Crystal structure and properties of the binary uranium telluride U_2Te_5

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Abstract

Single crystal X-ray studies of U_2Te_5 revealed that this compound crystallizes in the monoclinic system with $a = 34.42(2)$ Å, $b = 4.181(1)$ Å, $c = 6.074(3)$ Å, $\beta = 95.42(3)°$. The crystal structure was solved in the $C2/m$ space group and refined to final values of reliability factors $R(F) = 0.031$ and $R\omega(F) = 0.038$, corroborating other recent results. The two crystallographically independent uranium atoms are coordinated to eight tellurium atoms in a bicapped trigonal prismatic geometry. The layered structure is built up from stacking along the a-direction of UTe_2 slabs separated by Van der Waals gaps. Magnetic measurements reveal that U_2Te_5 exhibits paramagnetic behaviour down to 2K, and electrical resistivity measurements on a single crystal indicate semiconducting behaviour. © 1997 Elsevier Science S.A.

Keywords: Uranium telluride; Crystal structure; Magnetic properties; Electrical properties

1. Introduction

The first studies of the U-Te system revealed the existence of a large number of binary compounds with compositions ranging from UTe to UTe_3 [1-3]. Many of them remained poorly characterised for long time, using powder X-ray diffraction data which left some uncertainty about the existence of some of them, particularly at the tellurium-rich end of the phase diagram. Formulae U_3Te_7, U_2Te_5 and U_3Te_8 were first announced [2] as existing between UTe_2 and UTe_3 even though the reported phase diagram [4] showed only U_3Te_7. In more recent critical studies [5,6] the binary U_2Te_5 was reported as being the only compound existing in this region with an X-ray diffraction pattern indexed in the orthorhombic system ($a = 4.262$ Å, $b = 9.939$ Å and $c = 17.089$ Å) and

it was suggested [5] that the crystal structure derived from that of UTe_3 [7] with tellurium deficiencies.

The present single crystal X-ray study shows that the structure of U_2Te_5 is of a new type and corroborates recent results [8] published during the completion of this work. We report also on the magnetic and electrical properties of U_2Te_5.

2. Experimental

U_2Te_5 was obtained free of impurities by heating stoichiometric amounts of uranium and tellurium at 900°C for 10 days in an evacuated and sealed quartz tube. The reaction product was analyzed by X-ray powder diffraction using an Inel CPS 120 diffractometer with monochromatized CuK $\alpha 1$ radiation. Table 1 gives the list of observed and calculated intensities [9] which were computed with position parameters obtained from the structure determination. Single crystals of U_2Te_5 were obtained from the

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Table 1
Observed and calculated X-ray powder diffraction pattern of U_2Te_5

h	k	l	$d_{(obs)}$ (Å)	$d_{(calc)}$ (Å)	$I_{(obs)}$	$I_{(calc)}$
2	0	−1	5.877	5.879	6	4
6	0	0	5.712	5.711	7	3
2	0	1	5.546	5.540	17	15
4	0	−1	5.172	5.176	14	11
8	0	0	4.284	4.283	6	6
1	1	0	4.150	4.150	2	2
6	0	1	3.975	3.969	2	2
3	1	0	3.926	3.926	3	2
10	0	0	3.427	3.427	2	3
7	1	0	3.179	3.179	100	100
0	0	2	3.025	3.023	17	17
5	1	1	3.011	3.009	1	1
2	0	2	2.933	2.930	2	2
7	1	−1	2.887	2.888	1	2
9	1	0	2.815	2.815	4	4
6	0	−2	2.782	2.783	16	15
4	0	2	2.773	2.770	27	25
7	1	1	2.747	2.745	2	2
9	1	−1	2.622	2.623	4	4
8	0	−2	2.586	2.588	1	1
6	0	2	2.577	2.573	3	3
12	0	1	2.495	2.493	7	7
9	1	1	2.488	2.486	8	8
14	0	0	2.448	2.447	12	12
1	1	2	2.432	2.430	73	68
10	0	2	2.380	2.381	9	8
11	1	−1	2.372	2.373	14	13
3	1	2	2.360	2.359	15	14
14	0	−1	2.346	2.347	4	4
7	1	−2	2.260	2.261	3	4
5	1	2	2.255	2.253	1	1
11	1	1	2.251	2.249	5	5
13	1	0	2.230	2.230	6	5
10	0	2	2.171	2.168	4	3
0	2	0	2.090	2.090	26	25
6	0	−3	1.959	1.960	1	1
15	1	−1	1.951	1.952	2	2
4	2	−1	1.938	1.938	2	2
13	1	−2	1.866	1.867	6	3
11	1	2	1.860	1.858	3	3
15	1	1	1.859	1.867	4	4
14	1	2	1.822	1.821	1	2
2	2	−2	1.720	1.720	2	2
0	2	2	1.720	1.719	2	2
20	0	0	1.713	1.713	8	9
4	2	2	1.669	1.669	17	18
19	1	0	1.656	1.656	2	2
12	2	−1	1.648	1.649	4	4
19	1	−1	1.633	1.634	4	2
11	1	−3	1.629	1.630	3	4
8	2	−2	1.626	1.626	1	1
17	1	−2	1.617	1.619	4	2
15	1	2	1.612	1.610	3	2
12	2	1	1.602	1.602	5	4

