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# The Crystal Structure of $Na_4Ge_9O_{20}$

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Crystals of $Na_4Ge_9O_{20}$ are tetragonal, space group $I4_1/a$, with the dimensions $a = 14.98 \pm 0.01$ Å, $c = 7.384 \pm 0.005$ Å. The unit cell contains four formula units. Using three-dimensional Patterson and Fourier methods the germanium, oxygen and sodium positions have been determined. These positions have been refined using the method of least squares. The refined atomic coordinates are collected in Table 2. $Na_4Ge_9O_{20}$ is built up of $GeO_4$ tetrahedra and $GeO_6$ octahedra coupled together forming a three-dimensional network. (*cf.* Figs 2 a, b, and c). The Ge–O distances have been determined with a standard deviation of $\pm$ 0.015 Å. Table 3 gives the most important distances and angles in the structure. The mean Ge–O distance for octahedral coordination is $1.90_7$ Å (in the structure varying from $1.82_2$ Å to $1.99_8$ Å) and for tetrahedral coordination $1.74_3$ Å (in the structure varying from $1.71_5$ to $1.76_4$ Å).

In a previous paper [1] we described the preparation of crystalline $Na_4Ge_9O_{20}$, gave its crystallographic data and its germanium parameters. The aim of the present work is to determine the positions of the oxygen and sodium atoms and to refine the structure.

$Na_4Ge_9O_{20}$ was made by heating precipitated sodium germanate with its mother liquid (pH $\approx$ 9) in a closed vessel at 300°C. Using single crystals prepared in this way, Weissenberg photographs ($hk0$—$hk3$, $0kl$—$6kl$, $hhl$—$h$, $h + 7$, $l$) were taken, using Cu$K$ radiation. The cell dimensions of the tetragonal unit cell were found to be: $a = 14.98$ Å $c = 7.384$ Å. The characteristic space group is $I4_1/a$, No. 88 in the International Tables [2]. The unit cell contains four formula units ($Na_4Ge_9O_{20}$) giving a calculated density of 4.268 g.cm$^{-3}$ as compared with our observed value of 4.19 g.cm$^{-3}$.

The intensities of the reflexions were estimated visually using the multiple films technique and a calibrated scale. Lorentz and polarization corrections were made according to Lu [3]. No correction was made for the absorption. In this way the $|F_o|$ values of 693 independent, observed reflexions were obtained (*cf.* Table 1).

From a series of Patterson calculations we could determine the positions of the 36 germanium atoms in the unit cell.[1] We found:

| | Center of symmetry at 0 ¼ ⅛ | | | Center of symmetry at 000 | | |
|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| 4 $Ge_1$ in 4($a$) | 0 | 0 | 0 | 0 | ¼ | ⅛ |
| 16 $Ge_2$ in 16($f$) | 0.2030 | 0.1436 | −0.4227 | 0.1436 | 0.0470 | 0.7023 |
| 16 $Ge_3$ in 16($f$) | 0.0297 | 0.0970 | 0.3630 | 0.0970 | 0.2203 | 0.4880 |

## DETERMINATION OF THE OXYGEN AND SODIUM POSITIONS

In order to find the $x$ and $y$ parameters of the oxygen and sodium atoms the electron density projection $\varrho(xyp)$ was calculated. The phase angles of 37 of the 67 observed reflexions $hk0$ could be determined with certainty from the germanium contributions and the projection $\varrho(xyp)$ obtained from these values gave possible $x$ and $y$ coordinates of all oxygen and sodium atoms in the unit cell. Three-dimensional electron density calculations using all 693 reflexions with phase angles obtained from the germanium contributions only gave the oxygen and sodium $z$ parameters. The structure factors were then calculated taking into account all the atoms in the unit cell, and from a final three-dimensional electron density function the following parameters were obtained for the oxygen and sodium atoms:

| | Center of symmetry at 0 ¼ ⅛ | | | Center of symmetry at 000 | | |
|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| 16 $O_1$ in 16($f$) | 0.0953 | 0.4666 | 0.3745 | 0.0953 | 0.2166 | 0.2495 |
| 16 $O_2$ in 16($f$) | 0.0845 | 0.4795 | 0.8847 | 0.0845 | 0.2295 | 0.7597 |
| 16 $O_3$ in 16($f$) | 0.1894 | 0.3265 | 0.0303 | 0.1894 | 0.0765 | 0.9053 |
| 16 $O_4$ in 16($f$) | 0.0195 | 0.2995 | 0.8727 | 0.0195 | 0.0495 | 0.7477 |
| 16 $O_5$ in 16($f$) | 0.1584 | 0.3681 | 0.6381 | 0.1584 | 0.1181 | 0.5131 |
| 16 Na in 16($f$) | 0.0798 | 0.3104 | 0.2918 | 0.0798 | 0.0604 | 0.1668 |

The structure factors and the electron density projections were calculated on the electronic computer BESK using the programmes SNUSKMUS [4] and S 1 [5]. The three-dimensional electron density functions were calculated partly on the electronic computer Wegematic [6] and partly on a Ferranti Mercury computer.

## REFINEMENT OF THE STRUCTURE

To refine the parameters of the structure we used a least squares programme on the computer FACIT EDB [7] and started with the set of atomic positions given above. Atomic scattering factors published by Berghuis *et al.*[8] were used. For each atom, its coordinates and its isotropic temperature factor were refined together with the scale factors between the different Weissenberg photographs. The residuals $S = \sum_{hkl} w(|F_o|-|F_c|)^2$ were minimized, at first with only about 500 independent reflexions included in the calculations. For the weight $w$ we used the weight function given by Hughes [9]:

$$w = \tfrac{1}{16}|F_{o,\min}|^{-2} \text{ for } |F_o| \leq 4|F_{o,\min}| \text{ and } w = |F_o|^{-2} \text{ for } |F_o| > 4|F_{o,\min}|.$$

