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Electrostatic Charge Distributions in the Structure of Low Albite, NaAlSi₃O₈

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(Received 15 August 1968 and in revised form 28 October 1968)

Computer programs are described which calculate the positive charges contributed by the metallic cations to the surrounding oxygen anions in the low albite, NaAlSi₃O₈, structure. The unknown variables are taken to be the assumed pure Si-O and Al-O distances, and the coordination number of the sodium ion. The charges are distributed in amounts that are inversely proportional to the cation-anion distances. The most satisfactory charge distribution occurs when Si-O = 1.602 (± 0.002), Al-O = 1.777 (± 0.003) Å and C.N. = 6 for Na (single atom); the total charges on the four tetrahedral groups of oxygen ions are then: 8.007, 7.999, 8.001 and 7.995 e.s.u. (σ = 0.01₂ e.s.u.) giving a total 'charge unbalance' of 0.014 e.s.u. (σ = 0.02₄ e.s.u.) and a total Al content of 1.000 atoms (σ = 0.005). It is concluded that the crystal is ideally ionic and that the structure is 'largely ordered' with 82% Al in one site. It is thought that the small integral C.N. for the Na ion may have important implications for the nature of ionic bonding. An Appendix gives the derivation of relationships for determining the proportion of an oxygen atom shielded by closer atoms from a Na ion.

I. THEORETICAL CONSIDERATIONS AND METHOD

Introduction

The feldspar minerals which are mainly KAlSi₃O₈-NaAlSi₃O₈-CaAl₂Si₂O₈ are characterized by polymorphism which is now known to be due to silicon-aluminum (Si-Al) 'order-disorder'. High-temperature forms such as high albite (NaAlSi₃O₈) and sanidine (KAlSi₃O₈), analysed by three-dimensional methods in the 'quenched' state at room temperature, have disordered structures with the Si-Al atoms distributed randomly among the tetrahedral sites. In contrast, feldspars that are generally accepted from geological evidence to be low-temperature forms (cooled slowly to ordinary temperatures) such as low albite (NaAlSi₃O₈) and microcline (KAlSi₃O₈), also analysed by three-dimensional methods, are known to have structures in which the Si and Al atoms are segregated into structurally different tetrahedral sites.

The generally accepted view is that in low-temperature feldspars such as low albite and (maximum) micro-

cline, the Si and Al atoms are completely segregated, that is, the structures are fully ordered with respect to Si-Al. A dissenting view was put forth by Ferguson, Traill & Taylor (1958), who proposed that in such low-temperature feldspars the Si and Al atoms may not be completely segregated; in this case these structures would be only largely and not fully ordered with respect to Si-Al. The basis for this view was an interpretation of the structures as ionic, that is, that the atoms behave as ions and that therefore the most likely low-temperature feldspar would be, in general, the one with the most satisfactory electrostatic charge distribution. It can be shown that such a structure cannot have the Si and Al atoms fully ordered; in the case of low albite, for example, Ferguson *et al.* showed in 1958 that the ideal ionic structure has the Al atoms segregated to only about 75% into one site.

This ionic interpretation appeared to the authors (Ferguson, Traill & Taylor, 1958) to explain a number of the structural features of the feldspars, and in a later paper Ferguson (1960) extended these ideas particularly with reference to the alkali feldspar phase relationships implied by the ionic interpretation of the structures. However, exception to these views was taken by a number of authors, for example, MacKenzie & Smith

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(1959) (answered by Ferguson, Traill & Taylor, 1959), Laves & Goldsmith (1961), Brown & Bailey (1964), and Appleman & Clark (1965). Of the original authors, Ferguson in particular felt that these objections did not invalidate the basic hypothesis of an ionic interpretation of the feldspar structures, and he felt the ideas were worth pursuing. The publication since 1960 of three-dimensional refinements of several feldspar structures, and the close association with an interested colleague (R.I. Gait) led Ferguson to resume development of these ideas, the first phase of which is described here.

The approach and the complications

The work reported in this paper represents the first stage in an attempt to interpret all the main feldspar structures in terms of Pauling's well-known principles or rules governing the structures of ionic crystals (Pauling, 1929, 1960). The results for low albite are encouraging, and similar work on other feldspar structures will indicate whether Pauling's principles may be applied rigorously to all the feldspars and possibly to the silicate structures generally. Calculations on other feldspar structures are in progress.

When a structure is interpreted in terms of Pauling's rules, it is considered to consist of an assemblage of linked polyhedra of anions about cations; the atoms are thus regarded as ions, and the bonding force is considered to be the electrostatic force of attraction between the oppositely charged ions. Furthermore, the valency of a given cation is regarded as being divided equally among the surrounding anions, and the configuration of a given structure is considered to be the one with minimum potential energy. One can then think of a given cation-anion bond as having an 'electrostatic bond strength' of z/n where $+ze$ is the charge on the cation and n is the number of surrounding anions. Pauling's second rule (of five) is the most important in the present context, and it may be stated thus (Evans, 1964):

In a stable coordinated structure the total strength of the valency bonds which reach an anion from all the neighbouring cations is equal to the charge on the anion.

The application of this rule to a simple structure such as NaCl gives an electrostatic bond strength from the Na^+ cation to each of its six surrounding Cl^- anions of $+1/6$ e.s.u. so that each Cl^- anion receives a total of $+6/6$ e.s.u. from its six surrounding Na^+ cations, in conformity with the second rule.

When, however, this second rule is to be applied to more complex structures such as the feldspars, three kinds of complications may arise:

(1) If a cation is surrounded irregularly by anions (oxygen) as is the large cation (Na^+ , K^+ , etc.) in all the feldspars structures, the number of anions receiving charge from the cation, that is, the coordination number of the cation, is uncertain.

