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Crystal Structure of the Low-dimensional Uranium Pentatelluride: UTe_5

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Abstract

The crystal structure of UTe_5 ($a = 17.915(5)$, $b = 10.407(3)$, $c = 4.220(2)$ Å, *Pnma*, $Pn2_1a$, $Z = 4$) was refined from 822 intensities with $I > 3\sigma(I)$ to a conventional R factor of 0.060. The uranium coordination polyhedron is a three capped tellurium trigonal prism, and all the Te atoms are involved in Te–Te bonds. The structure is built up with infinite chains of prisms stacked in the $\vec{c}$ direction. The chains are linked into (b, c) layers by a single Te atom which exhibits some positional disorder.

Introduction

The binary transition metal chalcogenides with a high chalcogen content usually crystallize with a low dimensional structural framework, as a result of formation of Van der Waals gaps between chalcogen sheets. Considerable attention has been focused on these systems, particularly on the Vb and IVb trichalcogenides since the discovery of non-linear electronic properties associated with the onset of charge density wave distortion in $NbSe_3$ and TaS_3 [1–3].

Interest has been devoted recently to the quasi one-dimensional zirconium and hafnium pentatellurides $ZrTe_5$ and $HfTe_5$, which also show large resistivity anomalies [4, 5]. No electronically driven phase transition could be shown in these compounds [6, 7].

We have recently reported on the existence and characterization of a uranium pentatelluride UTe_5 [8], and single crystal studies have shown that UTe_5 is not isomorphous with $HfTe_5$ [9], but is of a new structural type.

Experimental

A single crystal, with dimensions 0.04 × 0.09 × 0.15 mm, was used for the crystal structure determination. As previously reported [8] UTe_5 crystallizes in the orthorhombic system: $a = 17.915(5)$, $b = 10.407(3)$, $c = 4.220(2)$ Å, space group *Pnma* or $Pn2_1a$. X-ray diffraction intensities were collected in the range $1 < \theta < 30$, with the ω–2θ scan method, on a Nonius CAD-4 four circle diffractometer using MoKα radiation ($\lambda = 0.71073$ Å). The intensities of 1201 unique reflections were measured, 822 of which were greater than $3\sigma(I)$. All subsequent calculations were performed using the SDP package [10].

Intensities were corrected for absorption, Lorentz and polarization effects and a secondary extinction coefficient was included in the last stages of the refinements. The weighting scheme was based on counting statistics: $1/\omega = \sigma^2_F = 1/4|\sigma_I^2/I + 0.006\,I|$.

Uranium was found from Patterson peaks to occupy a ($4c$) position (x, 1/4, z) in the *Pnma* space group, and tellurium atoms were located by difference Fourier syntheses in ($8c$): (x, y, z), 2 × ($4c$) and ($4a$): (0, 0, 0) positions. Full matrix least-square refinements of positional and isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.123$ and $R_\omega = (|\Sigma\omega(|F_o| - |F_c|)^2/\Sigma|F_o|^2)^{1/2} = 0.184$, which were reduced to $R = 0.060$, $R_\omega = 0.089$ when introducing anisotropic thermal factors.

The final positional and thermal parameters are given in Tables I and II*: the tellurium atom Te(4) located in the special ($4a$): (0, 0, 0) position exhibits very large and anisotropic thermal parameters, with a main root mean-square amplitude of thermal vibration of 0.44 Å, indicating some positional disorder. Subsequent refinements were performed in the noncentrosymmetric $Pn2_1a$ space group, where all atoms occupy general ($4a$) positions. The reliability factors

TABLE I. Final Positional Parameters and their e.s.d.s.

Atom	x	y	z
U	0.40793(7)	0.250	0.3861(3)
Te(1)	0.16384(9)	0.5652(2)	0.3879(4)
Te(2)	0.0408(1)	0.250	0.6211(6)
Te(3)	0.7399(1)	0.250	0.3540(6)
Te(4)	0	0	0

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*Structure factors tables can be obtained on request to the author.

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TABLE II. Anisotropic (β_{ij}) and Equivalent Isotropic (B(Å^2)) Thermal Parameters[a].

