



Crystal structure and magnetic susceptibility of uranium palladium sulfide bronze, $U_xPd_3S_4$

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Abstract

The lattice parameter of cubic $U_xPd_3S_4$ was measured by X-ray diffractometry for various apparent x values between 0.5 and 1.5. It seemed to change with x , but the existence of a non-stoichiometric range for uranium could not be definitely determined since the product was not in a single phase. The Rietveld refinement for $U_xPd_3S_4$ ($x=1$) showed that the compound was $U_{0.90}Pd_3S_4$ and that the space group was $Pm\bar{3}n$ with the final R_1 value of 0.052. The lattice parameter was 6.637(1) Å, and the isotropic temperature factors were 0.59, 0.70 and 0.70 Å² for U, Pd and S, respectively. The measured reciprocal magnetic susceptibility for $U_{0.90}Pd_3S_4$ was not a linear function of temperature. From the slope in a temperature range of 50–200 K, the effective magnetic moment was obtained, which showed that both the U^{4+} and U^{3+} ions are present in this compound in nearly the same amounts. © 1998 Elsevier Science S.A.

Keywords: Uranium; Palladium; Sulfide; Bronze; Crystal structure; Magnetic susceptibility

1. Introduction

The well known platinum oxide bronzes, $M_xPt_3O_4$, have been formed with the M metals of M=Li, Na, Ni, Cd etc. for various concentrations in the range $0 < x \leq 1$. Most of these bronzes crystallize in a cubic system showing metallic electrical conductivity [1]. Although there seems to be no report on the formation of the corresponding sulfides ($M_xPt_3S_4$), the palladium sulfur compounds, MPd_3S_4 , with various rare-earth M metals, i.e. M=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Yb are known to be formed [2–4]. The crystal structure and electrical conductivity have been closely examined for MPd_3S_4 (M=La, Nd and Eu) in a single phase [5]. The M metals which form palladium sulfur bronze are not limited to rare-earth elements. Daoudi and Noel [6] prepared $U_xPd_3S_4$ with $0.9 < x < 1$ and determined its crystal structure by X-ray diffraction method for single crystal and powder specimens. According to their results, the occupation factor of uranium was converged to 0.92 (i.e. $U_{0.92}Pd_3S_4$), giving a minimum R factor of 0.052 with the use of isotropic temperature factors. This R factor was further lowered to 0.044 using anisotropic temperature factors for the three component elements.

Another interesting point with regard to $U_xPd_3S_4$ is the valence state of uranium. In MPd_3S_4 (M=rare-earth

elements), the valence state of the M metals is considered to be +3 or intermediate between +3 and +2 [5]. But the +4 valence state is usual and the +3 state is rather rare for uranium in solid compounds. Daoudi and Noel [6] suppose the valence to be intermediate between +4 and +3 on the basis of the U–S distance in the crystal, which was 2.875 Å, i.e. between 2.82 and 2.93 Å for the crystal radii sums of $U^{4+}-S^{2-}$ and $U^{3+}-S^{2-}$ [7], respectively. The present work was undertaken to study the non-stoichiometry and valence state of uranium in $U_xPd_3S_4$. The change of the lattice parameter was measured by X-ray diffractometry for the compounds with various nominal concentrations of uranium. The other crystal data were calculated using the Rietveld program. Magnetic susceptibilities were measured in a temperature range from 7 K to room temperature. The effective magnetic moments obtained were discussed in relation to the uranium valence.

2. Experimental

2.1. Sample preparation

β - US_2 was prepared by heating $UO_2SO_4 \cdot 3H_2O$ at 1273 K for 2 h in a stream of N_2/CS_2 mixture gas, which was obtained by bubbling N_2 through CS_2 at room temperature. The measured lattice parameters of the orthorhombic β - US_2 were in good agreement with those reported [8]. For

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preparing $U_xPd_3S_4$, the calculated amounts of β - US_2 , palladium powder and sulfur were finely mixed in an agate mortar. Palladium and sulfur used were of purities 99.9 and 99.999%, respectively. The mixture was subsequently transferred into a quartz ampoule, which was then sealed under vacuum. The ampoules containing the mixtures of nominal x values of 0.5, 0.6, 0.7, 0.8, 0.9, 0.92, 1.0, 1.1, 1.2 and 1.5 were heated at 1173 K for 3 days in a muffle furnace. The ampoules were quenched to room temperature after the reaction.

