Crystal Field and Exchange Interactions in Cubic Uranium Semimetallic Compounds

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We have reviewed the aspects of the crystal field and exchange interaction effects in the series of the 1:1 and 3:4 uranium compoumds, having the NaCl and Th_3P_4 *type crystal structures respectively and semimetallic electrical properties. Attention is drawn to the strong connection of the above effects with the complex electronic structure of these materials. A general consideration of the appearance of the variety of magnetic structures in the pure compounds, as well as in their solid solutions, in view of both the degree of 5f electron delocalization and number of the conduction electrons is also given.*

Introduction

In the past decade a large effort has been directed towards the understanding of the electronic structure of the largest and simplest family of the uranium compounds, having cubic crystal structures. This large family includes the rocksalt type monocompounds: UC, UX (X = pnictogen) and UY (Y = chalcogen), as well as the Th_3P_4-type pnictides U_3X_4 (X = P, As, Sb and Bi) and chalcogenides U_3Y_4 (Y = Se and Te). The Laves phases are not considered in this review.

All the compounds mentioned above are magnetically ordered at low temperatures (except for UC) and show metallic character in their electrical conductivity. The monopnictides UX are antiferromagnets, while the monochalcogenides UY and the U_3X_4 pnictides are ferromagnets. The chalcogenides U_3Se_4 and U_3Te_4 are magnetically more complex and as yet they have not been examined satisfactorily.

We summarize below the various aspects of the magnetism of the pure compounds as well as of their solid solutions. However, despite the large efforts made in the past, magnetisms (especially of the monocompounds) have not been fully recognized so far.

Electronic Structure

To understand the striking magnetic behaviour of the uranium compounds their electronic structures (which intimately correlate) should be recognized.

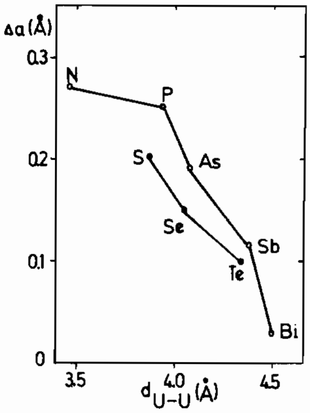

Fig. 1. The difference in the lattice parameters of the corresponding neodynium and uranium monocompounds as a function of the U-U spacing.

Rocksalt Uranium Compounds

In ionic compounds the number of electrons transferred to the anions is well established, and hence so is the electronic configuration of a given magnetic ion. In the case of an actinide ion this configuration is $5f^n$ (*e.g.* for the uranium ions: U^{3+}, U^{4+} and U^{5+}, n is equal to 3, 2 and 1, respectively). On the other hand, the situation in the metallic uranium compounds is more complex because their valence electrons are distributed to several adjacent electronic states, being usually hybridized to some extent. The latter effect implies a small deviation from a fixed valence of a given magnetic ion and suggests a possible non-integer f-electron occupation, supported (among others) by the observed trends in the experimental lattice parameters for the light actinide monocompounds [1]. In Fig. 1 the difference between the lattice parameters of the corresponding neodymium and uranium monocompounds is plotted as a function of the U–U spacing. There is clearly a large difference in the lattice parameters for the nitrides and an almost negligible one for the bismuthides. This may be indicative that the contribution of the 5f electrons to any chemical bonding strongly decreases with increasing interatomic distances.

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As shown by optical [2] and X-ray photoemission [3, 4] experiments, the electronic structure in the family is generally fairly constant. The differences appear between the monopnictides and monochalcogenides in the positions of the p-derived valence band and d-derived conduction band, whose separation is quite small for the monopnictides. This is indicative of a higher covalent bond effect in the UX series than in the UY series. There is also a small overlap between these two bands in the monopnictides, which gives rise to their semimetallic properties [5]. Their magnetic f-states, broadened by the hybridization effect, are located fairly close to the Fermi energy (E_F). However, the recent results of the photoemission study (using synchrotron radiation) on some uranium monocompounds also diluted by thorium and itrium homologues [6] have also shown some important differences in the photoemission density of states near E_F. These differences originate mainly from the presence of the d-electron band at E_F, which is rigidly filled with the electrons coming from increasing thorium or chalcogen content in the corresponding solid solutions.

These itinerant d-electrons are in resonance with the quasi-localized $5f^3$ states, which sink below E_F with a gap increasing with the U–U distances.

Th_3P_4-Type Compounds

The optical properties of U_3P_4 and U_3As_4, as well their thorium homologues, have recently been studied by Schoenes *et al.* [7]. The most striking feature of the electronic structure of the semimetallic uranium 3:4 pnictides (compared to the semiconducting thorium 3:4 pnictides) is the valence band shifting upwards in energy by 0.85 eV to give overlap with the conduction band. This finding also gives a localized position of the $5f^2$ electrons (U^{4+}) about 1.2 eV below E_F, and shows experimentally the presence of a strong p–f mixing effect in these uranium compounds.

Nature of Magnetism

Due to the unique electronic structure of the uranium atom in simple compounds, the question arises as to the proper description of the 5f electron magnetism, a question intensively debated for the last decade without reaching a final conclusion.

Experimental measurements still indicate evidence for a localized nature of the 5f electron, such as the Curie-Weiss behaviour, large values of the ordered moments μ_o (except for UN), the extended shape of the form factor dependence, as well as a good correlation between the temperature dependence of the Knight shift, relaxation time and magnetic susceptibility.

