The molecular packing of the DADA radicals (Figs. 1 and 2) is very similar in the iodide and the perchlorate. Contrary to the case of the iodide of the DADA radical, we did not find any abnormally short intermolecular distances in the perchlorate, except the distance C(7)–O(1).

It is noteworthy that the tetrahedral group ClO_4^- is oriented with the edge O(2)–O(2′) approximately parallel to the plane of the DADA radical. The explanation of this remarkable feature is at present not clear.

The authors are very grateful to Dr J. Honzl for providing the crystals and for numerous interesting discussions. We are also highly indebted to Dr B. Sedláček for his continuous interest in this work.

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A Reinvestigation of the Structure of Sodium Metasilicate, Na_2SiO_3

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New data have been used in a refinement which gives the mean dimensions of the metasilicate chain as Si–O (bridging) 1·672 ± 0·002 Å, Si–O (non-bridging) 1·592 ± 0·002 Å and ∠Si–O–Si 133·7°. These dimensions are interpreted in terms of π-bonding effects. The angular distortions in the tetrahedra in chlorate, sulphate, phosphate and silicate structures are examined, and distortions in silicates are shown to be consistent with non-bridging oxygen atoms having larger electronic charges than bridging oxygen atoms.

Introduction

The crystal structure of sodium metasilicate was determined by Grund & Pizy (1952). Their analysis used partial three-dimensional data, which were obtained photographically, and gave a residual R of 27%. They showed that the structure consists of infinite chains of silicate tetrahedra, with the chains linked together by coordination to sodium. The two types of Si–O bond were found to have lengths of 1·57 and 1·67 Å; the difference is unusually large for silicate structures but it could occur in this type of chain. However, the residual shows that the accuracy is likely to be low. The present reinvestigation was undertaken in order to determine accurately the Si–O bond lengths and angles, which are relevant to the discussion of π-bonding in second-row elements (Cruickshank, 1961).

Crystal data

Na_2SiO_3. $M = 122{\cdot}07$. Orthorhombic, $a = 10{\cdot}48$, $b = 6{\cdot}07$, $c = 4{\cdot}82$ Å; $V = 306{\cdot}6$ Å^3, $Z = 4$, $D_c = 2{\cdot}64$. $F(000) = 240$. Space group $Cmc2_1$ (no. 36). μ for Mo $K\alpha$ radiation $= 8{\cdot}5$ cm^{-1}.

Experimental

Crystals of Na_2SiO_3 were kindly supplied by Dr F. Liebau. They were prepared by fusion of equi-molar quantities of SiO_2 and Na_2CO_3 at 1100° and slow cooling of the melt. For the present work an approximately equi-dimensional crystal of mean diameter about 0·3 mm ($\mu R = 0{\cdot}13$) was selected and sealed in a Lindemann-glass capillary.

Cell dimensions were reported by Grund & Pizy (1952), and by Seeman (1956). In this work they were remeasured from precession photographs and on the linear diffractometer (Arndt & Phillips, 1961). The various measurements are given in Table 1. The

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Table 1. *Cell dimensions for* Na_2SiO_3

Determination	*a*	*b*	*c*
Grund & Pizy	10·43 Å	6·02 Å	4·81 Å
Seeman	10·52	6·075	4·825
Precession photography	10·484	6·070	4·813
Diffractometer	10·482	6·064	4·826

rounded dimensions given above under *Crystal Data* were used in the calculation of interatomic dimensions.

Three-dimensional data were collected on the linear diffractometer, with Mo $K\alpha$ radiation, balanced Sr and Zr filters, and a scintillation counter with pulse height discrimination. The intensities were corrected for Lorentz and polarization factors with programs written by J. G. Sime for the KDF9 computer. A small number of reflexions obtained at values not significantly above background were included at their observed values; this provided a simple means of treating 'unobserved' reflexions. Subsequent examination of the discrepancies between $|F_o|$ and $|F_c|$ indicated that the procedure was justifiable. In this way a total of 315 independent structure amplitudes was obtained.

Least-squares refinement

The structure-factor least-squares program written by J. G. F. Smith and D. W. J. Cruickshank for the KDF9 computer was used. The form factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962). The starting point for the refinement was the set of coordinates given by Grund & Pizy, with isotropic vibration parameters of $U=0{\cdot}01$ Å^2 for all atoms. An initial structure-factor calculation gave a residual $R=(\Sigma|\Delta|)/(\Sigma k|F_o|)$ of 19·6%. Two cycles of full-matrix refinement of the coordinates, individual isotropic vibration parameters, and the overall scale factor were carried out, the weighting scheme used being $w=1$ for $|F_o|<6$, $w=36/|F_o|^2$ for $|F_o|>6$. These reduced the residual to 5·0%. At this point an analysis of the ΔF showed that the weighting scheme was inadequate. There was a slight decrease in the accuracy of the data with increasing $|F_o|$, and a sharp decrease in accuracy at very low $\sin\theta$ values, probably arising from setting errors in the diffractometer at low angles. A few very strong reflexions seemed to be affected by extinction and required down-weighting. The weighting scheme was changed to

$$w=\frac{1-\exp\left[-4(\sin\theta/\lambda)^2\right]}{20+|F_o|+0{\cdot}02|F_o|^2}$$

and two further cycles of refinement were carried out, reducing the residual to 4·5%, with a considerable improvement in the standard deviations.

