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# Atomic Structure of a 4*H* GaSe Polytype Named δ-Type

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GaSe $\delta$, hexagonal, space group $P6_3mc$, $a=3·755$ (3), $c=31·990$ (10) Å, $Z=8$. The mean atomic distances in the layers are: Ga–Ga = 2·457 (10), Ga–Se = 2·463 (10) and Se–Se = 4·784 (15) Å. The mean atomic distances between the layers are: Se–Se = 3·880 (15), Ga–Se = 4·392 (16) Å. The interlayer Se–Se distance is less than twice the van der Waals radius.

## Introduction

Three forms of the GaSe-structure have been reported: $\beta$ (Hahn, 1953; Jellinek & Hahn, 1961), $\varepsilon$ (Schubert, Dörre & Kluge, 1955) and $\gamma$ (Schubert *et al.*, 1955; Jellinek & Hahn, 1961). The $\beta$ and $\varepsilon$ structures are 2*H* and the $\gamma$ is 3*R*. The earlier determinations were made with crystals, the more recent determination for the $\beta$ type was made with a powder sample. As Terhell & Lieth (1972) have shown powdering destroys the low degree of ordering in the $\varepsilon$-type, and the existence of a so-called $\beta$-type GaSe observed with the aid of powder pictures is therefore in question. We never observed the $\beta$-type of pure GaSe crystals in our structure determinations. Terhell & Lieth (1971) found the $\beta$-type only in mixed crystals $GaSe_{1-x}S_x$ for $x \geq 0·25$.

The data of Jellinek & Hahn (1961) on the $\beta$-type have been used for the calculation of the band structure, see for instance Bourdon (1971, 1974) and Schlueter (1972), and the results did not coincide with the experimental determination of the gap. Thus it was 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 height and diameter of 0·24 mm. Precession and Weissenberg photographs indicated the diffraction symbol $6/m\ mm\ P6_3\,.\,c$, compatible with the three space groups: $P6_3/mmc$, $P\bar{6}2c$ and $P6_3mc$. The last space group was confirmed during refinement of the structure.

We found $a=3·755$ (3) and $c=31·990$ (10) Å in good agreement with the values of Terhell & Lieth (1971) for 2*H*GaSe. Our value of $c$ confirmed a 4*H* structure.

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 0·03° s$^{-1}$ and the scan range: $a+b$ tg $\theta$ with $a=0·8$ and $b=0·3$. 402 independent reflexions up to a maximum $2\theta$ value of 80° 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. The linear absorption coefficient for GaSe is 346 cm$^{-1}$ and a spherical absorption correction of $\mu R=4$ was applied. 298 reflexions with $F_o^2 \geq 3\sigma(F_o^2)$ were used. The parameter $p$ for the calculation of standard deviations was set equal to 0·04 (Cotton, Deganello, Frenz & Shaver, 1973).

The following computer programs written for the IBM 168 were used: *ORFLS* (Busing, Martin & Levy, 1962), *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1965).

At first we thought that our 4*H* crystal was a polytype with an $\varepsilon$- or $\beta$-structure built by two types of layers *A* and *B* but none of the possible models allowed a refinement. The crystal actually has a new four-layer structure with the sequence

$$\underbrace{\overset{\Uparrow}{}\,A\;C\;A\;B\;\overset{\Uparrow}{}}A\ldots$$

In the asymmetric unit there are four independent Ga atoms and four independent Se atoms in the Wyckoff positions 2(*a*) and 2(*b*) for which only the $z$ coordinate is variable. We fixed arbitrarily the $z$ coordinate of the first Ga atom for the definition of the origin along the $6_3$ axis. Three cycles of isotropic refinement yielded agreement indices $R_1=0·098$, $R_2=0·117$. A cycle of constrained anisotropic refinement would not change these values because all the atoms have the same point symmetry $3m$ which imposes $\beta_{11}=\beta_{22}=2\beta_{12}$ and $\beta_{23}=\beta_{13}=0$; therefore the $\beta$ tensor has two degrees of freedom ($\beta_{11}$ and $\beta_{33}$ for instance) which are equal to the limit of errors. The scattering factors were taken from Cromer & Waber (1974). Anomalous dispersion effects were included and values for $\Delta f'$ and $\Delta f''$ were those of Cromer & Liberman (1970).

