

1 Magnetic and related properties of pnictides and chalcogenides

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

1.3 Pnictides and chalcogenides based on actinides

(Chap. 1.3.1 (Actinide monopnictides and monochalcogenides) see subvolume 27B6; chap. 1.3.2 (Binary non-equiatomic actinide pnictides and chalcogenides) see subvolume 27B7)

1.3.3 Ternary actinide pnictides and chalcogenides

1.3.3.1. Introduction

1.3.3.1.1 General

Ternary compounds of actinides with the elements from the 5th ($X = \text{P, As, Sb, Bi}$) and 6th ($Y = \text{S, Se, Te}$) group of the Periodic Table form a large family of phases, which exhibit a great variety of different stoichiometries, crystal structures and non-trivial physical properties. In general, the entire group may be divided into three distinct series, depending on the character of the third component, which can be: (i) a main group s- or p-electron element, (ii) a d-electron transition metal atom, or (iii) an f-electron lanthanide atom. The present compilation reports on as many as 457 different ternaries, namely 159 compounds containing s(p)-electron elements, 174 with d-electron elements, and 124 with 4f-electron elements. There are presented altogether 658 figures (299, 337 and 22 figures for the phases from the first, second and third series, respectively). It is worthwhile emphasizing that the previous edition of Landolt-Börnstein Tables (LBIII/12c from 1982) devoted to actinide pnictides (section 6.4 by R. R. Arons) and actinide chalcogenides (section 6.5 by H. Lütgemeier) contained hardly any information on ternary phases, mentioning only 17 compounds with s(p)-electron elements for which in total 10 figures were given. This huge disproportion in the volume of experimental data between the two compilations comes from the fact that the intense research on this family of compounds started not before the late eighties. Accordingly, the authors of the previous work have referred to only 19 articles, whereas the present review gives as many as 333 different reference items. Supplementary to numerous ternary systems the present compilation presents a few quaternary uranium and thorium chalcogenides. The reason is to account for recent significant development in the solid-state chemistry of such materials, that is stimulated by their relevance in thermoelectric, piezoelectric, ferroelectric, and non-linear optics applications.

Despite much advancement in the general knowledge on ternary actinide pnictides and chalcogenides, developed in last decades, up till now no monograph has appeared that would address a large variety of the physical behaviour in these compounds. The reader may be referred to several volumes of Gmelin Handbook of Inorganic Chemistry [G1-G5], however the information to be found in these compilations is restricted to a very small number of systems, and in any case it goes beyond elementary bulk properties. Moreover, some physical data are available in the chapters by Damien et al. [86DDT], Fournier and Troć [86FT] in Handbook on the Physics and Chemistry of the Actinides, as well as in a more recent review by Sechovsky and Havela [98SH] in Handbook of Magnetic Materials. For the readers interested in the preparation of actinide pnictides and chalcogenides, besides the above Gmelin's editions, one may also recommend the chapter by Dell and Bridger in the MTP International Review of Science [72DB], and the work by Spirlet and Vogt [84SV] in Handbook on the Physics and Chemistry of the Actinides, the latter summarising single crystal growth techniques appropriate for actinide-based materials.

1.3.3.1.2 Magnetic and related properties

As revealed in profound experimental and theoretical studies [for reviews see Handbook on the Physics and Chemistry of Actinides, eds. A. J. Freeman, G. H. Lander, C. Keller, Vol. 1-6 (North Holland, Amsterdam (1984-1991))], the magnetism of actinide-based compounds is quite complex because Coulomb, spin-orbit, crystal field and exchange energies are there of similar order of magnitude. An extended nature of the 5f wave functions makes the 5f electrons being usually neither fully localised nor itinerant. Their participation to bonding is particularly distinct in the case of uranium-based materials, which often exhibit unusual physical phenomena that arise due to the formation near the Fermi level of a narrow 5f-band with a high density of states. This electronic structure appears very sensitive to the strength of interaction of the 5f electrons with s-, p- and d-electronic states of surrounding atoms. Hence, it is sometimes possible that by introducing in a controlled manner some modifications in the neighbourhood of actinide atoms one is able to tune the physical characteristics of a given system towards desired behaviour. Usually, the best way for establishing the influence of f-s,p,d hybridisation on the physical properties is a systematic study of extended series of isostructural compounds, in which only one selected control parameter is varied, like for example the size or electronic character of the non-actinide component. Obviously, ternary systems, by a vast number of possible combinations, offer many possible routes for this type of research.

In what follows we attempt to give a brief overview of the present knowledge on the magnetic and related properties of ternary actinide pnictides and chalcogenides, with the main aim to identify the particular series of compounds, for which the experimental and theoretical data are compiled herein after in the form of figures and tables. For the clarity of presentation the materials are grouped into three categories: compounds with s- and p-electron constituents (alkali metals, alkaline earth metals, metalloids, p-electron metals, halogens), compounds containing 3d-, 4d- and 5d-electron transition metals, and compounds that form with lanthanides. It is remarkable that in each group the absolute majority of the physical data concerns uranium-based phases. There are some data available for thorium compounds (which have been studied mainly for the purpose of getting a nonmagnetic reference material to uranium systems) but to date only very few ternary series have been extended to transuranium elements and consequently hardly anything is known on the physical properties of such compounds. The obvious reason for that comes from difficulties in preparation and handling of these materials due to their scarcity, radioactivity, toxicity and reactivity.

Another problem in the solid-state physics of actinide pnictides and chalcogenides is little availability of high-quality single crystals having the size sufficient for physical property measurements. This deficiency is clearly reflected in the present compilation: while many crystal structures of compounds with different compositions have been studied on single crystals, most of the magnetic investigations have been performed on powders. The today's state-of-the-art single crystal growth techniques (chemical vapour transport, mineralisation, growth from tin-, lead- and reactive-fluxes, etc.) allow preparation of relatively large single crystals of a few uranium phosphides, arsenides or sulphides but only much smaller crystals have been obtained so far of ternary compounds with other pnictogen or chalcogen atoms. It must be emphasized that studying single-crystalline specimens is of the critical importance especially for actinide-based compounds, which usually exhibit strong anisotropy in their physical properties. For this reason a special attention is put in the following review on the magnetic and related data obtained on single-crystalline specimens.

