	111*
	6		58	54*		10		15	15		20		4	—	0			16	25
	8		35	37		12		7	11						2			10	19
	9		8	9		14		11	12	0	0	10	17	17	4			6	6
	10		47	43		16		7	12		2		4	—	6			50	49
	14		22	23		18		16	17		4		8	5	8			13	11
	16		13	15		20		6	6		6		2	—	10			33	30
	18		11	12		22		9	8		8		10	8	12			8	—
	20		16	16		24		9	8		10		12	12	14			3	—
	22		12	12		26		0	—		12		6	—	16			13	—
	24		9	8	0	0	6	5	9		14		8	8					
	26		4	—		2		37	36		16		7	6	16	0	2	3	—
						4		19	17		18		6	5	14			2	—
0	0	2	189	186*		6		32	30		20		2	—	12			7	—
	2		57	54*		8		55	51	0	0	11	19	20	10			37	36
	4		5	—		10		2	—		2		5	—	8			35	35
	6		90	90*		12		15	16		4		0	—	6			149	148*
	8		46	46		14		2	—		6		14	14	4			77	74*
	10		54	54*		16		5	—		8		6	9	2			162	155*
	12		6	10		18		21	19		10		4	—	0			189	186*
	14		33	34		20		2	—		12		3	—	2			55	54*
	16		43	38		22		16	17		14		3	—	4			152	151*
	18		7	—		24		9	7		16		8	9	6			18	23
	20		2	5		26		4	—		18		4	—	8			55	59
	22		13	13											10			5	—
	24		13	9	0	0	7	38	36	0	0	12	5	8	12			3	—
	26		11	12		2		38	36		2		1	—	14			13	12
						4		50	44		4		15	13	16			4	—
0	0	3	30	27		6		2	—		6		8	—	16	0	3	15	10
	2		4	5		8		18	22		8		9	9	14			6	—
	4		92	90*		10		6	9		10		2	—	12			30	25
	6		52	52		12		20	20		12		10	10	10			40	38
	8		60	62*		14		33	31		14		2	—	8			44	37
	10		2	9		16		13	13						6			27	28
	12		50	47		18		1	—	0	0	13	0	—	4			97	102*
	14		14	16		20		11	13		2		6	6	2			8	11
	16		6	7		22		2	—		4		6	6	0			30	27
	18		17	17		24		7	—		6		10	10	2			42	42
	20		10	12							8		12	13	4			50	49
	22		20	18	0	0	8	34	36		10		4	—	6			6	—
	24		9	10		2		2	—		12		8	—	8			6	—
	26		8	9		4		3	—						10			36	36
						6		23	22	0	0	14	11	13	12			12	—
0	0	4	24	26		8		0	—		2		1	—	14			9	—
	2		88	85*		10		8	8		4		2	—	16			5	—
	4		7	10		12		5	6		6		6	—					

Table 4 (cont.)

