nealing at and quenching (LN_2) from different temperatures.

It should be mentioned that results obtained with differential thermal analysis (DTA) did not agree with those obtained by metallographic and X-ray diffraction methods. For example, with DTA, $SmCo_{5\pm x}$ and Sm_2Co_{17} compounds were found to be peritectically melting in agreement with the results of Lihl *et al.* (1969) and Buschow & Van der Goot (1968). However, with X-ray diffraction and metallographic methods, these compounds were found to be congruently melting. A shift in the composition of the alloys due to oxidation, evaporation of Sm and chemical reactivity of Sm with crucible materials at elevated temperatures may lead to this discrepancy. In the case of metallographic and X-ray diffraction methods, this compositional shift can be detected and interpreted directly, whereas in the case of DTA this is not possible since the change in composition occurs gradually. Even if oxidation of the samples can be avoided by taking special precautions, however, evaporation and reaction (with crucible materials) of Sm are practically unavoidable.

The Co-rich part of the Sm–Co phase diagram (Fig. 3) differs from that even very recently reported (Buschow & Den Broeder, 1973) in the following respects:

(*a*) the two polymorphic forms of Sm_2Co_7 and Sm_2Co_{17} have been inserted correctly,

(*b*) no peritectic has been observed in the composition range $SmCo_{5+x}$ $(-0{\cdot}3\le x\le 1)$,

(*c*) one peritectoid and two eutectics have been inserted,

(*d*) the new phases $SmCo_{5-x}$ and $SmCo_{5+x}$ have been correctly inserted.

It should be noted that $SmCo_{5+x}$ and $Sm_2Co_{17}(h)$ are isostructural (*i.e.* of the $TbCu_7$-type with disordered substitutions). It means that we should obtain a homogeneous region from $SmCo_{5+x}$ to $Sm_2Co_{17}(h)$ in the phase diagram, at least, at temperatures near to the solidus. What we experimentally obtain is a eutectic in the neighbourhood of $SmCo_7$. An explanation for this discrepancy is still being sought.

The author wishes to thank Professor E. Kneller for valuable discussion, Mr B. Müller for help in preparing the alloys and Dr C. Herget from Th. Goldschmidt for material help.

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Crystal Structure of Monoclinic $NaCaHSiO_4$

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(*Received* 24 *October* 1973; *accepted* 25 *October* 1973)

Monoclinic $NaCaHSiO_4$ has a structure based on Ca^{2+} and Na^+ ions and $HSiO_4^{3-}$ groups, which are linked into chains by strong hydrogen bonds. The structure is similar to that of an orthorhombic form, from which it differs in the orientation of the silicate tetrahedra and the arrangement of hydrogen bonds.

$NaCaHSiO_4$, first synthesized by Thilo, Funk & Wichmann (1951), is important in relation to processes for extracting alumina from aluminosilicate materials. From chemical and other evidence, these workers suggested that it contained separate $HSiO_4^{3-}$ tetrahedra. This conclusion was supported by the spectroscopic studies of Stavitskaya, Ryskin & Mitropol'skii (1968), who concluded also that the tetrahedra were linked by strong hydrogen bonds. Gard, Ramsay & Taylor (1973) reported crystal data; they found the crystals to be monoclinic. In contrast, Lyutin, Kazak, Ilyukhin & Belov (1972) reported a structure determination on crystals that they had found to be orthorhombic, with cell parameters closely related to those given by Gard.

Ramsay & Taylor (1973). They confirmed the presence of separate SiO_4 tetrahedra, but the H atoms were assumed to occupy general positions, which implied that they were statistically distributed. The present paper describes a determination of the structure of monoclinic material.

