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The crystal structure of a new ternary germanide, $Ho_{26}Pd_4(Pd, Ge)_{19-x}$

O.L. Sologub, Yu.M. Prots', P.S. Salamakha*, V.K. Pecharsky, O.I. Bodak

Department of Inorganic Chemistry, L'viv State University, Lomonosov Str. 6, 290005 L'viv, Ukraine

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Abstract

The crystal structure of the compound $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ was determined by the single-crystal method (DARTCH-1 automatic diffractometer, Mo Kα radiation).

$Ho_{26}Pd_4(Pd, Ge)_{19-x}$ is a substitutional variant of the $Er_{26}Ge_{23-x}$ structure type: space group *P4/nmm*, $a = 14.523(6)$ Å, $c = 10.318(2)$ Å, $V = 2176(2)$ Å^3, $Z = 2$, $R_F = 0.0428$ for 841 unique reflections.

The coordination numbers of the holmium atoms are 14–17. For the germanium atoms tetragonal antiprisms and trigonal prisms are typical as coordination polyhedra. Those for the palladium atoms are trigonal prisms and cubes. All coordination polyhedra have additional atoms.

The structure of $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ can be interpreted as being built up of three kinds of fragment formed by rare earth atoms: (a) a stacking of tetragonal antiprisms and cubes; (b) a column of cubes; (c) a chain of trigonal prisms and tetragonal pyramids. The relationships between the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure and the $Er_{26}Ge_{23-x}$ and $Ce_{26}Li_5Ge_{22+x}$ structure types are discussed.

Keywords: Germanides; Arc melting; Annealing

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1. Introduction

Investigations of the ternary system Ho–Pd–Ge showed that besides the phases known in the literature – $HoPd_2Ge$ (YPd_2Si type) [1], HoPdGe ($CeCu_2$ type) [2], $HoPd_{1-x}Ge_2$ ($CeNiSi_2$ type), $HoPd_{0.6}Ge_{1.4}$ (AlB_2 type), Ho_2PdGe_6 (Ce_2CuGe_6 type), $HoPd_2Ge_2$ ($CeGa_2Al_2$ type) [3] and $Ho_3Pd_4Ge_4$ ($Gd_3Cu_4Ge_4$ type) [4] there exists a compound $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ with a structure similar to $Er_{26}Ge_{23-x}$ [5]. This paper presents the results of a structure determination of the new ternary $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ phase.

2. Experimental details

A sample of $Ho_{50}Pd_{15}Ge_{35}$ was prepared from high purity elements (Ho, 99.9 wt.%; Ge and Pd, 99.99 wt.%) by direct arc melting under an argon atmosphere, annealing at 870 K in evacuated quartz ampoules for 2 weeks and quenching in cold water. The weight loss during the synthesis of an ingot of mass 0.5 g was 0.1%.

Prism-like single crystals of the ternary germanide with dimensions of $0.015 \times 0.015 \times 0.050$ mm^3 were studied preliminarily using the Laue, rotation and Weissenberg methods (Mo Kα and Cu Kα radiation).

A survey of diffraction data for the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure was carried out using a DARTCH-1 automatic four-circle diffractometer with a graphite monochromator (1333 measured and 841 unique reflections, Mo Kα radiation, θ–2θ scanning, cut-off threshold $I(hkl) > 4\sigma(I)$ and absorption correction by the azimuthal scan technique). The unit cell parameters were refined from the 2θ values of 28 reflections (Mo Kα radiation, $16° < 2\theta < 33°$). Attempts to refine the displacement parameters of Pd1 atoms (2*c*) in the anisotropic approximation failed, so the isotropic approximation was used. The difference in the number of electrons of Pd and Ge atoms permitted us to distinguish easily their relative contributions to the diffraction pattern of $Ho_{26}Pd_4(Pd, Ge)_{19-x}$. The M1 and M2 sites are fully occupied statistically by Pd and Ge atoms. Only for one position, 2*c*, which is partially

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*Corresponding author.