h	k	l	F_c	F_o	h	k	l	F_c	F_o	h	k	l	F_c	F_o	h	k	l	F_c	F_o
$\overline{16}$	0	4	14	8	$\overline{8}$	0	8	42	39	$\overline{2}$	0	13	21	24	11	5	0	19	21
$\overline{14}$			25	26	$\overline{6}$			31	31	0			0	—	13			8	8
$\overline{12}$			25	29	4			40	40	2			9	—	15			13	13
$\overline{10}$			3	—	2			7	—	4			6	—	17			2	—
$\overline{8}$			23	20	0			34	36	$\overline{16}$	0	14	4	—	0	6	0	163	166
6			98	100*	2			8	10	$\overline{14}$			19	19	2			47	45
4			25	25	4			8	—	$\overline{12}$			1	—	4			55	55
2			201	210*	6			28	28	$\overline{10}$			15	—	6			49	50
0			25	26	8			11	—	$\overline{8}$			13	16	8			28	26
2			100	100*	10			15	15	4			2	—	10			13	13
4			47	46	$\overline{16}$	0	9	9	—	4			21	23	12			7	—
6			21	21	$\overline{14}$			21	20	2			6	—	14			6	—
8			53	53	$\overline{12}$			11	14	0			11	13	16			1	—
10			12	—	$\overline{10}$			54	51	2			7	—					
12			26	23	8			12	15						1	7	0	11	13
14			2	—	6			44	45						3			11	13
$\overline{16}$	0	5	13	—	4			56	59	2	0	0	$\overline{37}$	38	5			17	16
$\overline{14}$			14	15	2			3	—	4			129	130*	7			29	29
$\overline{12}$			46	40	0			46	43	6			96	99*	9			39	37
$\overline{10}$			47	46	2			5	—	8			1	—	11			18	16
$\overline{8}$			57	54	4			20	21	10			54	54	13			4	3
6			65	65*	6			9	—	12			11	15	15			9	9
4			98	101*	8			5	—	14			19	19	17			6	—
2			35	34	10			8	—	16			3	—					
0			45	44	$\overline{16}$	0	10	28	25	1	1	0	16	29	0	8	0	63	64
2			46	44	$\overline{14}$			5	—	3			60	60*	2			173	179*
4			19	17	$\overline{12}$			40	33	5			16	16	4			32	31
6			40	37	$\overline{10}$			1	—	7			73	78*	6			24	26
8			10	12	$\overline{8}$			14	15	9			31	30	8			49	49
10			12	—	6			22	22	11			35	33	10			12	13
12			7	—	4			12	11	13			6	—	12			26	25
14			—	—	2			17	20	15			5	—	14			8	10
$\overline{16}$	0	6	6	—	0			16	17	17			12	11	16			6	4
$\overline{14}$			34	34	2			18	14										
$\overline{12}$			22	29	4			10	—	0	2	0	27	32	1	9	0	54	54
$\overline{10}$			52	52				—	—	2			147	129*	3			26	25
$\overline{8}$			42	39	$\overline{16}$	0	11	11	—	4			45	44	5			73	77*
6			6	—	$\overline{14}$			4	—	6			49	47	7			23	26
4			10	10	$\overline{12}$			17	18	8			20	21	9			44	45
2			58	58*	$\overline{10}$			24	22	10			4	—	11			6	—
0			6	9	$\overline{8}$			13	—	12			20	19	13			6	8
2			58	60*	6			46	44	14			6	8	15			11	10
4			19	24	4			0	—	16			5	—	17			5	—
6			47	49	2			10	15	1	3	0	$\overline{112}$	104*	0	10	0	75	76*
8			3	—	0			19	20	3			21	25	2			2	—
10			2	—	2			3	—	5			70	72*	4			47	45
12			15	15	4			14	17	7			57	55	6			3	3
$\overline{16}$	0	7	0	—	$\overline{16}$	0	12	6	—	9			23	23	8			10	11
$\overline{14}$			21	20	$\overline{14}$			11	—	11			25	25	10			17	18
$\overline{12}$			24	23	$\overline{12}$			19	22	13			19	17	12			17	14
$\overline{10}$			35	34	$\overline{10}$			9	—	15			4	—	14			12	11
$\overline{8}$			43	41	$\overline{8}$			28	29	17			11	11	16			4	—
6			27	31	6			11	—										
4			71	71*	4			11	—	0	4	0	$\overline{116}$	113*	1	11	0	8	7
2			6	—	2			1	—	2			41	42	3			58	56
0			38	36	0			6	8	4			22	25	5			12	13
2			11	13	2			13	12	6			45	40	7			22	21
4			3	8	4			9	—	8			32	30	9			21	19
6			20	17	6			5	—	10			24	23	11			13	18
8			12	10				—	—	12			2	—	13			8	8
10			12	15	$\overline{16}$	0	13	5	—	14			0	—	15			7	8
12			2	—	$\overline{14}$			5	—	16			2	—	17			0	—
$\overline{16}$	0	8	29	28	$\overline{12}$			24	23	1	5	0	1	5	0	12	0	21	21
$\overline{14}$			0	—	$\overline{10}$			3	—	3			53	51	2			31	33
$\overline{12}$			5	—	$\overline{8}$			10	—	5			47	44	4			4	—
$\overline{10}$			31	31	6			24	25	7			13	13	6			4	2
					4			6	—	9			35	33	8			23	23

Table 4 (cont.)

