

1 Magnetic and related properties of pnictides and chalcogenides

(Chap. 1.1 see subvol. 27A, chap. 1.2 see subvol. 27B1, 27B2, 27B3, 27B4, 27B5)

1.3 Pnictides and chalcogenides based on actinides

(Chap. 1.3.1 see subvol. 27B6, chap. 1.3.3 see subvol. 27B8)

1.3.2 Binary non-equiatomic pnictides and chalcogenides

1.3.2.1 Introduction

1.3.2.1.1 General remarks

Binary compounds $An_x(X,Y)_y$ of actinides (An) with the Vth group ($X = N, P, As, Sb, Bi$) and VIth group ($Y = S, Se, Te$) elements of the Periodic Table form a large family of phases with different crystal and magnetic structures and a variety of physical properties. The previous edition of the Landolt-Börnstein Tables (LB III/12c from 1982) devoted to actinide pnictides (section 6.4 by R.R.Arons) and chalcogenides (section 6.5 by H.Lütgemeier) presented only a small number of such phases. No ample monograph on actinide binaries has been edited so far. Some limited information on their chemical and physical data is available in the chapters of a few volumes of the Gmelin Handbook of Inorganic Chemistry [G1-G5], or in the series of seven volumes of the Handbook on the Physics and Chemistry of the Actinides, edited by Freeman F.J., Lander G.H. and Keller C. In the latter editions especially the chapters on the bulk properties by Damian D. et al. [86DDT] and Fournier J.M. and Troć R. [85FT] may be recommended to the reader. Some valuable information on the subject may also be found in the chapter by Dell R.M. published in the series of the Pergamon Text Books in Inorganic Chemistry [75D].

The present work successively describes the magnetic and related properties of the binary actinide pnictides (i) and chalcogenides (ii) with the following compositions:

- i) An_4X_3 , An_5X_4 , An_5X_3 , An_3X_4 , U_2N_{3+x} and AnX_2 ,
- ii) An_3Y_4 , An_2Y_3 , An_3Y_5 , An_7Y_{12} , AnY_2 , An_2Y_5 , AnY_3 and UTe_5 .

At the end of the compilation a few compounds with compositions different from those given above are presented. Actinide monopnictides AnX and monochalcogenides AnY have been compiled separately and will be published in LBIII/27 subvolumes B6 α and β , respectively.

1.3.2.1.2 Synthesis of binary phases and their crystallochemistry

Polycrystalline samples

The existing phases being identified up to date among non-equiatomic binary actinide pnictides and chalcogenides are presented in Table 1 and 2, respectively.

Table 1. Binary actinide pnictides with a stoichiometry different from 1:1.

Composition	Element An					
	Th	Pa	U	Np	Pu	Am
AnX ₂			UN _{2-x}			
	α -ThP ₂	PaP ₂	α, β -UP ₂			
	α, β -ThAs ₂	PaAs ₂	UAs ₂	NpAs ₂		
	ThSb ₂	PaSb ₂	USb ₂	NpSb ₂	PuSb ₂	AmSb ₂
	ThBi ₂		UBi ₂			
An ₂ X ₃			α -U ₂ N _{3+x}			
			β -U ₂ N ₃			
An ₃ X ₄	α, β -Th ₃ N ₄					
	Th ₃ P ₄	Pa ₃ P ₄	U ₃ P ₄	Np ₃ P ₄		
	Th ₃ As ₄	Pa ₃ As ₄	U ₃ As ₄	Np ₃ As ₄		
	Th ₃ Sb ₄	Pa ₃ Sb ₄	U ₃ Sb ₄	Np ₃ Sb ₄		
	Th ₃ Bi ₄		U ₃ Bi ₄			
An ₄ X ₃					Pu ₄ Sb ₃	Am ₄ Sb ₃
An ₅ X ₃	Th ₅ Bi ₃					
An ₅ X ₄			U ₅ Sb ₄			

Table 2. Binary actinide chalcogenides with a stoichiometry different from 1:1.

Composition	Element An								
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
AnY ₃			US ₃ USe ₃	NpS ₃ NpSe ₃					
	ThTe ₃		α,β-UTe ₃	NpTe ₃	PuTe ₃	AmTe ₃	CmTe ₃	BkTe ₃	CfTe ₃
An ₂ Y ₅	Th ₂ S ₅		U ₂ S ₅	Np ₂ S ₅					
	Th ₂ Se ₅		U ₂ Se ₅ (?)	Np ₂ Se ₅					
AnY ₂			α,β,γ- US ₂	β-NpS _{2-x}	PuS _{2-x}	AmS _{2-x}	CmS _{2-x}	BkS _{2-x}	CfS _{2-x}
	β-ThS ₂	PaS ₂	α,β,γ- US ₂	β-NpS _{2-x}	PuS _{2-x}	AmS _{2-x}	CmS _{2-x}	BkS _{2-x}	CfS _{2-x}
	ThSe ₂	γ-PaSe ₂	α,β,γ- USe ₂	NpSe _{2-x}	PuSe _{2-x}	AmSe _{2-x}	CmSe _{2-x}	BkSe _{2-x}	CfSe _{2-x}
	ThTe ₂		UTe ₂	NpTe _{2-x}	PuTe _{2-x}	AmTe _{2-x}	CmTe _{2-x}	BkTe _{2-x}	CfTe _{2-x}
An ₃ Y ₅			U ₃ S ₅ U ₃ Se ₅ U ₃ Te ₅	Np ₃ S ₅ Np ₃ Se ₅					
An ₂ Y ₃				α,β,γ,η- Np ₂ S ₃	α,β,γ,η- Pu ₂ S ₃	α,β,γ,η- Am ₂ S ₃	α,γ,η- Cm ₂ S ₃	α,γ- Bk ₂ S ₃	γ-Cf ₂ S ₃
	η-Th ₂ S ₃		η-U ₂ S ₃	γ,η- Np ₂ S ₃	γ,η- Pu ₂ S ₃	γ,η- Am ₂ S ₃	γ,η- Cm ₂ S ₃	γ,η- Bk ₂ S ₃	γ-Cf ₂ S ₃
	η-Th ₂ Se ₃		η-U ₂ Se ₃	γ,η- Np ₂ Se ₃	γ,η- Pu ₂ Se ₃	γ,η- Am ₂ Se ₃	γ,η- Cm ₂ Se ₃	γ,η- Bk ₂ Se ₃	γ-Cf ₂ Se ₃
	Th ₂ Te ₃		γ,η- U ₂ Te ₃	γ,η- Np ₂ Te ₃	γ,η- Pu ₂ Te ₃	γ,η- Am ₂ Te ₃	γ,η- Cm ₂ Te ₃	ε-Bk ₂ Te ₃	
An ₃ Y ₄				Np ₃ S ₄	Pu ₃ S ₄	Am ₃ S ₄		Bk ₃ Se ₄	
			U ₃ Se ₄	Np ₃ Se ₄	Pu ₃ Se ₄	Am ₃ Se ₄			
			U ₃ Te ₄	Np ₃ Te ₄	Pu ₃ Te ₄	Am ₃ Te ₄	Cm ₃ Te ₄		
An ₇ Y ₁₂	Th ₇ S ₁₂								
	Th ₇ Se ₁₂		U ₇ Se ₁₂ U ₇ Te ₁₂						
AnY ₅			UTe ₅						

