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A neutron-diffraction study of the crystal structure of analcime, $NaAlSi_2O_6 \cdot H_2O$

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Auszug

Die Kristallstruktur des Analcims, $NaAlSi_2O_6 \cdot H_2O$, nach Röntgen-Untersuchungen zur Raumgruppe $Ia3d$ gehörend, wurde mittels Neutronenbeugung überprüft. Es wurden die Intensitäten der Reflexe in einem Oktanten des reziproken Gitters registriert, der außer der kubischen Symmetrie auch einigen geringer-symmetrischen Systemen entspricht. Die systematischen Auslöschungen entsprechen der Raumgruppe $Ia3d$; innerhalb der Fehlergrenzen stimmen die Intensitäten der sechs in der Lauegruppe $m3m$ symmetrischen Interferenzen überein. Aus Fourier-Differenz-Synthesen und Verfeinerung nach der Methode der kleinsten Quadrate folgt, daß die Neutroneninterferenzen wie die Interferenzen der Röntgenstrahlen im Einklang mit einer gemittelten $Ia3d$-Struktur sind. Die Vollmatrix-Verfeinerung ergab $R = 0{,}044$ für 194 unabhängige Reflexe. Die H-Atome sind über die Lagen $32e$ und $96h$ verteilt und nicht an Wasserstoffbindungen beteiligt. Der für den Winkel H—O—H gefundene Wert ist wahrscheinlich ein Mittelwert aus den verschiedenen Stellungen der Wassermoleküle in der Struktur; es wird versucht, dafür eine Deutung anhand statischer und dynamischer Modelle zu geben.

Abstract

The crystal structure of the mineral analcime, $NaAlSi_2O_6 \cdot H_2O$, known from x-ray analysis to approximate closely to the cubic space-group symmetry $Ia3d$, has been examined by neutron diffraction. Intensity data from a single crystal were collected for one octant so as to be representative of cubic and some lower symmetries. In general, the systematic absences were consistent with the space group $Ia3d$; within experimental error, the six reflections equivalent for Laue group $m3m$ were equal in intensity. From Fourier difference syntheses and least-squares refinements, it is concluded that the neutron data, like the x-ray data, are consistent with an averaged $Ia3d$ structure. Full-matrix

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least-squares refinement with the constraints required by the $Ia3d$ space group gave a final R value of 0.044 over 194 independent reflections. Hydrogen atoms are distributed in $32e$ and $96h$ positions and are not engaged in hydrogen bonds. Apparent values for the H—O—H angle probably depend on the averaging of arrangements for the water molecules; interpretations are suggested in terms of static and dynamic models.

Introduction

The hydrated alkali aluminosilicate analcite, or analcime, $NaAlSi_2O_6 \cdot H_2O$, occurs fairly widely in rocks, often in association with other zeolites (Deer, Howie and Zussman, 1963). Its essential crystal structure was established by Taylor (1930) but several other x-ray studies have been made (Taylor, 1938; Nàray-Szabò, 1938; Calleri and Ferraris, 1964; and Knowles, Rinaldi and Smith, 1965) in view of the apparent incompatibility with cubic symmetry of certain properties, both physical (especially the weak but definite optical birefringence of some samples) and chemical (particularly the remarkable constancy of the Al/Si ratio among naturally occurring analcites). As a result, the most plausible crystal structure involves 16 formula units in a cubic unit cell of space group $Ia3d$, with a random distribution of 16 aluminium and 32 silicon atoms on the $48g$ positions and a random distribution of 16 sodium atoms in the $24c$ positions; anionic oxygen atoms are in $96h$ general positions and water-oxygen atoms in $16b$ positions. Anionic oxygen atoms are shared between linked $(Si,Al)O_4$ tetrahedra so as to form an aluminosilicate framework involving rings of six and four tetrahedra. The water molecules are confined to channels within this framework, and the sodium ions are coordinated by four anionic oxygen atoms from this framework and by two water molecules.

