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Sodium Silicate Hydrates. III. The Crystal Structure of $Na_2O.SiO_2.6H_2O$ and of the Isostructural $Na_2O.GeO_2.6H_2O$.

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A new sodium germanate hydrate, of oxide formula $Na_2O.GeO_2.6H_2O$, has been prepared and found to be isostructural with the silicate $Na_2O.SiO_2.6H_2O$. A complete structure analysis of both compounds has been carried out with three-dimensional data, with a view to extending the structural knowledge of sodium silicate hydrates, comparing interatomic bond distances and investigating the hydrogen bond systems. The silicon and germanium atoms are each surrounded tetrahedrally by four oxygen atoms. The tetrahedra being interconnected by fairly short hydrogen bonds. At least some of the hydrogen atoms seem to show a statistical distribution such that between two and three are associated with each silicon–oxygen or germanium–oxygen tetrahedron. The sodium atoms are in approximately octahedral coordination, the octahedra alternately sharing faces and corners to form sheets.

Introduction

A previous structural study of $Na_2O.SiO_2.9H_2O$ (Jamieson & Dent Glasser, 1966*b*) has shown that this compound contains $(H_2SiO_4)^{2-}$ groups. As a continuation of work in this field, the structure of the hexahydrate was next investigated, to find if the anions differed and to compare bond distances.

As silicon, sodium and oxygen do not differ greatly in scattering power, it was thought that if an isostructural germanate could be prepared the structure determination would be simplified, because of the presence of the comparatively heavy germanium atom. Prior to this study, only one sodium germanate hydrate was known – $Na_2O.GeO_2.7H_2O$ (Pugh, 1926; Nowotny & Szekely, 1952) – for which there is no corresponding silicate. Weight-loss determinations on $Na_2O.GeO_2.7H_2O$ (Schwarz & Heinrich, 1932) suggest the existence of a hexahydrate.

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Experimental

The $Na_2O.SiO_2.6H_2O$ crystals used in this study were prepared as described in part I (Jamieson & Dent Glasser, 1966*a*). The crystals did not have very regular geometrical forms; the one selected for intensity measurement was not greater than 0.3 mm in its longest dimension.

For preparation of the germanate hydrate, mixtures of sodium hydroxide and germanium dioxide were first fused in a platinum crucible at 1250 °C. $Na_2O:GeO_2$ molar ratios were (i) 1.36:1 (ii) 1.57:1 and (iii) 1.84:1. The quenched material was divided into portions, a different volume of water being added to each. Many of the preparations yielded crystals of $Na_2O.GeO_2.7H_2O$ as identified by X-ray single-crystal and powder photographs and checked by chemical analysis. One solution [4.5 g of melt (ii) in 8 ml of water] which for the silicate series would be expected to yield $Na_2O.SiO_2.9H_2O$ was seeded with crystals of this. In a short time, very large clear crystals had grown, but as soon as these were handled in any way, they turned cloudy,

and on closer examination were found to consist of a great many very tiny needles of $Na_2O.GeO_2.7H_2O$, together with water. Careful analysis of the original crystals before complete decomposition gave the ratio $Na_2O:GeO_2:H_2O$ as 1:1:9.3. This is thought to indicate the possible metastable existence of $Na_2O.GeO_2.9H_2O$. Solutions seeded with sodium silicate penta- and octahydrate yielded either the heptahydrate or no crystals at all.

Crystals of $Na_2O.GeO_2.6H_2O$ grew from only one solution [4.26 g of melt (i) dissolved in 5 ml of water] which for the silicate series would not be expected to yield $Na_2O.SiO_2.6H_2O$. The solution had not been seeded. The composition of the crystals was checked by standard chemical analysis, and their refractive indices were measured. Rotation and Weissenberg photographs strongly indicated that the crystals were isostructural with $Na_2O.SiO_2.6H_2O$ (Table 1). The crystals readily absorbed water on standing in air to yield the heptahydrate in the form of a powder. The crystal used for intensity measurements (approximately $0.3\times0.2\times0.2$ mm) was protected by a thin layer of petroleum jelly and showed no signs of decomposition after a period of six months.

Intensity data for the (010) projection of the silicate were estimated visually, and later complete three-dimensional data were obtained using a Hilger & Watts automatic linear diffractometer with Mo $K\alpha$ radiation. Data for the germanate were initially estimated visually from *h*0*l*, *h*1*l*$\cdots$*h*5*l* Weissenberg photographs, using the multiple film pack technique and Cu $K\alpha$ radiation, but were later remeasured on the diffractometer with Mo $K\alpha$ radiation; the intensities measured in the two ways were in fair agreement.

The relative intensities, corrected for Lorentz and polarization factors, were converted to an approximately absolute scale by Wilson's statistical method which gave also an approximate value for the overall temperature factor. No corrections were made for absorption or extinction.

All processing of data and crystallographic calculations were performed on an Elliott 803 computer, using the programs of Daly, Stephens & Wheatley (1963), whose kindness in making them available is gratefully acknowledged. Structure factors were calculated with scattering factors taken from *International Tables for X-ray Crystallography* (1962) for Na^+, Si, Ge^{2+}, O^- and O. (It was assumed that the Ge–O bond had more ionic character than Si–O.)

Crystallographic data

The unit cells of $Na_2O.SiO_2.6H_2O$ and of $Na_2O.GeO_2.6H_2O$ (as refined on the linear diffractometer) are given in Table 1 along with the unit cell of $Na_2O.GeO_2.7H_2O$, included for comparison.

Refractive indices determined for $Na_2O.GeO_2.6H_2O$ were $\alpha=1.493$ and $\gamma=1.509$, and the density (measured by the suspension method) 2.05 (±0.05) g.cm^{-3}. The X-ray density, for $Z=2$, is 2.08 g.cm^{-3}.

Structure determination

Initially, an attempt was made to solve the (010) projection (which has the centrosymmetrical plane space group $p2$) of $Na_2O.SiO_2.6H_2O$ by direct methods. The authors acknowledge the help of Prof. M. M. Woolfson and Dr G. Germain, both formerly of the Manchester College of Science & Technology, in this part of the work. Unitary structure factors were calculated from the photographic intensity data and by means of Harker–Kasper inequalities, 16 signs were determined in terms of four sign symbols. Repeated use of the basic sign relationship

$$s(h, l)s(h', l')s(h+h', l+l')\approx+1$$

extended this to 60 signs in terms of two sign symbols. Fourier syntheses were calculated for all three possible combinations of sign symbols, and the electron density map obtained from the most likely combination is illustrated in Fig. 1(*a*), together with that for the final, correct structure [Fig. 1(*b*)]. Six of the signs determined were later proved to be incorrect.

Although the Fourier synthesis [Fig. 1(*a*)] contained much that was correct, including the locations of the silicon and sodium atoms, it was difficult to recognize any features and refinement proved slow. At this stage the germanate hydrate was prepared and it was decided to concentrate on the determination of this structure.

A two-dimensional Patterson synthesis was calculated from the germanate *h*0*l* intensity data. Although the germanium atom showed up very clearly, determination of other atomic positions was not simple, and attempts at refinement were again unsuccessful. A three-dimensional Patterson synthesis was calculated and used to prepare (graphically) a three-dimensional minimum function based on the germanium atom. By this method, the oxygen atoms forming a tetrahedron round the germanium atom were approximately located, as were another three, out of a possible seven (2Na and 5O) independent atoms.

A three-dimensional Fourier synthesis based on these atomic sites showed the 'ghosting' effect frequently encountered with non-centrosymmetric structures; for each peak at (x, y, z) there occurred a 'ghost' peak at $(\bar{x}, \bar{y}, \bar{z})$ whose magnitude was frequently as great as that of the 'true' peaks. Nevertheless, it was found possible to work out a plausible set of atomic positions. Further refinements (including a three-dimensional difference synthesis and several projection refinements) improved these positions and showed also which atoms were sodium and which oxygen.

The germanate structure was finally refined by the method of least squares (diagonal-block approximation), the procedure used closely following that of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961), incorporating the same weighting scheme and method of calculation of the estimated standard deviations. After seven least-squares cycles on the original data

(710 reflexions) the structure was refined as far as the data would permit, to an R index of 15.9%. The new data now became available, consisting of 1347 reflexions measured largely on the diffractometer; for reflexions whose intensities could not be determined because of the geometrical limitations of the diffractometer, visual data were used. Further refinements were carried out with these data, only isotropic temperature factors being refined in order to economize on computing time. After a further seven cycles, the maximum shift in atomic coordinates was two thirds of the e.s.d. and the average shift only 0.09 of the average e.s.d. With these parameters an R index of 11.9% was obtained for all 1347 reflexions; all measured reflexions were included, even those too weak to be statistically significant.

Structure factors were next calculated for the *h0l* data of $Na_2O.SiO_2.6H_2O$ using the atomic parameters finally obtained for the germanate, except for the oxygen atoms forming a tetrahedron round germanium which were moved closer to the central atom to allow

Table 2. *Peaks found on difference synthesis which may correspond to hydrogen atom positions in* $Na_2O.SiO_2.6H_2O$

Peak found near oxygen atom	Pointing towards oxygen atom	Hydrogen bond length (silicate)
O(3)	O(2)	2·89 Å
O(5)	O(1)	2·75
O(6)	O(7)	2·76
O(7)	O(1)	2·60
O(9)	O(2)	2·77

Table 1. *Unit cell data*

	a	*b*	*c*	*β*	Space group	*Z*
$Na_2O.SiO_2.6H_2O$	11·57 Å	5·96 Å	6·39 Å	102·1°	$P2_1$	2
$Na_2O.GeO_2.6H_2O$	11·51	6·15	6·36	102·1°	$P2_1$	2
$Na_2O.GeO_2.7H_2O$*	6·52	8·44	17·37		$P222_1$	4

* Nowotny & Szekely (1952).

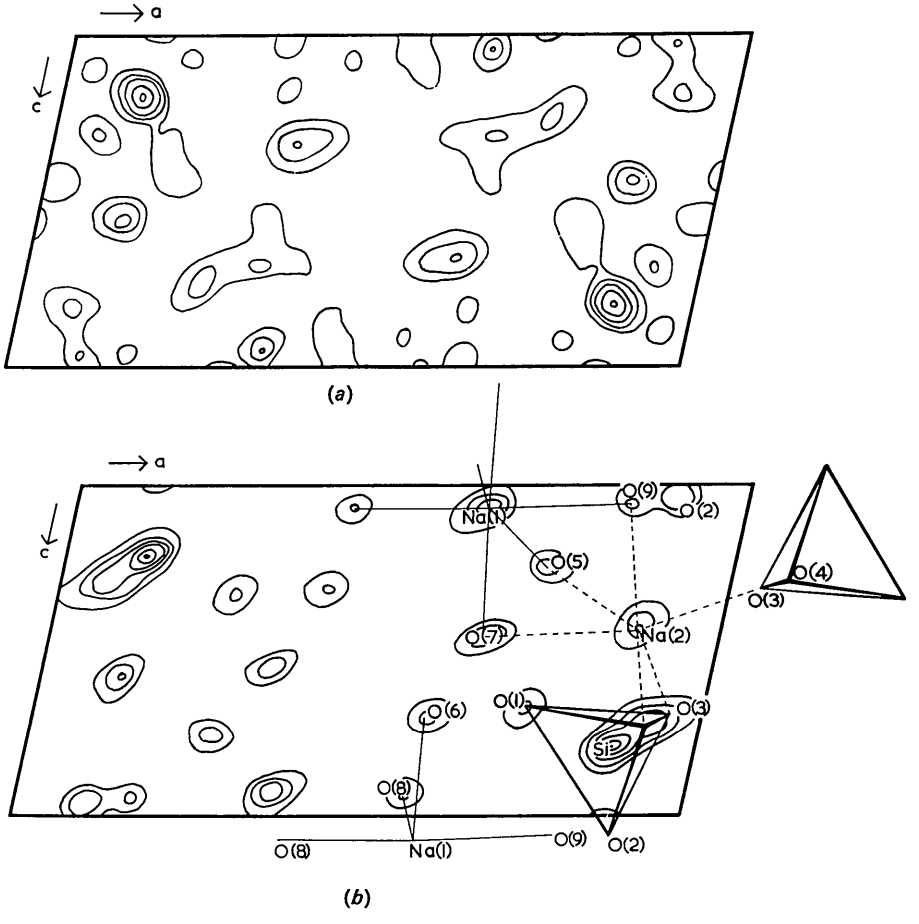

Fig. 1. (*a*) (010) electron density projection for $Na_2O.SiO_2.6H_2O$ calculated with signs developed by direct methods. (*b*) (010) electron density projection for $Na_2O.SiO_2.6H_2O$ calculated with final signs and complete *h0l* data.

