

The Crystal Structure of $\text{Sm}_{10}\text{Pd}_{21}$

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Abstract

$\text{Sm}_{10}\text{Pd}_{21}$ crystallizes in the monoclinic space group $C2/m$ with $a = 24.853(4)$, $b = 5.765(1)$, $c = 16.509(3)$ Å, $\beta = 90.88(2)^\circ$, $Z = 4$, $D_x = 10.50$, $D_m = 10.35$ Mg m⁻³ (by pycnometry), $\mu(\text{Mo } K\alpha) = 39.8$ mm⁻¹. The structure was solved by direct methods and refined by full-matrix isotropic least squares to a conventional R index of 0.077 over 2378 counter-measured observed reflexions. The determination of the atomic positions allowed the correct stoichiometry to be assigned. The structure consists of nets of hexagons, pentagons and triangles interleaved by 3⁶ nets of Pd atoms, all the layers being stacked normal to the y axis. The Sm–Pd contacts, always shorter than the sum of the corresponding metallic radii, play an important role in determining the coordination of each atom.

Introduction

Rare earths (R) with the Group VIII elements Fe, Co, Ni, Ru, Rh, Os, Ir and Pt are known to form compounds with 1:2 stoichiometry and crystal structures corresponding to the Laves phases, MgCu_2 or MgZn_2 type. With Pd, on the other hand, only Eu is known to form a compound, EuPd_2 , with MgCu_2 structure type, containing Eu in the divalent state (Iandelli & Palenzona, 1974). In all other known R –Pd phase diagrams, Y–Pd, Sm–Pd, Gd–Pd, Dy–Pd, Ho–Pd and Er–Pd investigated by Loebich & Raub (1973), phases are formed with 1:2 composition but their structures have not yet been determined. Moreover, in the Yb–Pd system around the 1:2 composition at least three phases are formed which give complex X-ray powder patterns (Iandelli & Palenzona, 1973).

Therefore it seemed worthwhile to undertake research on the RPd_2 phases; in this paper the crystal structure of $\text{Sm}_{10}\text{Pd}_{21}$ is reported.

Experimental

A careful examination of the above-mentioned R –Pd phase diagrams showed that SmPd_2 presents the most favourable thermal conditions of preparation in order

to obtain a single phase and, possibly, single crystals; therefore, a sample of composition $\text{Sm}_{36}\text{Pd}_{64}$ was prepared (Sm 99.5% and Pd 99.999% purity), sealed in a tantalum crucible under argon by arc welding, melted in an induction heating furnace and slowly cooled to room temperature. The homogeneity of the sample was checked by conventional micrographic techniques. Large crystals separated by a eutectic formed the principal phase. Small cavities in the bulk allowed the separation of single crystals.

A needle-like single crystal with dimensions $0.05 \times 0.07 \times 0.40$ mm (elongated parallel to the y axis, as observed later) was examined by X-ray photographic techniques. Monoclinic symmetry and extinctions for hkl with $h + k = 2n + 1$ indicated the possible space groups $C2$, Cm or $C2/m$. $C2/m$ was chosen for structure resolution on the basis of intensity statistics.

Lattice constants (see *Abstract*) and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) on a Philips PW 1100 automatic diffractometer. The ω -scan mode was used with scan width 2° , scan speed $0.045^\circ \text{ s}^{-1}$, and background time 10 s. A whole hemisphere of the reciprocal lattice was scanned for θ between 2 and 27.5° . Three standard reflexions were periodically monitored; no significant change in their intensities was observed. Lorentz and polarization corrections were applied; the absorption correction was made, following the procedure suggested by North, Phillips & Mathews (1968), by the use of 72 ψ -scan data from four strong $0k0$ reflexions. The discrepancy index among equivalent reflexions amounted to 2.3%; averaging gave 3008 independent reflexions.

The structure determination was accomplished using direct methods. The unusual intensity distribution, with very weak reflexions for k odd, led to difficulty in the solution of the phase problem. The structure was finally solved using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), kindly supplied by Dr P. Main. *MULTAN* was applied to 350 reflexions with $|E| \geq 1.56$ and to the corresponding 5000 strongest phase relationships. Owing to the particular intensity distribution, 100 weak reflexions and the corresponding 2523 phase relationships were retained for the PSI ZERO test and the respective figure of merit (FOM) was allotted a weight of 1.2.

This gave the best combined FOM for the correct solution, in spite of the presence of better values for the absolute FOM and for the residual among the 16 sets of starting phases considered.