Attempts at x-ray refinement of structural models of different symmetry, such as space group $I4_1/acd$, have been unsuccessful (Calleri and Ferraris, 1964). While the systematic absences conform to $Ia3d$ for most samples, some specimens show a few weak reflections, such as 200, which should be forbidden in this space group (Knowles, Rinaldi and Smith, 1965). The weak birefringence and other anomalies would require that the cubic symmetry be debased; this could be a consequence of the hydrogen-atom positioning and/or of ordering of the aluminium and silicon atoms, possibly with corresponding selective positioning of the sodium atoms. X-ray diffraction is somewhat insensitive to two of these effects: hydrogen scattering is weak; and the atomic scattering factors of Al^{3+} and Si^{4+} are very similar.

Moreover, lack of close O · · · O contacts involving the water molecules prevents inference of hydrogen sites from the plausible hydrogen bonds.

There are 32 hydrogen atoms in the unit cell and there is a special position (32*e*) of 32-fold multiplicity along the threefold axes of the cell. Not all the hydrogen atoms can occupy this position, however, since a linear water molecule would be implied. If the hydrogen atoms are ordered, then the symmetry must be lower than cubic, whereas for cubic symmetry there must be a degree of disorder.

Since aluminium and silicon have appreciably different scattering lengths for neutrons (0.35 and 0.42×10^{-12} cm, respectively), and since hydrogen has a scattering length comparable in magnitude (-0.372×10^{-12} cm) to those of the other elements present, it should be possible to resolve both the aluminium/silicon and the hydrogen-atom problems by neutron diffraction.

Experimental

Neutron intensity data were collected from a single crystal of analcime (Cyclopean Islands, sample no. 6612 from the collection of the Mineralogical Institute of the University of Turin) which showed a large cube face and some smaller faces of type $\{hk0\}$, had cross-section 4.5 × 4.5 mm, and was 3.0 mm thick. It was transparent and weakly birefringent, with extinction along [100] in the cube face.

The crystal was mounted with the [110] direction parallel to the φ axis of an automatic four-circle single-crystal neutron diffractometer at the PLUTO reactor at Atomic Energy Research Establishment, Harwell. Intensity data were collected at a wavelength monochromatized to 1.148 Å, with an ω-2θ step scan (22 steps of 0.08° in ω for the peak, and 4 steps on each side for the background; monitor count, 4×10^4). A typical background count for one step was 10—20; for the strongest reflection, the measured integrated intensity was 48,000 counts. Setting angles were computed for a cubic unit cell with $a = 13.73$ Å, the value from the latest x-ray studies (Calleri and Ferraris, 1964; Knowles, Rinaldi and Smith, 1965); this cell was used in all subsequent calculations. Data were collected for one complete octant to $2\theta = 100°$, for a body-centred unit cell. In addition, data for one octant to $2\theta = 30°$ were collected for a primitive cell; some reflections expected to be extinguished for space group *Ia3d*, but found to be non-zero, were re-measured with a monitor count five times greater than for the first measurements. None of these reflections had an integrated intensity significantly greater than its standard deviation, even with the increased counting time. The only observation in apparent violation of the *Ia*3*d* symmetry (200, with 020, 002, for which $|F_o| = 1.43 \times 10^{-12}$ cm) could be explained only partly as a $\lambda/2$ reflection from the very intense 400 reflection.

The punched-tape diffractometer output was converted to structure factors, with their standard deviations (based on counting statistics), by an ATLAS programme written by N. A. Curry. No absorption or extinction corrections were made. Nuclear scattering lengths used in the calculations were: H, −0.372; O, 0.577; Na, 0.35; Al, 0.35; Si, 0.42×10^{-12} cm (Bacon, 1969).

Order/disorder in analcime

Examination of the neutron intensity data showed that, within expected experimental error ($< \pm 10^{-12}$ cm on $|F_o|$), the six reflections which (in the general case) should be equivalent for the Laue group *m*3*m* had equal intensities. A "cubic unique set" of data was computed by averaging the six (or fewer) values of $|F_o|$ for the "cubic equivalent reflections" in the octant. This gave a set of 254 non-zero independent reflections; sixty of these were later excluded from the refinement because they were weak ($|F_o| \leq 1.5 \times 10^{-12}$ cm on the absolute scale and $|F_c| < |F_o|$).