Table 2
Crystal data and intensity collection details

Formulae	U_2Te_5
Space group	C2/m (n° 12)
Parameters:	
a (Å)	34.42(2)
b (Å)	4.181(1)
c (Å)	6.074(3)
$\beta°$	95.43(3)
Z	4
d_{cal} (g cm^{-1})	8.507
λ, monochromator	Mo Kα (0.71073 Å), graphite
Linear absorption coefficient (cm^{-1})	516.77
Scan type	$\omega - 2\theta$
Crystal dimensions (mm^3)	0.1 × 0.08 × 0.05
Absorption correction	Ψ scan
Transmission factors (min., max., average)	0.31, 0.99, 0.68
Secondary extinction parameter	5.40×10^{-7}
Number of refined parameters	43
Number of independent reflections	2283
Number of independent reflection	
$I > 1\sigma$	1998
$I > 2\sigma$	1997
$I > 3\sigma$	1880
Limits	$\theta \leq 35$
	$0 \leq h \leq 9, 0 \leq k \leq 6,$
	$-55 \leq k \leq 55$
$R(F)$ for $I > 3\sigma(I)$	3.1
$R\omega(F)$ for $I > 3\sigma(I)$	3.8
$R(F)$ for all	3.4
$R\omega(F)$ for all	3.9

stoichiometric ratio UTe_2/Te and with $TeCl_4$ as transporting agent in a temperature gradient of 770–730°C for 2 days. A small lustrous plate (0.1 × 0.08 × 0.03 mm^3) was selected for X-ray intensity data collection, performed using a four-circle diffractome-

ter CAD4 Enraf Nonius. Least squares refinements of the diffraction angles of 25 reflections resulted in a monoclinic lattice C with unit cell parameters $a = 34.42(2)$ Å, $b = 4.181(1)$ Å, $c = 6.074(3)$ Å, $\beta = 95.43(3)°$. The data processing and the crystal structure solution and refinement were performed with the structure determination program MoLEN [10] implemented on a VaxStation 3100 computer. All the main information concerning data collection, processing and structure calculations are given in Table 2.

The data were corrected for Lorentz and polarisation effects. A numerical absorption correction based on the psi-scan method was performed and the transmission factors were in the range 0.31–0.99. The general reflection condition (hkl): $h + k = 2n$, is consistent with C2, Cm and C2/m space groups. The crystal structure was successfully solved in the centrosymmetric space group C2/m. The atomic positions for uranium atoms and two tellurium atoms were obtained by direct methods using the program MULTAN [11] and by Fourier difference for the three remaining tellurium atoms. All the atoms were found on 4i positions and refinements of positional and isotropic displacements parameters converged to a $R(F)$ of 0.041. Taking into account anisotropic

Table 3
Fractional coordinates, equivalent isotopic and anisotropic displacement parameters with their estimated standard deviations in parentheses

