Characterization of the Binary Uranium and Thorium Tellurides U_7Te_{12} and Th_7Te_{12}

O. Tougait, M. Potel, and H. Noël*

Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511, CNRS,
Université de Rennes I, Avenue du Général Leclerc, 35042 Rennes, France

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Single crystals of U_7Te_{12} and Th_7Te_{12} were obtained by chemical vapor transport reactions in evacuated and sealed quartz tubes, starting from a slightly deficient tellurium stoichiometry and using iodine as the transporting agent in a temperature gradient of 1030−1000 °C. Their crystal structures were solved in the noncentrosymmetric hexagonal space group $P\bar{6}$ (No. 174), $Z = 1$. The cell constants are $a = 12.312(1)$ Å and $c = 4.260(1)$ Å for U_7Te_{12} and $a = 12.300(2)$ Å and $c = 4.566(1)$ Å for Th_7Te_{12}. The three nonequivalent actinoid (A = U, Th) atoms per unit cell, A(1), A(2), and A(3), occupy 1a, 3k, and 3j Wyckoff positions and the four nonequivalent tellurium atoms occupy two 3k and two 3j positions. All the actinoid atoms are centered in tricapped (A(1)) or bicapped (A(2), A(3)) tellurium trigonal prisms, which form infinite columns running along the [001] direction. The bicapped trigonal prisms around A(2) and around A(3) are linked also in both cases by edge-sharing, to form large distorted hexacapped trigonal prisms. U_7Te_{12} exhibits ferromagnetic ordering below 54 K and a semimetallic type conductivity.

Introduction

The crystal chemistry of binary actinide chalcogenides has been investigated by many authors, but some parts of the phase diagrams are still not perfectly characterized. The crystal structure of Th_7S_{12} was first described in the pioneering work of Zachariasen.[1] This compound is reported to crystallize in the hexagonal space group $P6_3/m$, with lattice parameters $a = 11.041(1)$ Å and $c = 3.983(1)$ Å with a structural disorder related to occupation of half of the thorium 2a positions. Some binary pnictides having similar 7/12 composition, such as $Cr_{12}P_7$, and related ternaries with atomic ratio 2/7/12 were reported to exhibit crystal structures related to the anti-Th_7S_{12} type but were described either in $P6_3/m$ with a disordered structure[2,3] or in $P\bar{6}$ with an ordered occupation of all the atomic positions.[4−6]

The binary uranium telluride U_7Te_{12}[7] was reported to be isostructural with Th_7S_{12}. The X-ray powder diffraction pattern was indexed with the hexagonal unit cell parameters $a = 12.309(4)$ Å and $c = 4.242(2)$ Å, and a reasonable agreement was assured between the diffracted intensities and those calculated using the Th_7S_{12} positional parameters. However, no residual factors were given and later a critical review on the U−Te system[8] also cast some doubt on the validity of this structural model proposed for U_7Te_{12}. Furthermore, to our knowledge no information concerning the formation of the corresponding thorium telluride Th_7Te_{12} has been reported up to now, and only some observations on Th−Te system[9] have indicated the existence of a phase composition around Th_2Te_3 with hexagonal symmetry.

In continuation of our studies on the U−Te system, we have prepared single crystals of U_7Te_{12}, as well as of the corresponding thorium telluride Th_7Te_{12}, to establish the real crystal structure of these types of compounds. We present here the syntheses, crystal structures, and physical properties of the binary thorium and uranium tellurides Th_7Te_{12} and U_7Te_{12}

Experimental Section

Synthesis. Single crystals of U_7Te_{12} and Th_7Te_{12} were grown by chemical vapor transport reactions, starting from slightly deficient tellurium stoichiometry corresponding to the atomic ratios of (U,Th)/Te = 2/3 and using 15 mg of iodine as transporting agent. The quartz tube (15 cm long, 1.5 cm diameter) containing 1 g of starting materials was slowly heated and held in the temperature gradient 1030 → 1000 °C for 1 week. Long needle-shaped crystals with hexagonal bases were obtained in the cold zone, together with some black lustrous plate-like single crystals identified as being UOTe or ThOTe.

Crystallography. The phase was identified and the purity was examined by X-ray powder diffraction with an INEL CPS 120 diffractometer using monochromatized Cu Kα_1 radiation and equipped with a curved position-sensitive detector calibrated with Si as standard.