Table 3. *Observed and calculated structure factors* ($\times 10$) *for* $Na_2O.SiO_2.6H_2O$

H	L	F	F	A	B
K= 0					
2	0	46	41	-41	0
3	0	55	36	-36	0
4	0	597	617	-617	0
5	0	220	148	-148	0
6	0	341	327	-327	0
7	0	202	176	176	0
8	0	243	209	209	0
9	0	93	16	-16	0
10	0	71	36	36	0
11	0	59	55	-55	0
12	0	83	75	-75	0
13	0	123	141	-141	0
14	0	47	28	-28	0
0	1	18	132	132	0
1	1	214	253	-253	0
2	1	137	160	-160	0
3	1	553	509	-509	0
4	1	247	198	-198	0
5	1	74	67	67	0
6	1	39	37	-37	0
7	1	33	35	35	0
8	1	59	58	-58	0
9	1	82	72	-72	0
10	1	12	10	10	0
11	1	83	83	83	0
12	1	30	19	19	0
13	1	45	59	59	0
14	1	43	45	45	0
2	-1	360	370	370	0
14	-1	100	123	-123	0
15	-1	47	60	-60	0
0	2	91	72	-72	0
1	2	102	84	-84	0
2	2	150	106	-106	0
3	2	81	52	-52	0
4	2	216	178	-178	0
5	2	374	363	363	0
6	2	402	384	384	0
7	2	112	112	-112	0
8	2	21	27	27	0
9	2	32	25	-25	0
10	2	116	119	-119	0
11	2	45	41	41	0
12	2	45	47	47	0
13	2	66	82	82	0
1	-2	348	334	-334	0
5	-2	43	35	-35	0
14	-2	81	105	-105	0
15	-2	33	41	-41	0
0	3	273	265	265	0
1	3	374	337	337	0
2	3	337	317	317	0
3	3	524	511	511	0
4	3	199	167	167	0
5	3	145	145	-145	0
6	3	184	173	-173	0
7	3	182	161	-161	0
8	3	167	171	-171	0
9	3	72	60	-60	0
10	3	52	68	68	0
11	3	127	137	137	0
12	3	50	55	55	0
13	3	21	24	-24	0
12	-3	111	122	122	0
13	-3	5	18	18	0
14	-3	10	13	13	0
15	-3	52	49	49	0
0	4	218	168	168	0
1	4	88	79	79	0
2	4	120	110	110	0
3	4	52	74	-74	0
4	4	178	131	-131	0
5	4	254	243	-243	0
6	4	52	43	-43	0
7	4	20	22	-22	0
8	4	52	29	-29	0
9	4	61	57	57	0
10	4	5	13	-13	0
11	4	83	101	101	0
12	-4	40	27	-27	0
13	-4	16	13	-13	0
14	-4	32	36	-36	0
15	-4	85	93	93	0
0	5	59	49	-49	0
1	5	330	317	317	0
2	5	35	39	-39	0
3	5	142	158	-158	0
4	5	54	38	-38	0
5	5	184	163	-163	0
6	5	94	84	84	0
7	5	49	42	42	0
8	5	94	98	98	0
9	5	148	146	146	0
10	5	47	53	-53	0
11	5	10	15	-15	0
9	-5	102	96	96	0
10	-5	70	47	47	0
11	-5	106	103	-103	0
12	-5	129	141	-141	0
13	-5	49	63	-63	0
0	6	165	138	-138	0
1	6	78	20	-20	0
2	6	49	35	-35	0
3	6	12	7	7	0
4	6	146	121	121	0
5	6	108	88	88	0
6	6	127	114	114	0
7	6	29	37	37	0
8	6	35	35	-35	0
9	-6	109	109	109	0
10	-6	87	90	90	0
11	-6	17	7	7	0
12	-6	21	12	12	0
13	-6	65	81	-81	0
0	7	77	73	-73	0
1	7	28	29	-29	0
2	7	67	61	61	0
3	7	68	55	55	0
4	7	53	48	48	0
5	7	48	63	-63	0
6	7	11	12	12	0
7	7	39	23	-23	0
8	7	109	115	-115	0
2	-7	30	19	-19	0
3	-7	37	42	42	0
4	-7	65	71	71	0
5	-7	45	45	45	0
6	-7	5	9	9	0
7	-7	74	72	-72	0
8	-7	12	1	-1	0
9	-7	48	37	37	0
10	-7	43	28	-28	0
0	8	158	155	-155	0
1	8	94	24	24	0
2	8	119	108	-108	0
3	8	11	37	37	0
4	8	118	109	109	0
5	8	38	24	24	0
6	8	115	109	109	0
7	8	35	18	18	0
8	8	42	37	-37	0
9	8	91	79	-79	0
10	8	49	53	-53	0
K= 1					
1	0	84	88	-51	71
2	0	303	305	-27	304
3	0	122	97	-9	-97
4	0	251	219	-3	219
5	0	354	318	-53	314
6	0	332	319	97	-304
7	0	235	231	191	-129
8	0	28	28	-18	22
9	0	61	58	34	47
10	0	113	108	74	79
11	0	30	33	-31	-13
12	0	56	61	8	61
13	0	24	24	-3	-24
14	0	65	75	-28	-69
15	0	20	29	-29	1
0	1	405	470	-37	468
1	1	220	233	27	231
2	1	182	202	-52	195
3	1	250	222	151	163
4	1	108	114	19	-112
5	1	191	171	79	-152
6	1	282	269	-19	-268
7	1	0	3	-1	3
8	1	115	105	69	79
9	1	140	156	-144	61
10	1	137	158	-41	152
11	1	62	74	-9	-74
12	1	83	94	-44	-84
13	1	53	68	-13	-66
14	1	48	59	-13	-58
1	-1	99	118	-26	-115
2	-1	197	349	116	329
3	-1	473	430	-24	429
4	-1	606	542	-404	362
5	-1	110	94	83	-45
6	-1	376	372	-77	-364
7	-1	206	198	-95	-174
8	-1	315	290	22	-289
9	-1	22	25	-8	-23
11	-1	85	77	-7	77
12	-1	140	149	77	127
13	-1	63	63	46	43
14	-1	28	39	16	-36
15	-1	30	45	29	-34
0	2	135	123	123	3
1	2	588	576	47	-574
2	2	112	105	-62	-85
3	2	165	139	136	-30
4	2	209	198	-133	-146
5	2	415	408	75	401
6	2	160	159	-121	104
7	2	84	81	-48	65
8	2	57	60	2	-60
9	2	208	210	-51	-204
10	2	36	36	29	22
11	2	86	92	-37	-85
12	2	60	76	69	-33
13	2	84	102	34	96
14	2	52	80	-2	80
1	-2	547	525	476	-222
2	-2	284	270	-117	-243
3	-2	107	70	47	53
4	-2	162	157	114	108
5	-2	62	72	-18	-69
6	-2	82	89	-28	84
7	-2	135	134	-102	87
8	-2	76	61	6	-61
9	-2	190	174	-129	-117
10	-2	105	109	-37	-103
11	-2	79	77	-38	-67
12	-2	44	46	-20	42
13	-2	58	56	25	50
15	-2	74	89	44	78
0	3	304	302	36	300
1	3	190	180	-61	-170
2	3	284	258	121	-133
3	3	61	64	-62	13
4	3	115	99	-93	33
5	3	307	287	89	273
6	3	94	85	-84	11
7	3	49	50	49	-8
8	3	26	27	23	-13
9	3	97	102	35	-96
10	3	54	60	51	-33
11	3	14	20	-9	-18
12	3	40	54	22	49
1	-3	278	263	88	262
2	-3	99	107	-34	67
3	-3	164	172	46	-166
4	-3	296	276	155	229
5	-3	57	56	-36	-55
6	-3	82	172	171	-21
7	-3	35	43	41	-13
8	-3	50	42	41	-11
9	-3	121	122	36	117
10	-3	88	77	-48	-60
11	-3	110	101	41	-92
12	-3	35	33	-28	17
13	-3	58	70	-64	27
14	-3	35	40	-37	16
15	-3	16	26	-25	5
0	4	120	113	76	-84
1	4	169	166	-88	-141
2	4	18	21	-11	18
3	4	266	238	74	226
4	4	241	205	-45	200
5	4	192	183	-35	180
6	4	99	96	49	-82
7	4	155	146	22	-145
8	4	91	96	1	-96
9	4	129	133	8	-132
10	4	31	34	-20	28
11	4	100	111	-21	109
12	4	42	52	-32	42
1	-4	322	308	-47	305
2	-4	132	112	-37	106
3	-4	147	128	-105	-73
4	-4	247	219	-55	-212
5	-4	397	384	-64	-379
6	-4	43	36	1	-36
7	-4	74	65	44	47
8	-4	150	141	-22	148
9	-4	293	280	22	279
10	-4	93	99	31	39
11	-4	74	74	56	-49
12	-4	66	71	24	-67
13	-4	94	104	32	-99
14	-4	14	16	17	4
0	5	128	128	-10	128
1	5	72	68	-41	44
2	5	85	81	-62	52
3	5	57	56	25	50
4	5	206	196	4	-196
5	5	32	24	20	-14
6	5	46	50	-38	33
7	5	57	58	18	-55
8	5	18	24	8	23
9	5	57	62	-48	40
10	5	32	40	-3	40
1	-5	139	145	108	97
2	-5	50	43	-43	2
3	-5	187	183	37	179
4	-5	156	155	-43	149
5	-5	209	205	-52	-198
6	-5	141	129	48	-120
7	-5	176	169	-131	-106
8	-5	57	54	-51	-19
9	-5	14	21	-21	4
10	-5	42	48	-38	29
11	-5	148	147	-9	146
12	-5	32	32	11	31
13	-5	48	53	39	-35
14	-5	26	24	6	-24
0	6	80	98	45	87
1	6	96	87	37	79
2	6	44	50	46	-21
3	6	35	32	13	-29
4	6	57	52	6	-52
5	6	48	44	44	-7
6	6	39	34	-27	20
7	6	32	31	-7	30
8	6	44	46	0	46
9	6	28	36	22	29
10	6	13	15	-8	-13
1	-6	145	127	78	101
2	-6	16	17	11	13
3	-6	123	102	-26	98
4	-6	119	119	102	63
6	-6	65	67	57	36
7	-6	124	109	-18	-107
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Table 3 (*cont.*)

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1	7	14	20	-2	-20
2	7	45	39	37	14
3	7	27	27	27	-4
4	7	44	34	33	-8
5	7	30	27	26	5
6	7	29	31	-11	-29
1	-7	33	29	-11	-26
2	-7	34	29	17	24
3	-7	89	89	-21	86
4	-7	44	40	38	10
5	-7	30	36	9	35
6	-7	23	23	-7	-22
7	-7	20	24	-10	-22
8	-7	59	56	-55	10
0	8	65	59	-51	-29
1	8	5	11	-8	-11
1	-8	88	82	-79	-24
2	-8	38	31	-26	-18
3	-8	26	21	20	5
4	-8	51	37	37	-3
5	-8	73	63	60	18
6	-8	85	72	72	7
7	-8	23	17	9	-15
8	-8	80	73	-67	30
K= 5					
3	0	187	185	-185	-5
4	0	102	93	-38	84
5	0	82	62	62	7
6	0	76	64	-34	-54
7	0	37	46	45	-6
8	0	28	34	26	-22
9	0	71	60	-25	55
10	0	63	52	-41	32
11	0	10	13	-9	10
12	0	60	57	48	31
13	0	29	29	26	-12
14	0	48	44	-3	-44
3	1	35	30	-14	26
4	1	90	78	46	-63
5	1	143	142	60	-129
6	1	103	95	16	-94
7	1	73	59	58	10
8	1	87	87	-49	72
9	1	14	22	-21	7
10	1	4	7	-3	6
11	1	23	23	-22	-4
12	1	70	75	37	-65
13	1	51	57	31	-47
14	1	14	20	-16	-12
4	-1	54	55	42	35
5	-1	111	107	-104	26
6	-1	114	110	-39	-103
7	-1	174	164	108	-123
8	-1	144	141	-55	-125
9	-1	4	9	-7	-4
10	-1	98	101	-5	101
11	-1	84	83	-15	81
12	-1	93	92	11	91
13	-1	28	39	-4	39
14	-1	13	10	10	0

Table 3 (*cont.*)

