$$dI_x = b\,dx\,I_x\,.$$

The total amount of light transmitted through the whole field of view is thus equal to Iab where

$$Iab = \int_{D_1}^{D_2} dI_x = b\int_{D_1}^{D_2} I_x dx\,.$$

Now, by definition of D_x

$$D_x = \log_{10}\,(I_0/I_x)$$

or

$$I_x = I_0 10^{-D_x}.$$

Hence,

$$Iab = bI_0\int_{D_1}^{D_2} 10^{-D_x}dx\,.$$

We have assumed that D_x varies uniformly across the area, *i.e.*

$$D_x = D_1 + \frac{(D_2-D_1)x}{a}$$

and

$$dD_x = \frac{(D_2-D_1)\,dx}{a}\,.$$

Hence,

$$\begin{aligned} Iab &= \frac{abI_0}{D_2-D_1}\int_{D_1}^{D_2} 10^{-D_x}dD_x \\ &= \frac{abI_0}{D_2-D_1}\cdot\frac{1}{\log_e 10}\,[10^{-D_1}-10^{-D_2}] \\ &= \frac{abI_0}{D_2-D_1}\cdot 0{\cdot}4343\,[\text{antilog}\,(-D_1)-\text{antilog}\,(-D_2)]. \end{aligned}$$

The average density measured by the microdensitometer is D' where

$$\begin{aligned} D' &= \log_{10}\,(I_0/I) \\ &= \log_{10}\left[\frac{D_2-D_1}{0{\cdot}4343\,[\text{antilog}\,(-D_1)-\text{antilog}\,(-D_2)]}\right]. \end{aligned}$$

The true average density is $(D_1+D_2)/2$ and we require the ratio $D'2/(D_1+D_2)$.

We shall put $D_1=0$ when this ratio becomes

$$\frac{2}{D_2}\log_{10}\left[\frac{D_2}{0{\cdot}4343\,[1-\text{antilog}\,(-D_2)]}\right].$$

From this equation the data given in Tables 1 and 2 have been derived.

Reference

Wooster, W. A. & Fasham, J. A. L. (1958). *J. Sci. Instrum.* **35**, 153.

Acta Cryst. (1964). **17**, 882

The Crystal Structures of Low and High Albites at −180 °C

By P. P. Williams* and Helen D. Megaw

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 17 *June* 1963 *and in revised form* 6 *August* 1963)

The structures of low and high albites determined by Ferguson, Traill & Taylor (1958) have been reinvestigated at −180 °C, particular attention being paid to the anisotropic peaks found at the sites of the sodium atoms at room temperature. Refinement of the structures has been conducted by means of (F_o-F_c) projections parallel to the [001] and [100] axes. The peaks found to be anisotropic at room temperature remain anisotropic at the lower temperature, the effect being more pronounced in high albite than in low. No observable change in the ellipticity of the sodium peaks occurs when the temperature is reduced. The structures of the minerals are discussed on the basis of theories of disorder in feldspar structures.

Introduction

The structures of low and high albites determined by Ferguson, Traill & Taylor (1958) showed an unusual feature which has since been the subject of much discussion, namely a marked anisotropy of the electron-density distribution at the site of the sodium atom. The effect was much more conspicuous in high albite than in low. It was to elucidate this feature that the present low-temperature study was undertaken. For practical reasons, it could only be two-dimensional; this, however, allowed convenient comparison with the work of Ferguson, Traill & Taylor.

The difficulty of distinguishing between thermal vibration amplitudes and disorder as a cause of broadening in electron-density peaks has long been recognized. In both cases, the observed distribution represents an average over a large number of unit cells, or subcells, in which the atom occupies a number of different positions. Thermal amplitudes are described by the use of a Gaussian temperature factor; disorder effects, when each atom is more or less

---

* Present address: Dominion Laboratory, Department of Scientific and Industrial Research, Wellington, New Zealand.

permanently 'frozen in' to one position in the range, are described by putting appropriate fractional atoms at each position. When the range of positions is fairly small, the experimental resolution may not be great enough to distinguish between the two.

For an elongated electron-density peak, the two simplest explanations postulate (i) a large anisotropic thermal amplitude, (ii) an 'average structure' containing two half-atom positions. When the thermal anisotropy or the half-atom splitting is fairly small, the distinction between these two models may be below the limit of resolution. It is then permissible to use either model, according to convenience, without prejudice to the physical interpretation it will ultimately be given. This has been done below in the description of the experimental results.

One may hope to obtain more information by a low-temperature study, because, while frozen-in disorder is likely to change very little, the thermal vibration amplitudes are in principle temperature-dependent. In practice, however, there are difficulties in predicting the temperature dependence. For simple substances with a single Debye temperature less than about 300 °C, it can be shown (*cf.* James (1948), p. 236) that at temperatures around -180 °C the variation of B with temperature should be approximately linear; but the assumptions involved here are not well fulfilled for feldspars. Thus it is not possible to say that an absence of measurable temperature dependence would be unambiguous evidence for disorder. This point will be considered further below.

It should be noted that even when the electron-density distribution can be attributed with confidence to half atoms, it is still not possible to say whether the distribution between the half-atom sites is statistical, with each cell uninfluenced by its neighbours, or perfectly ordered over a volume too small to give difference reflexions. The discussion of this must be based on other grounds: in speaking of the 'half-atom model' we do not prejudge this issue.

Previous work and present work

Ferguson, Traill & Taylor found differences between high and low albite as follows.

