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Structural and Magnetic Properties of the Tetragonal Actinide Compounds*

R. TROĆ

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, Box 937, Poland

Abstract

This paper deals with the systematics in the structural and magnetic properties of a large family of tetragonal actinide compounds. It is shown that all this family of compounds crystallize in structure types which, from the point of view of magnetic properties, have very close connections. In the analysis of earlier and newer magnetic data obtained for these compounds in the ordered state, special attention is paid to smooth dependences of the transition temperatures on the shortest interatomic distances, An–An, and to the types of their magnetic structures. In the paramagnetic state the up-to-date crystal field calculation attempts are reviewed and their results are compared to the experimental data of high-temperature susceptibility measurements.

Introduction

The actinide compounds exhibit a large variety of unusual magnetic phenomena, mainly governed by the relatively large spatial extent of the 5f states and their strong hybridization with bands of different angular momentum character. Hence, the binding energy of the 5f shell compares with that of valence electrons, implying a large sensitivity of the physical properties to chemical environments. Most of the actinide compounds have metallic character. Thus, owing to the proximity of the energies of the 5f electrons to the Fermi energy, several anomalies occur in the magnetic properties. Of course, in compounds with strongly electronegative atoms (such as oxygen, nitrogen and halogen), the 5f electrons are more or less localized and the interpretation of their magnetic properties is much easier than for those exhibiting complex metallic behaviour.

The best way to try to understand all this complex behaviour of metallic actinide compounds is to consider their magnetic properties in the framework of a series of compounds exhibiting similar crystallographic features. In the past, such considerations have been made for the simplest cubic actinide compounds; for example, a review was given by the present author at the preceding conference in Venice [1]. Now we present such systematics in structural and magnetic properties for another large series of compounds, which crystallize in closely related tetragonal structures. The first such review was published by Zygmunt [2] in 1981. At present, we give new aspects of recent studies performed on this large family of compounds, comprising the binary and ternary actinide compounds with the elements of Groups IV ($\tilde{X}$ = Si, Ge, Sn), V (X = P, As, Sb, Bi) and VI (Y = S, Se, Te) of the Periodic Table. Thus, in recent years there has been a growing interest in the physical properties of these tetragonal compounds, but especially directed to those also containing a transition metal (T) with the general formulae: UT_2X_2, UTX_2 and AnT_2 (Si, Ge)$_2$.

Crystal Structures

Among the large number of known up-to-date tetragonal actinide compounds, only a few structure types with either *P*4/*nmm* or *I*4/*mmm* space groups are represented. For the binary and ternary actinide compounds with non-metallic atoms (metalloids), the former space group is represented by the PbFCl type of structure or by its closely related modifications; *i.e.* the ZrSiS-type, usually referred to as ternary, and the anti-Cu_2Sb type of binary compounds. Examples of the latter space group are the two structure types UGeTe and Ce_2O_2Te. All these structures have one common and important feature: the actinide atoms (M) occupy equivalent sites with C_{4v} point symmetry. The metalloids form 9- or 8-fold coordination polyhedra, being square-antiprisms with different M–4Y and M–4X distances as well different sides a and $a/\sqrt{2}$, respectively, where a is the lattice constant. Additionally, the ninth Y atom in this polyhedron, with the distance M–1Y together with the remaining 4Y atoms, forms a square-pyramid, as shown in Fig. 1. An increase in the size of the anions Y increases the distances between M–4Y and M–1Y, causing in this way a gradual reduction of the cation coordination number from 9 to 8. For example, the

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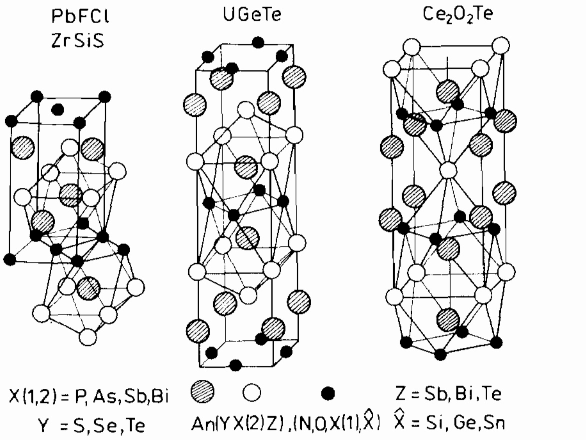

Fig. 1. The C_{4v} symmetry coordination polyhedron of uranium atoms in the PbFCl (ZrSiS), UGeTe and Ce_2O_2Te types of structure.

latter number is only true in the case of the Ce_2O_2Te-type (see Fig. 1). It should be mentioned that although the unit cells for the α-UP_2 phase [3] with the lattice parameters: $a' = a\sqrt{2}$, $c' = 2c$ (a and c are the lattice parameters for the high-temperature β-phase of UP_2) and for the orthorhombic Np-, Pu- and Am-diantimonides ($a' \approx b' \approx a\sqrt{2}$, $c' = 2c$) are different from those described above, the actinide atom coordination polyhedron is essentially the same, but is slightly distorted [4].

The PbFCl structure has been described in the literature many times (see e.g. ref. 5). In general, it can be inferred from the hypothetical mono-compound PbCl (AB) by shifting the Cl (B) atoms up or down from their positions in the NaCl structure, *i.e.* from the $z = 0$ and $z = \frac{1}{2}$ planes, respectively; also by simultaneous occupation of one half tetrahedral voids ($2a$) by the C atom in alternate layers. As a result the layers of atoms A, B and C are stacked along the c-axis in the sequence C–A–B–B–A–C.

