Tableau 3. *Principales distances interatomiques* (Å) *dans les polyèdres de coordination des cations associés*

Octaèdre CuO_6			
Cu–O($E12$)	1,999 (3)	Cu–O($W1$)	2,037 (3)
Cu–O($E22$)	2,055 (3)	Cu–O($W2$)	2,052 (3)
Cu–O($E32$)	2,156 (3)	Cu–O($W9$)	2,329 (4)
Polyèdre Na(1)O_6			
Na(1)–O($E22$)	2,395 (3)	Na(1)–O($W3$)	2,362 (4)
Na(1)–O($W1$)	2,744 (3)	Na(1)–O($W7$)	2,388 (3)
Na(1)–O($W2$)	2,415 (3)	Na(1)–O($W9$)	2,394 (3)
Polyèdre Na(2)O_6			
Na(2)–O($E21$)	2,386 (3)	Na(2)–O($W6$)	2,408 (4)
Na(2)–O($W4$)	2,387 (4)	Na(2)–O($W8$)	2,404 (4)
Na(2)–O($W6$)	2,591 (4)	Na(2)–O($W12$)	2,416 (4)
Polyèdre Na(3)O_5			
Na(3)–O($E21$)	2,399 (4)	Na(3)–O($W10$)	2,385 (4)
Na(3)–O($W5$)	2,386 (4)	Na(3)–O($W11$)	2,486 (4)
Na(3)–O($W6$)	2,433 (4)		

Les distances Na—O (Tableau 3) sont comprises:
–entre 2,362 et 2,744 Å dans le polyèdre Na(1)O_6;
–entre 2,386 et 2,591 Å dans le polyèdre Na(2)O_6;
–entre 2,386 et 2,484 Å dans le polyèdre Na(3)O_5.

Les atomes de cuivre sont entourés par trois molécules d'eau et par trois atomes d'oxygène à des distances variant de 1,999 à 2,329 Å. Les groupements P_3O_{10}, en s'enroulant autour des axes 2_1 situées en $x = \frac{1}{4}$ et $z = \frac{1}{4}$ d'une part, et en $x = \frac{3}{4}$ et $z = \frac{3}{4}$ d'autre part, délimitent deux canaux enfermant les octaèdres CuO_6 et Na(1)O_6. Ces deux derniers polyèdres partagent tantôt une face commune formée par O($W2$), O($W9$) et O($E22$), tantôt un sommet O($W1$), de façon à former un enchaînement infini Na(1)O_6–CuO_6–Na(1)O_6. . . .

Autour des deux autres axes 2_1 de la maille, on trouve deux canaux beaucoup plus grands que les précédents, délimités par six groupements P_3O_{10} dans lesquels se situent les polyèdres de coordination des atomes de sodium Na(2) et Na(3). Les polyèdres Na(2)O_6 et Na(3)O_5 partagent soit un sommet O($E21$) soit une arête O($W5$)–O($W6$) pour former une chaîne infinie se développant parallèlement à l'axe 2_1. La localisation complète des atomes d'hydrogène et leur affinement n'a pu être menée à bien.

Références

Averbuch-Pouchot, M. T. & Guitel, J. C. (1976). *Acta Cryst.* B**32**, 1670–1673.

Averbuch-Pouchot, M. T. & Guitel, J. C. (1977). *Acta Cryst.* B**33**, 1613–1615.

Frenz, B. A. (1978). *Enraf–Nonius CAD-4 SDP. A Real Time System for Concurrent X-ray Data Collection and Crystal-Structure Determination in Crystallography.* Dans *Computing in Crystallography*, édité par H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Herceg, M. (1974). 2ème Eur. Crystallogr. Meet. Keszthely, Hongrie, Août.

International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press.

Jouini, O. & Durif, A. (1983). *C.R. Acad. Sci.* A paraître.

Rakotomahanina, E., Averbuch-Pouchot, M. T. & Durif, A. (1972). *Bull. Soc. Fr. Minéral. Cristallogr.* **95**, 516–520.