Material and crystal data

The sample was made by grinding together solid NaOH, $Ca(OH)_2$ and quartz (0·6% Al_2O_3, 11200 cm^2 g^{-1}) in molar ratios 3:2:2 for a few minutes, without taking any special precautions to exclude atmospheric moisture, and heating the resulting powder in a sealed stainless steel vessel for 11 days at 280 °C. The presence of a little water is essential to the reaction. The product was washed with cold water. The powder pattern was identical with that given by Gard, Ramsay & Taylor (1973). A true single crystal of sufficient size could not be found, and a twinned crystal was used for the work. It was a prism elongated along **b**, of size 180 × 50 × 30 μm, twinned on (001), and contained equal amounts of the two components. Crystal data (from rotation, oscillation and Weissenberg photographs) agreed with those given by Gard, Ramsay & Taylor (1973).

Crystal data

Monoclinic, $P2_1$ or $P2_1/m$.
$a=5{\cdot}72$, $b=7{\cdot}06$, $c=5{\cdot}48$ Å, $\beta=122{\cdot}5°$, $V=186{\cdot}6$ Å^3, $Z=2$, $D_{obs}=2{\cdot}75$, $D_{calc}=2{\cdot}77$ g cm^{-3}.

Because the cell is geometrically nearly hexagonal, an unconventional *B*-centred monoclinic cell can be defined that has β nearly 90°, and there are three possible choices of axes which are nearly but not quite identical both for the primitive and for the *B*-centred cell; Gard, Ramsay & Taylor (1973) gave the parameters for all these cells.

Intensity measurement and structure determination

Intensities of 248 independent reflexions were estimated visually from multiple-film Weissenberg photographs of the *h*0*l* to *h*4*l* layers, taken with filtered Cu radiation. All reflexions were treated as observed. In general, reflexions were measured for both twin components and the results averaged; this provided a partial correction for absorption, but no other absorption correction was applied. For the 0*k*0 reflexions, intensities were obtained by powder diffractometry.

All calculations were made on an ICL 4/70 computer, with programs based on those kindly supplied by Dr F. R. Ahmed of the National Research Council of Canada, and adapted by Mr J. S. Knowles of the University of Aberdeen Computing Centre. Form factors (for Ca^{2+}, Na^+, Si, O, O^-, and H) were taken from *International Tables for X-ray Crystallography* (1962).

A trial structure, based on the orthorhombic structure reported by Lyutin, Kazak, Ilyukhin & Belov (1972), was refined by block-diagonal least-squares calculations, initially in $P2_1/m$ and later in $P2_1$. Individual, isotropic temperature factors were used. The H-atom position was based on crystal-chemical considerations, and no attempt was made to refine either the coordinates or the temperature factor assumed for this atom. In the final stages of refinement, the weighting scheme used was $w=1/[1+\{(|F_{obs}|-10{\cdot}0)/10{\cdot}0\}^2]$, and analyses against $|F_{obs}|$, $\sin^2\theta$ and k showed it to be satisfactory. The final R was 0·114 on all reflexions, and a final difference map showed no peaks outside the limits $\pm1{\cdot}5$ eÅ^{-3}, the largest values being near the Ca ions. Tables 1–3 give, respectively, the observed and calculated structure factors, atomic parameters, and the more important interatomic distances and angles. Fig. 1 shows the structure projected along **b**.

Table 1. *Observed and calculated structure factors* (× 10)

