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New ternary holmium–transition metal–germanides: Ho_2OsGe_2 of Sc_2CoSi_2 type and $Ho_3Pd_4Ge_4$ of $Gd_3Cu_4Ge_4$ type

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Abstract

Ho_2OsGe_2, $M_r = 665.24$, has amonoclinic structure of the Sc_2CoSi_2 type, *mS*20, (12) $C2/m$-i^5, $a = 10.691(2)$ Å, $b = 4.2618(7)$ Å, $c = 10.050(2)$ Å, $\beta = 118.07(1)°$, $V = 404.06(9)$ Å^3, $Z = 4$, $D_x = 10.936$ mg mm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 88.723$ mm^{-1}, $F(000) = 1096$, $T = 293$ K, $wR = 0.055$ for 490 unique reflections.

$Ho_3Pd_4Ge_4$, $M_r = 1210.75$, has an orthorhombic structure of the $Gd_3Cu_4Ge_4$ type, *oI*22, (71) *Immm*-*ljiha*, $a = 4.2348(8)$ Å, $b = 6.8373(9)$ Å, $c = 14.093(3)$ Å, $V = 408.1(1)$ Å^3, $Z = 2$, $D_x = 9.854$ mg mm^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 53.365$ mm^{-1}, $F(000) = 1026$, $T = 293$ K, $wR = 0.058$ for 329 unique reflections.

The structures of these new germanides were determined by the single-crystal diffraction method. Ho_2OsGe_2 and $Ho_3Pd_4Ge_4$ can be interpreted as being built up only of lamellae consisting of linked trigonal Ho_6 and Ho_4Ge_2 prisms centred by germanium and transition metal atoms respectively.

1. Introduction

Only a very small number of ternary phases are known for the systems Ho–Os–Ge and Ho–Pd–Ge: cubic $Ho_3Os_4Ge_{13}$ [1] of $Yb_3Rh_4Sn_{13}$ type (formerly called $Pr_3Rh_4Sn_{13}$ type), orthorhombic HoPdGe [2] of disordered $CeCu_2$ or KHg_2 type and orthorhombic $HoPd_2Ge$ [3] of YPd_2Si type, a substitution variant of the Fe_3C type. Here we report on the structures of two new ternary germanides.

2. Experimental details

Samples of nominal composition Ho_2OsGe_2 and $HoPdGe_2$ were prepared from high purity elements—holmium (99.9%), osmium, palladium and ger-

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manium (99.999%)—by arc melting under an argon atmosphere, annealed at 1073 K in evacuated quartz tubes for 2 weeks and quenched in water. The weight loss was 0.2% and 0.4% respectively. A needle-like single crystal of the osmium- (palladium-) containing compound with dimensions ±(100): 0.010 mm (0.048 mm), ±(010): 0.048 mm (0.016 mm) and ±(001): 0.010 mm (0.016 mm) was mounted on a Philips PW1100 automatic four-circle diffractometer (Mo Kα radiation) with a graphite monochromator. The unit cell parameters were refined from 2θ values of 26 (20) reflections (Mo Kα, $\lambda = 0.71073$ Å, $19° < 2\theta < 38°$) using the program LATCON [4].

From the values of the lattice constants, their ratios and the possible space groups derived from the conditions for observed reflections, it followed that the osmium-containing compound could be isotypic to monoclinic Sc_2CoSi_2 [5] and the palladium-containing compound isotypic to orthorhombic $Gd_3Cu_4Ge_4$ [6]. This was verified in subsequent structure refinements. The structure determinations and refinements, based on $|F|$ values, of the positional and anisotropic displacement parameters were made using programs from the XTAL3.0 system [7]. The details are compiled in Table 1. The atomic positional parameters were standardized using the STRUCTURE TIDY program

TABLE 1

Summary of details of structure determinations and refinements for Ho_2OsGe_2 and $Ho_3Pd_4Ge_4$