Acta Cryst. (1984). C**40**, 730–733

Two-Layer Structure of Tricalcium Germanate, $Ca_{3-X}[GeO_4](O_{1-2X},F_{2X})$ with $X \simeq 0{\cdot}275$

By Fumito Nishi and Yoshio Takéuchi

Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113, *Japan*

(*Received* 1 *December* 1983; *accepted* 18 *January* 1984)

Abstract. $M_r = 261{\cdot}6$, hexagonal, $P6_3mc$, $a = 7{\cdot}223$ (1), $c = 5{\cdot}681$ (1) Å, $V = 256{\cdot}7$ Å^3, $Z = 2$, $D_x = 3{\cdot}38$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 90{\cdot}7$ cm^{-1}, $F(000) = 252{\cdot}5$, $T = 298$ K, $R = 0{\cdot}062$ for 376 observed reflections. The structure may be regarded as a two-layer variant of the rhombohedral structure of tricalcium silicate which is of the nine-layer type. It consists of isolated GeO_4 tetrahedra located on the threefold axes and separate anions on the mirror planes. Each GeO_4 tetrahedron takes a statistical orientation; 62 (2)% of the tetrahedron points in one **c** direction, the remaining fraction pointing in the opposite **c** direction. The separate anion sites, which are not coordinated to Ge and in general are occupied by oxygen atoms in the structure type, contain 40·5% oxygen atoms and 59·5% fluorine atoms. The resulting deficiency of minus charge is balanced by the distribution of vacancies at the Ca site.

0108-2701/84/050730-04$01.50

Introduction. Polymorphism of tricalcium germanates Ca_3GeO_5 has been discussed by Eysel & Hahn (1970) and Boikova & Domansky (1974). Brenner, Eysel & Hahn (1971) and Breuer & Eysel (1983) have studied structural relationships between Ca_3GeO_5 and related compounds. Structural details of Ca_3GeO_5 are, however, left unknown.

As an extension of our detailed structural studies on the polymorphic forms of tricalcium silicates (Nishi & Takéuchi, 1981; Nishi, Takéuchi & Maki, 1982*a*,*b*, 1983), we have undertaken the structural study on the germanate analogue of tricalcium silicate. Our syntheses of tricalcium germanates have yielded to date four 'polytypic' forms. In the present paper we report the crystal structure of the simplest form containing two layers of oxygen atoms parallel to (001). This structure is closely related to the structure of $(Cd_{0\cdot5}Pb_{0\cdot5})_3SiO_5$ proposed by Eysel & Breuer (1983) based on X-ray powder data and denoted as a two-layer structure.