Actinide nitrides higher than monocompounds AnN are prepared by reacting thorium or uranium metal, being in the form of fine powders, with nitrogen at temperatures 500...1000°C. The highest nitrides obtained in this manner for thorium and uranium are $ThN_{1.33}$ and $UN_{1.75}$, respectively. Whereas the former nitride is strictly stoichiometric with the composition of Th_3N_4 , the latter one exists in a wide range of compositions as U_2N_{3+x} ($0.1 < x < 0.5$). Moreover, it was proved [64TT] to be possible obtaining even a higher composition of $UN_{1.86}$ yet using ammonia instead of nitrogen. In turn, the earlier reported chemical composition of UN_2 was shown not to form even under high pressure [64TT]. These high-content nitrides decompose to the respective mononitrides while heated in vacuum at temperatures above 1000°C. For transuranium elements only the mononitrides exist. These phases, together with ThN and UN , are the subject of consideration in LBIII/27B6a.

All binaries of high metalloid/actinide ratio with phosphorus, arsenic, antimony and bismuth are easily prepared by reacting the actinide hydride or directly actinide metal in the form of powder or thin turnings mixed together with the appropriate amount of the non-metal elements. Such a reaction is carried out in quartz tubes in which substrates are sealed under vacuum and heated at moderate temperatures of 400...950°C for several days. Sometimes the so pre-reacted product had to be crushed under neutral atmosphere of argon, pelletised, placed again in evacuated quartz tubes and annealed at the required temperature for a week or longer.

In the Faraday method of obtaining metalloid-rich actinide pnictides and chalcogenides, the reaction takes place between a finely divided metal and pnictogen or chalcogen vapour. This is possible by heating an evacuated quartz tube loaded with actinide metal and placed separately e.g. from sulphur, selenium or tellurium pieces. In some elder works, chalcogenides of various stoichiometries were typically synthesized by heating of uranium hydride with H_2S or H_2Se .

Preparation of binaries with low metalloid/actinide ratio turned out to be a more difficult task and several different methods are used. Some binary chalcogenides can be obtained by thermal dissociation of the richer in metalloid compounds, carried out in a vacuum-sealed tube with one end kept outside the furnace, where an excess of the non-metal from the sample is deposited. A more precise way for controlling the stoichiometry is using a vacuum thermobalance in the process [86DDT]. Sometimes actinide-rich binaries can be synthesized by direct reaction of the constituting elements, as described above.

The preparation scale depends mainly upon the availability or scarcity of a given actinide element. For example this is the gram range for Np and Pu , multimilligram range for Am and ^{244}Cm and only microgram range for ^{248}Cm , ^{249}Bk and ^{249}Cf [79DHP]. Scarcity, toxicity and radioactivity of transuranium elements limit not only the synthesis of their compounds but also to a large degree any researches of their physical properties. Apart from large costs, only few laboratories in the world are allowed to handle with transuranium compounds, having special facilities for this purpose. Normally the isotopes with the longest half-life, as e.g. ^{243}Am or ^{248}Cm , are preferred in the syntheses of their compounds [82H]. It is mainly because the properties of compounds containing shorter-lived isotopes are substantially damage-deformed by radiation and contaminated by the so-called daughter elements.

A summary concerned syntheses of various binary chalcogenides of actinide elements heavier than uranium is given e.g. in [82H].

Single crystals

A. Binary pnictides

Single crystals of thorium and uranium pnictides have been first synthesized at the Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences in Wrocław (Poland) [68H] using chemical vapour transport method (CVT; 1). This technique is based on a chemical transport reaction carried out in an evacuated sealed quartz tube, which contains except for a powder of a given compound also a transporting carrier agent as iodine, bromine or other halogen. The crystals grow on walls of the tube due to a temperature gradient being of about 100°C (see [84SV] and [85H]).

Modification of the above CVT method is the Van Arkel method (2) in which crystals form on an induction heated tungsten filament [77HM,79CSM]. Applying this technique Calestani et al. [79CSM] have grown single crystals of a series of the binary thorium and uranium pnictides but also the compounds containing protactinium such as $PaAs_2$, Pa_3As_4 and Pa_3Sb_4 .

If a binary uranium compound is highly soluble in liquid antimony, bismuth or other metallic solvent the method of high-temperature crystallization from solution (3) may be used [85H]. In this method uranium metal and the second component Sb or Bi , both in the proportion determined from the respective liquidus-solidus curve

(LSC) of the phase diagram, are placed in a corundum crucible and then sealed in a quartz tube under argon atmosphere. The tube is heated about 25°C above LSC and subsequently cooled down to the LSC temperature. After cooling down ingots containing single crystals and an excess of the solvent are obtained. The latter is removed either by sublimation or by dissolving in mercury (Sb or Bi). A somewhat different method (4) has been used to grow single crystals of U_3Bi_4 [97HWG]. In this case the crystals were obtained by evaporation of bismuth from a U-Bi liquid solution kept at constant temperature (1080°C) to provide low evaporation rate by a long time. The synthesis was carried out in an induction furnace using a graphite crucible of a special shape. Only limited experiences have been obtained so far with heavier actinide pnictides. Particularly worth mentioning are single crystals of Np_3As_4 [82WD] and NpAs_2 [81DD], which were successfully grown at the CEA Fontenay aux Roses (France).

A list of binary actinide pnictides obtained in single-crystalline form may be found in the chapter by Spirlet and Vogt [84SV]. Here, in order to demonstrate the applicability of different crystallization methods, Table 3 gathers a few examples of the obtained single crystals of uranium pnictides UX_2 and U_3X_4 .

Table 3. Crystallization methods used for preparing single crystals of binary uranium pnictides UX_2 and U_3X_4 . The numbers correspond to the methods described in the text.

