

The Unit Cell of α -Ga₂S₃

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The unit cell of α -Ga₂S₃ has been determined from single crystal and powder X-ray diffraction data. The structure has monoclinic symmetry with cell dimensions

$$a = 12.637, b = 6.41_1, c = 7.03_8 \text{ \AA}, \beta = 131.07^\circ.$$

The unit cell, which is centred on the C-face, contains 4 molecules. The space group requirements rule out the possibility of the wurtzite-type structure previously suggested by Hahn & Frank (1955).

1. Introduction

According to Hahn & Klingler (1949), Ga₂S₃ can crystallize in one of two modifications, a low-temperature form or a high-temperature form. The inversion temperature is thought to be between 550 and 600 °C., and Hahn & Klingler found that the low- and high-temperature phases have structures which are related to the zinc blende and wurtzite structures respectively, each having a random distribution of vacancies in the sites normally occupied by Zn in the model structures.

In a later paper, Hahn & Frank (1955) described a superstructure which they prepared by annealing the disordered high-temperature modification of Ga₂S₃ at 1000 °C. for several days. Hahn & Frank called this new form α -Ga₂S₃, as distinct from β -Ga₂S₃ (the disordered high-temperature phase) and γ -Ga₂S₃ (the disordered low-temperature phase). To avoid confusion it is proposed to adopt the same nomenclature in this paper. On the basis of X-ray powder data they concluded that the unit cell of α -Ga₂S₃ was hexagonal, having parameters

$$a = \sqrt{3}a' = 6.38 \text{ \AA} \quad \text{and} \quad c = 3c' = 18.09 \text{ \AA},$$

a' and c' being the parameters of a single wurtzite-type cell. They also considered that the space group might be $C_6^3 = P6_5$ or $C_6^2 = P6_1$ and suggested that the sulphur atoms are hexagonally close-packed in layers perpendicular to the c -axis as in wurtzite. The gallium atoms were supposed to lie in the tetrahedral positions occupied by Zn in the wurtzite structure, but with six of these sites empty per unit cell. These vacancies they thought were in equivalent positions along the 6_5 -axis of the space group.

It appears that Hahn & Frank failed to notice that the indices they assigned to their observed X-ray reflections were of the type $\pm h \mp k + 1 = 3n$, n being an integer. Thus their proposed structure should have had trigonal symmetry with a rhombohedral cell of dimensions $a = 7.07 \text{ \AA}$ and $\alpha = 53.71^\circ$.

Specimens of Ga₂S₃, prepared by the authors'

colleagues, have recently been studied using powder and single-crystal techniques. Each method of preparation (to be described in the next section) yielded material giving the same X-ray powder pattern, which, though almost identical with that found for α -Ga₂S₃ by Hahn & Frank, nevertheless shows extra reflections which are not reconcilable with a rhombohedral cell.

2. Preparation of specimens and their X-ray powder data

Specimens of Ga₂S₃ were prepared in two ways as follows:

(i) A mixture, containing appropriate amounts of gallium and sulphur, was heated in a sealed evacuated tube at 450 °C. for 5 days. The temperature was then raised at the rate of 50 °C./12 hr. and the material was heated for a further 7 days at a maximum temperature of 1100 °C.

(ii) Equivalent amounts of gallium and sulphur were contained separately in silica boats in a sealed evacuated tube. The portion of the tube containing the gallium was heated at 1150 °C. and that containing the sulphur at 450–500 °C. for 1 day, gallium sulphide forming in the boat initially containing the gallium.

Each method yielded a yellow polycrystalline mass of Ga₂S₃, but in the second method elongated plate-like crystals, of dimensions suitable for X-ray study, were formed on the rim of the silica boat.

X-ray powder photographs of the two specimens were taken with crystal-monochromatised Cu $K\alpha$ radiation using a de Wolff focusing camera of 22.9 cm. effective diameter. Calibration of the camera was accomplished by mixing aluminium powder with the specimen being X-rayed. The X-ray powder data, identical for each specimen, are given in column (iii) of Table 1, and for comparison the patterns found by Hahn & Klingler for β -Ga₂S₃ and by Hahn & Frank for α -Ga₂S₃ are shown in columns (i) and (ii) respectively.

