

*Acta Cryst.* (1973). B29, 2615**Refinement of the Crystal Structure of NaScSi<sub>2</sub>O<sub>6</sub>**

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**Abstract.** NaScSi<sub>2</sub>O<sub>6</sub>, C2/c. Cell constants at 20°C,  $a = 9.8438$  (4),  $b = 9.0439$  (4),  $c = 5.3540$  (2) Å,  $\beta = 107.215$  (2)°,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å. The structure is isomorphous with other Na-pyroxenes.

**Introduction.** The crystals were synthesized by Dr Jun Ito of Harvard University (Ito & Frondel, 1968). Precession photographs exhibited monoclinic symmetry. Reflexions with  $h+k=2n+1$  ( $hkl$ ) and  $l=2n+1$  ( $h0l$ ,  $0kl$ ) were absent. This is consistent with the space group C2/c observed in other sodic pyroxenes (Prewitt & Burnham, 1966; Clark, Appleman & Papike, 1969). A full data set out to a  $2\theta$  of 70° and consisting of 909 non-equivalent reflexions was collected from a crystal

with dimensions  $0.05 \times 0.06 \times 0.26$  mm with a Syntex PT automated diffractometer, a graphite monochromator, and Mo  $K\alpha$  radiation; a  $\theta$ - $2\theta$  scan technique was employed. Absorption corrections for polyhedral crystal shape were made by a quadrature integration procedure, and reduction of the data resulted in 781 observed reflexions. The structure refinement was made on a CDC 6400 computer by the least-squares method (REFINE program, Finger, 1969). Scattering factors for O<sup>-</sup> and fully ionized cations were taken from Cromer & Mann (1968) and coefficients for anomalous dispersion from Cromer (1965). The positional parameters of NaInSi<sub>2</sub>O<sub>6</sub> (Christiansen & Hazell, 1967) and the isotropic temperature factors for NaFeSi<sub>2</sub>O<sub>6</sub>

Table 1. *Atomic parameters for NaScSi<sub>2</sub>O<sub>6</sub>*The  $B_{1j}$  are  $\times 10^5$ .

	$x$	$y$	$z$	$B$ equiv.	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O1A1	0.1182 (1)	0.0785 (2)	0.1455 (3)	0.51 (2)	93 (11)	205 (14)	424 (42)	-17 (9)	-10 (17)	28 (18)
O2A1	0.3591 (2)	0.2479 (2)	0.3072 (3)	0.70 (2)	206 (13)	189 (14)	693 (47)	-80 (11)	84 (19)	-45 (20)
O3A1	0.3504 (2)	0.0082 (2)	0.0179 (3)	0.66 (2)	164 (13)	249 (14)	543 (48)	6 (11)	71 (19)	-92 (20)
SiA1	0.29130 (6)	0.08731 (6)	0.2439 (1)	0.40 (1)	102 (5)	128 (5)	362 (18)	-16 (4)	32 (7)	-6 (7)
M1	0	0.89627 (6)	$\frac{1}{4}$	0.42 (1)	117 (4)	117 (5)	390 (16)	0	27 (6)	0
M2	0	0.3036 (2)	$\frac{1}{4}$	1.31 (2)	497 (16)	286 (15)	773 (45)	0	-139 (21)	0

Table 2. *Selected interatomic distances in NaScSi<sub>2</sub>O<sub>6</sub> (Å)*

Si tetrahedron		M1 octahedron		M2 antiprism	
SiA1-O1A1	1.630 (3)	M1-O1A1, B1	2.183 (2)	M2-O1A1, O1B1	2.490 (2)
SiA1-O2A1	1.592 (2)	M1-O1A2, B2	2.105 (5)	M2-O2C2, O2D2	2.411 (6)
SiA1-O3A1	1.653 (2)	M1-O2C1, D1	2.017 (2)	M2-O3C1, O3D1	2.461 (4)
SiA1-O3A2	1.653 (3)	Mean	2.102	M2-O3C2, O3D2	2.894 (3)
Mean	1.632			Mean for 6	2.454
				Mean for 8	2.564
		O1A1-O1B1	2.865 (5)		
O1A1-O2A1	2.740 (4)	O2C1-O2D1	3.012 (4)	Cation-cation	
O1A1-O3A1	2.649 (3)	O1A1-O2C1	2.952 (2)	Si-SiA2	3.108 (1)
O1A1-O3A2	2.667 (7)	O1A1-O1A2	3.030 (1)	M1-M1(1)	3.269 (1)
O2A1-O3A1	2.651 (2)	O1A2-O2C1	3.003 (2)	M1-SiA1	3.356 (1)
O2A1-O3A2	2.589 (2)	O1A2-O2D1	3.085 (6)	M1-SiA2	3.279
O3A1-O3A2	2.681 (1)	O1A1-O1B2	2.777 (4)		
Mean	2.663		2.964		