UP_2	UAs_2	USb_2	UBi_2
(1)	(1)	(1,2,3)	(3)
U_3P_4	U_3As_4	U_3Sb_4	U_3Bi_4
(1,2)	(1,2)	(2)	(3, 4)

B. Binary chalcogenides

Binary chalcogenide single crystals such as US_2 , USe_2 , USE_3 , UTe_2 and UTe_3 were first obtained by Slovyanskikh et al. [66SEYK] by the chemical vapour transport method using bromine as a transporting agent. The growth mechanism in relation to various conditions of the synthesis has been systematically studied in [70SSE].

For description of other techniques of growing single crystals of binary actinide chalcogenides the interested reader is referred to [84SV] and the original papers.

1.3.2.1.3 Crystal structures and valence states

A. Binary pnictides

The phases known so far are gathered in Table 1. There is just one compound with the lowest X/An ratio, namely U_3Sb_4 , that crystallizes with a hexagonal structure of the Ti_5Ga_4 type (s.g. $\text{P6}_3\text{mcm}$) [94PRBD]. The atomic ratio $\text{X/An} < 1$ is found also for Pu_4Sb_3 and Am_4Sb_3 , which form in the cubic anti- Th_3P_4 -type structure (s.g. $\text{I}\bar{4}3\text{d}$). Both antimonides exhibit the properties similar to their isostructural rare-earth-based counterparts, and therefore are thought to contain trivalent actinide ions.

The thorium nitride with the 3:4 stoichiometry is completely unique and exists in two polymorphic modifications α and β having hexagonal and monoclinic symmetry, respectively. The other known An_3X_4 compounds with phosphorus, arsenic and antimony being formed by thorium, protactinium, uranium and neptunium (except for antimonide in the latter case), as well as the bismuthide U_3Bi_4 , all adopt cubic unit cells of the Th_3P_4 type (s.g. $\text{I}\bar{4}3\text{d}$) with $Z = 4$. By analogy to the Th_3X_4 phases the actinide atoms in the isomorphic 3:4 pnictides of Pa, U and Np are considered to be tetravalent. Compressibility and crystal structures of Th_3P_4 and uranium pnictides U_3X_4 , where $\text{X} = \text{P} \dots \text{Sb}$, were investigated at room temperature under hydrostatic pressures up to 50 GPa [90GSBL]. In this pressure range transitions to lower symmetry crystal structure were not observed.

The 2:3 stoichiometry is represented only by uranium nitrides that crystallize in a cubic α -form of the Mn_2O_3 type (s.g. $\text{Ia}\bar{3}$) or a trigonal β -form of the La_2O_3 type (s.g. $\text{P}\bar{3}\text{m1}$), depending on the exact composition [62TTL].

The cubic uranium nitrides exist in a wide composition range up to $\text{UN}_{1.75}$. The nitrides richer in nitrogen content, up to $\text{UN}_{1.86}$, have also a cubic unit cell but probably of the CaF_2 type. Addition of excess nitrogen atoms results in a contraction of the cubic lattice parameters. Such a wide range in the nitrogen content is possible only if uranium ions in these phases exist simultaneously in the 4+ and 5+ or likely 6+ oxidation states, depending on the nitrogen content (for discussion see [64TT]). In contrast to the α -form, the hexagonal β - U_2N_3 can be obtained only at high temperatures, far above 1000°C , and has probably a substoichiometric composition $\text{UN}_{1.45}$ [68LM].

The stoichiometry most widely occurred among the binary actinide pnictides is AnX_2 , as represented e.g. in the case of antimony by actinide elements from thorium to americium. On going from U to Am one observes a decreasing tendency to form such binaries first with phosphorus and then with arsenic. The dipnictides crystallize in two different crystal structures: i) a tetragonal structure of the anti- Cu_2Sb type (s.g. P4/nmm) and ii) an orthorhombic structure of the LaSb_2 type (s.g. Pnma). In general, the oxidation state of actinide atoms in tetragonal AnX_2 compounds is regarded as tetravalent. Interestingly, also PaAs_2 and PaSb_2 crystallize in the same structure [78HDHD], despite the fact that their single 5f electron is completely delocalised here, as deduced from the observation of the temperature independent paramagnetism [79CSM, 79HDC]. For UP_2 , the anti- Cu_2Sb -type structure was found only above room temperature. As proved by means of single crystal X-ray investigation [71PL], at lower temperatures the volume of the unit cell increases ($a = a_0\sqrt{2}$, $c = 2c_0$, where a_0 and c_0 are the lattice parameters of the anti- Cu_2Sb cell) due to small displacements of the uranium atoms, and in the new structure (s.g. I4mm) there are as many as three different positions for the uranium atoms. X-ray powder diffraction performed for UP_2 , UAs_2 and a mixed compound UAsS under pressure up to 60 GPa have revealed phase transformations to orthorhombic structures similar to that of PbCl_2 , occurring at 22, 15 and 46 GPa, respectively [90GSBD].

For the transuranium dipnictides the tetragonal crystal structure has been evidenced for NpAs_2 on the basis of single crystal neutron diffraction data [82BBDF]. All the transuranium diantimonides NpSb_2 , PuSb_2 and AmSb_2 crystallize in the orthorhombic LaSb_2 unit cells, alike the light rare-earth diantimonides (from La to Sm). The characteristic feature of this structure is the existence of short Sb-Sb bonds (e.g. 0.274 nm in NpSb_2), which are even shorter than those in elemental antimony (0.291 nm). Also the An-An distances in these compounds (ca. 0.42 nm) are considerably shorter than for example those in actinide ditellurides (0.43...0.44 nm). These differences seem to manifest a partial delocalisation of the 5f electrons in AnSb_2 that possibly participate in the bonding due to strong 5f-5f electron hybridisation. Such a hypothesis is strongly supported by the physical properties of the above diantimonides (see below).

B. Binary chalcogenides

The binary actinide chalcogenides identified so far are displayed in Table 2. In general, these phases form a few uniform groups with the compositions varying from An_3Y_4 to AnY_3 . In general, binaries with a high chalcogen content crystallize with low-dimensional structure frameworks with van der Waals gaps between chalcogen atoms sheets [85N1]. In the case of uranium tellurides two compositions especially rich in metalloid content have been reported, namely tetragonal $\text{UTe}_{3.38}$ [71BBW] and orthorhombic UTe_5 (s.g. $\text{Pn2}_1\text{a}$) [92BNSM].

The uranium and neptunium trisulphides and triselenides, as well ThTe_3 , crystallize with a monoclinic structure of the ZrSe_3 type (s.g. $\text{P2}_1/\text{m}$). From the fact that the triselenides of Ti, Zr, Hf and Th adopt the same structure, it was inferred that the actinide ions in these compounds are tetravalent. This requires the presentation of their general chemical formula as $\text{An}^{4+}(\text{Y-Y})^{2-}\text{Y}^{2-}$, which implies an assumption on the formation of polyanions $(\text{Y-Y})^{2-}$ [86DDT]. In turn, all the transuranium tritellurides from NpTe_3 to CfTe_3 crystallize with an orthorhombic unit cell of the NdTe_3 type (s.g. Cmcm). In this case, the presence of An^{3+} cations is postulated. For UTe_3 two modifications α and β are known with the monoclinic and orthorhombic crystal structures of the above types, respectively.