(2) For a given cation-anion polyhedron, if some or all of the cation-anion distances are unequal, as is

the case in the feldspar structures for any coordination number of the large cation, the question arises as to whether the cationic charge should be distributed among the coordinated anions (i) equally, or (ii) by invoking Coulomb's Law, namely, inversely as the squares of these distances.

(3) In aluminosilicates such as the feldspars where Si and Al may statistically occupy the same tetrahedral site, the proportion of each within a given site may be derived from the 'size' (mean tetrahedral cation-oxygen ($T-O$) distance) of the site provided the pure Si-O and Al-O distances are known. The problem is to know which pure Si-O and Al-O distances one should take for a given feldspar structure. The particular values taken determine the proportions of Si and Al that statistically occupy one tetrahedral site, and the derived (Si, Al)-content of a tetrahedron determines the effective positive charge on that site.

The method

Our method is to calculate for a given feldspar structure the positive charges distributed to the oxygen anions by the metallic cations for a number of reasonable values of the three uncertain factors – the pure Si-O distance, the pure Al-O distance, and the large cation coordination – and to see whether any combination of these yields a 'charge unbalance' of virtually zero on the whole structure of the low-temperature feldspar. If a combination of the uncertain factors can be shown to yield a near-zero charge unbalance, then we accept this low charge unbalance value as strong evidence in support of our assumptions, namely that the atoms do behave as ions (which is implicit in the Pauling approach), and that the particular Si-O and Al-O distances and the large cation coordination are valid for the structure in question.

The 'charge unbalance' of a structure might be expected to be the sum of the differences from exactly 2 e.s.u. of the positive charges contributed to each structurally different oxygen anion. However, the change from a high-temperature to a low-temperature feldspar structure involves the interchange of tetrahedrally coordinated Si^{4+} and Al^{3+} cations, and thus the oxygen anions will be affected in tetrahedral groups of four rather than individually. For this reason the charge unbalance is taken to be the sum of the differences from exactly 8 e.s.u. of the positive charges contributed to each structurally different tetrahedral group of four oxygen ions.

The manner in which the three complications described earlier were dealt with in the case of low albite are described in the following section.

(1) The coordination number of Na

In simple structures Na is often 6-coordinated, but in complicated structures it is usually surrounded irregularly by anions and it is difficult to say whether its coordination number is 5, 6, 7 or higher. If one thinks

of the large cation (Na^+) as simply a positively charged sphere, then one would expect the cation–oxygen (Na-O) bonds to be non-directed, and the positive charge from the cation (Na^+) to be distributed to all surrounding oxygen anions in amounts that take account in some way of the proportion of an oxygen anion ‘exposed’ to the cation. We considered this possibility, and with the help of Dr H. R. Coish of the Department of Physics of the University of Manitoba, derived angular relationships which were used to compute a ‘shielded fraction’ for any oxygen atom, this being the proportion of the oxygen atom shielded in relation to the centre of the cation, by other closer oxygen and/or sodium atoms. As one might expect, the shielded fractions of the oxygen atoms increase in a general way with increasing cation–oxygen distance, and for low coordinations of the cation, all the oxygen atoms would likely have negligible shielded fractions; in the case of low albite, the shielded fractions of the closest five oxygen atoms to Na are zero, and of the next four closest are <7%. Although the Na coordination in low albite proves to be 6 and the shielded fractions of the oxygen atoms are therefore of negligible importance, we feel it is worth putting on record our method of deriving the shielded fractions (see Appendix) because they constitute an essential aspect of one of our conclusions, namely that the large cation (Na^+) does not behave as a charged sphere in the sense of contributing charge to all the anions ‘exposed’ to it, but rather it has a definite integral coordination.

In order to include all reasonable possibilities, the charge distributions in low albite were computed for Na coordinations from about 4 to 17 (for several given Si–O and Al–O values), with account being taken of the shielded fractions of the oxygen atoms and, as described immediately below, of the Na–O distances.

(2) The variation in cation–oxygen distances

We agree with other authors, for example Jones & Taylor (1961) and Brown & Bailey (1964) that, in calculating the charge distribution in a feldspar, account should be taken in some way of the different cation–oxygen distances. Because the force of attraction is regarded as Coulombic, the positive charge on the cation was distributed to the anions inversely as the squares of the cation–oxygen distances. This was done not only for the Na–O polyhedra but also for the (Si, Al)–O or T–O tetrahedra for some of which there are marked variations in individual T–O lengths.

(3) The assumed pure Si–O and Al–O values

As early as 1940, Chao, Hargreaves & Taylor (1940) applied to a feldspar structure (orthoclase) the principle that the ‘size’ of a tetrahedron could be used to derive the statistical Si:Al ratio within the tetrahedron provided values for the pure Si–O and Al–O distances were known or assumed. Smith (1954) made a systematic study of published aluminosilicate structures and concluded at that time that the best values were

Si–O = 1.60 ± 0.01 , and Al–O = 1.78 ± 0.02 Å. Later Smith (1961, p. 41) expressed the opinion that the best values (presumably for the feldspars) are 1.603 ± 0.003 and 1.77 ± 0.01 Å respectively, and more recently Smith & Bailey (1963) concluded that the best values for the feldspars are Si–O = 1.61 and Al–O = 1.75 Å.

In deciding which Si–O and Al–O values to assume, we took account of the above factors as well as of the extreme mean T–O values of the structure we were considering. In low albite (Ribbe, Megaw & Taylor, 1969) the extremes of the four tetrahedral sizes are 1.610 and 1.764 Å, so that assumed values of Si–O greater than 1.610 Å and Al–O less than 1.746 Å would be meaningless if one is to relate tetrahedral size to Si–Al content. We thus felt that any assumed Si–O value between 1.610 and about 1.59 Å, and any assumed Al–O value between 1.746 and about 1.80 Å could be regarded as reasonable. If some particular values of Si–O and Al–O between these limits can be shown to yield a near-zero charge unbalance, then these are taken to be the best values of Si–O and Al–O for low albite.

