A THREE-DIMENSIONAL
REFINEMENT OF THE STRUCTURE OF LOW ALBITE

By

P. H. RIBBE[1], R. B. FERGUSON[2], and W. H. TAYLOR[1]

A three-dimensional refinement of the low-temperature form of albite, $NaAlSi_3O_8$, confirms the apparent anisotropy of the sodium atom that was shown in the two-dimensional structure analysis by Ferguson, Traill and Taylor (1958). "Split" sodium half-atoms approximate this anisotropy, and refinement procedes successfully using the half-atom positions of Williams (1961). The final coordinates indicate a 0.35 Å "splitting" for sodium. The mean Al/Si–O bond lengths are: $T_1(O)$, 1.744 Å; $T_1(m)$, 1.610 Å; $T_2(O)$, 1.616 Å; $T_2(m)$, 1.613 Å.

Introduction

The refinement in two dimensions of the structure of a low-temperature albite (compositional and dimensional data in Table 1) was published by Ferguson, Traill and Taylor (1958). At that time equi-inclination Weissenberg photographs of 26 upper levels were taken by one of us (R.B.F.) to provide data for three-dimensional work. A standard multifilm technique was used, and intensities were visually estimated, corrected for the Lorentz and polarization effects, and then simultaneously scaled and corrected for contraction and extension of spots, using intensity data from 4 a-axis levels and 5 c-axis levels. Absorption effects were assumed to be negligible for $MoK\alpha$ radiation, and no extinction was observed. The square roots of these corrected intensities gave the observed structure factors.

The refinement

The three-dimensional refinement was carried out on the computer, EDSAC II, in the Mathematical Laboratory, University of Cambridge, using a difference synthesis program by Wells (1961).

[1] Cavendish Laboratory, University of Cambridge.
[2] University of Manitoba.

Table 1. Composition and cell dimensions of low albite from Ramona, California.

Composition (Emmons (1953))

	mol. %
$KAlSi_3O_8$(Or)	1.0
$NaAlSi_3O_8$(Ab)	98.5
$CaAl_2Si_2O_8$(An)	0.5

Cell dimensions (Ferguson, Traill and Taylor (1958))

a	8.138 Å	$d(100)$	7.299 ± 0.005 Å
b	12.789 Å	$d(010)$	12.752 ± 0.001 Å
c	7.156 Å	$d(001)$	6.388 ± 0.002 Å
α	94°20′	α^*	$86°20′ \pm 02′$
β	116°34′	β^*	$63°32′ \pm 02′$
γ	87°39′	γ^*	$90°28′ \pm 02′$

Volume of cell	664.2 Å³
Calculated density	2.623 g cm⁻³
Space group	$C\bar{1}$

The history of the refinement is given in Table 2. The initial R-factor was 0.149, using the parameters of Ferguson, Traill and Taylor (1958). This reduced to 0.112 after a number of cycles. At this stage a single isotropic sodium atom was still being used, in spite of the evidence of anisotropy or "splitting" given by Ferguson, Traill and Taylor (1958) and confirmed by Williams (1961). Interatomic distances and

Table 2. History of the three-dimensional refinement of low albite.

Stage of refinement	$R = \dfrac{\sum \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert}{\sum \lvert F_o \rvert}$	Figure number	Comments
0	0.149		Parameters of Ferguson, Traill and Taylor (1958).
I	0.112	1a, 2a	Isotropic sodium at $x = .2686$, $y = .9883$, $z = .1472$.
IIa	0.104		"Split" sodium coordinates modified from Williams (1961).
IIb	0.101		Refined "split" sodium position.
III	0.095	1b, 2b	Final parameters, using $f_{Al}3+$ for $T_1(0)$ and $f_{Si}4+$ for $T_1(m)$, $T_2(0)$ and $T_2(m)$.

angles were then calculated for purposes of future comparison. The environment of the sodium atom is shown in Figures 1a and 2a, indicating its pronounced anisotropy.

Williams (1961) found that the sodium atom in low albite was "split" at room temperature by 0.017 Å in the x- and 0.285 Å in the y-direction. He did not determine the z-coordinates. He further discovered that at $-180\,°C$ the "splitting" was nearly the same ($x = 0.018$ Å; $y = 0.258$ Å; $z = 0.089$ Å) and therefore postulated that sodium in low albite occupies two distinct positions in its cavity quite at random.
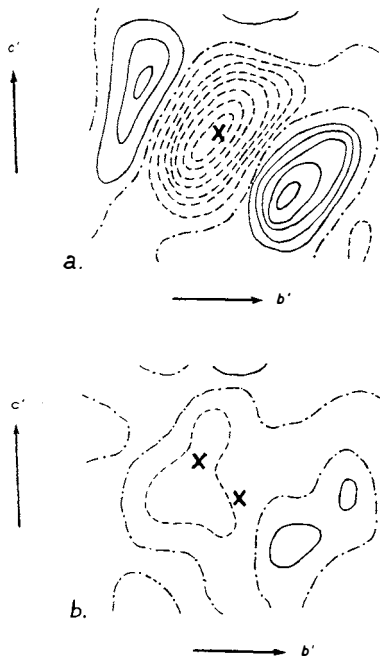

Figure 1. The sodium environment of low albite:

$(\varrho_o - \varrho_c)$ projected along [100]. Positive contours are in solid lines, zero contour in chained lines, and negative contours in dashed lines.