Least-squares full-matrix refinement with isotropic temperature factors was accomplished over the 2378 reflexions having $|F_o| \geq 6\sigma(F_o)$, with weights $w = [\sigma^2(F_o) + 0.062F_o^2]^{-1}$. The *SHELX 76* system of programs was used (Sheldrick, 1976). Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). At convergence for the 82 parameters, the conventional *R* index was 0.077. The final values of the

positional and thermal parameters are listed in Table 1.*

Discussion

As shown in Fig. 1, the structure of $\text{Sm}_{10}\text{Pd}_{21}$ is made up of layers parallel to the (010) plane. At $y = 0$ and $y = \frac{1}{2}$, Sm and Pd atoms in 1:1 ratio form somewhat distorted hexagon-pentagon-triangle nets placed in such a way that the atoms of one layer cover nearly exactly those of the other, each atom being overlapped by an atom of a different kind. The voids left in this structural network at the centres of the hexagonal and pentagonal prisms ($y \approx \frac{1}{4}$ and $y \approx \frac{3}{4}$) are occupied by Pd atoms which form two identical slightly irregular 3^6 nets.

Table 2 collects the interatomic distances up to values 21% greater than $\sum r$, i.e. the sum of the corresponding atomic radii (1.80 and 1.38 Å for Sm and Pd respectively). A more complete representation of the distribution of the neighbouring atoms is given in Figs. 2 and 3, where the number of surrounding atoms at a distance d is plotted against the ratio $d/\sum r$ for each atomic position, following a method outlined by Bruzzone, Fornasini & Merlo (1970).

A noticeable feature common to both graphs is that the Sm-Pd distances are always less than $\sum r$, whilst the Sm-Sm and Pd-Pd distances (with only two

Table 1. *Positional and thermal parameters* ($\times 10^4$) *for* $\text{Sm}_{10}\text{Pd}_{21}$ *with e.s.d.'s in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Sm(1)	3515 (1)	0	4813 (1)	45 (4)
Sm(2)	8554 (1)	0	6445 (1)	72 (4)
Sm(3)	3147 (1)	0	1978 (1)	67 (4)
Sm(4)	741 (1)	0	8135 (1)	70 (4)
Sm(5)	1186 (1)	0	1307 (1)	59 (4)
Sm(6)	2753 (1)	0	9211 (1)	68 (4)
Sm(7)	4288 (1)	0	190 (1)	55 (4)
Sm(8)	420 (1)	0	5941 (1)	53 (4)
Sm(9)	5339 (1)	0	2797 (1)	70 (4)
Sm(10)	7627 (1)	0	3516 (1)	56 (4)
Pd(1)	3487 (1)	5000	4752 (2)	77 (6)
Pd(2)	8590 (1)	5000	6643 (2)	68 (6)
Pd(3)	3131 (1)	5000	1963 (2)	124 (6)
Pd(4)	675 (1)	5000	7900 (2)	82 (6)
Pd(5)	1164 (1)	5000	1597 (2)	69 (6)
Pd(6)	2690 (1)	5000	9207 (2)	93 (6)
Pd(7)	4404 (1)	5000	172 (2)	88 (6)
Pd(8)	437 (1)	5000	5920 (2)	78 (6)
Pd(9)	5377 (1)	5000	2723 (2)	91 (6)
Pd(10)	7614 (1)	5000	3551 (2)	96 (6)
Pd(11)	2500	2500	5000	68 (6)
Pd(12)	7033 (1)	2542 (3)	2263 (1)	56 (4)
Pd(13)	3727 (1)	2496 (3)	3237 (1)	57 (4)
Pd(14)	1654 (1)	2350 (4)	9538 (1)	74 (5)
Pd(15)	567 (1)	2555 (3)	4397 (1)	71 (4)
Pd(16)	5158 (1)	2452 (3)	1168 (1)	65 (4)

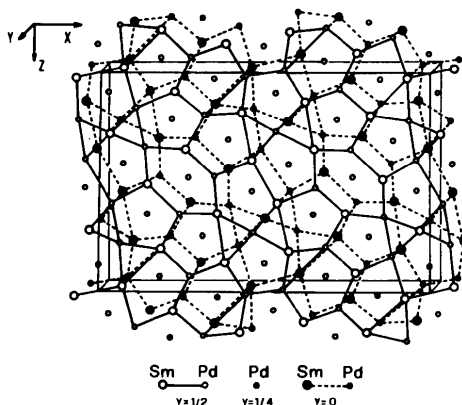


Fig. 1. A view of the structure (*a*, *b*/2, *c*) of $\text{Sm}_{10}\text{Pd}_{21}$.