If the tetrahedral position ($2a$) is occupied by a small C ion, e.g. by F^-, O^{2-} or N^{3-}, this position (owing to a large enough C–C distance) can be regarded as non-bonding and the normal valence rule is obeyed with full charge compensation, $\Delta = 0$. Consequently, in this type of structure the compounds crystallize with predominantly ionic chemical bonding, like the oxychalcogenides MOY (M = Th, U, Np, Pu) or oxyhalides PuO (Cl, Br, I) [6]. For these compounds the free parameter z_M of the M atoms is always below $\frac{1}{4}$, $\frac{c}{a} < 2$ (except for PuOI) and the distances M–4Y > M–4X. To this class of ionic compounds should also belong the uranium nitrochalcogenides UNSe and UNTe (UNS could not be prepared [7]), but here $\Delta = 1$ and, as shown in heat capacity measurements [8], these two compounds have distinct metallic character (high values of the electronic specific heat coefficient γ).

On the other hand, intralayer covalent and/or metallic chemical bonding occurs in the ZrSiS type of compounds when the element of Group IV ($\hat{X}$ = Si, Ge, Sn) or V (X = P, As, Sb, Bi – marked as X(1)) is placed at the $2a$ sites. Then the z_M parameters become larger than 1/4. This implies that the distances M–4Y < M–4X. Furthermore, the a-axis contracts and the c/a ratio increases to over 2 with respect to those of the PbFCl-type structure. For binary UX_2 and ternary $U\hat{X}Y$ compounds, as well as for the UXY-type compounds, the normal charge balance is no longer held and $\Delta = 2$ and 1, respectively, which roughly corresponds to the number of conduction electrons (see the results of positron annihilation studies in refs. 9 and 10). The other differences between these two structure types were discussed in detail by Flahaut [5]. At this time, it should be noted that in the anti-Cu_2Sb (or Fe_2As) structure only two neptunium binary compounds crystallize, namely $NpAs_2$ and $NpTe_{2-x}$ [6].

The body-centered UGeTe-type structure is preferred over the ZrSiS-type when we deal with a somewhat larger difference between the radius r_X of the $\hat{X}$ (X(1)) atoms and r_Y of the Y atoms. It has a lattice parameter a almost the same as in the ZrSiS-type unit cell, but the c parameter is about twice as large as that in the latter case. This structure simply arises by symmetrical joining along the c-axis of two unit cells of the ZrSiS-type (with simultaneous shifting of the origin by $(\frac{1}{2}, \frac{1}{2}, 0)$). Hence, the z_M and z_X parameters have to be doubled to be compared with those in the ZrSiS-type [11].

All the uranium ternary compounds known at present with both types of structures are collected in Table I.

TABLE I. Uranium Ternary Compounds $U\hat{X}Y$ and UXY having the UGeTe (hatched area) and ZrSiS-type Structures

M	X̂	X	X̂	Y
U	Si Ge	P As Sb		S
U	Si Ge	P As Sb		Se
U	Ge	P As Sb Bi	Sn	Te

There also exist the ternary compounds $Th\hat{X}Y$ with the UGeTe-type structure, but such compounds have not been prepared so far for the other actinides, probably due to the fact that this structure also requires a large value of r_M [11]. For example, all the known ternary compounds (Np, Pu)OY and (Np, Pu)XY crystallize either in the PbFCl or ZrSiS-type, respectively.

It is worth noting that in both structure types, *i.e.* ZrSiS and UGeTe, it is possible to occupy the remaining one-half of the tetrahedral $2a$ voids by

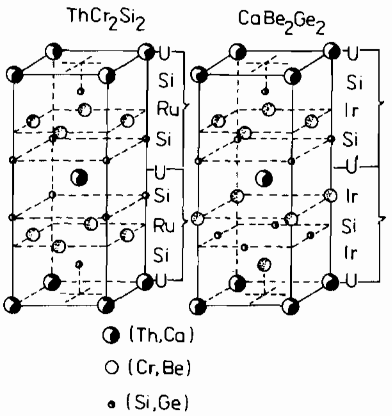

Fig. 2. The crystal structures of $ThCr_2Si_2$ (*I*4/*mmm*) and $CaBe_2Ge_2$ (*P*4/*nmm*) types. The atomic layers are marked for URu_2Si_2 and UIr_2Si_2, respectively.

the Ni or Cu atoms [12]. As a result one obtains for $UNiAs_2$ and $UCuAs_2$ [13] the filled ZrSiS-type, but the filled UGeTe-type structure for $UCuP_2$ [14]. In a similar way, a structure with an enormously elongated *c*-axis ($c/a \simeq 9.2$) has recently been found for $U_4Cu_4P_7$ ($UCuP_{1.75}$), where the incomplete segment $UCuP_{2-x}$ (deficiency of phosphorus atom in one position) of the filled UGeTe-type intergrows with the two unit cells of the $UCuAs_2$-type (filled ZrSiS-type) symmetrically along the *c*-axis on both sides of the former segment [15].

Similar uranium ternary compounds containing 3d-, 4d- and 5d-electron metals, but mostly with silicon or germanium as a third component, crystallize in the body-centered $ThCr_2Si_2$-type (*I*4/*mmm* space group). However, in some cases when T = Pt or Ir they crystallize in the primitive $CaBe_2Ge_2$-type unit cell (see a review by Suski in ref. 16). Both types of structure are illustrated in Fig. 2. The former structure, which has the largest number of representatives among the rare earth silicides and germanides, is also found for the phosphides $LnNi_2P_2$ and $LnPd_2P_2$ [17, 18]. So far there exists only one uranium compound, UNi_2P_2 [12, 18], having such a body-centred structure. Of the other actinides with this structure, only the $NpT_2(Si, Ge)_2$ compounds with T = a 3d-electron metal have been studied.

The point symmetry of the coordination polyhedron of the actinide atom [$AnSi_4$] or [$AnGe_4$] in the $ThCr_2Si_2$-type is D_{4h}. Despite the change in the point symmetry of the central atom with respect to that in the structures described above, from the point of view of layered structures we have still some analogy with the filled ZrSiS and UGeTe structures. For example, the UNi_2P_2 unit cell with $c/a \approx 2.5$ might be formed from two filled ZrSiS-type ones by removing the $z = 0$ planes of P atoms from the hypothetical $UNiP_2$ (such a compound could not be prepared) and symmetrically joining two new unit cells.

