

## Crystal Structures in the System Zn-In-S

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The crystal structures of the three nonstoichiometric compounds  $Zn_{1.685}In_{2.21}S_5$ ,  $Zn_{4.37}In_{2.42}S_8$  and  $Zn_{6.13}In_{2.58}S_{10}$  have been determined. Their hexagonal unit cells are of the Wurtzite type with  $a = 3.85 \text{ \AA}$ , the  $c$ -dimensions and space groups being  $30.85 \text{ \AA}$ ,  $P6_3mc$ ;  $24.96 \text{ \AA}$ ,  $P3m1$ ;  $31.30 \text{ \AA}$ ,  $P3m1$ , respectively. All atoms occupy positions on the triad rotation axes.

The layer structures show the same principle as all the other known structures in the Zn-In-S system (1-5). They are based on slightly distorted close packing of the sulfur atoms with Zn in tetrahedral voids, whereas In may occupy tetrahedral and octahedral voids in the same structure.

A survey of the existing Zn-In-S structures has been extended to indicate all the conceivable hexagonal Zn-In-S types not yet known.

### Introduction

Application of the method of chemical transport reaction with the elements Zn, In, and S allowed Nitsche (6) to synthesize a series of crystalline products. The elements of the effective binary components ZnS and  $In_2S_3$  have been mixed together in different ratios, and the cooler end of the temperature gradient has been varied between 1040 and 670°C. The soft and transparent crystals have the form of hexagonal plates up to  $1 \text{ cm}^2$ , often intergrown and cleaving easily perpendicular to [001]. Their color changes from bright yellow (Zn-rich) to orange (In-rich). The investigation of this material by analytical and X-ray methods will be the subject of this paper.

Zn-In-S crystals show a marked photo-semiconductivity (7, 8). Their layer structures are of interest from the crystal-chemical point of view: the chemical composition allows the thickness of the corresponding layer pack to be predicted (9). This relation has also been realized by Donika et al. (10); in addition, they observed many polytype forms of the stoichiometric compounds  $ZnIn_2S_4$ ,  $Zn_2In_2S_5$  and  $Zn_3In_2S_6$ .

\* Full details of the investigation methods, structure factors etc., are given in the Ph.D. thesis of this author.

### Primary Investigations and Solutions

The crystals have been analyzed on the ARL electronprobe microanalyzer, using their cleavage planes (001). The standard probes were synthetic ZnS and  $In_2S_3$ . Concentrations have been corrected for dead time, drift and background as well as for absorption, atomic number effect and fluorescence (11). The analytical data (reliability  $\pm 3\%$ ) show that all compositions fit into the binary system ZnS- $In_2S_3$ , i.e., the metals are in the valency states  $Zn^{II}$  and  $In^{III}$ . The chemical compositions are expressed by  $y = [Zn]/([Zn] + [In])$ . X-ray data were obtained mainly by single crystal precession techniques, using Mo  $K_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ).

In the following, we shall extend the symbols of Ramsdell (12), which are used for the description of polytype forms of SiC, ZnS, CdI<sub>2</sub>, etc., by adding a number  $s$  which indicates the thickness of one layer pack in units of one average metal-sulfur slab ( $\approx 3.1 \text{ \AA}$ ), if different from unity. Depending on the space group symmetry, one unit cell may contain several of these layer packs (= stacking units). The whole structure is generated from these stacking units by symmetry operations of the first kind (pure motions). Hence, our type symbol of the general

