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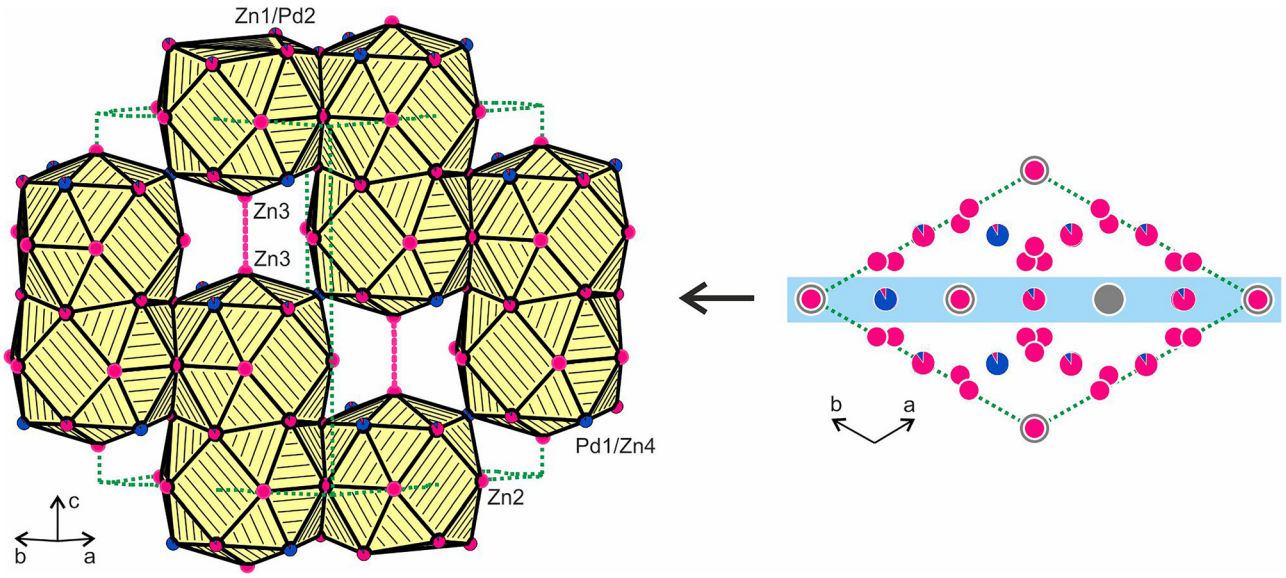
Crystal structure of $Eu_2Pd_{3.37(1)}Zn_{13.63(1)}$



Projection of the $Eu_2Pd_{3.37}Zn_{13.63}$ structure onto the *xy* plane (right). Europium, palladium and zinc atoms are drawn as medium grey, blue and magenta circles, respectively. Mixed occupied sites are indicated by segments. A cutout with one row of condensed Eu@(Pd/Zn)$_{19}$ polyhedra is shown left.

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Abstract

$Eu_2Pd_{3.37}Zn_{13.63}$, trigonal, $R\bar{3}m$ (no. 166), a = 9.1693(7) Å, c = 13.2443(13) Å, V = 964.34(14) Å^3, Z = 3, $R_{gt}(F)$ = 0.0268, $wR_{ref}(F^2)$ = 0.0287, T = 293 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Crystals of the title compound $Eu_2Pd_{3.37}Zn_{13.63}$ were obtained by induction melting of the elements (3:4:12 atomic ratio) in a sealed tantalum ampoule in a water-cooled sample chamber. Starting materials were europium ingots (American Elements, 99.99%), palladium sheets (Agosi, 99.99%) and zinc granules (99.9%, Merck). The sample was first heated to 1473 K, kept for 5 min and quenched. The ampoule was then sealed in an evacuated silica tube, heated to 1223 K with a heating rate of 100 K h^{-1}. The sample was kept at 1223 K for 24 h followed by slow cooling (1 K h^{-1}) to room temperature. $Eu_2Pd_{3.37}Zn_{13.63}$ is light grey with metallic luster and stable in air.

Experimental details

The $Eu_2Pd_{3.37}Zn_{13.63}$ crystals were selected from the mechanically fragmented sample of the nominal composition

Table 1: Data collection and handling.

Crystal:	Grey block
Size:	0.030 × 0.040 × 0.075 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	39.0 mm^{-1}
Diffractometer, scan mode:	IPDS Stoe, ω scans
θ_{max}, completeness:	33.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9175, 488, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 417
$N(param)_{refined}$:	26
Programs:	X-Area [1], JANA2006 [2], SUPERFLIP [3, 4]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*Y*	*z*	U_{iso}*/U_{eq}
Eu1	0	0	0.34506(2)	0.01304(7)
Pd1[a]	0.5	0	0.5	0.01283(13)
Zn1[b]	0.5	0	0.5	0.01283(13)
Zn2[c]	0.50154(2)	0.49846(2)	0.15132(4)	0.01548(15)
Pd2[d]	0.50154(2)	0.49846(2)	0.15132(4)	0.01548(15)
Zn3	0.29377(5)	0	0	0.01484(12)
Zn4	0	0	0.10343(5)	0.01629(16)

[a]Occupancy: 0.917(10), [b]Occupancy: 0.083(10), [c]Occupancy: 0.897(8), [d]Occupancy: 0.103(8).