Finally, we come back to the Ce_2O_2Te-type compounds, such as U_2N_2Z (Z = Sb, Bi, Te) and U, Np, Pu)$_2O_2Te$, which crystallize in the anti-type of $Th_2Cr_2Si_2$ structure, in which the actinide atoms occupy the Si atom positions with C_{4v} point symmetry. The sublattice of the actinide atoms in this structure is analogous to that in the UGeTe-type, but the size of the former is correspondingly smaller. This feature is of importance in describing the magnetic structure arrangements.

From the above analysis, one can conclude that the tetragonal actinide compounds always form layered crystal structures, with close analogy between one another in all structure types known so far. This has important consequences in any attempts to systemize their magnetic properties.

Magnetic Properties

The Ordered State

(a) Ionic–covalent compounds

It was recognized many years ago that the UX_2, UOY and UGeY-type compounds are antiferromagnetic, whereas the ternary compounds UXY and U_2N_2 (Sb, Bi, Te) are ferromagnetic (see ref. 7). Only two existing neptunium dipnictides, namely $NpAs_2$ and $NpSb_2$, are also magnetically ordered compounds at low temperatures. The most interesting is $NpAs_2$, which undergoes a ferro–antiferromagnetic transition at 18 K and has an unusual magnetic structure in the antiferromagnetic state between 18–52 K [19]. Both transitions are first-order. A tentative magnetic phase diagram for this compound has been given by Blaise *et al.* [20]. The diantimonides $NpSb_2$ and $PuSb_2$ have a deformed anti-Cu_2Sb unit cell of the $LaSb_2$-type. By this structural analogy, the cation valency in these compounds is assumed to be 3+ [21].

Previously, a short report was given on the results of susceptibility measurements over a wide temperature range of a series of UX_2, UXX′, UOY, UNSe, UNTe and USnTe compounds [22]. Now we present more detailed data for these measurements. Figure 3 displays the low-temperature susceptibility for the uranium dipnictides. As seen, the susceptibility (measured on the polycrystalline samples) increases slightly for UP_2 and UAs_2 on approaching the lowest temperature range, and that for USb_2 and UBi_2 even goes through a small maximum. Such unusual variation of the susceptibility in the ordered state could be explained on the basis of single crystal measurement results of Blaise and Henkie (unpublished data), which indicated a large anisotropy in the temperature dependences of the parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) susceptibilities to the *c*-axis. In contrast to these

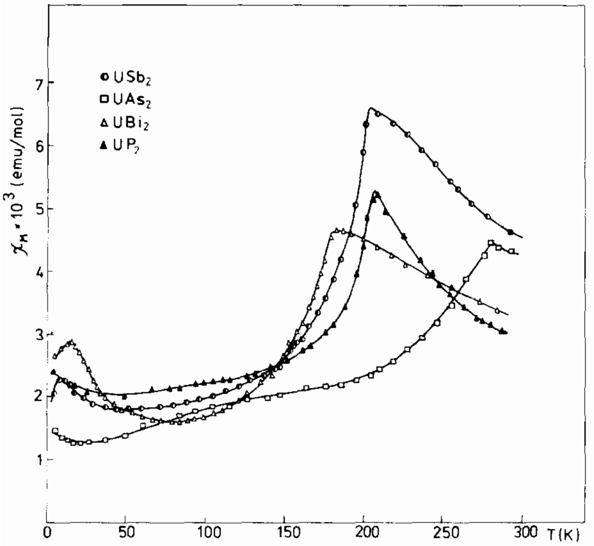

Fig. 3. The low-temperature magnetic susceptibilities for the UX_2 type of compounds, measured on the polycrystalline samples.

results, the average susceptibility of the UOY series decreases with temperature in the range below T_N without any peculiar anomalies.

Very recently Collard *et al.* [23] have investigated magnetic properties of NpOS. The $\chi(T)$ curve showed a rounded maximum around 8 K, and the hyperfine field measured at 2 K was 154 T, corresponding to a value of the ordered moment $\mu_o = 0.8\ \mu_B$. However, no conclusive results about the ordered state of NpOS could be obtained from neutron diffraction measurements. In turn, NpOSe is an antiferromagnet with $T_N = 11.6$ K, and the hyperfine field measured at 4.2 K was found to be 324 T, which corresponds to $\mu_o = 1.5\ \mu_B$ [24].

In the class of actinide nitrochalcogenides, so far only UNSe and UNTe have been prepared and studied magnetically [22]. The magnetization of these compounds, performed at 4.2 K in fields up to 5 T, is shown in Fig. 4. UNTe is a ferromagnet below 55 K with a distinct tendency to saturation of the magnetic moment to a value of 0.65 μ_B, somewhat less than the value found in neutron diffraction measurements (0.85 μ_B) [8]. As Fig. 5 illustrates, the thermal magnetization curves of UNTe taken in fields up to 5 T signal a large anisotropy of this compound as in the case of U_2N_2Te [25]. In contrast, the magnetization of UNSe at 4.2 K is linear, and as the neutron diffraction experiment pointed out [8] this compound does not undertake any transition to the ordered state. Such a transition could be suggested by a strong curvature of the reciprocal susceptibility observed near 90 K (see Fig. 11).

In recent years, in the class of ternary AnXY compounds, only USnTe [22], NpSbTe, NpAsTe [26] and $PuSb_{1-x}Te$ ($x = 0.34$) [27] have been studied magnetically. In agreement with the magnetic properties of the UGeY compounds [28], USnTe also shows antiferromagnetic properties, however in a much more complex manner.

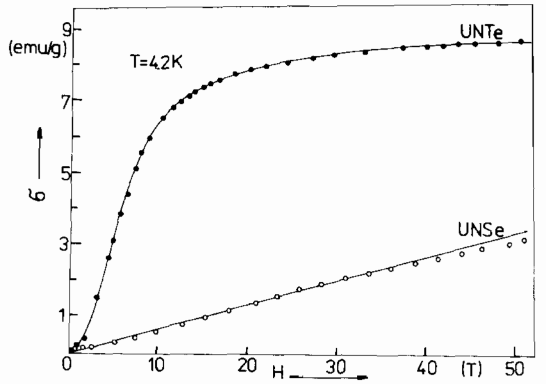

Fig. 4. Magnetization of UNSe and UNTe, measured on the polycrystalline samples in magnetic fields up to 5 T at 4.2 K.