Accordingly, a difference Fourier synthesis was computed in space group *Ia*3*d* with the atomic parameters given by Calleri and Ferraris (1964), i.e. with the oxygen atoms in 96*h*, Al/Si atoms randomly distributed in the 48*g* positions, and sixteen sodium atoms randomly distributed in the 24*c* positions. It showed only two negative peaks on a negative background around the water-oxygen atom: one on the threefold axis in a 32*e* position and another in a general 96*h* position. Thus a total of 128 sites is available for the 32 hydrogen atoms. The Fourier-peak heights suggested an occupancy of one quarter for each position (i.e., a total of eight H atoms in 32*e*, and 24 in 96*h*).

In order to check the Al/Si disorder and the Na-atom distribution, two least-squares refinements by the ORFLS programme (Busing, Martin and Levy, 1962) were carried out as follows, with the original full octant of structure-factor data:

1. In simulated triclinic symmetry, with atomic coordinates derived from the application of the symmetry operations of space

group $Ia3d$ to the coordinates given by CALLERI and FERRARIS (1964), the neutron scattering lengths were refined for six independent sodium atoms and twelve independent Al/Si atoms. The starting values of the variables were two thirds of the normal scattering length for sodium, and the weighted mean $(\mathrm{Al} + 2 \cdot \mathrm{Si})/3$ for Al/Si.

2. In simulated triclinic symmetry, with atomic coordinates derived from the application of the $I4_1/acd$ symmetry operations to the coordinates given by CALLERI and FERRARIS for this space group, the neutron scattering lengths were refined for four sodium atoms, four aluminium atoms, and eight silicon atoms. In this case, the starting values of the variables were the normal scattering lengths for these atoms.

Whereas no significant changes occurred in (1), in (2) the scattering lengths of the sodium atoms all decreased from the normal value of 0.35 to an average value of 0.26×10^{-12} cm, and the Si and Al scattering lengths became less disparate. These changes favour the existence of disordered cubic symmetry.

Least-squares refinement of the cubic structure

The starting parameters for the least-squares refinement were those from the CALLERI and FERRARIS x-ray refinement for Na, Al/Si, and O, together with hydrogen coordinates from the cubic neutron

