

Crystal Structure and Physical Properties of β USe_2 and $\text{USe}_{2-x}\text{Te}_x$ ($x = 0.24$ and 0.72)

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The uranium diselenide β USe_2 and the seleno-telluride $\text{USe}_{1.76}\text{Te}_{0.24}$ crystallize in the orthorhombic system, with the PbCl_2 type, space group $Pnma$, and lattice constants $a = 7.455(2)$, $b = 4.2320(5)$, $c = 8.964(2)$ Å for β USe_2 and $a = 7.542(1)$, $b = 4.2491(4)$, $c = 9.006(2)$ Å for $\text{USe}_{1.76}\text{Te}_{0.24}$. Their crystal structures were refined from single crystal X-ray diffraction data, with conventional R factors 0.064 and 0.046, respectively. Both compounds exhibit ferromagnetism with Curie temperatures of 14 K for the former and 33 K for the latter. The structural, electrical, and magnetic properties of these chalcogenides as well as of β US_2 , UTe_2 , and other mixed chalcogenides are discussed. © 1996 Academic Press, Inc.

1. INTRODUCTION

The crystal structures of the uranium dichalcogenides have been studied by many authors in the past years. Both uranium disulfide (1) and uranium diselenide (2) have been reported to exist with three different structure modifications, tetragonal α , orthorhombic β , and hexagonal γ , depending on the temperature and methods of preparation used.

The crystal structure of the α form was determined from single crystal X-ray diffraction data to be tetragonal and described in space group $P4/ncc$ (3) and later in $P4/n$ (4). In fact, the α dichalcogenides exhibit a rather wide homogeneity range, corresponding to a variable occupancy of the $4c$ site by uranium in $P4/ncc$, a result which has recently been confirmed by neutron diffraction (5). In the limiting case when this site is exactly half occupied, and after being left long time annealing at a moderate temperature, the ordering of the uranium atom occupation occurs on a $2c$ site in $P4/n$. This results from the splitting of the $4c$ position ($P4/ncc$) into two independent $2c$ positions ($P4/n$), one of which remains empty.

The crystal structure type of the γ form remained un-

known, but single crystals of γ USe_2 have been obtained, and the structure of this compound has been determined recently (9).

The crystal structure of β US_2 was first refined by Suski *et al.* (6) by using single crystal data, which confirmed the structure as a PbCl_2 -type, described in the space group $Pbnm$. The coordinates of the atoms and morphological features of the growth of single crystals for both β US_2 and β USe_2 have been studied by Ellert *et al.* (7). They were able to determine the predominant faces of the crystals, symmetry classes, and the point groups. However, the calculation of the positional parameters, which were carried out in the $Pnam$ space group, were refined only to $R = 0.148$ and 0.19 , respectively.

Although the polymorphic β - α transition was earlier questioned in studies of equilibrium diagrams of these dichalcogenides (8), Beck and Dausch (4) claimed this transition to be truly polymorphic. However, such a claim should be considered as being of a highly problematic nature, due to the generally associated change in the uranium to chalcogen ratio (3, 5).

In contrast to the uranium disulfide and diselenide, UTe_2 occurs in only one crystal structure modification, being also orthorhombic, but with space group $Immm$ (10, 11).

Recently, we reported the single crystal X-ray diffraction data obtained for the uranium mixed chalcogenides, USSe , USTe , and USeTe , which also crystallize in the PbCl_2 -type structure (12). As deduced from previous studies on powder samples (13, 14), the last mixed compound can exist over a broad region of homogeneity, $\text{USe}_{2-x}\text{Te}_x$, with $0.025 \leq x \leq 1.2$. Previously, we had obtained and studied single crystals with composition of $\text{USe}_{1.28}\text{Te}_{0.72}$ (12), and we now report on the crystal structure and magnetic measurements of single crystals with composition $\text{USe}_{1.76}\text{Te}_{0.24}$.