On the other hand, the band character of the f-electrons has strongly emerged from the earlier photoemission experiments [2–4] and from the large values of the low temperature heat capacities [8, 9], both pointing to the large density of states at E_F partially confirming the intensive band calculations performed for various uranium monocompounds [3, 10–12]. In addition, the inelastic neutron scattering experiments [13, 14] have revealed the existence of strong competition between magnetic (sharp spin wave excitations) and relaxational (very broad spin excitations) behaviour, where the predominance of the former features rapidly decreases with decreasing U–U distances.

Such a behaviour is believed to arise from the highly correlated 5f electron states, located in energy near E_F, and hence having many common features with the mixed-valent [7, 15] or Kondo lattice [14, 16] compounds, but all these appearances are certainly different from those of the rare earth compounds, due to the different energy-scaling involved.

It is clear that any simple model cannot correctly describe all of the known physical properties, particularly of the uranium monocompounds. In the latter compounds the contribution of the 6d electrons, not only to the transport properties but also to the total magnetism, additionally complicates the clear understanding of the magnetic behaviour.

Crystalline Field Effect

Rocksalt Compounds

Although the unique problem associated with the electronic structure of the rocksalt uranium compounds made it difficult to treat them in terms of existing simplified crystal field theories, there is strong evidence that the atomic-like character of the 5f electrons is, to a certain extent, preserved owing to the forming of a narrow 5f resonance state with high intra-atomic correlations. However, the large spatial extent of the 5f functions causes a large interaction with environments. In fact, the experimentally observed large crystal field interactions become quite comparable in magnitudes with the Coulomb and spin-orbit magnitudes. This fact alone leads to serious complications by breaking down the Russell-Saunders coupling, and as a consequence one needs to use an intermediate coupling scheme and J-mixing procedure (non-perturbative approach). Chan and Lam [17] reported the practical energy-level diagrams for several $5f^n$ configurations obtained for various strengths of the crystal field effect.

The uranium ions in the NaCl type crystal structure have an octahedral environment, for which the crystal-field potential, V_{CF}, in the Stevens O_m^n operator manner end for four-fold axis can be written as

$$V_{CF} = V_4(O_4^0 + 5 \cdot O_4^4) + V_6(O_6^0 - 21 \cdot O_6^4) \qquad (1)$$

where the crystal electric field (CEF) parameters V_m are related to the simple geometric, point charge model parameters A_m^n as

$$V_{\underline{m}} = A_m^n \langle r^m \rangle \chi \tag{2}$$

where $\langle r^m \rangle$ are the radial averages over the 5f electrons for a given ion, and χ is the corresponding Stevens multiplicative factor. However, a proper treatment of an actinide ion with the J-mixing effect requires the use of tensor operator techniques. Nevertheless, as Chan and Lam [17] pointed out, the J-mixing effect for the uranium ions U^{4+} and U^{3+} is less than 10% and in view of other contributions this can be neglected.

It is important to include into the total CEF Hamiltonian the contribution from the 6d-band electrons and the strong covalency effect (p–f mixing). At present such an approach is not available for the uranium compounds. There only exists an approach taking into account in the paramagnetic region for PuP a strong effect of the conduction electron polarization contribution into the total susceptibility [18]. This contribution is temperature-dependent and can be expressed as

$$\chi_{cep}(T) = -N(E_F)I_{sf}(o)(\langle S_z \rangle/H)\mu_B \tag{3}$$

where $N(E_F)$ is the total density of states at E_F, and $I_{sf}(o)$ is the exchange coupling parameter. The temperature dependence of the susceptibility comes from the $\langle S_z \rangle/H$ term being the spin projection on the magnetic field vector.

We expect the measured magnetic susceptibility of metallic rocksalt uranium compounds to have the following contributions to the measured susceptibility

$$\chi(T) = \chi_i(T) + \chi_{cep}(T) + \chi_{vv} + \chi_p \tag{4}$$

where $\chi_i(T) = C/(T + \theta_p)$ and may be related directly to the paramagnetic moment n_p of a given crystal-field ground state. The temperature-independent terms χ_{vv} and χ_p originate from the so-called Van-Vleck paramagnetism and from the Pauli paramagnetism, respectively. As mentioned above, χ_{cep}, is due to the polarization effect of the conduction electrons.

Hence, the magnetic properties of uranium compounds are often considered in view of the modified Curie-Weiss (MCW) law, because of a strong curvature of the $\chi(T)$ functions observed.

Troć and Lam [18] using the non-perturbative method have calculated for UP and UAs the temperature-dependent susceptibility and the spin projection $\langle S_z \rangle/H$, the latter being important in the Knight shift effect. They tried several $5f^n$ configurations where $2 \leqslant n \leqslant 6$, and crystal field strengths which ranged from 100–4000 cm^{-1} for $A_4\langle r^4 \rangle$ and from 0–1000 cm^{-1} for $A_6\langle r^6 \rangle$ taking into consideration both signs of these crystal-field parameters. The results of the best fitting obtained for $5f^3$ configuration for uranium ions (U^{3+}) are shown in Fig. 2.

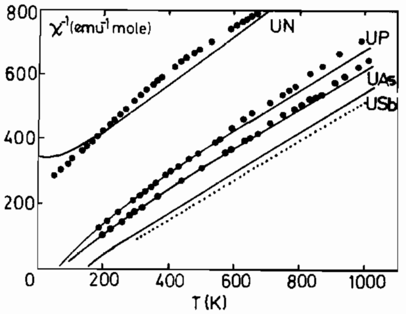

Fig. 2. Comparison of experimental χ_M^{-1} data for UN, UP, UAs and USb (closed points) with the theoretical data (full lines).

