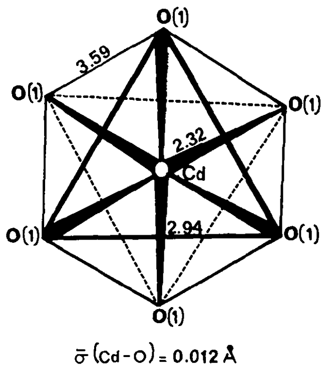

Fig. 2. Environnement de l'atome de cadmium.

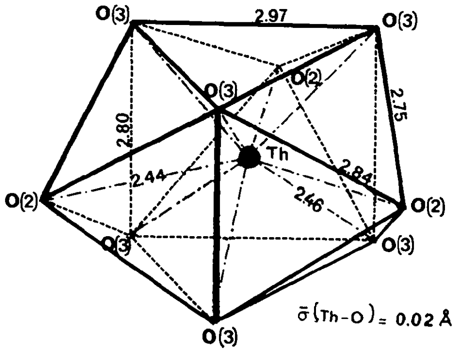

Fig. 3. Environnement de l'atome de thorium.

exemple en position $\frac{1}{3}\frac{2}{3}\frac{1}{4}$, entouré de trois tétraèdres MoO_4 au niveau $\frac{3}{4}$. Les atomes de thorium sont reliés par un pont O—Mo—O, répété par l'axe ternaire et la période *c* du cristal. Ces colonnes $[Th(MoO_4)_3]_\infty$ se placent parallèlement les unes aux autres suivant un assemblage hexagonal; on passe d'une colonne à l'autre par une translation $\frac{1}{3}\frac{1}{3}\frac{1}{2}$ (Fig. 1).

Entre ces colonnes se constitue un canal, centré par l'axe sénaire 6_3 dans lequel se logent les atomes de Cd (en 000 et $00\frac{1}{2}$). Les oxygènes des tétraèdres MoO_4 qui entourent le cadmium forment un octaèdre autour de celui-ci; ils se superposent les uns au-dessus des autres en mettant en commun une face.

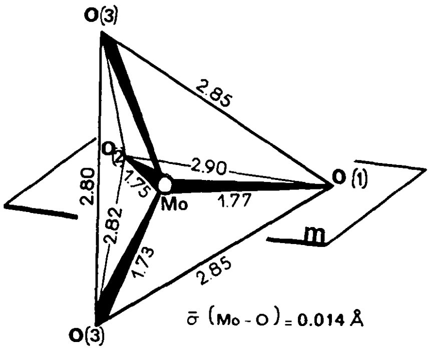

Fig. 4. Environnement de l'atome de molybdène.

La structure confirme la morphologie du cristal: des chaînes periodiques de liaison peuvent être suivies:

– d'une part, parallèlement à l'axe *c*, suivant les colonnes $[Th(MoO_4)_3]_\infty$ définies ci-dessus;

– d'autre part, parallèlement à (110) suivant deux autres chaînes qui partent du cadmium à l'origine (000 et $00\frac{1}{2}$) passant par un tétraèdre MoO_4, le thorium ($\frac{1}{3}\frac{2}{3}\frac{1}{4}$) et un tétraèdre MoO_4, le tout se répétant par l'axe binaire hélicoïdal pour aboutir aux atomes de Cd en 010 et $01\frac{1}{2}$; ces deux chaînes définissent une face du type *F* suivant Hartman (1973) de notation (110).

Les mesures diffractométriques ont été effectuées au Laboratoire de Chimie Structurale des matériaux de l'Université de Paris VI.

Références

AIT ALI SLIMANE, Z., SILVESTRE, J. P. & FREUNDLICH, W. (1978). *C. R. Acad. Sci.* **287**, 409–410.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1971). *ORXFLS* 3. Report ORNL-59-4-37. Oak Ridge National Laboratory, Tennessee.

HARTMAN, P. (1973). *Structure and Morphology in Crystal Growth. An Introduction.* Amsterdam: North-Holland.

International Tables for X-ray Crystallography (1974). Tome IV, Tableau 2.2A. Birmingham: Kynoch Press.

THORET, J. & LAUNAY, S. (1978). *C. R. Acad. Sci.* **287**, 9–11.