$LaPd_3S_4$ was prepared for correcting the measured magnetic susceptibilities. This compound was formed by the reaction of the calculated amounts of La_2S_3 , palladium powder and sulfur in an evacuated and sealed quartz ampoule under the same heating conditions as above.

2.2. X-ray diffraction analysis

X-ray powder diffractometry was carried out using a Rigaku RAD-IC diffractometer using $Cu\ K\alpha_1$ radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. The slit system was 1° - 1° -0.15-0.3 mm. The intensity and least-squares lattice parameter calculations were carried out with the LAZY-PULVERIX [9] and LCR2 [10] programs, respectively. The RIETAN program [11] was used for refining the diffraction data by the Rietveld method.

2.3. Magnetic susceptibility measurement

The magnetic susceptibilities of $U_xPd_3S_4$ were measured at temperatures between 7 K to room temperature at 10 kOe by a vibrating sample magnetometer (Riken Denshi Co.). The relation between the magnetization and the electromotive force in the detection coil was calibrated using Gd_2O_3 standard sample.

3. Results and discussion

A plot of the cubic lattice parameters against x values in $U_xPd_3S_4$ is shown in Fig. 1. It seems likely that the lattice parameter increases with increasing x value. In these specimens, however, the impurity UOS phase [12] was found to exist in the X-ray peaks although its amount was estimated to be 5–15% from the peak intensities. There were no systematics in the UOS amount with the x values in the range 0.7–1.2. However, a comparable amount of another unindexable phase was mingled in the specimens of low x values, i.e. $x=0.5$ and 0.6. On the other hand, a phase different from $U_xPd_3S_4$ was formed in a large amount for $x=1.5$. The impurity PdS of the order of 10% was also observed to exist in the specimens of $x=0.7$ and 0.8. This PdS phase is assumed to have been precipitated from the excess palladium and sulfur due to the smaller

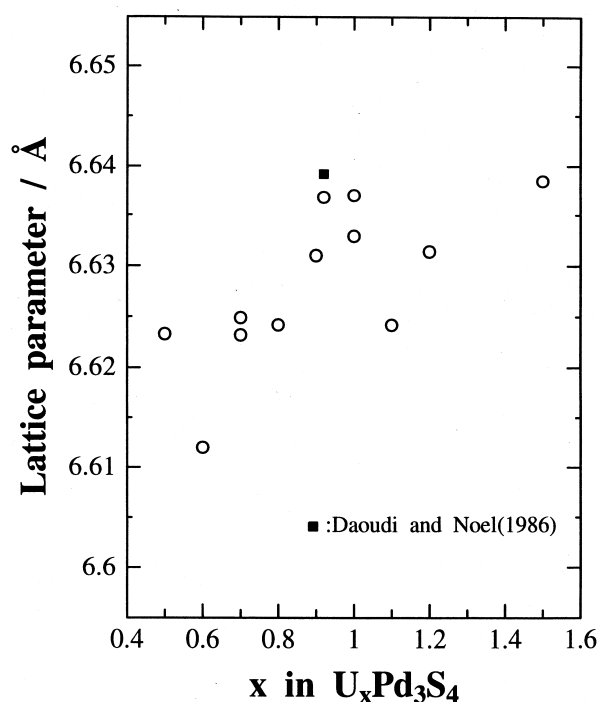


Fig. 1. Lattice parameter of cubic $U_xPd_3S_4$ as a function of apparent x value.

mixing ratios of uranium (disulfide) and the formation of UOS.

The lattice parameter of a compound in two-phase mixtures is expected to be unvaried under fixed gaseous pressure and temperature. The cubic lattice parameter of $U_xPd_3S_4$ in the present measurements seems to increase (Fig. 1) though the data are scattered. This is considered to be associated with the different gaseous pressures since the reaction was made in sealed ampoules. Because the amount of impurity UOS exceeded 10% in some cases, no definite conclusion can be drawn about the x range in $U_xPd_3S_4$. It is possible that the compound has some sulfur non-stoichiometry.