At this stage the isotropic refinement had converged, and anisotropic refinement was begun. One full-matrix cycle produced a highly significant degree of refinement and reduced the residual to 3·2%. A second cycle produced no significant shifts. The effect of anisotropic refinement, however, was to produce a great improvement in the ΔF for high-order reflexions, and a further change in the weighting scheme was indicated.

$$w=\frac{1-\exp\left[-0{\cdot}5(\sin\theta/\lambda)^2\right]}{1+0{\cdot}0001\,|F_o|^3}$$

was found to be more suitable, and two further cycles were carried out with this weighting scheme. No further reduction in the residual was obtained, but $R'=(\Sigma w\Delta^2)/(\Sigma w|kF_o|^2)$ and the standard deviations were appreciably reduced.

Two additional cycles were carried out with the form factor for Na^+ in place of that for the neutral atom. These produced no significant changes in the parameters or residual.

In polar space groups the imaginary component of the anomalous dispersion can often produce significant errors in coordinates in the polar directions (Ueki, Zalkin & Templeton, 1966); consequently further refinement was carried out with the form factors of Na and Si corrected for the real and imaginary components (*International Tables for X-ray Crystallography*, 1962). Although these quantities are quite small for Mo $K\alpha$ radiation, ($\Delta f''=0{\cdot}1$), they are not negligible in relation to the accuracy of the experimental data, for the resulting coordinate shifts were larger than the e.s.d.'s of the random errors. With the polar coordinate of sodium fixed at $z=0$, and assuming that the data had been collected in the $+l$ hemisphere, the z coordinates increased by 0·00115 for each oxygen atom and by 0·00045 for silicon after two cycles of least squares. If the data were assumed to be $hk\bar{l}$, the shifts were

Table 2. *Final fractional coordinates and e.s.d.'s*

	x	*y*	*z*
Na	0·16562 (9)	0·33880 (15)	0
Si	0	0·15737 (11)	0·53676 (32)
O(1)	0·12947 (15)	0·28733 (28)	0·48105 (47)
O(2)	0	0·08436 (37)	0·87224 (58)

Table 3. *Vibration tensor components and e.s.d.'s* (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Na	0·0117 (4)	0·0120 (4)	0·0163 (7)	−0·0006 (7)	−0·0011 (4)	−0·0008 (5)
Si	0·0057 (3)	0·0045 (3)	0·0087 (3)	0·0005 (5)	0	0
O(1)	0·0086 (6)	0·0128 (6)	0·0142 (6)	0·0021 (8)	0·0031 (8)	−0·0059 (11)
O(2)	0·0168 (9)	0·0071 (8)	0·0094 (7)	0·0034 (11)	0	0

$-0{\cdot}00115$ and $-0{\cdot}00037$ respectively. Neither polarity led to any appreciable reduction in R, but the negative polarity gave a marginally lower $\Sigma w\Delta^2$ (7·84 against 8·02) and reduced the difference between the chemically equivalent bonds, Si–O(2) and Si–O(2′), from 0·009 to 0·004 Å, whereas the positive polarity increased this difference to 0·014 Å. As the nominal e.s.d.'s of these bond lengths are about 0·002 Å, the result may indicate that the data are actually $hk\bar{l}$. However this is not proved, and we prefer to take the final coordinates as those from the refinement without anomalous dispersion, but to increase the bond length e.s.d.'s in the discussion.*

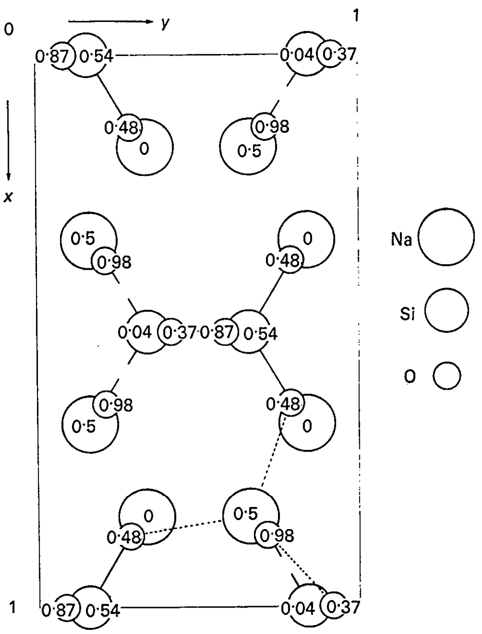

Fig. 1. Projection along [001].

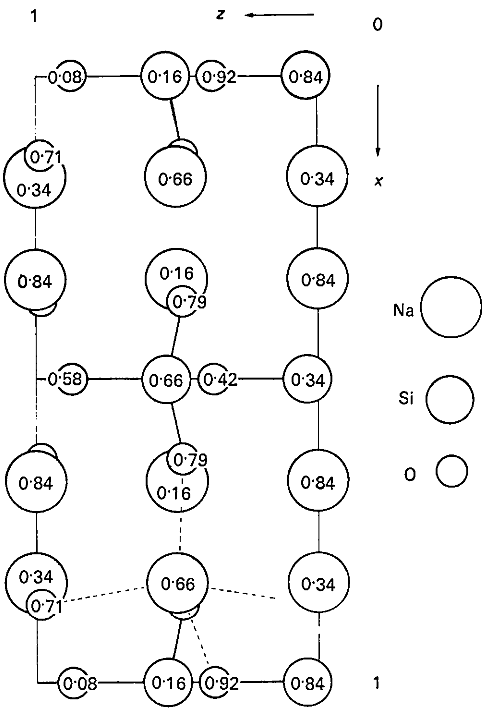

Fig. 2. Projection along [010].

