by Gschneidner in terms of a considerable homogeneity region. In order to check this interpretation the X-ray powder diagrams of three arc-cast samples annealed at 800°C and containing slightly different relative amounts of La and Al were compared (Table 4). The first (20·0 at.% La) was Buschow's original diagram, which had served for his determination of the '$\alpha$-$LaAl_4$' lattice constants; besides the $La_3Al_{11}$ lines, there are also weak lines of Al. The second, corresponding to the exact stoichiometric composition (21·4 at.% La) shows no other lines than those of pure $La_3Al_{11}$, whereas the third (22.2 at.% La) also contains $LaAl_3$ lines. This proves not only that the homogeneity region is rather small but also that $La_3Al_{11}$ is indeed the correct chemical formula. The invariance of the lattice constants tends to corroborate the former conclusion.

Since the high-temperature modification cannot be quenched (Buschow), one would think that all previous investigations, which were carried out at room temperature, would refer to the low-temperature phase. The question then arises why the orthorhombic structure had not earlier been recognized. Poor resolution of the X-ray diagrams might be held responsible, but such an explanation seems particularly unsatisfactory in the case of Rossi's work, which involves tetragonal Laue photographs of single-crystalline samples. We are inclined to believe, therefore, that the $BaAl_4$-type structure is stabilized by chemical impurities. Although this idea needs experimental verification, it should be noted that purer starting materials were available to us (La 99·9%, Al 99·99%) than to any of the previous investigators, and also that our method of sample preparation was probably less apt to introduce contamination.

Since it is impossible to quench the high-temperature modification, the $\alpha$ and the $\beta$ phases are likely to have the same chemical composition, in which case they should be designated as $\alpha$-$La_3Al_{11}$ and $\beta$-$La_3Al_{11}$. If so, and if Buschow's statement is correct that '$\beta$-$LaAl_4$' has the $BaAl_4$-type structure, the phase transition entails the ordering of vacancies by diffusion. This conclusion is not necessarily at variance with the reported sharpness (Buschow, 1965*a*) of the transition.

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# Crystal and Molecular Structure of *S*,*S*-Dimethyl-*N*-methylsulphonylsulphilimine, $(CH_3)_2SNSO_2CH_3$

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The crystal structure of *S*,*S*-dimethyl-*N*-methylsulphonylsulphilimine has been solved by three-dimensional Patterson and Fourier calculations. The parameters have been refined by the aid of Booth's differential syntheses, with a final $R=0·106$. The S–N distances [1·58$_1$(10) and 1·63$_3$(9) Å] indicate a delocalized S–N–S $d_\pi$ bond system. The S–N–S bond angle is 116·2 (6)°, the average S–O distance, 1·44$_6$ Å. The C(1)–S(VI) bond distance, 1·74$_9$ (12) is similar to other C($sp^3$)–S(VI) bonds. The C($sp^3$)–S(IV) bond distances [1·74 (7) and 1·74 (3) Å] are rather short, which can be explained only with the supposition of strong hyperconjugation. The large e.s.d.'s of the C(2)–S(IV) and C(3)–S(IV) bonds are due to the intensive thermal motion of the C(2) and C(3) atoms.

## Introduction

The structure and the stereochemistry of the *N*-acrylsulphilimines have been investigated by Kucsman and his collaborators (Kucsman, 1953, 1958; Kucsman & Kapovits, 1964). These investigations gave interesting results concerning the bond system and the configuration of these compounds. Among others the presence of a strong S(IV)–N $d_\pi$ bond in the *N*-sulphonylsulphilimines ($RR'SNSO_2Q$) has been proved by infrared spectroscopy (Kucsman, Ruff & Kapovits, 1966). It has not, however, been possible to draw any unambiguous conclusion concerning the character of the S(VI)–N bond from spectroscopic data. Moreover, in the infrared spectrum of the sulphilimines containing an $S(IV)CH_3$ group an anomalous phenomenon was revealed, which was described as the '*S*-methyl effect'.

To clear up this problem the complete structure determination of one of the sulphilimines (R,R′ and $Q=CH_3$) has been performed, as a first step towards the systematic structure analysis of the sulphilimine derivatives.

## Experimental

The crystals of the compound were prepared by the method of Schulz & Kresze (1963) and were recrystallized from a mixture of absolute benzene and alcohol. According to the infrared spectrum the colourless needle-like crystals are free from mother liquor impurities. The m.p. (122 °C) is in good agreement with the literature data.

*Crystal data*

$C_3H_9NO_2S_2$, $M=155{\cdot}25$
$a=5{\cdot}80_5\pm0{\cdot}012$, $b=13{\cdot}50_3\pm0{\cdot}009$, $c=9{\cdot}21_3\pm0{\cdot}012$ Å
$\beta=105{\cdot}15\pm0{\cdot}13°$, $V=697{\cdot}07$ Å$^3$, $Z=4$,
$D_x=1{\cdot}479$ g.cm$^{-3}$
$D_m=1{\cdot}47_3$ g.cm$^{-3}$ (by flotation).
$\mu=60$ cm$^{-1}$ (Cu $K\alpha$), $F_{000}=328$,
Space group $P2_1/c$ (from systematic absences).

The lattice parameters were determined by the precession camera, calibrated with sodium chloride. The intensities were measured by a Zeiss fast photometer on integrated, equi-inclination Weissenberg photographs, taken with Ni-filtered Cu $K\alpha$ radiation, using the multiple-film technique. The dimensions of the crystals investigated were reduced by our preparation device (Kálmán & Argay, 1965) below the value of $\mu R=0{\cdot}4$, and in this way the absorption correction could be neglected. Unfortunately the crystals slowly decomposed during the long X-ray irradiation. Therefore the investigated samples were changed after every second layer. It was hoped that the probable effect of this phenomenon upon the values of the intensities would be diminished by collection of data from repeated photographs, made around the three crystal axes, and controlling them by each other.

Photographs were taken from the following layers:

$hk0, \ldots\ldots\ldots hk6,$
$h0l, \ldots\ldots\ldots h4l,$
$0kl$, $1kl$* and $2kl$*

The spot shape correction on the non-equatorial layers and the multiple-film scaling were taken by hand calculations, measuring the intensities on both upper and lower parts of the films. Then the intensities were corrected for the Lp factor by a National Elliott 803B computer, using the program of Sasvári & Sánta (1964). After the interlayer scaling, made by hand, the absolute scale and the approximate temperature factors ($\bar{B}=3{\cdot}63$ Å$^2$) were determined by Wilson's method. In this way 1264 independent reflexions (81% of the possible ones) were collected. For the structure determination and refinement the 1027 non-zero reflexions were used.

## Structure analysis and refinement

The interpretation of the 3-D Patterson calculation using the 'satellite and rotation vector's relations' (Buerger, 1959) gave unambiguously all sulphur–sulphur vectors. The $(u,v,w)$ Patterson coordinates were transformed to the $(x,y,z)$ Fourier ones by the aid of the shortest vector, the absolute value of which was in good agreement with the estimated intramolecular S···S distance. The first 3-D Fourier synthesis was performed with the phases appropriate to the sulphur atoms. Three successive rounds of structure factor and Fourier calculations gave the positional parameters of all the atoms; $R$ was now 0·231.

The refinement was carried out with twelve cycles of Booth's differential synthesis (1948), two with the average, two with atomic isotropic and eight with anisotropic thermal parameters. The latter were calculated by the method of Nardelli & Fava (1960), using the

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* These intensities were used only to control the same ones collected from other layers.

Table 1. *Final positional (monoclinic*) parameters with their standard deviations*

| | $x$ | $y$ | $z$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| S(1) | 0·1301 | 0·1175 | 0·2137 | 0·0004 | 0·0001 | 0·0003 |
| S(2) | 0·1640 | −0·0785 | 0·2886 | 0·0005 | 0·0001 | 0·0003 |
| O(1) | 0·1705 | 0·2100 | 0·2936 | 0·0021 | 0·0006 | 0·0012 |
| O(2) | −0·1150 | 0·0963 | 0·1313 | 0·0017 | 0·0007 | 0·0013 |
| N | 0·2509 | 0·0353 | 0·3312 | 0·0017 | 0·0006 | 0·0012 |
| C(1) | 0·2913 | 0·1206 | 0·0777 | 0·0020 | 0·0006 | 0·0012 |
| C(2) | 0·4055 | −0·1399 | 0·2515 | 0·0144! | 0·0019 | 0·0068! |
| C(3) | 0·1800 | −0·1305 | 0·4639 | 0·0039! | 0·0009 | 0·0039! |

* For the calculation of the clinographical projections (Figs. 1 and 2) the orthogonalized parameters were used. The transformation matrix from monoclinic to orthogonal coordinates was:

$$\begin{pmatrix} 1 & 0 & \cos\beta \\ 0 & 1 & 0 \\ 0 & 0 & \sin\beta \end{pmatrix}$$

second derivatives of the electron densities from the differential syntheses. In view of the uncertainty in deriving the correct scale factors, the anisotropic thermal parameters, given in Table 2 have only limited physical meaning.