The magnetic properties of binary and mixed dichalcogenides in the polycrystalline form had been described in previous reports on these compounds. However, except for β US_2 (6), such studies on single crystals (5, 12) or ground single crystals (15), as well as electrical resistivity

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measurements for all the compounds mentioned above, have been carried out only recently (12, 15, 16).

2. EXPERIMENTAL

Single crystals of βUSe_2 and those within the solid solutions $\text{USe}_{2-x}\text{Te}_x$ ($x = 0.24$ and 0.72) were grown by chemical vapor transport reactions. In the cases of βUSe_2 and $\text{USe}_{1.76}\text{Te}_{0.24}$, bromine was used as a carrier gas with concentrations of 0.5 and 0.7 mg/cm^3 for the β -diselenide and mixed chalcogenide, respectively. To grow $\text{USe}_{1.28}\text{Te}_{0.72}$ single crystals, iodine (1.5 mg/cm^3) was used as a transporting agent. The starting substances for the preparation of βUSe_2 and $\text{USe}_{1.76}\text{Te}_{0.24}$ single crystals were thin turnings of metallic uranium and chips of the relevant chalcogen, earlier purified by multiple sublimations in sealed quartz ampoules. The USeTe powder previously obtained by heating stoichiometric mixtures of components in evacuated and sealed quartz ampoules at 900°C for 1 week was used as an initial material for the growing of $\text{USe}_{1.28}\text{Te}_{0.72}$.

Maintaining a temperature gradient of 800 – 870°C over 10 days for all cases, the crystals grew in the form of needles along the b -axis with the largest dimensions of the rectangular cross sections being $0.5 \times 0.1 \times 3 \text{ mm}^3$, $0.5 \times 0.5 \times 5 \text{ mm}^3$, and $0.1 \times 0.1 \times 0.8 \text{ mm}^2$ for βUSe_2 , $\text{USe}_{1.28}\text{Te}_{0.72}$, and $\text{USe}_{1.76}\text{Te}_{0.24}$, respectively. The thermodynamic parameters of the transport reactions were such that crystals of all the compounds grew in the cold part of the quartz ampoules. To study the range of the existence of βUSe_2 , we varied the selenium concentration of an initial USe_x compound ($1.9 < x < 2.5$), leaving the other parameters, such as temperature gradient and concentration of transporting agent, unchanged. Single crystals of βUSe_2 were obtained only in a very narrow range of starting concentrations, namely for $2.2 < x < 2.3$. The single crystals, which grew in the concentration region of $1.9 < x < 2.2$ were of αUSe_2 . On going to a more selenium-rich range ($2.3 < x < 2.5$), a crystal growth of USe_3 occurred. Our investigations indicated a more limited range of existence for βUSe_2 in comparison to previous data from Refs. (17) and (18). All crystals obtained were greyish-black with a metallic lustre. It is interesting to note that in the case of the $\text{USe}_{2-x}\text{Te}_x$ system, the starting substances with stoichiometries of $1:1:1$ and $1:1.8:0.2$ thus resulted in the single crystals of $\text{USe}_{1.28}\text{Te}_{0.72}$ and $\text{USe}_{1.76}\text{Te}_{0.24}$, respectively. The difference between the initial composition of the starting material and the final stoichiometry of the single crystals obtained is probably connected with the various rates of the chemical transport of Se and Te.

In this paper, we present the results of the crystal structure refinements of βUSe_2 and $\text{USe}_{1.76}\text{Te}_{0.24}$ from X-ray single crystal data, and discuss their physical properties, as well as those of βUS_2 and $\text{USe}_{1.28}\text{Te}_{0.72}$.