The final coordinates and standard deviations (from the last 'neutral-atom' cycle) are given in Table 2, and the vibration parameters and their standard deviations in Table 3. The estimated standard deviations in these tables are those given by inversion of the full matrix, without augmentation for anomalous dispersion. Observed and calculated structure factors are given in Table 4.

Table 4. *Observed and calculated structure factors*

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
2	0	0	35.3	36.5	3	5	1	59.2	62.1	10	2	3	15.3	15.3	7	1	5	8.2	8.8
4	0	0	21.6	18.3	5	5	1	15.5	15.3	12	2	3	32.1	32.2	9	1	5	21.9	22.2
6	0	0	92.4	105.5	7	5	1	6.2	5.9	1	3	3	13.9	14.0	11	1	5	12.2	12.7
8	0	0	41.9	42.5	9	5	1	35.1	35.4	3	3	3	24.5	25.3	13	1	5	8.5	8.6
10	0	0	9.6	9.6	11	5	1	14.3	13.7	5	3	3	16.3	15.9	0	2	5	28.7	29.3
12	0	0	33.4	33.5	0	6	1	27.2	26.7	7	3	3	10.7	10.3	2	2	5	11.6	11.6
14	0	0	16.4	16.9	2	6	1	4.4	4.3	9	3	3	9.0	8.9	4	2	5	9.8	9.7
3	1	0	81.7	88.4	4	6	1	9.6	9.1	11	3	3	11.6	11.7	6	2	5	25.4	25.9
5	1	0	27.7	25.2	6	6	1	12.6	12.3	13	3	3	6.6	6.3	8	2	5	11.3	11.7
7	1	0	10.1	9.0	8	6	1	14.6	14.1	0	4	3	22.2	21.8	10	2	5	7.7	7.9
9	1	0	36.9	36.3	1	7	1	6.9	6.9	2	4	3	6.9	6.9	12	2	5	17.5	17.9
11	1	0	10.7	14.0	3	7	1	26.2	26.5	4	4	3	7.6	7.8	1	3	5	1.6	1.4
13	1	0	9.5	9.1	5	7	1	5.2	5.3	6	4	3	24.5	24.7	3	3	5	13.4	13.5
0	2	0	75.2	77.8	7	7	1	5.1	5.4	8	4	3	12.5	12.5	5	3	5	8.8	8.7
2	2	0	13.7	12.1	0	8	1	42.3	42.6	10	4	3	4.0	4.3	7	3	5	2.5	2.5
4	2	0	42.2	40.4	2	8	1	11.2	11.1	12	4	3	21.2	20.9	9	3	5	2.6	2.7
6	2	0	29.8	30.3	2	0	2	7.7	3.5	1	5	3	12.4	12.6	11	3	5	7.8	7.9
8	2	0	15.9	16.1	4	0	2	31.0	30.4	3	5	3	38.3	39.4	0	4	5	21.2	21.1
10	2	0	5.6	5.0	6	0	2	66.0	72.2	5	5	3	10.2	10.4	2	4	5	15.5	15.2
12	2	0	2.8	3.3	8	0	2	25.5	24.9	7	5	3	10.7	10.6	4	4	5	9.6	9.8
14	2	0	4.7	4.9	10	0	2	4.1	3.6	9	5	3	23.8	24.1	6	4	5	17.4	17.4
1	3	0	11.5	10.5	12	0	2	24.2	24.1	11	5	3	8.8	8.7	8	4	5	17.6	17.1
3	3	0	90.3	100.0	14	0	2	10.7	10.7	0	6	3	19.7	19.4	10	4	5	9.6	9.5
5	3	0	19.8	18.8	1	1	2	10.5	8.7	2	6	3	5.1	5.1	12	4	5	13.4	13.1
7	3	0	4.1	3.7	3	1	2	50.9	51.1	4	6	3	10.6	10.3	1	5	5	17.2	17.3
9	3	0	43.9	44.2	5	1	2	10.1	8.5	6	6	3	9.6	9.6	3	5	5	23.4	23.3
11	3	0	16.9	16.7	7	1	2	2.7	2.2	8	6	3	10.7	10.7	5	5	5	13.1	12.9
13	3	0	9.9	9.8	9	1	2	24.6	23.9	1	7	3	3.7	3.9	7	5	5	15.0	14.8
0	4	0	41.0	41.0	11	1	2	7.4	6.9	3	7	3	15.5	15.9	9	5	5	16.5	16.7
2	4	0	15.3	15.1	13	1	2	4.4	3.9	5	7	3	3.5	3.9	0	6	5	11.1	11.2
4	4	0	25.0	25.4	0	2	2	66.0	66.1	0	8	3	25.8	26.2	2	6	5	4.3	4.4
6	4	0	40.6	40.3	2	2	2	15.1	14.1	2	0	4	23.3	23.9	4	6	5	9.5	9.5
8	4	0	3.7	3.3	4	2	2	30.3	29.2	4	0	4	34.7	36.3	6	6	5	7.2	6.0
10	4	0	12.0	11.5	6	2	2	31.2	31.5	6	0	4	36.2	37.1	8	6	5	6.2	6.3
12	4	0	28.2	28.5	8	2	2	17.2	17.4	8	0	4	12.4	12.0	1	7	5	8.2	8.1