TABLE I  
X-RAY AND ANALYTICAL DATA OF THE Zn-In-S PHASES IDENTIFIED IN OUR SERIES OF SPECIMENS

X-ray data			Analytical data			
Hexagonal unit cell $a(\text{\AA})$	Laue symmetry	Conditions limiting possible reflections	Type symbol, name (ref.)	$y$ Minimal	Maximal $y$	Stoichiometric formula
3.82 <sub>4</sub>	6/ <i>mmm</i>	if $h - k = 3n; l = 2n$	2H Wurtzite $\alpha$ -ZnS	0.96	0.99	1.0 (ZnS) <sub>2</sub>
5.41 <sub>0</sub> , cubic	<i>m3m</i>	$h + k, k + 1, (l + h) = 2n$	3C Zincblende $\beta$ -ZnS	0.95	1.0	1.0 (ZnS) <sub>3</sub>
3.82 <sub>0</sub>	6/ <i>mmm</i>	if $h - k = 3n; l = 4n$	4H Wurtzite (14)	0.98	0.99	1.0 (ZnS) <sub>4</sub>
3.82 <sub>5</sub>	6/ <i>mmm</i>	[if $h - k = 3n; l = 6n$ if $l = 6n; h - k = 3n$ ]	6H Wurtzite (14)	0.93	0.97	1.0 (ZnS) <sub>6</sub>
3.85 <sub>6</sub>	$\bar{3}m(?)$	$-h + k + 1 = 3n(?)$	36R12	0.75	0.85	0.82 (Zn <sub>9</sub> In <sub>2</sub> S <sub>12</sub> ) <sub>3</sub>
3.83 <sub>8</sub>	$\bar{3}m^a$	---	10H10	0.66	0.71	0.78 (Zn <sub>7</sub> In <sub>2</sub> S <sub>10</sub> )
3.84 <sub>5</sub>	6/ <i>mmm</i>	if $h - k = 3n; l = 2n(?)$	18H9	0.67	0.68	0.75 (Zn <sub>6</sub> In <sub>2</sub> S <sub>9</sub> ) <sub>2</sub>
3.85 <sub>7</sub>	$\bar{3}m^a$	---	8H8	0.64	0.65	0.71 (Zn <sub>5</sub> In <sub>2</sub> S <sub>8</sub> )
3.86 <sub>3</sub>	$\bar{3}m^a$	---	6H6 (2, 10)	0.52	0.57	0.60 (Zn <sub>3</sub> In <sub>2</sub> S <sub>6</sub> )
3.85 <sub>1</sub>	6/ <i>mmm</i>	if $h - k = 3n; l = 2n$	10H5 (4, 10)	0.39	0.46	0.50 (Zn <sub>2</sub> In <sub>2</sub> S <sub>5</sub> ) <sub>2</sub>
3.86 <sub>4</sub>	$\bar{3}m$	$-h + k + 1 = 3n$	12R4 (1)	0.25	0.34	0.33 (ZnIn <sub>2</sub> S <sub>4</sub> ) <sub>3</sub>
5.35 <sub>5</sub> , cubic	<i>m3m</i>	[ $h + k, k + 1, (l + h) = 2n$ $h, k, l = 2n + 1, 2n + 1, 2n + 1$ or $4n + 2, 4n + 2, 4n + 2$ or $4n, 4n, 4n$ ]	--- $\alpha$ -In <sub>2</sub> S <sub>3</sub>		0.08	0.0 (In <sub>2</sub> S <sub>3</sub> )

<sup>a</sup> The diffraction pattern simulates the symmetry 6/*mmm*; this is discussed in "Structure determinations."

TABLE II  
DATA OF THE CRYSTALS USED FOR INTENSITY MEASUREMENT

Zn-In-S type	10H5	8H8	10H10
Formula <sup>a</sup>	(Zn <sub>1.685</sub> In <sub>2.21</sub> S <sub>8</sub> ) <sub>2</sub>	(Zn <sub>4.37</sub> In <sub>2.43</sub> S <sub>8</sub> )	(Zn <sub>6.13</sub> In <sub>2.58</sub> S <sub>10</sub> )
Laue symmetry	6/ <i>mmm</i>	$\bar{3}m^b$	$\bar{3}m^b$
Cell parameters <i>a</i> (Å)	3.851 ± 2	3.857 ± 2	3.83 <sub>8</sub>
<i>c</i> (Å)	30.85 ± 2	24.961 ± 15	31.3 <sub>0</sub>
Number <i>Z</i> of formula units per cell	<i>Z</i> = 2	<i>Z</i> = 1	<i>Z</i> = 1
Space group	<i>P6<sub>3</sub>mc</i>	<i>P3m1</i>	<i>P3m1</i>
Calculated density ρ <sub>c</sub> (g/cm <sup>3</sup> )	4.336 ± 3	4.236 ± 3	4.23 <sub>0</sub>
Linear absorption coefficient μ <sub>MoKα</sub> (cm <sup>-1</sup> )	125	136	141
Approx. size of crystal (mm)	0.02 × 0.04 × 0.07	0.01 × 0.02 × 0.03	0.02 × 0.02 × 0.06
Apparatus used for intensity measurement	4-circle automatic PICKER diffractometer, Nb filtered MoKα-radiation		Leitz fotometer GIII (Precession, MoKα)
Number of independent reflections	277	666	184

<sup>a</sup> The crystals used for intensity measurement have been analyzed afterwards.