H	L	F_o	F_c	A_c	B_c
0	2	50	53	-48	-23
1	2	146	133	-33	-129
2	2	255	234	213	-96
3	2	93	86	76	-40
4	2	70	57	22	-53
5	2	91	85	-7	85
6	2	97	90	-32	85
7	2	35	41	-20	35
8	2	52	45	-32	-31
9	2	90	81	-44	-68
10	2	33	32	9	-30
11	2	56	54	21	-50
12	2	23	26	-23	12
1	-2	19	20	-17	-9
2	-2	204	203	162	-123
3	-2	59	61	-23	-57
4	-2	67	55	17	52
5	-2	42	45	-42	16
6	-2	37	42	-12	40
7	-2	97	91	80	43
8	-2	97	88	-76	-44
9	-2	139	122	40	-116
10	-2	69	75	8	-75
11	-2	18	20	2	-20
12	-2	43	35	25	24
13	-2	68	73	-59	43
14	-2	40	38	8	38
0	3	96	94	90	-27
1	3	71	72	51	-51
2	3	15	11	7	9
3	3	63	55	44	-33
4	3	88	79	-59	52
5	3	157	140	-83	113
6	3	43	51	-47	21
7	3	43	36	-33	13
8	3	51	58	58	-3
9	3	33	28	-1	-28
10	3	41	34	0	-34
11	3	19	19	16	-10
12	3	26	33	-11	32
1	-3	67	60	37	48
2	-3	49	46	46	2
3	-3	116	106	-89	-58
4	-3	55	54	32	43
5	-3	30	29	23	18
6	-3	80	55	-31	45
7	-3	25	26	11	24
8	-3	81	74	-73	13
9	-3	60	57	40	41
10	-3	81	68	39	-56
11	-3	34	26	3	-26
12	-3	55	57	57	5
13	-3	30	23	-16	-15
14	-3	26	31	-31	-2
0	4	90	83	-12	-82
1	4	83	65	-21	-61
2	4	63	53	-46	28
3	4	178	156	-27	154
4	4	135	125	-39	119
5	4	27	25	14	21
6	4	6	13	0	-13
7	4	83	80	29	-74
8	4	108	111	89	-66
9	4	42	56	-10	-55
10	4	9	15	-12	-9
1	-4	122	101	40	93
2	-4	79	83	-43	71
3	-4	107	88	-39	-73
4	-4	151	148	25	-146
5	-4	133	129	-5	-128
6	-4	53	54	28	-47
7	-4	75	70	-30	63
8	-4	99	91	-69	60
9	-4	124	115	19	113
10	-4	89	91	-24	87
11	-4	24	30	30	-7
12	-4	71	72	61	-39
13	-4	47	44	-17	-41
14	-4	5	5	5	1
0	5	58	50	-50	-4
1	5	67	62	-47	41
2	5	29	24	-7	23
3	5	65	59	57	11
4	5	68	63	-1	-63
5	5	73	58	41	-41
6	5	87	78	76	-19
7	5	25	29	-23	-11
8	5	21	18	9	16
9	5	21	15	-10	11
10	5	45	51	-41	30
1	-5	35	39	19	34
2	-5	43	45	-44	11
3	-5	112	96	-29	98
4	-5	45	47	42	21
5	-5	81	66	3	-66
6	-5	91	76	12	-76
7	-5	114	97	43	-87
8	-5	57	50	-28	-41
9	-5	19	25	-24	-8
10	-5	56	47	-26	25
11	-5	74	67	20	62
12	-5	38	37	9	36
0	6	60	54	-43	35
1	6	34	31	19	28
2	6	25	27	-27	2
3	6	73	70	67	-18
4	6	41	37	29	-25
5	6	31	19	-15	11
6	6	12	4	4	4
1	-6	54	47	14	45
2	-6	70	58	-51	27
3	-6	31	24	7	22
4	-6	82	72	-43	57
5	-6	34	25	-9	23
6	-6	40	35	34	-16
7	-6	81	58	10	-52
8	-6	5	9	2	-5
9	-6	26	36	34	-1
10	-6	17	16	12	-1

H	L	F_o	F_c	A_c	B_c
11	-6	41	35	-24	27
12	-6	19	19	-14	12
9	7	26	17	-3	17
1	7	29	32	-3	-31
2	7	91	81	-40	-70
1	-7	85	76	21	-73
3	-7	45	43	12	-42
1	-7	64	52	-50	-12
5	-7	45	35	-0	36
6	-7	94	79	-1	79
7	-7	76	70	-47	52
8	-7	34	27	24	-11
0	8	64	50	-15	-58
1	8	47	43	20	-38
1	-8	23	17	15	7
2	-8	44	42	-25	-33
3	-8	41	40	31	-26
4	-8	71	64	20	-61
5	-8	45	40	1	-40
6	-8	30	25	-18	-17
7	-8	45	40	-34	21

K= 6

H	L	F_o	F_c	A_c	B_c
3	0	131	128	-48	-119
4	0	120	106	-105	-6
5	0	64	68	-68	-2
6	0	89	71	-57	43
7	0	140	123	112	50
8	0	119	104	103	-11
9	0	56	60	34	49
10	0	14	14	-10	10
11	0	53	59	-54	-24
12	0	49	43	-48	-10
13	0	65	76	-75	-13
14	0	10	16	-12	12
0	1	3	39	-13	37
1	1	10	62	-58	-22
2	1	4	21	10	-18
3	1	50	53	-33	-41
4	1	32	27	12	24
5	1	61	51	10	50
6	1	79	71	2	71
7	1	53	65	13	64
8	1	74	60	-47	-37
9	1	25	26	-22	-13
10	1	54	50	-27	-42
11	1	45	42	-6	-41
12	1	25	19	11	16
13	1	24	32	26	-19
14	1	45	50	48	14
3	-1	52	41	41	-4
4	-1	73	58	-56	17
5	-1	75	69	-15	-68
6	-1	75	64	-59	-26
7	-1	31	43	-33	-27
8	-1	63	64	43	-47
9	-1	79	79	61	50
10	-1	96	88	88	1
11	-1	23	28	22	17
12	-1	20	26	3	26
13	-1	48	54	-12	-53
14	-1	41	54	-54	-1
0	2	46	37	-36	-9
1	2	46	48	-27	-40
2	2	27	25	-24	5
3	2	76	68	-27	-62
4	2	77	75	4	75
5	2	68	59	58	11
6	2	48	44	33	-29
7	2	84	73	-42	59
8	2	86	87	-18	-85
9	2	46	55	6	-55
10	2	12	14	-13	-6
11	2	9	13	13	-3
12	2	48	55	44	34
1	-2	47	42	18	38
2	-2	108	96	94	-18
3	-2	86	91	55	72
4	-2	95	96	-40	87
5	-2	84	86	-73	45
6	-2	75	66	-61	-25
7	-2	96	83	-62	-56
8	-2	51	58	-46	-35
9	-2	28	45	33	-30
10	-2	65	70	70	-5
11	-2	62	61	46	39
12	-2	39	33	27	19
13	-2	24	25	11	-23
14	-2	11	9	-8	2
0	3	54	56	1	-56
1	3	56	43	0	-43
2	3	104	99	76	65
3	3	154	133	119	-61
4	3	71	62	62	3
5	3	51	39	-30	24
6	3	106	94	-92	-20
7	3	58	47	-47	2
8	3	35	38	-34	-18
9	3	19	20	8	18
10	3	51	52	51	12
11	3	55	53	49	18
12	3	33	37	22	30
1	-3	104	97	-93	-26
2	-3	134	124	-75	-99
3	-3	94	74	-21	71
4	-3	85	71	61	36
5	-3	128	117	113	29
6	-3	100	95	16	94
7	-3	67	51	39	-34
8	-3	66	50	-24	-44
9	-3	97	96	-96	-8
10	-3	73	75	-75	1
11	-3	26	29	-28	8
12	-3	41	39	39	5
13	-3	25	29	9	28
14	-3	19	29	15	25
0	4	32	28	25	12
1	4	36	36	-1	36

H	L	F_o	F_c	A_c	B_c
2	4	77	85	58	63
3	4	33	21	6	-20
4	4	17	6	-4	-5
5	4	50	50	-50	2
6	4	40	31	-29	-11
7	4	38	35	-1	35
8	4	23	36	-21	15
9	4	23	28	20	19
10	4	26	19	11	16
1	-4	48	38	17	-34
2	-4	89	91	-63	-65
3	-4	51	45	-45	-5
4	-4	80	73	-57	-48
5	-4	50	35	31	17
6	-4	65	56	44	35
7	-4	86	74	67	-32
8	-4	89	82	79	23
9	-4	4	15	13	-9
10	-4	33	30	2	-29
11	-4	51	57	-56	4
12	-4	19	35	-26	-23
13	-4	5	14	-12	7
14	-4	34	45	-25	37
0	5	71	74	35	65
1	5	105	96	93	-24
2	5	57	50	21	45
3	5	57	52	-45	-26
4	5	53	54	-15	-52
5	5	38	33	-32	-8
6	5	16	11	-5	-10
7	5	35	41	-12	39
8	5	23	30	26	14
9	5	51	48	42	-24
10	5	14	14	-11	-8
1	-5	66	67	15	65
2	-5	56	38	-32	-21
3	-5	68	63	-58	26
4	-5	132	116	-115	-14
5	-5	87	78	-78	-5
6	-5	58	53	40	-35
7	-5	58	60	53	-29
8	-5	73	72	57	43
9	-5	29	35	34	8
10	-5	32	29	28	5
11	-5	5	18	-11	-14
12	-5	50	53	-47	-24
0	6	37	12	-1	12
1	6	51	50	-33	-37
2	6	66	53	-45	-37
3	6	33	34	-8	-33
4	6	47	39	30	-26
5	6	33	36	36	-6
6	6	45	32	28	16
1	-6	57	43	43	1
2	-6	61	51	48	17
3	-6	93	85	35	77
4	-6	38	30	24	-18
5	-6	36	32	-32	0
6	-6	67	63	-61	-17
7	-6	78	64	-39	-50
8	-6	39	37	-17	33
9	-6	17	8	5	7
10	-6	27	36	14	33
11	-6	34	33	18	28
12	-6	27	19	8	-17
0	7	47	47	-37	-29
1	7	44	47	-45	-12
2	7	5	7	6	-4
3	7	8	19	19	4
4	7	17	26	21	15
5	7	19	28	8	27
6	7	12	17	16	4
1	-7	33	32	-1	-32
2	-7	7	8	-8	1
3	-7	52	38	13	36
4	-7	39	30	28	12
5	-7	60	59	59	-4
7	-7	30	28	-12	-25
0	8	50	50	-49	8
1	-8	68	56	-54	-16
2	-8	69	58	-58	1
3	-8	21	8	-7	4
4	-8	23	15	15	-3
5	-8	35	30	21	22
6	-8	61	56	56	-3
7	-8	22	23	18	-14

K= 7

H	L	F_o	F_c	A_c	B_c
5	0	82	74	71	19
6	0	64	58	22	-54
7	0	82	82	48	-66
8	0	23	25	-16	20
9	0	38	32	-32	-5
10	0	35	38	-38	-6
11	0	31	35	-32	16
12	0	41	37	20	31
13	0	12	17	16	6
3	1	45	46	38	26
4	1	93	74	26	-69
5	1	94	76	3	-76
6	1	51	45	-32	-31
7	1	32	31	-25	19
8	1	59	55	-42	35
9	1	75	72	-65	30
10	1	23	27	-5	26
11	1	12	16	11	-11
12	1	25	27	27	-2
13	1	34	34	32	-13
5	-1	12	8	-7	-4
6	-1	14	21	0	-21
7	-1	105	91	74	-52
8	-1	75	62	10	-61
9	-1	53	44	14	-41
10	-1	56	54	31	44
11	-1	54	54	-35	41
12	-1	21	24	7	23
13	-1	19	17	-1	17