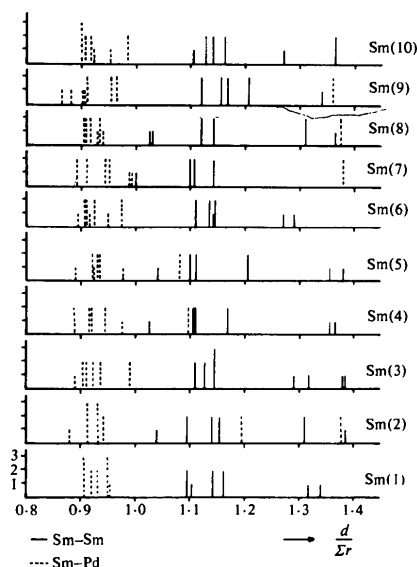


Fig. 2. Distribution of neighbouring atoms around the Sm atoms.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34431 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) in $\text{Sm}_{10}\text{Pd}_{21}$

E.s.d.'s are less than 0.01 Å.

Sm(1) - 2 Sm(2) 3.95	Sm(4) - 1 Sm(8) 3.70	Sm(7) - 1 Sm(7) 3.60	Sm(10) - 1 Sm(1) 3.99	Pd(1) - 1 Sm(2) 2.80	Pd(6) - 1 Sm(3) 2.83	Pd(11) - 2 Sm(10) 2.86	Pd(14) - 1 Sm(7) 2.84
- 1 Sm(10) 3.99	- 2 Sm(3) 4.00	- 2 Sm(5) 3.96	- 2 Sm(3) 4.07	- 2 Sm(1) 2.89	- 1 Sm(6) 2.85	- 2 Sm(1) 2.93	- 1 Sm(6) 2.95
- 2 Sm(8) 4.12	- 2 Sm(7) 4.00	- 2 Sm(4) 4.00	- 2 Sm(2) 4.12	- 1 Sm(10) 2.93	- 2 Sm(6) 2.89	- 2 Sm(2) 3.80	- 1 Sm(3) 2.98
- 2 Sm(10) 4.20	- 2 Sm(9) 4.21	- 1 Sm(3) 4.12	- 2 Sm(1) 4.20	- 1 Sm(8) 2.96	- 1 Sm(5) 2.93	- 2 Pd(10) 2.81	- 1 Sm(6) 3.10
- 2 Pd(1) 2.89	- 1 Pd(3) 2.81	- 1 Sm(6) 4.12	- 2 Pd(11) 2.86	- 2 Pd(11) 2.88	- 2 Pd(12) 2.90	- 2 Pd(1) 2.88	- 1 Sm(5) 3.44
- 1 Pd(8) 2.89	- 1 Pd(7) 2.82	- 2 Pd(14) 2.84	- 1 Pd(3) 2.87	- 2 Pd(13) 2.96	- 2 Pd(14) 2.95	- 2 Pd(11) 2.88	- 1 Sm(4) 3.49
- 2 Pd(11) 2.93	- 2 Pd(4) 2.91	- 2 Pd(7) 2.90	- 2 Pd(10) 2.88	- 2 Pd(15) 3.09	- 2 Pd(14) 3.05	- 1 Pd(14) 2.71	- 1 Pd(14) 2.71
- 2 Pd(15) 2.97	- 2 Pd(16) 2.92	- 2 Pd(16) 3.00	- 2 Pd(12) 2.92			- 1 Pd(3) 2.88	
- 1 Pd(2) 3.02	- 2 Pd(13) 3.01	- 2 Pd(16) 3.03	- 1 Pd(1) 2.93	Pd(2) - 1 Sm(9) 2.50	Pd(7) - 1 Sm(4) 2.82	Pd(12) - 1 Sm(6) 2.90	- 1 Pd(6) 2.95
- 2 Pd(13) 3.03	- 1 Pd(9) 3.10	- 1 Pd(5) 3.14	- 1 Pd(2) 3.03	- 2 Sm(2) 2.90	- 1 Sm(5) 2.83	- 1 Sm(10) 2.92	- 1 Pd(7) 3.00
- 1 Pd(10) 3.04	- 2 Pd(14) 3.49	- 1 Pd(4) 3.15	- 2 Pd(13) 3.13	- 1 Sm(1) 3.02	- 2 Sm(7) 2.90	- 1 Sm(2) 2.96	- 1 Pd(6) 3.05