<sup>b</sup> The diffraction pattern simulates the symmetry 6/*mmm*; this is discussed in "Structure determination."

TABLE III  
"STRUCTURE PARAMETERS OF TYPE 10H5

Atom	Position	<i>z</i>	B isotropic	Population parameter
S <sub>1</sub>	(b)	.000	0.62 ± 35	1.0
S <sub>2</sub>	(a)	.106 ± 1	0.92 ± 44	1.0
S <sub>3</sub>	(b)	.207 ± 1	0.91 ± 48	1.0
S <sub>4</sub>	(b)	.794 ± 1	0.30 ± 44	1.0
S <sub>5</sub>	(a)	.400 ± 1	1.80 ± 44	1.0
Zn <sub>1</sub>	(b)	.8757 ± 5	0.20 ± 18	1.05 ± 4
Zn <sub>2</sub>	(b)	.1300 ± 8	1.32 ± 31	0.60 ± 4
In <sub>1</sub>		.65 ± 32	0.27 ± 2	
In <sub>2</sub>	(a)	.0303 ± 5	1.47 ± 12	0.88 ± 2
In <sub>3</sub>	(a)	.2529 ± 5	0.93 ± 10	1.01 ± 3

<sup>a</sup> *a* = 3.851 ± 2 Å, *c* = 30.85 ± 2 Å, S.G. *P6<sub>3</sub>mc*, atomic positions: (a)0,0,*z*; 0,0,*z* + 1/2 (b) 1/3,2/3,*z*; 2/3,1/3,*z* + 1/2

form *pGs* contains the following information:

*p* = number of close-packed sulfur layers in the hexagonal unit cell ≈ [*c*(Å)/3.1 Å],

*G* = Bravais lattice type,

*s* = number of close-packed sulfur layers in the stacking unit;

(*p*, *s*, *p/s* = integral numbers).

The ratio *p/s* is equal to the number *Z* of formula units per unit cell and is determined by the systematically absent X-ray reflections. This relation is as follows:

$$\text{if } h - k = 3n : l = (p/s) \cdot m,$$

$$(m, n = \text{any integer}).$$

It may be interpreted as a pseudo-selection rule (13) due to pseudo-centering of the hexagonal cell on the triad rotation axes.

TABLE IV  
INTERATOMIC DISTANCES (Å) OF TYPE 10H5

In <sub>0</sub>	In <sub>3</sub> -S <sub>3</sub> = 2.638 ± 18	In <sub>3</sub> -S <sub>4</sub> = 2.565 ± 15	S <sub>3</sub> -S <sub>4</sub> = 3.497 ± 31
In <sub>t</sub>	In <sub>2</sub> -S <sub>1</sub> = 2.412 ± 6	In <sub>2</sub> -S <sub>2</sub> = 2.336 ± 38	S <sub>1</sub> -S <sub>2</sub> = 3.956 ± 29
Zn <sub>t</sub> , In <sub>t</sub>	Zn <sub>2</sub> -S <sub>2</sub> = 2.346 ± 14	Zn <sub>2</sub> -S <sub>3</sub> = 2.374 ± 39	S <sub>2</sub> -S <sub>3</sub> = 3.822 ± 37
Zn <sub>t</sub>	Zn <sub>1</sub> -S <sub>4</sub> = 2.512 ± 30	Zn <sub>1</sub> -S <sub>5</sub> = 2.348 ± 14	S <sub>4</sub> -S <sub>5</sub> = 3.951 ± 40
Empty layer			S <sub>1</sub> -S <sub>5</sub> = 3.799 ± 32