Table 3. *Selected interatomic angles for NaScSi<sub>2</sub>O<sub>6</sub> (°)*

Si tetrahedron		M1 octahedron		Chain angles	
O1A1-Si-O2A1	116.5 (1)	O1A1-M1-O1B1	82.0 (1)	SiA1-O3A1-SiA2	140.2 (1)
O1A1-Si-O3A1	107.6 (2)	O1A1-M1-O2C1	91.2 (1) $\times 2$	O3A2-O3A1-O3A2	173.6 (1)
O1A1-Si-O3A2	108.7 (2)	O1A1-M1-O1A2	89.9 (1) $\times 2$	SiA1-O1A1-M1	122.7 (1)
O2A1-Si-O3A1	109.5 (1)	O1A1-M1-O1B2	80.7 (1) $\times 2$	SiA2-O1A2-M1	122.2 (2)
O2A1-Si-O3A2	105.8 (1)	O1A2-M1-O2C1	91.4 (1) $\times 2$	SiC1-O2C1-M1	146.9 (1)
O3A1-Si-O3A2	108.4 (1)	O1A2-M1-O2D1	96.9 (1) $\times 2$	SiA1-O1A1-M2	113.6 (1)
Mean	109.4	O2C1-M1-O2D1	96.6 (1)	SiC2-O2C2-M2	96.7 (2)
		Mean	89.9		

(Clark *et al.*, 1969) were used as the initial structural model. After several cycles of full matrix least-squares refinement, the structure converged with a conventional  $R$  of 3.1% (observed reflexions) where the anisotropic temperature factors were of the form  $\exp(-\sum_{i=1}^3 \sum_{j=1}^3 h_i h_j \beta_{ij})$ . A correction for isotropic extinction was made at this point (Zachariasen, 1963) and the extinction coefficient was included as a variable in the refinement. Further refinement resulted in an  $R$  of 2.8% (observed reflexions) and 3.7% (all reflexions). Final parameters are given in Table 1. Interatomic distances and angles were selected from the output of program *ERRORS* (Finger, personal communication) and are presented in Tables 2 and 3 respectively.\*

**Discussion.** The structure is isomorphous with other sodic pyroxenes (Clark *et al.*, 1969). Na occupies the M2 site which may be considered as a very distorted cubic antiprism, and Sc occupies the M1 site which is a distorted octahedron. The sodic pyroxenes are of considerable interest as the change in structural detail between them is dependent solely on the radius ( $r$ ) of the cation occupying the M1 site and are, therefore, isomorphous in the strictest sense of the term (Baur, 1971); most structural parameters are either invariant or vary monotonically. The Si-O2Al distance is constant at 1.592 (4) Å from NaAlSi<sub>2</sub>O<sub>6</sub> ( $r_{M1}=0.53$  Å) to NaInSi<sub>2</sub>O<sub>6</sub> ( $r_{M1}=0.80$  Å) while the mean M1-O distance is a linear function of  $r$  (corr. coeff.=0.99). However, some non-monotonic parameters occur and give an insight into bonding characteristics. The variation of the M1-M1 approach distance across the shared O1-O1 edge with  $r$  for the refined sodic pyroxene structures is shown in Fig. 1; a smooth curve can be drawn through those points representing the Al, Fe, Sc and In members but NaCrSi<sub>2</sub>O<sub>6</sub> deviates significantly from the trend. A similar situation occurs in the corundum structures (Prewitt, Shannon, Rogers & Sleight, 1969) where not only Cr<sub>2</sub>O<sub>3</sub> is seen to be anomalous but also Ti<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>3</sub>. In these structures, the shorter metal-metal approaches were correlated with an increase in conductivity indicating the presence of metal-metal bonding. By implication we may predict that the short metal-metal distance in NaCrSi<sub>2</sub>O<sub>6</sub> and the suspected anomalous metal-metal distances in

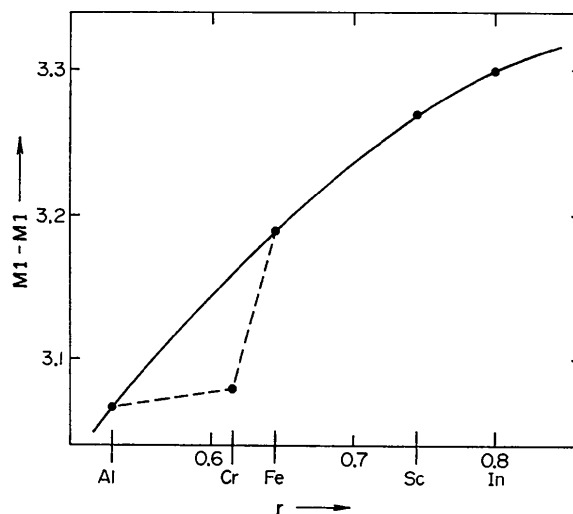


Fig. 1. Variation of the M1-M1 approach distance (Å) across the shared O1-O1 edge with the radius (Å) of the cation on the M1 site for the sodic pyroxenes. Points plotted are for NaXSi<sub>2</sub>O<sub>6</sub> where X=Al, Cr, Fe, Sc and In respectively.

NaTiSi<sub>2</sub>O<sub>6</sub> and NaVSi<sub>2</sub>O<sub>6</sub> (work in progress) should also be due to metal-metal bonds.

Examination of the Si-O distances across the Na-pyroxene series shows that those in NaCrSi<sub>2</sub>O<sub>6</sub> are anomalous and would suggest that any investigation into the effect of non-tetrahedral cations on Si-O bond lengths in this series should initially avoid those pyroxenes containing transition metals with non-spherical  $d$ -electron configurations. Further work is planned on sodic pyroxenes of this type.

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\* A list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30185 (7 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.