Table 1. *List of observed and calculated structure factors*

h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c
4 0 0	32.35	-33.80	11 2 1	12.30	11.63	16 2 2	1.97	- 2.12	12 5 3	2.03	- 1.75	15 6 5	6.32	7.08
8	32.59	32.55	17	6.98	- 6.63	3 3 2	13.77	13.82	14	1.64	- 1.87	8 7 5	4.95	4.80
12	12.93	-12.61	4 3 1	5.81	- 5.92	5	14.05	13.69	16	3.40	3.12	10	5.01	4.93
16	11.00	-10.96	6	6.19	6.20	7	14.72	-14.57	7 6 3	10.67	10.83	12	2.69	2.86
2 2 0	6.57	- 6.56	8	12.02	11.81	9	5.30	5.73	9	12.75	12.58	16	5.72	- 5.50
4	4.01	4.10	10	8.22	8.24	11	3.13	- 2.79	13	2.42	- 2.21	9 8 5	2.17	- 2.18
6	4.86	4.84	12	7.28	- 7.08	13	2.98	2.64	15	2.86	2.96	11	3.93	- 4.44
8	7.90	- 7.89	14	1.67	- 1.84	15	2.71	- 2.69	17	3.58	- 3.44	13	4.34	4.60
10	5.40	- 5.58	16	2.37	2.30	17	8.58	- 8.08	8 7 3	3.10	- 3.17	15	6.26	5.97
12	4.53	4.47	5 4 1	4.56	4.18	6 4 2	2.50	- 2.58	10	4.12	- 4.31	10 9 5	10.55	10.11
14	1.79	1.65	7	6.91	6.89	8	4.79	- 4.92	16	1.43	1.51	11 10 5	2.33	2.17
16	8.22	- 8.40	11	3.87	- 3.62	10	3.28	3.25	9 8 3	5.04	5.20	13	4.29	- 5.30
4 4 0	5.36	5.23	13	1.82	1.81	12	3.40	3.17	10 9 3	2.37	2.20	12 11 5	3.58	- 3.77
6	19.05	19.34	15	5.23	5.38	16	7.24	- 7.48	14	7.06	- 7.08	8 6 6	4.17	- 4.30
8	7.38	- 7.11	6 5 1	7.39	7.52	5 5 2	10.43	- 9.91	11 10 3	4.83	- 5.57	12	5.19	5.04
10	14.18	-13.96	8	4.56	4.24	7	10.37	10.20	15	5.31	4.52	16	1.61	- 1.36
12	4.58	4.52	10	15.85	15.42	11	6.08	- 6.15	12 11 3	3.93	4.86	7 7 6	15.61	-15.31
14	13.05	12.87	12	5.55	- 4.86	15	4.02	4.36	4 4 4	10.37	10.26	9	8.11	7.60
16	11.98	12.38	14	2.89	- 3.08	8 6 2	2.86	3.05	8	6.98	- 6.68	11	1.61	- 1.44
6 6 0	7.21	- 7.59	16	2.95	2.89	12	3.36	- 3.17	12	3.22	- 3.42	13	3.22	- 3.69
8	12.58	12.52	7 6 1	3.22	- 3.42	16	1.43	1.46	13 5 4	2.32	2.44	15	3.76	- 4.43
10	2.33	2.30	9	12.75	-12.50	7 7 2	19.13	18.92	17	4.29	- 4.02	12 10 6	2.15	- 2.01
12	8.51	- 8.47	11	6.88	- 6.25	9	5.45	- 5.23	6 6 4	2.50	2.43	11 11 6	3.58	3.96
14	4.10	- 3.78	13	5.96	6.13	11	1.73	1.80	8	1.43	1.26	13	4.83	- 5.44
8 8 0	10.37	10.29	15	2.42	- 2.33	13	1.81	1.89	10	3.10	3.09	10 7 7	4.73	4.81
10	10.01	9.70	8 7 1	13.94	-13.80	15	5.99	6.20	16	7.87	- 6.92	9 8 7	6.11	- 6.09
12	2.06	- 2.13	10	5.75	- 5.60	10 8 2	3.93	- 4.02	9 7 4	1.97	2.06	11	2.86	- 3.03
14	4.46	- 4.67	12	6.83	6.22	9 9 2	13.29	-13.20	11	3.40	- 3.23	10 9 7	5.55	- 6.06
16	7.51	- 7.13	14	3.44	3.74	13	6.35	6.79	14 8 4	3.67	- 3.66	12	1.43	1.64
10 10 0	4.65	- 4.21	11 8 1	9.84	9.36	15	5.01	- 4.31	11 9 4	1.43	- 1.56	14	5.01	6.03
14	3.39	3.57	13	2.90	- 3.05	12 10 2	4.02	3.91	12 10 4	2.50	2.72	11 10 7	5.72	6.26
2 1 1	12.10	12.52	15	11.44	-10.66	6 3 3	8.11	- 8.43	12 12 4	3.58	- 3.79	13	4.83	- 5.40
6	12.87	-13.22	10 9 1	7.33	- 6.83	10	9.05	9.21	6 5 5	3.46	- 3.51	8 8 8	8.22	7.96
10	14.77	-14.33	14	1.79	- 1.86	15	3.58	4.85	10	19.01	-18.41	12	4.73	- 5.65
14	6.25	5.99	11 10 1	5.19	5.28	9 4 3	2.38	- 2.12	14	3.58	3.56	11 9 8	5.28	6.40
18	5.19	- 4.28	13	4.12	3.99	11	2.11	- 2.23	7 6 5	6.35	6.23	12 10 8	2.33	- 2.48
3 2 1	4.82	4.97	4 2 2	5.12	5.23	6 5 3	5.12	- 4.71	9 6 5	10.16	9.38	10 9 9	13.41	-14.83
7	3.26	3.05	8	4.29	- 4.52	8	3.29	- 3.34	11	7.19	- 7.06	11 10 9	2.86	2.93
9	4.02	3.95	12	3.82	3.65	10	13.64	13.31	13	5.96	- 5.95			