Further, because the Si:Al ratio in a given tetrahedron depends upon the assumed Si–O and Al–O values, the Si:Al ratio in all the tetrahedra and hence the Si:Al ratio for the structure as a whole will also depend upon these assumed Si–O and Al–O values.

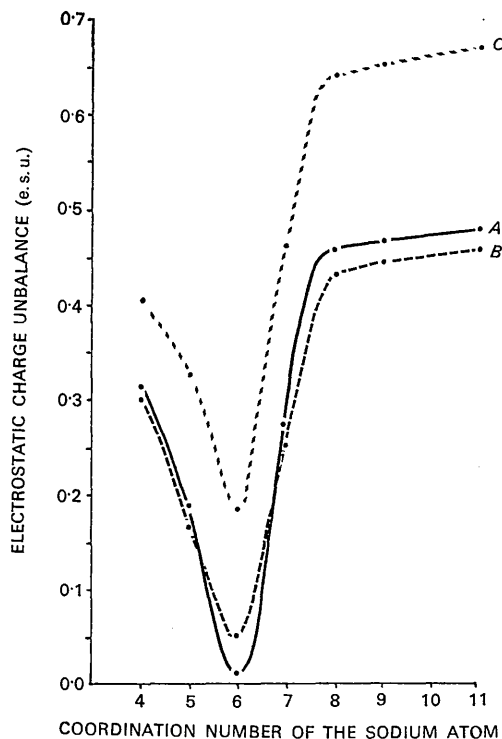


Fig. 1. Variation in electrostatic charge unbalance $\Sigma |A|$ in e.s.u. with C.N. of Na for three different combinations of Si–O and Al–O distance. Si–O and Al–O distances (Å) are: for curve A 1.602, 1.777; for curve B 1.600, 1.780 (Smith, 1954); for curve C 1.610 and 1.750 (Smith & Bailey, 1963).

Thus the closeness of this ratio to that expected, from the chemical composition, for the structure in question, is another criterion (besides the charge unbalance) for the reasonableness of the assumed Si-O and Al-O values.

The computer programming

The calculations were carried out with the aid of four computer programs that were written for feldspar structures with space group $C\bar{1}$ and applied to low albite. These programs were written by the authors in FORTRAN II for the IBM 1620 computer. It is the authors' intention to rewrite and combine these programs in FORTRAN IV for use on larger computers to facilitate similar calculations for other end-member feldspar structures. Details of the four programs used for low albite are given in the unpublished Ph.D. thesis of Gait (1967).

II. RESULTS FOR LOW ALBITE, $\text{NaAlSi}_3\text{O}_8$

Source data and preliminary calculations

The cell dimensions were those of Ferguson, Traill & Taylor (1958), and the atomic parameters those derived by three-dimensional methods by Ribbe, Megaw & Taylor (1969). The tetrahedral-oxygen (T -O) lengths were taken from Ribbe, Megaw & Taylor (1969) and they are shown in Table 1. The Na-O distances for the isotropic Na (single atom) rather than for the anisotropic Na (two 'half atoms') were recalculated by the present authors (Table 2).

Table 1. T -O bond lengths from Ribbe, Megaw & Taylor (1969)

Average 'standard errors' (standard deviations) in individual T -O bond lengths 0.004₆ Å, and in mean tetrahedral T -O bond lengths 0.002₃ Å.

$T1(0)$ -O $A(1)$	1.750 Å	$T2(0)$ -O $A(2)$	1.629 Å
-O $B(0)$	1.746	-O $B(0)$	1.592
-O $C(0)$	1.738	-O $C(m)$	1.615
-O $D(0)$	1.749	-O $D(m)$	1.623
Mean	1.746	Mean	1.615
$T1(m)$ -O $A(1)$	1.601	$T2(m)$ -O $A(2)$	1.641
-O $B(m)$	1.603	-O $B(m)$	1.617
-O $C(m)$	1.622	-O $C(0)$	1.587
-O $D(m)$	1.615	-O $D(0)$	1.604
Mean	1.610	Mean	1.612

The electrostatic charge distribution

As already stated, in our computer programming the charge distribution for the structure is calculated for one particular value of Si-O and one of Al-O over a range of Na coordination numbers. It became apparent after the first two or three runs on low albite that a coordination number of 6 for Na gave much lower charge unbalance values than did any other. This is illustrated by Fig. 1. It was then a matter of carrying out successive runs using different Si-O and Al-O distances until the smallest possible charge unbalance was

achieved. This smallest unbalance proved to be 0.014 e.s.u. and it occurs for Si-O = 1.602 and Al-O = 1.777 Å and for Na in 6 coordination. The details of these results are assembled in Table 3. Table 4 shows the charge unbalance values for Na in 6 coordination for several Si-O and Al-O distances close to the best, and Table 5 compares the present results with those obtained by Ferguson *et al.* (1958). Fig. 1 shows the variation in $\Sigma |A|$ for a range of C.N.'s of Na for (i) our best Si-O and Al-O distances (curve A), (ii) those of Smith (1954) (curve B), and (iii) those of Smith & Bailey (1963) (curve C).

