

COMPUTER CALCULATED ELECTROSTATIC CHARGE DISTRIBUTIONS
IN THE STRUCTURES OF THE FELDSPARS
LOW ALBITE, HIGH ALBITE AND ANORTHITE

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ABSTRACT

Electrostatic charge distributions have been computed for three feldspar structures for assumed reasonable values of the pure Si-O and Al-O distances and for reasonable coordination numbers of the large cations. The positive charges on the cations were distributed in proportion to the inverse squares of the interatomic distances, to the anions (oxygen). The measure of charge unbalance was taken to be the sum of the deviations from 8.000 e.s.u. on each tetrahedral group of four oxygens within the structure.

Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) was chosen first for study as it represents the most general case of the end-member feldspar structures; a FORTRAN IV program was written to carry out these calculations on an I.B.M. SYSTEM 360/DOS computer. Since no satisfactory low charge unbalance could be obtained for anorthite within a reasonable time, the study was directed towards the simpler low and high albite structures.

Calculations for low albite ($\text{NaAlSi}_3\text{O}_8$) were carried out with the aid of a set of four FORTRAN II programs written for the I.B.M. 1620 computer. The results revealed that low albite has an almost perfect electrostatic charge distribution (unbalance = 0.014 e.s.u.) for a 6-fold coordination of the sodium atom and for assumed Si-O and Al-O distances of 1.602 and 1.777 Å respectively; these distances indicate that the structure is about 82% ordered with respect to Si and Al.

High albite ($\text{NaAlSi}_3\text{O}_8$) exhibits an appreciable charge unbalance (0.27 e.s.u.) for sodium (treated as a single atom) in 6-fold coordination, whereas, for 10-fold or higher coordination, the structure has a small

unbalance value (about 0.06 e.s.u.) but not quite as small as for low albite. This result is interpreted as indicating that the sodium in high albite has the 'frozen in' coordination represented by the sodium atom at a high temperature when the thermal anisotropism is large and the sodium has a larger effective environment. It is proposed that as the temperature decreases, the thermal vibration of the sodium atom decreases until the low-temperature stable state is reached, that is when the effective coordination of the sodium is reduced to 6-fold and the structure has achieved the form of low albite. Electrostatic charge unbalance is invoked as the principal reason for the Si : Al ordering which occurs during the inversion from high-temperature to low-temperature albite (Ferguson, Traill and Taylor, 1958). Tetrahedral site T1(0) in high albite has marked excess electrostatic charge for 6-fold coordination of the sodium, and therefore the Al in the structure will migrate preferentially into this site in order to reduce the amount of excess positive charge.

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CHAPTER I

INTRODUCTION

(i) General Considerations

The research leading to this thesis was conducted in an attempt to clarify some of the fundamental crystallographic aspects of the feldspar group of minerals particularly with reference to silicon-aluminum order-disorder. In 1958, Ferguson, Traill and Taylor proposed that the most stable low-temperature feldspars were those whose Si-Al distribution leads to the most satisfactory electrostatic charge distribution within these structures. This interpretation is not in agreement with most other workers in this field who prefer the 'full ordering theory' which assumes that the most stable low-temperature feldspar is fully ordered with respect to Si-Al. Of the three authors who first proposed the 'charge balance' or 'ionic' theory in 1958, Ferguson has been the strongest proponent; he has considerably embellished the original ideas in a succeeding paper (Ferguson, 1960).

The present study was undertaken by the author under the direction of Dr. Ferguson to investigate more fully the charge balance theory of the feldspar structures. The study involved the calculation of electrostatic charge distributions within the low and high albite and the anorthite structures. In the first instance the subject of the thesis was suggested by Dr. R. B. Ferguson of the Department of Geology of the University of Manitoba. As has already been mentioned, Ferguson has done a considerable amount of work on the distribution of electrostatic

charges within various end-member feldspar structures, and he has considered the implications of these results (Ferguson, Traill and Taylor, 1958; Ferguson, 1960). The approach taken by Ferguson and his associates was directly related to their study of the structures of low and high albite in 1958 (Ferguson et al., 1958). At that time, it appeared that a study of the valence bond strengths within the structures would possibly explain some of the structural features, especially in relation to Si-Al order-disorder within the feldspar group. Preliminary calculations by Ferguson et al. (1958) at that time appeared to support the view that the feldspar minerals may be treated as if they were ionic in character. This in turn led to the prediction that the low-temperature varieties of the feldspars should be locally balanced as far as the distribution of electrostatic charges is concerned. The reverse should be true for the high-temperature feldspars. The calculations which were carried out for publication in 1958 were done for low and high albite using the atomic parameters derived from their two-dimensional Fourier refinements. The present study has revised and elaborated the method of these calculations, and has resulted in the development of a computerized method to complete iterative sets of calculations. A large number of variables have to be taken into account, and it is an extremely tedious task to carry through even a small part of these calculations by hand. The computer-based method is so designed as to handle the required variables, and the programs have been tested for the feldspar structures with the space group $C\bar{1}$ (low and high albite, and the microcline structures). Some modification of the programs will be required to deal with the other feldspar structure types.

A comparison between the results obtained by Ferguson et al. (1958) and the present set of calculations, reveals some important differences. The earlier results calculated using the two-dimensional parameters for low and high albite are considerably less conclusive than the present results using the more accurate parameters derived from the three-dimensional analysis by Ribbe, Megaw and Taylor (1967).

The earlier work on the feldspar minerals led Ferguson, Traill and Taylor to believe that important aspects of feldspar crystallography could be clarified by a study of the electrostatic charge distributions within the structures, and this in turn implies that the structures have to be treated as if they were ionic in character. This is the most fundamental assumption which has to be made in order to investigate the validity of the earlier authors' views. It can be demonstrated that valence or electrostatic charge is important in determining the possible elemental substitutions which may take place in the feldspar structures. The plagioclase group is often cited as an ideal example of this type of substitution. Albite ($\text{NaAlSi}_3\text{O}_8$) may be expressed as $\text{Na}^{+1}\text{Al}^{+3}\text{Si}_3^{+4}\text{O}_8^{-2}$; 16 positive charges satisfy 16 negative charges, which may be interpreted as the attainment of electrostatic charge balance. Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), the calcium-rich end-member of the plagioclase series, has an increased positive charge on the calcium atom (+2) compared to the charge on the sodium atom (+1) in the albite end-member, and this increased positive charge results in the requirement that sufficient trivalent aluminum be admitted into the structure in place of tetravalent silicon in order to balance the positive and negative charges. Various plagioclase minerals of inter-

mediate composition between albite and anorthite have long been recognized, and throughout the series similar changes in the $\text{Si}^{+4}:\text{Al}^{+3}$ ratio have to take place in order to satisfy the valence or electrostatic requirements necessitated by the $\text{Na}^{+1}:\text{Ca}^{+2}$ ratios of the particular plagioclase.

The second assumption which has to be made in connection with this type of study is that the low-temperature members will, with the attainment of a stable state, in general achieve local electrostatic charge balance, whereas the high-temperature members will not necessarily possess this characteristic.

The preliminary calculations by Ferguson et al. have shown that ^{these assumptions} appear to be ^{valid}; however, some caution should be observed as these calculations were carried out by hand and, owing to the length of the computation, only a few coordinations of the large cation could be tested. Furthermore, the work on the albite members was effected using the original parameters of the atoms derived from only the two-dimensional Fourier refinements. The following tabulation gives a brief summary of the electrostatic charge unbalance values given by Ferguson et al. (1958, Table 10):

Total Charge Unbalance on Low and High Albite derived by

Ferguson et al. (1958)

Feldspar Type	Large cation and Coordination No.	Total Charge Unbalance ($\Sigma \Delta$) e.s.u.
Low albite	Na (6)	0.12) Assumed Si-Al distribution
Low albite	Na (7)	0.33) identical
High albite	Na (6)	0.34) Assumed Si-Al distribution
High albite	Na (7)	0.22) identical

The above tabulation indicates that there is a ^{larger} charge unbalance for high albite compared to that for low albite with sodium in 6-fold coordination; and there is also a difference in the coordination of the sodium atom yielding the minimum charge unbalance. Further complications arise as to the degree of Si-Al ordering of the low albite structure. The present study was initiated in order to take account of these factors and to devise a practical computer program system to calculate charge distributions taking into account all the reasonable variables.

However, all the first calculations were carried out with respect to the anorthite structure because it represents the most general case of the end-member feldspars; any computer program applicable to anorthite would be sufficiently general that it could be fairly simply applied to other members of the feldspar group. Compared to the albite end-member of the plagioclase series, anorthite is more complex. The unit cell of anorthite is twice as large as the unit cell of albite, and furthermore has only a P lattice compared to the C lattice of albite; as a result, anorthite has four times the number of non-equivalent atoms, each of which has to be considered in detail in conducting studies of the electrostatic charge distributions. A computer program in FORTRAN IV language was written for the IBM SYSTEM 360/ DOS to take account of all the expected variables in the anorthite structure. A complete printout of this program and its description may be found in Appendix I with more details in Chapters II and III. Chapter II in particular describes in detail the progress of the work on anorthite, and presents various important changes in the train of thought which were required as more information became available as a result of these detailed calculations.

The results of the anorthite calculations were unsatisfactory owing to the complexity of the structure, and therefore the last part of the study was devoted to the simple albite structures.

(ii) Fundamental Feldspar Crystallography pertinent to the Distribution of Electrostatic Charges within the Structures

The basic structural components of the feldspar minerals are the (Si,Al)-O or (T-O) tetrahedra which are joined together to form 4-fold rings. The rings are linked in such a way as to produce chains of these rings set nearly at right angles to one another in an alternate fashion like a 'Greek Key' pattern. These chains lie parallel to the a-axes of the structures. This arrangement results in each oxygen atom being common to two tetrahedra. These chains of 4-fold rings of tetrahedra are connected to one another by a few T - O - T bonds and by alkali or alkali earth cations occupying the largest interstices between adjacent chains. Thus each oxygen atom in the structure is bonded to two tetrahedral cations and possibly to one or more of the large cations (Deer, Howie and Zussman, 1963 and 1966).

The tetrahedral sites vary in "size" (mean T-O bond length) depending upon the statistical amounts of Al and Si which occupy them. The pure Si-O tetrahedron is distinctly smaller than the pure Al-O tetrahedron. Since the experimental structural data represent the statistical average of virtually an infinite number of unit cells, the average sizes of these tetrahedra reflect the statistical amount of Si and Al occupying those sites; if the ideal Si-O and Al-O values can be determined, then the Si : Al ratio within a tetrahedron can be deduced.

Further discussion upon this matter follows in Chapter II where details of the charge distribution calculations are given.

The coordinations of the large cations (Na, K or Ca) are also an uncertain factor and they are usually deduced, more or less arbitrarily, by counting the number of nearest neighbouring oxygen atoms to the cation in question. As these cations occupy large, irregular cavities in the structure, the number of nearest neighbours may be a matter of opinion. This problem has been taken into consideration in the charge distribution calculations, and sets of calculations have been completed over a range of coordinations in an attempt to clarify this matter.

(iii) Sources of Primary Data

(a) Low-Temperature and High-Temperature Albites

Two sources of information were available to the author concerning the albite structures. The first is the original paper describing the two-dimensional refinement of these structures (Ferguson, Traill and Taylor, 1958), published in the interim while the authors prepared final data for the more accurate three-dimensional refinement. The latter information is not generally available as yet; however, Professor Ferguson has received the kind permission of Dr. W. H. Taylor of the Crystallographic Laboratory at Cambridge, England, to use the three-dimensional results which are about to be published (Ribbe, Megaw and Taylor, 1967); see also Ribbe, Ferguson and Taylor (1962).

(b) Anorthite

The primary data for the anorthite structure were taken from the three-dimensional refinement by Kempster, Megaw and Radoslovich (1962) and the discussion thereof by Megaw, Kempster and Radoslovich (1962).

(iv) Acknowledgements

The study represented by this thesis was conducted under the supervision of Dr. R. B. Ferguson of the University of Manitoba, and without his continuing support and assistance could not have been successfully completed. Throughout the entire period of research Dr. Ferguson's constructive criticism has been a source of inspiration and guidance and the author would therefore like to extend to Dr. Ferguson his most sincere appreciation of the help and cooperation which he has received. The research was partly financed through a grant to Dr. Ferguson from the National Research Council of Canada. The author would like to express his gratitude to Dr. H. R. Coish of the Physics Department of the University of Manitoba who provided him with the method and formulae needed to perform the calculations to determine the solid shielding angles described in the text of the thesis. Dr. F. R. Ahmed of the Pure Physics Division of the National Research Council in Ottawa kindly provided the author with a computer program which was used in the early stages of this research, to calculate interatomic distances in the feldspar structures. All the Staff and Graduate Students of the Department of Geology of the University of Manitoba deserve the thanks of the author for their interest and criticism in the course of his research. Mrs. Helen Wilson has done the typing, and the author would

like to thank her for her patience and skill in solving the many interminable problems which arise in work of this nature.

CHAPTER II

THE CALCULATION OF ELECTROSTATIC CHARGE DISTRIBUTION IN A
FELDSPAR USING THE ANORTHITE STRUCTURE AS
AN EXAMPLE

(i) Charge Distributions from the Cations to the Oxygens

Of the factors governing the structures of the rock forming minerals, the ionic size and the electrostatic charge may be considered as being most important. The latter is the principal force which holds ions together and is a force of electrical attraction between oppositely charged bodies. The set of principles or rules which are currently accepted for studies concerning the distribution of electrostatic charge were given by Pauling (1929). Pauling's rule may be stated as follows:

"Divide the valency of a given positive ion by the number of surrounding negative ions. The resulting fraction is the contribution of the positive ion towards satisfying the valency of each negative ion. If we now consider a given negative ion it is found that the sum of the contributions from its neighbouring positive ions is equal or approximately equal to its valency."

In a highly symmetrical structure such as NaCl, the distribution of electrostatic charges is greatly simplified by the obvious coordination number of the cations and by the fact that the cation-anion bond lengths are usually equal; these two facts negate the need for any complicated calculations. However, when attempting to apply similar methods to asymmetric structures like the feldspar minerals, the matter is greatly complicated by the irregular coordination of the large cations and by the fact that the cation-anion bond lengths are rarely equal. In an asymmetric structure, it is necessary to take account of the inter-atomic

distances. The simplest statement to describe the method used to distribute the charge is as follows: The positive charge on the cations is distributed proportionally, according to the inverse squares of the bond distances, to the surrounding anions. An alternative method would be to distribute the negative charges on the anions to the nearest cations in a similar manner. In practice the calculations are simplified if the former method is employed since there is a smaller number of cations than anions in the feldspar structures, and the decision as to which anions are the nearest neighbours to a particular cation is facilitated.

The actual method used here for calculating the charge distribution is best explained under two separate headings: (a) Electrostatic Charge Distribution within the Tetrahedral Groups, and (b) Electrostatic Charge Distribution from the Alkali or Alkali Earth Cations to the Surrounding Oxygens. For all the feldspar structures similar methods may be used, but anorthite, being the most general, is used as an example. An IBM SYSTEM 360/DISK OPERATING SYSTEM computer program was devised to process the data for the anorthite structure and a complete documentation of this program is given in Appendix I at the end of this thesis.

(a) Electrostatic Charge Distribution within the Tetrahedral Groups

The distribution of charges within the tetrahedral groups depends on the effective positive charge on a particular tetrahedral cation which is in turn determined by the statistical proportions of Si^{+4} and Al^{+3} occupying the site. This amount of positive charge is then

distributed proportionally according to the inverse square of the distances, to the four surrounding oxygen atoms.

Before treating the method in detail a few comments concerning the tetrahedra are required. Table 1 lists the tetrahedral oxygen distances for the anorthite structure as given by Megaw, Kempster and Radoslovich (1962). The tetrahedra are, in general, all asymmetric regardless of the feldspar variety. Hence in each tetrahedral group, there are four different tetrahedron-oxygen (T-O) distances to be taken into consideration. In general all the independent tetrahedra contain different proportions of Si and Al, although in the low-temperature structures there are usually two distinct groups, one with small (Si-rich) tetrahedra and one with large (Al-rich) tetrahedra. In the high-temperature varieties all the tetrahedra are nearly the same size, though they each show minor differences, and in both low- and high-temperature varieties of the feldspars, each T-O distance requires individual attention.

Anorthite with a cell content of $4 [\text{CaAl}_2\text{Si}_2\text{O}_8]$ has 16 non-equivalent tetrahedral sites; 8 of these are Si-rich and 8 are Al-rich. Each tetrahedral site has 4 oxygen atoms associated with it, but each oxygen is common to 2 tetrahedra. Thus there are 32 non-equivalent oxygen atoms in the structure. Despite this equivalence of the oxygen atoms, there are 64 T-O distances to be taken into consideration in performing the calculation.

The first step in the calculation is to assume possible ideal values for the pure Si-O and Al-O tetrahedral bond lengths. These

Key no. of tetrahedron	Atoms		Length	Mean T-O "Size"
	T	O		
1.	$T_1(0000)$	$O_A(1000)$ $O_B(0000)$ $O_C(0000)$ $O_D(0000)$	1.647 } 1.641 } 1.575 } 1.589 }	1.613
2.	$T_1(00i0)$	$O_A(10i0)$ $O_B(00i0)$ $O_C(00i0)$ $O_D(00i0)$	1.620 } 1.599 } 1.583 } 1.661 }	1.616
3.	$T_1(mz0c)$	$O_A(1z00)$ $O_B(mz0c)$ $O_C(mz0c)$ $O_D(mz0c)$	1.618 } 1.626 } 1.617 } 1.571 }	1.608
4.	$T_1(mzic)$	$O_A(1zi0)$ $O_B(mzic)$ $O_C(mzic)$ $O_D(mzic)$	1.643 } 1.600 } 1.623 } 1.637 }	1.626
5.	$T_2(0z00)$	$O_A(2z00)$ $O_B(0z00)$ $O_C(m0i0)$ $O_D(m00c)$	1.624 } 1.589 } 1.629 } 1.611 }	1.613
6.	$T_2(0zi0)$	$O_A(2zi0)$ $O_B(0zi0)$ $O_C(m000)$ $O_D(m0ic)$	1.606 } 1.652 } 1.617 } 1.566 }	1.610
7.	$T_2(m00c)$	$O_A(200c)$ $O_B(m00c)$ $O_C(0zic)$ $O_D(0z00)$	1.646 } 1.559 } 1.601 } 1.603 }	1.602
8.	$T_2(m0ic)$	$O_A(20ic)$ $O_B(m0ic)$ $O_C(0z0c)$ $O_D(0zic)$	1.634 } 1.628 } 1.622 } 1.629 }	1.628
9.	$T_1(0z00)$	$O_A(1z00)$ $O_B(0z00)$ $O_C(0z00)$ $O_D(0z00)$	1.820 } 1.753 } 1.701 } 1.755 }	1.758
10.	$T_1(0z10)$	$O_A(1zi0)$ $O_B(0z10)$ $O_C(0z10)$ $O_D(0z10)$	1.747 } 1.733 } 1.708 } 1.796 }	1.746
11.	$T_1(m00c)$	$O_A(1000)$ $O_B(m00c)$ $O_C(m00c)$ $O_D(m00c)$	1.794 } 1.723 } 1.735 } 1.754 }	1.752
12.	$T_1(m0ic)$	$O_A(10i0)$ $O_B(m0ic)$ $O_C(m0ic)$ $O_D(m0ic)$	1.757 } 1.757 } 1.755 } 1.695 }	1.741
13.	$T_2(0000)$	$O_A(2000)$ $O_B(0000)$ $O_C(mz10)$ $O_D(mz0c)$	1.784 } 1.749 } 1.723 } 1.730 }	1.746
14.	$T_2(00i0)$	$O_A(20i0)$ $O_B(00i0)$ $O_C(mz00)$ $O_D(mzic)$	1.782 } 1.792 } 1.745 } 1.692 }	1.753
15.	$T_2(mz0c)$	$O_A(2z0c)$ $O_B(mz0c)$ $O_C(00ic)$ $O_D(0000)$	1.754 } 1.747 } 1.706 } 1.769 }	1.744
16.	$T_2(mzic)$	$O_A(2zic)$ $O_B(mzic)$ $O_C(000c)$ $O_D(00i0)$	1.738 } 1.696 } 1.780 } 1.792 }	1.752

Table 1. Anorthite: The List of Tetrahedral-Oxygen Distances.
(after Megaw, Kempster and Radoslovich, 1962).

assumptions are treated in more detail in Section (ii) of this Chapter. From these ideal or assumed values it is possible to calculate the proportions of Si and Al in each one of the tetrahedral sites, following the method of J. V. Smith (Smith, 1954). The relationship may be expressed as follows:

$$Al = \frac{(TO_m - SiO)}{(AlO - SiO)} \dots\dots\dots(1)$$

where: Al is the statistical aluminum content of a tetrahedron expressed as an atomic fraction,

TO_m is the size or mean bond length of a particular tetrahedron (\AA),

SiO is the assumed size of a pure Si-O tetrahedron (\AA),

AlO is the assumed size of a pure Al-O tetrahedron (\AA).

In the computer program the Al-contents of all the non-equivalent tetrahedra in the unit cell of the anorthite structure are calculated by this method. The sum of all these Al-contents should approximate to the stoichiometric requirements of the structure. In the case of anorthite, this value (ΣAl) should be close to 8. Table 2 lists the Al-contents of the 16 non-equivalent tetrahedra in the anorthite structure for a particular case, namely for Si-O = 1.602 \AA and Al-O = 1.762 \AA ; the Table also shows the ΣAl value.

The amount of effective positive charge on a particular tetrahedral site may now be calculated from the following relationship:

$$P = 4 - Al \dots\dots\dots(2)$$

where: P is the positive charge on a tetrahedral site in e.s.u. and

Al is the fractional Al-content derived from equation (1).

T 1	-	T1(0000)	AL	CONTENT	T 1	0.069
T 2	-	T1(00i0)	AL	CONTENT	T 2	0.088
T 3	-	T1(mz0c)	AL	CONTENT	T 3	0.038
T 4	-	T1(mzic)	AL	CONTENT	T 4	0.150
T 5	-	T2(0z00)	AL	CONTENT	T 5	0.069
T 6	-	T2(0zi0)	AL	CONTENT	T 6	0.050
T 7	-	T2(m00c)	AL	CONTENT	T 7	0.0
T 8	-	T2(m0ic)	AL	CONTENT	T 8	0.163
T 9	-	T1(0z00)	AL	CONTENT	T 9	0.975
T10	-	T1(0zi0)	AL	CONTENT	T10	0.900
T11	-	T1(m00c)	AL	CONTENT	T11	0.938
T12	-	T1(m0ic)	AL	CONTENT	T12	0.869
T13	-	T2(0000)	AL	CONTENT	T13	0.900
T14	-	T2(00i0)	AL	CONTENT	T14	0.944
T15	-	T2(mz0c)	AL	CONTENT	T15	0.888
T16	-	T2(mzic)	AL	CONTENT	T16	0.938
TOTAL AL-CONTENT						= 7.975

Table 2. Anorthite: Example of Al-Contents of the 16 Non-Equivalent Tetrahedra.

Si-O = 1.602 Å and

Al-O = 1.762 Å.

Column 2 gives the Megaw (1956) notation for the tetrahedral sites.

The above relationship assumes that the charge on the silicon is +4 and that on the aluminum is +3. Therefore the amount of positive charge on a site which is statistically neither pure Si nor pure Al must be between 3 and 4 and is directly related to the amount of aluminum in that tetrahedral site.

A further factor must be taken into account before the actual electrostatic charge distribution can be calculated. If one considers that the electrostatic forces vary as the inverse squares of the bond distances, then this factor, called the 'weighting factor', has to be calculated in order to evaluate the proportion of the positive charge which is to be distributed to a particular oxygen atom as a function of the inverse square of the bond distance. The 'weighting factor' is the sum of the inverse squares of the four (T-O) distances which make up any one tetrahedron, and may be expressed as follows:

$$WT = \sum \left[\frac{1}{TO^2} \right] \dots\dots\dots(3)$$

where: WT is the 'weighting factor' or 'proportionality factor' and
TO is the T-O distance (Å).

This factor has to be calculated for each of the 16 non-equivalent tetrahedra.

The final step in this part of the calculation is the actual proportioning of the positive charge on the tetrahedral site to each of the surrounding four oxygen atoms, according to the inverse square of the distance of that oxygen from the centre of the tetrahedral site.

The calculation is effected as follows:

$$C_T = \frac{P}{(TO)^2 \times WT} \dots\dots\dots(4)$$

- where: C_T is the positive charge in e.s.u. given to a particular oxygen atom from a particular tetrahedral site,
- P is the effective positive charge in e.s.u. on a particular tetrahedral site, derived from equation (2),
- TO is the tetrahedral-oxygen distance (\AA), and
- WT is the 'weighting factor' calculated for a particular tetrahedron from equation (3).

This tetrahedral charge contribution calculation is carried out in the program for all oxygen atoms associated with each tetrahedron; in other words, this value must be calculated for 64 T-O bond lengths. Since these will include some T-O bonds for equivalent oxygen atoms, the values have to be sorted out and the positive charges which have been contributed to those oxygen atoms which are equivalent must be added together. In effect this reduces the number of final answers to 32, the number of non-equivalent oxygen atoms in a single anorthite unit cell. Each of these numbers will be composed of the sum of the positive charge contributions from 2 tetrahedra sharing a common oxygen. An example of a set of these tetrahedral charge contributions is given in Table 3.

(b) Electrostatic Charge Distribution from the Alkali or Alkali Earth Cations to their Surrounding Oxygens

The amount of charge available from the alkali or alkali earth cation is, of course, dependent upon its valency. In the case of the anorthite unit cell, there are 4 non-equivalent calcium atoms, each with a charge of +2. An appropriate set of calcium-oxygen distances must be

0 1	-	OA(1000)	TET CHARGE ON OXY	0 1	1.671
0 2	-	OA(1z00)	TET CHARGE ON OXY	0 2	1.682
0 3	-	OA(10i0)	TET CHARGE ON OXY	0 3	1.741
0 4	-	OA(1zi0)	TET CHARGE ON OXY	0 4	1.715
0 5	-	OA(2000)	TET CHARGE ON OXY	0 5	1.689
0 6	-	OA(2z00)	TET CHARGE ON OXY	0 6	1.738
0 7	-	OA(20i0)	TET CHARGE ON OXY	0 7	1.691
0 8	-	OA(2zi0)	TET CHARGE ON OXY	0 8	1.768
0 9	-	OB(0000)	TET CHARGE ON OXY	0 9	1.721
010	-	OB(0z00)	TET CHARGE ON OXY	010	1.770
011	-	OB(00i0)	TET CHARGE ON OXY	011	1.728
012	-	OB(0zi0)	TET CHARGE ON OXY	012	1.723
013	-	OB(m000)	TET CHARGE ON OXY	013	1.846
014	-	OB(mz00)	TET CHARGE ON OXY	014	1.743
015	-	OB(m0i0)	TET CHARGE ON OXY	015	1.728
016	-	OB(mzi0)	TET CHARGE ON OXY	016	1.809
017	-	OC(0000)	TET CHARGE ON OXY	017	1.770
018	-	OC(0z00)	TET CHARGE ON OXY	018	1.773
019	-	OC(00i0)	TET CHARGE ON OXY	019	1.829
020	-	OC(0zi0)	TET CHARGE ON OXY	020	1.810
021	-	OC(m000)	TET CHARGE ON OXY	021	1.758
022	-	OC(mz00)	TET CHARGE ON OXY	022	1.749
023	-	OC(m0i0)	TET CHARGE ON OXY	023	1.733
024	-	OC(mzi0)	TET CHARGE ON OXY	024	1.761
025	-	OD(0000)	TET CHARGE ON OXY	025	1.767
026	-	OD(0z00)	TET CHARGE ON OXY	026	1.755
027	-	OD(00i0)	TET CHARGE ON OXY	027	1.656
028	-	OD(0zi0)	TET CHARGE ON OXY	028	1.690
029	-	OD(m000)	TET CHARGE ON OXY	029	1.748
030	-	OD(mz00)	TET CHARGE ON OXY	030	1.827
031	-	OD(m0i0)	TET CHARGE ON OXY	031	1.868
032	-	OD(mzi0)	TET CHARGE ON OXY	032	1.768

Table 3. Anorthite: Example of the Tetrahedral Charges Contributed to the 32 Non-Equivalent Oxygen Atoms.

Si-O = 1.602 Å and
Al-O = 1.762 Å.

Column 2 gives the Megaw (1956) notation for the 32 non-equivalent oxygen atoms.

determined for each of these calcium atoms prior to the calculation of the charge distribution. The Ca-O environment is closely related to the Ca-O bond lengths, and to a first approximation, the nearest neighbours, say twelve, may be counted and taken as being bonded. In the course of the investigation it became apparent that the electrostatic charge distribution may involve either more or fewer oxygen atoms than the nearest twelve in each Ca-O environment; therefore a complete set of Ca-O bonds was calculated to a distance of 6.50 Å from each calcium atom, which involves about the nearest 50 oxygens in the environment of each calcium. An IBM 1620 computer program was written to effect these calculations and a full documentation is given in Appendix IIB. The atomic parameters and the derived Ca-O distances are given in Tables 4A and 4B.

Having now established the bond distances in the calcium-oxygen environments, the +2 charge on the calcium may be distributed to as many of the surrounding oxygens as are considered to be in coordination, in a manner similar to that which was done with the tetrahedral groups. Again the charge on the cation must be distributed proportionally to the inverse square of the distances.

In the first part of the calculation a 'weighting factor' has to be determined in order to proportionally distribute the charges according to the inverse square law. This 'weighting factor' is obtained from the following expression:

$$W = \sum \left[\frac{1}{CO^2} \right] \dots\dots\dots(5)$$

where: W is the 'weighting factor' for a particular large cation, and CO is a particular large cation-oxygen bond distance (Å).

Megaw Symbol	x/a (Fractions of Cell Edges x 10 ⁴)	y/b	z/c
Ca(000)	7353 (2647)	0156 (9844)	9127 (0873)
Ca(z00)	2684	0312	5438
Ca(0i0)	2268 (7732)	4646 (5354)	4578 (5422)
Ca(zi0)	2364 (7636)	4933 (5067)	9260 (0740)
OA(1000)	0276	1234	9957
OA(1z00)	9814	1237	4808
OA(10i0)	5127 (4873)	3744 (6256)	5135 (4865)
OA(1zi0)	4871 (5129)	3744 (6256)	0030 (9970)
OA(2000)	4276 (5724)	0091 (9909)	8549 (1451)
OA(2z00)	4268 (5732)	0099 (9901)	3602 (6398)
OA(20i0)	0732	4876	6330
OA(2zi0)	0755	4925	1363
OB(0000)	8114	1027	0792
OB(0z00)	8071	0996	6046
OB(00i0)	6637 (3363)	4062 (5938)	3955 (6045)
OB(0zi0)	7088 (2912)	3964 (6036)	9181 (0819)
OB(m000)	1852 (8148)	1484 (8516)	8546 (1454)
OB(mz00)	1910 (8090)	1490 (8510)	3982 (6018)
OB(m0i0)	2983	3575	6113
OB(mzi0)	3382	3606	1309
OC(0000)	0120	2780	1351
OC(0z00)	0177	2900	6486
OC(00i0)	4918 (5082)	2222 (7778)	3689 (6311)
OC(0zi0)	4898 (5102)	2031 (7969)	8500 (1500)
OC(m000)	9996 (0004)	3198 (6802)	8937 (1063)
OC(mz00)	9917 (0083)	3102 (6898)	3983 (6017)
OC(m0i0)	5150	1794	6090
OC(mzi0)	5067	1947	0974
OD(0000)	1795	1072	1919
OD(0z00)	2153	1057	6862
OD(00i0)	3008 (6992)	3969 (6031)	3221 (6779)
OD(0zi0)	3079 (6921)	3986 (6014)	8000 (2000)
OD(m000)	7073 (2027)	1277 (8723)	7894 (2106)
OD(mz00)	8246 (1754)	1443 (8557)	2830 (7170)
OD(m0i0)	6861	3637	7335
OD(mzi0)	6999	3691	1993

Values given in brackets are the original atomic parameters of Kempster et al. (1962), for atoms which have been inverted by the author into the asymmetric part of the unit cell.

Table 4A. Anorthite: The Original Atomic Parameters (Kempster et al., 1962) - transferred into the Asymmetric Part of the Unit Cell.

TABLE 4B

Anorthite: Calcium-Oxygen Distances less than 6.500Å.

- Note: (a) "OXYGEN NAME AND NO." gives the Megaw (1956) notation with a numerical, sequential number used in the computer program. This listing includes all equivalent oxygen atoms, and successive pairs are related by a centre of symmetry. e.g. OA(1000) and OA(100c); they are thus structurally equivalent and hence are assigned the same atom number.
- (b) Under each Ca-column, X, Y and Z refer to the translation components in relation to the atomic parameters listed in Table 4A.
- (c) "NN" refers to the 'nearness number', that is the oxygen atoms in order of nearness. Where two Ca-O distances are the same, their respective oxygen atoms are assigned the same 'nearness number'.
- (d) There is a small error (up to 2%) in these Ca-O distances as slightly incorrect interaxial angles were used in the calculation. These will be corrected when subsequent (post-thesis) work on anorthite is continued.