TABLE 1
Crystallographic Data for βUSe_2 and $\text{USe}_{1.76}\text{Te}_{0.24}$

Formula	βUSe_2	$\text{USe}_{1.76}\text{Te}_{0.24}$
Crystal dimensions (mm^3)	$0.06 \times 0.04 \times 0.015$	$0.06 \times 0.04 \times 0.04$
Crystal system	orthorhombic	orthorhombic
Space group	$Pnma$	$Pnma$
Lattice parameters (\AA)	$a = 7.455(2)$; $b = 4.2320(5)$; $c = 8.964(2)$	$a = 7.542(1)$; $b = 4.2491(4)$; $c = 9.006(2)$
Volume (\AA^3)	$V = 282.8$	$V = 288.6$
Formula units/cell	$Z = 4$	$Z = 4$
Formula weight	395.95	407.62
Calculated density (g/cm^3)	9.30	9.38
Radiation λ (\AA)	0.71069	0.71069
μ ($\text{MoK}\alpha$) (cm^{-1})	797	773
Scan mode	ω	$\omega - 2\theta$
2θ range ($^\circ$)	$<40^\circ$	$<40^\circ$
Reflections measured	1059	1406
Independent reflections ($I > 2\sigma(I)$)	377	462
Number of variables	20	21
$R = \sigma[F_o - F_c]/\Sigma F_o $	0.071	0.046
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2]^{1/2}$	0.064	0.043
Goodness of fit	1.73	0.949

The X-ray diffraction intensities were collected using an automated four-circle diffractometer (Enraf-Nonius CAD-4) with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Magnetization studies of the ferromagnetic samples were performed on a moving-sample magnetometer.

3. CRYSTAL STRUCTURE REFINEMENTS

Least squares refinements of the diffraction angles of 25 reflections for both compounds resulted in the lattice parameters given in Table 1. The obtained values for βUSe_2 are close to the previously published values deduced from powder (19) and crystal (7) data, except for the a parameter where the difference attains more than 0.1 \AA .

The lattice parameters of $\text{USe}_{1.76}\text{Te}_{0.24}$ lie in a region found for compositions between $x = 0$ and 0.5 , in polycrystalline samples of the $\text{USe}_{2-x}\text{Te}_x$ system reported by Pechennikov *et al.* (19).

The intensities were corrected for Lorentz and polarization effects and for absorption using the DIFABS program (20). The calculations were performed by full matrix least squares refinement using the MOLEN program system (21). The crystallographic and experimental data are summarized for both compounds in Table 1.

The starting positional parameters for U and chalcogen were taken from previously published data on single crystals of mixed dichalcogenides (12). All atoms occupy the positions (4c): $\pm(x, \frac{1}{4}, z)$; $(\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z)$ of the $Pnma$ space group. A series of refinement cycles gave the final conventional R and weighted R_w residual values displayed in Table 1. There are four formula units in the unit cell giving calculated densities of 9.30 and 9.38 g/cm^3 for β

TABLE 2
Positional Parameters and Isotropic Thermal Factors of the Atoms in β US₂ (6), β USE₂,
USE_{1.76}Te_{0.24}, and USE_{1.28}Te_{0.72} (12)

Atom	Occupancy	Position	x	y	z	B_{eq} (Å ²)
β US ₂ (6)						
U	1	4c	0.2523(2)	0.25	0.3772(2)	—
S(1)	1	4c	0.0290(12)	0.25	0.6662(14)	—
S(2)	1	4c	0.1439(12)	0.25	0.0664(12)	—
β USE ₂ (this work)						
U	1	4c	0.2554(3)	0.25	0.3723(2)	1.52(2)
Se(1)	1	4c	0.0305(5)	0.25	0.6626(4)	1.50(6)
Se(2)	1	4c	0.1409(5)	0.25	0.0689(4)	1.49(6)
USE _{1.76} Te _{0.24} (this work)						
U	1	4c	0.2599(1)	0.25	0.3711(1)	0.768(9)
(Se/Te)(1)	0.76/0.24	4c	0.0312(3)	0.25	0.6621(3)	0.68(3)
Se(2)	1	4c	0.1407(3)	0.25	0.0687(2)	0.84(3)
USE _{1.28} Te _{0.72} (12)						
U	1	4c	0.27191(8)	0.25	0.3691(6)	0.548(7)
(Se/Te)(1)	0.28/0.72	4c	0.03250(1)	0.25	0.66020(1)	0.43(7)
Se(2)	1	4c	0.14290(2)	0.25	0.06840(2)	0.43(2)

USE₂ and for USE_{1.76}Te_{0.24}, respectively. The value given in a previous publication (7) for β USE₂ is smaller (8.98 g/cm³).