H	L	F_o	F_c	A_c	B_c
2	2	59	45	43	-13
3	2	37	28	27	-6
4	2	80	59	-50	-31
6	2	95	81	-52	51
7	2	67	48	-17	45
8	2	6	15	9	-12
9	2	49	45	-12	-43
10	2	60	55	52	-19
11	2	44	37	16	-34
12	2	24	21	16	-13
13	2	35	32	20	25
2	-2	88	77	26	-72
3	-2	9	18	-17	5
4	-2	46	39	-32	-23
5	-2	86	82	-80	18
6	-2	94	83	-47	68
7	-2	39	28	-15	24
8	-2	4	2	-1	1
9	-2	64	55	3	-54
10	-2	38	31	23	-21
11	-2	22	28	19	21
12	-2	18	19	9	17
13	-2	17	33	-23	24
14	-2	22	31	-23	21
0	3	42	31	31	-1
1	3	42	24	-3	-24
2	3	69	67	55	-38
3	3	38	29	24	15
4	3	36	34	-13	31
5	3	53	43	22	37
6	3	15	14	-13	5
7	3	32	22	22	3
8	3	34	40	37	-14
9	3	32	37	20	-31
10	3	38	40	3	-40
11	3	25	28	-20	-20
1	-3	119	100	79	60
2	-3	68	65	63	-15
3	-3	68	59	9	-58
4	-3	92	85	80	-29
5	-3	32	20	-16	12
6	-3	28	21	-19	8
7	-3	33	38	-31	-22
8	-3	48	55	-54	11
9	-3	13	15	15	-5
10	-3	8	8	4	-7
11	-3	27	31	29	-12
12	-3	24	33	32	9
13	-3	36	36	-8	35
14	-3	22	20	-19	-7
0	4	99	84	47	-69
1	4	43	38	17	-34
2	4	29	29	8	28
3	4	75	61	19	58
4	4	88	74	-10	73
5	4	28	30	-7	29
6	4	54	48	3	-48
7	4	27	22	5	-21
8	4	37	34	15	-30
9	4	40	43	-31	-30
10	4	32	32	-32	5
11	4	26	30	-15	26
1	-4	111	95	-31	90
2	-4	37	37	-19	32
3	-4	21	17	-3	-17
4	-4	85	76	30	-69
5	-4	65	63	22	-59
6	-4	47	42	42	1
7	-4	19	12	7	-9
8	-4	64	61	-48	38
9	-4	43	43	2	43
10	-4	5	15	-1	15
11	-4	10	14	11	-8
12	-4	49	50	33	-38
13	-4	14	30	3	-30
0	5	15	8	-7	4
1	5	47	45	-44	5
2	5	84	77	-48	60
3	5	20	18	7	16
4	5	62	51	-38	-35
5	5	24	16	9	-13
6	5	25	18	17	-3
7	5	18	15	-14	-2
8	5	8	5	5	-2
1	-5	19	10	7	7
2	-5	74	74	-73	7
3	-5	58	47	-37	30
4	-5	56	45	-17	41
5	-5	28	30	-16	-25
6	-5	44	46	27	-37
7	-5	20	16	8	-14
8	-5	15	9	8	4
9	-5	19	14	-12	-6
10	-5	33	42	-18	38
11	-5	56	64	4	64
12	-5	5	7	-7	1
13	-5	27	24	-6	-23
0	6	48	42	-40	11
1	6	35	37	-37	6
2	6	11	20	-19	4
3	6	23	27	19	-20
4	6	28	28	28	-4
5	6	29	34	33	-8
6	6	16	15	9	-11
7	6	24	20	0	20
8	6	10	14	7	12
1	-6	69	65	65	2
2	-6	26	13	-12	-3
3	-6	13	18	-18	1
4	-6	20	16	-11	11
5	-6	41	37	-35	-10
6	-6	27	18	17	-6
7	-6	31	40	-12	-38
8	-6	7	31	18	-25
9	-6	46	41	37	19
10	-6	25	24	-12	20
0	7	28	14	-5	13
1	7	60	55	11	-54
1	-7	37	31	10	-29

for the difference between Ge–O and Si–O bond lengths. The initial R index of 32% was reduced after one cycle of least-squares refinement to 23%.

From this point on, the three-dimensional data from the diffractometer were used. Five cycles of least-squares refinement were carried out employing the 461 reflexions with $\sin\theta/\lambda < 0.55$, and a further six cycles on the complete data (1416 reflexions). At this stage, the maximum shift in atomic coordinates was a half of the e.s.d. and the average shift was 0.125 of the average e.s.d.

A three-dimensional difference synthesis was calculated in the hope of locating at least some of the twelve independent hydrogen atoms. Five peaks were

Table 4. *Final parameters for the non-hydrogen atoms of* $Na_2O.SiO_2.6H_2O$

Figures in brackets give the estimated standard deviation corresponding to the least significant digit.

	Coordinates (fractions of cell edge)			Isotropic temperature factor B
	x	y	z	
Si	0·1258 (2)	0·0143 (5)	0·2090 (3)	1·29 (2) Å^2
Na(1)	0·3828 (3)	0·4619 (8)	0·9264 (6)	2·10 (6)
Na(2)	0·1265 (3)	0·4986 (9)	0·5652 (6)	2·40 (6)
O(1)	0·2638 (5)	0·988 (1)	0·3362 (9)	1·4 (1)
O(2)	0·1017 (5)	0·988 (1)	0·951 (1)	1·4 (1)
O(3)	0·0482 (5)	0·812 (1)	0·312 (1)	1·5 (1)
O(4)	0·0807 (6)	0·260 (1)	0·279 (1)	1·7 (1)
O(5)	0·2730 (6)	0·144 (1)	0·745 (1)	2·3 (1)
O(6)	0·4130 (6)	0·320 (1)	0·301 (1)	2·3 (1)
O(7)	0·3383 (7)	0·633 (1)	0·562 (1)	2·5 (1)
O(8)	0·4190 (6)	0·853 (1)	0·058 (1)	2·2 (1)
O(9)	0·1841 (6)	0·552 (1)	0·944 (1)	2·2 (1)

Table 5. *Positions of oxygen atoms* O(3) *and* O(4)

		Coordinates (fraction of cell edge)			Isotropic temperature factor, B
		x	y	z	
(*a*) $Na_2O.GeO_2.6H_2O$ (first 'refined' structure)	O(3)	0·083	0·734	0·277	2·7 Å^2
	O(4)	0·047	0·197	0·326	1·8
(*b*) $Na_2O.SiO_2.6H_2O$	O(3)	0·048	0·812	0·312	1·5
	O(4)	0·081	0·260	0·279	1·8
(*c*) $Na_2O.GeO_2.6H_2O$ (final refined structure)	O(3)	0·045	0·820	0·323	0·9
	O(4)	0·088	0·288	0·270	1·2

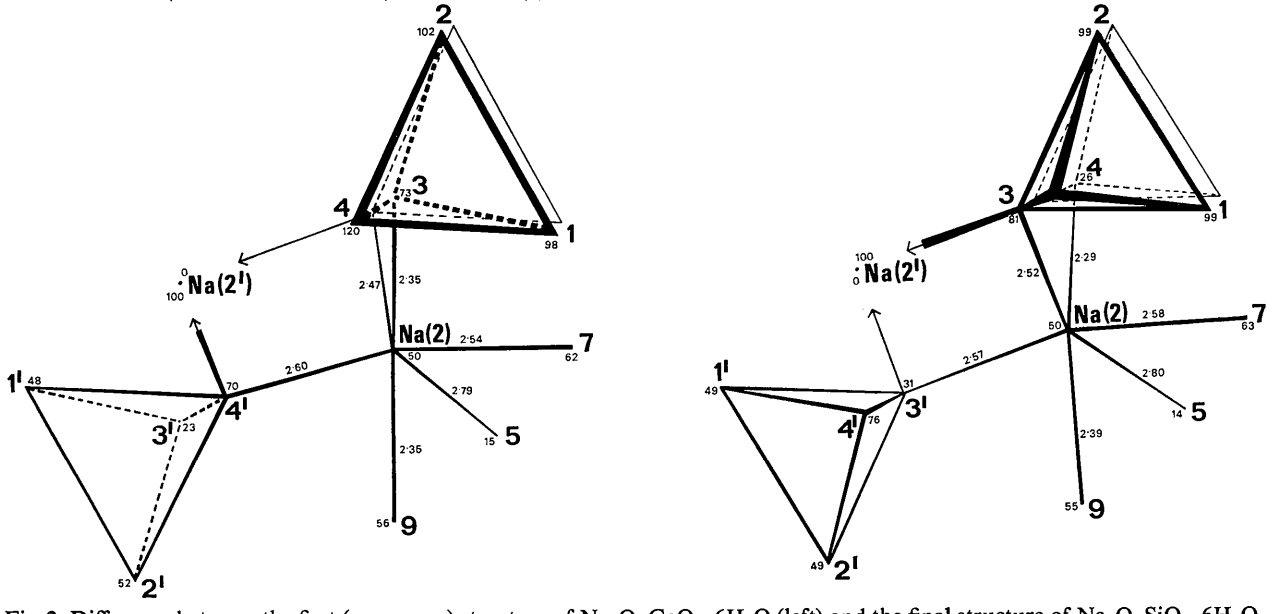

Fig. 2. Difference between the first (erroneous) structure of $Na_2O.GeO_2.6H_2O$ (left) and the final structure of $Na_2O.SiO_2.6H_2O$. Germanium–oxygen and silicon–oxygen tetrahedra are drawn. Large figures represent the numbers given to different oxygen atoms, with primes indicating different asymmetric units. y coordinates (small figures) are in hundredths of the cell side, and bond distances are in Å. The correct structure for $Na_2O.GeO_2.6H_2O$ is very similar to that of the silicate.

Table 6. *Observed and calculated structure factors* ($\times 10$) *for* $Na_2O.GeO_2.6H_2O$

