Les atomes lourds forment deux quadrillages dont les longueurs des côtés sont égales à $a/4$ dans la direction [100] et $b/3$ dans la direction [010]. Le premier est situé à la cote $z = \frac{1}{4}$ et le deuxième à la cote $z = \frac{3}{4}$, et ils sont décalés l'un de l'autre dans la direction [430] de $\mathbf{a}/8 + \mathbf{b}/6$. A ce quadrillage correspond une règle de renforcement des réflexions dans le réseau réciproque: les clichés de Weissenberg montrent que les réflexions hkl dont $h = 4n$ et $k = 3n'$ sont toujours très intenses.

Dans cette structure apparaissent des cavités octaédriques vides formées par les atomes de thallium. Les cavités mettent en commun des arêtes horizontales et forment ainsi des canaux parallèles à la direction **c**.

Conclusion

Tous les atomes métalliques de ce composé possèdent dans leur configuration électronique un doublet $6s^2$ non partagé. Pour le bismuth, ce doublet n'a pas ici d'action stéréochimique. Pour le thallium, au contraire, le doublet a une action stéréochimique évidente: il occupe pour les atomes Tl(1) et Tl(2) le sixième sommet d'un octaèdre dont les atomes de soufre forment les cinq autres sommets. Pour les atomes Tl(3) et Tl(4), le doublet occupe le cinquième sommet d'une bipyramide à base triangulaire dont les atomes de soufre forment les quatre autres sommets. De tels arrangements ont été observés dans Tl_4S_3 (Leclerc & Bailly, 1973).

De plus, suivant une règle fréquemment vérifiée, les doublets des quatre atomes de thallium sont localisés au voisinage les uns des autres, puisque les quatre atomes de thallium sont premiers voisins, et que leurs polyèdres de coordination sont au contact les uns des autres.

Dans $TlBiS_2$ où le thallium est relativement dilué dans la structure, l'activité stéréochimique des doublets n'intervient plus. Dans Tl_2S, elle est au contraire extrêmement marquée. Dans $Tl_4Bi_2S_5$, la proportion de thallium est suffisante pour qu'elle se manifeste.

Le cristal utilisé, lors de cette étude, a été préparé par Mlle M. Guittard, que nous remercions très vivement.

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Nd_5Ir_3: a New Tetragonal Phase with Ir-Centred Square Antiprisms of Nd Atoms

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Abstract

Nd_5Ir_3 crystallizes with a new structure type [tetragonal, space group $P4/ncc$, $a = 11{\cdot}157\ (6)$, $c = 6{\cdot}432\ (5)$ Å, $Z = 4$, $D_x = 10{\cdot}76$ Mg m^{-3}, $F(000) = 2058$, μ(Mo $K\alpha$) = 84·4 mm^{-1}; single-crystal diffractometry, spherical-absorption correction, least-squares refinement, $R = 0{\cdot}11$ for 355 independent reflexions]. The structure is characterized by square antiprisms of Nd atoms centred by Ir atoms. Comparison of Nd_5Ir_3 with the tetragonal W_5Si_3 type shows similar infinite columns of square antiprisms but in a different arrangement. Shifting some atomic planes of Nd_5Ir_3 along the **c** direction leads to an atomic arrangement identical to the W_5Si_3 type. R_5Ir_3 compounds (R = La, Pr, Sm, Gd) are isostructural with Nd_5Ir_3.

Introduction

A survey of the crystal structures of rare-earth–transition-metal compounds R_xT with $x \geq 1$ (T = Co, Rh, Ni, Pd) has been made (Parthé & Moreau, 1977). These structures may be grouped into those where all T

atoms are at the centres of trigonal prisms of R atoms and those where the T atoms are at the centres of either trigonal prisms, cubes, square antiprisms and/or truncated square antiprisms. To see if this classification is still valid for T = Pt and Ir, systematic studies of the R–Pt (Le Roy, Moreau, Paccard & Parthé, 1978), and R–Ir systems have been made. We report in this paper a new structure type, Nd_5Ir_3, and lattice parameters of isotypic compounds which have been identified in the R–Ir systems (R = La, Pr, Sm, Gd).