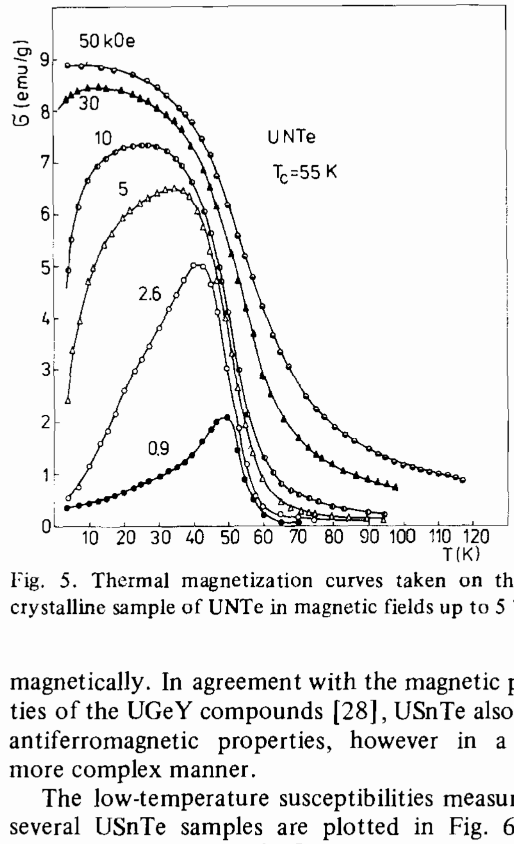

Fig. 5. Thermal magnetization curves taken on the polycrystalline sample of UNTe in magnetic fields up to 5 T.

The low-temperature susceptibilities measured for several USnTe samples are plotted in Fig. 6. In a previous publication [22], unusual two-peaked χ curves for this compound were demonstrated. Now, in Fig. 6 the susceptibility data measured for four samples of USnTe show apparent differences in the lattice parameters, probably due to some variation in the stoichiometry of this compound. However, there is a distinct correlation in the $\chi(T)$ behaviour. An increase in the c/a ratio from 2.144 (sample No. 1) to 2.155 (sample No. 4) causes a marked shift in the temperature of the χ maximum to lower temperatures and a gradual change in the shape of the χ peak to a very diffused one. Although for sample No. 1 the

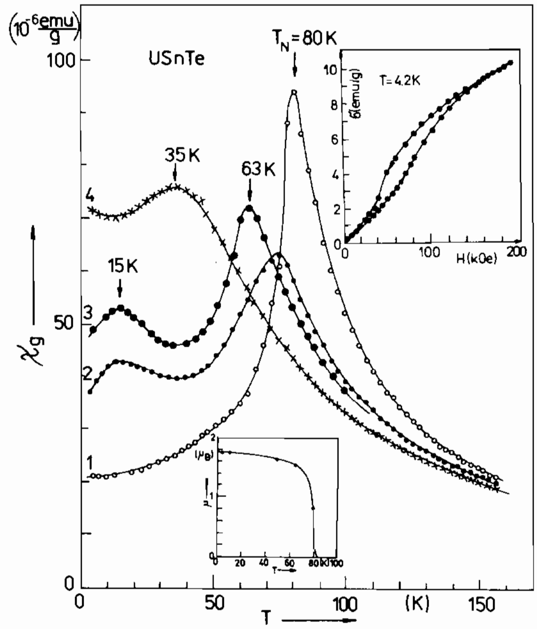

Fig. 6. Low-temperature magnetic susceptibility of USnTe, measured for four polycrystalline samples. Numbers 1 to 4 correspond to the samples (cited in the text) showing a variation in the lattice parameters. The insets represent a metamagnetic transition observed in magnetic fields above 4 T (upper) and temperature variation of sublattice magnetization (lower), determined in neutron diffraction measurements [29].

antiferromagnetic order below 80 K has been confirmed by neutron diffraction measurements [29] (see inset of Fig. 6), no such magnetic ordering has been observed for sample No. 4. Further investigation of this interesting compound should clear up the situation. In addition, USnTe (sample No. 2) exhibited a metamagnetic transition in fields above 4 T, as shown in the inset of Fig. 6. However, no saturation was reached even in fields as high as 20 T, utilizing the powder sample.

In recent years the investigation of the phases occurring in the U–(Cu,Ni)–(P, As) systems has been undertaken [12]. As mentioned in the preceding subsection, five tetragonal phases have been established to exist with the following compositions: $UCuP_2$, $UCuAs_2$, $U_4Cu_4P_7$, $UNiAs_2$ and UNi_2P_2. It appears that the first two compounds have ferromagnetic properties and the other three phases have antiferromagnetic properties with high transition temperatures. Quite recently, another tetragonal compound, $U_2Cu_4As_5$, with a so far unknown crystal structure, has been found, which is also an antiferromagnet below 190 K [30]. The magnetic susceptibilities of this compound and of the two nickel-containing ones are plotted against the temperature in Fig. 7.