<i>h k l</i>	<i>F_c</i>	<i>F_o</i>	<i>h k l</i>	<i>F_c</i>	<i>F_o</i>	<i>h k l</i>	<i>F_c</i>	<i>F_o</i>	<i>h k l</i>	<i>F_c</i>	<i>F_o</i>
10 12		10	13 19 0	5	8	3 27 0	11	12	9 9 1	4	—
12	6	4	15	5	—	5	3	—	10 10	8	—
14	1	—	17	2	—	7	10	8	11 11	7	—
16	1	—				9	2	—	12 12	8	10
			0 20 0	7	11	11	5	—	13 13	21	16
1 13 0	12	11	2	4	—	13	4	—	14 14	11	15
3	33	28	4	8	7						
5	6	4	6	3	—	0 28 0	3	—	14 14 2	2	—
7	33	34	8	4	—	2	5	—	13 13	18	18
9	9	7	10	7	8	4	2	—	12 12	2	—
11	8	10	12	2	—	6	3	—	11 11	16	18
13	10	13	14	2	—	8	4	—	10 10	32	31
15	1	—				10	1	—	9 9	4	—
17	7	—	1 21 0	13	10	12	2	—	8 8	70	72
			3	1	—				7 7	5	—
0 14 0	26	27	5	22	21	1 29 0	2	—	6 6	51	50
2	30	30	7	1	—	3	4	—	5 5	61	64
4	37	34	9	12	13	5	2	—	4 4	50	53
6	13	15	11	7	4	7	7	9	3 3	35	40
8	8	7	13	4	—	9	0	—	2 2	46	48
10	14	13	15	5	—	11	3	—	1 1	101	(—)
12	2	—	17	1	—				0 0	191	186*
14	5	—				0 30 0	13	12	1 1	58	50
			0 22 0	9	12	2	1	—	2 2	93	94*
1 15 0	1	—	2	24	24	4	9	10	3 3	12	12
3	5	6	4	7	4	6	5	—	4 4	53	(—)
5	1	—	6	11	12	8	0	—	5 5	50	46
7	10	13	8	12	13	10	6	—	6 6	34	31
9	7	7	10	1	—				7 7	18	18
11	12	13	12	8	—	<i>h h l</i>	<i>F_c</i>	<i>F_o</i>	8 8	0	—
13	1	—	14	1	—	1 1 0	16	27	9 9	31	30
15	0	—	16	3	—	2 2	148	134*	10 10	0	—
17	3	—				3 3	22	25	11 11	21	17
			1 23 0	0	—	4 4	22	25	12 12	12	11
0 16 0	78	83	3	1	—	5 5	48	44	13 13	7	—
2	2	—	5	3	—	6 6	52	50	14 14	12	—
4	40	37	7	4	—	7 7	30	29			
6	21	22	9	1	—	8 8	53	49	14 14 3	6	—
8	4	3	11	0	—	9 9	48	45	13 13	3	—
10	19	17	13	2	—	10 10	19	18	12 12	15	15
12	8	8				11 11	15	18	11 11	14	14
14	8	8	0 24 0	6	—	12 12	7	4	10 10	19	18
16	1	—	2	22	24	13 13	12	13	9 9	0	—
			4	10	10	14 14	6	—	8 8	39	43
1 17 0	1	—	6	10	8				7 7	21	24
3	40	36	8	8	8	14 14 1	2	—	6 6	37	37
5	18	19	10	1	—	13 13	23	20	5 5	61	(—)
7	27	28	12	7	—	12 12	8	10	4 4	4	6
9	8	11	14	1	—	11 11	22	20	3 3	44	46
11	10	11	16	2	—	10 10	5	—	2 2	23	26
13	3	—				9 9	3	—	1 1	55	53
15	3	—	1 25 0	12	12	8 8	26	28	0 0	30	27
17	5	—	3	1	—	7 7	2	—	1 1	80	72*
			5	16	15	6 6	8	10	2 2	42	43
0 18 0	5	14	7	2	—	5 5	3	—	3 3	10	—
2	39	39	9	10	10	4 4	78	73*	4 4	102	102*
4	4	—	11	0	—	3 3	75	74*	5 5	22	22
6	15	14	13	2	—	2 2	43	44	6 6	15	18
8	9	9	15	4	—	1 1	21	(—)	7 7	5	—
10	5	—							8 8	21	19
12	13	12	0 26 0	19	19	0 0 1	16	25	9 9	12	13
14	6	—	2	4	—	1 1	54	52	10 10	3	—
16	3	—	4	8	5	2 2	36	36	11 11	9	—
			6	4	—	3 3	38	36	12 12	13	14
1 19 0	22	21	8	1	—	4 4	34	34	13 13	1	—
3	5	—	10	6	—	5 5	54	51	14 14	8	—
5	22	20	12	5	—	6 6	21	22			
7	8	8	14	4	—	7 7	16	16	14 14 4	4	—
9	14	13				8 8	46	41	13 13	2	—
11	6	4	1 27 0	6	—				12 12	1	—

Table 4 (cont.)

h	h	l	F_c	F_o	h	h	l	F_c	F_o	h	h	l	F_c	F_o
$\overline{14}$	14	14	$\overline{5}$	—	$\overline{8}$	8	14	$\overline{3}$	—	3	3	14	$\overline{8}$	—
$\overline{13}$	13		0	—	$\overline{7}$	7		0	—	4	4		7	—
$\overline{12}$	12		1	—	$\overline{6}$	6		10	13	5	5		6	—
$\overline{11}$	11		5	—	$\overline{5}$	5		7	11	6	6		2	—
$\overline{10}$	10		4	—	$\overline{4}$	4		$\overline{16}$	17	7	7		4	—
$\overline{9}$	9		$\overline{12}$	14	$\overline{3}$	3		$\overline{5}$	—					

confirms this, but the details of the refinement process (as in (a) above) do not support any suggestion that still further refinement would result in the disappearance of the size-differences which we believe we have established.

(c) Indirect evidence of some Si, Al ordering in orthoclase is provided by the cell dimensions. Cole *et al.* (1949) directed attention to this fact in discussing the relationship between orthoclase and sanidine, and comparison of these with microcline shows differences as expected for the degrees of ordering established for microcline and now proposed for orthoclase.

(d) Studies of optical properties by Bailey (1954) and Hewlett (1959) are interpreted if, for potassium feldspars, the refractive index most nearly parallel to the b -axis is very sensitive to the degree of Si, Al ordering. The relatively large change observed in this index on converting orthoclase C to sanidine would thus indicate that disordering has occurred in the process (see Spencer (1937) or Cole *et al.* (1949), Table 1).

On these grounds it will be assumed, in the discussion which follows, that the small degree of Si, Al ordering deduced from tetrahedron size-differences is established.

