may be derived by stacking and in-filling of Kagomé nets perpendicular to a threefold axis, which includes the structures of the different types of Friauf-Laves phases. The symbol describing the layer sequence for $MgNi_2$ is: △△▽▽ and for the μ phase: |△0|. In our description the Kagomé nets are perpendicular to the plane of the paper containing the horizontal rows of secondary-net atoms. The Frank & Kasper symbols define our sequence in the vertical direction by replacing △ by *L*, ▽ by *R* and 0 by *V*.

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The Crystal Sructure of Yugawaralite

BY I. S. KERR AND D. J. WILLIAMS

The Physical Chemistry Laboratories, Department of Chemistry, Imperial College, London, S.W.7, England

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A single crystal of yugawaralite $Ca_2Al_4Si_{12}O_{32}.8H_2O$ was examined by X-rays and 1700 non-zero intensities were measured. An $N(z)$ test indicated the absence of a centre of symmetry and the space group *Pc* was adopted. Structural analysis has revealed an alumino-silicate framework consisting of 8-, 5- and 4-membered rings. In the course of the refinement the calcium cation appeared coordinated by four oxygen atoms and four water molecules, and aluminum and silicon were shown to be in an ordered arrangement from consideration of interatomic distances. With isotropic temperature factors the final reliability index was 0·065 and the $N(z)$ based on F_{calc} almost coincided with that of F_{obs}. Yugawaralite is a zeolite not belonging to any recognized family. It possesses a two-dimensional system of channels approximately 3·6 × 2·8 Å free diameter.

Introduction

Yugawaralite was described by Sakurai & Hayashi (1952) as a mineral of the zeolite family having the formula $Ca_4Al_7Si_{20}O_{54}14H_2O$ and a density of 2·20 g.cm^{-3}. More recently a crystal of yugawaralite found at Heinabergsjøkull, south-eastern Iceland, by Walker (1969) was used for further X-ray studies by Barrer & Marshall (1965). By means of Weissenberg and precession photographs they determined the unit cell as monoclinic with: $a = 6{\cdot}73 \pm 0{\cdot}01$ Å, $b = 13{\cdot}95 \pm 0{\cdot}01$ Å, $c = 10{\cdot}03 \pm 0{\cdot}01$ Å, $\beta = 111°30' \pm 2'$, giving unit-cell contents, with a certain degree of rounding, as $Ca_2Al_4Si_{12}O_{32}.8H_2O$. They applied the statistical test of Howells, Phillips & Rogers (1950), and the $N(z)$ plot suggested the absence of a centre of symmetry. From this and the noting of systematic absences they proposed the space group *Pc*. The structure has been briefly described by Kerr & Williams (1967); in the present paper a full and final description of the structure is given which includes the ordering of aluminum and silicon, and the cation and water positions.

Experimental

The present investigation is a continuation of that of Barrer & Marshall (1965) with a crystal of size 0·2 × 0·2 × 0·2 mm from the same source. A Buerger precession camera and Mo $K\alpha$ radiation were used for the systematic collection of three-dimensional X-ray intensity data. As it is not possible with a precession camera to use multiple film techniques, owing to the different angles of incidence of the two beams giving rise to the same diffraction spot, photographic data were obtained by taking a series of timed exposures of 27, 9, 3 and 1 hours and in some cases 20 minutes. The crystal was mounted so that it rotated about its *b* axis, thus enabling data to be collected up the two shorter axes without needing to remount the crystal. By use of a precession angle of 32·5° the following layers were taken: *nkl* where $n = 0, 1, 2$ and 3, and *hkn* where $n = 0$, 1, 2, 3 and 4.

A Joyce–Loebl integrating microdensitometer (of the flying spot scanner type) was used for measurement of all the data of about 6000 diffraction spots. It was found necessary to measure the background beside each spot as well as the spot itself, since there was a non-uniform variation in background over the film. The difference then gave the integrated intensity, which was found to be reproducible. However, in comparing ratios from different exposures of the same diffraction, a certain non-linearity was encountered. The cause of this non-linearity is still not apparent, as the only diffractions measured were those falling in the linear range claimed by the manufacturers of both film and densitometer. The problem was overcome on this particular occasion by applying a correction function of the type:

$$I_{\text{correct}} = I_{\text{obs}} + aI^2_{\text{obs}} + bI^4_{\text{obs}},$$

where a and b were constants derived by considering the overlapping data.This enabled film and interlayer ratios to be determined so that all diffractions could be put on a common scale and those measured more than once could be averaged.

Buerger-type-Lorentz and polarization factors were then applied resulting in a final list of 1700 non-zero structure amplitudes. On account of the low absorption coefficient of 0·96 mm^{-1}, correction for absorption was deemed unnecessary. All the calculations described in this paper were performed on the University of London Atlas computer.

Structural analysis

A statistical test was carried out on all the structure factor data, including those diffractions of negligible intensity. The graph of $N(z)$ appears in Fig. 1 and confirms the acentric nature of the yugawaralite data. At the same time a three-dimensional sharpened Patterson map was computed which showed Harker peaks due to the glide plane. These peaks enabled the y coordinates of most of the strongly scattering atoms to be determined, and groups of three atoms were readily picked out. The groups of three were then assembled in a number of trial structures, of which only one gave a sensible arrangement of six Al, Si atoms. The first Fourier synthesis was calculated on the basis of just six Al, Si positions and yielded five oxygen positions. These were included in the input for a second Fourier which showed the remaining two Al, Si atoms, six more oxygen atoms and a high peak attributed to calcium. The remaining five oxygen atoms were judiciously placed midway between Al, Si atoms lying about 3·2 Å apart. It was subsequently realized that some of these oxygen atoms were placed rather badly compared with those revealed by the Fourier synthesis.

For the Fourier and subsequent least-squares calculations, semi-ionized scattering factors were used for aluminum, silicon and oxygen. These were taken from Volume III of *International Tables for X-ray Crystallography* (1962) interpolating where necessary. Non-ionized scattering factors were found not to give such good agreement as the semi-ionized. In the early stages a mean value was used for Al, Si, weighted in accordance with the chemical formula. The fully ionized scattering factor was used for calcium, and water was represented by oxygen.

The least-squares refinement was undertaken weighting reflexions equally; except for a few of the very strongest which were given a lighter weight. In due course, four weak peaks surrounding the calcium ion appeared on an electron density map, and were attributed to partial or complete occupation by water. A check was kept of the Al, Si–O distances but it was not until twelve cycles of least-squares that two tetrahedra emerged with greater distances than the rest. From this point on, the respective scattering factors were used for aluminum and silicon. After four further cycles, refinement ceased with the reliability index equal to 0·065, with isotropic temperature factors. It was decided to try anisotropic factors on the calcium, aluminum and silicon atoms, but after three cycles of least-squares this again ceased to refine having brought about a negligible improvement with $R = 0{\cdot}061$.

Finally, the statistical test was applied to the calculated structure factors. The result is shown in Fig. 1 where it can be seen almost to coincide with that of F_{obs}.

Description of the structure and discussion

(*a*) *General*

The principal data concerning the structure of yugawaralite are listed in Tables 1–6. Table 1 contains the atomic coordinates with their standard deviations estimated from the shifts of the final two cycles of least-squares refinement. Tables 2 and 3 give distances and angles relating to the framework, Table 4 calcium environmental distances, Table 5 distances and angles concerning the water molecules and Table 6 the observed and calculated structure factors. A skeletal model of the framework is shown in Figs. 2, 3 and 4, viewed along the a, b and c axes respectively. The black tetrahedra represent aluminum and the remainder represent silicon atoms.