1.3.3.1.2.1 Ternary actinide pnictides and chalcogenides containing s- and p-electron elements

Unequivocally, the most extensively studied compounds belonging to this family have been those with the general chemical composition $AnOY$ and $AnXY$. The two series consist of numerous phases crystallising with tetragonal structures (space group $P4/nmm$) of the $PbFCl$ - and $ZrSiS$ (anti- Fe_2As)-type, respectively. Their unit cells exhibit very similar atom arrangements, and differ only slightly in the values of free positional parameters of actinide and chalcogen atoms. These differences, reflected also in the interatomic distances, bring about important changes in the chemical bonding. The $PbFCl$ -type compounds are considered to be stoichiometric and nearly ionic with equilibrium in charges. Indeed, the $AnOY$ oxychalcogenides show semiconductor-like electrical conductivity, and their unit cell volumes decrease in a regular manner on going from Th towards Pu, thus indicating a stable tetravalent state of the actinide ions (see Fig. 1a). In contrast, the $AnXY$ ternaries often show deviations from the ideal stoichiometry, and their unit cell volumes exhibit irregular variations across the given series (note Fig. 1b). Apparently, the lattice parameters reflect there different magnitude of the 5f-6d and

5f-np hybridisation that leads to some delocalisation of the 5f electrons. Consequently, all the AnXY compounds are metallic or semimetallic.

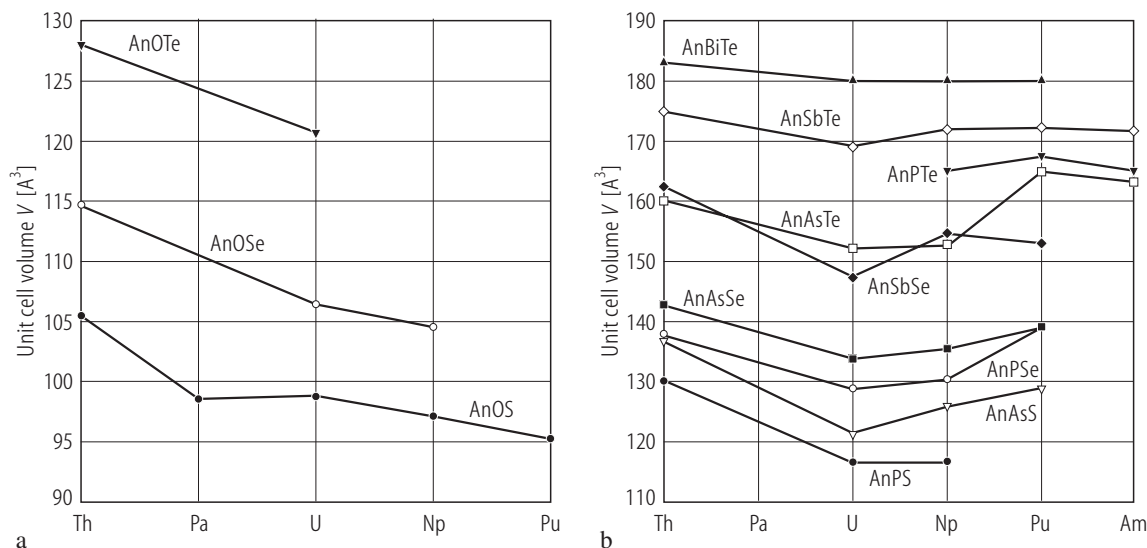


Fig. 1. Unit cell volume, V , of actinide oxychalcogenides AnOY (a) and actinide pnictochalcogenides AnXY (b).

The magnetic and related properties of the uranium oxychalcogenides UOY have been intensively studied by means of magnetic susceptibility [79TZ], electrical and thermal conductivity [64WP], heat capacity [63SNB, 84ABCH], and thermoelectric power [64WP] measurements. Moreover, for UOS inelastic neutron scattering experiments have been performed to address the issue of crystal field effect [95ABBC]. All three compounds are semiconductors that order antiferromagnetically at low temperatures due to the presence of well-localised magnetic moments on U^{4+} ions, coupled magnetically by superexchange via p-electron orbitals of neighbouring anions. The observed enormous magnetic anisotropy, with nearly temperature-independent transverse susceptibility in both ordered and paramagnetic regions [93KPGZ, 95ABBC], can be ascribed to crystalline electrical field interactions. The role of the C_{4v} crystal field potential on the magnetic and thermodynamic properties of UOS and UOSe has been studied by several authors using phenomenological methods [93KPGZ, 95ABBC and references cited therein]. The postulated crystal field levels schemes have always a uniaxial doublet being the ground state but differ in the sequence of higher lying energy levels and in the magnitude of the overall splitting of the $^3\text{H}_4$ multiplet. The proposed different crystal field models have recently been critically reviewed by Gajek [00G] who also calculated the electronic structure of UOY compounds, yet applying an ab initio approach. The models derived from the first principles account well for the available experimental data of UOS and UOSe.

The constitution studies of the equiatomic compounds AnOY have been extended to neptunium- and plutonium-based phases, however only for NpOS and NpOSe some magnetic data are available. Susceptibility, Mössbauer and neutron diffraction measurements have revealed in both compounds antiferromagnetic order [89ABBB]. Like in their uranium-based counterparts the strongly anisotropic magnetic behaviour of these chalcogenides is driven by interplay of superexchange coupling and crystal field interactions.

Isostructural with AnOY are the nitrido-chalcogenides ThNY and UNY with $\text{Y} = \text{Se}, \text{Te}$. The uranium selenide is paramagnetic down to 4.2 K, while the telluride orders ferromagnetically at low temperatures [79TZ]. A crystal field model accounting for the magnetic and thermodynamic properties of UNTe assumes a singlet ground state thus pointing to an induced nature of the ferromagnetism in this compound [86ABBG].