(1) The state of ordering of Si and Al among the tetrahedral sites is very different. In high albite it is random or nearly so, while in low albite all, or nearly all, the Al atoms are found in one of the four independent sites, $T_1(0)$.

(2) The detailed coordinates of all atoms differ considerably. Though this fact was not stressed at the time, it can now be seen that the differences are quite large compared with those between the corresponding coordinates in other feldspars, and it cannot be safely assumed that they are simply due to the different sizes of Si and Al.

(3) The degree of apparent anisotropy of the sodium atom is much greater for high albite than for low, though the major axis of the ellipsoid lies in nearly the same direction for both. In terms of the half-atom model, the separations are 0·6 Å for high albite, 0·1 Å for low.

Ferguson, Traill & Taylor considered that the magnitude of the anisotropy, at least in high albite, was too great to be attributed to thermal vibration. Their view was that the cavity available for Na is much larger than it can fill, and that it occupies one side of half the cavities and the other side of the other half. Megaw (1959) has put forward a modified suggestion for high albite: that the cavities themselves are of different shapes, each providing one specific site for Na, and that the two kinds alternate with perfect order over a small volume or domain at the boundaries of which a change of step occurs. Megaw's hypothesis is based on the resemblance of high albite to anorthite (Megaw, Kempster & Radoslovich, 1962). She suggests that the configuration of the framework in a structure with complete Si/Al disorder at any Si:Al ratio is not very different from that with complete order at a 1:1 ratio; that this configuration cannot form a stable repeat unit with a 7-Å c axis and base-centring; and that therefore the existence of two slightly different subcells alternating in some direction is necessary. (Whether the direction of the doubling is [110], [111], or some other direction remains an open question, as does the possibility of a further doubling to give four subcells.) This argument and explanation do not apply to low albite.

According to Megaw's model, all the other atoms besides Na should show half-atom (or quarter-atom) splittings, though perhaps very small ones. It was one of the objects of the present work to search for them, in the hope that the greater resolution obtainable at low temperatures might make them observable even with two-dimensional data. Unfortunately this did not prove to be the case; the resolution was not good enough to decide the issue.

The main object, however, was to see whether the anisotropy of the electron density of Na persisted down to low temperature. With this in mind, the work was planned to repeat at -180 °C that of Ferguson, Traill & Taylor. Any conspicuous differences of Si/Al order, or of atomic coordinates, as well as of electron density distribution at the Na site, would be shown up by this method. Because of the less extensive computing facilities available for the older work, it was necessary to check whether some of the small observed differences were due to incomplete refinement. For this purpose, some observations were repeated at room temperature. Unfortunately, time did not permit a complete repetition, and therefore detailed conclusions cannot be drawn about temperature changes of atomic coordinates and cell dimensions (and hence of bond lengths and bond angles). Whether two-dimensional work would have shown significant changes in atomic coordinates is in any case doubtful.

Material

The sample of low albite came from Ramona, San Diego County, California, and was the same as that used by Ferguson, Traill & Taylor, who gave its history and analysis.

The sample of high albite used by Ferguson, Traill & Taylor was an inverted Amelia albite, but attempts to prepare a similar sample for this work resulted in a material which showed polysynthetic twinning according to the albite law, and the crystals were severely cracked; it proved impossible to isolate a suitable fragment. A much more tractable sample was generously provided by Dr W. S. MacKenzie, to whom we are further indebted for the following information about the conditions of preparation. The crystals were grown hydrothermally from a glass of starting composition $Na_2O:Al_2O_3=1:1$, with considerably more SiO_2 than would correspond to the feldspar composition; the tube, however, was unsealed, and SiO_2 was escaping from the system. The temperature was 700 °C, the pressure of water vapour 1000 bars (14,700 lb.in^{-2}). Albite crystals grew at the top of the tube. By contrast with those usually formed from crystallization of albite glass, they were relatively few and relatively large. Some uncompleted work on the twinning showed that it was certainly not according to the albite law but might possibly have been according to the Carlsbad law. The value of the obliquity parameter, $2(\theta_{131}-\theta_{1\bar{3}1})$, was the same as that of ordinary hydrothermal crystals grown at 1000 °C, which is usually taken as characteristic of high albite.

Because of this identity of the obliquity parameter, it was initially assumed that any differences from the material studied by Ferguson, Traill & Taylor would be negligible. Later, when this was questioned, it was assumed that they would in any case be small, and their possible effect would be taken into consideration in discussing the results.

Lattice parameters

The axes of reference chosen are those conventional for the feldspars, according to which the space-group symbol is $C\bar{1}$. The lattice parameters determined by Ferguson, Traill & Taylor are given in Table 1. They were used throughout the present investigation, since their changes with temperature are too small to affect refinement.

Table 1. *Lattice parameters of albite*
(Ferguson, Traill & Taylor, 1958)

	Low albite	High albite
a	8·138 Å	8·149 Å
b	12·789	12·880
c	7·156	7·106
α	94° 20′	93° 22′
β	116 34	116 18
γ	87 39	90 17

Experimental

X-ray patterns were obtained from approximately equidimensional fragments with edges 0·2–0·3 mm. The low-temperature Weissenberg camera used was designed by Williams. Intensities were obtained from zero-level Weissenberg photographs taken at −180 °C about [100] and [001] with Mo $K\alpha$ radiation, with the standard multiple-film technique and visual estimation by reference to a comparison scale. The numbers of non-zero independent reflexions recorded were as follows: for low albite, 258 of type $hk0$ and 239 of type $0kl$; for high albite, with the same exposure times, 135 and 100 respectively. For low albite, reflexions were visible to the limit of the reflecting sphere, but for high albite, only to $(\sin\theta)/\lambda = 0{\cdot}9$. This emphasizes the greater degree of disorder in high albite, which manifests itself in the data as a larger overall 'temperature' factor.