*Table 1.* $F_o$ and $F_c$ for $Na_4Ge_9O_{20}$

| $h$ $k$ $l$ | $F_o$ | $F_c$ | $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 2 0 0 | 228 | 227.4 | 2 12 0 | 357 | 335.2 |
| 4 0 0 | 79 | − 76.3 | 4 12 0 | 277 | 286.3 |
| 6 0 0 | 188 | 186.9 | 6 12 0 | 69 | 66.0 |
| 8 0 0 | 30 | − 14.9 | 8 12 0 | 287 | −302.5 |
| 10 0 0 | 317 | 308.1 | 10 12 0 | 139 | −145.7 |
| 12 0 0 | 178 | −165.5 | 12 12 0 | < 20 | 20.1 |
| 14 0 0 | 30 | 29.7 | 14 12 0 | 158 | −123.1 |
| 16 0 0 | 208 | −202.8 | | | |
| 18 0 0 | 307 | −312.3 | 2 14 0 | 287 | 261.7 |
| | | | 4 14 0 | < 20 | 12.8 |
| 2 2 0 | 327 | −341.7 | 6 14 0 | 208 | −209.9 |
| 4 2 0 | 337 | −360.3 | 8 14 0 | 129 | 146.3 |
| 6 2 0 | 693 | 793.9 | 10 14 0 | 228 | 214.9 |
| 8 2 0 | 168 | 164.6 | 12 14 0 | 79 | 87.5 |
| 10 2 0 | 119 | −108.1 | | | |
| 12 2 0 | 30 | − 1.5 | 2 16 0 | 79 | − 87.9 |
| 14 2 0 | < 20 | 5.3 | 4 16 0 | 178 | 181.0 |
| 16 2 0 | 248 | 193.7 | 6 16 0 | 79 | − 90.6 |
| 18 2 0 | 248 | −170.5 | 8 16 0 | 168 | 166.0 |
| | | | 2 18 0 | 50 | 30.2 |
| 2 4 0 | 59 | 68.9 | 4 18 0 | 158 | −171.7 |
| 4 4 0 | 198 | −263.5 | | | |
| 6 4 0 | 327 | −358.1 | 1 0 1 | 209 | −204.4 |
| 8 4 0 | 99 | −118.4 | 3 0 1 | 318 | 389.5 |
| 10 4 0 | 137 | −153.1 | 5 0 1 | 100 | 95.6 |
| 12 4 0 | 347 | 381.4 | 7 0 1 | 134 | 177.3 |
| 14 4 0 | 218 | 180.4 | 9 0 1 | 142 | −135.6 |
| 16 4 0 | < 20 | − 29.9 | 11 0 1 | < 17 | − 15.0 |
| 18 4 0 | 49 | 42.9 | 13 0 1 | 42 | 47.9 |
| | | | 15 0 1 | < 17 | 24.2 |
| 2 6 0 | 376 | −402.4 | 17 0 1 | 234 | 216.5 |
| 4 6 0 | 149 | 56.0 | | | |
| 6 6 0 | < 20 | 13.3 | 2 1 1 | 251 | 181.3 |
| 8 6 0 | 119 | 103.4 | 4 1 1 | 142 | −162.9 |
| 10 6 0 | 426 | −383.6 | 6 1 1 | 117 | −149.6 |
| 12 6 0 | 347 | −310.2 | 8 1 1 | 67 | 59.8 |
| 14 6 0 | 297 | −237.9 | 10 1 1 | 167 | −145.5 |
| 16 6 0 | 337 | −316.6 | 12 1 1 | 326 | −314.5 |
| | | | 14 1 1 | 151 | −152.2 |
| 2 8 0 | 158 | 99.8 | 16 1 1 | 42 | − 54.2 |
| 4 8 0 | 614 | 647.9 | 18 1 1 | 42 | − 47.2 |
| 6 8 0 | 248 | 230.2 | | | |
| 8 8 0 | 50 | − 45.5 | 1 2 1 | 25 | − 35.5 |
| 10 8 0 | 109 | 121.2 | 3 2 1 | 167 | 186.7 |
| 12 8 0 | 267 | 265.8 | 5 2 1 | 243 | −319.4 |
| 14 8 0 | 347 | 317.9 | 7 2 1 | 268 | −324.7 |
| 16 8 0 | 168 | −150.9 | 9 2 1 | 201 | 204.8 |
| | | | 11 2 1 | < 17 | 0.1 |
| 2 10 0 | 505 | −507.3 | 13 2 1 | 92 | 75.7 |
| 4 10 0 | 386 | −384.5 | 15 2 1 | 226 | −192.2 |
| 6 10 0 | 89 | − 73.1 | 17 2 1 | 159 | −151.8 |
| 8 10 0 | 228 | −219.1 | | | |
| 10 10 0 | 149 | 161.3 | 2 3 1 | 276 | 299.1 |
| 12 10 0 | < 20 | 3.5 | 4 3 1 | 67 | 82.2 |
| 14 10 0 | 119 | −145.2 | 6 3 1 | 251 | 302.6 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ | $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 8 3 1 | 418 | 451.5 | 8 9 1 | < 17 | 30.1 |
| 10 3 1 | 251 | 227.8 | 10 9 1 | 125 | −129.0 |
| 12 3 1 | 84 | − 86.3 | 12 9 1 | 50 | − 36.7 |
| 14 3 1 | 92 | 109.9 | 14 9 1 | 59 | 42.8 |
| 16 3 1 | 92 | 90.2 | 16 9 1 | 234 | −188.3 |
| 18 3 1 | 125 | −122.4 | | | |
| | | | 1 10 1 | 209 | −192.2 |
| 1 4 1 | 176 | −206.7 | 3 10 1 | 268 | 269.4 |
| 3 4 1 | 92 | − 90.8 | 5 10 1 | 134 | −138.2 |
| 5 4 1 | 184 | 240.5 | 7 10 1 | < 17 | − 31.2 |
| 7 4 1 | 59 | 65.2 | 9 10 1 | 92 | − 81.9 |
| 9 4 1 | 268 | 287.5 | 11 10 1 | 217 | −200.9 |
| 11 4 1 | 100 | −114.0 | 13 10 1 | 259 | 207.0 |
| 13 4 1 | 84 | − 90.1 | 15 10 1 | < 17 | − 3.0 |
| 15 4 1 | 176 | 173.7 | | | |
| 17 4 1 | 50 | 61.2 | 2 11 1 | 268 | −261.6 |
| | | | 4 11 1 | 84 | 59.3 |
| 2 5 1 | 151 | −192.8 | 6 11 1 | 167 | 174.8 |
| 4 5 1 | 435 | −383.2 | 8 11 1 | 109 | − 86.1 |
| 6 5 1 | < 17 | − 4.6 | 10 11 1 | 50 | 47.2 |
| 8 5 1 | 84 | 77.9 | 12 11 1 | 251 | 212.3 |
| 10 5 1 | 92 | − 87.5 | 14 11 1 | 243 | 206.0 |
| 12 5 1 | 109 | −117.3 | | | |
| 14 5 1 | 134 | 120.4 | 1 12 1 | 109 | 88.8 |
| 16 5 1 | 209 | 205.6 | 3 12 1 | 184 | −171.0 |
| 18 5 1 | 25 | − 57.3 | 5 12 1 | < 17 | 12.0 |
| | | | 7 12 1 | < 17 | − 23.9 |
| 1 6 1 | 200 | 242.9 | 9 12 1 | 217 | 212.3 |
| 3 6 1 | 133 | −131.3 | 11 12 1 | 42 | − 30.0 |
| 5 6 1 | < 17 | 6.4 | 13 12 1 | 17 | − 18.7 |
| 7 6 1 | 284 | −298.8 | | | |
| 9 6 1 | 176 | −157.7 | 2 13 1 | 151 | −137.6 |
| 11 6 1 | 134 | 129.2 | 4 13 1 | 176 | −149.3 |
| 13 6 1 | 117 | −109.5 | 6 13 1 | 92 | − 71.6 |
| 15 6 1 | 59 | 53.5 | 8 13 1 | 376 | −314.3 |
| 17 6 1 | 134 | −127.6 | 10 13 1 | 201 | −175.6 |
| | | | 12 13 1 | 42 | 34.0 |
| 2 7 1 | 109 | 100.3 | | | |
| 4 7 1 | < 17 | 0.5 | 1 14 1 | < 17 | 16.8 |
| 6 7 1 | < 17 | 22.5 | 3 14 1 | 100 | − 10.8 |
| 8 7 1 | < 17 | 4.7 | 5 14 1 | 234 | 216.5 |
| 10 7 1 | 301 | −268.3 | 7 14 1 | < 17 | − 10.6 |
| 12 7 1 | 92 | −100.7 | 9 14 1 | 217 | −188.7 |
| 14 7 1 | 42 | 44.6 | 11 14 1 | 100 | − 82.8 |
| 16 7 1 | < 17 | − 9.0 | | | |
| | | | 2 15 1 | 184 | 153.5 |
| 1 8 1 | 125 | 112.5 | 4 15 1 | 192 | 171.9 |
| 3 8 1 | 67 | − 62.1 | 6 15 1 | 100 | 91.9 |
| 5 8 1 | 117 | −113.8 | 8 15 1 | < 17 | 4.3 |
| 7 8 1 | 460 | 437.7 | | | |
| 9 8 1 | 42 | 23.4 | 1 16 1 | 184 | 159.5 |
| 11 8 1 | 84 | 83.5 | 3 16 1 | < 17 | − 18.3 |
| 13 8 1 | 134 | −131.9 | 5 16 1 | 42 | − 53.7 |
| 15 8 1 | 117 | − 89.4 | 7 16 1 | 59 | 43.5 |
| | | | | | |
| 2 9 1 | 100 | − 84.1 | 2 17 1 | 42 | − 42.5 |
| 4 9 1 | 217 | 209.4 | 4 17 1 | 42 | 48.8 |
| 6 9 1 | 151 | 145.6 | 6 17 1 | 92 | − 95.3 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ | $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 1 18 1 | 259 | −246.9 | 11 5 2 | < 18 | − 27.0 |
| 3 18 1 | 75 | 38.7 | 13 5 2 | 45 | − 54.2 |
| 5 18 1 | 42 | − 43.0 | 15 5 2 | 99 | − 78.5 |
| | | | 17 5 2 | 27 | − 42.7 |
| 2 0 2 | 359 | −345.7 | | | |
| 4 0 2 | 99 | 78.6 | 2 6 2 | 72 | 44.1 |
| 6 0 2 | 126 | −135.7 | 4 6 2 | < 18 | − 25.2 |
| 8 0 2 | 233 | −242.0 | 6 6 2 | 126 | −112.0 |
| 10 0 2 | 440 | 399.1 | 8 6 2 | 413 | 377.6 |
| 12 0 2 | 45 | 54.5 | 10 6 2 | 90 | 81.8 |
| 14 0 2 | < 18 | 30.7 | 12 6 2 | 90 | − 85.9 |
| 16 0 2 | < 18 | − 29.9 | 14 6 2 | 99 | 86.9 |
| 18 0 2 | 126 | 122.7 | 16 6 2 | 224 | 173.6 |
| | | | | | |
| 1 1 2 | 162 | −145.9 | 1 7 2 | 135 | 125.2 |
| 3 1 2 | 233 | −195.7 | 3 7 2 | 135 | 118.5 |
| 5 1 2 | 72 | − 70.6 | 5 7 2 | 162 | 171.0 |
| 7 1 2 | 63 | 59.6 | 7 7 2 | 45 | − 32.6 |
| 9 1 2 | 287 | −276.8 | 9 7 2 | 45 | 60.5 |
| 11 1 2 | 45 | 47.0 | 11 7 2 | 108 | 104.5 |
| 13 1 2 | 45 | − 54.7 | 13 7 2 | 45 | − 30.9 |
| 15 1 2 | 188 | −172.4 | 15 7 2 | 45 | 54.1 |
| 17 1 2 | < 18 | − 18.9 | | | |
| | | | 2 8 2 | 72 | 69.4 |
| 2 2 2 | 54 | 49.6 | 4 8 2 | 45 | − 62.9 |
| 4 2 2 | 27 | 13.7 | 6 8 2 | 269 | −279.9 |
| 6 2 2 | 117 | 117.1 | 8 8 2 | 45 | − 58.9 |
| 8 2 2 | 305 | −318.2 | 10 8 2 | < 18 | − 8.8 |
| 10 2 2 | 63 | − 64.1 | 12 8 2 | 153 | −134.3 |
| 12 2 2 | 81 | − 62.4 | 14 8 2 | 79 | 168.5 |
| 14 2 2 | 215 | −204.4 | | | |
| 16 2 2 | 224 | 193.7 | 1 9 2 | 27 | 30.8 |
| 18 2 2 | 72 | 67.1 | 3 9 2 | 90 | 78.0 |
| | | | 5 9 2 | 117 | −130.4 |
| 1 3 2 | 206 | −205.8 | 7 9 2 | 72 | −103.7 |
| 3 3 2 | 197 | 203.5 | 9 9 2 | 72 | − 69.5 |
| 5 3 2 | 242 | 222.8 | 11 9 2 | < 18 | − 7.6 |
| 7 3 2 | 126 | 110.1 | 13 9 2 | 108 | −100.0 |
| 9 3 2 | 54 | 47.1 | | | |
| 11 3 2 | 27 | 75.8 | 2 10 2 | 72 | 71.5 |
| 13 3 2 | 153 | 121.5 | 4 10 2 | 171 | −188.5 |
| 15 3 2 | 63 | − 60.6 | 6 10 2 | 179 | 203.5 |
| 17 3 2 | 108 | 98.7 | 8 10 2 | 90 | 89.7 |
| | | | 10 10 2 | 63 | 67.6 |
| 2 4 2 | 341 | 446.4 | 12 10 2 | 171 | −183.7 |
| 4 4 2 | 144 | 156.9 | 14 10 2 | 108 | −135.1 |
| 6 4 2 | 179 | −180.1 | | | |
| 8 4 2 | 99 | 93.6 | 1 11 2 | 188 | 152.3 |
| 10 4 2 | 144 | −128.2 | 3 11 2 | 171 | 180.5 |
| 12 4 2 | 144 | 128.3 | 5 11 2 | 108 | −117.9 |
| 14 4 2 | 153 | −142.2 | 7 11 2 | 108 | 99.2 |
| 16 4 2 | 81 | − 54.3 | 9 11 2 | 72 | 99.0 |
| | | | 11 11 2 | 63 | 60.3 |
| 1 5 2 | 278 | −258.6 | 13 11 2 | 44 | 43.6 |
| 3 5 2 | 72 | − 70.0 | | | |
| 5 5 2 | 108 | 110.4 | 2 12 2 | 54 | 54.3 |
| 7 5 2 | 341 | −265.9 | 4 12 2 | < 18 | − 22.8 |
| 9 5 2 | 54 | − 48.3 | 6 12 2 | 215 | 232.9 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|
| 8 12 2 | 45 | 39.7 |
| 10 12 2 | 63 | − 73.7 |
| 12 12 2 | 117 | 161.0 |
| 1 13 2 | 27 | − 30.4 |
| 3 13 2 | 54 | 18.8 |
| 5 13 2 | 197 | −208.4 |
| 7 13 2 | 45 | − 56.6 |
| 9 13 2 | 18 | 20.0 |
| 11 13 2 | 162 | −143.5 |
| 2 14 2 | 144 | −140.4 |
| 4 14 2 | 224 | −225.6 |
| 6 14 2 | 90 | − 83.4 |
| 8 14 2 | 45 | 56.3 |
| 10 14 2 | 108 | −115.0 |
| 1 15 2 | 143 | 123.2 |
| 3 15 2 | < 18 | − 11.9 |
| 5 15 2 | 44 | 45.3 |
| 7 15 2 | < 18 | 17.2 |
| 9 15 2 | 188 | 148.9 |
| 2 16 2 | 135 | −121.4 |
| 4 16 2 | 215 | 176.3 |
| 6 16 2 | 45 | 48.0 |
| 1 17 2 | < 18 | 22.4 |
| 3 17 2 | 206 | −201.9 |
| 5 17 2 | 18 | − 11.9 |
| 1 0 3 | 253 | −270.5 |
| 3 0 3 | 71 | − 66.3 |
| 5 0 3 | 63 | − 46.0 |
| 7 0 3 | 237 | 272.1 |
| 9 0 3 | 205 | −218.9 |
| 11 0 3 | 268 | −306.6 |
| 13 0 3 | < 24 | − 8.4 |
| 15 0 3 | 118 | 101.6 |
| 17 0 3 | 110 | 134.1 |
| 0 1 3 | 253 | −270.5 |
| 2 1 3 | 284 | −344.7 |
| 4 1 3 | < 24 | 14.7 |
| 6 1 3 | 47 | − 30.9 |
| 10 1 3 | 4 | 20.0 |
| 8 1 3 | < 24 | − 7.2 |
| 12 1 3 | 79 | 75.0 |
| 14 1 3 | 142 | 134.5 |
| 16 1 3 | 95 | − 68.3 |
| 18 1 3 | 134 | 69.1 |
| 1 2 3 | 197 | 234.1 |
| 3 2 3 | 47 | 43.4 |
| 5 2 3 | 71 | − 65.8 |
| 7 2 3 | 39 | 31.9 |
| 9 2 3 | 87 | 73.4 |
| 11 2 3 | 79 | − 62.8 |
| 13 2 3 | 205 | 211.6 |
| 15 2 3 | < 24 | − 9.5 |
| 17 2 3 | 134 | −136.7 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|
| 2 3 3 | 221 | −236.2 |
| 4 3 3 | 71 | 29.2 |
| 6 3 3 | 95 | − 84.7 |
| 8 3 3 | 379 | −381.4 |
| 10 3 3 | 87 | 75.8 |
| 12 3 3 | < 24 | − 6.6 |
| 14 3 3 | 39 | 29.0 |
| 16 3 3 | 39 | 39.5 |
| 1 4 3 | 166 | −194.1 |
| 3 4 3 | 260 | −290.1 |
| 5 4 3 | 189 | 233.4 |
| 7 4 3 | 182 | 177.1 |
| 9 4 3 | 118 | −127.1 |
| 11 4 3 | 213 | −225.2 |
| 13 4 3 | < 24 | 0.4 |
| 15 4 3 | 63 | 67.8 |
| 17 4 3 | 79 | − 63.9 |
| 2 5 3 | 79 | 81.4 |
| 4 5 3 | 63 | 41.2 |
| 6 5 3 | 157 | 151.4 |
| 8 5 3 | 229 | −238.6 |
| 10 5 3 | < 24 | − 19.2 |
| 12 5 3 | < 24 | − 14.6 |
| 14 5 3 | 339 | −293.7 |
| 16 5 3 | 55 | − 64.9 |
| 1 6 3 | 189 | 188.8 |
| 3 6 3 | 71 | 64.3 |
| 5 6 3 | 189 | 194.9 |
| 7 6 3 | 158 | −141.0 |
| 9 6 3 | 213 | −208.7 |
| 11 6 3 | 213 | 215.8 |
| 13 6 3 | 237 | 232.1 |
| 15 6 3 | 79 | 63.7 |
| 2 7 3 | 189 | 198.9 |
| 4 7 3 | 149 | 137.4 |
| 6 7 3 | < 24 | 10.2 |
| 8 7 3 | 229 | 236.3 |
| 10 7 3 | 126 | 116.1 |
| 12 7 3 | 252 | 278.5 |
| 14 7 3 | 55 | 55.4 |
| 1 8 3 | 205 | −203.4 |
| 3 8 3 | 134 | −119.8 |
| 5 8 3 | 103 | − 68.5 |
| 7 8 3 | 71 | 50.3 |
| 9 8 3 | 150 | −122.8 |
| 11 8 3 | 55 | 48.9 |
| 13 8 3 | 118 | −106.5 |
| 15 8 3 | 150 | −189.3 |
| 2 9 3 | 229 | −221.9 |
| 4 9 3 | 87 | − 59.4 |
| 6 9 3 | 363 | −415.3 |
| 8 9 3 | 47 | 18.7 |