In Fig. 8 we plot the transition temperature of all the uranium compounds of which the magnetic properties have been described above as a function of the shortest U–U separation, corresponding to the lattice parameter *a* of a given compound. It is remarkable to note from this Figure that the apparent regularities within a given group of compounds are strongly revealed. Relatively, the highest values in the transition temperatures are observed for the uranium dipnictides, with a peak for UAs_2. Introduction of a plane of Ni atoms into the UAs_2 lattice decreases T_N by about 15%. There are two branches of curves for the UXY-type compounds: one with higher transition

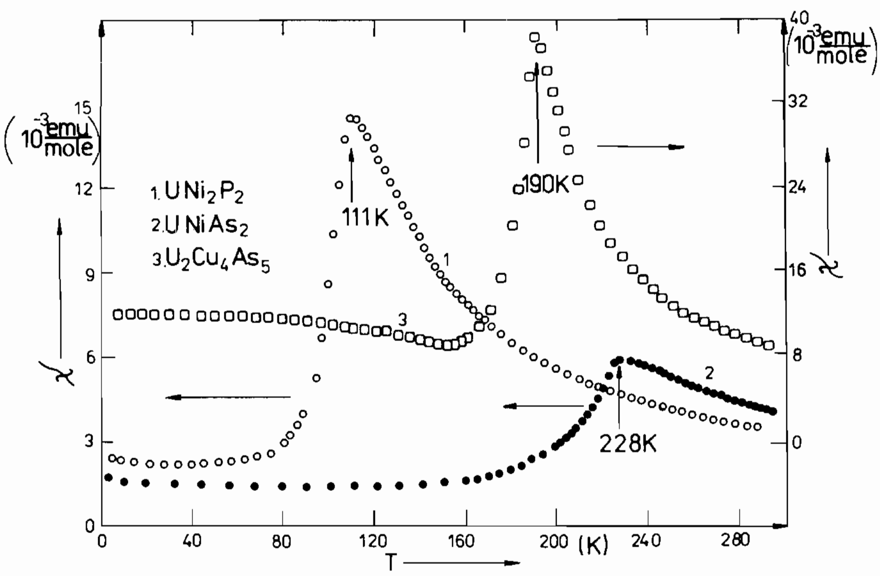

Fig. 7. Low-temperature magnetic susceptibility for the polycrystalline samples of UNi_2P_2, $UNiAs_2$ and $U_2Cu_4As_5$ [30].

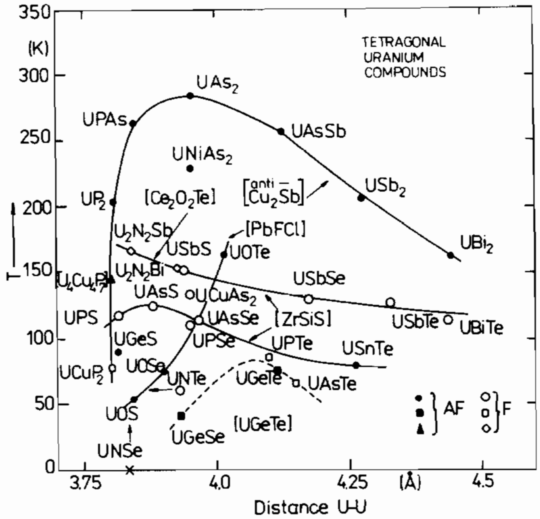

Fig. 8. The transition temperatures as a function of the shortest U–U separations for the ionic–covalent type of tetragonal uranium compounds with the PbFCl, ZrSiS, UGeTe and Ce_2O_2Te types of crystal structure. These temperatures for the compounds with filled-type structures are also plotted.

temperatures for more metallic ternary compounds containing Sb and Bi (with a continuation on the U_2N_2 (Sb, Bi) compounds); and one constituted by compounds with P and As content as well as by USnTe. The lowest transition temperatures are exhibited by the ternary compounds with the UGeTe-type structures, to which $UCuP_2$ also belongs. Comparing for example, the transition temperatures of UPS and UGeS, with both the same crystal structure and U–U distance, this temperature is lower for the latter compound. Finally, from Fig. 8 it is clear that on increasing the U–U separation in the ionic-type compounds UOY and UNY, the transition temperature rapidly increases.

Magnetic structures of a number of the tetragonal uranium compounds of the UGeY, UOY and UX_2 series were established in numerous neutron diffraction investigations (see refs. 7 and 31). Very recently the magnetic structure of USnTe has been determined [29]. The sequence of ferromagnetic sheets (001) is + + – –, like that in UGeTe [32] and UOS [33] or UOSe [34]. The magnetic unit cell is doubled with respect to the crystallographic one in the direction of the four-fold axis *c*, with the magnetic moment aligned parallel along this direction with a magnitude of 1.75 μ_B.

Among the compounds studied, but belonging to the *P*4/*nmm* space group, three different antiferromagnetic arrangements of the magnetic moments along the *c*-axis: AF I (+ –), AF II (+ – – +) and AF III (+ + – –) were found, according to the theoretical predictions based on the molecular field approach (MFA) [35a]. In addition, a ferromagnetic F (+ + ··) alignment was also postulated, commonly represented by the UXY and NpXY ternary compounds. Moreover, Przystawa [35b] obtained similar results using the RPA Green's function method. Furthermore, this author [36] considered the magnetic symmetry in the tetragonal lattice with the magnetic atoms in positions (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, z_U)$ and came to the conclusion that the *P*4/*nmm* group can be retained for the AF II type, but in cases of AF I and AF III types, the magnetic symmetry is lowered. Then, the AF II and AF III structures are essentially different because of the difference in the values of the structural uranium atom parameters. If $z_U < 1/4$ (the PbFCl-type compounds), the nearest sheets of uranium atom layers are ferromagnetically coupled (AF III type), but if $z_U > 1/4$ (the ZrSiS-type compounds) they are coupled antiferromagnetically (AF II type) in accordance with the experiments (see Table II).

TABLE II. Existing Types of Magnetic Structures for the Tetragonal Uranium Compounds with the PbFCl (ZrSiS) and UGeTe Type of Crystal Structures

Type	AF I	AF II	AF III	F
Sequence	+ –	+ – – +	+ + – –	+ +
Wave vector ($\bar{k}$)	[0 0 1]	[0 0 $\frac{1}{2}$]	[0 0 $\frac{1}{2}$]	[0 0 0]
[PbFCl]	UOTe		UOS UOSe	UNTe
[ZrSiS]	UBi_2	UP_2 UAs_2 USb_2	UGeS	UXY $UCuAs_2$
Sequence	+ – + –	+ – – +	+ + – –	+ + + +
Wave vector ($\bar{k}$)	[0 0 1]	[0 0 1]	[0 0 1]	[0 0 0]
[UGeTe]	UGeSe		UGeTe	UPTe UAsTe $UCuP_2$

Possible tetragonal magnetic structures and their stability conditions for the compounds which crystallize in the UGeTe-type (space group *I*4/*mmm*) were in turn discussed by Lorenc *et al.* [37] in terms of the MFA and the magnetic group theory. Magnetic atoms were taken in the $(0, 0, \pm z_U)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z_U)$ positions. Colinear magnetic moment arrangements similar to those above were found, but all spin arrangements obtained were formed only within the chemical unit cell. Experimentally, it was confirmed that UGeSe exhibited the AF I type, whereas UGeTe the AF III type [32]. The other compounds in this series are ferromagnets (see Table II).