TABLE V

<sup>a</sup> STRUCTURE PARAMETERS OF TYPE 8H8

Atom	Position	<i>z</i>	B isotropic	Population parameter
S <sub>1</sub>	(a)	.000	1.1 ± 4	1.0
S <sub>2</sub>	(c)	.125 ± 1	0.6 ± 4	1.0
S <sub>3</sub>	(a)	.251 ± 1	0.8 ± 3	1.0
S <sub>4</sub>	(c)	.378 ± 1	1.7 ± 5	1.0
S <sub>5</sub>	(a)	.5042 ± 6	0.0 ± 3	1.0
S <sub>6</sub>	(c)	.620 ± 1	1.3 ± 5	1.0
S <sub>7</sub>	(a)	.736 ± 1	0.9 ± 4	1.0
S <sub>8</sub>	(b)	.879 ± 1	1.2 ± 6	1.0
Zn <sub>1</sub>	(c)	.035 ± 2	3.9 ± 9	0.45 ± 5
Zn <sub>2</sub>	(a)	.156 ± 1	1.5 ± 1.4	0.58 ± 4
In <sub>2</sub>	(c)	.2864 ± 5	0.6 ± 1.2	0.42 ± 3
Zn <sub>3</sub>	(a)	.410 ± 2	0.8 ± 7	1.00 ± 3
Zn <sub>4</sub>	(c)	.534 ± 1	0.6 ± 5	0.38 ± 3
In <sub>4</sub>	(a)	.6862 ± 5	1.0 ± 1.8	0.62 ± 5
Zn <sub>5</sub>	(c)	.834 ± 1	3.3 ± 7	0.50 ± 2
In <sub>6</sub>	(b)	.975 ± 1	1.6 ± 1.2	.092 ± 4
Zn <sub>7</sub>	(a)		0.0 ± 6	0.60 ± 2
In <sub>7</sub>	(b)		1.7 ± 6	0.40 ± 2
Zn <sub>8</sub>	(c)		1.7 ± 5	0.59 ± 4

<sup>a</sup>  $a = 3.857 \pm 2 \text{ \AA}$ ,  $c = 24.961 \pm 15 \text{ \AA}$ , S.G.  $P3m1$ , atomic positions: (a) 0,0,*z* (b) 1/3,2/3,*z* (c) 2/3,1/3,*z*

Crystal-chemical considerations (Wurtzite supercells) make it obvious that the unit cells contain integral numbers  $p$  of sulfur atoms. In order to relate the chemical formulas to the actual structural units (layer packs), the former are written in brackets such as to contain  $s$  formula units of sulfur. If  $s \neq p$ , the bracket has an index which is equal to  $p/s = Z$ .

Table I shows that our nonstoichiometric Zn-In-S compounds do not differ very much

TABLE VII

<sup>a</sup>STRUCTURE PARAMETERS OF TYPE 10H10

Atom	Position	<i>z</i>	<sup>b</sup> Population parameter
S <sub>1</sub>	(c)	.0376 ± 37	1.0
S <sub>2</sub>	(b)	.1504 ± 37	1.0
S <sub>3</sub>	(c)	.2477 ± 88	1.0
S <sub>4</sub>	(b)	.3452 ± 40	1.0
S <sub>5</sub>	(c)	.4471 ± 69	1.0
S <sub>6</sub>	(b)	.5381 ± 36	1.0
S <sub>7</sub>	(c)	.6472 ± 39	1.0
S <sub>8</sub>	(b)	.7389 ± 37	1.0
S <sub>9</sub>	(c)	.8508 ± 63	1.0
S <sub>10</sub>	(b)	.9448 ± 40	1.0
Zn <sub>1</sub>	(b)	.0760 ± 24	1.31 ± 16
Zn <sub>2</sub>	(c)	.1755 ± 29	0.94 ± 19
Zn <sub>3</sub>	(b)	.2762 ± 27	1.00 ± 18
Zn <sub>4</sub>	(c)	.3759 ± 28	1.00 ± 19
In <sub>5</sub>	(a)	.5000 ± 22	0.66 ± 10
Zn <sub>6</sub>	(b)	.6135 ± 26	1.10 ± 17
Zn <sub>7</sub>	(c)	.7184 ± 27	1.20 ± 19
Zn <sub>8</sub>	(b)	.8157 ± 24	1.27 ± 17
Zn <sub>9</sub>	(c)	.9696 ± 28	1.00 ± 17

<sup>a</sup>  $a = 3.83_8 \text{ \AA}$ ,  $c = 31.3_0 \text{ \AA}$ , S.G.  $P3m1$ , atomic positions: (a) 0,0,*z* (b) 1/3,2/3,*z* (c) 2/3,1/3,*z*, B isotropic = 0.52 ± 10 for all atoms.

<sup>b</sup> All the atoms in tetrahedral voids have been refined as zinc atoms; their population parameters  $PP > 1$  indicate partial substitution by indium. The number of electrons per unit cell is 471 according to the chemical formula; refinement was made without restrictions on the sum of the PP and resulted in 457 electrons per unit cell.

from stoichiometric compositions compatible with their unit cell and space group symmetry. All but the two rhombohedral phases 36R12 and 12R4 show a tendency towards higher indium concentrations.