The occupancy parameters of the chalcogen atoms were allowed to vary in order to determine the actual composition of the crystals. No significant deviations from the full occupancies of the selenium positions were observed in β USE₂. For USE_{1.76}Te_{0.24}, the refinements confirmed that the position of Se(2) is always fully occupied, whereas the position of Se(1) can be occupied by both Se and Te. Taking these results into account, we can say that the solid solution in the β USE₂-UTE₂ system can be formulated as U(Se_{1-y}Te_y)(1)Se(2). Hence, the homogeneity range for this solid solution is probably limited only to the possible substitution of Se(1) by Te up to $y = 0.72$, which was reached when performing the crystal growth starting from the stoichiometric composition 1:1:1. This conclusion however is not compatible with the data from powder studies of this system (13, 14), where the Se component may be changed over a wider region of concentration. However, the lattice parameters are only weakly dependent on the concentration and it is rather difficult to determine the real substitution range from X-ray powder diffraction data.

Table 2 gives the refined positional and isotropic thermal parameters for β USE₂ and USE_{1.76}Te_{0.24}. The anisotropic thermal parameters are given in Table 3 and the main interatomic distances are gathered in Table 4. In addition, for the sake of comparison, the standardized (22) positional parameters (in the $Pnma$ space group) for β US₂ (6) and

for USE_{1.28}Te_{0.72} (12) have also been included in Table 2. While all these parameters are close to each other, there is however some significant difference with respect to those given in reference (7) for β USE₂.

4. CRYSTAL STRUCTURE DESCRIPTION

Figure 1 displays a view of the crystal structure of β USE₂. As described earlier (12), a uranium atom in a PbCl₂-type structure is bonded to nine chalcogen atoms, forming

TABLE 3
Anisotropic Displacement Parameters in β USE₂
and USE_{1.76}Te_{0.24}

Atom	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,3)$
β USE ₂				
U	1.15(4)	1.83(4)	1.58(4)	-0.12(6)
Se(1)	1.0(1)	2.1(1)	1.4(1)	0.2(1)
Se(2)	1.2(1)	1.5(1)	1.5(1)	0.1(1)
USE _{1.76} Te _{0.24}				
U	0.80(2)	0.71(2)	0.79(2)	-0.25(2)
(0.24 Te + 0.76 Se)(1)	0.82(6)	0.91(6)	0.77(5)	0.03(5)
Se(2)	0.69(6)	0.79(7)	0.56(5)	-0.01(5)

Note. The form of the anisotropic displacement parameter is: $\exp[-\frac{1}{4}(h^2a^{*2}\beta(1,1) + k^2b^{*2}\beta(2,2) + l^2c^{*2}\beta(3,3) + 2hka^*b^*\beta(1,2) + 2hla^*c^*\beta(1,3) + 2klb^*c^*\beta(2,3))]$, where a^* , b^* , and c^* are reciprocal lattice constants. $\beta(1,2) = \beta(2,3) = 0$.