| h k l | $F_o$ | $F_c$ | h k l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 10 9 3 | < 24 | — 15.5 | 1 1 4 | 351 | 337.2 |
| 12 9 3 | 158 | —133.1 | 3 1 4 | 94 | 73.1 |
| 14 9 3 | 55 | 60.9 | 5 1 4 | 334 | —329.2 |
| | | | 7 1 4 | 163 | 151.2 |
| 1 10 3 | 110 | —109.8 | 9 1 4 | < 17 | — 28.0 |
| 3 10 3 | 410 | 418.7 | 11 1 4 | 120 | 119.3 |
| 5 10 5 | 95 | 98.1 | 13 1 4 | 26 | — 41.1 |
| 7 10 3 | 134 | —125.2 | 15 1 4 | < 17 | 8.0 |
| 9 10 3 | < 24 | — 6.9 | | | |
| 11 10 3 | 89 | 66.6 | 2 2 4 | 94 | — 46.6 |
| 13 10 3 | 166 | 204.6 | 4 2 4 | 180 | 199.7 |
| 15 10 3 | 87 | — 11.2 | 6 2 4 | 488 | 536.0 |
| | | | 8 2 4 | 283 | 314.2 |
| 2 11 3 | 189 | 179.6 | 10 2 4 | 94 | 63.9 |
| 4 11 3 | 158 | 140.6 | 12 2 4 | < 17 | 40.8 |
| 6 11 3 | < 24 | 6.1 | 14 2 4 | 171 | 136.8 |
| 8 11 3 | < 24 | — 31.1 | 16 2 4 | 206 | 223.7 |
| 10 11 3 | 110 | 110.7 | | | |
| 12 11 3 | 158 | —184.5 | 1 3 4 | < 17 | — 10.5 |
| | | | 3 3 4 | 120 | 105.5 |
| 1 12 3 | 95 | — 90.6 | 5 3 4 | 326 | —324.0 |
| 3 12 3 | 126 | —101.8 | 7 3 4 | 103 | 92.3 |
| 5 12 3 | 134 | —130.4 | 9 3 4 | 129 | 93.1 |
| 7 12 3 | 189 | —182.2 | 11 3 4 | 274 | —220.4 |
| 9 12 3 | 189 | 187.8 | 13 3 4 | 60 | 42.7 |
| 11 12 3 | 63 | 67.5 | 15 3 4 | < 17 | 27.9 |
| 2 13 3 | 142 | 138.3 | | | |
| 4 13 3 | 134 | —131.8 | 2 4 4 | 77 | — 71.1 |
| 6 13 3 | 142 | 152.2 | 4 4 4 | 231 | —270.1 |
| 8 13 3 | 47 | 86.8 | 6 4 4 | 368 | —425.1 |
| 10 13 3 | 118 | 117.8 | 8 4 4 | 334 | —383.0 |
| | | | 10 4 4 | 103 | —103.0 |
| 1 14 3 | < 24 | — 14.3 | 12 4 4 | 129 | 124.1 |
| 3 14 3 | 103 | 85.4 | 14 4 4 | < 17 | 26.6 |
| 5 14 3 | 150 | 160.4 | | | |
| 7 14 3 | 47 | — 35.6 | 1 5 4 | 120 | 121.8 |
| | | | 3 5 4 | 69 | — 49.6 |
| 2 15 3 | 39 | 31.6 | 5 5 4 | 26 | — 27.6 |
| 4 15 3 | 142 | —129.6 | 7 5 4 | 69 | — 64.9 |
| 6 15 3 | < 24 | 0.8 | 9 5 4 | 188 | 174.1 |
| 8 15 3 | 71 | 78.4 | 11 5 4 | 214 | —175.6 |
| | | | 13 5 4 | < 17 | 37.7 |
| 1 16 3 | 158 | 152.8 | 15 5 4 | 94 | 98.4 |
| 3 16 3 | 47 | — 47.9 | | | |
| 5 16 3 | 150 | —162.4 | 2 6 4 | < 17 | — 2.2 |
| 7 16 3 | 47 | — 50.6 | 4 6 4 | 146 | 106.2 |
| 2 17 3 | 55 | — 47.7 | 6 6 4 | 180 | 167.1 |
| 4 17 3 | 55 | — 44.8 | 8 6 4 | 137 | 111.6 |
| | | | 10 6 4 | 146 | —111.0 |
| 0 0 4 | 583 | 567.2 | 12 6 4 | 180 | —160.8 |
| 2 0 4 | 206 | 194.4 | 14 6 4 | 206 | —176.8 |
| 4 0 4 | 137 | —117.0 | | | |
| 6 0 4 | 154 | —131.3 | 1 7 4 | 51 | 62.8 |
| 8 0 4 | < 17 | — 12.8 | 3 7 4 | 266 | —308.6 |
| 10 0 4 | < 17 | 25.6 | 5 7 4 | 120 | 102.7 |
| 12 0 4 | 171 | —165.6 | 7 7 4 | 69 | 94.0 |
| 14 0 4 | 120 | —144.3 | 9 7 4 | 77 | 74.1 |
| 16 0 4 | 248 | —317.0 | 11 7 4 | 26 | — 29.2 |
| | | | 13 7 4 | 26 | — 25.6 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ | $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 2 8 4 | < 17 | 19.1 | 9 0 5 | 152 | −144.3 |
| 4 8 4 | 257 | 284.8 | 11 0 5 | 54 | − 67.0 |
| 6 8 4 | < 17 | 11.1 | 13 0 5 | 54 | − 58.3 |
| 8 8 4 | 137 | −149.2 | 15 0 5 | 108 | −104.1 |
| 10 8 4 | < 17 | 20.4 | | | |
| 12 8 4 | 146 | 125.8 | 2 1 5 | < 18 | 0.7 |
| 14 8 4 | 180 | 150.9 | 4 1 5 | 295 | 275.6 |
| | | | 6 1 5 | < 18 | − 1.2 |
| 1 9 4 | < 17 | − 19.4 | 8 1 5 | < 18 | − 30.2 |
| 3 9 4 | 197 | −182.7 | 10 1 5 | < 18 | − 59.9 |
| 5 9 4 | 51 | 45.8 | 12 1 5 | 170 | −146.5 |
| 7 9 4 | 86 | 88.5 | 14 1 5 | 71 | 80.1 |
| 9 9 4 | 146 | −176.0 | | | |
| 11 9 4 | < 17 | 30.7 | 1 2 5 | 196 | 182.1 |
| 13 9 4 | 34 | 40.9 | 3 2 5 | 250 | 251.4 |
| | | | 5 2 5 | 98 | − 82.7 |
| 2 10 4 | 257 | −277.0 | 7 2 5 | 170 | −181.0 |
| 4 10 4 | 248 | −289.0 | 9 2 5 | 187 | 233.9 |
| 6 10 4 | < 17 | 15.2 | 11 2 5 | 268 | 259.0 |
| 8 10 4 | 256 | 31.3 | 13 2 5 | < 18 | 30.0 |
| 10 10 4 | 171 | 202.9 | 15 2 5 | 89 | − 86.0 |
| 12 10 4 | 111 | 100.2 | | | |
| | | | 2 3 5 | < 18 | 11.2 |
| 1 11 4 | 120 | −112.1 | 4 3 5 | 80 | 56.6 |
| 3 11 4 | < 17 | − 28.9 | 6 3 5 | 179 | 142.8 |
| 5 11 4 | < 17 | 14.3 | 8 3 5 | 62 | − 67.9 |
| 7 11 4 | 197 | 149.7 | 10 3 5 | 268 | 216.6 |
| 9 11 4 | 120 | −141.2 | 12 3 5 | < 18 | − 12.5 |
| 11 11 4 | < 17 | 7.3 | 14 3 5 | < 18 | 4.6 |
| 13 11 4 | 60 | 66.5 | | | |
| | | | 1 4 5 | 125 | − 99.7 |
| 2 12 4 | 94 | 98.1 | 3 4 5 | 161 | −140.9 |
| 4 12 4 | 86 | 61.7 | 5 4 5 | 134 | −114.6 |
| 6 12 4 | 94 | − 87.2 | 7 4 5 | < 18 | 31.1 |
| 8 12 4 | 283 | −227.1 | 9 4 5 | < 18 | 27.8 |
| 10 12 4 | 283 | −277.5 | 11 4 5 | 54 | − 45.4 |
| 12 12 4 | 86 | −111.3 | 13 4 5 | 250 | −202.0 |
| | | | | | |
| 1 13 4 | 283 | −219.8 | 2 5 5 | < 18 | 28.8 |
| 3 13 4 | 146 | 108.3 | 4 5 5 | 250 | −243.7 |
| 5 13 4 | 94 | 120.1 | 6 5 5 | 179 | 145.3 |
| 7 13 4 | 26 | 23.1 | 8 5 5 | < 18 | − 7.7 |
| 9 13 4 | 34 | − 40.0 | 10 5 5 | 98 | 75.4 |
| | | | 12 5 5 | 170 | 151.1 |
| 2 14 4 | 240 | 225.1 | 14 5 5 | < 18 | − 13.8 |
| 4 14 4 | 69 | 63.5 | | | |
| 6 14 4 | < 17 | − 12.2 | 1 6 5 | 321 | 293.1 |
| 8 14 4 | 291 | 244.6 | 3 6 5 | 232 | 185.5 |
| | | | 5 6 5 | 125 | −107.2 |
| 1 15 4 | 86 | − 95.2 | 7 6 5 | 152 | −100.4 |
| 3 15 4 | < 17 | − 20.9 | 9 6 5 | 89 | 60.0 |
| | | | 11 6 5 | < 18 | 47.9 |
| 2 16 4 | 146 | −176.3 | 13 6 5 | < 18 | − 8.6 |
| | | | | | |
| 1 0 5 | 286 | −269.1 | 2 7 5 | 134 | 140.1 |
| 3 0 5 | 286 | 260.3 | 4 7 5 | 107 | −113.1 |
| 5 0 5 | 62 | 58.9 | 6 7 5 | 241 | −215.4 |
| 7 0 5 | 125 | −108.5 | 8 7 5 | 89 | − 54.7 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|
| 10 7 5 | 339 | −255.2 |
| 12 7 5 | < 18 | 1.1 |
| 14 7 5 | 161 | −149.0 |
| 1 8 5 | < 18 | − 4.1 |
| 3 8 5 | 196 | −169.0 |
| 5 8 5 | 107 | − 97.9 |
| 7 8 5 | 134 | 129.9 |
| 9 8 5 | 179 | 182.9 |
| 11 8 5 | 116 | −106.3 |
| 13 8 5 | 268 | −231.2 |
| 2 9 5 | < 18 | 34.6 |
| 4 9 5 | 250 | 246.5 |
| 6 9 5 | < 18 | 20.8 |
| 8 9 5 | 312 | 247.0 |
| 10 9 5 | 98 | 70.5 |
| 12 9 5 | 54 | − 35.8 |
| 1 10 5 | 80 | 96.1 |
| 3 10 5 | 54 | 56.0 |
| 5 10 5 | < 18 | 24.2 |
| 7 10 5 | 54 | 48.0 |
| 9 10 5 | 45 | 9.4 |
| 11 10 5 | 89 | − 62.1 |
| 2 11 5 | 268 | −255.1 |
| 4 11 5 | < 18 | − 24.2 |
| 6 11 5 | < 18 | 1.9 |
| 8 11 5 | 116 | − 90.4 |
| 10 11 5 | 98 | 77.6 |
| 1 12 5 | 27 | 47.6 |
| 3 12 5 | 223 | −222.6 |
| 5 12 5 | 139 | −179.5 |
| 7 12 5 | 71 | 74.7 |
| 9 12 5 | < 18 | − 8.1 |
| 2 13 5 | < 18 | 39.9 |
| 4 13 5 | 143 | −171.1 |
| 6 14 5 | < 18 | 38.9 |
| 8 13 5 | 116 | −118.5 |
| 1 14 5 | < 18 | − 24.8 |
| 3 14 5 | < 18 | 55.7 |
| 5 14 5 | 98 | 200.9 |
| 7 14 5 | 205 | 157.3 |
| 2 15 5 | 98 | 123.8 |
| 2 0 6 | < 25 | − 20.4 |
| 4 0 6 | 218 | −221.5 |
| 6 0 6 | 151 | −137.4 |
| 8 0 6 | 42 | 70.3 |
| 10 0 6 | 42 | 58.2 |
| 12 0 6 | 142 | 145.5 |
| 1 1 6 | 75 | 75.9 |
| 3 1 6 | 59 | 57.0 |
| 5 1 6 | 100 | 79.3 |
| 7 1 6 | 117 | 136.0 |
| 9 1 6 | 159 | −160.0 |
| 11 1 6 | 167 | 159.4 |
| 13 1 6 | 75 | 86.0 |
| 2 2 6 | 176 | −156.7 |
| 4 2 6 | < 25 | − 18.0 |
| 6 2 6 | < 25 | 19.4 |
| 8 2 6 | < 25 | − 33.4 |
| 10 2 6 | 226 | −178.2 |
| 12 2 6 | 75 | − 62.5 |
| 1 3 6 | 335 | −338.5 |
| 3 3 6 | 176 | 147.5 |
| 5 3 6 | < 25 | − 9.1 |
| 7 3 6 | < 25 | 8.2 |
| 9 3 6 | 126 | − 96.5 |
| 11 3 6 | 50 | − 49.9 |
| 13 3 6 | 92 | 85.1 |
| 2 4 6 | 75 | 53.5 |
| 4 4 6 | 50 | 36.7 |
| 6 4 6 | 92 | 76.8 |
| 8 4 6 | < 25 | − 8.1 |
| 10 4 6 | 92 | 92.4 |
| 12 4 6 | < 25 | 71.5 |
| 1 5 6 | 134 | −132.4 |
| 3 5 6 | 201 | 196.2 |
| 5 5 6 | 134 | 125.1 |
| 7 5 6 | 167 | −176.7 |
| 9 5 6 | 142 | 131.3 |
| 11 5 6 | 92 | 88.5 |
| 13 5 6 | 142 | 137.2 |
| 2 6 6 | 126 | −108.2 |
| 4 6 6 | 125 | −111.5 |
| 6 6 6 | 201 | 176.0 |
| 8 6 6 | 159 | 141.7 |
| 10 6 6 | < 25 | 27.1 |
| 12 6 6 | 67 | 17.2 |
| 1 7 6 | < 25 | − 34.0 |
| 3 7 6 | 109 | − 90.6 |
| 5 7 6 | < 25 | 41.6 |
| 7 7 6 | 176 | −227.3 |
| 9 7 6 | 25 | − 17.7 |
| 11 7 6 | 42 | 22.4 |
| 2 8 6 | < 25 | 10.7 |
| 4 8 6 | < 25 | 32.0 |
| 6 8 6 | 134 | −109.1 |
| 8 8 6 | 84 | −112.7 |
| 10 8 6 | 59 | − 67.7 |
| 12 8 6 | < 25 | 13.0 |

