Inorganica Chimica Acta, 117 (1986) 183–185

Phase Relationships in the Uranium–Palladium–Sulfur System.
II. Characterisation and Crystal Structure of $U_xPd_3S_4$ $(0.9 < x < 1)$

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(Received July 13, 1985; revised December 10, 1985)

Abstract

The new ternary uranium–palladium–sulfide $U_xPd_3S_4$ $(0.9 < x < 1)$ crystallizes in the cubic system $a = 6.639(2)$ Å, space group *Pm*3*n*, with a platinum bronze type structure. Refinement of the structure of a single crystal grown by the chemical vapour transport method revealed an incomplete uranium site filling in the crystal lattice, corresponding to the formula: $U_{0.92}Pd_3S_4$. The crystal radius of the uranium is found to be intermediate between U^{3+} and U^{4+} so that the uranium is expected to be in an intermediate valence state.

Introduction

Investigations of phase behavior in some ternary palladium chalcogenides systems: Pd–M–(S, Se) with M = Nb, Ta, U, have recently led to the characterization of new compounds exhibiting original structural types: $(Nb, Ta)_2Pd_3Se_8$, $Nb_2Pd_{0.71}Se_{15}$ [1, 2], UPd_2S_4 [3] and PdU_2S_4 [4].

The existence of a series of ternary palladium and rare earth (RE) sulfides, with the formula $(RE)Pd_3S_4$, was also reported and these compounds were recognized to crystallize with a platinum bronze $(M_xPt_3O_4)$ type structure [5]. We report on the characterization of an isomorphous uranium compound: $U_xPd_3S_4$ $(0.9 < x < 1)$.

Experimental and Discussion

A new phase with composition UPd_3S_4 was prepared by heating stoichiometric mixtures of uranium disulfide, palladium powder and sulfur in an evacuated and sealed silica tube at 900 °C for 24 h; the reaction product was ground and annealed at 950 °C for one day. The X-ray powder diffraction analysis was made on a X-ray powder diffractometer using Cu Kα radiation and a proportional counter.

TABLE I. X-ray Powder Diffraction Pattern of UPd_3S_4

h k l	D_{obs}	D_{calc}	I/I_o
1 1 0	4.705	4.697	10
2 0 0	3.326	3.321	15
2 1 0	2.971	2.970	60
2 1 1	2.713	2.712	100
2 2 0	2.349	2.348	20
3 1 0	2.099	2.100	5
2 2 2	1.917	1.917	10
3 2 0	1.841	1.842	25
3 2 1	1.775	1.775	65
4 0 0	1.659	1.661	30
4 1 1 3 3 0	1.565	1.566	5
4 2 0	1.485	1.485	5
4 2 1	1.449	1.449	15
3 3 2	1.417	1.416	20
4 2 2	1.356	1.356	10

The X-ray powder diffraction pattern could be indexed in the cubic system (Table I), and a least square calculation yielded the lattice parameter: $a = 6.639(2)$ Å. Grey-black single crystals were obtained by the chemical vapor transport method, using iodine as transporting agent in a temperature gradient 940–880 °C for 10 days. Weissenberg photographs showed the systematic extinctions: *hhl*: $l \neq 2n$ compatible with the space group *Pm*3*n*, which confirmed UPd_3S_4 to crystallize with a platinum bronze type structure. This structural framework is characterized by its ability to accommodate incomplete filling of the M crystallographic site, but this property was not observed for $LaPd_3S_4$, the structure of which was refined from powder data [5]. Furthermore, such a substitution of the rare earths by uranium without any change of the crystal framework could suggest that uranium is also trivalent in this compound; but, although the U^{3+} valence state may occur in chalcogenides, U^{4+} is more usual, and an intermediate valency is a possible situation [6].

0020-1693/86/$3.50

TABLE II. Intensity Collection Parameters

Crystal dimensions	0.02 × 0.01 × 0.007 cm
Linear absorption coefficient	367 cm^{-1}
Unit cell volume	292.6 Å^3
Experimental density	7.67 ± 0.10 g cm^{-3}
Radiation	λ(Mo Kα)
Scan mode	$\omega - 2\theta$
Measurement conditions	$0 < h < 9$
	$0 < k < 9$
	$0 < l < 9$
Measurement limits	$\theta < 30°$
Number of observed reflections	381
Number of independent reflections $I > 3\sigma(I)$	137
Reliability factors	
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.044
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.050

TABLE IV. Interatomic Distances[a]

U–8S:	2.875 Å	Pd–4S:	2.347 Å
U–12Pd:	3.711 Å	Pd–2Pd:	3.319 Å
		Pd–4U:	3.711 Å
S–3Pd:	2.347 Å		
S–2U:	2.875 Å		
S–6S:	3.319 Å		

[a] All atoms in special positions: no estimated standard deviation calculation.

