phys. stat. sol. (a) 22, 75 (1974)

Subject classification: 18.2; 1.1; 22.8

Institute for Low-Temperature and Structure Research, Polish Academy of Sciences, Wrocław (a) and Institute of Nuclear Research, Świerk Research Establishment, Otwock (b)

The Crystal and Magnetic Structure of UPTe and UAsTe Studied by Neutron Diffraction

By

A. ZYGMUNT (a), A. MURASIK (b), S. LIGENZA (b), and J. LECIEJEWICZ (b)

Neutron-diffraction study confirmed the occurrence of an UGeTe type of structure in UPTe and UAsTe. The parameters of uranium and X (X = P, As) atoms were refined using the room temperature neutron data. Below the Curie point the magnetic moment alignment has been found to be along the fourfold axis, in accordance with previous magnetization measurements. The magnetic moment of the uranium ion at liquid helium temperature has been determined to be 1.44 and 1.59 BM in UPTe and UAsTe, respectively.

Проведенные нейтронографические исследования подтвердили, что соединения UPTe и UAsTe обладают кристаллической структурой типа UGeTe. На основании данных, полученных для комнатной температуры, были уточнены параметры положения атомов урана, фосфора и мышьяка. Найдено, что, в согласии с ранее проведенными измерениями намагничение, магнитные моменты при температурах ниже точки Кюри укладываются вдоль четырехкратной оси. Определенные для температуры жидкого гелия магнитные моменты иона урана в UPTe и UAsTe равны 1,44 и 1,59 М.Б., соответственно.

1. Introduction

A fairly large number of UXY compounds (X-pnigogen, Y-chalcogen) crystallize in the PbFCl type structure (space group P4/*nmm*) [1]. Lately, a new type of crystal structure has been found among UXY compounds [2, 3], namely, that of UGeTe (space group I4/mmm) [4]. UAsTe and UPTe, as X-ray measurements suggest, belong to the latter type. Magnetic measurements performed on powder and single-crystal samples revealed that both UAsTe and UPTe are strong uniaxial ferromagnets with the Curie point at 66 and 85 K, and magnetic moments amounting to 1.29 and 1.74 BM, respectively [2, 3, 5]. Now we report the results of a neutron diffraction study aiming at the determination of atomic parameters in the unit-cell and the confirmation of the magnetic structure.

2. The Crystal Structure

Neutron-diffraction patterns shown in Fig. 1 and 2 were obtained at the liquid helium and room temperature on the KSN-2 spectrometer at the EWA reactor. Powder samples, previously used in X-ray and magnetic measurements, were carefully tested for absence of preferred orientation effects before running them on the spectrometer.

The indices of the observed neutron peaks obeyed the extinction rule characteristic of a body-centred structure with lattice constants as determined before by X-rays, supporting thus the UGeTe type of crystal structure.

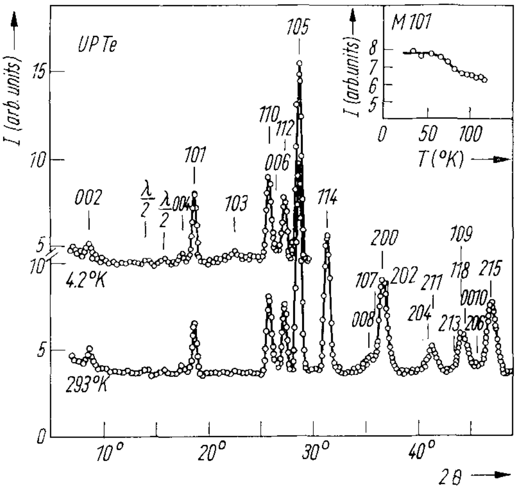


Fig. 1. Neutron-diffraction patterns of UPTe taken at room and liquid helium temperature

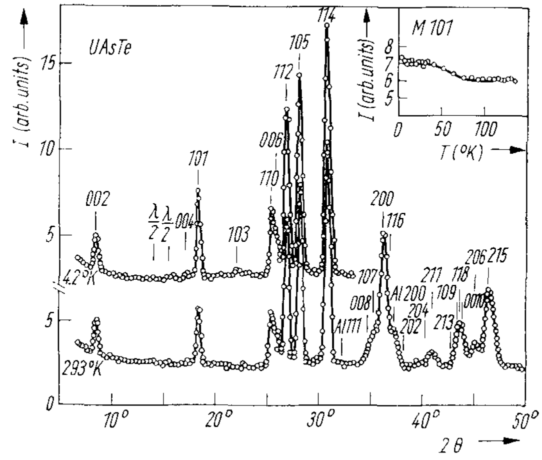


Fig. 2. Neutron-diffraction patterns of UAsTe taken at room and liquid helium temperature

The UGeTe type of crystal structure is described by the space group I4/mmm (D$^{17}_{4h}$) with the following atomic positions:

$(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$

4U in 4e: $0, 0, u;\ \ 0, 0, \bar{u};$

4Te in 4e: $0, 0, z;\ \ 0, 0, \bar{z};$

4Ge in 4c: $0, \frac{1}{2}, 0;\ \ \frac{1}{2}, 0, 0\ .$

We have carried out a refinement of the structure parameters u and z in UPTe and UAsTe basing on neutron diffraction patterns obtained at 293 K. The refinement was performed by a successive minimization of the R-factor with the help of a computer. The best agreement between the observed and calculated intensities was obtained locating the U and Te atoms in the 4e sites and the P or As atoms in 4e sites. With this distribution the following sets of structure parameters were obtained:

Table 1

	u	z	R
UPTe	0.1145	0.3095	0.11
UAsTe	0.1195	0.3145	0.06

Neutron scattering amplitudes for U, P, As, and Te were taken after [6]. No temperature factor was allowed for.

The calculated and observed intensities for the above structures are compared in Table 2.

Table 2

A comparison of calculated and observed neutron intensities for UPTe and UAsTe

	UPTe		UAsTe	
h k l	I_{obs}	I_{calc}	I_{obs}	I_{calc}
0 0 2	131	161	237	310
0 0 4	58	46	29	35
1 0 1	412	468	404	430
1 0 3	not observed	0.1	not observed	1.1
1 1 0 0 0 6	715	569	676	619
1 1 2	602	768	1213	1107
1 0 5	1936	1750	1576	1588
1 1 4	1492	1496	2030	2119
0 0 8 1 0 7 2 0 0 1 1 6 2 0 2	1726	1735	1983	2050
2 0 4 2 1 1	393	244	172	218
2 1 3	not observed	0.0	not observed	0.6
1 0 9 1 1 8 0 0 10 2 0 6 2 1 5	1989	2279	2570	2411

The principal interatomic distances are listed in Table 3. The crystallographic unit-cell of UAsTe and UPTe is shown in Fig. 3 and the coordination polyhedron around the U ion in Fig. 4. The latter is a tetragonally distorted square-based antiprism. Its point symmetry is C_{4v}. A comparison with the uranium coordination polyhedron in the PbFCl type reveals an important difference — the distance R_3 in the latter case is the same [7, 8] or almost the same [9] as R_2, whereas in the UGeTe type R_3 is larger than R_2, so that the fifth tellurium atom does not belong to the coordination polyhedron. The crystal structure of UGeTe type can be thus described as a sandwich-like arrangement of $[UX_4Y_4]$ polyhedra, explaining the strong tendency of the crystals to grow in the shape of thin plates along the [110] direction observed in both UAsTe and UPTe. UPTe and UAsTe belong to the UOY, UX_2, UXY type series of tetragonal uranium compounds, in which the change of the chemical bonding character is accom-

Table 3

Principal interatomic distances in UPTe and UAsTe

atom	neighbour	No. of neighbours	distance in Fig. 4	distances (Å)	
				UPTe	UAsTe
U	X	4	R_1	2.823	2.919
	Te	4	R_2	3.182	3.153
	Te	1	R_3	3.320	3.365
X	X	4	R_4	2.899	2.933
Te	Te	4	R_5	3.844	3.821
Te	Te	4		4.100	4.148
U	U	4		4.100	4.148
	U	4		5.464	5.389
	U	1		3.882	4.106

The lattice constants: UPTe [3] $a = (4.100 \pm 0.003)$ Å ,
$c = (17.026 \pm 0.005)$ Å
UAsTe [2] $a = (4.148 \pm 0.003)$ Å ,
$c = (17.256 \pm 0.005)$ Å

panied by a reduction of the coordination number of the uranium ion from 9 to 8. This is schematically illustrated in Fig. 5.

3. The Magnetic Structure

Liquid helium neutron patterns show that, except for (00*l*), the intensities of all reflections increase, suggesting the presence of ferromagnetic ordering, in

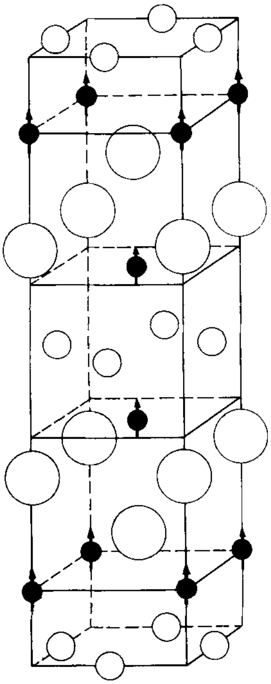
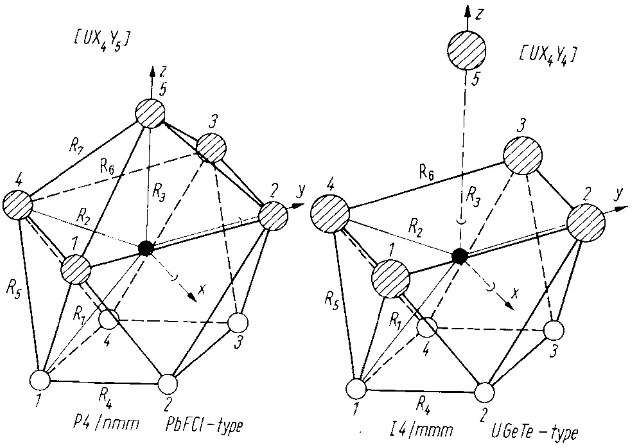


