

The Dierbium Dipalladium Silicide, $\text{Er}_2\text{Pd}_2\text{Si}$, Structure, a Periodic Intergrowth of CeCu_2 and MnP Structure-Type Segments

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Abstract. $M_r = 575.4$, orthorhombic, $Pnmm$, $a = 7.391$ (1), $b = 13.724$ (2), $c = 4.2807$ (8) Å, $Z = 4$, $D_x = 8.92$ Mgm^{-3} , $\mu(\text{Mo } K\alpha) = 47.98$ mm^{-1} , $F(000) = 987$, $T = 293$ K. The crystal structure of a single crystal of composition $\text{Er}_2\text{Pd}_{2.15}\text{Si}_{0.85}$ was determined by direct methods and refined to a weighted R of 0.091 [$w = 1/\sigma^2(F)$, 308 F_o , 16 variables]. Er forms strongly deformed trigonal prisms which are centred either by Pd atoms or by Pd/Si. The structure can be described as a periodic intergrowth of CeCu_2 and MnP structure-type segments with layers of Er atoms, corresponding to Ce or Mn atoms, common to both slabs. The compounds $\text{Dy}_2\text{Pd}_2\text{Si}$, $\text{Ho}_2\text{Pd}_2\text{Si}$ and $\text{Tm}_2\text{Pd}_2\text{Si}$ are isotypic to $\text{Er}_2\text{Pd}_2\text{Si}$.

Introduction. The ternary systems containing a rare-earth element (including Sc and Y) with palladium and silicon, germanium or gallium have not been studied in detail. A few ternary R -Pd-Si compounds have only recently been analysed structurally, for example ScPdSi with the TiNiSi ($oP12$) type structure (Hovestreydt, Engel, Klepp, Chabot & Parthé, 1982), $\text{Y}_3\text{Pd}_2\text{Si}_3$ with the $\text{Hf}_3\text{Ni}_2\text{Si}_3$ type ($oC32$) (Paccard, Le Roy & Moreau, 1982) and RPd_2Si with a ternary ordered Fe_3C -type variant ($oP16$) (Moreau, Le Roy & Paccard, 1982). In this paper we report on the structure determination of a compound with approximate composition $\text{Er}_2\text{Pd}_2\text{Si}$.

Experimental. A number of alloys in the ternary system Er -Pd-Si with 33 to 50 at.% Er were prepared. Starting materials were high-purity elements (Er: 99.9, Pd: 99.99 and Si: 99.999%) which were used for the preparation of the equiatomic binary master alloys ErPd and ErSi . Appropriate amounts of the crushed master alloys and Pd or Si powders were mixed, compacted by cold pressing and allowed to react by melting in an arc furnace under purified Ar. The $\text{Dy}_2\text{Pd}_2\text{Si}$, $\text{Ho}_2\text{Pd}_2\text{Si}$ and $\text{Tm}_2\text{Pd}_2\text{Si}$ alloys, as well as stoichiometric $\text{Er}_2\text{Pd}_2\text{Si}$, were prepared directly from the elements by arc melting.

Well developed single crystal of tabular shape ($90 \times 50 \times 30$ μm) selected from a sample with nominal composition $\text{Er}_{0.44}(\text{Pd}_{0.6}\text{Si}_{0.4})_{0.56}$; computer-controlled

four-circle diffractometer (Philips PW 1100, graphite-monochromated $\text{Mo } K\alpha$ radiation); preliminary investigations indicated orthorhombic symmetry, with systematic absences $0kl$ $k+l = 2n+1$ and $h0l$ $h+l = 2n+1$; possible space groups $Pnmm$ or $Pnn2$; the cell dimensions of $\text{Er}_2\text{Pd}_{2.15}\text{Si}_{0.85}$ [$\equiv \text{Er}_2\text{Pd}(\text{Pd}_{0.575}\text{Si}_{0.425})_2$] given in Table 1 were determined by least-squares refinement of the 2θ values of 24 reflections using $\text{Mo } K\alpha_1$ ($\lambda = 0.70930$ Å) radiation in the range $45^\circ < 2\theta < 54^\circ$; data collected for one octant of reciprocal space using the θ - 2θ scan mode ($6^\circ \leq 2\theta \leq 54^\circ$); the unique set consisted of 542 reflections from which 309 with $I > 3\sigma(I)$ were considered as significant; Lorentz, polarization and spherical absorption ($\mu R \sim 1.0$) corrections.

