

Structure of YPd_2Si , an Ordered Fe_3C Type

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Abstract. Yttrium dipalladium silicide, YPd_2Si , space group $Pnma$, $a = 7.303(2)$, $b = 6.918(2)$, $c = 5.489(1)$ Å, $Z = 4$, $\mu R(Mo K\alpha, \lambda = 0.71069 \text{ \AA}) = 1.6$, crystallizes with an ordered version of the Fe_3C -type structure with the Y and Pd atoms occupying the corresponding Fe sites. The structure was determined by direct methods; final $R = 0.11$ for 219 independent intensities. New compounds found to be isotypic are RPd_2Si with $R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu$ and RPt_2Si with $R = Gd, Tb, Dy, Ho, Er, Tm, Lu, Y$.

Introduction. The lattice parameters of R_3M binary alloys of rare earth (R) and transition metals (M) with the Fe_3C -type structure have been reported for $M = Ir, Pt$, by Le Roy, Moreau, Paccard & Parthé (1979), for $M = Co, Rh, Ni, Pd$ by Parthé & Moreau (1977) and for $M = Os, Ru$ by Palenzona (1979), Palenzona (1980), Sanjinez, Chabot & Parthé (1980). The Fe_3C structure can be derived from a hexagonal close-packed model, using the concept of unit-cell twinning as reported by Andersson & Hyde (1974) and Parthé & Moreau (1977). It could be expected that the Fe_3C model would still appear if the M atom, originally at the centre of R trigonal prisms, is replaced by the much smaller Si atom and some of the R atoms replaced by M atoms such as Pt or Pd. We report the structure of RM_2Si compounds with $R =$ rare earth and $M = Pt$ and Pd crystallizing with an Fe_3C -type derived structure.

The alloys were made from commercially available elements of high purity (rare earth: 99.9%, Pd: 99.99%, Pt: 99.99%, Si: 99.999%). Samples were prepared by conventional arc-melting techniques. Small crystals of YPd_2Si suitable for X-ray analysis were isolated by mechanical fragmentation from the crushed melt. Weissenberg photographs showed the crystals to have space group $Pnma$ or $Pn2_1a$.

YPd_2Si single-crystal intensities were measured with Zr-filtered Mo $K\alpha$ radiation on a computer-controlled three-circle goniometer in the $\theta/2\theta$ scan mode. Intensities of 328 independent reflections, to a limit of $\sin \theta/\lambda = 0.30 \text{ \AA}^{-1}$, were measured and corrected for background, Lorentz and polarization factors and 219 reflections with $I > 3\sigma(I)$ were considered as observed.

X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and were calibrated with Si powder. Lattice parameters reported in Table 1 were refined by least squares to fit values for 25 independent reflections observed on Guinier films from powdered samples.

All the computer programs used were from the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The crystal structure of YPd_2Si was solved by direct methods in the space group $Pnma$ with the programs *SINGEN* and *PHASE*, which generated

Table 1. Unit-cell dimensions (Å) for RT_2Si compounds with the ordered Fe_3C -type structure

E.s.d.'s are given in parentheses. N is the number of atoms in the unit cell.

	a	b	c	$(V/N)^{1/3}$
CePd ₂ Si	7.609 (2)	6.877 (1)	5.695 (1)	2.651
PrPd ₂ Si	7.561 (3)	6.885 (2)	5.672 (3)	2.643
NdPd ₂ Si	7.513 (2)	6.892 (2)	5.638 (1)	2.633
SmPd ₂ Si	7.445 (3)	6.905 (2)	5.584 (2)	2.618
GdPd ₂ Si	7.364 (2)	6.920 (2)	5.545 (1)	2.604
TbPd ₂ Si	7.323 (2)	6.906 (2)	5.513 (1)	2.593
DyPd ₂ Si	7.299 (1)	6.923 (2)	5.501 (1)	2.590
HoPd ₂ Si	7.265 (2)	6.923 (2)	5.484 (2)	2.583
ErPd ₂ Si	7.234 (2)	6.932 (3)	5.469 (2)	2.578
TmPd ₂ Si	7.201 (2)	6.927 (2)	5.452 (1)	2.571
LuPd ₂ Si	7.151 (2)	6.924 (3)	5.438 (2)	2.563
YPd ₂ Si	7.303 (5)	6.918 (4)	5.489 (4)	2.588
GdPt ₂ Si	7.356 (2)	6.916 (2)	5.515 (2)	2.598
TbPt ₂ Si	7.325 (2)	6.913 (2)	5.486 (2)	2.589
DyPt ₂ Si	7.288 (2)	6.909 (2)	5.469 (2)	2.582
HoPt ₂ Si	7.269 (2)	6.909 (2)	5.449 (2)	2.577
ErPt ₂ Si	7.234 (2)	6.909 (2)	5.431 (2)	2.570
TmPt ₂ Si	7.212 (3)	6.916 (3)	5.422 (2)	2.566
LuPt ₂ Si	7.170 (2)	6.917 (3)	5.398 (2)	2.558
YPt ₂ Si	7.282 (2)	6.912 (2)	5.461 (1)	2.580