H	L	Fo	Fc	Ac	Bc
K= 0					
2	0	101	86	-86	0
3	0	287	303	-303	0
4	0	911	962	-962	0
5	0	307	310	-310	0
6	0	149	168	-168	0
7	0	494	487	487	0
8	0	423	423	423	0
9	0	16	39	39	0
10	0	33	47	-47	0
11	0	221	228	-228	0
12	0	242	266	-266	0
13	0	154	172	-172	0
14	0	86	105	105	0
0	1	231	212	212	0
1	1	415	420	-420	0
2	1	483	466	-466	0
3	1	861	748	-748	0
4	1	274	205	-205	0
5	1	322	294	294	0
6	1	268	240	240	0
7	1	173	145	145	0
8	1	91	95	-95	0
9	1	218	216	-216	0
10	1	179	172	-172	0
11	1	27	14	-14	0
12	1	56	74	74	0
13	1	192	201	201	0
14	1	134	126	126	0
1	-1	318	310	310	0
2	-1	541	642	642	0
3	-1	306	338	338	0
4	-1	283	280	-280	0
5	-1	199	173	173	0
6	-1	433	484	-484	0
7	-1	164	163	-163	0
8	-1	224	217	217	0
9	-1	165	151	151	0
10	-1	418	458	458	0
11	-1	13	52	52	0
12	-1	131	144	-144	0
13	-1	163	166	-166	0
14	-1	204	228	-228	0
15	-1	33	7	-7	0
0	2	398	349	-349	0
1	2	435	388	-388	0
2	2	280	232	-232	0
3	2	86	88	88	0
4	2	167	171	171	0
5	2	696	662	662	0
6	2	385	384	384	0
7	2	284	269	-269	0
8	2	189	171	-171	0
9	2	242	228	-228	0
10	2	172	152	-152	0
11	2	204	205	205	0
12	2	227	234	234	0
13	2	156	163	163	0
14	2	32	12	-12	0
1	-2	447	409	-409	0
2	-2	217	244	244	0
3	-2	245	276	276	0
4	-2	93	76	-76	0
5	-2	20	25	25	0
6	-2	257	271	-271	0
7	-2	349	392	-392	0
8	-2	214	219	-219	0
9	-2	152	182	182	0
10	-2	390	429	429	0
11	-2	143	148	148	0
12	-2	66	70	70	0
13	-2	40	67	-67	0
14	-2	223	258	-258	0
15	-2	113	127	-127	0
0	3	66	54	54	0
1	3	398	334	334	0
2	3	629	552	552	0
3	3	883	824	824	0
4	3	297	251	251	0
5	3	302	252	-252	0
6	3	398	354	-354	0
7	3	395	358	-358	0
8	3	273	271	-271	0
9	3	37	42	42	0
10	3	256	256	256	0
11	3	279	267	267	0
12	3	31	49	49	0
13	3	110	114	-114	0
1	-3	819	786	-786	0
2	-3	470	446	-446	0
3	-3	333	310	-310	0
4	-3	346	370	370	0
5	-3	694	777	777	0
6	-3	53	43	-43	0
7	-3	59	65	65	0
8	-3	240	262	-262	0
9	-3	420	456	-456	0
10	-3	66	80	-80	0
11	-3	25	55	55	0
12	-3	225	238	238	0
13	-3	87	114	114	0
14	-3	15	16	16	0
15	-3	48	57	-57	0
0	4	290	266	266	0
1	4	327	289	289	0
2	4	353	301	301	0
3	4	44	60	-60	0
4	4	317	275	-275	0
5	4	452	404	-404	0
6	4	169	152	-152	0
7	4	15	22	-22	0
8	4	106	89	89	0
9	4	238	217	217	0
10	4	51	46	46	0
11	4	54	64	64	0
12	4	98	100	-100	0
1	-4	27	21	-21	0
2	-4	380	355	-355	0
3	-4	296	292	-292	0
4	-4	94	74	-74	0
5	-4	231	240	240	0
6	-4	120	117	117	0
7	-4	331	356	356	0
8	-4	107	120	120	0
9	-4	108	121	-121	0
10	-4	58	65	-65	0
11	-4	260	288	-288	0
12	-4	49	26	26	0
13	-4	67	86	86	0
14	-4	70	94	94	0
15	-4	182	205	205	0
0	5	214	191	191	0
1	5	455	407	407	0
2	5	159	149	-149	0
3	5	368	345	-345	0
4	5	197	170	-170	0
5	5	227	193	-193	0
6	5	201	202	202	0
7	5	244	230	230	0
8	5	264	244	244	0
9	5	166	140	140	0
10	5	206	204	-204	0
11	5	134	116	-116	0
1	-5	64	64	-64	0
2	-5	50	41	-41	0
3	-5	255	235	-235	0
4	-5	396	395	-395	0
5	-5	222	218	-218	0
6	-5	110	121	121	0
7	-5	248	267	267	0
8	-5	239	253	253	0
9	-5	125	135	135	0
10	-5	10	2	-2	0
11	-5	265	304	-304	0
12	-5	232	266	-266	0
13	-5	31	49	-49	0
14	-5	102	123	123	0
0	6	210	189	-189	0
1	6	180	171	-171	0
2	6	242	218	-218	0
3	6	60	70	-70	0
4	6	209	187	187	0
5	6	228	215	215	0
6	6	280	278	278	0
7	6	93	86	86	0
8	6	133	139	-139	0
1	-6	196	196	196	0
2	-6	314	282	282	0
3	-6	175	160	160	0
4	-6	165	164	164	0
5	-6	210	228	-228	0
6	-6	299	321	-321	0
7	-6	111	116	-116	0
8	-6	39	2	2	0
9	-6	204	227	227	0
10	-6	189	205	205	0
11	-6	20	7	7	0
12	-6	89	99	-99	0
13	-6	191	228	-228	0
0	7	261	265	-265	0
1	7	191	170	-170	0
2	7	30	29	29	0
3	7	133	115	115	0
4	7	175	166	166	0
1	-7	63	53	-53	0
2	-7	27	36	36	0
3	-7	187	172	172	0
4	-7	216	232	232	0
5	-7	99	110	110	0
6	-7	40	70	-70	0
7	-7	176	193	-193	0
8	-7	84	101	-101	0
9	-7	29	46	46	0
10	-7	58	58	58	0
0	8	246	222	-222	0
1	8	64	76	76	0
2	8	163	150	150	0
3	8	132	105	105	0
1	-8	215	201	-201	0
2	-8	174	225	-225	0
3	-8	29	35	35	0
4	-8	174	200	200	0
5	-8	140	136	136	0
6	-8	143	167	167	0
K= 1					
2	0	423	594	-52	592
3	0	95	76	-4	76
4	0	212	193	0	193
5	0	87	42	-26	32
6	0	618	633	158	-613
7	0	283	270	189	-193
8	0	145	150	-8	149
9	0	225	218	31	216
10	0	263	270	58	264
11	0	80	76	-35	67
12	0	37	26	10	-24
13	0	185	192	5	-192
14	0	165	188	-36	-185
0	1	672	738	-68	735
1	1	476	465	10	465
2	1	245	240	-55	234
3	1	211	190	188	-25
4	1	485	457	48	-455
5	1	384	357	91	-346
6	1	193	192	-20	-191
7	1	229	224	-9	223
8	1	305	306	31	305
9	1	216	256	-191	171
10	1	111	116	-26	113
11	1	258	283	-13	-283
12	1	261	276	-44	-272
13	1	101	107	1	-107
14	1	43	23	-14	19
1	-1	230	238	-13	-237
2	-1	396	489	108	477
3	-1	595	696	-92	690
4	-1	660	737	-450	584
5	-1	63	62	62	5
6	-1	531	582	-94	-575
7	-1	458	471	-81	-464
8	-1	452	465	38	-463
9	-1	30	31	5	30
10	-1	426	437	64	433
11	-1	222	238	-9	238
12	-1	250	275	85	262
13	-1	55	56	52	20
14	-1	173	192	17	-191
0	2	159	130	70	110
1	2	786	674	55	-672
2	2	390	349	-45	-346
3	2	382	343	160	-304
4	2	271	239	-134	-198
5	2	635	603	62	600
6	2	355	344	-148	310
7	2	199	208	-67	197
8	2	55	58	6	-58
9	2	322	338	-43	-335
10	2	151	153	39	-148
11	2	191	214	-19	-214
12	2	81	96	94	23
13	2	202	249	27	247
1	-2	824	735	526	-514
2	-2	511	485	-64	-480
3	-2	109	103	93	42
4	-2	285	297	89	283
5	-2	217	243	-32	241
6	-2	256	298	-69	290
7	-2	104	132	-109	74
8	-2	272	293	4	-293
9	-2	375	390	-139	-365
10	-2	158	177	-16	-176
11	-2	62	58	-47	-34
12	-2	181	187	-15	186
13	-2	207	218	14	217
14	-2	146	171	-52	163
0	3	152	146	61	133
1	3	542	494	-7	-494
2	3	473	411	235	-337
3	3	92	78	-55	55
4	3	293	261	-90	245
5	3	551	511	82	504
6	3	154	135	-91	100
7	3	87	39	67	-43
8	3	172	168	44	-162
9	3	278	293	50	-289
10	3	95	98	55	-81
11	3	70	84	-21	81
12	3	167	175	20	174
13	3	110	124	-2	124
1	-3	255	225	42	221
2	-3	220	212	-92	-192
3	-3	486	493	83	-486
4	-3	182	187	168	83
5	-3	25	20	-20	0
6	-3	255	269	181	198
7	-3	231	257	26	255
8	-3	135	135	62	120
9	-3	33	42	22	36
10	-3	230	241	-29	-239
11	-3	213	238	61	-230
12	-3	37	43	-43	-4
13	-3	90	102	-62	81
14	-3	127	131	-47	122
0	4	363	320	95	-305
1	4	269	255	-107	-231
2	4	183	157	-12	156
3	4	518	458	47	456
4	4	381	338	-82	328
5	4	169	164	-27	162
6	4	235	233	59	-225
7	4	320	318	32	-316
8	4	208	200	5	-200
9	4	88	91	-5	-91
10	4	191	200	-33	198
11	4	218	228	-47	223
1	-4	587	543	-85	536
2	-4	222	197	-65	186
3	-4	295	276	-134	-241
4	-4	522	483	-58	-480
5	-4	606	611	-72	-607
6	-4	74	81	14	-80
7	-4	198	200	35	197
8	-4	336	373	-42	370
9	-4	415	471	30	470
10	-4	88	94	92	17
11	-4	204	216	61	-207
12	-4	198	219	25	-218
13	-4	161	196	39	-192
14	-4	19	23	5	22
0	5	194	191	-41	186
1	5	241	221	-76	208
2	5	240	226	-92	208
3	5	76	75	24	72
4	5	316	308	10	-308
5	5	142	125	31	-121
6	5	100	92	-24	-88
7	5	78	89	31	-84
8	5	148	154	-4	154
9	5	166	188	-58	179
10	5	88	96	-2	96
11	5	44	35	-16	-31
1	-5	268	246	121	214
2	-5	215	201	-43	197
3	-5	351	339	26	338
4	-5	169	183	-55	174
5	-5	354	354	-41	-352
6	-5	314	316	46	-313
7	-5	248	241	-122	-208
8	-5	61	56	-55	-14
9	-5	143	154	-27	152
10	-5	187	213	-42	209
11	-5	195	212	-18	212
12	-5	41	46	18	-43
13	-5	173	183	31	-180
0	6	322	324	47	321
1	6	227	201	-36	198
2	6	82	86	59	-62
3	6	174	158	36	-154
4	6	224	222	28	-220
5	6	113	113	66	-92
6	6	58	73	-41	60
7	6	172	175	-4	175
1	-6	93	100	98	-23
2	-6	19	4	4	2
3	-6	257	243	-25	241
4	-6	287	281	98	263
5	-6	50	33	33	-6
6	-6	63	77	74	22
7	-6	225	237	-15	-237
8	-6	143	161	64	-147
9	-6	39	29	-1	29
10	-6	57	71	-71	8
11	-6	173	188	16	187
12	-6	123	144	-63	130
13	-6	19	16	-15	6
0	7	119	125	18	123
1	7	194	174	20	-172
2	7	323	305	46	-301
3	7	187	173	-15	-173
4	7	41	36	5	-36
5	7	124	123	-39	116
6	7	267	256	-19	256
7	7	154	150	-10	150
1	-7	230	255	-36	-253
2	-7	304	279	-61	-272
3	-7	175	151	-45	-145
4	-7	47	35	27	22
5	-7	228	213	-71	201
6	-7	336	340	25	340
7	-7	81	82	40	72
8	-7	71	82	11	-82
9	-7	165	169	71	-153
10	-7	205	223	16	-222
0	8	200	194	-28	-192
1	8	125	113	-44	-103
2	8	77	89	-21	-86
1	-8	106	94	-23	91
2	-8	149	145	11	-144
3	-8	172	159	8	-159
4	-8	178	164	-30	-161
5	-8	96	96	-31	-91
6	-8	106	115	-29	111
7	-8	182	190	-46	185
8	-8	155	167	-31	165
9	-8	19	10	-1	-10
K= 2					
1	0	343	391	383	77
2	0	559	491	-291	-396
3	0	553	524	-521	-57
4	0	731	698	-694	70
5	0	346	322	-275	-167
6	0	318	313	164	267
7	0	415	397	397	4
8	0	542	538	534	65
9	0	99	105	96	43
10	0	75	84	-57	-62
11	0	199	201	-196	44
12	0	309	317	-314	-40
13	0	63	59	-56	-18
14	0	67	77	74	24
0	1	304	298	273	-121
1	1	439	467	-175	433
2	1	342	296	-247	-166
3	1	187	134	79	-108
4	1	299	264	-152	216
5	1	443	410	377	161
6	1	472	425	419	69
7	1	74	55	20	51
8	1	84	78	-74	23
9	1	348	321	-299	-118
10	1	168	162	-157	-42
11	1	72	67	-56	-37
12	1	43	32	26	20
13	1	219	221	219	23
14	1	128	118	114	-30
1	-1	270	292	292	5
2	-1	383	394	383	95
3	-1	257	224	-120	-190
4	-1	270	263	-253	71
5	-1	284	304	-207	-223
6	-1	462	482	-481	9
7	-1	229	229	-228	-21
8	-1	225	224	194	-113
9	-1	279	282	277	49
10	-1	266	280	278	36
11	-1	88	103	89	53
12	-1	145	158	-128	-92
13	-1	191	211	-209	-29
14	-1	215	237	-237	13
0	2	77	13	12	-5
1	2	189	178	-165	-65
2	2	353	313	-300	90
3	2	91	82	31	-76

Table 6 (*cont.*)

H	L	F_o	F_o	A_c	B_c
4	2	236	196	158	-117
5	2	389	340	330	80
6	2	115	105	97	40
7	2	304	273	-256	-95
8	2	259	258	-240	-95
9	2	291	282	-279	-41
10	2	108	100	-97	-22
11	2	214	203	203	2
12	2	248	235	229	53
13	2	152	160	159	19
1	-2	213	203	-84	185
2	-2	529	511	509	37
3	-2	457	468	444	148
4	-2	167	181	100	151
5	-2	32	21	9	19
6	-2	389	411	-401	91
7	-2	327	358	-314	-172
8	-2	189	214	-175	-123
9	-2	114	125	70	103
10	-2	377	407	407	-4
11	-2	201	213	211	33
12	-2	59	64	45	46
13	-2	77	81	-75	-29
14	-2	217	239	-235	-46
0	3	400	361	-281	-226
1	3	210	170	169	12
2	3	269	236	227	-63
3	3	570	511	510	-33
4	3	199	172	172	-3
5	3	281	250	-230	-99
6	3	320	281	-275	56
7	3	382	361	-360	26
8	3	78	71	-63	-34
9	3	123	112	111	20
10	3	268	262	244	94
11	3	316	323	322	16
12	3	47	45	44	9
13	3	106	103	-100	24
1	-3	719	697	-697	-1
2	-3	510	497	-485	-108
3	-3	95	99	-76	-63
4	-3	459	483	451	174
5	-3	507	555	542	121
6	-3	227	241	230	73
7	-3	152	158	33	-155
8	-3	279	298	-296	32
9	-3	364	401	-400	-22
10	-3	82	104	-74	-73
11	-3	144	145	87	116
12	-3	203	211	210	16
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9	4	198	182	170	-65
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5	-8	202	195	189	48
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11	0	68	66	-60	29
12	0	95	85	83	-19
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6	1	293	277	-107	-255
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8	1	327	304	-37	302
9	1	227	221	-128	180
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6	-1	226	245	98	-225
7	-1	451	461	106	-449
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11	-1	209	223	-94	202
12	-1	138	154	-12	153
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14	-1	154	182	-5	-182
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7	-6	194	199	0	-199
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9	-6	57	55	54	-11
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9	0	99	105	89	55
10	0	44	58	-39	-43
11	0	183	198	-163	-112
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13	0	61	61	-7	-61
14	0	55	60	54	25
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2	1	392	357	-313	-171
3	1	382	334	-3	-334
4	1	223	184	-183	16
5	1	206	188	188	7
6	1	424	378	363	105
7	1	160	146	31	142
8	1	121	99	-11	-98
9	1	174	176	-175	-19
10	1	157	146	-126	-74
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13	1	174	173	173	4
14	1	104	120	100	65
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2	-1	292	325	325	4
3	-1	153	173	106	136
4	-1	103	146	-66	95
5	-1	197	205	-205	-3
6	-1	285	295	-295	4
7	-1	187	205	-202	-31
8	-1	140	154	154	-5
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5	2	352	294	266	127
6	2	178	158	105	118
7	2	171	163	-131	97
8	2	213	195	-171	-93
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12	2	174	168	159	54
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7	-3	86	103	44	-93
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Table 6 (*cont.*)

