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Atomic Structure of the 2*H* $GaS_{0.59}Se_{0.41}$ β-Type

BY A. KUHN

Laboratoire de Luminescence II, *Equipe de recherches, associée au CNRS, Université P. et M. Curie, 4 place Jussieu*, 75230 *Paris Cédex* 05, *France*

R. CHEVALIER AND CH. DESNOYERS

Laboratoire de Minéralogie–Cristallographie, associé au CNRS, Université P. et M. Curie, 4 place Jussieu, 75230 Paris Cédex 05, *France*

AND J. C. J. M. TERHELL

Department of Physics, Eindhoven University of Technology, Eindhoven, The Netherlands

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Abstract. β-$GaS_{0.59}Se_{0.41}$, hexagonal, space group $P6_3/mmc$, $a=3{\cdot}660$ (2), $c=15{\cdot}786$ (4) Å, $Z=4$. The mean atomic distances in the layer are: Ga–Ga = 2·447 (8), Ga–(S,Se) = 2·400 (3) and (S,Se–S,Se) = 4·722 (15) Å. The mean atomic distances between the layers are: (S,Se)–(S,Se) = 3·811 (9) and Ga–(S,Se) = 4·308 (14) Å.

Introduction. In a systematic study of interatomic distances in GaSe (Kuhn, Chevalier & Rimsky, 1975; Kuhn, Chevy & Chevalier, 1975) and GaS (Kuhn, Chevy & Chevalier, 1976*a*) for band structure calculations, we were interested in the determination of interatomic distances even in a mixed crystal with composition approximately $GaS_{0.5}Se_{0.5}$ and the $2H\beta$ structure as determined by Terhell & Lieth (1971).

Needle crystals grown by vacuum sublimation were used. The chemical composition of the $GaS_{(1-x)}Se_x$ data crystal was determined with an electron microprobe, CAMECA Model MS46. The corrections were made on computer with the program *EMPADR* VII (Rucklidge & Gasparini, 1969).

Three specimens (A_0, A_1, A_2) were analysed, representing basal cleavage lamellae from the prismatic single crystal; their sections did not exceed 250 μm. These hexagonal lamellae were stuck on a glass slide together with lamellae of the GaS and GaSe standard crystals. This mounting was simultaneously covered with a conductive layer of carbon (thickness approximately 150 Å).

The three elements Ga, S and Se were simultaneously analysed using their characteristic $K\alpha$ X-ray lines.

The beam size was less than 1 μm; an accelerating voltage of 20 kV, a specimen current of 20 nA and a counting time of 30 s for each point analysed were used.

The results of the analysis are given in Table 1. Taking into account the relative uncertainty due to the counting system the results from the three specimens are identical; the accuracy of the analysis and the homogeneity (hom. $=\sigma/\sqrt{N}$) of each specimen were checked by statistics. Each specimen exhibits good homogeneity.

The data crystal corresponds to $GaS_{0.59}Se_{0.41}$. It was a hexagonal prism with a height equal to the diameter of about 0·15 mm. The space group $P6_3/mmc$ was confirmed during refinement of the structure.

We found $a=3{\cdot}660$ (2) and $c=15{\cdot}786$ (4) Å in good agreement with the values of Terhell & Lieth (1971) for $GaS_{0.6}Se_{0.4}$.

Data were collected with Mo $K\alpha$ radiation on a four-circle diffractometer (PW 1100 Philips) equipped with a graphite-crystal incident monochromator. The θ–2θ scan technique was used. The scan rate was equal to 0·03° s^{-1} and the scan range was of the form $a+b\,\mathrm{tg}\,\theta$ with $a=0{\cdot}9$ and $b=0{\cdot}2$. We collected 357 independent and non-zero reflexions (using the maximum value of two equivalent reflexions *hkl* and *khl*) up to a maximum 2θ value of 100°. The intensities of three reflexions were measured every hour as a check on crystal stability and movement. The Lorentz–polarization correction was applied to the data. We did not apply an absorption correction because $\mu R<2$. 282

Table 1. *Results of the chemical analysis*

		Se	Ga	S	Σ
A_0	Wt %	27·04 ± 0·24	57·71 ± 0·46	15·59 ± 0·11	100·34
	At. % (base: 2 atoms)	41·0	100·2	58·8	200·0
A_1	Wt %	26·97 ± 0·38	57·56 ± 0·51	15·03 ± 0·15	99·55
	At. % (base: 2 atoms)	41·0	100·2	58·7	199·9
A_2	Wt %	26·77 ± 0·37	57·71 ± 0·46	15·54 ± 0·16	100·02
	At. % (base: 2 atoms)	41·0	100·2	58·7	199·9

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).