The chief differences between the powder patterns

Table 1. *X-ray powder data of gallium sulphide*

(Hahn & Klinger)		(Hahn & Frank)		(Goodyear, Duffin & Steigmann)	
β -Ga ₂ S ₃		α -Ga ₂ S ₃		α -Ga ₂ S ₃	
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
		5.28	<i>wm</i>	5.33	<i>ms</i>
		4.70	<i>wm</i>	{ 4.77 4.73	{ <i>m</i> <i>w</i>
		3.466	<i>w</i>	{ 3.515 3.488	{ <i>w</i> <i>wm</i>
3.193	<i>ms</i>	3.187	<i>ms</i>	3.209	<i>vs</i>
3.014	<i>m</i>	3.008	<i>m</i>	3.010	<i>s</i>
2.819	<i>ms</i>	2.823	<i>m</i>	{ 2.844 2.824	{ <i>wm</i> <i>ms</i>
		2.739	<i>vw</i>	2.742	<i>wm</i>
		2.640	<i>vw</i>	2.654	<i>w(b)</i>
		2.350	<i>vw</i>	{ 2.378 2.359	{ <i>vw</i> <i>vw</i>
2.194	<i>m</i>	2.192	<i>m</i>	{ 2.206 2.193 2.185	{ <i>m</i> <i>w</i> <i>w</i>
		2.085	<i>w</i>	{ 2.098 2.085	{ <i>vw</i> <i>wm</i>
		2.032	<i>vw</i>	{ 2.052 2.040	{ <i>vvw</i> <i>w</i>
		1.897	<i>vw</i>	{ 1.903 1.884	{ <i>vw(b)</i> <i>vw</i>
1.843	<i>s</i>	1.841	<i>vs</i>	1.851	<i>vs</i>
		1.811	<i>vw</i>	{ 1.824 1.810	{ <i>w</i> <i>vw</i>

b=rather broad.

of Ga₂S₃ in columns (ii) and (iii) lie in the observation by the present authors of closely separated doublets at about 4.75, 3.50, 2.83, 2.36, 2.09, 2.05, 1.90 and 1.81 Å, and a group of three reflections at about 2.19 Å, instead of the single reflections found by Hahn & Frank at these positions. Some of these pairs of lines are so closely spaced that, without the aid of a high-resolution instrument, they would most likely be recorded as single reflections. Since Hahn & Frank employed a Debye-Scherrer camera of 57.4 mm. diameter (private communication), it is almost certain that the difference between their data and those of the present writers is simply due to one of technique. In all other respects the agreement between the powder data is good enough to suggest that the material described here is indeed the same as the α -Ga₂S₃ of Hahn & Frank. This would also be expected from the mode of preparation of the specimens, since in each method the material was thought to be sufficiently annealed for complete ordering of the structure.

3. Structural considerations

A slight distortion of the rhombohedral cell of Hahn & Frank would explain the 'double' reflections of the

present powder data. However, it seemed better to determine the space lattice directly using single-crystal data.

Table 2. *Observed and calculated θ°_{Cu} for α -Ga₂S₃*

θ_o	<i>hkl</i>	θ_c	θ_o	<i>hkl</i>	θ_c
8.323	110	8.333	16.887	{ 220 002	{ 16.851 16.895
9.303	200	8.314	18.912	400	18.887
9.391	11 $\bar{1}$	9.399	19.077	22 $\bar{2}$	19.064
12.668	31 $\bar{1}$	12.676	20.455	51 $\bar{1}$	20.447
12.768	20 $\bar{2}$	12.769	20.578	203	20.576
13.901	020	13.915	20.658	313	20.650
14.840	40 $\bar{2}$	14.845	21.557	60 $\bar{2}$	21.541
15.727	310	15.719	21.698	51 $\bar{3}$	21.677
15.842	11 $\bar{2}$	15.847			
16.331	021	16.319			

A rotation photograph taken about the elongated axis of one of the single crystals showed layer lines whose spacings corresponded to an identity period of about 14.7 Å parallel to the rotation axis. A series of oscillation photographs about the same axis produced reflections which could be indexed in terms of a triclinic cell which, on reduction by Delaunay's method, indicated that the true symmetry of the lattice was monoclinic, the unit cell being centred on the *C*-face. In terms of the monoclinic cell the elongated axis of the single crystal is in the [021] direction and the extended face is (100). The parameters of the monoclinic cell, calculated from the more accurate powder data, are

$$a = 12.637, b = 6.411, c = 7.038 \text{ \AA}, \beta = 131.07^\circ.$$

A comparison between the observed and calculated θ -values is shown in Table 2. The primitive cell of the lattice is a slightly distorted rhombohedron, with translations 7.08₅, 7.08₅ and 7.03₈ Å and axial angles 54.13°, 54.13° and 53.80°, which is almost identical with the rhombohedral cell of Hahn & Frank. The relation of the latter to the monoclinic cell is shown in Fig. 1.