TABLE VI

INTERATOMIC DISTANCES (Å) OF TYPE 8H8

In <sub>o</sub>	In <sub>6</sub> -S <sub>6</sub> = 2.774 ± 48	In <sub>6</sub> -S <sub>7</sub> = 2.547 ± 39	S <sub>6</sub> -S <sub>7</sub> = 3.649 ± 60
Zn <sub>r</sub> , In <sub>r</sub>	Zn <sub>2</sub> -S <sub>2</sub> = 2.353 ± 12 Zn <sub>4</sub> -S <sub>4</sub> = 2.364 ± 25 Zn <sub>7</sub> -S <sub>7</sub> = 2.440 ± 44	Zn <sub>2</sub> -S <sub>3</sub> = 2.405 ± 20 Zn <sub>4</sub> -S <sub>5</sub> = 2.345 ± 65 Zn <sub>7</sub> -S <sub>8</sub> = 2.503 ± 20	S <sub>2</sub> -S <sub>3</sub> = 3.870 ± 35 S <sub>4</sub> -S <sub>5</sub> = 3.850 ± 35 S <sub>7</sub> -S <sub>8</sub> = 4.593 ± 71
Zn <sub>t</sub>	Zn <sub>1</sub> -S <sub>1</sub> = 2.391 ± 29 Zn <sub>3</sub> -S <sub>3</sub> = 2.388 ± 35 Zn <sub>5</sub> -S <sub>5</sub> = 2.353 ± 41 Zn <sub>8</sub> -S <sub>8</sub> = 2.406 ± 18	Zn <sub>1</sub> -S <sub>2</sub> = 2.251 ± 42 Zn <sub>3</sub> -S <sub>4</sub> = 2.296 ± 55 Zn <sub>5</sub> -S <sub>6</sub> = 2.127 ± 29 Zn <sub>8</sub> -S <sub>1</sub> = 2.309 ± 22	S <sub>5</sub> -S <sub>2</sub> = 3.835 ± 56 S <sub>3</sub> -S <sub>4</sub> = 3.864 ± 60 S <sub>5</sub> -S <sub>6</sub> = 3.647 ± 44 S <sub>8</sub> -S <sub>1</sub> = 3.749 ± 77

TABLE VIII  
INTERATOMIC DISTANCES (Å) OF TYPE 10H10

$\text{In}_0$	$\text{In}_5\text{-S}_5 = 2.20 \pm 15$	$\text{In}_5\text{-S}_6 = 2.45 \pm 19$
	$\text{Zn}_1\text{-S}_1 = 2.21 \pm 7$	$\text{Zn}_1\text{-S}_2 = 2.33 \pm 14$
	$\text{Zn}_2\text{-S}_2 = 2.35 \pm 5$	$\text{Zn}_2\text{-S}_3 = 2.26 \pm 29$
	$\text{Zn}_3\text{-S}_3 = 2.39 \pm 11$	$\text{Zn}_3\text{-S}_4 = 2.16 \pm 15$
$\text{Zn}_t, \text{In}_t$	$\text{Zn}_4\text{-S}_4 = 2.41 \pm 6$	$\text{Zn}_4\text{-S}_5 = 2.23 \pm 23$
	$\text{Zn}_6\text{-S}_6 = 2.36 \pm 14$	$\text{Zn}_6\text{-S}_7 = 2.45 \pm 6$
	$\text{Zn}_7\text{-S}_7 = 2.12 \pm 15$	$\text{Zn}_7\text{-S}_8 = 2.34 \pm 36$
	$\text{Zn}_8\text{-S}_8 = 2.40 \pm 14$	$\text{Zn}_8\text{-S}_9 = 2.47 \pm 18$
	$\text{Zn}_9\text{-S}_{10} = 2.35 \pm 5$	$\text{Zn}_9\text{-S}_1 = 2.13 \pm 14$

### Crystal Data

The five  $\text{Zn-In-S}$  types 10H5, 8H8, 10H10, 18H9 and 36R12 are new. The crystal structures could be determined for the former three ones; no suitable single crystals were obtained from the other two. The main data of the crystals used for structure determinations are listed in Table II.