| h k l | $F_o$ | $F_c$ |
|---|---|---|
| 1 9 6 | 251 | 234.8 |
| 3 9 6 | 176 | 160.4 |
| 5 9 6 | < 25 | 44.3 |
| 7 9 6 | < 25 | 25.5 |
| 9 9 6 | < 25 | 22.6 |
| 11 9 6 | 234 | 188.5 |
| 2 10 6 | < 25 | 21.7 |
| 4 10 6 | 100 | 80.7 |
| 6 10 6 | 92 | 61.2 |
| 8 10 6 | 50 | 47.3 |
| 1 11 6 | < 25 | − 18.6 |
| 3 11 6 | < 25 | 26.8 |
| 5 11 6 | 184 | −258.5 |
| 2 12 6 | < 25 | 20.7 |
| 4 12 6 | 209 | 218.9 |
| 6 12 6 | < 25 | 13.5 |
| 1 13 6 | < 25 | 28.0 |
| 3 13 6 | 117 | 119.9 |
| 5 13 6 | 42 | − 75.1 |
| 1 0 7 | 26 | − 40.8 |
| 3 0 7 | 26 | − 42.4 |
| 5 0 7 | 69 | 72.9 |
| 7 0 7 | 95 | 126.3 |
| 9 0 7 | < 17 | 30.1 |
| 11 0 7 | 138 | −144.3 |
| 2 1 7 | 95 | −103.1 |
| 4 1 7 | 112 | 86.2 |
| 6 1 7 | < 17 | − 32.2 |
| 8 1 7 | 215 | 195.3 |
| 10 1 7 | 190 | 164.1 |
| 12 1 7 | 52 | − 60.4 |
| 1 2 7 | 181 | 157.7 |
| 3 2 7 | 190 | −172.8 |
| 5 2 7 | 146 | −137.0 |
| 7 2 7 | 95 | − 77.0 |
| 9 2 7 | 78 | − 67.6 |
| 11 2 7 | < 17 | − 14.8 |
| 2 3 7 | 95 | −101.6 |
| 4 3 7 | 258 | −228.4 |
| 6 3 7 | 198 | −145.2 |
| 8 3 7 | 258 | −177.8 |
| 10 3 7 | 78 | − 28.8 |
| 12 3 7 | 155 | −152.7 |
| 1 4 7 | 52 | − 41.5 |
| 3 4 7 | 52 | − 68.8 |
| 5 4 7 | 146 | 151.3 |
| 7 4 7 | 250 | 323.6 |
| 9 4 7 | 86 | − 65.5 |
| 11 4 7 | < 17 | − 17.2 |
| 2 5 7 | 181 | 170.2 |
| 4 5 7 | < 17 | − 29.5 |
| 6 5 7 | 250 | 226.5 |
| 8 5 7 | 95 | 95.3 |
| 10 5 7 | 95 | − 83.1 |
| 1 6 7 | 181 | −161.3 |
| 3 6 7 | < 17 | 33.7 |
| 5 6 7 | < 17 | 5.8 |
| 7 6 7 | 164 | −122.7 |
| 9 6 7 | 146 | −125.3 |
| 2 7 7 | < 17 | 1.8 |
| 4 7 7 | < 17 | − 25.4 |
| 6 7 7 | < 17 | 31.0 |
| 8 7 7 | 103 | 106.0 |
| 10 7 7 | 86 | − 86.9 |
| 1 8 7 | 164 | −157.1 |
| 3 8 7 | 86 | − 94.8 |
| 5 8 7 | 146 | 164.4 |
| 7 8 7 | < 17 | − 28.3 |
| 9 8 7 | 69 | 53.4 |
| 2 9 7 | 155 | −185.6 |
| 4 9 7 | < 17 | − 34.2 |
| 6 9 7 | 69 | − 50.2 |
| 8 9 7 | 52 | 33.1 |
| 1 10 7 | < 17 | 1.3 |
| 3 10 7 | 103 | 92.2 |
| 5 10 7 | 121 | 157.2 |
| 7 10 7 | 129 | −139.9 |
| 2 11 7 | < 17 | − 38.7 |
| 4 11 7 | 138 | 107.3 |
| 1 12 7 | 52 | 66.3 |
| 0 0 8 | 211 | 170.4 |
| 2 0 8 | 339 | 307.4 |
| 4 0 8 | 101 | 94.6 |
| 6 0 8 | 55 | − 33.6 |
| 8 0 8 | < 28 | 50.9 |
| 1 1 8 | 55 | 59.3 |
| 3 1 8 | < 28 | − 23.3 |
| 5 1 8 | 119 | −113.5 |
| 7 1 8 | < 28 | − 14.7 |
| 9 1 8 | 101 | 86.4 |
| 2 2 8 | 119 | −113.7 |
| 4 2 8 | 202 | 193.8 |
| 6 2 8 | < 28 | 20.4 |
| 8 2 8 | 156 | 137.3 |