Because of the anomalous differences in $\varrho$ values of the carbon atoms, a 3-D $(F_o-F_c)$ synthesis was performed to verify the positional parameters of the C(2) and C(3) atoms. The result of the difference synthesis confirmed the coordinates of these atoms, obtained from the third 3-D Fourier synthesis. To find the reason of the difference in $\varrho$ values of the carbon atoms, the $(x,y)$ and $(x,z)$ projections of their electron densities were drawn, on the basis of the third 3-D Fourier cycle. These projections using an arbitrary limit of the electron density ($\varrho_0 \geq 3$ e.Å$^{-3}$) show that while C(1) has an almost spherical electron cloud, C(3) and especially C(2) have unusually deformed elliptical ones. The estimated volumes of these electron clouds are inversely proportional to the electron densities found in the atomic centres. These results are consistent with each other and with the unusually great thermal parameters of the C(2) and C(3) atoms.

After the seventh cycle of the refinement a correction of the accidental errors and of the effect of the secondary extinction upon the intensities was performed. Twenty reflexions in the centre of the reciprocal lattice ($\sin^2\theta/\lambda^2 \leq 0\cdot03$) were corrected by the method of Pinnock, Taylor & Lipson (1956).

The final coordinates with their e.s.d.'s (Cruickshank, 1949) are given in Table 1. In Table 3 are listed the observed and calculated values of the electron density and the second derivatives at the atomic peaks with e.s.d.'s. The determination of the hydrogen coordinates was not attempted, because of the great thermal motion of the methyl groups. The final reliability indices, $R$ (for the observed reflexions only) and $R'$ (including the non-observed ones, using $F_o = 0\cdot5F_{\min}$, when $F_c \geq F_{\min}$) are 0·106 and 0·128, respectively.

Table 2. *Anisotropic thermal parameters* (Å$^2$)

The parameters are values of $B_{ij}$ in the expression:

$$\exp\left[-\tfrac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{23}b^*c^*kl + 2B_{13}a^*c^*hl + 2B_{12}a^*b^*hk)\right]$$

| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|---|---|---|---|---|---|---|
| S(1) | 2·93 | 2·47 | 2·93 | 0·01 | 1·28 | 0·12 |
| S(2) | 4·64 | 2·80 | 2·96 | −0·18 | 0·42 | 0·33 |
| O(1) | 8·89 | 2·75 | 4·64 | −0·08 | 3·38 | −0·22 |
| O(2) | 2·88 | 4·40 | 6·90 | 1·70 | 1·22 | 0·60 |
| N | 4·15 | 3·13 | 3·21 | 0·20 | 0·89 | −0·23 |
| C(1) | 3·96 | 4·34 | 3·76 | 0·08 | 1·75 | −0·33 |
| C(2) | 16·20 | 6·25 | 9·67 | 1·05 | 9·05 | 4·17 |
| C(3) | 6·98 | 3·41 | 4·25 | −0·02 | 1·77 | −0·32 |

The scattering factors used throughout the calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen and carbon, and of Dawson (1960) for sulphur. The calculations were performed on the Olivetti Elea 6001/S computer of the Centro di Calcolo Elettronico of the University of Parma, using the programs of Nardelli, Musatti, Domiano & Andreetti (1964, 1965).

## Discussion

The atomic distances and angles are given in Table 4. The e.s.d.'s are calculated by the formula of Ahmed & Cruickshank (1953) for distances and from those of Darlow (1960) for angles. The clinographic projections of the molecule are shown in Figs. 1 and 2.

The sulphur atoms with different valence states [S(IV) and S(VI)] are linked by an $sp^2$-nitrogen atom, which is able to establish $\pi$-connexions. The S–N distances ($1\cdot58_1$ and $1\cdot63_3$ Å) indicate that a delocalized $d_\pi$ bond system is formed on the S–N–S atoms with strong $d_\pi$ bonds. The deviation between them is signi-

Table 3. *Comparison of peak heights* (e.Å$^{-3}$) *and curvatures* (e.Å$^{-5}$) *from the differential synthesis*

| | | $\varrho$ | $-A_{hh}$ | $-A_{kk}$ | $-A_{ll}$ | $A_{hk}$ | $A_{hl}$ | $A_{kl}$ |
|---|---|---|---|---|---|---|---|---|
| S(1) | obs. | 31·0 | 309 | 308 | 245 | 4 | 79 | −15 |
| | calc. | 30·9 | 308 | 308 | 245 | 4 | 78 | −14 |
| S(2) | obs. | 26·7 | 226 | 264 | 209 | 11 | 40 | −18 |
| | calc. | 26·7 | 227 | 264 | 208 | 11 | 40 | −18 |
| O(1) | obs. | 8·8 | 55 | 70 | 57 | −2 | 12 | 18 |
| | calc. | 8·8 | 57 | 70 | 57 | −3 | 12 | 19 |
| O(2) | obs. | 8·7 | 83 | 58 | 60 | −2 | 25 | 1 |
| | calc. | 8·7 | 82 | 58 | 60 | −2 | 25 | 1 |
| N | obs. | 8·5 | 67 | 60 | 56 | −3 | 13 | 0 |
| | calc. | 8·6 | 67 | 60 | 56 | −3 | 13 | 0 |
| C(1) | obs. | 7·4 | 61 | 66 | 59 | 1 | 16 | −2 |
| | calc. | 7·3 | 61 | 67 | 59 | 1 | 16 | −1 |
| C(2) | obs. | 4·0 | 16 | 34 | 19 | 8 | 10 | −5 |
| | calc. | 3·9 | 16 | 33 | 19 | 8 | 10 | −6 |
| C(3) | obs. | 5·7 | 39 | 46 | 18 | −7 | 8 | 1 |
| | calc. | 5·6 | 39 | 46 | 19 | −8 | 8 | 2 |
| | e.s.d. | 0·2 | 2 | 3 | 2 | 1 | 1 | 1 |

ficant according to the significance test of Cruickshank & Robertson (1953):

$$t_0=(l_1-l_2)(\sigma_1^2+\sigma_2^2)^{-\frac{1}{2}}=3\cdot54\,,$$

but can be explained on the basis of the different atomic radii and electronegativities of the S(IV) and S(VI) atoms (Truter, 1962*b*).

The S–O distances [$1\cdot43_8$ and $1\cdot45_5$ Å] indicate strong bonds comparable to those found in other sulphones and sulphonamides. The C(1)–S(VI) bond, $1\cdot74_9$ Å, is not significantly shorter ($t_{0,\max}=1\cdot64$) than other C($sp^3$)–S(VI) bonds, *e.g.*

| | |
|---|---|
| $1\cdot770\pm0\cdot009$ Å in | $(CH_3SO_2)_2C=C=NCH_3$ (Wheatley, 1954) |
| $1\cdot761\pm0\cdot01$ | $(CH_3SO_2)(C_6H_5SO_2)C=C=NCH_3$ (Bullough & Wheatley, 1957) |
| $1\cdot770\pm0\cdot007$ | $K_2CH_2(SO_3)_2$ (Truter, 1962*a*). |

The C(2)–S(IV) and C(3)–S(IV) bonds are considerably shorter than the theoretically calculated C($sp^3$)–S(IV) or the one found, for example, in rongalite, $1\cdot83\pm0\cdot01$ Å (Truter, 1962*b*). These unusually short distances, though their standard deviations are rather high, seem to originate from a hyperconjugation-like effect. This question nevertheless needs the thermal motion analysis of atoms as well as of the molecule, and this could not be performed at present because of lack of computer facilities. At any rate, the '*S*-methyl effect' mentioned above should clearly be associated with the shortening of the C($sp^3$)–S(IV) bond lengths and the intensive thermal motion of the methyl groups. The thermal vibration of the C(2) is considerably greater than that of C(3), for which, however, an unambiguous explanation could not be found.

Another remarkable fact is that the standard deviations of the S–O bond lengths are not influenced as significantly by the great thermal motion of the oxygen atoms as that of the C–S(IV) bond lengths by that of the carbon atoms.

The S(IV)–N–S(VI) bond angle, 116·2°, is less than the theoretical 120°. The lone electron pair of the nitrogen, which does not take part in the S–N–S delocalized $d_\pi$ system, presumably displays a repulsion effect upon the S–N bonds, and therefore the bond angle decreases. The O(1)–S(VI)–O(2), O(1)–S(VI)–C(1) and O(2)–S(VI)–C(1) bond angles are similar to the corresponding ones in the $CH_3SO_2$ groups of other compounds investigated (Wheatley, 1954; Bullough & Wheatley, 1957). The O(2)–S(VI)–N angle is considerably greater than the O(1)–S(VI)–N angle and those found in potassium imidodisulphate (Cruickshank & Jones, 1963) in the dinitrososulphite and sulphamate ions (Jeffrey & Stadler, 1951). The bond angles of the

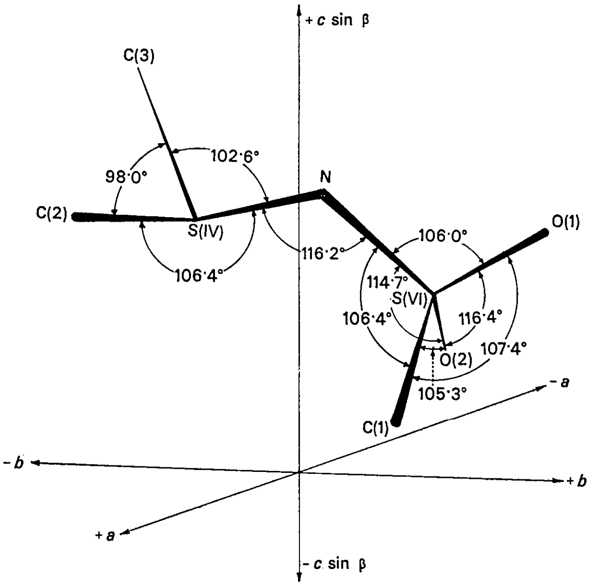

Fig. 1. The atomic distances and labelling of the atoms in sulphilimine.