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14	-4	113	129	113	61
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7	5	217	203	152	135
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7	-5	289	295	288	-65
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7	-2	121	124	107	61
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14	-2	103	96	8	95
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9	3	182	158	1	-158
10	3	79	65	-15	-63
11	3	67	66	-1	66
12	3	137	142	-63	128
13	3	104	112	-7	112
1	-3	78	73	71	17
2	-3	228	212	132	-166
3	-3	267	263	-54	-257
4	-3	63	63	50	-39
5	-3	69	75	-4	74
6	-3	261	251	-132	214
7	-3	190	212	-49	206
8	-3	141	152	-119	95
9	-3	77	68	68	-9
10	-3	210	203	81	-186
11	-3	139	128	35	-124
12	-3	78	100	99	-17
13	-3	66	59	-59	8
14	-3	92	106	-68	81
0	4	266	232	45	-227
1	4	167	144	-16	-144
2	4	163	138	-78	113
3	4	380	322	-64	316
4	4	239	202	-71	189
5	4	26	26	20	17
6	4	115	111	45	-102
7	4	257	216	84	-199
8	4	183	170	113	-127
9	4	32	47	-39	-25
10	4	102	114	-50	103
1	-4	295	265	-2	265
2	-4	144	129	-55	116
3	-4	232	212	-14	-211
4	-4	343	346	97	-332
5	-4	301	313	65	-306
6	-4	94	94	54	-76
7	-4	171	171	-52	163
8	-4	246	244	-122	211
9	-4	260	261	-7	261
10	-4	90	97	-31	92
11	-4	113	116	44	-107
12	-4	182	181	100	-150
13	-4	123	115	-23	-113
14	-4	35	22	-21	5
0	5	84	73	-71	17
1	5	204	183	-98	155
2	5	159	138	-41	131
3	5	69	56	28	48
4	5	194	166	98	-134
5	5	160	152	119	-94
6	5	46	48	-38	-29
7	5	112	104	2	104
8	5	131	121	-38	115
9	5	126	108	-82	70
1	-5	141	133	-23	131
2	-5	203	198	-127	152
3	-5	261	241	-108	215
4	-5	79	63	37	52
5	-5	188	174	13	-173
6	-5	221	222	72	-210
7	-5	204	216	118	-181
8	-5	78	69	-23	-64
9	-5	106	100	-29	96
10	-5	171	163	-45	157
11	-5	132	126	18	124
12	-5	34	14	14	2
0	6	247	218	-106	190
1	6	128	133	-26	130
2	6	61	61	-60	-10
3	6	140	131	98	-88
4	6	155	145	60	-132
5	6	66	57	-9	-56
6	6	19	23	10	21
7	6	122	131	-81	103
1	-6	78	65	45	-46
2	-6	97	73	-67	28
3	-6	152	146	-57	134
4	-6	227	230	-108	203
5	-6	130	125	-46	117
6	-6	60	36	30	-19
7	-6	167	159	51	-151
8	-6	105	100	25	-96
9	-6	65	68	61	-30
10	-6	47	24	-11	21
11	-6	158	139	-63	124
12	-6	79	90	-28	86
0	7	80	65	-18	62
1	7	110	102	14	-101
2	7	229	199	-21	-198
3	7	169	147	91	-115
4	7	34	22	-15	-17
5	7	88	85	-56	64
6	7	169	163	-29	160
7	7	106	104	-35	98
1	-7	225	212	61	-203
2	-7	251	235	33	-233
3	-7	121	119	49	-108
4	-7	92	78	-72	29
5	-7	163	147	-18	146
6	-7	204	215	-17	214
7	-7	88	98	-57	80
8	-7	90	82	44	-70
0	8	172	161	30	-158
1	8	145	146	74	-125
2	8	63	70	-16	-68
1	-8	35	36	-4	35
2	-8	93	104	-45	-94
3	-8	122	131	63	-115
4	-8	154	147	55	-136
5	-8	50	53	18	-50
6	-8	50	53	-19	49
7	-8	114	122	-51	110
8	-8	115	102	5	102
K= 6					
4	0	280	299	-295	-52
5	0	154	164	-163	7
6	0	101	87	-37	79
7	0	319	292	263	127
8	0	248	222	221	28
9	0	87	85	50	69
10	0	93	75	-61	-43
11	0	206	206	-170	-117
12	0	151	159	-155	-33
13	0	96	91	-87	-24
14	0	85	86	76	41
3	1	200	193	-171	-90
4	1	60	67	-24	63
5	1	185	154	111	107
6	1	226	181	129	127
7	1	140	130	75	106
8	1	123	94	-49	-80
9	1	141	117	-91	-74
10	1	203	170	-130	-110
11	1	95	79	-53	-60
12	1	79	70	51	47
13	1	130	123	123	10
14	1	135	138	115	78
4	-1	118	113	-112	-13
5	-1	204	185	-124	-137
6	-1	214	204	-196	-59
7	-1	56	61	-53	-30
8	-1	139	138	137	-17
9	-1	212	202	166	115
10	-1	198	181	176	41
11	-1	31	18	14	12
12	-1	33	61	-60	-14
13	-1	153	160	-113	-114
14	-1	113	121	-120	-15
0	2	240	217	-208	-62
1	2	242	228	-201	-109
2	2	139	116	-111	-35
3	2	85	76	52	-55
4	2	252	219	177	130
5	2	261	227	224	38
6	2	91	84	83	-11
7	2	138	115	-105	47
8	2	216	196	-111	-162
9	2	139	123	-92	-81
10	2	47	44	-41	15
11	2	93	90	88	22
12	2	152	163	144	77
1	-2	70	83	-54	63
2	-2	208	197	194	34
3	-2	234	242	192	147
4	-2	150	164	41	158
5	-2	62	60	-57	18
6	-2	191	192	-164	-100
7	-2	240	230	-191	-129
8	-2	150	127	-97	-82
9	-2	49	72	69	-19
10	-2	169	180	173	48
11	-2	173	168	117	122
12	-2	97	84	61	58
13	-2	62	46	-12	-44
14	-2	99	114	-113	-17
0	3	164	140	-84	-112
1	3	87	67	23	-63
2	3	275	254	227	114
3	3	372	325	322	-47
4	3	163	140	138	26
5	3	103	88	-82	33
6	3	253	227	-214	-78
7	3	198	178	-177	-19
8	3	102	103	-103	-10
9	3	75	77	49	59
10	3	194	163	153	55
11	3	143	132	126	37
12	3	54	40	13	38
1	-3	301	272	-258	-84
2	-3	242	214	-173	-127
3	-3	125	115	-21	113
4	-3	229	209	182	103
5	-3	282	278	260	100
6	-3	133	144	74	124
7	-3	89	91	21	-89
8	-3	212	208	-156	-137
1	-3	301	272	-258	-84
2	-3	242	214	-173	-127
3	-3	125	115	-21	113
4	-3	229	209	182	103
5	-3	282	278	260	100
6	-3	133	144	74	124
7	-3	89	91	21	-89
8	-3	212	208	-156	-137
9	-3	231	238	-230	-61
10	-3	109	108	-103	-30
11	-3	46	39	29	26
12	-3	160	165	144	81
13	-3	96	117	84	81
14	-3	54	56	28	49
0	4	126	107	96	47
1	4	188	14	113	77
2	4	210	179	141	111
3	4	39	38	-2	-38
4	4	105	97	-94	-23
5	4	204	185	-181	-40
6	4	127	117	-110	-40
7	4	87	75	-11	74
8	4	97	66	44	49
9	4	153	146	135	56
10	4	36	57	53	22
1	-4	80	52	-17	-49
2	-4	233	203	-156	-131
3	-4	187	159	-157	-26
4	-4	136	122	-99	-72
5	-4	130	123	111	52
6	-4	181	178	143	105
7	-4	191	187	187	1
8	-4	121	107	102	34
9	-4	95	93	-78	-51
10	-4	140	130	-106	-76
11	-4	124	139	-135	-31
12	-4	35	42	5	-41
13	-4	64	66	56	35
14	-4	95	101	64	78
0	5	211	186	135	129
1	5	174	140	140	-2
2	5	96	76	-52	54
3	5	223	193	-173	-86
4	5	174	144	-88	-113
5	5	67	65	-55	-34
6	5	68	65	65	8
7	5	129	137	108	84
8	5	157	137	134	30
9	5	76	66	63	-22
10	5	79	91	-89	-16
1	-5	198	182	111	145
2	-5	58	38	-18	-34
3	-5	151	134	-133	-15
4	-5	269	255	-242	-81
5	-5	182	165	-153	-62
6	-5	74	77	65	-40
7	-5	140	149	149	2
8	-5	189	197	151	126
9	-5	82	88	70	52
10	-5	19	8	-4	7
11	-5	113	138	-136	-21
12	-5	144	149	-137	-58
0	6	56	44	-28	35
1	6	162	144	-124	-73
2	6	214	166	-151	-69
3	6	97	88	-42	-78
4	6	100	94	85	-39
5	6	145	133	130	28
6	6	171	146	140	42
1	-6	158	137	128	50
2	-6	207	183	167	75
3	-6	174	165	107	126
4	-6	72	60	24	-55
5	-6	135	134	-120	-60
6	-6	180	177	-156	-84
7	-6	132	138	-84	-110
8	-6	48	51	10	50
9	-6	119	106	90	55
10	-6	127	131	98	87
11	-6	65	76	44	62
12	-6	55	53	-47	-24
0	7	161	148	-139	-50
1	7	155	134	-125	-46
2	7	36	12	-8	-9
3	7	75	56	53	21
4	7	121	112	98	55
5	7	103	79	63	47
6	7	0	18	15	-10
1	-7	71	58	-29	-50
2	-7	35	35	33	12
3	-7	137	139	95	102
4	-7	133	128	121	42
5	-7	95	94	94	8
6	-7	0	51	-25	-45
7	-7	122	124	-101	-72
8	-7	74	80	-70	-38
0	8	103	96	-95	-9
1	8	56	40	36	18
1	-8	164	144	-133	-54
2	-8	154	148	-140	-48
3	-8	19	9	-1	-9
4	-8	54	79	79	8
5	-8	116	125	103	70
6	-8	117	123	118	36

found near certain of the oxygen atoms (Table 2) which may represent hydrogen atoms, but it was not thought worth while to calculate structure factors with these included and no further refinement was carried out. The final R value was 11.1% for 1416 reflexions (Table 3); no omissions were made. Final parameters and estimated standard deviations are listed in Table 4.

Incorrectness of the 'refined' structure of $Na_2O.GeO_2.6H_2O$

A comparison of the silicate and germanate structures showed that agreement was generally good. The positions of the oxygen atoms O(3) and O(4), however, had changed considerably in the refinement of the silicate (Table 5) so that in the (010) projection the two atoms had virtually changed places, while retaining similar heights up y (Fig. 2). In addition, it should be noted that the x, y, z coordinates of O(3) in the germanate structure [Table 5(*a*)] become the $x, \bar{y}, z$ coordinates of O(4) in the silicate [Table 5(*b*)], with a similar effect for O(4) of the germanate.

Because of this inconsistency, it was suspected that one of the structures was wrong. Of the two, the silicate was considered more likely to be correct because (1) it had refined further from the germanate structure to give a lower final R value and (2) the final difference synthesis showed no unusual effects. Accordingly, a

Table 7. *Final parameters for the non-hydrogen atoms of* $Na_2O.GeO_2.6H_2O$

Figures in brackets give the estimated standard deviation corresponding to the least significant digit.

