(Devarajan & Glazer, 1986; Stadnicka, Glazer & Koralewski, 1988). We found it difficult even to determine the correct optical activity sign in our crystal by using the simplified model proposed by Glazer & Stadnicka (1986). In order to go on along this line further experimental information such as measurements of the refractive indices would be of great value.

Concerning the low-temperature phase, the precession photographs indicated that the number of molecules Z remained the same in both phases, so the transition is of ferrodistortive type. This fact, together with the splitting of the diffraction spots and the systematic extinctions detected, points to a reduction of the symmetry to a monoclinic group, which must necessarily be $P2_1$ if the transition is to be accounted for within the framework of the Landau theory.

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References

Aizu, K. (1972). *J. Phys. Soc. Jpn*, **32**, 1287–1301.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Devarajan, V. & Glazer, A. M. (1986). *Acta Cryst.* A**42**, 560–569.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 867–881.

Glazer, A. M. & Stadnicka, K. (1986). *J. Appl. Cryst.* **19**, 108–122.

Glazer, A. M. & Stadnicka, K. (1989). *Acta Cryst.* A**45**, 234–238.

Hempel, H., Maack, H. & Sorge, G. (1989). *Phys. Status. Solidi.* To be published.

Karppinen, M., Lundgren, J.-O. & Liminga, R. (1983). *Acta Cryst.* C**39**, 34–38.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mróz, B., Kiefte, H. & Clouter, M. J. (1988). *Ferroelectrics*, **82**, 105–110.

Pietraszko, A. & Lukaszewicz, K. (1988). *Z. Kristallogr.* **185**, 564.

Stadnicka, K., Glazer, A. M. & Koralewski, M. (1988). *Acta Cryst.* B**44**, 356–361.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY*72 system – Version of June 1972, modified by D. Schwarzenbach, Institut of Crystallography, Univ. of Lausanne, Switzerland. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Wolejko, T., Pakulski, G. & Tylczynski, Z. (1988). *Ferroelectrics*, **82**, 179–182.

Wolejko, T., Piskunowicz, P., Breczewski, T. & Krajewski, T. (1988). *Ferroelectrics*, **81**, 179–182.

Acta Cryst. (1990). C**46**, 1202–1204

Refinement of the Structure of Sodium Enneagermanate (Na$_4$Ge$_9$O$_{20}$)

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Abstract. Na$_4$Ge$_9$O$_{20}$, M_r = 1065·3, tetragonal, $I4_1/a$, a = 15·0263 (9), c = 7·3971 (9) Å, V = 1670·2 Å^3, Z = 4, D_x = 4·236 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 172·9 cm^{-1}, F(000) = 1968, room temperature, 2589 unique reflections, final R = 0·026. Five Ge atoms per formula unit are in tetrahedral coordination with oxygen [Ge(1)—O = 1·742 (2) Å; ⟨Ge(2)—O⟩ = 1·747 (2) Å] and four are in octahedral coordination [⟨Ge(3)—O⟩ = 1·900 (2) Å]. The sodium cation has seven oxygens within the 3·2 Å sphere, with four short bonds in the form of a nearly planar configuration, and its thermal ellipsoid is markedly anisotropic with its major axis almost parallel to the c axis.

Introduction. The structure of tetragonal sodium enneagermanate (Na$_4$Ge$_9$O$_{20}$) is of interest as a possible structural model for sodium germanate glasses (*e.g.* Kamiya, Yoko, Miki, Itoh & Sakka, 1987; Weber, 1982) and high-pressure silicate melts (*e.g.* Fleet, Herzberg, Henderson, Crozier, Osborne & Scarfe, 1984). Early confusion about the composition of sodium enneagermanate and its stability relative to that of the tetragermanate Na$_2$Ge$_4$O$_9$ was resolved by White, Shaw, Corwin & Pabst (1959) and by Murthy & Aguayo (1964) and Monnaye (1975), respectively. The structures of both of these germanates are based on polymerized GeO$_4$ tetrahedra (single chains in Na$_4$Ge$_9$O$_{20}$ and three-

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membered rings in $Na_2Ge_4O_9$) interconnected by GeO_6 octahedra. Tetragonal $Na_4Ge_9O_{20}$ has four Ge atoms per formula unit in octahedral coordination with oxygen (Ingri & Lundgren, 1963) and hexagonal $Na_2Ge_4O_9$, with a wadeite-like structure (Nowotny & Wittmann, 1954; Jolly & Myklebust, 1968; Choisnet, Deschanvres & Raveau, 1973), has one germanium per formula unit in octahedral coordination.