Single-crystal X-ray diffraction intensities were collected at ambient temperature using a four-circle diffractometer (CAD 4, Enraf Nonius). The orientation matrix was determined from least-squares analysis of the setting angles of 25 optimized reflections, confirming the hexagonal symmetry and the lattice parameters. To avoid a time-dependent reaction with moisture from the air, data collection was carried out under a stream of dry argon, and crystal stability was monitored with three standard reflections from different regions of reciprocal space whose intensities were checked every hour. No crystal decay was detected in either compound. The data processing and the crystal structure solution and refinement were performed with the structure determination program package MolEN[10] implemented on a VaxStation 3100 computer. All the main information concerning data collection, processing, and structure calculations is given in Table 1. The data were corrected from Lorentz factor and polarization effects, and a

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Table 1. Crystallographic Data for U_7Te_{12} and Th_7Te_{12}

	U_7Te_{12}	Th_7Te_{12}
space group	$P\bar{6}$ (No. 174)	$P\bar{6}$ (No. 174)
a (Å)	12.312(1)	12.300(2)
c (Å)	4.260(1)	4.566(1)
V (Å^3)	559.2(2)	598.2(2)
Z	1	1
fw	3197.9	3155.2
ρ_{cal} (g cm^{-3})	9.493	8.758
temp (K)	293	293
λ (Mo Kα) (Å)	0.710 73	0.710 73
linear abs coeff, μ (cm^{-1})	632.6	592.5
$R(F)$[a] for $I > 3\sigma(I)$	0.052	0.063
$R_w(F)$[b] for $I > 3\sigma(I)$	0.063	0.078

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

numerical Gaussian absorption correction[11] was processed using the program ABSCOR.

Results and Discussion

Crystal Structure Determination. As noted above, the crystal structure type Th_7S_{12} was previously described in the centrosymmetric space group $P6_3/m$, to which the systematic extinction condition $00l$, $l = 2n$, corresponds. Careful analysis of collected crystallographic data for both compounds did not reveal any extinction conditions so the initial model[7] proposed for U_7Te_{12} could not be kept for refinements, and the structure was solved in the noncentrosymmetric space group $P\bar{6}$.

Averaging in $6/m$ Laue symmetry was performed on 2862 reflections, giving internal R values of 6.3% and 3.8% based on I and F_o, respectively. The positional parameters for uranium atoms were determined from the resolution of the Patterson function, and those of the tellurium atoms were obtained by a difference Fourier synthesis. The uranium atoms occupy the three nonequivalent positions 1a, 3k, and 3j, and the tellurium atoms occupy two 3k and two 3j positions. Full-matrix least-squares refinements of the positional and anisotropic displacement parameters for all atoms led to the residual factors $R(F) = 0.052$ and $R_w(F) = 0.063$. All attempts to associate the 3k and 3j positions two by two by a centrosymmetric relation, which would give 6h positions in the $P6_3/m$ space group, led to inconsistent results.

The crystal structure of Th_7Te_{12} was also refined in space group $P\bar{6}$, using the atomic coordinates previously found for U_7Te_{12} as initial values. The final residual factors ($R(F) = 0.064$ and $R_w(F) = 0.076$) were obtained when positional and anisotropic displacement parameters were refined.

In both cases, the residual electron density peaks with maximum height of 1.4% of an actinoid were located near the three nonequivalent U and Th atoms in the final Fourier difference maps. Refinements of the occupancy factors did not reveal any deviation from full occupation of the crystallographic sites, confirming the phase composition 7/12. Table 2 gives the final positional and equivalent isotropic displacement parameters for U_7Te_{12} and Th_7Te_{12}. Selected interatomic distances are listed in Table 3.

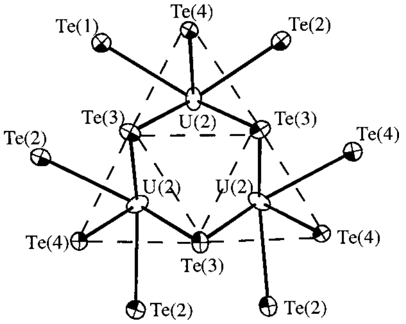

Figure 1. Edge-sharing arrangement of the U-centered trigonal prisms, forming a 6-fold capped triprism. Thermal ellipsoids are drawn at 90% probability.

