the same number of reflections is 0·0209 hour. Running time for the PEXRAD peripheral programs is small. In both INPUT and OUTPUT, printing time (on a 1401 machine) is additional to the times given.

It is a pleasure to thank Dr M. B. Wilk for valuable discussions of the standard deviation in the integrated intensity, Mrs G. Hansen for assistance with the FAP section of PEXRAD INPUT, Mr L. J. Cirincione for writing the IBM 1011 paper tape to magnetic tape program, and Mr J. L. Bernstein for running many calculations with these programs on the IBM 7090.

Note added in proof.— The K-values of N_j are no longer necessarily used in calculating $I(hkl)$ and $\sigma^2(I(hkl))$. Now, the program integrates from the first ten 'good' background points on one side of the principal maximum to the first ten 'good' background points on the other side of the same maximum. If this criterion is not met, the program then uses all K points.

References

Abrahams, S. C. (1962). *Rev. Sci. Instrum.* **33**, 973.

Bond, W. L. (1959). *International Tables for X-ray Crystallography*, II. Birmingham: Kynoch Press.

Buerger, M. J. (1960). *Crystal Structure Analysis*. New York: Wiley.

Prewitt, C. T. (1960). *Z. Kristallogr.* **114**, 355.

Sautter, J. (1961). Private communication.

Acta Cryst. (1963). **16**, 946

The Crystal Structure of α-Ga_2S_3

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The structure of α-Ga_2S_3 has been determined from single-crystal and powder diffraction data. The unit cell is monoclinic, space group Cc, $a = 11{\cdot}14_0$, $b = 6{\cdot}41_1$, $c = 7{\cdot}03_8$ Å, $\beta = 121{\cdot}22°$, and $Z = 4$. The structure, which is based on wurtzite with 4 cation vacancies per cell, differs from that proposed by Hahn & Frank mainly in the disposition of the vacant sites. Shrinkage of sulphur tetrahedra around these sites leads to some distortion from ideal close packing.

1. The unit cell and space group

The crystal structure of α-Ga_2S_3 was determined by Hahn & Frank (1955) as hexagonal, the sulphur atoms being in hexagonally close-packed layers perpendicular to the c axis and the gallium atoms filling some of the tetrahedral positions occupied by Zn in the wurtzite structure. Later, Goodyear, Duffin & Steigmann (1961) showed that the space lattice really has monoclinic symmetry, the unit cell being centred on the C face. They also pointed out that the lattice spacings observed by Hahn & Frank were in fact reconcilable with a rhombohedral cell closely related to their monoclinic cell.

Goodyear *et al.* found that their cell contained 4 molecules and, because of its shape and size, they concluded that the sulphur atoms must be nearly hexagonally close-packed in layers perpendicular to the $[\bar{1}01]$ axis. However, they did not consider the conventional and most convenient cell, which is formed by taking a new a axis along the [102] direction, giving new cell parameters $a = 11{\cdot}14_0$, $b = 6{\cdot}41_1$, $c = 7{\cdot}03_8$ Å, $\beta = 121{\cdot}22°$. The relation between the two cells is shown in Fig. 1; the conventional cell is still centred on the C face and the close-packed sulphur layers would now lie parallel to the (001) face.

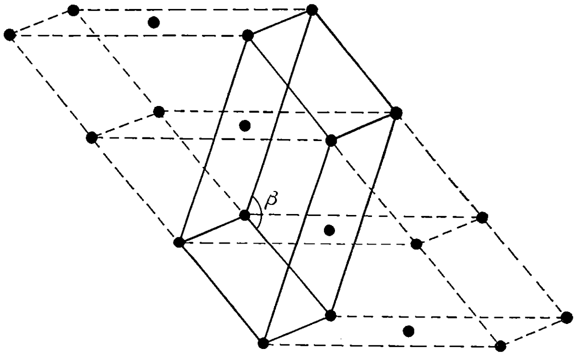

Fig. 1. The unit cell α-Ga_2S_3 (———— outline of conventional cell, - - - - outline of cell chosen by Goodyear, Duffin & Steigmann).