No corrections were applied for absorption, because, when typical absorption corrections were calculated for molybdenum radiation, they proved to be small compared with the likely random errors in the observed intensities.

For comparison, and as a check, a room-temperature photograph of low albite was taken about [001].

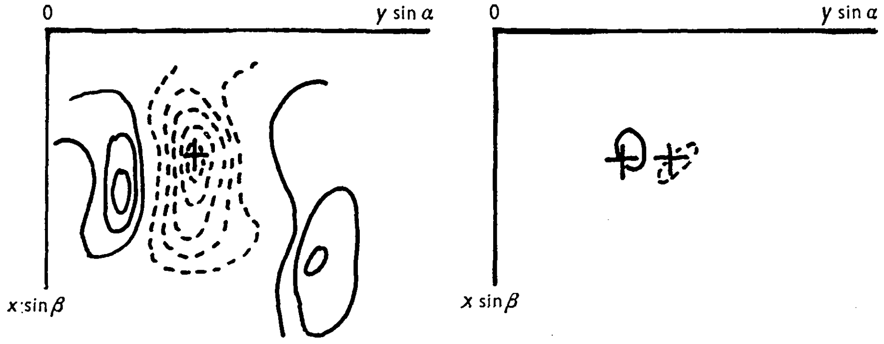
Atomic scattering factors and temperature factors

The atomic scattering curves of Bragg & West (1928), used by Ferguson, Traill & Taylor, incorporate temperature factors which would have been inapplicable at low temperatures. For the present work, atomic scattering factors were computed by fitting the analytic expressions of Forsyth & Wells (1959) to the curves given by Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Na and O, and by Viervoll & Øgrim (1949) for Si and Al. Curves for the neutral atoms were used. A mean scattering factor of $\frac{3}{4}f_{\rm Si}+\frac{1}{4}f_{\rm Al}$ was used for all atoms in tetrahedral sites, thus avoiding any initial assumptions concerning the kind of Si/Al order. The temperature factors were refined independently. All computations were performed on EDSAC II.

Refinement of the structures

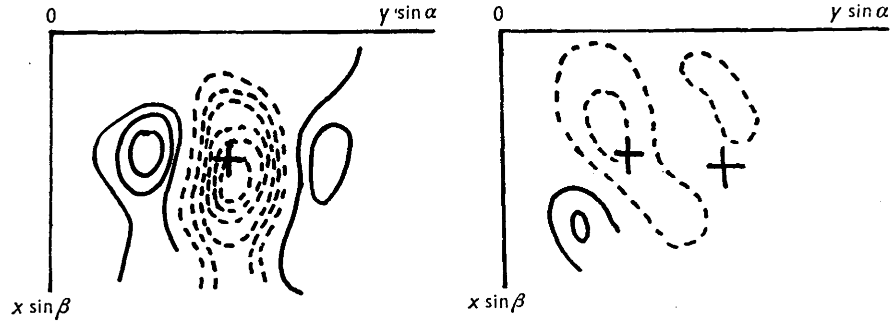
For the first trial structure, the coordinates of Ferguson, Traill & Taylor were used with an overall temperature factor of $B=0$, and $\varrho_o-\varrho_c$ syntheses were computed (Figs. 1(*a*), 2(*a*), 3(*a*), 4(*a*)). The marked anisotropy of the sodium atom in both projections of both structures is immediately apparent.

Two half atoms were substituted for the original sodium atom, and were initially given the same temperature factor. Later, independent temperature factors were allotted to each sodium half atom in high albite, as had been done already (in both low and high albite) for the tetrahedral atoms as a whole and for each separate oxygen atom. Refine-



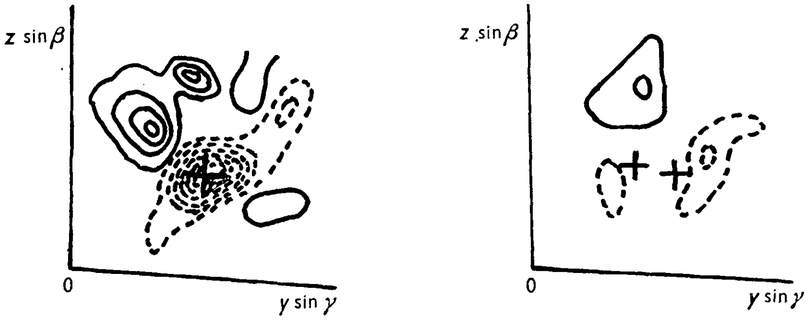
(a) (b)

Fig. 1. Low albite at −180 °C: $(\varrho_o - \varrho_c)$ synthesis in the neighbourhood of the sodium atom, projected down [100]. (a) First model, which has Ferguson, Traill & Taylor's coordinates, and $B = 0$. (b) Final model, with two half atoms. Contour intervals 0·19 e.Å^{-2}; negative contours shown by broken lines; zero contour omitted.