Table 2. Atomic Coordinates and Equivalent Isotopic Displacement Parameters

atom	site	x	y	z	B_{eq}[a] (Å^2)
		(a) U_7Te_{12}			
U(1)	1a	0	0	0	0.66(2)
U(2)	3k	0.1738(1)	0.4659(1)	0.5	0.76(1)
U(3)	3j	0.4335(1)	0.2676(1)	0	0.61(1)
Te(1)	3k	0.2173(1)	0.2094(1)	0.5	0.71(2)
Te(2)	3k	0.5257(1)	0.1349(1)	0.5	0.68(2)
Te(3)	3j	0.3769(1)	0.4956(1)	0	0.88(2)
Te(4)	3j	0.0168(1)	0.2644(1)	0	0.84(2)
		(b) Th_7Te_{12}			
Th(1)	1a	0	0	0	0.58(2)
Th(2)	3k	0.1759(1)	0.4607(1)	0.5	0.37(1)
Th(3)	3j	0.4556(1)	0.2735(1)	0	0.47(1)
Te(1)	3	0.2193(2)	0.2079(2)	0.5	0.77(3)
Te(2)	3k	0.5142(1)	0.1194(2)	0.5	0.62(2)
Te(3)	3j	0.3805(2)	0.4958(1)	0	0.51(2)
Te(4)	3kj	0.0164(2)	0.2629(1)	0	0.57(2)

All the equivalent isotropic displacement parameters have values close to those usually reported for thorium or uranium compounds, and no significant anisotropy can be assigned to any of the three independent U or Th atoms. Considering these results, all the actinoid chalcogenides with 7/12 stoichiometry should be described with this U_7Te_{12} type structure, in the space group $P\bar{6}$ with fully ordered uranium or thorium sublattices, rather than with the structure type previously claimed for Th_7S_{12} assuming disorder due to occupation of half of an actinoid sublattice.

Crystal Structure Description. The three independent uranium atoms have trigonal prismatic environments of tellurium atoms, and as for many other binary and ternary actinoid chalcogenides, the height of the prisms corresponds to one of the lattice parameters ($c = 4.260$ Å). The prisms form infinite columns running along the [001] axis by sharing their triangular faces.

The U(1) atoms located at the origin of the unit cell are coordinated by nine tellurium atoms, forming a tricapped trigonal prism, where the capping Te atoms are closer to uranium (3.157 Å) than the apex Te atoms (3.383 Å). This is also true in the thorium telluride, where the corresponding Th−Te distances are 3.137 and 3.483 Å.

U(2) and U(3) are both surrounded by eight tellurium atoms, forming bicapped trigonal prisms, which are linked three by three by edge-sharing, forming in both cases large distorted hexacapped triprisms with an empty central cavity (Figure 1). Such a motif of infinite columns of hexacapped triprisms was found recently to be the basic repeating structural unit of another binary uranium telluride: U_3Te_5.[12]

As seen in Figure 2, which gives the projection of the crystal structure of U_7Te_{12} in the hexagonal plane, the U(1) tricapped trigonal prisms are surrounded by six triprisms. They share common edges with three U(2) triprisms which are at the same z level, and the three Te capping atoms of the U(1) prisms form the apexes of three U(3) triprisms.

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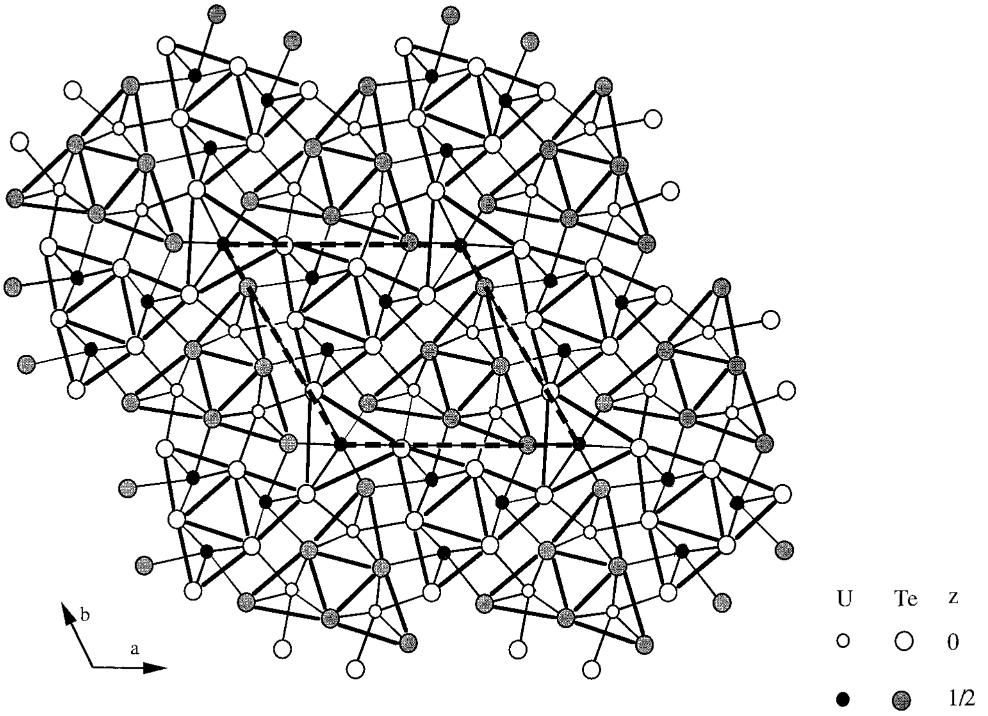

Figure 2. Crystal structure of $\mathrm{U_7Te_{12}}$ projected in the *ab* plane.