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Table 1
Structural data for $Ho_{26}Pd_4(Pd, Ge)_{19-x}$; $P4/nmm$, $a = 14.523(6)$ Å, $c = 10.318(2)$ Å, $V = 2176(2)$ Å^3, $Z = 2$, $R_F = 0.0428$

Atom	Wyckoff position	Occupation	x/a	y/b	z/c	$B_{eqv} \times 10^2$ (Å^2)
Ho1	4*f*	100	$\frac{3}{4}$	$\frac{1}{4}$	0.2690(3)	0.53(8)
Ho2	8*h*	100	0.3688(1)	$-x$	$\frac{1}{2}$	0.54(4)
Ho3	8*i*	100	$\frac{1}{4}$	0.0709(2)	0.9446(2)	0.76(6)
Ho4	8*i*	100	$\frac{1}{4}$	0.0665(2)	0.3844(2)	0.62(5)
Ho5	8*j*	100	0.3922(1)	x	0.6647(2)	0.58(4)
Ho6	16*k*	100	0.3805(1)	0.57087(3)	0.1745(2)	0.63(4)
Pd1	2*c*	0.5Pd	$\frac{1}{4}$	$\frac{1}{4}$	0.184(2)	1.5(3)
Pd2	8*j*	100	0.3682(2)	x	0.1729(4)	0.94(7)
Ge1	2*c*	100	$\frac{1}{4}$	$\frac{1}{4}$	0.7904(11)	1.0(2)
Ge2	8*i*	100	$\frac{1}{4}$	0.5379(3)	0.6926(5)	0.88(13)
Ge3	8*j*	100	0.4538(2)	x	0.3880(5)	0.60(10)
Ge4	8*j*	100	0.4420(2)	x	0.9597(5)	0.49(10)
M1	2*c*	0.79Ge + 0.21Pd	$\frac{1}{4}$	$\frac{1}{4}$	0.5396(9)	0.6(2)
M2	8*i*	0.73Ge + 0.27Pd	$\frac{1}{4}$	0.6300(3)	0.9716(4)	0.82(11)

$B_{eqv} = \frac{1}{3}(B_{11}a^{*2}a^2 + \ldots + 2B_{23}b^*c^*bc \cos \alpha)$. Estimated standard deviations are given in parentheses.

Table 2
Anisotropic parameters for the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ho1	0.21(14)	0.61(14)	0.75(14)	0	0	0
Ho2	0.55(5)	B_{11}	0.50(8)	−0.12(7)	−0.02(6)	$-B_{13}$
Ho3	0.50(9)	1.03(10)	0.74(10)	0	0	−0.01(10)
Ho4	0.55(9)	0.71(10)	0.57(9)	0	0	−0.02(9)
Ho5	0.64(5)	B_{11}	0.45(8)	−0.10(8)	−0.02(6)	$-B_{13}$
Ho6	0.75(6)	0.61(6)	0.51(7)	−0.12(5)	0.01(7)	−0.08(6)
Pd2	0.94(9)	B_{11}	0.9(2)	−0.05(13)	0.04(11)	$-B_{13}$
Ge1	0.8(3)	B_{11}	1.7(6)	0	0	0
Ge2	0.4(2)	0.5(2)	1.8(3)	0	0.5(2)	0
Ge3	0.55(14)	B_{11}	0.7(2)	−0.0(2)	0.06(4)	$-B_{13}$
Ge4	0.64(13)	B_{11}	0.6(2)	0.2(2)	−0.16(13)	$-B_{13}$
M1	0.7(3)	B_{11}	0.6(5)	0	0	0
M2	0.8(2)	1.5(2)	1.1(2)	0	0	−0.4(2)

$T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$.

filled (Pd1), could the type of occupying atoms not be determined absolutely. However, on the basis of crystallochemical considerations, we assumed that it was occupied by Pd atoms.