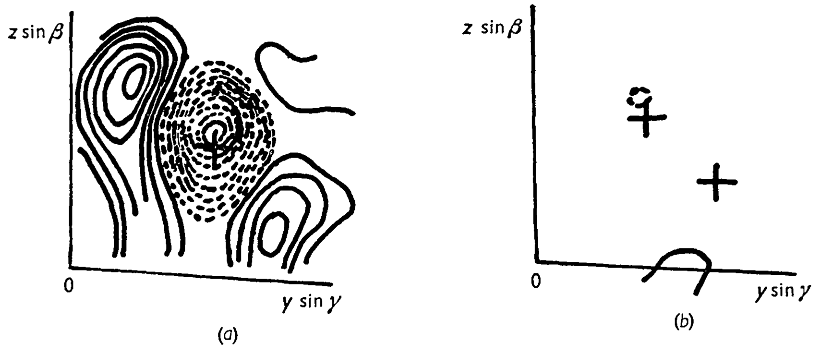
(a) (b)

Fig. 2. High albite at −180 °C: [100] projection, with contour intervals 0·19 e.Å^{-2} and different temperature factors for the two half atoms in (b); otherwise as Fig. 1.



(a) (b)

Fig. 3. Low albite at −180 °C: [001] projection, with contour intervals 0·24 e.Å^{-2}; otherwise as Fig. 1.



(a) (b)

Fig. 4. High albite at −180 °C: [001] projection, with contour intervals 0·24 e.Å^{-2}; otherwise as Fig. 2.

ment of coordinates and temperature factors proceeded together. Parts of the final $\varrho_o-\varrho_c$ map are shown in Figs. 1(*b*), 2(*b*), 3(*b*), 4(*b*).

The tetrahedral atoms remained in positive regions of the map throughout the refinement, with one exception, $T_1(0)$ in the [100] projection of low albite, which fell in a negative region. This result for $T_1(0)$ is in accordance with Ferguson, Traill & Taylor's conclusion that it is the only Al-rich site; but since in the [100] projection there is partial overlapping with another atom, $O_c(m)$, and in the [001] projection no comparable effect is observed, its significance is doubtful.

In the later stages of refinement of the [001] projection of low albite, the tetrahedral atoms appeared slightly anisotropic. Although very small, the effect was confirmed by an independent set of data from another crystal at room temperature. Nevertheless, we cannot claim any significance for it at this stage, since it might be due to incomplete refinement. Overlap of atoms would in any case have hidden it in the [100] projection.

The oxygen atoms in each projection of each structure fell into two groups, with large and small temperature factors respectively (Table 2). However, no obvious correlation was noticed between the groups from one projection to the other, or from one structure to the other. It is possible that the differences in different projections imply a slight anisotropy which is otherwise too small to be detected on $\varrho_o-\varrho_c$ maps. In both projections of both structures, the temperature factor of $O_A(2)$ is one of the smallest.

Table 2. *Temperature factors applied to oxygen atoms*

	Low albite		High albite	
	[100]	[001]	[100]	[001]
$O_A(1)$	0·3 Å^2	0·3 Å^2	1·0 Å^2	0·7 Å^2
$O_A(2)$	0·3	0·3	1·0	0·15
$O_B(0)$	0·7	0·5	1·6	1·6
$O_B(m)$	0·7	0·5	1·0	0·7
$O_C(0)$	0·7	0·5	1·0	0·7
$O_C(m)$	0·3	0·5	1·0	0·7
$O_D(0)$	0·3	0·5	1·0	1·6
$O_D(m)$	0·3	0·3	1·0	1·6

The sodium atoms in low albite need no special remark. The refinement of both the −180° data and the room-temperature data proceeded smoothly. In high albite, which was studied only at −180 °C, one half atom, Na(1), lay in a deeper negative region than did the other, Na(2), as long as their temperature factors were kept equal. To remedy this, two alternative models were tried. In the first, the half atoms were allowed different temperature factors. The *B* value for Na(1) increased considerably, while that of Na(2) changed little; the final values are those recorded in Table 3. In the second model, the temperature factors were kept equal, while Na(1) and Na(2) were allotted unequal weights, the best weighting being 0·45 Na(1) : 0·55 Na(2). Both models gave equally good $\varrho_o-\varrho_c$ maps, but the *R* indices were better for the first model (Table 4) which was adopted.

Table 3. *Temperature factors applied to sodium atoms*

	High albite, −180 °C		Low albite (Similar half atoms)	
	Na(1)	Na(2)	−180 °C	Room temperature
[100] projection	1·3 Å	0·8 Å	0·55 Å	—
[001] projection	1·3	0·65	0·55	1·4 Å

Table 4. *Final R indices*

		High albite	
	Low albite	Half atoms with different *B*	Weighted half atoms
[100] projection	11·1 %	11·4 %	11·5 %
[001] projection	9·4	9·7	12·9

A third model was tried with sodium atoms distributed along the major axis of the ellipsoid; the single sodium atom was split into twelve equal parts, at equal intervals along the line joining the refined positions of the half-atom model. Again the difference map was nearly as good, but the *R* index was rather worse.

The final *R* indices in Table 4 suggest that refinement has proceeded as far as is justified by the accuracy of the measurements.