1	5	0	22.6	21.7	10	2	2	7.5	7.2	10	0	4	15.4	15.6	3	7	5	11.1	10.7
3	5	0	22.2	21.5	12	2	2	8.8	8.9	12	0	4	17.5	17.9	2	0	6	19.9	21.5
5	5	0	1.1	2.3	1	3	2	18.7	17.8	1	1	4	17.1	17.2	4	0	6	27.1	27.8
7	5	0	14.4	15.9	3	3	2	73.6	80.5	3	1	4	21.9	21.3	6	0	6	23.6	24.3
9	5	0	1.9	0.4	5	3	2	17.9	17.3	5	1	4	10.2	10.1	8	0	6	11.8	11.7
11	5	0	5.4	5.1	7	3	2	13.1	12.6	7	1	4	12.5	12.6	10	0	6	15.5	15.4
0	6	0	38.2	38.1	9	3	2	38.0	38.3	9	1	4	12.9	12.8	12	0	6	16.9	16.8
2	6	0	1.8	0.9	11	3	2	15.5	15.0	11	1	4	5.9	6.1	1	1	6	13.4	14.4
6	6	0	31.6	31.9	13	3	2	9.0	9.3	13	1	4	5.1	5.2	3	1	6	15.7	16.0
1	7	0	10.2	10.6	0	4	2	29.5	28.6	0	2	4	36.5	37.0	5	1	6	11.2	11.0
3	7	0	15.5	15.0	2	4	2	7.2	6.8	2	2	4	8.2	7.7	7	1	6	12.0	11.8
5	7	0	3.0	2.6	4	4	2	15.7	15.1	4	2	4	16.0	15.5	9	1	6	11.9	11.7
7	7	0	10.0	10.5	6	4	2	30.4	29.6	6	2	4	21.2	21.0	11	1	6	7.6	7.4
0	8	0	10.2	10.2	8	4	2	5.2	5.0	8	2	4	12.0	12.0	13	1	6	6.4	6.2
1	1	1	35.2	33.0	10	4	2	7.4	7.1	10	2	4	5.6	5.4	0	2	6	13.4	13.4
3	1	1	45.7	49.4	12	4	2	22.5	22.5	12	2	4	8.4	8.4	2	2	6	4.5	4.5
5	1	1	26.9	24.9	1	5	2	16.6	16.3	1	3	4	21.8	21.2	4	2	6	11.5	11.5
7	1	1	20.6	21.0	3	5	2	26.3	26.2	3	3	4	45.2	45.9	6	2	6	7.5	7.4
9	1	1	51.4	53.5	5	5	2	10.7	10.5	5	3	4	15.0	14.4	8	2	6	3.8	3.6
11	1	1	9.8	9.8	7	5	2	13.3	12.8	7	3	4	17.5	17.0	10	2	6	4.7	4.5
13	1	1	5.8	5.4	9	5	2	8.9	9.0	9	3	4	25.8	25.8	12	2	6	5.2	5.6
0	2	1	61.3	63.9	11	5	2	8.8	8.8	11	3	4	11.0	11.0	1	3	6	18.0	17.8
2	2	1	23.4	21.5	0	6	2	41.9	42.5	0	4	4	19.3	19.1	3	3	6	21.5	21.2
4	2	1	19.1	18.2	2	6	2	17.3	17.2	2	4	4	11.6	11.0	5	3	6	10.7	10.5
6	2	1	58.6	58.6	4	6	2	16.0	16.0	4	4	4	8.3	8.0	7	3	6	15.4	15.2
8	2	1	13.7	13.1	6	6	2	34.6	35.3	6	4	4	17.6	17.2	9	3	6	15.2	14.9
10	2	1	9.9	9.3	8	6	2	13.2	13.4	8	4	4	12.5	12.5	11	3	6	7.4	7.1
12	2	1	35.6	35.9	1	7	2	16.6	16.8	10	4	4	6.5	6.7	0	4	6	15.5	15.6
14	2	1	6.6	6.9	3	7	2	20.7	21.4	1	5	4	6.4	6.4	2	4	6	11.4	11.1
1	3	1	32.5	30.7	5	7	2	11.8	11.9	3	5	4	20.5	20.6	4	4	6	8.0	7.7
3	3	1	20.6	20.0	0	8	2	6.7	6.9	5	5	4	9.4	9.3	6	4	6	12.5	12.4
5	3	1	10.7	10.0	2	8	2	1.4	2.3	7	5	4	5.9	6.0	8	4	6	12.6	12.2
7	3	1	18.7	18.8	1	1	3	26.4	25.7	9	5	4	7.7	7.6	10	4	6	7.3	7.0
9	3	1	7.7	7.6	3	1	3	47.2	48.9	0	6	4	31.1	31.4	1	5	6	5.5	5.4
11	3	1	7.9	8.0	5	1	3	22.7	22.7	2	6	4	13.1	13.5	3	5	6	8.7	8.4
13	3	1	3.5	3.4	7	1	3	19.6	20.3	4	6	4	12.3	12.4	5	5	6	3.8	3.9
0	4	1	43.4	43.5	9	1	3	41.8	42.4	6	6	4	26.2	26.6	7	5	6	5.4	5.5
2	4	1	13.1	12.6	11	1	3	14.9	14.5	8	6	4	11.2	11.3	9	5	6	2.1	1.5
4	4	1	27.6	27.4	13	1	3	10.5	10.3	1	7	4	12.6	12.7	0	6	6	11.7	11.7
6	4	1	45.1	46.1	0	2	3	60.5	62.4	3	7	4	17.4	17.3	2	6	6	5.9	6.2
8	4	1	1.5	1.5	2	2	3	25.8	25.6	5	7	4	9.8	10.2	4	6	6	4.9	5.1
10	4	1	10.0	9.9	4	2	3	24.9	25.0	1	1	5	9.3	9.9	6	6	6	10.4	10.0
12	4	1	33.6	33.5	6	2	3	50.9	52.5	3	1	5	25.4	25.6	1	7	6	2.0	2.1
1	5	1	7.4	7.3	8	2	3	19.3	19.0	5	1	5	16.0	16.2					