A quantitative inspection of the intensities of the spots on the b axis photographs indexed by Goodyear, Duffin & Steigmann has shown that the diffraction patterns were not strictly symmetrical about the zero layer line, indicating that the crystal was not oscillating about the true b axis. Consequently, these authors incorrectly indexed reflexions and assigned the structure to the wrong space group. Because of the near rhombohedral nature of the lattice, the [110] and $[\bar{1}10]$ directions in the conventional cell are pseudo-*b*-axes, and the photographs in question were taken erroneously about one of these.

Reflexions recorded on oscillation photographs about the true *b* axis have been indexed, and the systematically absent reflexions are *hkl* with $h+k$ odd, and *h*0*l* with *l* odd. The space groups compatible with these observations are $Cc\,(C_s^4)$ and $C2/c\,(C_{2h}^6)$, and a hexagonal close-packed array of sulphur atoms is possible with each. However, a qualitative survey of the intensities of *h*0*l* reflexions showed quite clearly that the cations were located in tetrahedral positions as in wurtzite, which immediately rules out the space group $C2/c\,(C_{2h}^6)$.

2. Intensity measurements

Single crystals of α-Ga_2S_3 prepared by the method described by Goodyear, Duffin & Steigmann were available for the investigation. In general, all the crystals were elongated along their [$\bar{1}$32] axes and were very thin in cross section; two such crystals were selected for study.

99 independent reflexions, from lattice planes parallel to the [$\bar{1}$10] and [$\bar{1}$32] crystal axes, were recorded on zero-layer lines of oscillation photographs taken with filtered Cu Kα radiation. The intensities of the spots were estimated visually from multiple-film exposures by comparison with a calibrated scale

Table 1. *Atomic parameters and temperature factors*

(Origin in glide-plane *C*)

	(i) Preliminary				(ii) Final			
Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)	*x*/*a*	*y*/*b*	*z*/*c*	*B* (Å^2)
Ga(1)	0·042	0·396	0·125	0·20	0·043 ± 0·001	0·400 ± 0·002	0·130 ± 0·002	1·17
Ga(2)	0·208	0·938	0·125	0·20	0·204 ± 0·001	0·935 ± 0·002	0·120 ± 0·002	0·52
S(1)	0	0·083	0	1·00	− 0·002 ± 0·002	0·081 ± 0·005	− 0·017 ± 0·004	1·33
S(2)	0·167	0·583	0	1·00	0·177 ± 0·001	0·580 ± 0·003	0·012 ± 0·003	0·62
S(3)	0·333	0·083	0	1·00	0·339 ± 0·002	0·090 ± 0·006	0·004 ± 0·005	1·35

Table 2. *Comparison of observed and calculated structure factors*

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α_c
002	191	239	56°
004	56	57	178
006	110	109	300
110	80	85	129
111	60	48	106
112	83	75	226
113	34	26	204
114	56	61	294
115	25	23	311
116	26	29	342
117	18	18	10
$11\bar{1}$	60	51	17
$11\bar{2}$	101	95	43
$11\bar{3}$	69	53	274
$11\bar{4}$	70	63	309
$11\bar{5}$	54	49	194
$11\bar{6}$	53	59	200
$11\bar{7}$	25	24	117
220	62	62	120
221	98	92	29
222	61	57	210
223	65	57	119
224	52	47	289
225	44	50	239
226	25	24	16
$22\bar{1}$	77	86	302
$22\bar{2}$	66	61	41
$22\bar{3}$	75	72	208
$22\bar{4}$	40	30	329
$22\bar{5}$	51	50	137
$22\bar{6}$	25	20	209
$22\bar{7}$	18	15	77
330	9	5	180
331	149	177	147
332	18	7	251°
333	38	39	253
334	0	7	341
335	86	81	32
$33\bar{1}$	186	259	91
$33\bar{2}$	9	4	145
$33\bar{3}$	152	160	34
$33\bar{4}$	0	5	92
$33\bar{5}$	31	39	259
$33\bar{6}$	0	5	5
$33\bar{7}$	96	91	148
440	42	48	241
441	40	47	294
442	38	39	337
443	40	52	5
444	34	32	69
$44\bar{1}$	46	50	192
$44\bar{2}$	42	45	147
$44\bar{3}$	57	58	106
$44\bar{4}$	47	42	39
$44\bar{5}$	46	46	13
$44\bar{6}$	42	41	314
$44\bar{7}$	58	48	278
550	52	52	102
551	40	47	318
552	38	33	190
553	29	37	41
$55\bar{1}$	53	55	230
$55\bar{2}$	52	49	15
$55\bar{3}$	53	59	152
$55\bar{4}$	49	44	284
$55\bar{5}$	39	41	77
$55\bar{6}$	40	28	210
660	107	93	233°
661	18	10	354
$66\bar{1}$	18	8	277
$66\bar{2}$	134	122	183
$66\bar{3}$	0	7	213
$66\bar{4}$	96	73	131
310	86	105	265
620	90	91	57
930	11	7	252
511	55	47	266
821	53	43	119
$42\bar{1}$	64	68	237
$73\bar{1}$	54	52	71
$10,4,\bar{1}$	27	27	287
402	46	39	72
712	47	46	289
$53\bar{2}$	39	38	317
$84\bar{2}$	42	33	212
$0\bar{2}3$	165	199	243
$3\bar{1}3$	38	25	80
$64\bar{3}$	81	81	179
$95\bar{3}$	72	65	90
$51\bar{4}$	47	53	158
$13\bar{4}$	43	36	234
$75\bar{4}$	44	37	256
$1\bar{3}5$	35	30	112
$4\bar{2}5$	9	15	269
$24\bar{5}$	51	57	173
$86\bar{5}$	32	34	299
$0\bar{4}6$	52	40	134
$3\bar{3}6$	0	6	78
$35\bar{6}$	85	85	154

