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Structural and magnetic properties of some new uranium ternary pnictides: UTX_2 ($T \equiv Fe$, Co, Ni, Cu; $X \equiv P$, As, Sb, Bi)

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Abstract

The crystallographic and magnetic data for several new uranium–transition metal–pnictides UTX_2 (where $T \equiv Fe$, Co, Ni, Cu and $X \equiv P$, As, Sb, Bi) are reported. The magnetic properties of these new phases are discussed in comparison with those of their parent compounds, namely dipnictides UX_2.

1. Introduction

Ternary uranium compounds with the nominal composition UTX_2, where $T \equiv$transition metal and $X \equiv P$, As, Sb, Bi, form a new family of uranium ternaries, closely related to the well-known UX_2 phases. They all crystallize in a tetragonal system with the ZrCuSiAs-type structure (space group, *P*/*nmm*) [1] that can be also described as a filled ZrSiS type [2]. The word 'filled' refers here to the intercalation of planes of transition metal atoms into the unit cell of the respective binary uranium dipnictide. The only exception known so far is the compound $UCuP_2$ [3] which is isotypic to $SrZnBi_2$ [4] and described as a filled UGeTe type (space group, *I*4/*mmm*).

Previously we reported in a series of publications the magnetic, transport and magneto-optical properties of $UCuAs_2$ [5–7] and $UCuP_2$ [5, 8, 9] single crystals as well as the results of neutron diffraction studies on polycrystalline $UNiAs_2$ [10] and $UPdAs_2$ [11]. Recently, the existence of two new ternaries in this class of compounds, namely $UNiSb_2$ and $UCoP_2$, has been recognized and briefly communicated [12]. In the following we present the crystallographic and magnetic data for seven new uranium–transition metal–pnictides with the 1:1:2 stoichiometry.

2. Experimental details

The ternary UTX_2 compounds were prepared in powder form by sintering the stoichiometric mixtures of the respective uranium dipnictides and the

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TABLE 1

Lattice parameters and ordering temperatures for the uranium pnictides isotypic to $UCuAs_2$

Compound	Lattice parameters		Magnetism	$T_{C,N}$ (K)
	a (Å)	c (Å)		
$UCoP_2$	3.812	9.293	?	–
$UFeAs_2$	3.958	9.176	?	–
$UCoAs_2$	3.953	9.037	Ferromagnetic	144
$UNiAs_2$ [10]	3.951	9.138	Antiferromagnetic	228
$UCuAs_2$ [5]	3.951	9.558	Ferromagnetic	133
$UPdAs_2$ [11]	3.987	9.493	Antiferromagnetic	240
$UNiSb_2$	4.316	9.104	Antiferromagnetic	174
$UCuSb_2$	4.312	9.640	Ferromagnetic	106
$UNiBi_2$	4.470	9.073	Antiferromagnetic	166
$UCuBi_2$	4.526	9.376	Antiferromagnetic	15, 51

powdered transition metal. The binary UX_2 compounds were synthesized as described in ref. 13. The nominal purity of the starting components in all cases was at least 99.9%. The pnictogen elements were repeatedly purified by distillation prior to the reactions. The UX_2+T mixtures were gradually heated in evacuated sealed quartz ampoules to about 700 °C and held at this temperature for 2 weeks. In the case of bismuthides the starting materials were additionally placed in a ceramic crucible to prevent the reaction of bismuth with quartz walls of a tube.

The X-ray powder examinations performed on a DRON 1.5 diffractometer revealed the samples to be single phase except for $UFeAs_2$ and $UCoP_2$ which showed a small admixture of U_3As_4 and U_3P_4 respectively. The X-ray patterns were easily indexed in a primitive tetragonal system with the lattice parameters listed in Table 1.

Magnetic susceptibility measurements were carried out in the temperature range 4.2–300 K using an RH Cahn electrobalance. Magnetization studies were done in applied magnetic fields up to 40 kOe and temperatures ranging from 4.2 K to slightly above the Curie point by using a moving-sample low frequency magnetometer with a superconducting coil.

3. Results

Magnetic susceptibility measurements have revealed $UNiSb_2$, $UNiBi_2$ and $UCuBi_2$ to be antiferromagnetically ordered below 174 K, 166 K and 51 K respectively. As an example, the temperature variation in the magnetic susceptibility of $UNiSb_2$ is presented in Fig. 1. Above 160 K the $\chi^{-1}(T)$ curve for this compound shows an almost straight-line behaviour with $\mu_{eff}=2.68$ μ_B (U atom)$^{-1}$ and $\Theta_p=42$ K. Contrary to $UNiSb_2$ which seems to be a simple antiferromagnet, an unusual two-peaked $\chi(T)$ dependence was found