The crystal has the space group $P6_3/mmc$ like the β type of GaS (Hahn & Frank, 1955) with a two-layer structure and stacking sequence:

$$\underset{\uparrow \quad \uparrow}{A\ B\ A}\cdots$$

In the asymmetric unit we have one independent Ga atom and one independent ($S_{0.59}Se_{0.41}$) 'atom' in the Wyckoff position 4(*f*).

Three cycles of anisotropic refinement yielded agreement indices $R_1 = 0{\cdot}065$, $R_2 = 0{\cdot}073$. The scattering factors were taken from Cromer & Waber (1974). The refinement of the structure was made with a form factor $f = 0{\cdot}59f_S + 0{\cdot}41f_{Se}$. The final coordinates and the thermal parameters are given in Table 2.*

Table 2. *Positional and thermal parameters*

	Ga	$S_{0.59}Se_{0.41}$
x	$\frac{1}{3}$	$\frac{1}{3}$
y	$\frac{2}{3}$	$\frac{2}{3}$
z	0·1725 (1)	0·6004 (1)
β_{11}	0·0136 (7)	0·0119 (8)
β_{22}	0·0136 (7)	0·0119 (8)
β_{33}	0·0010 (1)	0·0011 (1)
β_{12}	0·0068 (3)	0·0060 (4)
β_{23}	0	0
β_{13}	0	0
$B_{\text{iso equ.}}$ (Å^2)	0·7	0·7

From the values in Table 2 we calculated the r.m.s. components of thermal displacement, which reduce to two independent terms as a result of the point symmetry 3*m*, r_1 in the plane perpendicular to the *c* axis and r_2 along the *c* axis:

	r_1	r_2
Ga	0·085 (8) Å	0·113 (2) Å
$S_{0.59}+Se_{0.41}$	0·081 (8)	0·121 (3)

A final difference Fourier synthesis did not reveal any stacking fault.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31705 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Principal interatomic distances*

Intra layer	Inter layers	Atoms	Distances
1		(S,Se)–Ga	2·400 (3) Å
1		Ga–Ga	2·447 (8)
1		(S,Se)–(S,Se)	4·722 (15)
	1–2	(S,Se)–(S,Se)	3·811 (9)
	1–2	Ga–(S,Se)	4·308 (14)

Table 4. *Bond angles*

Intra layer	(S,Se)–Ga–(S,Se)	99·38 (0·14)°
Inter layers	(S,Se)–(S,Se)–(S,Se)	57·40 (0·16)

Discussion. Interatomic distances and bond angles are given in Tables 3 and 4.

It is interesting to note that the Ga–Ga intralayer distances are, within the limits of error, the same for $GaS_{0.59}Se_{0.41}$ as for GaSe (Kuhn, Chevalier & Rimsky, 1975) and GaS (Kuhn, Chevy & Chevalier, 1976*a*).

Because of the importance of the interatomic distances in GaS, GaSe and $GaS_{1-x}Se_x$ in solid state physics a comparison and detailed discussion will be given elsewhere (Kuhn, Chevy & Chevalier, 1976*b*).

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References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.

Cotton, F. A., Deganello, G., Frenz, B. A. & Shaver, A. (1973). *J. Organomet. Chem.* **50**, 227–240.

Cromer, D. T. & Waber, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

Hahn, H. & Frank, G. (1955). *Z. anorg. allgem. Chem.* **278**, 340–348.

Kuhn, A., Chevalier, R. & Rimsky, A. (1975). *Acta Cryst.* B**31**, 2841–2842.

Kuhn, A., Chevy, A. & Chevalier, R. (1975). *Phys. Stat. Sol.* (*a*) **31**, 469–475.

Kuhn, A., Chevy, A. & Chevalier, R. (1976*a*). *Acta Cryst.* B**32**, 983–984.

Kuhn, A., Chevy, A. & Chevalier, R. (1976*b*). *Phys. Stat. Sol.* To be published.

Rucklidge, J. & Gasparini, E. L. (1969). *EMPADR* VII, Univ. of Toronto, unpublished report (37 pp.).

Terhell, J. C. J. M. & Lieth, R. M. A. (1971). *Phys. Stat. Sol.* (*a*) **5**, 719–724.