Direct and Fourier methods of structure solution; the signs of 92 reflections with $E > 1.2$ were determined with the programs *SINGEN* and *PHASE* of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); corresponding E map revealed the Er and Pd positions; the positions of the two mixed sites were obtained from a corresponding Fourier map; preliminary least-squares refinement [$\sum(\Delta F)^2$ minimized] assuming a 1:1 occupation of the mixed sites by Pd and Si converged to an R value of 0.11; refinement of the population parameters for these two sites resulted in a slight decrease of R to 0.106; the 002 reflection was omitted for the final refinements, since it appeared to be severely affected by extinction; final $R = 0.101$ and $R_w = 0.091$; scattering factors for neutral atoms from Cromer & Mann (1968), anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Table 1. Lattice parameters and cell volume of compounds with orthorhombic $\text{Er}_2\text{Pd}_2\text{Si}$ type

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

	a (Å)	b (Å)	c (Å)	V (Å ³)
$\text{Dy}_2\text{Pd}_2\text{Si}$	7.419 (2)	13.857 (4)	4.305 (1)	442.6 (2)
$\text{Ho}_2\text{Pd}_2\text{Si}$	7.403 (2)	13.793 (3)	4.2910 (9)	438.2 (2)
$\text{Er}_2\text{Pd}_2\text{Si}$	7.391 (1)	13.724 (2)	4.2807 (8)	434.2 (1)
$\text{Er}_2\text{Pd}(\text{Pd}_{0.575}\text{Si}_{0.425})_2$	7.3986 (3)	13.756 (2)	4.2885 (2)	436.46 (7)
$\text{Tm}_2\text{Pd}_2\text{Si}$	7.380 (2)	13.658 (4)	4.269 (2)	430.3 (3)

Table 2. Atomic positions and thermal parameters ($\times 10^2$) for $\text{Er}_2\text{Pd}(\text{Pd}_{0.575}\text{Si}_{0.425})_2$ with space group $Pn\bar{m}$

All atoms are in equipoint 4(g). The equivalent isotropic temperature factors are expressed as $T = \exp[-2\pi^2 U(2\sin\theta/\lambda)^2]$ and were obtained from $U = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. E.s.d.'s are given in parentheses.

	x	y	z	U (\AA^2)
$\text{Pd}_{0.58}\text{Si}_{0.42}(1)$	0.164 (2)	0.5325 (7)	0	1.0 (2)
$\text{Pd}_{0.57}\text{Si}_{0.43}(2)$	0.167 (2)	0.0168 (7)	0	0.8 (2)
Pd	0.172 (1)	0.2262 (6)	0	0.9 (2)
Er(1)	0.4590 (5)	0.3723 (4)	0	1.0 (1)
Er(2)	0.5462 (5)	0.1264 (4)	0	1.0 (1)

Table 3. Interatomic distances (\AA) up to 3.8 \AA for $\text{Er}_2\text{Pd}(\text{Pd}_{0.575}\text{Si}_{0.425})_2$

Pd/Si indicates $\text{Pd}_{0.575}\text{Si}_{0.425}$. E.s.d.'s are given in parentheses.