3Eu:4Pd:12Zn. The crystal quality was first tested through Laue photographs (Buerger camera, image plate detection system). Single crystal X-ray diffraction was performed at room temperature on a Stoe IPDS–II diffractometer (graphite monochromatized MoK_α radiation; oscillation mode). A numerical absorption correction was applied. The starting atomic parameters were deduced with the charge-flipping algorithm [3] implemented in Superflip [4] and the structure was refined on F^2 with the Jana2006 software package [2], with anisotropic displacement parameters for all atoms. Separate refinement of the occupancy parameters indicated small degrees of Pd/Zn mixing for the 9*d* and 18*h* sites, which were refined as least-squares variables in the final cycles. The $Eu_2Pd_{3.37}Zn_{13.63}$ crystal is a reverse/obverse twin with a domain ratio of 0.971(4):0.029(4).

Comment

$Eu_2Pd_{3.37}Zn_{13.63}$ crystallizes with the Th_2Zn_{17} type structure [5], space group $R\bar{3}m$ and completes the series of $RE_2Pd_{3-x}Zn_{14+x}$ compounds [6]. Comparison with the $RE_2Pd_{3-x}Zn_{14+x}$ phases reveals two peculiarities: (i) the solid solution of the europium compound tends towards higher palladium content and (ii) the cell volume is larger than that of the lanthanum representative, indicating divalent europium. The Th_2Zn_{17} type structure has four crystallographically independent zinc sites and allows for different coloring variants (Table 3). Typical binary examples are Ce_2Fe_{17} [7], Zr_2Be_{17} [8] or Ba_2Mg_{17} [9]. Ternary ordered variants have been observed for $Ce_2Co_{15}Al_2$ [7] and $Gd_2Co_3Zn_{14}$ [6]. $Eu_2Pd_{3.37}Zn_{13.63}$ is close to the latter ordering variant, however, the 9*d* and 18*h* sites still show small degrees of Pd/Zn and Zn/Pd mixing, respectively. Such small homogeneity ranges have been observed for most of the many ternary Th_2Zn_{17} type representatives [10]. The europium atoms in the $Eu_2Pd_{3.37}Zn_{13.63}$ structure have the coordination number 19 by palladium and zinc. These $Eu@(Pd/Zn)_{19}$ polyhedra are condensed *via* common hexagon faces and these double units are stacked in ABC sequence (rhombohedral space group symmetry). The coordination polyhedron around europium is a slightly distorted hexa-capped hexagonal prisms with an additional Zn3 atom. This coordination reminds of the $CaCu_5$ type [11], one of the basic binary intermetallic structure types. Indeed, the Th_2Zn_{17} type derives from the $CaCu_5$ structure [12] by an ordered replacement of 2/3 of the calcium atoms by europium and of 1/3 by a $Zn3_2$ dumb-bell while the remaining palladium and zinc atoms replace the copper atoms. The $Zn3_2$ dumb-bells are emphasized in the figure between adjacent $Eu@(Pd/Zn)_{19}$ polyhedra. The Zn3–Zn3 distances of 274 pm are close to the Zn–Zn distances in *hcp* zinc (six times 266 and six times 291 pm) [13]. The Pd–Zn distances within the three-dimensional $[Pd_{3.37}Zn_{13.63}]$ network of $Eu_2Pd_{3.37}Zn_{13.63}$ range from 260 to 278 pm, which is slightly longer than the sum of the covalent radii [14] of 253 pm for Pd + Zn. This is similar to the series of dimorphic equiatomic *RE*PdZn phases [15].

Table 3: Examples of coloring variants for Th_2Zn_{17} type representatives (space group $R\bar{3}m$, Pearson code hR57 and Wyckoff sequence $hfdc^2$).

Compound	6*c*	6*c*	9*d*	18*f*	18*h*	Ref.
Th_2Zn_{17}	Th	Zn	Zn	Zn	Zn	[5]
Ce_2Fe_{17}	Ce	Fe	Fe	Fe	Fe	[7]
Zr_2Be_{17}	Zr	Be	Be	Be	Be	[8]
Ba_2Mg_{17}	Ba	Mg	Mg	Mg	Mg	[9]
$Ce_2Co_{15}Al_2$	Ce	Al	Co	Co	Co	[7]
$Gd_2Co_3Zn_{14}$	Gd	Zn	Co	Zn	Zn	[6]

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