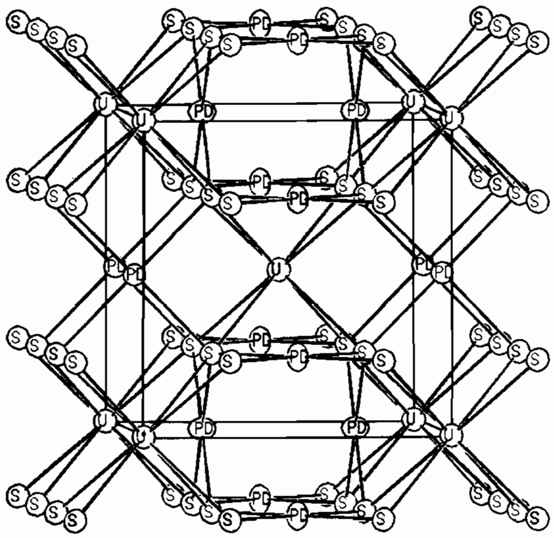

Fig. 1. ORTEP view of the structure of $\text{U}_x\text{Pd}_3\text{S}_4$.

A full structural determination was undertaken to shed some light on these problems.

Single crystal X-ray diffraction intensities were collected on a Nonius Cad4 four circle diffractometer, with the experimental conditions given in Table II. A numerical absorption correction was applied to the data, using the program ABSCOR [7]. All calculations were made with a PDP 11-60 computer, using the SDP program system [7].

In this structure, the U, Pd and S atoms occupy the fixed positions: 2a (0, 0, 0), 6d (1/4, 1/2, 0), and 8e (1/4, 1/4, 1/4) of the *Pm*3*n* space group. Full matrix least squares refinements of the isotropic thermal parameters afforded the residuals $R = 0.055$ and $R_w = 0.072$. The value of the thermal factor of uranium appeared then to be anomalously high relative to that of the lighter atoms, suggesting that too high an electron density was assigned to this crystallographic site. The uranium occupancy factor t was then allowed to vary in the further refinements, and converged to the value $t = 0.92(2)$, concomitantly with a small but significant decrease of the residuals to $R = 0.051$, $R_w = 0.066$. The last refinement cycles including anisotropic thermal parameters for all atoms yielded the final values $R = 0.044$, $R_w = 0.050$. The values of the thermal parameters are listed in Table III, the main interatomic distances are in Table IV, and Fig. 1 gives an ORTEP view of the structure.

These results show that about 10% of the uranium sites are empty in the investigated crystal, and suggest the existence of a non-stoichiometric domain for this compound. We have prepared phases with nominal compositions: $\text{U}_{0.9}\text{Pd}_3\text{S}_4$, $\text{U}_{0.95}\text{Pd}_3\text{S}_4$ and UPd_3S_4, for which no impurity lines were observed in X-ray powder diffraction patterns. But the expected variations of both the lattice parameters and of the experimental densities fall within the range of experimental error and thus do not give indications as to the expected variation of the uranium content in the lattice. It is worth mentioning that such an incomplete uranium site filling has already been

TABLE III. Anisotropic (β(i, j)) and Equivalent Isotropic B (Å^2) Thermal Parameters[a]

Atom	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$	B (Å^2)
U	1.08(1)	$\beta_{1,1}$	$\beta_{1,1}$	0	0	0	1.08(1)
Pd	1.60(5)	0.97(2)	$\beta_{2,2}$	0	0	0	1.18(2)
S	1.05(5)	$\beta_{1,1}$	$\beta_{1,1}$	0.06(5)	$\beta_{1,2}$	$\beta_{1,2}$	1.05(1)

[a] The form of the anisotropic thermal parameters is: $\exp(-1/4)\Sigma_{i,j} h_i h_j a_i^* a_j^* \beta_{i,j}$) where a^* is a reciprocal lattice constant.

observed in some other compounds, such as the binary chalcogenides U_7Te_{12} [8], αUS_2 and αUSe_2 [9]. This ability for uranium to occupy only partly its crystallographic site is a basically interesting property for this element.

As was pointed out above, another point of interest is the problem of the electronic structure of uranium in this compound. It is known that the uranium ion size, or crystal radius, varies significantly with the valence state, so that reliable information concerning the electron occupancy of the 5f shell may be extracted from crystallographic data [6]. It was shown that in compounds with an 8-fold sulfur coordination of uranium, the mean uranium-to-sulfur distances range typically from $d(U^{4+}-S) \simeq 2.82$ Å to $d(U^{3+}-S) \simeq 2.93$ Å [6]. In $U_xPd_3S_4$ the U–S distance has a value of 2.875 Å, which indicates that the uranium crystal radius is intermediate between those of U^{4+} and U^{3+}. We can thus postulate that the uranium electron configuration is intermediate between $5f^3$ (U^{3+}) and $5f^2$ (U^{4+}), whereas palladium, with a typical square planar coordination, remains divalent as in the rare-earth compounds. This implies a higher electron delocalisation in $U_xPd_3S_4$ than in the RE analogues (which can occur via a 5f–6d hybridization) and, like the RE analogues [5], $U_xPd_3S_4$ should exhibit a metallic type conductivity.

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