..... continued/

OXYGEN NAME AND NO.	CA1(O00)		CA2(Z00)		CA3(O10)		CA4(Z10)	
	X,Y,Z X,Y,Z	BOND NN						
OA(1000) 01	0 0 0	2.491(04)					0 0 0	5.304(33)
OA(100C) 01	0 -1 +1	2.652(06)					-1 0 +1	5.676(38)
OA(1Z00) 02			-1 0 0	2.501(04)	-1 0 0	4.858(27)		
OA(1Z0C) 02			0 0 0	6.351(48)	0 0 0	5.741(37)		
OA(1Z0C) 02	0 -1 0	6.235(46)	0 -1 0	2.705(07)				
OA(1010) 03			0 0 0	4.913(29)	0 0 0	2.482(04)	-1 0 0	6.353(49)
OA(101C) 03			-1 0 0	6.299(45)	-1 0 0	6.299(45)		
OA(1Z10) 04	0 0 +1	5.394(34)	0 -1 0	5.691(36)	0 0 0	2.806(07)	0 0 +1	2.500(04)
OA(1Z1C) 04	0 -1 0	5.659(35)					0 0 0	2.573(05)
OA(2000) 05	0 0 0	2.287(01)	0 0 0	4.064(11)				
OA(200C) 05	+1 0 0	6.056(43)	-1 -1 0	6.055(40)				
OA(2Z00) 06	0 -1 +1	6.238(47)	0 0 0	3.363(08)				
OA(2Z0C) 06	+1 0 +1	6.464(51)	-1 0 +1	6.226(42)	0 0 0	6.348(46)	0 0 0	3.776(11)
OA(2010) 07	0 -1 0	3.501(09)	0 -1 0	2.374(01)	0 0 0	3.225(08)	0 0 0	6.379(50)
OA(201C) 07			-1 -1 0	6.397(50)	+1 0 0	6.270(43)	0 0 +1	6.379(50)
OA(2Z10) 08			0 0 0	6.323(46)	0 0 0	4.226(14)	0 0 +1	3.734(10)
OA(2Z1C) 08					0 0 0	6.117(40)	+1 0 +1	6.211(46)
OA(2Z1C) 08							0 0 0	6.053(41)
OA(2Z1C) 08							-1 0 0	2.335(01)

Table 4B. (Continued)

OXYGEN NAME AND NO.	CA1(OOO)		CA2(ZOO)		CA3(OIO)		CA4(ZIO)	
	X,Y,Z X,Y,Z	BOND NN	X,Y,Z X,Y,Z	BOND NN	X,Y,Z X,Y,Z	BOND NN	X,Y,Z X,Y,Z	BOND NN
OB(O000) 09	0 0+1	2.359(02)	-1 0 0	6.185(41)	-1 0 0	6.497(53)		
OB(O00C) 09	0-1 0 +1-1 0	4.727(24) 4.010(11)	0-1 0	6.004(39)			0 0 0	5.232(32)
OB(OZ00) 010	0 0 0	4.831(26)	0 0 0 -1 0 0	4.165(13) 4.314(17)			-1 0 0	6.401(51)
OB(OZ0C) 010			0-1 0	2.449(03)	0 0 0	5.736(36)		
OB(O0IO) 011					0 0 0	4.106(13)	0 0+1	6.261(47)
OB(O0IC) 011			0-1 0	5.762(37)	-1 0 0	4.334(17)	0 0 0	5.194(31)
OB(OZIO) 012	0 0 0	4.912(28)			0 0 0	6.162(41)	0 0 0	4.140(12)
OB(OZIC) 012					0 0 0	5.953(39)	-1 0 0	4.406(17)
OB(M000) 013	0 0 0 +1 0 0	4.621(23) 4.416(17)	0 0 0	4.884(27)			0 0 0	4.455(19)
OB(M00C) 013	0-1+1	3.866(10)	-1-1 0	5.558(33)	0 0 0	4.070(12)	0 0+1	6.127(42)
OB(MZ00) 014	+1 0+1	6.355(48)	0 0 0	2.515(05)	0 0 0	6.363(48)		
OB(MZ0C) 014	0-1 0	5.034(29)	0-1 0	4.837(26)	0 0 0	5.18(05)	0 0 0	4.911(28)
OB(MOIO) 015	0 0 0	6.396(50)	-1-1 0 0 0 0	4.744(24) 4.222(14)	0 0 0	6.270(43)	0 0+1	6.148(43)
OB(MOIC) 015			-1-1 0	6.307(45)	-1 0 0	4.688(24)	0 0+1	3.277(08)
OB(MZIO) 016	+1 0+1	6.119(44)			0 0 0	5.187(31)		
OB(MZIC) 016	0-1 0	4.828(25)			0 0 0	5.639(34)	0 0 0	4.297(15)
							-1 0 0	4.878(27)

Table 4B (Continued)

OXYGEN NAME AND NO.	CA1(O00)		CA2(Z00)		CA3(O10)		CA4(Z10)	
	X,Y,Z X,Y,Z	BOND NN						
OC(O000) 017	+1 0+1	4.301(14)	0 0 0	6.370(49)	0 0 0	4.605(23)	0 0+1	5.023(29)
OC(O00C) 017	0-1 0	4.511(19)	0 0 0	4.456(21)	0 0 0	4.448(20)	-1 0 0	3.573(09)
OC(OZ00) 018			0 0 0	4.456(21)	0 0 0	4.448(20)	0 0 0	4.225(14)
OC(OZ0C) 018	+1 0 0	6.358(49)	-1-1 0	4.741(23)	+1 0 0	6.406(50)	0 0 0	
OC(O010) 019			+1 0 0	6.417(51)	-1 0 0	3.837(09)	0 0 0	
OC(O01C) 019	0-1 0	4.523(20)	0 0 0	4.462(22)	0 0 0	4.270(15)	0 0 0	
OC(OZ10) 020	0 0 0	3.117(07)	-1 0 0	6.397(50)	-1 0 0	6.270(43)	0 0+1	4.438(18)
OC(OZ1C) 020	0-1+1	5.369(33)	0-1 0	4.334(19)	0 0 0	6.296(44)	+1 0+1	6.001(40)
OC(M000) 021	0 0 0	4.494(18)	0 0 0	4.334(19)	0 0 0	6.296(44)	0 0 0	5.055(30)
OC(M00C) 021	+1-1+1	5.290(32)	-1 0 0	4.450(20)	0 0 0	5.501(33)	0 0 0	
OC(MZ00) 022			-1 0 0	4.450(20)	-1 0 0	2.553(06)	0 0 0	
OC(MZ0C) 022			0-1 0	5.089(31)	0 0 0	4.288(16)	0 0 0	
OC(MO10) 023	0 0 0	4.590(22)	0 0 0	2.550(06)	+1 0 0	6.354(47)	0 0 0	
OC(MO1C) 023			0 0 0	2.550(06)	0 0 0	4.574(22)	0 0 0	
OC(MZ10) 024	0 0+1	4.391(16)	0-1 0	4.236(15)	0 0 0	5.295(32)	0 0+1	4.773(25)
OC(MZ1C) 024	+1 0+1	6.017(41)	-1-1 0	6.278(43)	0 0 0	5.295(32)	0 0 0	
OC(MZ20) 024	0-1 0	3.262(08)	0-1 0	5.661(34)	0 0 0	5.295(32)	0 0 0	4.572(21)

Table 4B (Continued)

OXYGEN NAME AND NO.	CA1(O00)		CA2(Z00)		CA3(O10)		CA4(Z10)	
	X,Y,Z X,Y,Z	BOND NN						
OD(O000) 025	+1 0+1	4.138(13)	0 0 0	4.895(28)	0 0 0	5.644(35)	-1 0 0	6.183(44)
OD(O00C) 025	0-1 0	2.411(03)	0-1 0	4.960(30)				
OD(OZ00) 026	0 0 0	4.351(14)	0 0 0	2.385(02)	0 0 0	5.837(38)	0 0 0	5.802(39)
OD(OZ0C) 026	+1 0 0	6.162(45)	-1-1 0	4.148(12)				
OD(O010) 027	0-1+1	5.846(38)	0 0 0	5.892(38)	0 0 0	2.370(02)	0 0+1	5.637(36)
OD(O01C) 027	0-1 0	6.006(40)			0 0 0	4.051(11)	-1 0 0	4.645(23)
OD(OZ10) 028	0 0 0	6.039(42)	0 0 0	5.681(35)	0 0 0	4.745(25)	0 0 0	6.349(48)
OD(OZ1C) 028					-1 0 0	4.829(26)	0 0+1	4.189(13)
OD(M000) 029	0 0 0	2.537(05)	0 0 0	4.318(18)			-1 0 0	5.533(34)
OD(M00C) 029	+1-1+1	4.857(27)	-1 0 0	6.293(44)	0 0 0	6.465(52)	0 0+1	6.209(45)
OD(MZ00) 030	0 0+1	5.129(30)	-1 0 0	4.312(16)	-1 0 0	4.982(30)		
OD(MZ0C) 030	0-1 0	4.555(21)	0-1 0	3.732(09)			0 0 0	5.615(35)
OD(MO10) 031	+1-1 0	5.749(37)	0 0 0	5.193(32)	0 0 0	4.423(19)	0 0 0	5.660(37)
OD(MO1C) 031	0 0 0	5.240(31)	0-1 0	6.334(47)	0 0 0	6.164(42)	-1 0 0	4.354(16)
OD(MZ10) 032	0 0+1	5.992(39)			-1 0 0	4.375(18)	0 0+1	4.544(20)
OD(MZ1C) 032	0-1 0	5.742(36)	0-1 0	6.455(52)	0 0 0	6.452(51)	0 0 0	2.777(06)

Table 4B (Continued)

The 'weighting factor' is equal to the sum of the inverse squares of the large cation-oxygen bond distances of all those oxygen atoms which are taken to be coordinated with that large cation.

The actual charge distribution from the large cation to a neighbouring oxygen may now be calculated from the following equation:

$$C_C = \frac{P_C}{(CO)^2 \times W} \dots\dots\dots(6)$$

- where: C_C is the positive charge in e.s.u. contributed to a given oxygen atom from a given large cation,
 P_C is the positive charge in e.s.u. on the large cation,
 CO is the bond distance (\AA) of a given oxygen atom from a given large cation, and
 W is the 'weighting factor' calculated for a given large cation environment from equation (5).

In the anorthite structure, if for example 12-fold coordination is assumed for each of the 4 non-equivalent calcium atoms, the above calculation has to be done for each of the Ca-O distances which will result in 48 numbers. These numbers represent the positive charges contributed to each of 48 oxygen atoms, and it now remains to sum those positive charge contributions which have been given to equivalent oxygen atoms, thus arriving at a list of the 32 non-equivalent oxygen atoms and their corresponding amounts of charge received from the various calcium atoms.

Two separate sets of charge contributions have now been calculated, the tetrahedral-oxygen contributions and the calcium-oxygen contributions; these two numbers have to be summed for the non-equivalent oxygen atoms to determine the total amount of charge contributed to those oxygen atoms. These values should approximate to ~~the~~ 2 e.s.u. in order to satisfy the

requirements of the valency or the electrostatic balance. An example of these computed data for the anorthite structure are given in Table 5.

At this stage in the calculation all the basic information has been obtained for a complete calculation of the charge distribution within the anorthite structure, using assumed ideal values for Si-O and Al-O as well as assumed coordination numbers for the calcium atoms. The set of calculations described above has no meaning unless the ideal Si-O and Al-O tetrahedral sizes and the calcium coordination numbers are stated, and this has been done in Tables 2, 3, 5, 6 and 7. These computed data now require further processing so that their significance may be evaluated.

(ii) The Calculation of Charge Unbalance

It might be expected that, if the local electrostatic charge distribution is balanced for a given structure, the sum of the charge contributions to each of the oxygen atoms should approximate closely to 2.000 e.s.u. in order that the negative charge on these oxygen atoms would be neutralized. However, a more realistic view concerns the Si-Al distribution within the structure which is dependent, as we have seen earlier, upon the assumed ideal sizes of the pure Si-O and Al-O tetrahedra. The distribution of Si and Al in the structure is considered to be closely related to the electrostatic charge distribution and a test of this would be to evaluate the total charge contribution to each of the 16 tetrahedral groups of four oxygens. Ideally, if the structure exhibits perfect local electrostatic balance, the charge on each tetrahedral group of four oxygens should sum to 8.000 e.s.u. An example of these computed values for the anorthite structure is given in Table 6, from which it may

TOTAL CHARGE ON OXY	O 1	2.031
TOTAL CHARGE ON OXY	O 2	2.067
TOTAL CHARGE ON OXY	O 3	2.154
TOTAL CHARGE ON OXY	O 4	2.086
TOTAL CHARGE ON OXY	O 5	2.056
TOTAL CHARGE ON OXY	O 6	2.132
TOTAL CHARGE ON OXY	O 7	2.124
TOTAL CHARGE ON OXY	O 8	2.072
TOTAL CHARGE ON OXY	O 9	2.052
TOTAL CHARGE ON OXY	O10	2.016
TOTAL CHARGE ON OXY	O11	1.948
TOTAL CHARGE ON OXY	O12	1.998
TOTAL CHARGE ON OXY	O13	1.985
TOTAL CHARGE ON OXY	O14	1.996
TOTAL CHARGE ON OXY	O15	1.990
TOTAL CHARGE ON OXY	O16	1.983
TOTAL CHARGE ON OXY	O17	1.987
TOTAL CHARGE ON OXY	O18	1.914
TOTAL CHARGE ON OXY	O19	1.903
TOTAL CHARGE ON OXY	O20	1.931
TOTAL CHARGE ON OXY	O21	1.969
TOTAL CHARGE ON OXY	O22	1.942
TOTAL CHARGE ON OXY	O23	1.904
TOTAL CHARGE ON OXY	O24	1.934
TOTAL CHARGE ON OXY	O25	1.971
TOTAL CHARGE ON OXY	O26	2.016
TOTAL CHARGE ON OXY	O27	1.958
TOTAL CHARGE ON OXY	O28	1.969
TOTAL CHARGE ON OXY	O29	1.992
TOTAL CHARGE ON OXY	O30	1.966
TOTAL CHARGE ON OXY	O31	1.951
TOTAL CHARGE ON OXY	O32	1.979

Table 5. Anorthite: Example of the Total Charge Contributions to the 32 Non-Equivalent Oxygen Atoms.

Si-O = 1.602 Å.

Al-O = 1.762 Å.

Calcium in the following coordination:

Ca(OO)-16; Ca(zOO)-18; Ca(OiO)-14; Ca(ziO)-16.

TOTAL CHARGE ON TETRAHEDRON	T 1	8.041
TOTAL CHARGE ON TETRAHEDRON	T 2	7.962
TOTAL CHARGE ON TETRAHEDRON	T 3	7.971
TOTAL CHARGE ON TETRAHEDRON	T 4	7.983
TOTAL CHARGE ON TETRAHEDRON	T 5	8.045
TOTAL CHARGE ON TETRAHEDRON	T 6	7.990
TOTAL CHARGE ON TETRAHEDRON	T 7	7.988
TOTAL CHARGE ON TETRAHEDRON	T 8	7.996
TOTAL CHARGE ON TETRAHEDRON	T 9	8.013
TOTAL CHARGE ON TETRAHEDRON	T10	7.984
TOTAL CHARGE ON TETRAHEDRON	T11	7.978
TOTAL CHARGE ON TETRAHEDRON	T12	7.999
TOTAL CHARGE ON TETRAHEDRON	T13	8.007
TOTAL CHARGE ON TETRAHEDRON	T14	7.993
TOTAL CHARGE ON TETRAHEDRON	T15	8.002
TOTAL CHARGE ON TETRAHEDRON	T16	8.000
POSITIVE UNBALANCE	0.107	
NEGATIVE UNBALANCE	0.157	
SUM OF DEVIATION K =	88	0.264

Table 6. Anorthite: Example of the Total Charge Contributions to the 16 Non-Equivalent Tetrahedral Groups of Four Oxygens and the Total Charge Unbalance Value.

Si-O = 1.602 Å, and

Al-O = 1.762 Å.

Calcium in the following coordination:

Ca(OO)-16; Ca(zOO)-18; Ca(OiO)-14; Ca(ziO)-16.

K is the iteration number which is explained in the text.

be seen that there is small deviation from the predicted ideal values, either greater or less than 8.000 e.s.u.

A measure of the degree of electrostatic charge unbalance for the structure as a whole may now be obtained by summing the differences from 8.000 e.s.u. on each of the tetrahedra; this value represents the total electrostatic charge unbalance in the structure, and it is also shown in Table 6.

The above description of the calculation of electrostatic charge distribution is in its basic form and does not take into account variation in the ideal values of Si-O, Al-O and the calcium coordination numbers. Computations of this nature require that these variables be treated, and to do this, computer-based calculations are essential. The following section of this Chapter discusses and takes account of these variables.

(iii) Additional Variables

(a) Assumed Si-O and Al-O Values

The ideal values of Si-O and Al-O which are to be assumed for the purpose of these calculations are of great importance in relation to the Si-Al order-disorder problem in the feldspar structures. It is upon these values that the statistical Al-contents of the tetrahedra depend. A first attempt at reaching reasonable values for these distances was made by J. V. Smith (1954) who concluded from a study of various aluminosilicate structures that the best values should be as follows:

$$\text{Si-O} = 1.60 \pm 0.01 \text{ \AA} \quad \text{and} \quad \text{Al-O} = 1.78 \pm 0.02 \text{ \AA}.$$

Later, in conjunction with S. W. Bailey, Smith revised these distances (Smith and Bailey, 1963) and they proposed the following ideal values for the feldspars:

$$\text{Si-O} = 1.61 \text{ \AA} \quad \text{and} \quad \text{Al-O} = 1.75 \text{ \AA}.$$

As was mentioned in the discussion of the electrostatic charge balance calculations, ideal values for Si-O and Al-O have to be assumed in the first instance in order to calculate the statistical amount of Al present in a particular tetrahedral site so that the amount of positive charge on that site may be determined. The assumed values may, however, be varied later in order to establish more accurate ideal values for the structure under consideration. To fulfill this, the Si-O and Al-O values were inserted into the FORTRAN IV computer program as variables, so that sets of iterative calculations could be performed, varying the Si-O and Al-O values for each set of calculations. Starting values of Si-O and Al-O were arrived at by an examination of all the tetrahedral distances in the anorthite structure. The smallest mean tetrahedral bond length would represent the largest possible size for an ideal Si-O tetrahedron and so the actual ideal value could only be that value or *smaller*. In this way the number of iterations required to determine the best values was reduced and the starting values determined for anorthite were:

$$\text{Si-O} = 1.602 \text{ \AA} \quad \text{and} \quad \text{Al-O} = 1.758 \text{ \AA} \text{ (see Table 1, p. 13)}$$

The computer program is written such that after the first iteration, a value representing the total charge unbalance is obtained, and then an adjustment of -0.001 \AA is made to the Si-O value. The second iteration is then calculated and the total charge unbalance values are compared. If the total unbalance value has decreased, thus indicating an improved

charge distribution, then a similar change would be made to the Si-O value and the third iteration calculated. This would continue until the total charge unbalance value is larger than that of the previous iteration and the best ideal value of Si-O is attained. Now changes are made to the Al-O value of $+0.001 \text{ \AA}$, and similar changes continue to be made until the total charge unbalance on one iteration is greater than that of the previous iteration. In this way the best values of Si-O and Al-O are obtained. These two values are then kept constant for the remaining calculations during which a series of iterations are performed varying the coordination numbers of the calcium atoms as described in the next section. Additional details of this operation may be found in Appendix I where there is a complete description of the computer program including the printout and the complete program documentation.

(b) Coordination of the Calcium Atoms

The coordination numbers of the calcium atoms ^{are} uncertain and additional complications arise when one considers that it is possible that the four calcium atoms may have different coordination numbers. The iterative form of the computer program is suited to this kind of problem, and after the best Si-O and Al-O values have been determined, the succeeding iterations vary the coordinations of the calcium atoms. Here again the problem is compounded by the presence of 4 inter-dependent variables, and the impossibility of being able to treat them as such, owing to the magnitude of the calculation. As a compromise it was decided that the best approach would be to vary the coordination number of each calcium atom in turn, increasing them from a low reasonable value, say of 12.

The program was set up in such a way that it would accept or reject any oxygen into coordination depending on whether the increased coordination lowered or raised the total electrostatic charge unbalance value. Similar decisions were made for each of the 4 calcium atoms. Table 7 gives an example of the printed output from the program and gives the radius of the calcium environment scanned, and the number of oxygens within that environment which have been coordinated to the calcium atom. Since this anorthite is presumably a low-temperature feldspar it may be expected to have a charge unbalance near zero; consequently, decisions like the one above were used as a means of finding the correct combination of the coordination numbers which will yield a minimum unbalance value. The decision to accept a given oxygen into coordination with a given calcium atom is then based on whether the increased coordination reduces the charge unbalance in the structure. However, it became apparent during the investigation that there is a possibility that some of the closer oxygen atoms may be rejected in favour of others further away from the calcium atom. This may be explained in terms of a 'shielding effect' in which some of the closer oxygen atoms are unable to receive electrostatic charge from a calcium owing to their being shielded by other still closer atoms. More is said about this matter in Chapter III where some of the details of the results on the anorthite calculations are discussed.

In the program the following results are printed out for each iteration, an example of a complete printout for one iteration being given in Appendix I(f):

- (a) The Si-O and Al-O values used and the iteration number (K),
- (b) The Al-content (fractions of atoms) of each tetrahedron,

ITERATION NUMBER 88	
LIMIT FOR CAT-O 1	5.290
CO-ORD OF CAT1	16.
LIMIT FOR CAT-O 2	5.193
CO-ORD OF CAT2	18.
LIMIT FOR CAT-O 3	5.295
CO-ORD OF CAT3	14.
LIMIT FOR CAT-O 4	5.232
CO-ORD OF CAT4	16.

Table 7. Anorthite: Example of the Limiting Ca-O Distances and the Coordination Numbers of the 4 Non-Equivalent Calcium Atoms.

charge distribution, then a similar change would be made to the Si-O value and the third iteration calculated. This would continue until the total charge unbalance value is larger than that of the previous iteration and the best ideal value of Si-O is attained. Now changes are made to the Al-O value of $+0.001 \text{ \AA}$, and similar changes continue to be made until the total charge unbalance on one iteration is greater than that of the previous iteration. In this way the best values of Si-O and Al-O are obtained. These two values are then kept constant for the remaining calculations during which a series of iterations are performed varying the coordination numbers of the calcium atoms as described in the next section. Additional details of this operation may be found in Appendix I where there is a complete description of the computer program including the printout and the complete program documentation.

(b) Coordination of the Calcium Atoms

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- (c) The total Al-content of the structure (expressed as numbers of atoms),
- (d) The tetrahedral charge contributions (e.s.u.) to each of the 32 non-equivalent oxygen atoms,
- (e) The coordination numbers of the 4 calcium atoms and the corresponding radii (\AA) of the environments which have been examined to this stage in the calculations,
- (f) The total charge contributions (e.s.u.) to each of the non-equivalent oxygen atoms,
- (g) The total charge contributions (e.s.u.) summed for each tetrahedral group of 4 oxygens,
- (h) The sum of the excess positive charge (e.s.u.) on the tetrahedra and the sum of the charge deficiency on the tetrahedra, and
- (i) The total electrostatic charge unbalance (e.s.u.) in the *four tetrahedral units of the* structure and the iteration number (K) which may be used to refer to the variables used for that particular iteration.

When the calculations have been completed and a minimum charge unbalance has been determined for the whole structure, a summary of each iteration is printed out in tabular form. An example of such a summary is given in Table 8.

ITERATION NUMBER	SID VALUE	ALO VALUE	TOTAL AL CONTENT	CHARGE		CHARGE DIFFERENCE	COORDINATION NOS. OF			
				UNBALANCE	AL		CA1	CA2	CA3	CA4
1	1.602	1.758	8.180	1.002	12	0.0	12	12	12	12
2	1.601	1.758	8.229	1.037	12	-0.035	12	12	12	12
3	1.602	1.758	8.180	1.002	12	0.035	12	12	12	12
4	1.602	1.759	8.127	0.961	12	0.041	12	12	12	12
5	1.602	1.760	8.076	0.942	12	0.019	12	12	12	12
6	1.602	1.761	8.025	0.939	12	0.002	12	12	12	12
7	1.602	1.762	7.975	0.945	12	-0.005	12	12	12	12
8	1.602	1.761	8.025	0.939	12	0.0	12	12	12	12
9	1.602	1.761	8.025	0.914	13	0.025	13	12	12	12
10	1.602	1.761	8.025	0.816	13	0.098	13	13	12	12
11	1.602	1.761	8.025	0.900	13	-0.084	13	13	13	12
12	1.602	1.761	8.025	0.845	13	-0.028	13	13	12	13
13	1.602	1.761	8.025	0.662	14	0.154	14	13	12	12
14	1.602	1.761	8.025	0.629	14	0.033	14	14	12	12
15	1.602	1.761	8.025	0.650	14	-0.021	14	14	13	12
16	1.602	1.761	8.025	0.508	14	0.121	14	14	12	13
17	1.602	1.761	8.025	0.487	15	0.021	15	14	12	13
18	1.602	1.761	8.025	0.441	15	0.046	15	15	12	13
19	1.602	1.761	8.025	0.576	15	-0.136	15	15	12	14
20	1.602	1.761	8.025	0.475	16	-0.035	16	15	12	13
21	1.602	1.761	8.025	0.431	15	0.010	15	16	12	13
22	1.602	1.761	8.025	0.421	15	0.010	15	16	12	14
23	1.602	1.761	8.025	0.394	16	0.026	16	16	12	14
24	1.602	1.761	8.025	0.261	16	0.133	16	17	12	14
25	1.602	1.761	8.025	0.261	16	0.0	16	17	12	14
26	1.602	1.761	8.025	0.303	17	-0.042	17	17	12	14
27	1.602	1.761	8.025	0.291	16	-0.030	16	18	12	14
28	1.602	1.761	8.025	0.261	16	0.0	16	17	12	14
29	1.602	1.761	8.025	0.291	16	-0.030	16	18	12	14

Table 8. Anorthite: Example of a Summary of a Complete Set of Iterative Charge Balance Calculations.

CHAPTER III

RESULTS AND DISCUSSION OF THE ELECTROSTATIC CHARGE

CALCULATIONS FOR THE ANORTHITE STRUCTURE

(i) General Remarks

Chapter II dealt with the principles involved in the distribution of electrostatic charges within a complicated structure such as anorthite. This Chapter describes briefly some of the calculations of charge unbalance in the anorthite structure, pointing out some of the modifications in approach which were employed in an attempt to obtain more meaningful results. In the last section of this Chapter it is shown that the anorthite structure presented more of a challenge than had originally been anticipated, and that it was considered advisable by the author and his supervisor to embark on a thorough study of the simpler low- and high-temperature albite structures in order to establish a workable system that could, at a later date, be applied to the anorthite and other feldspar structures. Despite the fact that, at present, the work concerning the anorthite structure is incomplete, certain interesting features of the electrostatic charge distribution have come to light as a result of these first calculations.

Owing to the large number of non-equivalent atoms in the anorthite structure, programming is difficult as the equivalence of the oxygen atoms must be established during the tetrahedral part of the calculations so that the charge distributions may be summed on the non-equivalent atoms. An additional difficulty is the fact that there are 4 non-equivalent calcium

atoms and thus 4 sets of Ca-O distances are involved; even more difficult is the equivalence of the various oxygens in each of these 4 calcium atom environments. The over-riding control (the charge unbalance value) governing changes in the variables in the computer program is based on the assumptions that this anorthite is a low-temperature feldspar and that it can therefore be expected to yield a low total electrostatic charge unbalance value. Reference to the tabulation on page 4 indicates that the minimum charge unbalance hitherto obtained for any feldspar is that of 0.12 e.s.u. for low albite (Ferguson et al., 1958). A consequence of this is that the unbalance value for the anorthite structure must be at least comparable to that for low albite in order to support the original assumptions. As mentioned in the previous Chapter, the charge unbalance is measured by the sum of the deviations from 8.000 e.s.u. on each of the non-equivalent tetrahedral groups of 4 oxygens in a feldspar structure. Thus for low albite the unbalance value is given by the sum of the deviations on 4 independent tetrahedra. Since anorthite has 16 non-equivalent tetrahedra, the comparable charge unbalance value to that of low albite will differ by a factor of four, that is to say, $0.12 \times 4 = 0.48$ e.s.u.

(ii) Calculations Using the Same Coordination Numbers for each of the Four Calcium Atoms

The first calculations to be carried out concerning the electrostatic charge distributions within the structure of anorthite were attempted using equal coordinations for the 4 calcium atoms, and varying the ideal sizes of the pure Si-O and Al-O tetrahedra. It was thought

at this stage that a minimum charge unbalance value, comparable to that of low albite, could be obtained in this way. Table 9 shows a few selected values which characterize these calculations, and it may be seen that the minimum charge unbalance value (0.794 e.s.u.) was obtained using a coordination number of 11 for all the calcium atoms. This value of 0.794 e.s.u. is almost twice as great as the best comparable low albite value, although the best ideal values for Si-O and Al-O vary only slightly and appear to be reasonable. From information of this nature it was obvious that the variables, Si-O, Al-O and the coordination numbers of the calcium atoms are all strongly inter-dependent. The problem of allowing for this inter-dependency is virtually insuperable in the anorthite structure in that it would involve calculating all possible combinations of the several variables, and this would require very extensive computer time. At this point it was felt that the 4 calcium atoms may have different coordination numbers and the program was modified accordingly as described in the next Section.

(iii) Calculations Using Different Coordination Numbers for the Four Calcium Atoms

(a) Coordination by a Number of the Nearest Oxygen Atoms in each Calcium Environment

Continuing from the study described in the previous Section, it was thought that different coordination numbers of the different calcium atoms would possibly give more satisfactory results; consequently the computer program was modified in order to vary the coordination numbers of each calcium atom independently of the others. The coordination was again controlled by the charge unbalance value and a new attempt was made

BEST Si-O (Å)	BEST Al-O (Å)	CO-ORDINATION OF ALL FOUR Ca-ATOMS	TOTAL CHARGE UNBALANCE (e.s.u.)
1.602	1.767	6	2.211
1.600	1.763	10	1.067
1.602	1.763	11	0.794
1.602	1.763	12	0.835
1.602	1.766	13	1.215
1.602	1.762	14	1.083
1.602	1.762	15	0.813
1.602	1.764	16	0.859

Table 9. Anorthite: Examples of Electrostatic Charge Unbalance Values for Various Coordinations of the Calcium Atoms.

to reach a low charge unbalance value. The coordination numbers in these calculations represent the number of nearest oxygen atoms around a particular calcium atom. The program first attained the best Si-O and Al-O values with a low starting coordination for all four calcium atoms; then the coordination of the first calcium, Ca(000), was increased by one and a comparison made between the unbalance number obtained on the previous iteration with the unbalance obtained on the current iteration; if the charge unbalance had decreased, a similar change was made to the coordination of Ca(000) and again tested. This procedure was continued until the charge unbalance number on the current iteration was greater than that of the previous iteration, at which point the best coordination number for this calcium atom had been established. The program then moved on to adjust that coordination of the second calcium, Ca(z00), and arrived at its oxygen environment in a similar manner; and so on for the remaining 2 non-equivalent calcium atoms. Table 10 gives some selected values for various complete sets of iterations, and it can be seen that the minimum total electrostatic charge unbalance value is 0.734 e.s.u., representing a slight decrease from the minimum value given in Table 9. This value was obtained with generally large coordination numbers for the calcium atoms. These coordinations are considerably larger than those predicted by geometric considerations, and it was felt that they may be unreal. However, the large number of oxygen atoms in a given calcium environment suggested that possibly the charge on the calcium is effective to large distances, and that it may be necessary to consider an even larger calcium environment in order to attain a small charge unbalance value for the structure. Such an idea would be departing from the strict concept of coordination, but nevertheless it was thought advisable to investigate this possibility.

BEST Si-O(Å)	BEST Al-O(Å)	COORDINATION NOS. OF				TOTAL CHARGE UNBALANCE (e.s.u.)
		Ca1 (000)	Ca2 (z00)	Ca3 (0i0)	Ca4 (zi0)	
1.602	1.763	14	13	12	11	0.747
1.602	1.761	12	11	10	11	0.838
1.602	1.764	15	16	16	16	0.734
1.600	1.763	12	11	10	11	0.762

Table 10. Anorthite: Examples of Electrostatic Charge Unbalance Values for Different Coordination Numbers of each of the Four Calcium Atoms.

(b) The Investigation of a Larger Oxygen Environment for Each Calcium Atom taking into Account a 'Shielding Factor'

This investigation was based on a concept that the charge on the calcium atoms was effective for large distances in all directions around the atom. Therefore, if this were the case, it would be necessary to distribute the charges to all the oxygens in a wide environment about each calcium atom. The resulting coordinations would probably be large, but perhaps the number of oxygens involved in this environment should not be considered as being 'coordinated' in the accepted sense of the word.

The computer program was once again modified and provision was made to test an oxygen environment of radius 6.5 \AA about each of the 4 calcium atoms, in a manner similar to that described in Chapter II. This large environment would include about the nearest 50 oxygens to each calcium. The method involves testing each oxygen atom in order of increasing Ca-O distance, and if the total charge unbalance number is reduced, then that oxygen will be considered as an effective part of that calcium environment. Similar tests are then made on the oxygen environments of each of the other calcium atoms until they have all been examined to given limits. It was thought that with these modifications, the charge unbalance value would be a sensitive indicator as to whether or not a given oxygen was electrostatically bonded to a given calcium atom.

This approach also offered the possibility that some of the oxygen atoms might be taken into coordination with a calcium atom in favour of others which are closer to that calcium atom. This was explained

as being due to electrostatic 'shielding' of some oxygens by other closer atoms, either oxygens or calcium atoms. Using this new method described above, several sets of calculations were completed, and it became apparent that the inter-dependency of the variables was a real problem. This was brought to light by the fact that the final charge unbalance value produced by the program was strongly dependent upon the assumed starting coordinations for the calcium atoms. The starting values for the ideal Si-O and Al-O values appeared to be less significant. However, the coordination numbers assumed at the start of the program for the calcium atoms had a strong bearing on the final charge unbalance value. On account of this a further small modification to the computer program was made so that the coordinations of the calcium atoms could be varied in turn, thus gradually scanning through the environment, in such a manner that the radius of the scan remained approximately the same for all the calcium atoms at any given time. This appeared to be a compromise to the problem of treating the coordination numbers as inter-dependent variables. Table 11 gives an example of the summary of each iteration for a complete set of these calculations and it may be seen that a marked decrease in the charge unbalance value for the anorthite structure was effected.

Several more sets of these iterative calculations were performed using this method and using different starting values for Si-O and Al-O; scanning the calcium environment to 6.50 \AA , resulting in larger coordination numbers than are shown in Table 11. It may be seen from the examples shown in Table 12 that a further decrease in the charge unbalance value was effected, and that regardless of the starting values for the ideal

ITERATION NUMBER	SIO VALUE	ALO VALUE	TOTAL AL CONTENT	CHARGE UNBALANCE	CHARGE DIFFERENCE	COORDINATION NOS. OF			
						CA1	CA2	CA3	CA4
1	1.602	1.758	8.180	1.002	0.0	12	12	12	12
2	1.601	1.758	8.229	1.037	-0.035	12	12	12	12
3	1.602	1.758	8.180	1.002	0.035	12	12	12	12
4	1.602	1.759	8.127	0.961	0.041	12	12	12	12
5	1.602	1.760	8.076	0.942	0.019	12	12	12	12
6	1.602	1.761	8.025	0.939	0.002	12	12	12	12
7	1.602	1.762	7.975	0.945	-0.005	12	12	12	12
8	1.602	1.761	8.025	0.939	0.0	12	12	12	12
9	1.602	1.761	8.025	1.065	-0.126	13	12	12	12
10	1.602	1.761	8.025	1.029	-0.090	12	13	12	12
11	1.602	1.761	8.025	1.061	-0.122	12	12	13	12
12	1.602	1.761	8.025	0.926	0.014	12	12	12	13
13	1.602	1.761	8.025	0.900	0.025	13	12	12	13
14	1.602	1.761	8.025	0.845	0.055	13	13	12	13
15	1.602	1.761	8.025	0.894	-0.050	13	13	13	13
16	1.602	1.761	8.025	0.961	-0.116	13	13	12	14
17	1.602	1.761	8.025	0.908	-0.064	14	13	12	13
18	1.602	1.761	8.025	0.975	-0.131	13	14	12	13
19	1.602	1.761	8.025	0.916	-0.071	13	13	13	13
20	1.602	1.761	8.025	0.729	0.116	13	13	12	14
21	1.602	1.761	8.025	0.574	0.154	14	13	12	14
22	1.602	1.761	8.025	0.536	0.038	14	14	12	14
23	1.602	1.761	8.025	0.671	-0.135	14	14	13	14
24	1.602	1.761	8.025	0.621	-0.084	14	14	12	15
25	1.602	1.761	8.025	0.528	0.008	15	14	12	14
26	1.602	1.761	8.025	0.477	0.051	15	15	12	14
27	1.602	1.761	8.025	0.536	-0.059	15	15	13	14
28	1.602	1.761	8.025	0.565	-0.088	15	15	12	15
29	1.602	1.761	8.025	0.460	0.017	16	15	12	14

Table 11. Anorthite: A Set of Results Illustrating Changes in Coordination for the Four Calcium Atoms and their Effect on the Charge Unbalance Value.

BEST Si-O(Å)	BEST Al-O(Å)	CO-ORDINATION NOS. OF				TOTAL CHARGE UNBALANCE (e.s.u.)
		Ca1 (000)	Ca2 (z00)	Ca3 (0i0)	Ca4 (zi0)	
1.602	1.762	16	22	14	16	0.130
1.602	1.762	16	19	14	16	0.143
1.602	1.762	16	20	14	16	0.148
1.602	1.762	18	20	14	16	0.136

Table 12. Anorthite: A Comparison between Different Sets of Calculations which Yielded Small Charge Unbalance Values using Different Starting Values for the Ideal Si-O and Al-O Mean Tetrahedral Sizes.

Si-O and Al-O, the best values arrived at in each case are the same. The values listed in Table 12 are all extremely low for the total electrostatic charge unbalance for anorthite and are equivalent to even smaller values for the low albite structure. For example, 0.130 e.s.u. on anorthite is equivalent to $0.130/4 = 0.032$ e.s.u. on the low albite structure. However, examination of the structure model of anorthite, purchased from Crystal Structures Ltd., Cambridge, England, in conjunction with detailed studies of the results, indicated that some oxygen atoms were being taken into coordination with calcium which were completely shielded by other closer atoms. The realization of this fact made it clear that further calculations along similar lines would be of no value as the small charge unbalance values which had been obtained were of no significance since they had been produced mathematically without due regard to the actual crystal structure of the mineral.

Despite this, it may be said that the computer program in its present form (as detailed in Appendix I) provides a basic method of handling the calculations required for the anorthite structure, although modification is required to take account of crystal structure considerations.

(iv) Conclusions Regarding Anorthite

Although it must be admitted that the work on the electrostatic charge distributions within the structure of anorthite is incomplete, certain information may be considered as being of value. In the first place, all the calculations which were performed indicate that the ideal values for the sizes of the pure Si-O and Al-O tetrahedra for anorthite

are probably close to 1.602 Å and 1.762 Å respectively. The final values for the structure may be slightly different, but will almost certainly be of this order. Information concerning the best coordination numbers of the calcium atoms is unsatisfactory, and recent work dealing with the albite structures (described in the next Chapters) indicates that these coordination numbers may be considerably lower than those which were assumed for most of the calculations detailed above, say in the range 6-fold to 9-fold, rather than in the range 12-fold to 16-fold. However, it remains to be seen whether this is actually the case and further work along these lines is anticipated.

It now remains to comment on some of the very low charge unbalance values which were obtained for the anorthite structure, but which are considered as being unreal. It is rather surprising that any set of assumed values for several variables should yield a low unbalance even if they are unreal. This was one of the original assumptions which was used in designing the computer program to handle these calculations and, as has already been mentioned, these calculations were performed without due consideration of the actual crystal structure of anorthite.