H	FO	FC	ALPHA
K= 0, L= 0			
-1	127	117	0.00
-2	202	171	180.00
-3	481	404	0.00
-4	98	78	0.00
-5	139	157	0.00
-6	181	179	0.00
K= 0, L= 1			
0	94	84	0.00
1	529	600	0.00
2	120	122	0.00
3	221	205	0.00
4	217	226	0.00
-1	80	61	0.00
-2	533	575	0.00
-3	210	218	0.00
-4	121	156	0.00
-5	146	167	0.00
-6	30	22	0.00
K= 0, L= 2			
0	420	383	0.00
1	183	176	0.00
2	298	285	0.00
3	74	72	180.00
4	143	127	0.00
-1	695	673	0.00
-2	209	226	180.00
-3	69	82	0.00
-4	560	530	0.00
-5	121	108	0.00
-6	66	48	0.00
-7	147	135	0.00
K= 0, L= 3			
0	202	197	0.00
1	76	76	0.00
2	260	227	0.00
3	179	179	0.00
-1	113	100	0.00
-2	201	231	0.00
-3	413	442	0.00
-4	172	167	0.00
-5	30	4	180.00
-6	113	133	0.00
K= 0, L= 4			
0	209	195	0.00
1	259	256	0.00
2	60	12	0.00
-1	106	183	0.00
-2	181	189	0.00
-3	108	93	0.00
-4	162	184	0.00
-5	205	241	0.00
-6	78	92	0.00
K= 0, L= 5			
0	27	14	180.00
1	140	171	0.00
-1	83	80	0.00
-2	261	280	0.00
-3	152	174	0.00
-4	90	89	0.00
-5	121	117	0.00
-6	29	47	0.00
-7	156	147	0.00
K= 0, L= 6			
-1	171	130	0.00
-2	57	80	0.00
-3	146	80	0.00
-4	134	171	0.00
-6	82	96	0.00
K= 1, L= 0			
-1	150	169	0.24
-2	150	141	31.41
-3	126	134	161.54
-4	39	44	114.66
K= 1, L= 1			
0	185	256	359.76
1	76	62	209.09
2	91	94	203.18
3	96	107	337.84
4	56	52	257.65
-1	91	86	161.23
-2	170	171	179.66
-3	134	145	16.32
-4	72	71	133.33
K= 1, L= 2			
0	236	228	0.10
1	74	71	225.24
2	183	207	196.43
3	96	94	337.91
4	86	85	332.25
-1	85	98	188.33
-2	74	85	25.84
-3	24	53	105.66
-4	165	179	171.50
K= 1, L= 3			
0	83	83	199.73
1	76	46	326.20
2	58	65	324.88
3	102	94	210.48
-1	169	150	359.14
-2	139	111	164.70
-3	185	172	162.10
-4	201	200	11.56
K= 1, L= 4			
0	132	132	351.83
1	175	183	195.56
2	55	53	322.37
-1	178	158	358.85
-2	272	288	184.89
-3	120	112	17.45
-4	79	77	18.70
K= 1, L= 5			
0	73	67	346.00
1	79	76	342.29
-1	154	157	191.35
-2	56	50	349.40
-3	62	36	1.53
-4	55	64	166.10
K= 1, L= 6			
-1	69	50	340.02
-2	73	59	356.45
-3	162	141	183.28
-4	110	92	7.03
K= 2, L= 0			
0	149	150	209.73
-1	575	594	4.05
-2	382	362	2.78
-3	172	147	201.09
-4	260	290	5.75
K= 2, L= 1			
0	101	85	342.38
1	63	65	238.23
2	522	540	5.97
3	250	235	3.00
-1	343	384	2.02
-2	251	280	6.66
-3	259	307	4.86
-4	70	100	347.04
K= 2, L= 2			
0	429	457	3.18
1	336	297	4.45
2	110	95	207.09
3	244	249	4.58
4	117	132	3.27
-1	54	57	306.64
-2	432	417	5.14
-3	193	186	356.69
-4	31	47	249.39
K= 2, L= 3			
0	70	46	246.73
1	244	218	6.37
2	149	140	3.55
3	115	97	357.47
-1	285	232	0.27
-2	472	414	3.37
-3	159	139	354.60
-4	93	90	353.43
K= 2, L= 4			
0	229	233	5.44
1	33	33	338.37
2	144	125	2.20
-1	320	282	0.96
-2	32	34	308.64
-3	128	118	2.05
-4	239	207	0.04
K= 2, L= 5			
0	164	154	0.18
-1	109	142	2.85
-2	96	95	2.02
-3	219	208	356.59
-4	123	130	358.85
K= 2, L= 6			
-1	82	101	6.65
-2	85	84	351.20
-3	100	88	8.02
-4	187	192	3.67
K= 3, L= 0			
-1	107	125	34.03
-2	25	25	44.28
-3	20	56	90.00
-4	32	75	152.23
K= 3, L= 1			
0	184	175	180.12
1	244	241	0.52
2	191	162	354.31
3	107	170	201.37
4	72	70	234.36
-1	100	170	203.01
-2	20	52	49.68
-3	26	47	104.35
K= 3, L= 2			
0	232	181	200.95
1	99	121	198.76
2	132	111	352.70
3	56	54	257.02
-1	275	269	15.18
-2	47	40	74.45
-3	26	80	188.96
-4	30	70	49.52
K= 3, L= 3			
0	185	75	1.02
1	81	72	348.28
2	31	36	235.42
3	103	45	310.44
-1	322	286	193.34
-2	26	20	347.62
-3	234	251	19.01
K= 3, L= 4			
0	136	129	203.07
1	77	86	352.34
2	22	76	221.88
-1	31	35	225.34
-2	266	292	15.28
-3	203	169	109.87
-4	115	137	107.58
K= 3, L= 5			
0	98	63	215.93
1	15	35	241.21
-1	76	67	1.45
-2	102	94	199.90
-3	56	21	16.69
-4	121	126	21.11
K= 3, L= 6			
-1	14	18	264.83
-3	29	87	12.59
K= 4, L= 0			
0	702	657	12.89
-1	55	85	310.74
-2	57	68	204.74
-3	361	354	11.51
-4	64	49	326.18
-5	85	90	350.52
K= 4, L= 1			
0	212	205	355.82
1	372	308	11.14
2	57	54	203.56
3	123	118	352.66
4	193	209	0.02
-1	79	102	345.20
-2	296	280	0.19
-3	112	108	337.53
-4	151	143	3.25
-5	180	188	7.67
K= 4, L= 2			
0	109	118	358.87
1	132	128	340.37
2	260	282	10.27
4	66	91	357.97
-1	386	405	9.00
-2	49	95	271.21
-3	133	116	3.87
-4	358	337	18.99
-5	31	69	321.73
-6	39	46	348.44
K= 4, L= 3			
0	246	242	8.37
1	93	68	351.23
2	149	148	308.91
3	134	123	4.08
-1	138	138	348.38
-2	82	67	352.79
-3	266	265	5.32
-4	181	172	356.13
-5	31	48	355.15
-6	183	117	2.53
K= 4, L= 4			
0	115	119	350.57
1	181	196	9.07
-1	76	58	342.19
-2	266	214	4.30
-3	178	147	358.44
-4	186	99	9.19
-5	164	184	359.20
-6	81	91	348.22
K= 4, L= 5			
0	39	34	341.25
-1	151	90	356.79
-2	180	197	3.88
-4	133	112	351.94
-5	151	148	2.62
K= 4, L= 6			
-3	87	103	1.25
-4	118	130	3.27