Atom	β(1, 1)	β(2, 2)	β(3, 3)	β(1, 2)	β(1, 3)	β(2, 3)	B(Å^2)
U	1.08(4)	1.53(4)	0.85(4)	0	−0.10(4)	0	1.16(2)
Te(1)	1.74(5)	0.97(5)	1.58(6)	0.32(5)	0.05(5)	−0.09(5)	1.43(3)
Te(2)	1.32(7)	1.35(7)	1.16(8)	0	0.06(7)	0	1.27(4)
Te(3)	1.20(7)	1.74(8)	1.48(8)	0	−0.16(7)	0	1.47(4)
Te(4)	5.7(1)	10.3(2)	1.2(1)	6.9(1)	−0.2(1)	−0.5(1)	5.72(7)

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

were reduced to $R = 0.076$ ($R_\omega = 0.107$) with isotropic B parameters, but converged to values equivalent to those in *Pnma*: $R = 0.060$, $R_\omega = 0.088$ with anisotropic thermal factors. The y level of uranium being fixed to $y = 1/4$, the largest variations from the former (*Pnma*) positional parameters occur effectively for Te(4) which shifts slightly from the origin of the unit cell (Table III), but its thermal parameters remain (in $Pn2_1a$) larger and more anisotropic than those of the other tellurium atoms.

The number of varying parameters in the least square refinements is respectively 55 in $Pn2_1a$ and 35 in *Pnma*, and the crystal structure is described in the centrosymmetric space group. This description has to be considered as being a slightly idealized model, since the existence of weak superlattice reflections [8] indicates that some structural distortion is effective at ambient temperature.

TABLE III. Positional and Isotropic Thermal Parameters Refined in $Pn2_1a$ Space Group.

Atom	x	y	z	B(Å^2)
U	0.40785(7)	0.250	0.3861(3)	1.09(2)
Te(1)	0.1640(2)	0.5699(3)	0.3848(9)	1.63(6)
Te(2)	0.0410(1)	0.2539(7)	0.6215(6)	1.23(4)
Te(3)	0.7398(1)	0.2576(6)	0.3534(6)	1.37(4)
Te(4)	−0.0099(2)	−0.0219(5)	0.004(1)	2.23(6)
Te(5)	0.8362(2)	0.4392(3)	0.6086(7)	1.03(4)

Crystal Structure Description

Figure 1 displays a projection of the structure in the (a, b) plane. Uranium is situated approximately at the center of trigonal prisms of tellurium atoms

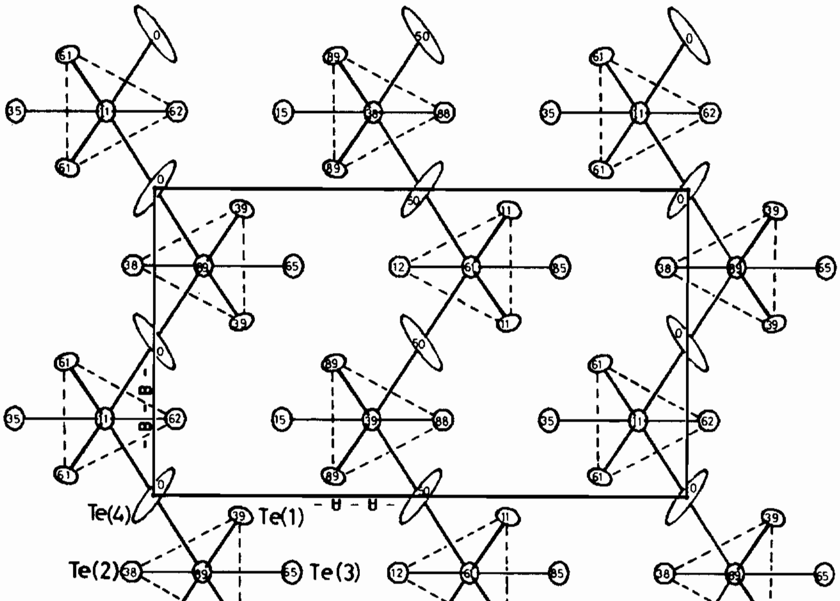

Fig. 1. Projection of the crystal structure in the (a, b) plane, with the z coordinate (×10^2) of each atom.

