

The Structure of a Triclinic Potassium Felspar

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The crystal structure of an intermediate microcline from Kodarma, India, has been determined. Using the atomic co-ordinates of sanidine as a starting point, initial refinement of the structure was made by seventeen successive F_o and $(F_o - F_c)$ Fourier projections parallel to the a and c axes. Final refinement was accomplished by two sets of three-dimensional Fourier sections and lines parallel to (001) and [001] respectively. An artificial temperature factor of $B = 4.0 \text{ \AA}^2$ was used to reduce diffraction effects, and a final correction was applied from a third set of back-synthesis sections and lines.

The mean bond lengths within the four non-equivalent tetrahedra were found to be 1.645, 1.700, 1.611 and 1.614 Å. A statistical analysis of the experimental and computational errors showed the differences between these values to be significant. It is concluded that this particular microcline has a partial ordering of Si and Al over the tetrahedral sites and that the polymorphism of sanidine and microcline is a result of this order-disorder relationship. The thermal vibration of the potassium atom is shown to be greater in the high-temperature form, sanidine, than in microcline. Examination of the stages of refinement provides a basis for assessing the possibility of detecting ordering of Si and Al in other similar structures by careful two-dimensional methods.

1. Introduction

The potassium felspar minerals (KAlSi_3O_8) occur in several polymorphic forms having different but intergradational optical and physical properties. Sanidine, the monoclinic high-temperature variety, occurs in volcanic tuffs, lava flows, and a few plutonic rocks. Common orthoclase, another monoclinic variety, and microcline, triclinic, are found in a wide variety of igneous and metamorphic rocks believed to have crystallized at intermediate to low temperatures. Adularia is the name usually given to the monoclinic and triclinic potassium felspars found in low-temperature hydrothermal veins and to many of the authigenic potassium felspars found in sedimentary rocks. Adularia is distinctive for a unique crystal habit, but its validity as a true polymorphic form is still in question.

The problem of the polymorphism of the potassium felspars has interested scientific investigators for many years. Mallard (1876) and Michel-Levy (1879) believed that these felspars were not truly polymorphous. They attempted to prove that the monoclinic varieties were actually composed of triclinic individuals twinned on a submicroscopic scale in such a manner that the resulting crystals showed monoclinic optical properties. Alling (1921, 1923, 1926) and Spencer (1937, 1938) showed that although this process seemed physically feasible it could not explain the different thermal reactions of the monoclinic and triclinic varieties or their differences in specific gravity and refractive index. Taylor, Darbyshire & Strunz (1934) further showed common orthoclase to be dimensionally

monoclinic and untwinned according to X-ray investigation. This proved the existence of polymorphism, although Laves (1950) later demonstrated that some optically monoclinic adularia actually may be composed of triclinic units twinned submicroscopically in accordance with the theory of Mallard and Michel-Levy.

The basic structure of the felspars was first determined by Taylor (1933) by trial-and-error procedure on a sanidine phenocryst from a volcanic block from Mount Vesuvius. Reference should be made to this early work for a general description of the felspar structure. Taylor pointed out the problem that the monoclinic holohedral symmetry assumed for sanidine demands two eightfold sets of equivalent 'silicon' atoms (Si_1 and Si_2) which must contain the 16 (Si+Al) atoms present in the unit cell. In all potassium felspars, however, there are 12 Si and 4 Al atoms, suggesting a division into four groups to preserve equivalence of atom types, three groups containing 4 Si each and one containing 4 Al. But such a grouping is possible only if the true symmetry is either triclinic or monoclinic hemihedral. Barth (1934) suggested that this discrepancy could be removed by considering the aluminium and silicon atoms to be distributed randomly over the structurally equivalent positions demanded by strict holohedral symmetry. Barth also suggested that in the microcline structure the aluminium atoms may be segregated into an equivalent group of four, in accordance with the change to triclinic symmetry. Barth's principle of an ordered versus disordered distribution of atoms over equivalent positions is accepted now as an explanation for the polymorphism of many minerals, the atomic distribu-

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tion varying with the temperature of formation and rate of cooling.

Order-disorder relationships can often be detected by simple X-ray investigation or by certain changes in refractive index and specific gravity, provided there is sufficient difference in the size or atomic number of the atoms involved. In the case of potassium feldspars the higher-temperature varieties do have the lower specific gravities and refractive indices to be expected from disordered structures. Superlattice X-ray reflexions, which in such cases are diagnostic of ordering, are not present in the lower-temperature forms, but would not be expected owing to the similarity in scattering power of aluminium and silicon and the low Al:Si ratio of 1:3.* The fact that the several potassium feldspar varieties can be correlated in their occurrence with different ranges of formation temperature, however, is in accord with the principle of order-disorder and with the idea that intermediate states should be expected between completely disordered and completely ordered structures. Laves (1952) and Goldsmith & Laves (1954a) have discussed much of the experimental and theoretical evidence for order-disorder in the feldspars.

Proof of the nature of the distribution of aluminium and silicon can be provided only by detailed atomic-structure determinations. Although electron-density values alone will not distinguish the two atoms, because of similarity in atomic number, aluminium is slightly larger than silicon so that precise interatomic-distance measurements should differentiate them. The original investigation of sanidine by Taylor (1933) was not attempted in enough detail to give any indication as to Si-Al distribution. Chao, Hargreaves & Taylor (1940) undertook the determination of accurate interatomic distances in a pegmatitic specimen of common orthoclase from Burma (Spencer *C*) by means of two-dimensional Fourier syntheses. They found the average Si-O distance in the tetrahedron around atom Si₁ to be 1.68 Å, and that in the non-equivalent tetrahedron about Si₂ to be 1.58 Å. On the basis of this difference they considered the Si-Al distribution to be ordered with 8 Si in the Si₂ sites and 4 Si+4 Al in the larger Si₁ sites. Further work by Cole, Sörum & Kennard (1949), however, showed that this conclusion was not justified in view of the limited experimental data used. These latter authors also examined in considerable detail the same orthoclase after sanidinization by heating at 1075° C. for 300 hr. They calculated three-dimensional Fourier section and line syntheses, using intensity data from 737 different reflexions. The mean Si-O distance was determined as 1.642 Å for both tetrahedral sites, indicating a disordered Si-Al distribution. Although the interatomic

distances of 1.62 and 1.72 Å assumed by the authors for pure Si-O and Al-O respectively are now known to be in error, the experimental value still indicates a disordered Si₁Al₁ distribution when compared with the most recent values of 1.60 Å for Si-O and 1.78 Å for Al-O (Smith, 1954). This detailed work on sanidine by Cole *et al.* is the most accurate study to date on the Si-Al distribution in a feldspar.

The present paper reports a similar high-accuracy structure determination on microcline, a triclinic potassium feldspar. Laves (1950, 1951) has reported the cell angles typical of most microclines; the angle α^* deviates by 0° 22' from 90° while γ^* deviates by 2° 10'. More recently, MacKenzie (1954) and Goldsmith & Laves (1954b) have recognized that there is a series of triclinic potassium feldspars with interaxial angles varying from nearly monoclinic to the maximum values cited by Laves. The microcline series was recognized independently by us, and is discussed by Bailey (1954) in relation to optical, chemical and X-ray data for a number of specimens. The structure determination reported here was made on an intermediate member of this microcline series, having interaxial angles roughly halfway between monoclinic symmetry and the maximum triclinic values.

