

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

1.3.1 Actinide monopnictides and monochalcogenides

1.3.1.1 Actinide monopnictides

1.3.1.1.1 Introduction

1.3.1.1.1.1 General considerations

Monopnictides are binary compounds AnX which besides an actinide element An contain one of the elements belonging to the V-th group of the periodic system, i.e. nitrogen, phosphorus, arsenic, antimony and bismuth, which are defined here as the X-element. In a similar way, such compounds containing elements of the VI-th group, i.e. sulfur, selenium and tellurium, are defined as AnY and are called actinide monochalcogenides. This edition of Landolt-Börnstein concerns the magnetic and related properties of the actinide monopnictides AnX , together with isostructural monocompounds containing the element of Group IV, carbon, as well as the mutual solid solutions with either cation or anion mixing. The anion mixing concerns here only the elements within the V-th group, or between nitrides and carbides. The magnetic and related properties of monochalcogenides together with the solid solutions between An -elements (cation mixing) and between elements within the VIth group or of the Vth and VIth group (anion mixing) are subject of another LB-volume, namely III/27B6 β .

The monocarbides are usually nonstoichiometric and defined as AnC_{1-x} . In several respects An monocarbides are similar in the physical properties to the transition metal carbides [64CL]. The basic reason to include also these monocarbides to the family of the AnX monocompounds was dictated by the fact of the formation of complete solid solutions, e.g. with mononitrides AnN , besides of having the same crystal structure. The latter together with the individual monocompounds AnC [64C] or AnN , have played for a long time an important role because of their importance in nuclear technology. This interest lies in their high melting points ($T_m > 2000^\circ C$), lack of phase transformations at suitable temperatures and stability under irradiation. In addition they exhibit a considerably higher thermal and electrical conductivity and higher density compared to UO_2 commonly used as a nuclear fuel. For example, the UC-UN solid solutions are more effective as an advanced fuel for fast breeder reactors than the individual components. In past years, many investigators have studied the thermodynamics of these solid solutions; see e.g. the references in [86TIMK]. Thus due to this importance there exists a huge literature, but often contained in numerous laboratory reports, conference Proceedings and so on, being usually difficult accessible. Therefore, they have been here omitted, as well as many technologically treated articles, which appeared in specific journals.

Previously, some limited information about the monopnictides has been included in Landolt-Börnstein, New series, Group III, Vol.12c (LBIII/12c), published in 1982, which concerned the magnetic and related properties of all kind of compounds formed by the actinides with elements of Group V. In turn, such information attributed to the actinide monocarbides has been included in the LB-volume III/19f2, which appeared in 1993. If one compares the reviewed above volumes with the present compilation it appears that the number of references and figures has increased many times.

The most intensive research on the monopnictides became possible with the moment of starting the production of single crystals of appropriate size and of good quality. This requirement comes from the fact that the actinide-based compounds usually exhibit strong anisotropic physical properties. Therefore, the present compilation is based on the data obtained mainly on AnX single crystals. In addition, a large number of comprehensive books and review articles have been published since 1982. In particular one should mention the volumes of the “*Handbook on the physics and chemistry of the actinides*” edited by A.J. Freeman and G.H. Lander (volumes I, II and V) or by A.J. Freeman and C. Keller (volumes III, IV and VI) published in 1984-91 from which several selected chapters are listed in the reference list of this volume. Another book dealing with the actinide binary compounds, including the

monopnictides was published in 1993 as “*Handbook on the Physics and Chemistry of Rare Earths*” edited by K.A. Gschneider Jr., L. Eyring, G.H. Lander and G.R. Choppin (volume 17). In the reference list there are cited 5 selected chapters from this book. The reader can take into account also several volumes of the *Gmelin Handbook of Inorganic Chemistry* [72HK], [81G], [81HK], [87HK] and others. They, however, contain mainly technological information cited in many unavailable reports and less bulk physical properties of actinide materials. Finally it should be mentioned that as a continuation of the book titled “*The physics of actinide compounds*” (Plenum, New York, 1983) by P. Erdős and J.M. Robinson, a vast compilation appeared in 1999 in Adv. Phys. of the authors P. Santini, R. Lemański and P. Erdős, titled: “*Magnetism of actinide compounds*” which gives a full account on the magnetic and related properties of actinide pnictides and chalcogenides (see [99SLE]).

Most of the references cited in this volume relate to the monopnictides of U and in less degree to those of Np and Pu or heavier members of the actinide family. This is dictated mainly by three factors: availability, radioactivity hazard and cost. If the first factor decreases considerably in going through the series from U (tons), Np and Pu (kilos), Am and Cm (grams) and finally to berkelium and californium (milligrams), the two latter factors go rapidly up in the same direction. Also the much greater radioactivity hazard has made that only very limited studies on the α -activity protactinium monocompounds are now available. On the other hand, despite the large availability and much less radioactivity of the thorium monopnictides they were useful, but in limited way, only as the reference compounds to the uranium counterparts due to the fact of not possessing the f-electrons in the Th-electronic shells.

Because of the large hazards for researchers only limited government research establishments, such as Argonne and Oak Ridge National Laboratories in the USA and CEN-Fontenay aux Roses in France, could initiate at all the transuranium works in the past. All the obtained hazard transuranium monopnictides, after having been doubly encapsulated in specially prepared containers, could next be safely studied outside a glove box for their physical properties in many other laboratories, like in CEN-Grenoble and Saclay (France) or AERE Harwell (England). In these studies it is of large importance to use the longest-lived isotopes, e.g. ^{243}Am and ^{248}Cm , to avoid a radiation damage and introducing daughter impurities that grow in the sample, as would be the case of using the short-lived isotopes. Fortunately, the first seven transuranium elements, i.e. from Np to Es, all have long-lived isotopes with half-lives of at least a year or more.