The crystal structure was solved by direct methods in the space group *P4/nmm* using a program from the CSD system [6]. The structure determination and refinements of the positional and anisotropic displacements of atoms based on $|F|$ values converged to the final values $R_F = 0.0428$ and $R_W = 0.0443$.

3. Results

The atomic positional parameters, anisotropic displacement parameters and interatomic distances are given in Tables 1–3 respectively.

The projection of the unit cell of the compound on the *XY* plane and the coordination polyhedra of the atoms are shown in Fig. 1. For simplicity, only half of the unit cell along [0 0 1] is given here. The other half of the unit cell may be obtained after transformation of the presented part by using the *n* plane perpendicular to [0 0 1]. The coordination polyhedra of the holmium atoms have 14–17 apexes: Ho1[$Ho_8Ge_2M_4$] (a), Ho2-[$Ho_{10}Ge_4$] (b), Ho3[$Ho_8Pd_3Ge_4M$] (c), Ho4[Ho_8Pd_3-Ge_3M] (d), Ho5[$Ho_{10}Ge_6M$] (e) and Ho6[$Ho_9PdGe_4M_2$] (f). Those of the palladium atoms are cubes with four additional atoms, Pd1[Ho_8Pd_4] (g), and distorted trigonal prisms with additional atoms, Pd2[Ho_6PdGe_2] (h). The Ge and M atoms occupy the centres of tetragonal antiprisms with additional atoms, Ge1[Ho_8M] (i) and M1[Ho_8Ge] (m), and distorted trigonal prisms

Table 3
Interatomic distances d (Å) in the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure (*CN*, coordination number)

Ho1–2M2	3.032(6)
2Ge2	3.106(8)
4Ho6	3.363(6)
4Ho2	3.411(5)
2M2	3.529(6)
	CN = 14
Ho2–2Ge2	2.959(7)
2Ge2	3.082(7)
2Ho1	3.411(5)
2Ho2	3.450(6)
2Ho6	3.476(3)
2Ho4	3.559(6)
2Ho5	3.879(6)
	CN = 14
Ho3–2Ge4	2.800(7)
M2	2.931(8)
Ge2	3.043(7)
2Pd2	3.046(6)
Ge1	3.049(9)
2Ho5	3.590(5)
Pd1	3.593(14)
2Ho6	3.668(5)
2Ho3	3.679(7)
2Ho6	3.990(6)
	CN = 16
Ho4–2Pd2	2.933(6)
2Ge3	2.974(7)
M1	3.109(8)
Pd1	3.368(12)
2Ho6	3.502(5)
Ge2	3.522(7)
2Ho2	3.556(6)
2Ho5	3.604(5)
2Ho4	3.768(6)
	CN = 15
Ho5–2Ge2	2.970(7)
Ge3	3.123(6)
M1	3.193(7)
Ge1	3.196(8)
Ge3	3.210(7)
Ge4	3.211(6)
2Ho3	3.590(5)
2Ho4	3.604(5)
2Ho5	3.734(6)
2Ho2	3.879(6)
2Ho5	4.131(6)
	CN = 17
Ho6–Ge4	2.932(7)
Pd2	2.949(7)
M2	2.952(6)
Ge3	2.980(7)
M2	3.010(6)
Ge4	3.035(6)
Ge2	3.172(6)
Ho1	3.363(6)
Ho2	3.476(3)
Ho4	3.502(5)
Ho3	3.668(5)
Ho5	3.734(6)
Ho6	3.736(3)
Ho6–Ho6	3.789(6)
Ho6	3.910(6)
Ho3	3.990(6)
	CN = 17
Pd1–4Pd2	2.430(7)
4Ho4	3.368(12)
4Ho3	3.593(14)
	CN = 12
Pd2–Pd1	2.430(7)
Ge4	2.672(7)
Ge3	2.831(7)
2Ho4	2.933(6)
2Ho6	2.949(7)
2Ho3	3.046(6)
	CN = 9
Ge1–M1	2.588(15)
4Ho3	3.049(9)
4Ho5	3.196(8)
	CN = 9
Ge2–2Ho2	2.959(7)
2Ho5	2.970(7)
Ho3	3.043(7)
Ho1	3.106(8)
2Ho6	3.172(6)
M2	3.175(8)
	CN = 9
Ge3–Pd2	2.831(7)
2Ho4	2.974(7)
2Ho6	2.980(7)
Ge3	2.993(8)
2Ho2	3.082(7)
Ho5	3.123(6)
Ho5	3.210(7)
	CN = 10
Ge4–Ge4	2.521(8)
Pd2	2.672(7)
2Ho3	2.800(7)
2Ho6	2.932(7)
2Ho6	3.053(6)
Ho5	3.211(6)
	CN = 9
M1–Ge1	2.588(15)
4Ho4	3.109(8)
4Ho5	3.193(7)
	CN = 9
M2–2M2	2.534(8)
Ho3	2.931(8)
2Ho6	2.952(6)
2Ho6	3.010(6)
Ho1	3.032(6)
Ge2	3.175(8)
	CN = 9

