

Crystal Structure of the Phase Pd₃₂S₁₄

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The crystal structure of the title compound has been determined by X-ray diffraction methods using 229 observed reflections ($\sin \theta/\lambda < 0.9$) collected on a counter diffractometer. The crystals are cubic, space group $I\bar{4}3m$ with the cell dimension $a = 8.954(2)$ Å. The structure was refined to a conventional R -factor of 0.037.

The structure contains Pd–Pd-contacts of lengths 2.79 and 2.94 Å; the Pd–S bond lengths are from 2.27 to 2.49 Å. The coordination around the palladium and sulfur atoms is discussed.

The existence of a phase of approximate composition Pd₂S has been reported by several authors (Ref. 1 and references therein). According to Grønvold and Røst the crystals of this phase are body-centered cubic with lattice constant $a = 8.930$ Å;¹ the composition was found to be near Pd_{2.5}S and the density 8.68 g cm⁻³ corresponding to 30.7 palladium and 13.9 sulfur atoms per unit cell. Samples show a weak paramagnetic susceptibility between liquid air temperature and 460 °C. Fischmeister found that this phase has a low electrical resistivity with a positive temperature coefficient indicating a metallic type conductivity.² According to Raub *et al.* Pd_{2.3}S is superconducting below 1.63 K.³

EXPERIMENTAL

Various samples of binary palladium–sulfur alloys were prepared by melting together calculated amounts of the elements in sealed evacuated silica tubes. The ground samples were annealed for one week at ca. 600 °C. Guinier X-ray powder photographs indicated that the composition of the resulting phase was approximately Pd_{2.35}S. Several fairly well developed crystals were obtained by slowly cooling a powdered sample which had been

annealed at 630 °C for several days. One of these (approximate dimensions 0.03 × 0.05 × 0.08 mm³) proved to be suitable for intensity data collection.

Determination of unit cell dimensions and collection of intensity data were carried out on a SYNTEX PI four-circle diffractometer using graphite crystal monochromated MoK α -radiation. The $\theta/2\theta$ scanning mode was employed with the 2θ scan speed of 1° min⁻¹ from 0.65° below $2\theta(\alpha_1)$ to 0.65° above $2\theta(\alpha_2)$; background counts were taken for 0.35 times the scan time at each of the scan range limits. Three standard reflections were measured after every 40 reflections; they showed no significant variation in intensity.

Of the 254 unique reflections with $\sin \theta/\lambda < 0.9$, 229 were measured to be larger than 2.5 $\sigma(I)$ and were regarded as observed. The data set was corrected for Lorentz and polarization effects and also for absorption and secondary extinction.

The atomic form factors used were those of Hanson *et al.*⁴ and the calculations were performed using the computer programs described in Ref. 5. The full-matrix least-squares refinement program minimizes the quantity $\sum w\Delta F^2$ where w is the inverse of the variance of the observed structure factors.

CRYSTAL DATA

Pd_{2.35}S, cubic, $a = 8.954(2)$ Å; $V = 717.7$ Å³. Unit cell content: 32 palladium and 14 sulfur atoms. Calculated density 8.916 g cm⁻³. $\mu(\text{MoK}\alpha) = 201$ cm⁻¹. Absent reflections: (hkl) for $h+k+l$ odd. Possible space groups: $I23$ (No. 197), $Im\bar{3}$ (No. 204), $I432$ (No. 211), $I\bar{4}3m$ (No. 217), and $Im3m$ (No. 229).

STRUCTURE DETERMINATION

The space groups $Im\bar{3}$ and $Im3m$ were excluded because statistical tests favoured a non-centred structure. The structure was solved

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$). The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Pd I	11624(13)	11624	11624	311(8)	311	311	-57(16)	-57	-57
Pd II	16979(8)	41829(11)	16979	245(7)	210(9)	245	8(11)	104(17)	8
S I	34392(40)	34392	34392	245(22)	245	245	-12(53)	-12	-12
S II	0	50000	0	154(36)	296(65)	154	0	0	0

by Patterson methods and a model was found which could be refined according to the space group $I\bar{4}3m$ (No. 217) in which eight palladium atoms (Pd I) are found in positions 8c and 24 (Pd II) in 24 *g*; eight sulfur atoms (S I) are situated in 8c and six (S II) in position 6b.