1.3.1.1.2 Historical view

The first publications on the physics (mainly magnetic properties) of actinide monopnictides date to the beginning of the sixties. In particular they comprised the uranium monocarbides [62TTL], mononitrides [62TTL], [75T], monophosphides [63TT], [64AJD], monoarsenides [64TSZ], monoantimonides [64TSZ] and monobismuthides [66TZ]. A summary on this subject was presented by W. Trzebiatowski first as conference articles [67T], [67TPST] and then as an extensive review [80T2].

These first studies showed that all the monopnictides denoted as UX (X = N...Bi) are AF-ordered at low temperatures, except for UC which is a temperature-independent paramagnet (TIP). After the first recognizing of their magnetic properties they have next been extensively studied in a wide aspect of physical properties up to now. During all this time an appreciable effort has been made to determine their physical properties.

The wide interest in this group of compounds has arisen due to their simple cubic crystal structure of the NaCl-type (s.g. Fm3m) and their easy availability as high-quality single crystals (see e.g. [84SV]). Then, at the end of the 60s and beginning of the 70s, the monopnictides of other An elements like Np and Pu as well as some heavier An elements, have been studied mainly in Oak Ridge and Argonne National Laboratories (USA) and a little later in Fontenay aux Roses (France) or in AERE Harwell (England)). At present such researches are continued mainly in the Transuranium Institute (TUI) in Karlsruhe (Germany) and partly in the Los Alamos National Laboratories (USA). In the former institute most of the transuranium monopnictides in the form of single crystals have been prepared.

1.3.1.1.3 Preparation and crystal structure

A. Synthesis of polycrystalline- and single-crystalline samples

A convenient method for preparation of actinide monocarbides is directly from elements by arc-melting or plasma-jet melting under inert atmosphere of helium or argon. There exist several other methods used in utilization of actinide monocompounds in nuclear technology (see e.g. review [75P]). First single crystals of uranium monocarbide [66EM], [83MHOK] and mononitride [D.E. Stellrecht, Battelle Columbus Ohio Laboratories-unpublished, see also [05DTSM]] were obtained by high-temperature heating of polycrystalline materials. Except for UC in the low-temperature range, the remaining monocarbides have variable compositions evidenced by examination of the phase diagrams: Th-C [69BS], U-C (Fig. I.17) and Pu-C (Fig. I.44). The lattice

parameters of AnC_{1-x} decrease with removal of carbide atoms, especially for ThC_{1-x} (Fig. I.10) and PuC_{1-x} (Fig. I.45) for which there exists an appreciable variation in homogeneity range. For all these light actinide monocarbides much effort has been directed in the past first of all toward obtaining reliable thermodynamic data at high temperature. Only a small part of such data is reflected in this issue. For a summary see ref. [67S3].

The monocompounds AnN , AnP and AnAs are simply prepared by thermal decomposition of the corresponding higher pnictides [75D1]. Usually, UP and UAs decompose during melting. Melting of UN is usually done under nitrogen high pressure. Finally the monoantimonides and monobismuthides may be obtained directly from elements by arc-melting, but getting pure and stoichiometric materials becomes a rather difficult task. In addition, UBi is extremely pyroforic. The situation is more simple in the case of plutonium because no richer pnictides exist, so plutonium reacts with phosphorus, arsenic, antimony and bismuth to form monocompounds directly. For some details concerning monocarbides see [75P], mononitrides [75D2] and those concerning monocompounds with phosphorus, arsenic, antimony and bismuth see [81G]. Most of the single crystals of monopnictides containing P, As, Sb, Bi were obtained by mineralization, which is described in detail in [84SV]. Single crystals of UP and UAs were also obtained by high-temperature solution growth [83HHR], while those of USb , besides mineralization, also by modified Van Arkel techniques [77HM].

Of particular interest in the magnetic and related properties are studies of mutual solid solutions, where either given cations or anions are mixed (see e.g. [87VM]). They allow for the systematic changes of several important parameters, like atomic separation, electron concentration, and also by dilution with nonmagnetic solvents (e.g. thorium, yttrium, lanthanum and lutetium counterparts) diminishes almost to zero the exchange magnetic and various other-type interactions leaving the CEF one approximately unchanged. Solid-solubility relationship in the pseudobinary systems, mainly between thorium, uranium and plutonium monocompounds, have been intensively studied in the past. As the dominant factor determining the extent of solid solubility between the NaCl-type compounds appeared to be the relative size difference of the component non-metal atoms [67B]. For example, a complete solubility has been found between UN-ThN , UN-PuN as well as between UN-RN and UN-TN , where $\text{R} = \text{Y, La, Ce, Pr, Nd}$ and $\text{T} = \text{Zr, Hf}$ (see review [86H]). When the lattice parameters of the two phases differ by more than 10...15% there is only a limited mutual solubility [67AD]. On the other hand, the solid solubility studies between UC , UN , UP , USi and US have established that the valence electron concentration (VEC) influences the solution behaviour greatly [67INS]. Thus, $\text{VEC} \approx 11$ favors the complete miscibility. All these studies started mainly in the sixties and have been stimulated by possible application of the solid solutions as nuclear fuel materials, while the later studies in the seventies and being continued up to nowadays have showed also their large importance in the knowledge of fundamental aspects in the physical properties. This is because the pseudobinary systems introduce unlimited possibilities to vary systematically numerous physical parameters.

B Crystal structure

The rocksalt NaCl-structure type (B1) is cubic with 4 FU/cell and belongs to space group $\text{Fm}\bar{3}\text{m}$. The atoms are distributed as follows:

Na: 4a $\text{m}\bar{3}\text{m}$ 0,0,0 Cl: 4b $\text{m}\bar{3}\text{m}$ $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

This is a relatively simple structure (Fig. R2). The magnetic atoms form a fcc lattice, which gives rise to a greater simplicity for theoretical treatment. However, the lattice parameters of the rock salt-type binary monocompounds do not vary regularly across an AnX series with the Z number of An element [see e.g. 79DHP1] and [86DDT], as do the corresponding rare earths (RE's) isomorphic REX compounds. The parameters of the AnX compounds go through a minimum close to the beginning of series, the depth of which decreases in going down the V-th element column (see Fig. R.5a).