Experimental

The alloys were made from commercially available elements of high purity: R 99·9%, Ir 99·99%. Samples were prepared by conventional arc-melting techniques. Initial stoichiometries were such that the Ir content ranged from 35 to 40 at.%. Small crystals of Nd_5Ir_3 suitable for X-ray analysis were isolated by mechanical fragmentation from the sample containing 38 at.% Ir. Weissenberg photographs showed the crystal to have space group $P4/ncc$ (systematic absences, $hk0$: $h + k = 2n$; $0kl$: $l = 2n$; hhl: $l = 2n$). 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 355 independent reflexions to a limit of $\sin\theta/\lambda$ = 0·60 Å^{-1} were measured and corrected for background, Lorentz and polarization factors. The crystal was approximately spherical with $R \simeq 36 \times 10^{-3}$ mm and isotropic absorption corrections were applied with μR = 3·0 (*International Tables for X-ray Crystallography*, 1972).

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 were refined by least squares to fit values for 20 independent reflexions.

Structure determination and refinement

All computer programs used were those of the XRAY system (1972). The phases of the largest (E > 1·0) normalized structure factors were determined by direct methods. On the corresponding E map, 20 Nd atoms and 12 Ir atoms were recognized. This was in agreement with calculations based on the atomic volume of the elements which indicated that the unit cell could accommodate four Nd_5Ir_3 units. Moreover, this stoichiometry agrees with the original composition of the sample from which the crystal was chosen. Positional and isotropic thermal parameters were refined satisfactorily by least-squares methods. Scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). R ($\equiv \sum |\Delta F| / \sum |F_o|$) was 0·11 for 344 observed independent reflexions[*] with $|F_{\text{obs}}| > 3\sigma_F$. The final positional and thermal parameters are listed in Table 1.

Table 1. *Atomic parameters for* Nd_5Ir_3 *with e.s.d.'s in parentheses*

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

The space group is $P4/ncc$, and the origin is at $\bar{1}$.

	Equipoint	x	y	z	U (Å^2)
Nd(1)	16(g)	0·0392 (4)	0·3384 (4)	0·1210 (5)	0·5 (2)
Nd(2)	4(b)	$\frac{3}{4}$	$\frac{1}{4}$	0	0·9 (2)
Ir(1)	8(f)	0·5964 (6)	−0·5964 (6)	$\frac{1}{4}$	0·9 (2)
Ir(2)	4(c)	$\frac{1}{4}$	$\frac{1}{4}$	0·3863 (7)	0·6 (2)

Table 2. *Lattice constants for compounds isotypic with* Nd_5Ir_3

E.s.d.'s are in parentheses, V = volume of the unit cell; n = number of atoms in the unit cell.

	a (Å)	c (Å)	$(V/n)^{1/3}$
La_5Ir_3	11·459 (6)	6·629 (5)	3·01
Pr_5Ir_3	11·276 (6)	6·499 (5)	2·95
Nd_5Ir_3	11·157 (6)	6·432 (5)	2·92
Sm_5Ir_3	11·035 (8)	6·372 (6)	2·89
Gd_5Ir_3	10·977 (4)	6·348 (3)	2·88

The isotypism of La_5Ir_3, Pr_5Ir_3, Sm_5Ir_3 and Gd_5Ir_3 with Nd_5Ir_3 was established by comparing observed and calculated powder diffraction intensities (Yvon, Jeitschko & Parthé, 1977). The lattice parameters reported in Table 2 were obtained by least-squares refinement of 2θ values of reflexions measured on films, calibrated with Si, taken with a Guinier camera (Cu $K\alpha$ radiation). The variation of the cell parameters is a consequence of the normal lanthanide contraction.

Discussion

Table 3 gives the interatomic distances (<4 Å). Having only eight Nd neighbours, every Ir atom is at the centre of a square antiprism and every Nd atom participates in the formation of such an antiprism. Thus the structure can be built up exclusively from Ir-centred square antiprisms of Nd atoms. In Fig. 1 the [001] projection shows how these antiprisms are linked together in the structure. The Ir(2)-centred antiprisms are regular and form two infinite columns parallel to the c axis. The Ir(1)-centred antiprisms are slightly deformed and have

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34315 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