The composition An_2Y_5 was found for sulphides and selenides of thorium, uranium and neptunium. All these phases crystallize with a tetragonal structure of the Th_2S_5 type [82NP]. As in the case of the AnY_3 compounds, the calculation of the interatomic distances points to the presence of short Y-Y bonds suggesting the chemical formula containing $(\text{Y-Y})^{2-}$ polyanions and thus An^{4+} cations: $(\text{An}^{4+})_2(\text{Y-Y})^{2-}(\text{Y}^{2-})_3$.

Like the trichalcogenides, the actinide dichalcogenides AnY_2 are represented from thorium to californium. Moreover, the thorium and uranium sulphides and selenides occur in three polymorphic forms α , β and γ depending on the deficiency in the Y atoms. The tetragonal α -phase of the uranium disulphide has a composition

range from $\text{US}_{1.80}$ to $\text{US}_{1.93}$, while the composition of the isotypic diselenide is $\text{USE}_{1.80}$ to $\text{USE}_{2.0}$. The β -phases of the uranium sulphide and selenide have orthorhombic PbCl_2 type structure (s.g. Pnma), in which crystallize also ThS_2 , ThSe_2 , PaS_2 and NpS_2 . The γ -type polymorphic modifications of US_2 and USE_2 adopt a hexagonal structure of the anti- Fe_2P type (s.g. $\text{P}\bar{6}2\text{m}$), found also for PaSe_2 . In turn, the transuranium element ($\text{An} = \text{Pu} \dots \text{Cf}$) disulphides and diselenides are represented in the literature as having a pseudotetragonal anti- Cu_2Sb -type crystal structure (s.g. P4/nmm) [86DDT]. In this unit cell there are two types of chalcogen atoms, and thus the ionic formula reads: $(\text{An}^{3+})_2(\text{Y}-\text{Y})^{2-}(\text{Y}^{2-})_2$. These transuranium element dichalcogenides also exhibit some deficiency in Y atoms, and so their compositions are given in Table 2 as AnY_{2-x} . In a few cases the stoichiometric compounds have different crystal structures. For example, $\text{PuS}_{1.9}$ crystallizes in the anti- Cu_2Sb -type cell, while the stoichiometric disulphide, PuS_2 , has a monoclinic symmetry of the CeS_2 type that is considered as a superstructure of the tetragonal unit cell [68MP]. The thorium and uranium ditellurides are stoichiometric and crystallize with two different structures of hexagonal and orthorhombic (s.g. Immm) symmetry [70KJ], respectively. In turn, the transuranium element ditellurides occur in the range of composition $\text{AnTe}_2 - \text{AnTe}_{2-x}$, but without any change in the type of their crystal structure (tetragonal, anti- Cu_2Sb type). On the basis of refinements of the single-crystalline data collected for $\text{AmTe}_{1.7}$ [79BDH], tellurium vacancies were found to be randomly distributed within the basal plane of the unit cell. It is interesting to note that the presence of tellurium vacancies brings about an increase in the c/a ratio, which becomes larger than 2. The transuranium elements in the ditellurides are assumed to be trivalent, as corroborated by their unit cell volumes being very similar to those found for the respective rare-earth-based counterparts.

The composition An_3Y_5 is adapted only by chalcogenides of uranium and neptunium. All of them crystallize in an orthorhombic crystal structure of the U_3S_5 type (s.g. Pnma). Detailed structural data have been established for U_3S_5 and U_3Se_5 in the course of diffraction studies of their single crystals [72MBW]. In the refined unit cell there are two metal sites 4(c) and 8(d) having different coordinations (7 and 8), which are occupied by actinide atoms with different valences: An^{3+} and An^{4+} . This feature was confirmed by Mössbauer effect measurements of Np_3S_5 and Np_3Se_5 [81TJPD], and furthermore it is firmly corroborated by the formation compounds like ThPu_2S_5 .

Table 4. Stability ranges of different forms of transuranium sesquichalcogenides.

	Element An					
	Np	Pu	Am	Cm	Bk	Cf
An_2S_3	α					
	β					
	γ					
	η					
An_2Se_3	γ					
	η					
An_2Te_3	γ					
	η					
	ϵ					

The actinide sesquichalcogenides An_2Y_3 crystallize with several different crystal structures denoted as α , β , γ , η and ϵ . Their stability is depicted in Table 4 in the form of double-end arrows. The α -phases possess orthorhombic symmetry of the La_2S_3 type (s.g. Pnma) with two metal sites of the coordination numbers 7 and 8, respectively. At higher temperature they transform into the γ -form. The latter modification is a body-centered cubic one of the Th_3P_4 type unit cell (s.g. $\text{I}\bar{4}3\text{d}$) with the coordination number 8. The γ -phases exist over a range of composition from An_2Y_3 ($\text{Y}/\text{An} = 1.5$) to An_3Y_4 ($\text{Y}/\text{An} = 1.33$). The η -sesquichalcogenides crystallize with an orthorhombic structure of the U_2S_3 (or Sb_2S_3) type (s.g. Pbnm), which exhibits two different crystalline sites of metal atoms, both having a coordination number of 7. At higher temperatures the η -phases transform into the cubic γ -phases. Finally, the ϵ -form of An_2Y_3 has only been found for Bk_2Te_3 . It is orthorhombic of the Sc_2S_3

type, with the coordination number 6. In all the sesquichalcogenides the valency of actinide elements is thought to be +3. On the one hand there exist close structural similarities between transuranium and rare-earth elements in forming such phases, but on the other hand one observes distinct differences in the case of the sesquichalcogenides of thorium and uranium. The latter compounds crystallize exclusively in the η -form, with the only exception being Th_2Te_3 that has a hexagonal structure.

For thorium and uranium the formation of phases An_7Y_{12} has been reported [72BB], which show a hexagonal symmetry of their own type (s.g. $\text{P6}_3\text{m}$).