	Ho_2OsGe_2	$Ho_3Pd_4Ge_4$
$(\sin\theta)/\lambda$ range (Å^{-1})	0.094–0.703	0.081–0.703
$h\ k\ l$ range with antireflections	$-14 \leqslant h \leqslant 14$ $0 \leqslant k \leqslant 5$ $0 \leqslant l \leqslant 13$	$0 \leqslant h \leqslant 5$ $0 \leqslant k \leqslant 9$ $0 \leqslant l \leqslant 19$
Standard reflections (maximum intensity variation in per cent)	−1 1 −2 (1.1) 0 −2 0 (0.8)	−2 0 0 (0.7) −1 −1 −4 (0.5)
Number of collected reflections	1372	740
Number of unique reflections	653	370
R_{int}	0.068	0.039
Linear absorption coefficient (mm^{-1})	88.723	53.365
Maximum and minimum transmission factors	0.4172 0.1212	0.4725 0.3441
Number of reflections with $\lvert F_{rel}\rvert > 3\sigma(\lvert F_{rel}\rvert)$	490	329
Number of parameters	32	23
Secondary extinction correction parameter ($\times 10^2$)	0.54 (6)	1.1 (1)
Maximum shift to error ($\times 10^4$)	0.6	0.8
Final residual electron density (Å^{-3})	+7.8 −8.5	+9.4 −7.5
S	2.344	2.845
R	0.067	0.075
wR, $w = 1/\sigma^2(\lvert F_{rel}\rvert)$	0.055	0.058

The reflections were collected in the ω–2θ mode. Absorption correction was made using the program LSABS [8]. The anomalous dispersion factors were taken from ref. 9.

[10]. The final structural data for Ho_2OsGe_2 are given in Table 2 and the interatomic distances in Table 3; the corresponding data for $Ho_3Pd_4Ge_4$ are given in Tables 4 and 5. One notes the high value of the displacement

TABLE 2

Structure data for Ho_2OsGe_2 of Sc_2CoSi_2 type, $mS20$, (12) $C2/m\text{–}i^5$, $a = 10.691(2)$ Å, $b = 4.2618(7)$ Å, $c = 10.050(2)$ Å, $\beta = 118.07(1)°$, $V = 404.06(9)$ Å^3, $Z = 4$, $wR = 0.055$. The atomic positional parameters listed here allow a direct comparison with the standardized data of Sc_2CoSi_2

Atom	Wyckoff position	x	y	z	$U_{eq} \times 100$ (Å^2)
Ho(1)	4(i)	0.9968(3)	0	0.3253(3)	0.69(8)
Ho(2)	4(i)	0.1848(3)	0	0.1130(3)	0.86(9)
Os	4(i)	0.2710(2)	0	0.6320(2)	0.86(7)
Ge(1)	4(i)	0.3585(6)	0	0.4386(6)	0.8(2)
Ge(2)	4(i)	0.4876(6)	0	0.1251(6)	0.8(2)

The equivalent atomic displacement factors are expressed as $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$. E.s.d.s are given in parentheses. The standardization procedure [10] for Sc_2CoSi_2 has led to the following transformation of the originally published cell vectors: $\boldsymbol{a}' = -\boldsymbol{a}$, $\boldsymbol{b}' = \boldsymbol{c}$, $\boldsymbol{c}' = \boldsymbol{a} + \boldsymbol{b}$; and an origin shift by 0 1/2 0.

TABLE 3

Interatomic distances in Ho_2OsGe_2 up to 4 Å for holmium and osmium atoms and up to 3.7 Å for germanium atoms

Ho(1)–2Ge(2)	2.900(5)	Os–2Ge(1)	2.457(3)
2Ge(1)	3.018(4)	Ge(1)	2.522(8)
Os	3.089(4)	Ge(2)	2.587(5)
Os	3.097(3)	Ho(1)	3.089(4)
2Ge(1)	3.100(6)	Ho(1)	3.097(3)
2Os	3.143(3)	2Ho(1)	3.143(3)
Ge(1)	3.479(7)	2Ho(2)	3.193(3)
Ho(1)	3.480(4)	2Os	3.264(3)
Ho(2)	3.554(5)		
2Ho(2)	3.678(3)	Ge(1)–2Os	2.457(3)
Ho(2)	3.889(4)	Os	2.522(8)
		Ge(1)	2.677(8)
Ho(2)–Ge(1)	2.905(5)	Ho(2)	2.905(5)
2Ge(2)	3.040(6)	2Ho(1)	3.018(4)
2Ge(2)	3.084(4)	2Ho(1)	3.100(6)
Ge(2)	3.182(8)	Ho(1)	3.479(7)
2Os	3.193(3)		
Ho(2)	3.511(3)	Ge(2)–Os	2.587(5)
Ho(1)	3.554(5)	Ge(2)	2.650(9)
2Ho(1)	3.678(3)	2Ho(1)	2.900(5)
2Ho(2)	3.824(4)	2Ho(2)	3.040(6)
Ho(1)	3.889(4)	2Ho(2)	3.084(4)
		Ho(2)	3.182(8)

E.s.d.s are given in parentheses.