	Coordinates (fractions of cell edge)			Isotropic temperature factor,
	x	y	z	B
Ge	0·1312 (1)	0·0122 (4)	0·2092 (1)	0·77 (1) Å^2
Na(1)	0·3826 (3)	0·4681 (8)	0·9298 (6)	1·35 (6)
Na(2)	0·1314 (3)	0·500 (1)	0·5694 (6)	1·83 (6)
O(1)	0·2768 (5)	0·984 (1)	0·344 (1)	0·8 (1)
O(2)	0·1033 (5)	0·978 (1)	0·934 (1)	0·8 (1)
O(3)	0·0450 (6)	0·820 (1)	0·323 (1)	0·9 (1)
O(4)	0·0876 (6)	0·288 (2)	0·270 (1)	1·2 (1)
O(5)	0·2769 (7)	0·149 (2)	0·748 (1)	1·8 (1)
O(6)	0·4172 (7)	0·325 (2)	0·294 (1)	2·2 (1)
O(7)	0·3427 (7)	0·625 (2)	0·568 (1)	2·1 (1)
O(8)	0·4193 (6)	0·856 (2)	0·056 (1)	1·3 (1)
O(9)	0·1849 (6)	0·556 (2)	0·944 (1)	1·8 (1)

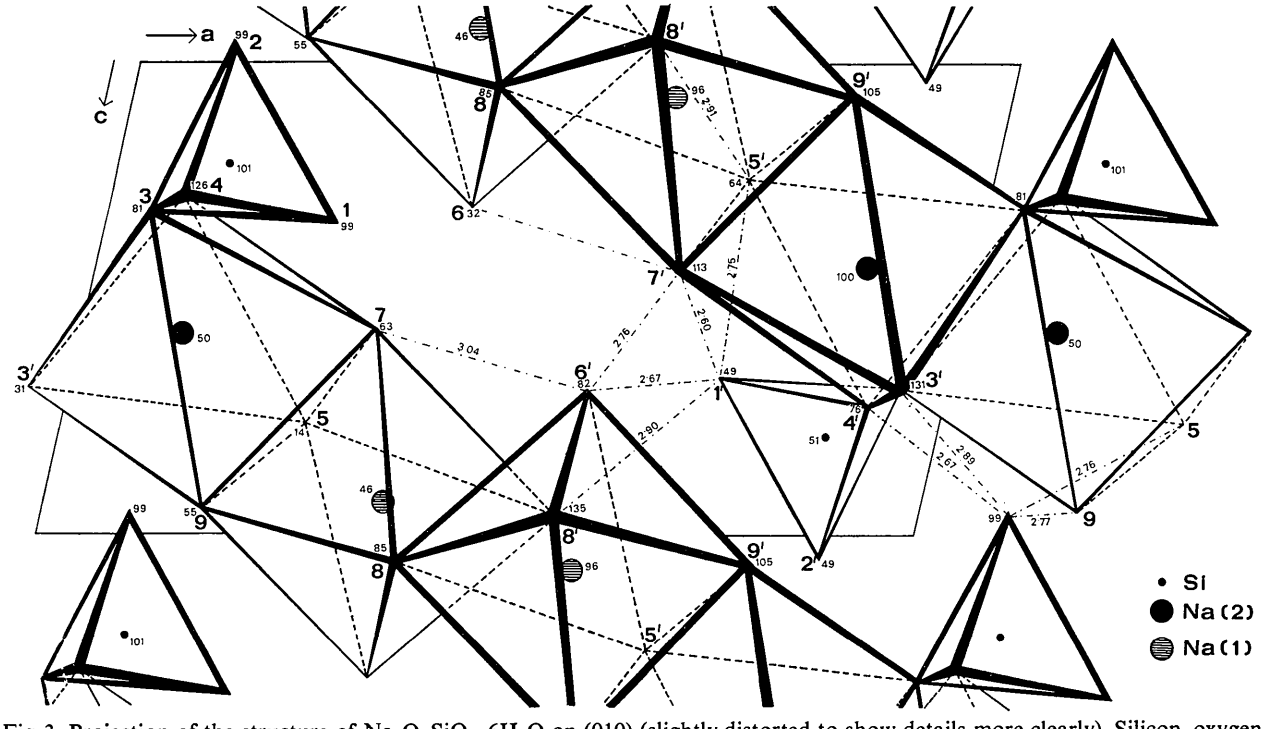

Fig. 3. Projection of the structure of $Na_2O.SiO_2.6H_2O$ on (010) (slightly distorted to show details more clearly). Silicon–oxygen tetrahedra and sodium–oxygen octahedra are drawn, oxygen atoms occurring at the corners. Figures have the same significance as in Fig. 2, and some hydrogen bond lengths are given in Å. The sodium–oxygen octahedra share the faces O(5)–O(7)–O(9) and the corners O(3) and O(8).

further sequence of least-squares refinements on $Na_2O.GeO_2.6H_2O$ was undertaken, this time employing the parameters for O(3) and O(4) taken from the silicate structure.

The initial R value was slightly higher than previously obtained, at 13.0%, but the atoms O(3) and O(4) did not tend to return to their original positions. A total of ten further least-squares cycles on the full data were required for complete refinement. At this stage, the maximum shift in atomic coordinates was 0.167 of the e.s.d. and the average shift 0.066 of the average e.s.d. The final R index was reduced to 8.5% (from 11.9%) for 1347 reflexions (Table 6). Final parameters and standard deviations are listed in Table 7.

The experience outlined here shows the danger in accepting too readily the results of least-squares refinements, however plausible, and especially where a 'heavy' atom is involved.

Description of the structure

The (010) projection of the structure of $Na_2O.SiO_2.6H_2O$ is illustrated in Fig. 3. It could equally well represent the germanate structure, with minor alterations to the atomic positions and bond distances.

Each silicon and germanium atom is surrounded by four oxygen atoms at the corners of a somewhat distorted tetrahedron [Table 8(*a*) and Fig. 4]; in the ensuing discussion, these will be called 'tetrahedral' oxygen atoms to distinguish them from the 'water' oxygen atoms. Si–O bond distances vary from 1.62 to 1.71 Å and Ge–O distances from 1.72 to 1.83 Å. A surprising difference is that in the silicate there is one outstandingly long bond [Si–O(3)], the other three being of a similar length, while in the germanate there are two long bonds and two shorter ones. The tetrahedra are isolated, but approach each other fairly closely [Table 8(*c*)], indicating the presence of hydrogen bonds (to be discussed later).

There are two independent sodium atoms. Na(1) is surrounded entirely by 'water' oxygen atoms in the form of a fairly regular octahedron [Table 8(*b*)]. Bond lengths vary from 2.36 to 2.52 Å in the germanate and from 2.37 to 2.50 Å in the silicate. Na(2) is coordinated by three 'tetrahedral' oxygen atoms and three 'water' oxygen atoms; the resulting octahedron shows far more distortion [Table 8(*b*)]. Bond lengths vary considerably: from 2.28 to 2.82 Å in the germanate and from 2.29 to 2.80 Å in the silicate. The sodium–oxygen octahedra are linked together in an unusual manner to produce sheets (Fig. 3).

Table 8(*e*) shows the coordination of the 'water' oxygen atoms. Three of these, O(6), O(8) and O(9), have roughly tetrahedral coordination. O(5) and O(7) are five-coordinated, in the shape of what may be described most nearly as an irregular trigonal bipyramid.

Hydrogen bonding system

There are twelve independent hydrogen atoms to be located. Table 8(*c*) and (*d*) lists all twelve O–O distances less than 3.25 Å for atoms not bonded to the same silicon, germanium or sodium atom. It is assumed that each of these represents some sort of hydrogen bond. The distance O(4)–O(9) in the silicate (3.18 Å) seems too long for this, but if O(9) is in fact a water molecule, then it must have a hydrogen atom pointing somewhere in the direction of O(4).

The shortest distances between the tetrahedra, taken to represent hydrogen bonds, are from O(2) to O(3) and from O(2) to O(4). This means that at least two hydrogen atoms must be associated with each tetrahedron, and as they cannot both be near O(2), at least one must be near O(3) or O(4). The Si–O(3) bond is long and a peak was found near O(3) on the difference synthesis, leading to the conclusion that O(3) is a hydroxyl group. In support of this argument, the Na–O(3) distances calculated are consistently fairly long (average 2.55 Å), indicating that O(3) is not charged.

On the other hand, the Na(2)–O(4) distance is outstandingly short for both silicate and germanate, and in the silicate Si–O(4) is not much longer than Si–O(2). No peak was found near O(4) on the difference synthesis, and it is difficult to decide whether the hydrogen

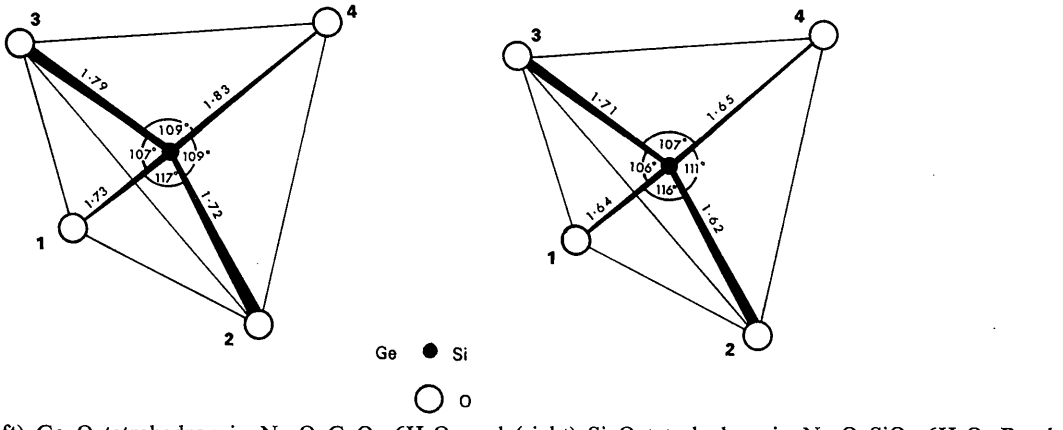

Fig. 4. Details of (left) Ge–O tetrahedron in $Na_2O.GeO_2.6H_2O$, and (right) Si–O tetrahedron in $Na_2O.SiO_2.6H_2O$. Bond lengths in Å.

Table 8. *Interatomic distances and bond angles for* $Na_2O.GeO_2.6H_2O$ *and* $Na_2O.SiO_2.6H_2O$

Figures in brackets represent the estimated standard deviation corresponding to the least significant digit.

(*a*) Germanium–oxygen and silicon–oxygen tetrahedra.

$Na_2O.GeO_2.6H_2O$	Bond distance	$Na_2O.SiO_2.6H_2O$	Bond distance
Ge–O(1)	1·726 (8) Å	Si–O(1)	1·640 (7) Å
Ge–O(2)	1·723 (8)	Si–O(2)	1·623 (7)
Ge–O(3)	1·792 (8)	Si–O(3)	1·712 (7)
Ge–O(4)	1·833 (9)	Si–O(4)	1·646 (8)
O(1)–O(2)	2·94 (1)	O(1)–O(2)	2·767 (9)
–O(3)	2·83 (1)	–O(3)	2·679 (9)
–O(4)	2·83 (1)	–O(4)	2·632 (9)
O(2)–O(3)	2·87 (1)	O(2)–O(3)	2·718 (9)
–O(4)	2·90 (1)	–O(4)	2·701 (9)
O(3)–O(4)	2·95 (1)	O(3)–O(4)	2·704 (9)
	Bond angle		Bond angle
O(1)–Ge–O(2)	116·6 (4)°	O(1)–Si–O(2)	116·0 (3)°
–O(3)	107·1 (4)	–O(3)	106·1 (3)
–O(4)	105·5 (4)	–O(4)	106·5 (3)
O(2)–Ge–O(3)	109·3 (4)	O(2)–Si–O(3)	109·2 (3)
–O(4)	108·9 (4)	–O(4)	111·4 (4)
O(3)–Ge–O(4)	109·1 (4)	O(3)–Si–O(4)	107·3 (4)

(*b*) Sodium–oxygen octahedra.

	$Na_2O.GeO_2.6H_2O$ Bond distance	$Na_2O.SiO_2.6H_2O$ Bond distance
Na(1)–O(5)	2·46 (1) Å	2·43 (1) Å
–O(6)	2·43 (1)	2·49 (1)
–O(7)	2·45 (1)	2·50 (1)
–O(8)′	2·37 (1)	2·37 (1)
–O(8)	2·52 (1)	2·48 (1)
–O(9)	2·36 (1)	2·39 (1)
	Bond angle	Bond angle
O(5)–Na(1)–O(6)	97·3 (4)°	98·5 (3)°
–O(7)	84·0 (4)	83·6 (3)
–O(8′)	99·3 (3)	102·2 (3)
–O(9)	79·5 (3)	77·6 (3)
O(8)–Na(1)–O(6)	93·2 (3)	90·8 (3)
–O(7)	84·9 (3)	85·4 (3)
–O(8′)	99·7 (3)	98·7 (3)
–O(9)	82·5 (3)	82·4 (3)
O(6)–Na(1)–O(8′)	83·8 (3)	85·7 (3)
–O(9)	90·8 (4)	88·5 (3)
O(7)–Na(1)–O(8′)	98·2 (4)	99·3 (3)
–O(9)	87·3 (4)	86·5 (3)
	Bond distance	Bond distance
Na(2)–O(3)	2·58 (1) Å	2·52 (1) Å
–O(3′)	2·53 (1)	2·57 (1)
–O(4)	2·28 (1)	2·29 (1)
–O(5)	2·82 (1)	2·80 (1)
–O(7)	2·55 (1)	2·58 (1)
–O(9)	2·36 (1)	2·39 (1)
	$Na_2O.GeO_2.6H_2O$ Bond angle	$Na_2O.SiO_2.6H_2O$ Bond angle
O(3) –Na(2)–O(3′)	105·6 (3)°	108·6 (3)°
–O(4)	86·6 (3)	87·5 (3)
–O(7)	90·9 (3)	88·8 (3)
–O(9)	119·2 (4)	122·7 (3)
O(5) –Na(2)–O(3′)	89·9 (3)	89·7 (2)
–O(4)	84·6 (3)	82·9 (3)
–O(7)	75·3 (3)	75·1 (3)
–O(9)	72·4 (3)	70·7 (3)
O(3′)–Na(2)–O(4)	85·7 (3)	84·8 (3)
–O(9)	81·1 (3)	79·5 (3)
O(7) –Na(2)–O(4)	102·4 (4)	104·4 (3)
–O(9)	84·9 (4)	84·5 (3)

Table 8 (*cont.*)

(*c*) Hydrogen bonds linking the tetrahedra directly.

