As-containing and empty layers; in each case, the distances between two consecutive iodine layers are 3·670 and 3·455 Å respectively.

Within the 'arsenic' layers, the As atoms and the lone pair sit in octahedra sharing edges and corners, $\frac{2}{3}$ of them being occupied.

The lone pair of As^{III} is stereochemically active, explaining the two sets of As–I distances in the octahedron (Table 2). The angle I–As–I is close to the value of 100° obtained by electron diffraction (Morino, Ukaji & Ito, 1966).

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & WABER, J. T. (1974). In *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.
ENJALBERT, R. & GALY, J. (1978). *C. R. Acad. Sci. Sér. C,* **287**, 259–260.
ENJALBERT, R. & GALY, J. (1979). *Acta Cryst.* **B35**, 546–550.
HEYWORTH, D. (1931). *Phys. Rev.* **38**, 351–359.
MORINO, Y., UKAJI, T. & ITO, T. (1966). *Bull. Chem. Soc. Jpn,* **39**, 71–77.
TROTTER, J. (1965). *Z. Kristallogr.* **121**, 81–86.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Refinement of the 3R γ-Indium Monoselenide Structure Type

By J. RIGOULT AND A. RIMSKY

Laboratoire de Minéralogie-Cristallographie, Université P. et M. Curie, 4 place Jussieu, 75230 Paris CEDEX 05, France

AND A. KUHN

Laboratoire de Luminescence II (Equipe de Recherche associée au CNRS), Université P. et M. Curie, Tour 13, 4 place Jussieu, 75230 Paris CEDEX 05, France

Abstract. The structure factors of the 3R γ-InSe structure type [space group R3m, a = 4·002 (1), c = 24·946 (6) Å (hexagonal axes), Z = 6, μ(Ag Kᾱ) = 13·57 mm⁻¹] have been measured carefully at room temperature by X-ray diffraction and then used in a new refinement of the crystal structure. A residual R(F) factor of 0·015 was obtained after statistical stacking faults had been analysed and taken into account in the refinement. No important modifications were found in the structure itself but more accurate lattice and atomic parameters are given, leading to a better knowledge of the atomic geometry, useful for band-structure calculations. This study forms the basis of a charge-density analysis of γ-InSe.

Introduction. Indium monoselenide is a semiconductor of the A_{III}–B_{VI} group of layered compounds. The gap is about 1·3 eV at room temperature. It is possible to prepare large crystals (Chevy, Kuhn & Martin, 1977), and a high photovoltaic effect can be observed in structures prepared from these crystals. InSe has other interesting physical properties.

The first synthesis of InSe was performed by Klemm & Vogel (1934); the first determination of its structure was made by Schubert, Dörre & Günzel (1954).

InSe is peritectic and this is why there was a certain confusion in some later publications about its structure determination, as shown by Chevy, Kuhn & Martin (1977).

For a systematic study of interatomic distances in the A_{III}–B_{VI} layered compounds GaSe (Kuhn, Chevy & Chevalier, 1975; Kuhn, Chevalier & Rimsky, 1975), GaS (Kuhn, Chevy & Chevalier, 1976a), and $GaSe_xS_{1-x}$ (Kuhn, Chevy & Chevalier, 1976b), it was important to have a good knowledge of these distances in InSe for band-structure calculations. Even for the determination of the electron density distribution in InSe it was necessary to determine the structure factors and to refine γ-InSe with higher accuracy than in the previous best publication, namely that of Likforman, Carré, Etienne & Bachet (1975).

The preparation of the data crystal was very difficult. InSe monocrystals are soft and any mechanical treatment such as cutting, sawing or even cleaving

creates irreversible deformations. This is why we could not use our large crystals and were obliged to grow small InSe monocrystals from the vapour phase, to be used directly.

The growth mechanism of InSe monocrystals is not the same as for GaS and GaSe, where the needle crystals grow with a screw dislocation displaying the same stacking sequence. In the growth of InSe monocrystals from the vapour phase there is a successive deposition of the layers and in consequence any crystal has stacking faults, often twinning and even different polytypes in small regions.

We prepared the data crystals by transport reaction. We were obliged to select the data crystal, having a minimum concentration of stacking faults and no twinning, from a great number of tested crystals. The data crystal had the form of a truncated pyramid with dimensions along **a**, **b** and **c** of 0·2, 0·2 and 0·07 mm.

Details of the experimental procedures are given in Table 1. The sample chosen for data collection was fixed by grease to the end of a quartz rod to prevent any damage to the crystal by glueing it. The diffraction data were treated by the *STEPSCAN* (Rigoult, 1979) program which is a modification of the *PROFILE* program for background, dead-time and Lorentz–polarization corrections. The variance of the diffracted intensities was found by statistics from three periodically measured reflections: $\sigma^2(F_o^2) = \sigma^2_{counting}(F_o^2) + (0 \cdot 01 F_o^2)^2$.