As is well known, the odd number of electrons on the unfilled 5f shell under crystal field effect gives Krammers-type ground states. For the U^{3+} ions a Γ_6 doublet and two quarters $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$ are possible.

The calculation for both these monocompounds proved the ground state to be quartet $\Gamma_8^{(2)}$, being rich in the $|M = 9/2\rangle$ component. On the contrary, Sinha *et al.* [20] made measurements of the magnetic form factor for single crystalline UAs and unexpectedly found an oblate magnetization density shape, quite opposite to that expected for the ground state function of $\Gamma_8^{(2)}$ (prolate). Similarly Lander *et al.* [21] measured an anisotropy of the magnetic form factor on a single crystal of USb. An excellent agreement was attained for only one model incorporating a $5f^3$ uranium ion state (U^{3+}) with $\Gamma_8^{(1)}$ crystal field ground state, which is rich in the $|M = 7/2\rangle$ component, and its magnetization density has an oblate shape. Surprisingly, this state implies a change in sign for the crystal field parameters V_4 and V_6, as if the Sb metalloids have positive charges. However, in view of the presence of itinerant d-electrons at E_F, the conduction electrons may considerably affect V_{CF}, leading in consequence to change of even the CEF parameter signs. Zołnierek (unpublished) has calculated the χ_M^{-1} *vs.* T function for USb based on the CEF parameters incorporated from neutron diffraction measurements, and found a good agreement with the χ-data of Bush *et al.* [22], which are displayed in Fig. 2.

The crystal field level sequence is $\Gamma_8^{(1)}$, $\Gamma_8^{(2)}$ and Γ_6 with energies 0, 371 and 440 K. The ground level quartet $\Gamma_8^{(1)}$ has the following composition

$$\left\{ \begin{array}{l} 0.015|\pm 9/2\rangle + 0.247|\pm 1/2\rangle - 0.969|\mp 7/2\rangle \\ 0.564|\pm 5/2\rangle - 0.826|\mp 3/2\rangle \end{array} \right\} \tag{5}$$

which leads to $n_p = 2.31\ \mu_B$ and $\mu_o = 2.37\ \mu_B$.

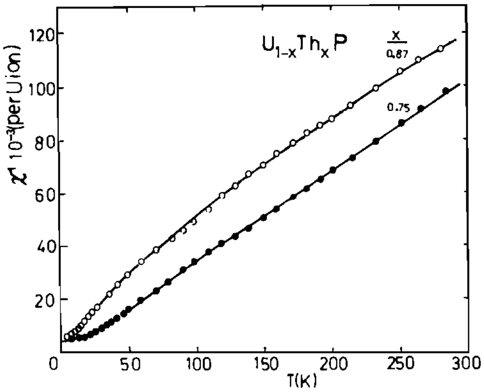

Fig. 3. Reciprocal susceptibility per uranium atom of the two compositions of the (U, Th)P system, as a function of temperature (see [32]).

As also shown in Fig. 2, the results of the calculations by Lemmer and Lowther [23] for UN, based on the two crystal field model and on an assumption of a $5f^2$ electron configuration for uranium ion, follow unsatisfactorily the experimental results [24].

For the uranium monochalcogenides there were attempts to fit the theoretical results obtained by assuming different electronic configurations for uranium atom (from $5f^1$ to $5f^4$) to the experimental susceptibility data [17] without, however, attaining any reasonable agreement. It seems that the observed pronounced curvatures of the χ^{-1} *vs.* T function for UY at higher temperatures are caused by a large contribution of Pauli susceptibility, due to the 6d-electrons. On the other hand the low temperature χ-data follow the Curie-Weiss law with high accuracy [25], yielding values somewhat low for the effective moments (μ_{eff} = 2.4–2.9 μ_β). For the U^{3+} ion they are usually considered to be markedly larger. The deduction of the ground wave function from the neutron diffraction experiments, performed for US [26] as well as for UTe and $USb_{0.8}Te_{0.2}$ [27], becomes difficult because of the lack of an anisotropic behaviour in their form factors.

Finally, it should be emphasized that no sign of discrete crystal field transitions were found in some lighter UX and UY compounds using neutron spectroscopy [20, 28, 30]. This failure, as well as the Schottky type anomalies [31], is probably a result of the strong f–d interactions [14]. However, for the monocompounds USb [29] and UTe [30] with the fairly large lattice constants the f–d fluctuations become slower, therefore allowing the appearance of relatively flat crystal-field type transitions at 8.5 and 6 THZ, respectively.

Rocksalt Type Solid Solutions

Until now there have been no systematic studies of the paramagnetic characteristics for the solid solutions formed by a given uranium monocompound with a nonmagnetic isomorphous monocompound, like UX–ThX, UY–ThY, UX–YX *etc.* The most striking and important results are those for most diluted solutions. As shown in Fig. 3 in the case of dilute UP–ThP samples an apparent levelling off of the susceptibility to the constant value at the lowest temperature is observed [32]. Moreover, the small saturation magnetization obtained for $U_{0.1}Th_{0.9}P$ [32] and $U_{0.1}Th_{0.9}Sb$ [33] are more pertinent to the four than the trivalent uranium state, as Fig. 4 indicates [33]. Figure 4 compares the theoretical magnetization curves of U^{3+} and U^{4+} ions, calculated by using the CEF parameters as obtained for USb [21] and for USb-ThSb [34], with the experimental results obtained for the two above compositions.