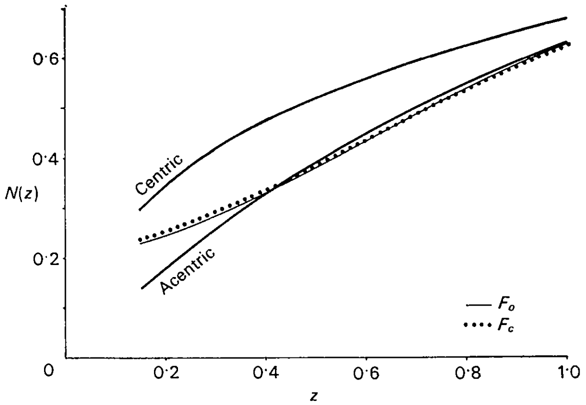

Fig. 1. The statistical $N(z)$ plot for the yugawaralite data. The F_{observed} (thin line) and $F_{\text{calculated}}$ (dotted line) are seen against the two reference curves.

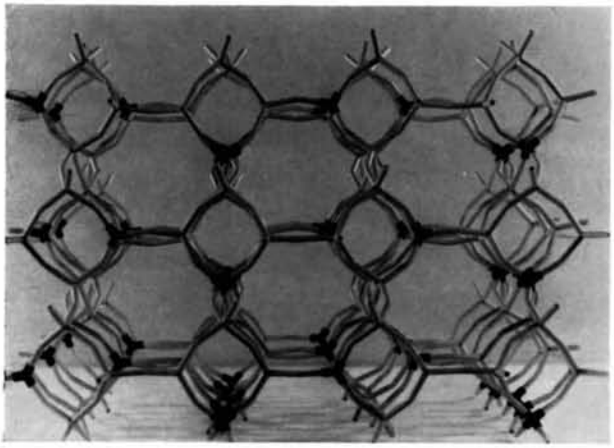

Fig. 2. A model of the framework of yugawaralite viewed down the *a* axis. The black apices represent Al while the lighter ones represent Si. Oxygen atoms must be imagined to be midway along each bond.

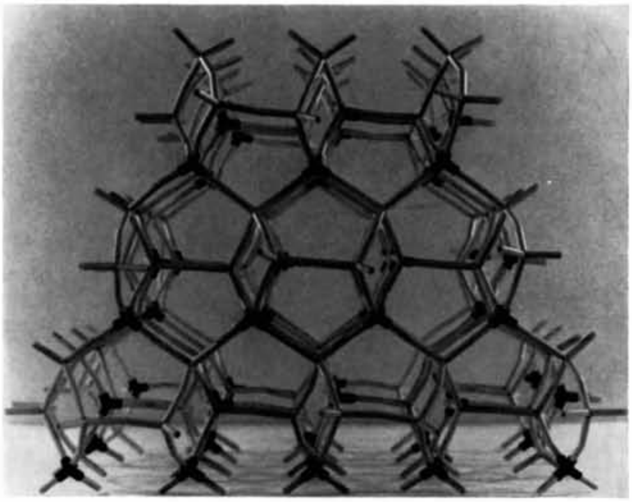

Fig. 3. Model viewed along the *b* axis.

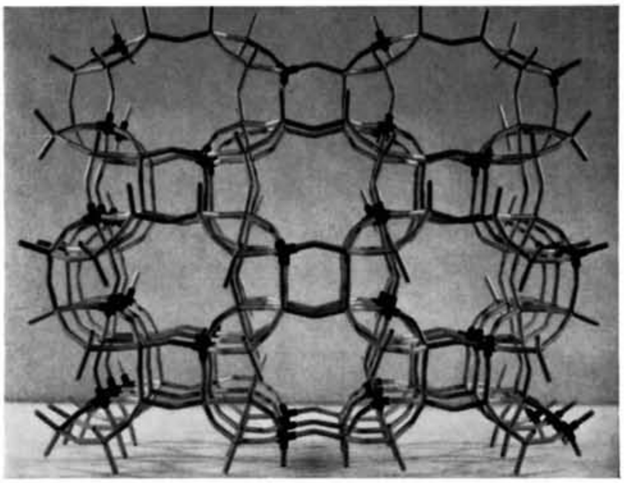

Fig. 4. Model viewed along the *c* axis.

Table 1. *Atomic coordinates with standard deviations estimated from the shifts of the last two cycles of least-squares*

	x	y	z	B (Å^2)
Ca	0·0439	0·2157	0·4253	0·95
σCa	0·0001	< 0·0001	< 0·0001	0·09
Al(1)	0	0·0071	0	0·50
Al(2)	0·3947	0·3554	0·6540	0·60
σAl	0·0001	0·0001	0·0001	0·05
Si(1)	0·3406	0·1489	0·9832	0·47
Si(2)	0·7103	0·0371	0·1923	0·52
Si(3)	0·4084	0·1253	0·6955	0·44
Si(4)	0·0265	0·4760	0·4401	0·44
Si(5)	0·3583	0·3733	0·9620	0·42
Si(6)	0·7398	0·4981	0·6231	0·50
σSi	0·0002	< 0·0001	< 0·0001	0·05
O(1)	0·1076	0·1067	0·9523	1·25
O(2)	0·8502	0·0463	0·0970	1·46
O(3)	0·1911	0·0756	0·5952	1·07
O(4)	0·5083	0·1093	0·1326	0·88
O(5)	0·4292	0·1212	0·8605	1·39
O(6)	0·6155	0·0726	0·6867	0·84
O(7)	0·8469	0·0651	0·3550	0·82
O(8)	0·3381	0·2636	0·0008	1·00
O(9)	0·4004	0·2324	0·6357	1·32
O(10)	0·1661	0·4290	0·9903	1·16
O(11)	0·8328	0·4837	0·4980	1·20
O(12)	0·1686	0·3817	0·5002	0·70
O(13)	0·5769	0·4104	0·0833	0·94
O(14)	0·3590	0·3906	0·8071	1·47
O(15)	0·6237	0·4007	0·6390	1·30
O(16)	0·9292	0·4705	0·2665	0·86
σO	0·0003	0·0001	0·0002	0·04
H_2O(1)*	0·9758	0·2536	0·1757	2·28
H_2O(2)*	0·9058	0·2319	0·6272	1·22
H_2O(3)	0·6945	0·2880	0·3365	2·05
H_2O(4)*	0·3396	0·1500	0·3627	2·86
σH_2O	0·0006	0·0001	0·0002	0·04

* These sites have an occupancy factor of 0·75.