Table 2. *Final fractional atomic coordinates together with refined values of thermal parameters* B_{ij} *(Å^2) (above) and* U_{ij} *(below).* Estimated standard deviations are given in parentheses

Atom	x/a	y/b	z/c	B_{11} U_{11}	B_{22} U_{22}	B_{33} U_{33}	B_{12} U_{12}	B_{13} U_{13}	B_{23} U_{23}
O	0.10428(14)	0.13440(16)	0.21932(12)	3.02(8) 0.00401(11)	3.63(9) 0.00482(12)	1.65(6) 0.00219(8)	0.44(6) 0.00058(8)	0.47(5) 0.00062(6)	0.23(6) 0.00031(8)
Si/Al	0.66208(15)	-0.41208(15)	0.12500	1.23(6) 0.00163(8)	1.23(6) 0.00163(8)	1.46(10) 0.00194(13)	-0.10(8) -0.00013(10)	0.11(6) 0.00014(8)	0.11(6) 0.00014(8)
Na	0.12500	0.00000	0.25000	3.32(38) 0.0044(5)	2.94(23) 0.0039(3)	2.94(23) 0.0039(3)	— —	— —	-1.28(30) -0.0017(4)
W (water oxygen)	0.12500	0.12500	0.12500	6.64(23) 0.0088(3)	6.64(23) 0.0088(3)	6.64(23) 0.0088(3)	2.04(45) 0.0027(6)	2.04(45) 0.0027(6)	2.04(45) 0.0027(6)
H(1)	0.0791(37)	0.0791(37)	0.0791(37)	10.0(2.1) 0.0133(28)	10.0(2.1) 0.0133(28)	10.0(2.1) 0.0133(28)	-1.5(2.5) -0.0020(33)	-1.5(2.5) -0.0020(33)	-1.5(2.5) -0.0020(33)
H(2)	0.1402(20)	0.1006(29)	0.0548(23)	6.3(1.2) 0.0084(16)	11.5(2.2) 0.0153(29)	5.9(1.2) 0.0079(16)	0.5(1.2) 0.0006(16)	3.2(1.1) 0.0043(15)	0.5(1.1) 0.0006(15)

Table 3. *Bond lengths and bond angles of* Si/Al *polyhedron*
Estimated standard deviations in parentheses. (See Fig. 1)

Si/Al(I)–O(I)	1.647(2) Å	O(I) –Si/Al(I)–O(II)	112.2(1)°
Si/Al(I)–O(III)		O(I) –Si/Al(I)–O(III)	104.2(1)
		O(I) –Si/Al(I)–O(IV)	111.2(1)
Si/Al(I)–O(II)	1.649(2)	O(II) –Si/Al(I)–O(III)	111.2(1)
Si/Al(I)–O(IV)		O(II) –Si/Al(I)–O(IV)	106.0(1)
O(I) –O(II)	2.737(3)	O(III)–Si/Al(I)–O(IV)	112.2(1)
O(III)–O(IV)		O(I) –O(IV)–O(I′)	148.5(1)
O(I) –O(III)	2.599(3)	O(I) –O(IV)–O(II′)	108.2(1)
O(II) –O(IV)	2.633(3)	O(I) –O(IV)–O(III′)	141.9(1)
O(I) –O(IV)	2.720(3)	O(II) –O(IV)–O(I′)	138.5(1)
O(II) –O(III)		O(II) –O(IV)–O(II′)	156.0(1)
		O(II) –O(IV)–O(III′)	115.6(1)
Si/Al(I)–Si/Al(I′)	3.137(2)	O(III)–O(IV)–O(I′)	147.6(1)
		O(III)–O(IV)–O(II′)	95.2(8)
		O(III)–O(IV)–O(III′)	87.5(8)
		Si/Al(I)–O(IV)–Si/Al(I′)	144.3(2)