Atom	Site	x	y	z	B_{eq} (Å^2)	U(1,1)	U(2,2)	U(3,3)	U(1,3)
U(1)	4i	0.15062(1)	0	0.58067(5)	0.71(1)	0.0084(1)	0.0086(1)	0.0098(1)	0.0001(1)
U(2)	4i	0.55535(1)	0	0.02934(5)	0.65(1)	0.0065(1)	0.0085(1)	0.0095(1)	−0.0001(1)
Te(1)	4i	0.00002(1)	0	0.24932(8)	0.66(1)	0.0069(2)	0.0099(2)	0.0080(2)	0.0000(2)
Te(2)	4i	0.12059(2)	0	0.06400(9)	0.72(1)	0.0070(2)	0.0113(2)	0.0090(2)	0.0003(2)
Te(3)	4i	0.29686(2)	0	0.1562(1)	1.10(1)	0.0126(3)	0.0141(3)	0.0144(2)	−0.0027(2)
Te(4)	4i	0.29832(2)	0	0.6332(9)	1.06(1)	0.0117(2)	0.0140(2)	0.0147(2)	0.0023(2)
Te(5)	4i	0.41729(2)	0	0.45587(9)	0.74(1)	0.0073(2)	0.0116(2)	0.0089(2)	−0.0001(2)

U(1,2) = U(2,3) = 0 for all atoms.
The form of the anisotropic displacement parameter is: $\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$ where a, b and c are reciprocal lattice constants.

atomic displacement parameters and the secondary extinction coefficient, the final values $R(F) = 0.031$ and $R\omega(F) = 0.038$ were obtained. A subsequent difference Fourier synthesis did not reveal any significant electronic density peak. Atomic positional parameters and anisotropic displacement parameters are listed in Table 3 and selected interatomic distances are listed in Table 4. The given atomic parameters have been standardized using the program Structure-Tidy [12], which implies a shift of [1/2, 0, 1/2] of the origin of the unit cell compared to that given in another recent structure determination published during the completion of this work [8]. Taking into account the origin shift, the two sets of data are in full agreement.
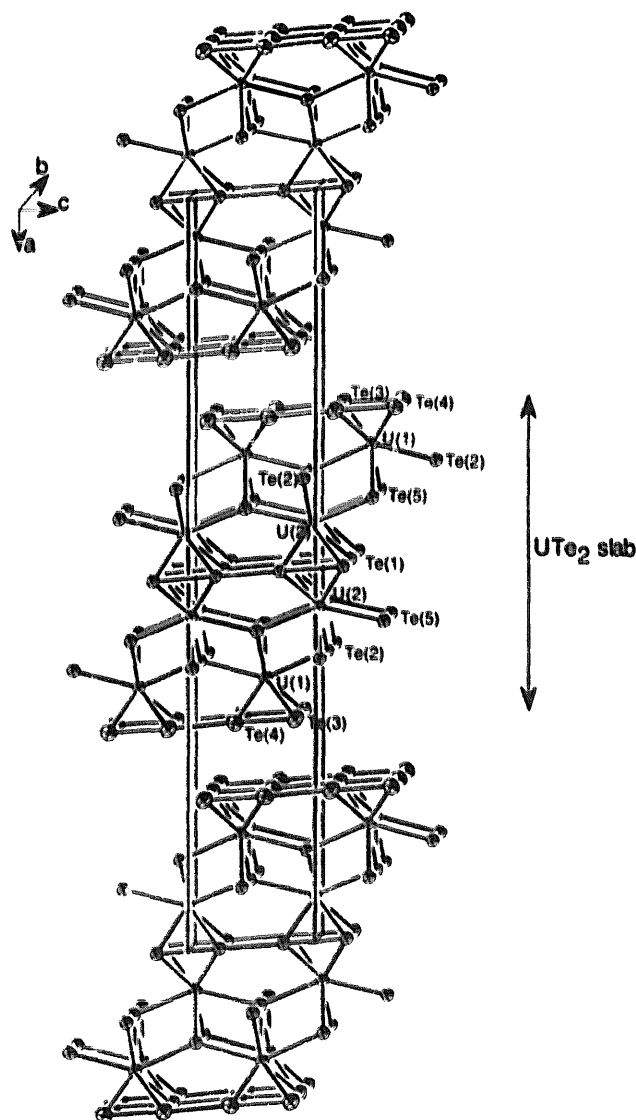
3. Structure description