During reduction of the diffractometer data ( $LP$ -correction; no correction for absorption and extinction), large and unsystematic discrepancies between symmetry-related reflections could be observed for both types 10H5 and 8H8. The internal residuals

$$R_{\text{int}} = \frac{\sum_i \Delta_i}{\sum_i I_i},$$

were 0.16 and 0.17, respectively, where  $I_i$  stands for the individual intensity,  $\Delta_i$ , being the difference between  $I_i$  and its corresponding symmetry related mean.

### Structure Determinations

The relationship between the unit cells and the Wurtzite cell justifies the hypothesis that all the atoms occupy positions on triad rotation axes with minimal point symmetry  $3m$ . Our results confirmed this assumption. Possible additional symmetry elements are the inversion center  $\bar{1}$ , the mirror plane  $m$  and the screw axis  $6_3$ . Considering the rhombohedral centering of the hexagonal cell as well, we derive the following eight possible space groups:

$$P3m1, P\bar{3}m1, P\bar{6}m2, P6_3mc, P6_3/mmc, R3m, R\bar{3}m, F\bar{4}3m.$$

The group  $F\bar{4}3m$  corresponds to the special case of a rhombohedral cell with  $\alpha = \beta = \gamma = 60^\circ$ , compatible with the cubic close packing.

The systematically absent X-ray reflections of type 10H5 fit the groups  $P6_3mc$  and  $P6_3/mmc$ . Because the types 8H8 and 10H10 simulate the Laue symmetry  $6/mmm$ , the space group  $P\bar{6}m2$  was assumed at first. However, the structure determination led to the space group  $P3m1$  [1]. This can partly be explained as follows: Due to the special positions  $x, y, z = 0, 0, z$  and  $1/3, 2/3, z$  and  $2/3, 1/3, z$  with space group symmetry  $P3m1$  (Laue symmetry  $\bar{3}m1$ ), the structure amplitudes  $|F_{hkl}|$  and  $|F_{\bar{h}\bar{k}\bar{l}}|$  are equal, if the condition  $-h + k = 3n$  is fulfilled. In the Laue group  $\bar{3}m1$ , the triplets  $hkl$  are in general (exception:  $h = k$ ) not symmetry-related to  $h\bar{k}\bar{l}$ , but they are symmetry-equivalent in the Laue group  $6/mmm$ .

The structure of type 10H5 was solved in the following steps:

—one-dimensional “trial and error” with 20 structure factors  $F_{00l}$  determined the sequence of  $\text{Zn}_t\text{-In}_0\text{-Zn}_t\text{-In}_t$  in the 5-sulfur-layer pack ( $\text{Zn}_t =$

<sup>1</sup> Donika et al. seem to have encountered the same problem concerning the structure of  $\text{Zn}_3\text{In}_2\text{S}_6$ , type 6H6: in their first short paper (1966) they assumed the space group  $P\bar{6}m2$ , but later (1968) they found the space group  $P\bar{3}m1$  (2).

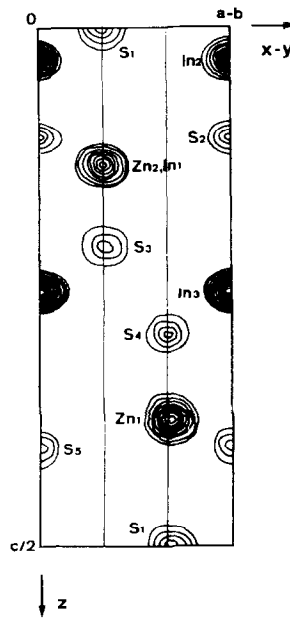
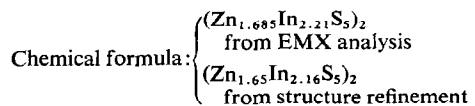


FIG. 1.  $\rho(x-y, z)$  of type 10H5,  $R = 0.133$ .