The final least-squares calculations with the refinement of positional and anisotropic thermal parameters converged to a conventional *R*-factor of 0.037 ($R_w = 0.041$) including all observed reflections; the overdetermination ratio is 16 and the goodness of fit ($S = (\sum w\Delta F^2/n - m)^{1/2}$) is 1.68. Final parameters are listed in Table 1; the structure factor listing is available from the authors.

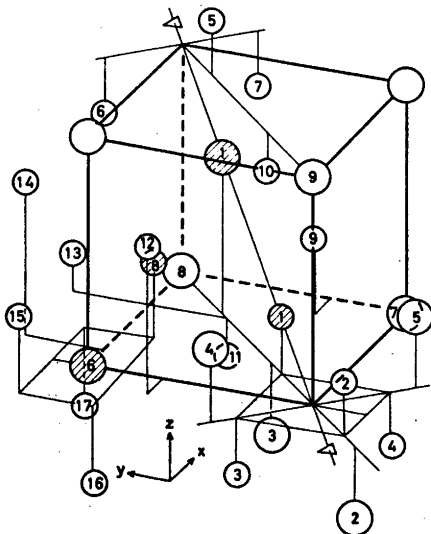


Fig. 1. One octant of the unit cell of $\text{Pd}_{22}\text{S}_{14}$. Small and large circles represent palladium and sulfur atoms, respectively. The hatched circles are atoms referred to in Tables 1 and 2. The numbering is as follows: S I: 1-5; S II: 6-9; Pd I: 1-7; Pd II: 8-17.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

It has been shown by the structure determination that the phase has a stoichiometric composition containing 32 palladium and 14 sulfur atoms per unit cell, corresponding to 69.57 atomic-% palladium or a formula of $\text{Pd}_{2.286}\text{S}$.

The thermal parameters indicate nearly isotropical vibration for all atoms; the average root mean square amplitudes of vibration are 0.11, 0.10, 0.10, and 0.09 Å for Pd I, Pd II, S I, and S II, respectively.

A perspective figure of one octant of the unit cell is presented in Fig. 1. In order to illustrate the various environments some atoms external to this volume are included. Interatomic distances are listed in Table 2. In the following discussion only interatomic distances less than 3.0 Å will be considered.

The coordination about S I and Pd I may be seen from Fig. 2 where a projection of a part of the structure into the mirror plane (1,1,0) is shown. Around the space diagonal

Table 2. Interatomic distances (Å). Estimated standard deviations are less than 0.002 Å for Pd-Pd and 0.004 Å for Pd-S bond lengths. Numbering of atoms may be seen from Figs. 1, 2 and 3.

Pd I (1)-Pd I (2,3,4)	2.944
-Pd II (8,9,10)	2.788
-S I (3,4,5)	2.490
Pd II (8)-Pd I (1)	2.788
-Pd II (11,12,13,14)	2.785
-S I (1)	2.303
-S II (6)	2.271
S I (1)-Pd I (5,6,7)	2.490
-Pd II (8,9,10)	2.303
S II (6)-Pd II (8,15,16,17)	2.271

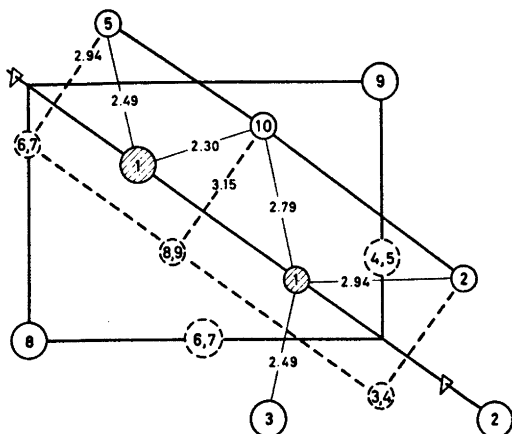


Fig. 2. Projection of the structure into the mirror plane (1,1,0) showing the atomic environments of Pd I and S I. Atoms in the mirror plane are drawn with solid lines.