Experimental. Single crystals of tricalcium germanate were synthesized from equimolar mixtures of Ca_2GeO_4 and CaF_2 plus small amounts of Al_2O_3 at 1720 K. In the resulting products, we identified the existence of 24-layer and 9-layer variants in addition to 2-layer Ca_3GeO_5. Electron microprobe analyses of the 2-layer material yielded: 60·14 wt% CaO, 36·48 wt% GeO_2, 0·88 wt% Al_2O_3; the total is 2·50 wt% deficient from 100%. If we assume that the entire 2·50 wt% not otherwise accounted for is due to the fluorine content, we obtain the chemical composition $Ca_{5\cdot45}Ge_{1\cdot91}Al_{0\cdot09}$-$O_{8\cdot81}F_{1\cdot19}$ for the material. Crystal ground to shape of a sphere with diameter 0·275 mm; Laue and precession photographs showing $hk1$ reflections revealed the crystal had hexagonal symmetry; cell dimensions obtained by least squares of $\sin 2\theta$ values of 24 reflections, Rigaku AFC5 single-crystal diffractometer, graphite monochromatized Mo $K\alpha$ radiation. $hk0$ precession photograph obtained after a long exposure to X-rays (48 h, 120 mA, 40 kV) revealed several very weak extra reflections (Fig. 1), indicating that the above cell is in fact a subcell of a large true cell. The limited number and exceedingly weak intensities of the extra reflections did not permit us to derive the 'true cell' definitively, and we did not take account of the extra reflections in the present study; ω–2θ scan, 752 reflections, $2\theta_{\max} = 100°$, 693 with $F_o > 2\sigma(|F_o|)$, $0 \le h \le 13$, $0 \le k \le 7$, $0 \le l \le 11$, 3 standard reflections, intensity variation 1·1% (of $|F_o|$ value), Lorentz, polarization and absorption correction (transmission coefficients: max. 0·3, min. 0·24). Comparison between $F_o(hkl)$ and $F_o(khl)$ pairs showed that they were essentially of the same value. Each pair of values was averaged to give 376 independent structure factors which were used for structure determination and least-squares refinement. In addition to $|F_o(hkl)| = |F_o(khl)|$, reflections occur only if $l = 2n$ for $00l$ and $l = 2n$ for $hh\overline{2h}l$ reflections; space group $P6_3mc$ finally confirmed through structure refinement; initial atomic coordinates deduced from those of '9-layer' rhombohedral structure of tricalcium silicate (Nishi & Takéuchi, 1981); structure factors calculated using only Ge, Ca and the separate anions which do not coordinate to the Ge atom. Fourier map based on the phases of the F_c's showed statistical orientations of the GeO_4 tetrahedra, thus hindering straightforward refinement of the structure. We therefore assumed a regular-shape tetrahedron for GeO_4 with Ge—O = 1·77 Å, and refined the positions, along **c**, occupancies in both orientations and the anisotropic thermal parameters of each atom of the tetrahedron; remaining atoms in the structure subjected to ordinary anisotropic refinement; $\sum \Delta F^2$ minimized, unit weights, $R = 0{\cdot}062$, $wR = 0{\cdot}048$, max. $\Delta/\sigma = 0{\cdot}53$, mean $\Delta/\sigma < 0{\cdot}1$, max., min. height in final $\Delta\rho$ map $-$ 1·2, $-0{\cdot}8$ e Å^{-3}, isotropic extinction correction applied $[g_{\rm iso} = 0{\cdot}079\,(6) \times 10^{-4}]$, neutral scattering factors with correction for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974), $f'_{\rm Ge} = 0{\cdot}20$, $f'_{\rm Ca} = 0{\cdot}20$, $f''_{\rm Ge} = 1{\cdot}80$, $f''_{\rm Ca} = 0{\cdot}40$, computer program for least squares: *ORFLS* (Busing, Martin & Levy, 1962).

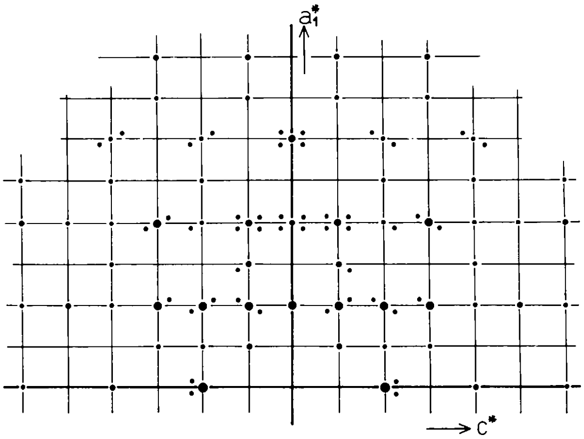

Fig. 1. The $h0l$ section of the weighted reciprocal lattice, showing the locations of the extra reflections observed. The size of the solid circles representing the extra reflections is greatly exaggerated.

Discussion. Table 1 gives the final atomic parameters.[*] The structure is illustrated in Figs. 2(*a*), (*b*). As will be observed in this figure, the tetrahedra in two orientations do not share the same Ge positions, the difference being 0·329 (6) Å. The fraction of the

---

[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39197 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetrahedron that points in the +**c** direction is 62 (2)%, the remaining fraction pointing in the opposite **c** direction.

The tetrahedra are joined together by Ca atoms, with occupancy 90·8 (6)% [9·2 (6)% vacant]. The coordination number of Ca may be evaluated by summing up the 'occupancies' of the Ca—O bonds, the sum being 6·0. Each Ca—O bond length (Table 2) was weighted by the bond occupancy and used to derive a mean Ca—O length of 2·384 (6) Å. The sum of bond valence at each anion was calculated using the procedure provided by Donnay & Allmann (1970) (Table 2), the result showing that the valence at the separate anion is significantly lower than two. We thus propose that the fluorine atoms in the structure are distributed at the separate anion site O(3) with an occupancy of 59·5% (oxygen occupancy 40·5%). The deficiency of minus charge, owing to substitution of F^{1-} for O^{2-}, is thus compensated by a distribution of vacancies around the Ca site; the neutrality of the crystal is accordingly attained.