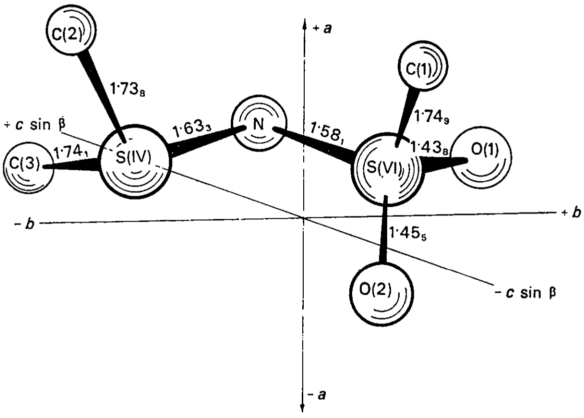

Fig. 2. The bond angles and labelling of the atoms in sulphilimine.

Table 4. *Interatomic distances and bond angles with their e.s.d.'s*

| | | | |
|---|---|---|---|
| S(VI)–O(1) | $1\cdot438\pm0\cdot009$ Å | S(VI)–N–S(IV) | $116\cdot2\pm0\cdot6$° |
| S(VI)–O(2) | $1\cdot455\pm0\cdot012$ | O(1)–S(VI)–O(2) | $116\cdot4\pm0\cdot6$ |
| S(VI)–N | $1\cdot581\pm0\cdot010$ | O(1)–S(VI)–N | $106\cdot0\pm0\cdot6$ |
| S(VI)–C(1) | $1\cdot749\pm0\cdot012$ | O(1)–S(VI)–C(1) | $107\cdot4\pm0\cdot6$ |
| S(IV)–N | $1\cdot633\pm0\cdot009$ | O(2)–S(VI)–N | $114\cdot7\pm0\cdot6$ |
| S(IV)–C(2) | $1\cdot74\pm0\cdot07$ | O(2)–S(VI)–C(1) | $105\cdot3\pm0\cdot6$ |
| S(IV)–C(3) | $1\cdot74\pm0\cdot03$ | N–S(VI)–C(1) | $106\cdot4\pm0\cdot5$ |
| S···S | $2\cdot729\pm0\cdot003$ | N–S(IV)–C(2) | $106\cdot4\pm1\cdot7$ |
| | | N–S(IV)–C(3) | $102\cdot6\pm0\cdot7$ |
| | | C(2)–S(IV)–C(3) | $98\cdot0\pm1\cdot9$ |

$CH_3S(IV)$–N group can be compared with those of dimethyl sulphoxide (Thomas, Shoemaker & Eriks, 1966) which has a similar electron structure:

| | Sulphilimine | | Sulphoxide |
|---|---|---|---|
| C(2)–S(IV)–C(3) | 98·0° | C(1)–S(IV)–C(2) | 98·2° |
| C(2)–S(IV)–N | 106·4 | C(1)–S(IV)–O | 106·7 |
| C(3)–S(IV)–N | 102·6 | C(2)–S(IV)–O | 107·5 |

As has been emphasized throughout this paper, some atoms of the molecule had unusually great thermal vibrations. This question suggests that the structure should be reinvestigated and refined with more accurate intensities collected at low temperature, as suggested by Cruickshank (1960) and Jensen (1962) in such cases. The observed slow decomposition of the crystals during X-ray irradiation may also be connected with the great thermal motion of the structure. Perhaps an electron spin resonance study of the irradiated crystals will give some information concerning this phenomenon.

The conformation of the molecule from the organic chemical aspect will be discussed elsewhere (Kucsman, Kálmán & Kapovits, 1966).

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Table 5. *Observed and calculated structure factors*

Unobserved reflexions are marked by a dot.