Table 2. Atomic positions for YPd_2Si

E.s.d.'s are given in parentheses. The isotropic temperature factors for YPd_2Si are expressed as $\exp[-2\pi^2 \times 10^{-2} U(2 \sin \theta/\lambda)^2]$.

	x	y	z	$U(\text{Å}^2)$
Y	0.0303 (9)	$\frac{1}{4}$	0.144 (2)	0.1 (2)
Pd	0.1767 (5)	0.0517 (5)	0.5928 (8)	0.12 (9)
Si	0.362 (3)	$\frac{1}{4}$	0.853 (5)	1.2 (5)

Table 3. *Interatomic distances in YPd₂Si up to 3.45 Å*

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

Pd—Si	2.40 (2)	Y—Si	2.90 (3)
—Si	2.49 (2)	—2Pd	2.957 (7)
—Si	2.69 (2)	—Si	3.00 (3)
—Pd	2.748 (5)	—Si	3.03 (3)
—Pd	2.865 (5)	—2Pd	3.004 (6)
—Y	2.957 (7)	—2Pd	3.020 (9)
—Y	3.004 (6)	—Si	3.03 (3)
—Y	3.020 (9)	—2Pd	3.201 (7)
—Pd	3.036 (6)		
Si—2Pd	2.40 (2)		
—2Pd	2.49 (2)		
—2Pd	2.69 (2)		
—Y	2.90 (3)		
—Y	3.00 (3)		
—Y	3.03 (3)		

the phases with $|E(hkl)| > 1.3$. The positions of the Y and Pd atoms were revealed in the corresponding E map, while the Si positions were obtained by difference Fourier syntheses. Full-matrix least-squares refinement converged after a few cycles to a conventional $R(\equiv \sum |AF| / \sum |F_o|)$ of 0.11.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional parameters are listed in Table 2, interatomic distances in Table 3. Refinement in the $Pn2_1a$ space group did not significantly improve the R factor.

Discussion. The isotypism of the YPd₂Si structure of Fe₃C type was not expected at first from determination of lattice constants owing to differences in b/a and c/a ratios. But comparison of atomic positional parameters of YPd₂Si and Y₃Pt shows that the only difference (9%) is in the value of the z parameter of Pd and Si atoms when compared with Y(2) and Pt (Le Roy *et al.*, 1979). In Fig. 1 the Y₃Pt and YPd₂Si models are represented in projection along the c axis. Chains of atoms which characterize the hexagonal close-packed model are similar to those of Fe₃C. Trigonal prisms surrounding Si atoms in YPd₂Si are similar to those surrounding Pt atoms in Y₃Pt and consequently these two structures can be considered as isotypic.

In Fig. 1 one can see that two Pd—Pd edges of each trigonal prism are parallel to the b axis so that the value of the b parameter should be mainly dependent on the Pd—Pd distance and not dependent on the size of the rare earth. This is demonstrated in Fig. 2 where we have plotted the values of the unit-cell parameters for

* A list of structure factors of YPd₂Si has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36841 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

RPd₂Si and RPt₂Si compounds as a function of the radius of the trivalent rare-earth ion (Templeton & Dauben, 1954). The variation of the a and c parameters is a consequence of the normal lanthanide contraction, but the variation of the b parameter is