The structure refinement of sodium enneagermanate by Ingri & Lundgren (1963) was based on visually estimated film intensities for 840 reflections and yielded $R = 0{\cdot}135$. The general features of the structure were firmly established but the refined isotropic thermal parameters for oxygen were very low (0·00 to 0·61 $Å^2$) and the stereochemical environment of the sodium cation was unclear.

Experimental. Sodium enneagermanate crystals were grown using a nutrient of germanium albite ($NaAlGe_3O_8$) composition. A 2 g stoichiometric mixture of Na_2CO_3, Al_2O_3 and GeO_2 and 18 g of hydrous sodium tungstate were contained in a platinum crucible with a well fitting lid, soaked at 1173 K for two days, and cooled at 4 K h^{-1} to about 773 K. The products consisted of fine-grained germanium albite and a few light-pink prismatic crystals of $Na_4Ge_9O_{20}$, up to 0·5 × 5 mm in size. Sodium enneagermanate was characterized by optical microscopy, electron microprobe analysis and powder and single-crystal diffraction.

The crystal was cubical, with approximate dimensions 0·10 × 0·12 × 0·11 mm and a calculated volume of $1{\cdot}30 \times 10^{-3}$ mm^3. Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ X-radiation. 20 reflections in 2θ range 50·1–59·1° for cell parameters. Data collected by θ–2θ scan; scan angle $(2\theta) = 2{\cdot}4°$, with dispersion correction. 5609 *hkl* reflections allowed by space group $I4_1/a$ out to $2\theta = 80°$ measured; $0 \le h \le 27$, $-27 \le k \le 27$, $0 \le l \le 13$. Standard reflections 240, $4\bar{2}0$, 004; $R_{\rm int} = 0{\cdot}01$, no significant variation in intensity. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a 12 × 12 × 12 grid) varied from 0·159 for 020 to 0·277 for 2,3,13. 2589 unique reflections: 1357 reflections considered unobserved on the basis of $I < 3\sigma(I)$ $\{\sigma(I) = [I_m + 0{\cdot}002^2(I_m - B)^2 + 0{\cdot}005^2 \times (I - I_m)^2]^{1/2}$, I_m, measured intensity and B, background$\}$.

Structure refinement proceeded from the positional parameters of Ingri & Lundgren (1963). $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$; unobserved reflections were given a low weight ($\sigma = 1000$). Refinement using all reflections out to $2\theta = 80°$ and 76 variable parameters converged to $R = 0{\cdot}026$, $wR = 0{\cdot}025$ for reflections with $I \ge 3\sigma(I)$, $S = 0{\cdot}443$, $(\Delta/\sigma)_{\max} = 2 \times 10^{-7}$, $\Delta\rho = -0{\cdot}7$ e $Å^{-3}$ (at 0·10,0·05,0·65) to 2·1 e $Å^{-3}$ (at 0·0,0·25,0·21). The isotropic extinction parameter for type I extinction (g; Coppens & Hamilton, 1970) is $0{\cdot}128\,(8) \times 10^{-4}$. Scattering factors for neutral atomic species and f', f'' taken, respectively, from Tables 2.2B and 2.3.1 of *International Tables for X-ray Crystallography* (1974). Computations carried out with *DATAP77* and *LINEX77* (State University of New York at Buffalo).

Discussion. Positional parameters are given in Table 1 and selected interatomic distances and bond angles in Table 2.* Compared to the present refinement of the structure of $Na_4Ge_9O_{20}$, the sodium and oxygen positional parameters of Ingri & Lundgren (1963) are generally within ±0·002, Ge—O bond distances are within ±0·01 Å, and Na—O distances are generally within ±0·02 Å; the only marked discrepancy is for the Na—O($5^{\rm iii}$) distance (−0·05 Å).

The overall features of the structure are illustrated in Fig. 2 of Ingri & Lundgren (1963) and in Fig. 3 of Kamiya, Yoko, Miki, Itoh & Sakka (1987) and details of the stereochemistry of the sodium cation in Fig. 1. The Ge(3)O_6 octahedra are associated into Ge_4O_{16} groups by sharing edges, as in the rock-salt structure, and then linked by Ge(1)O_4 tetrahedra to form columns parallel to the c axis. These columns of mixed Ge(3)O_6 octahedra and Ge(1)O_4 tetrahedra are linked by spiral single chains of Ge(2)O_4 tetrahedra also parallel to the c axis. The bond angles associated with the shared octahedral edges [O(2)—Ge(3)—O(2)] are markedly distorted in a manner consistent with cation–cation repulsion (*cf.* Fleet, 1974) and the Ge(1)O_4 tetrahedron is correspondingly stretched in the a_1,a_2 plane (compressed in the **c** direction).

