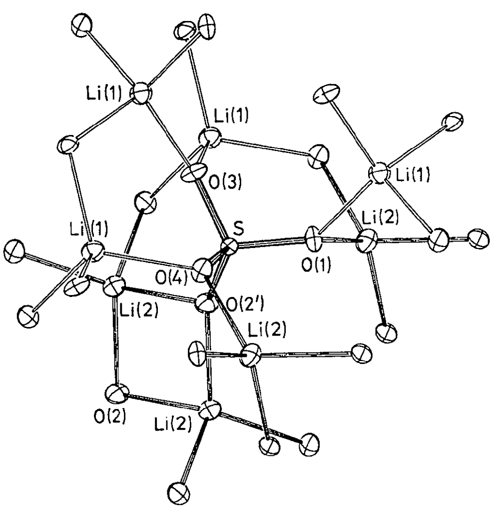

Fig. 1. An *ORTEP* diagram of part of the $\beta$-$Li_2SO_4$ structure, with one sulphate ion connected to eight $LiO_4$ tetrahedra. The edge shared between two $LiO_4$ tetrahedra, O(2)–O(2′), is 2·737 (2) Å. The angle O(2)–Li(2)–O(2′) is 88·6 (1)°.

The crystal structure is built up of $SO_4$ and $LiO_4$ tetrahedra. The $SO_4$ tetrahedra are almost regular with the S–O distances in the range 1·470 (1) to 1·478 (1) Å. There are two different kinds of $LiO_4$ tetrahedra. One of these, around Li(1), is almost regular with O–Li(1)–O angles within 106·5 (1)–115·2 (1)°; the other, around Li(2), is somewhat more distorted with O–Li(2)–O angles within 88·6 (1)–124·6 (1)°. All the $LiO_4$ tetrahedra are more nearly regular than suggested by Albright (1932), who deduced the lithium atom positions solely from spatial considerations. Some interatomic distances and angles are given in Table 2.

Each oxygen in the structure is linked to one sulphur and two lithium atoms, *i.e.* each $SO_4$ tetrahedron is connected with eight $LiO_4$ tetrahedra. Mostly the tetrahedra share corners; however, two adjacent $Li(2)O_4$ tetrahedra share an edge as shown in Fig. 1. The edge-sharing O–O distance is only 2·737 (2) Å, in contrast with 3·105 (1)–3·467 (1) Å for the other O–O distances within the $LiO_4$ tetrahedra. The angle O(2)–Li(2)–O(2′) (*cf.* Fig. 1) is 88·6 (1)°. Further details of this work are available from the author.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the* $\beta$-$Li_2SO_4$ *structure*

The distances marked with an asterisk have been corrected for thermal vibrations according to the riding-motion model (Busing & Levy, 1964).

| | This work | This work | Alcock, Evans & Jenkins (1973) |
|---|---|---|---|
| S–O(1) | 1·470 (1) | 1·474* | 1·468 (4) |
| –O(2) | 1·471 (1) | 1·476* | 1·479 (3) |
| –O(3) | 1·478 (1) | 1·482* | 1·470 (4) |
| –O(4) | 1·473 (1) | 1·476* | 1·471 (5) |
| Average | 1·473 | 1·477* | 1·472 |
| Li(1)–O(1) $(x-\frac{1}{2},\frac{1}{2}-y,z)$ | | 1·963 (3) | 1·98 (1) |
| –O(3) $(x,1+y,z)$ | | 1·975 (2) | 1·98 (1) |
| –O(3) $(\frac{1}{2}-x,\frac{1}{2}+y,1-z)$ | | 1·914 (3) | 1·91 (1) |
| –O(4) $(x,y,z)$ | | 1·975 (2) | 1·94 (1) |
| Average | | 1·957 | 1·95 |
| Li(2)–O(1) $(x,1+y,z)$ | | 1·962 (2) | 1·94 (1) |
| –O(2) $(\frac{1}{2}-x,\frac{1}{2}+y,-z)$ | | 1·929 (3) | 1·93 (1) |
| –O(2) $(\frac{1}{2}+x,\frac{1}{2}-y,z)$ | | 1·990 (2) | 1·98 (1) |
| –O(4) $(x,y,z)$ | | 1·980 (2) | 1·99 (1) |
| Average | | 1·965 | 1·96 |
| O(1)–S–O(2) | | 109·0 (1) | 108·8 (2) |
| O(1)–S–O(3) | | 110·0 (1) | 109·6 (2) |
| O(1)–S–O(4) | | 109·7 (1) | 110·4 (2) |
| O(2)–S–O(3) | | 107·7 (1) | 108·0 (2) |
| O(2)–S–O(4) | | 110·9 (1) | 110·7 (2) |
| O(3)–S–O(4) | | 109·6 (1) | 109·5 (3) |

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## Refinement of the 2*H* GaS β-type.

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GaS $\beta$, hexagonal, space group $P6_3/mmc$, $a=3{\cdot}587$ (3), $c=15{\cdot}492$ (7) Å, $Z=4$. The mean atomic distances in the layers are: Ga–Ga = 2·447 (9), Ga–S = 2·334 (4) and S–S = 4·599 (18) Å. The mean atomic distances between the layers are: S–S = 3·768 (11) and Ga–S = 4·223 (14) Å. The interlayer S–S distance is more than twice the van der Waals radius.