[1,1,1], a three-fold axis, one finds slightly deformed trigonal prisms with palladium atoms in the corners: Pd I (2,3,4); Pd II (8,9,10); Pd I (5,6,7) *etc.* The Pd I–Pd I distances are 2.944 Å and the Pd II–Pd II distances 3.147 Å. Pd I and S I are situated alternately near the centers of every second of the prisms. The distances from this Pd I atom to the six surrounding palladium atoms are 2.944 Å [of the Pd I-type, forming a regular tetrahedron around the empty corner (0,0,0)] and 2.788 Å (Pd II). In addition the Pd I atom is bonded to three S I atoms (3,4,5) outside the quadrangular faces of the prism at distances of 2.490 Å. The S I atoms in prismatic centers are

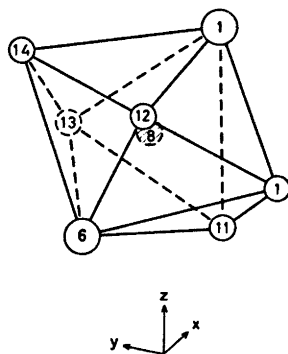


Fig. 3. The pentagonal bipyramidal coordination of Pd II (8). Symbols as in Fig. 1.

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bonded to three Pd I-type atoms and three Pd II-type atoms at distances of 2.490 Å and 2.303 Å, respectively. No other atoms are closer than 3.50 Å to S I.

The coordinations of S II and Pd II are quite different from those of S I and Pd I. Atom S II (*cf.* Fig. 1, sulfur atom No. 6) is coordinated by four palladium atoms (8,15,16, 17) in a flattened tetrahedral arrangement; the Pd–S distances are 2.271 Å. The arrangement about Pd II is visualized in Fig. 3. To a central palladium atom (8) are bonded five palladium atoms (1,11,12,13,14) in a nearly planar pentagonal arrangement in distances of 2.788 Å (1) and 2.785 Å (11–14). The central palladium atom is also bonded to two sulfur atoms which form the apices of a pentagonal bipyramid with distances 2.271 Å (S II, 6) and 2.303 Å (S I, 1). The palladium atoms of the equatorial plane are coplanar within 0.2 Å; the central bond angles are in the range 68.8–74.6° and the S–Pd II (8)–Pd angles are from 84 to 97°.

The crystal structures of the following palladium–sulfur compound have so far been determined: PdS,⁶ PdS,⁷ Pd_{2.286}S (present work), Pd₃S⁸ and Pd₄S,⁹ all of which seem to be stoichiometric. Accordingly no extended range of homogeneity has been found.

Short S–S distances corresponding to covalent bonds are found only in PdS₂, whereas intermetallic Pd–Pd bonds exist in all compounds richer in palladium than PdS; these are all longer than the Pd–Pd bond (2.751 Å) in metallic palladium. The coordination polyhedra around both sulfur and palladium atoms are irregular.

A distorted tetrahedral arrangement of palladium atoms around a sulfur atom is found in PdS with bond lengths within the range 2.26 to 2.45 Å; the corresponding bond length is 2.271 Å for the tetrahedral environment of S II in the present structure. A trigonal prismatic coordination comparable to that about S I is not found in any of the other palladium sulfides. This arrangement is, however, observed in several other palladium compounds, such as in PdTe (NiAs-type structure) and in palladium-rich phosphides.

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