Table 2. *Interatomic distances* (Å) *within the framework*

(*a*) Al–O distances

Al(1)–O(1)	1·715	Al(2)–O(9)	1·730
Al(1)–O(2)	1·728	Al(2)–O(12)	1·766
Al(1)–O(3)	1·734	Al(2)–O(14)	1·712
Al(1)–O(7)	1·761	Al(2)–O(15)	1·725
Mean	1·735	Mean	1·733

(*b*) Si–O distances

Si(1)–O(1)	1·598	Si(4)–O(10)	1·598
Si(1)–O(4)	1·610	Si(4)–O(11)	1·615
Si(1)–O(5)	1·600	Si(4)–O(12)	1·611
Si(1)–O(8)	1·612	Si(4)–O(16)	1·624
Mean	1·605	Mean	1·612

Table 2 (*cont.*)

(*b*) Si–O distances

Si(2)–O(2)	1·575	Si(5)–O(8)	1·598
Si(2)–O(4)	1·622	Si(5)–O(10)	1·622
Si(2)–O(6)	1·652	Si(5)–O(13)	1·616
Si(2)–O(7)	1·603	Si(5)–O(14)	1·576
Mean	1·613	Mean	1·603
Si(3)–O(3)	1·601	Si(6)–O(11)	1·609
Si(3)–O(5)	1·612	Si(6)–O(13)	1·635
Si(3)–O(6)	1·609	Si(6)–O(15)	1·605
Si(3)–O(9)	1·603	Si(6)–O(16)	1·597
Mean	1·606	Mean	1·612

(*c*) O–O distances, AlO_4 tetrahedra

(1) O(1)–O(2)	2·770	(2) O(9)—O(12)	2·661
O(1)–O(3)	2·874	O(9)—O(14)	2·876
O(1)–O(7)	2·922	O(9)—O(15)	2·785
O(2)–O(3)	2·865	O(12)–O(14)	2·875
O(2)–O(7)	2·878	O(12)–O(15)	2·879
O(3)–O(7)	2·670	O(14)–O(15)	2·873
Mean	2·830	Mean	2·825

(*d*) O–O distances, SiO_4 tetrahedra

(1) O(1)–O(4)	2·645	(4) O(10)–O(11)	2·582
O(1)–O(5)	2·655	O(10)–O(12)	2·644
O(1)–O(8)	2·626	O(10)–O(16)	2·635
O(4)–O(5)	2·589	O(11)–O(12)	2·668
O(4)–O(8)	2·568	O(11)–O(16)	2·638
O(5)–O(8)	2·636	O(12)–O(16)	2·623
Mean	2·620	Mean	2·632
(2) O(2)–O(4)	2·610	(5) O(8)—O(10)	2·568
O(2)–O(6)	2·666	O(8)—O(13)	2·551
O(2)–O(7)	2·612	O(8)—O(14)	2·673
O(4)–O(6)	2·642	O(10)–O(13)	2·592
O(4)–O(7)	2·618	O(10)–O(14)	2·666
O(6)–O(7)	2·656	O(13)–O(14)	2·635
Mean	2·634	Mean	2·614
(3) O(3)–O(5)	2·636	(6) O(11)–O(13)	2·640
O(3)–O(6)	2·666	O(11)–O(15)	2·607
O(3)–O(9)	2·553	O(11)–O(16)	2·611
O(5)–O(6)	2·585	O(13)–O(15)	2·690
O(5)–O(9)	2·686	O(13)–O(16)	2·555
O(6)–O(9)	2·606	O(15)–O(16)	2·680
Mean	2·622	Mean	2·631

(*e*) Mean distances

Overall mean Al–O	1·734 ± 0·018
Overall mean Si–O	1·609 ± 0·016
Mean Si–O in Si–O–Al bonds	1·597 ± 0·013
Mean Si–O in Si–O–Si bonds	1·614 ± 0·014
Mean O–O in AlO_4 tetrahedra	2·827 ± 0·083
Mean O–O in SiO_4 tetrahedra	2·625 ± 0·039

Table 3. *Angles of* Al, Si–O–Si *bonds, in degrees*

Al(1)–O(1)–Si(1)	136·9	Al(2)–O(9)—Si(3)	152·2
Al(1)–O(2)–Si(2)	156·8	Si(4) –O(10)–Si(5)	139·4
Al(1)–O(3)–Si(3)	163·7	Si(4) –O(11)–Si(6)	152·5
Si(1) –O(4)–Si(2)	140·0	Al(2)–O(12)–Si(4)	134·6
Si(1)–O(5)–Si(3)	150·0	Si(5)–O(13)–Si(6)	141·3
Si(2) –O(6)–Si(3)	139·0	Al(2)–O(14)–Si(5)	153·4
Al(1)–O(7)–Si(2)	130·4	Al(2)–O(15)–Si(6)	143·4
Si(1)–O(8)–Si(5)	156·9	Si(4)–O(16)–Si(6)	146·1

Table 4. *Calcium environment, distances in* Å

Ca–O(3)	2·546
Ca–O(7)	2·449
Ca–O(9)	2·564
Ca–O(12)	2·486
Ca–$H_2O(1)$	2·435
Ca–$H_2O(2)$	2·530
Ca–$H_2O(3)$	2·414
Ca–$H_2O(4)$	2·474
Mean	2·487 ± 0·051

The yugawaralite framework can be described as a plane chequered pattern comprising separate 4-membered rings, which are linked to their nearest neighbours by the opposite corners of other 4-membered rings, turned so that their free corners lie out of the plane. Fig2 shows the original 4-rings normal to the angle of viewing, while the linking rings are seen inclined. The latter rings are joined to layers above and below with their free corners and in doing so 5-mem-

Table 5. *Distances and angles relating to water molecules*

Those in heavy type are thought to be hydrogen bonds.

(*a*) Distances in Å

$H_2O(1)$–O(2)	**3·037**	$H_2O(3)$–O(4)	3·180
$H_2O(1)$–O(16)	3·210	$H_2O(3)$–O(7)	3·261
$H_2O(1)$–$H_2O(3)$	**2·943**	$H_2O(3)$–O(11)	3·140
$H_2O(1)$–$H_2O(4)$	**2·875**	$H_2O(3)$–O(12)	3·285
		$H_2O(3)$–O(13)	**2·922**
$H_2O(2)$–O(3)	**3·002**	$H_2O(3)$–O(16)	3·209
$H_2O(2)$–O(6)	3·160	$H_2O(3)$–$H_2O(4)$	3·157
$H_2O(2)$–O(9)	3·302		
$H_2O(2)$–O(12)	3·285	$H_2O(4)$–O(3)	3·039
$H_2O(2)$–O(15)	3·058	**$H_2O(4)$–O(4)**	**2·980**
$H_2O(2)$–$H_2O(3)$	**2·850**	**$H_2O(4)$–O(9)**	**2·860**

(*b*) Angles in degrees

O(2) —$H_2O(1)$–$H_2O(3)$	97·1	**O(13) —$H_2O(3)$–$H_2O(1)$**	**69·0**
O(2) —$H_2O(1)$–$H_2O(4)$	**77·3**	O(13) –$H_2O(3)$—$H_2O(2)$	157·9
$H_2O(3)$–$H_2O(1)$–$H_2O(4)$	106·9	$H_2O(1)$–$H_2O(3)$–$H_2O(2)$	109·6
O(3) —$H_2O(2)$–O(15)	174·9	O(3) —$H_2O(4)$–O(4)	149·0
O(3) —$H_2O(2)$–$H_2O(3)$	**101·0**	O(3) —$H_2O(4)$–O(9)	51·2
O(15) —$H_2O(2)$–$H_2O(3)$	75·1	**O(4) —$H_2O(4)$–O(9)**	**149·1**