The accuracy of the low albite results

In order to assess the accuracy of the results, we have calculated the standard deviation of the charge unbalance, $\sigma_{\Sigma |A|}$, based on the errors in the cation-oxygen distances given by Ribbe *et al.* (1969), and using established relationships for the standard deviation of one number that is a function of two or more other experimentally determined numbers. The relevant standard deviation relationships given in a work such as Baird (1962) are:

For

$$\bar{z} = \bar{x} + \bar{y}, \quad \sigma_{\bar{z}}^2 = \sigma_{\bar{x}}^2 + \sigma_{\bar{y}}^2$$

and for

$$\bar{z} = \bar{x}^a \bar{y}^b, \quad \sigma_{\bar{z}}^2 / \bar{z}^2 = a^2 \sigma_{\bar{x}}^2 / \bar{x}^2 + b^2 \sigma_{\bar{y}}^2 / \bar{y}^2.$$

The standard deviations relating to the present results are given in Table 6. All 'exposure factors' were taken as unity because, as indicated earlier, the calculations showed the 'shielding factors' to be negligible for coordination numbers of $\text{Na} \leq 7$. It is important to note that the standard deviations of the charges received by the oxygen ions and hence of the charge unbalance $\sigma_{\Sigma |A|}$, arise from only two sources: (i) the fact that the Al-content and hence the effective positive charge of a given T site depends upon its mean T -O bond length having error $\sigma_{\overline{T-O}}$, and (ii) the fact that the positive charges are distributed from the cations to the oxygen anions in amounts that are inversely proportional to the squares of the cation-oxygen distances having errors $\sigma_{(T-O)}$ and $\sigma_{(Na-O)}$. Thus although the value of $\Sigma |A|$ is, of course, strongly dependent upon the Si-O and Al-O distances assumed, the value of $\sigma_{\Sigma |A|}$ is independent of these provided they are taken to four significant figures as are the observed T -O distances.

Table 6 shows that $\sigma_{\overline{C}}$, the standard deviation of the mean positive charge contributed by Na^+ to one oxygen anion, 0.0005₇ e.s.u. is negligible compared with that contributed by one T atom $\sigma_{\overline{CT}}$, 0.004₂ e.s.u. so that $\sigma_{\bar{z}}$ and hence σ_{Σ} and $\sigma_{\Sigma |A|}$ are independent of the C.N. of Na for any reasonable coordination.

The single most important result shown in Table 5 is that the standard deviation of the charge unbalance $\sigma_{\Sigma |A|}$ is equal to 0.02₄ e.s.u. Its importance is discussed in the next section.

Conclusions from the low albite results

The authors regard the most striking aspect of these results to be the fact that there exists a set of reasonable values of Si-O distance, Al-O distance and Na coordination number which yields, for the low albite structure, a charge unbalance $\Sigma|\Delta|$ of 0.014 e.s.u., and that this value is less than the standard deviation of the charge unbalance, $\sigma_{\Sigma|\Delta|}$, 0.024 e.s.u. Thus within the limit of error of the observed cation-oxygen distances, the charge unbalance is zero for the assumed conditions. In addition, as Table 3 shows, the best assumed Si-O and Al-O distances yield a total Al-content of 1.000 atoms, the standard deviation for which (from Table 6) is 0.004₆ atom. Thus the Si:Al ratio corresponding to the assumed Si-O and Al-O distances is also exactly that required by the ideal chemical formula, NaAlSi₃O₈, even though, as Table 4 shows, there are other combinations of Si-O and Al-O distances that result in an ideal Al-content.

The authors feel that these and the related results provide strong evidence for the following conclusions concerning low albite:

(1) The structure can reasonably be interpreted as conforming exactly to Pauling's second rule governing ionic crystals. The atoms behave as though they are fully ionized with the electrostatic charges distributed in amounts that are inversely proportional to the squares of the metal-oxygen distances.

(2) Because, from Table 6, $\sigma_{\Sigma|\Delta|} = 0.024$ e.s.u., it follows that $\Sigma|\Delta|$ must be ≤ 0.024 e.s.u. in order for a

structure to have zero charge unbalance within the experimental error. Considering in this light the $\Sigma|\Delta|$ values given in Table 4, we conclude that the best T-O values for low albite are: Si-O = 1.602 ± 0.002 ; Al-O = 1.777 ± 0.003 Å.

These are appreciably different from the most recent distances proposed by Smith & Bailey (1963), 1.61 and 1.75 Å, but they are within the limits of Smith's (1954) original values, 1.60 ± 0.01 and 1.78 ± 0.02 Å, and they are close to the values suggested by Smith (1961) 1.603 ± 0.003 Å, and 1.77 ± 0.01 Å.

(3) The Si-Al distribution is the one which leads to the most satisfactory charges on the tetrahedral groups of four oxygen anions rather than the one with the Si and Al atoms fully ordered, that is, the one with 100% Al in one site. On the basis of best electrostatic charge distribution, the Si-Al distribution is the one shown in Table 3 with sites $T1(0)$, $T1(m)$, $T2(0)$ and $T2(m)$ occupied statistically by 0.823, 0.046, 0.074 and 0.057 Al atom respectively. With $\sigma_{\bar{Al}} = 0.002$ atom (Table 6), we conclude that the last three sites contain small but real amounts of Al. According to this interpretation, the structure has about 82% Al in one site; we call such a structure 'largely' ordered to contrast it with a 'fully' ordered one that implies 100% Al in one site.

(4) The Na atom (ion) is coordinated to (gives charge to) the closest 6 oxygen atoms as Fig. 1 indicates. In connection with the coordination of Na by oxygen atoms, the following points deserve emphasis:

(i) A C.N. of 6 for Na appears reasonable and even likely in view of the many other structures in which Na