There are changes of up to 0·12 Å in the z coordinates and up to 0·05 Å in the y coordinates as compared with the results of Grund & Pizy.

Discussion of the structure

General description

Projections of the structure down [001] and [010] are shown in Figs. 1 and 2. The metasilicate chains are parallel to the c axis and have $mc2_1$ symmetry with two

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* *Note added in proof:–* The hypothesis that the data are $hk\bar{l}$ rather than hkl is significant at the 0·01 level according to Hamilton's (1965) statistical tests, The discussion in the main text is thus overcautious.

tetrahedra in the repeat unit. The silicon and the bridging oxygen lie in the mirror plane. The oxygen atoms are further coordinated to sodium atoms, which link the chains together in the **a** and **b** directions. Li_2SiO_3 (Seeman, 1956), Na_2GeO_3 (Ginetti, 1954), and Li_2GeO_3 (Hahn & Theune, 1957) have been shown to have the same structure as Na_2SiO_3.

Relationship to the wurtzite structure

Grund & Pizy (1952) noted that sodium metasilicate shows pseudo-hexagonal symmetry. The reason for the pseudo-symmetry may be seen by reference to Fig. 3, which shows the tetrahedra of oxygen atoms around silicon and sodium projected down the c axis, assuming tetrahedral coordination of the sodium. One layer of the structure is shown. The repeat distance of the cell covers two such layers, related by the 2_1 axis. The pattern of tetrahedra is that found in the ZnS wurtzite structure type. In Na_2SiO_3 two-thirds of the zinc atoms are replaced by sodium and one-third by silicon, thus destroying the hexagonal symmetry. These atoms, however, remain close to the hexagonal positions, and the oxygen atoms are shifted from the positions which correspond to S in wurtzite owing to the ~0·7 Å difference between Si–O and Na–O bond lengths. Because of the similar scattering powers of sodium and silicon the diffraction pattern shows pseudo-hexagonal symmetry, particularly in the $hk0$ projection. The dimensions of the pseudo-hexagonal cell of Na_2SiO_3 are $a'=a/3=3{\cdot}49$, $b'=b/\sqrt{3}=3{\cdot}50$, $c'=c=4{\cdot}82$ Å; the actual space group $Cmc2_1$ is a subgroup of $P6_3mc$, the wurtzite space group, with the orthorhombic cell volume six times that of the hexagonal cell. Table 5 shows the fractional coordinates of the atoms in sodium metasilicate together with the values they would be required to have in the hexagonal structure. For silicon and sodium the correspondence is quite close.

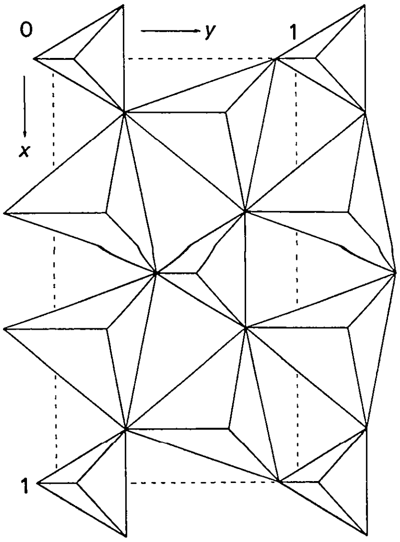

Fig. 3. The oxygen tetrahedra, projected down [001].

Table 5. *Comparison of coordinates*

	Found in Na_2SiO_3			Required for hexagonal structure		
Na	0·166,	0·339,	0	0·167,	0·333,	0
O(1)	0·129,	0·287,	0·481	0·167,	0·333,	z
Si	0,	0·157,	0·537	0,	0·167,	$\frac{1}{2}$
O(2)	0,	0·084,	0·872	0,	0·167,	$z+\frac{1}{2}$

The sodium coordination

The bond lengths and angles at sodium are given in Table 6. Ignoring anomalous dispersion the e.s.d.'s are 0·002 Å for the lengths and 0·08° for the angles; however Na–O(1) and Na–O(1‴) have large components in the polar direction and to allow for anomalous dispersion their e.s.d.'s should be increased to 0·005 Å. As discussed in the previous section, the structure is related to the tetrahedrally coordinated structure of wurtzite. Apart from the effects of the differing Si–O and Na–O distances, the main distortion is the increase of the sodium coordination from four to five. The 'extra' Na–O bond is that to O(1‴), with the longest distance of 2·55 Å. The polyhedron of five oxygen atoms is a distorted trigonal bipyramid in which O(1‴) is involved in the largest distortions.

