JOURNAL OF SOLID STATE CHEMISTRY 60, 131–134 (1985)

Phase Relationships in the Uranium–Palladium–Sulfur System

I. Characterization and Crystal Structure of UPd_2S_4

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Received December 28, 1984

The new compound UPd_2S_4 was prepared by reacting stoichiometric amounts of US_2, Pd, and S in evacuated quartz ampoules. UPd_2S_4 crystallizes in the tetragonal system, $a = b = 6.734(1)$, $c = 11.841(4)$ Å, space group $I4_1/a$, $Z = 4$. The crystal structure was determined from single-crystal X-ray diffraction data and refined to a conventional R factor of 0.054. Palladium has a square planar sulfur coordination with Pd–S distances = 2.33 Å. Uranium is coordinated with eight sulfur atoms, with a mean U–S distance of 2.83 Å characteristic of uranium in the tetravalent state.

Introduction

The existence of a number of ternary uranium sulfides with alkaline earths, 3*d*, and rare earth elements, has been reported in the past years (*1–4*). With M = 3*d*, series of compounds with general formula MUS_3, MU_2S_5, and MU_8S_{17} were isolated (*2*) in which the 3*d* elements have an octahedral-type sulfur coordination and uranium an eightfold sulfur coordination. A study of ternary systems involving the noble 4*d* metals is being carried out, and we report here on the first new compound characterized in the U–Pd–S system.

Synthesis and Characterization of UPd_2S_4

The search for ternary compounds in the U–Pd–S system was carried out by heating calculated mixtures of US_2, palladium powder, and sulfur in evacuated and sealed quartz tubes. Because of the sensitivity of uranium sulfides to oxygen and moisture, all mixings were performed in a dry-argon-filled glovebox. The reaction products were analyzed by the X-ray powder diffraction method, and preliminary investigations showed that at least three new ternaries form in these systems. Evolution of the X-ray diffraction patterns with composition revealed that a mixture (US_2 + 2 Pd + 2 S) heated and annealed at 900°C for 2 days yields a single-phase material UPd_2S_4.

Single crystals were obtained by the chemical vapor transport method using iodine as transporting agent in a two-zone furnace with the temperature gradient 920–860°C. The unit cell constants were derived from oscillation and Weissenberg photographs. UPd_2S_4 crystallizes in the tetragonal system $a = b = 6.734(1)$, $c = 11.841(4)$ Å; the systematic extinctions hkl: $h + k + l \neq 2n$, $hk0$: h, $(k) \neq 2n$, and $00l$: $l \neq 4n$ are compatible with the space group $I4_1/a$. Ta-

0022-4596/85 $3.00

TABLE I

X-RAY POWDER DIFFRACTION DATA OF UPd_2S_4

hkl	d_{obs} (Å)	d_{calc} (Å)	I/I_0
101	5.854	5.854	12
112	3.711	3.708	47
103	3.409	3.403	50
200	3.361	3.363	21
202	2.921	2.925	100
114	2.515	2.513	11
213	2.392	2.392	9
105	2.234	2.232	39
312	2.002	2.002	40
303	1.950	1.950	27
224	1.855	1.854	46
321	1.845	1.843	38
116	1.823	1.822	16
206	1.702	1.701	15
400	1.683	1.682	13
305	1.628	1.628	9
332	1.532	1.532	7
413	1.508	1.508	20
217	1.474	1.474	17
422	1.458	1.458	15
316	1.447	1.446	12

TABLE II

POSITIONAL PARAMETERS OF UPd_2S_4

Atom	*x*	*y*	*z*
U	0	0.250	0.625
Pd	0	0	0
S	0.3033(5)	0.1032(5)	0.0742(3)

TABLE IV

INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

U–S	2.788(3) × 4	S–S	3.160(1) × 2
–S	2.881(2) × 4	–S	3.306(5)
Pd–S	2.329(3) × 2	–S	3.427(4) × 2
–S	2.332(2) × 2	–S	3.470(5)
U–U	4.483(0)	–S	3.798(2) × 2
U–Pd	4.045(0)	–S	4.034(4)
Pd–Pd	3.367(0)		
–Pd	3.799(0)		

ble I gives the X-ray powder pattern of UPd_2S_4.

The experimental density $d_{exp} = 6.98$ is in agreement with the theoretical density $d_{th} = 7.16$ calculated with $Z = 4$.

Crystal Structure Determination

A single crystal with dimensions 0.06 × 0.09 × 0.09 mm was used for the structure determination. The X-ray diffraction intensities were measured on a Nonius CAD-4 four-circle diffractometer, using Mo$K\alpha$ (λ = 0.71073 Å) radiation and the $\omega - 2\theta$ scan mode.