Table 3. *Observed and calculated powder data*

I'_o = Recorded intensity measured with microdensitometer.
$I_c = |F_c|^2 p f_1(\theta) \times 10^{-4}$, where p is the multiplicity and $f_1(\theta)$ is the angular factor defined by Goodyear & Duffin (1957). The absorption factor was almost constant for all reflexions, so no correction was made for this.

hkl	d_c	d_o	I_o	I_c	I_c	I'_o
110	5·32	5·32	*ms*	252	252	235
200	4·76	4·77	*m*	156	224	213
$\bar{1}11$	4·72	4·72	*w*	68		
111	3·514	3·514	*w*	32	100	80
$\bar{2}02$	3·486	3·486	*wm*	68		
$\bar{3}11$	3·210	3·211	*vs*	334	500	474
020	3·203			166		
$\bar{1}12$	3·020	3·014	*s*	92	380	332
002	3·011			288		
310	2·845	2·843	*wm*	100	371	359
021	2·828	2·824	*ms*	118		
$\bar{3}12$	2·821			153		
$\bar{2}21$	2·741	2·741	*wm*	61	61	59
220	2·658	2·657	*w*	29	62	42
$\bar{4}02$	2·650	2·651	*w*	33		
400	2·382	2·379	*vw*	22	22	12
$\bar{2}22$	2·359	2·359	*vw*	23	23	13
112	2·345	2·342	*vw*	34	34	18
221	2·208	2·206	*m*	45	215	212
311	2·207			62		
022	2·194	2·193	w^+	58		
$\bar{3}13$	2·185	2·182	w^+	50		
202	2·101	2·099	*w*	28	28	23
$\bar{4}21$	2·089	2·086	*wm(b)*	21	74	70
$\bar{1}13$	2·087			13		
$\bar{5}12$	2·086			29		
130	2·084			11		
$\bar{5}11$	2·053	2·050	*vvw*	9	52	41
$\bar{1}31$	2·042	2·041	*w*	30		
$\bar{4}22$	2·042			13		
420	1·911	1·901	*w(vb)*	12	39	32
131	1·904			21		
$\bar{5}13$	1·898			6		
$\bar{2}23$	1·884	1·884	*vw*	20	20	17
$\bar{6}02$	1·855	1·852	*vs*	130	369	472
$\bar{3}31$	1·851			239		
510	1·826	1·824	*w*	26	26	33
$\bar{1}32$	1·812	1·810	*vw*	9	28	23
$\bar{4}23$	1·809			19		
330	1·772	—	—	0·1	0·1	—
$\bar{3}32$	1·766	—	—	0·03	11	9
222	1·757	1·756	*vvw*	11		
$\bar{4}04$	1·743	1·742	*vvw*	14	14	10
113	1·721	—	—	2	2	—
$\bar{2}04$	1·712	1·708	*m*	4	372	398
312	1·710			119		
023	1·701	1·700	*m*	120		
$\bar{3}14$	1·694	1·693	*m*	129		
421	1·636	1·635	*vvw*	10	10	7
132	1·629	—	—	4	4	—
$\bar{5}14$	1·621	1·621	*vvw*	14	14	14
$\bar{6}22$	1·605	1·603	*wm(b)*	40	57	80
040	1·602			17		
600	1·588	1·586	wm^-	50	241	328
331	1·581	1·580	*wm*	83		
$\bar{3}33$	1·572	1·572	*wm*	66		
$\bar{1}14$	1·572			10		
$\bar{6}04$	1·571			32		