The present compound may be compared with the related crystalline phases $Ca_{12}Si_4O_{19}F_2$ (Tanaka, Sudoh & Akaiwa, 1968) and high-$(Cd_{0\cdot5}Pb_{0\cdot5})_3SiO_5$ (Breuer & Eysel, 1983), which have both been studied by X-ray powder diffraction. The reported orthorhombic cell for the former is expressed by a hexagonal cell $a = 7\cdot092$, $c = 5\cdot689$ Å (Tanaka *et al.*, 1968). The latter has a hexagonal cell $a = 7\cdot133$, $c = 5\cdot990$ Å at 1010 K (Breuer & Eysel, 1983). Although Eysel & Breuer (1983) assigned a space group *P*3*m*1 to the latter, the indices of the powder lines (Eysel & Breuer, 1983) are consistent with *P*6$_3$*mc*. In addition, if the atomic coordinates proposed by Eysel & Breuer (1983) are shifted by $\frac{1}{3}(\mathbf{a}_2-\mathbf{a}_1)$, they are essentially the same as those of the present structure. Therefore, it is very likely that both of the structures have not space group *P*3*m*1 but *P*6$_3$*mc* and are isotypic with our structures.

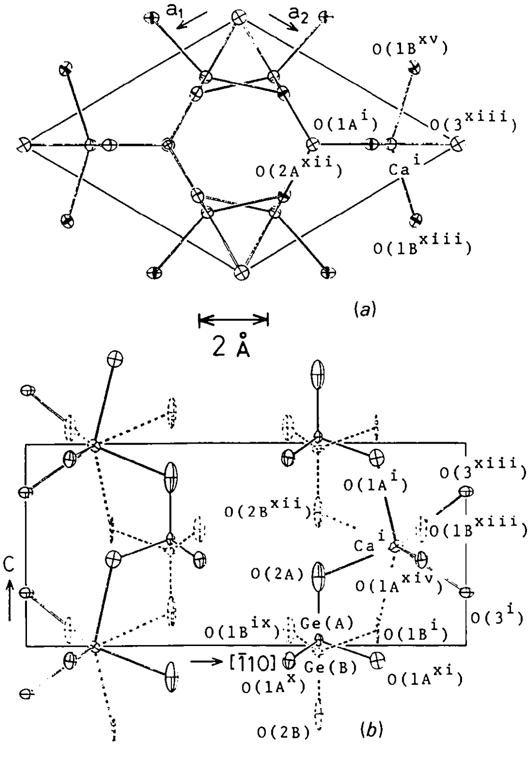

Fig. 2. The crystal structures (*a*) viewed down **c** and (*b*) viewed along [110], showing the cations, together with their neighbouring anions, in the mirror plane passing through the long diagonal of the cell. The GeO_4 groups having an occupancy of 62% are indicated by solid lines, those with an occupancy of 38% by broken lines.

Table 1. *Atomic parameters* (×10^4 *except for x, y special positions*) *for tricalcium germanate*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	*x*	*y*	*z*	B_{eq}(Å^2)
Ca	0·908 (6)	1558 (1)	−1558 (1)	4936 (15)	2·4
Ge(*A*)	0·62 (2)	$\frac{1}{3}$	$\frac{2}{3}$	300	1·5
Ge(*B*)	0·38 (2)	$\frac{1}{3}$	$\frac{2}{3}$	−280 (10)	2·1
O(1*A*)	0·62 (2)	2000	−2000	9260	3·5
O(1*B*)	0·38 (2)	2000	−2000	764	4·3
O(2*A*)	0·62 (2)	$\frac{1}{3}$	$\frac{2}{3}$	3416	6·5
O(2*B*)	0·38 (2)	$\frac{1}{3}$	$\frac{2}{3}$	−3392	6·0
O(3)	0·405 O 0·595 F	0	0	2610 (30)	3·0

Table 2. Ca—O *bond lengths* (Å) *and estimated valence sums* (v.u.)