Table 2. Na-O and Na-Na distances < 4.52 Å

(1) 'Nearness number'	(2) Oxygen	(3) EQV	(4)			(5)	(6)	(7)	(8)
			X	Y	Z	X/A	Y/B	Z/C	(Å)
1	OA(2)	1	1	0	0	1.0929	0.4974	0.2808	2.377
2	OD(0)	3	0	0	0	0.7075	0.6091	0.3890	2.435
3	OB(0)	4	1	0	-1	0.6876	0.3899	-0.1905	2.455
4	OA(1)	1	0	0	0	0.4945	0.3692	0.0336	2.537
5	OA(1)	2	0	0	-1	0.5055	0.6308	-0.0336	2.664
6	OC(0)	1	1	0	0	1.0132	0.3035	0.2690	2.953
7	OD(M)	1	0	0	0	0.6840	0.3681	0.4348	2.991
8	OC(M)	3	0	0	0	1.0239	0.6935	0.2291	3.262
9	OB(M)	2	0	0	-1	0.6800	0.6488	-0.2587	3.465
10	OA(2)	2	0	0	-1	0.9071	0.5026	-0.2808	3.719
11	OA(2)	2	0	0	0	0.9071	0.5026	0.7192	3.726
12	NA	2	0	0	-1	0.2318	0.5112	-0.1462	3.915
13	OB(0)	3	-1	0	0	0.3124	0.6101	0.1905	4.095
14	OD(0)	4	0	0	-1	0.2925	0.3909	-0.3890	4.199
15	OC(M)	4	1	0	-1	0.9761	0.3065	-0.2291	4.278
16	OD(0)	4	1	0	0	1.2925	0.3909	0.6110	4.281
17	OC(0)	2	0	0	0	0.9868	0.6965	0.7310	4.447
18	OD(M)	2	1	0	0	1.3160	0.6319	0.5652	4.482
19	OB(M)	1	1	0	0	1.3200	0.3512	0.2587	4.499
20	OB(M)	1	0	0	0	0.3200	0.3512	0.2587	4.518

Column (1): The 'nearness number' of the 20 closest oxygen atoms surrounding the Na atom.

Column (2): The symbolic name (Megaw, 1956) of the oxygen or Na atoms.

Column (3), EQV: A code number which indicates the equivalent position of the oxygen atom in space group $C\bar{1}$ thus: 1, x, y, z ; 2, $\bar{x}, \bar{y}, \bar{z}$; 3, $x + \frac{1}{2}, y + \frac{1}{2}, z$; 4, $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Column (4), XYZ: The translational components of the oxygen atom relative to the equivalent position designated in column (3).

Columns (5), (6) and (7), X/A, Y/B, Z/C: The parameters of the oxygen atom in fractions of the cell edges.

Column (8), (Å): The bond length in Å.

is 6-coordinated. However, from a consideration of the Na–O distances in low albite (Table 2), the fact that the seventh Na–O distance, 2.991 Å, is only slightly greater than the sixth, 2.953 Å, might suggest that the C.N. of

Na should be 7. Our results suggest that coordination number, rather than Na–O distance as such, is significant in low-symmetry silicate structures where Na is irregularly surrounded by oxygen atoms.

Table 3. Summary of conditions yielding a near-zero electrostatic charge unbalance

Cell dimensions of Ferguson, Traill & Taylor (1958).
Atomic parameters of Ribbe, Megaw & Taylor (1969).
All cations considered as fully ionized, Na⁺, Al³⁺, Si⁴⁺, and all cationic charges distributed in amounts that are inversely proportional to the squares of the cation–oxygen distances.

Si–O 1.602 Å, Al–O 1.777 Å.

Al-contents of tetrahedra in fractions of atoms:

<i>T</i> 1(0)	0.823
<i>T</i> 1(<i>m</i>)	0.046
<i>T</i> 2(0)	0.074
<i>T</i> 2(<i>m</i>)	0.057
Total	1.000

Coordination of Na by oxygen atoms: 6

'Nearness number'	Symbol	Na–O length	Shielded fraction	Charge received from Na ⁺ (e.s.u.)
1	OA(2)	2.377 Å	0	0.192
2	OD(0)	2.435	0	0.183
3	OB(0)	2.455	0	0.180
4	OA(1)	2.537	0	0.322
5	OA(1)	2.664	0	
6	OC(0)	2.953	0.03	0.121

Total positive charges received from all cations by each non-equivalent oxygen atom (e.s.u.)

OA(1)	2.113	OC(0)	1.940
OA(2)	2.108	OC(<i>m</i>)	1.955
OB(0)	1.984	OD(0)	1.970
OB(<i>m</i>)	1.977	OD(<i>m</i>)	1.954

Total positive charges (Σ) received by each tetrahedral group of four oxygen atoms, and differences from 8.000 (|Δ|) (e.s.u.)

<i>T</i> 1(0)–OA(1)	2.113	<i>T</i> 1(<i>m</i>)–OA(1)	2.113
–OB(0)	1.984	–OB(<i>m</i>)	1.977
–OC(0)	1.940	–OC(<i>m</i>)	1.955
–OD(0)	1.970	–OD(<i>m</i>)	1.954
Σ	8.007	Σ	7.999
Δ	0.007	Δ	0.001
<i>T</i> 2(0)–OA(2)	2.108	<i>T</i> 2(<i>m</i>)–OA(2)	2.108
–OB(0)	1.984	–OB(<i>m</i>)	1.977
–OC(<i>m</i>)	1.955	–OC(0)	1.940
–OD(<i>m</i>)	1.954	–OD(0)	1.970
Σ	8.001	Σ	7.995
Δ	0.001	Δ	0.005

Total electrostatic charge unbalance, Σ |Δ| (e.s.u.): 0.014.

Table 4. Summary of the T–O distances yielding the smallest charge unbalance values (Σ |Δ|) for C.N. of Na = 6

Si–O (Å)	Al–O (Å)	Al-content, atomic proportion	Positive charges Σ received by tetrahedral groups of four oxygen atoms (e.s.u.)				Total charge unbalance, Σ Δ (e.s.u.)
			<i>T</i> 1(0)	<i>T</i> 1(<i>m</i>)	<i>T</i> 2(0)	<i>T</i> 2(<i>m</i>)	
1.601	1.780	1.000	8.015	7.994	7.997	7.994	0.030
1.601	1.781	0.994	8.020	7.996	7.998	7.997	0.029
1.602	1.777	1.000	8.006	7.999	8.001	7.994	0.014
1.602	1.778	0.994	8.011	8.000	8.002	7.997	0.016
1.603	1.774	1.000	7.998	8.003	8.005	7.994	0.016
1.603	1.775	0.994	8.003	8.005	8.007	7.997	0.018
1.603	1.776	0.988	8.008	8.007	8.008	8.002	0.025
1.604	1.771	1.000	7.988	8.008	8.009	7.994	0.035

Derived best T–O distances: Si–O 1.602 ± 0.002 Å, Al–O 1.777 ± 0.003 Å.