with additional atoms, $Ge2[Ho_8M]$ (j), $Ge3[Ho_8PdGe]$ (k), $Ge4(Ho_7PdGe]$ (l) and $M2[Ho_6GeM_2]$ (n).

4. Discussion

According to Fig. 2, where a simplified projection of the considered structure on the *XZ* plane is presented,

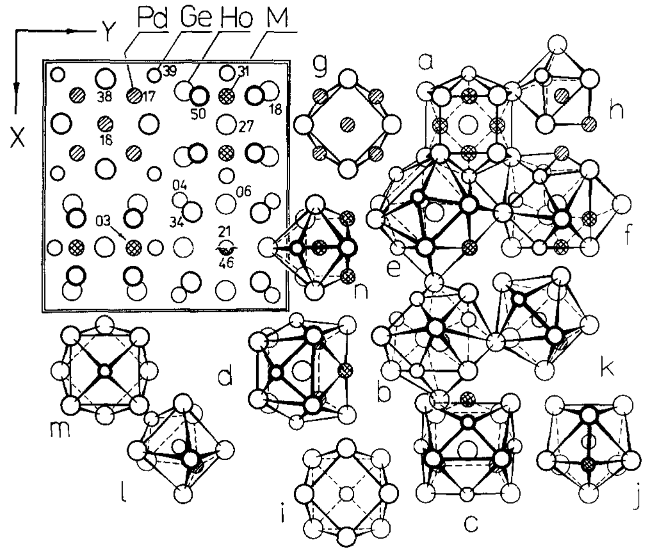

Fig. 1. Projection of the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ unit cell in the region (0–0.5)z on the XY plane and coordination polyhedra of the atoms.