	$Na_2O.GeO_2.6H_2O$ Bond distance	$Na_2O.SiO_2.6H_2O$ Bond distance
O(2)–O(3′)	2·97 (1) Å	2·89 (1) Å
O(2)–O(4′)	2·58 (1)	2·67 (1)

(*d*) Other hydrogen bonds

O(1)–O(5)	2·76 (1) Å	2·75 (1) Å
–O(6)	2·71 (1)	2·67 (1)
–O(7)	2·65 (1)	2·60 (1)
–O(8)	2·82 (1)	2·90 (1)
O(2)–O(5)	2·74 (1)	2·76 (1)
–O(9)	2·75 (1)	2·77 (1)
O(4)–O(9)	3·04 (1)	[3·18 (1)]
O(5)–O(8)	2·90 (1)	2·91 (1)
O(6)–O(7′)	2·98 (1)	3·04 (1)
–O(7)	2·80 (1)	2·76 (1)

(*e*) Coordination of the 'water' oxygen atoms.

	$Na_2O.GeO_2.6H_2O$ Bond distance	$Na_2O.SiO_2.6H_2O$ Bond distance
O(5)–Na(1)	2·46 (1) Å	2·43 (1) Å
–Na(2)	2·82 (1)	2·80 (1)
–O(1)	2·76 (1)	2·75 (1)
–O(2)	2·74 (1)	2·76 (1)
–O(8)	2·90 (1)	2·91 (1)
	Bond angle	Bond angle
Na(1)–O(5)–Na(2)	76·9 (3)°	79·6 (3)°
–O(1)	129·4 (4)	129·2 (3)
–O(2)	115·7 (4)	113·0 (3)
–O(8)	91·4 (3)	88·2 (3)
Na(2)–O(5)–O(1)	91·4 (3)	88·4 (3)
–O(2)	92·5 (3)	90·9 (3)
–O(8)	161·9 (4)	161·4 (3)
O(1)—O(5)–O(2)	113·8 (4)	116·3 (3)
–O(8)	106·8 (4)	110·2 (3)
O(2)—O(5)–O(8)	80·2 (3)	81·0 (3)
	Bond distance	Bond distance
O(6)–Na(1)	2·43 (1) Å	2·49 (1) Å
–O(1)	2·71 (1)	2·67 (1)
–O(7′)	2·98 (1)	3·04 (1)
–O(7)	2·80 (1)	2·76 (1)
	Bond angle	Bond angle
Na(1)–O(6)–O(1)	114·2 (4)°	111·7 (3)°
–O(7′)	110·2 (4)	109·6 (3)
–O(7)	112·7 (4)	110·7 (3)
O(1)—O(6)–O(7′)	99·7 (4)	107·0 (3)
–O(7)	100·7 (4)	97·9 (3)
O(7′) –O(6)–O(7)	118·4 (5)	118·2 (3)

	$Na_2O.GeO_2.6H_2O$ Bond distance	$Na_2O.SiO_2.6H_2O$ Bond distance
O(7)–Na(1)	2·45 (1) Å	2·50 (1) Å
–Na(2)	2·55 (1)	2·58 (1)
–O(1)	2·65 (1)	2·60 (1)
–O(6)	2·80 (1)	2·76 (1)
–O(6′)	2·98 (1)	3·04 (1)
	Bond angle	Bond angle
Na(1)–O(7)–Na(2)	82·5 (4)°	82·9 (3)°
–O(1)	144·2 (5)	145·9 (4)
–O(6)	107·6 (4)	105·0 (3)
–O(6′)	84·6 (4)	83·2 (3)
Na(2)–O(7)–O(1)	95·0 (4)	93·0 (3)
–O(6)	102·8 (4)	102·5 (3)
–O(6′)	161·4 (5)	162·5 (4)
O(1)—O(7)–O(6)	107·7 (4)	108·9 (4)
–O(6′)	87·6 (4)	92·5 (3)
O(6)—O(7)–O(6′)	93·9 (4)	91·4 (3)

Table 8 (*cont.*)

	Bond distance	Bond distance
O(8)–Na(1′)	2·37 (1) Å	2·37 (1) Å
–Na(1)	2·52 (1)	2·48 (1)
–O(1)	2·82 (1)	2·90 (1)
–O(5)	2·90 (1)	2·91 (1)
	Bond angle	Bond angle
Na(1′)–O(8)–Na(1)	112·6 (4)°	111·5 (3)°
–O(1)	125·4 (4)	128·1 (3)
–O(5)	104·3 (4)	107·3 (3)
Na(1) –O(8)–O(1)	113·0 (3)	112·8 (3)
–O(5)	109·9 (4)	107·2 (3)
O(1) —O(8)–O(5)	86·7 (3)	84·9 (3)
	Bond distance	Bond distance
O(9)–Na(1)	2·36 (1) Å	2·39 (1) Å
–Na(2)	2·36 (1)	2·39 (1)
–O(2)	2·75 (1)	2·77 (1)
–O(4)	3·04 (1)	3·18 (1)
	Bond angle	Bond angle
Na(1)–O(9)–Na(2)	88·4 (3)°	89·4 (3)°
–O(2)	123·6 (4)	123·3 (3)
–O(4)	113·4 (4)	114·2 (3)
Na(2)–O(9)–O(2)	95·6 (4)	96·7 (3)
–O(4)	123·6 (4)	122·9 (3)
O(2)—O(9)–O(4)	110·7 (4)	108·9 (3)

atom indicated by the short O(2)–O(4) distance is associated with O(2), with O(4), or (most probably) shared by the two atoms. The long Ge–O(4) distance may mean that in the germanate the hydrogen atom is more firmly attached to O(4), although the Na(2)–O(4) distance remains short.

The rest of the structure can be explained on the basis of O(5) to O(9) being water molecules, but if the fact that only a few peaks could be picked up on the difference synthesis is significant, it seems probable that there is some sort of statistical distribution of hydrogen atoms throughout the structure. If this is the case, then some of the 'water' oxygen atoms could tend towards $(OH)^-$ and others towards $(H_3O)^+$.

Discussion

The Si–O bond lengths for the $(H_2SiO_4)^{2-}$ ion in $Na_2H_2SiO_4.8H_2O$ (Jamieson & Dent Glasser, 1966*b*) are 1.672 and 1.591 ± 0.008 Å.

A recent structure refinement of Na_2SiO_3 (McDonald & Cruickshank, 1967) has shown distances of 1.672 and 1.592 ± 0.002 Å for the bridging and non-bridging Si–O bonds respectively. For this reason, it is thought that the lengths in $Na_2H_2SiO_4.8H_2O$ are a true indication of the distinction between Si–OH and Si–O. McDonald & Cruickshank (1967) have pointed out that these distances agree with the π-bonding theory developed for bond lengths in acid phosphates (Cruickshank & Robinson, 1966).

The distance Si–O(3) (1.712 Å) in $Na_2O.SiO_2.6H_2O$ is thus considerably longer than would be expected for Si-OH. This may be explained by the fact that O(3) is coordinated also by two sodium atoms. The remaining Si–O distances lie about midway between expected lengths for Si–O and Si–OH, supporting the conclusion that the hydrogen atoms have a statistical distribution. It seems likely, from a study of bond lengths, that the formula of the anion in $Na_2O.SiO_2.6H_2O$ lies somewhere between $(H_2SiO_4)^{2-}$ and $(H_3SiO_4)^-$.

The structure of the sodium silicate hydrate $Na_2O.SiO_2.5H_2O$ has recently been solved (Jost & Hilmer, 1966). This structure shows many similarities to that of $Na_2O.SiO_2.6H_2O$, and Si–O bond distances are 1.61, 1.61, 1.64 and 1.70 Å. It is probable that the hydrogen atoms again take up a statistical distribution.

Several hydrogen germanates are known in addition to $Na_2O.GeO_2.7H_2O$. These have been formulated as $MH_3Ge_2O_6$ [M = Li, Na, K, NH_4, Rb, Cs] (Nowotny & Wittmann, 1953; Nowotny & Szekely, 1952), $M_3HGe_7O_{16}4H_2O$ [M = Li, Na, K, NH_4, Rb, Cs, Tl, Ag] (Wittmann & Nowotny, 1956), $BaH_2GeO_4.4H_2O$ and SrH_2GeO_4 (Nowotny & Szekely, 1952). The latter has been shown to be isostructural with KH_2PO_4, thus providing evidence for the existence of the $(H_2GeO_4)^{2-}$ ion. No accurate values for Ge–OH distances are, however, known. Bond distances for Ge–O in quartz-like GeO_2 (Smith & Isaacs, 1964) are 1.739 ± 0.003 Å.

Germanium-oxygen distances in $Na_2O.GeO_2.6H_2O$ may indicate that the formula of the anion is more nearly $(H_2GeO_4)^{2-}$ as compared with the silicate. In view of the doubt as to the location of the hydrogen atoms, however, it would be unwise to assign an exact formula to either of these compounds.

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Crystal Structures of Mesotartaric Acid

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Triclinic mesotartaric acid monohydrate crystallizes in $P\bar{1}$ with $Z=2$ and $a=5{\cdot}516$, $b=9{\cdot}220$, $c=7{\cdot}330$ Å and $\alpha=115{\cdot}11$, $\beta=93{\cdot}62$, $\gamma=93{\cdot}64°$; the monoclinic monohydrate in $P2_1/c$ with $Z=4$ and $a=5{\cdot}215$, $b=5{\cdot}019$, $c=25{\cdot}92$ Å and $\beta=99{\cdot}72°$; the triclinic anhydrous modification in $P\bar{1}$ with $Z=2$ and $a=9{\cdot}459$, $b=6{\cdot}464$, $c=5{\cdot}396$ Å and $\alpha=68{\cdot}99$, $\beta=76{\cdot}36$, $\gamma=75{\cdot}77°$; and the orthorhombic anhydrous modification in $Pbn2_1$ or $Pbnm$ with $Z=16$ and $a=19{\cdot}05$, $b=9{\cdot}88$, $c=12{\cdot}16$ Å. The first three structures were solved by application of the correlation method to projections and refined by three-dimensional least squares.

The molecules are not centrosymmetric but have the staggered conformations as found earlier in mesotartrates. In the monoclinic modification the carbonyl group in one of the planar halves of the molecule is, surprisingly, not at the side of the α-hydroxyl group. The other intramolecular bond lengths and angles are approximately the same for the three structures. In the networks of hydrogen bonds, carboxylic acid dimers and hydrated links are of primary importance.

Introduction

The object of this investigation was to determine the conformation of the mesotartaric acid molecule in several crystal modifications. Moreover, the structure determinations of these substances, containing only light atoms, served as test cases for the correlation method (de Vries, 1965).

In the literature, three modifications of mesotartaric acid are described, namely a triclinic hydrate (Longchambon, 1926) and two anhydrous forms, one of which is orthorhombic (Longchambon, 1926) and the other triclinic (Schneider, 1928).

By recrystallization of the triclinic hydrate from water at different temperatures, the three modifications mentioned in the literature were obtained, as well as a monoclinic monohydrate (Bootsma & Schoone, 1964). Though no thermodynamic data are available it is reasonable to assume that at room temperature the monoclinic hydrate is not the stable modification.

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Experimental

In the determination of cell-dimensions 2θ values were measured on the single-crystal diffractometer. For the intensity measurements spherical crystals (diameter ~0·3 mm), ground by the technique described by Schuijff & Hulscher (1965), were used. The intensities were recorded on integrated Weissenberg photographs or collected with a General Electric diffractometer provided with a single-crystal orienter and a scintillation counter. Each reflexion was counted once and the background was measured for 15 seconds at both ends of the scanning region (3–4°). Copper radiation was used in all cases.

The intensities were corrected for Lorentz–polarization and absorption factors and for non-linearity of the counter.

Cell data

The cell dimensions were refined by a least-squares treatment of $\sin^2\theta$ values. In Table 1 our values are compared with those reported by Longchambon and Schneider.