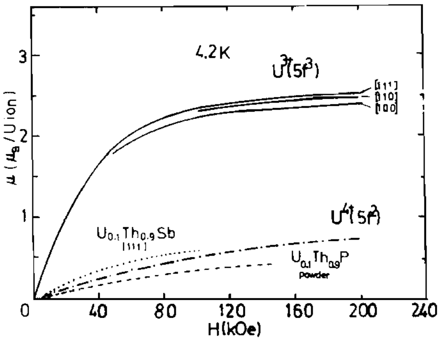

Fig. 4. Theoretical magnetization curves for U^{3+} and U^{4+} ions, compared with the magnetization curve of $U_{0.1}Th_{0.9}$-Sb, after Cooper and Vogt [33]. Magnetization data for $U_{0.1}$-$Th_{0.9}P$ are from [32].

The results obtained on other systems, like UY–ThY [35, 36], seem to be similar to those of UX–ThX type in the dilute region, with the exception of UTe–ThTe [37], for which the different crystal structure of ThTe(CsCl-type) leads to a magnetic ground state for uranium, even in the most dilute region of concentrations.

An explanation of all the above experimental data is the occurrence of a strong antiferromagnetic coupling mechanism between localized 5f electrons and the conduction electrons, giving rise to the so-called Kondo compensated states being by nature non-magnetic. This implies that χ changes from a constant value for $T < T_k$, where T_k is the Kondo temperature, to a MCW behaviour for $T > T_k$, indicating the existence at low temperatures of a transition from the non-magnetic to magnetic state [38]. The electrical measurements of most diluted samples of UY–ThY [1, 36] and USb-ThSb [38] have confirmed their Kondo-like behaviour.

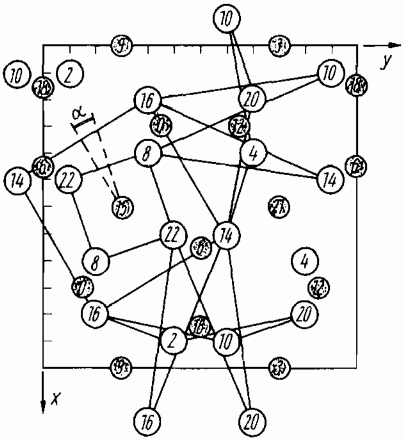

Fig. 5. The projection of the Th_3P_4 type structure on the (xy) plane. The small and large circles indicate the uranium and ligand atoms, respectively. The numbers give the z-component.

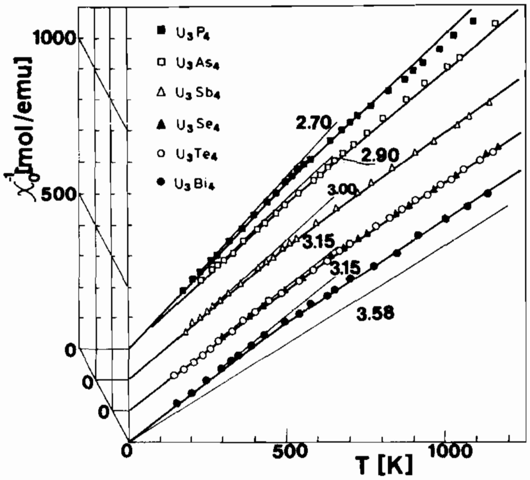

Fig. 6. The χ^{-1} *vs.* T dependences for the $U_3(X;Y)_4$ type compounds, corrected for the presence of the exchange interactions. The full lines are calculated according to eqn. (7). The data are from Ref. [39].

Th_3P_4-Type Compounds

Although the $U_3(X;Y)_4$ compounds also crystallize in a cubic structure, the Th_3P_4 type structure (space group T_d^6-$I\bar{4}3d$) is considerably more complex than that of the NaCl type. The projection of this structure on the (xy) plane is illustrated in Fig. 5.

Here there are three octaverticons built by X or Y atoms around each U ion, with S_4 point symmetry. The most striking feature of this structure is that the elongated axes $\bar{4}$ of these octaverticons are perpendicular to one another, yielding an unusual three-axial CEF anisotropy [39]. Due to S_4 point symmetry, V_{CF} is here more complicated with the general form

$$V_{CF} = B_2O_2^o + B_4(O_4^o + aO_4^4 - bO_4^{4\prime}) + \\ + B_6(O_6^o + cO_6^4 + dO_6^{4\prime}) \qquad (5)$$

First a simplified calculation [39], and then a more extended one made by J. Mulak (unpublished), leads to the following ground state

$$\left\{ \begin{array}{l} 1/\sqrt{2}\,|4\rangle - 1/\sqrt{2}\,|\bar{4}\rangle \\ \epsilon|4\rangle + \epsilon|\bar{4}\rangle + \gamma|0\rangle \end{array} \right\} \qquad (6)$$

being a pseudodoublet, and to the first excited doublet: $\alpha|\mp3\rangle + \beta|\mp1\rangle$, where α, β, ϵ and γ are the amplitudes.

The dependences of χ^{-1} *vs.* T in the range 77–1200 K, measured for all six $U_3(X;Y)_4$ compounds and corrected for the presence of the exchange interactions, are curvilinear [39], as Fig. 6 illustrates.