The structure of U$_2$Te$_5$ is displayed in Fig. 1 which reveals clearly the bidimensional character of this

Table 4
Selected interatomic distances (Å), with standard deviations in parentheses

U(1)			U(2)		
	=2Te(4)	3.093(1)		=2Te(2)	3.061(1)
	=2Te(3)	3.107(1)		=Te(5)	3.175(1)
	=2Te(5)	3.128(1)		=Te(5)	3.179(1)
	=Te(2)	3.201(1)		=2Te(1)	3.202(1)
	=Te(2)	3.210(1)		=2Te(1)	3.203(1)
	=U(1)	4.181(1)		=U(2)	3.791(1)
	=U(2)	4.915(1)		=U(1)	4.915(1)
Te(1)	=2U(2)	3.202(1)	Te(2)	=2U(2)	3.061(1)
	=2U(2)	3.203(1)		=U(1)	3.201(1)
	=Te(1)	3.027(1)		=U(1)	3.210(1)
	=Te(1)	3.045(1)		=Te(4)	3.818(1)
	=Te(5)	3.835(1)		=Te(3)	3.865(1)
				=Te(5)	3.907(1)
Te(3)	=2U(1)	3.107(1)	Te(4)	=2U(1)	3.093(1)
	=Te(4)	2.891(1)		=Te(3)	2.891(1)
	=Te(4)	3.181(1)		=Te(3)	3.181(1)
	=Te(2)	3.865(1)		=Te(2)	3.818(1)
Te(5)	=2U(1)	3.128(1)			
	=U(1)	3.175(1)			
	=U(2)	3.179(1)			
	=Te(1)	3.835(1)			
	=Te(1)	3.837(1)			
	=Te(2)	3.907(1)			

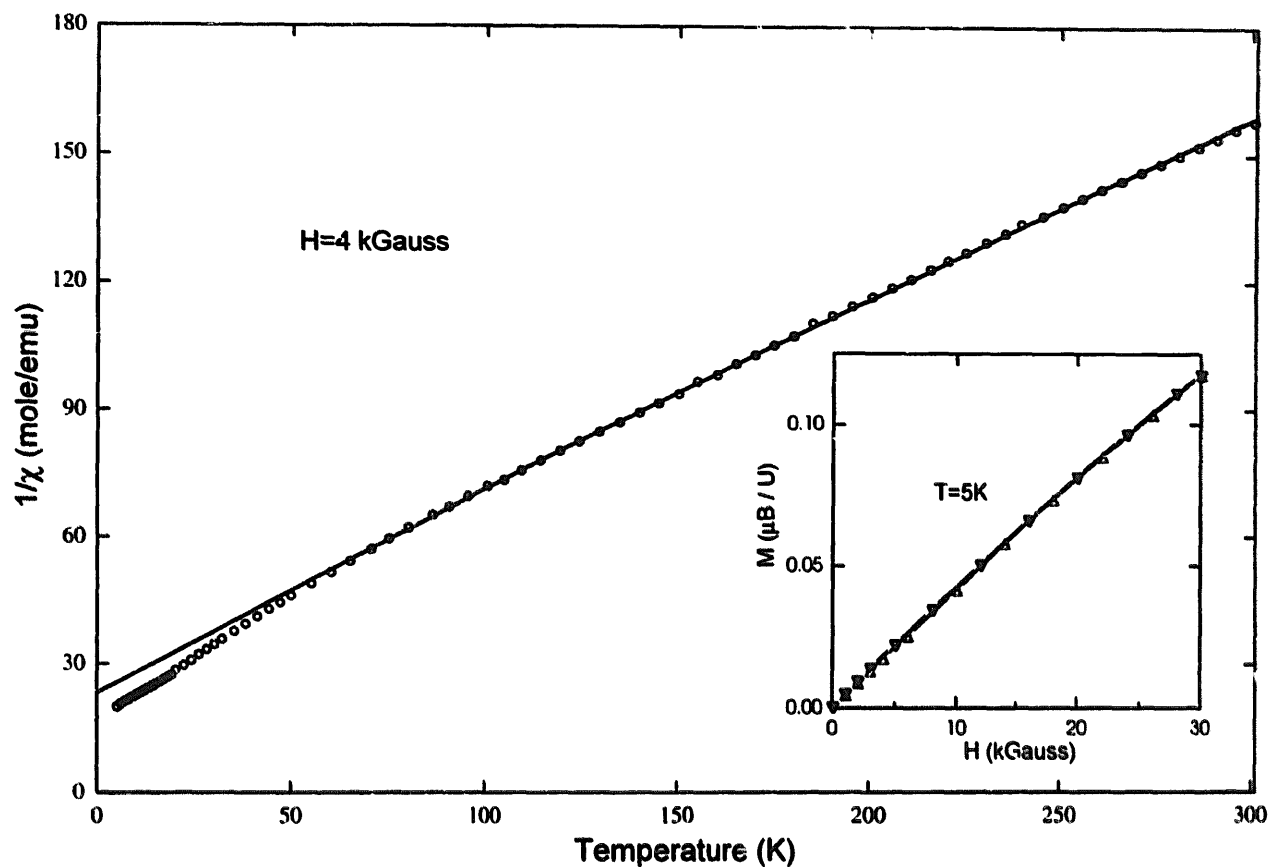Fig. 1. Ortep view of the crystal structure of U$_2$Te$_5$.