Results

Table 5. *Final two-dimensional atomic coordinates*

	Low albite			High albite		
	x	*y*	*z*	*x*	*y*	*z*
Na(1)	0·2675	0·9802	0·1510	0·2650	0·9843	0·1565
Na(2)	0·2653	0·0000	0·1385	0·2770	0·0252	0·1135
$T_1(0)$	0·0095	0·1680	0·2075	0·0075	0·1665	0·2130
$T_1(m)$	0·0053	0·8207	0·2380	0·0045	0·8163	0·2300
$T_2(0)$	0·6910	0·1100	0·3105	0·6895	0·1069	0·3195
$T_2(m)$	0·6797	0·8818	0·3595	0·6830	0·8770	0·3505
$O_A(1)$	0·0065	0·1283	0·9678	0·0065	0·1343	0·9825
$O_A(2)$	0·5905	0·9962	0·2785	0·5850	0·9940	0·2730
$O_B(0)$	0·8169	0·1070	0·1943	0·8080	0·1150	0·1890
$O_B(m)$	0·8191	0·8525	0·2612	0·8157	0·8500	0·2445
$O_C(0)$	0·0095	0·3011	0·2680	0·0115	0·2923	0·2690
$O_C(m)$	0·0247	0·6936	0·2295	0·0223	0·6870	0·2160
$O_D(0)$	0·2085	0·1087	0·3885	0·1950	0·1105	0·3880
$O_D(m)$	0·1844	0·8674	0·4345	0·1750	0·8690	0·4220

Mean standard deviations of the coordinates are:

Low albite:

$\sigma(\mathrm{Na})=0{\cdot}018$ Å, $\sigma(T)=0{\cdot}0036$ Å, $\sigma(\mathrm{O})=0{\cdot}011$ Å.

High albite:

$\sigma(\mathrm{Na})=0{\cdot}057$ Å, $\sigma(T)=0{\cdot}0068$ Å, $\sigma(\mathrm{O})=0{\cdot}025$ Å.

The final two-dimensional coordinates are given in

Table 6. *Bond lengths and bond angles in low and high albite*

(*a*) *T*–O bond lengths (Å)

	Low albite				High albite			
	This work		F.T.T.*		This work		F.T.T.	
$T_1(0)$–$O_A(1)$	1·738	1·737	1·762	1·742	1·662	1·668	1·652	1·652
–$O_B(0)$	1·741		1·702		1·686		1·654	
–$O_C(0)$	1·724		1·762		1·642		1·645	
–$O_D(0)$	1·745		1·744		1·683		1·658	
$T_1(m)$–$O_A(1)$	1·611	1·617	1·596	1·590	1·639	1·631	1·646	1·639
–$O_B(m)$	1·629		1·626		1·646		1·633	
–$O_C(m)$	1·626		1·553		1·673		1·641	
–$O_D(m)$	1·603		1·583		1·567		1·636	
$T_2(0)$–$O_A(2)$	1·649	1·622	1·618	1·636	1·622	1·638	1·646	1·642
–$O_B(m)$	1·580		1·627		1·615		1·635	
–$O_C(0)$	1·607		1·649		1·636		1·640	
–$O_D(0)$	1·652		1·649		1·680		1·645	
$T_2(m)$–$O_A(2)$	1·633	1·616	1·640	1·616	1·712	1·654	1·637	1·647
–$O_B(0)$	1·600		1·597		1·598		1·633	
–$O_C(m)$	1·617		1·618		1·635		1·668	
–$O_D(m)$	1·613		1·611		1·671		1·649	

Standard deviation of *T*–O bond length in this work:
Low albite = 0·012 Å High albite = 0·025 Å

* Ferguson, Traill & Taylor (1958).

(*b*) O–O bond lengths (Å)

		Low albite		High albite	
$T_1(0)$	$O_A(1)$–$O_B(0)$	2·726	2·833	2·641	2·722
	$O_A(1)$–$O_C(0)$	2·947		2·780	
	$O_A(1)$–$O_D(0)$	2·737		2·635	
	$O_B(0)$–$O_C(0)$	2·877		2·695	
	$O_B(0)$–$O_D(0)$	2·851		2·830	
	$O_C(0)$–$O_D(0)$	2·857		2·753	
$T_1(m)$	$O_A(1)$–$O_B(m)$	2·630	2·641	2·617	2·663
	$O_A(1)$–$O_C(m)$	2·702		2·727	
	$O_A(1)$–$O_D(m)$	2·591		2·582	
	$O_B(m)$–$O_C(m)$	2·640		2·751	
	$O_B(m)$–$O_D(m)$	2·669		2·628	
	$O_C(m)$–$O_D(m)$	2·611		2·672	
$T_2(0)$	$O_A(2)$–$O_B(0)$	2·665	2·646	2·670	2·673
	$O_A(2)$–$O_C(m)$	2·576		2·560	
	$O_A(2)$–$O_D(m)$	2·640		2·720	
	$O_B(0)$–$O_C(m)$	2·687		2·591	
	$O_B(0)$–$O_D(m)$	2·656		2·701	
	$O_C(m)$–$O_D(m)$	2·652		2·799	
$T_2(m)$	$O_A(2)$–$O_B(m)$	2·597	2·637	2·710	2·700
	$O_A(2)$–$O_C(0)$	2·594		2·659	
	$O_A(2)$–$O_D(0)$	2·640		2·722	
	$O_B(m)$–$O_C(0)$	2·652		2·666	
	$O_B(m)$–$O_D(0)$	2·624		2·671	
	$O_C(0)$–$O_D(0)$	2·717		2·770	

Standard deviation of O–O bond length:
Low albite = 0·016 Å
High albite = 0·035 Å

