JOURNAL OF SOLID STATE CHEMISTRY 47, 219–224 (1983)

Crystal Chemistry, Magnetic, and Electrical Properties of the Tetragonal Plutonium Oxide Telluride Pu_2O_2Te

J. M. COSTANTINI* AND D. DAMIEN
DECPu–SEFCAE, CEN, BP 6, 92260 Fontenay-aux-Roses, France

C. H. DE NOVION
DECPu–SESI, CEN, BP 6, 92260 Fontenay-aux-Roses, France

A. BLAISE
DRF/SPhS, CEN-G, 85-X, 38041 Grenoble Cedex, France

AND A. COUSSON, H. ABAZLI, AND M. PAGÈS
Institut du Radium, 11 Rue Pierre et Marie Curie,
75321 Paris Cedex 05, France

Received April 27, 1982; in revised form August 6, 1982

We describe the preparation and some physical properties of Pu_2O_2Te. The plutonium oxide telluride is isostructural with the corresponding rare-earth oxide tellurides which crystallize in the tetragonal system of La_2O_2Te-type. Magnetic susceptibility data from 4 K to room temperature are reported together with resistivity measurements. Pu_2O_2Te is found to be an antiferromagnet below 56 K and a semiconductor with an intrinsic energy gap of 0.65 eV. The magnetic behavior is interpreted in terms of superexchange coupling interactions via nonmetal *p* orbitals, i.e., in terms of $5f$–p overlaps. This conclusion is supported by crystal chemistry considerations by comparison of cell volumes of Pu_2O_2Te and Nd_2O_2Te. In Pu_2O_2Te, the Pu crystal radius is found to be much lower than that of Nd in Nd_2O_2Te, suggesting some $5f$ electron "delocalization" leading to a crystal radius shrinkage. As for the hexagonal Pu_2O_2X compounds, with X = O, S, Se, the measured gap may be considered as the energy separation between the chalcogen *np* band and the $6d$–$7s$ conduction band, the occupied $5f$ states lying just below the *np* band with some $5f$–np overlap.

Nous décrivons la préparation et quelques propriétés physiques de Pu_2O_2Te. L'oxytellurure de plutonium est isostructural des oxytellurures correspondants de terres rares qui cristallisent dans le système quadratique de type La_2O_2Te. On a mesuré sa susceptibilité magnétique ainsi que sa résistivité entre 4 K et la température ambiante. Pu_2O_2Te est antiferromagnétique au-dessous de 56 K et semiconducteur avec un gap intrinsèque de 0.65 eV. Le magnétisme a été interprété en terme d'interactions de superéchange à travers les orbitales *p* des non-métaux c'est-à-dire en terme de recouvrements $5f$–p. Cette conclusion est confirmée par des considérations cristallochimiques en comparant les volumes de maille de Pu_2O_2Te et de Nd_2O_2Te. Dans Pu_2O_2Te, le rayon cristallin de Pu est bien inférieur à celui de Nd dans Nd_2O_2Te. Cela suggère que les électrons $5f$ se "délocalisent" ce qui conduit à une réduction du rayon cristallin. Comme pour les composés hexagonaux Pu_2O_2X où X = O, S, Se le gap mesuré peut être considéré comme la différence d'énergie entre la bande np du chalcogène, et la bande de conduction $6d$–$7s$, les états $5f$ occupés se trouvant juste au-dessous de la bande *np* en la recouvrant partiellement.

---

* To whom correspondence should be addresed: D. Tech./SELECI, CEA–CEN Saclay, 91191 GIF-sur-Yvette Cedex, France.

0022-4596/83 $3.00

Introduction

In a previous study on the hexagonal oxide chalcogenides Pu_2O_2X, $X = O, S, Se$ (*1*), we showed that a $5f$–p covalent bonding should exist in these antiferromagnetic compounds. Moreover, we stressed the influence of the chalcogen ion (X) on the magnitude of the $5f$–np overlaps which lead to a delocalization of the $5f$ electrons. This effect was correlated with the increase of the Néel point and with the shrinkage of the Pu^{3+} crystal radius along this series of compounds.