Table 2. *Atomic parameters (e.s.d.'s on last digits in parentheses)*

	x/a	*y/b*	*z/c*	*B* (Å^2)
Ca	−0·013 (1)	0	−0·007 (2)	0·86 (5)
Na	0·640 (2)	0·271 (3)	0·379 (2)	2·2 (2)
Si	0·340 (1)	0·259 (2)	0·714 (1)	0·9 (1)
O(1)	0·670 (2)	0·261 (5)	0·870 (2)	1·5 (2)
O(2)	0·233 (3)	0·264 (5)	0·934 (2)	1·4 (2)
O(3)	0·214 (3)	0·073 (3)	0·501 (3)	1·6 (3)
O(4)	0·206 (3)	0·454 (3)	0·505 (3)	1·4 (3)
H	0·039	0·501	0·501	4·0

The deviation from the more symmetrical space group, $P2_1/m$, is small, and a final attempt was made to refine in this space group; *R* was 0·122 on all reflexions. Application of Hamilton's (1965) test, with either conventional or weighted *R* values, showed that the structure with space group $P2_1/m$ could be rejected at the 0·005 level. The space group $P2_1/m$ implies that the H bonds are symmetrical, and gives an O–H–O distance of 2·51 Å. The space group $P2_1$ allows them to be unsymmetrical, and gives an O–H···O distance of 2·53 Å; this may be considered more probable on crystal-chemical grounds. In subsequent references in this paper to the monoclinic structure, that with space group $P2_1$ is implied.