The exchange interactions in the above described compounds were considered in detail by Zygmunt [2]. He came to the conclusion that the occurrence of magnetic ordering is due to the superexchange interactions, formed by means of the metalloid layers being either in the ionic or covalent states. The superexchange via the ionic layers U^{4+}–Y^{2-}–U^{4+} and covalent ones U–X(1)–U is ferromagnetic (except for UOTe and UBi_2) and that via the ionic U^{4+}–$X(2)^{3-}$–U^{4+} and covalent U–$\hat{X}$–U layers is antiferromagnetic.

It should be emphasized that in all the above cases the exchange interaction in the uranium atom (001) plane itself is always strongly ferromagnetic and only the differences in distances between these planes and the variation in the kind of superexchange drive a given sequence of these ferromagnetic planes.

A quite different magnetic structure has been found in $NpAs_2$ [19]. Although the magnetic moments are also aligned here along the *c*-axis, however, they order with a pure sine wave modulation, propagating along a [100] direction of the tetragonal unit cell. Mössbauer spectra [38] and polarized neutron measurements [39] pointed to the Np^{4+} ($5f^3$) configuration; this leads to a Kramers doublet as a ground state in this compound. Probably the observed strong Ising anisotropy (unusual for the Kramers ion), together with competitive exchange interactions, give rise to that unusual magnetic structure.

(b) The $UT_2(Si, Ge)_2$-type compounds

A survey on the magnetic properties of the silicides and germanides of uranium, containing also the 3d-, 4d- or 5d-electron metals, has very recently been given by Leciejewicz and Szytuła [40]. Most of these compounds crystallize in the fully ordered $ThCr_2Si_2$ type of structure with the sequence of layers M–$\hat{X}$–T–$\hat{X}$–M (see Fig. 2). It has been found that apart from the uranium ions only the Mn ions of all the remaining transition metals show magnetically ordered sublattices in this kind of compound. Besides the ferromagnetic structures found for $UMn_2\hat{X}_2$ and UCu_2Si_2, two antiferromagnetic colinear coupling schemes, namely AF I (UCo_2Si_2 and UNi_2Ge_2) and AF II (UCu_2Ge_2), as well as a few non-colinear structures (being cosinusoidally modulated spin waves, propagating along the *c*-axis, e.g. UNi_2Si_2, UPd_2Si_2 and UPd_2Ge_2), have been observed [41, 42]. As the authors [40] stated, the magnetic properties of these kinds of compounds, in contrast to the previously described ones, are governed by two factors:

(i) exchange interactions which can be described by the RKKY model (see ref. 42);

(ii) crystal electric field (especially by the sign of the B_2^0 coefficient in the CEF Hamiltonian).

In their isotropic RKKY model with a spherical Fermi surface, a strong dependence of the magnetic structure on the a/c ratio and the number of free electrons has been found. For example, the colinear antiferromagnetic ordering takes place for $a/c < 0.415$, and that exhibiting oscillatory character of the magnetic moments for $a/c > 0.415$.

However, the most interesting finding among these compounds has been the discovery of the heavy-electron behaviour, first in URu_2Si_2 [43] and then in UIr_2Si_2 [44]. Heavy-electron behaviour arises when the Fermi level is located at or near the top of an extremely narrow f-band, evidenced by the very high value of the electronic specific heat. In addition, URu_2Si_2 exhibits superconductivity below 1.2 K, coexisting with a very strange magnetic structure with an unusually small value for the ordered magnetic moment [45].

In Fig. 9 we give the dependences of the transition temperature of the $UT_2(Si, Ge)_2$ ternary compounds on the U–U distance, within the uranium atom layer, in a way similar to Fig. 8. Again, one can see from this Figure distinct regularities in these dependences. It is interesting to note that the transition temperatures of the ternary compounds with the 3d-electron metal lie between those containing, on the one hand Rh or Pd, and on the other Ir, Ru and Pt. UOs_2Si_2 shows only Pauli paramagnetism [46], and URh_2Ge_2 has probably some transition at very low temperatures [47]. The transition temperature for UPd_2Si_2 is plotted twice in Fig. 9, because of the two different values existing in the literature [42, 48]. Also in Fig. 9 are given the values of the Curie point for the U_2N_2Z-type compounds because of close similarity in the crystal structure to the $UT_2(Si, Ge)_2$-type compounds (see preceding subsection). It is also apparent from this Figure that U_2N_2Te differs from the two remaining nitro ternary compounds. This difference originates from the fact that the magnetic structure of U_2N_2Te is quite unique; the magnetic moment is tilted by about 70° from the *c*-axis (see ref. 25 and 49). A similar canted magnetic structure, but with the antiferromagnetic alignment of the magnetic moments, has also been found for $NpCo_2Si_2$ [50]. The other neptunium 3d-transition metal silicides and germanides have predominantly ferromagnetic

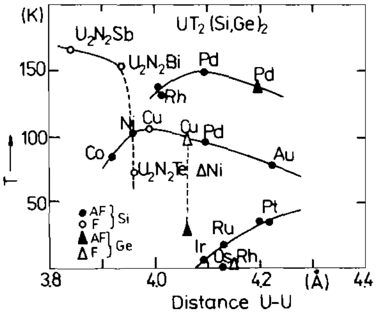

Fig. 9. The transition temperatures as a function of the shortest U–U separation for the metallic uranium silicides and germanides, containing also the *n*d-transition metals. For comparison the Curie points of the U_2N_2Z-type compounds are also plotted.

properties (see ref. 51). A study of the Mössbauer effect on the ^{237}Np ion in this series of compounds has allowed determination of the magnitudes of ordered neptunium moments (around 1.5 μ_B).