| $h$ $k$ $l$ | $F_o$ | $F_c$ | $h$ $k$ $l$ | $F_o$ | $F_c$ |
|---|---|---|---|---|---|
| 1 3 8 | 92 | − 66.4 | 2 8 8 | 275 | 291.8 |
| 3 3 8 | < 28 | − 29.1 | 4 8 8 | 110 | 86.1 |
| 5 3 8 | 156 | −129.7 | | | |
| 7 3 8 | 92 | 89.7 | 1 9 8 | < 28 | 45.6 |
| | | | 3 9 8 | 83 | − 87.3 |
| 2 4 8 | 73 | 63.9 | | | |
| 4 4 8 | < 28 | 21.0 | 1 0 9 | < 18 | − 6.6 |
| 6 4 8 | 257 | −278.5 | 3 0 9 | 55 | 63.2 |
| 8 4 8 | 119 | −170.0 | 5 0 9 | 258 | 247.9 |
| 1 5 8 | 101 | 93.7 | | | |
| 3 5 8 | 83 | 58.9 | 2 1 9 | 138 | −136.4 |
| 5 5 8 | < 28 | − 16.5 | 4 1 9 | 101 | 111.9 |
| 7 5 8 | 46 | 9.6 | | | |
| | | | 1 2 9 | 147 | 133.0 |
| 2 6 8 | < 28 | 42.2 | 3 2 9 | 28 | − 32.5 |
| 4 6 8 | 147 | −147.6 | | | |
| 6 6 8 | < 28 | 14.9 | 2 3 9 | 92 | 86.7 |
| | | | 4 3 9 | 147 | 144.9 |
| 1 7 8 | < 28 | 21.5 | | | |
| 3 7 8 | 193 | −170.5 | | | |
| 5 7 8 | 55 | 97.8 | 1 4 9 | 46 | − 47.9 |