The very low charge unbalance value was obtained as a result of several factors. The first is that the program was designed to reach a minimum value on the basis of the total electrostatic charge unbalance value. This means that once the best Si-O and Al-O tetrahedral values were established, the coordination of the calcium atoms was varied, the method of variation being based on the assumption that if any change in coordination yielded a reduction in the charge unbalance value, then

that change in coordination was considered to be acceptable. Thus the final results for the low charge unbalance values gave coordinations for the calcium atoms which were quite high, and not only different from each other, but also not necessarily representing the nearest number of oxygen atoms to a given calcium atom. Examination of the crystal structure model indicated that some of the oxygens which had been taken into coordination were unreasonable in that they were completely shielded from the calcium atom by other atoms closer to the calcium than the given oxygen. This, taken into consideration with the fact that the program was designed to yield a minimum charge unbalance value, led to the unrealistic arrangement of oxygens (considered as coordinated oxygens) about a given calcium atom which yielded the smallest charge unbalance values. Thus, in the opinion of the author, all these values are unreal and no conclusions may be drawn using these numbers. In fact they may be considered as being the product of a 'mathematical game'.

Recent work concerning the albite structures has shown that the lowest charge unbalance value can be obtained by systematically varying the coordination of the sodium atom. This, however, only involves the single sodium atom and the complications which may arise are minimized. Nevertheless, it may be practical to use a similar method to solve the anorthite structure; it is necessary to consider the oxygen environment about the calcium atoms in order of nearness, and to calculate their solid shielding angles in order to determine the amount of a given oxygen which is shielded from a given calcium atom, by atoms closer than itself. This method is at least crystallographically sound and has been shown to be of

value in similar calculations concerning the albite structures. The remaining alternative concerning anorthite is that the assumed coordination numbers of the calcium atoms are considerably less than had been anticipated and that there is a possibility that a small charge unbalance value may be obtained using smaller coordination numbers, possibly different for each of the four non-equivalent calcium atoms.

(v) Conclusions Leading to the Study of Low and High Albite

The foregoing discussion concerning the results obtained in attempting to distribute the electrostatic charges within the structure of anorthite, indicate the changes in the lines of thought which came to light during the progress of the research.

The last series of calculations concerning anorthite ^{was} based on the false premise that the measure of electrostatic charge unbalance would be a sensitive measure of the 'shielding' effects. It is evident that some atoms are shielded by others and that these atoms are unlikely to receive any charge contributions from the calcium atoms. It also became apparent, by visual examination of the anorthite structure model, that some of the oxygen atoms are only partially shielded by other atoms. It was therefore strongly evident that charge balance calculations such as have been described should take careful account of these factors. Every oxygen atom in the structure should be examined and the amount of shielding by atoms closer to a given calcium atom than itself should be determined. This last view appeared to be the logical conclusion to the previous studies and various means of determining the amount of shielding were investigated.

At the outset it was apparent that visual estimation with the aid of the crystal structure model would be unsatisfactory since the charge distribution is extremely sensitive to all changes in the variables as is shown in previous sections of this Chapter. Therefore it appeared that the amount of shielding would have to be arrived at by mathematical means. Dr. H. R. Coish of the Physics Department of The University of Manitoba was kind enough to assist in this matter and he derived the required formulae which could be used to accurately calculate the amount of shielding of any given atom by other closer ones. These formulae included the use of solid geometry and consequently required calculations which were expected to be extensive. The large number of non-equivalent atoms in the unit cell of anorthite made the task extremely formidable and it was considered advisable to assess the feasibility of these calculations by a study of simpler structures such as low and high albite. In this matter the author received the complete cooperation of his supervisor.

CHAPTER IV

ELECTROSTATIC CHARGE DISTRIBUTION WITHIN

THE LOW ALBITE STRUCTURE

(i) Description of the Method

The method used to calculate the electrostatic charge distributions within the structures of low and high albite was the outcome of studies concerning the charge distribution in anorthite. The method was developed using the IBM 1620 computer since it was more readily available to the author than the IBM SYSTEM 360 used for anorthite; also, it provided a quick method of 'de-bugging' the programs because it was in the direct control of the author. The method of calculating the charge distribution may be equally well applied to both low and high albite, and with the present set of IBM 1620 FORTRAN II programs, may be applied to any feldspar structure with the space group $C\bar{1}$. Documentation of the 4 programs required to do these calculations is given in Appendix II at the end of this thesis. The main difference between these calculations and those of the anorthite structure is that account is now taken of the 'shielding' of the outlying oxygen atoms, a factor which at the start of the albite project was thought to be important. The amount of shielding which occurs for each oxygen in relation to a particular sodium atom is calculated, and from this, the fraction of that oxygen exposed to the sodium charge may be derived; from this, in turn, is calculated the proportion of positive charge it receives from the sodium. It is upon this basis that the electrostatic charge distribution was carried out for the albite structures.

The four programs were written especially for the above calculation, and in their present state require a small amount of handling before the data from one program can be used for the next. Following are brief notes describing the four programs:

Program #1 - Scan of Interatomic Distances: A program to calculate, within given limits (\AA), all the interatomic distances in a given environment about a particular atom.

Program #2 - Scan of Interbond Angles and Shielding Angles: This program used the cation-oxygen distances obtained from Program #1 (re-arranged in increasing order of bond length), and calculates all the required angles in order to establish the overlap relationships between the atoms.

Program #3 - The Solid Angle Shielding Effect: This program uses data directly from Program #2 without modification in order to calculate the shielded fractions of the oxygen atoms relative to the large cations.

Program #4 - The Electrostatic Charge Distribution Program: This program uses data from Program #3 with minor modification and also requires additional data, namely the list of T-O distances (\AA). It calculates the distribution of the electrostatic charges within the given structure, and takes into account the shielding of one oxygen by other atoms closer than itself to the large cations.

Listing and documentation of these Programs may be found in Appendices IIA, IIB, IIC, and IID.

(a) Program #1 - Scan of Interatomic Distances

The first operation required to process the original data is the calculation of the interatomic distances in Angstrom units. The original cell dimensions were those of Ferguson et al. (1958) and the original parameters were those derived by three-dimensional methods by Ribbe et al. (1967). These parameters have to be transferred, if necessary, into an asymmetric part of the unit cell. An asymmetric part of the unit cell for the albite structures with space group $C\bar{1}$ is $1a$, $\frac{1}{2}b$ and $\frac{1}{2}c$. The parameters thus defined are given in Table 13, and these are taken as being the original positions of the atoms throughout this text. The computer program is so designed as to calculate the complete list of bonds within a particular distance around a given atom. Upper and lower limits are provided in order to reduce the number of calculations. Since a complete scan of the environment of a given atom is required, this involves a complete set of translation operations of $+1$ and -1 for each atom in each of the equivalent positions. For example, equivalent position (x, y, z) would be translated as follows:

$x+1, y, z$; $x, y+1, z$; $x, y, z+1$; $x+1, y+1, z$; $x+1, y+1, z+1$; etc.,

until a complete environment has been scanned. Only those bonds falling within the given limits are recorded, and for each of these the following information is punched on cards (see Table 14):

- Column (1) The number of the atom in a given environment whose symbolic name, Megaw notation (1956), is given in column 3.
- (2) The symbolic name of the atom whose environment is being scanned (NA).
- (3) The Megaw notation for the atom in the given environment, corresponding to the atom number in (1).

ATOM+NO.		X/A	Y/B	Z/C
NA	01	7682	4888	1462
OA(1)	06	4945	3692	0336
OA(2)	07	0929	4974	2808
OB(O)	08	8124	1101	1905
OB(M)	09	3200	3512	2587
OC(O)	10	0132	3035	2690
OC(M)	11	5239	1935	2291
OD(O)	12	2075	1091	3890
OD(M)	13	6840	3681	4348

Table 13. Low Albite: The Original Parameters
(Ribbe et al., 1967) Transferred into
the Asymmetric Part of the Unit Cell.
(Expressed as fractions of cell edges x 10^4).

- (4) EQV - The number which indicates the equivalent position of that atom. The code in the case of $\bar{C}\bar{I}$ is:
- 1 - x, y, z
 - 2 - $\bar{x}, \bar{y}, \bar{z}$
 - 3 - $x+\frac{1}{2}, y+\frac{1}{2}, z$
 - 4 - $x-\frac{1}{2}, y-\frac{1}{2}, \bar{z}$
- (5) X Y Z - The amount of translation, in terms of x, y and z which has taken place relative to that equivalent position.
- (6)
- (7)
- & (8) X/A, Y/B, Z/C - The derived parameters of the atom in fractions of the cell edges.
- (9) BOND (A) - The bond length (\AA).
- (10) SER. NO. - A serial number referring to that particular bond.

A listing of the Na-O and Na-Na bond lengths less than 6.500\AA calculated for the low albite structure by this method is given in Table 14, arranged in order of calculation in Table 14A and in order of increasing bond length in Table 14B.

(b) Program #2 - Scan of Interbond Angles and Shielding Angles

The second series of calculations are performed using the data obtained from Program #1, re-arranged in order of increasing bond length (Table 14B), as well as the cell dimensions given by Ferguson et al. (1958). These are the calculations which provide the angular relationships between the bonds necessary for calculating the 'shielding factors'. The angles calculated are defined as follows (Fig. 1):

ATOM	TO	ATOM	EQV.	X	Y	Z	X/A	Y/B	Z/C	BOND(A)	SER. NO.
1	NA	NA	1	0	0	0	.7682	.4888	.1462	0.000	1
6	NA	OA(1)	1	0	0	0	.4945	.3692	.0336	2.537	2
7	NA	OA(2)	1	0	0	0	.0929	.4974	.2808	5.984	3
8	NA	OB(O)	1	0	0	0	.8124	.1101	.1905	4.865	4
9	NA	OB(M)	1	0	0	0	.3200	.3512	.2587	4.518	5
11	NA	OC(M)	1	0	0	0	.5239	.1935	.2291	4.536	6
13	NA	OD(M)	1	0	0	0	.6840	.3681	.4348	2.991	7
7	NA	OA(2)	1	0	0	-1	.0929	.4974	.7192	6.178	8
9	NA	OB(M)	1	0	0	-1	.3200	.3512	.7413	5.903	9
13	NA	OD(M)	1	0	0	-1	.6840	.3681	.5652	4.954	10
6	NA	OA(1)	1	1	0	0	1.4945	.3692	.0336	6.423	11
7	NA	OA(2)	1	1	0	0	1.0929	.4974	.2808	2.377	12
9	NA	OB(M)	1	1	0	0	1.3200	.3512	.2587	4.499	13
10	NA	OC(O)	1	1	0	0	1.0132	.3035	.2690	2.953	14
12	NA	OD(O)	1	1	0	0	1.2075	.1091	.3890	5.803	15
7	NA	OA(2)	2	0	0	0	.9071	.5026	.7192	3.726	16
9	NA	OB(M)	2	0	0	0	.6800	.6488	.7413	4.912	17
10	NA	OC(O)	2	0	0	0	.9868	.6965	.7310	4.447	18
12	NA	OD(O)	2	0	0	0	.7925	.8909	.6110	5.870	19
13	NA	OD(M)	2	0	0	0	.3160	.6319	.5652	5.862	20
1	NA	NA	2	0	0	-1	.2318	.5112	.1462	3.915	21
6	NA	OA(1)	2	0	0	-1	.5055	.6308	.0336	2.664	22
7	NA	OA(2)	2	0	0	-1	.9071	.5026	.2808	3.719	23
9	NA	OB(M)	2	0	0	-1	.6800	.6488	.2587	3.465	24
10	NA	OC(O)	2	0	0	-1	.9868	.6965	.2690	5.035	25
11	NA	OC(M)	2	0	0	-1	.4761	.8065	.2291	4.951	26
13	NA	OD(M)	2	0	0	-1	.3160	.6319	.4348	4.592	27
1	NA	NA	2	1	0	0	1.2318	.5112	.8538	4.768	28

Table 14A. Low Albite: List of Bonds less than 6.500 Å given in order of Calculation (For details, see text).

.....continued/

Table 14A. (continued)

ATOM	TO	ATOM	EQV.	X	Y	Z	X/A	Y/B	Z/C	BOND(A)	SER.NO.
6	NA	OA(1)	2	1	0	0	1.5055	.6308	.9664	6.444	29
13	NA	OD(M)	2	1	0	0	1.3160	.6319	.5652	4.482	30
1	NA	NA	2	1	0	-1	1.2318	.5112	-.1462	5.092	31
7	NA	OA(2)	2	-1	0	-1	-.0929	.5026	-.2808	6.269	32
10	NA	OC(O)	2	-1	0	-1	-.0132	.6965	-.2690	6.263	33
6	NA	OA(1)	3	0	0	0	.9945	.8692	.0336	5.510	34
8	NA	OB(O)	3	0	0	0	1.3124	.6101	.1905	4.621	35
9	NA	OB(M)	3	0	0	0	.8200	.8512	.2587	4.647	36
10	NA	OC(O)	3	0	0	0	.5132	.8035	.2690	4.657	37
11	NA	OC(M)	3	0	0	0	1.0239	.6935	.2291	3.262	38
12	NA	OD(O)	3	0	0	0	.7075	.6091	.3890	2.435	39
13	NA.	OD(M)	3	0	0	0	1.1840	.8681	.4348	5.729	40
12	NA	OD(O)	3	0	0	-1	.7075	.6091	-.6110	5.547	41
8	NA	OB(O)	3	-1	0	0	.3124	.6101	.1905	4.095	42
8	NA	OB(O)	3	-1	0	-1	.3124	.6101	-.8095	6.432	43
12	NA	OD(O)	4	0	0	0	.2925	.3909	.6110	6.337	44
9	NA	OB(M)	4	0	0	-1	.1800	.1488	-.2587	6.132	45
10	NA	OC(O)	4	0	0	-1	.4868	.1965	-.2690	4.580	46
11	NA	OC(M)	4	0	0	-1	-.0239	.3065	-.2291	6.245	47
12	NA	OD(O)	4	0	0	-1	.2925	.3909	-.3890	4.199	48
8	NA	OB(O)	4	1	0	0	.6876	.3899	.8095	5.321	49
9	NA	OB(M)	4	1	0	0	1.1800	.1488	.7413	6.091	50
11	NA	OC(M)	4	1	0	0	.9761	.3065	.7709	4.771	51
12	NA	OD(O)	4	1	0	0	1.2925	.3909	.6110	4.281	52
13	NA	OD(M)	4	1	0	0	.8160	.1319	.5652	5.554	53
1	NA	NA	4	1	0	-1	.7318	.0112	-.1462	6.279	54
6	NA	OA(1)	4	1	0	-1	1.0055	.1308	-.0336	5.191	55
8	NA	OB(O)	4	1	0	-1	.6876	.3899	-.1905	2.455	56
11	NA	OC(M)	4	1	0	-1	.9761	.3065	-.2291	4.278	57
13	NA	OD(M)	4	1	0	-1	.8160	.1319	-.4348	6.058	58

ATOM	TO	ATOM	EQV.	X	Y	Z	X/A	Y/B	Z/C	BOND(A)	SER.NO.
7	NA	OA(2)	1	1	1	1	1.0929	.4974	.2808	2.377	12
12	NA	OD(O)	3	1	1	1	.7075	.6091	.3890	2.435	39
8	NA	OB(O)	4	-1	-1	-1	.6876	.3899	-.1905	2.455	56
6	NA	OA(1)	1	1	1	1	.4945	.3692	.0336	2.537	2
6	NA	OA(1)	2	-1	-1	-1	.5055	.6308	-.0336	2.664	22
10	NA	OC(O)	1	1	1	1	1.0132	.3035	.2690	2.953	14
13	NA	OD(M)	1	1	1	1	.6840	.3681	.4348	2.991	7
11	NA	OC(M)	3	1	1	1	1.0239	.6935	.2291	3.262	38
9	NA	OB(M)	2	-1	-1	-1	.6800	.6488	-.2587	3.465	24
7	NA	OA(2)	2	-1	-1	-1	.9071	.5026	-.2808	3.719	23
7	NA	OA(2)	2	-1	-1	-1	.9071	.5026	.7192	3.726	16
1	NA	NA	2	-1	-1	-1	.2318	.5112	-.1462	3.915	21
8	NA	OB(O)	3	1	1	1	.3124	.6101	.1905	4.095	42
12	NA	OD(O)	4	-1	-1	-1	.2925	.3909	-.3890	4.199	48
11	NA	OC(M)	4	-1	-1	-1	.9761	.3065	-.2291	4.278	57
12	NA	OD(O)	4	-1	-1	-1	1.2925	.3909	.6110	4.281	52
10	NA	OC(O)	2	-1	-1	-1	.9868	.6965	.7310	4.447	18
13	NA	OD(M)	2	-1	-1	-1	1.3160	.6319	.5652	4.482	30
9	NA	OB(M)	1	1	1	1	1.3200	.3512	.2587	4.499	13
9	NA	OB(M)	1	1	1	1	.3200	.3512	.2587	4.518	5
11	NA	OC(M)	1	1	1	1	.5239	.1935	.2291	4.536	6
10	NA	OC(O)	4	-1	-1	-1	.4868	.1965	-.2690	4.580	46
13	NA	OD(M)	2	-1	-1	-1	.3160	.6319	-.4348	4.592	27
8	NA	OB(O)	3	1	1	1	1.3124	.6101	.1905	4.621	35
9	NA	OB(M)	3	1	1	1	.8200	.8512	.2587	4.647	36
10	NA	OC(O)	3	1	1	1	.5132	.8035	.2690	4.657	37
11	NA	NA	2	-1	-1	-1	1.2318	.5112	.8538	4.768	28

Table 14B. Low Albite: List of Bonds less than 6.500 Å given in order of Increasing Bond Length (For details, see text).

.....continued/

Table 14B. (continued)

ATOM	TO	ATOM	EQV.	X	Y	Z	X/A	Y/B	Z/C	BOND(A)	SER.NO.
11	NA	OC(M)	4	-1	-1	-1	.9761	.3065	.7709	4.771	51
8	NA	OB(O)	1	1	1	1	.8124	.1101	.1905	4.865	4
9	NA	OB(M)	2	-1	-1	-1	.6800	.6488	.7413	4.912	17
11	NA	OC(M)	2	-1	-1	-1	.4761	.8065	.2291	4.951	26
13	NA	OD(M)	1	1	1	1	.6840	.3681	.5652	4.954	10
10	NA	OC(O)	2	-1	-1	-1	.9868	.6965	.2690	5.035	25
1	NA	NA	2	-1	-1	-1	1.2318	.5112	.1462	5.092	31
6	NA	OA(1)	4	-1	-1	-1	1.0055	.1308	.0336	5.191	55
8	NA	OB(O)	4	-1	-1	-1	.6876	.3899	.8095	5.321	49
6	NA	OA(1)	3	1	1	1	.9945	.8692	.0336	5.510	34
12	NA	OD(O)	3	1	1	1	.7075	.6091	.6110	5.547	41
13	NA	OD(M)	4	-1	-1	-1	.8160	.1319	.5652	5.554	53
13	NA	OD(M)	3	1	1	1	1.1840	.8681	.4348	5.729	40
12	NA	OD(O)	1	1	1	1	1.2075	.1091	.3890	5.803	15
13	NA	OD(M)	2	-1	-1	-1	.3160	.6319	.5652	5.862	20
12	NA	OD(O)	2	-1	-1	-1	.7925	.8909	.6110	5.870	19
9	NA	OB(M)	1	1	1	1	.3200	.3512	.7413	5.903	9
7	NA	OA(2)	1	1	1	1	.0929	.4974	.2808	5.984	3
13	NA	OD(M)	4	-1	-1	-1	.8160	.1319	.4348	6.058	58
9	NA	OB(M)	4	-1	-1	-1	1.1800	.1488	.7413	6.091	50
9	NA	OB(M)	4	-1	-1	-1	.1800	.1488	.2587	6.132	45
7	NA	OA(2)	1	1	1	1	.0929	.4974	.7192	6.178	8
11	NA	OC(M)	4	-1	-1	-1	.0239	.3065	.2291	6.245	47
10	NA	OC(O)	2	-1	-1	-1	.0132	.6965	.2690	6.263	33
7	NA	OA(2)	2	-1	-1	-1	.0929	.5026	.2808	6.269	32
1	NA	NA	4	-1	-1	-1	.7318	.0112	.1462	6.279	54
12	NA	OD(O)	4	-1	-1	-1	.2925	.3909	.6110	6.337	44
6	NA	OA(1)	1	1	1	1	1.4945	.3692	.0336	6.423	11
8	NA	OB(O)	3	1	1	1	.3124	.6101	.8095	6.432	43
16	NA	OA(1)	2	-1	-1	-1	1.5055	.6308	.9664	6.444	29

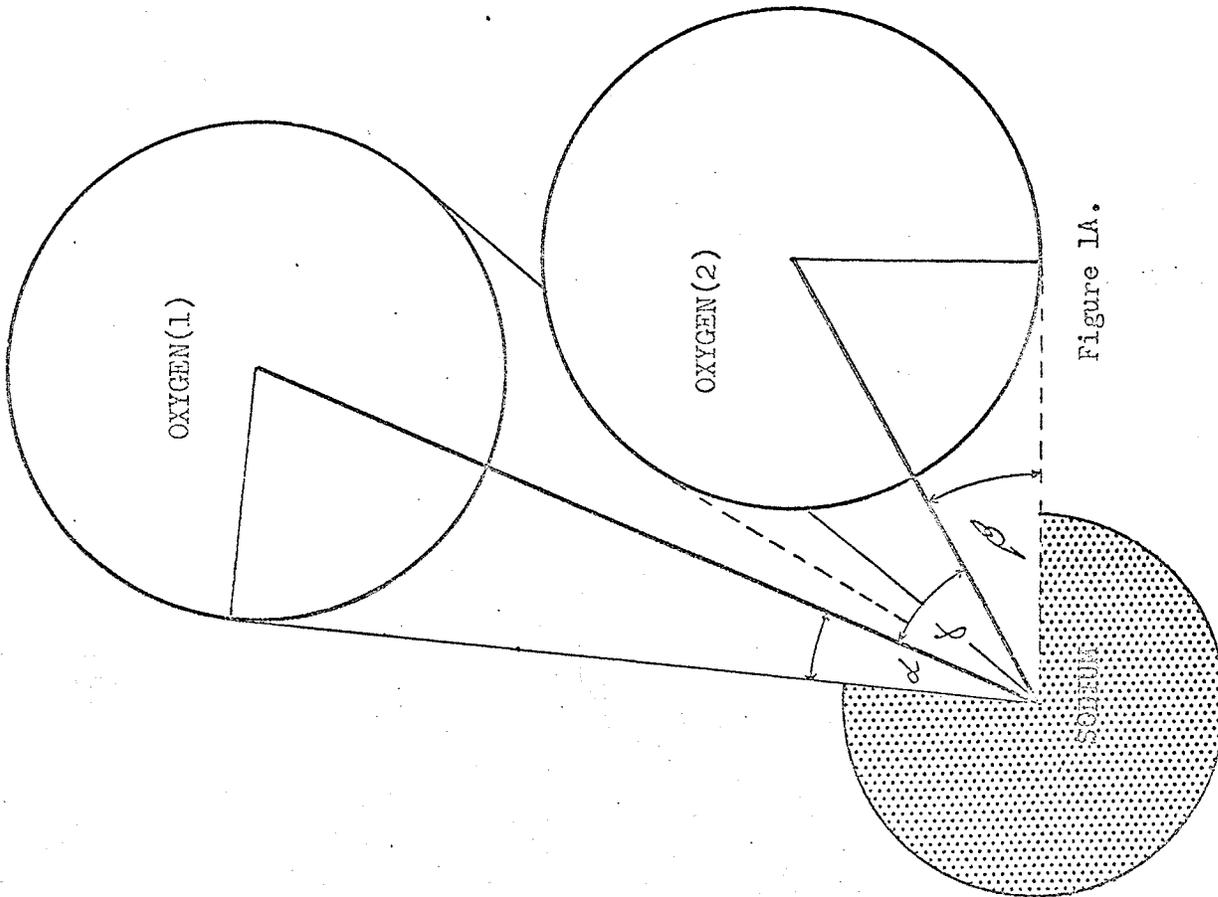


Figure 1A.

Fig. 1 Description of the Angles α , β and γ .

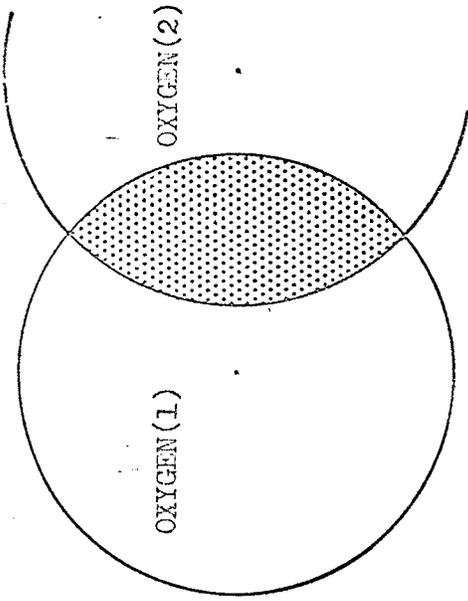


Figure 1B.

Description of the Figures

Figure 1A. Diagrammatic View of Two Na-O Bonds and the Definitions of their Angular Relationships.

Figure 1B. The Relationship between Oxygen(1) and Oxygen(2) when viewed along the Na-Oxygen(1) Bond. The Stippled area represents that part of Oxygen(1) which is Shielded by Oxygen(2).

α is the plane angle subtended at the centre of the sodium atom by the radius of the oxygen being shielded.
 $\text{Sin } \alpha = R_{\text{ox}}/\text{Na-O}.$

Assumed values of $R_{\text{ox}} = 1.32 \text{ \AA}.$

β is the plane angle subtended at the centre of the sodium atom by the radius (R) of the closer atom causing the shielding. $\text{Sin } \beta = R_{\text{ox}}/\text{Na-O}$ or $\text{sin } \beta = R_{\text{Na}}/\text{Na-O},$ and

γ is the inter-bond angle subtended at the centre of the sodium atom by the atom being shielded and by the shielding atom (oxygen or sodium).

The output from this program lists only those angular values which indicate that overlap does occur, but it does not calculate that overlap. Table 15 lists these values for the low albite structure, and the following information is contained in this Table:

- Columns (1)
(2) and (3) The serial number of the atom which is being shielded, its Megaw symbol and distance (\AA) from the sodium atom.
(4) The symbol of the cation under consideration (NA).
(5) and (6) The Megaw symbol of the atom which is causing the shielding, and its distance (\AA) from the sodium atom.
(7), (8), (9) The three angles $\alpha^\circ, \beta^\circ$ and $\gamma^\circ,$ defined as above and shown in Fig. 1.
(10) The sequential number from Program #1 of the Na-O bond distance of the atom which is being shielded.

The angles α, β and γ are sufficient to determine if there is an overlap, this occurring when $\gamma < (\alpha + \beta)$. Only if this relation is true are the angles recorded.

From these data it is now possible to determine the amount of overlap which has occurred and hence to calculate the amount of shielding which takes place with respect to a particular oxygen atom.

ATOM NO.	ATOM	TO	ATOM	ALPHA α	BETA β	GAMMA γ	BOND NO.
10	OC(O)	2.953	-NA-	OA(2)	2.377	56.499	
13	OD(M)	2.991	-NA-	OA(1)	2.537	26.551	14
11	OC(M)	3.262	-NA-	OA(2)	2.377	54.908	7
9	OB(M)	3.465	-NA-	OA(1)	2.664	51.205	38
7	OA(2)	3.719	-NA-	OB(O)	2.455	48.147	24
7	OA(2)	3.726	-NA-	OD(M)	2.991	45.529	23
7	OA(2)	3.726	-NA-	OD(O)	2.435	44.064	16
8	OB(O)	4.095	-NA-	OA(1)	2.664	44.843	16
8	OB(O)	4.095	-NA-	OD(O)	2.435	41.240	42
12	OD(O)	4.199	-NA-	OA(1)	2.537	43.638	42
12	OD(O)	4.199	-NA-	OB(O)	2.455	39.231	48
11	OC(M)	4.278	-NA-	OA(2)	3.719	41.706	48
11	OC(M)	4.278	-NA-	OB(O)	2.455	18.322	57
12	OD(O)	4.281	-NA-	OC(O)	2.953	17.972	57
12	OD(O)	4.281	-NA-	OA(2)	2.377	36.562	52
10	OC(O)	4.447	-NA-	OA(2)	3.726	34.655	52
10	OC(O)	4.447	-NA-	OD(O)	2.435	38.159	18
13	OD(M)	4.482	-NA-	OC(M)	3.262	35.328	18
13	OD(M)	4.482	-NA-	OA(2)	2.377	17.267	30
9	OB(M)	4.499	-NA-	OC(O)	2.953	17.128	30
9	OB(M)	4.499	-NA-	OA(2)	2.377	17.061	13
9	OB(M)	4.518	-NA-	OD(M)	2.991	17.061	13
9	OB(M)	4.518	-NA-	OA(1)	2.537	26.188	5
11	OC(M)	4.536	-NA-	OD(M)	2.991	16.987	5
11	OC(M)	4.536	-NA-	OA(1)	2.537	16.987	6
10	OC(O)	4.580	-NA-	OA(1)	2.537	16.918	6
10	OC(O)	4.580	-NA-	OA(1)	2.537	16.918	46
13	OD(M)	4.592	-NA-	OB(M)	3.465	16.750	46
13	OD(M)	4.592	-NA-	OB(M)	2.664	16.750	27
8	OB(O)	4.621	-NA-	OC(M)	3.262	16.705	27
						16.597	35

Table 15. Low Albite: Inter-Bond Angles and Overlap Angles for all Oxygens with Na-O less than 6.500 Å (for details, see text).
continued/

ATOM NO.	ATOM	TO	ATOM	ALPHA α	BETA β	GAMMA γ	BOND NO.
8	OB(O)	4.621	-NA-	OA(2)	2.377	24.833	35
9	OB(M)	4.647	-NA-	OC(M)	3.262	33.085	36
10	OC(O)	4.657	-NA-	OA(1)	2.664	36.098	37
10	OC(O)	4.657	-NA-	OD(O)	2.435	31.120	37
11	OC(M)	4.771	-NA-	OA(2)	3.726	32.243	51
11	OC(M)	4.771	-NA-	OD(M)	2.991	30.283	51
8	OB(O)	4.865	-NA-	OC(O)	2.953	33.379	4
9	OB(M)	4.912	-NA-	OA(2)	3.726	31.687	17
9	OB(M)	4.912	-NA-	OD(O)	2.435	15.058	17
11	OC(M)	4.951	-NA-	OB(M)	3.465	32.826	17
11	OC(M)	4.951	-NA-	OA(1)	2.664	15.462	26
13	OD(M)	4.954	-NA-	OA(2)	3.719	15.462	26
13	OD(M)	4.954	-NA-	OB(O)	2.455	15.453	10
10	OC(O)	5.035	-NA-	OA(2)	3.719	15.198	25
10	OC(O)	5.035	-NA-	OB(M)	3.465	15.198	25
6	OA(1)	5.191	-NA-	OC(O)	2.953	14.731	55
8	OB(O)	5.321	-NA-	OA(2)	3.726	14.363	49
8	OB(O)	5.321	-NA-	OD(M)	2.991	14.363	49
6	OA(1)	5.510	-NA-	OB(M)	4.647	13.860	34
6	OA(1)	5.510	-NA-	OC(M)	3.262	13.860	34
12	OD(O)	5.547	-NA-	OA(2)	3.719	13.766	41
12	OD(O)	5.547	-NA-	OB(M)	3.465	13.766	41
13	OD(M)	5.554	-NA-	OC(M)	4.536	13.748	53
13	OD(M)	5.554	-NA-	OD(M)	2.991	13.748	53
13	OD(M)	5.729	-NA-	OB(M)	4.647	13.320	40
13	OD(M)	5.729	-NA-	OC(M)	3.262	13.320	40
12	OD(O)	5.803	-NA-	OC(O)	2.953	13.148	15
13	OD(M)	5.862	-NA-	OB(O)	4.095	13.013	20
13	OD(M)	5.862	-NA-	OD(O)	2.435	13.013	20
12	OD(O)	5.870	-NA-	OC(O)	4.657	12.995	19

ATOM NO.	ATOM	TO	ATOM	ALPHA α	BETA β	GAMMA γ	BOND NO.	
12	OD(O)	5.870	-NA-	OB(M)	4.647	25.863	12.995	19
12	OD(O)	5.870	-NA-	OC(O)	4.447	28.144	12.995	19
12	OD(O)	5.870	-NA-	OD(O)	2.435	24.361	12.995	19
9	OB(M)	5.903	-NA-	OD(O)	4.199	23.331	12.921	9
9	OB(M)	5.903	-NA-	OB(O)	2.455	22.006	12.921	9
7	OA(2)	5.984	-NA-	OB(M)	4.518	24.104	12.743	3
7	OA(2)	5.984	-NA-	OB(O)	4.095	21.775	12.743	3
13	OD(M)	6.058	-NA-	OA(1)	5.191	25.016	12.585	58
13	OD(M)	6.058	-NA-	OC(M)	4.278	21.778	12.585	58
13	OD(M)	6.058	-NA-	OB(O)	2.455	23.783	12.585	58
9	OB(M)	6.091	-NA-	OC(M)	4.771	24.138	12.516	50
9	OB(M)	6.091	-NA-	OC(O)	2.953	27.293	12.516	50
9	OB(M)	6.132	-NA-	OC(O)	4.580	23.039	12.430	45
9	OB(M)	6.132	-NA-	OA(1)	2.537	13.392	12.430	45
7	OA(2)	6.178	-NA-	OD(M)	4.592	22.429	12.336	8
7	OA(2)	6.178	-NA-	OD(O)	4.199	19.653	12.336	8
11	OC(M)	6.245	-NA-	OA(1)	2.537	15.673	12.202	47
10	OC(O)	6.263	-NA-	NA	3.915	20.815	12.166	33
10	OC(O)	6.263	-NA-	OA(1)	2.664	19.772	12.166	33
7	OA(2)	6.269	-NA-	NA	3.915	3.739	12.155	32
7	OA(2)	6.269	-NA-	OA(1)	2.537	39.271	12.155	32
12	OD(O)	6.337	-NA-	OB(M)	4.518	20.566	12.022	44
12	OD(O)	6.337	-NA-	OD(M)	2.991	26.833	12.022	44
6	OA(1)	6.423	-NA-	OB(M)	4.499	18.815	11.859	11
6	OA(1)	6.423	-NA-	OA(2)	2.377	31.201	11.859	11
8	OB(O)	6.432	-NA-	OD(M)	4.592	20.358	11.842	43
8	OB(O)	6.432	-NA-	OB(M)	3.465	27.932	11.842	43
6	OA(1)	6.444	-NA-	NA	4.768	19.763	11.820	29
6	OA(1)	6.444	-NA-	OD(M)	4.482	17.917	11.820	29
6	OA(1)	6.444	-NA-	OA(2)	2.377	37.020	11.820	29

(c) Program #3 - The Solid Angle Shielding Effect

Program #3 was written to process the data obtained from Program #2, and to calculate the amount of shielding. The mathematical relationships are given in detail in Appendix IIC and may be referred to there. At this point it will be sufficient to note that there are four possible angular relationships which may exist, and their consequences with respect to overlap:

- (1) When $\gamma > (\beta + \alpha)$ no overlap occurs.
- (2) When $\beta \leq \gamma \leq \alpha$ the amount of maximum overlap is equal to or less than the effective radius of the atom which is being shielded.
- (3) When $\gamma \leq \beta \leq (\gamma + \alpha)$ the amount of maximum overlap is greater than the effective radius of the atom which is being shielded.
- (4) When $\beta \geq (\gamma + \alpha)$ the atom in question is being totally shielded by the closer atom.

The four cases require slightly different mathematical treatment, and a series of tests are made at the beginning of the program to determine which case is true in a given situation. Once this is determined, the calculation proceeds along the appropriate channel until the amount of shielding for that case has been calculated. This continues for each of the data cards which represent overlap occurrences. The program takes into account cases where more than one oxygen is shielding another, adding all the shielding values for one oxygen when necessary. Table 16 lists the shielded fractions for all oxygen atoms in the sodium environment to a distance of 6.500 \AA , defining the atom by its atom number (Table 13), and by its bond length (\AA), and the corresponding serial number from Table 14A.

SER.NO.	SHIELDED FRACTION	ATOM NO.	NA-O BOND
1	0.0000	1	0.000
2	0.0000	6	2.537
3	.4387	7	5.984
4	.2026	8	4.865
5	.7150	9	4.518
6	.6874	11	4.536
7	.0161	13	2.991
8	.5545	7	6.178
9	1.1825	9	5.903
10	1.0912	13	4.954
11	.9636	6	6.423
12	0.0000	7	2.377
13	.9011	9	4.499
14	.0269	10	2.953
15	1.0000	12	5.803
16	.1573	7	3.726
17	1.0773	9	4.912
18	.5398	10	4.447
19	1.0234	12	5.870
20	.9071	13	5.862
21	0.0000	1	0.000
22	0.0000	6	2.664
23	.1114	7	3.719
24	.0364	9	3.465
25	.3175	10	5.035
26	.9240	11	4.951
27	.5557	13	4.592
28	0.0000	1	0.000

.....continued/

Table 16. Low Albite: Shielded Fractions of the Oxygen Atoms Involved in the Bonds Listed in Tables 14A and 14B.