2. Experimental

The microcline selected for analysis was specimen *U*, a transparent and colourless crystal collected by Dr E. Spencer from a pegmatite in Kodarma, Bihar, India. The chemical analysis and optical and physical properties determined by Spencer (1937) are listed in Table 1. On the basis of these properties and its semi-

Table 1. *Chemical analysis and physical properties of specimen U*

(Results taken from Spencer (1937) except for extinction on (001).)

SiO ₂	64.38	Specific gravity	2.5692
Al ₂ O ₃	19.50	Refractive indices	α 1.5195
Fe ₂ O ₃	0.11		β 1.5232
CaO	0.28		γ 1.5255
MgO	Trace	Birefringence ($\gamma - \alpha$)	0.0060
K ₂ O	14.32	2 <i>V</i> _{calc.}	76.5°
Na ₂ O	1.48	2 <i>V</i> _{meas.}	76.2°
Loss	0.28	Extinction on (010)	7.5°
Total	100.35	Extinction on (001)	9.0°
Or	84.63 wt. %		
Ab	12.51		
An	1.40		

glassy appearance, Spencer believed his specimen *U* to be unusual and not representative of most microclines. This is in accord with our placement of the sample as intermediate in the microcline series.

Specimen *U* is a micropertthite but the weak extra X-ray reflexions from the unmixed sodium feldspar component do not seriously overlap those from the potassic host. Considerable trouble was encountered

* In the plagioclase feldspars albite (NaAlSi₃O₈) is similar to microcline in its Al:Si ratio of 1:3 and the absence of superlattice reflexions. Anorthite (CaAl₂Si₂O₈), with a larger Al:Si ratio of 2:2, however, does show superlattice reflexions and a doubled *c* axis relative to albite and microcline.

Table 2. *Lattice constants of specimen U*

Cube No.	a^* (\AA^{-1})	b^* (\AA^{-1})	c^* (\AA^{-1})	α^*	β^*	γ^*
1	0.129753	0.077168	0.154330	89° 53'	63° 59'	89° 09'
2	0.129747	0.077165	0.154338	89° 52'	—	89° 08'
3	0.129746	0.077175	0.154333	89° 52'	—	89° 10'
4	0.129750	0.077167	0.154331	89° 55'	63° 58'	89° 10'
5(a)	0.129760	0.077172	0.154345	89° 57'	63° 57'	89° 12'
(b)	—	0.077170	0.154333	89° 55'	—	—
Weighted average	0.129749	0.077169	0.154333	89° 55'	63° 58'	89° 10½'
	a (\AA)	b (\AA)	c (\AA)	α	β	γ
	8.5784	12.9600	7.2112	89° 42'	115° 58'	90° 52½'

In the above table the reciprocal-lattice constants for cubes No. 1-4 were obtained by the θ -method, 5(a) from precession-camera measurements corrected for shrinkage, and 5(b) by graphical extrapolation from 43° oscillation-photograph measurements.

in isolating untwinned fragments, since the crystal has patchy areas of typical microcline cross-hatch twinning. By exercising great care, however, several small untwinned cubes were cut with a razor blade from regions in between the cross-hatched areas of a cleavage flake. Unit cell dimensions, as listed in Table 2, were obtained on these cubes by the θ -method (Weisz, Cochran & Cole, 1947), by precession-camera measurements, and by graphical extrapolation. The positive directions of the axes were chosen to make the reciprocal-cell angles acute, in accordance with previous convention. Laves (1951) has suggested a new choice of axes such that the system of co-ordinates is rotated 180° about the b axis. The present work was advanced too far at that time to warrant following the suggested change. The orientation of Table 2 was retained, therefore, and will be used throughout this paper.

Photographs suitable for determining the intensities of a large number of reflexions were obtained by the Weissenberg equi-inclination technique, using filtered Mo radiation. A Unicam two-crystal Weissenberg was used, modified for use with one crystal and employing a special lead trap to cut down scattered radiation. Multiple-film packs consisting of three films separated by tin foil 0.025 mm. thick were used to reduce the intensities of the strongest reflexions to a measurable range. Three such packs were required for a complete record of each layer line, using exposures of 120, 15, and 1½ hr. Cube No. 1 of Table 2, measuring 0.17 × 0.17 × 0.17 mm. and having an extinction angle of 9° on (001), was used to record a total of 13 different reciprocal-lattice levels perpendicular to the b axis. At this point cube No. 1 was lost, and all further data were obtained from cube No. 4. It measured 0.12 × 0.12 × 0.10 mm. and was found to have the same cell dimensions and optical properties as the first specimen. Nine reciprocal levels perpendicular to the a axis and five levels perpendicular to the c axis were recorded from cube No. 4. In all, a total of 27 different levels were recorded, furnishing intensity data for 3,875 different reflexions.

All intensity measurements were made visually by matching the intensity of a given reflexion with one of a series of spots on a standard scale. The standard

scale was made by exposure of a multiple-film pack to a strong reflexion from cube No. 1, the limit stops on the Weissenberg being set so that the crystal oscillated back and forth through the reflexion angle a desired number of times. This ensures that the intensity-scale spots have about the same shape as the experimental spots and that each film of a multiple pack has its own corresponding intensity scale. Altogether 2,652 different reflexions with measurable intensities were recorded, while 1,223 reflexions in the same $\sin \theta/\lambda$ range had intensities too low to be observable for the exposures used. It is estimated that the intensity of each reflexion was measured an average of four to five times because of the use of multiple-film packs and the occurrence of most reflexions on more than one reciprocal level.

X-ray reflexions occurring on one half of a non-equatorial Weissenberg film are contracted while those on the other half are extended. The effect becomes more marked for reciprocal levels of increasing ζ value and with decreasing θ value within any one level. Visual matching of intensities against standard scales tends to over-estimate the intensities of the contracted spots and to under-estimate those of the extended spots owing to the change in size of the spots. Kaan & Cole (1949) have shown that when the same reflexion occurs on both halves of the film the average of the two intensities is close to the true value. For a triclinic crystal most reflexions occur on only one half of the film, requiring a correction to obtain the true intensity. By using the intensities of those reflexions which were present on both halves of the film, empirical correction curves were determined for each reciprocal level of specimen U by plotting $(\sin \theta/\lambda)^2$ versus $(I_B - I_T)/2I_B$ and $(I_B - I_T)/2I_T$. I_B and I_T are the measured intensities of the same reflexion on the bottom and top halves of the film respectively, where I_B is measured from a contracted spot and I_T from an extended spot. Then multiplication of a given I_B value by the appropriate value of $(I_B - I_T)/2I_B$ from the curve gives $(I_B - I_T)/2$, the correction to be subtracted from I_B to give the true intensity. A similar procedure using I_T and the other curve yields the correction to be added to I_T . Typical empirical curves are illustrated in Fig. 1.

The graphical method of Cochran (1948) was followed in correcting for the Lorentz polarization factor. No correction was applied for the absorption factor. Absorption effects were made as small as possible, however, by using small crystals and Mo radiation.