For a large number of AnX compounds the stability of crystal structure has been studied under pressure up to 50 GPa (see a review [93BH]). It appears that ThC and ThN have remarkable structural stability, no phase transition takes place in the pressure range up to 50 GPa (see Table 5). Also AmN , CmN and CfN keep the fcc structure up to 50 GPa (Table 7). In contrast to the above monocompounds, UN and UP have been shown to transform into a rhombohedral structures at 29 [85SGB], and 10 GPa [88SGBD], respectively. This finding can be treated as a signal of some participation of the 5f-electrons in chemical bonding of the crystal. The high-pressure experiments on the AnX containing a large anion, such as As, Sb, Bi lead to the transformation of the rock-salt structure into the CsCl-type structure (B2) under applying pressure (see Table 5). ThBi has this structure already at ambient pressure [82BBF]. The $\text{B1} \leftrightarrow \text{B2}$ transformation is usually sluggish and shows pronounced hysteresis. The An compounds, containing cations $\text{An} = \text{Np}$ and Pu and anions $\text{X} = \text{Sb}$ and Bi favor a tetragonal high-pressure structures, which can be recognized as a distorted B2 structure.

The unit cell volume in the B1 phase as a function of pressure can be described by the Murnaghan and Birch first-order equations of state. These two equations yield almost the same results and allow to determine the bulk moduli B_0 and its pressure derivatives B_0' (see Tables 6 and 7). At this first-order transition the relative volume, $(V_{B1}-V_{B2})/V_{B1}$, collapses by about 10%. In general, there is a trend to decreasing B_0 with increasing Z .

1.3.1.1.4 Physical properties

A. Electronic structure

The main task in studies of the physics of actinide compounds in general and of such structurally simple materials as the mononictides in particular, is to understand the unusual role of the 5f-electrons in creating a large diversity of their physical properties. Despite the appreciable attempts which have been undertaken in the past, the nature of the 5f electrons in the NaCl-type actinide compounds is still not well understood. They are spanned between an itinerant and localized scenario depending on the ratio of Coulomb interaction U and the band width W . The low or high value of the U/W ratio decides about applying in their description either a one-electron band theory or classical localized type approaches, as e.g., the CEF-theory, respectively. From simple volume considerations one can conclude the trivalent An^{3+} states to be existent in all these compounds with the possible exception of the carbide and nitride monocompounds. So the charge transfer fills the p band giving rise to semimetallic behaviour, while the carbide and nitride monocompounds are treated as metallic materials.

From a practical point of view Hill in 1970 [70H] introduced the An-An separation as the pertinent parameter allowing to divide these two different regions of behaviour. It was rather a crude assumption with a meaning that direct 5f - 5f electron wave function overlap is the only parameter governing the 5f bandwidth W . Some times later it became clear that the dominant factor determining the physical properties is the strength of the hybridization of An f-electrons with band electrons, both valence and conduction ones. This comes from the fact that the 5f wave functions in the lighter actinide atoms are appreciably extended and hence they interact to a greater extent with the chemical surrounding. Thus, the region spread between uranium and plutonium and between light and heavy pnictogens should be considered as cross-over regimes where a progressive localization of 5f electrons occurs, and already the 5f⁶ electronic configuration of the americium ion in its monocompounds is fully considered to be localized. So the transplutonium monocompounds become similar in their physical properties to those of rare earth counterparts. This also means that the 5f states do not participate in any electronic bonding redistribution. Nevertheless the inspection of Fig. V.12A gives clear evidence in the difference in the degree of localization of 4f and 5f electrons.

There are several tools for studying the electronic structure experimentally, like photoemission, X-ray absorption, optical, magneto-optical as well as neutron, Mössbauer, muon and other spectroscopies. Photoemission spectroscopy (PES) and its inverse one (BIS) have become the major tool in the investigation of the electronic structure of solids [87R2], and they practically do not need single crystals. PES operates in a wide energy scale of 5...1500 eV. It allows to differ itinerant and localized 5f-electron states by studying the final-state effects in the VB and core 4f-regimes. Especially, the latter effect, where the holes were left behind in a photo excitation process makes a disturbance in the initial ground state. For discussion see [82B1] and [84B4]. As to the VB, the 5f-emission for AmN moves away from E_F to higher binding energies (BE) and exhibits the spectral shape of a 5f⁶ final-state multiplet, i.e. 5f⁶ initial state (see e.g. Fig. II.109). In general there are distinct differences among the various PE spectra for the UX compounds (Fig. R.23). For UN the PES (40 eV) shows a 1.4 eV-wide 5f-6d hybridized conduction band cut by E_F according to the theory [84B1]. By applying angle resolved (AR) PES one gets more striking results as for example a new BZ for $T < T_N$, despite the same unit cell of crystal and magnetic structures [83RHH]. While this study proves the 5f band dispersion, i.e. the itinerant character of the 5f electrons in UN, the recent high-resolution ARPES data [01IKST] present two non-dispersive bands located close to E_F (see Fig. II.22), instead of the highly dispersive U 5f-6d hybridized bands predicted by calculations [79EK2], [84B1]. Nevertheless, a clear difference occurs in comparison of the data for UN (Fig. II.22) and USb (Fig. V.20 and 21). The more itinerant U 5f electrons of UN located closest to E_F contribute much to the heavy-electron metallic nature of this compound (compare in Table 3 that $\gamma(0)_{UN} \gg \gamma(0)_{USb}$). Simultaneously, there is also a localized character of U 5f electrons in UN as evident from the U 5f²-final state-multiplet satellite in its ARPES spectrum. All this points to a new idea of a dual (itinerant and localized) character for both monocompounds UN and USb, though the itinerancy in UN is considerably stronger than that marked in USb. The intermediate mononictides UP and UAs can be described in a similar way but with only different weight of these two f electron characters.