Table 16. (continued)

SER.NO.	SHIELDED FRACTION	ATOM NO.	NA-O BOND
29	.7972	6	6.444
30	.7736	13	4.482
31	0.0000	1	0.000
32	1.0798	7	6.269
33	1.1109	10	6.263
34	.6659	6	5.510
35	.9022	8	4.621
36	.1379	9	4.647
37	.7534	10	4.657
38	.0678	11	3.262
39	0.0000	12	2.435
40	1.0487	13	5.729
41	.7972	12	5.547
42	.2522	8	4.095
43	.4489	8	6.432
44	.6970	12	6.337
45	1.1597	9	6.132
46	.6733	10	4.580
47	1.0000	11	6.245
48	.3767	12	4.199
49	.9717	8	5.321
50	.5248	9	6.091
51	.3677	11	4.771
52	.5730	12	4.281
53	.4203	13	5.554
54	0.0000	1	0.000
55	.3723	6	5.191
56	0.0000	8	2.455
57	.4031	11	4.278
58	1.2051	13	6.058

(d) Program #4 - The Electrostatic Charge Distribution Program

Program #4 uses data derived from Program #3 with minor modification. The charge distribution program is essentially similar to that described for the anorthite structure in Chapter II where details of the tetrahedral cation to oxygen charge calculations are given. The difference between this program and the basic form of the anorthite program is that account is now taken of the amount of a particular oxygen atom which is exposed to receive charge from the large cation. The amount of exposure (EX) is calculated from (1 - the shielding factor). The following equations were developed, and reference numbers to the corresponding equations in Section (i)b of Chapter II are given for the purposes of comparison:

To calculate the 'weighting factor' W (Equation #5 in Chapter II):

$$\begin{aligned} W &= \sum \left[\frac{1}{CO^2} \times EX \right] \\ &= \sum \left[\frac{EX}{CO^2} \right] \end{aligned}$$

where EX is the amount of a given oxygen atom exposed to the sodium atom.

To calculate the charge contribution of a sodium atom to a given oxygen atom (Equation #6 in Chapter II):

$$\begin{aligned} C_C &= \frac{P_C}{(CO)^2 \times W} \times EX \\ &= \frac{+1 \times EX}{(CO)^2 \times W} \\ &= \frac{EX}{(CO)^2 \times W} \end{aligned}$$

where EX is defined as above.

In the interests of saving time, Program #4 does not vary the ideal Si-O and Al-O values as does the program for anorthite. The albite charge distribution program assumes ideal values of Si-O and Al-O and proceeds to calculate the charge unbalance for a series of different sodium coordination numbers. These results may then be examined to determine the coordination number of the sodium atom which results in the minimum charge unbalance value, and then minor adjustments can be made to the ideal Si-O and Al-O values by successive runs of the program.

(ii) Presentation of Results

Using the method described above, several sets of calculations were carried out on low albite using the original x,y and z parameters taken from the three-dimensional structure refinement by Ribbe, Megaw and Taylor (1967). All the values quoted in this part of the text are computed and they have not been rounded off. They are given to the fourth decimal place and the remainders have simply been removed. A satisfactorily small unbalance value of 0.014 e.s.u. for the whole structure was, in due course, derived using the following values of the variables: Si-O = 1.602 Å, Al-O = 1.777 Å and a coordination number of the sodium atom of 6. The numerical results of the computations are presented in two ways, first as the print-out of the data in Table 17, and then graphically in Fig. 2. Table 17 gives the complete listing of the computed results for the set of calculations yielding the smallest charge unbalance value.

Table 17

Low Albite : Print-out of the Complete Set of Electrostatic Charge Balance Calculations for Coordination Numbers of the Sodium from 4-fold to 17-fold with Si-O = 1.602 and Al-O = 1.777 Å. This Set Includes that with 6-fold Coordination of the Sodium which Yielded the Smallest Unbalance Value Obtained, 0.014 e.s.u.

The Table occupies six pages and the following information is given for each of the tested coordinations of the sodium atom:

- (1) The ideal values of Si-O and Al-O assumed for this set of calculations (recorded only in the first set of results, i.e. the set for sodium coordination of 4).
- (2) The Al-contents of each tetrahedron and the total Al-content of the structure as fractions of atoms (also only recorded as the data in (1)).
- (3) The coordination number of the sodium and the maximum Na-O value to which it corresponds.
- (4) The charge contributed by the sodium to each non-equivalent oxygen (e.s.u.) (These are identified by their atom number listed in Table 13).
- (5) The total charge on each of the non-equivalent oxygen atoms (e.s.u.).
- (6) The total charge contributions to each of the non-equivalent tetrahedral groups of four oxygens (e.s.u.).
- (7) The total electrostatic charge unbalance value (e.s.u.) for that set of variables.

DMAX VALUE IS 2.538
COORD OF SODIUM 4
6 .232
7 .265
8 .248
9 0.000
10 0.000
11 0.000
12 .252
13 0.000

SIO= 1.602 ALO= 1.777

AL CONTENT OF TET 1 .8228
AL CONTENT OF TET 2 .0457
AL CONTENT OF TET 3 .0742
AL CONTENT OF TET 4 .0571

TOTAL AL CONTENT .9999
TOTAL CHARGE ON OXYGEN NO. 6 2.0233
TOTAL CHARGE ON OXYGEN NO. 7 2.1805
TOTAL CHARGE ON OXYGEN NO. 8 2.0522
TOTAL CHARGE ON OXYGEN NO. 9 1.9769
TOTAL CHARGE ON OXYGEN NO.10 1.8182
TOTAL CHARGE ON OXYGEN NO.11 1.9551
TOTAL CHARGE ON OXYGEN NO.12 2.0396
TOTAL CHARGE ON OXYGEN NO.13 1.9539
CHARGE ON TETRAHEDRON NO. 1 7.9335
CHARGE ON TETRAHEDRON NO. 2 7.9093
CHARGE ON TETRAHEDRON NO. 3 8.1419
CHARGE ON TETRAHEDRON NO. 4 8.0154
CHARGE UNBALANCE ON LOW ALBITE .3144

DMAX VALUE IS 2.668
COORD OF SODIUM 5
6 .366
7 .219
8 .205
9 0.000
10 0.000
11 0.000
12 .208
13 0.000

TOTAL CHARGE ON OXYGEN NO. 6 2.1571
TOTAL CHARGE ON OXYGEN NO. 7 2.1342
TOTAL CHARGE ON OXYGEN NO. 8 2.0088
TOTAL CHARGE ON OXYGEN NO. 9 1.9769
TOTAL CHARGE ON OXYGEN NO.10 1.8182
TOTAL CHARGE ON OXYGEN NO.11 1.9551
TOTAL CHARGE ON OXYGEN NO.12 1.9955
TOTAL CHARGE ON OXYGEN NO.13 1.9539
CHARGE ON TETRAHEDRON NO. 1 7.9797
CHARGE ON TETRAHEDRON NO. 2 8.0431
CHARGE ON TETRAHEDRON NO. 3 8.0522
CHARGE ON TETRAHEDRON NO. 4 7.9250
CHARGE UNBALANCE ON LOW ALBITE .1905

DMAX VALUE IS 2.958
COORD OF SODIUM 6
6 .322
7 .192
8 .180
9 0.000
10 .121
11 0.000
12 .183
13 0.000
TOTAL CHARGE ON OXYGEN NO. 6 2.1126
TOTAL CHARGE ON OXYGEN NO. 7 2.1076
TOTAL CHARGE ON OXYGEN NO. 8 1.9839
TOTAL CHARGE ON OXYGEN NO. 9 1.9769
TOTAL CHARGE ON OXYGEN NO.10 1.9396
TOTAL CHARGE ON OXYGEN NO.11 1.9551
TOTAL CHARGE ON OXYGEN NO.12 1.9702
TOTAL CHARGE ON OXYGEN NO.13 1.9539
CHARGE ON TETRAHEDRON NO. 1 8.0063
CHARGE ON TETRAHEDRON NO. 2 7.9986
CHARGE ON TETRAHEDRON NO. 3 8.0007
CHARGE ON TETRAHEDRON NO. 4 7.9944
CHARGE UNBALANCE ON LOW ALBITE .0140

DMAX VALUE IS 2.998
COORD OF SODIUM 7
6 .287
7 .171
8 .161
9 0.000
10 .108
11 0.000
12 .163
13 .106
TOTAL CHARGE ON OXYGEN NO. 6 2.0781
TOTAL CHARGE ON OXYGEN NO. 7 2.0871
TOTAL CHARGE ON OXYGEN NO. 8 1.9646
TOTAL CHARGE ON OXYGEN NO. 9 1.9769
TOTAL CHARGE ON OXYGEN NO.10 1.9266
TOTAL CHARGE ON OXYGEN NO.11 1.9551
TOTAL CHARGE ON OXYGEN NO.12 1.9506
TOTAL CHARGE ON OXYGEN NO.13 2.0607
CHARGE ON TETRAHEDRON NO. 1 7.9201
CHARGE ON TETRAHEDRON NO. 2 8.0710
CHARGE ON TETRAHEDRON NO. 3 8.0676
CHARGE ON TETRAHEDRON NO. 4 7.9413
CHARGE UNBALANCE ON LOW ALBITE .2773

DMAX VALUE IS	3.268	
COORD OF SODIUM	8	
6	.265	
7	.158	
8	.148	
9	0.000	
10	.099	
11	.078	
12	.150	
13	.098	
TOTAL CHARGE ON OXYGEN NO. 6		2.0556
TOTAL CHARGE ON OXYGEN NO. 7		2.0736
TOTAL CHARGE ON OXYGEN NO. 8		1.9520
TOTAL CHARGE ON OXYGEN NO. 9		1.9769
TOTAL CHARGE ON OXYGEN NO.10		1.9181
TOTAL CHARGE ON OXYGEN NO.11		2.0335
TOTAL CHARGE ON OXYGEN NO.12		1.9377
TOTAL CHARGE ON OXYGEN NO.13		2.0524
CHARGE ON TETRAHEDRON NO. 1		7.8635
CHARGE ON TETRAHEDRON NO. 2		8.1185
CHARGE ON TETRAHEDRON NO. 3		8.1116
CHARGE ON TETRAHEDRON NO. 4		7.9064
CHARGE UNBALANCE ON LOW ALBITE		.4601

DMAX VALUE IS	3.468	
COORD OF SODIUM	9	
6	.247	
7	.147	
8	.138	
9	.067	
10	.093	
11	.073	
12	.140	
13	.091	
TOTAL CHARGE ON OXYGEN NO. 6		2.0378
TOTAL CHARGE ON OXYGEN NO. 7		2.0630
TOTAL CHARGE ON OXYGEN NO. 8		1.9420
TOTAL CHARGE ON OXYGEN NO. 9		2.0439
TOTAL CHARGE ON OXYGEN NO.10		1.9114
TOTAL CHARGE ON OXYGEN NO.11		2.0282
TOTAL CHARGE ON OXYGEN NO.12		1.9276
TOTAL CHARGE ON OXYGEN NO.13		2.0458
CHARGE ON TETRAHEDRON NO. 1		7.8189
CHARGE ON TETRAHEDRON NO. 2		8.1559
CHARGE ON TETRAHEDRON NO. 3		8.0791
CHARGE ON TETRAHEDRON NO. 4		7.9460
CHARGE UNBALANCE ON LOW ALBITE		.4700

DMAX VALUE IS 3.728
COORD OF SODIUM 11
6 .224
7 .228
8 .125
9 .060
10 .084
11 .066
12 .127
13 .083
TOTAL CHARGE ON OXYGEN NO. 6 2.00144
TOTAL CHARGE ON OXYGEN NO. 7 2.1435
TOTAL CHARGE ON OXYGEN NO. 8 1.9289
TOTAL CHARGE ON OXYGEN NO. 9 2.0376
TOTAL CHARGE ON OXYGEN NO.10 1.9026
TOTAL CHARGE ON OXYGEN NO.11 2.0213
TOTAL CHARGE ON OXYGEN NO.12 1.9143
TOTAL CHARGE ON OXYGEN NO.13 2.0371
CHARGE ON TETRAHEDRON NO. 1 7.7603
CHARGE ON TETRAHEDRON NO. 2 8.1105
CHARGE ON TETRAHEDRON NO. 3 8.1310
CHARGE ON TETRAHEDRON NO. 4 7.9981
CHARGE UNBALANCE ON LOW ALBITE .4830

DMAX VALUE IS 4.098
COORD OF SODIUM 12
6 .216
7 .220
8 .154
9 .058
10 .081
11 .064
12 .123
13 .080
TOTAL CHARGE ON OXYGEN NO. 6 2.0071
TOTAL CHARGE ON OXYGEN NO. 7 2.1360
TOTAL CHARGE ON OXYGEN NO. 8 1.9575
TOTAL CHARGE ON OXYGEN NO. 9 2.0356
TOTAL CHARGE ON OXYGEN NO.10 1.8998
TOTAL CHARGE ON OXYGEN NO.11 2.0192
TOTAL CHARGE ON OXYGEN NO.12 1.9101
TOTAL CHARGE ON OXYGEN NO.13 2.0344
CHARGE ON TETRAHEDRON NO. 1 7.7746
CHARGE ON TETRAHEDRON NO. 2 8.0964
CHARGE ON TETRAHEDRON NO. 3 8.1472
CHARGE ON TETRAHEDRON NO. 4 7.9818
CHARGE UNBALANCE ON LOW ALBITE .4871

DMAX VALUE IS 4.208
COORD OF SODIUM 13
6 .211
7 .215
8 .150
9 .057
10 .079
11 .062
12 .145
13 .078
TOTAL CHARGE ON OXYGEN NO. 6 2.0016
TOTAL CHARGE ON OXYGEN NO. 7 2.1305
TOTAL CHARGE ON OXYGEN NO. 8 1.9536
TOTAL CHARGE ON OXYGEN NO. 9 2.0341
TOTAL CHARGE ON OXYGEN NO.10 1.8978
TOTAL CHARGE ON OXYGEN NO.11 2.0176
TOTAL CHARGE ON OXYGEN NO.12 1.9322
TOTAL CHARGE ON OXYGEN NO.13 2.0323
CHARGE ON TETRAHEDRON NO. 1 7.7853
CHARGE ON TETRAHEDRON NO. 2 8.0858
CHARGE ON TETRAHEDRON NO. 3 8.1341
CHARGE ON TETRAHEDRON NO. 4 7.9947
CHARGE UNBALANCE ON LOW ALBITE .4397

DMAX VALUE IS 4.288
COORD OF SODIUM 15
6 .203
7 .207
8 .144
9 .055
10 .076
11 .082
12 .155
13 .075
TOTAL CHARGE ON OXYGEN NO. 6 1.9935
TOTAL CHARGE ON OXYGEN NO. 7 2.1222
TOTAL CHARGE ON OXYGEN NO. 8 1.9478
TOTAL CHARGE ON OXYGEN NO. 9 2.0319
TOTAL CHARGE ON OXYGEN NO.10 1.8947
TOTAL CHARGE ON OXYGEN NO.11 2.0375
TOTAL CHARGE ON OXYGEN NO.12 1.9426
TOTAL CHARGE ON OXYGEN NO.13 2.0293
CHARGE ON TETRAHEDRON NO. 1 7.7788
CHARGE ON TETRAHEDRON NO. 2 8.0925
CHARGE ON TETRAHEDRON NO. 3 8.1370
CHARGE ON TETRAHEDRON NO. 4 7.9916
CHARGE UNBALANCE ON LOW ALBITE .4590

DMAX VALUE IS	4.448	
COORD OF SODIUM	16	
6	.200	
7	.203	
8	.142	
9	.054	
10	.091	
11	.081	
12	.153	
13	.074	
TOTAL CHARGE ON OXYGEN NO. 6		1.9903
TOTAL CHARGE ON OXYGEN NO. 7		2.1189
TOTAL CHARGE ON OXYGEN NO. 8		1.9456
TOTAL CHARGE ON OXYGEN NO. 9		2.0311
TOTAL CHARGE ON OXYGEN NO.10		1.9092
TOTAL CHARGE ON OXYGEN NO.11		2.0362
TOTAL CHARGE ON OXYGEN NO.12		1.9402
TOTAL CHARGE ON OXYGEN NO.13		2.0281
CHARGE ON TETRAHEDRON NO. 1		7.7854
CHARGE ON TETRAHEDRON NO. 2		8.0859
CHARGE ON TETRAHEDRON NO. 3		8.1290
CHARGE ON TETRAHEDRON NO. 4		7.9996
CHARGE UNBALANCE ON LOW ALBITE		.4299

DMAX VALUE IS	4.488	
COORD OF SODIUM	17	
6	.198	
7	.202	
8	.141	
9	.053	
10	.090	
11	.080	
12	.152	
13	.081	
TOTAL CHARGE ON OXYGEN NO. 6		1.9888
TOTAL CHARGE ON OXYGEN NO. 7		2.1174
TOTAL CHARGE ON OXYGEN NO. 8		1.9445
TOTAL CHARGE ON OXYGEN NO. 9		2.0307
TOTAL CHARGE ON OXYGEN NO.10		1.9086
TOTAL CHARGE ON OXYGEN NO.11		2.0356
TOTAL CHARGE ON OXYGEN NO.12		1.9390
TOTAL CHARGE ON OXYGEN NO.13		2.0351
CHARGE ON TETRAHEDRON NO. 1		7.7810
CHARGE ON TETRAHEDRON NO. 2		8.0904
CHARGE ON TETRAHEDRON NO. 3		8.1328
CHARGE ON TETRAHEDRON NO. 4		7.9958
CHARGE UNBALANCE ON LOW ALBITE		.4463

Fig. 2 is a plot of the essential results of Table 17, namely a plot of the total electrostatic charge unbalance against the coordination number of the sodium. The diagrammatic form is the more satisfactory presentation as the rate and amount of change in the total electrostatic charge unbalance value with coordination number of the sodium atom can be seen very easily.

From these results for low albite, especially as they are shown in Fig. 2, it is clear that the electrostatic balance is almost perfect (0.014 e.s.u.) for a coordination number of 6 oxygens around the sodium atom, and for Si-O = 1.602 Å and Al-O = 1.777 Å (Table 18). These results strongly support the original premise that local charge unbalance should ideally be zero in this low-temperature feldspar structure. Furthermore, Fig. 2 shows that the unbalance value for any coordination of sodium other than six is large and that there can be no doubt that 6-fold coordination of sodium is the most favourable to the low-temperature albite structure. The oxygen atoms which are involved in this coordination with the sodium atom are the nearest six and these are listed in Table 18.

As previously mentioned, the smallest charge unbalance for the calculations presented in this thesis for the low albite structure is 0.014 e.s.u. This represents a marked reduction from the smallest value ^(0.12 e.s.u.) obtained by Ferguson, Traill and Taylor (1958) also using a 6-fold coordination for the sodium atom. Several significant differences between these two calculations should be pointed out. The calculations of Ferguson et al. (1958) did not take account of the cation-oxygen distances, and also they used Smith's (1954) ideal values for Si-O and Al-O,

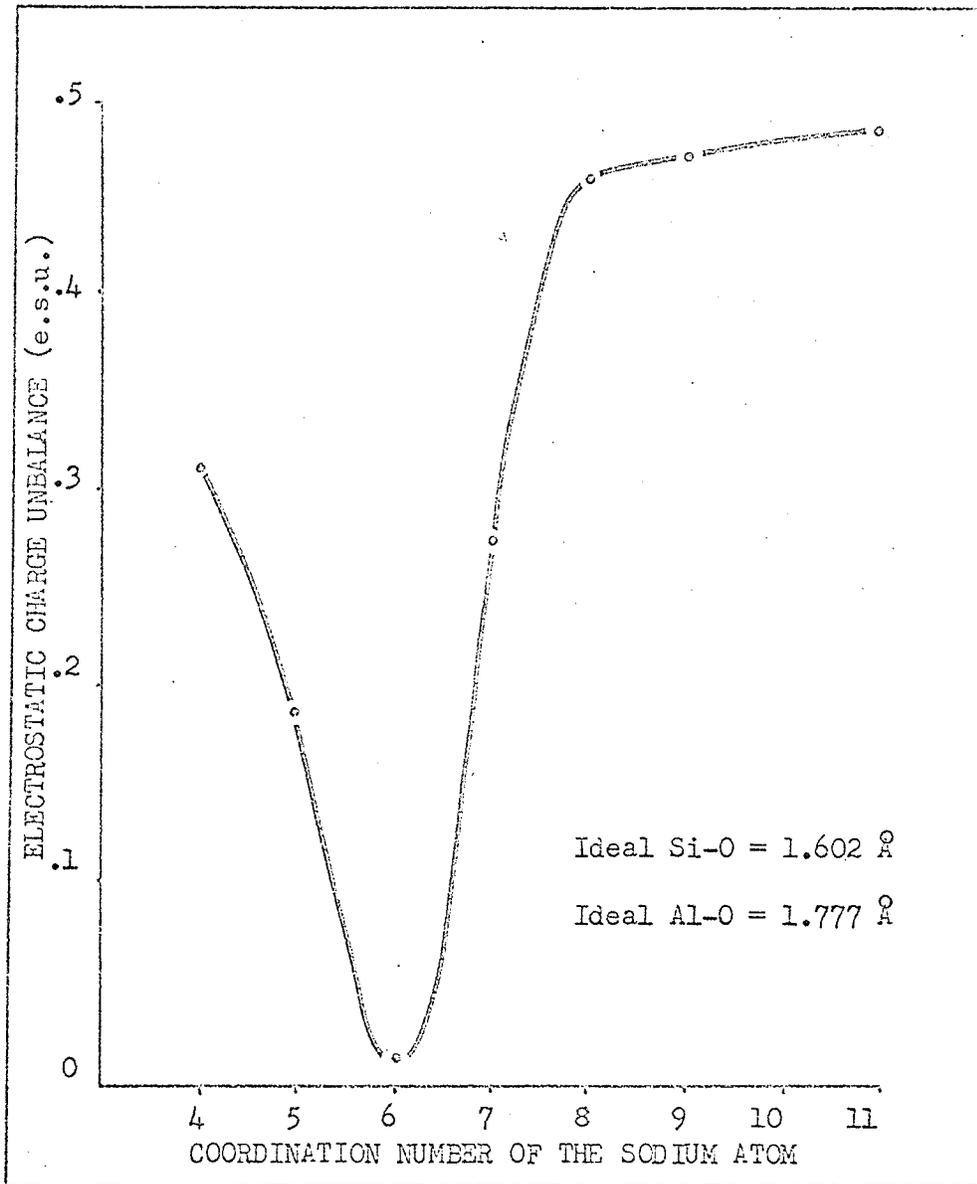


Fig. 2. Low Albite: Variation in Electrostatic Charge Unbalance with Coordination Number of the Sodium Atom for Si-O = 1.602 Å and Al-O 1.777 Å.

Table 18

Low Albite: Summary of the Conditions

Yielding Near-Zero Electrostatic

Charge Unbalance

Original Cell Dimensions of Ferguson et al. (1958) and the original three-dimensional atomic parameters of Ribbe et al. (1967).

All cation charges distributed according to the inverse square of the cation-oxygen distances.

Si-O = 1.602 Å Al-O = 1.777 Å

Al-contents of tetrahedra in fractions of atoms

T1(O)	0.823
T1(M)	0.046
T2(O)	0.074
T2(M)	<u>0.057</u>

Total Al-Content 1.000

Coordination of Sodium by 6 Oxygens

Nearness Number	Megaw Symbol	Na-O (Å)	Fractions Shielded	Charge Contributions from the Sodium
1.	OA(2)	2.377	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

.....continued/

Table 18 - Continued

Total Positive Charges Received by Each Non-equivalent Oxygen, e.s.u.

OA(1)	2.113
OA(2)	2.108
OB(O)	1.984
OB(M)	1.977
OC(O)	1.940
OC(M)	1.955
OD(O)	1.970
OD(M)	1.954

Total Positive Charges (Σ) Received by each Tetrahedral Group of Four Oxygens and Differences from 8.000 (Δ), e.s.u.

T1(O) - OA(1)	2.113	T1(M) - OA(1)	2.113
OB(O)	1.984	OB(M)	1.977
OC(O)	1.940	OC(M)	1.955
OD(O)	1.970	OD(M)	1.954
$\Sigma =$	8.007	$\Sigma =$	7.999
$ \Delta =$	0.007	$ \Delta =$	0.001

T2(O) - OA(2)	2.108	T2(M) - OA(2)	2.108
OB(O)	1.984	OB(M)	1.977
OC(M)	1.955	OC(O)	1.940
OD(M)	1.954	OD(O)	1.970
$\Sigma =$	8.001	$\Sigma =$	7.995
$ \Delta =$	0.001	$ \Delta =$	0.005

TOTAL ELECTROSTATIC CHARGE UNBALANCE FOR LOW ALBITE, $\Sigma|\Delta| = 0.014$ e.s.u.

1.600 and 1.780 Å respectively. If a given tetrahedron was calculated to have less than zero for an Al-content, this value was adjusted to zero. These two facts, together with the less accurate two-dimensional structure refinement of Ferguson et al. (1958), account for the differences in the smallest charge unbalance value for the low albite structure, compared to those given in this thesis. Of further note is that in 1962 Paul Pushkar (personal communication to Dr. Ferguson) re-calculated the charge unbalance on low albite using a 6-fold coordination of the sodium atom, taking account of the Na-O and T-O distances, and he arrived at a total charge unbalance value of 0.064 e.s.u. It should be noted that at the time these calculations were carried out, Ferguson was strongly in favour of the idea that if proper account were taken of the crystallographic considerations, i.e., the cation-anion distances, and the Al-contents of the tetrahedra, *a nearly* perfect balance for this low albite could be calculated.

Several other sets of calculations were carried out for the low albite structure (Ribbe et al., 1967) for comparative purposes and some of the details of the results are shown in Table 19, and graphically in Fig. 3. The tabulation given below compares the curves shown in Fig. 3:

Curve in Fig. 3	Ideal Si-O(Å)	Ideal Al-O(Å)	Al-content (Atoms)	Coord. of Na	Minimum Unbalance Value (e.s.u.)
A	1.602	1.777	0.9999	6	0.014
B	1.600 (Smith, 1954)	1.780	1.016	6	0.050
C	1.610 (Smith and Bailey, 1963)	1.750	1.021	6	0.187

Table 19

Low Albite: A Summary of the Most Important Results which Led to the Calculations

Yielding the Smallest Charge Unbalance Value

SiO Å	Al-O Å	Total Al-content (Atoms)	Total Charge Contributions to the Independent Tetrahedral Groups of Four Oxygens (e.s.u.)			Total Charge Unbalance (e.s.u.)	
			T1(O)	T1(M)	T2(O)		
1.601	1.780	0.9999	8.015	7.994	7.997	7.994	0.029
1.601	1.781	0.994	8.020	7.996	7.998	7.997	0.028 *
<u>1.602</u>	<u>1.777</u>	<u>0.9999</u>	<u>8.006</u>	<u>7.999</u>	<u>8.001</u>	<u>7.994</u>	<u>0.014</u>
1.602	1.778	0.994	8.011	8.000	8.002	7.997	0.017
1.603	1.775	0.994	8.003	8.005	8.007	7.997	0.017
1.603	1.776	0.988	8.008	8.007	8.008	8.002	0.023
1.603	1.774	0.9999	7.998	8.003	8.005	7.994	0.016
1.604	1.771	0.9999	7.988	8.008	8.009	7.994	0.035

* The set of assumed values yielding the smallest electrostatic charge unbalance is underlined.

The best mean tetrahedral sizes for Si-O and Al-O are:

Best Si-O = 1.602 Å and

Best Al-O = 1.777 Å.

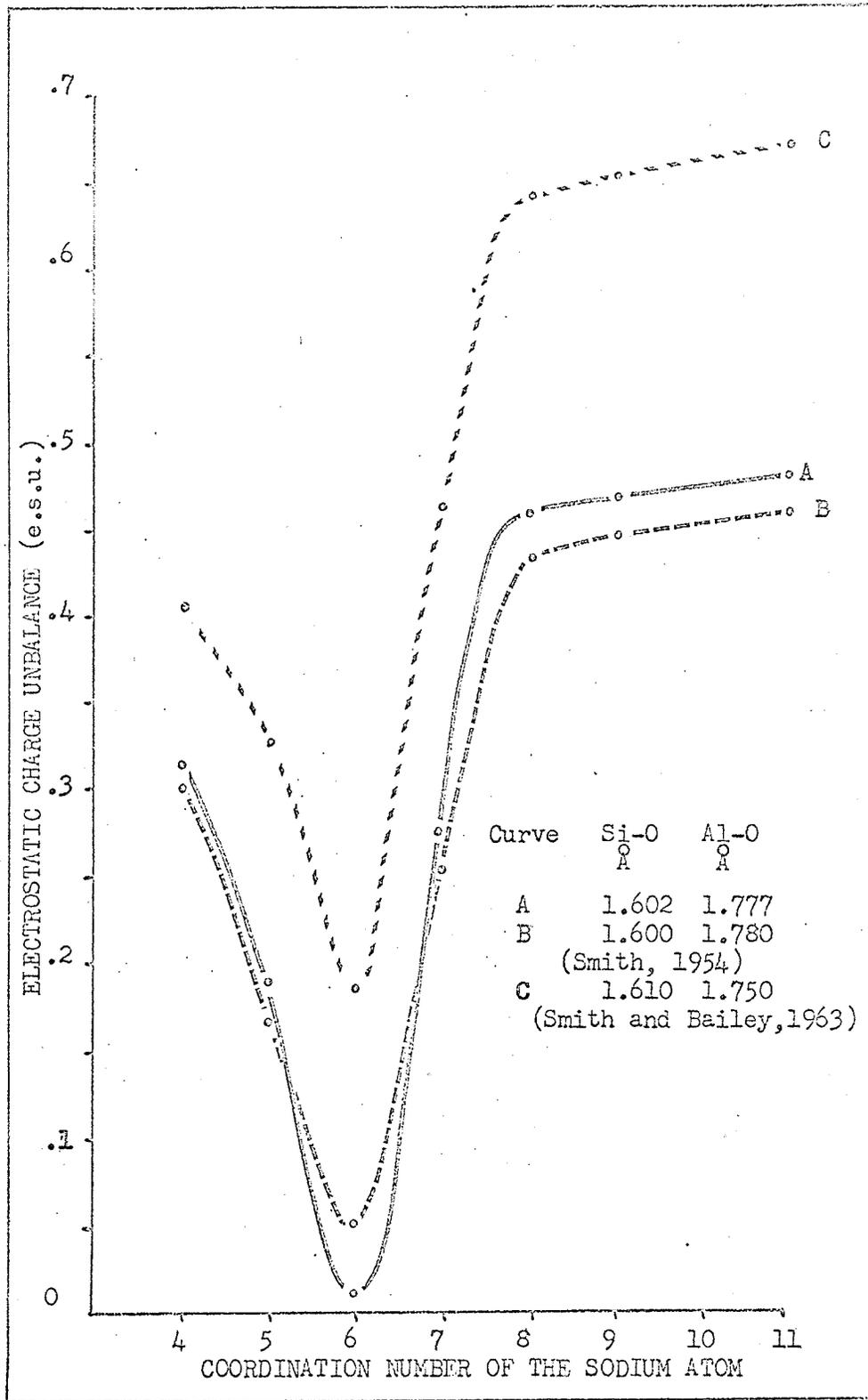


Fig. 3. Low Albite: Curves Showing the Variation in Electrostatic Charge Unbalance with Coordination Number of the Sodium Atom for Different Ideal Values of Si-O and Al-O.

Fig. 3 compares the best results with those using the ideal values of $\text{Si-O} = 1.60 \text{ \AA}$ and $\text{Al-O} = 1.78 \text{ \AA}$ proposed by Smith in 1954 and with the revised ideal values of 1.61 \AA and 1.75 \AA put forth by Smith and Bailey in 1963. The latter values gave a minimum charge unbalance (also for 6-fold coordination of the sodium) of 0.187 e.s.u. , about three times greater than the value yielded by Smith's 1954 ideal values, for which the unbalance is 0.050 e.s.u. The two curves remain essentially the same shape and both categorically define the 6-fold coordination of the sodium. On the assumption that this low-temperature feldspar should have a minimum charge unbalance of ideally zero, the author is obliged to accept the Si-O and Al-O values close to those first proposed by Smith in 1954. This leads to the further conclusion that low albite is only about 82% ordered with respect to Si-Al.

Although the most important point about the charge distribution is, as mentioned earlier, the closeness to 8 e.s.u. of the positive charges contributed to the tetrahedral groups of four oxygens, it is of some value to consider the total charges contributed to the oxygens individually. The total positive charge contributions to the non-equivalent oxygens in the structure are given in Table 18 for the conditions that yield the lowest charge unbalance value of 0.014 e.s.u. The greatest deviation from the ideal value of 2.000 e.s.u. is for oxygen OA(1) which is $+0.1126 \text{ e.s.u.}$ and results from the fact that two of the equivalent atoms of this kind are close to the sodium atom (the 4th and 5th closest atoms). Consequently, when treated as a non-equivalent atom, it receives almost one-third of the total positive charge of $+1$ from the sodium atom (Table 18). The other oxygen atom which receives an excess charge ($+0.1076 \text{ e.s.u.}$) is OA(2) and

this results from the fact that this oxygen is involved in the shortest Na-O bond length in the structure of 2.377 Å ; thus, it receives more charge from the sodium atom than another other single oxygen by virtue of the inverse square law used in distributing the charges.

The remaining oxygen atoms in the structure are all slightly undercharged but to a lesser extent than the OA oxygens are overcharged. The least charged oxygen is OC(0) with 1.9396 e.s.u. It is the sixth nearest oxygen to be coordinated with the sodium and hence is at the greatest distance; it is also partly shielded by OA(2).

Considering now the oxygens taken in tetrahedral groups of four, (Table 18), it may be seen that the sum of the charges in each such group is extremely close to 8.000 e.s.u. and that the maximum deviation is +0.0063 e.s.u. on Tl(0). The sum of the deviation from 8.000 e.s.u. for the four independent tetrahedra, as emphasized earlier, is 0.014 e.s.u. From these results it may be concluded with confidence that the electrostatic charge distribution in low albite is locally balanced with particular reference to the tetrahedral groups of four oxygens. The results indicate clearly that the Al is concentrated to the extent of 82%, but only to that extent, in the one site Tl(0), and that any appreciable change in the assumed amount of Al in this site would upset the almost perfect balance of electrostatic charge which this structure exhibits.

(iii) Summary of Conclusions

1. Low albite possesses a nearly perfect electrostatic charge distribution provided a reasonable set of assumptions is

accepted. Because this is so, the atoms in the structure are thought of as behaving as ions. It implies that the structure is ionic in character.

2. This near-zero electrostatic charge balance is attained only if the sodium atom is taken as being in 6-fold coordination with the nearest 6 oxygen atoms. Therefore, one may say that the electrostatic influence of the sodium atom extends to a radius of more than 2.953 Å but less than 2.991 Å from the centre of the sodium atom.
3. Ideal values for the pure mean sizes of the Si-O and Al-O tetrahedra that yield the smallest unbalance value are Si-O = 1.602 Å and Al-O = 1.777 Å; these values are close to those proposed by Smith in 1954. Using the new ideal values of Si-O and Al-O, the total Al-content of the structure is 0.9999 atoms, and the following are the Al-contents of the 4 independent tetrahedra, expressed as fractions of atoms: T1(O) = 0.8228, T1(M) = 0.0457, T2(O) = 0.0742, and T2(M) = 0.0571.
4. From the above information, low albite is not fully ordered, but is only largely ordered, about 82%, with respect to Si-Al.

CHAPTER V

ELECTROSTATIC CHARGE DISTRIBUTION WITHIN

THE HIGH ALBITE STRUCTURE

(i) General Remarks

The unit cell of high-temperature albite has the same size, cell content and space group as low-temperature albite. Slight differences in the positions of the atoms are evident from their parameters as determined by the refinements of the structure. On account of the close similarity between the structures it is possible to apply to high albite the methods used to calculate the distribution of electrostatic charges in low albite. Thus the same four computer programs may be used and corresponding values obtained: Na-O and Na-Na bond lengths in a given sodium environment and the corresponding inter-bond angles, overlap angles and shielded fractions of the oxygen atoms. The reader is referred to the introductory section of Chapter IV on low albite, and to the four IBM 1620 FORTRAN II programs in Appendix II for the details of the computation method.

The cell dimensions used for this high albite are those of Ferguson et al., (1958) and the original atomic parameters are those of Ribbe et al., (1967) derived from the three-dimensional structure refinement. Both the papers referred to above noted strong anisotropism of the sodium atom and have pointed out the difficulty of defining exactly the position of this atom. For the purposes of these calculations

the sodium atom has been treated as a single atom and its parameters are taken as those given by Ribbe et al., (1967) for the single atom.