To discuss the extension of these conclusions to a less electronegative anion, we prepared the oxide telluride Pu_2O_2Te and studied its electrical and magnetic properties in relation with the $5f$ electron delocalization.

Experimental

Sample preparations and crystallographic data. Two different methods were used to prepare Pu_2O_2Te. The first one, already reported (*2*), is based upon the reaction

$$PuO_2 + PuTe \rightarrow Pu_2O_2Te.$$

Stoichiometric amounts of plutonium dioxide and monotelluride were cold pressed. The resulting pellet was then heated up to 800°C in a vacuum-sealed silica tube.

In the second method plutonium hydride was reacted with tellurium vapor and plutonium dioxide in stoichiometric amounts according to the reaction

$$PuO_2 + Te + PuH_x(2 < x < 3) \rightarrow Pu_2O_2Te + \frac{x}{2} H_2.$$

The reaction was carried out in a vacuum-sealed silica tube which was first heated at 400°C, then reactants were heated up to 800°C for some days to complete the reaction. The amount of hydrogen evolved in the reaction, from 1 g maximum of hydride, was small enough to prevent any hazard of rupture of the sealed tube. Both Pu_2O_2Te samples were black colored. X-ray powder patterns of both samples were taken using a 114.6-mm diameter Norelco camera and Cu$K\alpha$ radiation. The film dilatation corrections were performed.

Magnetic susceptibility measurements. The magnetic susceptibility of a powdered sample was measured with the Faraday method from 4 K to room temperature, at 6 kG, the sample being encapsulated in an ultrapure aluminium container. Preliminary measurements at varying applied fields were performed at room temperature to check that the sample was free from magnetic impurities.

Electrical resistivity measurements. The electrical resistivity was also measured in the same temperature range using a 4-point method on a pelletized sample ($\phi = 3$ mm, $l \simeq 5$ mm) which was sintered at 1200°C and sealed in a copper container.

Full experimental details have been previously given in (*3*).

Results

X-ray data. The X-ray patterns were indexed in the tetragonal system (Table I). The examination of the line intensities suggests that Pu_2O_2Te is isostructural with tetragonal U_2O_2Te (*4*), La_2O_2Te (*6*) and other rare-earth oxide tellurides $(RE)_2O_2Te$ (*7*, *9*). The lattice parameters are reported in Table II. They were fitted with the computer program POWD (*5*) and are in rather good agreement with the previous determination (*2*).

Magnetic susceptibility results. The plot of the reciprocal molar susceptibility $1/\chi_M$ versus temperature is shown on Fig. 1. The diamagnetic contributions of Pu^{3+}, O^{2-}, and Te^{2-}, as given in (*10*), are substracted from data as well as the blank value. A slight field-dependence correction, due to a small ferromagnetic impurity content, is also performed, according to the Honda–Owen plot (*15*). The curve $1/\chi_M = f(T)$ (Fig. 1) suggests that Pu_2O_2Te undergoes an antiferromagnetic transition at $T_N = 56$ K.

TABLE I

X-RAY POWDER PATTERN OF Pu_2O_2Te (a = 4.008 (1) Å, c = 12.659 (2) Å; z = 0.34)[a]