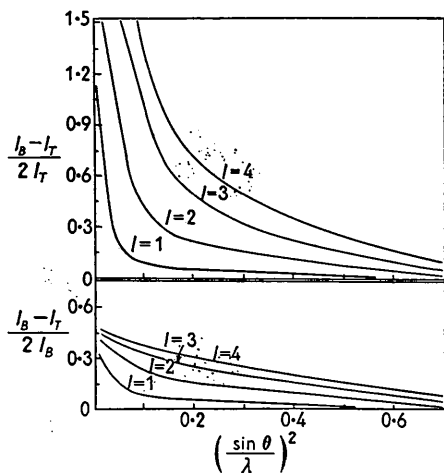


Fig. 1. Empirical correction curves for the Weissenberg contraction-extension effect on the first four reciprocal levels normal to the c axis. The upper set of curves is for use with reflexions which occur only on the top half of the film, the lower set for reflexions which occur only on the bottom half of the film.

In addition, the cubes were rolled on fine emery paper to round off the cube corners and make the path lengths of different reflexions as similar as possible. Although no definite extinction effects were noted, F_c values were substituted for several of the largest F_o values at the stage of three-dimensional Fourier syntheses as a precautionary measure.

After correction, the intensity data of the 27 reciprocal levels were placed on a single relative scale by comparison of the intensities of those reflexions occurring on more than one level. The final F^2 values were converted to F values and placed on a rough absolute scale by comparison with F_c values computed from the monoclinic sanidine structure. For this purpose an $f(\theta)$ curve was used, plotting F_o/F_c versus small ranges of $(\sin \theta/\lambda)^2$. Only the $(h0l)$ reflexions were used for this curve on the assumption that these values would be least affected in the transition from monoclinic to triclinic symmetry. The $(0kl)$ and $(hk0)$ reflexions then were used to derive more precise atomic parameters of microcline by two-dimensional refinement. At the completion of this refinement, and prior to three-dimensional syntheses, a second $f(\theta)$ curve, involving approximately 1800 of the medium-intensity reflexions, was constructed to place all reflexions on a more accurate absolute scale. The final $f(\theta)$ curve is illustrated in Fig. 2.

Since microcline is triclinic, the two standard space groups are $P\bar{1}$ and $P1$. In this investigation, however, the alternative and larger C cell, used in the mono-

clinic feldspars, is retained for convenience. With this selection of axes the systematic absences of type $h+k = 2n+1$ are also valid for specimen U . The two space groups are $C\bar{1}$ and $C1$. In the absence of definite tests for symmetry centres, all feldspar structures to

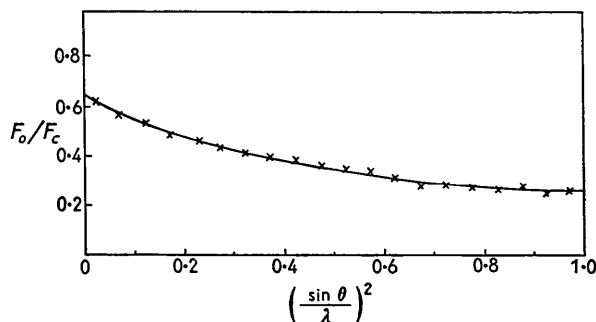


Fig. 2. Final $f(\theta)$ curve to place all structure amplitudes of specimen U on an absolute scale. The crosses represent values of $\Sigma F_o/\Sigma F_c$ for all medium-intensity reflexions in successive 0.05 ranges of $(\sin \theta/\lambda)^2$. The F_c values are based on the final two-dimensional atomic co-ordinates.

date have been worked out on the assumption of centrosymmetry. The recent application of statistical tests to X-ray intensities by Wilson and his colleagues now allows determination of the exact space groups. Bailey, Ferguson & Taylor (1951) justified the assumption of centrosymmetry by earlier workers by showing centres of symmetry to be present in sanidine, common orthoclase and albite. We have applied three tests to show that microcline also is centrosymmetric. 955 reflexions of types $(hk0)$, $(hk1)$, $(hk2)$, $(hk3)$ and $(hk4)$, fully corrected and placed on a single intensity scale, were divided into four $(\sin \theta/\lambda)^2$ groups. The results of the $N(z)$ test (Howells, Phillips & Rogers, 1950) are illustrated in Fig. 3. Table 3 lists the experimental and theoretical ratios determined for the Wilson ratio test (Wilson, 1949; Howells *et al.*, 1950) and the variance test (Wilson, 1951). From the very close agreement of the experimental curves and ratios

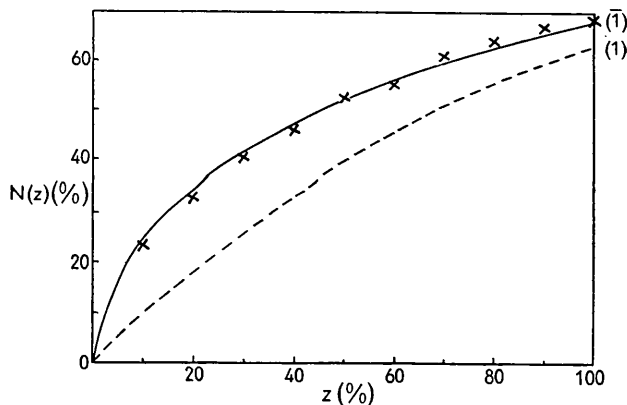


Fig. 3. $N(z)$ test for centrosymmetry in specimen U . The theoretical curve for $(\bar{1})$ is indicated as a solid line, that for (1) as a dashed line.

Table 3. *Statistical tests for centrosymmetry*

Number of reflexions	Type of reflexions	Limits of $(\sin \theta/\lambda)^2$	Number of groups	Wilson ratio $\langle F ^2 \rangle / \langle I \rangle$	Variance average $\langle (I - \langle I \rangle)^2 \rangle / \langle I \rangle^2$
955	$hk0, hk1, hk2, hk3, hk4$	0.025—0.400	4	0.612	2.04
		Theoretical values	($\bar{1}$)	0.637	2.00
			(1)	0.785	1.00

Table 4. *Atomic co-ordinates of specimen U determined by two-dimensional refinement, compared with those for sanidinized specimen C published by Cole et al. (1949)*

Atom	Number in cell	Sanidinized specimen C			Specimen U		
		θ_1	θ_2	θ_3	θ_1	θ_2	θ_3
K	4	102.85	0	49.65	102.2	1.3	49.6
Si ₁	4	{ 3.5	66.6	80.4	3.5	65.95	82.8
Si _{1'}	4						
Si ₂	4	{ 255.2	42.4	124.0	254.5	42.2	124.8
Si _{2'}	4						
O _{A1}	4	0	53.0	0	0.4	51.0	4.0
O _{A2}	4	228.5	0	102.9	230.8	359.3	100.7
O _{B1}	4	{ 298.0	52.9	80.8	296.1	51.8	85.6
O _{B2}	4						
O _{C1}	4	{ 12.3	111.6	92.7	13.3	111.9	93.45
O _{C2}	4						
O _{D1}	4	{ 64.5	45.7	144.9	64.0	44.7	148.1
O _{D2}	4						

In the above table $\theta_1, \theta_2, \theta_3$ are the angular co-ordinates defined by the expressions $\theta_1 = 360 x/a^\circ, \theta_2 = 360 y/b^\circ, \theta_3 = 360 z/c^\circ$, where x, y, z are the atomic co-ordinates in Ångström units and a, b, c are the axial lengths as given in Table 2. 1° in $\theta_1, \theta_2, \theta_3$ equals 0.0238, 0.0360, 0.0200 Å respectively. Silicon and aluminium atoms are not distinguished. Atoms linked by brackets are equivalent to one another by symmetry in monoclinic sanidine but are non-equivalent in triclinic microcline.

with the theoretical values for centrosymmetry we conclude that a symmetry centre is present and, therefore, that the space group is $C\bar{1}$. We are not prepared, however, to assess the effect on these statistical tests of minor deviations from centrosymmetry such as might arise (for example) from the difference between Si and Al atoms.