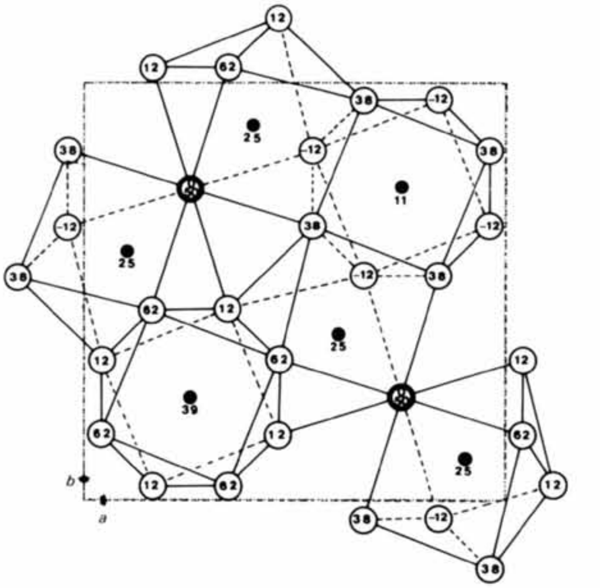

Fig. 1. Arrangement of the Ir-centred square antiprisms in Nd_5Ir_3. The drawing represents a [001] projection. Only antiprisms in the lower half of the unit cell are shown. Ir atoms are represented by small black circles, Nd atoms by large white circles. Numbers indicate the values of the z parameters (× 100).

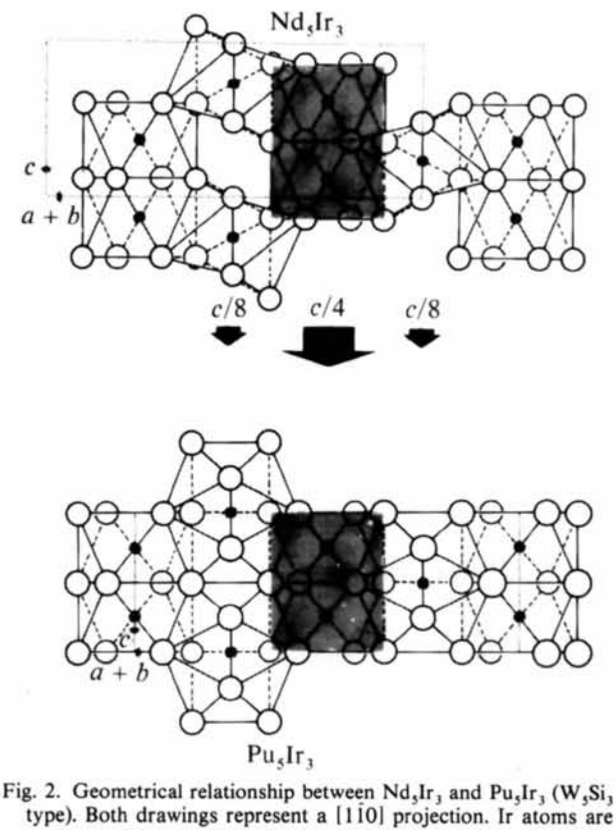

Fig. 2. Geometrical relationship between Nd_5Ir_3 and Pu_5Ir_3 (W_5Si_3 type). Both drawings represent a [1$\bar{1}$0] projection. Ir atoms are represented by small black circles, Nd or Pu atoms by large white circles. From the Nd_5Ir_3 model shifts of atomic planes indicated by black arrows lead to the Pu_5Ir_3 model.

Table 3. *Interatomic distances* (<4 Å) *in* Nd_5Ir_3

All e.s.d.'s are less than 0·008 Å; the Nd atoms forming the surrounding square antiprisms are marked with asterisks.

Nd(1)–Ir(1)	2·917 Å	Nd(2)–4Ir(1)	2·908 Å
–Ir(2)	2·963	–2Nd(2)	3·216
–Ir(1)	3·063	–4Nd(1)	3·462
–Ir(2)	3·068		
–Ir(1)	3·204	Ir(1)–2Nd(2)*	2·908
–Nd(2)	3·462	–2Nd(1)*	2·917
–Nd(1)	3·576	–2Nd(1)*	3·062
–2Nd(1)	3·606	–2Nd(1)*	3·204
–2Nd(2)	3·751		
–2Nd(1)	3·772	Ir(2)–4Nd(1)*	2·963
		–4Nd(1)*	3·068
		–2Ir(2)	3·216

one common face with an antiprism in each of these two columns. In Fig. 2 the [1$\bar{1}$0] projection shows how the Ir(1)-centred antiprisms connect the parallel columns of Ir(2)-centred antiprisms. Moreover, each column is displaced from the neighbouring one by $c/4$ or one half the height of an antiprism.

