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5f-LIGAND HYBRIDIZATION AND MAGNETISM IN UTX COMPOUNDS

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Investigations of magnetic and related electronic properties of UTX compounds have revealed a variety of magnetic phenomena ranging from weak paramagnetism to various types of magnetic ordering. The observed systematics of ground-state properties is discussed with respect to the development of the electronic structure related to the expected variations of the 5f-ligand hybridization. The huge magnetic anisotropy observed in all studied materials is tentatively attributed mainly to the hybridization-mediated anisotropic two-ion interaction.

1. Introduction

The specific ingredients in intermetallic compounds containing U, Np or Pu, are the 5f electrons which can contribute, on one hand, to the metallic bonding and, on the other hand, to the formation of magnetic moments. The character of 5f states ranges from itinerant to nearly localized depending on the kind of the actinide atom and its surrounding. Consequently, the 5f states form a more or less narrow band at E_F . The two dominating contributions to 5f-band formation are the direct 5f-wave function overlap and the 5f-ligand hybridization [1, 2]. The role of electronic configurations of ligands, interatomic spacings and 5f-atom coordination (being intimately connected with bonding conditions and the crystal structure) in these effects is obvious.

The rich system of equiatomic ternaries AnTX (T is a transition metal and X a p-metal) provides a useful tool for systematic studies of the gradual localization of 5f electrons and the related attributes in electronic properties. The main isostructural groups of UTX compounds are summarized in table I. The occurrence of specific structures with respect to the Periodic Table seems to be influenced also by the d-electron concentration in the T metal. We concentrate on the two largest groups of the Fe_2P (ZrNiAl) and $CeCu_2$ (TiNiSi) types of structure [3]. U–U spacings in the former group range from about 350 pm (UFeAl,

UCoAl) to nearly 400 pm (UTSn and UTIn compounds). All materials of the latter one have d_{U-U} in the critical region 340–360 pm [4, 5].

2. Results and discussion

Investigation of bulk properties of UTX compounds, such as the magnetic susceptibility, the specific heat in fields up to 5 T, and the low-temperature magnetization in fields up to 40 T, have revealed a variety of magnetic phenomena ranging from weak paramagnetism to different types of magnetic ordering of stable 5f moments. The basic characteristics are summarized in figs. 1(a) and (b), from which the following general features can be deduced.

(a) Magnetic ordering of the highest magnetic moments is found in compounds with T metals from the end of transition metal series (UNiX, UPdX, UPtX). By reducing the d-band occupation the gradual

Table 1
Schematic table of the occurrence of various crystal structures with respect to the transition metal constituent in UTX compounds.

Mn	Fe	Co	Ni	Cu
Tc	Ru	Rh	Pd	Ag
Re	Os	Ir	Pt	Au
MgZn ₂ -hex.	Fe_2P (ZrNiAl)-hex.			MgAgAs-cub.
	$CeCu_2$ (TiNiSi)-or.			CaIn ₂ -hex.

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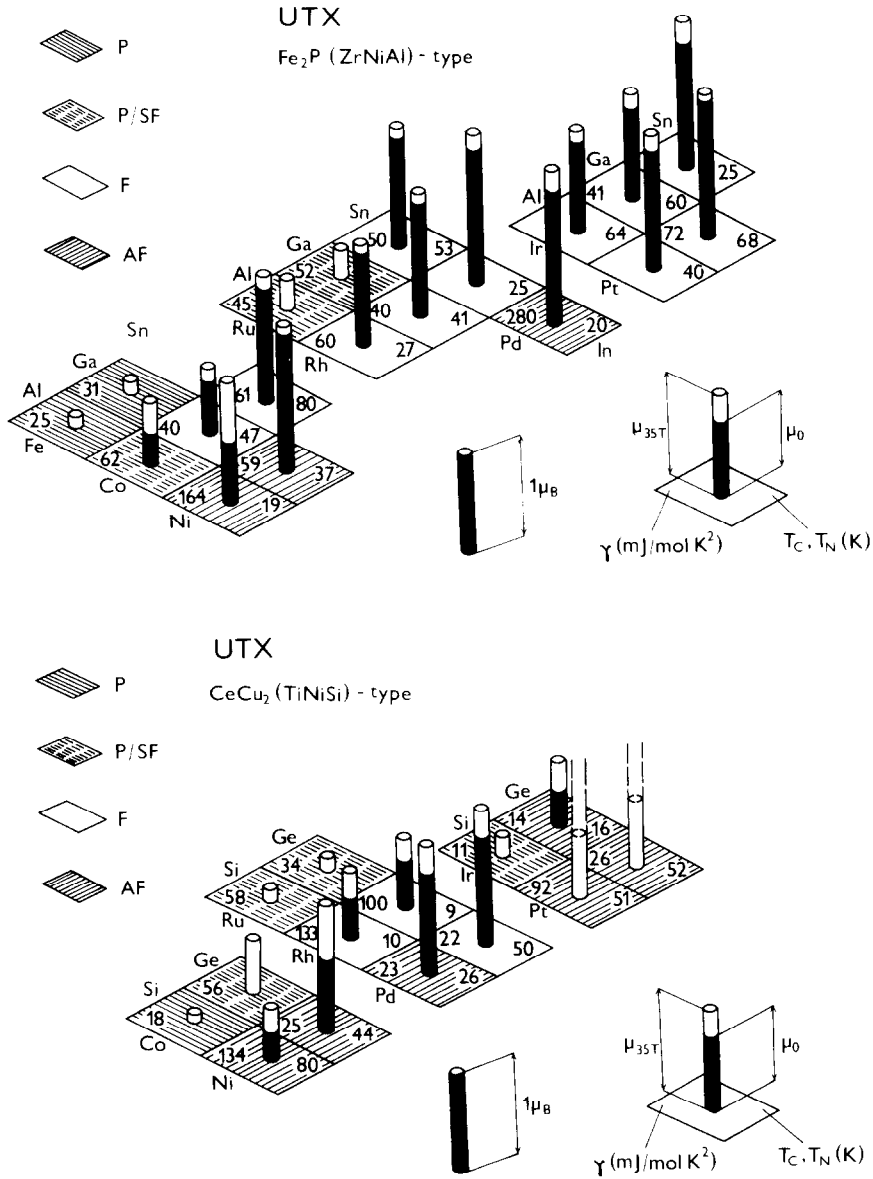