Er(1)–Pd(3)	2.922 (9)	Er(2)–Pd/Si(2)	2.89 (1)
2Pd(3)	2.987 (7)	2Pd/Si(1)	2.946 (8)
2Pd/Si(2)	3.050 (8)	Pd(3)	3.089 (9)
2Pd/Si(2)	3.070 (8)	2Pd(3)	3.095 (7)
Pd/Si(1)	3.08 (1)	Pd/Si(2)	3.18 (1)
Pd/Si(1)	3.10 (1)	2Pd/Si(1)	3.184 (9)
Er(2)	3.443 (7)	Er(1)	3.443 (7)
Er(1)	3.566 (7)	Er(2)	3.543 (7)
2Er(2)	3.732 (4)	2Er(1)	3.732 (4)
Pd/Si(1)–2Pd/Si(2)	2.491 (8)	Pd/Si(2)–2Pd/Si(1)	2.491 (8)
Pd/Si(1)	2.58 (2)	Pd/Si(2)	2.52 (2)
2Er(2)	2.946 (8)	Pd(3)	2.88 (1)
Er(1)	3.08 (1)	Er(2)	2.89 (1)
Er(1)	3.10 (1)	2Er(1)	3.050 (8)
2Er(2)	3.184 (9)	2Er(1)	3.070 (8)
2Pd(3)	3.63 (1)	Er(2)	3.18 (1)
Pd(3)–Pd/Si(2)	2.88 (1)		
Er(1)	2.922 (9)		
2Er(1)	2.987 (7)		
Er(2)	3.089 (9)		
2Er(2)	3.095 (7)		
2Pd/Si(1)	3.63 (1)		

Powder diffraction data showed stoichiometric $\text{Er}_2\text{Pd}_2\text{Si}$ to be isotypic with $\text{Er}_2\text{Pd}(\text{Pd}_{0.575}\text{Si}_{0.425})_2$. A comparison of the intensities with those calculated by *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) (in particular a comparison between the intensities of the 111 and 031 reflections) showed a tendency of the Pd and Si atoms to order on the mixed sites. Mixed site (1) is preferentially occupied by Pd atoms and mixed site (2) by Si atoms; however, there is no complete ordering. No effort was made to determine the ordering in more detail. As seen in Table 2 in the case of the single crystal $\text{Er}_2\text{Pd}_{2.15}\text{Si}_{0.85}$ no preferential site occupation could be found.

Discussion. The final structural parameters are given in Table 2, a list of interatomic distances in Table 3.*

A projection of the $\text{Er}_2\text{Pd}_2\text{Si}$ structure along the short c axis is shown in the middle of Fig. 1. The structure consists of a space-filling arrangement of strongly deformed trigonal prisms of Er atoms with their prism axes parallel to the crystallographic b axis. Depending on the kinds of atoms that are found in the centres of the trigonal prisms the structure can be described as a stacking of two different prism sheets. One kind of slab, where every prism centre is occupied by a mixture of Pd and Si atoms, corresponds to the CeCu_2 type as found for example with ErPdGe (Hovestreydt *et al.*, 1982) and is shown on the left of Fig. 1. The second slab,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38390 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