Fig. 2. Reverse magnetic susceptibility as a function of temperature of U_2Te_5. The solid line represents a fit according to the modified Curie–Weiss law in the temperature range 100–300 K. Insert: Magnetization as a function of the applied field at 5 K.
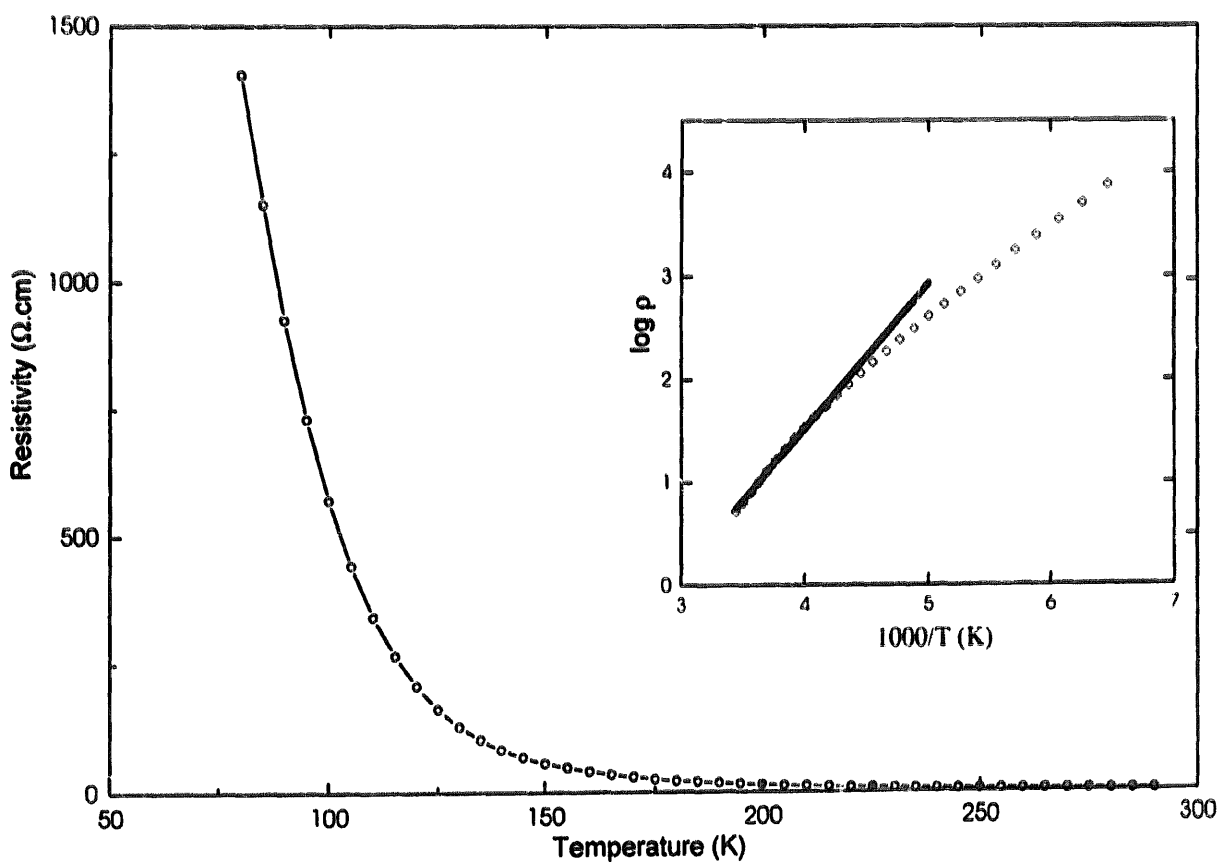