	2 θ		Intensities	
hkl	Observed	Calculated[b]	Observed[c]	Calculated[d]
002	13.84	13.99	vw	2
101	23.26	23.28	vw	0.2
004	28.17	28.19	vw	0.6
103	30.83	30.76	vs	100
110	31.63	31.57	s	45
114	42.82	42.83	w	2
006		42.86		7
200	45.27	45.25	m	20
202	47.56	47.59	vw	0.3
211	51.48	51.49	vw	0.1
204	54.23	54.17	m	0.5
116		54.19		18
213	55.76	55.72	s	38
206	64.07	64.08	w	9
220	65.90	65.92	w	7
301	70.97	70.93	w	<0.1
109		71.02		5
303	74.66	74.50	m	8
217		74.54		1
310		74.93		8
314	81.83	81.87	w	0.8
226		81.89		5
321	88.35	88.24	m	<0.1
219		88.31		6
1011		88.33		3
323	91.57	91.64	m	11
307		91.68		0.5
400	100.61	100.60	vw	3
402	102.50	102.33	vw	<0.1
318		102.40		3
411	105.49	105.39	w	<0.1
309		105.47		3
2111		105.51		5
1013	109.06	109.12	m	0.5
413		108.95		9
327		108.99		0.9
332	111.35	111.20	vw	0.1
2012		111.35		2
334	116.87	116.78	vw	0.3
406		116.81		4
0014		116.99		1
420	118.72	118.68	w	6
3110		118.80		1
424	126.79	126.77	vw	0.4
336		126.80		5
417	128.53	128.42	vw	1
2113		128.57		1
426	138.35	138.33	m	11
2014		138.57		5
3112	144.01	143.91	w	4
501	149.26	149.03	w	<0.1
431		149.03		0.1
419		149.18		10
3211		149.26		10
433	156.26	156.45	s	24
503		156.46		12

[a] Atomic position parameter of Ce_2O_2Te taken from (*9*).

[b] Calculations done with computer program POWD (*5*).

[c] Legend: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

[d] Calculations were done with the computer program TENSIT (*8*). Intensities were corrected with the appropriate Lorenz polarization factor, but neither absorption coefficient nor temperature factor were taken into account. Space group *I4/m m m* was assumed as in U_2O_2Te and La_2O_2Te (see text) (*4*, *6*).

Above T_N the paramagnetic behavior is complex since the effective moment per Pu atom, deduced from a Curie–Weiss fit, is

TABLE II

LATTICE PARAMETERS OF TETRAGONAL Pu_2O_2Te

	This work		Literature (*2*)
	1st prep.	2nd prep.	
a (Å)	4.008 (1)	4.008 (1)	4.03
c (Å)	12.659 (2)	12.669 (4)	12.66
c/*a*	3.16		3.14

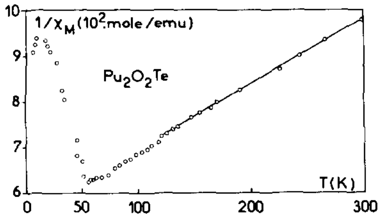

FIG. 1. Thermal dependence of the reciprocal molar susceptibility of Pu_2O_2Te ($1/\chi_M$).

markedly higher (~1.65 μ_B) than the Pu^{3+} free ion value (~1.23 μ_B) (*11*). The high negative value of the Curie paramagnetic temperature ($\theta_p \simeq -380$ K) compared to T_N, suggests that strong interactions might exist between paramagnetic moments.

Electrical resistivity results. Pu_2O_2Te is a semiconductor but with high resistivity values ($\rho \simeq 10^6\ \Omega \cdot$ cm at room temperature), as it can be seen from the plot of ρ versus $1/T$ on Fig. 2. From the linear plot, an intrinsic energy gap is deduced: Eg = 0.65 eV (measured on two different samples). This value is quite consistent with those of the similar hexagonal compounds Pu_2O_2X (X = S, Se) for which Eg values are in the 0.5–0.6-eV range (*1*). As for these compounds sample resistivity becomes very high below 200 K ($\rho > 10^8\ \Omega \cdot$ cm) preventing one from making reliable measurements at lower temperatures.

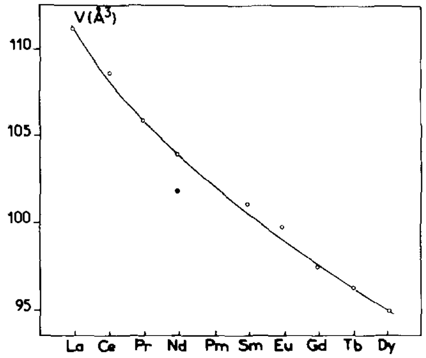

FIG. 3. Molar volumes of rare-earth oxytellurides $(RE)_2O_2Te$ as a function of rare-earth atomic number (*9*). The black dot symbolizes the molar volume of the Pu-based compound.