3. Two-dimensional refinement

The determination of the structure of specimen *U* can be considered as essentially a refinement of the monoclinic structure of sanidine. The atomic parameters of sanidine have been determined very precisely by Cole *et al.* (1949) and are also listed in Table 4 of this paper. Specimen *U* is slightly triclinic but is sufficiently similar to sanidine in cell dimensions, physical properties and X-ray patterns to justify the assumption of similarity of crystal structure as well. It is likely that the atomic positions are displaced only slightly from those of sanidine. As a result of the change in symmetry from the monoclinic space group $C2/m$ of sanidine to the triclinic space group $C\bar{1}$ of microcline, all symmetry axes and planes of the former are lost. This means that the number of equivalent general positions per set is reduced from 8 to 4 and, therefore, that the 12 Si+4 Al in the unit cell must now be distributed among four non-equivalent sets of tetrahedral positions instead of two sets. The 32 oxygen

atoms must lie on eight different sets of equivalent general positions, and the four potassium atoms on one set. No atoms lie in special positions. The atomic parameters of 13 different atoms must be determined for microcline in contrast to those of 8 atoms for sanidine.

As a starting point the phases to be associated with the experimental structure amplitudes were computed from the sanidine structure. Two-dimensional electron-density projections along the a and c axes were then calculated. Since (010) is expected to be nearly, but not quite, a reflexion plane of symmetry in microcline, projection along the b axis would not be profitable because of partial overlap of atoms which would superimpose exactly in monoclinic symmetry. 192 ($0kl$) reflexions were summed for the projection along the a axis and 228 ($hk0$) reflexions for the projection along the c axis. No artificial temperature factor was employed, except that already present in the Bragg & West (1928) scattering factors used to determine the absolute scale. In the projection made along the a axis only atoms O_{A1}, O_{A2} and K were resolved.* All other atoms overlapped to such a degree that their atomic centres could not be determined with any accuracy. All three of the resolved atoms lie in special positions

* The designation of atoms used in this paper is the same as that used for the triclinic albite structure by Taylor *et al.* (1934).

in the sanidine structure, but in this microcline were found to have shifted slightly away from the monoclinic symmetry elements. The projection along the c axis was more informative in that atoms O_{A2} , O_{C1} , O_{C2} , Si_2 , Si'_2 and K were resolved. Both atoms O_{A2} and O_{C1} have shifted towards Si'_2 , while the overlapping atoms O_{B1} and O_{D2} appear to have shifted away from Si_1 and Si'_1 , relative to their positions in sanidine. This suggests that a concentration of the larger Al atoms in the latter tetrahedral sites may have taken place. The amount of overlap of most atoms was not unexpected. The main purpose of these projections was to derive information as to the heights and shapes of the resolved peaks for use as constants in the correction equations for $(F_o - F_c)$ syntheses.

Starting with the positions determined from the previous two projections, gradual refinement of the structure was achieved by a series of 15 $(F_o - F_c)$ projections parallel to the a and c axes. This type of synthesis gives a map of the actual electron density minus the density given by a set of atoms of known location and scattering power. As a result of this subtraction process the difficulties caused by the overlap of electron density between adjacent atoms and by diffraction ripples due to finite termination of series are minimized. Cochran (1951) has given a correction formula whereby those atoms which are found to lie on gradients of electron density in the difference maps and, therefore, not at their true positions may be moved up slope to their true locations. The F_c values used in the coefficients of these syntheses were calculated manually, using two-figure cosine tables and the Bragg & West (1928) scattering factors of atoms. No distinction was made at first between Si and Al, and 3% albite was assumed to be in solid solution in the microcline. The Fourier syntheses were computed using an IBM Card Programmed Electronic Calculator (CPC, Model I). The control panels were wired so that the electron density at any desired two-dimensional point could be computed by plugging the co-ordinates of the point into one panel and feeding the amplitudes and wave numbers of the series into the tabulator by means of a pack of reflexion cards. Since the series must be summed electronically at each point at which an electron density is desired, the method is not much faster for an entire projection than the hand summation of Beever-Lipson strips. It proved especially convenient, however, for calculating electron-density gradients, for which only a few points in the regions of atomic centres are needed. The co-ordinates of the points could be changed on the control panels by intervals as small as 1° , if desired.

The final atomic parameters selected after completion of the series of $(F_o - F_c)$ syntheses are listed in Table 4. The amount of refinement which had been achieved can be estimated from the decrease of the reliability factor $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. For the $(0kl)$ and $(hk0)$ reflexions, respectively, this factor dropped from initial values of 0.205 and 0.174, based

on F_c values computed from the sanidine atomic sites, to final figures of 0.095 and 0.098. The Si-O interatomic distances calculated from the final two-dimensional atomic sites are listed in Table 5. The mean

Table 5. Si-O *interatomic distances for specimen U, as determined by two-dimensional refinement*

Si ₁	-O _{A1}	1.641 Å	Si' ₁	-O _{A1}	1.733 Å
	-O _{B1}	1.699		-O _{B2}	1.696
	-O _{C1}	1.669		-O _{C2}	1.749
	-O _{D1}	1.656		-O _{D2}	1.684
	Mean	1.666		Mean	1.715
Si ₂	-O _{A2}	1.637 Å	Si' ₂	-O _{A2}	1.620 Å
	-O _{B1}	1.545		-O _{B2}	1.588
	-O _{C2}	1.577		-O _{C1}	1.605
	-O _{D2}	1.637		-O _{D1}	1.623
	Mean	1.599		Mean	1.609

Si-O distances in the tetrahedra around Si_1 and Si'_1 are 1.67 and 1.715 Å, while those in the tetrahedra around Si_2 and Si'_2 are 1.60 and 1.61 Å. The deviations within the Si_2 tetrahedra are too great to put much significance on the mean value, but the precision in the other three tetrahedra is considerably better. The tentative conclusion may be drawn that the larger Al atoms have segregated out of the Si_2 and Si'_2 sites into the Si_1 and Si'_1 sites. In particular, the Si'_1 tetrahedron seems to be a favoured site for Al. The reliability of these two-dimensional results relative to the final three-dimensional values will be discussed in § 6.