TABLE 4
Interatomic Distances [\AA] in βUSe_2 and $\text{USe}_{1.76}\text{Te}_{0.24}$

	βUSe_2	$\text{USe}_{1.76}\text{Te}_{0.24}$		βUSe_2	$\text{USe}_{1.76}\text{Te}_{0.24}$
U–1 Se(2)	2.850(4)	2.868(2)	Se(1)–2 U	3.020(3)	3.070(2)
2 Se(2)	2.860(3)	2.871(2)	1 U	3.096(6)	3.137(2)
1 Se(2)	2.922(5)	2.923(2)	2 U	3.250(3)	3.246(2)
2 (Se/Te)(1)	3.020(3)	3.070(2)	2 Se(2)	3.344(5)	3.368(2)
1 (Se/Te)(1)	3.096(4)	3.137(2)	2 Se(2)	3.450(4)	3.475(2)
2 (Se/Te)(1)	3.250(3)	3.246(2)	1 Se(2)	3.569(5)	3.605(2)
2 U	4.232(1)	4.249(1)	2 (Se/Te)(1)	3.630(6)	3.641(7)
2 U	4.324(1)	4.356(1)	1 Se(2)	3.734(6)	3.754(3)
			2 (Se/Te)(1)	4.044(3)	4.090(3)
			2 (Se/Te)(1)	4.232(3)	4.249(1)
			Se(2)–1 U	2.850(4)	2.868(2)
			2 U	2.860(3)	2.871(2)
			1 U	2.922(5)	2.923(2)
			2 Se(2)	3.227(6)	3.248(3)
			2 (Se/Te)(1)	3.344(5)	3.368(2)
			2 (Se/Te)(1)	3.450(4)	3.475(2)
			1 (Se/Te)(1)	3.569(5)	3.605(3)
			1 (Se/Te)(1)	3.734(6)	3.754(3)
			2 Se(2)	4.232(6)	4.243(1)

a tricapped trigonal prism. In the βUSe_2 unit cell, the coordination number for atom Se(1) is 5 (irregular pyramid) and for Se(2) it is 4 (distorted tetrahedron) with the average distances $\text{U–Se}(1) = 3.127 \text{ \AA}$ and $\text{U–Se}(2) = 2.873 \text{ \AA}$. The corresponding distances for $\text{USe}_{1.76}\text{Te}_{0.24}$ are 3.154 and 2.883 \AA . It is clear from this that the Te atom, being larger in size than Se, will show a preferential tendency to occupy the chalcogen (1) position due to steric constraints.

The shortest distances between selenium atoms in β

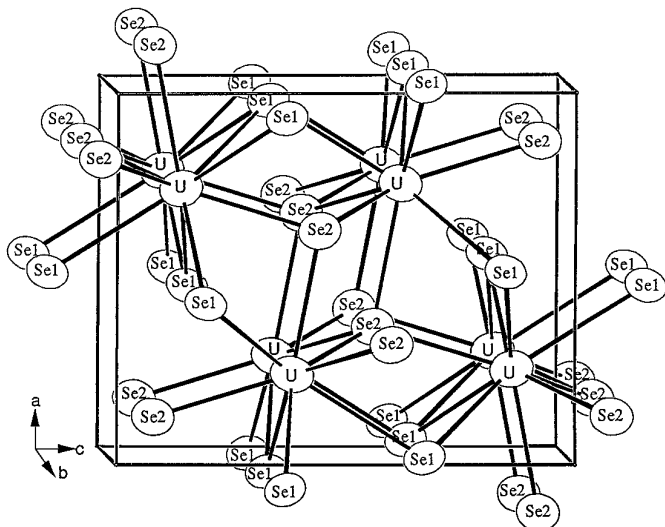


FIG. 1. ORTEP view of the crystal structure of βUSe_2 .

USe_2 are in the range from 3.227 (Se(2)–Se(1)) to 3.630 \AA (Se(1)–Se(1)). All of them are above bonding distance values.