To check and increase the accuracy of the absorption correction, which is fundamental, 77 reflections were collected by rotation about the scattering vector. These observations were the basis of a least-squares fit of sample dimensions following a procedure described previously (*FACIES* program; Rigoult, Tomas & Guidi-Morosini, 1979).

The adjusted dimensions were used for the absorption correction by numerical integration with a 16 × 16 × 6 Gaussian grid (Coppens, Leiserowitz & Rabinovich, 1965). The transmission factor was between 0·17 and 0·41. At this stage, the equivalent reflections were averaged because extinction (if isotropic) was expected to affect these reflections in a

similar manner. The agreement factor $R(F^2)$ between equivalent reflections was 2·2%.

The atomic parameters published by Likforman *et al.* (1975) were the starting point for full-matrix least-squares refinements based on F_o^2, with $\bar{\sigma}^2(F_o^2)$ as weights and scattering factors (including anomalous dispersion) for neutral In and Se atoms from *International Tables for X-ray Crystallography* (1974).

There are two independent In and Se atoms per unit cell lying in the positions $00z$ with site symmetry $3m$; The only non-vanishing anisotropic thermal parameters U_{ij} are thus U_{11}, U_{22}, U_{33} and U_{12} ($U_{11} = U_{22} = 2U_{12}$). Together with the atomic parameters (z, U_{11} and U_{33}) and the scale factor an isotropic extinction parameter was also refined using the program *LINEX* 74 (Becker & Coppens, 1975). The best fit was found for a type I crystal and no improvement was obtained with anisotropic extinction. In order to determine the absolute structure, the refinement was reproduced with inversion of the sign of anomalous dispersion f'': a better convergence is found for the refinement with

Table 2. *Results of refinements*

Values without standard deviations were not refined.

Refinement	(I)	(II)	(III)
sin θ/λ range (Å^{-1})	0·00–1·20	0·50–1·20	0·75–1·20
Scale factor k	0·758 (1)	0·751 (2)	0·739 (4)
Extinction parameter g ($\times 10^4$)	0·120 (4)	0·120	0·120
Stacking faults (%)	6·3 (1)	6·3	6·3
$R(F)$	0·017	0·020	0·028
$R_w(F)$	0·015	0·015	0·018
$R(F^2)$	0·023	0·024	0·032
$R_w(F^2)$	0·030	0·029	0·034
S^*	2·25	1·81	1·46
N_o	398	332	227
N_v	14	12	12
Maximum extinction correction y	0·63		

* $S = [\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

Table 1. *Experimental conditions for data collection* (293 K)

Wavelength: λ(Ag $K\bar{\alpha}_1$) = 0·5594075 Å
Apparatus: Philips PW 1100 four-circle diffractometer
Monochromator: pyrolitic graphite (cos$^2 2\theta_M$ = 0·9722)
Scanning mode: θ–2θ step scan [80 steps (0·02° θ per step) with a counting time of 2 s per step]
Background determination: correlation algorithm
(sin $\theta/\lambda)_{max}$ = 1·2 Å^{-1}
Crystal size (along **a**, **b**, **c**): 0·2 × 0·2 × 0·07 mm
Number of reflections measured: 1336
Number of symmetry-independent reflections: 398

Table 3. *Atomic parameters: fractional coordinate* z ($\times 10^5$) *and* U_{ij} ($\times 10^{-4}$ Å^2)

Refinement sin θ/λ range (Å^{-1})	(I) 0·0–1·20	(II) 0·50–1·20	(III) 0·75–1·20
In(1) z	0	0	0
U_{11}	135 (1)	133 (1)	130 (1)
U_{33}	180 (3)	179 (3)	183 (7)
In(2) z	11102 (2)	11104 (3)	11112 (5)
U_{11}	136 (1)	134 (1)	131 (1)
U_{33}	176 (3)	174 (3)	174 (5)
Se(1) z	82834 (4)	82840 (4)	82857 (7)
U_{11}	122 (1)	119 (1)	116 (1)
U_{33}	166 (4)	161 (4)	171 (7)
Se(2) z	61666 (4)	61674 (4)	61689 (7)
U_{11}	130 (1)	128 (1)	127 (1)
U_{33}	159 (4)	154 (4)	128 (8)

negative f''. At this stage the residual factors are already fairly good: $R(F^2) = 0.054$, $R_w(F^2) = 0.068$, $S = 5.12$. However, a difference-Fourier synthesis shows residual peaks of about 6 e Å^{-3}, which indicates the presence of stacking faults. Indeed, the extinction condition $h - k + l \neq 3n$ (reverse lattice) is not perfectly fulfilled and reflections hkl with $-h + k + l = 3n$ and $l \neq 3n$ (obverse lattice) give significant diffracted intensities whose ratio to the corresponding reflections $\bar{h}\bar{k}\bar{l}$ fluctuates over a large range. This situation excludes the possibility of a twin, and the statistical nature of the defects is also confirmed by weak streaks on monochromatized precession photographs. The stacking faults (layers rotated by 60° around the c axis) can be accurately included in the refinement, the new atoms lying on the obverse lattice.