				- 1 Sm(10) 3.03	- 2 Pd(16) 2.88	- 1 Sm(5) 2.97	- 1 Pd(14) 3.06
				- 2 Pd(12) 2.81	- 2 Pd(16) 2.88	- 1 Sm(3) 3.15	
				- 1 Pd(5) 2.96	- 2 Pd(14) 3.00	- 1 Pd(2) 2.81	Pd(15) - 1 Sm(8) 2.91
				- 2 Pd(15) 3.07	- 1 Pd(7) 3.03	- 1 Pd(5) 2.82	- 1 Sm(1) 2.97
						- 1 Pd(12) 2.83	- 1 Sm(8) 2.97
						- 1 Pd(6) 2.90	- 1 Sm(2) 2.99
				Pd(3) - 1 Sm(4) 2.81	Pd(8) - 2 Sm(5) 2.88	- 1 Pd(10) 2.92	- 1 Sm(9) 3.04
				- 1 Sm(10) 2.87	- 1 Sm(1) 2.89	- 1 Pd(12) 2.93	- 1 Pd(15) 2.82
				- 2 Sm(3) 2.88	- 1 Sm(9) 2.89	- 1 Pd(13) 3.14	- 1 Pd(8) 2.90
				- 1 Sm(6) 2.91	- 2 Pd(13) 2.87		- 1 Pd(8) 2.91
				- 2 Pd(14) 2.88	- 2 Pd(15) 2.90		- 1 Pd(15) 2.95
				- 2 Pd(13) 2.93	- 2 Pd(15) 2.91	Pd(13) - 1 Sm(3) 2.89	- 1 Pd(2) 3.07
				- 2 Pd(12) 3.14	- 1 Pd(4) 3.31	- 1 Sm(8) 2.89	- 1 Pd(11) 3.09
						- 1 Sm(4) 3.03	- 1 Pd(9) 3.16
						- 1 Sm(10) 3.13	
				Pd(4) - 1 Sm(9) 2.75	Pd(9) - 2 Sm(9) 2.89	- 1 Pd(4) 2.81	Pd(16) - 1 Sm(4) 2.92
				- 2 Sm(4) 2.91	- 1 Sm(2) 2.97	- 1 Pd(8) 2.87	- 1 Sm(5) 2.95
				- 1 Sm(3) 2.93	- 1 Sm(8) 2.99	- 1 Pd(13) 2.88	- 1 Sm(7) 3.00
				- 1 Sm(7) 3.15	- 1 Sm(4) 3.10	- 1 Pd(13) 2.89	- 1 Sm(7) 3.03
				- 2 Pd(13) 2.81	- 1 Sm(5) 3.11	- 1 Pd(3) 2.89	- 1 Sm(9) 3.07
				- 2 Pd(16) 2.96	- 2 Pd(16) 3.00	- 1 Pd(3) 2.93	- 1 Pd(16) 2.83
				- 1 Pd(8) 3.31	- 2 Pd(15) 3.16	- 1 Pd(1) 2.96	- 1 Pd(7) 2.88
						- 1 Pd(10) 3.17	- 1 Pd(7) 2.88
				Pd(5) - 1 Sm(9) 2.87	Pd(10) - 2 Sm(10) 2.88		- 1 Pd(16) 2.94
				- 2 Sm(5) 2.92	- 1 Sm(2) 2.90		- 1 Pd(5) 2.95
				- 1 Sm(6) 3.02	- 1 Sm(3) 2.93		- 1 Pd(4) 2.96
				- 1 Sm(7) 3.14	- 1 Sm(1) 3.04		- 1 Pd(9) 3.00
				- 2 Pd(12) 2.82	- 2 Pd(11) 2.81		
				- 2 Pd(16) 2.95	- 2 Pd(12) 2.92		
				- 1 Pd(2) 2.96	- 2 Pd(13) 3.17		