For the purpose of prediction of valence state in binary neptunium chalcogenides the Mössbauer isomer shift (IS) related to NpAl_2 has been successfully used, as shown in Fig. 1i. For example for the neptunium 3:5 polychalcogenides the corresponding isomer shifts are 29.0(5) mm/s for the Np^{3+} site and $-4.5(3)$ mm/s for the Np^{4+} site. In this figure there are marked two different ranges of IS corresponding to two different oxidation states III and IV of neptunium in various non-equiatomic binary chalcogenides. The observed spread in IS values assigned to a given charge state results from the difference in chemical bonding, mainly in the extent of covalency character. In general, one can conclude that Np in its chalcogenides shows an intermediate position within the actinide family, forming the compounds of uranium type (e.g. NpS_3), where it is tetravalent, as well as compounds of transuranium type (e.g. NpTe_{2-x}) where it is trivalent.

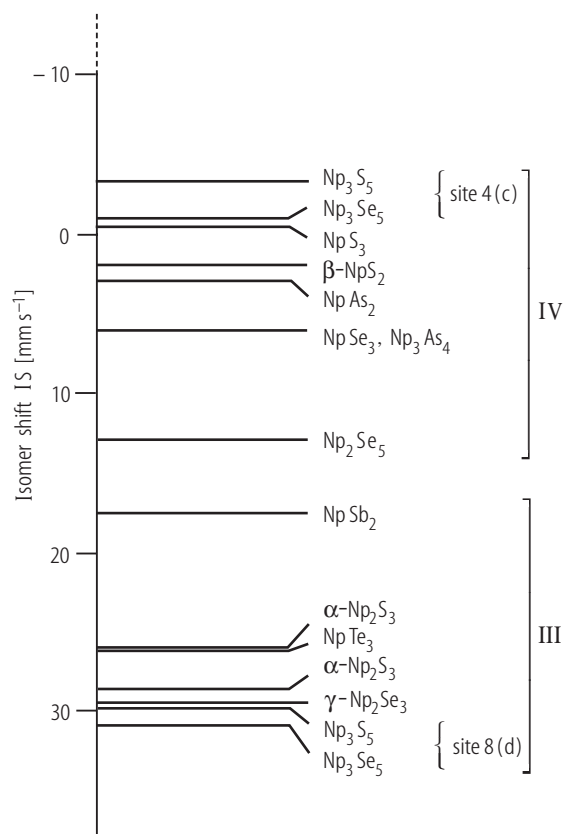


Fig. 1i. Isomer shifts for neptunium binary chalcogenides (modified after [84TJP]). The electron density decreases from top to bottom. For comparison the data for NpAs_2 , NpSb_2 and Np_3As_4 are also shown.

1.3.2.1.4 Physical properties

The main aim of this presentation is not to review thoroughly all the properties that have been determined by many authors for various binaries, but rather to emphasize some of the most important achievements in the studies of a few isostructural series, namely those with the stoichiometries 3:4, 1:2 and 1:3.

$An_3(X,Y)_4$ -type compounds

In the past, the 3:4 group of actinide pnictides and chalcogenides was intensively studied and many theoretical and experimental results have been gained, especially at first for U_3P_4 and U_3As_4 , and then for U_3Sb_4 and U_3Bi_4 . Except for bulk magnetic and electrical transport measurements, several other techniques have been applied, e.g. optical, X-ray photoemission, positron annihilation, de Haas-van Alphen and Shubnikov-de Haas spectroscopies, as well as various electronic band structure calculations. Nevertheless, in the following we shall concentrate mainly on the data on the bulk magnetic and transport properties.

The thorium-based phases Th_3N_4 , Th_3P_4 and Th_3As_4 are either weakly paramagnetic or diamagnetic. All these compounds are semiconductors with the activation energies of 1.4, 0.4 and 0.44 eV, respectively [81KTMN, 78HM]. In contrast, the antimonide Th_3Sb_4 exhibits a metallic conductivity. All the uranium-based pnictides U_3X_4 were found to be ferromagnetic in the low temperature region [80T]. The chalcogenides U_3Y_4 ($Y = Se, Te$) have more complicated and so far not well defined magnetic behaviour [72SMR].

Large interest in studying the magnetic properties of the An_3X_4 pnictides and the An_3Y_4 chalcogenides arises from their unique crystal structure in which the nearest atomic configuration around each An ion forms an octahedron of S_4 point symmetry. In this structure the elongated -4 axes of three such octahedrons are perpendicular to one another, yielding an unusual three-axial crystal field anisotropy. The magnetic behaviour of the 3:4 pnictides was generally described in terms of crystal field effect acting on fourvalent actinide ion. In the early work by Troć et al. [71TMS] on the $U_3(X,Y)_4$ compounds an average magnetic susceptibility in the paramagnetic region was successfully expressed by a simple model assuming a pseudodoublet ground state. Also for Np_3As_4 a proper explanation of the bulk magnetic behaviour and the Mössbauer spectroscopy data was given in the framework of a crystal field model with Np^{4+} ions [87ABFB].

The studies of single-crystalline samples of U_3P_4 and U_3As_4 have revealed both these pnictides to be extremely strongly anisotropic with a net magnetization along the [111] direction [69B]. Later on, single crystal neutron diffraction examinations indicated that the magnetic structures of these compounds have a three-axial character with the uranium magnetic moments tilted from the easy axis [111] by a small angle θ [81BRTH]. The values of this angle were subsequently a matter of intense debate from both experimental [99WGH] and theoretical [00KSK] point of view. Quite unexpectedly for the two other uranium pnictides, i.e. U_3Sb_4 and U_3Bi_4 , a (pseudo)collinear arrangement of the magnetic moments with the easy magnetization axis [100] and hard axes [111] and [110] was found by neutron diffraction [87HMOP, 96GWH].

While for U_3P_4 the magnetization along its hard direction [100] increases smoothly up to 50 T (the strongest field studied) [82GLLO], for U_3As_4 [76NS] and U_3Sb_4 [87HMOP, 89MHFV] first-order phase transitions induced by an applied magnetic field occur. The critical fields measured at 4.2 K are: $B_c = 21$ T (along [100]) and 4.9 T (along [111]) for the arsenide and $B_c = 17.6$ T (along [110]) for the antimonide. The renormalization group approach applied for U_3As_4 [81TSNM] has demonstrated the existence of a tricritical point below which the magnetization jump vanishes at a temperature close to $T_c/2$, in agreement with the experiments. From the temperature dependence of the magnetization jump in the [100] direction it was possible to derive for the arsenide the temperature variations of cubic anisotropy constants K_1 and K_2 [80BLOY, 81TSNM]. The magnetic anisotropy in the U_3X_4 compounds is exceptionally high. Certainly, it is related to the formation of very narrow Bloch walls with a thickness of about 2.4 Å [79GNM]. To explain such a large anisotropy some authors [82TYK, 83STNT] have attempted to apply the p-f mixing effect, in analogy to cerium-based mononpnictides. Moreover, it is worth noting that for U_3P_4 the spontaneous magnetostriction λ_s along the [111] direction is of the order of 10^{-3} (at 78 K) [71THBD], which can only be compared to the λ_s values determined for heavy rare-earth metals.