All the uranium pnictochalcogenides UXY, crystallising with the ZrSiS-type structure, exhibit at low temperatures strongly anisotropic ferromagnetic properties with the tetragonal c -axis being the easy magnetisation direction [72BZ, 94KNPZ, 95KNZ]. The compounds UPS and UAsY show semimetallic-like electrical conductivity, with a logarithmic decrease of the resistivity with rising temperature in the paramagnetic region, characteristic of Kondo systems [72WHK, 01WWH]. The dominant mechanisms leading to the

occurrence of magnetic ordering in these materials are superexchange via the metalloid atoms and RKKY interactions mediated by conduction electrons. The observed huge magnetic anisotropy has its main origin in strong crystal field interactions and the hybridisation between the uranium 5f electrons and the valence p-electrons of the non-magnetic ligands. Moreover, the 5f electrons are partly delocalised due to substantial f-d hybridisation [96OBAK].

Among the UXY compounds those with $X = \text{As}$ have been most intensively studied on high-quality single crystals. First of all one should recall UAsSe that has been comprehensively characterised by means of bulk methods, i.e. magnetic susceptibility, magnetisation, electrical resistivity, magnetoresistivity, thermoelectric power, Hall effect, specific heat and neutron diffraction measurements, as well as by means of various spectroscopies: optical, magnetooptical, NMR, XPS, ARPES and positron annihilation (see the references cited in [02CHWP]). The compound focused so much attention mainly because of its unusual electrical behaviour in the ferromagnetic region, dominated by an upturn in the resistivity below ca. $0.5T_C$ [72WHK, 01CHGL]. This extraordinary behaviour has been interpreted [98HCPF] as a manifestation of electron-assisted quantum tunnelling of atoms that arises owing to some disorder in the anion sublattice [01HPWK]. This so-called two-level system (TLS) Kondo effect has been proven to describe well the properties of UAsSe as well as of deliberately disordered compounds $\text{UAs}_{1-x}\text{Se}_{1+x}$ [01HWWK, 02CHWP]. Recently, a low-temperature electrical behaviour very similar to that in UAsSe has been established for UPS and likewise attributed to the TLS phenomenon [01WWH]. Ideal candidates for testing the TLS scenario seem thorium-based phases ThXY , which all are diamagnetic [68H] and not before recently have been studied exclusively for the purpose of comparison of their temperature-dependent electrical resistivity and specific heat with the behaviour of the corresponding uranium ternaries. Indeed, the electrical properties of ThAsS and ThAsSe fit very well with the theoretical predictions of the nonmagnetic TLS Kondo model [01HPWK, 02HW].

Constitution studies on the equiatomic actinide pnictochalcogenides have been extended to transuranium compounds ($\text{An} = \text{Np}, \text{Pu}$ and Am), however up to now only few of them have been recognized in respect of their physical properties. The neptunium-based phases NpAsY ($Y = \text{S}, \text{Se}, \text{Te}$) are semimetallic ferromagnets, showing some unusual features in the ordered state [77BCSW, 84BCFC, 85W]. Very similar behaviour is displayed by the plutonium-based analogues PuAsY ($Y = \text{Se}, \text{Te}$) [77BCSW]. In turn, NpSbTe remains a Curie-Weiss paramagnet down to 1.8 K [84BCFC].

Closely related to the UXY compounds are the double-pnictides UPAs, UAsSb and USbBi , crystallising with a tetragonal crystal structure of the same type. At low temperatures UPAs orders antiferromagnetically, whereas USbBi is ferromagnetic [79TZ]. No information is available on the magnetic behaviour of UAsSb .

Worth mentioning at this place are also the ternaries UMY with $M = \text{Si}, \text{Ge}$ or Sn , which crystallise either with the ZrSiS -type structure (sulphides and USnTe) or the UGeTe -type structure (selenides and UGeTe). All three compounds with germanium and USnTe are antiferromagnetic [77Z, 87T]. So far nothing is known on the magnetic properties of the silicon containing materials.

Another interesting series of equiatomic actinide ternaries, yet crystallising with a considerably different crystal structure than all those discussed above, is a group of the double-chalcogenides $\text{UY}_2\text{Y}'$. These latter compounds adopt an orthorhombic unit cell of the PbCl_2 -type in which the uranium atoms are located in a low-symmetry tricapped trigonal prismatic site. All three phases order ferromagnetically at low temperatures, and their electrical resistivity shows a semimetallic behaviour [94TKSP]. As the crystal field ground state is there probably a non-magnetic singlet, it was postulated that the observed ferromagnetism has an induced nature and develops via strong polarisation of conduction electrons.

The ternary actinide compounds with the overall composition $\text{An}_2(\text{N/O})_2(\text{X/Y})$ focused considerable attention in the past. It was proven that all the phases with $X = \text{P}, \text{As}$ and $Y = \text{S}, \text{Se}$ adopt the hexagonal $\text{Ce}_2\text{O}_2\text{S}$ -type structure, whereas those containing p-electron elements with larger ionic radius, i.e. $X = \text{Sb}, \text{Bi}$ and $Y = \text{Te}$, crystallise with a body-centred tetragonal structure of the $\text{La}_2\text{O}_2\text{Te}$ -type. In the hexagonal unit cell the actinide atoms have a capped triangular antiprismatic environment, with three chalcogens comprising one face of the prism and four nitrogen/oxygen atoms making up the opposite face and cap. In the case of the tetragonal compounds the actinide atoms are located at distorted square antiprismatic sites, being sandwiched between layers of N(O) and X(Y) atoms.

All the hexagonal $\text{U}_2\text{N}_2(\text{X/Y})$ phases order antiferromagnetically with the uranium magnetic moments aligned along the c -axis [76ZT]. Their properties are governed by strong crystal field interactions that cause splitting of the $^3\text{H}_4$ multiplet of the U^{4+} ion into a set of energy levels with a doublet ground state. The striking feature of $\text{U}_2\text{N}_2\text{P}$ and $\text{U}_2\text{N}_2\text{As}$ are their very high ordering temperatures ($T_N = 363$ and 403 K, respectively),

which are the highest Néel points known so far among actinide compounds. In contrast, all the tetragonal $U_2N_2(X/Y)$ materials exhibit strongly anisotropic ferromagnetism at low temperatures [78ZT]. In the pnictides U_2N_2Sb and U_2N_2Bi the crystal field ground state is a uniaxial non-Kramers doublet and the moments are aligned along the four-fold axis. A distinct exception occurs in U_2N_2Te in which the spins form an angle with the c -axis, due to a peculiar scheme of low-lying crystal field levels (singlet-singlet-doublet), which are closely spaced in energy [78ZT].