Table 20 lists the atomic parameters of the non-equivalent sodium and the ^{eight} oxygen atoms for the high albite structure. These have been moved into an asymmetric part of the unit cell which for the space group $C\bar{1}$ is $1a, \frac{1}{2}b, \frac{1}{2}c$. Table 20 is directly analagous to Table 13 in Chapter IV.

In Chapter IV it was mentioned that for low albite the Na-O and Na-Na bonds were calculated to a distance of 6.500 \AA from the original sodium atom. It was found that this included an unnecessarily large environment, and therefore the bonds for the environment of the original sodium atom in the high albite structure were calculated to a maximum distance of 4.600 \AA . This considerably reduced the calculation time for the programs and it produced equally satisfactory results.

(ii) Preliminary Data Required for the Distribution of Electrostatic Charges

The following Tables give all the data necessary for calculating the actual charge distribution in the high albite structure and are directly analagous to those given for low albite in Chapter IV:

Table 21. High Albite: List of Bonds Less Than 4.600 \AA
Given in Order of Increasing Bond Length.

Table 22. High Albite: Inter-Bond Angles and Overlap Angles
for all Oxygens with Na-O less than 4.600 \AA .

Table 23. High Albite: Shielded Fractions of the Oxygen Atoms
Involved in the Bonds Listed in Table 21.

(Tables 21, 22 and 23 are analagous to Tables 14B, 15 and 16
respectively in Chapter IV.)

ATOM+NO.	X/A	Y/B	Z/C
NA 01	2743	0076	1320
OA(1) 06	4943	3651	0149
OA(2) 07	0923	4910	2781
OB(O) 08	8213	1091	2002
OB(M) 09	3187	3477	2456
OC(O) 10	0158	2906	2765
OC(M) 11	5217	1870	2191
OD(O) 12	1957	1123	3877
OD(M) 13	6884	3679	4260

Table 20. High Albite: The Original Parameters (Ribbe et al., 1967) Transferred into the Asymmetric Part of the Unit Cell (expressed as fractions of the cell edges $\times 10^4$).

ATOM	TO	ATOM	EQV.	X	Y	Z	X/A	Y/B	Z/C	BOND(A)	SER.NO.
7	NA	OA(2)	3	0	-1	0	.5923	-.0090	.2781	2.342	13
12	NA	OD(O)	1	0	0	0	.1957	.1123	.3877	2.506	6
8	NA	OB(O)	2	0	-1	-1	.1787	-.1091	-.2002	2.526	9
6	NA	OA(1)	4	0	0	-1	.0057	.1349	-.0149	2.604	19
6	NA	OA(1)	3	-1	-1	0	-.0057	-.1349	.0149	2.713	15
11	NA	OC(M)	1	0	0	0	.5217	.1870	.2191	2.909	5
13	NA	OD(M)	3	-1	-1	0	.1884	-.1321	.4260	3.133	16
9	NA	OB(M)	4	0	0	-1	.1813	.1523	-.2456	3.169	21
10	NA	OC(O)	3	0	-1	0	.5158	-.2094	.2765	3.367	14
7	NA	OA(2)	4	0	0	-1	.4077	.0090	-.2781	3.533	20
7	NA	OA(2)	4	0	0	0	.4077	.0090	.7219	3.834	17
1	NA	NA	2	-1	-1	-1	-.2743	-.0076	-.1320	4.007	11
8	NA	OB(O)	1	-1	0	0	-.1787	.1091	.2002	4.138	7
12	NA	OD(O)	2	-1	-1	-1	-.1957	-.1123	-.3877	4.174	12
11	NA	OC(M)	2	0	-1	-1	.4783	-.1870	-.2191	4.272	10
13	NA	OD(M)	4	1	0	0	.8116	.1321	.5740	4.331	23
9	NA	OB(M)	1	0	0	0	.3187	.3477	.2456	4.391	3
10	NA	OC(O)	4	0	0	0	.4842	.2094	.7235	4.432	18
8	NA	OB(O)	1	0	0	0	.8213	.1091	.2002	4.445	2
13	NA	OD(M)	4	0	0	-1	-.1884	.1321	-.4260	4.479	22
12	NA	OD(O)	2	0	-1	0	.8043	-.1123	.6123	4.506	8
10	NA	OC(O)	1	0	0	0	.0158	.2906	.2765	4.509	4

Table 21. High Albite: List of Bonds less than 4.600 Å given in order of Increasing Bond Length. (For details, see Chapter IV, Section (i)a.)

SER.NO.	SHIELDED FRACTION	ATOM NO.	NA-O BOND
1	0.0000	1	0.000
2	.8028	8	4.445
3	.1360	9	4.391
4	.8041	10	4.509
5	.0183	11	2.909
6	0.0000	12	2.506
7	.4379	8	4.138
8	.7367	12	4.506
9	0.0000	8	2.526
10	.3123	11	4.272
11	0.0000	1	0.000
12	.3991	12	4.174
13	0.0000	7	2.342
14	.0626	10	3.367
15	0.0000	6	2.713
16	0.0000	13	3.133
17	.1206	7	3.834
18	.3903	10	4.432
19	0.0000	6	2.604
20	.0497	7	3.533
21	.0123	9	3.169
22	.5005	13	4.479
23	.6397	13	4.331

Table 23. High Albite: Shielded Fractions of the Oxygen Atoms involved in the Bonds listed in Table 21. (For details, see Chapter IV, end of Section (i)c.)

(iii) Presentation of the Results

Using the method described in Chapter IV, the electrostatic charge distribution within the structure of high albite was calculated. The procedure is directly comparable to that used for the low albite structure. Several sets of charge distributions were calculated, each set using different assumed ideal values for the pure Si-O and Al-O distances, but each covering a range of coordination numbers for the sodium atom from 5 to 16. The charge was again distributed proportionally according to the inverse square of the bond length (\AA) taking the shielding effect into account. The smallest charge unbalance value obtained for any set of calculations was 0.062 e.s.u. using a 12-fold coordination for the sodium atom, and with Si-O = 1.600 \AA and Al-O = 1.778 \AA . This set is accordingly used to illustrate the detailed results for high albite, and the print-out of these results is given in Table 24. Fig. 4 shows graphically, for this same set of calculations, the variation in electrostatic charge unbalance as a function of the coordination number of the sodium atom.

As indicated earlier, several sets of calculations were carried out for different Si-O and Al-O values, and Fig. 5 is a plot of some of the charge unbalance values obtained for the high albite structure. The following list details the values of the variables used and the corresponding smallest unbalance values:

Table 24

High Albite: Print-out of a Complete Set of Electrostatic
Charge Balance Calculations for Coordination Numbers
of the Sodium from 5-fold to 16-fold with Si-O = 1.600 Å
and Al-O = 1.778 Å. This Set includes that with
12-fold Coordination of the Sodium which
Yielded the Smallest Unbalance
Value Obtained, 0.062 e.s.u.

Note: This Table occupies the following six pages and is
analogous to Table 17 in Chapter IV. Additional
notes concerning the content of this Table may be
found at the beginning of Table 17.

DMAX VALUE IS 2.900
COORD OF SODIUM IS 5
6 .362
7 .233
8 .200
9 0.000
10 0.000
11 0.000
12 .203
13 0.000

SIO= 1.600 ALO= 1.778

AL CONTENT OF TET 1 .269
AL CONTENT OF TET 2 .247
AL CONTENT OF TET 3 .219
AL CONTENT OF TET 4 .241
TOTAL AL CONTENT .977
TOTAL CHARGE ON OXYGEN NO. 6 2.217
TOTAL CHARGE ON OXYGEN NO. 7 2.087
TOTAL CHARGE ON OXYGEN NO. 8 2.084
TOTAL CHARGE ON OXYGEN NO. 9 1.923
TOTAL CHARGE ON OXYGEN NO.10 1.875
TOTAL CHARGE ON OXYGEN NO.11 1.883
TOTAL CHARGE ON OXYGEN NO.12 2.057
TOTAL CHARGE ON OXYGEN NO.13 1.894
CHARGE ON TETRAHEDRON NO. 1 8.234
CHARGE ON TETRAHEDRON NO. 2 7.918
CHARGE ON TETRAHEDRON NO. 3 7.949
CHARGE ON TETRAHEDRON NO. 4 7.942
CHARGE UNBALANCE ON HIGH ALBITE .424

DMAX VALUE IS 2.910
COORD OF SODIUM IS 6
6 .315
7 .203
8 .174
9 0.000
10 0.000
11 .129
12 .177
13 0.000

TOTAL CHARGE ON OXYGEN NO. 6 2.171
TOTAL CHARGE ON OXYGEN NO. 7 2.057
TOTAL CHARGE ON OXYGEN NO. 8 2.058
TOTAL CHARGE ON OXYGEN NO. 9 1.923
TOTAL CHARGE ON OXYGEN NO.10 1.875
TOTAL CHARGE ON OXYGEN NO.11 2.012
TOTAL CHARGE ON OXYGEN NO.12 2.030
TOTAL CHARGE ON OXYGEN NO.13 1.894
CHARGE ON TETRAHEDRON NO. 1 8.135
CHARGE ON TETRAHEDRON NO. 2 8.001
CHARGE ON TETRAHEDRON NO. 3 8.022
CHARGE ON TETRAHEDRON NO. 4 7.886
CHARGE UNBALANCE ON HIGH ALBITE .272

DMAX VALUE IS 3.140
COORD OF SODIUM IS 7

6	.283	
7	.182	
8	.156	
9	0.000	
10	0.000	
11	.116	
12	.159	
13	.101	
TOTAL CHARGE ON OXYGEN NO. 6		2.138
TOTAL CHARGE ON OXYGEN NO. 7		2.036
TOTAL CHARGE ON OXYGEN NO. 8		2.040
TOTAL CHARGE ON OXYGEN NO. 9		1.923
TOTAL CHARGE ON OXYGEN NO.10		1.875
TOTAL CHARGE ON OXYGEN NO.11		1.999
TOTAL CHARGE ON OXYGEN NO.12		2.012
TOTAL CHARGE ON OXYGEN NO.13		1.996
CHARGE ON TETRAHEDRON NO. 1		8.067
CHARGE ON TETRAHEDRON NO. 2		8.057
CHARGE ON TETRAHEDRON NO. 3		8.072
CHARGE ON TETRAHEDRON NO. 4		7.847
CHARGE UNBALANCE ON HIGH ALBITE		.350

DMAX VALUE IS 3.170
COORD OF SODIUM IS 8

6	.258	
7	.166	
8	.142	
9	.089	
10	0.000	
11	.105	
12	.145	
13	.092	
TOTAL CHARGE ON OXYGEN NO. 6		2.113
TOTAL CHARGE ON OXYGEN NO. 7		2.019
TOTAL CHARGE ON OXYGEN NO. 8		2.026
TOTAL CHARGE ON OXYGEN NO. 9		2.012
TOTAL CHARGE ON OXYGEN NO.10		1.875
TOTAL CHARGE ON OXYGEN NO.11		1.988
TOTAL CHARGE ON OXYGEN NO.12		1.998
TOTAL CHARGE ON OXYGEN NO.13		1.987
CHARGE ON TETRAHEDRON NO. 1		8.013
CHARGE ON TETRAHEDRON NO. 2		8.102
CHARGE ON TETRAHEDRON NO. 3		8.022
CHARGE ON TETRAHEDRON NO. 4		7.906
CHARGE UNBALANCE ON HIGH ALBITE		.232

DMAX VALUE IS 3.370
COORD OF SODIUM IS 9

6	.240	
7	.154	
8	.132	
9	.083	
10	.070	
11	.098	
12	.134	
13	.086	
TOTAL CHARGE ON OXYGEN NO. 6		2.095
TOTAL CHARGE ON OXYGEN NO. 7		2.008
TOTAL CHARGE ON OXYGEN NO. 8		2.016
TOTAL CHARGE ON OXYGEN NO. 9		2.006
TOTAL CHARGE ON OXYGEN NO.10		1.945
TOTAL CHARGE ON OXYGEN NO.11		1.981
TOTAL CHARGE ON OXYGEN NO.12		1.988
TOTAL CHARGE ON OXYGEN NO.13		1.980
CHARGE ON TETRAHEDRON NO. 1		8.045
CHARGE ON TETRAHEDRON NO. 2		8.064
CHARGE ON TETRAHEDRON NO. 3		7.987
CHARGE ON TETRAHEDRON NO. 4		7.948
CHARGE UNBALANCE ON HIGH ALBITE		.174

DMAX VALUE IS 3.540
COORD OF SODIUM IS 10

6	.225	
7	.205	
8	.124	
9	.078	
10	.065	
11	.092	
12	.126	
13	.081	
TOTAL CHARGE ON OXYGEN NO. 6		2.080
TOTAL CHARGE ON OXYGEN NO. 7		2.059
TOTAL CHARGE ON OXYGEN NO. 8		2.008
TOTAL CHARGE ON OXYGEN NO. 9		2.001
TOTAL CHARGE ON OXYGEN NO.10		1.940
TOTAL CHARGE ON OXYGEN NO.11		1.975
TOTAL CHARGE ON OXYGEN NO.12		1.980
TOTAL CHARGE ON OXYGEN NO.13		1.975
CHARGE ON TETRAHEDRON NO. 1		8.010
CHARGE ON TETRAHEDRON NO. 2		8.033
CHARGE ON TETRAHEDRON NO. 3		8.019
CHARGE ON TETRAHEDRON NO. 4		7.982
CHARGE UNBALANCE ON HIGH ALBITE		.080

DMAX VALUE IS 3.840
COORD OF SODIUM IS 11

6	.215	
7	.241	
8	.119	
9	.074	
10	.062	
11	.088	
12	.120	
13	.077	
TOTAL CHARGE ON OXYGEN NO. 6		2.070
TOTAL CHARGE ON OXYGEN NO. 7		2.095
TOTAL CHARGE ON OXYGEN NO. 8		2.002
TOTAL CHARGE ON OXYGEN NO. 9		1.997
TOTAL CHARGE ON OXYGEN NO.10		1.937
TOTAL CHARGE ON OXYGEN NO.11		1.971
TOTAL CHARGE ON OXYGEN NO.12		1.974
TOTAL CHARGE ON OXYGEN NO.13		1.971
CHARGE ON TETRAHEDRON NO. 1		7.985
CHARGE ON TETRAHEDRON NO. 2		8.011
CHARGE ON TETRAHEDRON NO. 3		8.041
CHARGE ON TETRAHEDRON NO. 4		8.006
CHARGE UNBALANCE ON HIGH ALBITE		.073

DMAX VALUE IS 4.140
COORD OF SODIUM IS 12

6	.209	
7	.235	
8	.140	
9	.072	
10	.061	
11	.085	
12	.118	
13	.075	
TOTAL CHARGE ON OXYGEN NO. 6		2.065
TOTAL CHARGE ON OXYGEN NO. 7		2.089
TOTAL CHARGE ON OXYGEN NO. 8		2.024
TOTAL CHARGE ON OXYGEN NO. 9		1.996
TOTAL CHARGE ON OXYGEN NO.10		1.936
TOTAL CHARGE ON OXYGEN NO.11		1.969
TOTAL CHARGE ON OXYGEN NO.12		1.971
TOTAL CHARGE ON OXYGEN NO.13		1.970
CHARGE ON TETRAHEDRON NO. 1		7.997
CHARGE ON TETRAHEDRON NO. 2		8.000
CHARGE ON TETRAHEDRON NO. 3		8.053
CHARGE ON TETRAHEDRON NO. 4		7.993
CHARGE UNBALANCE ON HIGH ALBITE		.062

DMAX VALUE IS 4.180
COORD OF SODIUM IS 13

6	.204	
7	.230	
8	.136	
9	.071	
10	.059	
11	.083	
12	.140	
13	.073	

TOTAL CHARGE ON OXYGEN NO. 6	2.060
TOTAL CHARGE ON OXYGEN NO. 7	2.083
TOTAL CHARGE ON OXYGEN NO. 8	2.020
TOTAL CHARGE ON OXYGEN NO. 9	1.994
TOTAL CHARGE ON OXYGEN NO.10	1.934
TOTAL CHARGE ON OXYGEN NO.11	1.966
TOTAL CHARGE ON OXYGEN NO.12	1.993
TOTAL CHARGE ON OXYGEN NO.13	1.968
CHARGE ON TETRAHEDRON NO. 1	8.009
CHARGE ON TETRAHEDRON NO. 2	7.989
CHARGE ON TETRAHEDRON NO. 3	8.039
CHARGE ON TETRAHEDRON NO. 4	8.006
CHARGE UNBALANCE ON HIGH ALBITE	.066

DMAX VALUE IS 4.280
COORD OF SODIUM IS 14

6	.199	
7	.223	
8	.133	
9	.069	
10	.058	
11	.108	
12	.136	
13	.071	

TOTAL CHARGE ON OXYGEN NO. 6	2.054
TOTAL CHARGE ON OXYGEN NO. 7	2.077
TOTAL CHARGE ON OXYGEN NO. 8	2.017
TOTAL CHARGE ON OXYGEN NO. 9	1.992
TOTAL CHARGE ON OXYGEN NO.10	1.933
TOTAL CHARGE ON OXYGEN NO.11	1.991
TOTAL CHARGE ON OXYGEN NO.12	1.989
TOTAL CHARGE ON OXYGEN NO.13	1.966
CHARGE ON TETRAHEDRON NO. 1	7.994
CHARGE ON TETRAHEDRON NO. 2	8.004
CHARGE ON TETRAHEDRON NO. 3	8.052
CHARGE ON TETRAHEDRON NO. 4	7.993
CHARGE UNBALANCE ON HIGH ALBITE	.068

DMAX VALUE IS 4.340
COORD OF SODIUM IS 15

6	.196	
7	.220	
8	.131	
9	.068	
10	.057	
11	.106	
12	.134	
13	.084	

TOTAL CHARGE ON OXYGEN NO. 6	2.052
TOTAL CHARGE ON OXYGEN NO. 7	2.074
TOTAL CHARGE ON OXYGEN NO. 8	2.015
TOTAL CHARGE ON OXYGEN NO. 9	1.991
TOTAL CHARGE ON OXYGEN NO.10	1.932
TOTAL CHARGE ON OXYGEN NO.11	1.989
TOTAL CHARGE ON OXYGEN NO.12	1.988
TOTAL CHARGE ON OXYGEN NO.13	1.978
CHARGE ON TETRAHEDRON NO. 1	7.987
CHARGE ON TETRAHEDRON NO. 2	8.011
CHARGE ON TETRAHEDRON NO. 3	8.058
CHARGE ON TETRAHEDRON NO. 4	7.986
CHARGE UNBALANCE ON HIGH ALBITE	.095

DMAX VALUE IS 4.400
COORD OF SODIUM IS 16

6	.190	
7	.214	
8	.127	
9	.096	
10	.055	
11	.103	
12	.130	
13	.081	

TOTAL CHARGE ON OXYGEN NO. 6	2.046
TOTAL CHARGE ON OXYGEN NO. 7	2.068
TOTAL CHARGE ON OXYGEN NO. 8	2.011
TOTAL CHARGE ON OXYGEN NO. 9	2.019
TOTAL CHARGE ON OXYGEN NO.10	1.930
TOTAL CHARGE ON OXYGEN NO.11	1.986
TOTAL CHARGE ON OXYGEN NO.12	1.984
TOTAL CHARGE ON OXYGEN NO.13	1.976
CHARGE ON TETRAHEDRON NO. 1	7.972
CHARGE ON TETRAHEDRON NO. 2	8.028
CHARGE ON TETRAHEDRON NO. 3	8.042
CHARGE ON TETRAHEDRON NO. 4	8.002
CHARGE UNBALANCE ON HIGH ALBITE	.100

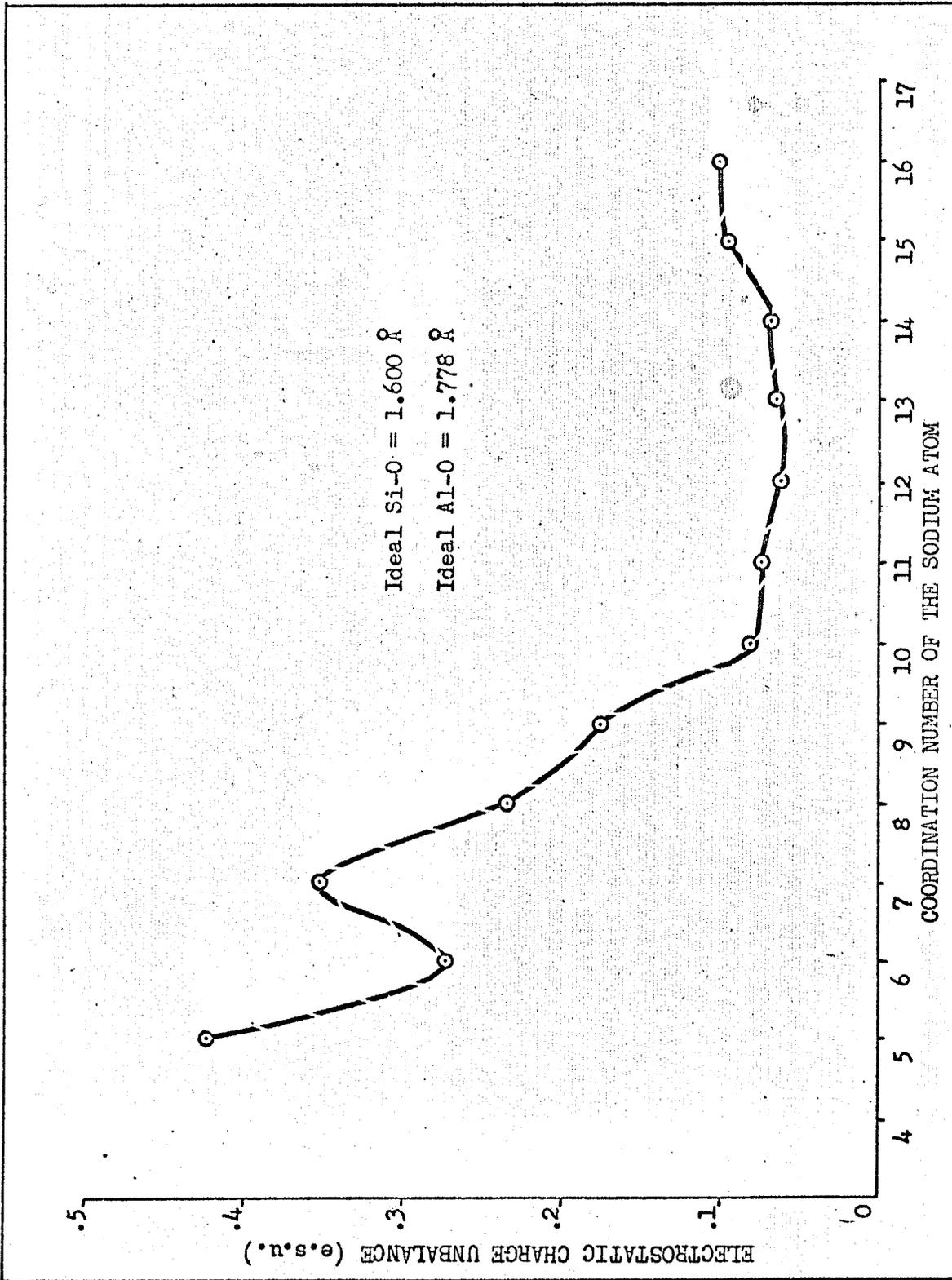


Fig. 4. High Albite: Variation in Electrostatic Charge Unbalance with Coordination Number of the Sodium Atom for Si-O = 1.600 Å and Al-O = 1.778 Å.

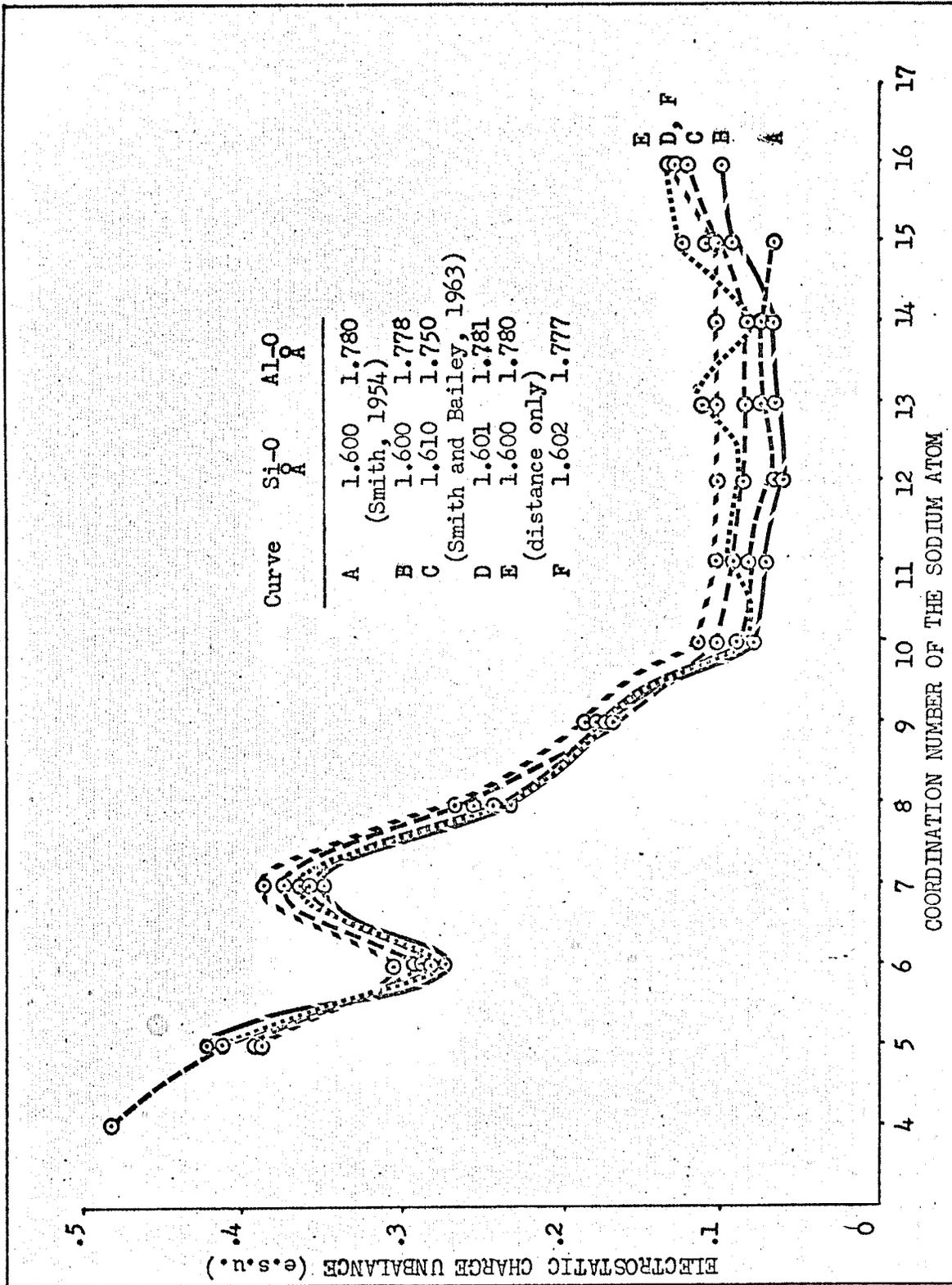


Fig. 5. High Albite: Curves Showing the Variation in Electrostatic Charge Unbalance with Coordination Number of the Sodium Atom for Different Ideal Values of Si-O and Al-O.

Curve in Fig. 4	Ideal Si-O(\AA)	Ideal Al-O(\AA)	Al-content (Atoms)	Coord. of Na	Minimum Unbalance Value (e.s.u.)
A	1.600 (Smith, 1954)	1.780	0.966	12	0.068
B	1.600	1.778	0.977	12	0.062
C	1.610 (Smith and Bailey, 1963)	1.750	0.957	12, 13 & 14	0.085
D	1.601	1.781	0.944	11,12,13,14 and 15	0.111
E	1.600 (No account taken of shielding)	1.780	0.966	14	0.074
F	1.602	1.777	0.9999	11,12,13,14 and 15	0.103

(iv) Summary of the Main Features of the Charge Distribution Results for High Albite

The lowest charge unbalance value for high albite was 0.062 e.s.u. and was obtained using Si-O = 1.600 \AA and Al-O = 1.778 \AA with a coordination number for the sodium atom of 12. (Table 24 and Fig. 4). However, this value (0.062 e.s.u.) is only one of several nearly as low unbalance values for sodium coordinations of 10-fold and higher (Table 24). Several other complete sets of calculations were performed using different values of Si-O and Al-O (see Tabulation above) and all these calculations yielded low unbalance values for coordinations greater than 10-fold (see Fig. 5). Another striking characteristic common to the curves shown in Figs. 4 and 5 is a marked charge unbalance value for a 6-fold coordination of the sodium (about 0.30 e.s.u.), but this unbalance value is still appreciably higher than the unbalance values for 10-fold or greater coordinations of the sodium atom, ranging from 0.06 to 0.13 e.s.u.

Because the interpretation of these results is closely related to the interpretation of the low albite results, it is held over to the next Chapter.

CHAPTER VI

DISCUSSION OF THE CHARGE DISTRIBUTION RESULTS FOR
HIGH ALBITE IN COMPARISON WITH THOSE FOR
LOW ALBITE

(i) Consideration of the Sodium-Oxygen Environment in High Albite

A major issue in the charge distribution in high albite is the low unbalance value of 0.062 e.s.u. obtained with a high coordination of the sodium atom. This value is fairly close to zero and at first appears to be contrary to the hypothesis proposed by Ferguson, Traill and Taylor (1958) that high albite should exhibit a distinct electrostatic charge unbalance. This new value is appreciably smaller than that derived by Ferguson et al. of 0.28 e.s.u., obtained with low coordination of the sodium atom.

The main issue appears now to be whether to treat the low coordination of sodium or the high coordination of sodium as the most representative of the structure. If the smallness of the charge unbalance value is to be taken as the sole criterion, then one would have to accept an indefinite coordination of sodium ranging between 10-fold and 16-fold, and possibly even higher. However, the low albite results strongly suggest that the best charge unbalance value can be obtained if the coordination of sodium is taken as 6-fold, and/or the charge on the sodium is only effective to a distance of about 2.96 \AA from the centre of the sodium atom. If one were to apply this principle to high albite, treating

the sodium as a single isotropic atom, rather than as an anisotropic atom, then it seems unreasonable to consider the oxygens in more than 6-fold coordination with the sodium because they will be beyond the 'influence' of the charge on the sodium atom. Ferguson, Traill and Taylor (1958), and Ribbe, Megaw and Taylor (1967), have clearly shown that the sodium atom in high albite is markedly anisotropic, roughly parallel to the b-axis of the structure, and ascribed to either spatial or temporal causes. Williams and Megaw (1964) conducted structure refinements on low and high albites at -180°C . and noted that the degree of anisotropism of the sodium in high albite had not changed. Their conclusion was that this suggested a spatial rather than a temporal variation in the position of sodium in the high albite structure. Ribbe et al. (1967) show that the strong anisotropism of the sodium atom may be interpreted as the effect of two "half-atoms" which are separated by a distance of about 0.61 \AA . They calculated the Na-O distances from the two "half-atoms", and these values are reproduced in Table 25. A study of this list (Table 25) shows that there is only one non-equivalent oxygen, OC(O), which is not amongst the closest 6, or within 2.96 \AA , of either "half-atom". Therefore, it may be argued that a high coordination of the single sodium atom is in keeping with the sodium coordination and/or the Na-O bonded distances derived from the low albite results, as the sodium in high albite behaves as two "half-atoms" with appreciable separation.

It was not possible for this thesis to calculate the electrostatic charge distributions in terms of "half-atoms" for the sodium, but the present results suggest that the high albite structure may exhibit almost

perfect charge balance if the closest 6 oxygens around the two "half-atoms" were considered. By studying Table 25 it can be seen that a coordination of the 6 closest oxygen atoms to each sodium "half-atom" corresponds to a coordination ~~of a coordination~~ of a single sodium atom of 8-fold, but in the latter case it involves four oxygens receiving proportionally large shares of charge from two "half-sodium atoms" (effectively one whole sodium atom), these particular oxygen atoms and their corresponding "sodium half-atom" to oxygen distances being: OA(1) at 2.74 Å ; OB(M) at 2.88 Å ; OC(M) at 2.68 Å, and OD(M) at 2.84 Å. Thus the charge unbalance for the closest 8 oxygens taken in coordination with the sodium atoms is quite large (0.232 e.s.u., Table 24). However, as the coordination increases around the single sodium, the proportion of charge contributed to each oxygen atom is, of course, reduced and this apparently approximates more closely to the best situation; say 6-fold coordination about two sodium "half-atoms"; since the charge unbalance value decreases rapidly as 10-fold coordination of sodium is approached and remains nearly unchanged through the higher coordination numbers, this suggests that these coordinations are all nearly equally satisfactory. It is necessary to re-state here that the 'shielding factors' have all been calculated for the oxygen atoms and that these are all taken into account during these calculations; thus the actual numbers are indicative of the given situation since careful consideration has been given to the crystal structures of both high and low albite. From a different and more general viewpoint, it may be said that in an ideally disordered high albite, all the oxygens are shared by two tetrahedral cations, both of which have the same effective positive charge; it follows therefore that all the oxygens in the structure receive essentially the same amount of tetrahedral

Table 25

High Albite: Details Relating to Oxygen Atoms around the Sodium Atom

Nearness Number	Na-O Dist. Å		Shielded Fraction	Oxygen	Na-O Dist. Å	Total Charge Contributions (e.s.u.)	Nearness No. from single Na-atom	Oxygen Distances (Å) Around Sodium "Half-Atoms"	
	Oxygen	Oxygen						Na1-O (Å)	Na2-O (Å)
1	OA(2)	2.342	0	OA(1)	2.604	2.065	(4)	2.54(3)	2.48(2)
2	OD(O)	2.506	0		2.713		(5)	2.74(5)	2.92
3	OB(O)	2.526	0	OA(2)	2.342	2.089	(1)	2.37(1)	2.34(1)
4	OA(1)	2.604	0		3.533				3.33
5	OA(1)	2.713	0		3.834				
6	OC(M)	2.909	0.018	OB(O)	2.526	2.024	(3)	2.57(4)	2.53(3)
7	OD(M)	3.133	0		4.138				
8	OB(M)	3.169	0.012	OB(M)	3.169	1.996	(8)	3.45	2.88(6)
9	OC(O)	3.367	0.062	OC(O)	3.367	1.936	(9)	3.20	3.57
10	OA(2)	3.533	0.050	OC(M)	2.909	1.969	(6)	3.12	2.68(5)
11	OA(2)	3.834	0.121	OD(O)	2.506	1.971	(2)	2.46(2)	2.58(4)
12	OB(O)	4.138	0.438	OD(M)	3.133	1.970	(7)	2.84(6)	3.44

charge; thus the equal distribution of the charge on the sodium atom to all the non-equivalent oxygen atoms would lead to an ideally perfect balance. It may be suggested that the coordination numbers from 10 and greater approximate to this ideal condition. However, this is not the case with the low albite structure since the tetrahedral charges are not distributed equally to all the oxygen atoms, and this leads to a large difference in the charge unbalance values for low and high albite at high coordinations of the sodium as indicated in Fig. 6.

As mentioned previously, the curves for high albite (Figs. 4 and 5) have a low charge unbalance value at the 6-fold coordination of the sodium atom, but not as low as for coordination numbers higher than 10-fold. In attempting to explain this feature of the high albite curves, the reasoning follows in a manner similar to that given immediately above. Again, by comparing single atom Na-O distances with the two sets of "half-atom" Na-O distances in Table 25, it may be seen that the smallest six single-atom Na-O distances include five of the smallest "half-atom" Na-O distances, but not in the same order, and not the same five. For example, the 7th smallest single-atom Na-O length includes one of the 6th smallest "half-atom" Na-O lengths, and the 8th smallest single-atom Na-O length includes the other 6th smallest "half-atom" Na-O length. It is difficult to analyze these numbers further except to suggest that the low unbalance value at the 6-fold coordination of the sodium is probably related to the 6-fold coordination requirement of sodium as deduced from the low albite results.

If it is possible to carry out similar calculations treating the sodium as two "half-atoms", a clearer understanding of these relationships between charge unbalance and coordination in high albite will probably result.