In general, the average susceptibility for these compounds can be expressed by a simple equation as

$$\bar{\chi} = 2.56\,\epsilon/T + B \qquad (7)$$

where B is the temperature independent term and hence $\mu_o = 4.53 \cdot \epsilon\ \mu_B$, being dependent only on the coefficient ϵ in eqn. (7).

The paramagnetic behaviour of the cubic U_3Se_4 and U_3Te_4 is more complicated because of the problem of stoichiometry and instability of Th_3P_4-type unit cells at low temperatures.

Magnetic Exchange Interactions

The magnetically ordered state is widely spread out in most of the metallic uranium compounds. It initially became clear that the magnetic ordering mechanism should be driven by the spin polarization effect of conduction electrons; the mechanism known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [41]. As is known, this interaction, characterized by the integral J_{sf}, is isotropic in nature. By contrast, more detailed magnetic investigations have shown that the cubic uranium compounds are anomalously anisotropic materials, presumably due to the existence of highly anisotropic exchange interactions.

Chan [42] was first to consider the angular anisotropy of the 5f orbitals and their role in exchange interactions through hybridization with 6d and 7s electrons and overlap with the p orbitals of the anions.

An explanation of the strange features met in the magnetic properties for both cerium and uranium monopnictides is based on the highly anisotropic two-ion Coqblin-Schrieffer (CS)-type interaction, which effectively causes f-electron hybridization with band electrons. A summary of the occurrences and consequences of this interaction has recently been given by Cooper [43], who has also emphasized the fact that CS–two-ion interaction is generically of a RKKY type. In the latter the band electrons provide a medium for generating an anisotropic coupling between predominantly localized ionic moments. In contrast to the isotropic RKKY interaction, in the CS exchange one has to assume a modest amount of f-electron delocalization.

On the other hand, a theoretical model which also explains the origin of unusual magnetic anisotropy in both Ce and U monopnictides whose magnetic properties in many aspects are similar to each other has recently been developed [44]. The model is based on the anisotropic mixing mechanism between f-states and the valence band, known as the f–p mixing exchange interactions. This mixing to be active requires the proximity of the f and Fermi levels, as well as the presence of even small amounts of the valence band holes. The latter interactions indicate the importance of the superexchange interaction in the case of the uranium compounds.

As Hill [45] pointed out more than a decade ago, the uranium–uranium spacing plays an important role in determining the magnetic and other physical properties.

It is clear that the small U–U distances favour a greater overlap of neighbouring 5f orbitals, being spatially more extended in real space than the 4f orbitals; as a result of the strong 5f–5f interaction (metallic bonding) the bandwith W_f of the 5f states increases to an appreciable extent. In addition, the hybridization effect of the 5f states with 6d and/or 7s states, but especially with the anion p-states (covalent bonding), effectively also increases W_f [46]. The latter interaction then produces the f-character in the valence band and the p-character close to the Fermi energy, effects which have both recently been confirmed experimentally [6, 7].

For example, the large 5f–6d–7s hybridization effect in uranium metal (d_{U-U} = 2.8 Å) gives rise to its non-magnetic behaviour (almost temperature-independent paramagnetism). For larger U–U distances (3.0–3.4 Å), but with W_{total} being still higher than the Coulomb correlation energy, U_C, the itinerant electron magnetism, can take place with different magnetic characteristics than the localized one, like *e.g.* UPt (weak ferromagnet with $T_C \cong 25$ K, $\mu_o = 0.5\ \mu_B$ per U atom and $\gamma(0) = 110$ mJ/K^2 mol. (see Ref. [47]). Here, the ferromagnetic properties of UPt originate from the band effect, *i.e.* the exchange splitting between the up and down spin sub-bands. On further increasing the U–U distances, the amplitudes of the local spin density fluctuations (see Moriya [48]) become sufficiently large to lead to the localized character of the magnetic moments. This implies a simultaneous rapid damping of the spin fluctuations driven here by the f–d hybridization effect and the 5f states, due to their energy narrowing, almost reach an integral occupation.

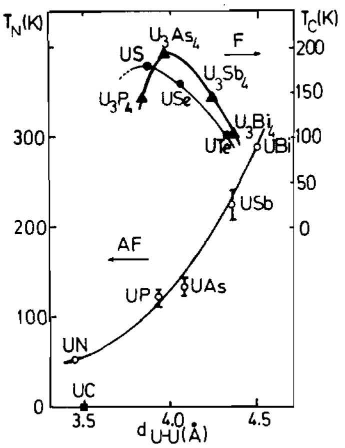

Fig. 7. The transition temperatures for the UX and UY series as well as for the U_3X_4 pnictides as a function of the U–U spacing. In the case of the latter compounds only the closest distances were taken into account.

Rocksalt Monocompounds

As already stated, all uranium monopnictides are antiferromagnets with increasing trends of both Néel temperatures (T_N) and magnetic-ordered moments (μ_o) on going down the pnictide column (Fig. 7). This fact indicates a monotonic growth in the strength of magnetic exchange interactions with increasing U–U separations and with more pronounced localized character of the 5f electrons. On the other hand, the trend in the Curie temperature (T_C) of the ferromagnetic uranium monochalcogenides (Fig. 7) is reversed. Although the μ_o's also rise, their values are relatively low (see Table I). Moreover, for the uranium monochalcogenides (which have more d-valence electrons due to divalence of chalcogens as compared to trivalence of pnictogens) a large conduction polarization effect has been observed [26, 27]. The neutron-diffraction derived values of the ordered moment are higher than those determined from the saturation magnetization (see Table I), so that the 6d-electron moment (μ_d) is antiferromagnetically aligned to the 5f-derived moment (μ_f) thus, the saturation moment $\mu_s = \mu_f - \mu_d$. The presence of the d-electrons at E_F in the uranium monochalcogenides (confirmed unambiguously by experiment) plays a crucial role in the difference in their magnetic behaviour with respect to the uranium monopnictides.