| h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ | h | k | l | $10F_o$ | $10F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 960 | 909 | -2 | 1 | 1 | 530 | 575 | -1 | 9 | 1 | 160 | 174 | -4 | 2 | 2 | 25 | 25 | 5 | 10 | 2 | 8. | 7 | 1 | 5 | 3 | 12. | -30 |
| 2 | | | 610 | -630 | 3 | | | 76 | 64 | 2 | | | 191 | -179 | 5 | | | 13. | -12 | -5 | | | 43 | 40 | -1 | | | 429 | 383 |
| 3 | | | 671 | -689 | -3 | | | 50 | 54 | -2 | | | 162 | 146 | -5 | | | 13. | -14 | 0 | 11 | | 11. | -11 | 3 | | | 247 | -204 |
| 4 | | | 337 | -362 | 4 | | | 107 | 88 | 3 | | | 110 | -101 | 6 | | | 35 | -26 | 1 | | | 270 | 249 | -3 | | | 119 | 106 |
| 5 | | | 113 | -103 | -4 | | | 239 | -253 | -3 | | | 110 | 91 | -6 | | | 13. | -8 | -1 | | | 312 | 312 | 4 | | | 19. | 4 |
| 6 | | | 76 | 70 | 5 | | | 71 | 54 | 4 | | | 11. | -27 | 0 | 3 | | 724 | -723 | 2 | | | 206 | 214 | -4 | | | 218 | -197 |
| 1 | 1 | | 151 | -149 | -5 | | | 225 | -238 | -4 | | | 12. | -37 | 1 | | | 488 | -515 | -2 | | | 332 | 331 | 5 | | | 39 | 41 |
| 2 | | | 107 | -91 | 6 | | | 56 | 54 | 5 | | | 10. | 31 | -1 | | | 212 | 219 | 3 | | | 67 | 52 | -5 | | | 237 | -231 |
| 3 | | | 67 | 30 | -6 | | | 98 | -94 | -5 | | | 110 | -121 | 2 | | | 71 | 68 | -3 | | | 98 | 91 | 6 | | | 121 | -118 |
| 4 | | | 62 | -57 | 0 | 2 | | 309 | -364 | 6 | | | 56 | -83 | -2 | | | 110 | -89 | 4 | | | 43 | -38 | 0 | 6 | | 84 | -73 |
| 5 | | | 11. | 17 | 1 | | | 680 | -656 | 0 | 10 | | 464 | -479 | 3 | | | 297 | 304 | -4 | | | 141 | -149 | 1 | | | 344 | -340 |
| 6 | | | 76 | 69 | -1 | | | 116 | 125 | 1 | | | 278 | -291 | -3 | | | 193 | -206 | 5 | | | 6. | -42 | -1 | | | 13. | -1 |
| 0 | 2 | | 429 | 415 | 2 | | | 25 | -25 | -1 | | | 222 | 217 | 4 | | | 260 | 264 | -5 | | | 148 | -173 | 2 | | | 150 | -105 |
| 1 | | | 158 | 155 | -2 | | | 124 | -91 | 2 | | | 158 | 141 | -4 | | | 143 | -131 | 0 | 12 | | 35 | 33 | -2 | | | 168 | -126 |
| 2 | | | 145 | -162 | 3 | | | 148 | 116 | -2 | | | 195 | -193 | 5 | | | 80 | 64 | 1 | | | 98 | 99 | 3 | | | 150 | 132 |
| 3 | | | 98 | -115 | -3 | | | 8. | -7 | 3 | | | 203 | 216 | -5 | | | 107 | -74 | -1 | | | 13. | -46 | -3 | | | 198 | -186 |
| 4 | | | 43 | -30 | 4 | | | 182 | 179 | -3 | | | 254 | -267 | 6 | | | 80 | -85 | 2 | | | 134 | 133 | 4 | | | 150 | 112 |
| 5 | | | 50 | -11 | -4 | | | 141 | -125 | 4 | | | 110 | 120 | -6 | | | 13. | -23 | -2 | | | 71 | -53 | -4 | | | 132 | -128 |
| 6 | | | 67 | 12 | 5 | | | 195 | 205 | -4 | | | 164 | -169 | 0 | 4 | | 259 | 301 | 3 | | | 56 | 55 | 5 | | | 25 | 31 |
| 1 | 3 | | 305 | 309 | -5 | | | 156 | -148 | 0 | 11 | | 50 | 44 | 1 | | | 325 | 321 | -3 | | | 76 | -81 | -5 | | | 19. | 12 |
| 2 | | | 335 | 361 | 6 | | | 91 | 66 | 1 | | | 67 | 64 | -1 | | | 52 | 4 | 4 | | | 43 | -44 | -6 | | | 87 | 93 |
| 3 | | | 80 | 73 | -6 | | | 25 | -28 | -1 | | | 12. | -23 | 2 | | | 76 | 48 | -4 | | | 50 | -36 | 0 | 7 | | 349 | -340 |
| 4 | | | 181 | -185 | 0 | 3 | | 119 | -122 | 2 | | | 12. | -22 | -2 | | | 226 | 212 | 0 | 13 | | 13. | -28 | 1 | | | 392 | -362 |
| 5 | | | 80 | -67 | 1 | | | 257 | 273 | -2 | | | 12. | 1 | 3 | | | 254 | -251 | 1 | | | 94 | -94 | -1 | | | 84 | 43 |
| 6 | | | 62 | 66 | -1 | | | 273 | -278 | 3 | | | 11. | -4 | -3 | | | 181 | -126 | -1 | | | 13. | -37 | 2 | | | 17. | -31 |
| 0 | 4 | | 1086 | -1047 | 2 | | | 199 | 222 | -3 | | | 11. | -35 | 4 | | | 171 | -176 | 2 | | | 91 | -88 | -2 | | | 361 | 333 |
| 1 | | | 337 | -383 | -2 | | | 121 | -135 | 4 | | | 10. | 32 | -4 | | | 300 | -301 | -2 | | | 84 | -82 | 3 | | | 252 | 208 |
| 2 | | | 7. | 55 | 3 | | | 113 | 99 | -4 | | | 11. | -29 | 5 | | | 62 | -49 | 3 | | | 11. | 4 | -3 | | | 152 | 146 |
| 3 | | | 307 | 310 | -3 | | | 215 | -219 | 0 | 12 | | 231 | -217 | -5 | | | 87 | -75 | -3 | | | 57 | -34 | 4 | | | 143 | 134 |
| 4 | | | 303 | 311 | 4 | | | 50 | -28 | 1 | | | 84 | -68 | 6 | | | 10. | 1 | 4 | | | 50 | 44 | -4 | | | 19. | 19 |
| 5 | | | 127 | 124 | -4 | | | 67 | 36 | -1 | | | 121 | 114 | -6 | | | 80 | 83 | 0 | 14 | | 56 | -30 | -5 | | | 91 | -64 |
| 6 | | | 67 | -49 | 5 | | | 56 | -44 | 2 | | | 76 | 61 | 0 | 5 | | 203 | 201 | 1 | | | 62 | 61 | -6 | | | 50 | -38 |
| 1 | 5 | | 121 | 111 | -5 | | | 170 | 158 | -2 | | | 12. | -26 | 1 | | | 177 | -167 | -1 | | | 12. | -47 | 0 | 8 | | 56 | 47 |
| 2 | | | 281 | 297 | 6 | | | 35 | -46 | 3 | | | 67 | 85 | -1 | | | 224 | -179 | 2 | | | 91 | 90 | 1 | | | 127 | -85 |
| 3 | | | 119 | 122 | -6 | | | 91 | 84 | -3 | | | 91 | -99 | 2 | | | 362 | -393 | -2 | | | 43 | -36 | -1 | | | 182 | -173 |
| 4 | | | 50 | -45 | 0 | 4 | | 204 | 218 | 4 | | | 50 | 60 | -2 | | | 303 | -266 | 3 | | | 56 | 40 | 2 | | | 127 | -94 |
| 5 | | | 143 | -138 | 1 | | | 138 | 166 | -4 | | | 80 | -87 | 3 | | | 76 | -60 | -3 | | | 10. | -2 | -2 | | | 17. | -19 |
| 6 | | | 71 | -71 | -1 | | | 176 | -184 | 0 | 13 | | 62 | -58 | -3 | | | 87 | -101 | 0 | 15 | | 43 | 23 | 3 | | | 19. | -9 |
| 0 | 6 | | 505 | -540 | 2 | | | 127 | -118 | 1 | | | 11. | -1 | 4 | | | 124 | 124 | 1 | | | 101 | -112 | -3 | | | 110 | 89 |
| 1 | | | 345 | -368 | -2 | | | 121 | 99 | -1 | | | 67 | -62 | -4 | | | 80 | 77 | -1 | | | 124 | -138 | 4 | | | 56 | 31 |
| 2 | | | 98 | 94 | 3 | | | 193 | -201 | 2 | | | 11. | 41 | 5 | | | 71 | 74 | 2 | | | 98 | -132 | -4 | | | 50 | 36 |
| 3 | | | 292 | 303 | -3 | | | 224 | 233 | -2 | | | 11. | -29 | -5 | | | 188 | 176 | -2 | | | 132 | -148 | 5 | | | 13. | 32 |
| 4 | | | 188 | 194 | -4 | | | 84 | 87 | 3 | | | 62 | 61 | 6 | | | 9. | 7 | 3 | | | 43 | -46 | -5 | | | 18. | 9 |
| 5 | | | 43 | 26 | 5 | | | 107 | 108 | -3 | | | 10. | -15 | -6 | | | 71 | 72 | -3 | | | 62 | -68 | -6 | | | 13. | -6 |
| 6 | | | 56 | -57 | -5 | | | 67 | -64 | 4 | | | 62 | 74 | 0 | 6 | | 330 | 339 | 0 | 16 | | 9. | -20 | 0 | 9 | | 246 | -199 |
| 1 | 7 | | 71 | -50 | 6 | | | 67 | 67 | -4 | | | 8. | -13 | 1 | | | 118 | 91 | 1 | | | 67 | -85 | 1 | | | 91 | -56 |
| 2 | | | 35 | 11 | -6 | | | 87 | -89 | 0 | 14 | | 182 | 179 | -1 | | | 345 | 391 | -1 | | | 9. | 35 | -1 | | | 246 | -201 |
| 3 | | | 116 | 92 | 0 | 5 | | 219 | -235 | 1 | | | 143 | 146 | 2 | | | 248 | -253 | 0 | 17 | | 87 | -43 | 2 | | | 218 | 170 |
| 4 | | | 62 | 44 | 1 | | | 141 | 168 | -1 | | | 67 | -61 | -2 | | | 84 | 84 | 0 | 1 | 3 | 91 | 81 | -2 | | | 176 | -162 |
| 5 | | | 80 | -73 | -1 | | | 295 | -328 | 2 | | | 10. | -22 | 3 | | | 274 | -272 | 1 | | | 198 | 257 | 3 | | | 215 | 190 |