The Paramagnetic State

It is well known that crystal-field interaction in the actinide compounds is relatively strong compared to the rare earth counterparts and is important in an understanding of their magnetic behaviour even at high temperatures. Hence, knowledge of high-temperature susceptibility variation is needed to perform any analysis of the crystal-field (CF) effect acting in these compounds. In the past, such measurements up to about 1000 K have been carried out for UAsY [52], UPTe [53], U_2N_2Z [25] and UX_2, UOY, UNY (Y = Se, Te) or USnTe [22] compounds. All these studies have shown that the $\chi^{-1}(T)$ functions are strongly curvilinear and in many cases they may be described with the analytical equation:

$$\chi^{-1} = (A/T + B)^{-1} \pm \lambda \tag{1}$$

where the first term in brackets corresponds to $\chi_0(T)$ in the absence of an exchange interaction, and λ is a molecular field constant. Hence, the paramagnetic Curie temperature θ_p, may be defined as

$$\lim_{T \to \theta_p} \chi^{-1}(T) = 0, \qquad \theta_p = \frac{A}{1/\lambda - B} \tag{2}$$

The magnitudes of the constants A, B and λ obtained by the least-squares method, together with the values of θ_p, are given in ref. 22 for some compounds chosen from the above series.

TABLE III. Parameters Determined from the Two-level CF Model Fit to the Experimental Susceptibility Data

Compound	μ_o (μ_B)	Parameters of eqn. (4)			
	($a = \mu_o{}^2/4$)	b	c	d[K]	λ
UOS	2.0	0.0076	0.0064	244	+7
UOSe	2.2	0.0036	0.0027	480	0
UOTe	2.0	0.0052	0.0044	430	−12
USb_2	1.9	0.0081	0.0065	230	−79
USnTe	1.75	0.0288	0.0281	90	−50

The crystal-field potential of the tetragonal symmetry, relevant to C_{4v} and D_{4h} point groups has been described in detail in ref. 25 as well as the semi-quantitative method of analysing the CF-level scheme in the tetragonal compounds. There, it was shown that a Γ_{5t} doublet might be expected to be the ground-state CF level in many uranium or neptunium tetragonal compounds (with the above point symmetry) with these atoms in the 4+ and 3+ valent state (*i.e.* with $5f^2$ electron configuration), respectively.

The wavefunction of the doublet Γ_{5t} takes the form:

$$|\Gamma_{5t}\rangle = \cos\alpha|\pm 3\rangle \pm \sin\alpha|\pm 1\rangle \tag{3}$$

It has a strong uniaxial character that leads to strong anisotropic behaviour of the magnetic susceptibility, since the susceptibility component perpendicular to the c-axis, $\chi_\perp$, is zero. Such a situation implies that the paramagnetic moment μ_p and the ordered one μ_o should have the same magnitude.

Analysis of the CF behaviour in the above scheme, performed for the UOY and UX_2 types of compounds [22], showed that $\mu_{eff} \geqslant \mu_o$. This probably results in the presence of a singlet CF level, not far from the ground state doublet in energy, in accordance with the CF-splitting diagram presented in ref. 25. Previously [22], we proved it for the case of UOSe, but now we have treated other uranium compounds in this way. We have used here the two-level Van Vleck relation:

$$\chi(T) = \frac{a/T + b - c\exp(-d/T)}{2 + \exp(-d/T)} \tag{4}$$

with the assumption of a ground doublet and a singlet as the first excited level. The results of this analysis for several compounds of interest are given in Table III.

Figure 10 demonstrates such a fitting to UOS and compares the results of *ab initio* calculations made for this compound by Amoretti *et al.* [54]. The latter calculations are in good agreement with the Schottky effect observed in UOS and UOSe [54]. A similar situation like that mentioned above also takes place for the remaining UOY-type compounds, despite the fact that they are the most suited to such an analysis (predominant ionic chemical bonding, available Schottky effect results and the molecular

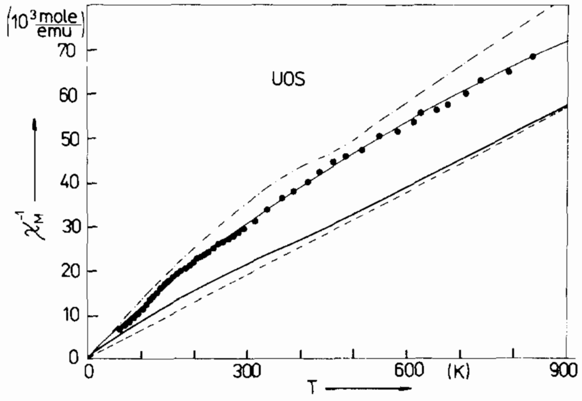

Fig. 10. The temperature dependence of the inverse magnetic susceptibility for UOS. The solid line, drawn through the experimental points, is the fitting curve to eqn. (4). The weak solid is drawn on the basis of the *ab initio* determined crystal-field parameters, given in ref. 54. The dot-dashed line represents the experimental data of ref. 33.

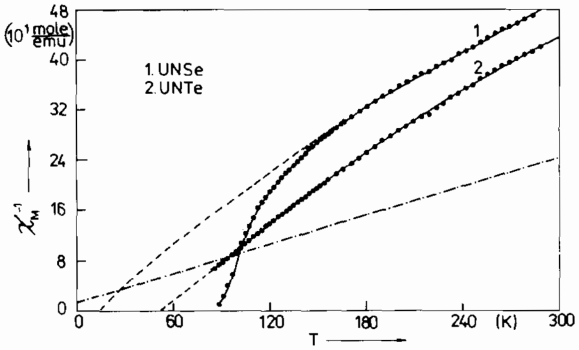

Fig. 11. The reciprocal magnetic susceptibility as a function of temperature for the polycrystalline samples of UNSe and UNTe. The dot–dashed line is drawn on the basis of the *ab initio* determined crystal-field parameters given in ref. 8. No distinct difference was found between such calculated curves for UNSe and UNTe CF parameters.