This procedure is easily performed by the introduction of just one additional parameter, which is the occupancy of the obverse layers; the atomic parameters of the atoms of the obverse layers are constrained to be equal to those of the reverse layers. The agreement factors and refined parameters are given in Tables 2 and 3 for refinements with all data and high-order data. Table 2 shows the improvement obtained by introduction of the stacking faults which appear with a weight of about 6% for all the sample. The high-order refinements (II) and (III) were undertaken in order to obtain atomic parameters unbiased from bonding effects and suitable for charge-density analysis (Coppens, 1977).

Refinement (III) is, in theory, less unbiased from bonding effects; however, correlations for it are greater, so the parameters obtained from refinement (II) seem more reliable as the basis of a charge-density study. Indeed, thermal parameters from refinement (II) are always slightly smaller than those from refinement (I), as may be expected for real thermal motion of the nuclei.

Discussion. The interatomic distances found by us and by Likforman *et al.* (1975) are compared in Table 4.* The bond angles are given in Table 5. For the In(1)—Se(2) and In(2)—Se(1) distances the differences between our values and those of Likforman *et al.* (1975) are in the limits of error, but for the other distances the differences are higher. We explain these differences by the higher accuracy of our refinement and the values $c = 24.946$ Å used by us and $c = 25.32$ Å used by Likforman *et al.* (1975).

The Se(1)—Se(2) interlayer distances are less than twice the van der Waals radius of Se (Pauling, 1945). This could explain an overlapping of their wave functions.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35000 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Principal interatomic distances* (Å)

	Present study	Likforman *et al.* (1975)
In(1)—In(2)	2.7696 (5)	2.818 (6)
In(2)—Se(1)	2.6335 (6)	2.636 (3)
Intralayer		
In(1)—Se(2)	2.6259 (6)	2.627 (3)
Se(1)—Se(2)	5.2808 (14)	5.358 (7)
Interlayer		
Se(1)—Se(2)	3.8140 (14)	3.864 (7)

Table 5. *Bond angles* (°)

Intralayer		Interlayer	
In(2)—In(1)—Se(2)	118.368 (4)	Se(1)—Se(2)—Se(1)	63.288 (9)
In(1)—In(2)—Se(1)	118.673 (5)	Se(2)—Se(1)—Se(2)	63.289 (9)
Se(2)—In(1)—Se(2)	98.898 (2)		
Se(1)—In(2)—Se(1)	99.287 (2)		

It is interesting to note that the two In(1)—Se(2) and In(2)—Se(1) distances are not identical and that there is a small asymmetry in the layers, as will be confirmed later by the electron density determination and as can be seen from the differences of the intralayer bond angles in Table 5.

References

BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425.
CHEVY, A., KUHN, A. & MARTIN, M. S. (1977). *J. Cryst. Growth*, 38, 118–122.
COPPENS, P. (1977). *Isr. J. Chem.* 16, 159–167.
COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* 18, 1035–1038.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
KLEMM, W. & VOGEL, H. U. (1934). *Z. Anorg. Chem.* 219, 45–64.
KUHN, A., CHEVALIER, R. & RIMSKY, A. (1975). *Acta Cryst,* B31, 2841–2842.
KUHN, A., CHEVY, A. & CHEVALIER, R. (1975). *Phys. Status Solidi A*, 31, 469–475.
KUHN, A., CHEVY, A. & CHEVALIER, R. (1976a). *Acta Cryst.* B32, 983–984.
KUHN, A., CHEVY, A. & CHEVALIER, R. (1976b). *Phys. Status Solidi A*, 36, 181–187.
LIKFORMAN, A., CARRÉ, D., ETIENNE, J. & BACHET, B. (1975). *Acta Cryst.* B31, 1252–1254.
PAULING, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
RIGOULT, J. (1979). *J. Appl. Cryst.* 12, 116–118.
RIGOULT, J., TOMAS, A. & GUIDI-MOROSINI, C. (1979). *Acta Cryst.* A35, 587–590.
SCHUBERT, K., DÖRRE, E. & GÜNZEL, E. (1954). *Naturwissenschaften,* 41, 448.