(*c*) O–*T*–O interbond angles

	Low albite		High albite	
		Mean values		Mean values
$O_A(1)$–$T_1(0)$–$O_B(0)$	102° 59′	109° 22′	104° 08′	109° 28′
$O_A(1)$–$T_1(0)$–$O_C(0)$	116 41		114 34	
$O_A(1)$–$T_1(0)$–$O_D(0)$	103 34		103 55	
$O_B(0)$–$T_1(0)$–$O_C(0)$	112 38		108 08	
$O_B(0)$–$T_1(0)$–$O_D(0)$	109 17		114 14	
$O_C(0)$–$T_1(0)$–$O_D(0)$	110 59		111 44	
$O_A(1)$–$T_1(m)$–$O_B(m)$	108 56	109 29	105 38	109 26
$O_A(1)$–$T_1(m)$–$O_C(m)$	112 37		110 49	
$O_A(1)$–$T_1(m)$–$O_D(m)$	107 52		107 17	
$O_B(m)$–$T_1(m)$–$O_C(m)$	108 01		111 58	
$O_B(m)$–$T_1(m)$–$O_D(m)$	111 35		109 51	
$O_C(m)$–$T_1(m)$–$O_D(m)$	107 52		111 02	
$O_A(2)$–$T_2(0)$–$O_B(0)$	110 43	109 23	111 11	109 26
$O_A(2)$–$T_2(0)$–$O_C(m)$	104 30		103 35	
$O_A(2)$–$T_2(0)$–$O_D(m)$	105 57		110 52	
$O_B(0)$–$T_2(0)$–$O_C(m)$	115 20		105 41	
$O_B(0)$–$T_2(0)$–$O_D(m)$	110 37		110 05	
$O_C(m)$–$T_2(0)$–$O_D(m)$	109 10		115 10	
$O_A(2)$–$T_2(m)$–$O_B(m)$	110 21	109 26	109 49	109 27
$O_A(2)$–$T_2(m)$–$O_C(0)$	110 46		105 11	
$O_A(2)$–$T_2(m)$–$O_D(0)$	104 14		107 05	
$O_B(m)$–$T_2(m)$–$O_C(0)$	114 38		111 08	
$O_B(m)$–$T_2(m)$–$O_D(0)$	109 08		109 36	
$O_C(0)$–$T_2(m)$–$O_D(0)$	107 08		113 50	

(*d*) *T*–O–*T* interbond angles

	Low albite		High albite	
		Mean values		Mean values
$T_1(0)$–$O_A(1)$–$T_2(0)$	140° 47′	140° 36′	142° 38′	140° 19′
$T_2(0)$–$O_A(2)$–$T_2(m)$	130 01		127 02	
$T_1(0)$–$O_B(0)$–$T_2(0)$	139 43		140 38	
$T_1(m)$–$O_B(m)$–$T_2(m)$	162 07		158 01	
$T_1(0)$–$O_C(0)$–$T_2(m)$	128 58		129 13	
$T_1(m)$–$O_C(m)$–$T_2(0)$	135 49		134 55	
$T_1(0)$–$O_D(0)$–$T_2(m)$	133 59		134 40	
$T_1(m)$–$O_D(m)$–$T_2(0)$	153 26		153 09	

Table 5, with their standard deviations,* the bond lengths and bond angles in Table 6. The bond lengths of Ferguson, Traill & Taylor are given for comparison in Table 6(*a*).

The final temperature factors for sodium and oxygen atoms are given in Tables 2 and 3; that for the tetrahedral atoms is zero.

The values of F_o and F_c are not sufficiently different from those of Ferguson, Traill & Taylor to warrant their inclusion in this paper. They are recorded at the Cavendish Laboratory.

Discussion

(1) Si/Al *distribution*

The general resemblance of the present results to those of Ferguson, Traill & Taylor is very obvious. From the average bond lengths, Al contents of all the sites have been calculated (Table 7), using the new values of Smith & Bailey (1962) for the Al and Si radii.

For low albite, we attach no significance to the difference between our bond lengths and those of Ferguson, Traill & Taylor. Effects of thermal expansion, if not wholly negligible, cannot be distinguished from those of experimental error. Within our limits of error, the results are consistent with perfect Si/Al order.

Table 7. Al *contents of tetrahedral sites*

	Low albite (Ramona)		High albite	
	This work	Ferguson, Traill & Taylor	Synthetic, this work	Heated Amelia, Ferguson, Traill & Taylor
$T_1(0)$	0·91	0·94	0·41	0·30
$T_1(m)$	0·05	(−0·14)	0·15	0·21
$T_2(0)$	0·09	0·19	0·21	0·23
$T_2(m)$	0·04	0·04	0·31	0·26
Total	1·09	(1·17)	1·08	1·00

(Values assumed for Si–O and Al–O are 1·61 and 1·75 Å, (Smith & Bailey, 1962)).

For high albite, we have to consider the fact that our material has a different thermal history from that of Ferguson, Traill & Taylor, and therefore may show differences not only in the *degree* of order but in the *kind* of order, which Megaw (1962) suggests is a more fundamental characteristic. Suppose that high albite, in true thermal equilibrium, has a different kind of order (underlying whatever disorder may be present) from low albite. Then the transition from low to high albite may have to proceed through complete site disorder as an intermediate stage, just as a reconstructive transition must proceed through a complete break-up of the crystal structure. If there are no further discontinuous changes in the kind of order at higher temperatures, it is then quite possible for a synthetic high albite to show more site order than a heated low albite, since the second, re-ordering, stage of the low-high transition is likely to be very sluggish indeed. It has been pointed out to us by P. H. Ribbe (private communication) that the optic axial angle, $2V$, of Ferguson, Traill & Taylor's material, indicates that it was not fully inverted, having the value 125–135° instead of 155°.

Assuming (from the analogy with low albite) that the effects of thermal expansion between −180 °C and 20 °C are negligible, we have therefore to examine whether the Si/Al occupation in synthetic high albite is significantly different from that in heat-inverted albite, and whether the tetrahedra in the synthetic albite are significantly different from one another. The arguments are as follows.