(ii) *Electron densities in tetrahedra*

The resolution of peaks in our two-dimensional projections of orthoclase is insufficient to justify an attempt to count the total number of electrons associated with each peak. Table 3 shows, however, that there is a significant difference in peak height between Si_1 and Si_2 in the final $[\overline{110}]F_o$ synthesis, and if electron-content goes in parallel with peak height the difference is in the right direction to correspond* to a higher proportion of Al in Si_1 . The most interesting feature is, however, the *magnitude* of the difference: it is much larger than would correspond to the small degree of ordering as determined above from the sizes of the tetrahedra.

To examine this point further, $[\overline{110}]F_o$ syntheses were prepared for sanidine (using the data of Cole *et al.*, 1949) and microcline (using the data of Bailey, 1954), for direct comparison with the same projection for orthoclase. For sanidine the average† peak height for Si_1 is identical with that for Si_2 , as expected for a

completely random Si, Al distribution. For microcline the peak heights for $Si_2(O)$ and $Si_2(m)$ are identical, as expected for nearly identical Al-contents 0.07 and 0.08 (Bailey & Taylor, 1955): the peak heights for $Si_1(O)$ and $Si_1(m)$ are smaller, which is again as expected for the larger Al-contents in these sites; but there is no significant difference in peak height between $Si_1(O)$ with 0.25 Al and $Si_1(m)$ with 0.56 Al.

Table 5. *Peak heights and peak widths in microcline*

Atom	$Si_1(O)$	$Si_1(m)$	$Si_2(O)$	$Si_2(m)$
Peak height (e.Å ⁻³)	27.1	26.3	28.4	(28.1)
Peak width (arbitrary units)	12.7	12.5	10.3	(11.6)
Al content	0.25	0.56	0.07	0.08

Figures supplied by Dr S. W. Bailey.

Peak width, in arbitrary units, measured at a given height in a section parallel to (001).

Numerical values for $Si_2(m)$, enclosed in brackets, are less accurately comparable than the others in the table.

Notation for atoms is that of Bailey & Taylor (1955).

A scrutiny of the three-dimensional measurements for microcline, kindly carried out for us by Dr Bailey, led to the results summarized in Table 5. Peak height now varies approximately linearly with Al-content, but there is a significant difference in peak width between the two Al-rich peaks on the one hand, and the two Al-poor on the other. The only tentative interpretation of this three-dimensional study which we can suggest is that the rather small reduction in total electron-content of the 'average' atom at a tetrahedron centre, as Al-content rises to about 0.25, is shown as a considerable reduction in peak height partly compensated by increased peak width. This interpretation assumes that the two-dimensional study reveals only the major difference in peak heights as between $Si_2(O)$, $Si_2(m)$ and $Si_1(O)$, $Si_1(m)$, and that even the three-dimensional study reveals only the major difference in peak *widths* as between these two groups of atoms but not the difference in width between $Si_1(O)$ and $Si_1(m)$ which would be expected in view of the observed difference in height.

A careful study of the two-dimensional projections for microcline and orthoclase gave no indication of differences in widths of the peaks. No three-dimensional data are available for orthoclase. Direct comparison of peak-widths with those of sanidine (for which three-dimensional data are available) would be impossible because there is no correlation of the overall temperature factors.

* Assuming neutral atoms $Si(14)$, $Al(13)$ or at least only partially-ionized atoms.

† Each type of peak occurs twice in this projection.

The position reached is, therefore, that in both orthoclase and microcline there is a larger difference in peak heights as between atoms Si₁ and atoms Si₂ than would correspond to the Al-content as deduced from dimensional differences between the tetrahedra; that no difference in peak heights is observed in sanidine; and that in microcline there is some evidence that this difference is associated with a compensating difference in peak width. No simple explanation can be suggested. (See also Section 5, (vi)).

(iii) *The potassium atom*

In the structure analyses of sanidine and microcline the atomic *f*-curves of Bragg & West (1928) were found to be satisfactory for Si (with Al) and O, but Bailey & Taylor (1955) pointed out that both in their own work on microcline and in the study of sanidine by Cole *et al.* (1949) the K atom was better represented by the atomic *f*-curves of James & Brindley (1931) when suitably modified by the application of temperature factors $B=1.0 \text{ \AA}^2$ for microcline and $B=1.9 \text{ \AA}^2$ for sanidine. Even the smaller value of B is larger than that which is effectively incorporated into the empirical curves of Bragg & West. No evidence of anisotropic thermal vibration was observed in F_o syntheses in either case.

Table 6. *Temperature factors for potassium feldspars*

(i) Orthoclase

O	isotropic	$B = 1.2 \text{ \AA}^2$	
Si(Al)	isotropic	$B = 0.6 \text{ \AA}^2$	
K	anisotropic	$B_X = 1.0 \text{ \AA}^2$ with orientation	$X = a^*$
		$B_Y = 1.8 \text{ \AA}^2$	$Y = b$
		$B_Z = 1.5 \text{ \AA}^2$	$Z = c$

All the above are applied to the *f*-curves of Tomiie & Stam (1958).