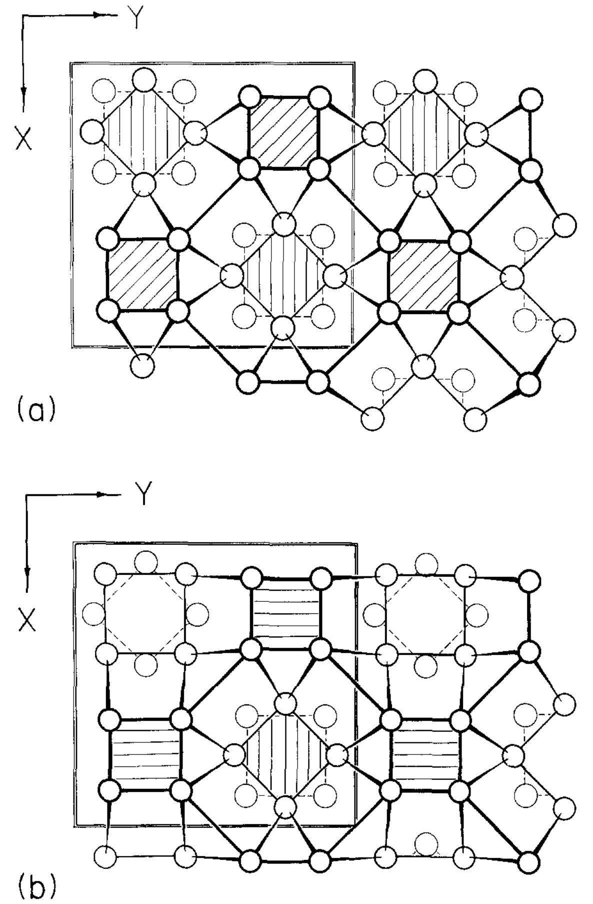

Fig. 3. Stacking of the basic fragments in the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure (projection on the XY plane): a, section in the region (0.18–0.62)z; b, section in the region (0.62–1.18)z.

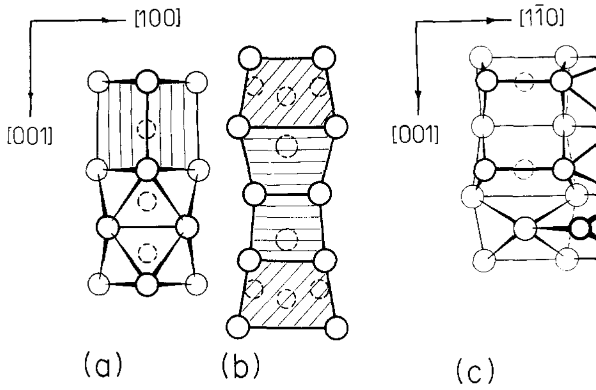

Fig. 2. Three basic fragments in the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure (projection on the XZ plane): a, column of tetragonal antiprisms and cube 1 (vertical lines); b, column of distorted cubes 2 (diagonal lines) and 3 (horizontal lines); c, chain of trigonal prisms and tetragonal pyramids.

one can pick out three basic fragments. Columns of tetragonal antiprisms and cubes in the ratio 2:1 centred by Pd and Ge atoms form the first fragment (Fig. 2a). Similar links exist in the Ru_3Sn_7 structure type [7]. The second fragment is formed only from distorted cubes occupied by X atoms (diagonal lines in Fig. 2b) or Ho atoms (horizontal lines in Fig. 2b) in the ratio 1:2. Each column is surrounded by four chains of trigonal prisms and tetragonal pyramids (Fig. 2c) to give the third fragment. For a better perception, this fragment is shown along the [1 1 0] direction. Cubes 1, 2 and 3 are shaded by vertical, diagonal and horizontal lines respectively. The same type of shading has been used in Fig. 3.

The joining of these fragments can be easily seen from the sections of the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure along the [0 0 1] direction shown in Fig. 3. Here we neglect the distortion of the cubes. Cube 2 and four empty tetragonal pyramids are connected by common planes (Fig. 3a). The environment of cube 3 differs from that of cube 2 by the presence of two trigonal prisms instead of two tetragonal pyramids. The apexes of four tetragonal pyramids form the common plane for cube 1 and the tetragonal antiprisms (Figs. 3a and 3b). Four trigonal prisms are connected by a plane common to two antiprism edges.

The crystal structure of $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ represents a substitutional variant of the $Er_{26}Ge_{23-x}$ structure type [5]. The difference between the two structures lies only in the replacement of germanium atoms by palladium atoms in positions 2c and 8j and the presence of a statistical distribution of Ge and Pd atoms in positions 2c and 2i. A reduction of the interatomic distances exists in both structures. In the $Ho_{26}Pd_4(Pd, Ge)_{19-x}$ structure they are within the usual limits for intermetallic compounds, i.e. 7%–11% shorter than the sum of the atomic radii of the components (Ho, 1.766 Å; Pd, 1.376 Å; Ge, 1.369 Å [8]). Other isotypical ternary phases are not yet known. Only the compound $Ce_{26}Li_5Ge_{22+x}$ [9], where the Li atoms occupy empty tetragonal pyramids, has a similar structure.

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