Kalkowski *et al.* [87KKBS1, 2] studied a series of mononictides of U, ²³⁷Np and ²³⁹Pu by the near-edge X-ray absorption (XA) spectroscopy at the L₃ threshold. The spectra exhibit single-peaked white lines at threshold,

which shift by up to 6 eV to lower energies relative to the tetravalent dioxides (see Fig. IV.1). These shifts systematically increase from U to Np and next to Pu, or with increasing Z number of the X-element reflecting increasing localization and occupancy of the 5f states, in analogy with the rare-earth situation.

Optical spectroscopy covering large photon energies between 0.03 and 12 eV, needs large single crystals. The first data were obtained by J. Schoenes on USb and UO_2 [78SV]. Since 1978 a large number of such investigations have been done which are described in vast reviews [80S1-3], [84S3], [86R], [90RS] and [98S]. This spectroscopy gives information on the allowed dipole transitions from the VB (mainly p-electrons) to CB (mainly derived from U 6d electrons) and the transitions between U 5f \rightarrow U 6d and Xnp \rightarrow U7s. The d-band splits in the octahedral symmetry into two bands, which in atomic notation are t_{2g} and e_g . The peaks, e.g., observed in the real (ϵ_1) and imaginary (ϵ_2) dielectric functions depending on photon energy (see Fig. V.73a), were interpreted in terms of f \rightarrow d and p \rightarrow d transitions which allowed to construct, e.g., for USb, the energy level scheme (Fig. V.73b). Both occupied and empty parts of the band structure contribute to the spectra. An increased hybridization of the U 5f states with U 6d or/and X 2p leads to a distribution of the spectral weights over a large energy scale.

B. Crystal electric field approach

In the case of 5f-electron localization, the four main energies scale as follows:

1) the intra-atomic Coulomb interaction is about 5 eV, 2) the spin-orbit (SO) splitting is about 0.3 eV, while 3) the crystal electric field (CEF) and 4) the exchange magnetic interactions are of about 0.1 eV and 0.01 eV, respectively. Due to being much less screened, the 5f-electrons are much stronger influenced by the CEF interactions compared to those experienced by the 4f-electrons in the lanthanide isomorphous compounds. The electronic energy levels of the lighter actinide ions were first recognized by Carnall and Wyborne [64CW]. Since the SO and CEF splitting energies are comparable for the lighter actinides, the admixture of different J -excited states into the ground state should be taken into account (see ref. [74CL]). Thus, the combination of strong both SO and CEF interactions causes that a so-called intermediate coupling (IC) scheme should be used in the interpretation of magnetic characteristics of actinide compounds. The energy diagrams in the terms of irreducible representations of the point group symmetry operation, Γ 's, found by the IC- approach for the low lying states at the $f^2 \dots f^6$ electron configurations are presented in Fig. R.10.

A review on the light actinide ions being in octahedral (O_h) electric crystal field, including intermediate coupling has been presented by Chan and Lam [74CL], which in turn can be compared with a review on lanthanide ions located in such a symmetry which has been presented by Hulliger [78H]. The values of p_{eff} and p_0 in the Russell-Saunders (R-S) and intermediate coupling (IC) schemes, depending on 5fⁿ electron configuration is displayed in Table I.

Table I. Paramagnetic effective moments p_{eff} and ordered moments p_0 in both L-S and intermediate coupling (IC) models as a function of the number of equivalent 5f electrons n [87HN]. Ground state level split by CEF (R-S) in octahedral symmetry.

n	$p_{\text{eff}}(L-S)$ [μ_B]	$p_{\text{eff}}(IC)$ [μ_B]	$p_0(L-S)$ [μ_B]	$p_0(IC)$ [μ_B]	Ion An ³⁺	Level
0	0	0	0	0	—	Γ_1
1	2.54	2.54	2.14	2.14	U ⁵⁺	Γ_7
2	3.58	3.63	3.20	3.24	U ⁴⁺ ³ H ₄	Γ_1
3	3.62	3.79	3.27	3.42	U ³⁺ ⁴ I _{9/2}	$\Gamma_8^{(1,2)}$ or Γ_6^*
4	2.68	2.89	2.40	2.59	Np ³⁺ ⁵ I ₄	Γ_1 or Γ_5
5	0.84	1.24	0.71	1.04	Pu ³⁺ ⁶ H _{5/2}	Γ_7
6	0	0	0	0	Am ³⁺ ⁷ F ₀	Γ_1
7	7.94	7.6	7.0	6.7	Cm ³⁺ ⁸ S _{7/2}	Γ_8 or Γ_7
8	9.72	9.3	9	8.6	Bk ³⁺ ⁷ F ₆	Γ_2 or Γ_1
9	10.63	10.2	10.0	9.6	Cf ³⁺ ⁶ H _{15/2}	Γ_7 or Γ_8
10	10.60	10.3	10.0	9.7	Es ³⁺ ⁵ I ₈	Γ_3 or Γ_1
11	9.59	9.5	9.0	8.9	Fm ³⁺ ⁴ I _{15/2}	Γ_7 or Γ_8
12	7.57	—	7.0	—	—	Γ_2 or Γ_1
13	4.54	—	4.0	—	—	Γ_6
14	0	—	0	0	—	Γ_1

*) The ground state depends on the parameter ratio B_4/B_6 in the CEF potential.

The latter coupling scheme changes completely the LLW diagrams [62LLW], which are important in the case of the R-S coupling into those shown in Fig. R.10. Thus, these Chan-Lam's diagrams give an idea about the ground state CEF levels in the case of so-called $J - J$ state mixing. Such calculations, applied to determine $\chi(T)$ for the first time, were done for UP and UAs (see Fig. III.19 and Fig. IV.18, respectively) as well as for PuP (Fig. III.90).