The family of $An_2O_2(X/Y)$ compounds is one of very few ternary series, which besides thorium and uranium phases comprise also transuranium-based materials. There are available in the literature brief reports on the formation of Pu_2O_2Sb , Am_2O_2Bi , Cm_2O_2X ($X = Sb, Bi$), Np_2O_2Y and Pu_2O_2Y ($Y = S, Se, Te$), Am_2O_2Y and Cm_2O_2Y ($Y = S, Te$), and even Bk_2O_2S and Cf_2O_2S [87B]. However, up to date only the plutonium compounds have been examined for their physical behaviour. The hexagonal phases Pu_2O_2S and Pu_2O_2Se as well as the tetragonal telluride Pu_2O_2Te are all antiferromagnetic semiconductors [83CDDb1, 83CDDb2]. Alike in the case of uranium ternaries, their magnetic properties result from strong superexchange interactions between the actinide atoms via p -orbitals of neighbouring non-magnetic ligands. The semiconducting properties originate from the formation of a gap between chalcogen p valence band and $6d$ - $7s$ conduction band. The $5f$ states overlap the bottom of valence band that brings about some delocalisation of $5f$ electrons.

Besides the above reviewed 1:1:1 and 2:2:1 series, there are reports in the literature on several other (but by far less rich) families of actinide ternaries containing s - or p -electron elements. One should mention here the orthorhombic phases U_2BY_5 ($B = Ca, Sr, Ba$; $Y = S, Se$) and Th_2AY_6 ($A = K, Rb, Cs$; $Y = Se, Te$), as well as the compounds $An_4O_4Y_3$ ($An = U, Np, Pu$; $Y = S, Te$), which crystallise either with tetragonal ($U_4O_4Te_3$) or monoclinic unit cells. However, until now hardly anything is known on the physical properties of these materials. Th_2RbSe_6 has been reported to be a diamagnetic semiconductor [98CPBW], and semiconducting character was found also for Th_2KSe_6 and Th_2CsTe_6 [96Cl, 98CPBW]. Unusual magnetic behaviour with initially ferro-, ferri- or canted antiferromagnetic ordering and re-orientational magnetic phase transition taking place at lower temperatures has been established for single crystals of semimetallic $U_4O_4Te_3$ [95KTSN]. There, the complex properties result probably from the competition between two different uranium sublattices with different electronic configurations, i.e. $5f^2$ (U^{4+}) and $5f^3$ (U^{3+}).

The compound $UTl_{0.56}Te_3$, which is structurally closely related to the orthorhombic Th_2AY_6 phases, has been shown to be a Curie-Weiss paramagnet down to 2 K [97TDPN]. Similarly, no long-range magnetic ordering has been found for the monoclinic selenide U_8MgSe_{17} , despite the presence of well-localised magnetic moments on uranium atom sites [79NT]. In turn, a possible antiferromagnetic ground state was ascribed to the orthorhombic compound UK_4Se_8 [97SK], and ferromagnetism was suggested for the tetragonal sulphide UKS_2 [66PL]. The ternaries UNa_2S_3 and $UCsTe_6$ that crystallise with hexagonal and orthorhombic structures, respectively, are both semiconductors [99MFSY2, 95CI] but their magnetic properties have not been determined yet.

Recently, much interest is devoted to quaternary uranium and thorium chalcogenides containing alkali metals, which usually crystallise in very complex low-dimensional structures with large coordination numbers. To this novel group of materials belong the monoclinic compounds U_2RbSbS_8 and $U_2RbSbSe_8$ [99CK], the trigonal telluride $URbSb_{0.33}Te_6$ [01CK], as well as the orthorhombic selenide $U_2Rb_4P_4Se_{26}$ [97CK], all identified as Curie-Weiss paramagnets. Additionally, the compound $URbSb_{0.33}Te_6$ has been characterised in respect of its electrical properties and found to be a narrow-gap semiconductor with holes as dominant charge carriers [01CK]. Strongly paramagnetic behaviour has also been reported for the series of quaternaries: $UKOS$, $U_2K_2O_2S_3$ and $U_2K_2O_2S_5$, yet the magnetic susceptibility measurements were performed for them only above 80 K [66PL]. Finally, a few thorium-based compounds are worthwhile to be mentioned: triclinic $ThK_2P_3Se_9$ and $ThRb_2P_3Se_9$ [00BASD], monoclinic $Th_2Cs_4P_5Se_{17}$ [00BASD] and orthorhombic $Th_2Cs_4P_4Se_{26}$ [01BASD], for which not only the structural data are available but also some Raman spectra measured on single-crystalline samples.

1.3.3.1.2.2 Ternary actinide pnictides and chalcogenides containing d-electron elements

Interest in the magnetic properties of actinide-based materials containing d -electron transition metals and elements from the Vth or VIth group of the Periodic Table began not before the late 1970s with pioneering studies on ternary uranium chalcogenides [76WFBN, 77WB]. Since that time over 170 different compounds have been reported in the literature but only very few of them have been investigated in depth, all the other being characterised until now almost entirely in respect of their crystal structures. It is also remarkable that except for Chevrel phases with neptunium, plutonium and americium [81DDH] no attempts have been made to prepare

