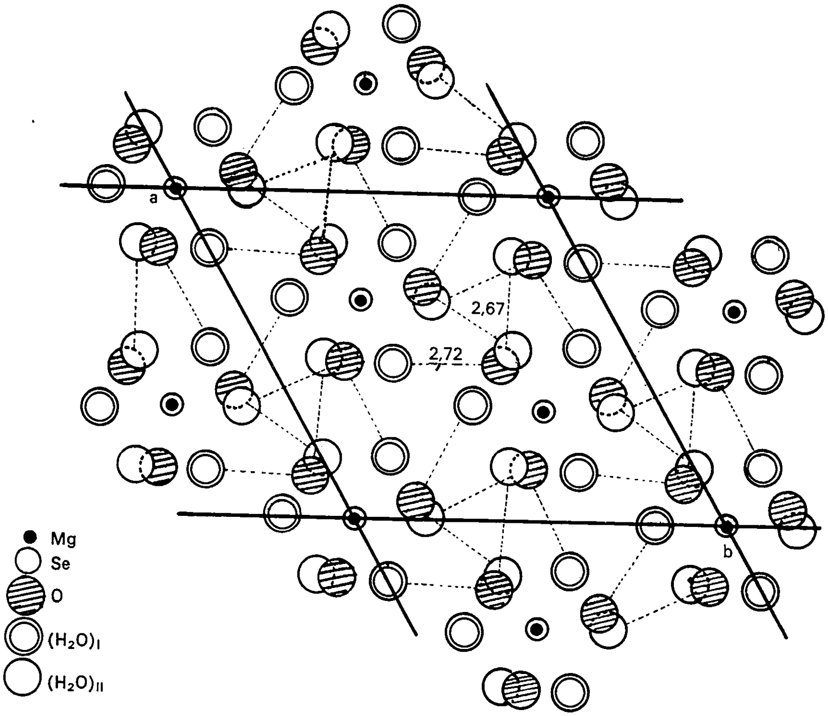

Fig. 2. Projection de la structure suivant [001].

de ces liaisons hydrogène sont représentées par des traits en pointillé; la troisième est visible sur la Fig. 1.

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Crystalline Phases in the System In–In_2S_3

By W. J. Duffin and J. H. C. Hogg

Department of Physics, The University, Hull, England

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Phases existing at room temperature in the In – In_2S_3 system are established as InS and In_6S_7 and their properties related to previous work. Crystallographic data are presented and InS is confirmed as orthorhombic with $a=3{\cdot}944$, $b=4{\cdot}447$, $c=10{\cdot}648$ Å, space group $Pmnn$, $Z=4$. In_6S_7 is found to be monoclinic with $a=9{\cdot}090$, $b=3{\cdot}887$, $c=17{\cdot}705$ Å, $\beta=108{\cdot}20°$, space group $P2_1/m$, $Z=2$. Evidence for the existence of crystalline In_2S is also examined.

Introduction

While the structures of α- and β-In_2S_3 have been well established by Hahn & Klingler (1949) and by Steigmann, Sutherland & Goodyear (1965), considerable confusion exists over the other crystalline phases in the In–In_2S_3 system which are stable at room temperature. In a detailed investigation of the phase diagram, Stubbs, Schufle, Thompson & Duncan (1952) reported the existence of InS and, with some uncertainty in composition, In_5S_6: no other phases were found, apart from In_3S_4 which is stable only above 370°C. X-ray powder data for both the InS and the In_5S_6 reported by Stubbs *et al.* have been published in the ASTM index by Schufle, but seem to bear little relation to the structure of InS reported by Schubert, Dörre & Günzel (1954) or to the lattice parameters of a compound listed as In_4S_5 also given by Schubert *et al.* Moreover, a phase with composition In_2S was reported by Klemm & von Vogel (1934) together with X-ray data and, although its existence is doubtful, the original evidence has not previously been critically examined.

In view of the importance of many group III – group VI compounds as semiconductors, an investigation to clarify the situation described above was instituted in this department. The present paper covers the whole range of compositions and is intended to identify the various phases and establish crystallographic data for them. Further work on the individual structures is in progress.

Experimental procedure

All specimens were prepared by mixing weighed amounts of In_2S_3 and metallic indium and heating the mixture above the melting point in an evacuated sealed-off quartz tube. The tube was then cooled slowly to a temperature appropriate to the phase(s) required [according to the phase diagram of Stubbs *et al.* (1952)] and held there for an hour or so. The tube was then removed from the furnace and quenched to room temperature in air before breaking the seal. The range of compositions of the original mixtures varied from about 73% by weight of In (corresponding to In_3S_4) to 85% In (nearly In_2S).