(ii) Comparison with microcline and sanidine

	Microcline	Orthoclase	Sanidine
B_X	0.7 \AA^2	1.0 \AA^2	1.3 \AA^2
B_Y	1.2	1.8	2.3
B_Z	1.0	1.5	1.9

Computed for microcline and sanidine by assuming the ratios $B_X:B_Y:B_Z$ to be the same as for orthoclase. The orthoclase values are computed to correspond to zero absorption: a similar correction for absorption in the real crystal would slightly reduce the values for microcline and sanidine.

In our analysis of orthoclase we have used the atomic *f*-curves of Tomiie & Stam (1958) modified by the application of the temperature factors for O and Si(Al) shown in Table 6, and by an isotropic temperature factor $B=1.4 \text{ \AA}^2$ for K. In this case, however, difference syntheses show a marked anisotropy in the K peak, corresponding to the values B_X, B_Y, B_Z with the orientations listed in Table 6. Since F_o syntheses do not reveal the anisotropy of this peak in orthoclase, difference syntheses for various projections of sanidine and microcline were studied in order to check the

apparent isotropy of the K-peak as seen in F_o syntheses of these structures. For sanidine the F_o values of Cole *et al.* (1949) were used, with F_c values obtained by applying to the atomic *f*-curves of Tomiie & Stam the isotropic temperature factors for O and Si(Al) shown in Table 6 (as for orthoclase) and for K an isotropic temperature factor equal to the average orthoclase value for the projection concerned. For microcline Bailey's (1954) $(hk0-6)^* F_o - F_c$ synthesis was used, together with the $(0kl-2)^* F_o - F_c$ synthesis kindly prepared for us by Dr Bailey, who has also calculated that at a particular electron density value the diameter of the three-dimensional K-peak is about 10% greater along y than along x . (It may be noted that the *f*-curve of Tomiie & Stam for K⁺ is very similar to that of James & Brindley used in the study of microcline, so that no serious inconsistency is involved in our comparison of the orthoclase projections and new sanidine projections with the microcline projections *in the neighborhood of the K-peak*). A study of these syntheses suggests that the K peak shows similar slight anisotropy in all three structures. We have not attempted a direct quantitative estimate of its magnitude for sanidine and microcline but if the ratio $B_X:B_Y:B_Z$ is assumed to be the same for microcline and sanidine as for orthoclase, then the average (isotropic) temperature factors for the K atom of 1.0 \AA^2 and 1.9 \AA^2 proposed by Bailey & Taylor (1955) lead to the numerical values listed in the lower part of Table 6.

For low and high albites Ferguson *et al.* (1958) have suggested that the apparent anisotropic thermal vibration which results in an effectively elongated Na atom may represent a random distribution of the Na atoms between two sites. The corresponding interpretation of the slightly disc-like K atom in the potassium feldspars may represent a distribution of K-atom positions varying with the Si, Al ordering in its immediate neighbourhood, which *must* vary from cell to cell when the fiction of the 'average atom' (Si_nAl_{1-n}) is replaced by the true model. This point is mentioned again below (v).

(iv) *Configuration of the tetrahedral groups*

It is usually assumed implicitly that the tetrahedral SiO₄ or AlO₄ group is perfectly regular and that the departures from regularity shown in the measurements of (e.g.) oxygen-oxygen tetrahedron edges in an actual structure are due to experimental errors or incomplete refinement. Consideration of the forces operative in the structure suggests, however, that perfect regularity is not necessarily to be expected, the close approximation to regularity and fixed size being no more than a consequence of the strength of the bonds within the tetrahedron in relation to forces external to it.

Direct evidence in support of this more sophisticated

* The numbers 6 and 2 indicate the 6th ($hk0$) and 2nd ($0kl$) syntheses described by Bailey (1954).

interpretation is accumulating as accurate analyses of feldspar structures become available. Thus on comparing the O-O distances for orthoclase in Table 2 with those for sanidine (Cole *et al.*, 1949—their Table 4) and for microcline (Bailey & Taylor, 1955—their Table 8) certain features corresponding to *departures* from perfectly regular tetrahedral groupings are seen to be common not only to orthoclase and sanidine (as would be expected, in view of their close similarity in all respects, already discussed in (5)(i)(b) above) but also to microcline. For example, OA-OC is longer than the mean for tetrahedra around Si₁ (or around Si₁(O) and Si₁(*m*) in triclinic microcline), but shorter than the mean for tetrahedra around Si₂ (or Si₂(O) and Si₂(*m*)). This difference is also found in celsian BaAl₂Si₂O₈ (Newnham & Megaw, 1960) although in this material the Si, Al ordering scheme is totally different. The difference must therefore be due to the general balance of forces as between Si(Al) and O, on the one hand, and K (or Ba) on the other.

Similar features can be seen in the low albite and high albite structures, but in view of the somewhat lower accuracy claimed (Ferguson *et al.*, 1958) and the greater anisotropy of the Na atom, a detailed discussion should probably await the forthcoming three-dimensional refinement of these structures.