In order to explain the magnetic properties of the U_3X_4 compounds several theoretical approaches were made. Initially, the molecular field approximation and a modified free-electron model had been applied to calculate the ordering temperatures and the exchange interaction constants, as well as to establish the stability ranges of various magnetically ordered states [73AI]. A model taking into account the crystal field (D) and exchange (J) interactions was considered by Przystawa and Praveczi [72PP]. Then the latter model was

subsequently extended by Oleksy and Przystawa [87HMOP] by including a new type of the anisotropic exchange interactions (K) compatible with the overall cubic symmetry, in addition to a three-axial type of crystal field anisotropy and exchange interactions within the MFA approach. This improved model yielded an explanation of the ground state magnetic behaviour of the U_3X_4 compounds and their magnetic phase diagrams. It also provided a scheme of phase transitions in high magnetic fields and gave a description of spin excitations [90OP]. At $T = 0$ K as many as three possible spin structures were found, namely two non-collinear three-axial ferromagnetic structures: C-type with easy [111] axis and P-type with easy [110] axis, as well as one collinear L-type structure with easy [100] axis. Most recently, the magnetic structures of the 3:4 uranium pnictides and their thermodynamic behaviour were successfully interpreted in terms of a Heisenberg Hamiltonian, using a symmetry analysis and the Landau theory of phase transitions within the mean-field approach [97OP].

As an alternative to localized moment approaches described above, the itinerant electron model was proposed by Sandratskii and Kübler [95SK] within the local approximation to spin-density functional theory. In this model the relativistic spin-orbit coupling is the principal mechanism leading to the formation of non-collinear magnetic structures in the 3:4 compounds with the Th_3P_4 -type crystal structure. It is worth to note however that the angle of non-collinearity calculated in [95SK] is much smaller (1.43 deg) than that observed for U_3P_4 by polarized neutron diffraction scattering (13 deg) [81BRTH].

As it has already been mentioned, in contrast to the 3:4 phosphide and arsenide, U_3Sb_4 and U_3Bi_4 have collinear magnetic structures with a [100] easy axis. In these compounds there are present two different sublattices of uranium atoms with different values of the magnetic moment being in the ratio of 1.29 and 1.17 for U_3Sb_4 and U_3Bi_4 , respectively [96GWH]. The different values of the magnetic moments on different atomic sites result from a low local symmetry of the uranium ion environment. Such a magnetic structure was predicted theoretically by Oleksy [88O] in the framework of the $S = 1$ model and the mean field approximation, and confirmed by neutron diffraction measurements [87HMOP, 96GWH]. However, according to Knöpfle et al. [00KSK] the collinear magnetic structure is generally not possible to exist in the case of the S_4 symmetry and for this reason the latter authors put forward another solution for the spin arrangement in U_3Sb_4 and U_3Bi_4 , namely a (pseudo)collinear one.

The analysis of the magnetic susceptibility and spontaneous magnetization data of U_3P_4 allowed Troć and Aldred to derive the critical exponents [83TA]. It was found that the values of the exponents α , δ , and ν are close to those calculated for a three-dimensional Ising system but the exponent $\beta = 0.39$ is considerably different from the predicted value of 0.315. More recently a critical study made by Strydom et al. [93SDKT], based on the inelastic neutron scattering results, has yielded also for the critical exponent β a value being very close to the theoretical one.

The optical studies of U_3P_4 revealed that the p-electron valence band in this compound is shifted by 0.85 eV towards the Fermi level with respect to its position in Th_3P_4 . This effect results in closing the semiconducting gap in U_3P_4 and leads to semimetallic conductivity. The binding energy of the 5f-states in U_3P_4 was estimated to be 1.2 eV, which points to their well localized character. Spectacularly, Reim and Schoenes discovered in U_3P_4 a giant magneto-optical Kerr effect of about 6 deg [90RS], thus corroborating the conclusions on localised magnetism in this compound.

The first accurate electrical measurements on single crystals of U_3P_4 , U_3As_4 and U_3Sb_4 were done by Henkie et al. [71HB, 81HMK]. They revealed a semimetallic behaviour of all these pnictides with fairly high room-temperature resistivities. Another indication that the phosphide and the arsenide are compensated semimetals comes from the character of their low-temperature magnetoresistance that varies as a squared magnetic field in a wide angular region [01IWMA]. The temperature variations of the resistivity in the magnetically ordered state exhibit abnormal convex curvature, which may be attributed to a complex domain effect in polyaxial magnetic structures. Recently, the resistivity under high pressure was measured for U_3P_4 [02TTKA]. The $T_C(p)$ dependence reaches a quantum critical point (QCP) at about 5 GPa, yet no superconductivity has been observed, probably because of the lack of an inversion symmetry in the crystal structure of the Th_3P_4 type.

Measurements of the Hall effect and the thermoelectric power of U_3P_4 , U_3As_4 and U_3Sb_4 were also made by Henkie et al. [72H, 81HMK]. For all these pnictides the ordinary Hall coefficient is positive and several orders of magnitude lower than the anomalous Hall coefficient related to their magnetism. The thermopower of U_3P_4 is positive in the entire paramagnetic region studied up to 800 K, but for U_3As_4 it changes its sign from negative above 370 K to positive at lower temperatures. In the case of U_3Sb_4 there occur two sign inversions, with the Seebeck coefficient being positive only between 133 and 236 K. In each compound the thermoelectric power exhibits a maximum in its temperature dependence at the respective T_C .

The de Haas-van Alphen studies of the Fermi surface in U_3P_4 and U_3As_4 made by Henkie et al. [83HJAC] were the very first investigations of this type done for magnetically ordered actinide compounds. Later on Japanese authors [93IATS, 01IWMA] continued such measurements on U_3P_4 and showed more details of closed Fermi surfaces. The observed cyclotron effective masses are large, ranging from 5 to 70 m_0 , being thus consistent with the established enhanced values of the electronic specific coefficient. The experimental data were compared to the theoretically derived Fermi surfaces [99AHYP].