which form infinite chains in the *c* direction by sharing the triangular bases (Te(1)–Te(1)–Te(2)) with adjacent prisms. The chains are linked into zigzag (*b*, *c*) layers by Te(4) atoms, which are inversion centers in *Pnma*, and the layers are coupled together by Van der Waals forces. As already suggested [8], the observed structural distortion of such a bidimensional structural framework is likely to result from weak interlayer bonding. Moreover the refinements have shown that Te(4) has not a very settled position; this reflects a tendency to disorder and thus indicates relatively weak interchain bonding, giving some one dimensional character to the anisotropy of the crystal structure. These structural features can, in fact, be observed macroscopically: the growing process of UTe$_5$ single crystals by the chemical vapor transport method has led, in different experiments, either to needles or to plate-like crystals, the largest dimension of the crystals being always the *c* crystallographic axis.

Figure 2 shows the coordination polyhedron of uranium, which is surrounded by nine tellurium atoms. The rectangular faces of the trigonal prism are capped by Te(3) and two Te(4) atoms which are not located as they usually are in the median plane of the prism, but which are sufficiently close to the triangular faces so as to form Te(1)–Te(3)–Te(1) and Te(4)–Te(2)–Te(4) bonds. The interatomic distances (Table IV), d (Te(3)–Te(1)) = 2.803 Å are close to that existing in elemental tellurium (2.83 Å) or between the Te–Te pairs (d = 2.763 and 2.980 Å) in HfTe$_5$ [9]. The Te(4)–Te(2) pairing is weaker (d = 3.14 Å) but contributes to the linkage between two adjacent columns of prisms.

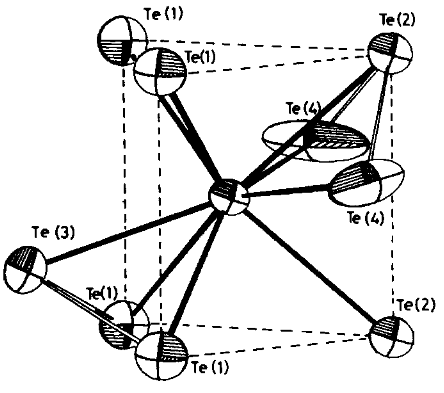

Fig. 2. Environment of uranium. Thermal ellipsoids are drawn at 90% probability.

TABLE IV. Interatomic Distances (Å) with Standard Deviations in Parentheses, Calculated from Positional Parameters in *Pnma*.

U–2 Te(4)	3.118(1)	Te(3)–2 Te(1)	2.803(2)
U–2 Te(1)	3.126(2)	Te(2)–2 Te(4)	3.140(1)
U–2 Te(1)	3.137(2)	Te(1)–Te(4)	3.429(1)
U–Te(2)	3.162(2)	Te(1)–Te(3)	3.696(1)
U–Te(3)	3.176(2)	Te(2)–Te(4)	3.765(1)
U–Te(2)	3.202(2)	Te(1)–Te(1)	3.847(2)
U–U	4.220(0)	Te(1)–Te(4)	3.968(1)
		Te(1)–Te(1)	3.978(2)

The tritelluride UTe$_3$ is isomorphous with HfTe$_3$, but the crystal structure of UTe$_5$ differs largely from that of HfTe$_5$. All are built up from chains of tellurium trigonal prisms but in HfTe$_5$ only two of the rectangular faces are capped by other tellurium atoms so that hafnium has a 8-fold coordination; the tellurium atom corresponding to Te(3) in UTe$_5$ is involved in a bridging Te–Te pair between two columns of prisms in HfTe$_5$. All Te atoms in UTe$_5$ are involved in Te–Te bonds while they are not in the HfTe$_5$ type. The contribution of Te atoms to band structure is thus quite different in the two compounds.

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