Table 6. *Bond lengths and angles*

Bond	
Na–O(1)	2·370 Å
Na–O(1′)	2·303
Na–O(1″)	2·282
Na–O(1‴)	2·549
Na–O(2)	2·404
Si—O(1)	1·592
Si—O(2)	1·677
Si—O(2′)	1·668

Angle	
O(1)—Na–O(1′)	98·19°
O(1)—Na–O(1″)	98·36
O(1)—Na–O(1‴)	156·94
O(1)—Na–O(2)	92·90
O(1′) –Na–O(1″)	118·95
O(1′) –Na–O(1‴)	93·29
O(1′) –Na–O(2)	120·29
O(1″)–Na–O(1‴)	93·41
O(1″)–Na–O(2)	116·99
O(2)—Na–O(1‴)	64·06

Angle	
O(1)–Si–O(1′)	116·89°
O(1)–Si–O(2)	107·07
O(1)–Si–O(2′)	110·83
O(2)–Si–O(2′)	103·06

Bond	
O(1)–O(1′)	2·714 Å
O(1)–O(2)	2·630
O(1)–O(2′)	2·685
O(2)–O(2′)	2·619

Angle	
Si—O(1)–Na	128·98°
Si—O(1)–Na′	128·45
Si—O(1)–Na″	111·50
Si—O(1)–Na‴	91·25
Na—O(1)–Na′	100·04
Na—O(1)–Na″	86·16
Na—O(1)–Na‴	82·07
Na′ –O(1)–Na″	83·26
Na′ –O(1)–Na‴	79·39
Na″–O(1)–Na‴	156·94

Angle	
Si—O(2)–Si′	133·72°
Si—O(2)–Na	94·43
Si′ –O(2)–Na	116·33
Na–O(2)–Na′	92·46

Oxygen coordination

The bond angles at oxygen are given in Table 6. O(2) is linked to two silicon and to two sodium atoms.

For sodium to achieve a coordination of five, O(1) must also become five-coordinate. It is linked to one silicon and to four sodium atoms. The arrangement is a highly distorted trigonal bipyramid.

The metasilicate chain

The bond lengths and angles of the metasilicate chain are given in Table 6. The anisotropic vibration amplitudes of the oxygen atoms are a little greater than those of silicon, so that some corrections to the bond lengths may be required to allow for librations of the chain or internal torsional motions. A proper analysis would be difficult and as the maximum correction can be estimated as only 0·004 Å, corrections will be ignored in the following discussion. The e.s.d.'s estimated from the inverse least-squares matrix are 0·002 Å for lengths and 0·1° for angles. These should perhaps be increased by 50% to allow for uncertainties in the cell dimensions and the neglect of any librational corrections. In addition, the e.s.d.'s of the two bonds which have large components in the *z* direction must be increased to about 0·007 Å because of the uncertainty of the polarity when correcting for anomalous dispersion. The two Si–O(2) bond lengths, 1·677 and 1·668 Å, are therefore not significantly different. This additional uncertainty does not apply to the mean of Si–O(2), since the effect of anomalous dispersion is to increase one length and decrease the other by a similar amount.

The bridging Si–O bonds, of mean length 1·672 Å, and the non-bridging ones, of length 1·592 Å, show an unusually large difference. Cruickshank's (1961) discussion of bond lengths in terms of $d-p$ π-bonding suggests that there should be a considerable difference between the lengths of bridging and non-bridging bonds. The fact that such differences are not normally observed in silicate structures may be attributed to the tendency of the silicate 'ion' to shed its negative charge, and with this some of its π-bonding potential, by forming partial covalent bonds to the cations. In the case of sodium metasilicate, where there is a rather electropositive cation this tendency is minimized and an appreciable difference in the length of the two types of bond should be found.

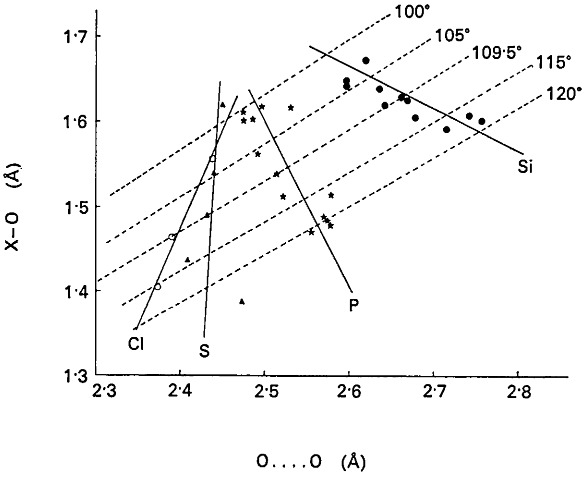

Fig. 4. Plot of O···O *versus* X···O distances for perchlorates, sulphates, phosphates and silicates.