Table I shows also the existing differences between the UX compounds in the antiferromagnetic state. Now we will briefly describe these differences.

TABLE I. Magnetic Properties of Uranium Monopnictides and Monochalcogenides.

Compound	Magnetism	Ordering temperature (K)	Ordered moment (μ_B/U atom)	Saturation moment (μ_B/U atom)	μ_{eff} (μ_B/U atom)
UN	AFI–1k*	52 ± 2	0.75	–	3.1
UP	1. AFI–2k	<22	1.93	–	3.2
	2. AFI–1k	125 ± 2	1.72		
UAs	1. AFIA–2k	<63	2.25	–	3.4
	2. AFI–1k	127 ± 2	1.95		
USb	AFI–3k	217–246	2.8	–	3.6
UBi	AFI–(?)	~285	3.0	–	(?)
US	F [111]	~180	1.70	1.55	2.3
USe	F [111]	~160	2.00	1.81	2.5
UTe	F [111]	~105	2.25	1.91	2.7

*The notation and meaning of different antiferromagnetic structures are in [58].

UN is a type I–1k antiferromagnet, having the smallest U–U distance (3.45 Å), T_N (52 K) and μ_o (0.75 μ_B/U atom) in the whole uranium monocompound family (if one does not take into account the nonmagnetic *UC* with a similar U–U distance). In the latter compound a strong covalent bonding between the 5f (U) and 2p (C) orbitals causes a complete electron delocalization [49].

All the above mentioned features of UN makes this compound intermediate between the electron itinerant and localized types of magnetism. Its electron itinerant character is shown by the same pressure dependence of T_N and μ_o [50], required by the theory, as well as by the large contraction in the lattice constant (Fig. 1) which has also been supported by theoretical calculations [51]. The same conclusions can also be drawn by analysing the inelastic neutron-scattering data [30, 52], the low temperature heat capacity [8] which yields a value of $\gamma(0) = 50$ mJ/K^2 mole, and from angle-resolved photoemission measurements below T_N [53].

Nevertheless, the magnetism of UN may roughly be treated in the framework of the pseudolocalized state with a 5f^2 (U^{4+}) electron configuration [54], requiring a promotion of one 5f electron to the conduction band in order to account for a good metallic electrical conductivity [55], and a relatively large number of the carriers (~0.9), inferred from the Hall effect (cited by Ref. [41]). Moreover, UN exhibits a well-defined Curie–Weiss law until about 500 K with a high value of μ_{eff} (=3.1 μ_B) [24] and its temperature-dependence of the sublattice magnetization obeys a two-level crystal field approximation with inclusion of the magnetic excitations and induced moment fluctuations [56]. Finally, the antiferromagnetic structure of UN showed no change under magnetic fields up to 40 T [57].

The most complex magnetic properties in zero and high magnetic fields, as well as in the critical region of temperatures, have been analysed for *UP* and *UAs*. Both compounds show a first order transition from the non-collinear to collinear magnetic structures with the [110] and [100] orientations of the magnetic moments, respectively. This transformation, which for UP is between AFI–2k to AFI–1k and for UAs between AFIA–2k to AFI–1k (see for review Refs. [58] and [59]), is accompanied by a rapid drop in the μ_0-value and by other physical properties [19, 60].

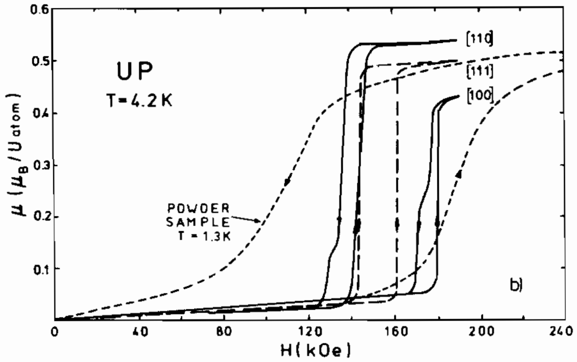

Fig. 8. The magnetization *vs.* magnetic field H for UP: a) single crystals (Ref. [61]) and b) powder sample (Ref. [57]).

Applying high magnetic fields to single UP and UAs crystals along the principal crystallographic axes up to 18 T [61, 62] or to powder samples up to 40 T [57] has revealed new ferrimagnetic multi-k structures [59]. Figure 8 exemplifies the critical magnetic fields for UP.

The initial powder [63] and single crystal [21] neutron-diffraction experiments on *USb* showed type 1k magnetic ordering, as is the case for UN. However, Rossat-Mignod *et al.* [58] have proved the structure to be of Kouvel-Kasper type, *i.e.* AFI–3k, with the moments lying along the [111] directions, according to the 5f wave functions determined earlier by Lander *et al.* [21] (the positive sign of V_4). A high field magnetization study on polycrystalline USb up to 40 T [57] showed only a linear behaviour. Similarly to UN, this points to the high stability of the type I structure under magnetic fields.

The magnetic properties of *UBi* are less well known. Trzebiatowski and Zygmunt [64] obtained the antiferromagnetic rocksalt phase of UBi by a rapid quenching from high temperatures, while the ferromagnetic phase occurred in the slow-cooled processes. The NaCl-UBi phase has also a type I structure [65], but the direction of the magnetic moments has not so far been established. One can also expect the AFI–3k type, as for USb. However, due to the extremely pyrophoric properties of UBi, any growing or handling with crystals is very difficult.