(v) *Electrostatic charge balance*

The importance of local electrostatic balance of charge as a factor in determining the stability of the alkali feldspars has recently been considered by Ferguson *et al.* (1958, 1959—see also MacKenzie & Smith, 1959) who pointed out that on this view the most stable potassium feldspar would be monoclinic with or-

dering (0.36 Al + 0.64 Si) in site Si₁ and (0.14 Al + 0.86 Si) in site Si₂. They further suggested that orthoclase might in fact represent this structure.

The degree of ordering deduced in (i) above is less than that predicted for 'ideal orthoclase', and though the accuracy of our determination is not such as to exclude completely the possibility that Spencer C is identical with 'ideal orthoclase', we believe that this is unlikely. Comparable figures for the balance of charge in orthoclase (Spencer C), sanidine, ideal orthoclase and microcline are shown in Table 7, with the degree of Si, Al ordering for each structure.

In discussing balance of charge for a structure in which a given site is occupied at random, sometimes by Si, sometimes by Al, so as to give a specified average Si, Al content, it is necessary to keep in mind that the calculation is essentially one involving a process of taking the average over a number of unit cells which differ in respect to the Si, Al occupation of the tetrahedron sites. This point has been sufficiently emphasized in the publications listed above. It is mentioned here because of its possible significance for the interpretation of the shape of the K peak, to which attention has already been directed in (iii) above.

Ferguson *et al.* (1958) use bond strengths given by the cation charge divided by the number of bonds to anions, without taking account of any variations in bond lengths within the group under consideration. This procedure is obviously satisfactory for the internal tetrahedron bonds which are almost identical in length. For K-O contacts each bond is assigned strength 1/9, but the justification for this is less obvious in view of the appreciable range in the contact distances listed by

Table 7. Si, Al ordering and balance of charge in potassium feldspars

Tetrahedron	Microcline	Sanidine	Orthoclase (Spencer C)	Orthoclase (‘Ideal’)
Si ₁ (O)	0.25 Al 8.11	0.25 Al 8.05	0.30 Al 8.03	0.36 Al 8.00
Si ₁ (<i>m</i>)	0.56 Al 7.87			
Si ₂ (O)	0.07 Al 8.00	0.25 Al 7.94	0.19 Al 7.98	0.14 Al 8.00
Si ₂ (<i>m</i>)	0.08 Al 8.08			
Σ Δ	0.32	0.22	0.10	0

For each structure the table gives first the degree of Si, Al ordering (represented by the fraction of Al), then the total bond strength contributed to O⁻² atoms, for each tetrahedral group.

The total deviations from balance Σ|Δ| are shown for *four* tetrahedral groups in each case.

The nomenclature for (triclinic) microcline is that of Bailey & Taylor (1955); the figures for balance of charge for microcline, sanidine and ideal orthoclase are taken from Ferguson *et al.* (1958).

Table 8. Si, Al ordering and K-O contact distances (Å) in potassium feldspars

	Averaged microcline	Orthoclase	Sanidine
Si, Al ordering	‘Si ₁ ’ = 0.41 Al + 0.59 Si ‘Si ₂ ’ = 0.08 Al + 0.92 Si	Si ₁ = 0.30 Al + 0.70 Si Si ₂ = 0.19 Al + 0.81 Si	Si ₁ = 0.25 Al + 0.75 Si Si ₂ = 0.25 Al + 0.75 Si
Distances K-OA ₁	2.889 (mean)	2.898	2.919
OA ₂	2.758	2.698	2.698
OB	3.101 (mean)	3.029	3.026
OC	3.132 (mean)	3.135	3.129
OD	2.953 (mean)	3.111	2.948

Nine K-O contacts = 1 with OA₂, 2 each with other atoms.

Cole *et al.* (1949) (their Table 4) for sanidine and by Bailey & Taylor (1955) (their Table 8) for microcline. Comparison of these distances with the corresponding distances for orthoclase (Table 2) suggests a rather more detailed treatment. For this the distinction between $\text{Si}_1(\text{O})$ and $\text{Si}_1(m)$, and between $\text{Si}_2(\text{O})$ and $\text{Si}_1(m)$, in triclinic microcline may be ignored, and we therefore collect together in Table 8 data for sanidine, orthoclase and 'microcline' in which the degree of Si, Al ordering in the tetrahedral groups and the K–O contact distances are averaged in this way. The Si, Al ordering increases from sanidine to orthoclase to microcline, and at the same time the bonds K– OA_1 diminish steadily, while the bond K– OA_2 increases as between (sanidine and orthoclase) and microcline. Now OA_1 is linked only to Si_1 atoms which contain higher proportions of Al as order increases, and OA_2 is linked only to Si_2 atoms in which the proportion of Al falls as order increases. Therefore, if the strength of K–O bonds may be assumed to vary (inversely) with length, the trends observed in the potassium feldspar series correspond to a change in strength of potassium bonds with OA_1 and OA_2 . The decrease in the strength of K– OA_2 and increase of K– OA_1 correspond to the change in Si, Al–O bond strength to these atoms with increase in the degree of Si, Al ordering. This is in harmony with the assumption that charge-balance is an important factor in controlling the structural detail. It may be permissible to press the argument further; the total increase in the bond length K– OA_2 (from sanidine to microcline) is much greater than the total corresponding decrease in the bonds K– OA_1 ; this may be supposed to be due to the fact that an atom OA_1 has bonds with *two* K atoms, whereas an atom OA_2 has only one K bond.