Apart from excess In_2S_3 and In, only two intermediate crystalline phases were obtained in any specimens: red crystals, identified as InS; and almost black crystals, corresponding to Stubbs's 'In_5S_6'. Single crystals of both phases large enough for X-ray work were easily obtained, but it proved impossible to make polycrystalline specimens consisting of a single phase. Nevertheless, it did prove possible to prepare specimens containing so little of one phase that the X-ray powder patterns yielded by them consisted only of lines from the other phase.

X-ray powder patterns were obtained both with a de Wolff focusing camera of effective diameter 22·9 cm and with a Geiger counter diffractometer. Cu *Kα* radiation was used and internal calibration with metallic indium mixed with the specimens minimized systematic errors. The agreement between photographic and diffractometer measurements of spacings was good enough in all cases to confirm that systematic errors (which arise from different causes in the two techniques) were small. The observed powder data given in the tables are those obtained by the photographic method with intensities measured with a microdensitometer. This is because some very weak reflexions were more certainly recorded photographically, particularly where they were adjacent to strong ones.

InS

The structure of InS reported by Schubert *et al.* (1954) gives it an orthorhombic unit cell with $a=3{\cdot}94_0$, $b=4{\cdot}44_3$, $c=10{\cdot}64_2$ Å and a space group $Pmnn$ (D_{2h}^{12}). There are 4 formula units per cell, 4 In atoms in 4(*g*) with $y=0{\cdot}125$, $z=0{\cdot}121$ and 4 S atoms in 4(*g*) with $y=-0{\cdot}005$, $z=0{\cdot}355$ (see also *Structure Reports*, Vol. 18, p. 382). They give no single-crystal data, and the only powder pattern on record is that of Schufle in the ASTM index in which the reflexions are indexed on a cubic cell.

Rotation and Weissenberg photographs of the red InS crystals obtained in the present investigation confirmed the space group and approximate lattice parameters of Schubert *et al.* Observed and calculated structure factors were obtained for reflexions appearing on an *a*-axis Weissenberg photograph and the agreement was sufficiently good for us to assume that Schubert's atomic positions are substantially correct.

The powder data are given in Table 1, and the lattice parameters yielding the values of d_{calc} therein are $a=3{\cdot}944$, $b=4{\cdot}447$, $c=10{\cdot}648$ Å. The agreement between calculated and observed spacings is good enough for the error in *a* and *b* to be no more than ±0·001 Å and in the *c* parameter no more than ±0·002 Å. The observed and calculated intensities of Table 1 show good agreement, although some preferred orientation undoubtedly occurred since the specimens for the X-ray photographs were prepared by sedimentation. By comparing diffractometer powder patterns of specimens with a flat surface with some of specimens whose surface had been disturbed with the points of a brush, it was found that the peak intensity of the 004 reflexion was somewhat enhanced by preferred orientation, while those of the 122 and 204 reflexions were reduced. These account for most of the differences in the table.

Comparison of the spacings with those of Schufle shows that his pattern had some weaker reflexions missing and some stronger ones unresolved. The fact that the reflexions remaining could be approximately indexed on a cubic cell is probably fortuitous.

InS crystals show frequent twinning of an interesting nature which will be reported elsewhere.

In_6S_7

The black crystalline phase occurring in the specimens of Stubbs *et al.* (1952) corresponded, according to them, to a binary compound containing 75–76% In: this they said 'would seem to correspond to In_5S_6 (74·9% In)'. Powder data for this phase were also published by Schufle in the ASTM index.

Somewhat later, Schubert, Dörre & Günzel (1954) quoted lattice parameters but no other data for a compound In_4S_5 (74·1% In) and Hansen (1958) concluded that this was now the composition of the phase previously reported by Stubbs *et al.* In private correspondence with the authors, however, Dr Schubert gave the

Table 1. *Powder data for* InS

I_c = calculated intensity from $p|F_c|^2 f_1(\theta)$ where p is the multiplicity and $f_1(\theta)$ is the angular factor for the de Wolff camera as defined by Goodyear & Duffin (1957).
I_o = observed integrated intensity obtained from microdensitometer recordings.
I_c and I_o are scaled so that $I_{110} = 100$.