An(X,Y)₂-type compounds

1. Dipnictides

PaAs_2 and PaSb_2 display a temperature independent paramagnetism, which indicates the 5f-electron delocalisation and formation of Pa^{5+} ions [79H]. All the other dipnictides crystallizing with the anti- Cu_2Sb -type crystal structure order magnetically at low temperatures with high Néel temperatures and fairly large magnetic moments oriented along the c -direction. These features are indicative of localized f-electrons. The magnetic properties of UX_2 compounds were interpreted theoretically by Amoretti et al. [84ABM] by means of crystal field model with three lowest lying singlets (configuration $5f^2$) and molecular field approximation. Such an approach gives rise to the antiferromagnetic order induced by molecular field. Initially, three possible types of antiferromagnetic structures (AFI, AFII and AFIII) and one ferromagnetic (F) arrangement of the actinide moments in the tetragonal dipnictides were considered by Przystawa and Suski [67PS], in terms of the Smart's method with three integrals and the molecular field approximation. Then, the same authors discussed five different exchange integrals, what caused an increase in the number of possible antiferromagnetic structures up to seven. Among the UX_2 compounds the experimentally observed structures were AFI (UBi_2) and AFIII (UP_2 , UAs_2 and USb_2). For the bismuthide the magnetic unit cell is of the same size as the chemical one, whereas for the latter type structure the magnetic unit cell is doubled along the [001] direction with respect to the chemical cell.

The layered character of the crystal structure of UX_2 compounds, where the conductive uranium (001) planes are separated by the sequence of nonconductive X planes stacked along the [001] direction, gives rise to the two-dimensional Fermi surface. A proof of a distinct change of the Fermi surface in these systems, occurring at the onset of magnetic ordering, comes from the observation of a huge jump in the electrical resistivity measured with the current flowing along the [001] axis. The elongated magnetic unit cell brings about a flat magnetic Brillouin zone that is reduced by half the volume. The Fermi surfaces in UP_2 [01WAWs], UAs_2 [00WAWM] and USb_2 [00AWMS] were derived from the Shubnikov-de Haas and de Haas-van Alphen effects studies. They have a cylindrical form with nearly circular cross section, which manifests the two-dimensional character of the electrical conduction. Clearly, UP_2 , UAs_2 and USb_2 are compensated semimetals with equal number of electrons and holes. A good agreement was also obtained between the calculated total electronic specific heat coefficient and the experimental data. For example, for UP_2 the electronic specific heat coefficient calculated for all the observed branches of the Shubnikov-de Haas oscillations is 25 mJ/mol K^2 as compared to the experimental result of 27 mJ/mol K^2 . The largest cyclotron masses within the UX_2 series were observed for UP_2 . Hence, it has been concluded that some 5f electrons in this compound become itinerant contributing significantly to the conduction band. Moreover, it was also discussed that the 5f delocalisation is stronger within the (001) plane in which the magnetic moments are ferromagnetically coupled than along the [001] direction. In consequence, the magnetic behaviour of UP_2 is strongly anisotropic. A very similar situation occurs for the uranium diarsenide and diantimonide. In contrast, the Fermi surface in UBi_2 , derived from the de Haas-van Alphen data [00AWMS] is not flattened. It consists of a cylindrical hole sheet that is very close to the Brillouin zone boundary and a spherical electron sheet centred at Γ of the magnetic Brillouin zone.

Self-consistent calculations of the electronic band structures of USb_2 and UBi_2 in the paramagnetic and ordered states were done using a fully relativistic spin-polarised LAPW method in the LSD approximation (Yamagami H., unpublished). This theory could give a systematic explanation of the observed Fermi surfaces and the magnetic moments in both compounds, thus being in favour of an itinerant 5f-electron picture.

Most recently, hyperfine interactions in the antiferromagnetic states of the uranium dipnictides have been studied by means of ^{238}U -Mössbauer measurements [04TNNH]. The nuclear quadrupole interaction of ^{238}U is almost zero in UBi_2 , due to a mutual cancellation of the 5f-electron and lattice contributions, whereas the sign of this interaction in UP_2 , UAs_2 and USb_2 is negative. This distinct difference in the nuclear quadrupolar interactions, observed between UBi_2 and the other dipnictides, originates mainly from the 5f-quadrupole

contribution. This finding strongly indicates that the nuclear quadrupolar interactions in UX_2 phases are closely correlated with their magnetic structures.

In Fig.2i there are plotted against the interatomic U-U distance the magnetic ordering temperatures of three groups of uranium compounds, which crystallize with crystal structures being very related to one another. These are the UX_2 binaries (anti- Cu_2Sb type), the uranium oxychalcogenides UOY (PbFCl type) as well as the mixed uranium pnictides UXX' and pnictochalcogenides UXY (ZrSiS type). The magnetic and transport properties of these ternaries were presented in detail in LBIII/27B8. As seen from the figure, the dependence of T_N on D_{UU} follows for both the UX_2 and UXX' -type pnictides (except for $USbBi$) a smooth curve passing through a marked maximum for T_N of UAs_2 . It is worthwhile to recall that a similar dependence constructed for the U_3X_4 pnictides exhibits a maximum in T_C vs. D_{UU} also just for the uranium arsenide, i.e. for U_3As_4 . This finding clearly indicates an important role played by the ligands in the magnetic exchange interactions. Interestingly, all the remaining ferro- and antiferromagnetic ternaries displayed in this figure have the transition temperatures considerably lower than those of the UX_2 binaries and the UXX' ternaries, and show the magnetic ordering within nearly the same region of D_{UU} as in the dipnictides, i.e. between 0.375 and 0.450 nm. The pressure dependence of the Néel temperature was studied for UP_2 and USb_2 [91HWF]. Within the uncertainty limit the coefficients dT_N/dp are equal to the pressure coefficients of the Curie temperature of the corresponding U_3X_4 pnictides. The variations of the ordering temperatures with pressure are related to their dependencies on the nearest U-U distance D_{UU} , which in turn are completely controlled by the ligand substitution [92HMWF].

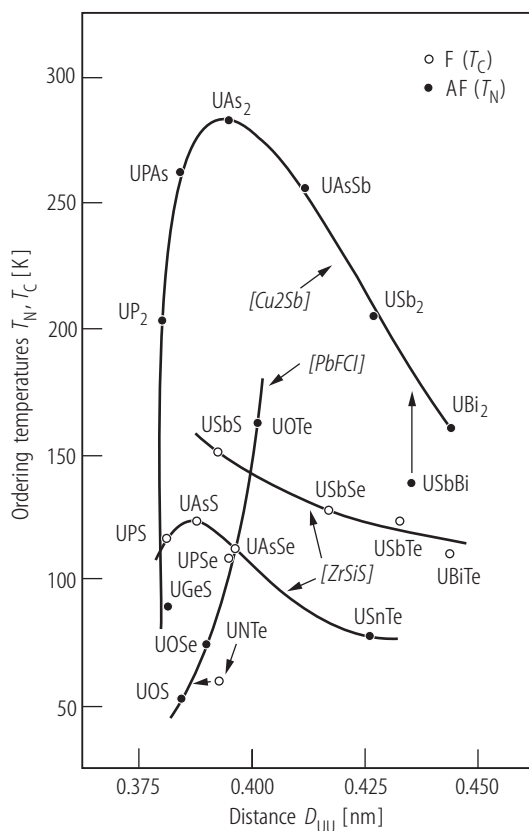


Fig. 2i. Magnetic ordering temperatures, $T_N(T_C)$, versus the interatomic U-U distance, D_{UU} , for the UX_2 binary pnictides, compared to the corresponding data for the ternary compounds from the series UOY , UXX' and UXY [87T].