A number of other metasilicates have recently been refined accurately giving e.s.d.'s for the mean lengths of 0·004 Å or better. In wollastonite, $CaSiO_3$ (Buerger & Prewitt, 1961), the bridging Si–O bonds have mean length 1·655 Å, and the non-bridging ones are of mean length 1·598 Å. In bustamite, $CaMn(SiO_3)_2$ (Peacor & Buerger, 1962) they are 1·642 Å and 1·603 Å respectively, while in rhodonite, $(Mn_{0\cdot80}Ca_{0\cdot16}X_{0\cdot04})SiO_3$ (Peacor & Niizeki, 1963), mean lengths of 1·648 and 1·608 Å were found. The less accurate structure of stokesite, $CaSnSi_3O_9.2H_2O$ (Vorma, 1963), shows mean lengths of 1·630 and 1·612 Å. These smaller differences parallel the lower electropositive character of calcium, manganese and tin compared with sodium. Associated with the smaller difference in bond lengths is an increase in the angle at the bridging oxygen. The angle of 133·7° in sodium metasilicate should be compared with the mean values of 143, 144, 137 and 147° in the four calcium metasilicates mentioned above. For a metasilicate chain with a bridging angle of 120°, and no 'shedding' of the negative charge, Cruickshank (1961) gave theoretical estimates of 1·70 and 1·56 Å for the bridging and non-bridging bonds. Extrapolation from the above experimental results suggests that the theoretical estimates are reasonable as a limit, but that the dimensions of the hypothetical isolated chain cannot be realized in an actual structure.

The distortions of the bond angles at silicon from tetrahedral values are quite marked; in particular the O(2)–Si–O(2′) angle is 103° and the O(1)–Si–O(1′) angle is 117°. These distortions are in the same directions as in polyphosphates and polysulphates, and are similar to those in rubidium metaphosphate (Cruickshank, 1964), which has angles of 103° and 120°. It is not possible to attribute these distortions in the silicate *solely* to a tendency of repulsions between the non-bonded oxygen atoms of a tetrahedron to equalize the O···O distances (granted that the Si–O lengths have been made unequal by π-bonding effects): for O(2)···O(2′) is actually 0·10 Å *less* than O(1)···O(1′), whereas with tetrahedral angles and the determined Si–O distances O(2)···O(2′) would be the larger.

Comparative study of tetrahedral distortions

The preceding observation on the distortions of the bond angles at silicon prompted a comparative study of silicates, phosphates, sulphates and perchlorates. The results are shown in Fig. 4, in which is plotted for individual tetrahedra the mean length of a pair, X–O_a and X–O_b, against the distances $O_a\cdots O_b$. More explicitly, for structures such as rings or chains, having tetrahedra $X(O_c)_2(O_d)_2$ with two pairs of types of oxygen, the points plotted are $X\text{–}O_c$(mean) against $O_c\cdots O_c$, and $X\text{–}O_d$(mean) against $O_d\cdots O_d$. For such structures as X_2O_7 or P_4O_{10} with tetrahedra of the type $X(O_c)_3O_d$, the points plotted are $X\text{–}O_c$(mean) against $O_c\cdots O_c$, and the mean of $X\text{–}O_c$ and $X\text{–}O_d$ against $O_c\cdots O_d$. A representative selection of reasonably accurate structures was included in the survey, though for the perchlorates only two structures, ClO_4^- and Cl_2O_7 (Beagley, 1965), are available. No acids were included because of the substantial effects of the hydrogen bonds (Cruickshank & Robinson, 1966).

For each element Si, P, S and Cl, the points fall into groups which may be roughly represented by straight lines. The striking feature is the very different slopes of these lines. Assuming that the mean bond lengths in the tetrahedra of a given element are constant (Cruickshank, 1961), and if π-bonding only alters bond lengths while angles remain tetrahedral, all the points would lie along the dashed line marked 109·5°. Only the chlorate line is anywhere near this. If π-bonding gave rise to various X–O lengths within a tetrahedra, but the angles altered so that the six $O\cdots O$ distances remained constant [as in the hard-sphere model of non-bonded repulsions (Bartell, 1960)], then the points would lie on vertical lines characteristic to each element. This situation is roughly realized for the sulphates (for which the simple π-bonding theory seems to work best). Some degree of non-bonded repulsion may also be at work in the chlorates. However, for the phosphates and, more particularly, for the silicates the lines are of negative slope. This is directly related to the previous observation for sodium metasilicate that $O(2)\cdots O(2')$ is 0·10 Å less than $O(1)\cdots O(1')$, despite Si–O(2) being 0·08 Å longer than Si–O(1). For bustamite and rhodonite the differences in the $O\cdots O$ distances are even more marked ($\sim$0·15 Å).

The negative slope of the silicate line seems best explained by supposing that the repulsive forces between pairs of external oxygen atoms are substantially greater than those between pairs of bridge oxygen atoms. This is in the sense of the elementary electrostatic picture in which external oxygen atoms are more negatively charged than bridge oxygen atoms. Similar but smaller repulsions may be postulated for phosphates.