During seven cycles of refinement the disagreement index

$$R = \sum_{hkl} ||F_o| - |F_c|| \,/\, \sum_{hkl} |F_o|$$

fell from 0.288 to 0.176. With all the 693 observed, independent reflexions, six additional cycles reduced the index $R$ from 0.176 to 0.120. Finally, the non-observed reflexions were also introduced in the least-squares refinement. Their $F_o$ values were then taken as the threshold value of the photographs that they should have appeared in. After eight cycles of refinement for 693 observed and 147 non-observed reflexions a final $R$ value of 0.135 was obtained. At this stage, the average coordinate shifts for the oxygen and sodium atoms were 2 % of their standard deviations. It was thus concluded that the data did not merit further refinement.

*Table 2.* Final set of atomic coordinates, isotropic temperature factors and their standard deviations, $\sigma$, in the structure of $Na_4Ge_9O_{20}$.

*Space group: I* $4_1/a$, No. 88 in the International Tables [2].

| *Atom* | $x$ | $\sigma_x$ | $y$ | $\sigma_y$ | $z$ | $\sigma_z$ | $B$ | $\sigma_B$ |
|---|---|---|---|---|---|---|---|---|
| $Ge_1$ in 4(*a*) | 0.0000 | | 0.2500 | | 0.1250 | | 0.474 | 0.05 |
| $Ge_2$ in 16(*f*) | 0.1366 | 0.0002 | 0.0460 | 0.0002 | 0.7009 | 0.0003 | 0.299 | 0.03 |
| $Ge_3$ in 16(*f*) | 0.0956 | 0.0002 | 0.2180 | 0.0002 | 0.4912 | 0.0003 | 0.262 | 0.03 |
| $O_1$ in 16(*f*) | 0.0928 | 0.0010 | 0.2127 | 0.0010 | 0.2448 | 0.0019 | −0.003 | 0.21 |
| $O_2$ in 16(*f*) | 0.0824 | 0.0010 | 0.2227 | 0.0010 | 0.7476 | 0.0021 | 0.227 | 0.23 |
| $O_3$ in 16(*f*) | 0.1889 | 0.0010 | 0.0739 | 0.0010 | 0.9074 | 0.0021 | 0.199 | 0.22 |
| $O_4$ in 16(*f*) | 0.0253 | 0.0011 | 0.0446 | 0.0011 | 0.7555 | 0.0023 | 0.609 | 0.25 |
| $O_5$ in 16(*f*) | 0.1554 | 0.0010 | 0.1088 | 0.0010 | 0.5070 | 0.0021 | 0.302 | 0.24 |
| Na in 16(*f*) | 0.0878 | 0.0006 | 0.0544 | 0.0006 | 0.1702 | 0.0014 | 0.840 | 0.15 |

4(*a*): $(000),(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (0\frac{1}{2}\frac{1}{4})$.
16(*f*): $(000)$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (xyz)$, $(x,\frac{1}{2}+y,z)$, $(\frac{1}{4}+y,\frac{3}{4}-x,\frac{3}{4}-z)$, $(\frac{1}{4}+y,\frac{1}{4}-x,\frac{1}{4}+z)$.

The coordinates have been given so that the structure has its center of symmetry at the origin.

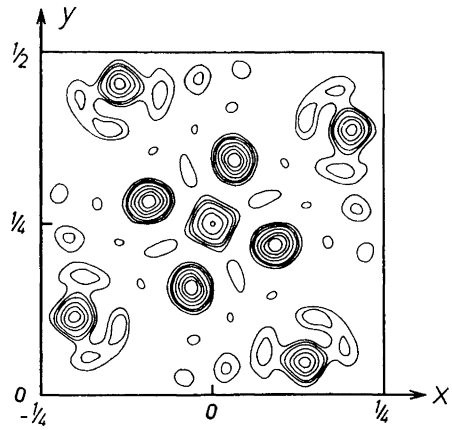


*Fig. 1.* The final Fourier projection $\varrho(xyp)$ for $Na_4Ge_9O_{20}$. In the large peaks only every second contour has been drawn. The negative values have been omitted.

The final positional parameters obtained and their standard deviations $\sigma$ are shown in Table 2. The refined isotropic thermal parameters are also given there. It should be remembered that the X-ray intensities were not corrected for absorption errors, which probably influenced the values obtained for the apparent thermal factors. Table 1 gives the final set of observed and calculated structure factors for $Na_4Ge_9O_{20}$. The electron density projection $\varrho(xyp)$ calculated with the signs obtained from the parameters given in Table 2 is shown in Fig. 1.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $Na_4Ge_9O_{20}$ is built up of $GeO_6$ octahedra and $GeO_4$ tetrahedra coupled together forming a three-dimensional network. Four $GeO_4$ octahedra share edges to form $Ge_4O_{16}$ groups. The groups are then connected with each other along the $z$ axis over a Ge atom which is four-coordinated, thus forming chains of the composition $(Ge_5O_{16})_n$. Such a chain is drawn in Fig. 2a. The chains are then joined by $(GeO_3)_n$ spirals consisting of $GeO_4$ tetrahedra sharing corners so that every one of these spirals links together four $(Ge_5O_{16})_n$ chains to a three-dimensional arrangement. In Fig. 2b such a $(GeO_3)_n$ spiral has been drawn. The three-dimensional arrangement of the chains and spirals is depicted in Fig. 2c.