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Cerium–Iridium Ce_5Ir_3 and Ce_5Ir_4

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Abstract. Ce_5Ir_3, $P4/ncc$, $Z = 4$, $a = 11{\cdot}267$ (4), $c = 6{\cdot}367$ (3) Å. This structure is of the Pu_5Rh_3 type. Ce_5Ir_4, $Pnma$, $Z = 4$, $a = 7{\cdot}436$ (5), $b = 14{\cdot}776$ (7), $c = 7{\cdot}626$ (6) Å; final $R = 0{\cdot}09$ for 246 independent intensities. The structure is intermediate between Sm_5Ge_4 and Gd_5Si_4 and is isotypic with Pu_5Rh_4.

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Introduction. Structural data on R_5Ir_3 compounds (R = La, Pr, Nd, Sm, Gd) have been published (Paccard, Le Roy & Moreau, 1979). At that time, Ce_5Ir_3 was also prepared, but the structure was not recognized from an examination of the powder diagram due to a large difference in the c/a ratio compared to Pr_5Ir_3. We also include the lattice parameters of Ce_5Ir_3 and those of Pu_5Rh_3 (Beznosikova, Chebotarev, Luk'yanov, Chernyi & Smirnova, 1974) for comparison, as it appears (Cromer, 1979) that all these structures are isotypic.

The crystal structure of Ce_5Rh_4 has been established by Raman (1976). The author used film techniques for intensity measurements and due to poor experimental conditions 'the refined structure could be treated only as a first approximation'. Ce_5Ir_4 was recognized as being isotypic with Ce_5Rh_4, but the relationship to the similar structures Gd_5Si_4 (Iglesias & Steinfink, 1972) and Sm_5Ge_4 (Smith, Johnson & Tharp, 1967) has not been deduced precisely. We report the results of our single-crystal X-ray investigation on Ce_5Ir_4 and discuss the relationship between the structure and other M_5X_4 structures.

The alloys were made from commercially available elements of high purity: Ce 99·9%, Ir 99·99%. Samples were prepared by conventional arc-melting techniques. Small crystals of Ce_5Ir_4 suitable for X-ray analysis were isolated by mechanical fragmentation from the crushed melt. Weissenberg photographs showed the crystal to have space group *Pnma* (systematic absences, $0kl$: $k + l = 2n$; $hk0$: $h = 2n$). Intensities were measured with Zr-filtered Mo $K\alpha$ (λ = 0·71069 Å) radiation on a computer-controlled three-circle goniometer in the $\theta/2\theta$ scan mode. Intensities of 476 independent reflexions, to a limit of $\sin\theta/\lambda$ = 0·50 Å^{-1}, were measured and corrected for background, Lorentz and polarization factors.

Powdered samples of Ce_5Ir_4 and Ce_5Ir_3 were obtained after annealing at 1173 K for 7 d. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation (λ = 1·5418 Å) and were calibrated with Si powder. Lattice parameters (see *Abstract*) were refined by least squares to fit values for 20 independent reflections.

All computer programs used were those of the XRAY system (1972). With the assumption of the centrosymmetric space group *Pnma* and Pu_5Rh_4-type structure, positional and isotropic thermal parameters of Ce_5Ir_4 were refined by full-matrix least squares. Scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). R ($=\sum|\Delta F|/\sum|F_o|$) was 0·11 for 246 observed independent reflexions* with $|F_o| > 3\sigma_F$. The final positional and thermal parameters of Ce_5Ir_4 are listed in Table 1, together with the corresponding positional parameters for Sm_5Ge_4, Gd_5Si_4 and Pu_5Rh_4.

Table 1. *Comparison of the atomic parameters of M_5X_4 structures*

Space group *Pnma*. Similar axial ratios. E.s.d.'s are given in parentheses.

	Equipoint		Sm_5Ge_4^{a}	Gd_5Si_4^{b}	Pu_5Rh_4^{c}	Ce_5Ir_4^{d}
M(1)	4(c)	x	0·2880 (8)	0·3560 (1)	0·3225 (1)	0·320 (2)
		z	0·9976 (8)	0·0113 (1)	0·01077 (9)	0·018 (1)
M(2)	8(d)	x	0·3795 (5)	0·3164 (1)	0·3424 (1)	0·341 (1)
		y	0·6157 (3)	0·6223 (0)	0·62196 (4)	0·6228 (4)
		z	0·1612 (5)	0·1795 (1)	0·16361 (6)	0·1680 (9)
M(3)	8(d)	x	0·9747 (5)	0·0289 (1)	0·0015 (1)	0·009 (1)
		y	0·3996 (3)	0·4028 (0)	0·40796 (4)	0·4089 (4)
		z	0·1781 (5)	0·1827 (1)	0·17796 (6)	0·1783 (9)
X(1)	4(c)	x	0·176 (2)	0·241 (1)	0·1898 (3)	0·198 (1)
		z	0·367 (2)	0·375 (1)	0·3529 (2)	0·369 (1)
X(2)	4(c)	x	0·413 (2)	0·479 (1)	0·4602 (3)	0·456 (1)
		z	0·612 (2)	0·599 (1)	0·6114 (2)	0·620 (1)
X(3)	8(d)	x	0·221 (1)	0·1435 (6)	0·1845 (2)	0·1796 (9)
		y	0·5449 (6)	0·5395 (3)	0·5391 (1)	0·5392 (3)
		z	0·469 (1)	0·4716 (7)	0·4609 (1)	0·4583 (6)