A rough calculation of the charge difference may be made if we assume a valence force-field for a silicate tetrahedron. Herzberg (1945) does not list force constants for silicates, but from the force constants k of 1·18 mdyn.$Å^{-1}$ for SO_4^{2-}, 0·90 for PO_4^{3-}, and 0·47 for SiF_4, a value of 0·6 seems plausible for the $O\cdots O$ coordinate in a silicate. In Na_2SiO_3, $O(1)\cdots O(1')$ is 0·11 Å larger than if the angles were tetrahedral, while $O(2)\cdots O(2')$ is the same amount shorter. With the assumed force constant, these length changes would be caused if O(1) carries an effective charge about one-third of an electron greater than O(2). Such a charge difference is not unreasonable.*

We need now to consider the question: granted that the charge repulsions alter the angles, what will be the effects on Si–O lengths? Could π-bonding be discounted? Lengths might be affected in two ways, directly by a change in the attractive force between a positive Si and a negative O, or indirectly through a change in the hybridization of the σ-bonds consequent on the changes in bond angles. Since the Si–O bond length changes only from 1·61 Å in the neutral tetrahedra of quartz to 1·63 Å in a formal SiO_4^{4-} tetrahedron (Smith & Bailey, 1963), whereas in the metasilicate we have a range from 1·59 to 1·67 Å, it seems unlikely that the actual charges are large enough to have a direct effect on the lengths. However, by considering the $O\cdots O$ repulsions as well as the $Si\cdots O$ attractions, it might be possible to choose charges for Si, O(external) and O(bridge), together with a stretching force-constant, such as to reproduce the observed bond lengths. But to pursue this further seems an over-speculative exercise. The hybridization effects are also probably not of major importance, for the angle changes in bustamite and rhodonite are as large as in Na_2SiO_3 yet the Si–O bond-length differences are smaller. Thus we may retain the π-bonding theory as a working hypothesis for silicates (π-bonding seems indisputable in chlorates and sulphates).

Further evidence for π-bonding is provided by the recent results for $Na_2H_2SiO_4.8H_2O$ (Jamieson & Dent Glasser, 1966) where the bond lengths in the $H_2SiO_4^{2-}$ ion are 1·672 and 1·591 ± 0·008 Å, practically identical with those in Na_2SiO_3. Cruickshank & Robinson (1966) have shown that bond lengths in acid phosphates are adequately represented on π-bonding theory if O(H) is treated as 65% O(R) and 35% O^-. The above bond lengths in $H_2SiO_4^{2-}$ also agree with these proportions on assuming the same order/length relation as for the hypothetical isolated metasilicate chain mentioned earlier. An ion $R_2SiO_4^{2-}$ ought to show a larger difference between the two sorts of Si–O length.

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* Here it is suggested that the charge on an external oxygen atom is greater than that on a bridge oxygen atom by about 0·3, whereas for thortveitite (Cruickshank, Lynton & Barclay, 1962) one of us suggested the reverse. There may well be some extra electronic charge on the bridge oxygen atom in thortveitite as compared with the metasilicate, since the bridge angle there is 180°, but the suggestions in that paper were based on a guess of the covalent character in the Sc–O bonds and the argument was primarily intended to show that the formal charges implied by an $Si_2O_7^{6-}$ formula could not possibly explain the packing features.

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A Reinvestigation of the Structure of $Na_4P_2O_7.10H_2O$

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New data have been used in a refinement which leads to molecular dimensions P–O (bridge) 1·612 ± 0·005 Å, P–O (outer) 1·523 ± 0·004 Å and ∠P–O–P 130·2°.

Introduction

The crystal structure of sodium pyrophosphate decahydrate, $Na_4P_2O_7.10H_2O$, was determined by MacArthur & Beevers (1957) from photographic data for three projections. These data were later used by Cruickshank (1964) in a least-squares refinement, which yielded bond lengths in the pyrophosphate group with standard deviations of about 0·015 Å. In order to obtain more accurate dimensions, fresh three-dimensional data were collected and a full refinement carried out.

Crystal data

$Na_4P_2O_7.10H_2O$. $M = 446·06$.
Monoclinic, $a = 17·01 \pm 0·02$, $b = 6·96 \pm 0·01$, $c = 14·85 \pm 0·02$ Å, $\beta = 112·0 \pm 0·2°$;
$V = 1630$ Å^3, $Z = 4$, $D_c = 1·817$, D_m (MacArthur & Beevers, 1957) $= 1·817$. $F(000) = 920$. Space group $C2/c$.

Experimental

The cell dimensions given above were measured from zero-layer precession and Weissenberg photographs. They are in agreement with the values given by Corbridge (1957) and by MacArthur & Beevers (1957) for the $I2/c$ cell.

Intensities were estimated visually from equi-inclination Weissenberg photographs of the layers $h0l$ to $h5l$, taken with Cu $K\alpha$ radiation. They were corrected for Lorentz and polarization factors with a DEUCE computer program written by J. G. Sime. This yielded a set of 1022 independent structure amplitudes, requiring six different scale factors. A structure factor calculation, using the coordinates and vibration parameters of Cruickshank (1964) transferred to the $C2/c$ cell, gave preliminary values for the layer scale factors and showed an initial residual R of 14·2%.

Least-squares refinement

The structure-factor least-squares program of J. G. F. Smith and D. W. J. Cruickshank for the KDF9 computer was used. The form-factors were taken from *International Tables for X-ray Crystallography* (1962) and the weighting scheme was

$$w = 1/(10 + |F_o| + 0·005|F_o|^2).$$

Two cycles of full-matrix least-squares refinement of the coordinates and individual vibration parameters, together with an overall scale factor, reduced the residual to 9·2%. After two cycles of block-diagonal anisotropic refinement, a small number of indexing errors were corrected and the individual layers rescaled. Two more cycles then produced convergence to a residual of 7·8%.

An $(F_o - F_c)$ Fourier synthesis was then computed and of the twenty highest peaks, 0·5 to 0·7 e.Å^{-3}, nine were in positions expected for hydrogen atoms. No peak could be found at the position expected for the remaining hydrogen, H(42). However, since the posi-

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