and were corrected for Lorentz, polarization and absorption factors.

Absorption corrections were made by assuming the specimens to be cylindrical in shape and applying the correction factors given by Bond (1959). The crystal used for [$\bar{1}32$] axis photographs had an approximate cross section of 0·08 × 0·05 mm², mean $\mu r = 0{\cdot}9$ with $\mu = 272$ cm^{-1}. A thinner crystal, of approximate cross section 0·03 × 0·03 mm², was used for [$\bar{1}10$] axis photographs and, although the crystal was tipped at about 29° to the oscillation axis, the absorption was assumed to be the same as that for a cylinder of mean $\mu r = 0{\cdot}5$ when the incident beam is normal to the specimen axis.

The intensities of X-ray powder reflexions, recorded with Cu $K\alpha$ radiation and a de Wolff focusing camera of 22·9 cm effective diameter, were estimated visually and measured quantitatively with a microdensitometer.

3. The determination of the structure

For initial intensity calculations, the space group was taken to be $Cc\,(C_s^4)$ and a wurtzite-type structure with four cation vacancies per cell was assumed. Atomic scattering factors used for these calculations were those of Freeman (1959) for Ga^{3+} and Wilson (1960) for S^{2-}. With atoms located in idealized positions, agreement with the observed data was reasonably good; but in order to account for several $h3l$ (l even) reflexions of medium strength, small arbitrary displacements of the gallium atoms were made parallel to the b axis, giving the atomic coordinates listed in part (i) of Table 1. Agreement between observed and calculated data was further improved by assuming temperature factors of 0·2 Å² for Ga and 1·0 Å² for S. At this stage the R index, $\Sigma|F_o - F_c|/\Sigma|F_o|$, was 16·4% for 73 observed hhl reflexions and 18·6% for 26 reflexions recorded on [$\bar{1}32$] axis photographs.

With these preliminary data, a three-dimensional least-squares refinement with individual isotropic temperature factors was undertaken by Dr H. H. Sutherland, using the program of Schoone (1960) on the Zebra computer installed at Queen's College, Dundee. After several cycles of refinement, the R indices were reduced to 13·6% and 12·9% for the two zones respectively, the final atomic parameters being those given in part (ii) of Table 1. The standard