Charge-balance and space-fitting requirements result in the sodium cation being displaced away from the central channel within the spiral $[Ge(2)O_4]_n$ chains to form bonds with the oxygens of the shared octahedral-tetrahedral corners. There are seven O atoms within the 3·2 Å sphere about the sodium cation. However, there are only four short distances to oxygens, forming a nearly planar configuration (Table 2) (see also Fig. 1). Three of these short distances are to shared octahedra-tetrahedral corners and therefore serve to charge balance the oxygens in question [O(1), O(4), O(5)]. The fourth is to the O atom bridging Ge(2)O_4 tetrahedra [O(3)]. The thermal ellipsoid for the sodium cation is markedly anisotropic with its major axis almost normal to the

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* Tables of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52681 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters* (Å^2) *for sodium enneagermanate* ($Na_4Ge_9O_{20}$)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

Origin at $\bar{1}$.

	Equi-point	x	y	z	B_{eq}
Na	16 (*f*)	0·08666 (9)	0·05566 (8)	0·16931 (21)	2·010 (25)
Ge(1)	4 (*a*)	0	$\frac{1}{4}$	$\frac{1}{8}$	0·527 (8)
Ge(2)	16 (*f*)	0·13657 (2)	0·04603 (2)	0·70097 (4)	0·540 (5)
Ge(3)	16 (*f*)	0·09568 (2)	0·21773 (2)	0·49080 (4)	0·509 (4)
O(1)	16 (*f*)	0·09204 (12)	0·21194 (13)	0·24544 (25)	0·801 (27)
O(2)	16 (*f*)	0·08005 (12)	0·22213 (13)	0·74549 (25)	0·655 (27)
O(3)	16 (*f*)	0·18871 (12)	0·07324 (13)	0·90670 (26)	0·817 (29)
O(4)	16 (*f*)	0·02503 (12)	0·04537 (12)	0·75873 (27)	0·848 (29)
O(5)	16 (*f*)	0·15385 (13)	0·10846 (12)	0·50551 (27)	0·789 (28)

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *in sodium enneagermanate*

Na—O(1)	2·416 (2)	Ge(2)—O(3)	1·760 (2)
Na—O(1^{ii})	2·713 (2)	Ge(2)—O(3^{iii})	1·753 (2)
Na—O(3)	2·489 (2)	Ge(2)—O(4)	1·730 (2)
Na—O(4)	3·179 (3)	Ge(3)—O(1)	1·818 (2)
Na—O(4^{v})	2·325 (2)	Ge(3)—O(5)	1·863 (2)
Na—O(5)	2·799 (2)	Ge(3)—O(2)	1·900 (2)
Na—O(5^{iii})	2·508 (2)	Ge(3)—O(2^{ii})	1·993 (2)
Ge(1)—O(1)	1·742 (2)	Ge(3)—O(2^{i})	1·974 (2)
Ge(2)—O(5)	1·743 (2)	Ge(3)—O(4^{i})	1·850 (2)

O(1)—Na—O(3)	93·33 (8)	O(1)—Ge(3)—O(2)	171·14 (8)
O(1)—Na—O(4^{v})	127·26 (8)	O(1)—Ge(3)—O(2^{ii})	90·32 (8)
O(1)—Na—O(5^{iii})	144·46 (9)	O(1)—Ge(3)—O(2^{i})	94·40 (8)
O(3)—Na—O(4^{v})	133·85 (9)	O(1)—Ge(3)—O(4^{i})	92·91 (9)
O(3)—Na—O(5^{iii})	95·30 (8)	O(5)—Ge(3)—O(2)	91·76 (8)
O(4^{v})—Na—O(5^{iii})	65·49 (7)	O(5)—Ge(3)—O(2^{ii})	96·69 (8)
O(1)—Ge(1)—O(1^{ii})	105·17 (6)	O(5)—Ge(3)—O(2^{i})	172·99 (8)
O(1)—Ge(1)—O(1^{iv})	118·47 (12)	O(5)—Ge(3)—O(4^{i})	89·71 (8)
O(5)—Ge(2)—O(3)	121·73 (9)	O(2)—Ge(3)—O(2^{ii})	81·19 (8)
O(5)—Ge(2)—O(3^{iii})	106·79 (9)	O(2)—Ge(3)—O(2^{i})	81·69 (8)
O(5)—Ge(2)—O(4)	110·63 (9)	O(2)—Ge(3)—O(4^{i})	95·24 (8)
O(3)—Ge(2)—O(3^{iii})	102·82 (11)	O(2^{ii})—Ge(3)—O(2^{i})	79·90 (8)
O(3)—Ge(2)—O(4)	102·66 (9)	O(2^{ii})—Ge(3)—O(4^{i})	172·74 (8)
O(3^{iii})—Ge(2)—O(4)	112·01 (9)	O(2^{i})—Ge(3)—O(4^{i})	93·37 (8)
O(1)—Ge(3)—O(5)	91·73 (9)		