During the course of the refinement it was noticed that the centre of the K atom was always located in a hollow of negative electron density. On the assumption that this meant a higher percentage of albite in solid solution in the microcline, the scattering factor for K was reduced accordingly for the later F_c calculations. Since the $(F_o - F_c)$ maps constructed at this time were computed for only small regions around the atomic centres, however, it was not possible to see the entire shape of the K peak. Later three-dimensional syntheses showed the observed peak to be both lower and broader than the calculated peak. This is probably due to a larger temperature factor for the K atom, a point which will be discussed in more detail in § 6

4. Three-dimensional refinement

Further refinement of the structure was carried out by means of standard three-dimensional section and line Fourier syntheses. For this purpose the phases of all reflexions were calculated from the atomic sites determined by two-dimensional refinement. A highly efficient method involving use of the CPC unit was developed for this computation, calculating F_c values for 3,700 reflexions in 10 hr. In this operation the atomic parameters were placed in storage in the unit, and the control panels were wired to perform the computation

Table 6. Co-ordinates of three-dimensional sections and lines

Section	θ_3	Line	θ_1	θ_2	Line	θ_1	θ_2	
First set	1*	86.0	1*	230.8	0	8*	254.5	45.0
	2*	123.5	2*	102.2	0	9*	245.2	135.0
	3*	146.0	3*	3.5	65.5	10*	75.6	135.0
	4*	4.0	4*	192.4	65.5	11*	183.6	112.6
	5	50.0	5*	0	51.4	12*	13.3	112.6
	6	100.0	6*	296.1	51.4	13*	115.9	128.0
Second set	7*	81.0	7*	64.0	45.0			
	8*	93.0						
	9*	102.5						

In the above table $\theta_1, \theta_2, \theta_3$ are angular co-ordinates as defined in Table 4. Back syntheses were computed for the sections and lines marked by asterisks (*).

$$F_c(hkl) = 4 \sum_{n=1}^{13} f_n \cos [2\pi(hu_n + kv_n + lw_n)].$$

The index and scattering-factor data were coded on individual reflexion cards, and the atomic parameters (u, v, w) were called out of storage as needed during the computation. The scattering factors of the Si atoms were slightly altered for the calculation. Si_2 and Si'_2 were given the scattering powers of pure silicon, while Si_1 and Si'_1 were given factors corresponding to $Si_1Al_{1/2}$. The tentative scattering curve constructed for potassium was parallel to that of Bragg & West but reduced in height by 16%. Both silicon (and aluminium) and oxygen were assumed to be 50% ionized and potassium completely ionized. At this point the $f(\theta)$ curve shown in Fig. 2 was constructed, and all F_o values were converted to an absolute scale. On the basis of all observable reflexions the reliability factor R_1 is 0.154.

The first set of three-dimensional sections and lines consisted of six sections parallel to (001) and thirteen lines parallel to the c axis at co-ordinates listed in Table 6. The computations were carried out at 3° intervals over one half of the unit cell by the method described by Hodgson, Clews & Cochran (1949),

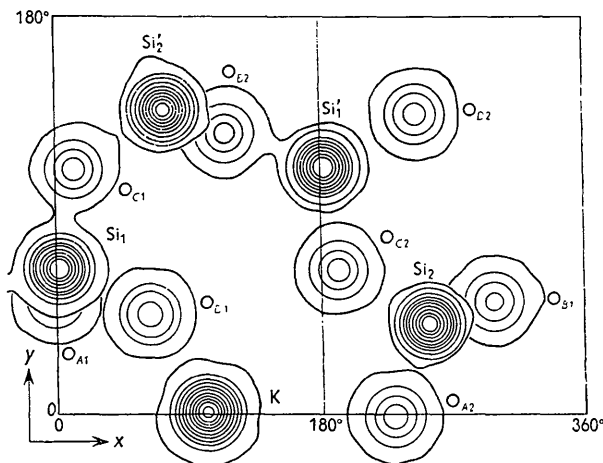


Fig. 4. Maxima of the first set of three-dimensional sections superimposed on (001). Contours are drawn at arbitrary intervals of 1000 units starting at 500, where one unit equals $0.00278 \text{ e.}\text{\AA}^{-3}$.

modified to allow machine sorting. All observed reflexions were used but 240 of the weaker reflexions of doubtful accuracy were given reduced weight by replacing the original F_o values by $wF_o + (1-w)F_c$, where w is the weight factor. Three of the highest-intensity reflexions were replaced by their F_c values ($w = 0$), to take into account possible extinction effects. To reduce the diffraction effects due to finite termination of series an artificial temperature factor was applied to all reflexions by multiplying the F_o values by $\exp[-B(\sin \theta/\lambda)^2]$. The value $B = 4.0 \text{ \AA}^2$ was chosen as large enough to reduce the observed structure amplitudes of highest $(\sin \theta/\lambda)^2$ values to nearly zero but not so large that it would cause serious overlapping by spreading out the electron densities of the atoms.

The contoured maps of the first set of three-dimensional sections and lines showed all atoms well resolved and symmetrical but with small ripples of negative electron density still present. Fig. 4 shows the maxima of all the sections superimposed on (001). The positions of the electron-density maxima were determined by a graphical modification of the parabola method of Booth (1948), and the true atomic parameters were then derived by the method of Parry & Pitt (1949). Calculation of the Si-O distances showed a great improvement in the precision within each tetrahedron, but with several values still deviating from the mean by 0.01–0.02 Å.

A new set of F_c values was calculated on the basis of the new atomic parameters, and three additional sections (Table 6) were computed. This second set of sections was selected to pass closer to the centres of six of the atoms than did the first set and, in particular, to derive better values for the atoms of greatest deviation from the mean Si-O distances. The signs of 18 of the weaker reflexions were changed as a result of the new F_c values, and weighting factors were applied to 120 additional reflexions. The changes in atomic parameters and the improvement in the precision of the Si-O values as a result of the second set of sections proved to be small, leading to the conclusion that further refinement by this approach would not be worth the labour involved. It seemed likely that the deviations existing in the Si-O bond lengths at this stage were due primarily to shifts in the electron-

density maxima as a result of incomplete removal of the finite termination-of-series effects and of distortion due to the artificial temperature factor used. The reliability factor calculated on the basis of a new set of F_c values was 0.138. Although the atomic parameters and resulting Si-O distances at all the stages of the refinement procedure are not included in this paper for reasons of brevity, they may be found in the reference by Bailey (1954) along with a complete listing of the experimental F_o values and the F_c values obtained at this stage.

Corrections for the remaining diffraction effects and the overlapping of electron-density peaks were applied by means of the back-synthesis method of Booth (1946, 1947). Seven three-dimensional sections and thirteen lines (Table 6) were computed, using F_c values as coefficients and retaining the same artificial temperature factor. Since the F_c values used as coefficients here were obtained as a result of two sets of F_o sections and computed at slightly different co-ordinates, the back-synthesis results are not strictly valid as corrections to either set. The error involved, however, is not believed to be large. The final atomic parameters are listed in Table 7, and the interatomic bond lengths and angles calculated from these values are listed in Table 8.