Fourier (eight hydrogen atoms randomly distributed in 32*e*, and twenty-four in 96*h*). A full-matrix least-squares refinement with the ORFLS programme (Busing, Martin and Levy, 1962) was subject to the following constraints required by the symmetry:

Silicate O : no constraints;
Si/Al : $y = \frac{1}{4} - x$, $B_{22} = B_{11}$, $B_{23} = B_{13}$;
Na : $B_{33} = B_{22}$, $B_{12} = B_{13} = 0$;

Water O (designated W) : $B_{11} = B_{22} = B_{33}$, $B_{12} = B_{13} = B_{23}$;
H(1) : $z = y = x$, $B_{11} = B_{22} = B_{33}$, $B_{12} = B_{13} = B_{23}$;
H(2) : no constraints (Peterse and Palm, 1966).

With unitary weights, the refinement converged successfully to a final R value of 0.044; Table 1 gives the final list of observed and calculated structure factors. A final difference Fourier synthesis showed only randomly distributed positive and negative peaks with maximum heights of about $\pm 0.02 \times 10^{-12}$ cm Å^{-3}, which is no greater than those found for other structures which we have studied recently (Ferraris, Jones and Yerkess, 1971*a*, 1971*b*).

Table 2 gives the final fractional coordinates (with estimated standard deviations in parentheses) of all the atoms, together with

Table 4. *Bond lengths and angles involving sodium atom and water molecule*
Estimated standard deviations in parentheses. (See Fig. 2)

Na(1)—W(1) Na(1)—W(2)	2.427(2) Å	O(1)—O(2) O(3)—O(4)	2.599(3) Å
Na(1)—O(1) Na(1)—O(2) Na(1)—O(3) Na(1)—O(4)	2.499(2)	O(2)—O(3) O(1)—O(4)	4.275(3)
Na(1)—O(7) Na(1)—O(9) Na(1)—O(13) Na(1)—O(14)	3.673(2)	W(1)—Na(1)—W(2)	180°
O(1)—O(7)	2.633(2)	O(1)—Na(1)—O(2) O(3)—Na(1)—O(4)	117.6(1)°
W(1)—O(1) W(1)—O(3) W(1)—O(5) W(1)—O(7) W(1)—O(9) W(1)—O(11)	3.406(2)	O(2)—Na(1)—O(3) O(1)—Na(1)—O(4)	62.7(1)
W(1)—O(2) W(1)—O(4) W(1)—O(6) W(1)—O(8) W(1)—O(10) W(1)—O(12)	3.560(2)	W(1)—Na(1)—O(1) W(1)—Na(1)—O(3)	87.5(1)
W(2)—O(1) W(2)—O(3)	3.560(2)	W(1)—Na(1)—O(2) W(1)—Na(1)—O(4)	92.5(1)
W(2)—O(2) W(2)—O(4)	3.406(2)	W(1)— O(1)—W(2)	88.3(1)
		W(2)—Na(1)—Na(2)	120°
		O(1)— W(1)—O(3)	94.3(1)
		O(2)— W(1)—O(4)	89.1(1)
		O(1)— W(1)—O(4) O(2)— W(1)—O(3)	75.7(1)
		O(3)— W(1)—O(4) O(1)— W(1)—O(2)	43.8(1)

B_{ij} coefficients in the expression $\exp\{-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\}$ and refined values of the U_{ij} thermal parameters. In Table 3, which lists the most important bond lengths and angles in the Si/Al polyhedron, the labelling follows that of Fig. 1; Fig. 2 shows the arrangement of Na atoms and water molecules corresponding to Table 4. Table 5 gives the orientation parameters for the thermal ellipsoids of all the atoms.