TABLE 4

Structure data for $Ho_3Pd_4Ge_4$ of $Gd_3Cu_4Ge_4$ type, *oI*22, (71) *Immm-ljiha*, $a = 4.2348(8)$ Å, $b = 6.8373(9)$ Å, $c = 14.093(3)$ Å, $V = 408.1(1)$ Å^3, $Z = 2$, $wR = 0.058$

Atom	Wyckoff position	x	y	z	$U_{eq} \times 100$ (Å^2)
Pd	8(*l*)	0	0.3050(4)	0.3297(2)	2.6(1)
Ho(1)	4(*j*)	1/2	0	0.3728(1)	0.76(6)
Ge(1)	4(*i*)	0	0	0.2176(3)	1.6(2)
Ge(2)	4(*h*)	0	0.1880(8)	1/2	1.3(1)
Ho(2)	2(*a*)	0	0	0	0.98(9)

The equivalent atomic displacement factors are expressed as $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. E.s.d.s are given in parentheses.

TABLE 5

Interatomic distances in $Ho_3Pd_4Ge_4$ up to 4 Å

Ho(1)–4Pd	3.033(2)	Pd–Ge(2)	2.529(4)
2Ge(1)	3.045(4)	2Ge(1)	2.589(2)
4Ge(2)	3.058(3)	Ge(1)	2.617(4)
2Pd	3.150(4)	Pd	2.666(4)
Ho(1)	3.585(3)	2Ho(1)	3.033(2)
2Ge(1)	3.648(2)	Ho(1)	3.150(4)
2Ho(2)	3.860(1)	2Pd	3.178(3)
		2Ho(2)	3.467(3)
Ho(2)–4Ge(2)	3.006(4)		
2Ge(1)	3.066(5)	Ge(1)–4Pd	2.589(2)
8Pd	3.467(3)	2Pd	2.617(4)
4Ho(1)	3.860(1)	2Ho(1)	3.045(4)
		Ho(2)	3.066(5)
		2Ho(1)	3.648(2)
		Ge(2)–2Pd	2.529(4)
		Ge(2)	2.571(8)
		2Ho(2)	3.006(4)
		4Ho(1)	3.058(3)

E.s.d.s are given in parentheses.

parameter of the palladium atoms. Attempts to refine the occupancy factor and displacement parameter of the palladium position did not allow us to improve the results. With the parameter U fixed at 1.5×10^{-2} Å^2 the occupation of the palladium site refined to 87.7(9)% but the R value increased to 0.091 ($wR = 0.069$).

3. Discussion

3.1. Ho_2OsGe_2 of Sc_2CoSi_2 type

The Sc_2CoSi_2 [5] or Zr_2CoSi_2 type [11] has been described before as an intergrowth of $MgCuAl_2$-type columns and CrB-type slabs [12]. A different description of this structure is based on its relation to the monoclinic Dy_3Ni_2 type [13] or to a hypothetical monoclinic R_3T_2 type obtained by unit cell twinning of a cubic close-packed structure [14]. As shown in Fig. 1, in Ho_2OsGe_2 are found the infinite lamellae, similar to those in both binary structures, consisting of four columns of face-sharing centred trigonal prisms. However, the prisms of the ternary structure are characterized by different occupations not only of the prism vertices (holmium and germanium atoms participate) but also of the prism centres (occupied by osmium and germanium atoms). The mutual orientation of the infinite prism lamellae in Ho_2OsGe_2 is different from that observed in the Dy_3Ni_2 type but is the same as in the hypothetical R_3T_2 structure mentioned above. The Sc_2CoSi_2 structure can thus be described as a substitution derivative of this hypothetical R_3T_2 structure, where one of the R and one of the T sites are occupied by silicon atoms.

No ternary substitution derivative structure of the Dy_3Ni_2 type is known. However, for the geometrically related Y_3Co_2 structure [15] (an orthorhombic stacking variant of Dy_3Ni_2) the Mo_2IrB_2 structure is known as a substitution variant [16]. As in Sc_2CoSi_2, the vertices of the trigonal prisms are occupied