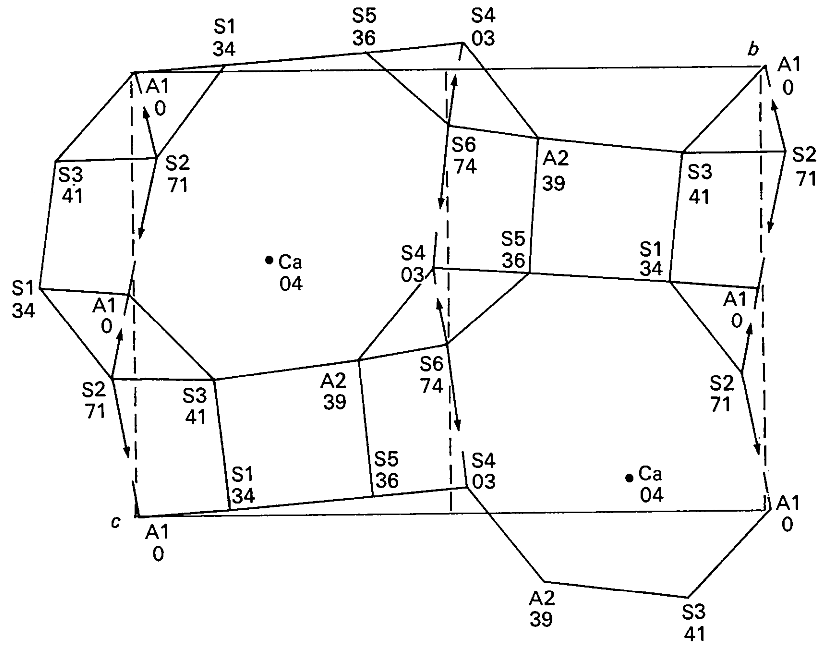

Fig. 5. Projection of yugawaralite onto the *bc* plane. The heights in hundredths of the *a* axis are indicated for Al, Ca and Si atoms. Al, S1 stand for Al(1), Si(1), *etc.*

Table 6. *Observed and calculated structure factors*

The latter are scaled up by five.

H	K	L	FO	FC
0	0	2	432	496
0	0	4	490	486
0	0	6	440	461
0	0	8	163	147
0	0	10	79	79
0	0	12	118	105
0	1	1	119	116
0	1	2	177	169
0	1	3	307	396
0	1	4	145	130
0	1	5	190	189
0	1	6	363	361
0	1	7	162	150
0	1	8	129	121
0	1	9	172	167
0	1	10	207	206
0	1	11	138	125
0	1	12	96	86
0	1	13	92	74
0	2	0	331	407
0	2	1	91	90
0	2	2	208	220
0	2	3	120	91
0	2	4	157	129
0	2	5	159	142
0	2	7	242	243
0	2	8	129	121
0	2	9	107	100
0	2	10	97	95
0	2	11	79	77
0	2	12	125	118
0	2	13	99	96
0	3	0	234	200
0	3	1	290	309
0	3	2	203	192
0	3	3	110	91
0	3	4	156	149
0	3	5	167	153
0	3	6	227	229
0	3	7	207	197
0	3	10	94	100
0	3	12	84	84
0	4	1	126	106
0	4	2	112	81
0	4	3	138	129
0	4	5	217	216
0	4	6	164	151
0	4	7	156	146
0	4	8	141	131
0	4	9	87	84
0	4	10	218	207
0	4	11	137	127
0	4	12	143	136
0	5	1	366	391
0	5	2	212	206
0	5	3	159	157
0	5	4	147	142
0	5	5	193	190
0	5	7	230	226
0	5	8	77	72
0	5	11	126	125
0	5	12	130	132
0	6	0	159	114
0	6	1	144	120
0	6	2	144	127
0	6	3	65	62
0	6	4	180	171
0	6	5	208	203
0	6	6	119	100
0	6	7	230	224
0	6	8	117	100
0	6	9	194	197
0	6	11	87	75
0	6	13	154	157
0	7	0	247	236
0	7	1	394	349
0	7	2	120	115
0	7	3	130	121
0	7	4	338	338
0	7	5	98	94
0	7	6	297	289
0	7	7	146	131
0	7	8	146	130
0	7	9	104	101
0	7	10	204	195
0	7	11	137	125
0	7	13	65	64
0	8	0	476	487
0	8	1	427	424
0	8	2	188	186
0	8	3	58	64
0	8	4	214	202
0	8	5	247	245
0	8	6	265	265
0	8	7	119	93
0	8	8	117	187
0	8	11	102	105
0	8	12	78	75
0	8	13	72	69
0	9	0	185	94
0	9	1	78	63
0	9	3	100	98
0	9	4	131	128
0	9	5	137	95
0	9	6	92	89
0	9	8	135	130
0	9	9	131	111
0	10	1	108	122
0	10	2	112	109
0	10	3	86	84
0	10	4	99	96
0	10	5	92	58
0	10	6	139	137
0	10	7	88	85
0	10	9	80	67
0	10	10	165	149
0	11	0	187	170
0	11	1	123	107
0	11	2	140	147
0	11	3	207	203
0	11	4	175	171
0	11	5	94	87
0	11	6	71	79
0	11	7	86	73
0	11	10	99	103
0	11	11	98	77
0	11	12	65	69
0	12	0	162	135
0	12	1	222	219
0	12	2	172	164
0	12	3	98	96
0	12	4	195	193
0	12	5	96	94
0	12	6	85	60
0	12	8	219	210
0	12	11	149	133
0	13	1	86	69
0	13	2	265	261
0	13	3	143	145
0	13	4	144	148
0	13	6	92	88
0	13	7	118	108
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2	16	8	98	42
2	17	-11	111	57
2	17	-9	75	75
2	17	-4	150	140
2	17	1	198	195
2	17	2	230	211
2	17	6	126	118
2	17	8	114	99
2	18	-3	94	94
2	18	-1	185	173
2	18	1	115	115
2	18	3	86	92
2	18	4	83	79
2	18	5	92	95
2	18	6	92	62
2	18	8	79	39
2	19	-9	127	41
2	19	-6	86	71
2	19	-5	113	91
2	19	-4	90	65
2	19	0	124	118
2	19	4	72	70
2	19	6	127	113
2	19	7	140	65
3	0	-12	111	111
3	0	-8	219	225
3	0	-6	252	244
3	0	-2	241	220
3	0	0	570	599
3	0	2	156	153
3	0	4	539	547
3	0	6	158	157
3	0	8	125	135
3	0	10	62	56
3	1	-14	116	111
3	1	-12	174	177
3	1	-10	199	206
3	1	-9	169	187
3	1	-8	131	142
3	1	-7	131	129
3	1	-6	498	494
3	1	-3	266	282
3	1	-2	114	119
3	1	-1	97	98
3	1	0	50	47
3	1	1	133	144
3	1	2	173	158
3	1	3	185	174
3	1	4	288	286
3	1	5	87	109
3	1	6	147	153
3	1	7	136	125
3	1	8	132	104
3	1	9	125	123
3	1	10	219	223
3	1	11	108	109
3	2	-13	141	143
3	2	-12	149	158
3	2	-8	126	124
3	2	-7	88	101
3	2	-6	53	53
3	2	-3	117	109
3	2	-2	53	64
3	2	0	158	159
3	2	1	132	127
3	2	2	192	177
3	2	3	40	46
3	2	4	119	128
3	2	5	39	29
3	2	6	49	57
3	2	7	114	107
3	2	9	60	63
3	2	11	66	72
3	3	-12	102	110
3	3	-10	55	73
3	3	-8	134	109
3	3	-7	78	82
3	3	-6	229	241
3	3	-3	86	95
3	3	-2	246	230
3	3	-1	324	323
3	3	0	130	129
3	3	1	163	159
3	3	2	80	60
3	3	3	160	161
3	3	4	99	98
3	3	5	132	100
3	3	6	165	159
3	3	7	48	51
3	3	9	51	98
3	3	10	117	119
3	4	-13	79	97
3	4	-12	129	151
3	4	-11	61	78
3	4	-10	232	227
3	4	-9	80	87
3	4	-8	48	47
3	4	-7	163	185
3	4	-6	199	206
3	4	-3	188	189
3	4	-2	180	184
3	4	-1	229	228
3	4	0	139	148
3	4	1	99	97
3	4	2	95	94
3	4	3	144	148
3	4	4	151	151
3	4	5	41	98
3	4	6	68	71
3	4	7	108	99
3	4	8	79	90
3	4	10	133	128
3	4	11	118	112
3	5	-12	99	108
3	5	-8	133	144
3	5	-7	289	293
3	5	-6	79	71
3	5	-4	157	172
3	5	-3	321	326
3	5	-2	96	47
3	5	-1	104	171
3	5	0	213	213
3	5	1	327	298
3	5	2	272	177
3	5	3	274	466
3	5	4	91	99
3	5	5	233	239
3	5	6	98	87
3	5	7	148	155
3	5	8	59	59
3	6	-13	108	204
3	6	-9	189	207
3	6	-8	158	158
3	6	-6	119	118
3	6	-5	217	236
3	6	-4	142	139
3	6	-3	108	107
3	6	-2	411	413
3	6	-1	296	243
3	6	0	311	491
3	6	1	98	82
3	6	2	48	91
3	6	3	126	176
3	6	4	169	147
3	6	5	134	149
3	6	6	113	118
3	6	7	77	40
3	6	8	81	87
3	6	9	87	91
3	6	11	91	60
3	7	-12	114	116
3	7	-11	84	91
3	7	-10	149	151
3	7	-9	48	69
3	7	-8	97	117
3	7	-7	271	267
3	7	-6	355	380
3	7	-5	98	91
3	7	-4	197	195
3	7	-3	112	174
3	7	-2	141	134
3	7	-1	219	170
3	7	0	139	145
3	7	1	167	173
3	7	2	144	147
3	7	3	128	134
3	7	4	251	254
3	7	5	119	112
3	7	6	125	125
3	7	8	214	214
3	7	9	57	97
3	7	10	173	164
3	8	-12	67	71
3	8	-9	68	113
3	8	-8	40	56
3	8	-6	152	169
3	8	-5	213	413
3	8	-4	57	64
3	8	-3	122	111
3	8	-2	244	243
3	8	-1	298	470
3	8	0	358	364
3	8	1	137	143
3	8	3	248	254
3	8	4	159	172
3	8	5	238	243
3	8	6	93	107
3	8	7	63	71
3	8	8	87	105
3	8	9	97	103
3	9	-14	77	95
3	9	-13	68	85
3	9	-12	121	139
3	9	-11	96	105
3	9	-10	59	61
3	9	-9	122	125
3	9	-8	151	152
3	9	-7	73	83
3	9	-6	119	113
3	9	-5	282	293
3	9	-4	195	157
3	9	-3	218	227
3	9	-2	54	56
3	9	0	71	94
3	9	1	243	247
3	9	2	90	93
3	9	3	123	119
3	9	4	83	96
3	9	5	114	128
3	9	6	131	117
3	9	7	101	102
3	9	9	95	97
3	10	-12	95	101
3	10	-11	69	78
3	10	-10	111	123
3	10	-7	84	81
3	10	-6	160	166
3	10	-5	50	66
3	10	-4	122	122
3	10	-3	57	74
3	10	-2	128	135
3	10	-1	179	174
3	10	1	131	101
3	10	2	64	72
3	10	3	75	74
3	10	4	91	94
3	10	7	129	130
3	10	10	81	89
3	11	-14	96	108
3	11	-10	75	94
3	11	-8	68	71
3	11	-5	112	128
3	11	-4	133	145
3	11	-3	111	124
3	11	-2	92	103
3	11	-1	134	160
3	11	0	84	90
3	11	1	47	41
3	11	2	96	109
3	11	5	114	127
3	11	6	63	79
3	11	7	99	104
3	11	10	74	93
3	11	11	118	120
3	12	-13	65	78
3	12	-11	86	97
3	12	-10	99	112
3	12	-9	79	85
3	12	-8	219	230
3	12	-7	191	267
3	12	-4	211	211
3	12	-3	159	171
3	12	-2	72	92
3	12	0	174	170
3	12	2	87	91
3	12	3	77	79
3	12	4	127	132
3	12	5	74	94
3	12	6	140	141
3	12	7	59	69
3	12	8	189	181
3	12	11	71	79
3	13	-12	93	105
3	13	-11	128	134
3	13	-9	93	99
3	13	-7	128	139
3	13	-4	174	183
3	13	-3	117	127
3	13	-2	193	201
3	13	0	176	187
3	13	1	62	56
3	13	2	263	202
3	13	5	96	108
3	13	6	156	198
3	14	-10	81	95
3	14	-8	149	157
3	14	-6	73	82
3	14	-5	123	131
3	14	-2	140	156
3	14	-1	104	209