(i) The standard deviations of tetrahedral means for the two determinations are 0·013 Å and 0·009 Å respectively (half the standard deviations of the individual bonds); and the difference between the $T_1(0)$ mean bond lengths is 0·016 Å. The ratio $0{\cdot}016/[(0{\cdot}013)^2+(0{\cdot}009)^2]^{\frac{1}{2}}$ is 1·0, giving a probability of 84% against the occurrence of such a discrepancy because of random error. Though this probability is too small to allow a definite conclusion that the state of order in the two structures is truly different (especially in view of the fact, observed in anorthite, that small real differences in tetrahedral size may be due to strain rather than to different Si/Al content), it is nevertheless large enough to provide very suggestive evidence in favour of such a hypothesis.

(ii) For synthetic high albite, the difference of the $T_1(0)$ tetrahedral mean from the overall mean is 0·020 Å; the ratio 0·020/0·013 is 1·54, corresponding to a 94% probability against the attribution of the difference to random error. Here again the evidence is in favour of the reality of ordering, but not conclusively so.

A three-dimensional analysis of this synthetic high albite would be of interest, to compare with the three-dimensional analysis of heat-inverted albite recently completed† (Ribbe, 1963).

(2) *Temperature factors*

The value $B=0$ for tetrahedral atoms is not unexpected. Previous work (for example on anorthite and bytownite) suggests that values of 0·2 to 0·5 Å²

---

* Standard deviations of coordinates were derived by a program which used the calculated curvature of the atom rather than the observed. They are thus sensitive not only to any errors in the temperature factors but also to any disorder at atomic positions; the latter effect, which may well occur in high albite, would tend to produce an overestimate of the error.

† We are indebted to Mr P. H. Ribbe for information about the results of this refinement. They do not change any of the above conclusions substantially, though they slightly strengthen the arguments in favour of a real difference between the materials. If the standard deviation of bond-lengths for synthetic albite is correct, it would be too high to allow of conclusive proof of the difference even if the standard deviation for heat-inverted albite were zero.

are usual at room temperature; if a linear temperature dependence holds, one expects values of 0·07 to 0·2 Å^2 at −180 °C, which might not be experimentally distinguishable from zero.

For oxygen, the situation is less clear. The Bragg & West curves used by Ferguson, Traill & Taylor at room temperature incorporate a B value of about 1·5 Å^2; in orthoclase (Jones & Taylor, 1961) and in bytownite (Fleet, 1962) $B = 1·0$ to 1·2 Å^2; in anorthite (Kempster, Megaw & Radoslovich, 1962) $B = 0·6$ Å^2. If we accept 0·6 Å^2 for an ordered structure and take the spread of positions due to Si/Al disorder as having an r.m.s. value equal to half the difference of Si–O and Al–O, 0·07 Å, we predict a disorder contribution to the 'temperature factor' of $8\pi^2 \times (0·07)^2$, or 0·4 Å^2, and hence an apparent temperature factor for a disordered structure of (0·6+0·4) Å^2 at room temperature, and (0·2+0·4) Å^2 at −180 °C. This must be recognized as a very rough order-of-magnitude calculation. It includes the doubtful assumptions that B for an ordered structure is linear with temperature, and that it should be combined with the disorder term by simple addition; moreover, if (as suggested above) the distortions of a disordered structure are not simply due to differences in the radii of Si and Al, the r.m.s. value of the disorder spread may well be much higher. Comparing these results with the actual B values at −180 °C, the low-albite values of 0·3 to 0·7 Å^2 do not give clear evidence for or against its being fully ordered, but the high-albite values of 0·7 to 1·6 Å^2 (omitting one exceptional value of 0·15 Å^2 for $O_A(2)$ in the [001] projection) are an indication of disorder. It is rather interesting, though it could be a coincidence, that the exceptionally small value is found for the atom with the exceptionally short Na–O distance, and in the projection containing this bond.

For discussing the sodium atom, we assume the half-atom model. For low albite, the B value in Table 3 decreases with decreasing temperatures in the way expected from the simple theory (the room-temperature value of 1·4 Å^2 being comparable to Ferguson, Traill & Taylor's estimate of 1·6 Å^2 for the unsplit atom). For high albite, the value for Na(1) at −180 °C is surprisingly high, especially by contrast with that for Na(2); no reliable room-temperature estimate is available for comparison. It seems likely that there is still disorder of a kind not allowed for by the half-atom model; even if the difference between Na(1) and Na(2) can be explained by unequal concentrations in the two sites (see above), the temperature factor is still too high to suggest that the positions are wholly defined. Here it is of considerable interest to note that in transitional anorthite (P. H. Ribbe, private communication) the Ca atoms at positions corresponding to Na(1) have much larger (isotropic) temperature factors than those corresponding to Na(2); the same effect was noticed in low anorthite (Kempster, Megaw & Radoslovich, 1962) though no special attention was drawn to it.

(3) *Anisotropy of sodium*

The persistence of the sodium anisotropy at −180 °C in both high and low albite is a striking result. Details are given in Table 8. Though it was expected in high albite, in low albite it is more surprising.

Table 8. *Separation of sodium half-atoms*

	Low albite	High albite
Separation	0·27 Å	0·62 Å
Inclination to y axis	19°	29°

For low albite, the half-atom separation is considerably greater than the 0·1 Å estimated by Ferguson, Traill & Taylor, and its direction is inclined to the y axis, not parallel to it. Refinement of the new room-temperature data for the [001] projection gave a result in agreement with that at −180 °C, so the apparent difference is probably due to the less complete refinement of the older work.