Thermal parameters for Ce_5Ir_4 {the Debye–Waller factor is defined as $\exp[-2\pi^2 \times 10^{-2}\, U \times (2\sin\theta/\lambda)^2]$}

	U (Å^2)		U (Å^2)
Ce(1)	3·6 (9)	Ir(1)	5·0 (8)
Ce(2)	3·4 (6)	Ir(2)	4·7 (8)
Ce(3)	3·7 (6)	Ir(3)	3·6 (5)

References: (a) Smith, Johnson & Tharp (1967). (b) Iglesias & Steinfink (1972). (c) Cromer (1977). (d) This work.

Discussion. The R_5Ir_3 structure can be considered as a shift variation of the W_5Si_3 structure type. All Ir atoms are at the centres of square antiprisms of R atoms. Some of these antiprisms form regular infinite columns with square faces perpendicular to c and other antiprisms are slightly inclined between two columns and have one face common with an antiprism in each of these two columns (Paccard, Le Roy & Moreau, 1979).

Table 2. *Lattice parameters of R_5M_3 compounds with* Pu_5Rh_3 *structure type*

Space group $P4/ncc$.

	a (Å)	c (Å)	c/a	$(V/n)^{1/3}$	References
La_5Ir_3	11·459 (6)	6·629 (5)	0·578	3·007	(a)
Ce_5Ir_3	11·267 (4)	6·367 (3)	0·565	2·934	(b)
Pr_5Ir_3	11·276 (6)	6·499 (5)	0·576	2·955	(a)
Nd_5Ir_3	11·157 (6)	6·432 (5)	0·576	2·925	(a)
Sm_5Ir_3	11·035 (8)	6·372 (6)	0·577	2·894	(a)
Gd_5Ir_3	10·977 (4)	6·348 (3)	0·578	2·880	(a)
Pu_5Rh_3	10·941	6·020	0·550	2·824	(c)

References: (a) Paccard, Le Roy & Moreau (1979). (b) This work. (c) Beznosikova *et al.* (1974).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34908 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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.

References

Beznosikova, A. V., Chebotarev, N. T., Luk'yanov, A., Chernyi, A. V. & Smirnova, E. A. (1974). *At. Energy (USSR)*, **37**, 144–148.

Cromer, D. T. (1977). *Acta Cryst.* B**33**, 1993–1995.

Cromer, D. T. (1979). Private communication.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Iglesias, J. E. & Steinfink, H. (1972). *J. Less-Common Met.* **26**, 45–52.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Le Roy, J., Moreau, J. M., Paccard, D. & Parthé, E. (1978). *Acta Cryst.* B**34**, 3315–3318.

Paccard, D., Le Roy, J. & Moreau, J. M. (1979). *Acta Cryst.* B**35**, 1315–1318.

Parthé, E. & Moreau, J. M. (1977). *J. Less-Common Met.* **53**, 1–23.

Raman, A. (1976). *J. Less-Common Met.* **48**, 111–117.

Smith, G. S., Johnson, Q. & Tharp, A. G. (1967). *Acta Cryst.* **22**, 269–272.

XRAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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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: $a_H = 7 \cdot 193\ (2)$, $c_H = 21 \cdot 372\ (7)$ Å, $V = 958$ Å^3, $Z = 2$. For 451 selected $hk \pm l$ reflections the final $R = 0 \cdot 033$. 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 $\cdots A-(\mathrm{As}E)-B-A-(\mathrm{As}E)-B-A-(\mathrm{As}E)-B-A\cdots$. The structure can be described as being built up of discrete AsI_3 molecules [As–I = 2·591 (1) Å and ∠IAsI = 99·67 (5)°].

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