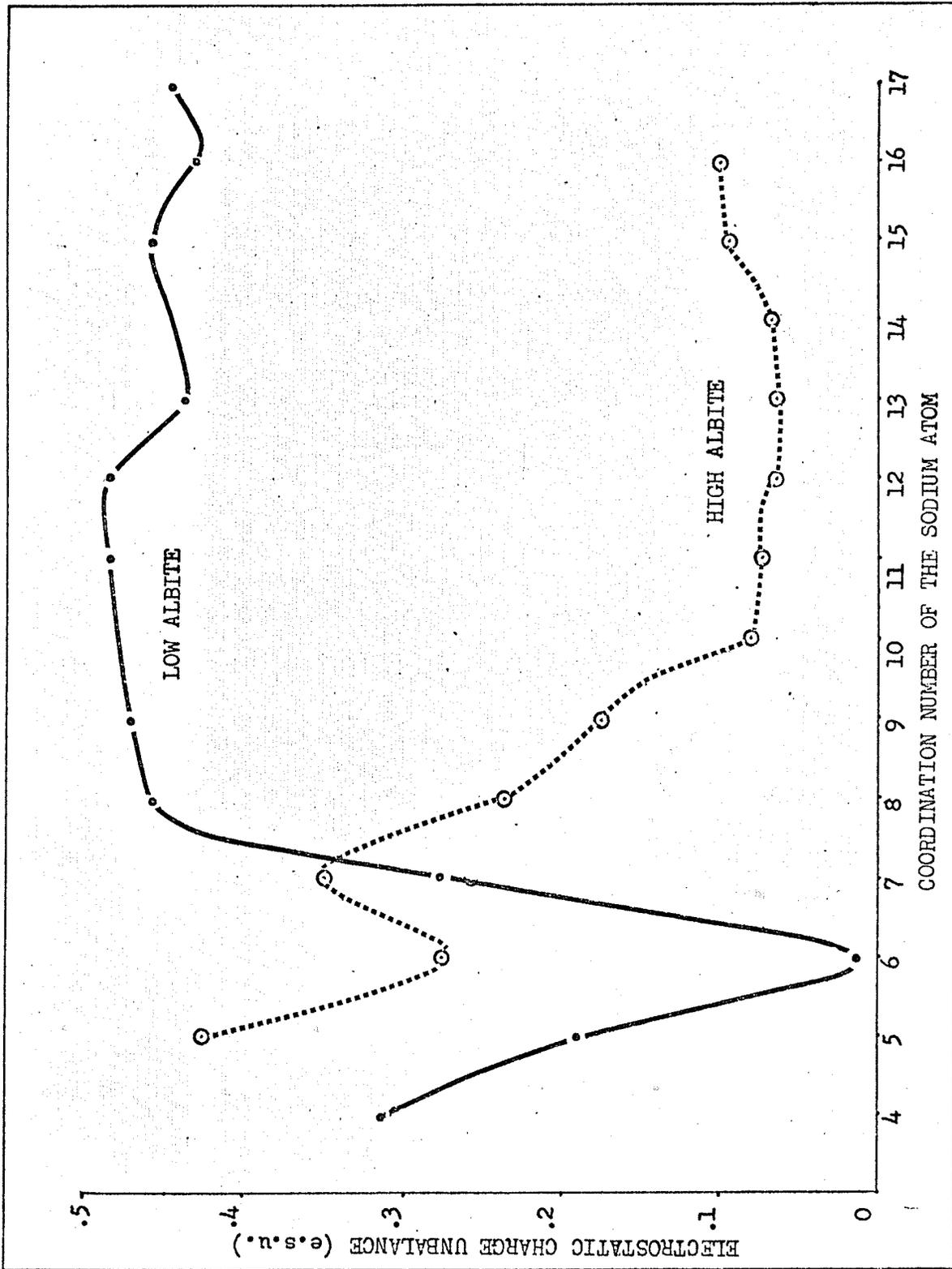


Figure 6: A Comparison between the Minimum Electrostatic Charge Unbalance Curves for Low and High Albite.

(ii) Consideration of the Tetrahedra in High Albite

In 1958, Ferguson et al. concluded that high albite has a distinctly higher minimum charge unbalance value than low albite, and they proposed that differences in charges contributed to corresponding tetrahedral groups of four oxygens offered a general explanation as to why the aluminum in disordered high albite tends to migrate preferentially into a particular tetrahedral site, Tl(O), in low albite.

In considering the new and more accurate results of charge distribution in these structures, the most important development is that a set of conditions has been established which will yield a low charge unbalance value for high albite (0.062 e.s.u.). This value is not quite as low for all the possibilities tested, as that for low albite (0.014 e.s.u.) but nevertheless, sufficiently low that it may no longer be reasonable to invoke a difference in the unbalance values to explain why high albite tends to order the Si-Al towards the low albite distribution. In the next Section, a related but new reason is offered as an explanation as to why there is the tendency for Si-Al ordering.

At present it must be established if there is a reason why the Al^{+3} in disordered high albite will tend to migrate into the particular tetrahedral site Tl(O) in low albite. To evaluate this, it is necessary to compare charge contributions to corresponding tetrahedral groups of four oxygens in high albite and in low albite. The values to be considered for low albite are clearly those yielding the smallest charge unbalance, but the matter is not as obvious in considering the high albite structure;

there are two possibilities, either the set of values yielding the smallest charge unbalance (say 12-fold coordination of the sodium atom), or the set of values corresponding exactly to the set of conditions which yielded the smallest charge unbalance value in low albite (i.e., 6-fold coordination of the sodium). The Tabulation given below illustrates these alternatives:

	LOW ALBITE	HIGH ALBITE	
Si-O Å	1.602	1.600	1.602
Al-O Å	1.777	1.778	1.777
C.N. of Na	6	12	6
T1(O)	8.006 e.s.u.	7.997 e.s.u.	8.150 e.s.u.
T1(M)	7.999	8.000	8.016
T2(O)	8.001	8.053	8.037
T2(M)	<u>7.994</u>	<u>7.993</u>	<u>7.901</u>
$\Sigma \Delta$	0.014	0.062*	0.302

* This value has been summed from four values which have not been rounded off and are listed only to three decimal places. The summed value is correct if rounding off of the numbers is considered.

If the above values are compared and one considers first the values for high albite which yield the smallest unbalance (0.062 e.s.u.), there is no reason why the Al^{+3} should migrate into any particular site or even migrate at all. In comparing the second set of values, however, one may see that these offer strong confirmation of the suggestion by Ferguson, Traill and Taylor (1958) that the Al^{+3} would tend to migrate

into site Tl(O) so as to reduce the high excess charge of +0.150 e.s.u. on that (disordered) tetrahedral group of four oxygens. Reasons are offered in the next Section as to which interpretation is regarded as the more likely, and also how to reconcile the two concepts.

(iii) A Possible Reason for the High Albite to Order Si-Al to Low Albite on Prolonged Cooling

The problems involved in making this kind of interpretation have been stated in the previous Section; if high albite has nearly as low a charge unbalance value as low albite, there appears little or no reason for Si-Al ordering to occur. It is reasonable to examine the charge distribution for a 6-fold coordination of the sodium atom in high albite as a possible explanation of the migration of Al^{+3} into the tetrahedral site Tl(O).

The answer to these difficulties appears to lie in the strong anisotropism of the sodium atom in high albite. The reasoning may be given as follows:

High albite, existing at a high temperature, has Si-Al disorder as a result of the high thermal motion. Because of the Si-Al disorder and the presumed strong thermal vibration of the sodium atoms, these atoms occupy large cavities anisotropically, either in point of time or space or both. Such conditions can be thought of as being "frozen in" when the crystal cools relatively quickly to normal temperature.

As discussed in Section (i) of this Chapter, the 12-fold coordination of the single-atom sodium in high albite which yields the smallest charge unbalance is only one of several equally small values

yielded by coordination numbers of 10 or greater. It was further indicated that the unbalance values for the single sodium atom are probably reasonable, approximating to the values which would have been obtained had it been possible to calculate charge unbalance values for two "half-atoms" taken in 6-fold coordination, the deduced ideal coordination from the low albite calculations.

Thus it may be said that high albite has largely satisfied the charge distribution requirements for a strongly anisotropic sodium atom. However, as the high albite crystal cools slowly, the thermal vibration would tend to decrease and therefore the effective coordination of the single-atom sodium could also be expected to decrease, in due course approximating 6-fold coordination, at which stage the charge distribution would be similar to that shown in column 3 of the Tabulation in Section (ii) of this Chapter, and at which stage, furthermore, there would be strong charge unbalance mainly represented by excess charge on site T1(0) which would tend to cause Al^{+3} to migrate into this site; hence the structural framework would begin to adopt the Si-Al configuration that it finally achieves at normal temperatures, that of low albite, about 82% ordered.

CHAPTER VII

SUMMARY AND CONCLUSIONS

(i) Assumptions and General Method of Calculation

The original assumptions in this work were fundamental, and there was no way of establishing their validity until the work had been completed. The first assumption was that the feldspars may be treated as ionic compounds, and as a consequence the electrostatic charge unbalance could be used as a measure of the stability of their structures. The second assumption was that the low-temperature feldspars would, in general, exhibit a perfect local charge balance and that the high-temperature feldspars would be less well balanced. The third and final assumption was that the particular values for pure Si-O and Al-O that resulted in a near-zero charge unbalance could be considered as the "ideal" values for that structure. These ideal Si-O and Al-O values are important in that they determine the distribution of silicon and aluminum in the structure which is important in determining the Si-Al order-disorder relationship.

In order to examine the validity of these assumptions, a method was devised for calculating the distribution of electrostatic charge throughout a particular structure. The first attempt at the application of these methods was made with the anorthite structure as it was considered to be the most general case; the crystallographic requirements were such that if a computer program were written to deal with this structure, the same program would be sufficiently flexible that it could be used for the

other feldspar minerals. In the course of the study on the anorthite structure a number of complications arose which greatly increased the difficulties which were being encountered, and thus the full details of this structure were left unfinished while complete studies were conducted for the low and high albite members of the feldspar group.

The electrostatic charge distribution calculations were performed in two parts. First, the positive charges on the tetrahedral sites were distributed to their immediate tetrahedral oxygen environment proportionally according to the inverse squares of the T-O distances. In this way the values for the tetrahedral charge contributions to the non-equivalent oxygen atoms were obtained. It should also be mentioned here that the influence of the positive charge on a given tetrahedral site is unlikely to extend beyond the immediate tetrahedral group of four oxygens, as this grouping results in the small, positively charged atom being completely enclosed by its oxygen environment.

The second part of the calculation involved the distribution of the electrostatic charges from the large cations (sodium in low and high albite) to the neighbouring oxygen atoms. This similarly took account of the inverse squares of the Na-O bond lengths (\AA) and also the fraction of that particular oxygen atom which was not shielded either by other oxygen atoms or by other sodium atoms. The total charge contributions were then summed for the non-equivalent oxygens, and these values again summed for the appropriate tetrahedral group of four oxygens. Since the balance of charge is basically dependent upon the distribution of silicon and aluminum in the tetrahedral sites of the structure, it was considered

that the sum of the deviations from 8.000 e.s.u. was the most realistic measure of the degree of charge unbalance in the structure. The albite calculations were programmed for the IBM 1620 in the FORTRAN II language, and the program allowed a number of charge distribution calculations to be performed for a range of coordinations of the large cation (sodium) for fixed assumed Si-O and Al-O values. In this way the unbalance value could be related directly to the coordination of the sodium atom.

The programs for albite mentioned above were developed as a result of a long series of calculations for the anorthite structure which were done using a FORTRAN IV program written by the author for the IBM SYSTEM 360/DOS. The experience gained from the numerous failures and inconsistencies that arose during the progress of developing this program greatly assisted the writing of the IBM 1620 programs for albite.

(ii) The Anorthite Structure

Chapters II and III contain a detailed account of the studies conducted on the anorthite structure. The results are inconclusive as the calculations are incomplete; this came about since the numbers of variables which had to be treated were large, and even with the elaborate computer program it was not possible to treat them inter-dependently. Although some of the latest results produced near-zero charge unbalance values for anorthite, it was felt that these were unrealistic. All the first calculations yielded high charge unbalance values, and on account of these the program was modified through various successive stages in an attempt to reduce the charge unbalance value. Most of the high unbalance values were obtained using large coordination numbers for the calcium atoms, and this is considered to be the reason for the high unbalance. More recent

studies concerning low and high albite have suggested that the effective coordination number of the large cation reduces from the high-temperature structure to the low-temperature structure. Thus, since the anorthite studied was considered to be a low-temperature feldspar, the coordination number of the calcium atoms is likely to be smaller than those for which the majority of the calculations were carried out. It is thought therefore that the coordination of the calcium atoms is likely to be between 6-fold and 12-fold, rather than 12-fold or higher. Time did not permit further calculations of this nature but it is believed that these smaller coordination numbers may yield a low or near-zero charge unbalance for the structure. This would probably result in a change in the ideal values for the sizes of the pure Si-O and Al-O tetrahedra obtained by the author so far for the anorthite structure.

The study on anorthite was finally left incomplete in favour of a study of the simpler albite structures. The information obtained from the anorthite calculations was useful in determining the approach which was applied to the albites.

(iii) Low-Temperature and High-Temperature Albites

A description and discussion of the electrostatic charge balance studies of low and high albite are detailed in Chapters IV, V and VI. The final results were of great interest, and are best considered in comparison with each other. The main conclusions are given below:

1. An almost ^{zero} charge unbalance value of 0.014 e.s.u. was obtained for low albite for one set of assumed conditions. Perfect charge unbalance is considered as being the most stable

state for this low albite, and the conclusions are therefore based upon the set of ideal conditions which gave rise to this unbalance value.

2. For the best unbalance value of 0.014 e.s.u., the mean sizes of the pure Si-O and Al-O tetrahedra assumed for this low albite are 1.602 and 1.777 Å respectively. These values are close to those suggested by Smith in 1954, Si-O = 1.601 Å and Al-O = 1.781 Å. Under these conditions this low albite is about 82% ordered with respect to Si and Al. It is not fully ordered.
3. The coordination number of the sodium atom in low albite with the best unbalance value is 6-fold, and this represents the most satisfactory arrangement of oxygen atoms with respect to the sodium atom.
4. The high albite studied yielded a low charge unbalance value of 0.062 e.s.u. with a coordination number of 12 for the sodium atom and with Si-O = 1.600 Å and Al-O = 1.778 Å. This low unbalance value is about four times greater than the smallest obtained for the low albite. Again the ideal Si-O and Al-O values are close to those proposed by Smith in 1954.
5. Anisotropism of the sodium atom is thought to account for the marked difference between the best coordination number for the low albite structure (6) compared to that for high albite (12). It is suggested that the anisotropism gives the sodium atom a greater effective radius of influence in high albite, and therefore

the number of oxygens which are coordinated to the sodium in high albite, (12), is much larger than the number of oxygens coordinated to sodium in low albite, (6). As the high albite passes through a long period of cooling, the anisotropism decreases and therefore the radius of influence of the sodium atom decreases, thus reducing the effective coordination of that atom.

6. Comparison between the set of conditions yielding the minimum charge unbalance for low albite and the same set of conditions for the high albite structure gives some significant information. A reason for the Si - Al ordering is suggested by a study of the total positive charge contributions to the tetrahedral groups of four oxygens. In high albite the site Tl(O) has excess positive charge and this is considered to be the reason why the trivalent Al will tend to migrate preferentially into that site in order to reduce the positive charge contributions to that group of oxygen atoms, so as to achieve near perfect charge balance.

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APPENDIX I

APPENDIX I

AN IBM SYSTEM 360/DOS COMPUTER PROGRAM TO CALCULATE
THE DISTRIBUTION OF ELECTROSTATIC CHARGES
WITHIN THE ANORTHITE STRUCTURE

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* As Appendix I is exceptionally long, a Table of Contents is given in order to facilitate its use.

APPENDIX I

A. THE BASIC DESCRIPTION OF THE COMPUTER PROGRAM

Since these calculations are extremely long and tedious, and in view of the fact that a large number of iterations are required to arrive at a minimum charge unbalance value, it was necessary that the calculations be adapted to a computer program. The calculations themselves involve simple arithmetic, but nevertheless the crystallographic relationships and the changes required to make the various adjustments to the variables resulted in the program being fairly long. The program was written originally for the IBM 1620 Data Processing Unit in FORTRAN II language and later translated in FORTRAN IV in order that it may be operated on the IBM SYSTEM 360/65 Disk Operating System which was acquired by the University of Manitoba in September 1966. The main advantage of this system is that the time required to perform a large number of calculations is remarkably short in comparison with the IBM 1620 Unit.

The Program is divided into a MAIN Program with four subroutines, and this division provides a suitable breakdown for the description of the program. The complete printout and simplified flow diagrams for the program are found in this Appendix.

(a) THE MAIN PROGRAM

The MAIN Program essentially controls the subroutines which handle the bulk of the calculations. It is here that the variables are

dimensioned and defined for use by the subroutines, and also several of the 'counters' required to handle the crystallographic requirements are defined. The outline of the MAIN Program is given below in point form:

1. Dimension the necessary variables.
2. Read in the crystallographic control numbers. These were established in order to give the program greater versatility, and to make it applicable to other feldspar structures with a minimum of modification.
3. Read in the assumed ideal values of the Si-O and Al-O distances. Read in all the tetrahedral-oxygen distances, including the average size of each tetrahedron.
4. Set the iteration counter (K).
5. Subroutine TETRA is called in for use, and this carries out the electrostatic charge distribution from the tetrahedral sites to the surrounding oxygens and then sums the values on equivalent oxygens so that a list of the tetrahedral charge contributions to the non-equivalent oxygens may be printed out. (See Section (b) in this Chapter concerning TETRA).
6. Subroutine ALKI is called, and this carries out the main part of the calculation involving the distribution of the charge on the alkali or alkali earth atoms to the oxygen environment. It also sums these values on the non-equivalent oxygens and, in addition, sums these numbers with the tetrahedral charges on all the non-equivalent oxygens.

In this way a complete list of the non-equivalent oxygen atoms is printed out giving the total positive contribution to each from the surrounding cations.

7. Subroutine ALKI2 is called and this calculates the total charge on each of the tetrahedral groups. It also determines the charge difference from the ideal value of 8,000 e.s.u. and arrives at the sum of these differences. This number represents the electrostatic charge unbalance in the structure.
8. Subroutine COORD is called and is used to adjust the coordination of the alkali or alkali earth atom, depending upon the structure type.
9. Return to the MAIN Program where a summary of the final results of each iteration are printed out under the following headings: Iteration Number; Si-O Value; Al-O Value; Total Al-content; Charge Unbalance; Charge Difference (from one iteration to the previous one); and Coordination Numbers of the alkali or alkali earth atoms. An example is given in Table 8.
10. End of Program.

The following sections involve a more detailed view of the manner in which the calculations are performed in each of the subroutines:

(b) SUBROUTINE TETRA

Subroutine TETRA is the least complex of all. The calculations are as follows:

1. Calculation of the aluminum content of each tetrahedral site.
2. Summation of the Al-contents of all these tetrahedral sites in order to obtain the number of Al-atoms in the structure.
3. Calculation of the statistical positive charge on each tetrahedral site.
4. Calculation of the 'weighting factor' used to proportion the positive charge according to the inverse squares of the distances of the oxygen atoms from the tetrahedral site.
5. The calculation of the actual amounts of charge contributed to each of the four oxygens associated with each of the tetrahedral groups.
6. The location of those oxygen atoms which are equivalent is given in order that the tetrahedral charges on equivalent oxygens may be summed; this results in a list of the tetrahedral charges on the non-equivalent oxygens. This is one of the sections of the program where it was impossible to create versatility. For each different feldspar structure this list has to be changed to suit that particular structure.

7. The aluminum content of each tetrahedral site is printed out.
8. The total number of Al-atoms in the ideal structure is listed.
9. The tetrahedral charges on all the non-equivalent oxygen atoms are listed.

(c) SUBROUTINE ALKI

The sequence of calculations performed by subroutine ALKI are expressed in point form:

1. The calcium-oxygen distances are read, and a control card is also read which enables the subroutine to determine the starting coordinations of the alkali or alkali earth atoms.
2. The coordination of the large cations is determined by comparing the list of data against the control card. Those cation-oxygen distances, less than those given on the control card, may be taken as being in coordination.
3. The 'weighting factor' is calculated from the sum of the inverse squares of large cation-oxygen distances, as determined in step 2.
4. The positive charge on the cation is distributed proportionally according to the inverse squares of the cation-oxygen distances for each one of the oxygens in the coordination scheme.

5. The positive charges on the equivalent oxygens are summed and the resulting list of large cation contributions to the non-equivalent oxygens is added to the list of the tetrahedral charge contributions to the same non-equivalent oxygen atoms. The result of this operation is a complete amount of positive charge contributed by all the cations in the structure.

6. The following information is printed out:

The radius of the sphere encompassing the oxygen atoms which are in coordination with the large cations.

The coordination numbers of the large cations.

The total positive charge contributions to the non-equivalent oxygens.

(d) SUBROUTINE ALKI2

This subroutine is a continuation of Subroutine ALKI. The steps followed in the manipulation of the data are as follows:

1. A list of the non-equivalent oxygens associated with each of the non-equivalent tetrahedra is given. It should be noted that this list represents a part of the program which has to be changed to suit different types of feldspar structures. This list sums the total positive charge contributed to each one of the tetrahedra.
2. The difference of the total charge on the tetrahedra from the ideal value of 8.000 e.s.u., is calculated. These

differences are then totalled and this number is taken to represent the electrostatic charge unbalance of the structure, measured in e.s.u.

3. The following information is printed out:

A list giving the total charge contributed to the non-equivalent tetrahedra.

The amount of electrostatic charge unbalance in the structure for the particular set of variables used.

The amount of positive charge unbalance and the amount of negative charge unbalance.

The amount of charge unbalance in the structure is used throughout the program as the deciding factor in the calculations with particular reference to the assumed values of ideal Si-O, ideal Al-O, and the coordination of oxygen atoms about the alkali or alkali earth atoms. Various adjustments are made to these values and if these give a smaller charge unbalance value, then similar changes are again made to the variables mentioned above.

(e) SUBROUTINE COORD

This subroutine was written to handle changes in the coordination numbers of the alkali or alkali earth atoms in the structures. It is so arranged that a certain number of the nearest neighboring oxygens may be taken into consideration during the first series of iterations when the ideal Si-O and Al-O distances are being adjusted. After the best ideal values of these two distances have been obtained, this subroutine comes into play to adjust the coordination values of the alkali or alkali earth atoms, keeping the best ideal Si-O and Al-O values constant. The various steps in the manipulation are as follows:

1. The coordination of the first of the alkali or alkali earth atoms (if there are two or more of these non-equivalent atoms in the structure) is increased. In other words, the next nearest oxygen is allowed to take part in the charge distribution calculation. The charge unbalance is calculated in the next iteration which proceeds through the whole program.
2. If the charge unbalance is less than that of the previous iteration, then provision is made for that oxygen to be considered as being coordinated with the alkali or alkali earth atom in question. The next nearest oxygen of the succeeding cation will then be brought into coordination for the succeeding iteration and the program moves again through the next iteration.
3. If, in this case, the amount of charge unbalance is greater than that obtained on the previous iteration, then this subroutine will reject that oxygen as being structurally coordinated with the alkali or alkali earth atom and it will print out this information, indicating the distance of the oxygen from the cation and also the number of the oxygen which may be related to the sequential numbering system used in the treatment of the data.
4. This procedure is followed with respect to each one of the alkali or alkali earth atoms in turn until all those

oxygen atoms within a radius of 6.500 Å of the cation have been considered. Thus the coordination of each non-equivalent alkali earth atom is increased in turn and decisions made as to whether the particular oxygen atom in question should be accepted into coordination or rejected.

In order to facilitate the sequential storage of the data, the interatomic distances were stored on the basis of the Megaw Notation (1956) for the feldspars.

APPENDIX I

B. PROGRAM DOCUMENTATION

APPENDIX I

B. PROGRAM DOCUMENTATION

(a) PROGRAM DEFINITIONS

Title: ELECTROSTATIC CHARGE BALANCE CALCULATIONS FOR
FELDSPAR STRUCTURES

Author: R. I. GAIT, University of Manitoba (1967)

Language: FORTRAN IV

Operation: IBM SYSTEM/360 DOS

Capacity: Maximum storage space reserved to handle the
anorthite structure. Up to 300 iterations
may be processed.

Core: COMMON 20,600 bytes
MAIN 7,128 bytes
TETRA 1,320 bytes
ALKI 1,756 bytes
ALKI2 1,628 bytes
COORD 16,196 bytes
Total Core 48,628 bytes

Time: For 221 iterations including compiling time:
21 minutes 31 seconds.

Output: All printout.

The complete program is listed on the following pages.

(b) PROGRAM PRINTOUT

The complete program may be found on the following nine pages.

```
C ELECTROSTATIC CHARGE BALANCE CALCULATIONS
C FOR FELDSPAR STRUCTURES
C APRIL, 1967
C
C MAIN PROGRAM
C
C ODIMENSION A(16,5),W(16,5),OC(32),SIO(300),ALO(300),D(128,4),
C 1DX(300,4),C(128),SUMX(4),DV(300),SUMOC(128),DVD(300),
C 2SUMCO(300,4),T(16),SUMC(128),SUMO(128),ZM(300),N(300,4)
C
C COMMON K,A,W,OC,SIO,ALO,D,DX,C,SUMX,DV,SUMOC,DVD,SUMCO,T,SUMC,
C 1SUMO,ZM,IOX,ICAT,ITET,IEQX,CHCAT,KMAX,IPUN,JOK,JOKE,MULT,IT,ISI,
C 2IAL
C
C 2 FORMAT(5F5.3)
319 FORMAT(5I2,F2.1)
C 4 FORMAT(2F5.3)
C
C READ (1,319)IOX,ICAT,ITET,IEQX,MULT,CHCAT
C READ (1,4)S1,S2
C IEQX=IEQX*2
C MULT=MULT*2
C KMAX=0
C WRITE (3,109)
C IT=2
C JOK=1
C JOKE=1
C DVD(1)=0.000
C K=1
C SIO(K)=S1
C ALO(K)=S2
C K=0
C READ (1,2)((A(I,J),J=1,5),I=1,ITET)
C 1 K=K+1
C IF(K-299)401,400,401
400 KMAX=K-1
C GO TO 153
401 IF(IT-4)314,54,314
314 CALL TETRA
C GO TO 300
54 ZM(K)=ZM(K-1)
C SIO(K)=SIO(K-1)
C ALO(K)=ALO(K-1)
300 CALL ALKI
C CALL ALKI2
C IF(IT-4)11,331,11
11 GO TO 1
331 CALL COORD
C IF(KMAX-K)603,153,603
603 GO TO 1
153 WRITE (3,154)KMAX
C WRITE (3,41)
C WRITE (3,40)
C WRITE (3,42)((D(I,J),J=1,ICAT),I=1,IEQX)
C WRITE (2,45)((D(I,J),J=1,ICAT),I=1,IEQX)
162 CONTINUE
C DO 164 K=1,KMAX
C DO 164 J=1,ICAT
C N(K,J)=SUMCO(K,J)
164 CONTINUE
```

```
M=1
L=30
443 WRITE (3,50)
    WRITE (3,53)
    DO 52 K=M,KMAX
    IF(K-L)55,444,55
444 L=L+30
    M=L-30
    GO TO 443
55 WRITE (3,51)K,SIO(K),ALO(K),ZM(K),DV(K),DVD(K),N(K,1),N(K,2),N(K,
1),N(K,4)
52 CONTINUE
    WRITE (3,165)K

C
40 FORMAT(1H ,10X,5HCA1-O,10X,5HCA2-O,10X,5HCA3-O,10X,5HCA4-O)
41 FORMAT(1H1,10X,32HLIST OF CALCIUM OXYGEN DISTANCES)
42 FORMAT(1H ,4(10X,F6.3))
45 FORMAT(4F10.3)
50 FORMAT(1H1,10X,86H ITERATION      SIO      ALO      TOTAL AL      CHAR
1E      CHARGE      COORDINATION NOS. OF )
51 FORMAT(1H ,10X,I7,4F10.3,F12.3,5X,4I5)
53 FORMAT(1H ,10X,86H  NUMBER      VALUE      VALUE      CONTENT      UNBALA
ICE DIFFERENCE      CA1 CA2 CA3 CA4 )
109 FORMAT(1H ,10X,21HFELDSPAR CALCULATIONS,15X,8HR.I.GAIT)
154 FORMAT(1H ,10X,20HMAXIMUM VALUE OF K =,I3)
165 FORMAT(1H ,10X,37HMINIMUM CHARGE UNBALANCE ON ITERATION,I4)

C
60 CALL EXIT
    END
```

SUBROUTINE TETRA

C

ODIMENSION A(16,5),W(16,5),OC(32),SIO(300),ALO(300),D(128,4),
1DX(300,4),C(128),SUMX(4),DV(300),SUMOC(128),DVD(300),
2SUMCO(300,4),T(16),SUMC(128),SUMO(128),ZM(300)

C

COMMON K,A,W,OC,SIO,ALO,D,DX,C,SUMX,DV,SUMOC,DVD,SUMCO,T,SUMC,
1SUMO,ZM,IOX,ICAT,ITET,IEQX,CHCAT,KMAX,IPUN,JOK,JOKE,MULT,IT,ISI,
2IAL

C

ZM(K)=0.
DO 3 I=1,ITET
Z=(A(I,1)-SIO(K))/(ALO(K)-SIO(K))
ZM(K)=ZM(K)+Z
16 IF(I-1)17,15,17
15 WRITE (3,6)K,SIO(K),ALO(K)
17 WRITE (3,7)I,Z
98 CONTINUE
Y=4.-Z
X=(1./(A(I,2)*A(I,2)))+(1./(A(I,3)*A(I,3)))
1+(1./(A(I,4)*A(I,4)))+(1./(A(I,5)*A(I,5)))
DO 3 J=2,5
W(I,J)=Y/(A(I,J)*A(I,J)*X)
3 CONTINUE

C

C

WRITE (3,199)ZM(K)
THE FOLLOWING CARDS MUST BE CHANGED FOR DIFFERENT FELDSPARS
ANORTHITE NON-EQUIVALENT OXYGENS RECEIVING TETRAHEDRAL CHARGE

OC(1)=W(1,2)+W(11,2)
OC(2)=W(3,2)+W(9,2)
OC(3)=W(2,2)+W(12,2)
OC(4)=W(4,2)+W(10,2)
OC(5)=W(7,2)+W(13,2)
OC(6)=W(5,2)+W(15,2)
OC(7)=W(8,2)+W(14,2)
OC(8)=W(6,2)+W(16,2)
OC(9)=W(1,3)+W(13,3)
OC(10)=W(5,3)+W(9,3)
OC(11)=W(2,3)+W(14,3)
OC(12)=W(6,3)+W(10,3)
OC(13)=W(7,3)+W(11,3)
OC(14)=W(3,3)+W(15,3)
OC(15)=W(8,3)+W(12,3)
OC(16)=W(4,3)+W(16,3)
OC(17)=W(1,4)+W(16,4)
OC(18)=W(8,4)+W(9,4)
OC(19)=W(2,4)+W(15,4)
OC(20)=W(7,4)+W(10,4)
OC(21)=W(6,4)+W(11,4)
OC(22)=W(3,4)+W(14,4)
OC(23)=W(5,4)+W(12,4)
OC(24)=W(4,4)+W(13,4)
OC(25)=W(1,5)+W(15,5)
OC(26)=W(7,5)+W(9,5)
OC(27)=W(2,5)+W(16,5)
OC(28)=W(8,5)+W(10,5)
OC(29)=W(5,5)+W(11,5)
OC(30)=W(3,5)+W(13,5)
OC(31)=W(6,5)+W(12,5)
OC(32)=W(4,5)+W(14,5)

13 WRITE (3,5)(I,OC(I),I=1,IOX)

C

```
5 FORMAT(1H ,10X,20HTET CHARGE ON OXY  O,I2,F9.3)
6 FORMAT(1H1,10X,14HSIO,  ALO,  K=,I4,2F7.3)
7 FORMAT(1H ,10X,14HAL  CONTENT  T,I2,F9.3)
199 FORMAT(1H ,10X,30HTOTAL ALUMINUM IN STRUCTURE  ,F9.3)
```

C

```
102 RETURN
    END
```

SUBROUTINE ALKI

```
C
ODIMENSION A(16,5),W(16,5),OC(32),SIO(300),ALO(300),D(128,4),
1DX(300,4),C(128),SUMX(4),DV(300),SUMOC(128),DVD(300),
C
2SUMCO(300,4),T(16),SUMC(128),SUMO(128),ZM(300)
COMMON K,A,W,OC,SIO,ALO,D,DX,C,SUMX,DV,SUMOC,DVD,SUMCO,T,SUMC,
1SUMO,ZM,IOX,ICAT,ITET,IEQX,CHCAT,KMAX,IPUN,JOK,JOKE,MULT,IT,ISI,
2IAL
C
32 FORMAT(4F5.3)
33 FORMAT(4F10.3)
IF(K-1)196,197,196
197 READ (1,32)(DX(1,J),J=1,ICAT)
READ (1,33)((D(I,J),J=1,ICAT),I=1,IEQX)
196 DO 433 I=1,IEQX
SUMOC(I)=0.
SUMC(I)=0.
SUMO(I)=0.
433 CONTINUE
DO 445 J=1,ICAT
SUMX(J)=0.
SUMCO(K,J)=0.
445 CONTINUE
WRITE (3,10)K
DO 203 J=1,ICAT
71 WRITE (3,75)J,DX(K,J)
DO 202 I=1,IEQX
IF(DX(K,J)-D(I,J))38,39,39
39 SUMCO(K,J)=SUMCO(K,J)+1.
SUMX(J)=SUMX(J)+(1./(D(I,J)*D(I,J)))
38 C(I)=0.
202 CONTINUE
77 WRITE (3,79)J,SUMCO(K,J)
40 DO 203 I=1,IEQX
IF(DX(K,J)-D(I,J))204,205,205
204 SUMC(I)=SUMC(I)+0.
GO TO 203
205 SUMC(I)=(CHCAT/(D(I,J)*D(I,J)*SUMX(J)))+SUMC(I)
203 CONTINUE
DO 207 I=1,IOX
IPN=I*MULT
N=MULT-1
DO 5 J=1,N
L=IPN-J
SUMOC(I)=SUMC(L)+SUMOC(I)
5 CONTINUE
SUMOC(I)=SUMOC(I)+SUMC(IPN)+OC(I)
207 CONTINUE
WRITE (3,22)
81 WRITE (3,84)(I,SUMOC(I),I=1,IOX)
41 CONTINUE
C
10 FORMAT(1H1,16HITERATION NUMBER,I4)
75 FORMAT(1H ,10X,15HLIMIT FOR CAT-O,I2,F7.3)
79 FORMAT(1H ,10X,13HCO-ORD OF CAT,I1,F7.0)
22 FORMAT(1H1)
84 FORMAT(1H ,10X,22HTOTAL CHARGE ON OXY O,I2,F7.3)
RETURN
END
```

SUBROUTINE ALKI2

ODIMENSION A(16,5),W(16,5),OC(32),SIO(300),ALO(300),D(128,4),
1DX(300,4),C(128),SUMX(4),DV(300),SUMOC(128),DVD(300),
2SUMCO(300,4),T(16),SUMC(128),SUMO(128),ZM(300)

COMMON K,A,W,OC,SIO,ALO,D,DX,C,SUMX,DV,SUMOC,DVD,SUMCO,T,SUMC,
1SUMO,ZM,IOX,ICAT,ITET,IEQX,CHCAT,KMAX,IPUN,JOK,JOKE,MULT,IT,ISI,
2IAL

THE FOLLOWING CARDS MUST BE CHANGED FOR DIFFERENT FELDSPARS
ANORTHITE TOTAL CHARGE ON 16 NON-EQUIVALENT TETRAHEDRA

T(1)=SUMOC(1)+SUMOC(9)+SUMOC(17)+SUMOC(25)
T(2)=SUMOC(3)+SUMOC(11)+SUMOC(19)+SUMOC(27)
T(3)=SUMOC(2)+SUMOC(14)+SUMOC(22)+SUMOC(30)
T(4)=SUMOC(4)+SUMOC(16)+SUMOC(24)+SUMOC(32)
T(5)=SUMOC(6)+SUMOC(10)+SUMOC(23)+SUMOC(29)
T(6)=SUMOC(8)+SUMOC(12)+SUMOC(21)+SUMOC(31)
T(7)=SUMOC(5)+SUMOC(13)+SUMOC(20)+SUMOC(26)
T(8)=SUMOC(7)+SUMOC(15)+SUMOC(18)+SUMOC(28)
T(9)=SUMOC(2)+SUMOC(10)+SUMOC(18)+SUMOC(26)
T(10)=SUMOC(4)+SUMOC(12)+SUMOC(20)+SUMOC(28)
T(11)=SUMOC(1)+SUMOC(13)+SUMOC(21)+SUMOC(29)
T(12)=SUMOC(3)+SUMOC(15)+SUMOC(23)+SUMOC(31)
T(13)=SUMOC(5)+SUMOC(9)+SUMOC(24)+SUMOC(30)
T(14)=SUMOC(7)+SUMOC(11)+SUMOC(22)+SUMOC(32)
T(15)=SUMOC(6)+SUMOC(14)+SUMOC(19)+SUMOC(25)
T(16)=SUMOC(8)+SUMOC(16)+SUMOC(17)+SUMOC(27)