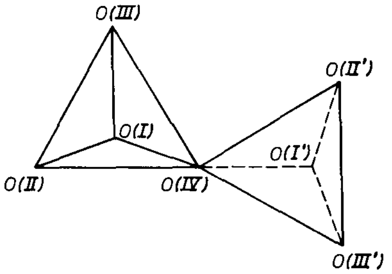

Fig. 1. Atomic arrangement in two contiguous silicon tetrahedra. Oxygen coordinates here and in Table 3 are: O(I): x, y, z; O(II): $\frac{1}{4} - x, -\frac{3}{4} + z, \frac{3}{4} - y$; O(III): $\frac{1}{4} - y, \frac{1}{4} - x, 1\frac{1}{4} - z$; O(IV): $1 - z, x, \frac{1}{2} + y$; $x = 0.1043$, $y = 0.1344$; $z = 0.7193$

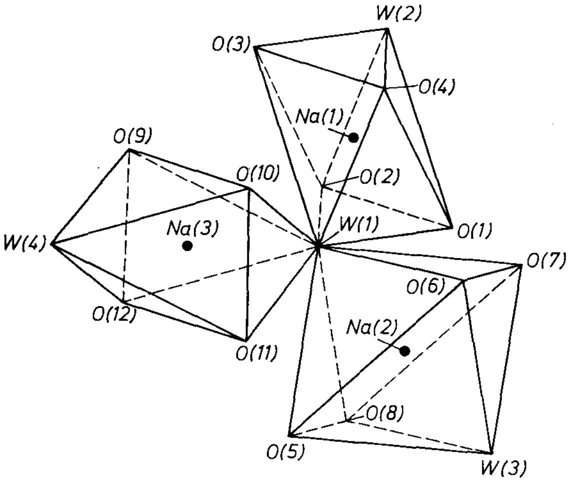

Fig. 2. Arrangement of three sodium polyhedra around water site. Oxygen coordinates here and in Table 4 are: O(1): x, y, z; O(2) $\frac{1}{4} - x, -\frac{1}{4} + z, \frac{1}{4} + y$; O(3) $\frac{1}{4} - x, \frac{1}{4} - z, \frac{1}{4} - y$; O(4) $x, -y, \frac{1}{2} - z$; $x = 0.2193$; $y = -0.1043$; $z = 0.1344$

Discussion

Hydrogen atoms apart, the present analysis confirms the essential features of the crystal structure of analcite reported previously (Calleri and Ferraris, 1964; Knowles, Rinaldi and Smith, 1965). Thus the 32 Si and 16 Al atoms are disordered in their sharing of a common set of 48 equivalent sites, and the 16 Na atoms have a disordered distribution over the 24 sites available to them. Whereas Knowles, Rinaldi and Smith (1965) reported eight oxygen atoms

Table 5. *Parameters characterizing the principal directions* 1, 2, 3 *of thermal vibration for the atoms: root-mean-square displacements (A) and angles which the principal directions make with the x (B), y (C) and z (D) axes*

Arrows indicate that the orientation of the ellipsoid of revolution is not defined

		A	*B*	*C*	*D*
O	1	0.19 Å	35°	122°	78°
	2	0.22	60	32	79
	3	0.14	106	93	16
Si/Al	1	0.13	45	135	90
	2	0.14	75	75	21
	3	0.12	49	49	111
Na	1	0.21	0	90	90
	2	0.23	90	135	45
	3	0.15	90	45	45
W (water oxygen)	1	0.33	↷	↷	↷
	2	0.33	↷	↷	↷
	3	0.18	54.7	54.7	54.7
H(1)	1	0.38	↷	↷	↷
	2	0.38	↷	↷	↷
	3	0.30	54.7	54.7	54.7
H(2)	1	0.34	45	105	49
	2	0.39	79	15	79
	3	0.19	133	90	43

distant 3.68 Å from a sodium atom, Table 4 and Fig. 2 indicate that there are only four. It will be seen from Fig. 2 that the water-oxygen atom lies at the common vertex of three sodium polyhedra. The closest approach of other oxygen atoms to the water oxygen is 3.406 Å (Table 4).