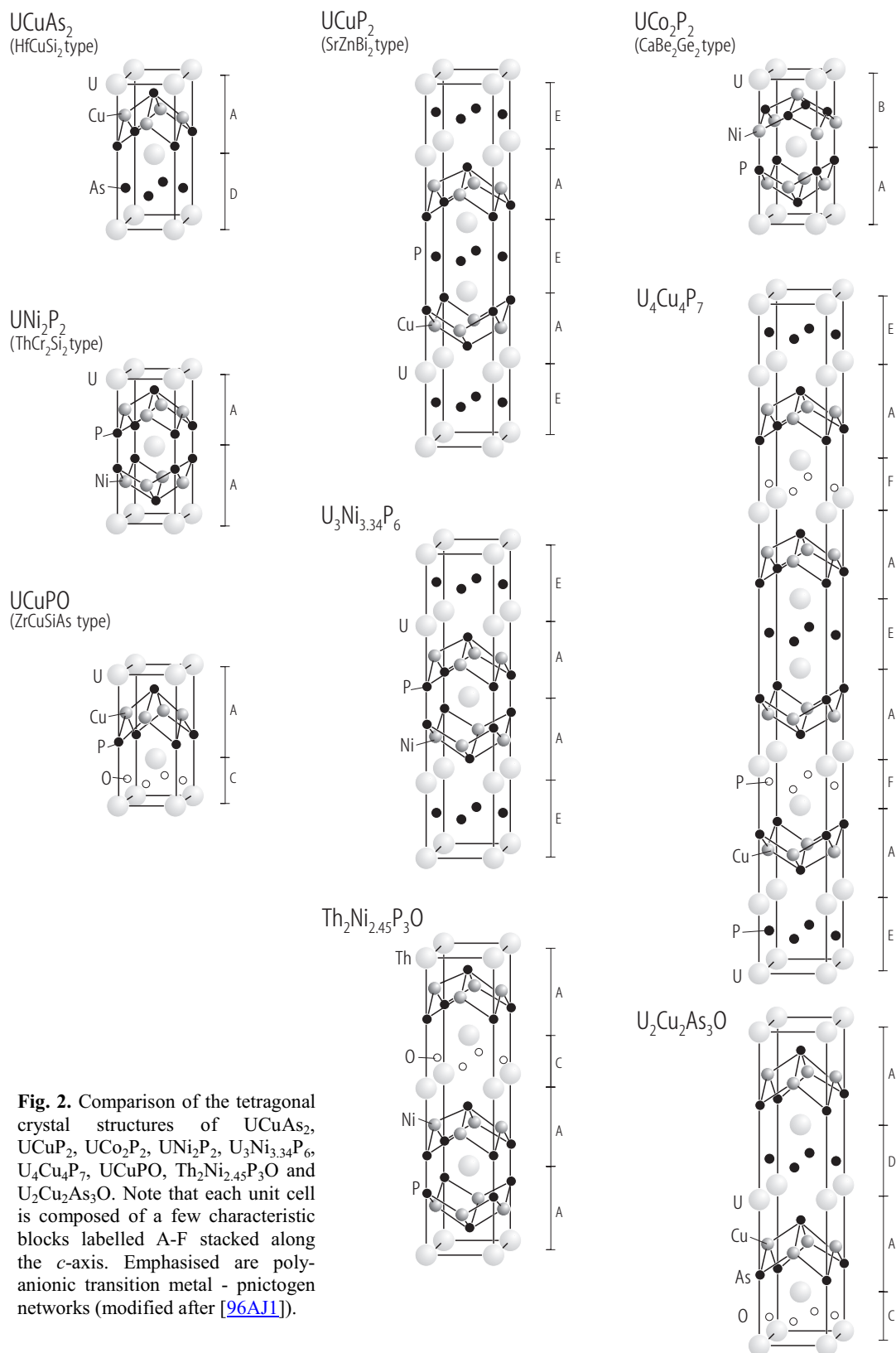
transuranium analogues to thorium- and uranium-based phases. These two facts clearly indicate that in spite of some progress in the field this particular research area still remains in its initial stage.

To date the most intensively investigated have been uranium pnictides with the overall composition UTX_2 or UT_2X_2 . The UTX_2 compounds crystallise with the tetragonal $HfCuSi_2$ -type structure with the only exception of $UCuP_2$ that adopts a closely related tetragonal structure of the $SrZnBi_2$ -type. In turn, nearly all the UT_2X_2 phases crystallise with the $ThCr_2Si_2$ - or $CaBe_2Ge_2$ -type structures, both derived from the tetragonal $BaAl_4$ -type structure. In Fig. 2 (see next page) there are shown the unit cells of the UTX_2 or UT_2X_2 compounds, together with the crystal structures of some other actinide pnictides to be mentioned below. A remarkable feature is that all the presented structures are closely related to one another being built of a few structural motives (blocks) stacked in a given order along the four-fold axis. In every case the uranium atoms are located at the sites of C_{4v} point symmetry. The U-U distances are always larger than the Hill limit for uranium (3.5 Å) and the nearest neighbours of U-atoms are usually pnictogens. Hence, it can be expected that the magnetic properties in the entire series are governed by indirect magnetic exchange interactions (superexchange and RKKY-type) and strongly influenced by 5f-p hybridisation.

Among UTX_2 pnictides thoroughly studied have been $UCuP_2$ and $UCuAs_2$. For these compounds detailed measurements of the magnetisation, magnetic susceptibility, electrical resistivity, Hall effect, magnetoresistivity, thermal conductivity, heat capacity, elastic effects, optical and magnetooptical behaviour have been performed, not only on powders but also on high-quality single crystals [91KTN, 92MMKJ, and references cited therein]. Both phases order ferromagnetically at low temperatures showing huge uniaxial anisotropy. Both are semimetals with low free carrier concentrations and exhibit pronounced Kondo effect. Similar properties have been established for ferromagnetic $UCoAs_2$ [00KNP]. Two other isostructural compounds, $UNiAs_2$ [89FMKT] and $UPdAs_2$ [90MFK], have been found to be antiferromagnets. The related antimonides $UTSb_2$ have been investigated by means of magnetic and electrical measurements, neutron diffraction and Mössbauer spectroscopy [98KKSM]. Most of these compounds order magnetically at low temperatures with ferromagnetic (for T = Cu, Ag, Au) or antiferromagnetic (for T = Ni, Ru, Pd) structures. Their electrical behaviour is governed by an interplay of crystal-field and Kondo interactions. From the bismuthides only $UCuBi_2$ has been studied magnetically and found to exhibit two subsequent antiferromagnetic phase transitions at low temperatures [92K]. It is worthwhile noting that in all UTX_2 pnictides only the uranium atoms carry the magnetic moments. In each case they are aligned along the four-fold axis and form ferromagnetic planes perpendicular to this axis. The adjacent planes couple with each other either in ferro- or antiferromagnetic manner. The magnetic properties of the entire family of UTX_2 compounds have been discussed in [98KKSM] in terms of f-ligand hybridisation effects. The strong anisotropy characteristic of all these ternaries has been attributed to pronounced 5f-p mixing and crystal field interactions, whereas the type of magnetic ordering has been associated with the magnitude of 5f-d overlap.