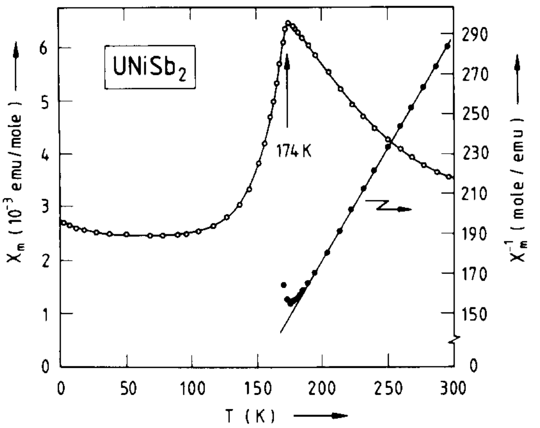
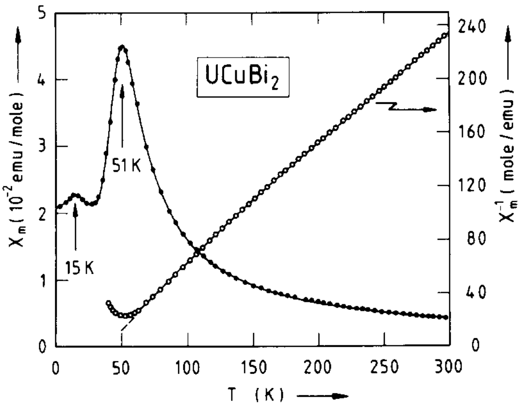


Fig. 1. Thermal dependence of molar magnetic susceptibility (left-hand scale) and inverse molar susceptibility (right-hand scale) of UNiSb$_2$.



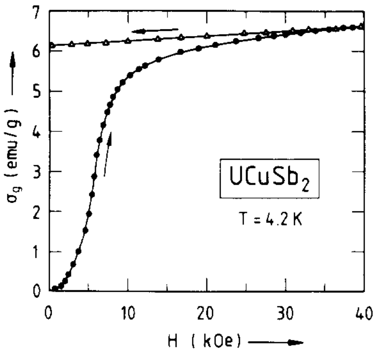


Fig. 2. Thermal dependence of molar magnetic susceptibility (left-hand scale) and inverse molar susceptibility (right-hand scale) of UCuBi$_2$.

Fig. 3. Magnetization of UCuSb$_2$ measured at 4.2 K in magnetic fields up to 40 kOe.

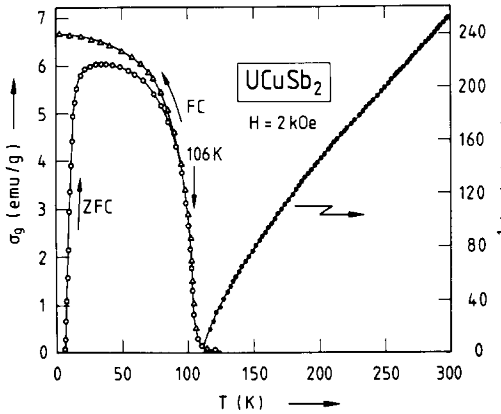
for UCuBi$_2$ (Fig. 2). The two observed susceptibility maxima, the first at 15 K and the second at 51 K, strongly indicate that except for the paramagnetic-to-antiferromagnetic transition at higher temperatures there is also an additional magnetic order–order transition at low temperatures. It is worthwhile noting that a very similar behaviour of the magnetic susceptibility was found before for example for USnTe [14]. The $\chi^{-1}(T)$ variation for UCuBi$_2$ in the paramagnetic region is rather curvilinear and follows a modified Curie–Weiss (MCW) law with the parameters: $C=1.078$ K emu mol^{-1}, $\chi_0=2.5\times10^{-4}$ emu mol^{-1} and $\Theta_p=31$ K. The effective magnetic moment amounts here to 2.94 μ_B (U atom)$^{-1}$.

Magnetization studies have shown that UCuSb$_2$ and UCoAs$_2$ are ferromagnets with $T_C=106$ K and $T_C=144$ K respectively. As an example in Fig.

3 we present the magnetization *vs.* magnetic field dependence for $UCuSb_2$. As seen, the $\sigma(H)$ curve tends to saturate in high magnetic fields reaching a value of 6.67 emu g^{-1} at 40 kOe. The thermal variation in the magnetization for $UCuSb_2$ is plotted in Fig. 4. The $\sigma(T)$ dependences were measured in two regimes of cooling the sample; an applied magnetic field *i.e.* field cooled with and without applied magnetic field (*i.e.* zero field cooled). The shape of these curves points to a large anisotropy of $UCuSb_2$. A characteristic broad maximum occurring in the $\sigma(T)_{ZFC}$ function results from competition between the temperature-induced domain movement leading to an increase in the sample magnetization and the thermally driven disordering in the magnetic moment system. In the paramagnetic region the reciprocal magnetic susceptibility as a function of temperature for $UCuSb_2$ is strongly curvilinear and may be described by the MCW law with $C = 0.550$ K emu mol^{-1}, $\chi_0 = 1.06 \times 10^{-3}$ emu mol^{-1} and $\Theta_p = 111$ K. The effective magnetic moment for this compound is 2.10 μ_B (U atom)$^{-1}$.