Fig. 3. Resistivity as a function of temperature of U_2Te_5.

binary compound. The two crystallographically independent uranium atoms U(1) and U(2) are surrounded by eight Te atoms, in a bicapped trigonal prismatic type coordination. The prisms share their triangular faces and form columns parallel to the b-axis. The U(2) prisms also share Te(1) rectangular faces, forming fourfold capped biprisms. The existence of short intra and interprism Te–Te distances (Table 4) indicates the formation of infinite -Te(1)-Te(1)-Te(1)- and -Te(3)-Te(4)-Te(3)- chains parallel to the c-axis. These chains form tellurium planes parallel to (b,c).

The network of U(1) prisms interpenetrates the network of U(2) prisms, giving rise to a structural arrangement which constitutes the basic structural block of the binary uranium ditelluride UTe_2 [13,14], in which the $[UTe_2]$ slabs are piled up by sharing the tellurium planes, forming consecutive maps of biprisms, while in U_2Te_5 the $[UTe_2]$ slabs are separated by Van der Waals gaps. All the U–Te distances fall within the range 3.061(1)–3.210(1) Å with average distances of 3.133 Å and 3.161 Å, respectively, for the U(1) and U(2) coordination polyhedra, which are close to the U–Te distances found in the uranium ditelluride UTe_2.

4. Physical properties

Magnetic measurements on a pressed pellet of a pure polycrystalline sample were performed in the temperature range 2–300 K using an S.H.E. SQUID magnetometer. The thermal variation of the reverse susceptibility reveals paramagnetic behaviour down to 2 K (Fig. 2). Magnetization as a function of the applied field at 5 K (insert on Fig. 3) is reversible but slightly curvilinear, probably due to the paramagnetic saturation effect. The magnetic susceptibility was fitted with a modified Curie–Weiss law $\chi = \chi_0 + C/(T - \theta_p)$ in the temperature range 100–300 K, giving the effective magnetic moment $\mu_{eff} = 2.83 \ \mu_B/U$, the paramagnetic Curie temperature $\theta_p = -48$ K and the temperature independent contributions $\chi_0 = 5.7 \times 10^{-4}$ emu mol^{-1}. The deviation from the modified Curie–Weiss law below 60 K results from crystal field effects. On account of the existence of the short Te–Te bonding distances, U_2Te_5 has to be considered as a polytelluride, in which uranium is undoubtedly in

the tetravalent state. The above value of the effective magnetic moment is in agreement with this, assuming a large crystal field splitting of the ground state.

Electrical conductivity measurements on single crystal of U_2Te_5 mounted with four indium contacts revealed a room temperature resistivity of 2.05 Ω cm. The electrical resistivity increases exponentially with decreasing temperature (Fig. 3), indicating thermally activated semiconducting behavior. The thermal activation energy E_a of 0.03(1) eV for electron conduction, estimated from the linear portion of the plot log(ρ) vs. 1000/T in the temperature range 230–300 K, is in agreement with the values usually found for this type of material in which inter and intralayer Te...Te contacts govern the electronic properties [15,16].

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