Much less studied have been the tetragonal UT_2X_2 pnictides. Detailed magnetic data are available for $UNi_{2-x}P_2$, UCo_2P_2 and $UNi_{2-x}As_2$ but only for the latter compound the measurements have been carried out on single crystals. The Ni-containing phosphide crystallises with the body-centred $ThCr_2Si_2$ -type structure, while the other two ternaries have primitive unit cells of the $CaBe_2Ge_2$ -type (see Fig. 2). Interestingly, both compounds with nickel exhibit a tendency to be deficient on T-metal sites. $UNi_{2-x}P_2$ is a simple antiferromagnet with uranium moments arranged in a manner described above for the UTX_2 compounds [90MFK]. The other two phases exhibit complex magnetic behaviour manifested by multiple magnetic phase transitions. The magnetic structure of $UNi_{2-x}As_2$ consists of two sublattices associated with two inequivalent uranium sites arising due to ordering of defects at Ni-atoms positions [94TBNK]. In the case of UCo_2P_2 the unusual magnetic properties originate from the presence of magnetic moments on some of the cobalt atoms in addition to the magnetic moments on uranium sites [94RVJ].

Amidst AnT_2X_2 compounds there are also a few phases that crystallise with non-tetragonal symmetry. Worth mentioning are $ThRu_2P_2$ and URu_2P_2 for which an orthorhombic structure of its own type has been determined [92GAJB]. In turn, the copper containing compound UCu_2P_2 is the only known representative of uranium pnictides that adopts the hexagonal $CaAl_2Si_2$ -type structure. For this latter phosphide quite detailed investigations of magnetic, electrical, optical and magnetooptical properties have been performed on single-crystalline samples. The compound was found to be a uniaxial ferromagnet with the highest Curie temperature ($T_C = 216$ K) among all studied to date actinide-based materials, and with huge magnetocrystalline anisotropy in both ordered and paramagnetic regions [90KT]. It shows semimetallic-type electrical conductivity with strongly damped free-carrier concentration and exhibits exceptionally large polar Kerr effect [89SFRK].



Unusual magnetic properties have been reported also for some other uranium pnictides that crystallise with tetragonal structures closely related to those mentioned above, e.g. $\text{U}_4\text{Cu}_4\text{P}_7$ and UCuPO (see Fig. 2). In $\text{U}_4\text{Cu}_4\text{P}_7$ the complex properties arise due to the presence of trivalent and tetravalent uranium ions in the lattice that carry different magnetic moments [94BTKN]. The oxypnictide UCuPO offers a unique possibility to study magnetic behavior of the uranium atom coordinated jointly by pnictogen and oxygen ions. Presumably just this uncommon environment is responsible for the highly anomalous susceptibility measured for this compound at low temperatures [94KANJ]. This hypothesis should be confronted with the magnetic behaviour of the other uranium oxypnictides reported in the literature, i.e. UMnAsO [97NJPB] and $\text{U}_2\text{Cu}_2\text{As}_3\text{O}$ [94KPN], but for both these compounds only the structural data are available as yet.

A very interesting series of ternary actinide pnictides are those crystallising with the “filled” skutterudite structure. The most prominent example is $\text{UFe}_4\text{P}_{12}$ that exhibits properties of a ferromagnetic semiconductor [86TRMM, 87GRTM]. This unusual behaviour arises due to strong f-electron hybridisation with the conduction electrons, as corroborated by the fact that its non-magnetic counterpart $\text{ThFe}_4\text{P}_{12}$ shows regular metallic conductivity [87TCDG]. The formation of two other Th-based skutterudites, namely $\text{ThRu}_4\text{P}_{12}$ and $\text{ThOs}_4\text{As}_{12}$, has been reported [80BJ], but nothing is known so far about their physical properties.

Similarly, the strength of f-ligand hybridisation is believed to be the main mechanism determining the low-temperature properties of equiatomic UTSb phases with cubic or hexagonal unit cells as well as $\text{U}_3\text{T}_3\text{Sb}_4$ compounds, which crystallise with “filled” Th_3P_4 -type cubic structure. It has been found that URhSb is an antiferromagnetic small-gap semiconductor, URuSb is a ferromagnetic metal, while UPdSb is a narrow domain-wall ferromagnet showing semiconductor-like electrical resistivity [87PNVV]. Amidst $\text{U}_3\text{T}_3\text{Sb}_4$ antimonides those with $\text{T} = \text{Co}$ and Cu are metallic ferromagnets [90ENMB], whereas the compounds with $\text{T} = \text{Ni}$, Pd and Pt exhibit behaviour of narrow gap semiconductors [90TMFA2, 92CLTS]. Worth mentioning here is also the thorium-based compound $\text{Th}_3\text{Co}_3\text{Sb}_4$ that is a metallic ferromagnet at room temperature due to magnetism of Co atoms, rarely observed in this type of materials [01SK].