| 6 | | | 56 | -68 | 2 | | | 260 | 280 | -2 | | | 67 | 76 | -3 | | | 235 | -191 | -1 | | | 514 | -561 | -3 | | | 18. | -17 |
| 0 | 8 | | 204 | 199 | -2 | | | 209 | -214 | 3 | | | 76 | -90 | 4 | | | 67 | -63 | 2 | | | 212 | 220 | 4 | | | 84 | 72 |
| 1 | | | 56 | 52 | 3 | | | 107 | 99 | -3 | | | 101 | 111 | -4 | | | 199 | -173 | -2 | | | 685 | -720 | -4 | | | 145 | 125 |
| 2 | | | 87 | 46 | -3 | | | 124 | -126 | 4 | | | 35 | -70 | 5 | | | 67 | 59 | 3 | | | 179 | 155 | -5 | | | 127 | 115 |
| 3 | | | 25 | -12 | 4 | | | 67 | -57 | -4 | | | 76 | 92 | -5 | | | 50 | -40 | -3 | | | 247 | -226 | -6 | | | 71 | 60 |
| 4 | | | 116 | -103 | -4 | | | 141 | 142 | 0 | 15 | | 43 | -29 | 6 | | | 67 | 57 | 4 | | | 19. | 6 | 0 | 10 | | 307 | 304 |
| 5 | | | 113 | -112 | 5 | | | 76 | -75 | 1 | | | 80 | -82 | -6 | | | 56 | 46 | -4 | | | 286 | 320 | 1 | | | 136 | 96 |
| 6 | | | 10 | -19 | -5 | | | 225 | 239 | -1 | | | 10. | 36 | 0 | 7 | | 426 | 447 | 5 | | | 87 | -50 | -1 | | | 355 | -351 |
| 1 | 9 | | 290 | -227 | 6 | | | 43 | -50 | 2 | | | 50 | -62 | 1 | | | 129 | 135 | -5 | | | 269 | 279 | 2 | | | 107 | -85 |
| 2 | | | 261 | -251 | -6 | | | 104 | 107 | -2 | | | 56 | 64 | -1 | | | 243 | -215 | 6 | | | 62 | -36 | -2 | | | 87 | 58 |
| 3 | | | 25 | -21 | 0 | 6 | | 148 | 123 | 3 | | | 6. | 4 | 2 | | | 248 | -255 | -6 | | | 94 | 97 | 3 | | | 134 | -124 |
| 4 | | | 62 | 52 | 1 | | | 495 | 514 | -3 | | | 43 | 51 | -2 | | | 62 | -41 | 0 | 2 | | 184 | -137 | -3 | | | 370 | 348 |
| 5 | | | 80 | 81 | -1 | | | 8. | 22 | 0 | 16 | | 156 | 162 | 3 | | | 228 | -223 | 1 | | | 160 | 207 | 4 | | | 94 | -73 |
| 6 | | | 43 | 57 | 2 | | | 110 | 118 | -1 | | | 80 | -92 | -3 | | | 12. | -17 | -1 | | | 192 | -170 | -4 | | | 244 | 229 |
| 0 | 10 | | 250 | 222 | -2 | | | 9. | 4 | 2 | | | 35 | -42 | 4 | | | 67 | -64 | 2 | | | 188 | 234 | -5 | | | 16. | -18 |
| 1 | | | 196 | 186 | 3 | | | 176 | -194 | -2 | | | 35 | 27 | -4 | | | 110 | 98 | -2 | | | 113 | 120 | 0 | 11 | | 71 | 51 |
| 2 | | | 10. | -1 | -3 | | | 67 | 65 | 0 | 17 | | 43 | 42 | 5 | | | 11. | 6 | 3 | | | 17. | 36 | 1 | | | 139 | 110 |
| 3 | | | 150 | -133 | 4 | | | 203 | -211 | 0 | 0 | 2 | 1215 | -1228 | -5 | | | 177 | 168 | -3 | | | 233 | 247 | -1 | | | 19. | -24 |
| 4 | | | 124 | -130 | -4 | | | 206 | 210 | 1 | | | 60 | -82 | 6 | | | 6. | 40 | 4 | | | 160 | -132 | 2 | | | 76 | 44 |
| 5 | | | 62 | -56 | 5 | | | 98 | -98 | -1 | | | 795 | -918 | -6 | | | 67 | 71 | -4 | | | 43 | 23 | -2 | | | 107 | -79 |
| 1 | 11 | | 355 | -365 | -5 | | | 107 | 99 | 2 | | | 406 | 440 | 0 | 8 | | 35 | 30 | 5 | | | 145 | -131 | 3 | | | 76 | -67 |
| 2 | | | 267 | -267 | 6 | | | 8. | 8 | -2 | | | 220 | -180 | 1 | | | 236 | -210 | -5 | | | 124 | -93 | -3 | | | 80 | -47 |
| 3 | | | 50 | -42 | -6 | | | 56 | -61 | 3 | | | 370 | 400 | -1 | | | 226 | 191 | 6 | | | 76 | -52 | 4 | | | 76 | -57 |
| 4 | | | 76 | 74 | 0 | 7 | | 91 | 64 | -3 | | | 505 | 546 | 2 | | | 254 | -244 | -6 | | | 76 | -59 | -4 | | | 67 | -36 |
| 5 | | | 84 | 104 | 1 | | | 172 | 154 | 4 | | | 182 | 157 | -2 | | | 50 | -24 | 0 | 3 | | 334 | 309 | 5 | | | 43 | 31 |
| 0 | 12 | | 162 | -145 | -1 | | | 154 | -146 | -4 | | | 421 | 445 | 3 | | | 13. | -15 | 1 | | | 25 | 29 | 0 | 12 | | 110 | 91 |
| 1 | | | 12. | -27 | 2 | | | 121 | 117 | 5 | | | 25. | 21 | -3 | | | 43 | 15 | -1 | | | 254 | 260 | 1 | | | 62 | 28 |
| 2 | | | 11. | 35 | -2 | | | 209 | -219 | -5 | | | 62 | 35 | 4 | | | 110 | 112 | 2 | | | 213 | -214 | -1 | | | 94 | -53 |
| 3 | | | 5 | 9 | 3 | | | 119 | -82 | 6 | | | 71 | -34 | -4 | | | 94 | 90 | -2 | | | 56 | 39 | 2 | | | 18. | -4 |
| 4 | | | 9. | 13 | -3 | | | 94 | 76 | -6 | | | 127 | -112 | 5 | | | 116 | 121 | 3 | | | 203 | -184 | -2 | | | 87 | 31 |
| 5 | | | 43 | 52 | 4 | | | 127 | -116 | 0 | 1 | | 420 | -408 | -5 | | | 43 | 32 | -3 | | | 121 | 85 | 3 | | | 25 | -28 |
| 1 | 13 | | 71 | 67 | -4 | | | 110 | 115 | 1 | | | 6. | -2 | 0 | 9 | | 113 | 106 | 4 | | | 19. | -26 | -3 | | | 76 | 90 |
| 2 | | | 104 | 90 | 5 | | | 11. | -34 | -1 | | | 378 | 411 | 1 | | | 265 | 262 | -4 | | | 136 | -99 | 4 | | | 50 | -30 |
| 3 | | | 50 | 36 | -5 | | | 11. | 25 | 2 | | | 289 | 293 | -1 | | | 177 | 160 | 5 | | | 18. | 18 | -4 | | | 80 | 56 |
| 4 | | | 7. | 1 | 6 | | | 55 | 52 | -2 | | | 345 | 362 | 2 | | | 179 | 179 | -5 | | | 145 | -118 | 0 | 13 | | 164 | 148 |
| 0 | 14 | | 14. | 26 | -6 | | | 8. | 38 | 3 | | | 185 | 172 | -2 | | | 302 | 287 | 6 | | | 50 | 28 | 1 | | | 176 | 139 |
| 1 | | | 10. | -27 | 0 | 8 | | 56 | 62 | -3 | | | 62 | -44 | 3 | | | 71 | -39 | -6 | | | 76 | -57 | -1 | | | 113 | 80 |
| 2 | | | 43 | -33 | 1 | | | 104 | 73 | 4 | | | 94 | 95 | -3 | | | 62 | 57 | 0 | 4 | | 372 | -357 | 2 | | | 67 | -33 |
| 3 | | | 43 | -44 | -1 | | | 10. | -30 | -4 | | | 182 | -168 | 4 | | | 94 | -100 | 1 | | | 25 | -35 | -2 | | | 43 | 31 |
| 4 | | | 6. | 11 | 2 | | | 80 | 58 | 5 | | | 12. | 12 | -4 | | | 84 | -77 | -1 | | | 346 | 380 | 3 | | | 177 | -151 |
| 1 | 15 | | 166 | 169 | -2 | | | 113 | -127 | -5 | | | 143 | -144 | 5 | | | 71 | -64 | 2 | | | 259 | 274 | -3 | | | 87 | -63 |
| 2 | | | 143 | 156 | 3 | | | 11. | -33 | 6 | | | 62 | -57 | -5 | | | 94 | -93 | -2 | | | 56 | 71 | 4 | | | 8. | -103 |
| 3 | | | 50 | 60 | -3 | | | 67 | -52 | -6 | | | 43 | -44 | 0 | 10 | | 166 | -155 | 3 | | | 173 | 188 | -4 | | | 107 | -90 |
| 0 | 16 | | 50 | 47 | 4 | | | 91 | -82 | 0 | 2 | | 194 | -179 | 1 | | | 139 | -118 | -3 | | | 226 | -174 | 0 | 14 | | 152 | -141 |
| 1 | | | 35 | 27 | -4 | | | 94 | 86 | 1 | | | 104 | 103 | -1 | | | 143 | -151 | 4 | | | 50 | -35 | 1 | | | 121 | -91 |
| 2 | | | 6. | 1 | 5 | | | 50 | -58 | -1 | | | 289 | -280 | 2 | | | 67 | 64 | -4 | | | 184 | -184 | -1 | | | 127 | 115 |
| 1 | 17 | | 62 | 79 | -5 | | | 62 | 68 | 2 | | | 145 | 153 | -2 | | | 50 | -31 | 5 | | | 127 | -98 | 2 | | | 14. | 6 |
| 0 | 1 | 1 | 38 | -10 | 6 | | | 6. | -19 | -2 | | | 43 | 26 | 3 | | | 143 | 138 | -5 | | | 104 | -69 | -2 | | | 56 | -40 |
| 1 | | | 876 | -894 | -6 | | | 8. | 21 | 3 | | | 71 | 55 | -3 | | | 107 | 91 | 6 | | | 11. | -35 | 3 | | | 84 | 60 |
| -1 | | | 1072 | 1030 | 0 | 9 | | 116 | 111 | -3 | | | 148 | 125 | 4 | | | 67 | 69 | -6 | | | 71 | 46 | -3 | | | 160 | -151 |
| 2 | | | 294 | 326 | 1 | | | 104 | -88 | 4 | | | 13. | 7 | -4 | | | 84 | 95 | 0 | 5 | | 355 | 306 | -4 | | | 121 | -118 |