Symmetry code: (i) $\frac{1}{4}-y,\frac{1}{4}+x,\frac{1}{4}-z$; (ii) $\frac{3}{4}+y,\frac{1}{4}-x,\frac{1}{4}-z$; (iii) $\frac{1}{4}-y,\frac{3}{4}+x,\frac{3}{4}+z$; (iv) $-x,\frac{1}{2}-y,z$; (v) $-x,-y,-z$.

plane close to the four short bonds and making an angle of 23° with the *c* axis.

There is an interesting correlation between the size of the thermal ellipsoids for Ge atoms and structural topology. In tetrahedral sodium enneagermanate, B_{eq} for germanium is 0·51 to 0·54 Å^2 (Table 1). This range of values may be compared with 0·47 to 0·53 Å^2 for three germanate sodalites (Fleet, 1989), which have open-framework structures, and 0·21 to 0·22 Å^2 for $(Ni,Mg)_{10}Ge_3O_{16}$ (Fleet & Barbier, 1989), which has a close-packed structure. Clearly, the thermal ellipsoids in sodium enneagermanate are broadened by concerted motion.

All three germanium positions in sodium enneagermanate have weak residual electron density at $z \simeq \pm 0{\cdot}1$. This is clearly unrelated to bonding but may represent a static distortion in the structure related to crystal defects and/or the marked anisotropy in the thermal ellipsoid for the sodium cation.

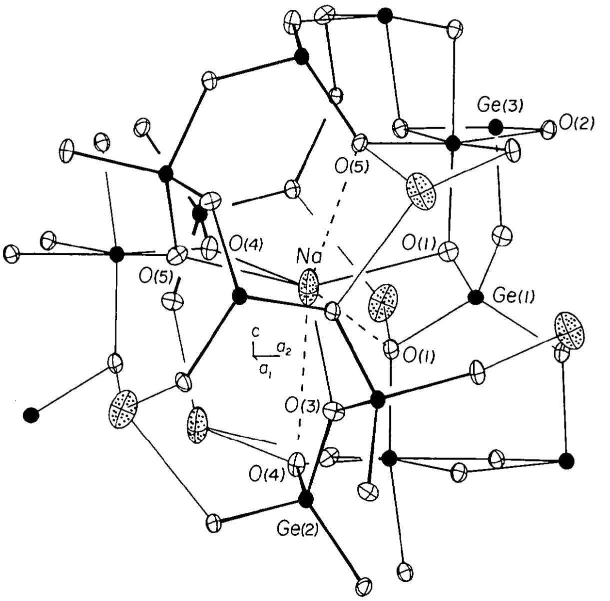

Fig. 1. Coordination environment of the sodium cation in sodium enneagermanate ($Na_4Ge_9O_{20}$): bonds to oxygens at 2·6 to 3·2 Å are indicated by broken lines.

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References

Choisnet, J., Deschanvres, A. & Raveau, B. (1973). *J. Solid State Chem.* 7, 408–417.
Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A26, 71–83.
Fleet, M. E. (1974). *Am. Mineral.* 59, 1083–1093.
Fleet, M. E. (1989). *Acta Cryst.* C45, 843–847.
Fleet, M. E. & Barbier, J. (1989). *Acta Cryst.* **B45**, 201–205.
Fleet, M. E., Herzberg, C. T., Henderson, G. S., Crozier, E. D., Osborne, M. D. & Scarfe, C. M. (1984). *Geochim. Cosmochim. Acta*, **48**, 1455–1466.
Ingri, N. & Lundgren, G. (1963). *Acta Chem. Scand.* **17**, 617–633.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Jolly, J. H. & Myklebust, R. L. (1968). *Acta Cryst.* **B24**, 460–461.
Kamiya, K., Yoko, T., Miki, Y., Itoh, Y. & Sakka, S. (1987). *J. Non-Cryst. Solids*, **91**, 279–292.
Monnaye, B. (1975). *Rev. Chim. Minér.* **12**, 268–287.
Murthy, M. K. & Aguayo, J. (1964). *J. Am. Ceram. Soc.* **47**, 444–447.
Nowotny, H. & Wittmann, A. (1954). *Monatsh. Chem.* **85**, 558–574.
Weber, H.-J. (1982). *Mater. Res. Bull.* **17**, 1313–1318.
White, J. F., Shaw, E. R., Corwin, J. F. & Pabst, A. (1959). *Anal. Chem.* **31**, 315–316.