Bonds between K and OB, OC, OD cannot be discussed in this simple way, since each such O atom is linked to one atom Si_1 and one atom Si_2 . Nor can the albite structures be included directly, since there are considerable differences between the coordination groups around the large K atom and the small Na atom.

We conclude that, although too much emphasis should not be given to arguments such as these, they may point to the need for some refinement in detail in the use of the charge-balance hypothesis.

(vi) *The real symmetry of orthoclase*

The final results of the structure analysis, and all the discussion in Sections 5(i) to 5(v), are presented on the assumption that the unit cell structure is truly monoclinic, space group $C2/m$. Since it has been suggested that 'orthoclase' is built up from triclinic microcline (Laves, 1952) the question of the real symmetry of our orthoclase structure needs careful consideration.

We have no experimental evidence suggesting that the unit-cell dimensions of our orthoclase depart from

monoclinic symmetry. Differences in the measured intensities of certain pairs of reflexions which must be identical if the structure is truly monoclinic have been assumed to be due to the effects of absorption and extinction. Diffuse streaks adjacent to Bragg reflexions have (peak) intensities so exceedingly feeble that we have ignored them in our structure analysis. (For fuller discussion of these experimental observations, see Section 3(i).) We conclude, therefore, that (to a close approximation) there is nothing in the direct experimental data which is not in accordance with our assumed monoclinic symmetry.

However, at a fairly early stage in the refinement process (based on $C2/m$) the difference syntheses showed an interesting feature—near the position of a Si(Al) atom a pair of +ve peaks and, forming a right-angled cross, a pair of –ve peaks. The corresponding effect in a Fourier (F_o) synthesis would be a slight elongation of the atomic peak along the direction joining the pair of +ve peaks in the difference synthesis. This feature may be explicable as follows:

(a) It may arise from imperfect corrections for absorption (see Section 3(ii)). For two reasons we consider this rather unlikely. First, if this were the explanation, every atom should be represented in the difference synthesis by a \pm cross oriented in the same direction. This is not observed. Second, in the case of the [010] projection, the application of an absorption correction produced no apparent alteration in the effect.

(b) It may indicate that the atom suffers anisotropic thermal vibration with maximum amplitude (in projection) along the line of the pair of +ve peaks. An attempt to select anisotropic temperature factors for the Si(Al) atoms did not result in satisfactory flattening of the background in the difference syntheses, nor was much improvement in the R -value obtained beyond about 11%. This explanation, therefore, is not considered very probable.

(c) The true symmetry of the structure may be lower than that of the holohedral monoclinic space group on which the refinement has so far been based. Thus in considering the projection along [010] the desired flattening of the background in the difference synthesis (i.e. the removal of the \pm cross) was quickly obtained, with reduction of the R -value to about 8.5%, on removing the mirror plane m of the space-group $C2/m$. For the two atoms of a pair which are exactly superimposed in the projection along [010] in $C2/m$ can then be moved independently in x and z directions in the new space group $C2$; one atom of such a pair is moved towards one +ve peak, the other towards the other +ve peak, the displacements involved being small. Similarly, in dealing with the 'anisotropy' of the Si(Al) peaks also seen in the difference syntheses in [001] and [100] projections, it would be necessary to remove the axis 2, thus reducing the symmetry to triclinic. This procedure was, however, abandoned: for there was considerable doubt about the reality of

a refinement process in which the improvement is obtained simply by increasing the number of variables available. If this reasoning is valid, we may conclude that no great reliance could be placed upon the details of a structural interpretation of these features of the difference syntheses which depended upon the assumption of a triclinic atomic arrangement within a dimensionally-monoclinic unit cell.

The true cell may, however, be doubled in one direction, while remaining monoclinic, with small out-of-phase domains blurring out the additional maxima which correspond to the larger spacing. The observed electron density map is then an average of the two halves of the unit cell. An effect of this kind is obtained in celsian (Newnham & Megaw, 1960) if the weak maxima with l odd are deliberately omitted from the synthesis.

(*d*) The partial character of the Si, Al order itself constitutes a type of 'disorder'. The structure finally determined in the refinement process may represent only the average arising from this type of disorder, or it may correspond to the average of constituents disordered in relation to structural details other than the type of atom (Si or Al) at the centres of tetrahedra. On continuing the refinement of this 'average' orthoclase, using $C2/m$, and with an isotropic temperature factor for the Si(Al) atoms, the final R -value was 7.2% (Table 4). In the final difference syntheses the pairs of +ve and -ve peaks near (Si(Al) atoms remain, especially in the [010] projection, and similar but less marked effects may be distinguished with some of the O atoms.