Table 5 (*cont.*)

| h | k | l | $10F_o$ | $10F_c$ |
|---|---|---|---|---|
| 0 | 15 | 3 | 15. | 12 |
| 1 | | | 67 | 42 |
| -1 | | | 15. | 9 |
| 2 | | | 43 | 30 |
| -2 | | | 14. | -8 |
| 0 | 16 | | 91 | -97 |
| 1 | | | 56 | -42 |
| -1 | | | 87 | 67 |
| 0 | 0 | 4 | 406 | 400 |
| 1 | | | 154 | -121 |
| -1 | | | 482 | 492 |
| 2 | | | 84 | -53 |
| -2 | | | 127 | -84 |
| 3 | | | 80 | -54 |
| -3 | | | 501 | -548 |
| 4 | | | 94 | -65 |
| -4 | | | 233 | -254 |
| 5 | | | 22. | -3 |
| -5 | | | 129 | 118 |
| 6 | | | 13. | 17 |
| -6 | | | 148 | 156 |
| 0 | 1 | | 62 | 55 |
| 1 | | | 104 | 103 |
| -1 | | | 141 | -163 |
| 2 | | | 84 | -69 |
| -2 | | | 393 | -364 |
| 3 | | | 210 | -208 |
| -3 | | | 50 | 23 |
| 4 | | | 145 | -138 |
| -4 | | | 158 | 146 |
| 5 | | | 15. | 5 |
| -5 | | | 121 | 104 |
| 6 | | | 16. | 56 |
| -6 | | | 35 | 40 |
| 0 | 2 | | 107 | -58 |
| 1 | | | 124 | -110 |
| -1 | | | 160 | 133 |
| 2 | | | 13. | -20 |
| -2 | | | 62 | 30 |
| 3 | | | 16. | 9 |
| -3 | | | 121 | -108 |
| 4 | | | 17. | 9 |
| -4 | | | 43 | -41 |
| 5 | | | 15. | 20 |
| -5 | | | 17. | 29 |
| 6 | | | 8. | 13 |
| -6 | | | 25 | 34 |
| 0 | 3 | | 426 | 414 |
| 1 | | | 336 | 370 |
| -1 | | | 227 | -232 |
| 2 | | | 94 | -85 |
| -2 | | | 80 | -88 |
| 3 | | | 350 | -378 |
| -3 | | | 226 | 215 |
| 4 | | | 242 | -236 |
| -4 | | | 179 | 175 |
| 5 | | | 25 | 9 |
| -5 | | | 67 | 50 |
| -6 | | | 25 | 4 |
| 0 | 4 | | 243 | -241 |
| 1 | | | 219 | -218 |
| -1 | | | 110 | 136 |
| 2 | | | 116 | -120 |
| -2 | | | 317 | 298 |
| 3 | | | 43 | 52 |
| -3 | | | 260 | 245 |
| 4 | | | 71 | 86 |
| -4 | | | 43 | 43 |
| 5 | | | 14. | 33 |
| -5 | | | 94 | -84 |
| 6 | | | 80 | -94 |
| 0 | 5 | | 11. | -11 |
| 1 | | | 80 | 81 |
| -1 | | | 110 | 112 |
| 2 | | | 84 | 89 |
| -2 | | | 242 | 208 |
| 3 | | | 16. | -7 |
| -3 | | | 14. | 5 |
| 4 | | | 38 | -26 |
| -4 | | | 71 | -59 |
| 5 | | | 21 | 3 |
| -5 | | | 98 | -106 |
| 6 | | | 80 | -71 |
| 0 | 6 | | 118 | -88 |
| 1 | | | 87 | 80 |
| -1 | | | 228 | -213 |
| 2 | | | 168 | 162 |
| -2 | | | 56 | -43 |
| 3 | | | 76 | 72 |
| -3 | | | 143 | 125 |
| 4 | | | 16. | -44 |
| -4 | | | 101 | 103 |
| 5 | | | 80 | -63 |
| -5 | | | 43 | 25 |
| 6 | | | 50 | -57 |
| 0 | 7 | | 302 | -278 |
| 1 | | | 80 | -58 |
| -1 | | | 87 | 289 |
| 2 | | | 156 | 156 |
| -2 | | | 113 | 102 |
| 3 | | | 161 | 196 |
| -3 | | | 119 | -93 |
| 4 | | | 43 | 96 |
| -4 | | | 127 | -113 |
| 5 | | | 11. | 5 |
| -5 | | | 91 | -100 |
| 6 | | | 62 | -61 |
| 1 | 8 | | 250 | 250 |
| -1 | | | 232 | -223 |
| 2 | | | 259 | 263 |
| -2 | 8 | 4 | 280 | -270 |
| 3 | | | 43 | 39 |
| -3 | | | 143 | -141 |
| 4 | | | 76 | -123 |
| -4 | | | 56 | 54 |
| 5 | | | 87 | -103 |
| -5 | | | 101 | 93 |
| 0 | 9 | | 162 | -152 |
| 1 | | | 62 | -55 |
| -1 | | | 25 | 22 |
| 2 | | | 204 | -203 |
| 3 | | | 35 | 41 |
| -3 | | | 80 | -60 |
| 4 | | | 23 | 28 |
| -4 | | | 76 | 66 |
| 5 | | | 8 | 12 |
| -5 | | | 94 | 86 |
| -6 | | | 25 | 24 |
| 0 | 10 | | 67 | 35 |
| 1 | | | 25 | 18 |
| -1 | | | 50 | 56 |
| 2 | | | 17. | -21 |
| -2 | | | 17. | -24 |
| 3 | | | 15. | -20 |
| -3 | | | 80 | -69 |
| 4 | | | 12. | 2 |
| -4 | | | 16. | 30 |
| 5 | | | 23 | -9 |
| 0 | 11 | | 67 | -55 |
| 1 | | | 91 | -93 |
| -1 | | | 160 | -170 |
| 2 | | | 35 | -57 |
| -2 | | | 259 | -278 |
| 3 | | | 50 | -54 |
| -3 | | | 84 | -78 |
| 4 | | | 10. | -20 |
| -4 | | | 127 | 135 |
| -5 | | | 119 | 150 |
| 0 | 12 | | 35 | -38 |
| 1 | | | 121 | -130 |
| -1 | | | 56 | 54 |
| 2 | | | 158 | -181 |
| -2 | | | 136 | 139 |
| 3 | | | 50 | -47 |
| -3 | | | 136 | 140 |
| 4 | | | 13. | -3 |
| -5 | | | 67 | -69 |
| 0 | 13 | | 62 | 50 |
| 1 | | | 15. | 15 |
| -1 | | | 16. | -31 |
| 2 | | | 13. | -14 |
| -2 | | | 15. | 37 |
| 3 | | | 16 | -20 |
| -3 | | | 25 | 17 |
| 0 | 14 | | 71 | 56 |
| 1 | | | 71 | -68 |
| -1 | | | 87 | 87 |
| 2 | | | 94 | -128 |
| -2 | | | 80 | 83 |
| 3 | | | 19 | 30 |
| 0 | 15 | | 12. | -16 |
| 1 | | | 43 | 32 |
| -1 | | | 104 | 99 |
| 2 | | | 62 | 42 |
| -2 | | | 80 | 105 |
| 0 | 16 | | 80 | 56 |
| 0 | 1 | 5 | 250 | -243 |
| 1 | | | 190 | -192 |
| -1 | | | 182 | 190 |
| 2 | | | 50 | -26 |
| -2 | | | 434 | 409 |
| 3 | | | 35 | -21 |
| -3 | | | 225 | 227 |
| 4 | | | 12. | -3 |
| -4 | | | 136 | -139 |
| 5 | | | 9. | 17 |
| -5 | | | 176 | -193 |
| -6 | | | 98 | -94 |
| 0 | 2 | | 154 | 127 |
| 1 | | | 256 | -262 |
| -1 | | | 294 | -316 |
| 2 | | | 366 | -393 |
| -2 | | | 445 | -470 |
| 3 | | | 193 | -185 |
| -3 | | | 148 | -178 |
| 4 | | | 124 | 104 |
| -4 | | | 134 | 137 |
| 5 | | | 134 | 148 |
| -5 | | | 143 | 148 |
| -6 | | | 124 | 124 |
| 0 | 3 | | 30 | -73 |
| 1 | | | 136 | 106 |
| -1 | | | 350 | -321 |
| 2 | | | 80 | 65 |
| -2 | | | 113 | -84 |
| 3 | | | 76 | 60 |
| -3 | | | 62 | 47 |
| 4 | | | 62 | 52 |
| -4 | | | 124 | 111 |
| 5 | | | 9. | 11 |
| -5 | | | 76 | 65 |
| -6 | | | 35 | 40 |
| 0 | 4 | | 154 | 152 |
| 1 | | | 186 | -173 |
| -1 | | | 393 | -370 |
| 2 | | | 276 | -292 |
| -2 | | | 265 | -244 |
| 3 | | | 113 | -105 |
| -3 | | | 35 | 7 |
| 4 | | | 76 | [illegible] |
| -4 | 4 | 5 | 152 | 151 |
| 5 | | | 67 | 81 |
| -5 | | | 134 | 127 |
| 6 | | | 43 | 32 |
| 0 | 5 | | 25 | -23 |
| 1 | | | 154 | 159 |
| -1 | | | 327 | -308 |
| 2 | | | 113 | 100 |
| -2 | | | 226 | -208 |
| 3 | | | 35 | 30 |
| -3 | | | 25 | -5 |
| 4 | | | 11. | 11 |
| -4 | | | 104 | 109 |
| 5 | | | 8. | 0 |
| -5 | | | 110 | 116 |
| -6 | | | 53 | 92 |
| 0 | 6 | | 101 | 82 |
| 1 | | | 215 | 198 |
| -1 | | | 189 | 185 |
| 2 | | | 134 | 123 |
| -2 | | | 374 | 376 |
| 3 | | | 67 | 57 |
| -3 | | | 134 | 121 |
| 4 | | | 16 | -21 |
| -4 | | | 71 | -75 |
| 5 | | | 56 | -57 |
| -5 | | | 62 | -54 |
| -6 | | | 62 | -84 |
| 0 | 7 | | 327 | 327 |
| 1 | | | 207 | 177 |
| -1 | | | 212 | 224 |
| 2 | | | 56 | -43 |
| -2 | | | 154 | -153 |
| 3 | | | 181 | -174 |
| -3 | | | 233 | -244 |
| 4 | | | 110 | -113 |
| -4 | | | 134 | -150 |
| 5 | | | 5. | 2 |
| -5 | | | 18 | 16 |
| -6 | | | 43 | 49 |
| 0 | 8 | | 56 | 54 |
| 1 | | | 113 | 114 |
| -1 | | | 194 | 182 |
| 2 | | | 101 | 108 |
| -2 | | | 215 | 198 |
| 3 | | | 62 | 55 |
| -3 | | | 35 | 21 |
| 4 | | | 9. | -9 |
| -4 | | | 71 | -61 |
| -5 | | | 71 | -67 |
| 0 | 9 | | 132 | 124 |
| 1 | | | 12. | 7 |
| -1 | | | 228 | 216 |
| 2 | | | 71 | -73 |
| -2 | | | 110 | 101 |
| 3 | | | 110 | -114 |
| -3 | | | 76 | -77 |
| 4 | | | 67 | -77 |
| -4 | | | 98 | -114 |
| -5 | | | 62 | -64 |
| 0 | 10 | | 101 | -78 |
| 1 | | | 12. | 20 |
| -1 | | | 158 | 153 |
| 2 | | | 11. | 15 |
| -2 | | | 35 | -24 |
| 3 | | | 16 | -11 |
| -3 | | | 160 | -153 |
| 4 | | | 6. | 11 |
| -4 | | | 113 | -117 |
| -5 | | | 11 | -7 |
| 0 | 11 | | 101 | -91 |
| 1 | | | 80 | -83 |
| -1 | | | 67 | -67 |
| 2 | | | 11. | -7 |
| -2 | | | 25 | 24 |
| 3 | | | 67 | 74 |
| -3 | | | 76 | 70 |
| -4 | | | 87 | 92 |
| -5 | | | 8. | 14 |
| 0 | 12 | | 43 | -40 |
| 1 | | | 11. | -13 |
| -1 | | | 12. | 4 |
| 2 | | | 35 | -20 |
| -2 | | | 71 | -60 |
| 3 | | | 25 | -19 |
| -3 | | | 80 | -87 |
| -4 | | | 43 | -46 |
| -5 | | | 43 | 37 |
| 0 | 13 | | 134 | -173 |
| 1 | | | 124 | -122 |
| -1 | | | 113 | -130 |
| 2 | | | 50 | 58 |
| -2 | | | 10. | -7 |
| -3 | | | 96 | 119 |
| -4 | | | 80 | 117 |
| 0 | 14 | | 56 | 52 |
| 1 | | | 25 | 22 |
| -1 | | | 50 | -40 |
| 2 | | | 6. | 4 |
| -2 | | | 43 | 56 |
| -3 | | | 50 | 57 |
| 0 | 15 | | 7. | -33 |
| 1 | | | 35 | -30 |
| -1 | | | 43 | 30 |
| -2 | | | 35 | 31 |
| -3 | | | 2. | [illegible] |
| 0 | 0 | 6 | 3. | -52 |
| 1 | | | 101 | 83 |
| -1 | | | 80 | -85 |
| 2 | | | 13. | [illegible] |