Reflections (453) were collected within the limits $\theta \leq 30°$, $0 \leq h \leq 9$, $0 \leq k \leq 9$, $0 \leq l \leq 16$; 378 intensities with $I \geq 3\sigma(I)$ were regarded as observed and averaged to yield 292 independent reflections which were used in the structure determination. All the calculations were performed using the SDP

TABLE III

ANISOTROPIC ($\beta_{i,j}$) AND EQUIVALENT ISOTROPIC (B (Å^2)) THERMAL PARAMETERS

Atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$	B (Å^2)
U	1.03(2)	$\beta(1,1)$	0.21(3)	0	0	0	0.76(1)
Pd	0.94(4)	1.06(5)	0.23(4)	−0.06(4)	0.07(4)	−0.03(4)	0.74(2)
S	0.87(9)	1.1(1)	0.33(9)	−0.04(9)	0.09(9)	−0.0(1)	0.76(5)

Note. The form of the anisotropic thermal parameter is $\exp\left(-\frac{1}{4}\sum_{i,j} h_i h_j a_i^* a_j^* \beta(i,j)\right)$; were a^* is a reciprocal lattice constant.

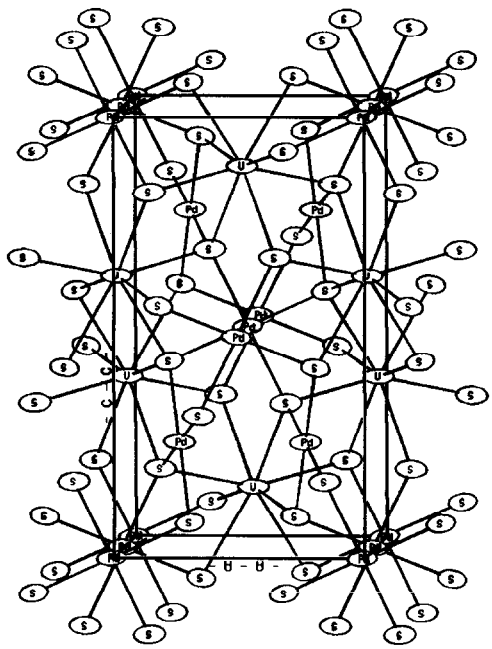

FIG. 1. View of the crystal structure of UPd_2S_4.

package (*5*). The intensities were corrected for Lorentz and polarization effects, and for absorption by approximating the crystal as a sphere with $\mu r = 1.8$. Uranium was found by the Patterson method to occupy the (4b): $(0, \frac{1}{4}, \frac{5}{8})$ special position and a difference Fourier map revealed the locations of Pd and S atoms in (8c): (0, 0, 0) and (16f): (x, y, z) positions, respectively. Full matrix least-square refinements of the positional and isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.085$ and $R_\omega = |\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2|^{1/2} = 0.097$ with $\omega = 1/\sigma^2 F$. Subsequent refinement cycles, with anisotropic thermal factors for all atoms, led to $R = 0.054$, $R_\omega = 0.067$.

Tables II and III give the final positional and thermal parameters, and the main interatomic distances are listed in Table IV.[1]

[1] A list of the observed and calculated structure factors may be obtained on request to the authors.

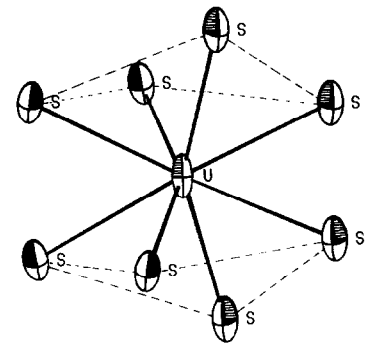

FIG. 2. Environment of uranium.

Crystal Structure Description

Figure 1 displays a view of the crystal structure of UPd_2S_4. Representative of the anisotropy of the thermal vibrations, all the thermal ellipsoids are flattened perpendicularly to the $\bar{4}$ axis; the calculated root mean square amplitude of thermal vibrations in (a, b) planes are ~0.11 Å for all atoms.

Palladium, located on an inversion center, has a square planar-type sulfur coordination. The S–Pd–S angle is 85°37′ and the palladium-to-sulfur distance, 2.33 Å, is very close to those found in other ternary compounds: 2.34 Å in $K_2Pd_3S_4$ (*6*), 2.35–2.39 Å in Na_2PdS_2 (*7*), where palladium, in a divalent state, has also a square planar sulfur coordination.

Uranium is surrounded by eight near-neighbor sulfur atoms, with a coordination polyhedron which can be regarded as being a distorted antiprism (Fig. 2). The mean uranium-to-sulfur distance is $d = 2.83$ Å, a value which was found to characterize the uranium U^{4+} ion ($5f^2$ configuration) in an eightfold sulfur coordination (*8*). Assuming no electron delocalization, i.e., an insulating or a large-gap semiconducting behavior, the simple charge balance calculation also indicates a tetravalent state for uranium in UPd_2S_4.

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