(ii) The charge unbalance of zero (within the limit of error) for low albite depends upon the distribution of the Na⁺ charge to the six surrounding oxygen ions in amounts that are inversely proportional to the square of the Na-O distance. However, the small, integral C.N. of the Na atom, 6, indicated by our results, appears to belie the simple view of the Na atom behaving as a charged sphere. The Na atom in low albite is surrounded irregularly by many oxygen atoms with the more distant oxygen atoms 'shielded' from the Na to a lesser or greater extent by closer atoms. If the Na atom did in fact behave simply as a charged sphere, one might reasonably expect it to distribute its charge to *all* the surrounding oxygen atoms in amounts that take account in some way of both the Na-O distances and the proportion of a given oxygen atom 'exposed' to the

Na. We carried out charge distribution calculations under such assumptions for C.N.'s for Na as high as 17, but as Fig.1 shows, the charge unbalance values were all much greater than those for C.N. 6. The authors feel that the small, integral coordination number for Na indicated by their results may have important implications regarding the nature of ionic bonding. We feel also that, in view of the observed coordination of Na in low albite, it is probably not necessary to take account of 'shielded fractions' of oxygen atoms in relation to the large cations in other feldspar structures.

Discussion

The authors have made it clear that they feel they have strong evidence for an ionic interpretation of the low

Table 5. Comparison of best charge unbalance conditions of Ferguson *et al.* (1958) with those of present authors

	Ferguson, Traill & Taylor (1958)	This paper
Method of structure refinement	Two-dimensional	Three-dimensional (Ribbe <i>et al.</i> , 1969)
Method of distributing cationic charges to surrounding oxygen atoms	Equally	Inversely proportional to the square of the cation-O distance
C.N. of (single) Na	6	6
Assumed Si-O distance (Å)	1.60	1.602
Assumed T-O distance (Å)	1.78	1.777
Al-contents of tetrahedra, fractions of atoms	$\left\{ \begin{array}{l} T1(0) \\ T1(m) \\ T2(0) \\ T2(m) \end{array} \right.$	$\left\{ \begin{array}{l} 0.823 \\ 0.046 \\ 0.074 \\ 0.057 \end{array} \right.$
Σ Al, fractions of atoms	1.12	1.000
Positive charges contributed to tetrahedral groups of 4 oxygen atoms (e.s.u.)	$\left\{ \begin{array}{l} T1(0) \\ T1(m) \\ T2(0) \\ T2(m) \end{array} \right.$	$\left\{ \begin{array}{l} 8.007 \\ 7.999 \\ 8.001 \\ 7.995 \end{array} \right.$
Charge unbalance, Σ Δ (e.s.u.)	0.12	0.014
σ Σ Δ (e.s.u.)	n.d.	0.024

Table 6. Standard deviations of Al-content, charge distributions and charge unbalance Σ|Δ|

For single T-O bond length, 'average standard error',	$\sigma_{(T-O)} = 0.004_6 \text{ \AA}$	} Ribbe, Megaw & Taylor (1969), Tables 5 and 8
For one tetrahedral group of four oxygen atoms, 'standard error in mean T-O bond lengths',	$\sigma_{(T-O)} = 0.002_3 \text{ \AA}$	
'Average standard error in Na-O bond lengths',	$\sigma_{(Na-O)} = 0.005_7 \text{ \AA}$	
For mean Al-content of one T site,	$\sigma_{Al} = 0.002_3$ (atoms)	
For total Al-content (4 T sites),	$\sigma_{\Sigma Al} = 0.004_6$ (atoms)	
For effective positive charge on tetrahedral cation, P _T ,	$\sigma_{PT} = 0.002_3$ (e.s.u.)	
For mean effective positive charge contributed by T to one oxygen ion, CT,	$\sigma_{CT} = 0.004_2$ (e.s.u.)	
For mean positive charge contributed by large cation (Na) to one oxygen ion, CC,	$\sigma_{CC} = 0.0005_7$ (e.s.u.)	
For mean positive charge received by one oxygen from two T's and/or two T's and one Na and/or two T's and two Na's,	$\sigma_{\bar{O}} = 0.005_9$ (e.s.u.)	
For mean positive charge received by four (tetrahedral) oxygens, Σ,	$\sigma_{\Sigma} = 0.01_2$ (e.s.u.)	
For charge unbalance, Σ Δ ,	$\sigma_{\Sigma \Delta} = 0.02_4$ (e.s.u.)	

albite structure. It remains to answer the most serious critics of this interpretation [as presented by Ferguson *et al.* (1958)]. We restrict our discussion here to the purely crystallographic criticism of Brown & Bailey (1964), Clark & Appleman (1960) and Appleman & Clark (1965), and make no attempt to deal with the closely related but much broader mineralogical criticism of such authors as Laves & Goldsmith (1961).