	Oxygen atom		Ca—O bond	
		Symmetry code	Multiplicity	Length (Å)
Ca	O(1*A*)	(vii)	0·62 (2)	2·309 (2)
	O(1*A*)	(viii)	0·62 (2)	2·309 (2)
	O(1*B*)	(v)	0·38 (2)	2·325 (2)
	O(1*B*)	(vi)	0·38 (2)	2·325 (2)
	O(3)		1·0	2·355 (11)
	O(2*A*)	(ii)	0·62 (2)	2·383 (3)
	O(2*B*)	(iii)	0·38 (2)	2·416 (4)
	O(1*B*)		0·38 (2)	2·433 (10)
	O(3)	(iv)	1·0	2·472 (12)
	O(1*A*)		0·62 (2)	2·518 (8)
		Total	6·0	
		Average		2·384 (6)

	Ca	Ge(*A*),(*B*)	Valence sum
O(1*A*)	0·260 × 0·62	1·0 × 0·62	
	0·335 × 1·24		
O(1*B*)	0·285 × 0·38	1·0 × 0·38	O(1*A*) + O(1*B*) =
	0·325 × 0·76		1·932
O(2*A*)	0·305 × 1·86	1·0 × 0·62	
			O(2*A*) + O(2*B*) =
O(2*B*)	0·295 × 1·14	1·0 × 0·38	1·903
O(3)	0·315 × 3		
	0·275 × 3		1·770

Symmetry code: None x, y, z; (i) $x, 1+y, z$; (ii) $x, -1+y, z$; (iii) $x, -1+y, 1+z$; (iv) $-x, -y, \frac{1}{2}+z$; (v) $y, -x+y, \frac{1}{2}+z$; (vi) $x-y, x, \frac{1}{2}+z$; (vii) $x-y, x, -\frac{1}{2}+z$; (viii) $y, -x+y, -\frac{1}{2}+z$; (ix) $-x+y+1, 1+y, z$; (x) $-x+y+1, 1+y, -1+z$; (xi) $x, 1+y, -1+z$; (xii) $-x+y, y, 1+z$; (xiii) $x-y, 1+x, \frac{1}{2}+z$; (xiv) $x-y, 1+x, -\frac{1}{2}+z$; (xv) $y, -x+y+1, \frac{1}{2}+z$.

References

BOIKOVA, A. I. & DOMANSKY, A. I. (1974). *Cem. Concr. Res.* **4**, 773–784.

BRENNER, P., EYSEL, W. & HAHN, TH. (1971). *Neues Jahrb. Mineral. Monatsh.* **4**, 175–179.

BREUER, K. H. & EYSEL, W. (1983). *Z. Kristallogr.* **162**, 289–297.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

DONNAY, G. & ALLMANN, R. (1970). *Am. Mineral.* **55**, 1003–1015.

EYSEL, W. & BREUER, K. H. (1983). *Z. Kristallogr.* **163**, 1–17.

EYSEL, W. & HAHN, TH. (1970). *Z. Kristallogr.* **131**, 40–59.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NISHI, F. & TAKÉUCHI, Y. (1981). Ann. Meet. Mineral. Soc. Japan, Abstract 62.

NISHI, F., TAKÉUCHI, Y. & MAKI, I. (1982*a*). Ann. Meet. Mineral. Soc. Japan, Abstract 43.

NISHI, F., TAKÉUCHI, Y. & MAKI, I. (1982*b*). Ann. Meet. Crystallogr. Soc. Japan, Abstract 89.

NISHI, F., TAKÉUCHI, Y. & MAKI, I. (1983). Ann. Meet. Mineral. Soc. Japan, Abstract 37.

TANAKA, M., SUDOH, G. & AKAIWA, S. (1968). Proc. 5th Int. Symp. Chemistry of Cement, Tokyo, pp. 122–135.