4. Discussion

The crystal structure of the UTX_2 compounds investigated is shown in Fig. 5 together with its parent structure of the ZrSiS type in which all the UX_2 pnictides crystallize. As seen, the only difference between these two



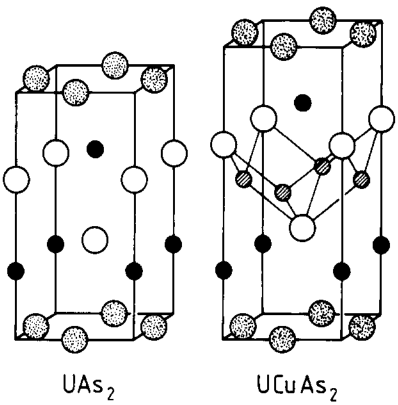


Fig. 4. Thermal dependence of magnetization (left-hand scale) and magnetic susceptibility (right-hand scale) of $UCuSb_2$ measured in a magnetic field of 2 kOe. The field-cooled (FC) and zero-field-cooled (ZFC) curves correspond to the regimes of cooling the sample with and without an applied field respectively.

Fig. 5. Comparison of the crystal structures of UAs_2 (ZrSiS type) and $UCuAs_2$ (filled ZrSiS type). An expansion of the UAs_2 unit cell after the intercalation of the copper atom layer is clearly shown. Thin lines mark a pyramidal arrangement of T and X(2) atoms, characteristic of the $UCuAs_2$-type structure (see ref. 2). ●, U; ◍, Cu; ◌, As1; ○, As2.

structures is an additional layer of transition metal atoms placed between the sheets of the As(2) atoms. The intercalation of this extra layer results in an expansion of the UX_2 unit cell and may cause important changes in the magnetic properties of a given parent compound in which the T atom is incorporated.

For example, a 'filling' of the UAs_2, USb_2 and UBi_2 unit cells by the nickel atoms results in an increase in the lattice parameter c of about 13%, 4% and 2% respectively, the a parameter for all these compounds remaining almost unchanged. At the same time, the Neél temperature of the parent compound is reduced by about 17%, 15% and 8% respectively (see Table 1).

On the contrary, not only does an introduction of copper atoms into the same unit cells cause a large expansion of the lattice (the c parameter increases by about 18%, 10% and 5% for the arsenide, antimonide and bismuthide respectively) but also it leads to changes in the kind of magnetic ordering. Whereas all the UX_2 compounds are antiferromagnets, the $UCuX_2$ phases, except for $UCuBi_2$, order ferromagnetically at low temperatures (see Table 1). As to the latter compound, which is an antiferromagnet and shows two successive magnetic phase transitions, it behaves here quite anomalously, probably in a similar manner to UBi_2 among the UX_2 compounds [15]. The reason for this feature might be the strongly metallic character of bismuth resulting in a strongly covalent bonding between uranium and Bi(1) atoms and some metallic bonding between Bi(1) atoms themselves.

The question remains of how the exchange interactions between the uranium atoms are modified when the atoms of a given transition metal are embedded in the UX_2-type unit cell (as neutron diffraction studies have shown, T atoms in UTX_2 are always non-magnetic [10, 11]). In general, the magnetic ordering in the UTX_2 compounds is probably driven by competition between the superexchange via metalloid anions and the Ruderman–Kittel–Kasuya–Yoshida (RKKY) interactions via conduction electrons. It is quite natural that some changes in the U–U distances accompanying an expansion of the lattice as well as an increase in the number of conduction electrons must both invoke some changes in the strength of RKKY-type interactions. These two phenomena may explain the differences in the magnetic properties of the UTX_2 compounds in comparison with those of the parent UX_2 phases. However, it is hardly conceivable that they alone are responsible for the observed variety of magnetic behaviours within the UTX_2 series. The differences in the atomic radii of particular transition metal atoms appear to be not very distinct (except for palladium and perhaps copper), and moreover all the 3d atoms introduce to the UTX_2 lattice the same number of s-electrons, *i.e.* two. On the contrary, the replacement of the T atom in UTX_2 may lead to a change in the number of d electrons (holes). Therefore it seems likely that the hybridization between the U f states and the T d states must play an important role in determining the magnetic properties of these compounds. A more detailed discussion of this point on the example of the $UTAs_2$ compounds will be published elsewhere.

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