Table 6 (*cont.*)

H	K	L	FO	FC
3	14	0	137	119
3	14	1	79	84
3	14	2	83	81
3	14	3	95	104
3	14	4	100	103
3	14	5	71	81
3	14	6	129	132
3	14	7	107	111
3	14	8	78	78
3	15	-11	76	78
3	15	-9	111	119
3	15	-8	74	89
3	15	-7	112	124
3	15	-6	71	98
3	15	-5	83	91
3	15	-4	93	95
3	15	-3	125	133
3	15	-1	121	131
3	15	0	120	115
3	15	1	76	81
3	15	2	145	143
3	15	3	69	78
3	15	4	63	60
3	15	5	133	101
3	15	6	67	58
3	15	9	120	119
3	16	-14	84	93
3	16	-8	72	83
3	16	-7	114	120
3	16	-4	91	98
3	16	-3	116	118
3	16	-2	100	112
3	16	-1	167	163
3	16	0	79	89
3	16	1	74	81
3	16	2	75	76
3	16	8	66	73
3	17	-10	72	71
3	17	-8	64	84
3	17	1	128	137
3	17	5	73	80
3	17	6	62	73
3	18	-10	60	72
3	18	-6	74	87
3	18	-5	140	157
3	18	-4	82	88
3	18	-1	103	105
3	18	1	65	64
3	18	5	93	108
3	18	9	69	75
3	19	-4	81	89
3	19	-2	152	154
3	19	0	68	72
3	19	2	191	177
3	19	4	93	130
4	0	-4	94	116
4	0	-2	456	468
4	0	0	235	218
4	0	2	387	372
4	0	4	82	87
4	1	-4	249	236
4	1	-3	169	176
4	1	-1	151	144
4	1	1	341	335
4	1	2	119	110
4	1	3	346	352
4	2	-4	86	105
4	2	-3	177	183
4	2	-2	172	174
4	2	-1	158	143
4	2	0	171	170
4	2	1	84	77
4	2	2	131	123
4	2	3	79	72
4	2	4	127	129
4	3	-4	370	395
4	3	-3	132	146
4	3	-2	116	118
4	3	0	145	161
4	3	1	177	175