Discussion and Conclusion

The molar volumes of Pu_2O_2Te and Nd_2O_2Te (*9*) are compared on Fig. 3 (in this tetragonal structure, there are two formula units per cell). Although crystal radii of Nd^{3+} and Pu^{3+} are very close in ionic compounds (where Pu 5f-electrons are well localized), i.e., in trihalides (*12*) and in sesquioxides (*1*), in the oxide telluride Pu crystal radius is clearly lower than that of Nd. From this shrinkage of Pu crystal radius, we conclude that the shield effect of the 5*f* shell, between the nucleus and the 6*s* and 6*p* outer shells, is reduced because of

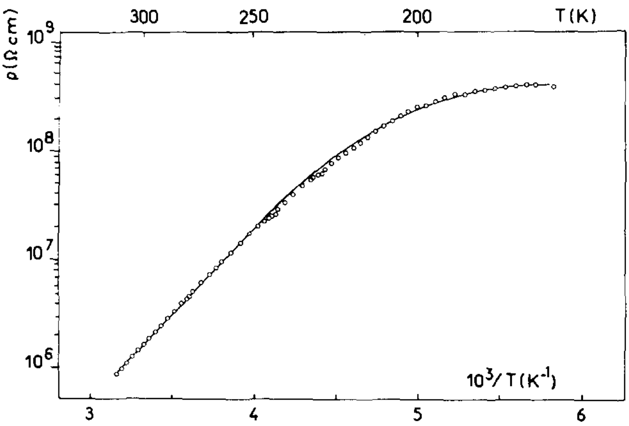

FIG. 2. Electrical resistivity (ρ) of Pu_2O_2Te in log units versus reciprocal temperature.

$5f$–p overlaps between plutonium and anion orbitals. A similar effect was observed for Pu_2O_2S and Pu_2O_2Se (*1*).

The shortest Pu–Pu distance ($d \simeq 3.6$ Å) in Pu_2O_2Te was assessed using atomic coordinates of Ce_2O_2Te (*9*); d is nearly the same as the shortest distance calculated for the hexagonal compounds ($\simeq$3.7 Å) (*1*). It is shorter than the lattice parameter ($a \simeq 4.0$ Å), yet it is longer than the critical distance (~3.4 Å) found in the Hill plot of Pu-based compounds (*13*). Since the $5f$ shell mean radius is shorter than 1 Å, superexchange coupling interactions via p orbitals of O^{2-} and Te^{2-} must occur to explain the magnetic transition. A similar effect was also found for the hexagonal Pu_2O_2X compounds but with smaller Néel points ($\leq$34 K) (*1*). For these compounds it was shown that differences of anion electronegativity and of p radial extent could account for the small T_N differences encountered from one compound to another. Yet here such an important rise of T_N between Pu_2O_2Se (34 K) and Pu_2O_2Te (56 K) is likely to be due to geometrical factors favoring larger $5f$–p overlaps in the tetragonal structure. We assume that both structures of Pu_2O_2Te and of hexagonal Pu_2O_2X (Fig. 4) are made of (Pu–O) layers alternating with chalcogen sheets as in the similar rare-earth compounds (*4*). In Pu_2O_2Te, (Pu–O) layers are made of chains of equispaced Pu and O atoms while in the hexagonal structure, $(Pu_2O_2)^{2+}$ ions form isolated patterns inside the layer. This might well explain why $5f$–p overlap is larger in the telluride and why superexchange interactions might be enhanced.