hkl	d_c	d_o	I_c		I_o
011	4·104 Å	4·104 Å	22		25
101	3·699	3·699	49		48
012	3·413	3·413	72		68
110	2·951	2·951	100		100
111	2·843	2·843	39		39
013	2·775	2·775	3		4
004	2·662	2·662	58		61
103	2·638	2·636	10		10
113	2·269	2·269	26		24
020	2·224	2·224	2		1
021	2·177	2·177	19		9
114	1·977	1·977	51	74	66
200	1·972	1·973	23		
015	1·921	1·920	7		9
023	1·884	1·885	14		13
105	1·874	1·873	14		15
122	1·820	1·822	50		34
211	1·777	1·778	5		5
115	1·727	1·727	7		6
212	1·707	1·707	20	21	17
024			1		
016	1·648	1·647	8		5
204	1·585	1·584	24		15
025	1·538	1·538	5		2
221	1·461	1·461	11		9
131	1·376	1·376	4	9	6
215			5		

Table 2. *Powder data for* In_6S_7

I_o is scaled so that $I_{212} = 100$.
(*b*) = broad.
Bracketed reflexions in the second column are unresolved by eye, in the fourth column are unresolved by the microdensitometer. Separate intensities given for the latter are based on visual estimates.

hkl	d_c	d_o		I_o
002	8·410 Å	8·406 Å		21
003	5·606	5·614		10
102	5·260	5·264		15
$20\bar{1}$	4·537	4·539		26
$20\bar{2}$	4·446	4·444		9
$10\bar{4}$	4·353	4·358		50
103	4·148	4·154		26
$20\bar{3}$	4·094	4·096		2
201	3·899	3·897		7
011	3·787	3·787		36
$20\bar{4}$	3·632	3·631		5
110	3·545	3·543	25	123*
$10\bar{5}$	3·529	3·531	98	
012	3·529			
202	3·430	3·430		53
$11\bar{2}$	3·427			
104	3·387	3·387		65
111	3·382			
013	3·195	3·188		92
$11\bar{3}$	3·186			
$20\bar{5}$	3·178			
$30\bar{2}$	3·028	3·031		5
203	2·998	2·997		93
$30\bar{1}$	2·997			

Table 2 (*cont.*)

hkl	d_c	d_o		I_o
$21\bar{1}$	2·952	2·952		27
$21\bar{2}$	2·927	2·924		8
$11\bar{4}$	2·900	2·900		10
210	2·889	2·888		5
014	2·854	2·855		10
$30\bar{4}$	2·821	2·821		63
$21\bar{3}$	2·819			
$20\bar{6}$	2·781	2·782		29
211	2·753	2·752		91
$21\bar{4}$	2·654	2·655		54
$30\bar{5}$	2·630	2·632		48
204	2·630			
212	2·572	2·570		100
$10\bar{7}$	2·528	2·526		7
106	2·451	2·449		12
$20\bar{7}$	2·450			
$31\bar{2}$	2·389	2·389		23
$31\bar{3}$	2·357	2·358	7	35
$11\bar{6}$	2·350	2·349	28	
$31\bar{4}$	2·283	2·285	16	70
016	2·274	2·274	54	
$40\bar{1}$	2·231	2·234		4
$30\bar{7}$	2·216	2·217		6
$31\bar{5}$	2·178	2·179		8
214	2·178			
$20\bar{8}$	2·177			
400	2·159	2·161		6
107	2·148	2·148		10
$40\bar{5}$	2·147			
$40\bar{6}$	2·047	2·046		30
313	1·971	1·971		31
$20\bar{9}$	1·952	1·952	44	136*
402	1·950			
020	1·944	1·943	92	
$41\bar{1}$	1·935	1·930		53
$41\bar{4}$	1·930			
$31\bar{7}$	1·925			
$11\bar{8}$	1·919	1·920		19
108	1·910	1·909		13
$21\bar{8}$	1·899	1·898		16
410	1·887	1·886		44
117	1·880	1·880		33
415	1·879			
009	1·869	1·868		6
207	1·866			
018	1·849	1·848		21
403	1·832	1·832		23
$41\bar{6}$	1·811	1·808(*b*)		11
$50\bar{2}$	1·807			
$22\bar{1}$	1·787	1·786		4
$12\bar{4}$	1·775	1·774		11
$2,0,\overline{10}$	1·765	1·763		8
$41\bar{7}$	1·731	1·731		20
315	1·716	1·715		22
$12\bar{5}$	1·703	1·703		19
208	1·694	1·695		10
124	1·686	1·685		12
$31\bar{9}$	1·673	1·672		4
$50\bar{7}$	1·671			
413	1·657	1·659		6
$22\bar{5}$	1·658			
$51\bar{3}$	1·647	1·646		12
$51\bar{2}$	1·638	1·639		16
223	1·631	1·630		31
$32\bar{1}$	1·631			

* With non-focusing cameras, these groups of reflexions may be unresolved and could appear as very strong single reflexions.

analysis of his specimens as being $In_{11}S_{13}$ (75·2% In) and it seems possible that the formula In_4S_5 was adopted following a suggestion of Thiel & Luckmann (1928).