So far, from transuranium dipnictides only the arsenide NpAs_2 (ferromagnetic below $T_C = 18$ K and antiferromagnetic between 18 K and $T_N = 52$ K) and the antimonides NpSb_2 ($T_C = 45$ K) and PuSb_2 ($T_N = 21$ K) have been investigated. Both magnetic transitions in NpAs_2 have a first order character. Magnetic phase diagrams of NpAs_2 were constructed on the basis of the magnetization [82BFDW] and neutron diffraction [82RBQB] data. In the antiferromagnetic state the neptunium magnetic moments in NpAs_2 are aligned along the c -axis and form a sine-wave modulated structure propagating along the [100] direction and extending over seven Np sites ($\mathbf{k} = 0.141, 0, 0$) in its incommensurate magnetic lattice. The first polarized neutron scattering experiment made by Delapalme et al. [82DMBF] points to a well localized character of the 5f electrons in this compound.

There are known only three transuranium diantimonides. These are ferromagnetic NpSb_2 ($T_C = 45$ K), antiferromagnetic PuSb_2 ($T_N = 21$ K) and non-magnetic AmSb_2 , all crystallizing with an orthorhombic structure of the LaSb_2 type. The observed magnetic properties and a distinct increase in the unit cell volume of the orthorhombic diantimonides compared to the tetragonal anti- Cu_2Sb type diantimonides are both a clear illustration of the progressive localization of the 5f electrons and establishing the 3+ oxidation state for the Np ion. However, the unit cell volumes of the transuranium diantimonides are still smaller than those of the corresponding Np...Am ditellurides and this arises due to much more extended character of the 5p-antimony orbitals which overlap to some extent with the 5f orbitals, thus pushing them to some degree of delocalisation.

2. Dichalcogenides

As already stated, the actinide dichalcogenides crystallize in various types of crystal structure and show a strong tendency to be nonstoichiometric. A numerous family of nearly stoichiometric compounds ($\text{An} = \text{Pa} \dots \text{Np}$) is that of orthorhombic phases with the PbCl_2 -type unit cells, such as PaS_2 , $\beta\text{-US}_2$, $\beta\text{-USE}_2$ and others. All these materials are semiconductors with an excitation gap of the order of 1 eV. In the uranium compounds, because of low local symmetry of the actinide ion, the crystal field effect yields only singlets. Indeed, they show non-magnetic properties with the magnetic susceptibility levelling off at low temperatures, which clearly reflects the formation of a singlet ground state. Similar behaviour is observed for UTe_{2-x} , which has also an orthorhombic structure yet of different type. Most unexpectedly, the solid solutions $\text{USE}_{2-x}\text{Te}_x$ exhibit ferromagnetism despite the terminal dichalcogenides are non-magnetic [96NPTS].

The tetragonal phases $\alpha\text{-US}_2$ and $\alpha\text{-USE}_2$ show some magnetic and thermodynamic anomalies at low temperatures, which might be related to the magnetic behaviour, however this issue has not been deeply addressed so far. A similar unclear situation is for chalcogenides with intermediate stoichiometries between 3:4 and 1:3. Their magnetic and related properties remain still as a large field for future investigations.

AnY₃-type compounds

In the past some interest has been devoted to the group of actinide trichalcogenides, mainly due to their monoclinic crystal structure of the ZrSe_3 type that exhibits a marked two-dimensional character. In this structure two of the inequivalent chalcogen atoms form tightly bound pairs causing that the actinide ion is tetravalent and a full charge compensation occurs, which brings about a semiconducting behaviour of the compounds. Despite extensive attempts made in the seventies, the magnetic properties of this group of phases have not fully been recognized up to now. It is believed that all the uranium trichalcogenides have singlet ground state and exchange interactions in these systems are weak compared to the crystal field effect. The most recent magnetic data obtained on single crystals of US_3 and USE_3 indicate the presence of broad maxima in the temperature-dependent susceptibility measured with the magnetic field applied along the b -axis. Some smaller anomalies in the susceptibility are also observed when the field is applied parallel to the a - and c -axes. These features have not been fully explained until now but it is believed that they manifest the low-dimensionality of the trichalcogenides. A two-dimensional antiferromagnetic ordering in the sulphide and the selenide was suggested on the basis of the Raman studies [87NZRL]. The susceptibility measured on single-crystalline and polycrystalline samples of $\alpha\text{-UTe}_3$ (ZrSe_3 type) shows some anomalies at low temperatures, which indicate an antiferromagnetic ordering below about 5 K. As expected, this phase is a semiconductor at low temperatures. On the other hand, $\beta\text{-UTe}_3$ that adopts the orthorhombic NdTe_3 -type structure, exhibits a ferromagnetic order below 12 K.

1.3.2.1.5 Arrangement of figures and tables

The overall organisation of this review is similar to that used in the volume on the binary actinide oxides (LBIII/27C2). The electronic, structural, magnetic, thermodynamic, electrical transport, thermal transport and related properties of binary actinide pnictides and chalcogenides are presented in the form of figures and tables. The surveys allow easy finding the interesting physical data for a given material by providing the numbers/labels of the required figure/table and referring to the relevant literature. The macroscopic state of the investigated specimen is defined here by using the following labels: “sc” for single crystal, “poly” for polycrystalline sample, “sintered” and “cold pressed” for so-prepared powders. The lack of any label means that the quoted experiment was made on a free-powder sample.

The compounds are grouped into series with different stoichiometries, and arranged according to decreasing atomic ratio between actinide and non-actinide components. Within each series the substances are ordered from light to heavy actinide element An. For a given An the compounds are arranged according to rising atomic mass of pnictogen X or chalcogen Y, i.e. X from N to Bi and Y from S to Te. First pnictides are discussed, then chalcogenides. For each compound the physical properties are presented in the following sequence:

- electronic band structure
- crystal structure
- bulk magnetic characteristics
- Mössbauer, NMR, EPR data
- neutron diffraction results
- crystal field models
- heat capacity data
- electrical transport properties
- optical and magnetooptical characteristics
- others (elastic constants, positron annihilation spectra, XPS spectra, ...)