87 WRITE (3,89)(I,T(I),I=1,ITET)
198 CONTINUE
SX=0.0
SY=0.0
DO 50 I=1,ITET
IF(8.-T(I))45,46,46
46 X=8.-T(I)
SX=SX+X
GO TO 50
45 Y=T(I)-8.
SY=SY+Y
50 CONTINUE
DV(K)=SX+SY
GO TO 15
IF(K-1)3,4,3
4 SIO(K+1)=SIO(K)-0.001
11 ALO(K+1)=ALO(K)
GO TO 113
3 DVD(K)=DV(K-1)-DV(K)
IF(IT-4)16,15,16
16 IF(ISI-4)7,8,7
8 IF(IAL-4)14,15,14
7 IF(DVD(K))5,4,4
5 SIO(K+1)=SIO(K-1)
ISI=4
GO TO 11
14 IF(DVD(K))9,10,10
10 ALO(K+1)=ALO(K)+0.001
12 SIO(K+1)=SIO(K)
GO TO 113
9 ALO(K+1)=ALO(K-1)

```
IAL=4
GO TO 12
15 IT=4
   SIO(K+1)=SIO(K)
   ALO(K+1)=ALO(K)
113 DO 115 J=1,ICAT
   DX(K+1,J)=DX(K,J)
115 CONTINUE
   WRITE (3,117)SY
   WRITE (3,118)SX
   WRITE (3,116)K,DV(K)
C
89 FORMAT(1H ,10X,30HTOTAL CHARGE ON TETRAHEDRON T,I2,F9.3)
116 FORMAT(1H ,10X,20HSUM OF DEVIATION K =,I4,F7.3)
117 FORMAT(1H ,10X,18HPOSITIVE UNBALANCE,F7.3)
118 FORMAT(1H ,10X,18HNEGATIVE UNBALANCE,F7.3)
C
RETURN
END
```

SUBROUTINE COORD

C

ODIMENSION A(16,5),W(16,5),OC(32),SIO(300),ALO(300),D(128,4),
1DX(300,4),C(128),SUMX(4),DV(300),SUMOC(128),DVD(300),
2SUMCO(300,4),T(16),SUMC(128),SUMO(128),ZM(300),
3CO(4),COD(4),CX(300,4),DMAX(300,4),CAMCO(300,4)

C

COMMON K,A,W,OC,SIO,ALO,D,DX,C,SUMX,DV,SUMOC,DVD,SUMCO,T,SUMC,
1SUMO,ZM,IOX,ICAT,ITET,IEQX,CHCAT,KMAX,IPUN,JOK,JOKE,MULT,IT,ISI,
2IAL

C

IF(JOKE-2)30,31,30
30 READ (1,27)(DMAX(1,J),J=1,ICAT)
IALK=0
IAKE=ICAT+1
31 DO 26 JIK=1,ICAT
CX(K,JIK)=DX(K,JIK)
26 CAMCO(K,JIK)=SUMCO(K,JIK)
JOKE=2
JIL=0
DO 33 JAC=1,ICAT
IF(CX(K,JAC)-DMAX(1,JAC))33,34,34
34 JIL = JIL+1
33 CONTINUE
IF(JIL-ICAT)37,36,37
36 KMAX = K
GO TO 12
42 IF(JOK-IAKE)43,44,43
43 IF(JOK-IALK)48,6,48
48 IF(CX(K,JOK)-DMAX(1,JOK))46,47,47
47 IF(JOK-ICAT)7,49,7
49 IALK=ICAT
46 CX(K,JOK)=CX(K,JOK)+0.001
COD(JOK)=0.
CAMCO(K,JOK)=CAMCO(K,JOK)+1.
DO 3 I=1,IEQX
IF(CX(K,JOK)-D(I,JOK))3,4,4
4 COD(JOK)=COD(JOK)+1.
3 CONTINUE
IF(CAMCO(K,JOK)-COD(JOK))5,6,5
5 CAMCO(K,JOK)=CAMCO(K,JOK)-1.
GO TO 43
6 JOK = JOK+1
GO TO 12
37 DO 21 L=1,IEQX
M=K-L
IF(DVD(M))21,23,23
23 DVD(K)=DV(M)-DV(K)
GO TO 25
21 CONTINUE
25 IF(DVD(K))24,42,42
24 JOK=JOK-1
DO 7 I=1,IEQX
IF(CX(K,JOK)-D(I,JOK))7,8,8
8 IF(DX(K-1,JOK)-D(I,JOK))9,7,7
9 WRITE (3,10)JOK,I,D(I,JOK)
D(I,JOK)=7.000
7 CONTINUE
JOK=JOK+1
IF(JOK-IAKE)45,44,45

```
44 JOK=1
45 GO TO 43
12 DO 14 I=1,JOK
   DX(K+1,I)=CX(K,I)
14 CONTINUE
   SIO(K+1)=SIO(K)
   ALO(K+1)=ALO(K)
```

```
C 10 FORMAT(1H ,16X,2HCA,I2,2H-O,I3,1H=,F5.3,12H      REJECTED)
C 27 FORMAT(4F5.3)
```

```
RETURN
END
```

APPENDIX I

(c) LIST OF VARIABLE NAMES

The COMMON Dimensioned Variables

- A(16,5) The tetrahedral-oxygen distances. The five values on each card are as follows: the first is the average size of the tetrahedron, the remaining four are the T-O distances in Angstrom units.
- ALO(200) The values of the ideal Al-O distances used in each successive iteration.
- C(64) A 'dummy' storage.
- D(64,4) The alkali or alkali earth to oxygen distances in Angstrom units. Provision is made for the handling of up to four non-equivalent large cations. (e.g., the four calcium atoms in the anorthite structure).
- DV(200) The total charge unbalance on each iteration.
- DVD(200) The difference between the charge unbalance on one iteration and the unbalance on the previous iteration.
- DX(200,4) The values which control the coordination numbers of the large cations, expressed as limiting alkali or alkali earth to oxygen distances.
- OC(32) The total tetrahedral charge on the non-equivalent oxygens.
- SIO(200) The values of the ideal Si-O distances used in each successive iteration.
- SUMC(64) The positive charge contribution of the alkali or alkali earth atoms to the coordinated oxygens.
- SUMCO(200,4) The coordination numbers of the alkali or alkali earth atoms.
- SUMO(64) Not used.
- SUMOC(64) The total positive charge contribution to the equivalent oxygens in the structure.
- SUMX(4) The 'weighting factor' for up to four alkali or alkali earth atoms and their oxygen environment.
- T(16) The total positive charge contributions to the non-equivalent tetrahedra.
- W(16,5) The storage spaces reserved for the tetrahedral positive charge contributions to the oxygen atoms.
- ZM(200) The space reserved for the total number of aluminum atoms in the ideal structure, as calculated on each iteration, and dependent upon the ideal Si-O and Al-O distances used.

The Remaining COMMON Variables

CHCAT	The charge on the alkali or alkali earth atoms.
IAL	A counter used to establish the attainment of the best ideal Al-O value.
ICAT	The number of non-equivalent alkali or alkali earth atoms.
IEQX	The number of equivalent oxygens in one unit cell of the structure.
IOX	The number of non-equivalent oxygens.
IPUN	Not used.
ISI	A counter used to establish the attainment of the best ideal Si-O value.
IT	A counter used to establish the attainment of both the best ideal Si-O and Al-O values.
ITET	The number of non-equivalent tetrahedra.
JOK	A counter used in the subroutine COORD.
JOKE	A counter used throughout the program.
KMAX	The maximum number of iterations calculated.
MULT	The multiplicity of the structure type.

Additional Variables Used in the MAIN Program

Dimensioned Variables

N(64,4)	A fixed point variable used to change the coordination numbers of the alkali or alkali earth atoms to integers from floating point numbers.
---------	---

Simple Variables

L and M	Simple counters.
---------	------------------

Additional Variables Used in Subroutine TETRA

X	The 'weighting factor' used in the tetrahedral calculation.
Y	The positive charge calculated for a tetrahedral site.
Z	The statistical aluminum content of a tetrahedron expressed as a fraction of 1.

Additional Variables Used in Subroutine ALKI

IPN, L and N Simple counters.

Additional Variables Used in Subroutine ALKI2

SX The amount of negative electrostatic charge unbalance.

SY The amount of positive electrostatic charge unbalance.

Additional Variables Used in Subroutine COORD

Dimensioned Variables

CAMCO(200,4) Directly equivalent to SUMCO(200,4).

CO(4) Not used.

COD(4) A simple counter.

CX(200) Directly equivalent to DX(200).

Simple Variables

I, J, L, M } Simple counters
IALK, IAKE }
JAC and JIL) or indicators.

APPENDIX I

(d) SIMPLIFIED FLOW CHARTS

The Flow Charts of the program are given in this section as follows:

Figure 1:

Simplified Flow Chart of the MAIN Program

Figure 2:

Simplified Flow Chart for Subroutine TETRA

Figure 3:

Simplified Flow Chart for Subroutine ALKI

Figure 4:

Simplified Flow Chart for Subroutine ALKI2

Figure 5:

Simplified Flow Chart for Subroutine COORD

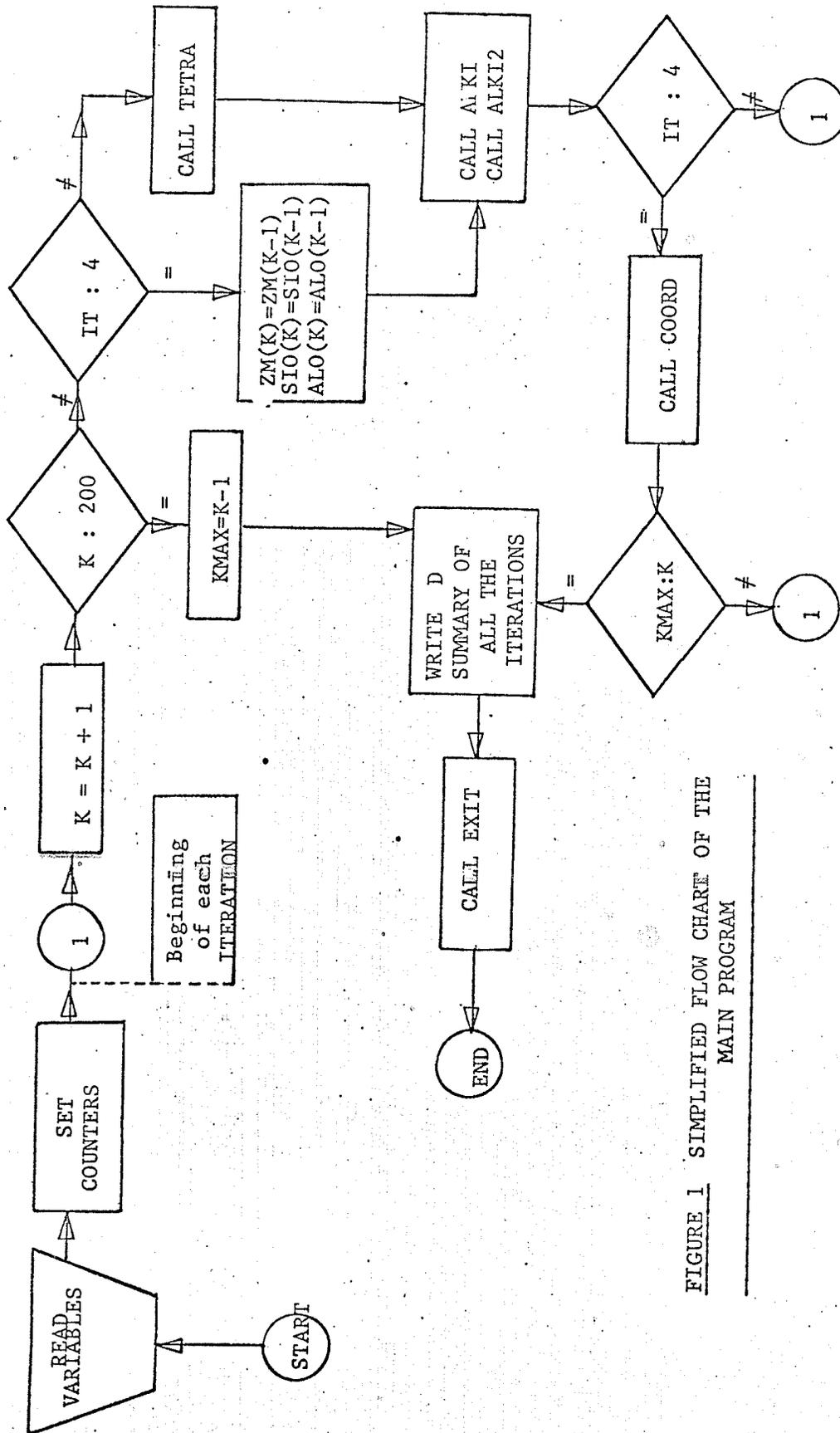


FIGURE 1 SIMPLIFIED FLOW CHART OF THE MAIN PROGRAM

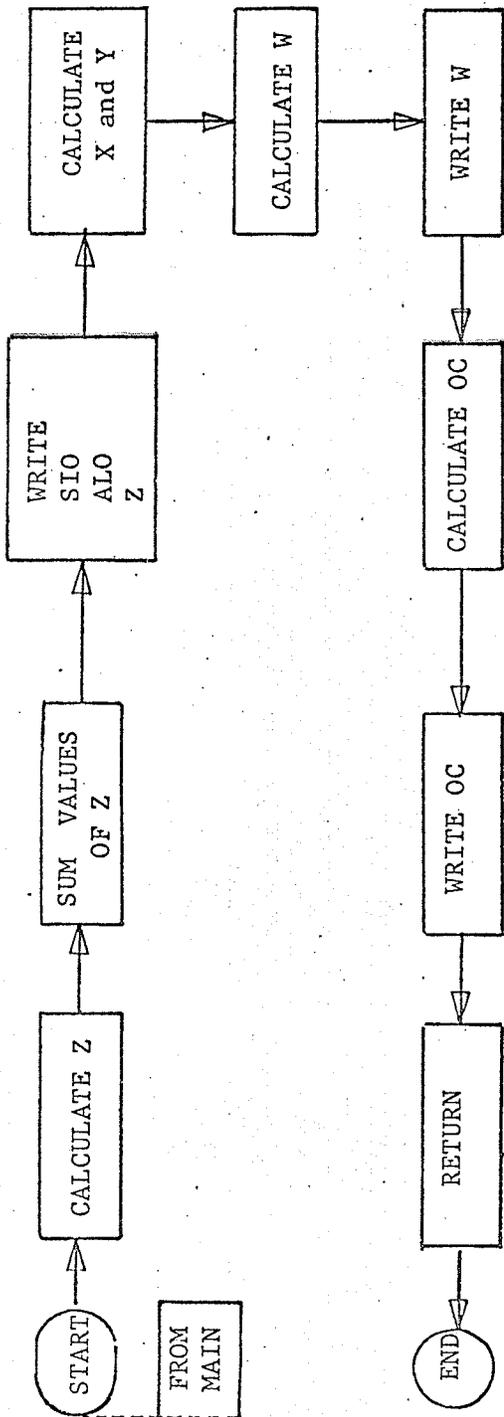


FIGURE 2 SIMPLIFIED FLOW CHART FOR SUBROUTINE TETRA

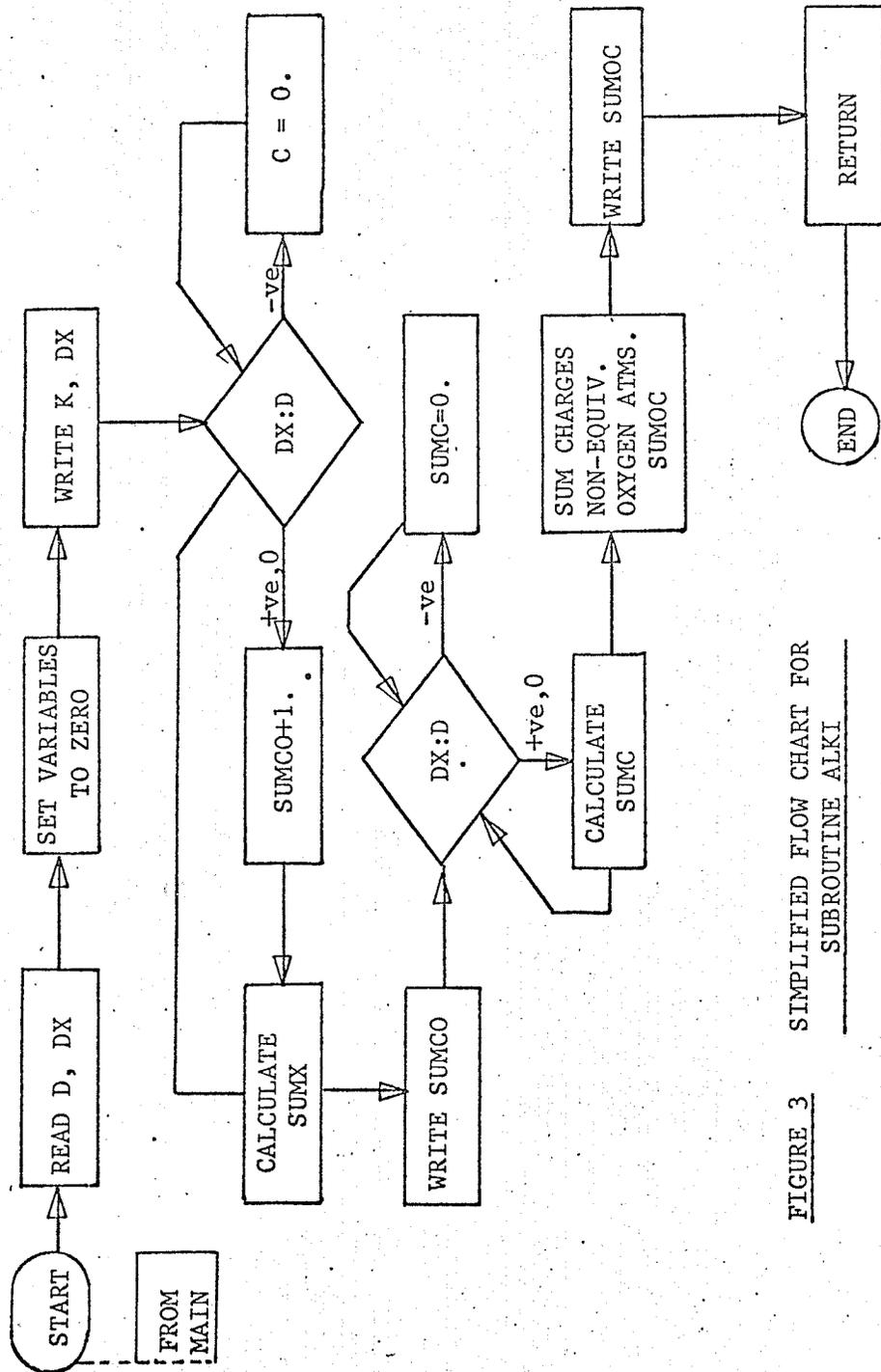


FIGURE 3 SIMPLIFIED FLOW CHART FOR SUBROUTINE ALKI

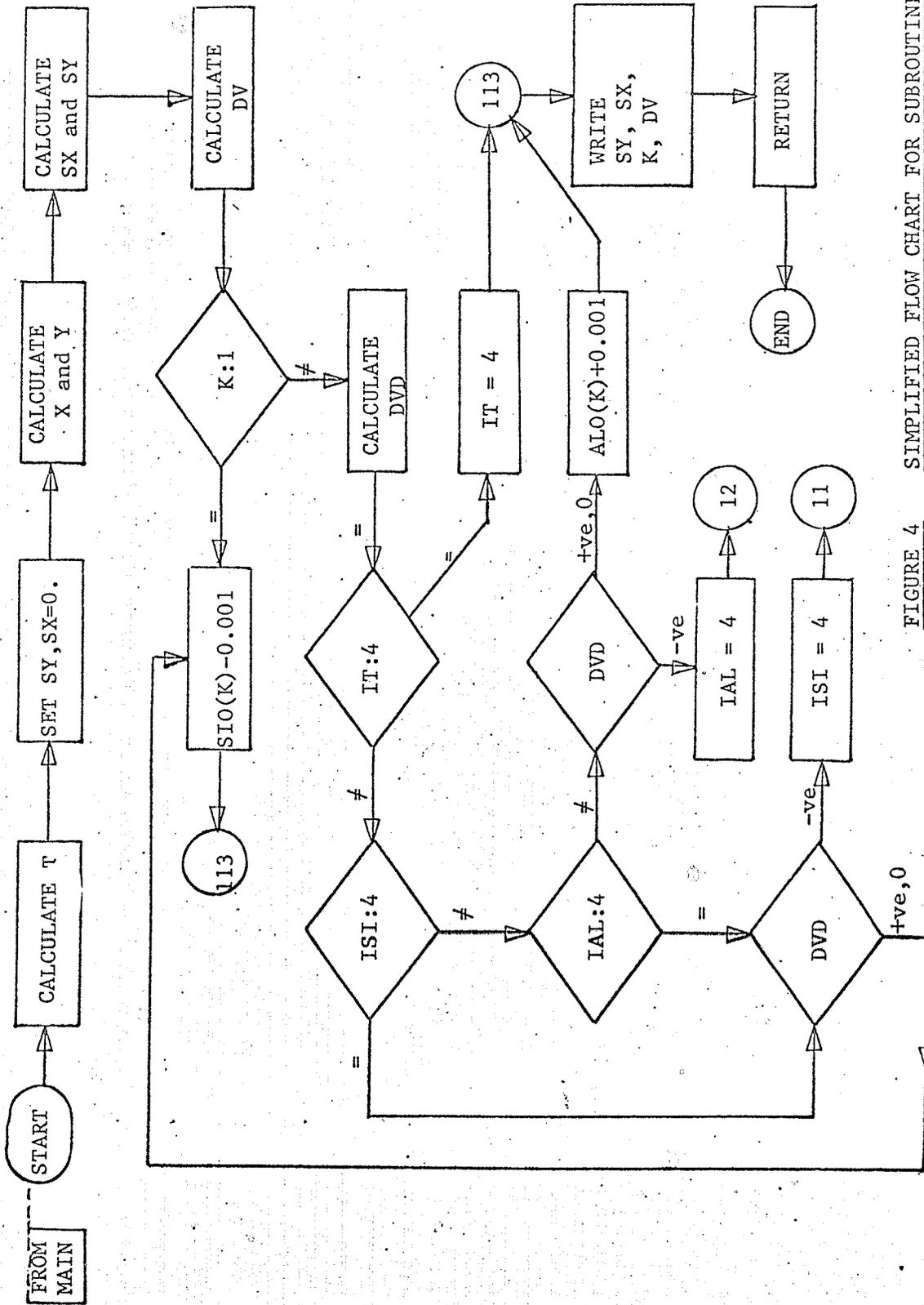


FIGURE 4 SIMPLIFIED FLOW CHART FOR SUBROUTINE ALK12

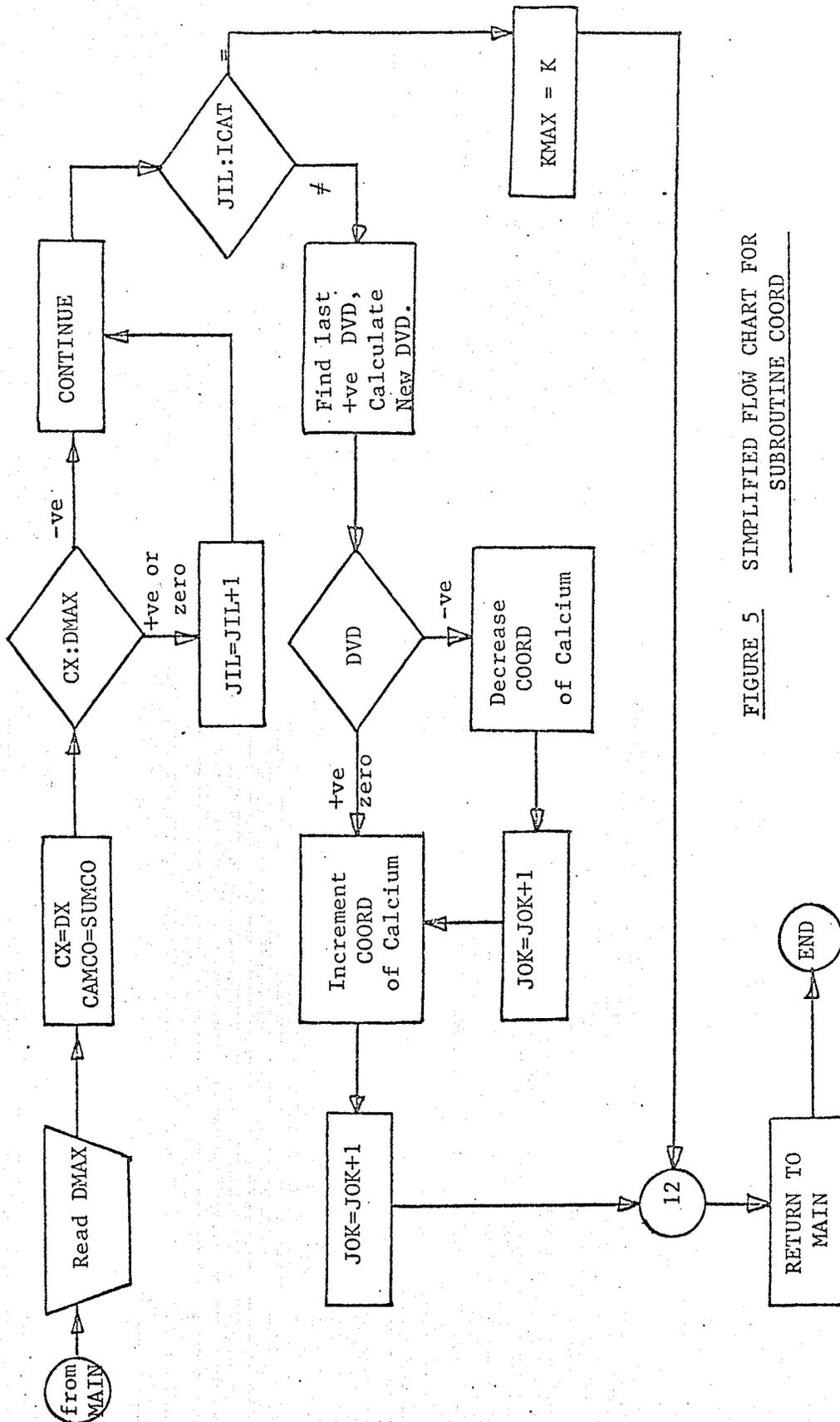


FIGURE 5 SIMPLIFIED FLOW CHART FOR SUBROUTINE COORD

APPENDIX I

(e) EXAMPLES OF THE PRIMARY DATA

The primary data is entered into the program in the following form:

(i) Si-O and Al-O Ideal Distances (2F5.3)

<u>Field #</u>	<u>1</u>	<u>2</u>
Cols. 1-10	X.XXX	X.XXX
Example	1.602	1.759

One card only.

(ii) The Tetrahedral Distances (5F5.3)

<u>Field #</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Cols. 1-25	X.XXX	X.XXX	X.XXX	X.XXX	X.XXX
Example	1.613	1.610	1.620	1.601	1.611

Field #1 is the average size of the tetrahedron.

Fields #2-5 are the distances from the centre of the tetrahedral site to the surrounding four oxygen atoms.

One card for each non-equivalent tetrahedron in the structure (Anorthite: 16 cards).

(iii) The Crystallographic Control Card (5I2.F2.1)

<u>Field #</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>					
Cols. 1-12	xxx	xxx	xxx	xxx	xxx	xxx					
Example	3	2	0	4	1	6	6	4	0	2	2

Field #1 The number of non-equivalent oxygen atoms.

Field #2 The number of non-equivalent alkali or alkali earth atoms.

Field #3 The number of non-equivalent tetrahedra.

Field #4 The number of equivalent oxygens.

Field #5 The multiplicity.

Field #6 The positive charge on the alkali or alkali earth atoms.

(The numerical examples given are for the anorthite structure).

One card only.

(iv) Control Card for the Determination of the Initial Coordination of the Alkali or Alkali Earth Atoms (4F5.3)

Field # 1 2 3 4

Cols. 1-20 X.XXX~~X~~.XXX~~X~~.XXX~~X~~.XXX

Example 4.1394.1494.0714.140

Field #1 The distance of the 12 closest oxygen to the alkali earth atom. The program will then use this number to determine that the alkali or alkali earth atom has 12-fold coordination.

Fields

#2,3,&4 Additional fields for another 3 non-equivalent alkali or alkali earth atoms.

(The numerical example is given for the anorthite structure with 4 non-equivalent calcium atoms).

One card only.

(v) List of Alkali or Alkali Earth to Oxygen Distances (4F5.3)

Field #1

Cols. 1-10 XXXXXX.XXX

Example 2.500

Field #2

Cols. 11-20 XXXXXX.XXX

Example 8.000

Field #3

Cols. 21-30 XXXXXX.XXX

Example 8.000

Field #4

Cols. 31-40 XXXXXX.XXX

Example 4.171

These four fields are placed on one card, and there will be one card for each of the equivalent oxygen atoms; in the anorthite structure there will be 64 cards.

These fields represent the list of alkali or alkali earth cation to oxygen distances punched in the appropriate space for a given oxygen. Some of these spaces will not be used as they represent some oxygen atoms which are too far from the large cation to be coordinated. In this case a dummy number (8.000) is used.

(vi) Limiting Control Card for Alkali or Alkali Earth to Oxygen Distances (4F5.3)

<u>Field #</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Cols. 1-20	X.XXX	X.XXX	X.XXX	X.XXX
Example	6.0006	.0006	.0006	.000
Fields #1,2,3,4	Similar to data card (iv) but the upper limit of the alkali or alkali earth to oxygen distances in Angstrom units. In the numerical example above, the program will end only after all the oxygen atoms in each non-equivalent alkali or alkali earth environment has been considered out to a distance of 6.000 Å.			

(The numerical example is given for the anorthite structure).

One card only.

APPENDIX I

(f) RESULTS OF A COMPLETE ITERATION

The following three pages give the computer listing for one complete iteration of the FORTRAN IV Program described in this Appendix.

SIO,	ALO,	K# 74	1.602	1.761
AL	CONTENT	T 1	0.069	
AL	CONTENT	T 2	0.088	
AL	CONTENT	T 3	0.038	
AL	CONTENT	T 4	0.151	
AL	CONTENT	T 5	0.069	
AL	CONTENT	T 6	0.050	
AL	CONTENT	T 7	0.0	
AL	CONTENT	T 8	0.164	
AL	CONTENT	T 9	0.981	
AL	CONTENT	T10	0.906	
AL	CONTENT	T11	0.943	
AL	CONTENT	T12	0.874	
AL	CONTENT	T13	0.906	
AL	CONTENT	T14	0.950	
AL	CONTENT	T15	0.893	
AL	CONTENT	T16	0.943	
TOTAL ALUMINUM IN STRUCTURE				8.025
TET	CHARGE	ON OXY	0 1	1.669
TET	CHARGE	ON OXY	0 2	1.681
TET	CHARGE	ON OXY	0 3	1.739
TET	CHARGE	ON OXY	0 4	1.714
TET	CHARGE	ON OXY	0 5	1.688
TET	CHARGE	ON OXY	0 6	1.737
TET	CHARGE	ON OXY	0 7	1.689
TET	CHARGE	ON OXY	0 8	1.767
TET	CHARGE	ON OXY	0 9	1.719
TET	CHARGE	ON OXY	010	1.768
TET	CHARGE	ON OXY	011	1.727
TET	CHARGE	ON OXY	012	1.722
TET	CHARGE	ON OXY	013	1.844
TET	CHARGE	ON OXY	014	1.742
TET	CHARGE	ON OXY	015	1.726
TET	CHARGE	ON OXY	016	1.807
TET	CHARGE	ON OXY	017	1.768
TET	CHARGE	ON OXY	018	1.771
TET	CHARGE	ON OXY	019	1.827
TET	CHARGE	ON OXY	020	1.808
TET	CHARGE	ON OXY	021	1.756
TET	CHARGE	ON OXY	022	1.747
TET	CHARGE	ON OXY	023	1.732
TET	CHARGE	ON OXY	024	1.760
TET	CHARGE	ON OXY	025	1.766
TET	CHARGE	ON OXY	026	1.754
TET	CHARGE	ON OXY	027	1.654
TET	CHARGE	ON OXY	028	1.689
TET	CHARGE	ON OXY	029	1.747
TET	CHARGE	ON OXY	030	1.825
TET	CHARGE	ON OXY	031	1.867
TET	CHARGE	ON OXY	032	1.766

ITERATION NUMBER 74

LIMIT FOR CAT-0 1 5.034

CO-ORD OF CAT1 16.

LIMIT FOR CAT-0 2 4.914

CO-ORD OF CAT2 18.

LIMIT FOR CAT-0 3 4.926

CO-ORD OF CAT3 14.

LIMIT FOR CAT-0 4 4.912

CO-ORD OF CAT4 15.

TOTAL CHARGE ON OXY	0 1	2.031
TOTAL CHARGE ON OXY	0 2	2.067
TOTAL CHARGE ON OXY	0 3	2.154
TOTAL CHARGE ON OXY	0 4	2.095
TOTAL CHARGE ON OXY	0 5	2.056
TOTAL CHARGE ON OXY	0 6	2.132
TOTAL CHARGE ON OXY	0 7	2.126
TOTAL CHARGE ON OXY	0 8	2.079
TOTAL CHARGE ON OXY	0 9	2.008
TOTAL CHARGE ON OXY	010	2.016
TOTAL CHARGE ON OXY	011	1.948
TOTAL CHARGE ON OXY	012	2.004
TOTAL CHARGE ON OXY	013	1.985
TOTAL CHARGE ON OXY	014	1.996
TOTAL CHARGE ON OXY	015	1.990
TOTAL CHARGE ON OXY	016	1.987
TOTAL CHARGE ON OXY	017	1.989
TOTAL CHARGE ON OXY	018	1.914
TOTAL CHARGE ON OXY	019	1.903
TOTAL CHARGE ON OXY	020	1.931
TOTAL CHARGE ON OXY	021	1.973
TOTAL CHARGE ON OXY	022	1.942
TOTAL CHARGE ON OXY	023	1.904
TOTAL CHARGE ON OXY	024	1.934
TOTAL CHARGE ON OXY	025	1.971
TOTAL CHARGE ON OXY	026	2.016
TOTAL CHARGE ON OXY	027	1.958
TOTAL CHARGE ON OXY	028	1.975
TOTAL CHARGE ON OXY	029	1.992
TOTAL CHARGE ON OXY	030	1.966
TOTAL CHARGE ON OXY	031	1.951
TOTAL CHARGE ON OXY	032	1.984
TOTAL CHARGE ON TETRAHEDRON	T 1	7.999
TOTAL CHARGE ON TETRAHEDRON	T 2	7.962
TOTAL CHARGE ON TETRAHEDRON	T 3	7.971
TOTAL CHARGE ON TETRAHEDRON	T 4	8.000
TOTAL CHARGE ON TETRAHEDRON	T 5	8.045
TOTAL CHARGE ON TETRAHEDRON	T 6	8.007
TOTAL CHARGE ON TETRAHEDRON	T 7	7.988
TOTAL CHARGE ON TETRAHEDRON	T 8	8.004
TOTAL CHARGE ON TETRAHEDRON	T 9	8.013
TOTAL CHARGE ON TETRAHEDRON	T10	8.005
TOTAL CHARGE ON TETRAHEDRON	T11	7.981
TOTAL CHARGE ON TETRAHEDRON	T12	7.999
TOTAL CHARGE ON TETRAHEDRON	T13	7.963
TOTAL CHARGE ON TETRAHEDRON	T14	8.000
TOTAL CHARGE ON TETRAHEDRON	T15	8.002
TOTAL CHARGE ON TETRAHEDRON	T16	8.013
POSITIVE UNBALANCE	0.088	
NEGATIVE UNBALANCE	0.138	
SUM OF DEVIATION K =	74	0.226

APPENDIX II

APPENDIX II

PROGRAM DOCUMENTATION OF A SERIES OF
IBM 1620 PROGRAMS TO CALCULATE ELECTROSTATIC
CHARGE DISTRIBUTION WITHIN THE LOW AND
HIGH ALBITE STRUCTURES

- A. FORTRAN II Program to Calculate Interatomic Distances
- B. FORTRAN II Program to Calculate Inter-Bond Angles and Solid Shielding Angles
- C. FORTRAN II Program to Calculate the Shielding Factors
- D. FORTRAN II Program to Calculate the Distribution of Electrostatic Charge Within the Structures

APPENDIX II

A. FORTRAN II PROGRAM TO CALCULATE INTERATOMIC DISTANCES

(i) A Description of Program #1

The FORTRAN II Program described here is entitled : SCAN OF INTERATOMIC DISTANCES, and was primarily written in order to calculate a complete list of sodium-oxygen and sodium-sodium bonds in a given environment of the original sodium atom. The environment of the sodium atom is defined as a sphere of certain radius within which a number of oxygen atoms and other sodium atoms are located.