A relatively large body of literature is devoted to pnictides with a metal/non-metal ratio equal or close to 2:1. To this class of compounds belong hexagonal phases: $\text{An}_2\text{T}_{12}\text{X}_7$ ($\text{An} = \text{Th}, \text{U}$; $\text{T} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Rh}$; $\text{X} = \text{P}, \text{As}$) crystallising with $\text{Zr}_2\text{Fe}_{12}\text{P}_7$ -type structure, $\text{U}_6\text{T}_{20}\text{X}_{13}$ ($\text{T} = \text{Ni}, \text{Rh}$; $\text{X} = \text{P}, \text{As}$) adopting the $\text{Zr}_6\text{Ni}_{20}\text{P}_{13}$ -type unit cell, and the compound $\text{U}_6\text{Ni}_{15}\text{P}_{10}$ isostructural with $\text{Ce}_6\text{Ni}_{15}\text{P}_{10}$. The family comprises also the phosphides UT_4P_2 ($\text{T} = \text{Mn}, \text{Ni}$) with tetragonal ZrFe_4Si_2 -type structure, UNi_3P_2 isostructural to orthorhombic HoCu_3P_2 , UMn_5P_3 crystallising with orthorhombic YCo_5P_3 -type structure, hexagonal and orthorhombic modifications of UCr_6P_4 , as well as monoclinic phases UT_5P_3 ($\text{T} = \text{V}, \text{Cr}$). Despite a large variety in the crystal structures, all these ternaries can be classified by different linkages of trigonal prisms built of metal atoms surrounding the pnictide atoms. It is regrettable that for most of them the structural studies (usually performed on single crystals) have not been followed so far by physical property measurements. Some magnetic data are available for $\text{U}_2\text{Ni}_{12}\text{P}_7$ and UNi_4P_2 that order ferromagnetically at low temperatures [98EAJ], antiferromagnetic UNi_3P_2 [98EAJ] and the compounds $\text{U}_6\text{T}_{20}\text{P}_{13}$ ($\text{T} = \text{Ni}, \text{Rh}$), both showing antiferromagnetic ordering [87GCMS, 98EAJ]. In the case of UMn_4P_2 the magnetic behaviour is more complex, with two subsequent antiferromagnetic phase transitions arising from the formation of magnetic moments on both uranium and manganese sites [90JTRP].

Unusual magnetic features have been found for the uranium phosphide $\text{U}_3\text{Ni}_{3.34}\text{P}_6$ that crystallises with a tetragonal structure closely related to those of UTX_2 and UT_2X_2 phases (see Fig. 2). In this compound the presence of two non-equivalent uranium sites in the unit cell brings about ferrimagnetic ordering with a distinctly marked compensation point [96REJS]. More typical properties have been reported for the tetragonal compound $\text{U}_2\text{Cu}_5\text{As}_5$ [91KNT] and hexagonal antimonide $\text{U}_3\text{Cu}_2\text{Sb}_3$ [86DB], which show antiferromagnetic and strongly anisotropic ferromagnetic behaviour, respectively.

The actinide ternary chalcogenides containing d-electron metals have generally been less studied than the pnictides. The reason for that may be the unstable character against air and moisture shown by many of them. Nevertheless, there is at least one long series of compounds which attracted much attention in the past because of unusual magnetic properties, namely the AnTY_3 phases ($\text{An} = \text{Th}, \text{U}$; $\text{T} = \text{Sc}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Nb}, \text{Ru}, \text{Rh}, \text{Ta}, \text{Pd}$; $\text{Y} = \text{S}, \text{Se}$). All these chalcogenides crystallise with orthorhombic symmetry either in a three-dimensional structure (space group Pnma) or in a layered structure (space group Cmcm), both comprising chains of corner-shared TY_6 octahedra with actinide atoms located in interstitial sites. The UTY_3 sulphides and selenides with $\text{T} = \text{V}, \text{Cr}$ and Co exhibit at low temperatures ferromagnetic order with a strong antiferromagnetic component and show extremely large magnetocrystalline anisotropy. The complex behaviour arises due to magnetic interactions

between d-electron and f-electron magnetic sublattices. As established by powder neutron diffraction [76WFBN], in UCrS_3 the chromium magnetic moments form a collinear antiferromagnetic structure whereas the uranium moments are arranged in a noncollinear antiferromagnetic manner. Alternatively, the same authors have proposed another model in which Cr moments are collinear and antiparallel but uranium moments are delocalised. Such an unusual scenario has been derived also for UVS_3 [77WF] as well as for UVSe_3 and UCrSe_3 [77NWF]. In turn, the magnetic structure in UCoS_3 consists of ferromagnetically aligned uranium moments and cobalt moments that form a canted antiferromagnetic sublattice [81CWBN]. The corresponding selenide UCoSe_3 is also a ferromagnet with antiferromagnetic component [89DN] but its magnetic structure has not been determined yet. Similarly, only bulk magnetic data are available for the other known AnTY_3 chalcogenides. The sulphides UNbS_3 , URuS_3 and UTaS_3 are ferromagnetic [85NCKS, 87DN], while the compounds URhS_3 and UPdS_3 show antiferromagnetism [85NCKS, 89DN]. More recently, ferromagnetic ordering of the moments carried by manganese atoms was found for ThMnTe_3 [00NI].

Complex magnetic properties have been reported for the monoclinic uranium sulphides U_2TS_5 with $\text{T} = \text{Fe}$ or Co [77WB, 79WBFN]. The behaviour in U_2FeS_5 is dominated by strong Fe-Fe magnetic exchange interactions, observed also in the isostructural thorium-based compound Th_2FeS_5 that is ferromagnetic [80BFNW]. The U-U exchange is too small to set long-range ordering but the U moments are polarised by substantial U-Fe interaction. As a result, the compound exhibits at the lowest temperatures a non-compensated antiferromagnetic ordering with a strong ferromagnetic component on both U and Fe sublattices, which changes considerably with rising temperature [77WB]. U_2CrS_5 shows similar bulk magnetic properties, yet in this case only the uranium moments are canted, while the chromium moments form a purely collinear antiferromagnetic structure [79WBFN]. In the literature there have been reported also U_2TS_5 phases with $\text{T} = \text{Ti}$ and Zr , crystallising with orthorhombic unit cells, and U_2HfS_5 that is cubic [84NCKS2]. The magnetic properties of these compounds have been studied only down to 80 K, and ferromagnetic ordering has been established for U_2HfS_5 .