(a) Stage I,   (b) Stage III.
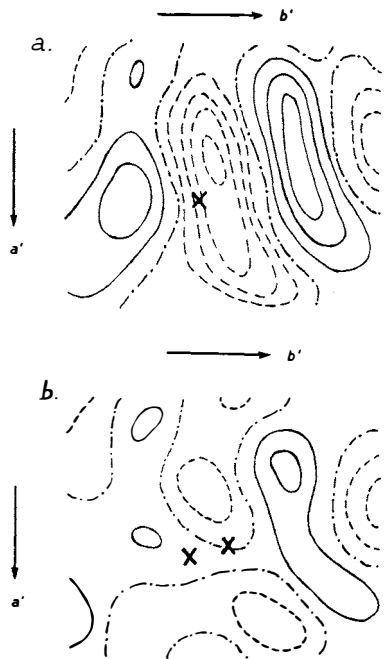
Figure 2. The sodium environment of low albite:

$(\varrho_o - \varrho_c)$ projected along [001]. Convention for contours as in Figure 1.

(a) Stage I,   (b) Stage III.

The refined sodium position (Stage I) was then used as a median point from which Williams' splittings were applied. An immediate improvement was registered, and as the split half-atom positions refined the R-factor eventually reached 0.101.

At this point, a 0.350 Å splitting was indicated for the Na_1–Na_2 half-atoms. The $(\varrho_o - \varrho_c)$ maps in Figures 1b and 2b show their final positions in projections along [100] and [001]. Until this time an average atomic scattering factor curve had been used for the T (for Tetrahedral) atom, $Al_{\frac{1}{4}}Si_{\frac{3}{4}}$, assuming a completely random distribution of Al/Si in the tetrahedral sites. But the bond lengths calculated at Stage I has indicated that the Al^{3+} predominately occupied the $T_1(0)$ site (Smith (1954); Smith and Bailey (forthcoming)), and in a final cycle the $T_1(0)$ atom was given the scattering curve for Al^{3+} and the other T atoms were given the Si^{4+} curve. The R-factor dropped to 0.095, and work was discontinued.

Table 3. The atomic coordinates of low albite in decimal fractions of the unit-cell dimension.

	x	y	z
$O_A(1)$	.0057	.1307	.9669
$O_A(2)$	.5923	.9972	.2801
$O_B(0)$	.8124	.1102	.1904
$O_B(m)$	.8205	.8517	.2585
$O_C(0)$	.0140	.3032	.2695
$O_C(m)$	.0239	.6934	.2292
$O_D(0)$	.2068	.1086	.3894
$O_D(m)$	.1838	.8682	.4352
$T_1(0)$	.0087	.1695	.2083
$T_1(m)$	.0044	.8203	.2378
$T_2(0)$	.6919	.1103	.3148
$T_2(m)$	.6814	.8819	.3605
Na_1	.2715	.9779	.1613
Na_2	.2651	.9993	.1310

The final atomic coordinates based on this three-dimensional refinement are given in Table 3. Except for Na, they do not differ from those calculated at the end of Stage I, nor do the final bond lengths and bond angles which are shown in Table 4.

Table 4. Interatomic distances and interbond angles of low albite calculated from the final three-dimensional parameters.

Mean Oxygen-Oxygen distances.

Tetrahedron	Mean O–O distance
$T_1(0)$	2.844 Å
$T_1(m)$	2.629 Å
$T_2(0)$	2.636 Å
$T_2(m)$	2.631 Å

Al/Si–O Distances.

$T_1(0)–O_A(1)$	1.751	
$-O_B(0)$	1.745	1.744 Å
$-O_C(0)$	1.730	
$-O_D(0)$	1.751	
$T_1(m)–O_A(1)$	1.604	
$-O_B(m)$	1.601	1.610 Å
$-O_C(m)$	1.623	
$-O_D(m)$	1.612	
$T_2(0)–O_A(2)$	1.635	
$-O_B(0)$	1.592	1.616 Å
$-O_C(m)$	1.614	
$-O_D(m)$	1.621	
$T_2(m)–O_A(2)$	1.643	
$-O_B(m)$	1.620	1.613 Å
$-O_C(0)$	1.585	
$-O_D(0)$	1.602	

Mean Interbond Angles.

$O–T_1(0)–O$	109°22′
$O–T_1(m)–O$	109°29′
$O–T_2(0)–O$	109°25′
$O–T_2(m)–O$	109°25′
T–O–T	140°17′

Accuracy and conclusions

The standard deviations of coordinates have at this point only been roughly calculated, and for that reason are not given here. It is expected that they will show considerable improvement over those given in Ferguson, Traill and Taylor (1958) for the two-dimensional

case. Interpretations of the results of this structural analysis of low albite will appear elsewhere after a more detailed study of the three-dimensional difference map is completed.

Acknowledgements

REFERENCES

EMMONS, R. C., ed. (1953): Selected petrogenic relationships of plagioclase. Geol.Soc. Amer., Mem. 52, p. 19.

FERGUSON, R. B., TRAILL, R. J. and TAYLOR, W. H. (1958): The crystal structures of low-temperature and high-temperature albites. Acta Cryst., vol. 11 (1958) pp. 331.

SMITH, J.V. (1954): A review of the Al–O and Si–O distances. Acta Cryst., vol. 7 (1954) pp. 479.

WELLS, M. (1961): Two structures in the system $(Na,K)NbO_3$ and some programs for EDSAC II. Ph. D. Thesis, Cambridge.

WILLIAMS, P. P. (1961): A study of apparently anisotropic atoms using low-temperature X-ray methods. Ph.D.Thesis, Cambridge.