| -2 | 0 | 6 | 56 | -55 |
| 3 | | | 121 | -92 |
| -3 | | | 177 | 134 |
| 4 | | | 94 | -54 |
| -4 | | | 267 | 256 |
| 5 | | | 9. | 10 |
| -5 | | | 25 | -4 |
| -6 | | | 179 | -180 |
| 0 | 1 | | 217 | -202 |
| 1 | | | 84 | -79 |
| -1 | | | 156 | 142 |
| 2 | | | 10 | 9 |
| 3 | | | 127 | 125 |
| -3 | | | 145 | -157 |
| 4 | | | 80 | 87 |
| -4 | | | 91 | -84 |
| 5 | | | 9. | 10 |
| -5 | | | 84 | -57 |
| -6 | | | 13. | 5 |
| 0 | 2 | | 67 | 44 |
| 1 | | | 12. | 18 |
| -1 | | | 7. | -24 |
| 2 | | | 14. | -6 |
| -2 | | | 50 | -37 |
| 3 | | | 15. | -2 |
| -3 | | | 50 | 50 |
| 4 | | | 13. | -13 |
| -4 | | | 80 | 67 |
| 5 | | | 8. | -21 |
| -5 | | | 15. | 6 |
| -6 | | | 35 | -39 |
| 0 | 3 | | 433 | -446 |
| 1 | | | 212 | -195 |
| -1 | | | 279 | 256 |
| 2 | | | 153 | 126 |
| -2 | | | 148 | -136 |
| 3 | | | 247 | 231 |
| -3 | | | 302 | -323 |
| 4 | | | 134 | 123 |
| -4 | | | 152 | -133 |
| 5 | | | 18 | -19 |
| -5 | | | 43 | -30 |
| -6 | | | 43 | 94 |
| 0 | 4 | | 141 | 139 |
| 1 | | | 94 | 87 |
| -1 | | | 173 | -153 |
| 2 | | | 67 | 54 |
| -2 | | | 278 | -267 |
| 3 | | | 87 | 82 |
| -3 | | | 145 | -137 |
| 4 | | | 13. | 34 |
| -4 | | | 35 | -33 |
| 5 | | | 25 | -40 |
| -5 | | | 84 | 66 |
| -6 | | | 121 | 121 |
| 0 | 5 | | 56 | 53 |
| 1 | | | 80 | -73 |
| -1 | | | 170 | -160 |
| 2 | | | 14. | -14 |
| -2 | | | 91 | -81 |
| 3 | | | 50 | 34 |
| -3 | | | 104 | 111 |
| 4 | | | 25 | -16 |
| -4 | | | 50 | 48 |
| -5 | | | 50 | 52 |
| 0 | 6 | | 62 | 39 |
| 1 | | | 84 | -69 |
| -1 | | | 118 | 108 |
| 2 | | | 87 | -81 |
| 3 | | | 14. | 14 |
| -3 | | | 94 | -78 |
| 4 | | | 80 | 60 |
| -4 | | | 76 | -78 |
| -5 | | | 56 | -39 |
| 0 | 7 | | 234 | 228 |
| 1 | | | 14. | 12 |
| -1 | | | 297 | -256 |
| 2 | | | 62 | -64 |
| -2 | | | 14. | 27 |
| 3 | | | 76 | -82 |
| -3 | | | 198 | 205 |
| 4 | | | 84 | -77 |
| -4 | | | 119 | 110 |
| -5 | | | 56 | 46 |
| 0 | 8 | | 76 | -49 |
| 1 | | | 131 | -174 |
| -1 | | | 246 | 235 |
| 2 | | | 162 | -164 |
| -2 | | | 237 | 270 |
| 3 | | | 67 | -66 |
| -3 | | | 91 | 84 |
| 4 | | | 43 | 59 |
| -4 | | | 50 | -63 |
| 5 | | | 107 | -102 |
| 0 | 9 | | 15. | 11 |
| 1 | | | 15. | 7 |
| -1 | | | 15. | 5 |
| 2 | | | 15. | -10 |
| -2 | | | 71 | 71 |
| 3 | | | 12. | 20 |
| -3 | | | 15. | 15 |
| -4 | | | 14. | -13 |
| -5 | | | 67 | -71 |
| 0 | 10 | | 15. | -21 |
| 1 | | | 14. | -21 |
| -1 | | | 15. | 10 |
| 2 | | | 50 | -14 |
| -2 | | | 71 | 67 |
| 3 | | | 10. | -28 |
| 4 | | | 15. | 5 |
| -5 | 10 | 6 | 10. | -4 |
| 0 | 11 | | 14. | 7 |
| 1 | | | 15. | 13 |
| -1 | | | 71 | 64 |
| 2 | | | 12. | [illegible] |
| -2 | | | 76 | 77 |
| 3 | | | 8. | 11 |
| -3 | | | 13. | 31 |
| -4 | | | 62 | -51 |
| -5 | | | 101 | -110 |
| 0 | 12 | | 13. | 4 |
| 1 | | | 91 | 101 |
| -1 | | | 116 | -114 |
| 2 | | | 94 | 123 |
| -2 | | | 107 | -113 |
| -3 | | | 56 | -56 |
| -4 | | | 10 | 15 |
| 0 | 13 | | 12. | 13 |
| 1 | | | 10. | 0 |
| -1 | | | 12. | -13 |
| -2 | | | 12. | -6 |
| -3 | | | 10. | 22 |
| -4 | | | 7. | -3 |
| 0 | 14 | | 10. | -22 |
| 1 | | | 76 | 106 |
| -1 | | | 129 | -127 |
| -2 | | | 113 | -122 |
| -1 | 15 | | 50 | -63 |
| 0 | 1 | 7 | 43 | 17 |
| 1 | | | 62 | -63 |
| -1 | | | 127 | 122 |
| 2 | | | 76 | -69 |
| -2 | | | 80 | 80 |
| 3 | | | 50 | -40 |
| -3 | | | 139 | -116 |
| 4 | | | 14. | 9 |
| -4 | | | 14. | 1 |
| -5 | | | 101 | 103 |
| -6 | | | 11. | 26 |
| 0 | 2 | | 35 | 36 |
| 1 | | | 266 | 325 |
| -1 | | | 256 | 291 |
| 2 | | | 207 | 231 |
| -2 | | | 310 | 358 |
| 3 | | | 50 | 44 |
| -3 | | | 182 | 170 |
| 4 | | | 35 | -61 |
| -4 | | | 35 | -36 |
| -5 | | | 156 | -156 |
| -6 | | | 139 | -178 |
| 0 | 3 | | 108 | 93 |
| 1 | | | 56 | 59 |
| -1 | | | 104 | 74 |
| 2 | | | 23. | 15 |
| -2 | | | 116 | -80 |
| 3 | | | 21. | -24 |
| -3 | | | 84 | -53 |
| 4 | | | 15. | -52 |
| -4 | | | 101 | -67 |
| -5 | | | 43 | -33 |
| -6 | | | 17. | 16 |
| 0 | 4 | | 14. | 14 |
| 1 | | | 215 | 223 |
| -1 | | | 260 | 229 |
| 2 | | | 136 | 174 |
| -2 | | | 226 | 209 |
| 3 | | | 13. | -3 |
| -3 | | | 62 | 48 |
| 4 | | | 43 | -77 |
| -4 | | | 67 | -46 |
| -5 | | | 113 | -95 |
| -6 | | | 62 | -50 |
| 0 | 5 | | 56 | 48 |
| 0 | 6 | | 87 | -82 |
| 0 | 7 | | 271 | -270 |
| 0 | 8 | | 56 | -48 |
| 0 | 9 | | 136 | -130 |
| 0 | 10 | | 13. | 29 |
| 0 | 11 | | 119 | 113 |
| 0 | 12 | | 11. | 0 |
| 0 | 13 | | 158 | 178 |
| 0 | 0 | 8 | 136 | -146 |
| 1 | | | 25. | 0 |
| -1 | | | 134 | -124 |
| 2 | | | 104 | 69 |
| -2 | | | 94 | 78 |
| 3 | | | [illegible] | 67 |
| -3 | | | 25. | 32 |
| 4 | | | [illegible] | 54 |
| -4 | | | 101 | -35 |
| 5 | | | 56 | 59 |
| -6 | | | 91 | 86 |
| 0 | 1 | | 152 | 142 |
| 1 | | | 110 | 100 |
| -1 | | | 14. | -18 |
| 2 | | | 35 | -22 |
| -2 | | | 50 | 40 |
| 3 | | | 67 | -57 |
| -3 | | | 104 | 104 |
| 4 | | | 5. | [illegible] |
| -4 | | | 94 | 100 |
| -5 | | | 71 | 53 |
| -6 | | | 62 | -50 |
| 0 | 2 | | 15. | -30 |
| 1 | | | 15. | -16 |
| -1 | | | [illegible] | 0 |
| 2 | | | 17. | -13 |
| -2 | | | 43 | [illegible] |
| 3 | | | 14. | [illegible] |
| -3 | | | [illegible] | [illegible] |
| 4 | 2 | 8 | 9. | 22 |
| -4 | | | 43 | -30 |
| -5 | | | 25 | -24 |
| -6 | | | 12. | 13 |
| 0 | 3 | | 306 | 302 |
| 1 | | | 170 | 133 |
| -1 | | | 179 | -149 |
| 2 | | | 132 | -90 |
| -2 | | | 139 | 86 |
| 3 | | | 116 | -115 |
| -3 | | | 247 | 236 |
| -4 | | | 198 | 195 |
| -5 | | | 67 | 57 |
| -6 | | | 76 | -93 |
| 0 | 4 | | 43 | 40 |
| 1 | | | 54 | -59 |
| -1 | | | 156 | 151 |
| 2 | | | 67 | -30 |
| -2 | | | 145 | 130 |
| 3 | | | 10. | -68 |
| -3 | | | 94 | 73 |
| 4 | | | 12. | -21 |
| -5 | | | 129 | -132 |
| -6 | | | 94 | -80 |
| 0 | 5 | | 43 | 41 |
| 0 | 6 | | 43 | 43 |
| 0 | 7 | | 121 | -121 |
| 0 | 8 | | 14. | -9 |
| 0 | 9 | | 62 | -35 |
| 0 | 10 | | 11. | -22 |
| 0 | 11 | | 10. | 16 |
| 0 | 1 | 9 | 14. | 25 |
| 1 | | | 98 | 104 |
| -1 | | | 90 | -89 |
| 2 | | | 84 | 79 |
| -2 | | | 104 | -107 |
| 3 | | | 43 | 29 |
| -3 | | | 25 | -27 |
| -4 | | | 25 | -32 |
| -5 | | | 11. | -4 |
| -6 | | | 35 | 27 |
| 0 | 2 | | 35 | 46 |
| 1 | | | 121 | -128 |
| -1 | | | 158 | -153 |
| 2 | | | 94 | -127 |
| -2 | | | 170 | -164 |
| 3 | | | 9. | -20 |
| -3 | | | 110 | -78 |
| -4 | | | 101 | 89 |
| -5 | | | 113 | 135 |
| 0 | 3 | | 43 | -43 |
| 1 | | | 22. | -72 |
| 2 | | | 17. | -27 |
| -2 | | | 22. | 28 |
| 3 | | | 9. | 23 |
| -3 | | | 110 | 73 |
| -4 | | | 132 | 108 |
| -5 | | | 17. | 1 |
| 0 | 4 | | 84 | -75 |
| 1 | | | 94 | -139 |
| -1 | | | 84 | -92 |
| 3 | | | 6. | 41 |
| -3 | | | 14. | -57 |
| -4 | | | 12. | 33 |
| -5 | | | 84 | 69 |
| 0 | 5 | | 20. | -22 |
| 0 | 6 | | 80 | -68 |
| 0 | 7 | | 129 | 129 |
| 0 | 8 | | 67 | 25 |
| 0 | 9 | | 119 | 77 |
| 0 | 0 | 10 | 119 | 139 |
| 1 | | | 101 | 89 |
| -1 | | | 104 | 81 |
| 2 | | | 13. | -25 |
| -2 | | | 22. | -25 |
| -3 | | | 113 | -93 |
| -4 | | | 101 | -80 |
| 5 | | | 14. | -45 |
| 0 | 1 | | 84 | -84 |
| 1 | | | 62 | -66 |
| -1 | | | 13. | 27 |
| 2 | | | 7. | -3 |
| -2 | | | 80 | -55 |
| -3 | | | 121 | -130 |
| -4 | | | 71 | -63 |
| 0 | 2 | | 12. | 25 |
| 1 | | | 13. | 22 |
| -1 | | | 16. | 17 |
| 2 | | | 9. | 11 |
| -2 | | | 17. | -17 |
| -3 | | | 43 | -35 |
| -4 | | | 14. | -12 |
| 0 | 3 | | 136 | -145 |
| 1 | | | 16. | -45 |
| -1 | | | 152 | 128 |
| 2 | | | 9. | 43 |
| -2 | | | 20. | -29 |
| -3 | | | 179 | -191 |
| -4 | | | 113 | -136 |
| 0 | 4 | | 80 | -75 |
| 1 | | | 43 | -47 |
| -1 | | | 25 | -48 |
| 0 | 5 | | 13. | -20 |
| 0 | 6 | | 67 | -35 |
| 0 | 7 | | 43 | 52 |
| 2 | 1 | 11 | 87 | 114 |
| -2 | | | 50 | 61 |
| [illegible] | | | 35 | -27 |