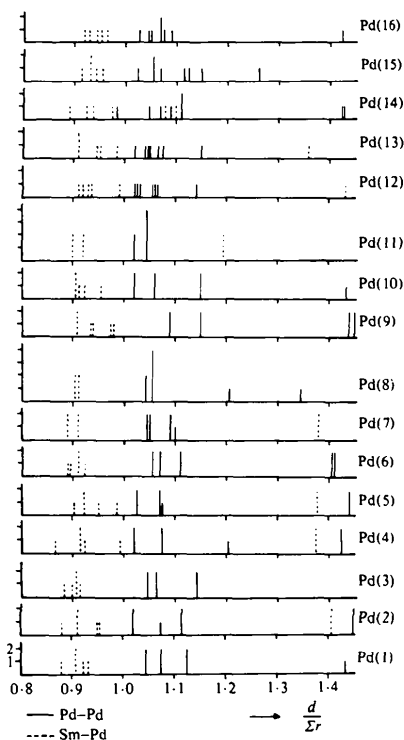


Fig. 3. Distribution of neighbouring atoms around the Pd atoms.

exceptions) are greater than $\sum r$. This causes the first gap in the distribution between the nearest group of the Sm-Pd contacts and the others. So, evaluating the coordination is questionable, since one can either count

only the closest atoms up to $d/\sum r = 1.0$, excluding longer distances between atoms of the same type, or count all the atoms up to $d/\sum r = 1.21$, as listed in Table 2, reaching the second gap in the distance distribution. In the last case the Sm and Pd mean coordination numbers, 17.7 and 11.3 respectively, are quite acceptable for a rare-earth intermetallic compound with 1:2 stoichiometry, as compared, for example, with the corresponding values of 16 and 12 for the Laves phases. On the other hand, from a chemical point of view, the pronounced gap between Sm-Pd contacts and distances to atoms of the same kind suggests that they cannot be reasonably mixed to build up coordination polyhedra. We prefer to take into account only the nearest neighbours and this criterion will be adopted in the following description.

Regarding the Sm coordination, Sm(1), Sm(3), Sm(6) and Sm(10), surrounded by 11 Pd atoms, lie at the centre of a pentagon with two triangles above and below the plane of the pentagon (Fig. 4); Sm(7) has the same coordination, except that a Pd atom is replaced by Sm(7), which gives the only Sm-Sm short contact. Sm(9) has 10 Pd atoms in a characteristic coordination polyhedron similar to that found around the Co atom in the structure of CoSn (Pearson, 1972); Sm(2), Sm(4) and Sm(5) have nearly the same environment, but with a Pd missing, while for Sm(8) the 10 Pd atoms are slightly rearranged. The two principal kinds of coordination around the Sm atoms can be well represented by the polyhedra of Sm(9) and Sm(10), drawn in Fig. 4 by means of the program ORTEP (Johnson, 1965).

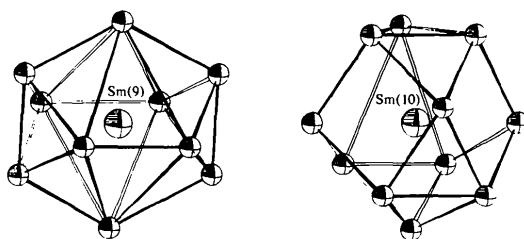


Fig. 4. Coordination polyhedra of Sm(9) and Sm(10). Assumed sphere radii are proportional to atomic radii.

In spite of the complexity of the structure which presents 16 site sets for the Pd atoms, they are four, five or six coordinated with Sm atoms in only a few ways. Around Pd(7), Pd(8) and Pd(11), the Sm atoms form a slightly puckered square; Pd(1), Pd(2), Pd(3), Pd(4), Pd(5), Pd(6) and Pd(10) are at the centre of a more or less irregular trigonal bipyramid; the environment of Pd(12), Pd(13), Pd(15) and Pd(16) appears to approximately tetragonal pyramidal but with the axial Sm–Pd bond generally longer than the equatorial ones; Pd(9) is octahedrally surrounded; finally, Pd(14) is a hybrid, as it is coordinated with four Sm and one Pd(14), the latter giving the only Pd–Pd distance which shows a slight contraction (2.71 Å).

Finally, we compare the present structure with that of the previously mentioned cubic Laves phase, which is adopted by Eu and by the alkaline earths Ca, Sr and Ba (Pearson, 1967) in the corresponding MPd_2 compounds. Although these two structural types do have something in common (*e.g.* both are layered), they are quite different. In $Sm_{10}Pd_{21}$ short contacts occur only between atoms of a different kind. Moreover, whereas in the Laves phase Pd is surrounded by an icosahedron, *i.e.* a bicapped pentagonal antiprism, in $Sm_{10}Pd_{21}$, even if all the atoms up to the second gap are considered, the environments around Pd(12),

Pd(13), Pd(15) and Pd(16) can be described as bicapped pentagonal prisms, and the situation differs further for the remaining Pd atoms.

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Synthesis and Crystal Structure of Diamagnetic ReP_4 , a Polyphosphide with Re–Re Pairs

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Abstract

Microcrystalline ReP_4 was prepared by heating the elemental components in the presence of iodine. Single crystals were obtained by reaction of the components

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in molten tin. They are orthorhombic, $Pbca$, $a = 6.227$ (2), $b = 9.231$ (2), $c = 10.854$ (3) Å, $Z = 8$. The structure is of a new type. It was determined and refined from single-crystal diffractometer data to $R = 0.042$ for 1195 structure factors. The Re atoms have

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