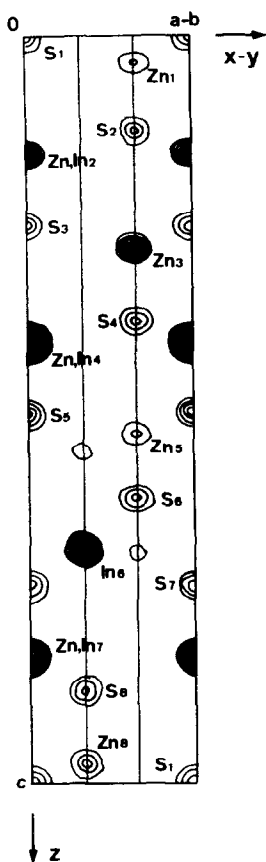
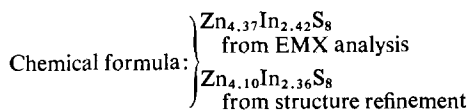


FIG. 2.  $\rho(x-y, z)$  of type 8H8,  $R = 0.189$ .



zinc atom in tetrahedral void;  $\text{In}_o$ ,  $\text{In}_t$  = indium atom in octahedral and tetrahedral void, respectively).

—The two-dimensional Patterson function  $P(u-v, w)$  uniquely defined the arrangement of the metal atoms, leaving three possible sulfur stacking sequences.

—For one of the three models, the refinement of the  $z$  parameters, isotropic temperature factors and—for Zn and In only—of population parameters by the method of least squares converged to  $R = 0.133$ .

The structures of types 8H8 and 10H10 (8 and 10 layer packs, respectively) asked for more computing display. A series of trial models were tested by Fourier methods, and the least-squares refinements resulted in final  $R = 0.189$  (8H8) and 0.265 (10H10).

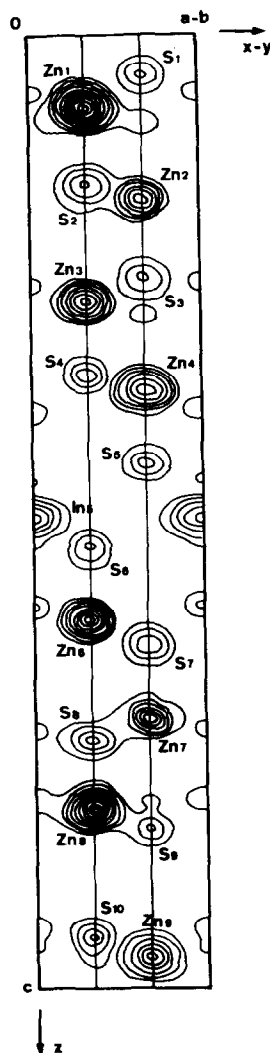
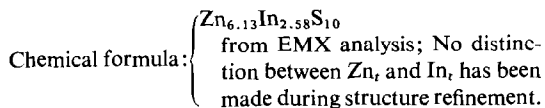


FIG. 3.  $\rho(x-y, z)$  of type 10H10,  $R = 0.265$ .



The parameters and interatomic distances of the three structures are listed in Tables III–VIII, their Fourier maps are shown in Fig. 1–3. The computing programs used were mainly those of the system “X-RAY 67” (15).

### Discussion of the Structures

Common to all the known Zn–In–S structures is an octahedrally coordinated indium atom  $\text{In}_o$ , which has tetrahedrally coordinated atoms