5. Accuracy of results

Cruickshank (1949) has recommended that statistical significance tests be applied to any measurements which are subject to error before attempting to compare their values. We have evaluated the standard

deviation of errors in atomic parameters and Si-O distances and have applied the significance levels suggested by Cruickshank. We have assumed the final results to be free from finite-summation errors and, therefore, have considered only the magnitudes of the experimental and computational errors. In doing this we have assumed specimen *U* to be monoclinic for ease of computation and have evaluated the experimental errors only in the *y* direction, since the standard deviations should be the same in all directions for spherically symmetric atoms. The experimental error is a function of the error present in the structure amplitudes. Use of $\Delta F = F_o - F_c$ in the past as an estimate of the structure-amplitude error has led to over-estimates of the experimental error since the value of ΔF is influenced by several factors which do not affect atomic positions. We have followed an alternative procedure suggested by Lipson & Cochran (1953), using the expression

$$\sigma(y_n) = \{(\delta D/\delta y)^2\}^{1/2}/C_n,$$

where $\sigma(y_n)$ is the standard deviation of the error in position of a given atom along the *y* direction, $\delta D/\delta y$ is the slope in the *y* direction of a map of type $D = \rho_o - \rho_c$, and C_n is the central curvature of the electron-density peak of the atom. To evaluate this expression, values of D were obtained by subtracting ρ_c of the back syntheses from ρ_o of the regular syntheses. Average values of the slope of D were then taken over all points in the seven sections where the expected value of the electron density was zero. Corroborating figures for the experimental error were obtained by assuming the error in the structure amplitude to be a

Table 7. *Final atomic co-ordinates of specimen U, as determined by three-dimensional sections and lines and corrected by back syntheses*

Atom (notation as in earlier feldspar papers)	θ_1	θ_2	θ_3	<i>u</i>	<i>v</i>	<i>w</i>	Atom (proposed systematic notation)
K	102.32	1.19	49.88	0.2842	0.0033	0.1386	K
Si ₁	3.31	66.11	82.04	0.0092	0.1836	0.2279	Si ₁ (<i>o</i>)
Si ₁ '	183.43	112.91	79.95	0.0095	0.8136	0.2221	Si ₁ (<i>m</i>)
Si ₂	254.45	41.72	124.61	0.7068	0.1159	0.3461	Si ₂ (<i>o</i>)
Si ₂ '	75.21	137.52	123.37	0.7089	0.8820	0.3427	Si ₂ (<i>m</i>)
O _{A1}	0.11	52.28	2.39	0.0003	0.1452	0.0066	O _A (1)
O _{A2}	230.00	359.51	102.98	0.6389	0.9986	0.2861	O _A (2)
O _{B1}	298.25	52.04	84.68	0.8285	0.1446	0.2352	O _B (<i>o</i>)
O _{B2}	116.21	127.88	80.12	0.8228	0.8552	0.2226	O _B (<i>m</i>)
O _{C1}	13.45	111.24	94.68	0.0374	0.3090	0.2630	O _C (<i>o</i>)
O _{C2}	192.21	66.22	91.71	0.0339	0.6339	0.2548	O _C (<i>m</i>)
O _{D1}	63.63	45.51	147.80	0.1767	0.1264	0.4106	O _D (<i>o</i>)
O _{D2}	246.20	135.76	146.26	0.1839	0.8771	0.4063	O _D (<i>m</i>)

In the above table $\theta_1, \theta_2, \theta_3$ are angular coordinates as defined in Table 4, and *u, v, w* are fractional coordinates. For atoms Si₁', Si₂', O_{B2}, O_{C2}, O_{D2} the values of *u, v, w* correspond to atoms having angular coordinates $\pm 180^\circ + \theta_1, 180^\circ + \theta_2, \theta_3$, the \pm sign being chosen so that the atom lies within the unit cell. For all other atoms the values of *u, v, w* correspond to the values of $\theta_1, \theta_2, \theta_3$.

Comparison with atomic positions given in Table 4, and with feldspar structures previously determined, is facilitated by the use of the angular coordinates $\theta_1, \theta_2, \theta_3$. The atoms chosen for representation in Fig. 4 correspond to the use of these angular coordinates.

The symbols shown in the last column are in harmony with the systematic notation for feldspar structures which it is proposed to introduce (Megaw, in preparation). The selection of appropriate representative atoms from each of the equivalent groups previously named Si₁', Si₂', O_{B2}, O_{C2}, O_{D2} is as required by the rules governing the use of the systematic notation.

Table 8. *Final interatomic distances and angles for specimen U*

Interatomic distances in Ångström units												
Si-O				K-O								
Si ₁		Si ₁ '		Si ₂		Si ₂ '		K				
O _{A1}	1.643	O _{A1}	1.697	O _{A2}	1.611	O _{A2}	1.618	O _{A1}	2.882	2.897	O _{C1}	3.209
O _{B1}	1.646	O _{B2}	1.698	O _{B1}	1.608	O _{B2}	1.607	O _{A2}	2.758	(3.405)	O _{C2}	3.054
O _{C1}	1.644	O _{C2}	1.698	O _{C2}	1.609	O _{C1}	1.616	O _{B1}	3.096		O _{D1}	2.985
O _{D1}	1.647	O _{D2}	1.705	O _{D2}	1.614	O _{D1}	1.615	O _{B2}	3.105		O _{D2}	2.920
Mean	1.645	Mean	1.700	Mean	1.611	Mean	1.614					

O-O							
Si ₁		Si ₁ '		Si ₂		Si ₂ '	
O _{A1} -O _{B1}	2.650	O _{A1} -O _{B2}	2.690	O _{A2} -O _{B1}	2.603	O _{A2} -O _{B2}	2.624
O _{A1} -O _{C1}	2.744	O _{A1} -O _{C2}	2.834	O _{A2} -O _{C2}	2.552	O _{A2} -O _{C1}	2.577
O _{A1} -O _{D1}	2.640	O _{A1} -O _{D2}	2.704	O _{A2} -O _{D2}	2.613	O _{A2} -O _{D1}	2.630
O _{B1} -O _{C1}	2.714	O _{B2} -O _{C2}	2.830	O _{B1} -O _{C2}	2.649	O _{B2} -O _{C1}	2.650
O _{B1} -O _{D1}	2.700	O _{B2} -O _{D2}	2.794	O _{B1} -O _{D2}	2.647	O _{B2} -O _{D1}	2.656
O _{C1} -O _{D1}	2.665	O _{C2} -O _{D2}	2.795	O _{C2} -O _{D2}	2.703	O _{C1} -O _{D1}	2.673
Mean	2.686	Mean	2.775	Mean	2.628	Mean	2.635

Interatomic angles			
O-Si-O		Si-O-Si	
O _{A1} -Si ₁ -O _{B1}	107° 20'	O _{A1} -Si ₁ '-O _{B2}	104° 44'
O _{A1} -O _{C1}	113° 12'	O _{A1} -O _{C2}	112° 59'
O _{A1} -O _{D1}	106° 44'	O _{A1} -O _{D2}	105° 14'
O _{B1} -O _{C1}	111° 10'	O _{B2} -O _{C2}	112° 45'
O _{B1} -O _{D1}	109° 48'	O _{B2} -O _{D2}	109° 45'
O _{C1} -O _{D1}	104° 42'	O _{C2} -O _{D2}	110° 22'
Mean	108° 49'	Mean	109° 18'
O _{A2} -Si ₂ -O _{B1}	107° 58'	O _{A2} -Si ₂ '-O _{B2}	108° 55'
O _{A2} -O _{C2}	104° 52'	O _{A2} -O _{C1}	105° 37'
O _{A2} -O _{D2}	108° 16'	O _{A2} -O _{D1}	108° 52'
O _{B1} -O _{C2}	110° 54'	O _{B2} -O _{C1}	110° 35'
O _{B1} -O _{D2}	110° 29'	O _{B2} -O _{D1}	111° 02'
O _{C2} -O _{D2}	114° 01'	O _{C1} -O _{D1}	111° 39'
Mean	109° 25'	Mean	109° 27'

constant percentage of $|F_o|$ and applying the expression (Lipson & Cochran, 1953)

$$\sigma(y_n) = \frac{K}{\sqrt{2} \cdot Z_n} \left(\frac{\pi}{2p} \right)^{\frac{1}{2}} \left(\frac{1}{V} \sum_{n=1}^N Z_n^2 \right)^{\frac{1}{2}},$$

where K is the constant percentage, V is the volume of the unit cell, Z_n is the atomic number of the atom involved, and p is a function of the atomic shape. The results, using $K = 0.10$ and 0.15 , are set out in Table 9 and may be seen to bracket the values obtained by the previous method.