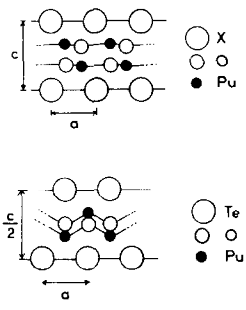

FIG. 4. Layer structures of hexagonal Pu_2O_2X (X = O, S, Se) and of tetragonal Pu_2O_2Te projected on (1, 0, 0) plane along the **a** axis. For Pu_2O_2S: Pu ± ($\frac{1}{3}$ $\frac{2}{3}$ 0.3), O ± ($\frac{1}{3}$ $\frac{2}{3}$ 0.6), S (000) (atomic coordinates taken from Ce_2O_2S (*16*). For Pu_2O_2Te: Pu (000.3) 0 ($\frac{1}{2}$ 0 $\frac{1}{4}$) and (0 $\frac{1}{2}$ $\frac{1}{4}$), Te (000) (atomic coordinates taken from Ce_2O_2Te (*9*).

For some rare-earth based oxide telluride which were also reported to be antiferromagnetic, Néel points were always found to be much lower ($T_N \lesssim 10$ K) (*9*). This shows the greater sensitivity of $5f$ orbitals to interactions with neighboring p orbitals compared to the $4f$ ones, because $4f$ electrons are more internal than the $5f$ ones, and because of a smaller radial extent of $4f$ orbitals compared to the $5f$ ones.

As in the hexagonal oxide chalcogenides (*1*) the energy gap Eg is assumed to correspond to the energy difference between the $7s$–$6d$ conduction band and the $4p$ valence band. The $5f$ localized states are considered to overlap the bottom of $4p$ band.

Conclusion. It has been shown that plutonium oxide telluride could be prepared by the direct reaction in a vacuum-sealed silica tube:

$$PuO_2 + Te + Pu\,H_x(2 < x < 3) \rightarrow Pu_2O_2Te + \frac{x}{2} H_2.$$

Pu_2O_2Te was found to be a semiconducting antiferromagnet with a gap of 0.65 eV and a Néel point of 56 K. We also showed that the chemical bonding in Pu_2O_2Te has a $5f$–p covalent character leading to superexchange interactions and $5f$ "delocalization" through covalency. Such a situation was already reported for the hexagonal Pu_2O_2X compounds (*1*) but in the oxide telluride covalency effects seem to be particularly enhanced due to the larger p radial extent of Te^{2-} and its lower electronegativity together with favorable geometrical factors.

Acknowledgment

The authors are particularly indebted to Professor R. Guillaumont for helpful discussions and advice.

References

1. J. M. Costantini, D. Damien, *et al.*, *J. Solid State Chem.* **47,** 210 (1983).
2. M. Allbutt and A. R. Junkison, AERE, R 5541 (1967).
3. J. M. Costantini, CEA, R 5046 (1980).
4. E. W. Breeze and N. H. Brett, *J. Nucl. Mater.* **40,** 113 (1971).
5. D. E. Williams, U.S. Atomic Energy Commission Document I.S. 1052 (1964).
6. R. Balestracci, *C.R. Acad. Sci. Paris B* **264,** 1736 (1967).
7. M. P. Pardo, J. Flahaut, and L. Domange, *C.R. Acad. Sci. Paris C* **255,** 937 (1962).
8. D. K. Smith, U.S. Atomic Energy Commission Document UCRL-7196 (1963).
9. Y. Abbas, Thèse Grenoble (1976).
10. L. N. Mulay, *in* "Magnetic Susceptibility," p. 1782, Wiley–Interscience, New York (1966).
11. J. D. Lam and A. T. Aldred, *in* "The Actinides, Electronic Structure and Related Properties," Vol. 1, Chap. 3, Academic Press, New York (1974).
12. C. Keller, *in* "The Chemistry of the Transuranium Elements" Vol. 3, p. 125, Verlag Chemie Weinheim (1971).
13. H. H. Hill *in* "Plutonium 1970" (W. Miner, Ed.), p. 2, Metallurgical Society of AIME, New York (1970).
14. P. Caro, *J. Less-Common Met.* **16,** 367 (1968).
15. L. F. Bates, *in* "Modern Magnetism," p. 133, Cambridge Univ. Press, London/New York, (1951).
16. W. H. Zachariasen, *Acta Crystallogr.* **2,** 60 (1949).