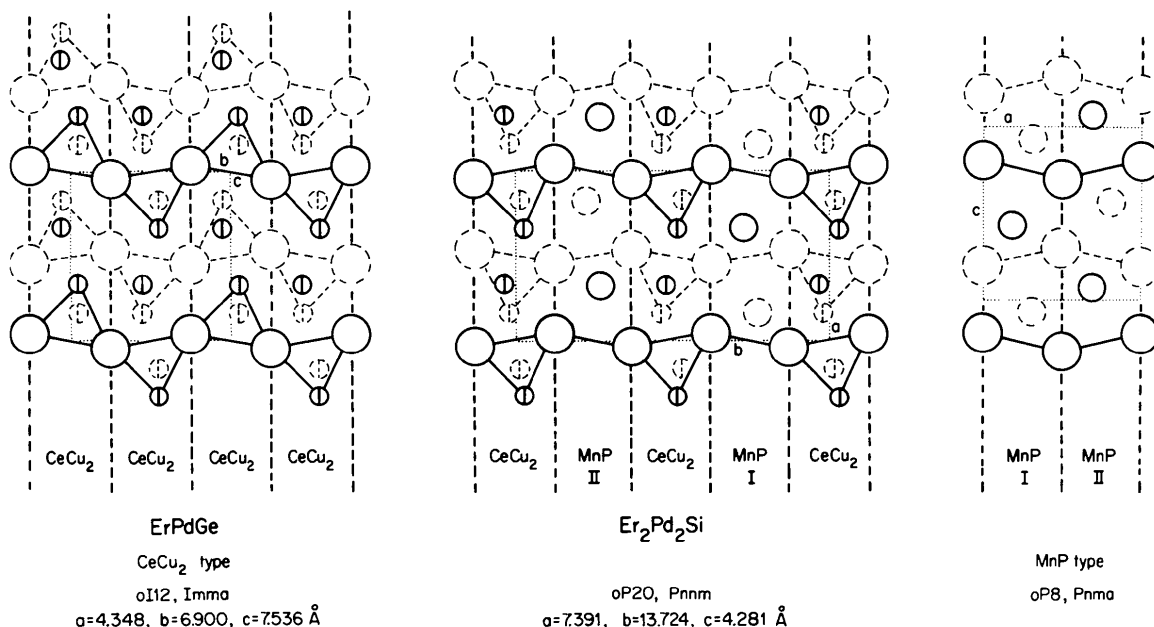


Fig. 1. The structure of $\text{Er}_2\text{Pd}_2\text{Si}$ interpreted as periodic intergrowth of CeCu_2 and MnP-type slabs. Large circles: Er, medium circles: Pd, small barred circles: randomly occupied by Pd and Ge or Si respectively. Filled circles in plane of projection; dashed circles differ by $\frac{1}{2}$ of the translation unit in height.

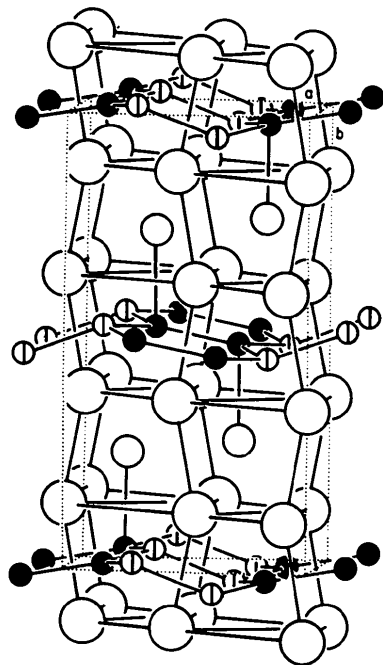


Fig. 2. Perspective drawing of Er₂Pd₂Si with the two kinds of mixed sites for Pd and Si indicated by small circles (full and barred). Medium circles: Pd, large circles: Er.

where every other prism centre is occupied by a Pd atom only, is a segment of the MnP type, as shown on the right of Fig. 1. No rare-earth compounds with the MnP type are known.*

* DyPd, HoPd and ErPd have high-temperature modifications with the CsCl type (Loebich & Raub, 1973; Palenzona & Cirafici, 1975). The low-temperature modifications give very diffuse diffraction lines. In the case of DyPd the lines have been indexed by assuming an FeB-type structure (Klepp & Parthé, 1982).

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Structure de l'Orthophosphate Double NaCuPO₄-α

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Abstract. α-NaCuPO₄ (low-temperature form), $M_r = 181.5$, orthorhombic, $P2_12_12_1$, $a = 9.708$ (5), $b = 4.805$ (2), $c = 7.166$ (4) Å, $Z = 4$, $D_m = 3.55$, $D_x = 3.606$ Mgm⁻³, $V = 334.3$ Å³, $T = 293$ K, $F(000) =$

The two mixed sites in the corrugated layer in the CeCu₂-type slab have different coordinations. If one considers only the close (Pd/Si)–Pd and (Pd/Si)–(Pd/Si) distances, (Pd/Si)(1) (open small circles in Fig. 2) has three neighbours and (Pd/Si)(2) (filled small circles in Fig. 2) has four neighbours, one being a Pd atom from a neighbouring MnP-type slab. The weak preferential site occupation noted during the study of powder photographs of stoichiometric Er₂Pd₂Si corresponds to the filled circles being occupied by Si atoms and the open circles by Pd atoms.

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