Table 3. Selected Distances (Å), with Standard Deviations in Parentheses

	A = U	A = Th		A = U	A = Th
A(1)−Te(4) × 3	3.157(2)	3.137(2)	A(3)−Te(4)	3.080(2)	3.188(2)
A(1)−Te(1) × 6	3.383(1)	3.483(1)	A(3)−Te(2) × 2	3.192(2)	3.257(2)
A(1)−A(1) × 2	4.260(1)	4.566(1)	A(3)−Te(1) × 2	3.198(2)	3.270(2)
			A(3)−Te(3)	3.213(2)	3.294(2)
A(2)−Te(4) × 2	3.103(2)	3.195(1)	A(3)−Te(2) × 2	3.217(2)	3.459(2)
A(2)−Te(3) × 2	3.164(2)	3.263(2)	A(3)−A(3) × 2	4.260(0)	4.015(2)
A(2)−Te(3) × 2	3.171(2)	3.322(2)			
A(2)−Te(2)	3.433(2)	3.303(2)			
A(2)−Te(1)	3.456(2)	3.409(2)			
A(2)−A(2) × 2	3.917(2)	3.973(2)			
Te(1)−A(3) × 2	3.198(2)	3.459(2)	Te(2)−A(3) × 2	3.192(2)	3.257(2)
Te(1)−A(1) × 2	3.383(2)	3.483(2)	Te(2)−A(3) × 2	3.217(2)	3.270(2)
Te(1)−A(2)	3.456(2)	3.409(2)	Te(2)−A(2)	3.433(2)	3.303(2)
Te(1)−Te(4) × 2	3.571(2)	3.686(2)	Te(2)−Te(4) × 2	3.654(2)	3.654(2)
Te(1)−Te(4) × 2	3.671(2)	3.722(2)	Te(2)−Te(3) × 2	3.680(2)	3.634(2)
Te(1)−Te(3) × 2	3.727(2)	3.829(2)	Te(2)−Te(2) × 2	3.771(3)	4.064(2)
Te(3)−A(2) × 2	3.164(2)	3.263(2)	Te(4)−A(3)	3.080(2)	3.188(2)
Te(3)−A(2) × 2	3.171(2)	3.322(2)	Te(4)−A(2) × 2	3.103(2)	3.195(2)
Te(3)−A(3)	3.213(2)	3.294(2)	Te(4)−A(1)	3.157(2)	3.137(2)
Te(3)−Te(2) × 2	3.680(2)	3.634(2)	Te(4)−Te(1) × 2	3.571(2)	3.686(2)
Te(3)−Te(1) × 2	3.727(2)	3.829(2)	Te(4)−Te(2) × 2	3.654(2)	3.654(2)

The coordination number of the tellurium atoms is 4 for Te(4) in a distorted tetrahedral geometry and 5 for the other Te atoms in a square pyramidal environment of uranium atoms.

The average U−Te distances are 3.31, 3.22, and 3.19 Å for U(1), U(2), and U(3), respectively, and they are 0.06−0.12 Å smaller than the corresponding Th−Te distances of 3.37, 3.28, and 3.31 Å for Th(1), Th(2), and Th(3), respectively. Thorium is typically a tetravalent element, and this difference corresponds roughly to that of the crystal radii of $\mathrm{Th^{4+}}$ and $\mathrm{U^{4+}}$ so that uranium could be expected to be tetravalent in this binary telluride, although the ratio 7/12 indicates a formal oxidation state lower than 4, and intermediate valence states could also be considered as for the other binaries $\mathrm{U_3Te_5}$[12] and $\mathrm{UTe_2}$.[13] This assumption is supported by our preliminary resistivity measurements giving values of $\rho_{77} = 3.3 \times 10^{-3}\ \Omega$ cm at 77 K and $\rho_{300} = 3.5 \times 10^{-3}\ \Omega$ cm at 300 K, indicating semimetallic behavior, so that some of the 5f electrons are probably delocalized via f−d hybridization.