H	K	L	FO	FC
4	3	2	188	174
4	3	3	155	144
4	3	4	73	76
4	4	-4	262	276
4	4	-3	183	215
4	4	-2	112	109
4	4	-1	92	98
4	4	0	462	470
4	4	1	185	188
4	4	2	195	174
4	4	4	237	235
4	5	-4	244	241
4	5	-3	239	261
4	5	-2	61	59
4	5	-1	142	138
4	5	0	104	114
4	5	1	194	199
4	5	2	148	152
4	5	3	130	139
4	5	4	160	164
4	6	-4	66	73
4	6	-3	118	137
4	6	-2	55	59
4	6	-1	60	61
4	6	0	193	189
4	6	1	86	78
4	6	2	160	154
4	6	3	127	123
4	6	4	56	57
4	7	-4	144	159
4	7	-3	164	168
4	7	-2	183	180
4	7	-1	119	110
4	7	1	241	239
4	7	2	175	167
4	8	-4	64	69
4	8	-3	293	317
4	8	-2	83	82
4	8	-1	218	213
4	8	1	145	148
4	8	2	173	169
4	8	3	133	132
4	8	4	183	180
4	9	-4	106	113
4	9	-3	121	131
4	9	-2	163	163
4	9	-1	70	71
4	9	0	85	91
4	9	1	139	140
4	9	2	231	185
4	9	3	136	140
4	9	4	116	124
4	10	-4	114	125
4	10	-2	238	203
4	10	-1	193	191
4	10	0	179	192
4	10	3	60	66
4	10	4	64	64
4	11	-4	61	69
4	11	-3	157	172
4	11	-2	110	107
4	11	-1	168	158
4	11	2	85	88
4	11	4	127	127
4	12	-3	71	73
4	12	-2	188	185
4	12	0	90	104
4	12	1	110	147
4	12	3	82	91
4	13	-3	105	108
4	13	0	109	133
4	13	1	91	102
4	13	2	89	86
4	13	3	64	63
4	13	4	157	163
4	14	-4	89	93
4	14	-1	83	87
4	14	1	72	65
4	14	2	99	108
4	14	3	104	105

H	K	L	FO	FC
4	14	4	124	127
4	15	-3	122	129
4	15	-2	178	177
4	15	0	69	62
4	15	2	119	114
4	15	3	80	78
4	15	4	100	99
4	16	-4	93	95
4	16	-3	102	104
4	16	-2	177	175
4	16	-1	68	67
4	16	0	83	90
4	16	4	116	119
4	17	-4	149	160
4	17	-2	176	185
4	17	2	141	132
4	17	4	85	94
4	18	-2	102	110
4	18	-1	192	189
4	18	0	61	57
4	18	1	93	87
4	18	3	116	115
4	19	-4	78	83
4	19	-1	68	69
4	19	0	144	128
4	19	1	57	62
5	0	-4	59	69
5	0	-2	133	148
5	0	0	239	261
5	0	2	227	207
5	0	4	193	202
5	1	-4	244	232
5	1	-3	188	238
5	1	-1	90	98
5	1	0	147	156
5	1	1	358	356
5	1	2	87	82
5	1	3	81	76
5	2	-4	135	111
5	2	-3	81	93
5	2	-2	219	219
5	2	-1	151	145
5	2	0	63	64
5	2	1	62	59
5	2	2	231	190
5	2	4	122	125
5	3	-4	200	213
5	3	-3	151	178
5	3	-2	270	268
5	3	-1	165	169
5	3	1	193	195
5	3	3	110	117
5	3	4	101	105
5	4	-4	104	116
5	4	-3	151	177
5	4	-2	394	384
5	4	-1	255	254
5	4	0	166	175
5	4	2	356	348
5	4	3	129	133
5	4	4	217	214
5	5	-4	197	206
5	5	-3	68	76
5	5	-2	209	205
5	5	-1	58	66
5	5	0	121	95
5	5	3	131	134
5	6	-4	164	174
5	6	-3	210	255
5	6	-2	110	114
5	6	-1	111	116
5	6	0	69	68
5	6	1	62	66
5	6	2	110	101
5	7	-4	164	182
5	7	-3	124	135
5	7	-2	194	198
5	7	0	82	93
5	7	2	157	154
5	8	-4	145	150

H	K	L	FO	FC
5	8	-3	107	121
5	8	-2	71	76
5	8	-1	64	70
5	8	0	189	200
5	8	1	145	142
5	8	3	114	110
5	9	-4	61	74
5	9	-3	220	246
5	9	-2	68	77
5	9	-1	84	86
5	9	0	168	189
5	9	1	168	162
5	9	2	137	91
5	9	4	94	95
5	10	-4	81	96
5	10	-3	71	74
5	10	-2	98	107
5	10	-1	81	82
5	10	1	85	86
5	10	2	122	127
5	10	3	132	135
5	10	4	200	199
5	11	-3	99	111
5	11	-2	144	144
5	11	0	72	76
5	11	1	84	86
5	11	3	101	100
5	12	-1	133	129
5	12	0	78	80
5	12	1	87	89
5	12	3	137	148
5	12	4	109	112
5	13	-3	99	106
5	13	-2	118	121
5	13	0	84	78
5	13	1	107	103
5	13	4	102	107
5	14	-4	78	85
5	14	-2	157	158
5	14	-1	85	89
5	14	0	103	108
5	14	2	71	53
5	15	-4	78	98
5	15	-3	110	112
5	15	-1	119	116
5	15	0	164	166
5	15	1	91	79
5	15	2	82	75
5	15	3	82	76
5	15	4	104	111
5	16	-4	164	171
5	16	-2	103	103
5	16	-1	64	56
5	16	0	102	106
5	16	2	77	80
5	17	-4	106	109
5	17	0	160	164
5	17	2	127	110
5	18	-3	103	106
5	18	-1	147	134
5	18	3	140	138
5	19	-1	62	58
6	0	-4	110	120
6	0	-2	411	405
6	0	0	326	347
6	0	2	277	282
6	0	4	314	325
6	1	-4	138	154
6	1	-3	77	94
6	1	-2	239	234
6	1	-1	190	203
6	1	0	67	67
6	1	1	86	101
6	1	2	59	56
6	1	3	57	62
6	1	4	130	128
6	2	-3	88	94
6	2	-2	166	172
6	2	-1	192	196
6	2	2	69	63

H	K	L	FO	FC
6	3	-3	62	74
6	3	-2	138	133
6	3	0	89	96
6	3	1	113	114
6	3	2	82	77
6	4	-3	137	122
6	4	1	139	103
6	4	3	86	87
6	4	4	125	125
6	5	-4	76	91
6	5	-3	170	223
6	5	-2	58	54
6	5	-1	66	66
6	5	0	135	119
6	5	1	202	199
6	5	2	69	75
6	5	3	60	60
6	5	4	118	116
6	6	-2	178	177
6	6	-1	114	120
6	6	0	78	72
6	6	2	87	86
6	6	3	73	63
6	6	4	177	171
6	7	-4	132	152
6	7	-3	127	152
6	7	-2	166	172
6	7	-1	60	54
6	7	0	162	181
6	7	1	108	116
6	7	4	89	80
6	8	-4	91	120
6	8	-3	59	74
6	8	-2	213	218
6	8	-1	250	239
6	8	0	68	77
6	8	1	110	110
6	8	2	129	126
6	8	3	214	215
6	8	4	188	191
6	9	-4	138	123
6	9	-2	70	81
6	9	-1	73	80
6	9	0	74	93
6	9	1	130	137
6	9	3	77	70
6	10	-4	77	75
6	10	-2	118	107
6	10	-1	95	133
6	10	3	64	66
6	11	-3	89	100
6	11	0	116	124
6	11	1	96	95
6	11	2	93	88
6	11	3	135	147
6	12	-4	221	230
6	12	0	122	127
6	12	1	83	82
6	13	-4	83	87
6	13	-3	129	133
6	13	-2	119	106
6	13	0	135	146
6	13	1	77	68
6	13	2	196	178
6	14	-4	122	127
6	14	-2	143	143
6	14	-1	102	102
6	14	1	73	80
6	14	2	73	79
6	14	3	104	115
6	14	4	88	96
6	15	-3	91	98
6	15	-1	78	73
6	15	0	75	72
6	15	1	104	94
6	15	2	118	113
6	16	-4	82	111
6	16	-3	81	87
6	16	-2	74	73
6	16	-1	76	68