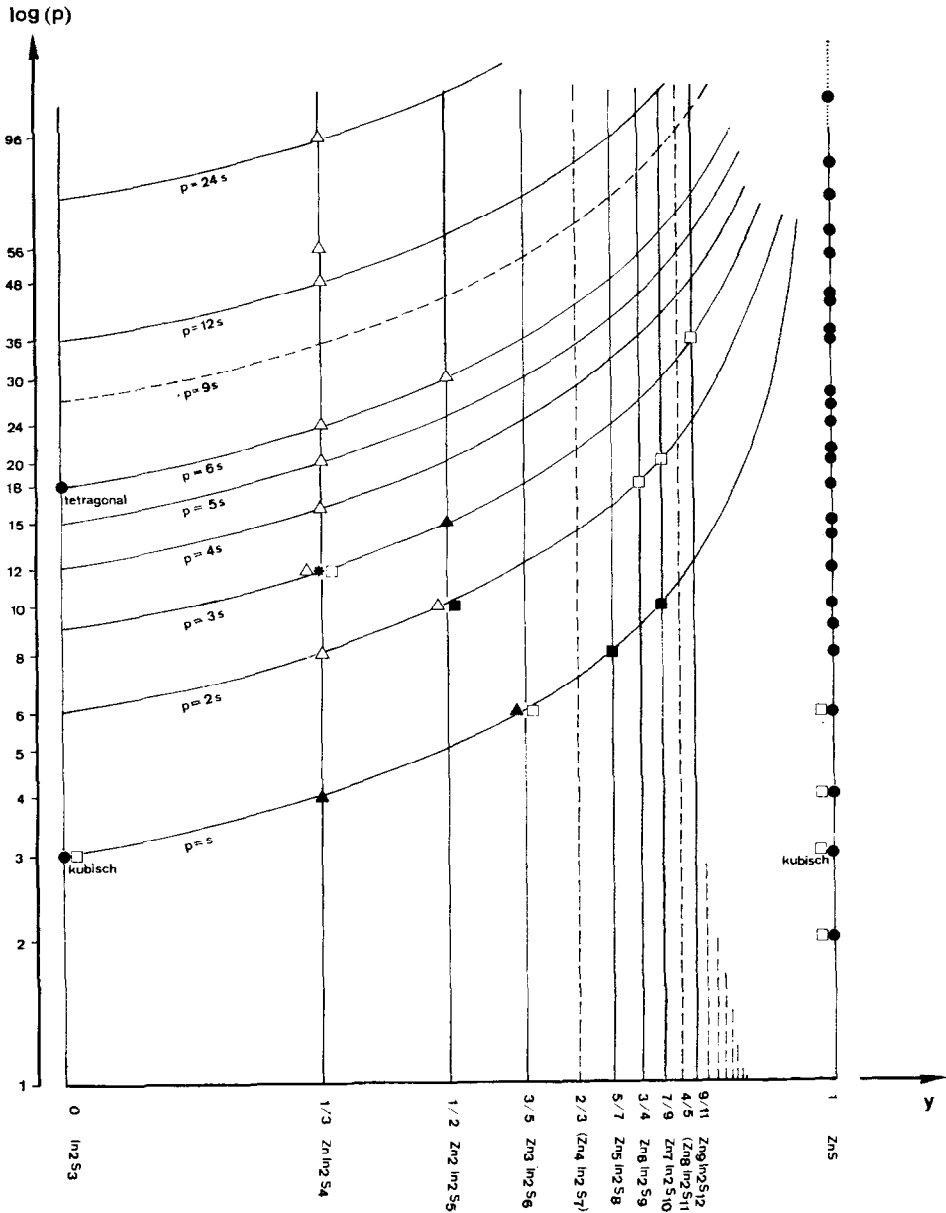


FIG. 4. Geometrical relationship between stoichiometric formula and cell dimension (number of sulfur layers).  $y = [\text{Zn}]/([\text{Zn}] + [\text{In}])$ ;  $p$  = number of close-packed sulfur layers in the hexagonal unit cell  $\approx [c(\text{\AA})/3.1(\text{\AA})]$ ;  $s$  = number of close-packed sulfur layers in the stacking unit; ● =  $\text{ZnS}$  and  $\text{In}_2\text{S}_3$  phases; \* = structure determined by Lappe *et al.* (1); ▲ = structures determined by Donika *et al.* (2-5); △ = phases identified by Donika *et al.* (10); ■ = structures determined in this work; □ = phases identified in this work.

( $\text{Zn}_t$  or  $\text{In}_t$ ) as neighbors. These three atoms are always arranged in the same way: both Zn, In tetrahedra are oriented such as to point towards the  $\text{In}_o$  layer. Their bases may be in one of the three different positions corresponding to the three possible stacking sequences . .ABAB. .,

. .ABAC. ., . .ABCA. . for the four sulfur atoms. Such structural units exist in the polytype forms of  $\text{ZnIn}_2\text{S}_4$  (1, 3, 5). Increasing the Zn concentration (and, therefore, the thickness of one layer pack as well) provides additional tetrahedra which are always pointing towards the  $\text{In}_o$ .

In order to preserve electroneutrality (replacement of 3 Zn<sup>II</sup> by two In<sup>III</sup>), the Zn-In-S layer packs always contain approximately two indium atoms. The empty layer in the sulfur packing explains the cleavage form (001).

A similar series of such layer structures have been proposed in the ZnO-In<sub>2</sub>O<sub>3</sub> system (16).

Figure 4 illustrates the geometrical relationship between the Zn:In ratio and the possible hexagonal structure types. In addition to the phases found in this work as well as by Donika *et al.* (2-5), we may predict the existence of further types.

Each intersection between the vertical lines (locus for a certain composition) and the curves with constant integral ratio  $p/s$  (locus for constant number  $Z$  of formula units per cell) represents possible types.

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