Discussion

The structure is based on Ca^{2+}, Na^+ and $HSiO_4^{3-}$ ions, and does not differ greatly from the orthorhombic structure reported by Lyutin, Kazak, Ilyukhin & Belov (1972). The most important differences are in the orientation of the silicate tetrahedra and the system of H bonds. In the monoclinic structure, the tetrahedra are so oriented that there are two different O(3)–O(4) distances between atoms of adjacent tetrahedra; some of these O–O vectors are 2·53 Å long and are presumed to contain the H atoms, while the others are 3·44 Å and do not. The H bonds link the tetrahedra into zigzag chains parallel to **b**. In the orthorhombic structure, the equivalent O–O vectors are all equal in length at 2·99 Å. Lyutin, Kazak, Ilyukhin & Belov (1972) suggested that the H atoms were contained in them. It follows from the space-group symmetry ($C222_1$) that the H bonds are symmetrical and that the H atoms are statistically distributed over twice the number of O–O vectors; the tetrahedra are linked by H bonds into sheets.

The Si–O bond distances and O–Si–O angles agree well with the suggested H atom position, the bond to O(4), which carries the H atom, being relatively long and those O–Si–O angles that include O(4) relatively small. The Ca coordination is octahedral. The Na coordination is best described as a distorted trigonal bipyramid, with the two axial bonds much longer than

Table 4. *Coordination of the oxygen atoms*

Oxygen atom	Coordinated atoms	Distance(s) Å	E.s.v. sum
O(1)	Si	1·60	2·07
	Na	2·61, 2·88	
	Ca	2·38, 2·42	
O(2)	Si	1·62	1·87
	Na	2·30	
	Ca	2·25, 2·46	
O(3)	Si	1·65	2·03
	Na	2·25	
	Ca	2·41	
	H	1·5	
O(4)	Si	1·68	2·03
	Na	2·37	
	Ca	2·35	
	H	1·0	

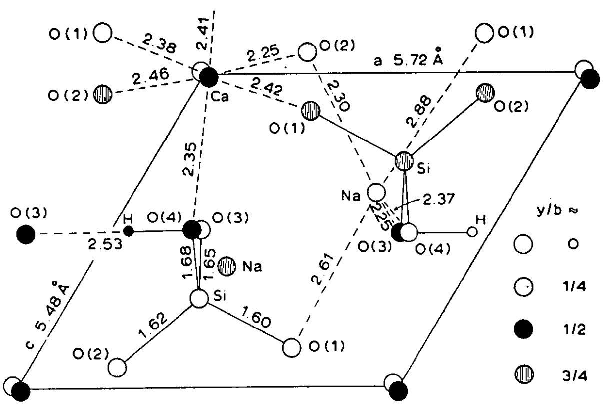


Fig. 1. The structure (space group $P2_1$) projected along **b**. Bond lengths in Å.

Table 3. *Interatomic distances* (Å) *and angles (e.s.d.'s on last digits in parentheses)*

Ca–O(1)	2·42 (3)	Na–O(1)	2·61 (1)	Si–O(1)	1·60 (2)
Ca–O(1)	2·38 (3)	Na–O(1)	2·88 (2)	Si–O(2)	1·62 (2)
Ca–O(2)	2·46 (3)	Na–O(2)	2·30 (2)	Si–O(3)	1·65 (2)
Ca–O(2)	2·25 (3)	Na–O(3)	2·25 (3)	Si–O(4)	1·68 (2)
Ca–O(3)	2·41 (2)	Na–O(4)	2·37 (3)		
Ca–O(4)	2·35 (2)				