Fig. 3 shows the most important distances in $Na_4Ge_9O_{20}$ and in Table 3 a detailed survey of the interatomic distances and angles in the structure is given. As is seen the Ge—O distances within the $GeO_4$ tetrahedra are all of the same magnitude, the range being $1.71_5$—$1.76_4$ Å with a mean of $1.74_0$ Å. The octahedral Ge—O distances seem to be of two kinds: one longer about 2.00 Å (range $1.99_2$—$1.99_8$ Å) and one shorter about 1.86 Å (range $1.82_2$—$1.90_5$ Å). The standard deviation in the Ge—O distances is $\pm 0.01_5$ Å which means that the experimental error should be given as $\pm$ 0.04 Å, if we want to have a reliability of 95 % in the Ge—O distances. The distances Ge—O within the octahedra should then be of two types: one with Ge—O = $(1.99_5 \pm 0.04)$

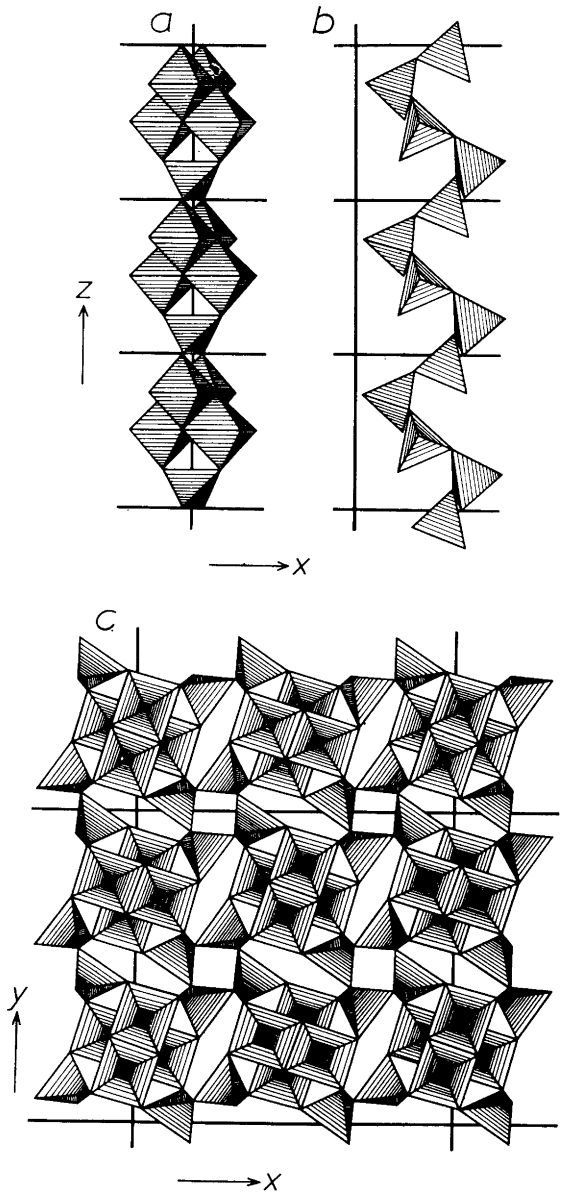


*Fig. 2.* The structure of $Na_4Ge_9O_{20}$: a) $Ge_4O_{16}$ groups connected with four-coordinated Ge atoms forming a chain of the composition $(Ge_5O_{16})_n$. b) $GeO_4$ tetrahedra sharing two corners forming a spiral, $(GeO_3)_n$. c) The connection of chains and spirals in $Na_4Ge_9O_{20}$. The structure is viewed along [001].

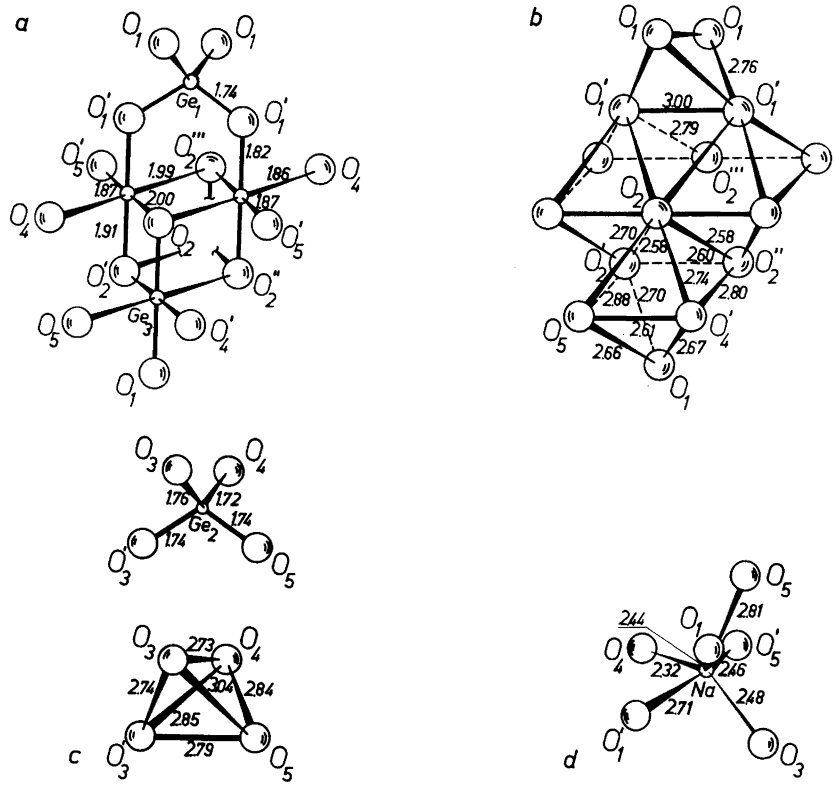


*Fig. 3.* The structure of $Na_4Ge_9O_{20}$: a) Ge—O distances in the chain $(Ge_5O_{16})_n$. b) O—O distances in the chain $(Ge_5O_{16})_n$. c) Ge—O and O—O distances in tetrahedra of the spiral $(GeO_3)_n$. d) Distances between sodium atoms and their coordinated oxygen atoms.

Å and one with Ge—O = $(1.86_3 \pm 0.04)$ Å. We may note that three of the six oxygen atoms belonging to a $GeO_6$ octahedron are each bound to three germanium atoms whereas the remaining three are each bound only to two germanium atoms. The distances Ge—O for the former group are longer ($1.99_8$, $1.99_2$ and $1.90_5$ Å) than the distances for the latter group ($1.86_9$, $1.85_5$ and $1.82_2$ Å).

The mean value of the Ge—O distances within the $GeO_6$ octahedra in $Na_4Ge_9O_{20}$ is $1.90_7$ Å, which is in good agreement with the average value of $1.89 \pm 0.03$ Å published in the International Tables for X-ray Crystallography, Vol. III [10]. (For a coordination Ge—4O no corresponding average value is given.)

In 1954, Nowotny and Wittmann [11] published a paper on the structure of $Me_3HGe_7O_{16}(H_2O)_4$ with Me = $Li^+$, $Na^+$, $K^+$, $NH^+_4$, $Rb^+$, and $Cs^+$, where they proposed an atomic arrangement, isotypic with that of pharmakosiderite [12] giving both four- and six-coordination around the germanium atoms. The $GeO_6$ octahedra and $GeO_4$ tetrahedra are there joined by common edges and

*Table 3.* Interatomic distances and angles in $Na_4Ge_9O_{20}$. Distances and O—Ge—O angles in octahedra around $Ge_3$ (*cf.* Figs. 3a and 3b):

| | | | | | |
|---|---|---|---|---|---|
| $Ge_3-O_1$ | $1.82_2$ Å | $O_1-O_2'$ | $2.70_4$ Å | $O_1-Ge_3-O_2$ | 172.7° |
| $Ge_3-O_2$ | $1.90_5$ Å | $O_1-O_2''$ | $2.72_2$ Å | $O_1-Ge_3-O_2'$ | 90.2° |
| $Ge_3-O_2'$ | $1.99_2$ Å | $O_1-O_4'$ | $2.66_9$ Å | $O_1-Ge_3-O_2''$ | 93.8° |
| $Ge_3-O_2''$ | $1.99_8$ Å | $O_1-O_5$ | $2.65_5$ Å | $O_1-Ge_3-O_4'$ | 93.1° |
| $Ge_3-O_4'$ | $1.85_5$ Å | $O_2-O_2'$ | $2.58_1$ Å | $O_1-Ge_3-O_5$ | 92.0° |
| $Ge_3-O_5'$ | $1.86_9$ Å | $O_2-O_2''$ | $2.58_1$ Å | $O_2-Ge_3-O_2'$ | 82.9° |
| Average | $1.90_7$ Å | $O_2-O_4'$ | $2.74_0$ Å | $O_2-Ge_3-O_2''$ | 82.8° |
| | | $O_2-O_5$ | $2.69_5$ Å | $O_2-Ge_3-O_4'$ | 93.5 |
| | | $O_2'-O_2''$ | $2.60_1$ Å | $O_2-Ge_3-O_5$ | 91.1° |
| | | $O_2'-O_5$ | $2.87_5$ Å | $O_2'-Ge_3-O_2''$ | 81.4° |
| | | $O_2''-O_4'$ | $2.80_2$ Å | $O_2'-Ge_3-O_4'$ | 173.9° |
| | | $O_4'-O_5$ | $2.60_6$ Å | $O_2'-Ge_3-O_5$ | 96.2° |
| | | | | $O_2''-Ge_3-O_4'$ | 93.2° |
| | | | | $O_2''-Ge_3-O_5$ | 173.7° |
| | | | | $O_4'-Ge_3-O_5$ | 88.8° |