The distribution found for the hydrogen atoms implies that half of the water molecules have one hydrogen atom in a 32*e* position and the other in a 96*h* position. Crystallographically, there are 12 such arrangements, plus one (which would require a linear water molecule) in which both hydrogen atoms are in a 32*e* position. The remaining half of the water molecules have both hydrogen atoms in 96*h* sites in fifteen possible H-O-H arrangements. Figure 3 shows the six equivalent 96*h* and two 32*e* positions associated with the oxygen

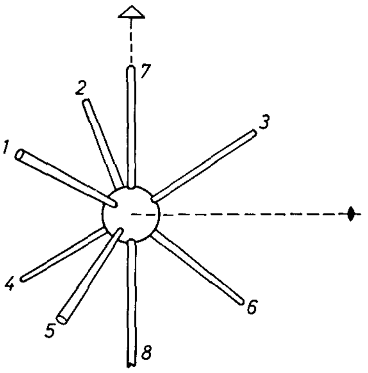

Fig. 3. Potential sites for water-hydrogen atoms. 96*h* sites are labelled 1—6 and 32*e* sites are labelled 7, 8. Thus the group of sites 1—3 is related by three twofold axes (one of which is shown) to the group 4—6, while individual members of each of the groups are related by the threefold axis. Positions 7 and 8 lie along the threefold axis

atom of the water molecule. The final refinement leads to the following apparent H—O—H angles:

H(1)—W—H(2) = 87(3)°; H(1)—W—H(4) = 129(3)°;
H(1)—W—H(5) = 137(3)°; H(1)—W—H(6) = 74(3)°;
H(7)—W—H(4) = 127(3)°; and H(7)—W—H(1) = 53(3)°.

While the water molecules may be expected to take up any of the orientations in Fig. 3 (or their symmetry equivalents), none of the above angles accords with the normal geometry of the water molecule. Evidently, overlap of the various symmetry-equivalent true hydrogen positions gives an average from which the above apparent angles have been derived. The large temperature factors found for the hydrogen atoms and for the water-oxygen atoms may be indicative of substantial disorder.

A plausible model for the hydrogen-atom positions could be the following. For every group of three Na polyhedra, there is one polyhedron without its Na atom [say Na(1) in Fig. 2]; one of two water molecules [e.g. W(1)] of this polyhedron has one hydrogen atom on the threefold axis [at 2.903 Å from O(6), O(10) and O(2)] and the second one on the general position 96*h*. The second water molecule [W(2) in Fig. 2] could have both its hydrogen atoms in the general position with at least one of them inside the empty Na polyhedron. According to this model, every group like that in Fig. 2 accounts for one hydrogen atom in 32*e* (eight for the eight groups in the unit cell) and three in 96*h* (i.e. 24 for the eight groups in the unit cell). (If silicon and aluminium atoms are statistically distributed, the same could be true for the empty Na polyhedron and water molecules). There are two further possibilities. In its normal chemical configuration, each water molecule may jump from one position to the next in a field of cubic symmetry. Alternatively, the "single" crystals of analcime may in reality be multiple twins approximating to cubic symmetry. In the latter case, true single crystals must be in a space group devoid of threefold axes and with a multiplicity of general positions no higher than eight; otherwise, hydrogen atoms could not be arranged around the oxygen atom in an ordered way.

That a deficiency or abundance of water molecules as revealed by chemical analysis (e.g. DEER, HOWIE and ZUSSMAN, 1963) could be responsible for optical anomalies is not unreasonable in the light of the structure. Absence of bonding to the water molecule means that some variation in orientation is more likely than a fixed one and that some deficiency can be tolerated; moreover the cavity within the empty sodium polyhedron is large enough to accommodate additional water molecules, possibly with strong hydrogen bonds.

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