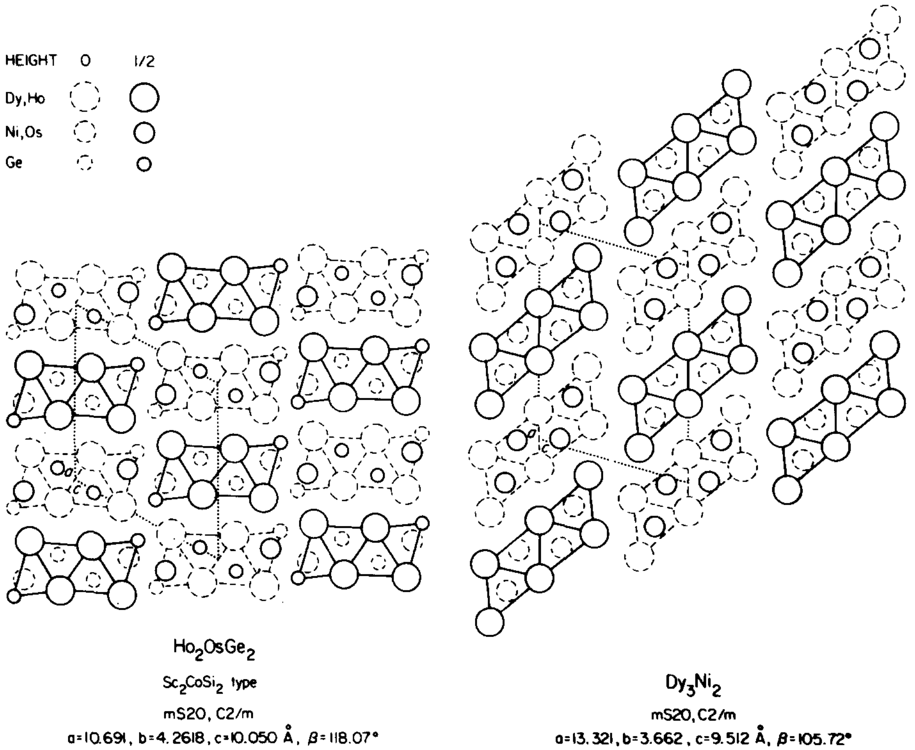

Fig. 1. Projections of the Ho_2OsGe_2 and Dy_3Ni_2 structures along [0 1 0]. The lamellae consisting of four trigonal prism columns are indicated.

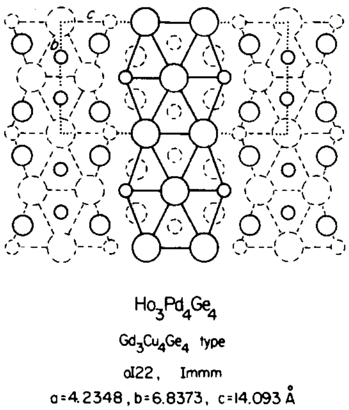

Fig. 2. Projection of the $Ho_3Pd_4Ge_4$ structure along [1 0 0]: large circles, holmium; medium circles, palladium; small circles, germanium. The atoms drawn with full lines are at height 1/2, with dashed lines at 0. Slabs built up of lamellae are emphasized.

by two kinds of atoms (molybdenum and iridium), but unlike Sc_2CoSi_2, at the centres only one kind of atom is found (boron).

The Ho_2OsGe_2 structure is also related to the monoclinic Y_4Co_4Ga structure [17], where it is also possible to recognize lamellae of four linked prism columns. However, these lamellae now share their outer edges in such a way that sheets are formed. The occupation of the prism vertices is the same, with yttrium atoms on holmium sites and gallium on the germanium site, but all prism centres are occupied by cobalt atoms. The mutual arrangement of the lamellae in Ho_2OsGe_2 and of the sheets in Y_4Co_4Ga is such that both structures can be sliced (along particular directions) into two-dimensional segments with an atom arrangement as in the CrB type.

The Sc_2CoSi_2 type is not common; only three scandium (zirconium) silicides with cobalt or iron are known. The new representative is the first lanthanide germanide with a heavy transition element.

3.2. *$Ho_3Pd_4Ge_4$ of $Gd_3Cu_4Ge_4$ type*

The $Gd_3Cu_4Ge_4$ [6] or $Sr_3Li_4Sb_4$ [18] type has been described before as an intergrowth of $MgCuAl_2$-type slabs and pairs of columns of germanium-centred trigonal Gd_6 prisms [12]. From another point of view, as demonstrated in Fig. 2, it is possible to recognize in $Ho_3Pd_4Ge_4$ slabs, perpendicular to [0 0 1], built up only of lamellae, each consisting of three trigonal prism columns sharing rectangular prism faces, the prisms being centred by palladium and germanium atoms. The lamellae are interconnected via common faces. Similar lamellae of trigonal prisms, but interconnected via edges and with only one kind of atom (cobalt) at the centres of trigonal prisms, are found in the Y_3Co_3Ga structure [19].

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