Rounding off results during the course of computation also gives rise to small errors which can be estimated by considering the details of the method of summation and the method of determining the positions of the electron-density maxima. When the three-point parabola method is used to obtain the positions of the maxima the expression

$$\sigma(q) = \frac{\sqrt{3}}{2n} \sigma(\rho) / C_n$$

is valid, where $\sigma(q)$ is the standard deviation of the error in position of a maximum, $\sigma(\rho)$ is the standard deviation of the error in the electron density, and n is the summation interval in Ångström units. After $\sigma(\rho)$ has been evaluated by considering the rounding-off errors during summation, $\sigma(q)$ may be converted into values of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ for any atom by substituting the appropriate values of the curvature and summation interval into the expression. The results listed in Table 9 show that computational errors are negligible when compared with the experimental errors.

Cruckshank has defined P as the probability that by chance a bond length A could be observed as greater than bond length B by at least δl , although really equal to B . He has suggested certain significance levels for use when comparing bond lengths, and for a Gaussian distribution of random errors these may be reduced to:

$$P > 5\%, \quad \delta l / \sigma < 1.645, \quad \text{difference not significant};$$

Table 9. *Analysis of accuracy of results for three-dimensional syntheses of specimen U*

	Experimental errors $\sigma(y_n)$		Details of atom peaks ($B = 4.0 \text{ \AA}^2$)			
	O	Si	Atom	$-C_n$ (e. \AA^{-5})	p	Z
(a) From $D = \rho_o - \rho_c$ map	0.0080 \AA	0.0024 \AA	O (average)	100.75	4.66	8
			Si (average)	334.60	6.28	14
			K	334.69	5.58	19
(b) $\sigma(F_o) = K F_o $ with						
K = 10%	0.0067	0.0028				
K = 15%	0.0100	0.0042				
Average $\sigma(y)$	<u>0.0082</u>	<u>0.0031</u>				
	Computational errors		Total error			
	O	Si	$\sigma(r)$ (O)	0.0083 \AA		
$\sigma(x)$	0.0017 \AA	0.0005 \AA	$\sigma(r)$ (Si)	0.0031		
$\sigma(y)$	0.0011	0.0003	σ (Si-O)	0.0088		
$\sigma(z)$	0.0017	0.0005	$\sigma = \sqrt{2} \cdot \sigma$ (Si-O)	0.0124		
Average	<u>0.0015</u>	<u>0.0004</u>				

5% > P > 1%, $2.327 > \delta l/\sigma > 1.645$,
difference possibly significant;

1% > P > 0.1%, $3.090 > \delta l/\sigma > 2.327$,
difference significant;

$P < 0.1\%$, $\delta l/\sigma > 3.090$,
difference highly significant;

where $\sigma^2 = \sigma^2(A) + \sigma^2(B)$. For specimen U we have $\sigma = 0.0124 \text{ \AA}$ (Table 9), and by applying these significance-level tests to the differences in the mean Si-O bond lengths of the four non-equivalent tetrahedra (Table 8) we find that all differences are significant or highly significant except the minor difference between the Si_2 and Si'_2 tetrahedra:

$$\text{Si}_2 - \text{Si}'_2: \delta l/\sigma = 0.003/0.0124 = 0.242;$$

$$\text{Si}_2 - \text{Si}_1: \delta l/\sigma = 0.0325/0.0124 = 2.621;$$

$$\text{Si}_2 - \text{Si}'_1: \delta l/\sigma = 0.0875/0.0124 = 7.056;$$

$$\text{Si}_1 - \text{Si}'_1: \delta l/\sigma = 0.0550/0.0124 = 4.435.$$

6. Discussion of results

We have translated our mean Si-O bond lengths into relative contents of Si and Al by use of Smith's (1954) linear graph of (Si, Al)-O distance versus tetrahedral composition:

Tetrahedron	Mean bond length	Al-content
Si_1	1.645 \AA	0.25
Si'_1	1.700	0.56
Si_2	1.611	0.07
Si'_2	1.614	0.08
	Total	<u>0.96</u>

The results are consistent with the total of one Al which must be present for each three Si in the unit cell. We conclude that this microcline is partially ordered with respect to Si and Al. Relative to sanidine, with a statistical distribution of $\frac{1}{4}\text{Al} + \frac{3}{4}\text{Si}$ in each tetrahedron, the aluminium atoms have migrated almost completely out of the Si_2 and Si'_2 tetrahedra into the Si'_1 site. The Si_1 tetrahedron retains the sanidine distribution of

$\frac{1}{4}\text{Al} + \frac{3}{4}\text{Si}$. Partial ordering in specimen U is in accord with our placement of the sample as intermediate in the microcline series, and strongly suggests that the variation in cell angles between different microclines is due primarily to variation in the degree of order. This view is supported by the larger refractive indices and optic angles of the maximum microclines, and suggests that such minerals have all the aluminium concentrated in one tetrahedron. Further work is in progress on the microcline series. The structures of both sanidine and microcline now have been examined in considerable detail. We regard the evidence which has been provided by these investigations as definite proof that the polymorphism of these two minerals is a result of an order-disorder relationship between Si and Al.

As might be expected, the O-O distances in specimen U differ with the tetrahedra involved. Table 8 shows greater O-O bond lengths in the two tetrahedra, Si_1 and Si'_1 , which contain appreciable percentages of Al. As in other feldspars, the co-ordination of oxygen around potassium is very irregular. There are nine closest neighbours at distances ranging from 2.758 to 3.209 \AA . A tenth oxygen is somewhat more distant at 3.405 \AA . The predominance of packing considerations over charge in controlling the co-ordination is illustrated by the fact that the closest neighbour is O_{42} , as in sanidine and common orthoclase. O_{42} is the only oxygen bonded to two nearly pure Si atoms, Si_2 and Si'_2 , and therefore can contribute little or no bond to potassium.