5. PHYSICAL PROPERTIES

The magnetic characteristics for most uranium chalcogenides, apart from the uranium monochalcogenides, have mainly been reported for powder samples. For example, the results of magnetic studies on limited solid solutions $\text{USe}_{2-x}\text{Te}_x$ (where x ranges from 0.5 to 1.2), in the temperature interval 77–600 K, were given by Pechennikov *et al.* (19). They found that the susceptibility followed the Curie–Weiss law, with the paramagnetic Curie temperatures, θ_p , ranging from 48 to 96 K with increasing tellurium content, but the effective magnetic moment appeared to maintain almost a constant value of 2.8–2.9 μ_B . On the basis of positive values of θ_p , the above authors suggested the ferromagnetic properties of these solid solutions. Indeed, our single crystal magnetic measurements on $\text{USe}_{1.76}\text{Te}_{0.24}$ (this paper) and on $\text{USe}_{1.28}\text{Te}_{0.72}$ (12) have confirmed ferromagnetism in these materials. Figure 2 shows the temperature dependence of the magnetization taken at $B = 0.2 \text{ T}$ for these two solid solutions. We have deduced the Curie temperatures, which are 33 and 69 K respectively, from the inflection points. The effective moment of uranium was found to be around $(3.0 \pm 0.1) \mu_B$.

Our single crystal magnetization studies of βUSe_2 revealed the ferromagnetic properties for this compound with $T_C \sim 14 \text{ K}$ (15). This is incompatible with the results of Pechennikov *et al.* (19), who ascribed a value $\theta_p = -48$

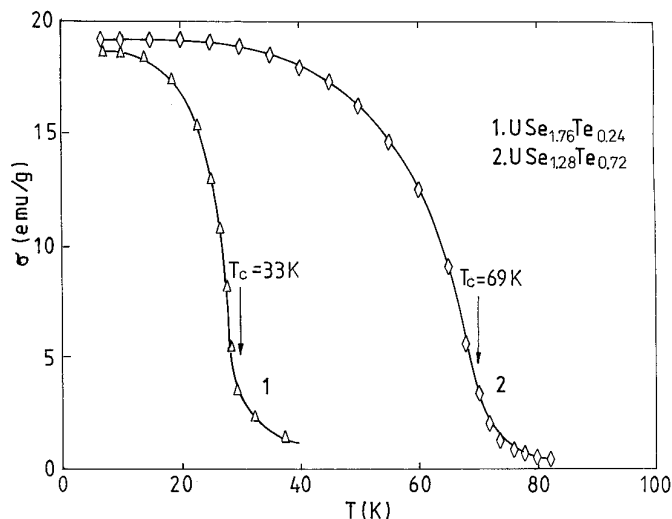


FIG. 2. Magnetization as a function of temperature for $\text{USe}_{1.76}\text{Te}_{0.24}$ and $\text{USe}_{1.28}\text{Te}_{0.72}$ in an applied field of 0.2 T.

K for their β USe_2 powder sample. The onset of magnetic order means that the exchange interactions in β USe_2 , as for the mixed chalcogenides (12), is larger than the crystal field interactions, as is required in a singlet-level only system (orthorhombic symmetry). This, however, contrasts with the results for β US_2 (6) and UTe_2 (23, 24) which are both Van Vleck paramagnets at the lowest temperatures.

The temperature dependence of the electrical resistivity, taken for single crystals of β US_2 (6), β USe_2 (15, 16) and USSe (12), have revealed their semiconducting properties. The β disulfide can be characterized as an intrinsic semiconductor with a large forbidden gap $\Delta E = 1.2$ eV (6), while the remaining compounds of this group have a gap of only a few meV (12, 16). Hence, they can be fairly easily changed into the semimetallic state in applied magnetic fields, as shown on the basis of magnetoresistivity measurements of e.g., β USe_2 (15, 16). Thus, the large difference in the forbidden gap values between these chalcogenides accounts for the difference in the observed magnetic properties.

Finally, we should add that UTe_2 and USTe or

$\text{USe}_{1.24}\text{Te}_{0.76}$ are all semimetallic. Hence, it is surprising that UTe_2 is nonmagnetic. It seems that despite the metallic character of this compound, the crystal field effect still predominates over the exchange interactions and does not allow for the appearance of the magnetic state in this material.

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