A relatively numerous family is that of U_8TY_{17} compounds. Monoclinic sulphides and selenides form with this composition for $\text{T} = \text{Ti}$, V , Cr , Mn , Fe , Co , Ni , and most of these compounds order antiferromagnetically below 70 K [79NT]. Antiferromagnetic ground state has been found also for $\text{U}_6\text{Ir}_2\text{S}_{15.5}$, $\text{U}_6\text{Ir}_2\text{Se}_{15.5}$ and $\text{U}_6\text{Rh}_2\text{S}_{15.5}$, crystallising with complex cubic crystal structure [96DN]. In turn, the sulphides U_3TS_6 ($\text{T} = \text{Ti}$, Zr) that adopt an orthorhombic structure of the Sb_2S_3 -type remain Curie-Weiss paramagnets down to 80 K [84NCKS2].

In the course of intense investigations of Chevrel phases in early 1980s the actinide-based selenides with $\text{An} = \text{Np}$, Pu and Am have been prepared and tested for possible superconductivity. Strong diamagnetism and drop in the resistivity below $T_c = 5.5$ K has been found only for NpMo_6Se_8 [81DDG], whereas the plutonium and americium compounds appeared to be paramagnetic down to 3 K [81DDH]. More recently, incipient superconductivity at 3 K has been found in $\text{Th}_{0.81}\text{Mo}_6\text{S}_8$ [96DPN]. The uranium sulphide UMo_6S_8 (in which the uranium atoms are said to have a nonintegral valence) is paramagnetic down to 2K [96DPN], and the selenide $\text{U}_{0.82}\text{Mo}_6\text{Se}_8$ exhibits a weak ferromagnetism at low temperatures [96DPN].

Besides the compounds reviewed above the magnetic and/or electrical properties have been studied for a few other systems. The monoclinic tellurides Th_2CuTe_6 and $\text{U}_2\text{Cu}_x\text{Te}_6$ have been found to be paramagnetic semiconductors [98NI, 01PBBK], the monoclinic compounds $\text{U}_6\text{Cu}_2\text{Y}_{13}$ ($\text{Y} = \text{S}$, Se) and the cubic sulphide $\text{U}_{0.9}\text{Pd}_3\text{S}_4$ have been shown to remain Curie-Weiss paramagnets down to 4.2 K [80N, 98FSYM], whereas for the hexagonal phases $\text{U}_3\text{Cu}_2\text{S}_7$ and $\text{U}_3\text{Cu}_2\text{Se}_7$ the paramagnetic and antiferromagnetic behaviour, respectively, has been established at low temperatures [96DLLN].

In recent years one observes a growing interest in quaternary uranium chalcogenides containing alkali metals. Within this group of compounds the physical properties have been reported for the orthorhombic phases UCuKSe_3 [96SAHK] and UTiCsTe_5 [95CI], as well as for the cubic sulphide $\text{U}_2\text{Cu}_{12}\text{K}_6\text{S}_{15}$ [00SPSK]. All these materials are paramagnetic down to 6 K. The latter compound shows metallic-like conductivity, in contrast to the other two quaternaries, which are semiconductors.

1.3.3.1.2.3 Ternary actinide pnictides and chalcogenides containing 4f-electron elements

Some limited information can be found in the literature on mixed actinide-lanthanide compounds with p-electron constituents. These are mainly chalcogenides based on uranium and thorium that form with various compositions and crystal structures. Until now most of these phases have been studied exclusively by means of X-ray diffraction. Most recently, the constitution of pseudobinary antimonides $U_{2/3}Ln_{1/3}Sb_2$ (adopting a tetragonal structure of the $NdTe_3$ -type) and $(U_{0.5}Ln_{0.5})_3Sb_7$ (crystallizing with its own tetragonal structure) has been reported [01SJ] but their physical properties are still unknown.

Some preliminary magnetic data have been reported for the $U_5Ln_4S_{16}$ ($Ln = Y, Tb, Dy, Ho, Er$) and $U_5Dy_4Se_{16}$ compounds, that crystallise with a monoclinic structure of its own type [81PLSK3, 82CNPS] as well as for the selenides $U_{0.5}Ln_{0.5}Se_2$ ($Ln = Y, Tb, Dy, Ho, Er, Tm, Yb$), crystallising with two different orthorhombic structures [84NCCC]. All these phases exhibit Curie-Weiss paramagnetism above 100 K.

From a few tellurides with the formula $U_{0.5}Ln_{0.5}Te_3$ only the compound with $T = Tb$ has been investigated for its magnetic behaviour and found to order ferromagnetically at low temperatures [85SKGK].

Fairly better studied have been the magnetic properties of several compounds from the series U_2LnS_5 , ULn_2S_5 , ULn_2Te_5 , $ThLn_2S_5$ and $ThULnS_5$, which all are derived from the corresponding An_3Y_5 binaries by substituting one or two lanthanide atoms for actinide atoms, while the crystal structure of the U_3S_5 -type is kept unchanged. The magnetic susceptibility measurements indicated that all the sulphides with $Ln = La, Ce, Pr, Nd, Sm$ are paramagnetic down to 4.2 K, except for the U_2LnS_5 phases that always show weak ferromagnetism [80NP]. In turn, the ULn_2Te_5 tellurides with $Ln = La, Pr, Nd, Gd$ have been studied magnetically down to 80 K and characterised as Curie-Weiss paramagnets [84NCCC].

1.3.3.1.3 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 ternary 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 three main chapters 1.3.3.3, 1.3.3.4 and 1.3.3.5 describe compounds with s- and p-electron, d-electron and f-electron constituents, respectively. The compounds are grouped into series with different stoichiometries, and arranged according to increasing number of actinide atoms in the formula and 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 P to Bi and Y from S to Te . Finally, for a fixed X/Y element the phases are presented in the order governed by increasing atomic mass of the third component (s-, p-, d- or f-electron atom).

For a given 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 magneto-optical characteristics
- others (elastic constants, positron annihilation spectra, XPS spectra, ...)