Fig. 1. Schematic diagram illustrating the development of some electronic properties (the type of ground state [P: paramagnetic, P/SF: paramagnetic with spin fluctuations, F: ferromagnetic, AF: antiferromagnetic], μ_{35T} the magnetic moment measured at 35 T along the easy magnetization direction, μ_0 the magnetic moment obtained by an extrapolation of the high-field magnetization data to $B = 0$ T and the coefficient γ of the specific heat) through the UTX series with the Fe₂P (ZrNiAl) (a) and the CeCu₂ (TiNiSi) (b) type of structure. The broken lines denote the not yet well-established moments (higher magnetic fields than presently used are necessary to be applied in the cases of UPtSi and UPtGe in order to complete the metamagnetic transitions). Some results of [3–5] are also included.

weakening of the magnetism amounts to a depression of the magnetic moments and, consequently, to a loss of magnetic ordering. Magnetic correlations then can survive in the form of spin-fluctuation effects and/or the metamagnetic behaviour at low temperatures (URuX, UCoAl) [3, 6, 7].

(b) For a particular T metal, the magnetism becomes more pronounced in the sequences UTAI, UTGa, UTSn, UTIn and UTSi, UTGe.

The characteristic feature of these materials is the 5f band pinned at E_F , while the d states are in higher binding energies due to the higher electronegativity of the late transition metals. The strong hybridization of the 5f and d bands causes a redistribution of 5f and 3d states in the DOS curve (see fig. 2); a part of 5f states is shifted below E_F , while some 3d states appear at lower binding energies. This picture suggests the 5f contribution to the magnetism to be dominant.

The ground-state development in UTX compounds is then consistent with the expected tendencies for the 5f ligand hybridization [2], which acts as a destabilizing factor on the formation of 5f magnetic moments: (a) the 5f–d hybridization is reduced due to lowering the 5f–d degeneracy when the d states are pulled more below E_F (due to higher population of the d states when moving with the T constituent to the right in the d series), and (b) the 5f–p hybridization with X-ligand states weakens with increasing X atomic volume, i.e., moving down in the p-element column.

The 5f magnetic moment is expected to be built up of the orbital contribution μ_L and the spin contribution μ_S of the opposite sign as calculated by Eriksson

et al. [7] and experimentally proved by Wulff et al. [6] for UCoAl. The development of magnetic moments in the UTX series indicates that μ_L is affected by the 5f-electron delocalization (due to the hybridization and the direct 5f-wave function overlap) more than μ_S . The considerable high-field-induced magnetization, especially in U3dX compounds (see fig. 1.) might be explained by the opposite field-induced changes of μ_L and μ_S . The contribution from the polarized conduction electrons should also be taken into account.

The most spectacular feature of the UTX ternaries is a huge magnetic anisotropy found already in the non-magnetic state. The estimated anisotropy fields in magnetically ordered substances exceed 100 T. This observation together with the anisotropy of other electronic properties (e.g. electrical resistivity) can be associated with the anisotropic 5f-ligand hybridization, which yields a strong anisotropy of $N_{sf}(E_F)$. As a consequence, mainly the hybridization-mediated anisotropic two-ion interaction can be tentatively accounted for the giant magnetic anisotropy. Such phenomena have been treated theoretically by Cooper et al. [8] for Ce and light-actinide pnictides and chalcogenides giving a satisfactory explanation of experimental results. The uniaxial anisotropy of the hexagonal UTX compounds suggests the strongest interaction within the (U, T) basal-plane layers (within which the U moments are coupled ferromagnetically along the *c*-axis). The interaction between these ferromagnetic layers is mediated by (X, T) layers coupling them in a parallel or antiparallel way.

The orthorhombic symmetry of the CeCu₂ (TiNiSi) type of compounds probably leads to multiaxial anisotropy and complicated magnetic structures.

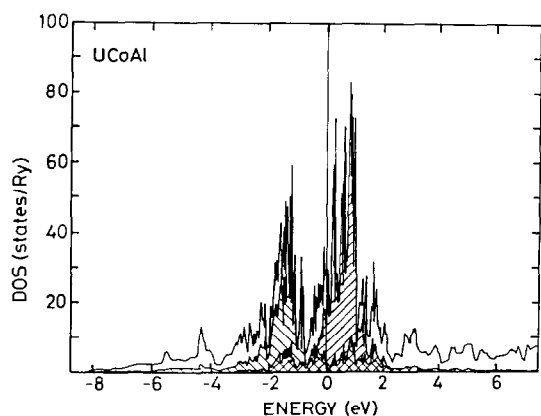


Fig. 2. Self-consistently calculated scalar relativistic density of states (DOS) for UCoAl [7]. The Fermi energy is at zero. The shading /// marks the 5f band and \\ the 3d band.

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