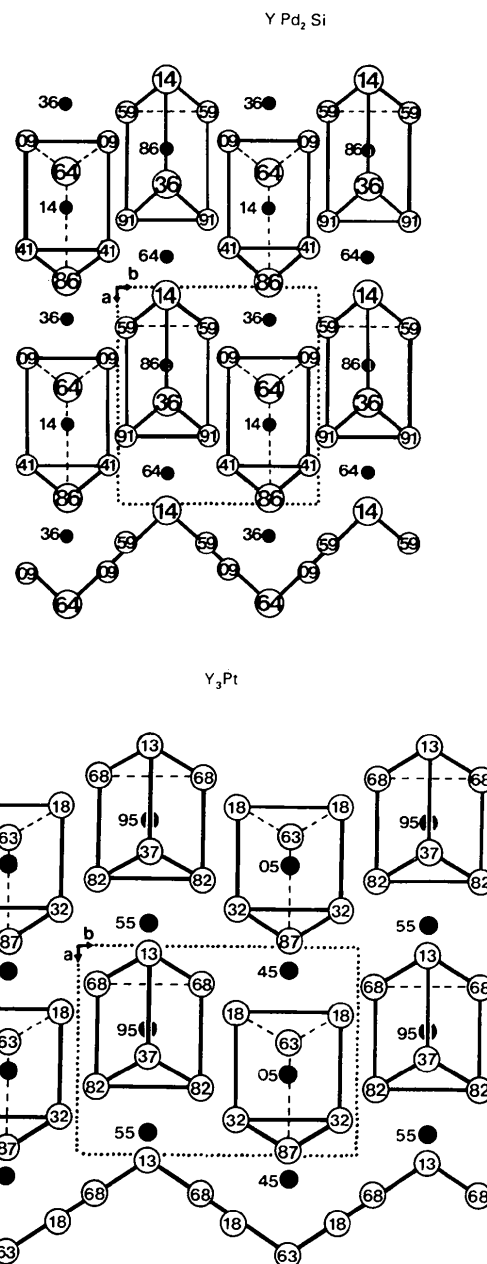


Fig. 1. Projection along the c axis for YPd₂Si and Y₃Pt with Fe₃C-type structure. Numbers within circles correspond to z parameters multiplied by 100. Drawing of trigonal prisms becomes significant if 100 is added to inscribed values of 100z for upper edges. YPd₂Si: big circles are Y atoms, small circles Pd atoms and full circles Si atoms. Y₃Pt: big circles are Y atoms and full circles Pt atoms.

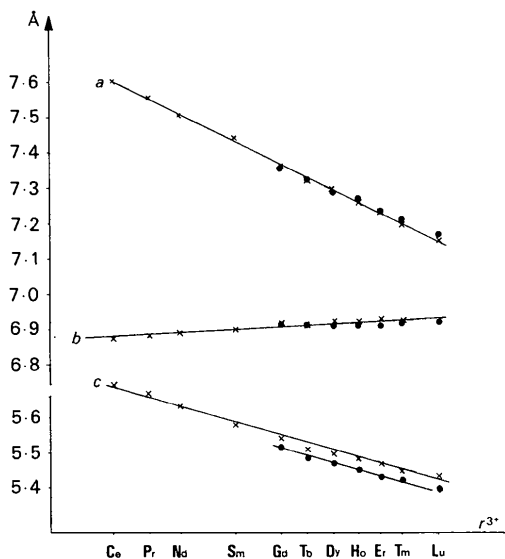


Fig. 2. Unit-cell parameters a , b , c , for orthorhombic RPd_2Si (x) and RPt_2Si (●) compounds versus ionic radius r^{3+} for rare-earth elements.

almost independent and it can be concluded that the bigger the rare earth, the shorter is the Pd–Pd distance along the b axis.

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Orthorhombic Palladium Yttrium Silicide $Y_3Pd_2Si_3$ and Rhodium Yttrium Silicide $Y_3Rh_2Si_3$ with $Hf_3Ni_2Si_3$ Structure Type

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Abstract. $Y_3Pd_2Si_3$ is orthorhombic, space group $Cmcm$ with $a = 4.251$ (3), $b = 10.406$ (8), $c = 14.123$ (7) Å, $\mu R = 1.4$, $Z = 4$. The structure was determined by direct methods; final $R = 0.08$ for 182 independent intensities. $Y_3Rh_2Si_3$ is isotypic; $a = 4.174$ (2), $b = 10.598$ (4), $c = 13.726$ (5) Å. Both structures are isotypic with $Hf_3Ni_2Si_3$.

Introduction. In the ternary system Y–Pd–Si we investigated first the system YPdSi–YSi to see whether it would be possible to find structures based on trigonal prisms of Y and Pd atoms surrounding Si atoms. A phase corresponding to $2(YPdSi) + YSi$, or $Y_3Pd_2Si_3$, was found and the structure was solved.

The alloys were made from commercially available elements of high purity (Y 99.9, Pd 99.99, Rh 99.99, Si 99.9999%). Samples were prepared by conventional arc-melting techniques. Small crystals of $Y_3Pd_2Si_3$ and

$Y_3Rh_2Si_3$ suitable for X-ray analysis were isolated by mechanical fragmentation from the crushed melt. Weissenberg photographs showed the crystals to have space group $Cmcm$.

$Y_3Pd_2Si_3$ single-crystal intensities were measured with Zr-filtered $Mo K\alpha$ ($\lambda = 0.71069$ Å) radiation on a computer-controlled three-circle goniometer in the θ – 2θ scan mode. Intensities of 231 independent reflections, to a limit of $\sin \theta/\lambda = 0.30$ Å^{–1}, were measured and corrected for background, Lorentz and polarization factors and 182 reflections with $I > 3\sigma(I)$ were considered as observed. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and were calibrated with Si powder. Lattice parameters (see *Abstract*) were refined by least squares to fit values for 23 independent reflections observed on films from powdered samples.

All the computer programs used were from the XRAY system (Stewart, Kruger, Ammon, Dickinson