The occurrence in UP, UAs and USb of the multi-k structures may be accounted for by a strong competition between an anisotropic exchange interaction, favouring the k-vector alignment along [100], and one ion anisotropy, preferring the [110] and [111] directions.

Experimentally it was possible to measure the anisotropy of spin correlations in cubic fcc lattices by using neutron scattering techniques. In the anisotropic model the experiments made for UN [66], UAs [20] and USb [29] have shown that the J^{zz} exchange integrals within the (001) planes are 13, 37 and 49 times larger than its planar representatives: J^{xx} and J^{yy}. This finding has many close analogues with Ising models, and clearly points to the extremely large anisotropy in the exchange interactions acting in these cubic systems.

In view of this competition Sinha *et al.* [20] have proposed an effective Hamiltonian of the form

$$H = -\Sigma\, J^{\alpha\alpha}(\overline{R_{ij}})S_i^{\alpha}S_j^{\alpha} - K\Sigma(S_i^{\alpha})^4 \tag{9}$$

where $J^{\alpha\alpha}(R_{ij})$ is the anisotropic interaction integral, S_i is the α component of the spin operator and K is a constant connected with the single ion anisotropy.

Recently, Sznajd [67] has developed this model and pointed out that the Hamiltonian can describe three classes of antiferromagnetic phases with the moment directions along [001], [110] and [111] axes, having various propagation vectors. The competition between the exchange and single-ion terms can cause the transitions between some of the phases, but not that observed in UAs, *i.e.* between AFIA–2k to AFI–1k. Probably such transition could be explained by using the fourth-order interaction terms in a Landau expansion of the free energy.

However, in contrast to Sinha *et al.*'s [20] conclusions, one needs neither a competition between second and fourth-order terms in exchange interactions nor the vicinity of the Lifshitz point in order to explain the first order transition in UP and UAs from the AFI–1k to the paramagnetic phase. Such transition results simply from the existence of the cubic crystal field anisotropy.

For a similar purpose as above Thayamballi and Cooper [68] have adopted the CS type two ion anisotropic interaction to f^2 and f^3 electronic configurations of uranium ions at zero temperature and zero magnetic field. They were able to obtain for the f^3 configuration the AFI–2k ground state and the AFI–1k state at slightly higher energy, by adding to the CS interaction a small antiferromagnetic and isotropic RKKY interaction and also a crystal field interaction with a positive V_4 term. Thus, it seems quite likely that this 2k–1k transition, first experimentally observed for UP, may appear with increasing temperature. In turn, the change in sign of the V_4 term leads, *e.g.*, to the ground state with the AFI–3k phase, realized by USb. Unfortunately the authors have not yet investigated the AFIA–2k phase.

Rocksalt Solid Solutions

It is of great interest to study the magnetic properties of various rocksalt solid solutions, for example, between the following series:

a) uranium monocompounds, especially between those having different kinds of magnetic ordering, like the UX–UY solid solutions,

b) uranium and thorium (or itrium) monocompounds, for which a magnetic dilution effect is attained,

c) uranium and light rare earth (L) monocompounds (where L stands for Pr and Nd) which are isoelectronical to the uranium atom.

The frequent formation of the mutual solid solutions among all the mentioned above rocksalt compounds gives a unique possibility for continuous change of the charge numbers and the degree of localization or hybridization of 5f electrons with variation of lattice constants or a valence of anions.

The group a) of solid solutions is ideal for studying the transition from anti- to ferromagnetism. Until now quite a large number of the solid solutions of the general form UX–UY have been examined, like UP–US [69], UP–USe [7], UAs-US [71], UAs–USe [72, 73] and USb–UTe [58, 59]. On the contrary, there exist only limited data for the UX′–UX″ type solid solutions, which indicate changes in antiferromagnetic structures, like UP–UAs [74].

In the dilute systems b) so far the data have been reported for both the dilute monopnictides like UP–ThP [75], UAs–ThAs [76, 77], USb–ThSb [59, 78], UAs–YAs [79] or USb–YSb [34] and the dilute monochalcogenides like US–ThS [80], USe–ThSe [36] and UTe–ThTe [37].

In order to summarize these experimental results we present in Fig. 9 a practical magnetic phase diagram, being fairly arbitrarily constructed. The hori-

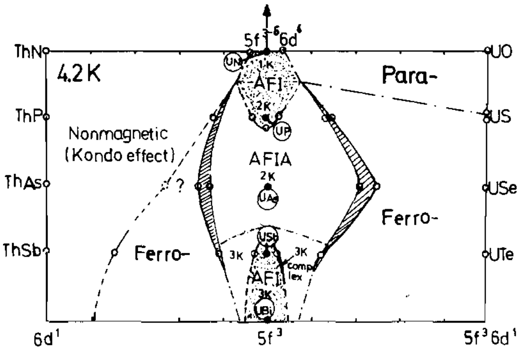

Fig. 9. A summary magnetic phase diagram showing the stability regions of different magnetic or non-magnetic phases, formed in the concentrated (UX–UY) or dilute (UX–ThX) systems. The hatched area indicates more complex than the multi-k antiferromagnetic structures. (The meaning of the axes is given in the text).

zontal concentration axis is replaced in the case of concentrated solid solutions (the right hand side) by the variation in the number of d-electrons in the form $5f^3 6d^1_x$, while in the case of dilute solid solutions (the left hand side) by both decreasing number of magnetically active ions and increasing number of d-electrons in the form $5f^3_{1-x}6d^1_x$. The vertical axis gives the degree of the hybridization (delocalization) by means of $5f^{3-\delta}6d^{\delta}$, where δ increases on going from UBi to UN. The above notations were taken from Ref. [6].