Brown & Bailey (1964) calculated the charge distributions and the charge unbalances for the low and high albite structures, and for the principal potassium feldspar structures using several different reasonable coordinations of the large cations and the Si-O and Al-O distances of Smith and Bailey (1963). They show that, under these assumptions, low albite has about 92% Al in one site, and a charge unbalance comparable to that in maximum microcline and greater than that in orthoclase, intermediate microcline, sanidine and high albite. From these calculations they conclude that 'there is no valid basis for using charge balance computations of this particular type to judge the relative stabilities of different structures.' In our view, the particular Si-O and Al-O distances assumed for any charge distribution calculation are of paramount importance, and we feel that the distances of Smith & Bailey (1963), 1.61 and 1.75 Å, used by Brown & Bailey (1964) in their charge calculations, are not necessarily the best for the feldspars. Our present results suggest other appreciably different T-O distances for the feldspars, and thus we cannot accept their criticism of the ionic interpretation of the alkali feldspars based on charge calculations using the T-O distances of Smith & Bailey (1963). In our opinion, it is more than chance that our T-O distances for low albite, taken with a C.N. of Na of 6, would yield a charge unbalance of virtually zero and an Al-content of one for low albite.

The criticism of Clark & Appleman (1960) of the ionic interpretation of the low albite structure results from their interpretation of the structure of reedmergnerite, NaBSi₃O₈, the boron analogue of albite, which they analysed (Appleman & Clark, 1965). Reedmergnerite and low albite are closely isostructural, and the three tetrahedral sites *T1(m)*, *T2(0)* and *T2(m)* are very nearly the same size, about 1.614 Å, in both structures. Site *T1(0)* in reedmergnerite is 1.465 Å and in low albite 1.746 Å. Because statistical substitution of B for Si in a reedmergnerite site would make the tetrahedron smaller whereas the substitution of Al for Si in an albite site would make the tetrahedron larger, Clark & Appleman (1960) argue that the close similarity in size of the three sites *T1(m)*, *T2(0)* and *T2(m)* in both structures is evidence that both sites must be pure Si, from which it follows that the remaining site *T1(0)* must be pure B in reedmergnerite and pure Al in low albite. They further invoke the T-O distances of Smith & Bailey (1963) to reinforce their fully ordered interpretation of low albite.

For reasons given in our discussion of Brown & Bailey's (1964) paper, we reject Smith & Bailey's (1963) T-O

distances as a valid basis for closely determining Si-Al distribution. Clark & Appleman's (1960) argument based on the closeness in size of the three tetrahedra in both structures has considerable strength. However, it is known that T-O bond lengths depend upon environment; for example, Smith & Bailey (1963) point out that T-O distances in layer silicates are appreciably different from those in framework silicates. For this reason we feel that it is not necessarily sound to conclude that the existence of tetrahedra of the same size in the two structures is evidence that both sets of tetrahedra are pure Si. The effective pure Si-O distance in the borosilicate reedmergnerite may be appreciably different from that in the aluminosilicate low albite.

At the time of submission of this paper for publication, the re-assessment of Smith & Bailey's (1963) T-O distances by Ribbe & Gibbs (1967) and Jones (1968) came to the authors' attention. Using data from 13 feldspar structures, refined by three-dimensional methods, and excluding reedmergnerite, these authors arrived at the following values:

	Si-O (Å)	Al-O (Å)
Ribbe & Gibbs (1967)	1.605 ₂ , $\bar{\sigma}$ 0.001 ₂	1.757 ₃ , $\bar{\sigma}$ 0.002 ₅
Jones (1968)	1.603 ₃ , $\bar{\sigma}$ 0.001	1.760 ₈ , $\bar{\sigma}$ 0.001

The close agreement of our Si-O value with theirs, and their increase of the Al-O value (although small) over that of Smith & Bailey (1963), adds strength to the validity of our values. It is possible that the difference between our Al-O value and the two similar values of the recent papers is related to the long extrapolation of the T-O distance from 0.5 Al to 1.0 Al.

In view of the satisfactory interpretation we have been able to make of the low albite structure using the ionic approach, we plan to extend it to the other feldspar structures. This will involve combining our existing computer programs for a faster computer, and modifying them to take account of (i) large cations that are appreciably 'split' such as Na in high albite, (ii) change of cell size from that of low albite to one such as anorthite, and (iii) change of symmetry from triclinic to monoclinic for minerals such as orthoclase and sanidine. The authors recognize that it will require calculations and results comparable to these for low albite for all the principal feldspar structures before they can argue that the feldspars generally conform closely to purely ionic structures.

The authors are grateful to Dr W. H. Taylor and Dr Helen D. Megaw for providing us, prior to publication, with the experimental data essential to this investigation, namely the results of the three-dimensional refinement of low albite carried out with Dr P. H. Ribbe. We are grateful to Dr F. R. Ahmed of the National Research Council, Ottawa, for use of interatomic distance computer programs provided by him. This research was generously financed by the National Research Council (of Canada).

APPENDIX

The derivation of the proportion of an oxygen atom shielded by closer atoms from a sodium atom

This Appendix describes equations which permit one to determine whether a given oxygen atom is, in relation to the Na atom, partially or completely shielded by closer oxygen and/or Na atoms, and if the oxygen is partially shielded, to calculate the amount of this shielding. This amount is called the 'shielded fraction', and it is the ratio of the solid angle subtended at the centre of the Na atom by the shielded area of the (partially) shielded oxygen atom to the solid angle subtended by the same oxygen atom entirely exposed.

The equations

The amount of shielding of an oxygen atom in relation to an Na atom is governed by three angles named and defined as follows and as shown in Fig.2(a):

α , the plane angle subtended at the centre of the central sodium atom by the radius of the oxygen atom O(1) being shielded. If $[Na-O(1)]$ is the sodium-oxygen distance, and if R_{ox} is an assumed radius of the oxygen atom (ion); then $\sin \alpha = R_{ox}/[Na-O(1)]$.

β , the plane angle subtended at the centre of the central sodium atom by the radius of the closer atom, say oxygen O(2), causing the shielding. $\sin \beta = R_{ox}/[Na-O(2)]$. A comparable relationship holds if the closer shielding atom is (another) Na.

γ , the interbond (plane) angle subtended at the centre of the central sodium atom by the centre of the oxygen atom being shielded O(1) and by the centre of the

shielding atom, say oxygen O(2), that is, angle O(1)-Na-O(2) in Fig.2(a).