The complementary technique of inelastic neutron scattering (INS), used so effectively for determining the CEF schemes for systems containing the 4f-ions [86FL] within the spectroscopic ground state terms, $(^{2S+1})L_J$, has been completely ineffective in 5f systems [85BH], probably because of the hybridization effect and large magnetic exchange interactions with respect to the former systems causing a broadening of conventional CEF levels [88HKBC]. Only in the case of very magnetically diluted systems, like $U_{0.08}Y_{0.92}Sb$ (Fig. V.108) and $U_yNd_{1-y}P$ (Fig. III.74b), it has partly been successful. It should be emphasized that the commonly observed absence of sharp CEF excitation in the actinide compounds is caused by many features, not only due to the possible itinerancy of f-electrons.

So far only the experiments aimed at determining the magnetic form factor of USb (Fig. V.34a), PuP (Fig. III.92) and PuSb (Fig. V.135) have allowed one to anticipate a $5f^3$ (U^{3+}) or a $5f^5$ (Pu^{3+}) ground state configuration for these highly localized NaCl-type actinide materials.

For small scattering vector Q ($= 4\pi/\sin\theta$) in the dipole approximation the form factor is expressed as an expansion in terms of Bessel transforms of magnetization $M(r)$

$$f(Q) = \langle j_0 \rangle + C_2 \langle j_2 \rangle + \dots \quad (1)$$

The coefficient C_2 numerically lies between 3.6 and 4.6 for all the localized systems.

Especially for the latter two cases (PuP and PuSb), where the magnetic amplitude increases as the scattering angle increases and the form factor goes through a maximum for the scattering vector $Q > 0$ (see Fig. V.135), one can obtain practically unambiguous information about the ground state of these plutonium monopnictides and about the spatial extent of the 5f functions. In turn, a study of the form factor of USb showed also that the magnetization density of the ground state function is *oblate* in shape being appropriate for a $\Gamma_8^{(1)}$ state, while for a $\Gamma_8^{(2)}$ state, this density is *prolate* (see Fig. V.34b). However, if no CEF excitations have been found for pure USb (see Fig. V.33), it was seen for the magnetically dilute system $U_{0.08}Y_{0.92}Sb$ (Fig. V.108) in the form of a magnetic inelastic peak at 20 meV [80FV]. In the literature there are also cases of describing magnetic excitations in USb (Fig. V.42) or the p_U vs. T dependence (Fig. V.35) based on the so-called HMTII model described below in view of LLW-parameters used.

By analyzing the angular dependence of the scattering of thermal neutrons, it is possible to determine the individual orbital p_l and spin p_s components of the total magnetic moments for actinide compounds [92L], [93L2]. The ratio p_l/p_s was found to be related to the Landé g splitting factor as follows:

$$p_l/p_s = C_2/(1 - C_2) = (1 - g/2)/(g - 1) \quad (2)$$

Here, the C_2 coefficient is experimentally determined from the measured $f(Q)$ curves (see relation (1)). The results for USb and PuSb are plotted together with other actinide compounds as a function of f^n in Fig. V.57, which follows well a prediction of the single-ion theory, including intermediate coupling [92L].

C. Energy band structure

The first attempts to determine the energy band structures (EBS) of actinide NaCl-type compounds were calculations without self consistency. Both approaches, the non-relativistic and the relativistic ones with crystalline field effects included in the latter, were made by Adachi and Imoto with the tight-binding (TB) approximation, based on the rigid band concept [69AI]. These calculations showed that it was indispensable to consider the spin-orbit interaction (SOI) in EBS calculations for the NaCl-type actinide compounds. The SOI splits the 6d and 5f levels into $6d_{3/2, 5/2}$ (~ 0.4 eV) and $5f_{5/2, 7/2}$ (~ 0.7 eV), respectively. With the same method the band structures of the ThX series ($X = C, N, P, S$), including the parametrization improvement, have been also calculated [75IAH]. They resulted in the resolution of the DOS curves into four components s, p, d_g and dt_{2g} and in the nature of bonding in ThX compounds.

The next calculations based on the KKR [74D] and LMTO [79AB] methods revealed the f-electron bandwidths to be broader than those in the TB calculations, because of neglecting in the latter the effect of hybridization between cation f-states and anion p-states. However, the latter reproduces the correct trends in an

unhybridized band width W and lattice parameters (see Fig. R.21). The former-type calculations were made for the following actinide monocompounds: ThP, PuN, NpSb and US. All potentials were obtained here by using relativistic Hartree-Fock-Slater wave functions for the actinide atoms, while the non-actinide atomic wave functions were the non-relativistic ones.

Furthermore, Weinberger and Mallet [79MW] have based their calculations on the relativistic single-site scattering phase shift model applied to the uranium monochalcogenide and monpnictide series. For results of the latter approach see Fig. R.20, where resonant χ -like differential Friedel summands for uranium and X-nonmetals are shown. The calculations indicated that the U 5f-electrons form a narrow well-localized band in this series. In the next step the results of RKKR calculations for UN ([80WMPN], [82W]) and UC ([79WPMN], [82M]) have been reported. One should mention also the RAPW calculations for UC [77FK] and molecular orbital (MO) calculations of UN [80JG] as well as the cluster calculations using self-consistent cellular multiple scattering techniques for UC and UN [79EK2] or for UN [79KE]. The ground-state properties of all the NaCl-type series were then treated by the sc-LMTO method [80BG1, 2]. It appeared that these band calculations give a rather similar picture for the electronic structure of all the UX compounds, namely the hybridized 5f-6d bands are cut by E_F , and several eV below this energy the anion derived p bands set in. The linearized KKR ASA equations were next used to determine trends in energy band structure across the series [84B2], but with neglecting the spin-orbit coupling. The obtained charge densities in the uranium and pnictogen spheres are given in Fig. R.22. On this basis the decrease in the fractional volume occupied by the uranium atoms leads to a narrowing of the d-f band and concomitant increase in DOS at E_F . In turn the RLMT0 calculations made for the actinide nitride series from Th to Am ([82B2], [84B1, 3]) have shown their band structure trends.