H	K	L	FO	FC
6	16	0	39	48
6	16	3	70	84
6	17	-3	81	89
6	17	1	76	71
6	18	-1	84	65
6	19	-1	63	62
6	19	2	141	125
6	19	4	69	60
7	0	-2	134	150
7	0	0	117	124
7	0	2	220	224
7	1	-4	125	130
7	1	-3	60	60
7	1	-2	73	83
7	1	0	113	121
7	1	1	131	131
7	1	3	81	79
7	2	-3	78	101
7	2	-2	197	202
7	2	0	167	171
7	2	1	69	65
7	2	4	120	112
7	3	-4	146	155
7	3	-3	152	122
7	3	-2	72	76
7	3	-1	58	53
7	3	0	135	148
7	4	-4	80	86
7	4	-2	145	142
7	4	0	179	185
7	4	1	93	90
7	4	2	68	70
7	4	4	172	172
7	5	-3	88	165
7	5	-2	64	71
7	5	-1	161	168
7	5	1	158	164
7	5	2	127	103
7	5	4	129	108
7	6	-1	174	185
7	6	1	87	81
7	6	2	71	69
7	6	3	91	88
7	7	-4	133	144
7	7	0	68	80
7	7	1	77	68
7	8	-4	67	62
7	8	-3	157	173
7	8	1	193	190
7	8	2	84	86
7	8	3	79	81
7	9	-4	127	135
7	9	-3	108	111
7	9	-2	74	75
7	9	0	78	79
7	9	1	147	136
7	9	2	156	145
7	9	3	83	83
7	10	-4	148	146
7	10	-3	74	85
7	10	-2	177	178
7	10	-1	158	174
7	10	0	61	70
7	10	1	65	66
7	10	3	72	83
7	10	4	95	104
7	11	-4	75	72
7	11	-3	83	97
7	11	-1	98	94
7	11	0	87	94
7	11	1	129	126
7	11	2	131	99
7	11	3	71	70
7	12	-2	197	197
7	12	-1	90	92
7	12	0	56	58
7	12	2	84	80
7	12	3	81	83
7	13	-4	74	82
7	13	0	127	136

H	K	L	FO	FC
7	13	1	69	48
7	13	4	80	94
7	14	-4	81	92
7	14	0	71	66
7	15	-2	78	82
7	15	2	73	69
7	16	-4	79	82
7	16	1	30	30
7	16	2	61	61
7	17	-1	47	54
7	17	2	133	114
7	18	-3	80	81
7	18	-2	66	57
7	19	4	78	69
8	0	-4	135	118
8	0	-2	119	120
8	0	0	74	98
8	1	-4	176	183
8	1	-3	69	164
8	1	-2	65	60
8	1	-1	101	110
8	1	0	71	72
8	1	1	184	195
8	2	-4	129	124
8	2	-3	62	43
8	2	0	97	105
8	2	1	83	60
8	2	2	136	125
8	3	-4	157	180
8	3	-3	65	81
8	3	-2	124	132
8	3	0	73	80
8	3	1	64	51
8	4	-2	145	145
8	4	-1	64	40
8	4	1	92	89
8	4	2	212	210
8	5	-4	125	131
8	5	-2	73	85
8	6	-3	130	121
8	6	-2	80	84
8	6	1	139	115
8	7	-4	95	103
8	7	-2	75	77
8	7	2	130	97
8	8	-2	168	173
8	8	-1	72	70
8	8	0	134	163
8	9	-3	91	104
8	9	-1	114	120
8	9	0	163	176
8	9	1	134	138
8	10	-3	114	136
8	10	-1	72	77
8	10	0	60	61
8	10	2	92	86
8	11	-4	80	102
8	11	-3	130	124
8	11	-2	96	103
8	11	-1	78	98
8	11	0	49	54
8	11	1	90	88
8	12	1	75	77
8	13	1	57	61
8	14	-2	77	84
8	14	-1	88	87
8	16	-2	84	89
8	17	-2	67	68
9	0	-2	197	191
9	1	-4	88	96
9	1	-2	104	108
9	3	-2	100	99
9	5	-3	67	70
9	7	-2	139	136
9	8	-4	76	98
9	8	-2	126	128
9	12	-4	85	90
9	13	-3	83	92
9	15	-4	110	48
9	18	-3	63	77

bered rings are produced, which can be seen to advantage on Fig. 3. A projection of the structure on to the *bc* plane is shown in Fig. 5.

The structure possesses a two-dimensional system of wide channels in the *ac* plane, the widest being in the [101] direction. Free passage along this channel is restricted to 3·6 × 2·8 Å by the 8-membered ring shown in Fig. 6. There are channels parallel to the *a* axis, also bounded by 8-membered rings. Here the free diameter would be 4·3 × 3·2 Å, but for the cation which sits in the plane of the window and restricts the aperture to 3·2 × 2·3 Å (Fig. 7). A molecule proceeding in the **c** direction must penetrate both windows mentioned above.

The geometric framework of yugawaralite can be idealized to possess a centre of symmetry, although one does not occur in the real structure. The reason for this omission appears to be the cation which takes up a non-centrosymmetric position, thus causing the partially ionized aluminum atoms, which are attracted to the calcium, to occupy asymmetric positions. The X-ray scattering powers of aluminum and silicon differ only slightly and this alone could not account for the strongly acentric $N(z)$. However the sizes of AlO_4 and SiO_4 tetrahedra differ more appreciably and cause displacements of all other atoms. It is these displacements which are a prime cause of the acentricity. Of special note are the mean deviations from centrosymmetric positions which are only 0·16 Å for Al, Si and 0·45 Å for oxygen.