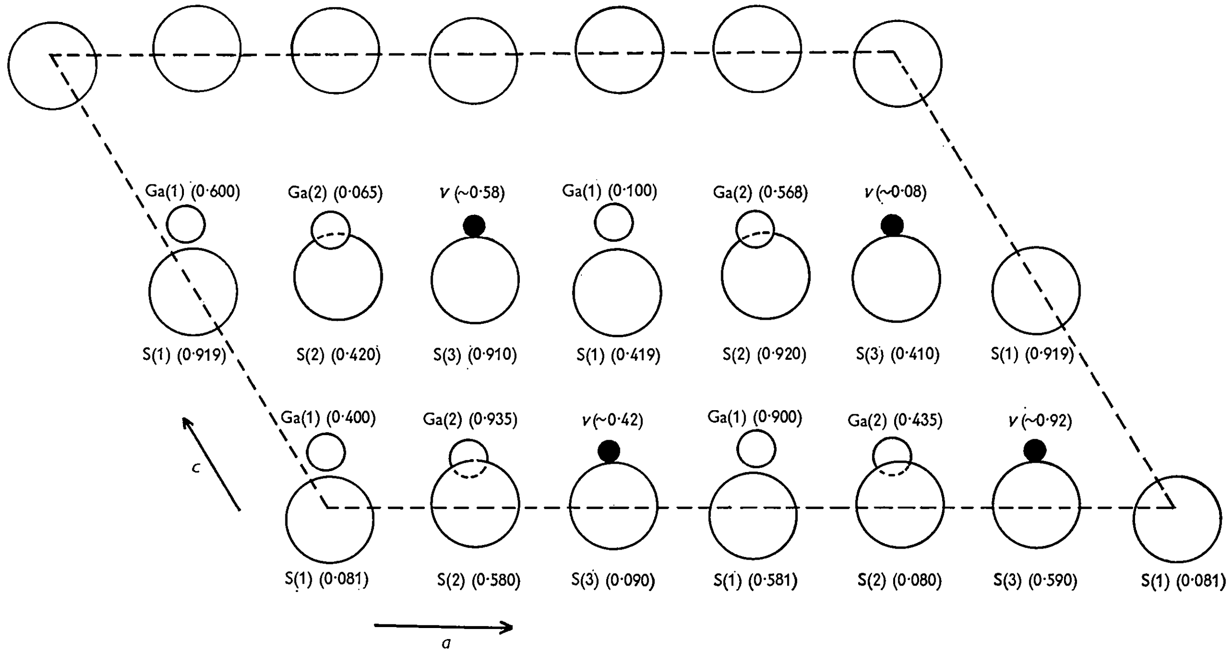

Fig. 2. Projection of the structure on the (010) cell face. The *b* axis is directed into the plane of the figure and the numbers are the *y*/*b* parameters of the atoms. *V* denotes vacant tetrahedral site.

deviations of the atomic coordinates, calculated by the formulae of Cruickshank (1949), are greater than the corresponding shifts in the final cycle of the refinement. The differences in the temperature factors of Ga(1) and Ga(2), and S(2) and S(1) (S(3)), are not readily explained in terms of atomic environments; they are possibly due to anisotropy in the thermal vibrations.

The observed and calculated structure factors are listed in Table 2, and observed and calculated intensity data for the powder reflexions are compared in Table 3.

4. Description of the structure

A projection of the structure on the (010) cell face is shown in Fig. 2, vacant tetrahedral cation sites which would be occupied in a wurtzite-type structure being indicated. Ignoring distortion from perfect close-packing, these vacancies are arranged in hexagonal arrays parallel to the (001) face. The structure differs principally from that proposed by Hahn & Frank in the relative orientation of successive arrays. According to Newman's (1961) proposed scheme of stacking sequences in $A_2^{III}B_3^{VI}$ compounds with tetrahedral binding, the present structure corresponds to the sequence –II–VI–II–VI–, whilst that of Hahn & Frank is of the type –II–II–II–II–.

Distortion from an idealized wurtzite-type structure is due mainly to shrinkage of tetrahedra surrounding vacant cation sites. The average S–S distances in tetrahedra enclosing Ga(1), Ga(2) and a vacancy are 3·75, 3·73 and 3·63 Å, respectively, the mean deviation being 0·05 Å in each case. Vacancies occur most frequently parallel to the *c* axis, which is one of Hahn & Frank's rhombohedral axes, and this causes a contraction in this direction, explaining why the lattice is monoclinic rather than rhombohedral. Finally, S(1) atoms are each linked to two gallium atoms, whereas S(2) and S(3) atoms are each linked to three. Consequently, Ga(1)–S(1) and Ga(2)–S(1) bond lengths (2·22 Å and 2·18 Å, respectively) are somewhat shorter than the average bond length, 2·32 Å, between Ga(1)(Ga2) and S(2)(S(3)) atoms.

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References

Bond, W. L. (1959). *Acta Cryst.* **12**, 375.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.
Goodyear, J. & Duffin, W. J. (1957). *Acta Cryst.* **10**, 597.
Goodyear, J., Duffin, W. J. & Steigmann, G. A. (1961). *Acta Cryst.* **14**, 1168.
Hahn, H. & Frank, G. (1955). *Z. anorg. Chem.* **278**, 333.
Newman, P. C. (1961). Mullard Research Report No. 420.
Schoone, J. C. (1960). *Computing Methods and the Phase Problems in X-ray Analysis*. London: Pergamon Press.
Wilson, A. J. C. (1960). *X-ray Diffraction by Polycrystalline Materials*. London: Institute of Physics.