Table 3. *Interatomic distances in Ce_5Ir_4 (Å)*

All e.s.d.'s are 0·01 Å. The Ce atoms forming the trigonal prisms surrounding Ir atoms are marked with *. The Ce atoms forming the cube around Ce(1) are marked with †.

Ce(1)–Ir(1)	2·82	Ir(1)–Ir(2)	2·72
–Ir(2)	2·90	–Ce(1)	2·82
–Ir(1)	2·94	–Ce(1)	2·94
–2Ir(3)	3·15	–2Ce(2)*	2·97
–Ir(2)	3·20	–2Ce(3)*	3·10
–2Ce(2)†	3·45	–2Ce(3)*	3·31
–2Ce(2)†	3·47		
–2Ce(3)†	3·51		
–2Ce(3)†	3·58		
Ce(2)–Ir(3)	2·80	Ir(2)–Ir(1)	2·72
–Ir(3)	2·88	–2Ce(2)*	2·90
–Ir(2)	2·90	–Ce(1)	2·90
–Ir(2)	2·92	–2Ce(2)*	2·92
–Ir(3)	2·97	–Ce(1)	3·20
–Ir(1)	2·97	–2Ce(3)*	3·29
–Ce(1)	3·45		
–Ce(3)	3·59		
Ce(3)–Ir(3)	2·96	Ir(3)–Ce(2)*	2·80
–Ir(1)	3·10	–Ce(2)*	2·88
–Ir(3)	3·14	–Ce(3)*	2·96
–Ir(3)	3·20	–Ce(2)*	2·97
–Ir(3)	3·28	–Ir(3)	2·98
–Ir(2)	3·29	–Ce(3)*	3·14
–Ir(1)	3·31	–Ce(1)	3·15
–Ce(1)	3·51	–Ce(3)*	3·20
–Ce(1)	3·58	–Ce(3)	3·28
–Ce(2)	3·59		

A comparison of unit-cell parameters in Table 2 shows that the c/a ratios for Ce_5Ir_3 and Pu_5Rh_3 are the smallest. Since in the former the c direction is perpendicular to the square faces of the Ce antiprisms, it seems that this structure allows the antiprisms to be squeezed together along this direction.

Examination of the parameters in Table 1 shows that Ce_5Ir_4 is isotypic with Pu_5Rh_4 (Cromer, 1977) which is intermediate between the Gd_5Si_4 and Sm_5Ge_4 types.

The whole structure can be described by a stacking of Ce-centred cubes of Ce atoms and Ir-centred trigonal prisms of Ce atoms as indicated in the list of interatomic distances in Table 3.

The parameters of Ce_5Rh_4 (Raman, 1976) are similar to those of Pu_5Rh_4 and thus all R_5Rh_4 compounds (R = La, Ce, Pr, Sm, Gd) should be considered to be of the Pu_5Rh_4 type (Raman, 1976; Parthé & Moreau, 1977). R_5Pt_4 compounds (R = Tb, Dy, Ho, Er, Y) are also isotypic with Pu_5Rh_4 (Le Roy, Moreau, Paccard & Parthé, 1978) and it has been shown that this structure can be described as a regular stacking of U_3Si_2-like layers of cubes and trigonal prisms and FeB-like layers of trigonal prisms only.

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Refinement of the Structure of Arsenic Triiodide

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Abstract. AsI_3, rhombohedral, $R\bar{3}$, has the following parameters in the hexagonal setting: $a_H = 7·193$ (2), $c_H = 21·372$ (7) Å, $V = 958$ Å^3, $Z = 2$. For 451 selected $hk \pm l$ reflections the final $R = 0·033$. In the hexagonal close packing of iodine, the As atoms with their lone pair E are located in $\frac{2}{3}$ of the octahedra every two layers $\cdots A-(AsE)-B-A-(AsE)-B-A-(AsE)-B-A\cdots$. The structure can be described as being built up of discrete AsI_3 molecules [As–I = 2·591 (1) Å and $\angle IAsI = 99·67$ (5)°].

Introduction. In view of the stereochemical effects of lone pairs on coordination, packing and phase transitions occurring in the trihalides MX_3 of the Group Va elements (M = N, P, As, Sb, Bi), precise information was needed about AsI_3 (Enjalbert & Galy, 1978, 1979).