For high albite, the magnitude of the separation is the same as that found by Ferguson, Traill & Taylor, but the direction is very similar to that in low albite, *i.e.* inclined to the y axis in the yz plane.

We conclude that at present there is no evidence for any qualitative change in the 'half-atom splitting' between room temperature and −180 °C, but that further work would be needed to show if there were small quantitative differences.

The magnitude of the splitting in high albite is so great that it seems unlikely that an anisotropic temperature factor would fit the observed electron density equally well; this, however, was not tested directly. For low albite, the splitting is too small to allow a distinction between the two models to be made with certainty on this evidence. We should like to emphasize that in using the 'half-atom' model for low albite we do so primarily for convenience of calculation and convenience of comparison with high albite, and not because we think it more likely to be the correct one.

It was pointed out in the introductory section that the conditions of the simple theory predicting a linear variation of B with temperature are not fulfilled in feldspars. Broadly speaking, they are linked with the assumption of the Debye theory of specific heat, that all interatomic forces in the structure are roughly equal. This may be true of the forces in the Si/Al–O framework, but not true of those holding the Na atoms in position. Alternatively, one could say that a linear variation of mean square amplitude with temperature implies a potential well which is roughly harmonic, and has smoothly sloping sides; an atom in a square potential well would have an amplitude independent of its energy and therefore of the temperature. Now the potential well of the sodium atom is likely to be a shallow bowl bounded by steep cliffs; the shallow bowl corresponds to the slowly varying electrostatic field in the cavity, and the steep walls to the positions where the repulsive forces become important. In these circumstances it is not possible to argue that an unchanged anisotropic spread at −180 °C must indicate disorder. The question remains open.

It should also be noticed that, even if the 'half-atom splitting' is real (as we think it is in high albite), it does not necessarily mean that this represents a physically important distance in the structure. Fig. 5 is a sketch diagram showing the projection on (010) of two pairs of sodium half atoms, P_1, P_2, and Q_1, Q_2, related by the centre of symmetry at O, the origin. The 'splitting' considered here is the vector P_1P_2. The simplest picture takes P_1 and P_2 as sites within the same cavity, and P_1P_2 as the distance between them (projected on (010)). But, according to Megaw, the atom cannot move from P_1 to P_2 without substantial changes in the surrounding framework; in other words, P_1 and P_2, here plotted with respect to a common origin O, are in reality separated by P_1P_2 plus a lattice translation vector. It is the cation–cation vector which is physically important, according to Megaw, Kempster & Radoslovich (1962), because a repulsive force acts along it; for this reason, it is likely to remain centrosymmetric. Then vectors P_1Q_1 and P_2Q_2 represent the directions of this force in different subcells, and the splitting vector, P_1P_2, has its use in describing the difference of their directions.

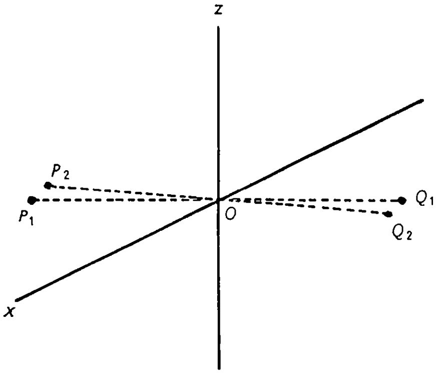


Fig. 5. Sketch diagram of 'split-sodium' positions projected on (010).

Summary and conclusion

The study of high albite at −180 °C makes it extremely likely that there is disorder which results in 'half-atom splitting' of the sodium atoms, but gives no evidence as to whether the half atoms are due to statistical occupation of two sites or to an ordered alternation within small domains. In low albite, it is not possible to say whether the anisotropy persisting at −180 °C is due to a 'half-atom splitting' or to an anisotropic thermal vibration. In both, the resemblances of the effects at room temperature and −180 °C are more striking than their differences, but there is an indication (not amounting to conclusive proof) that synthetic high albite and heat-inverted albite are not strictly identical.

Though the work does not give any direct answers to the questions still outstanding about the two albite structures, the observed facts seem of sufficient interest to put on record. They may be of interest for comparison with other feldspar studies, and in particular with the results of three-dimensional work on the albites now in progress in this laboratory.

We are grateful to Dr W. H. Taylor for suggesting this problem, and for his continued interest and encouragement. One of us (P. P. W.) also wishes to acknowledge with gratitude the award of a National Research Fellowship by the Department of Scientific and Industrial Research, New Zealand, during the tenure of which this work was performed.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.

Bragg, W. L. & West, J. (1928). *Z. Kristallogr.* **69**, 118.

Ferguson, R. B., Traill, R. J. & Taylor, W. H. (1958). *Acta Cryst.* **11**, 331.

Fleet, S. G. (1962). Thesis, Cambridge.

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.

Jones, J. B. & Taylor, W. H. (1961). *Acta Cryst.* **14**, 443.

Kempster, C. J. E., Megaw, H. D. & Radoslovich, E. W. (1962). *Acta Cryst.* **15**, 1005.

Megaw, H. D. (1959). *Miner. Mag.* **32**, 226.

Megaw, H. D. (1962). *Norsk. Geol. Tidsskr.* **42** (2), 104.

Megaw, H. D., Kempster, C. J. E. & Radoslovich, E. W. (1962). *Acta Cryst.* **15**, 1017.

Ribbe, P. H. (1963). Thesis, Cambridge.

Smith, J. V. & Bailey, S. W. (1962). Abstract of November Meeting of Geol. Soc. America, p. 147.

Viervoll, H. & Øgrim, O. (1949). *Acta Cryst.* **2**, 277.