Four possible relationships may exist between these angles. These relationships, their consequences with respect to overlap, and the equations for calculating the 'shielded fractions' in the cases of partial overlap, are as follows:

Case 1. No shielding

If $\gamma > \alpha + \beta$, no overlap occurs and 'shielded fraction' = 0.

Case 2. Small fraction shielded

If $\beta \leq \gamma < \alpha + \beta$, overlap occurs and the width of the area shielded does not exceed the radius of the atom being shielded. This case is shown in Fig.2. The area shielded is bounded by two curves, boundary 1 and boundary 2 as shown in Fig.2(b). Using polar coordinate angles φ , θ with the Na-O(1) bond as polar axis and φ as the azimuthal angle about this axis, the equation for boundary 2 is simply

$$\theta = \alpha$$

and the equation for boundary 1 is

$$\cos \beta = \cos \gamma \cos \theta + \sin \gamma \sin \theta \cos \varphi,$$

from which

$$\cos \varphi = \frac{\cos \beta - \cos \gamma \cos \theta}{\sin \theta \sin \gamma},$$

giving

$$\varphi = F(\theta) = \cos^{-1} [\cos \beta \csc \gamma \csc \theta - \cot \gamma \cot \theta].$$

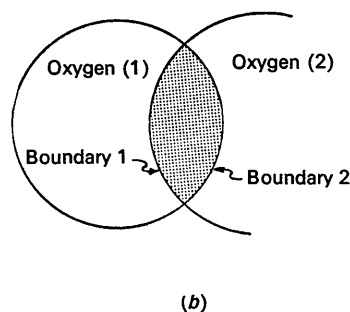
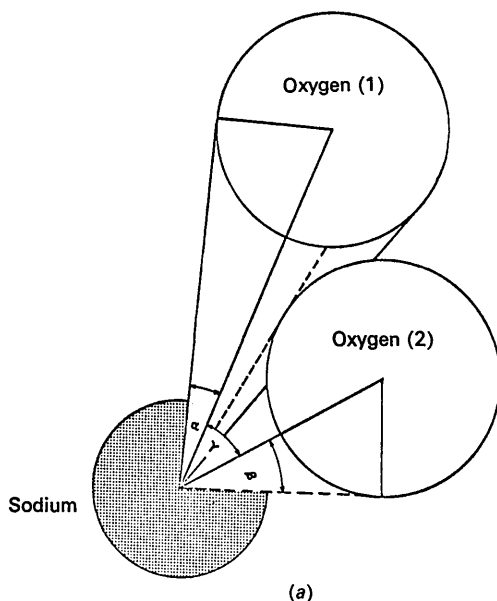


Fig.2.(a) Diagrammatic representation of a sodium atom, a shielded oxygen atom O(1) and a shielding oxygen atom O(2) showing the angles α, β, γ . (b) Projection along the Na-O(1) bond showing (stippled) the part of oxygen(1) shielded by closer oxygen (2).

Then Ω , the solid angle shielded is given by

$$\begin{aligned}\Omega &= 2 \int_{\gamma-\beta}^{\alpha} \int_0^{F(\theta)} \sin \theta \, d\theta \, d\varphi \\ &= 2 \int_{\gamma-\beta}^{\alpha} \sin \theta \, F(\theta) \, d\theta.\end{aligned}$$

Finally we get the 'shielded fraction' by dividing by the total solid angle subtended by oxygen O(1).

$$\text{Shielded fraction} = \frac{\Omega}{2\pi(1-\cos\alpha)}.$$

Case 3. Large fraction shielded

If $\gamma < \beta < \alpha + \gamma$, overlap occurs and the width of the area shielded lies between the radius and the diameter of the atom being shielded. In this case the solid angle shielded = $A + B$,

$$\begin{aligned}\text{where } A &= \int_0^{\beta-\gamma} \int_0^{2\pi} \sin \theta \, d\theta \, d\varphi \\ &= 2\pi[1 - \cos(\beta - \gamma)]\end{aligned}$$

$$\text{and } B = 2 \int_{\beta-\gamma}^{\alpha} \sin \theta \, F(\theta) \, d\theta.$$

Then for the 'shielded fraction' we have

$$\text{'Shielded fraction'} = \frac{A+B}{2\pi(1-\cos\alpha)}.$$

Case 4. Complete shielding

If $\beta \geq \alpha + \gamma$ the oxygen atom is completely shielded and

$$\text{'Shielded fraction'} = 1.$$

Acta Cryst. (1970). B26, 77

Neutron Diffraction Refinement of the Structure of Potassium Oxalate Monohydrate

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(Received 19 February 1969)

The structure of potassium oxalate monohydrate has been refined to a high degree of precision using three-dimensional neutron diffraction data. The conventional R value is 0.026 and the estimated standard deviations of atomic coordinates are between 0.001 and 0.003 Å. The oxalate ion is not quite planar with a separation of 0.037 (6) Å between the two parallel carboxyl planes. The C-C bond length is 1.581 (2) Å and the two C-O bond lengths are 1.262 (2) and 1.256 (2) Å. The O-H distance in the hydrogen bonds from the water molecule to the oxalate ion is 0.963 (3) Å; the O...O distance is 2.754 (2) Å, the O-H...O angle is 169.66 (22)° and the H-O-H angle, 107.62 (33)°. The root-mean-square amplitude of thermal motion of the water oxygen atom is considerably larger than that of the hydrogen atoms in some directions. The structure is compared with a recent X-ray structure of the same crystal and the agreement is excellent.

Introduction

In an earlier paper (Chidambaram, Sequeira & Sikka, 1964) (CSS) we reported a two-dimensional neutron

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diffraction study of the structure of potassium oxalate monohydrate. In that study the water molecule was shown to have a rather unusual type of coordination with neither of its two lone-pairs of electrons being