The program involves the standard form of the interatomic distance calculation, but scans the complete environment of the original sodium atom, after the given atoms have been moved into the asymmetric part of the unit cell. The complete scan of bonds is obtained by translation of the atoms, along the axes x, y and z, by all combinations of +1 and -1, for each of the equivalent positions defined for a particular structure.

Provision is made for only those bonds within a given upper limit to be recorded on punched cards.

(ii) The Program Printout

The complete printout of the program is given on the following pages, and the description of the input data is given in Section (iii).

```
C SCAN OF INTERATOMIC DISTANCES
C
C PROGRAM 1 - DATA ARE THE ORIGINAL STRUCTURAL PARAMETERS
C
C DIMENSION X(40),Y(40),Z(40),S(40),NAT(40),PN(4),NN(4),S1(40)
C DIMENSION TX(40),TY(40),TZ(40)
C
1 FORMAT(I2,8X,3F6.3,3F8.5,F4.2,2I2,F4.2)
3 FORMAT(A3,A2,I3,3(F6.4))
4 FORMAT(36HCALCULATION OF INTERATOMIC DISTANCES)
7 FORMAT(I2,3F3.1,3F8.4)
11 FORMAT(I2,2(2X,A3,A2),2X,I2,2X,3I2,3F9.4,F10.3,I15)
LL=0
READ 1,N,A,B,C,COSA,COSB,COSC,DMAX,NEQ,ICAT
DO 2 I=1,N
READ 3, S(I),S1(I),NAT(I),X(I),Y(I),Z(I)
2 CONTINUE
TYPE 4
C1=A*A
C2=B*B
C3=C*C
C4=A*B*COSC
C5=C*A*COSB
C6=B*C*COSA
NM=N-1
NJ=ICAT+1
DO 6 IJ=1,NEQ
14 READ 7,KEQ,EQX,EQY,EQZ,PX,PY,PZ
PN(1)=+0.
PN(2)=+1.
PN(3)=0.-1.
DO 6 K=1,3
DO 6 L=1,3
DO 6 M=1,3
DO 10 I=NJ,N
TX(I)=(X(I)*EQX)+PX+PN(K)
TY(I)=(Y(I)*EQY)+PY+PN(L)
TZ(I)=(Z(I)*EQZ)+PZ+PN(M)
10 CONTINUE
IEQX=EQX
IEQY=EQY
IEQZ=EQZ
NN(K)=PN(K)
NN(L)=PN(L)
NN(M)=PN(M)
J=0
IPUN=0
DO 6 J=1,ICAT
DO 6 II=ICAT,NM
XA=(TX(II+1)- X(J))
YB=(TY(II+1)- Y(J))
ZC=(TZ(II+1)- Z(J))
XAB=2.*XA*YB*C4
XAC=2.*ZC*XA*C5
XBC=2.*YB*ZC*C6
DIST=SQRT(((XA*XA)*C1)+((YB*YB)*C2)+((ZC*ZC)*C3)+XAB+XAC+XBC)
IF(DIST-DMAX)8,8,6
8 BOND=DIST
LL=LL+1
PUNCH 11,NAT(II+1),S(J),S1(J),S(II+1),S1(II+1),KEQ,NN(K),NN(L),
```

```
1NN(M),TX(II+1),TY(II+1),TZ(II+1),BOND,LL  
6 CONTINUE  
  IF(NEQ-KEQ)9,5,9  
9 GO TO 14  
5 CALL EXIT  
  END
```

(iii) Examples of the Data

The primary data are entered into the program in the following form:

(a) The Main Control Card for the Program

Cols. 1 and 2 XX
 Example 13
 Name N
 Description: N is the number of non-equivalent atoms involved in the calculation.

Cols. 3 to 10 blank
 1 2 3
 Cols. 11 to 28 XX.XXX|XX.XXX|XX.XXX
 Example 08.149|12.880|07.106
 Names A B C
 Description: A, B and C are the cell dimensions (Å) of the structure.

 1 2 3
 Cols. 29 to 52 +X.XXXXX+X.XXXXX+X.XXXXX
 Example -0.05873|-0.44307|-0.00495
 Names COSA COSB COSC
 Description: The cosines of the angles, alpha, beta and gamma for the structure.

 1 2 3
 Cols. 53 to 60 X.XXXXX
 Names DMAX,NEQ,ICAT
 Description: DMAX is the upper limit for the bonds calculation.
 NEQ is the number of equivalent positions for the structure.
 ICAT is the number of non-equivalent atoms whose inter-bond distances are required.

(b) The Atomic Parameters of the Structure (transferred to the Asymmetric Part of the Unit Cell)

One card must be given for each non-equivalent atom. On each card the following information must be given:

 1 2 3 4 5
 Cols. 1 to 26 XXXXXXXX|XXXXX|XXXXX|XXXX
 Example NA 01 2743 0076 1320
 Names S1,S2,NAT, X, Y, Z.
 Description: S1,S2 is an alphabetic field for the Megaw name of the atom.
 NAT is a sequential number given to that atom.
 X,Y and Z are the atomic parameters of the atoms expressed as fractions of the cell dimensions.

(c) The Definition of the Equivalent Positions

The number of cards must equal the number of equivalent positions (NEQ). On each card the following information must be given:

	1	2	3	4	5	6	7		
Cols. 1 to 35	XX	-X	-X	-X	XXX	XXX	XXX	XXX	XXX
Example	01	+1	+1	+1	0.0000	0.0000	0.0000	0.0000	
Names	KEQ, EQX, EQY, EQZ, PX, PY, PZ								
Description	KEQ is the equivalent position number. EQX, EQY and EQZ are factors which will change x, y and z parameters into \bar{x} , \bar{y} , and \bar{z} if necessary. PX, PY and PZ are the necessary fractions of the cell dimensions which must be added to the x/a, y/b and z/c fractions in order to complete the requirements of the equivalent position.								

APPENDIX II

B. FORTRAN II PROGRAM TO CALCULATE INTER-BOND ANGLES
AND SOLID SHIELDING ANGLES

(i) A Description of Program #2

The FORTRAN II Program described here is entitled: SCAN OF INTERBOND ANGLES AND SOLID SHIELDING ANGLES, and was written in order to prepare data for the third program of this series (Appendix IIC). The angles calculated here are a necessary step before the calculation of the shielded fractions of the oxygen atoms in the environment of a given sodium atom. Considerable assistance was given to the author by Dr. H. R. Coish of the Physics Department at the University of Manitoba.

The principal steps in the calculation are given below in point form:

- (1) The inter-bond angles are calculated using the standard method. For the purposes of these calculations, the inter-bond angle is designated as gamma (γ).

See Figure 1 in Appendix IIC.

- (2) Two solid angles are calculated in addition to the inter-bond angle. These are designated as alpha (α) and beta (β).

See Figure 1 in Appendix IIC for the definitions of these solid angles.

- (3) The angles, alpha (α) and beta (β), taken in relation to the angle gamma (γ), determine whether overlap or shielding occurs of an oxygen atom in a given sodium environment. This shielding may be due to another closer oxygen atom, or to a sodium atom.
- (4) A simple test is made to determine if overlap occurs. If gamma is less than alpha plus beta ($\gamma < \alpha + \beta$) then overlap occurs and the angular relationships of this overlap are recorded on punched cards, defining the angles and the atoms concerned. In this way, this program prepares data which is directly applicable to the next program in the series. (Program #3 described in Appendix IIC).

(ii) The Program Printout

The printout of the above Program follows on the next page, and a description of the input data are given in Section (iii).

```
C   SCAN OF INTERBOND ANGLES AND SHIELDING ANGLES
C
C   PROGRAM 2 USING DATA FROM PROGRAM 1
C
1  FORMAT(I2,8X,3F6.3,3F8.5)
3  FORMAT(I2,2(2X,A3,A2),2X,I2,2X,3I2,3F9.4,F10.3,11X,I4)
4  FORMAT(3F7.4,A4)
6  FORMAT(I4,2X,A3,A2,F7.3,1X,A4,1X,A3,A2,F7.3,3F11.3,I10)
C
   DIMENSION NAT(60),S(60),S1(60),OS(60),OS1(60),KEQ(60),IEQX(60),
1  IEQY(60),IEQZ(60),BOND(60),ETX(60),ETY(60),ETZ(60),LL(60)
C
   READ 1, N,A,B,C,COSA,COSB,COSC
   READ 4, XNA,YNA,ZNA,SO
   DO 2 I=1,N
2  READ 3, NAT(I),S(I),S1(I),OS(I),OS1(I),KEQ(I),IEQX(I),IEQY(I),
1  IEQZ(I),ETX(I),ETY(I),ETZ(I),BOND(I),LL(I)
   C1=A*A
   C2=B*B
   C3=C*C
   C4=A*B*COSC
   C5=C*A*COSB
   C6=B*C*COSA
C
   DO 5 I=1,N
   IF(NAT(I+1)-1)5,5,9
9  ALPH=(ATAN(1.32/(SQRT((BOND(I+1)*BOND(I+1))-(1.32*1.32)))))*180.
1 /3.1416
   DO 5 J=1,I
   K=(I+1)-J
   IF(NAT(K)-1)11,10,11
10 RAD=1.
   GO TO 12
11 RAD=1.32
12 BETA=(ATAN(RAD / (SQRT((BOND(K)*BOND(K) )-(RAD *RAD )))))*180.
1 /3.1416
   X1=ETX(I+1)-XNA
   X2=ETX(K)-XNA
   Y1=ETY(I+1)-YNA
   Y2=ETY(K)-YNA
   Z1=ETZ(I+1)-ZNA
   Z2=ETZ(K)-ZNA
   ABC=(X1*X2*C1)+(Y1*Y2*C2)+(Z1*Z2*C3)
   XAB=((X1*Y2)+(Y1*X2))*C4
   YCA=((Z1*X2)+(X1*Z2))*C5
   ZBC=((Y1*Z2)+(Z1*Y2))*C6
   COSG=(ABC+XAB+YCA+ZBC)/(BOND(I+1)*BOND(K))
   THG=SQRT((1.-COSG)/(1.+COSG))
   GAMMA=((ATAN(THG))*180.*2.)/3.1416
   IF(GAMMA)5,8,8
8  ALBE=ALPH+BETA
   IF((GAMMA+2.)-ALBE)7,5,5
7  PUNCH 6,NAT(I+1),OS(I+1),OS1(I+1),BOND(I+1),SO,OS(K),OS1(K),
1  BOND(K),GAMMA,ALPH,BETA,LL(I+1)
5  CONTINUE
   CALL EXIT
   END
```

(iii) Examples of the Input Data

The data for this program are derived from Program #1 and are entered in the following form:

(a) A Control Card for the Structure Type

Cols. 1 and 2 XX
Example 23
Name N
Description: N is the number of bonds calculated
 in program #1.

Cols. 3 to 10 blank

 1 2 3
Cols. 11 to 52 XX.XXX|XX.XXX|XX.XXX
Example 08.149|12.880|07.106
Names A B C
Description: A, B and C are the cell dimensions (Å)
 of the structure being studied.

 1 2 3
Cols. 29 to 52 +X.XXXXX+X.XXXXX+X.XXXXX
Example -0.05873-0.44307-0.00495
Names COSA COSB COSC
Description: The cosines of the crystallographic angles
 for the structure.

(b) The Original Parameters of the Sodium Atom (1 Card Only)

 1 2 3
Cols. 1 to 21 XX.XXXXXX.XXXXXX.XXXX
Example .2743 .0076 .1320
Names XNA YNA ZNA
Description: XNA = x/a for the sodium atom.
 YNA = y/b for the sodium atom.
 ZNA = z/c for the sodium atom.

Cols. 22 to 25 XXXX
Example -NA-
Name SO
Description: SO is the name for the alphabetic field
 defined above.

(c) The Data Cards as produced by Program #1

Note: The bond list has to be arranged in increasing order of bond length.

	1	2	3	4	5	6	7
Cols. 1 to 28	XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX						
Example	6	NA	QA(1)	1	0	0	0
Names	NAT,S1,S2,OS,OS1,KEQ,IEQX,IEQY,IEQZ						

Description: NAT is the serial number of the atom.
S1,S2 are the fields for the alphabetic representation of the name of that atom whose environment is being determined.
OS,OS1 are the fields reserved for the alphabetic representation of the atom in a given environment.
KEQ is the number of a given equivalent position.
IEQX,IEQY and IEQZ are numbers representing the translation of the atom (defined by its serial number in cols. 1 and 2) along the axes x, y and z.

	1	2	3
Cols. 29 to 55	XXX.XXXXXXXXX.XXXXXXXXX.XXXX		
Example	.4945	.3692	.0336
Names	ETX	ETY	ETZ

Description: ETX = x/a plus translation and the operation of symmetry according to the equivalent position number.
ETY = y/b plus translation and the operation of symmetry according to the equivalent position number.
ETZ = z/c plus translation and the operation of symmetry according to the equivalent position number.

	1	2
Cols. 56 to 80	XXXXXX.XXXXXXXXXXXXXXXXXXXXX	
Example	2.537	2
Names	BOND	LL

Description: BOND is the length of the bond between the atoms defined.
LL is the sequential number of that bond in order of calculation.

The punched card output from this program may then be used as data for Program #3 which is defined and documented in the following section of this Appendix.

APPENDIX II

C. FORTRAN II PROGRAM TO CALCULATE THE SHIELDING FACTORS

(i) A Description of Program #3

The FORTRAN II Program described here is entitled: THE SOLID ANGLE SHIELDING EFFECT, and was written by the author to process the data which had been obtained from the previous Program (Appendix IIB) and to prepare the final data for use in Program #4. The assistance which the author received from Dr. H. R. Coish of the Physics Department of this University was mainly in connection with these calculations. It is in this Program that the angles calculated by Program #2 are examined and categorized to determine the four different angular relationships between the angles alpha, beta and gamma which require different formulae for the integration which calculates the fraction of a given atom which is shielded.

This Program initially examined these angles and determined which of the four cases is being dealt with. It then proceeds to the appropriate part of the program which performs these calculations. Thus the Program may be thought of as being in four parts. These parts are marked in the program by COMMENT cards. In order to assist in determining which atom is being dealt with during any given part of the calculation, the Program refers to the sequential number of the bond as calculated in Program #1. This number, in effect, defines a particular atom and the calculated amount representing a shielded fraction is listed in punch card form, together with the fraction of that atom shielded, the

Na-O bond length describing that atom, and the serial number of that atom, are punched out as data cards for Program #4.

(ii) Some of the Mathematic Considerations Used in this Program

Figure 1 defines the angular relationships for a general example of overlap between a pair of oxygen atoms which have bonds to a common sodium atom. The angles alpha, beta and gamma are defined; the expressions used in the integrated calculation of the fraction shielded are also given.

(iii) A Brief Description of the Formulae Used to Calculate the Shielded Fraction of an Atom

CASE 1 - NO SHIELDING

When gamma is greater than beta + alpha, no shielding occurs. This case is taken account of during the preparation of the angles listed from Program #2. The expression may be stated as follows:

If $\gamma < \beta + \alpha$ the solid angle eclipsed = 0

CASE 2 - SMALL FRACTION SHIELDED

Statement : $\beta \leq \gamma \leq \beta + \alpha$

$$\text{Solid Angle Eclipsed} = 2 \int_{\gamma-\beta}^{\alpha} \sin \theta F(\theta) d\theta$$

Note: This case takes effect when the width of the area eclipsed by one atom does not exceed the radius of the atom being eclipsed.

CASE 3 - LARGE FRACTION SHIELDED

Statement : $\gamma < \beta < \gamma + \alpha$

Solid Angle Eclipsed = $A + B$

$$A = \int_0^{\beta-\gamma} \int_0^{2\pi} \sin \theta d\theta d\phi = 2\pi [1 - \cos(\beta-\gamma)]$$

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

Note: This case takes effect when the width of the area eclipsed by one atom exceeds the radius of the atom being eclipsed.

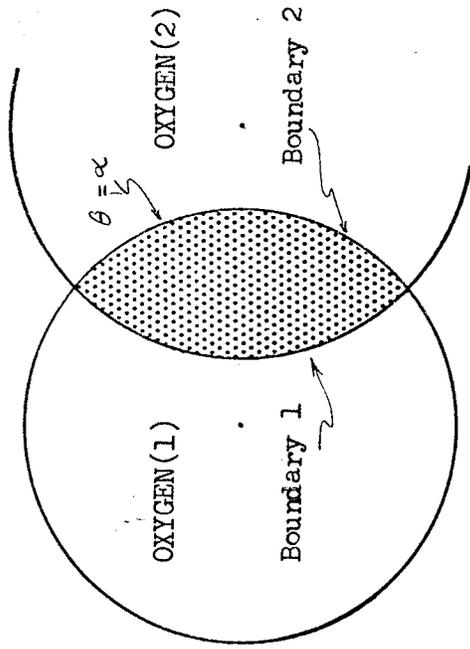


Figure 1B
Appendix II

The Figures represented here are the same as those shown in Figures 1A and 1B in the Text of this Thesis.

The Formula to Define Boundary 1 may be expressed as:

$$\cos \beta = \cos \delta + \sin \delta \sin \theta \sin \phi$$

$$\cos \phi = \frac{\cos \beta - \cos \delta \sin \theta}{\sin \theta \sin \delta}$$

and Boundary 2 may be expressed as:

$$\theta = \alpha$$

The amount of Shielding may then be calculated from:

$$\phi = F(\theta) = \cos^{-1} [\cos \beta \csc \delta \csc \theta - \cot \delta \cot \theta]$$

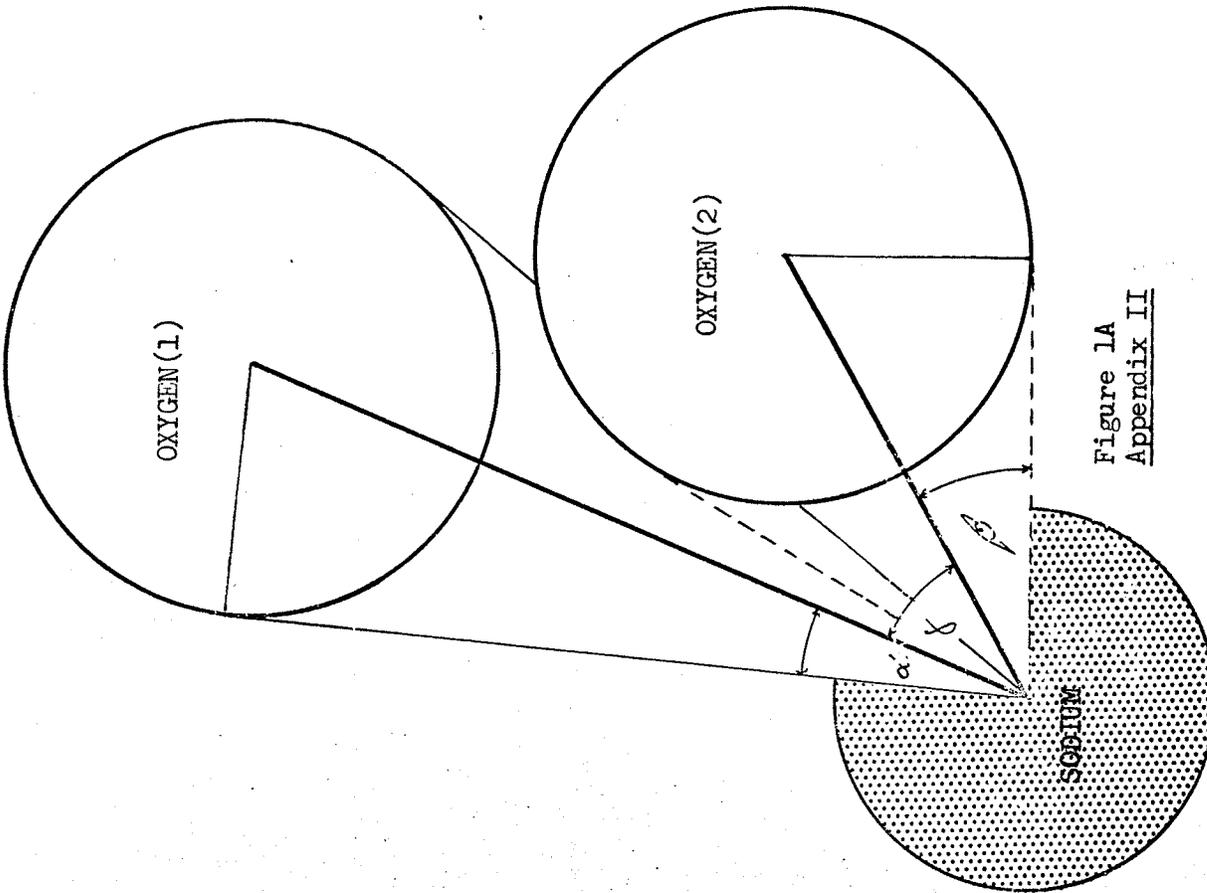


Figure 1A
Appendix II

CASE 4 - COMPLETE SHIELDING

Statement : $\beta \geq \gamma + \alpha$

In all four cases given above, the final answer is expressed as a fraction of the total exposure of that particular atom. In other words, this number represents the shielded fraction of a given oxygen atom. These values are directly applied to the electrostatic charge balance calculations which are described in Appendix IID.

(iv) The Program Printout

The printout of this Program is given on the following two pages.

(v) Examples of the Input Data

(a) Control Card:

	1	2
Cols. 1 to 8	XXXXXXX	
Example	58	90
Names	N	M

Description: N is the number of bonds calculated by Program #1.
M is the number of shielding occurrences calculated by Program #2.

```
C THE SOLID ANGLE SHIELDING EFFECT
C
C PROGRAM 3 USING DATA FROM PROGRAM 2
C N IS THE NUMBER OF BONDS CALCULATED
C M IS THE NUMBER OF SHIELDING OCCURENCES
C
C DIMENSION NAT(100),S(100),S1(100),BO(100),SO(100),SO1(100),
1BON(100),GAM(100),ALPH(100),BETA(100),NSER(100),SHI(58),
2IAT(58),BOND(58)
C
C 6 FORMAT(I4,2X,A3,A2,F7.3,6X,A3,A2,F7.3,3F11.3,8X,I2)
14 FORMAT(I14,F14.4,I6,F12.3)
20 FORMAT(I4)
50 FORMAT(2I4)
C
C READ 50, N,M
DO 11 JJ=1,N
BOND(JJ) = 0.
SHI(JJ)=0.000001
11 IAT(JJ)=1
DO 17 J=1,M
READ 6,NAT(J),S(J),S1(J),BO(J),SO(J),SO1(J),BON(J), GAM(J),
1 ALPH(J), BETA(J),NSER(J)
II=NSER(J)
IAT(II)=NAT(J)
BOND(II)=BO(J)
17 CONTINUE
DO 19 I=1,N
IF(NAT(I)-1)19,18,19
18 SHI(I)=1.000
19 CONTINUE
DO 16 I=1,M
GAM(I)=GAM(I)*3.1416/180.
ALPH(I)=ALPH(I)*3.1416/180.
16 BETA(I)=BETA(I)*3.1416/180.
DO 12 J=1,M
ICASE=0
TYPE 20,J
TH=0.
EC=0.
AGA= GAM(J)+ ALPH(J)
ALBE= ALPH(J)+ BETA(J)
GMB= GAM(J)- BETA(J)
ALF= ALPH(J)
IF(BETA(J)-GAM(J))30,30,31
30 IF(GAM(J)-ALBE)2,2,31
31 IF(BETA(J)-AGA)3,4,4
C
C SHIELDING EFFECT CASE 1 - NO SHIELDING
C
C SHIELDING EFFECT CASE 2
C
C 2 TH=ALPH(J)+.005
22 TH=TH-.005
IF(ICASE-3)41,40,41
41 IF(GMB-TH)15,10,10
40 IF(BEG-TH)15,10,10
15 CO = (COS(BETA(J))-(COS(GAM(J))*COS(TH)))
COP1 = SIN(GAM(J))*SIN(TH)
COP= CO/COP1
```

```
THP=SQRT((1.-COP)/(1.+COP))
PHI = (ATAN(THP))*2.
EC1 =SIN(TH)*PHI
EC2= EC1*2.*0.005
EC=EC+EC2
GO TO 22
```

```
C
C
C   SHIELDING EFFECT CASE 3
3  BEG=BETA(J)-GAM(J)
   A=2.*3.1416*(1.-COS(BEG))
   ICASE=3
   GO TO 2
10 IF(ICASE-3)25,24,25
24 EC=EC+A
C
25 ECC= 2.*3.1416*(1.-COS(ALPH(J)))
   ECL=EC/ECC
   I=NSER(J)
   SHI(I)=ECL+SHI(I)
   GO TO 12
C
C   SHIELDING EFFECT CASE 4 - COMPLETE SHIELDING
C
4  CONTINUE
   I=NSER(J)
   SHI(I)=1.+SHI(I)
12 CONTINUE
   DO 26 I=1,N
26 PUNCH 14, I,SHI(I),IAT(I),BOND(I)
C
   CALL EXIT
   END
```

(b) The Data Cards

The data cards are used directly from Program #2. Each card contains the following information:

	1	2	3
Cols. 1 to 18	XXXXXXXXXXXXXXXXX.XXX		
Example	10	OC(O)	2.953
Names	NAT, S,S1, EO		
Description:	NAT the serial number of the atom being shielded.		
	S,S1 the alphabetic field reserved for the name of the above atom.		
	EO the Na-O bond of the above atom.		

Cols. 19 to 24	XXXXXX
Example	-NA-
Name	none - considered as blanks for this input.

Cols. 25 to 36	5	6
	XXXXXXXXX.XXX	
Example	OA(2)	2.377
Name	SO,S01,BON	
Description:	SO and S01 are the alphabetic fields reserved for the name of the atom which is causing the shielding.	
	BON is the Na-O bond length of the above atom.	

Cols. 37 to 69	7	8	9
	XXXXXXXXX.XXXXXXXXXXX.XXXXXXXXXXX.XXX		
Example	56.499	26.551	33.732
Names	GAM	ALPH	BETA
Description:	GAM = the angle gamma (γ).		
	ALPH= the angle alpha (α).		
	BETA= the angle beta (β).		

These angles are defined in section (ii) of this Appendix.

Cols. 70 to 80	10	
	XXXXXXXXXXXXX	
Example	14	
Name	NSER	
Description:	NSER is the sequential number of the bond in question given in order of calculation from Program #2.	

APPENDIX II

D. FORTRAN II PROGRAM TO CALCULATE THE DISTRIBUTION
OF ELECTROSTATIC CHARGE WITHIN THE STRUCTURES

(i) A Description of Program #4

The FORTRAN II Program described here is entitled: THE ELECTROSTATIC CHARGE DISTRIBUTION PROGRAM, and was written in order to use data as processed in turn by Programs #1, #2, and #3. The resulting data from Program #3 require only slight modification for use with this program and represent the fraction of each oxygen atom shielded, and the Na-O bond distance and the atom serial number serve as identification for the oxygen atom in question. The program is designed to calculate the electrostatic charge distribution within the structures of low and high albite, taking into account the inverse squares of the bond distances, and where applicable the fraction of a given oxygen atom which is exposed to receiving charge from the sodium.

In its basic principles this program uses the general method described in detail in Chapter IA. A few significant changes have been made. The first is that the positive charge contributions from sodium to a given number of coordinated oxygen atoms is calculated before the tetrahedral charge distribution is carried out. In this way less emphasis is placed on the relative amounts of silicon and aluminum in the structure than was done in connection with the anorthite calculation. Secondly, the electrostatic charge from the sodium is distributed proportionally to the inverse square of the bond length, taking into account the effect of shielding.

Other differences are described below:

- (a) Assumed values of Si-O and Al-O are fixed for a set of calculations.
- (b) The coordination of the sodium is increased taking the oxygens in order of nearness. (The coordination of the sodium is controlled by means of the radius of the sphere (Å) encompassing those oxygen atoms whose Na-O bond lengths are less than this radius. The limiting value is a variable in this program).
- (c) The program makes no decisions as to the nature of changes which may be required for the variables.

(ii) A Summary of the Operations Performed in these Calculations

The following outline of the operations performed by this Program is given in point form, and many details are omitted. The program printout is given in Section (iii):

- (1) A control card is read which defines: the number of atoms which may have to be considered in coordination with the sodium, say about 20; the serial number of the atom; the desired maximum limit of the radius of the sphere of environment around the sodium; and finally, the minimum limit of the same sphere.
- (2) The data cards are read in, and the number of these must be equal to the number of atoms which may have to be considered in coordination with the sodium. The following information is contained on each of these cards: the fraction of a given atom which is shielded; the serial number of the atom in question; and the Na-O bond distance for that atom.
- (3) The first calculation is the determination of the amount of a given oxygen atom which is exposed to receive charge from the sodium. This is obtained by subtracting the shielded fraction from 1.000. In those cases where an oxygen is completely shielded from a sodium, this number will be negative, or zero, and it will never be coordinated with the sodium atom.
- (4) The electrostatic charge contributions of the sodium to the surrounding oxygen atoms is calculated, and these values are summed for the set of non-equivalent oxygen atoms in the structure.

- (5) The assumed values for Si-O and Al-O and all the tetrahedral-oxygen distances are read in as data.
- (6) The amount of aluminum in each tetrahedral site is calculated and expressed as a fraction of an atom. When this is complete, the summation of these values gives the total amount of aluminum which is present in the structure, and which of course, is a theoretical value dependent upon the ideal values of Si-O and Al-O which are assumed at the beginning of the calculation.
- (7) The positive charge contributions from the tetrahedral sites to their appropriate oxygen atoms are calculated and those values given to equivalent oxygens are summed, in order to prepare a list of the tetrahedral charge contributions to the non-equivalent oxygen atoms in the structure.
- (8) The total positive charge contributions to the non-equivalent oxygen atoms are summed from the values of the tetrahedral contributions plus the sodium atom contribution. These values should now approximate to 2 e.s.u.
- (9) The total charge on the four non-equivalent tetrahedra are calculated from the summation of the total positive charge on those four oxygen atoms which make up a particular tetrahedron. These values should closely approximate to 8.000 e.s.u.
- (10) The total charge unbalance value for the whole structure is calculated from the summation of the differences from eight of these total tetrahedral charge contributions. For an ideal low-temperature feldspar, provided suitable values for Si-O and Al-O have been used in conjunction with the correct coordination value number for the sodium, this value should be close to 0.000 e.s.u.

The Program is designed to treat, on an iterative basis, various coordination numbers of the sodium atom. Thus, depending upon the limits given to the calculation at the beginning of the Program, a series of coordination numbers will be used for a given pair of ideal Si-O and Al-O values. It is from results like that the data for Chapters IV, V and VI were obtained. See Tables 17 and 22 for examples of these data concerning the low albite and high albite structures respectively.

(iii) The Program Printout

The complete printout of Program #4 is given on the following two pages.

(iv) Examples of the Primary Input Data

(a) A Control Card:

	1	2
Cols. 1 to 8	XXXXXXXX	
Example	23	13
Names	N	NTM

Description: N is the number of bonds calculated in Program #1.
NTM is the number of non-equivalent atoms in the structure.

	3	4
Cols. 9 to 28	XXXXXX.XXXXXXXXXX.XXX	
Example	2.900	4.400
Names	DMAX	DLIM

Description: DMAX is the maximum limit of the radius of the environment about the sodium atom.
DLIM is the minimum radius of the same environment.

(b) The Data Cards:

Cols. 1 to 14 are read as blanks.

	1	2	3
Cols. 15 to 46	XXXXXXXXXX.XXXXXXXXXXXXXXXXXXXXXX.XXX		
Example	.4387	7	5.984
Names	ECL	NAT	D

Description: ECL is the fraction of a given oxygen which is shielded (or eclipsed) by other atoms.
NAT is the serial number identification of the above atom.
D is the Na-O bond length involving that particular oxygen atom.

Note: The number of cards must correspond to the number of bonds calculated by Program #1.

```
C THE ELECTROSTATIC CHARGE DISTRIBUTION PROGRAM
C
C PROGRAM 4 USING DATA FROM PROGRAM 3
C
C DIMENSION ECL(58),NAT(58),CACH(58),EXPO(58),D(58)
C DIMENSION A(4,5),SIO(50),ALO(50),TCH(4,5),CHOX(13),CHT(4)
C
1 FORMAT(2F5.3)
2 FORMAT(5F5.3)
9 FORMAT(26HTOTAL CHARGE ON OXYGEN NO.,I2,F10.3)
10 FORMAT(26HCHARGE ON TETRAHEDRON NO.,I2,F10.3)
11 FORMAT(30HCHARGE UNBALANCE ON LOW ALBITE,F10.3//)
15 FORMAT(17HAL CONTENT OF TET,I2,F7.3)
16 FORMAT(17HTOTAL AL CONTENT,F7.3)
25 FORMAT(14X,F14.4,I6,F12.3)
26 FORMAT(I10,F10.3)
32 FORMAT(55X,F10.3)
34 FORMAT(4HSIO=,F10.3,8H ALO=,F10.3)
36 FORMAT(18HCOORD OF SODIUM IS,I4)
52 FORMAT(13HDMAX VALUE IS,F8.3)
55 FORMAT(14X,F14.4,I6)
62 FORMAT(2I4,2F10.3)
C
READ 62,N,NTM,DMAX,DLIM
C
DO 33 I=1,N
33 READ 25, ECL(I),NAT(I),D(I)
ICY = 0
ITEM = 3
40 SUMX = 0.
NACO=0
DO 22 J=1,NTM
22 CACH(J)=0.00001
DO 21 I=1,N
IF(NAT(I)-1)41,21,41
41 EXPO(I)=1.-ECL(I)
IF(EXPO(I))21,21,44
44 IF(D(I)-DMAX)23,21,21
23 SUMX= (EXPO(I)/(D(I)*D(I)))+SUMX
NACO = NACO +1
21 CONTINUE
IF(ITEM-NACO)50,37,37
50 ITEM = NACO
DO 24 I=1,N
CHNA = 0.
IF(NAT(I)-1)45,24,45
45 IF(EXPO(I))24,24,35
35 IF(D(I)-DMAX)29,24,24
29 CHNA = EXPO(I)/(D(I)*D(I)*SUMX)
J=NAT(I)
28 CACH(J)=CACH(J)+CHNA
24 CONTINUE
PUNCH 52, DMAX
PUNCH 36,NACO
DO 27 J=6,NTM
27 PUNCH 26, J,CACH(J)
IF(ICY-1)61,60,61
C
61 K = 1
READ 1, SIO(K),ALO(K)
```

```
PUNCH 34,SIO(K),ALO(K)
ZM=0.
DO 3 I=1,4
SX=0.
READ 2, (A(I,J),J=1,5)
Z=(A(I,1)-SIO(K))/(ALO(K)-SIO(K))
ZM=ZM+Z
PUNCH 15,I,Z
Y=4.-Z
SX=(1./(A(I,2)*A(I,2)))+(1./(A(I,3)*A(I,3)))
1+(1./(A(I,4)*A(I,4)))+(1./(A(I,5)*A(I,5)))
DO 30 J=2,5
TCH(I,J)= Y/(A(I,J)*A(I,J)*SX)
30 CONTINUE
3 CONTINUE
PUNCH 16, ZM
```

C

```
60 CHOX(6)=TCH(1,2)+TCH(2,2)+CACH(6)
CHOX(7)=TCH(3,2)+TCH(4,2)+CACH(7)
CHOX(8)=TCH(1,3)+TCH(3,3)+CACH(8)
CHOX(9)=TCH(2,3)+TCH(4,3)+CACH(9)
CHOX(10)=TCH(1,4)+TCH(4,4)+CACH(10)
CHOX(11)=TCH(2,4)+TCH(3,4)+CACH(11)
CHOX(12)=TCH(1,5)+TCH(4,5)+CACH(12)
CHOX(13)=TCH(2,5)+TCH(3,5)+CACH(13)
DO 12 I=6,NTM
12 PUNCH 9,I,CHOX(I)
```

C

```
CHT(1)=CHOX(6)+CHOX(8)+CHOX(10)+CHOX(12)
CHT(2)=CHOX(6)+CHOX(9)+CHOX(11)+CHOX(13)
CHT(3)=CHOX(7)+CHOX(8)+CHOX(11)+CHOX(13)
CHT(4)=CHOX(7)+CHOX(9)+CHOX(10)+CHOX(12)
DO 14 I=1,4
14 PUNCH 10, I,CHT(I)
```

C

```
UNBAL =0.
DO 8 I=1,4
TX=8.-CHT(I)
IF(TX)6,8,8
6 TX=TX*(0.-1.)
8 UNBAL=UNBAL+TX
PUNCH 11, UNBAL
```

C

```
IF(DMAX-DLIM)37,38,38
37 DMAX = DMAX + .01
ICY = 1
GO TO 40
38 CALL EXIT
END
```