Heyworth (1931) published the structural determination of AsI_3, indicating that I atoms were hexagonally closed packed and that As atoms were octahedrally coordinated. Nevertheless, the author pointed out the difficulty of precisely locating As atoms and suggested that the lone pair should push As atoms towards a trigonal face of the I octahedron. Trotter (1965) confirmed both structures and remarks and showed that the AsI_3 structure could be described as built up from discrete AsI_3 molecules. The structure was refined using only $hk0$ and $h0l$ film data to R factors of 0·11 and 0·16. A new refinement using full spatial X-ray data was performed.

Orange-red hexagonal plates of AsI_3 were grown in carbon disulfide under microscope control until they increased to a suitable size, compatible with reasonable absorption. The crystal mounted on the diffractometer had three identical distances between the faces {100} {1$\bar{1}$0} {010}, *i.e.* 0·124, and 0·05 mm in thickness.

For the determination of the cell parameters and the collection of intensities a CAD-4 Nonius diffractometer was used with graphite-monochromatized Mo $K\alpha$ radiation. In the structure analysis 451 reflections with $I > 3\sigma(I)$ were used. Corrections were applied for Lorentz–polarization and absorption effects (μ = 20·0 mm^{-1}). The transmission factor evaluated by numerical integration varied between 0·133 and 0·378. In spite of some relations such as pseudo equality between $I(hkl)$ and $I(khl)$ which are not imposed by

$R\bar{3}$, this space group was confirmed by crystal-chemistry reasoning and crystallographic calculations. The refinements were performed by full-matrix least-squares calculations with anisotropic temperature factors for both As and I atoms. Atomic-scattering factors (Cromer & Waber, 1974) with real and imaginary dispersion corrections (Cromer & Liberman, 1970) were used. A parameter to correct for secondary extinction was stabilized at g = 0·352 × 10^{-7} (Zachariasen, 1967). The refinement converged to R = 0·033 and R_w = 0·046 for 14 variables. The final parameters are given in Table 1 and compared with those published by Trotter (1965).*

Discussion. A projection of the structure on to the (001) plane, slightly idealized, is given in Fig. 1. In spite of a change in the referential, this structure determination confirms the occurrence of discrete AsI_3 molecules, the I atoms being hexagonally close packed. The tripling of the c parameter is due to the succession of

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35004 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic temperature factors (with e.s.d.'s in parentheses)*

	Trotter (1965)*	Present work
As [6(c)] x	0	0
y	0	0
z	0·1985	0·80451 (8)
B (Å^2)	4·5	1·2
I [18(f)] x	0·3485	0·31750 (9)
y	0·3333	−0·00662 (9)
z	0·0822	0·74749 (3)
B (Å^2)	4·8	2·4

Anisotropic temperature factors β_{ij} for As and I

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	0·0127 (2)	=β_{11}	0·00134 (4)	=$\frac{1}{2}\beta_{11}$	0	0
I	0·0162 (2)	0·0211 (2)	0·00199 (2)	0·01123 (1)	0·00150 (4)	0·00149 (4)

The form of the anisotropic thermal ellipsoid is

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

* The cell parameters published by Trotter (1965) were a = 7·208, and c = 21·436 Å.
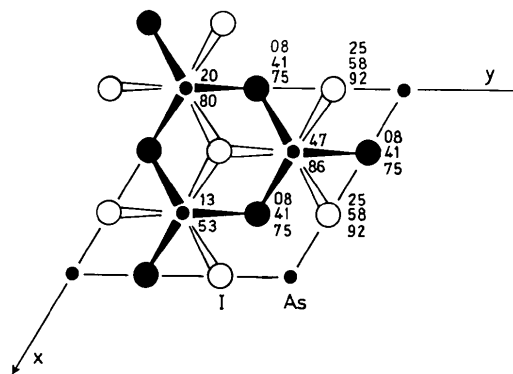

Fig. 1. Slightly idealized projection of the structure on to the (001) plane.

Table 2. *Interatomic distances (Å) and angles (°)*

Intramolecular

As–I	2·591 (1)	I···I	3·959 (1)
I–As–I	99·67 (5)		

Intermolecular

As···I	3·467 (2)		
I···I	4·151 (2)	4·237 (2)	4·247 (2)
	4·259 (2)	4·324 (2)	4·417 (2)
As···As	4·332 (2)		

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).

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Refinement of the 3R γ-Indium Monoselenide Structure Type

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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 $K\bar{\alpha}$) = 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