gesting this work and for the preparing the crystals. Thanks are due to Dr K. Sasvári for his valuable suggestions, to Mrs J. Matkó for measuring the intensities and to the team of the Centro di Calcolo Elettronico of the University of Parma for the calculations. A fellowship for four months was granted by the Italian Government.

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# Sodium Silicate Hydrates. III. The Crystal Structure of $Na_2O.SiO_2.6H_2O$ and of the Isostructural $Na_2O.GeO_2.6H_2O$.

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A new sodium germanate hydrate, of oxide formula $Na_2O.GeO_2.6H_2O$, has been prepared and found to be isostructural with the silicate $Na_2O.SiO_2.6H_2O$. A complete structure analysis of both compounds has been carried out with three-dimensional data, with a view to extending the structural knowledge of sodium silicate hydrates, comparing interatomic bond distances and investigating the hydrogen bond systems. The silicon and germanium atoms are each surrounded tetrahedrally by four oxygen atoms. The tetrahedra being interconnected by fairly short hydrogen bonds. At least some of the hydrogen atoms seem to show a statistical distribution such that between two and three are associated with each silicon–oxygen or germanium–oxygen tetrahedron. The sodium atoms are in approximately octahedral coordination, the octahedra alternately sharing faces and corners to form sheets.

## Introduction

A previous structural study of $Na_2O.SiO_2.9H_2O$ (Jamieson & Dent Glasser, 1966*b*) has shown that this compound contains $(H_2SiO_4)^{2-}$ groups. As a continuation of work in this field, the structure of the hexahydrate was next investigated, to find if the anions differed and to compare bond distances.

As silicon, sodium and oxygen do not differ greatly in scattering power, it was thought that if an isostructural germanate could be prepared the structure determination would be simplified, because of the presence of the comparatively heavy germanium atom. Prior to this study, only one sodium germanate hydrate was known – $Na_2O.GeO_2.7H_2O$ (Pugh, 1926; Nowotny & Szekely, 1952) – for which there is no corresponding silicate. Weight-loss determinations on $Na_2O.GeO_2.7H_2O$ (Schwarz & Heinrich, 1932) suggest the existence of a hexahydrate.

## Experimental

The $Na_2O.SiO_2.6H_2O$ crystals used in this study were prepared as described in part I (Jamieson & Dent Glasser, 1966*a*). The crystals did not have very regular geometrical forms; the one selected for intensity measurement was not greater than 0.3 mm in its longest dimension.

For preparation of the germanate hydrate, mixtures of sodium hydroxide and germanium dioxide were first fused in a platinum crucible at 1250 °C. $Na_2O:GeO_2$ molar ratios were (i) 1.36:1 (ii) 1.57:1 and (iii) 1.84:1. The quenched material was divided into portions, a different volume of water being added to each. Many of the preparations yielded crystals of $Na_2O.GeO_2.7H_2O$ as identified by X-ray single-crystal and powder photographs and checked by chemical analysis. One solution [4.5 g of melt (ii) in 8 ml of water] which for the silicate series would be expected to yield $Na_2O.SiO_2.9H_2O$ was seeded with crystals of this. In a short time, very large clear crystals had grown, but as soon as these were handled in any way, they turned cloudy,

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