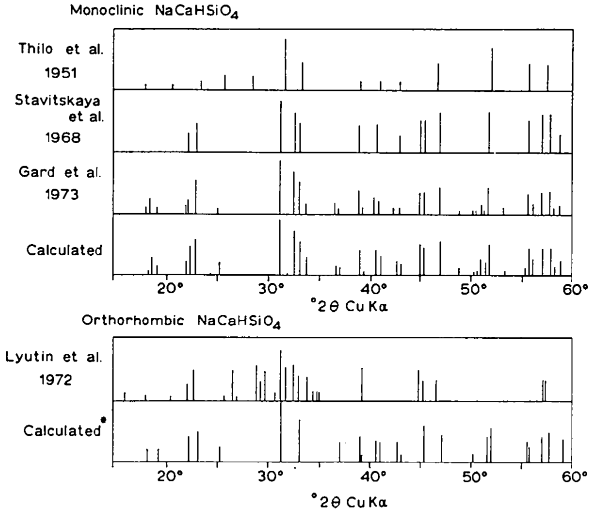
O–O within SiO_4 tetrahedra:	min.	2·64 (3)
	max.	2·71 (2)
O(3)–O(4) (H-bond)		2·53 (3)
Other O–O between tetrahedra:	min.	3·05 (2)
Si–O–H angle (assuming linear H-bond):		112 (1)°

Angles at Si	
O(1)–O(2)	114 (1)°
O(1)–O(3)	109 (1)
O(2)–O(3)	110 (1)
O(1)–O(4)	109 (1)
O(2)–O(4)	106 (1)
O(3)–O(4)	108 (1)

the three radial ones; for the orthorhombic structure Lyutin, Kazak, Ilyukhin & Belov (1972) described the coordination of this atom as tetrahedral. Table 4 gives the coordination of the oxygen atoms. Pauling's electrostatic valency rule is approximately satisfied if the Ca, Na, Si and H atoms are assumed to form bonds of strength $\frac{1}{3}$, $\frac{1}{5}$, 1 and $\frac{1}{2}$ respectively; the resulting underbonding of O(2) would explain the relative shortness (2·25 Å) of its bond to Ca.

Stavitskaya, Ryskin & Mitropol'skii (1968) concluded from the infrared spectrum that $NaCaHSiO_4$ contains strong H bonds, with an $O–H\cdots O$ distance of about 2·59 Å. Broad line n.m.r. gave a second moment of 1·5 Oe^2 at 77° K for the proton band; the authors concluded that the compound contained $HSiO_4^{3-}$ groups linked by the H bonds into zigzag chains. The present results agree reasonably well with these data; the second moment, calculated by van Vleck's formula [see, for example, Andrew (1955)] and assuming either of the space groups $P2_1$ or $P2_1/m$, is about 1·0 Oe^2.

Fig. 2 gives various sets of X-ray powder data. The observed data for the present sample (Gard, Ramsay & Taylor, 1973) agree closely in both spacings and intensities with those calculated from the parameters found in the present work. They also agree well with the observed data of Stavitskaya, Ryskin & Mitropol'skii (1968) and moderately well with those of Thilo, Funk & Wichmann (1951). We have also prepared a sample by one of the methods used by these workers, namely, treatment of Na_2CaSiO_4 with saturated water vapour at 180°C; the powder pattern of the product showed it to consist of the monoclinic phase studied here mixed with a semi-crystalline calcium silicate hydrate. It thus seems clear that this monoclinic phase is identical with the compounds described by these earlier workers.



* from the unit cell and atomic coordinates given by Lyutin et al.

Fig. 2. X-ray powder patterns.

Lyutin, Kazak, Ilyukhin & Belov (1972) stated that their sample was prepared hydrothermally at 300–700°C and 1000–3000 atm with an alkali concentration of about 30%, and that their crystals had been identified by single-crystal and powder examination; they considered them to be the same as those studied by Thilo, Funk & Wichmann (1951) and by Stavitskaya, Ryskin & Mitropol'skii (1968). However, their observed powder data do not agree with those of any of the other workers, and are moreover incompatible with the unit cell and atomic coordinates that they obtained from their structure determination (Fig. 2). $NaCaHSiO_4$ thus appears to exhibit polymorphism, but further work is needed to define the conditions of formation and powder pattern of the orthorhombic phase.

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