In the band calculations the strong correlation effect of 5f electrons was usually treated by LSDA, which however turned out to be not sufficient for more localized systems. Hence for a realistic description of the electronic structure, e.g. of the Am-[01PSTS] or Pu-[02PSTS] rocksalt phases, both correlations and valency fluctuations have been taken into account. The methods capable of describing electron localization is the self-interaction corrected (SIC)-LSDA which was successfully used for these two cases. This approach (see Fig. R.1) allows for an integer number of states to be localized, while the others are available for band formation. In other words the experimental data can be interpreted in terms of the coexistence of both localized and delocalized f-states, somehow defining the so called *dualism* of f-electrons.

1.3.1.1.1.5 Magnetic properties

A. Magnetic structures

The rocksalt-type monocompounds can be considered as ideal models for studying the magnetic properties of the 5f electrons (see Table 2). Nevertheless, despite many research efforts which have been made during more than the last 40 years of studies of the magnetism for this type of compounds its nature is still not completely understood. Early models were based on analogies with corresponding lanthanide monocompounds involving CEF and MF interactions of localized 5f electrons. A little later it turned out that the physics of all those NaCl-type compounds is first of all determined by already mentioned hybridization of 5f electrons with ligand's electrons, leading to the sizeable mixing of f with band s, p, and d (valence and/or conduction) electrons. The hybridization term has been introduced by Anderson and described by its well known Hamiltonian, which includes the band-f Coulomb exchange and the band-f hybridization on equal footing. As a result of the above electron mixing, the magnetic properties of actinide group of materials are very strongly anisotropic and have a different magnetization easy axis than in the situation caused by crystal electric field interactions (single-ion anisotropy) only, and hence the conventional localized crystal electrical field (CEF) theory can not be applied in such cases. These problems concern mainly the first representatives of the actinide series. If one proceeds to heavier members of the actinide family, i.e. to the transplutonium ones or down the Vth group of ligands, the 5f electrons become more localized with a simultaneous decreasing of the hybridization effect. Already for the AmX compounds and beyond the 5f electrons are localized and their magnetic properties resemble those of homologous 4f compounds, i.e. the Eu^{3+} counterparts. So, by progressing across the actinide series beyond Pu, the 5f electrons in their behaviour start to resemble the rare-earth 4f-electrons. On the other hand, the studies of the actinide monocompounds containing heavier An elements are very limited due to minute quantities available and their high radioactivity. Therefore a somewhat better recognition of their magnetic properties in the near future seems to be rather unattainable.

In order to recognize the magnetic properties of the mononpnictides considered here, besides conventional magnetic measurements, neutron scattering, both elastic (see [84RLB]) and inelastic (see [85BH]) ones, and recently developed resonance X-ray magnetic scattering (see below), have now become one of the most important probes for these purposes. It is indispensable to know all about the formed magnetic structures and their dependence on external variables (temperature, magnetic field, pressure and uniaxial stress) [82RBQE], [95LB].

The first determinations of magnetic structures, performed on polycrystalline samples, date in the 1960's, as for example on UN [65C], UP [66C], [66SVA], UAs [68LMT], USb [68LMT], [69KLB] and UBi [69KLC]. They are all commensurate and mainly type-I (Fig. R.14). These structures are characterized by ferromagnetic (001) planes perpendicular to the c-axis and coupled antiferromagnetically with a stacking $+ - + -$. The magnetic unit cell has the same size as the chemical one, i.e. with a wavevector $k = 1$. The exception is a second structure (type IA) (Fig. R.14) formed in UAs at roughly about $T_N/2$ with $k = 0.5$ and the stacking $(+ - - +)$, being a new type of magnetic ordering not predicted by the MFA theory for fcc structures (see [68LMT] or [68LKB]).

The availability of single crystals of UX compounds, starting since 1974, and their neutron diffraction studies performed under uniaxial stress or in magnetic fields done mainly by Rossat-Mignod and his coworkers [87R1] have revealed that the magnetic structures are much more complicated than it was known from the first investigations on polycrystalline samples. These studies have established e.g. for UP and UAs at low-temperatures, far below their T_N 's, the presence of multi- k structures and also for USb, but at all temperatures below T_N [84RLB]. The multi- k configuration is defined by the presence of more than one propagation vector k needed to fully describe a given magnetic structure. The variety of such structures in the framework of the type-I and type-IA structures are presented in Fig. R.14 and the reduced volumes of Brillouin zones associated with such ordering in Fig. R.15. The multi- k structures are realized due to a competition between single-ion anisotropy and an exchange anisotropy [87R1]. For a better understanding of the multi- k structures, the reader is referred to the literature [83MW], [84RLB], [87R1] and [95LB]. As already mentioned above, the discovery of multi- k structures in AnX was possible due to applying an external perturbation allowing to change the domain population, which without external perturbation is usually random, for each domain with a volume of 1/3. In general these structures prevail at low temperatures, except for NpP (see MPD in Fig. III.80). This was done for the first time by Rossat Mignod *et al.*, who have pointed out that just the change in the random domain population in AnX allows to notice a difference between the diffracted neutron intensities of single- k and multi- k cases.

Earlier neutron diffraction (ND) experiments, especially done on mixed uranium systems showed that the ferromagnetic (001) planes could be arranged in a variety of ways, in commensurate or incommensurate magnetic unit cells. For example, the performed ND-experiments made on Np mononpnictides [74ADHL] revealed the longitudinal magnetic structures with periodicity of $3+3-$ (NpP) or $4+4-$ (NpAs). For these two Np mononpnictides also incommensurate magnetic structures were found close to T_N , which locked into commensurate modulations at a temperature $T_0(T_{IC})$ being lower than T_N . Studies of UAs by diffuse neutron scattering in the temperature range above T_N have shown that the spin correlations in this compound are strongly anisotropic with tendency to form a precursory incommensurate magnetic order (see e.g. Fig. IV.49). However this is stopped at T_N where the first order transition to commensurate AFI- $1k$ structure takes place.