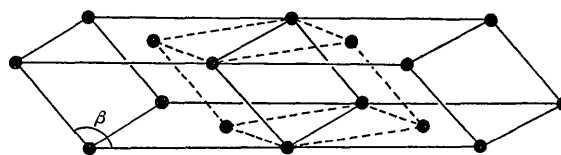


Fig. 1. Relation of the unit cell of Hahn & Frank to the *C*-face centred monoclinic cell. (-----, outline of the unit cell of Hahn & Frank).

Reflections recorded on oscillation photographs about the monoclinic *b*-axis were indexed, the only systematically absent reflections being those with *h*+*k* odd, indicating that the space group must be $C_2^3 = C2$, $C_{2h}^3 = C2/m$ or $C_s^3 = Cm$. If one assumes that the sulphur atoms are more-or-less hexagonally close-packed in layers perpendicular to the [101] axis of the monoclinic cell, i.e. approximately in the same orientation as suggested by Hahn & Frank, then

4 Ga₂S₃ molecules would be required per unit cell giving a calculated density of 3.64 g.cm.⁻³. This agrees well with the measured macroscopic density of 3.65 g.cm.⁻³ given in *Handbook of Chemistry and Physics* (1957-58). Although the symmetry of the space group *C*2 would be satisfied by this disposition of sulphur atoms, this would not be so for the tetrahedral positions in which the gallium atoms might be supposed to lie. It appears then that the structure of α -Ga₂S₃ is not related to the wurtzite structure. On the other hand, the space-group requirements would permit the gallium atoms to be octahedrally co-ordinated, but this

possibility must remain tentative until the full structure analysis has been completed.

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The Effect of Temperature on Local Order Diffuse Scattering from Alloys. I*

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The theory of the diffuse scattering of X-rays from binary alloys with local order has been extended to include explicitly the effects of thermal vibrations. By adopting certain simplifying assumptions about the lattice vibrations it is found that the thermal effects can be expressed in the form of appropriate Debye-Waller factors modifying the usual diffuse scattering terms. Experimental measurements verify the predicted general nature and magnitude of the temperature effect. Neglect of this effect appears to be a significant source of error in past experimental determinations of local order in alloys.

Introduction

Diffraction theory describing the diffuse X-ray scattering arising from local ordering† of the atoms in a binary alloy has been extended to include the modifying effects of static displacements due to differing atomic sizes by several authors [see, for example, Huang (1947); Warren, Averbach & Roberts (1951); Borie (1957), (1959)], but the analogous extension to include the effects of the dynamic displacements due to thermal vibrations has received relatively little attention. Muldower (1954) attempted to develop a scattering theory in which the lattice vibrations were explicitly included, but his theory was not carried beyond a first formal step. Münster & Sagel (1957) developed a theory of the local order diffuse scattering in powder patterns in terms of continuous interatomic pair probability density functions, thus including thermal displacements implicitly; these continuous

probability functions were then to be determined from each experiment.

We give here an approximate theory of local order diffuse X-ray scattering in which the modifying effects of the thermal vibrations are explicitly described. The theory is limited to binary alloys with only short range atomic correlations, and for simplicity it is further restricted to alloys with monatomic face-centered or body-centered cubic lattices. In this paper we develop the theory in detail for alloys with no atomic size effects and demonstrate the nature and magnitude of the predicted temperature effects with calculated examples and experimental measurements. The extension of the theory to alloys with size-effect static displacements following the model of Borie (1957) is given in a following paper.

Theory

The intensity of X-rays scattered by an array of atoms, neglecting extinction and absorption, is given in electron units as

$$I = \sum_m \sum_n f_m f_n \exp [i\mathbf{K} \cdot (\mathbf{r}_m - \mathbf{r}_n)], \quad (1)$$

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† The term local order is taken to include both the conventional type of short range order and the clustering of like atoms preceding precipitation.