The crystal structures of $\mathrm{U_7Te_{12}}$ and $\mathrm{Th_7Te_{12}}$ are related to an empty $\mathrm{Zr_2Fe_{12}P_7}$[4] structure type. The latter is also described according to orientation and linkage of centered trigonal prisms with correspondence between the actinoid and tellurium atoms and the iron and phosphorus atoms, respectively, and with the above-mentioned empty cavity in $\mathrm{A_7Te_{12}}$ compounds being occupied by zirconium in $\mathrm{Zr_2Fe_{12}P_7}$.

Magnetic Properties. Figure 3 displays the results of magnetic measurements performed on a pressed pellet of a pure polycrystalline sample of $\mathrm{U_7Te_{12}}$, using a SQUID magnetometer in the temperature and field ranges $5 < T < 300$ K and $0 < H < 30$ kG.

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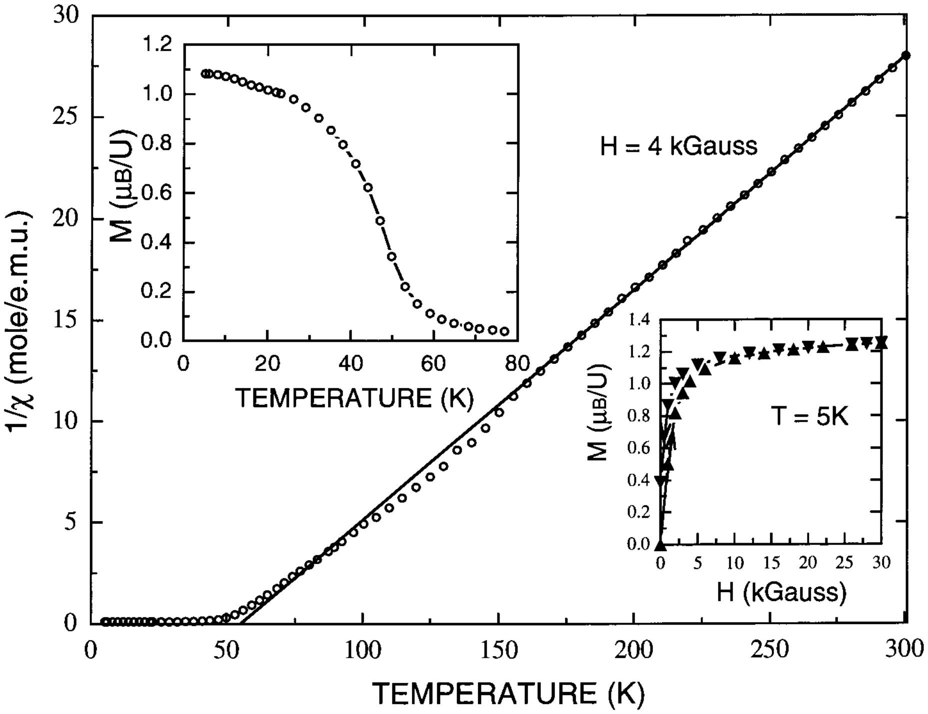

Figure 3. Inverse magnetic susceptibility as a function of temperature of U_7Te_{12}. The solid line represents a fit according to the modified Curie–Weiss law in the temperature range 180–300 K. Left inset: Magnetic susceptibility as a function of temperature. Right inset: Magnetization as a function of applied field at 5 K.

The magnetization as a function of magnetic field at 5 K reveals ferromagnetic behavior, with a saturation moment of ~1.25 μ_B/U atom, already reached under 10 kG and a weak remanent magnetization of ~0.39 μ_B/U atom, indicating soft ferromagnetic behavior. This is in contrast with ferromagnetic sulfide and selenide, which usually exhibit large magnetocrystalline anisotropy and hard magnetic behavior due to the presence of thin Bloch walls separating magnetic domains. The temperature dependence of the magnetization of the sample measured under an applied field of 4 kG, indicated a Curie temperature $T_C \approx 54$ K, which is significantly lower than the previously reported ordering temperature of 73 K.[14]

In the paramagnetic range, the susceptibility was fitted according to the Curie–Weiss law $\chi = C/(T - \Theta_p)$ with $180 < T < 300$ K, giving a Weiss constant Θ_p of 54 K and an effective moment μ_{eff} of 3.18(1) μ_B/U. The valence state of uranium cannot be unambiguously derived from this value, as the theoretical free-ion magnetic moments in the Russel–Saunders coupling scheme are 3.62 and 3.58 μ_B for U^{3+} and U^{4+}, respectively. Lower experimental values are always found and are generally ascribed to strong crystal field effects in chalcogenides.

Supporting Information Available: Listings of crystallographic data and anisotropic displacement parameters for all atoms of U_7Te_{12} and Th_7Te_{12} (2 pages). Ordering information is given on any current masthead page.

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