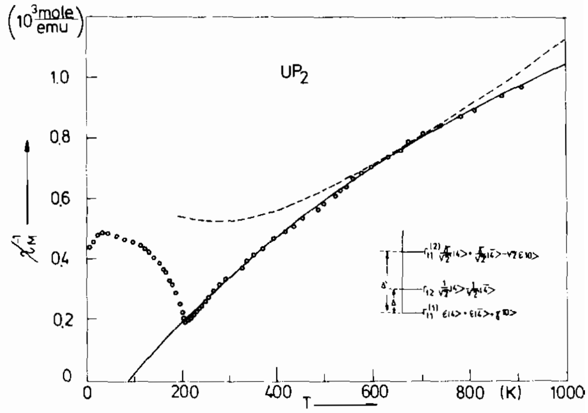

Fig. 12. The temperature dependence of the reverse magnetic susceptibility of polycrystalline UP_2, compared to the calculated dependence (dashed line), obtained on the basis of the CF-splitting scheme, also given. The values of parameters were taken from ref. 55. The solid line is the least-squares fitting to eqn. (1) with $A = 0.486$, $B = 3.32 \times 10^{-4}$ and $\lambda = -174$.

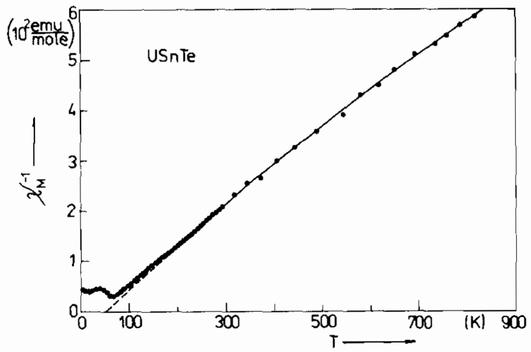

Fig. 13. The temperature dependence of the inverse magnetic susceptibility of polycrystalline USnTe. The solid line is the least-squares fitting to eqn. (4).

field parameter λ close to 0). Also, the recent results of CF calculations by Amoretti *et al.* [8] are compared in Fig. 11 with the low-temperature reciprocal susceptibilities obtained for UNSe and UNTe. In these calculations, which are in good agreement with the specific heat and neutron diffraction ones [8], a singlet Γ_{4t} and a doublet Γ_{5t} as the ground and excited states, respectively, were assumed for the reason given below.

The approximation with the two-level CF scheme in eqn. (4), also applied to the UX_2 (X = P, As and Sb) compounds, gave reasonable *b*, *c* and *d* parameters (*a* is always assumed from the value of the ordered moment) only for USb_2, as shown in Table III. However, for UP_2 and UAs_2, eqn. (4) did not yield a satisfactory solution. Also the CF problem for these compounds was the subject of a phenomenological approach, in which a simple two-parameter CF model, based on the available data of ordered moment μ_0, ordering temperature T_N and magnetic entropy S_M, was applied [55]. The low values of the measured magnetic entropy, determined in specific heat measurements on the UX_2-type compounds [56] were the basic point to assume that the only singlets $\Gamma_{1t}^{(1)}$, Γ_{2t} and $\Gamma_{1t}^{(2)}$, mutually connected by the molecular field along the easy *z*-axis (*c*-axis), are needed to describe the system. This CF scheme is given in Fig. 12 with the composition of states. Thus, the required parameters are only the energy splitting, Δ, between $\Gamma_{1t}^{(1)}$ and Γ_{2t} and the coefficient, ε, of the ground state. The energy splitting Δ′ (Fig. 12) could be found from its relation to the remaining two parameters. In accordance to the authors' statement [55], the above assumption becomes questionable on going from UP_2 to USb_2. In Fig. 12 we have also plotted the calculated susceptibility as $\chi_{calc}^{-1}(T) + \lambda$ (λ is given in ref. 55), based on the above model for UP_2, and compared the obtained curve with that found experimentally. As could be expected, a set of singlets would yield a concave instead of a convex $\chi_{calc}^{-1}(T)$ curve.

Of the UXY ternary compounds we present in Fig. 13 the high-temperature χ results obtained for USnTe. We have obtained a reasonable fitting of eqn. (4) to the experimental run of the χ^{-1} *versus* *T* curve and the parameters of this fitting are listed in Table III. It is interesting to note that an interpretation of the UAsY-type compounds, based on the two CF lowest-energy levels and molecular field approach has been given by Markowski [57].

Finally, we present the method of CF calculation applied by Amoretti *et al.* [58] to $NpAs_2$ with the $J = 9/2$ ground multiplet. As a starting point a CF wavefunction was taken of the doublet as a ground state already known from the best fit of the Np^{4+} magnetic form factor [39]. This approach allowed Amoretti *et al.* to reduce greatly the possible sets of CF parameters and deduce a suitable energy-level scheme for $NpAs_2$. The obtained results are somewhat different from those proposed previously, also for this compound, but based on an electrostatic 'layer' model [59]. In this model the most important CF interactions are within the layers of the ionic bond character, *i.e.* in the M–Y–Y–M ones, while the extra anionic charge ($\Delta \neq 0$) is uniformly distributed in the covalent X-planes. This means that the basal planes can be considered as electrostatic screens for the CF interactions. In contrast to the above assumptions, in the UNY type of compounds the interplanar spacings and the distances within the planes would rather suggest that the sandwich composition for these compounds should be inverted, *i.e.* Y–M–X–M–Y, which in consequence leads to a singlet ground state level, Γ_{4t}, separated by about 40 K from the excited doublet state Γ_{5t} [8].

In the future much more effort should be directed to a better understanding of this large (but not so complex in magnetic behaviour) family of compounds.

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