### Introduction

GaS crystallizes only in the 2*H* $\beta$ structure, as determined by Hahn (1953), Hahn & Frank (1955) and Terhell & Lieth (1971). Because an exact knowledge of the interatomic distances is important for band-structure calculations (Bourdon, 1976), we thought that a structure determination of higher accuracy would be of interest.

We used needle crystals grown by vacuum sublimation. The data crystal was a hexagonal prism with a length and diameter of 0·09 mm. The space group $P6_3/mmc$ was confirmed during refinement of the structure. The lattice parameters obtained, $a = 3{\cdot}587\,(3)$ and $c = 15{\cdot}492\,(7)$ Å, are in good agreement with the values of Hahn & Frank (1955) and Terhell & Lieth (1971).

Data were collected with Mo $K\alpha$ radiation on a four-circle diffractometer (PW 1100 Philips) equipped with a graphite-crystal incident monochromator. The $\theta$–$2\theta$ scan technique was used. The scan rate was 0·01° $s^{-1}$ and the scan range, $a + b\mathrm{tg}\theta$ with $a = 0{\cdot}9$ and $b = 0{\cdot}2$. 309 independent and non-zero reflexions (using the maximum value of two equivalent reflexions $hkl$ and $khl$) up to a maximum $2\theta$ value of 100° were collected.

The intensities of three reflexions were measured every hour to check crystal stability and movement. Lorentz and polarization corrections were applied to the data. An absorption correction was not made because of the small crystal dimensions ($\mu R < 1$). 261 reflexions with $F_o^2 \geq 3\sigma(F_o^2)$ were used in the refinement. The parameter $p$ for the calculation of standard deviations was set equal to 0·04 (Cotton, Deganello, Frenz & Shaver, 1973).

The computer programs *ORFLS* (Busing, Martin & Levy, 1962) and *ORFFE* (Busing, Martin & Levy, 1964), written for the IBM 168, were used.

The crystal has the space group $P6_3/mmc$ as found by Hahn & Frank (1955) with a two-layer structure with the sequence

$$\underbrace{A \quad B \quad A} \; . \; . \; . \; . \; .$$

In the asymmetric unit there is one independent Ga atom and one independent S atom in the Wyckoff position $4(f)$ for which only the $z$ coordinate is variable. Two cycles of anisotropic refinement yielded agreement indices: $R_1 = 0{\cdot}089$, $R_2 = 0{\cdot}118$. The scattering factors were taken from Cromer & Waber (1974). The final coordinates and the thermal parameters are given in Table 1.*

From the values of Table 1 we have calculated the r.m.s. components of thermal displacement, which reduce to two independent terms because of the point symmetry $3m$: $r_1$ in the plane perpendicular to the $c$ axis and $r_2$ along the $c$ axis. These values are:

| | $r_1$ | $r_2$ |
|---|---|---|
| Ga | 0·078 (7) | 0·090 (7) |
| S | 0·071 (7) | 0·094 (7) |

Table 1. *Positional and thermal parameters*

| | Ga | S |
|---|---|---|
| $x$ | $\frac{1}{3}$ | $\frac{1}{3}$ |
| $y$ | $\frac{2}{3}$ | $\frac{2}{3}$ |
| $z$ | 0·1710 (1) | 0·6016 (3) |
| $\beta_{11}$ | 0·0126 (8) | 0·0102 (16) |
| $\beta_{22}$ | 0·0126 (0) | 0·0102 (0) |
| $\beta_{33}$ | 0·0007 (1) | 0·0007 (1) |
| $\beta_{12}$ | 0·0055 (0) | 0·0051 (0) |
| $\beta_{13}$ | 0 | 0 |
| $\beta_{23}$ | 0 | 0 |
| $B_{\mathrm{iso\ equ.}}$ (Å$^2$) | 0·4 | 0·4 |

## Discussion

Interatomic distances found by us and calculated by using the values of $a$, $c$ and $z$ of Hahn & Frank (1955) are given in Table 2.

Table 2. *Principal interatomic distances*

| | | Present study | Hahn & Frank |
|---|---|---|---|
| Intra-layer | S—Ga | 2·334 (4) Å | 2·337 Å |
| | Ga–Ga | 2·447 (9) | 2·480 |
| | S—S | 4·599 (18) | 4·65 |
| Inter-layers | S—S | 3·768 (11) | 3·727 |
| | Ga–S | 4·223 (14) | 4·185 |

We can explain the differences between our values and those of Hahn & Frank by the higher accuracy of our refinement. The bond angles are: intralayer S–Ga–S 100·44 (0·19)°, interlayers S–S–S 56·86 (0·20)°. It is interesting to note, that the S–S interlayer distances are more than twice the van der Waals radius of S (Pauling, 1945). The Ga–Ga intralayer distances are, within the limits of error, the same for GaS and GaSe (Kuhn, Chevalier & Rimsky, 1975).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31501 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.