On balance, therefore, we favour an interpretation in terms of an 'average' structure described by the parameters of Table 1; the very small magnitude of the effects which suggest this interpretation, and the weakness of the diffuse streaks observed, must be taken as evidence that the structure of the true unit cell must differ only very slightly from the average structure thus determined.

It is an obvious step to suppose that the 'true' unit cell is that of microcline, which—on this view—when finely twinned on albite and pericline laws produces our 'average' orthoclase structure with apparently monoclinic symmetry. Support for this suggestion would be provided if a twinned microcline structure were to predict \pm crosses in the observed orientations: we have, unfortunately, failed to satisfy ourselves that there is any way in which this can be done, partly on account of the ill-defined nature of some of the observed \pm crosses. It must not be forgotten that 'microcline' in such a multiply-fine-twinned structure may be distorted from the microcline structure in the single-crystal specimen, so that attempts to discuss the geometry of an 'average' structure must be rather vague.

An alternative suggestion as to the true nature of orthoclase has been made by Megaw (1959), based on stacking disorder in a 14 Å structure in which the

Si, Al distribution is similar to that in the anorthite 14 Å structure. Our analysis, leading to a very slight concentration of the Al atoms into sites Si_1 , does not confirm the particular faulting tentatively proposed by Megaw. There is no reason to suppose that an appropriate system of stacking faults could not be devised, but it seems unlikely that a definite decision as to its validity could be given on the basis of our measurements.

At this stage it also becomes necessary to ask whether meaning can be attached to a discussion in terms of regions of recognizable microcline structure, or in terms of a hypothetical faulted structure, or whether it is not more realistic to think only in terms of local 'disorder' arising as a consequence of the concentration of Al in sites of type Si_1 both in microcline and in orthoclase, whereas sites Si_2 tend to contain a smaller proportion of Al. The observed difference in peak heights between Si_1 and Si_2 in both structures (already discussed in 3(ii)), whether or not it is associated with greater peak width in orthoclase as it is in microcline, is certainly suggestive in this connection. The apparent anisotropy of the K atom may also have some bearing on this problem.

We finally conclude that our analysis falls short of the accuracy and resolution which might permit a definite decision on the nature of the presumed 'average' or disordered structure represented by the orthoclase parameters of Table 1. Such evidence as we have inclines to the view that an attempt to discuss our orthoclase structure as though it were made up from multiply-twinned units with a well-defined microcline structure is unlikely to be physically realistic, but leaves unsettled the possibility that orthoclase represents a faulted 14 Å structure.

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Matrix Theoretical Derivation of Inequalities. II.

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The present paper shows a way starting from a matrix-theoretical representation of Fourier series and leading to the reduction by the symmetry properties of the matrix of Karle and Hauptman (1950) type, so that a general form of fundamental inequalities involving structure factors can be derived for any given space group.

It has been reported (Taguchi & Naya, 1958) that when the Karle & Hauptman matrix is slightly modified by the cyclic matrix, the matrix F can be diagonalized completely, so that the characteristic numbers may correspond to the electron densities; namely,

$$\varrho = UFU^{-1}, \quad (1)$$

where ϱ and F are the following N -dimensional matrices with N large:

$$\varrho = \begin{bmatrix} \varrho_0 & & & & 0 \\ & \ddots & & & \\ & & \varrho_r & & \\ & & & \ddots & \\ 0 & & & & \varrho_{N-1} \end{bmatrix}, \quad (2)$$

$$F = \frac{1}{N} \begin{bmatrix} F_0 & F_{-1} & F_{-2} & \dots & F_2 & F_1 \\ F_1 & F_0 & F_{-1} & \dots & F_3 & F_2 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ F_{-1} & F_{-2} & F_{-3} & \dots & F_1 & F_0 \end{bmatrix},$$

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U being a unitary matrix used in the transformation. Introducing the regular representation for the cyclic group of order N ,

$$C = \begin{bmatrix} 1, C, \dots, C^h, \dots, C^{N-1} \\ \begin{bmatrix} 0 & \dots & \dots & 0 & 1 \\ 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & 1 & \dots \\ 0 & 0 & \dots & 0 & 1 & 0 \end{bmatrix} \\ C^N = 1, \end{bmatrix} \quad (3)$$

F can be written as

$$F = \frac{1}{N} \sum_{h=0}^{N-1} F_h C^h. \quad (4)$$

We shall extend equation (4) for the one-dimensional case to the three-dimensional one. The resultant expression becomes to be

$$F = \frac{1}{N^3} \sum_{h=0}^{N-1} \sum_{k=0}^{N-1} \sum_{l=0}^{N-1} F_{hkl} C^h \times C^k \times C^l = \frac{1}{N^3} \sum_{\mathbf{h}=0}^{N-1} F_{\mathbf{h}} C^{\mathbf{h}}, \quad (5)$$