Our first task was to establish that the phases of Stubbs and of Schubert were the same, for it did not seem possible to index Schufle's pattern on the basis of Schubert's cell. Powder patterns of the black phase, obtained in precisely the same way as with InS, together with rotation and Weissenberg photographs enabled the unit cell and space group to be determined. The unit cell is monoclinic with lattice parameters $a = 9{\cdot}090 \pm 0{\cdot}005$, $b = 3{\cdot}887 \pm 0{\cdot}001$, $c = 17{\cdot}705 \pm 0{\cdot}004$ Å, $\beta = 108{\cdot}20 \pm 0{\cdot}05$, which are very close to those of Schubert. The agreement between observed and calculated spacings (Table 2) is not so good as with InS because of the large number of weak and overlapping reflexions. Schubert's cell is not the conventional one because there does exist a monoclinic cell with the same a and b but with smaller c and with β nearer to 90°, but to avoid further confusion in the literature it was thought better to leave the cell as quoted above.

Careful examination of Schufle's pattern showed that it could be identified with that in Table 2 provided it was assumed that it omitted many medium and weak reflexions and that a gross systematic error occurred in his spacings.

Weissenberg photographs about the a axis showed that the only absences are $0k0$ with k odd, giving a space group of either $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). A full structure determination of this phase is in progress and will be published in due course: preliminary results indicate that the structure has a centre of symmetry and that the space group is thus $P2_1/m$. Intensities calculated from unrefined atomic positions show very close agreement with the observed values given in Table 2.

There remains the question of composition. Although Schubert and Stubbs differ in their formulae, their estimates of composition are not in conflict: Schubert, 75·2% In; Stubbs, 75–76% In. It has not proved possible for us to obtain specimens of the phase sufficiently free from contamination to carry out an analysis, either by chemical means or by X-ray fluorescent techniques, which could give a composition to an accuracy better than 1%, although crude analyses confirm that the phase does indeed contain about 75% In. However, when a full structure determination was begun, it became clear that all atoms possessed atomic y coordinates of $\frac{1}{4}$ or $\frac{3}{4}$ and Patterson projections on (010) showed that the unit cell probably contained 12 In atoms. Further work showed that the unit cell could accommodate no more than 14 S atoms and at this stage the possibility of a formula In_6S_7 (75·4% In) with $Z = 2$ presented itself.

Calculated densities for the various possible formulae are:

In_4S_5, $Z = 2$ $\varrho = 3{\cdot}46$ (74·1% In)
$Z = 3$ $\varrho = 5{\cdot}19$
In_5S_6, $Z = 2$ $\varrho = 4{\cdot}28$ (74·9% In)
In_6S_7, $Z = 2$ $\varrho = 5{\cdot}11$ (75·4% In)

Measured densities are difficult to obtain accurately, but flotation methods have shown that the phase has a density certainly greater than 4·5 and displacement methods using toluene indicate a density of about 5·08. This clearly eliminates all but two possibilities and, coupled with the evidence from the structure determination, we concluded that the phase is in fact In_6S_7 with $Z = 2$ formula units per cell. It will be noted that this is in better agreement with the compositions given by Stubbs and Schubert than are the formulae suggested by them.

Other phases

No other phases have been found in any specimens, even in those quenched from points where In_3S_4 might be expected to be frozen in. A high-temperature investigation of the existence of In_3S_4 is projected.

It seems certain that the In_2S phase first reported by Thiel & Luckmann (1928) does not exist in crystalline form. The main evidence for its existence rests on a diagram of its X-ray powder pattern given by Klemm & von Vogel (1934). We have, as far as is possible on such a small scale illustration, examined carefully this particular diagram and find that the majority of reflexions are identical with those of InS. The remaining reflexions are almost certainly those of metallic indium and their specimen would thus appear to be a mixture of InS and In. The densities of 5·87 and 5·92 reported for this phase by Klemm & von Vogel and by Thiel & Luckmann respectively lie between those of InS (5·28) and In (7·28).

This conclusion seems to verify that of Klanberg & Spandau (1961) who report the existence of a gaseous In_2S phase, but suggest that on condensing into a solid the In_2S is unstable and breaks down to InS and In.

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