The refinement of the crystal structure was carried out for $U_xPd_3S_4$ with apparent x value of one by the Rietveld method [11]. Since the calculation showed the presence of 3.1 mol.% UOS as impurity (but no PdS and US_2), further calculation was made excluding the peaks of UOS by changing the sulfur position in $8e(u,u,u)$ of the space group $P\bar{4}3n$ from $u=0.235$ to 0.265 with a width of 0.01. The minimum R_1 value was obtained at $u=0.25$, i.e. the space group was $Pm\bar{3}n$ as in most MPd_3S_4 (M =rare-earth element) compounds [2–4].

The occupation factor of uranium was calculated to be 0.90 at 2a site. This value accords with 0.92 obtained by Daoudi and Noel [6]. The crystal data calculated by the Rietveld method are given in Table 1. The final R_1 and R_F factors of $U_xPd_3S_4$ were 0.052 and 0.035, respectively, and those of UOS were 0.069 and 0.036, respectively. The interatomic distances in $U_{0.90}Pd_3S_4$ were $r(U-S)=2.874$,

Table 1

Crystal data of $U_xPd_3S_4$ after Rietveld refinement. Space group: $Pm\bar{3}n$ (O_h^3); lattice parameter: 6.637(1) (Å)

		Occupation factor	Isotropic temperature factor B (Å ²)	Atom parameters		
				x	y	z
U	2a	0.90	0.59	0	0	0
Pd	6d	1.00	0.70	1/4	1/2	0
S	8e	1.00	0.70	1/4	1/4	1/4

$r(\text{Pd-S})=2.347$ and $r(\text{S-S})=3.319$ Å. Agreement of these values with those of Daoudi and Noel [6] is quite good. In Fig. 2, the observed data points (shown by dots) and the calculated peaks (solid line) are compared. The diffraction intensities were collected three times for 1.2 s with a 0.02° (2θ) step angle. The difference intensity pattern of the I_{obs} and the refined I_{calc} shown in the lower part of Fig. 2 indicates that the I_{calc} were satisfactorily well fitted to I_{obs} .

The measured magnetic susceptibilities of $U_xPd_3S_4$ ($x=0.90$) were corrected for Pd^{2+} by subtracting the magnetic susceptibilities of LaPd_3S_4 in which La^{3+} was non-magnetic, although the paramagnetism of LaPd_3S_4 was virtually zero. The variation of corrected reciprocal magnetic susceptibilities for $U_xPd_3S_4$ with temperature is shown in Fig. 3. The curve tends to flatten at higher temperatures showing a significant departure from the Curie-Weiss law. As has been reported for Li_7UO_6 [13], such flattening is caused by the additional temperature independent magnetic susceptibility. In this work, however, the effective magnetic moment (μ_{eff}) was calculated from the slope in two restricted temperature ranges. Straight line (1) for a temperature range 50–200 K was expressed as $\chi^{-1}=27.17+1.180T$, which gave $\mu_{\text{eff}}=2.60 \mu_B$ and $\Theta=-23.0$ K in $\chi=N\mu_{\text{eff}}^2/[3k(T-\Theta)]$, while for $T=30$ –270 K (line (2) in Fig. 2), $\chi^{-1}=28.70+1.092T$ was obtained. In this case, the effective magnetic moment and the Weiss constant were $\mu_{\text{eff}}=2.71 \mu_B$ and $\Theta=-26.3$ K.

If uranium is in a U^{4+} oxidation state, the ninefold

degenerate ground state 3H_4 of the uranium $5f^2$ electrons splits into Γ_1 , Γ_3 , Γ_4 and Γ_5 levels by the eightfold cubic crystal field of sulfur ions around a uranium ion, the lowest being the triplet Γ_5 level [14]. The magnetic susceptibility can be calculated by

$$\chi = \frac{N\mu_B^2\mu_{\text{eff}}^2}{3kT} = \frac{N\mu_B^2}{ZkT} \sum_{m(lf)} \sum_{n(lf)} | \langle m | L_z + 2S_z | n \rangle |^2,$$

where Z stands for the degeneracy of the lowest level [15]. The effective magnetic moment calculated is $\mu_{\text{eff}}=2.83 \mu_B$.