The final coordinates and the thermal parameters are given in Table 1. A final difference Fourier synthesis revealed two stacking-fault peaks for Ga(3) at $z=0·2078$ and Ga(4) at $z=0·2945$ which show small displacements respectively downwards and upwards in comparison with the normal positions. These

Table 1. *Positional and thermal parameters*

| | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| Ga(1) | 0 | 0 | −0·0380 (0) | 1·7 (0·3) |
| Ga(2) | 0 | 0 | 0·0394 (6) | 0·9 (0·3) |
| Ga(3) | $\frac{1}{3}$ | $\frac{2}{3}$ | 0·2119 (7) | 1·4 (0·2) |
| Ga(4) | $\frac{1}{3}$ | $\frac{2}{3}$ | 0·2880 (6) | 1·1 (0·1) |
| Se(1) | $\frac{2}{3}$ | $\frac{1}{3}$ | −0·0745 (6) | 1·1 (0·1) |
| Se(2) | $\frac{2}{3}$ | $\frac{1}{3}$ | 0·0752 (6) | 1·3 (0·1) |
| Se(3) | 0 | 0 | 0·1781 (6) | 0·8 (0·2) |
| Se(4) | 0 | 0 | 0·3274 (6) | 1·8 (0·3) |

Table 2. *Principal interatomic distances*

| Intralayer | Interlayer | | |
|---|---|---|---|
| 1 | | Se(1) –Ga(1) | 2·465 (10) Å |
| 1 | | Ga(1)–Ga(2) | 2·476 (18) |
| 1 | | Ga(2)–Se(2) | 2·454 (10) |
| 1 | | Se(1) –Se(2) | 4·789 (15) |
| | 1–2 | Se(2) –Se(3) | 3·945 (16) |
| | 1–2 | Ga(2)–Se(3) | 4·439 (16) |
| 2 | | Se(3) –Ga(3) | 2·425 (10) |
| 2 | | Ga(3)–Ga(4) | 2·437 (18) |
| 2 | | Ga(4)–Se(4) | 2·510 (10) |
| 2 | | Se(3) –Se(4) | 4·779 (15) |
| | 2–3 | Se(4) –Se(5) | 3·816 (16) |
| | 2–3 | Se(4) –Ga(5) | 4·306 (16) |
| | 2–3 | Ga(4)–Se(5) | 4·399 (16) |

Table 3. *Bond angles*

| Intra-layer | Inter-layer | | |
|---|---|---|---|
| 1 | | Se(1)–Ga(1)–Se(1) | 99·4 (0·7)° |
| 1 | | Se(2)–Ga(2)–Se(2) | 100·0 (0·8) |
| | 1–2 | Se(2)–Se(3) –Se(2) | 56·9 (0·5) |
| 2 | | Se(3)–Ga(3)–Se(3) | 101·6 (0·8) |
| 2 | | Se(4)–Ga(4)–Se(4) | 97·0 (0·7) |
| | 2–3 | Se(4)–Se(5) –Se(4) | 59·0 (0·5) |

two maxima were less than 0·6% of the normal peaks.*

## Discussion

Fig. 1 is a stereoscopic drawing of the unit cell. Interatomic distances and bond angles are given in Tables 2 and 3. Differences between the interatomic distances Se–Ga and Ga–Ga in layers 1 and 2 and even between the Se–Se interlayer distances are observed. We are not sure whether these differences are the result of the stacking faults of Ga(3) and Ga(4) or the consequence of one Coulombic interaction between Ga(2) and Se(3) respectively from layers 1 and 2 and two Coulombic interactions between Se(4) and Ga(5) and between Ga(4) and Se(5) respectively from layers 2 and 3. It is interesting to note that the Se–Se interlayer distances are less than twice the van der Waals radius of Se (Pauling, 1945). This could explain an overlapping of their wave functions and the high mobility of holes in the direction of the *c* axis observed by Minder & Zschokke-Gränacher (1974).

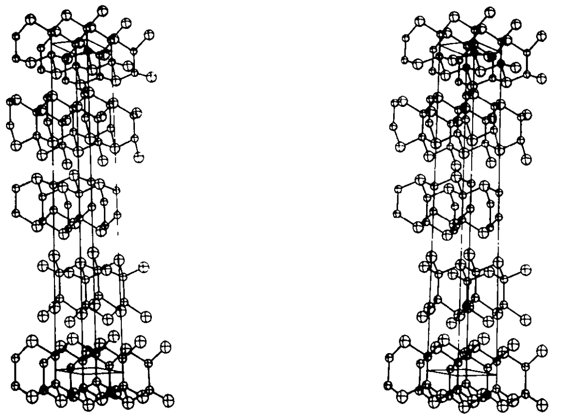

Fig. 1. A stereoscopic pair showing the three-dimensional structure of the GaSe δ-type unit cell. The *c* axis is vertical. Ga atoms are represented with a probability of 50%.

Because of the importance of the structures and interatomic distances of GaSe in solid state physics for band structure calculations, lattice dynamics, Raman scattering, *etc*., a detailed discussion of our results and a comparison with published results will be given elsewhere (Kuhn, Chevy & Chevalier, 1975).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31236 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.