Distances and O—Ge—O angles in tetrahedra around $Ge_2$ (*cf.* Fig. 3c):

| | | | | | |
|---|---|---|---|---|---|
| $Ge_2-O_3$ | $1.76_4$ Å | $O_3-O_3'$ | $2.74_5$ Å | $O_3-Ge_2-O_3'$ | 103.1° |
| $Ge_2-O_3'$ | $1.74_0$ Å | $O_4-O_5$ | $2.84_4$ Å | $O_3-Ge_2-O_4$ | 103.4° |
| $Ge_2-O_4$ | $1.71_5$ Å | $O_4-O_3$ | $2.73_1$ Å | $O_3-Ge_2-O_5$ | 120.8° |
| $Ge_2-O_5$ | $1.73_6$ Å | $O_4-O_3'$ | $2.85_2$ Å | $O_3'-Ge_2-O_4$ | 111.3° |
| Average | $1.73_9$ Å | $O_5-O_3$ | $3.04_4$ Å | $O_3'-Ge_2-O_5$ | 107.0° |
| | | $O_5-O_3'$ | $2.79_4$ Å | $O_4-Ge_2-O_5$ | 111.0° |

Distances and O—Ge—O angles in tetrahedra around $Ge_1$ (*cf.* Fig. 3a and 3b):

| | | | | | |
|---|---|---|---|---|---|
| $Ge_1-O_1$ | $1.74_0$ Å | $O_1-O_1'$ | $2.76_0$ Å | $O_1-Ge_1-O_1'$ | 105.0° |
| | | $O_1'-O_1'$ | $2.99_6$ Å | $O_1'-Ge_1-O_1'$ | 118.9° |

Distances between germanium atoms

| | |
|---|---|
| $Ge_1-Ge_3$ | $3.09_7$ Å |
| $Ge_3-Ge_3$ | $3.02_0$ Å |
| $Ge_3-Ge_3$ | $2.91_0$ Å |
| $Ge_2-Ge_3$ | $3.06_8$ Å |
| $Ge_2-Ge_3$ | $3.03_3$ Å |
| Average | $3.02_6$ Å |

Distances and O—Na—O angles in the coordination figure around Na (*cf.* Fig. 3d):

| | | | | | |
|---|---|---|---|---|---|
| $Na-O_1$ | $2.43_6$ Å | $O_1-O_1$ | $2.76_0$ Å | $O_1-Na-O_1'$ | 64.6° |
| $Na-O_1'$ | $2.71_4$ Å | $O_1-O_3$ | $3.55_0$ Å | $O_1-Na-O_3$ | 92.5° |
| $Na-O_3$ | $2.47_9$ Å | $O_1-O_5$ | $2.65_5$ Å | $O_1-Na-O_4'$ | 126.3° |
| $Na-O_4'$ | $2.31_8$ Å | $O_1'-O_3$ | $3.68_2$ Å | $O_1-Na-O_5$ | 60.4° |
| $Na-O_5$ | $2.80_6$ Å | $O_1'-O_4'$ | $3.50_6$ Å | $O_1-Na-O_5'$ | 144.7° |
| $Na-O_5'$ | $2.45_6$ Å | $O_3-O_5'$ | $3.68_0$ Å | $O_1'-Na-O_3$ | 90.2° |
| Average | $2.53_5$ Å | $O_4-O_5'$ | $2.60_6$ Å | $O_1'-Na-O_4'$ | 88.0° |
| | | $O_5-O_5'$ | $3.56_8$ Å | $O_1'-Na-O_5$ | 118.8° |
| | | | | $O_1'-Na-O_5'$ | 149.0° |
| | | | | $O_3-Na-O_4'$ | 135.0° |
| | | | | $O_3-Na-O_5$ | 116.0° |
| | | | | $O_3-Na-O_5'$ | 96.5° |
| | | | | $O_4'-Na-O_5$ | 103.9° |
| | | | | $O_4'-Na-O_5'$ | 66.1° |
| | | | | $O_5-Na-O_5'$ | 85.1° |

common corners as given in Fig. 2a in this paper, but, since the crystals of $Me_3HGe_7O_{16}(H_2O)_4$ are cubic (with $a \approx 7.7$ Å), the same types of chain could be cut out along all three unit cell directions. In $Me_3HGe_7O_{16}(H_2O)_4$, the octahedron groups $Ge_4O_{16}$ are thus joined by single tetrahedral $GeO_4$ groups along the $x$-, $y$- and $z$-directions. In $Na_4Ge_9O_{20}$, however, they are connected in this way only in the $z$ direction whereas in the $x$ and $y$ directions they are joined over two $GeO_4$ groups.

Nowotny and Wittman [11] obtained Ge—O = 1.61 Å and 1.74 Å in $GeO_4$ tetrahedra and 2.08 Å in $GeO_6$ octahedra in $Me_3HGe_7O_{16}(H_2O)_4$. However, they based their investigation on powder photograph data and consequently these distances cannot be considered as accurate as those obtained for $Na_4Ge_9O_{20}$.

Eulenberger, Wittmann and Nowotny [14] also proposed that the "tetragermanates" $MeGe_4O_9$ with Me = $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$, $Pb^{2+}$ should be related to the mineral benitoite (= $BaTiSi_3O_9$) and thus contain both four- and six-coordinated germanium atoms. The "tetragermanates" ($Me_2Ge_4O_9$) of $Na^+$, $K^+$, $Rb^+$, and $Tl^+$ should in the same way be related to the mineral wadeite (= $K_2ZrSi_3O_9$).

An accurate determination of the bond distances in the rutile form of $GeO_2$ was made by Baur [15,16]. In this compound all the germanium atoms are octahedrally coordinated to six oxygen atoms and he found the distances Ge—O to be 1.87 ± 0.2 Å and 1.91 ± 0.03 Å. The mean value, 1.89 Å, which is probably that quoted in the International Tables for X-ray Crystallography Vol. III [10], is also in good agreement with our mean value of $1.90_7$ Å.

Another determination of Ge—O distances for Ge in octahedral coordination was made by Strunz and Giglio [17], who determined the structure of stoettite, $FeGe(OH)_6$. The mean distance Ge—OH is given as 1.96 Å, which is somewhat longer than what we have found in $Na_4Ge_9O_{20}$. Strunz and Giglio [17] have not published any standard deviation in their Ge—O distances but since their determination of the structure is based on only 31 $hk0$- and 35 $0kl$-reflexions, the standard deviations are certainly larger than those of $Na_4Ge_9O_{20}$. Strunz and Giglio's [17] value of 1.96 Å for octahedral Ge—O bond distances might then not be significantly different from our mean value of $1.90_7$ for $Na_4Ge_9O_{20}$.

Bond distances Ge—O in tetrahedral coordination have recently been published by Hilmer [18]. He found the four Ge—O distances within a $GeO_4$ tetrahedron in the high-temperature form of $BaGeO_3$ to be 1.89 Å, 1.84 Å, 1.71 Å, and 1.70 Å with a mean value of 1.78 Å. No standard deviation is given, but since the structure determination was based on 67 $h0l$- and 70 $0kl$-reflexions they must be larger than those of $Na_4Ge_9O_{20}$. Hilmer's [18] mean value, 1.78 Å, is thus probably not significantly different from our value of $1.74_0$ Å for tetrahedral Ge—O distances. Geller *et al.*[19] discussed tetrahedral Ge—O distances and found that a reasonable distance would be 1.73 Å which is in excellent agreement with our result of $1.74_0$ Å in $Na_4Ge_9O_{20}$.

In addition to these accurate results, there are some others, less accurate since they are based on powder photograph data or on structure determinations which have not been refined. Thus, Nowotny and Szekely [20] found tetrahedral Ge—O distances in $SrH_2GeO_4$ to be 1.73 Å. Durif [21] found geometrically

that for $UGeO_4$ the distances Ge—O are 1.74 Å within the $GeO_4$ groups. Ginetti [22,23] made two determinations, one on $CuGeO_3$ and one on $Na_2GeO_3$, from which he found tetrahedral Ge—O distances of 1.84—1.86 Å. Finally, for the hexagonal modification of $GeO_2$, isomorphous with quartz, no accurate tetrahedral distances Ge—O have been determined [24].

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