Fig. 3. The crystallographic and magnetic unit-cell of UPTe and UAsTe. Black circles: U; small empty circles: P, As(X); large empty circles: Te(Y)

Fig. 4. The coordination around the U ion (black circle) in the crystal structure of UGeTe type and PbFCl type. Empty circles: P, As(X); hatched circles: Te(Y)



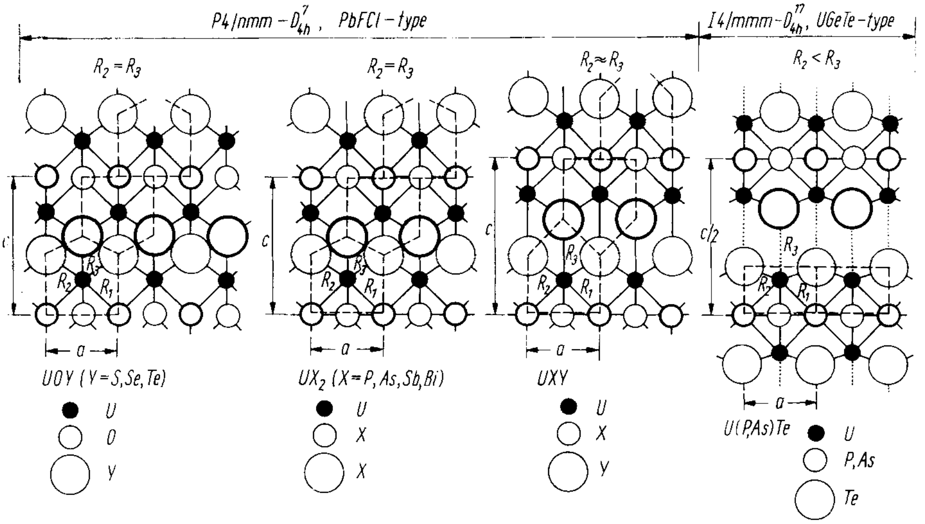


Fig. 5. Illustration of both the change of the chemical bonds and the reduction of the coordination number of uranium occurring in the UOY, UX_2, UXY type series. The bonds between the atoms are given by full lines

accordance with previous magnetization measurements [3, 5]. The magnetic moment per U ion at 4.2 K was found from the intensities at the (101) peaks which have the largest magnetic contribution. In UPTe it amounts to (1.44 ± 0.15) BM and in UAsTe to (1.59 ± 0.15) BM, assuming the form factor $5f^2$ for uranium [10].

The absence of magnetic contributions to the $(00l)$ reflections indicates that the moments are aligned along the fourfold axis, in good agreement with results of magnetization measurements which have shown that the c-axis is the axis of easy magnetization [3, 5].

Acknowledgements

The authors would like to express their appreciation to Prof. W. Trzebiatowski for his kind interest in this work, to Mrs. D. Świątkowska for preparing the programme for the ODRA computer, and to St. Cichecki, B. Halkiewicz, A. Zawadski, and R. Chojnacki for their technical assistance.

References

[1] F. Hulliger, J. less-common Metals **16**, 113 (1968).
[2] A. Zygmunt and M. Duczmal, phys. stat. sol. (a) **9**, 659 (1972).
[3] A. Zygmunt and A. Czopnik, phys. stat. sol. (a) **18**, 731 (1973).
[4] A. J. Klein Haneveld and F. Jellinek, J. less-common Metals **18**, 123 (1969).
[5] C. Bazan and A. Zygmunt, phys. stat. sol. (a) **12**, 649 (1972).
[6] G. E. Bacon, Acta cryst. **A28**, 357 (1972).
[7] A. Murasik, W. Suski, R. Troć, and J. Leciejewicz, phys. stat. sol. **30**, 61 (1968).
[8] J. Leciejewicz, R. Troć, A. Murasik, and A. Zygmunt, phys. stat. sol. **22**, 517 (1967).
[9] J. Leciejewicz and A. Zygmunt, phys. stat. sol. (a) **13**, 657 (1972).
[10] B. C. Frazer, G. Shirane, D. K. Cox, and C. E. Olsen, Phys. Rev. **150**, A1448 (1965).

(Received December 6, 1973)