The structures of tetragonal Nd_5Ir_3 and Pu_5Ir_3 (Cromer, 1977) present similar features. The Pu_5Ir_3 structure is of the W_5Si_3 type and is shown in Fig. 2 in the [1$\bar{1}$0] projection. As in the Nd_5Ir_3 type, there are infinite columns of Ir-centred square antiprisms but these columns are not displaced from one another along the c axes. The main difference between the two structure types of Fig. 2 is the nature of the coordination polyhedron of the Ir atoms placed between the columns. In Nd_5Ir_3 the coordination number is eight and the resulting polyhedron is a square antiprism, whereas in Pu_5Ir_3 the coordination number is six and the resulting polyhedron can be described by two equivalent figures: either a plane pentagon with one corner replaced by a pair of atoms perpendicular to the plane of the pentagon, or a square antiprism with two opposite corners through the centre of the antiprism missing. This coordination figure is also found in the tetragonal Y_3Rh_2 type (Moreau, Paccard & Parthé, 1976). However, it is possible to obtain the Pu_5Ir_3 model from Nd_5Ir_3 by shifting atomic planes along the **c** direction as is shown in Fig. 2. If the whole intermediate column of antiprisms in Nd_5Ir_3 is shifted by $c/4$ and the atomic planes placed between the columns are shifted by $c/8$ then the Pu_5Ir_3 model is obtained. Thus Nd_5Ir_3 and Pu_5Ir_3 (W_5Si_3 type) can be considered as shift structure variants. Similar geometrical relationships have been found previously between Y_3Co_2 and Dy_3Ni_2 (Moreau, Parthé & Paccard, 1975) or CrB, FeB and TbNi types (Hohnke & Parthé, 1966; Lemaire & Paccard, 1970), AlB_2 and $ThSi_2$ (Parthé, 1967) and CeAl and DyAl (Becle & Lemaire, 1967).

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A New GTB-Type Thallium Niobate

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Abstract

A new compound in the system Tl–Nb–O has been synthesized as single crystals of composition very close to $TlNb_7O_{18}$. It crystallizes in the tetragonal system with $a = b = 27{\cdot}50$ (2), $c = 3{\cdot}94$ (1) Å, space group $P4/mbm$, and $Z = 8$. The structure was refined to $R = 6\%$ for 1089 reflections $[I \geq 3\sigma(I)]$. The excess of cations found by refinement of the structure is not sufficient for charge balance. The suggested formula, $Tl_{7\cdot7}Nb_{54+x}O_{146-y}$, may be a result of the combined effect of the excess of cations and stacking faults involving the O atoms.

Introduction

Synthesis of single crystals in the system Tl–Nb–O led to the formation of several new oxides. One of these, with an interlinked tunnel structure (Gasperin, 1977), proved to have cationic-exchange and ionic-conductivity properties. Another, the subject of this paper, is isotypic with Rb or K niobates, the formulae of which are not well defined. A preliminary study of one of these (Gatehouse, Lloyd & Miskin, 1972) showed an unknown octahedral arrangement and was named GTB (Gatehouse Tungsten Bronze). However, the proposed scheme which gives the formula $Rb_3Nb_{54}O_{146}$ does not lead to charge balance.

It appeared worthwhile to pursue as far as possible the structure of this Tl compound because it often happens that the structural and chemical formulae do not agree for non-stoichiometric niobates.

Synthesis and description

Single crystals were obtained by the flux-growth method. The best results occurred when a mixture of Tl_2CO_3, Nb_2O_5 and B_2O_3 in the proportion 4:2:16 was heated at 1373 K in a Pt crucible. After cooling at a constant rate (6 K h^{-1}) to 773 K, the boron glass formed was extracted with boiling water. The resulting product was homogeneously crystallized, giving colourless needles.

The chemical analysis, with 17·1% Tl, and the measured density (5·0 Mg m^{-3}) correspond to the formula $TlNb_7O_{18}$ with $Z = 8$. However, owing to the large amount of Tl volatilized during the heating, it is not certain that the composition of the single crystal selected is the same as the whole.

Lattice parameters and systematic absences were determined from rotation and Weissenberg photographs. The crystals are rectangular prisms elongated along [001] and flattened in the [110] direction. They crystallize in the tetragonal system with $a = b = 27{\cdot}50$ (2), $c = 3{\cdot}94$ (1) Å and the extinctions (0*kl* only

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