(*b*) *The cation environment*

The calcium ion is situated in one of the main channels and is in contact with oxygens 3, 7, 9 and 12 of the frame-

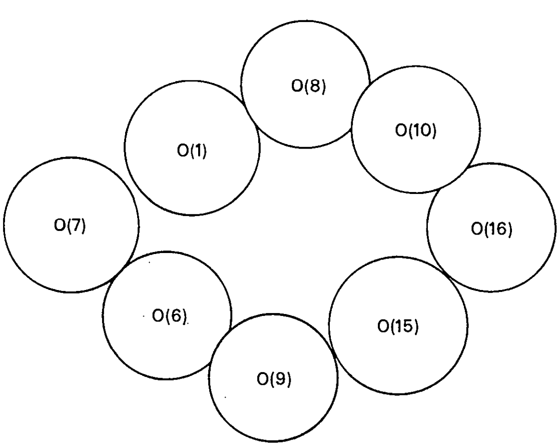

Fig. 6. The 8-membered window constricting the [101] channel. The oxygen atoms are projected onto the best plane which can be drawn through the eight centres.

work, all of which belong to AlO_4 tetrahedra. The coordination sphere is completed by four water molecules so that altogether there are eight atoms lying at a mean distance of 2·49 Å, as shown in Fig. 8

The cation environment is most similar to that occurring in gismondite (Fischer, 1963) where the Ca^{2+} is surrounded by 2 oxygen atoms and six water positions, of which only 5 can be occupied at a time. The mean Ca–O, H_2O distance is here 2·47 Å. The environment in yugawaralite may also be likened to that of Na^+ in natrolite – 4 oxygen atoms and two water positions (Meier, 1960), Sr^{2+} in brewsterite – 4 oxygen atoms and 5 water positions (Perrotta & Smith, 1964), Ba^{2+} in harmotome – 6 oxygen atoms and 4 water positions (Sadanaga, Marumo & Takéuchi, 1961) and Ca^{2+} in levynite where one highly occupied site is surrounded by 3 oxygen atoms and 3 water positions (Kerr, 1968).

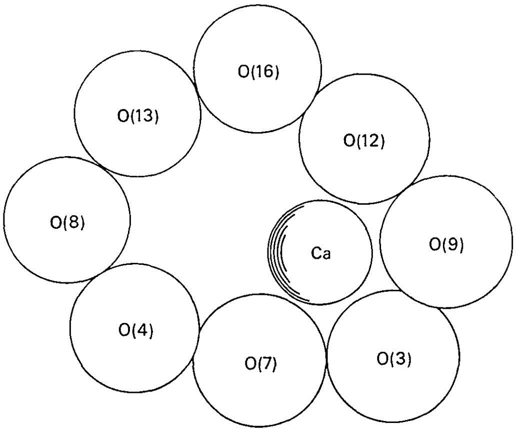

Fig. 7. A similar view of the 8-membered window constricting the *a* channel. This window is almost planar.

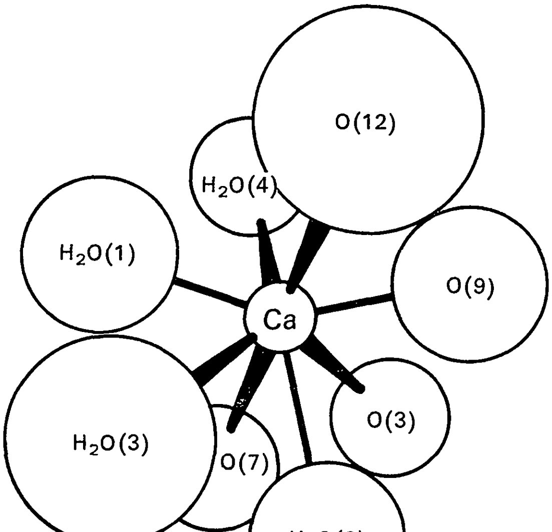

Fig. 8. The cation and its coordinating sphere of eight atoms.

In all the examples quoted above as being comparable to yugawaralite, the cation is coordinated partly by oxygen atoms of the framework and partly by water of hydration. A closer examination of these examples suggests a subdivision into two kinds of cation position. The first type occurs in yugawaralite, gismondite, harmotome and levynite, where the cation could be said to be attached to the cavity wall, while the second type occurs in natrolite and brewsterite, where owing to the smaller dimensions of the cavity or channel, the cation is situated centrally in the vacant space and has contact with framework oxygen atoms on opposite sides. In both cases the parts of the surface of the cation still exposed are coordinated by water.

A third type of cation position must also be mentioned here for distinction from those referred to above. It may occur in zeolites possessing large cavities where it is possible for a cation situated within the cavity to be insulated from direct contact with the frame work by a sphere of hydration. Examples of this occur in levynite where a second less highly occupied site is coordinated by 9 water atoms and in the related mineral chabazite where the Ca^{2+} is reported as possessing an incomplete sphere of hydration (Smith, Rinaldi & Dent Glasser, 1963). All three Ca^{2+} ions in heulandite are situated in the channels practically surrounded by water (Merkle & Slaughter, 1967, 1968).

(*c*) *Hydrogen bonds*

The presence of hydrogen bonds is inferred from the close proximity between water molecules and other atoms. Fig. 9 is an interpretation of the situation giving distances and ∠OOO angles. Since the positions of hydrogen atoms are not revealed by X-rays, conclusions cannot be drawn with certainty, for example there are three distances from $H_2O(4)$ to neighbouring oxygen atoms which fall within the range of hydrogen bonds. The longest bond may have to be discarded, or there may be an arrangement where both O(3) and O(9) are brought within the interaction of a single hydrogen atom.

The ∠OOO angles show an unusually large spread about the expected mean value of 109°– the mean ∠HOH angle. However, provided the two hydrogen bonds of each water molecule are bent equally, there is no need for ∠OHO angles to be less than 160° which compares favourably with 154° in $CuSO_45H_2O$ and 156° in oxalic acid (Bacon & Curry, 1962). All the hydrogen bonds in yugawaralite must be described as long or very long. They are therefore weak and it is to be expected that weak bonds will be considerably bent (Hamilton, 1962) Yugawaralite may be a profitable mineral to study by neutron diffraction.

(*d*) Al, Si-*ordering and conclusions*

The discovery of the ordering of aluminum and silicon has been a notable result of the present investigation. In zeolites ordering has been convincingly proved by considering interatomic distances, only in the cases of natrolite and gismondite. Yugawaralite has a high density of 18·2 Al, Si per 1000 Å^3 and the other two ordered zeolites have densities only slightly lower. Further research may reveal ordering in structures where the arrangement of Al, Si atoms was thought to be random, but it seems most likely that this will occur in zeolites with high Al, Si densities. One justification for this may be the influence upon ordering of a cation attached to the cavity wall. Owing to the larger Al–O distance in an Al–O–Si bond, the Si–O distance is slightly shortened from its mean value [see Table 2(*e*)].

It is difficult to place yugawaralite in any of the seven recognized groups of zeolites, although it shows certain similarities to both mordenite and heulandite in that all three structures have 4-, 5- and 8-membered rings. It does not, however, possess the zigzag layer which is characteristic of the mordenite group, nor the configuration of tetrahedra common to the heulandite group (Meier, 1968). Thus it may be that yugawaralite stands in a group on its own, unless some synthetic zeolites are found to join it.

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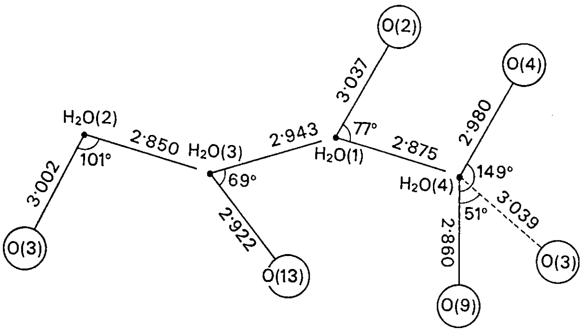

Fig. 9. Hydrogen bonds occurring in yugawaralite. This interpretation must be considered tentative until an investigation is done by neutron diffraction. There is much uncertainty concerning the status of the $H_2O(4)$–O(3) bond.

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