More detailed studies of magnetic structures of the AnX monocompounds have recently become possible by applying the resonant X-ray magnetic scattering (RXMS) technique first applied to UAs [90MVII], [92LS]. This technique uses X-rays produced by a synchrotron tuned to one of the absorption edge L_3 , M_4 and M_5 energies (for e.g. M_4 , $h\nu = 3.728$ keV for uranium, 3.852 keV for neptunium and 3.968 keV for plutonium). However, due to the limitation by the penetration depth of the material by X-rays to about 1200 Å, this technique is very sensitive to the near-surface volume of the sample, which may introduce the difference between the surface and body states of the investigated sample. Nevertheless, a careful experiment performed by using RXMS has shed light on new many details in studies of magnetic structures of AnX compounds. For reviews see: [92LS], [95LSLG], [99MLLR], [99CS] and [99SC].

The stabilization of the multi- k structures requires high-order terms in the free energy expansion. This is provided by the presence of large anisotropic exchange interactions. Moreover, the quadrupolar effects were responsible for the $1k - 2k$ transition in UAs [78C]. Synchrotron experiments have provided a more complicated critical scattering picture and suggested at least two components (sharp and broad) and thus two correlation lengths (see e.g. for USb Figs. V.48,49 and 56). It is claimed that strains in the surface region of the sample is the origin of this phenomena [95ANP]. It has turned out very recently, that RXMS gives access to magnetic

Bragg reflections which are forbidden in neutron and non-resonant X-ray diffraction [02LPBL]. This yields new possibilities to study multi- k structures, without applying external forces.

Mössbauer spectroscopy is also an excellent tool for electron structure and magnetic properties studies, but is limited to the constituent, which is active in this spectroscopy. This is mainly appropriate for the Np nucleus and to a lesser degree to the Am nucleus (see for a review [85DK] or [93PKG]). The Mössbauer effect investigations in NpX undertaken by Kalvius and his coworkers in the early 1970s have added much to our knowledge about these Np series. As shown next by Dunlap and Lander [72DK], [74DL] a simple linear relation exists between the hyperfine field B_{hf} and the ordered magnetic moment of Np^{n+} ($n = 3, 4$). This relation is as follows

$$B_{\text{hf}}/p_0 = 215 \text{ T}/\mu_{\text{B}} \quad (3)$$

and is presented in Fig. R.48 in the form of the slope of the B_{hf} vs. p_0 straight line. The B_{hf} values and other parameters for NpC and NpX compounds are given in Table 13.

B. Theoretical considerations

Despite the rich and unusual magnetic and electronic properties of the NaCl-type actinide monocompounds developed during the last 40 years by many experimentalists, only small numbers of theoreticians have been working on this fascinating subject, probably due to the large complexity of these structurally simplest compounds. For the NaCl-type uranium compounds the stability range of magnetic ordering of their various types were first studied by Grunzweig-Genossar et al. [68GK] and [68GKF] using the RKKY theory (see Fig. R.13b). It seems however that the RKKY interaction is insufficient and that *superexchange* through the anions should play also an important role in the NaCl-type actinide compounds [70AI]. This is evidenced when one deals with the solid solutions where the X atoms are mixed. Then, a MFA consideration was reported to be used to calculate T_{N} and Θ_{p} and the exchange interaction constant J_{nm} for different uranium pnictides including the monocompounds [73AI2]. However, the theoretical description of the actinide compounds is much more difficult and complex than in the case of their similar counterparts in the RE-family, i.e. Ce and Yb. The latter have one f-electron or one f-hole on their 4f-electron shell, respectively, while the light actinides have them from 3 to 6 on the corresponding 5f-shell. This multitude in f-electrons leads to the main sources of difficulty in the treatment of the hybridization between the f- and conduction (k) or valence (p) states.

The electron-delocalization model applied to some uranium monocompounds like UP, UAs and NpC [73RE] and solid solutions U(P,As), U(P,S) and U(As,S) [74RE] was proposed by Robinson and Erdös (see their book [83ER]). They have assumed that the transition $5f^n \rightarrow 5f^{n-1}$ (6d–7s) occurs for a certain fraction of the ions at different temperatures (see Fig. R.13a). The free energy is minimized with respect to the occupation numbers in two different configurations (see e.g. Fig. III.24). The model has been shown to provide a quantitative explanation of the experimental sublattice magnetization, magnetic susceptibility, magnetic phase changes and the fractional valence of the actinide ions as a function of temperature (see e.g. Fig. III.25).

Next B. Cooper and his coworkers [85CSYT], by using a Schrieffer-Wolf transformation, giving an effective two-body (k-f) coupling between conduction electrons (CE) and magnetic and electric multipoles of the 5f electrons, have eliminated charge fluctuations in the f-orbitals by second-order perturbation theory. This gives rise to a Coqblin-Schrieffer-type exchange Hamiltonian, which next is reduced to an effective Hamiltonian, H_{ij} , describing interaction between the U ions at different sites. Solution of H_{ij} has become the base of hybridization-mediated two-ion-interaction (HMTII) model, which with a success has been applied to Ce and U-monopnictides. A phenomenological parameter E_{ij} was introduced to this Hamiltonian which describes the distance function between i and j ions. The interactions derived depend on the number n of f-electrons and on the intraionic coupling. Thus, in the framework of this model, Thayamballi and Cooper [85TC] have performed among others a theoretical description of the magnetic behaviour of the uranium monopnictides: UP, UAs and USb (see Figs. III.26, IV.26 and V.35, respectively). However, in addition to HMTII they had to put a small isotropic Heisenberg interaction H_{ij} and a crystal-field term (expressed in the LLW-parameters W and x) to obtain the observed experimentally phase transitions and the magnitudes of the ordered magnetic moment. The effective-interaction model mentioned above was used within a MFA for a fcc cubic lattice of U^{3+} ions and the non-collinear structures in some UX monopnictides could be theoretically reproduced by a special choice of the phenomenological parameters E_n or H_n (for details see ref. [85TC]). The problem appeared however to reproduce the I/IA magnetic transition in UAs.