Finally, in group c) one expects the magnetic properties to vary more smoothly, as compared to the thorium and itrium solid solutions owing to markedly less active dilution processes.

So far as many as four such solid solutions have been investigated, namely UP–PrP, UP–NdP, US–PrS and US–NdS. A summary about the magnetic phase diagrams of these systems is given in Ref. [81]. The most interesting finding in these systems seems however to be the forming of the spin-glass like materials within certain ranges of the concentrations.

Th_3P_4-Type Compounds

All U_3X_4 pnictides are ferromagnets with T_C's going through a maximum for U_3As_4, as Fig. 7 indicates. As already mentioned, the strong three-axial nature of the crystal field anisotropy of the U_3X_4 compounds, together with an isotropic exchange interaction, may lead to a non-collinear magnetic structure [39, 82]. Indeed, the recent single crystal neutron-diffraction examinations of U_3P_4 and U_3As_4 [83] have indicated the magnetic ordering to be three-axial, where the magnetic moments of uranium atoms are tilted from the easy axis [111] by an angle θ of about 13 and 25 degree for the former and latter compounds respectively. The apparent difference in the net ordered moments of uranium in these two pnictides reflects the difference in the CEF effect, rather than a consequence of a simple μ_0 projection on the [111] direction. The last conclusion is supported by the large difference in the magnetic entropy values for these two compounds [84].

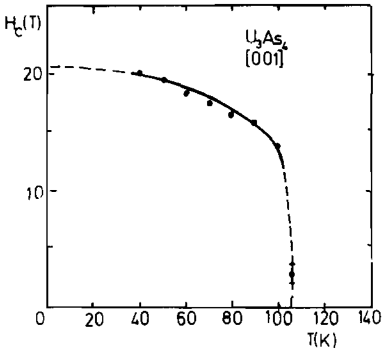

Fig. 10. The variation of the critical field with temperature for a first order transition observed in U_3As_4 (Ref. 89).

The problems of magnetic ordering, in particular the θ dependence on the exchange (J) and CEF (D) energy ratio in the U_3X_4 type compounds, has been considered theoretically [86, 87]. Only for very small values of the J/D ratio, is θ expected to increase rapidly towards its limited value of 54°50′.

The results have been obtained by applying high pulsed magnetic fields. While the magnetization of U_3P_4 along its hard direction [100] increases smoothly up to a measured limit of 50 T [87], for U_3As_4 a first order transition then occurs [88]. Figure 10 shows the change of the critical field for this transition with temperature, determined in stationary fields up to 20.5 T [89].

The occurrence of the first order transition in U_3As_4 has been the subject of intensive theoretical considerations. Kowalczyk [90] explained this transition by also including in Walasek's [85] Hamiltonian the fourth-order, single ion anisotropy term, but only if $S_{eff} \geqslant 2$. Sznajd [89], by means of the renormalization approach, has demonstrated the existence of a tri-critical point below which the magnetization jumps (first order transition) vanishes. Experimentally, the latter quantity was indeed observed to vanish at a temperature close to $T_C/2$ (see Fig. 10).

The measured temperature dependence of the magnetization discontinuity of U_3As_4 (jumps) in the [100] direction was used for determining the temperature variation of cubic anisotropy constants: K_1 and K_2 [89, 91]. Their temperature variation is shown in Fig. 11.

To explain the presence of such a giant anisotropy in the U_3X_4 pnictides (see Fig. 11), Takegahawa *et al.*

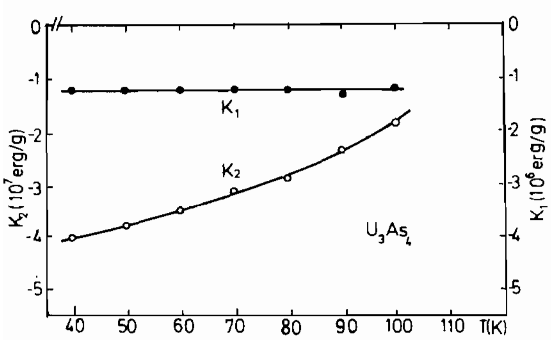

Fig. 11. The temperature variation of the anisotropy constants K_1 and K_2 for U_3As_4 (Ref. [89]).

[92] have attempted to apply the p–f mixing effect, as in the case of the Ce–monopnictides. As Schoenes *et al.* [7] recently reported, such an effect indeed has been confirmed experimentally.

Conclusions

The magnetic properties of numerous cubic uranium compounds in pure state or in their various solid solutions are strictly associated, even with a small variation in the uranium electronic state; *i.e.* depending on the degree of the localization of the 5f electrons and on the presence and to some extent also on the number of the 6d itinerant electrons in the conduction band.

Consequences of such complex electronic structure include the strong competitions between the magnetic moment exchange interactions (being in their nature very anisotropic), the spin-fluctuations due to the strong hybridization effect, and strong crystal field interactions. Moreover, in the dilute systems, the exchange interaction between the f states (located close to the Fermi energy) and the band electrons leads to the appearance of the Kondo effect.

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