On the other hand, if uranium takes on the oxidation state of U^{3+} , the ten-fold degeneracy of the ground state $^4I_{9/2}$ of $5f^3$ uranium configuration is partly removed by the eightfold cubic crystal field forming Γ_6 , $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$ levels. The lowest level is assumed to be Kramer's doublet Γ_6 [14]. The effective magnetic moment becomes $\mu_{\text{eff}}=2.31 \mu_B$ in this case.

These values of theoretical magnetic moments enable us to estimate the ratio of U^{4+} and U^{3+} ions in $U_xPd_3S_4$. For line (1) in Fig. 3, the U^{4+} and U^{3+} fractions are calculated to be 0.53 and 0.47. For line (2), the fractions are 0.75 and 0.25. Since the measured reciprocal magnetic susceptibility does not change linearly with temperature, the ratio

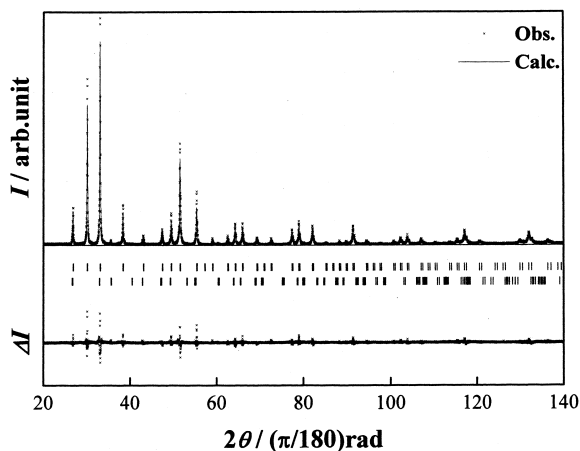


Fig. 2. Rietveld refinement of X-ray powder data of $U_xPd_3S_4$ as compared with the observed intensities. ΔI , difference of observed and calculated intensities.

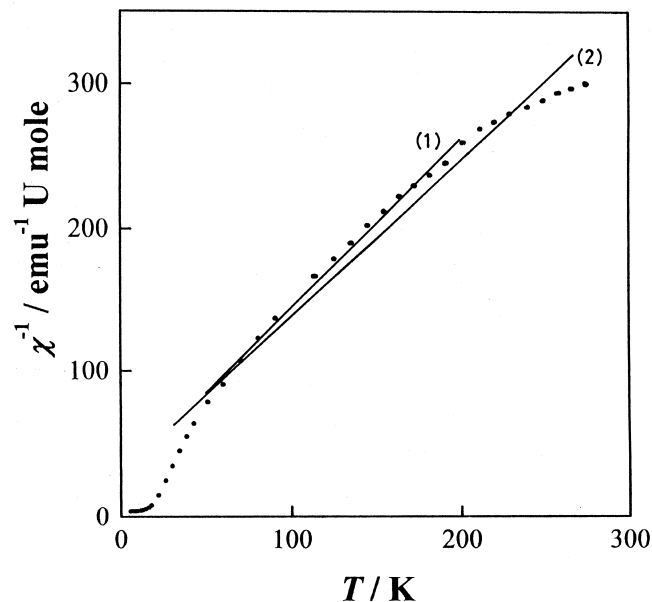


Fig. 3. Reciprocal magnetic susceptibility of $U_{0.90}Pd_3S_4$ as a function of temperature. Line (1): 50–200 K; line (2): 30–270 K.

changes with the temperature range taken. If the data above 50 K are taken as more usual for such cases, it can be said that the U^{4+} and U^{3+} ions are present in nearly the same amounts. Daoudi and Noel [6] assume the mixed valence state of U^{4+} and U^{3+} ions on the basis of the intermediate U–S bonding length observed between those of $U^{4+}-S^{2-}$ and $U^{3+}-S^{2-}$ expected bonding lengths. The results of this work are in good agreement with their results.

The uranium and sulfur atoms in $U_xPd_3S_4$ possibly form partial molecular orbitals as suggested by the curvature in the χ^{-1} vs. T plot [16]. It seems likely that the magnetic ordering takes place below 10 K from the inverse susceptibility curve at low temperatures.

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