On the other hand, it was also possible to explain the broad continuum of magnetic excitations in UP (Fig. III.27) and UAs (Fig. IV.27) by calculation of the dynamical susceptibility $\chi^{\alpha\beta}(\mathbf{q})$ by applying to the above described model a projection-operator method [88HC], [89HCL] and [93HC].

Finally there should be mentioned the theory of Cooper et al. and its relation to experiment in the case of PuSb. For example this theory was successful in predicting in this compound the transition from the ferro- to a type I antiferromagnetic phase (see Fig. V.132), though with much larger moments than were observed. A number of attempts were made by these authors to explain the magnetic excitations in PuSb [86BC].

1.3.1.1.6 Transport properties

The electrical transport properties of the AnX compounds have not been studied so far with satisfying attention. The earliest electrical resistivity measurements, made often in a wide temperature range for the monocarbides and mononitrides of Th, U and Pu or for their mutual solid solutions, were dictated by the development of nuclear energy. Hence, there were many studies of physical properties on the post irradiation examined samples. Usually they were carried out on hot pressed sintered or arc-melted samples (see e.g. Fig. I.34). The measurements evidenced their metallic character. The first measurements on single crystals of these materials were carried out by [83MHOK] for UC and [76NKMT] for UN. Several years later the Hall effect (R_H), magnetoresistance (MR) and dHvA effect for single-crystalline UC were investigated [90OUKS]. The resistivity follows an aT^2 dependence up to 160 K [88MKY], probably caused by electron-phonon scattering, while MR gives evidence of equal carrier numbers of holes and electrons what surprisingly makes UC rather a semimetal than a metal, despite the low values of the resistivity ($\rho \approx 40 \mu\Omega\text{cm}$ at RT). There exists a mass enhancement up to 15 m_0 associated with the spin fluctuations of the 5f electrons [01YHMI]. The detailed electrical transport single crystal measurements of UN have recently been carried out by [05DTSM] and compared to previous ones [76NKMT] and [77VD3] (see Figs. II.56-66).

The first electrical resistivity measurements performed on bulk materials of UP and UAs [74TK] were in agreement with later such measurements made on single crystals by [84SFV]. For both these compounds the $\rho(T)$ curves taken under high pressure and in magnetic fields are dominated by two first-order magnetic phase transitions at T_N and T_t (see Figs. III.38 and IV. 50-54). The $\rho(T)$ curve of USb is markedly different [84SFV] from that of UP and UAs. Not only this difference is marked for all values but first of all for the shape of $\rho(T)$ (see Fig. V.58). It is dominated by a very large broad maximum centered at 140 K, which can be explained by the formation of new Brillouin-zone boundaries due to the different periodicity of the magnetic structure being of AF-3k type. It is interesting to analyze the low-temperature resistivity following aT^2 , aT^3 and aT^4 power laws for UC, UN and USb respectively. The aT^4 or $T^2 \exp(-\Delta/k_B T)$ behaviour of $\rho(T)$ in USb found up to 45 K is probably due to following a linear magnon dispersion function as is predicted for an antiferromagnet and being confirmed by experiment (see Fig. V.40). Thus, exclusively for USb the other transport properties like Hall coefficient, thermoelectric power and critical scattering, have been determined. It turns out, as shown by electrical transport measurements that NpAs and NpSb also display a high sensitivity of the Fermi surface to their triple-k type I antiferromagnetic structures (see Figs. IV.114 and V.116), while in NpBi gaps are opened at low temperatures (Fig. VI.11). Among the other transuranium NaCl-type compounds only for PuSb some detailed measurements were made [85BCFR], [87TBFR]. Above T_N , $\rho(T)$ has a broad maximum, above which a Kondo-like behaviour has been detected (Fig. V.138). The Hall resistivity which goes through a pronounced maximum at T_C is shown in Fig. V.142. For the neptunium monocompounds interesting transport studies have been made under pressure (Figs. IV.114-117 for NpAs, Figs. V.116-119 for NpSb and Figs. VI.11-14 for NpBi).

1.3.1.1.7 Arrangement of tables and figures

In the present compilation the order of presentation is as follows: the data are arranged according to the position of the non-actinide element in the periodic table, first monocarbides and then mononitrides, monophosphides, monoarsenides, monoantimonides and finally monobismuthides. In each group the data are presented according to increasing atomic number of a given actinide elements, starting from thorium and ending at californium. The pseudobinary systems are located immediately after the binary compounds in which the actinide or non-actinide components are mixed.

In the compilation the electronic, structural, magnetic, thermodynamic, electrical and thermal transport or related properties of actinide mononitrides are presented in the form of figures and tables. The surveys providing main data and literatures for a given monocompound allow easy finding the interesting physical properties and relevant literature. The labels "s.c.", "poly" (in some special cases), "sintered", "thin film" were

used to determine the macroscopic status of the investigated materials. The lack of any label means that the data were found for powder or polycrystalline samples without the needs to emphasise it.

The information about the physical properties for a given monocompound or a solid solution compiled in the surveys, tables and figures may be subdivided into several distinct groups:

- a) Electronic and structural properties: band structure, Fermi surface, photoemission spectra etc;
- b) Lattice parameters, their temperature and pressure dependencies, elastic constants and phonon dispersion curves;
- c) Magnetic properties: temperature, field and pressure dependencies of the susceptibility and magnetization. Crystal electrical field interactions. Magnetic structures under normal or in externally perturbed conditions. Magnon dispersion curves, (T, B, p) magnetic phase diagrams obtained in elastic, inelastic, polarized and unpolarized, neutron and resonance X-ray magnetic scattering;
- d) Electron transport properties: electrical resistivity, magnetoresistivity, Hall coefficients, thermoelectric power etc.
- e) Thermal properties: heat capacity, Schottky effect, magnetic entropy and thermal conductivity.
- f) Spectroscopic properties: NMR, optic, magneto optic, Mössbauer and muon etc.