The three-dimensional syntheses show that the observed electron-density peak for potassium is considerably broader than the peak calculated from the Bragg & West scattering factor for potassium, although the heights were made to agree by scaling down the latter on a percentage basis. The observed and calculated peaks for both silicon and oxygen, on the other hand, are in close agreement. Cochran (1953) has devised a method for checking the electron content corresponding to any theoretical scattering-factor curve, and we have applied his technique to test the

correctness of the Bragg & West scattering factors as well as the factors for the same atoms as given by James & Brindley (1931). We have sampled the scattering curves at an interval 0.1 in $\sin \theta/\lambda$, multiplying the values by a temperature factor $\exp[-4(\sin \theta/\lambda)^2]$. Substitution of these modified f values in a Fourier series has given the electron contents listed in Table 10. The Bragg & West f values are admittedly empirical, being those found to work best in the analysis of several silicate structures. Table 10 shows that the electron contents for the

Table 10. *Electron contents derived from theoretical f curves*

Atom	Bragg & West (1928)	James & Brindley (1931)	
O (8)	8.9	O (neut.)	8.05
Si (14)	12.0	{ Si (neut.)	12.6
Al (13)	11.4	{ Si ⁺²	11.8 ₅
K (19)	19.3	{ Al (neut.)	12.4
Na (11)	10.3	{ K ⁺¹	18.3 ₅
Ca (20)	19.8	{ Na (neut.)	10.3 ₅
Mg (12)	11.5 ₅	{ Na ⁺¹	10.1
Fe (26)	25.4	{ Ca ⁺²	18.4
F (9)	9.7	{ Mg ⁺²	11.2
Cl (17)	17.3	{ F ⁻¹	9.7
		{ Cl ⁻¹	17.4 ₅

In the above table the atomic number of each atom is listed in parentheses.

O, Si and Al atoms are those corresponding to 50% ionized atoms, a state which is not unreasonable in silicates. The f values listed by Bragg & West for many of the other atoms, however, do not correspond to total electron counts which are consistent with our knowledge of the degree of ionization in silicates. For example, although the numbers of electrons determined from the f values of Na and F approximate to the numbers in the monovalent ions, those determined from K, Ca, Mg, Fe and Cl are closer to the numbers contained in the neutral state. The f values given by James & Brindley for Si(neut.), Al(neut.), Na(neut.), Mg⁺², and Cl⁻¹ also must deviate in some manner from the true scattering factors. We are especially

interested in potassium, and since the James & Brindley curve calculated from the Hartree model yields a more reasonable electron content than that given by Bragg & West we have used the former for our further investigation of the potassium peak.

Fig. 5(a) contrasts a profile through potassium for the observed two-dimensional electron-density maximum with that calculated using the Bragg & West scattering factors for Si and O and the James & Brindley factors for K. It was found that the observed peak could be approximated closely by multiplying the James & Brindley f values for K by a temperature factor of the form $\exp[-B(\sin \theta/\lambda)^2]$ with $B=1.0 \text{ \AA}^2$. This value is considerably larger than the temperature factor incorporated in the Bragg & West curves, and indicates a larger thermal vibration for K than for its neighbours. This is not unreasonable in view of the weak and irregular co-ordination of K in the feldspar structure. It should be equally true in other feldspars, and an even greater vibration might be expected in a high-temperature form, such as sanidine. As a check on this point, profiles through K were computed in exactly the same manner for sanidine (Fig. 5(b)). The $(0kl)$ intensity data published by Cole *et al.* were used to compute the observed profile. Although both sanidine peaks are smaller than those of microcline, owing to the use of fewer reflexions in the syntheses, a considerably larger temperature factor of $B = 1.9 \text{ \AA}^2$ was required to scale down the shape of the calculated peak to that of the observed peak. There was no evidence of anisotropic thermal vibration in either sanidine or microcline.

Detailed electron counts have not been attempted for any of the microcline syntheses. Our electron-density maps still have small diffraction ripples present which make it difficult to decide on the exact allocation of density. Somewhat smaller ripples in the case of sanidine proved to give erratic electron counts. This uncertainty would tend to mask the small differences to be expected from Al versus Si with which we are primarily concerned in this paper. It should be noted at this point that there were no significant differences in any of the peak heights themselves for the four non-equivalent Si atoms.

It is interesting to note that in all feldspars whose structures have been examined in any detail the tendency for ordering always has been to concentrate the Al in the Si₁ or Si₁' tetrahedra rather than in Si₂ or Si₂'. Thus, we have found a primary concentration of Al in the Si₁' site for specimen *U* with lesser amounts in Si₁. The inconclusive structure of common orthoclase (Chao, Hargreaves & Taylor, 1940) was interpreted as a segregation of Al in the Si₁ tetrahedra (Si₁ and Si₁' are equivalent in monoclinic symmetry), although, as Cole *et al.* have noted, this may or may not be a valid conclusion. Further work on orthoclase is now under way in this laboratory. Likewise in the plagioclase feldspars, Sörum (1953) has found the Al concentrated almost equally in the Si₁ and Si₁' sites of a 72% An

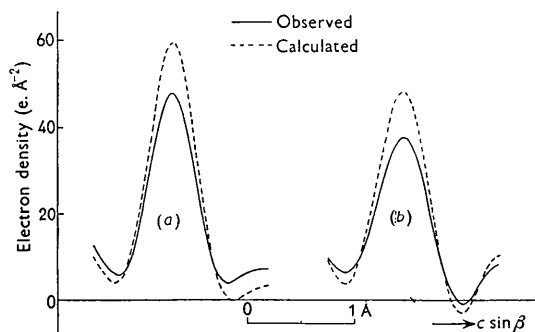


Fig. 5. Profiles through the observed and calculated two-dimensional electron-density maxima of the potassium atom for (a) specimen *U* using all $(0kl)$ reflexions, (b) sanidinized specimen *C* using the $(0kl)$ data of Cole *et al.* (1949).

specimen. Other structure analyses now in progress should prove whether or not this trend is real. In the case of specimen *U* the increased size of the Si_1' tetrahedron has been accommodated by the concordant contraction of the neighbouring Si_2 and Si_2' tetrahedra and by a slight shift of the whole Si_1 tetrahedron parallel to the *c* axis. In the feldspar structure there are chains of linked tetrahedra running parallel to the *a* axis. Adjacent chains are joined to one another in the *b* and *c* directions by the O_{A2} and O_{A1} atoms respectively. As a result of this linkage, O_{A2} is common to two tetrahedra, Si_2 and Si_2' , which are orientated parallel to *b*, while O_{A1} is common to the Si_1 and Si_1' tetrahedra, which are orientated parallel to *c*. Concentration of Al in the Si_1 and Si_1' tetrahedra and of Si in the Si_2 and Si_2' tetrahedra, therefore, results in an increase in the *c* axial length and a decrease in the *b* axial length relative to the disordered state. This in itself may be a useful indicator of the locus of Al concentration. It is noteworthy that an exactly similar relationship in axial lengths has been recorded by Cole *et al.* for specimen *C* and its sanidinized equivalent and by Laves (1952) for albite and analbite, the sodium analogues.

In view of the revised bond length determined for Al–O by recent workers, Smith (1954) has suggested that it may be possible to detect Si–Al ordering by two-dimensional Fourier syntheses and avoid the great labour of three-dimensional methods. As a test of this we can compare the results of the various stages of refinement of the structure of specimen *U*. The mean Si–O distances in the four tetrahedra are

	Two- dimensions	Three- dimensions	Difference
Si_1	1.666 Å	1.645 Å	0.021 Å
Si_1'	1.715	1.700	0.015
Si_2	1.599	1.611	0.012
Si_2'	1.609	1.614	0.005
		Mean	0.013

The two-dimensional results are valid in that they also indicate partial ordering of Si–Al, although the absolute values may be in error by a maximum of 0.02 Å. The average difference is 0.013 Å, corresponding to a tetrahedral composition difference of 0.07 Al. Careful two-dimensional refinement, therefore, should detect ordering of Si–Al, provided the degree of order or the Si:Al ratio is such that an error of 0.01–0.02 Å will not be significant.

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