Acta Cryst. (1984). C**40**, 733–736

Location and Anisotropic Refinement of Deuterium Atoms in Deuterium Sodium Silicate–Deuterium Oxide (1/8) $Na_2D_2SiO_4.8D_2O$ by Neutron Diffraction; Hydrogen Bonding at 173 K

BY RUDOLF L. SCHMID AND J. FELSCHE

Fakultät für Chemie, Universität Konstanz, Postfach 5560, *D*-7750 *Konstanz, Federal Republic of Germany*

AND G. J. MCINTYRE

Institut Laue – Langevin, BP 156 *X*, 38042 *Grenoble CEDEX, France*

(*Received* 1 *July* 1983; *accepted* 5 *December* 1983)

Abstract. $M_r = 302\cdot1$, orthorhombic, *Ibca*, $a = 11\cdot658\,(5)$, $b = 16\cdot927\,(4)$, $c = 11\cdot477\,(3)$ Å, $V = 2264\cdot79$ Å^3, $Z = 8$, $D_m = 1\cdot75$ (296 K), $D_x = 1\cdot77$ Mg m^{-3}, $\lambda = 1\cdot2640$ Å, $\mu(n) = 0\cdot001$ mm^{-1}, $F(000) = 160\cdot96$, $T = 173$ K, $R = 0\cdot037$ for 1015 independent reflections. All deuterium atoms have been located and the hydrogen-bond structure of $Na_2D_2SiO_4.8D_2O$ has been determined by single-crystal neutron diffraction. Coordinates and anisotropic temperature factors have been refined by full-matrix least squares for all atoms, deuterium atoms included. The crystal structure of $Na_2D_2SiO_4.8D_2O$ consists of isolated $[D_2SiO_4]^{2-}$ anions and linear chains of edge-linked $[Na(D_2O)_6]^+$ cations running parallel to the *a* axis which are connected by hydrogen bonds. Coordination numbers observed are CN = 6 for Na with almost octahedral geometry and CN = 4 and 5 for the D_2O-Na,D polyhedra.

Introduction. Two series of crystalline hydrate phases exist in the system Na_2O–SiO_2–H_2O: $Na_3HSiO_4.nH_2O$ ($n = 5,2,1,0$) with an $Na_2O:SiO_2$ ratio of 3:2; and $Na_2H_2SiO_4.nH_2O$ ($n = 8,7,5,4$) with an $Na_2O:SiO_2$ ratio of 1:1. Members of the first series are built up of isolated $[HSiO_4]^{3-}$ anions, as shown for $Na_3HSiO_4.5H_2O$ (Smolin, Shepelev & Butikova, 1973) and $Na_3HSiO_4.2H_2O$ (Schmid, Huttner & Felsche, 1979; Schmid, Szolnay, Felsche & Hutter, 1981), whereas the members of the second series are built up of isolated $[H_2SiO_4]^{2-}$ anions as shown for $Na_2H_2SiO_4.8H_2O$ (Jamieson & Dent-Glasser, 1966*a,b*), $Na_2H_2SiO_4.7H_2O$ (Dent-Glasser & Jamieson, 1976), $Na_2H_2SiO_4.5H_2O$ (Jamieson & Dent-Glasser, 1967; Williams & Dent-Glasser, 1971) and $Na_2H_2SiO_4.4H_2O$ (Jost & Hilmer, 1966).

The hydrogen-atom positions and the hydrogen-bonding schemes have been determined, in most cases by X-ray diffraction, for the above phases (see references above) except for $Na_2H_2SiO_4.8H_2O$ and $Na_2H_2SiO_4.4H_2O$. $Na_2H_2SiO_4.8H_2O$ is of particular interest as it shows unique thermal and physicochemical properties as it is the only member of the 1:1 series which undergoes a solid–solid decomposition reaction forming a lower hydrate phase, namely $Na_2H_2SiO_4.4H_2O$. A knowledge of the complete structure, including the positions of the hydrogen atoms, should provide a sound basis upon which to explain these properties and which will be published elsewhere.

In this paper we present the results of a single-crystal neutron diffraction study on deuterated $Na_2H_2SiO_4.8H_2O$ (hereafter $Na_2D_2SiO_4.8D_2O$) at 173 K. The results of a 296 K measurement, including thermal-motion analysis and *X–N* analysis, will be published later.

0108-2701/84/050733-04$01.50