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Heavy fermion behavior of U_2T_2X compounds

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Magnetic and specific-heat studies of U_2T_2X compounds show a frequent occurrence of the γ enhancement in conjunction with the onset of antiferromagnetic ordering. The largest value of 830 mJ/mol K^2 was observed in U_2Pt_2In, which is nonmagnetic down to 1.2 K. Variations of electronic structure are documented by optimized relativistic LCAO calculation.

I. INTRODUCTION

Magnetic and other electronic properties of light actinides in intermetallic compounds are strongly affected by the hybridization of the $5f$ states with electronic states of ligands. In compounds with transition metals, the most significant delocalizing effect comes from the $5f$-d hybridization, which is reduced with filling the d band. The reason follows from electronic structure calculations, which show how the gradual filling of the d states leads to a reduced overlap of the $5f$ states, forming a band pinned at E_F, with the d transition metal states, which are pushed down to higher binding energies. Thus irrespective of stoichiometry or crystal structure we can observe variations of the $5f$ electron magnetism, with a crossover from nonmagnetic to magnetic ground state by the end of transition metal series. There is a common belief that heavy fermion phenomena occur only with very narrow $5f$ bands, which do not order magnetically (or which show very small ordered moments). However, it remains an open question as to why the onset of magnetism is *not* accompanied by a significant γ enhancement in many cases. In other words, the heavy fermion compounds remain rather unique and it is unclear where to place them in the systematics of other uranium intermetallics.

Here we describe results of investigations of the recently discovered compounds of the U_2T_2X type,[1] which can contribute to heavy fermion research due to a systematic occurrence of γ enhancement. The U and Np compounds of the 2:2:1 stoichiometry exist with nearly all transition metals of the Fe, Co, and Ni column. X represents Sn or In. They all crystallize in the tetragonal U_3Si_2 structure type with U-U distances in the range 3.45–3.8 Å.[1]

II. EXPERIMENTAL RESULTS

We studied polycrystalline samples prepared by arc melting stoichiometric amounts of the constituent elements. Most of them were single phase. A several percent contamination was found in U_2Pt_2In (UPt) and in U_2Ir_2Sn and U_2Ir_2In (UIr).

Most of the compounds with Ni, Pd, and Pt display antiferromagnetic (AF) order at low temperatures. The only exception is **U_2Pt_2In**, which exhibits a strongly enhanced susceptibility χ at low temperatures (23×10^{-8} m^3/mol at 4.2 K—note that 1 mol f.u. contains 2 U atoms). No phase transition was indicated in the specific heat down to 1.2 K. The $\chi(T)$ dependence (Fig. 1) can, at high temperatures, be approximated by a modified Curie–Weiss (MCW) law similar to the majority of compounds described here:

$$\chi = C/(T-\Theta_p)+\chi_0, \tag{1}$$

yielding for U_2Pt_2In the parameters $\mu_{\rm eff}=2.4$ μ_B/U, $\Theta_p=-106$ K, and $\chi_0=9.7\times10^{-8}$ m^3/mol. Below 100 K, $\chi(T)$ deviates from the MCW fit towards larger χ values. The low-temperature data are contaminated by the UPt impurity[2] (which has spontaneous magnetization of 0.4 μ_B/U below $T=25$ K[3]), but the large susceptibility at 4.2 K was confirmed by high-field magnetization measurements. The specific heat displays a pronounced upturn of C/T vs T (Fig. 2), which is insensitive to applied magnetic field of 5 T. Although the fit involving a $T^2 \ln T$ term accounts well for the data only in a very limited temperature range (up to 5 K), it can be used to estimate the γ value in the zero K limit, $\gamma\cong830$ mJ/mol K^2.

The highest ordering temperatures were observed in the two Pd compounds, **U_2Pd_2Sn** ($T_N=41$ K) and **U_2Pd_2In** ($T_N=38$ K). The susceptibility analysis in terms of Eq. (1) yields smaller negative Θ_p values (−30 and −32 K for Sn and In, respectively) than in other compounds from this series. The relatively strong $5f$ localization is indicated by sizeable U magnetic moments (1.89 and 1.40 μ_B, respec-

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tively) determined from neutron-diffraction experiments. They show in both cases a noncollinear AF structure with moments within the basal plane and oriented along directions of the [110] type.[4] Despite magnetic ordering, a pronounced upturn in the C/T vs T dependence was found also for U_2Pd_2In, leading to γ=393 mJ/mol K^2 (65 mJ/mol K^2 is obtained by extrapolation from paramagnetic range). No such upturn was found in U_2Pd_2Sn, but the linear coefficient of the specific heat was still high: γ=203 mJ/mol K^2. The $5f$ local-moment magnetism in the Pd compounds is corroborated by the magnetic entropy estimate $(1-2\times R \ln 2)$.

Unlike U_2Pt_2In, **U_2Pt_2Sn** is magnetically ordered (T_N=15.5 K). A much smaller magnetic entropy (about $0.2\times R \ln 2$) is suggestive of itinerant magnetism. γ=334 mJ/mol K^2 was extracted from the low-temperature range, whereas 390 mJ/mol K^2 can be obtained above T_N.

U_2Ni_2In exhibits a similar behavior (T_N=15 K). Magnetic susceptibility analysis in terms of Eq. (1) yields Θ_p=−80 K and μ_{eff}=2.0 μ_B/U. The low-temperature γ=200 mJ/mol K^2 is substantially smaller than the high-temperature value of 350 mJ/mol K^2. The magnetic entropy is about $0.4\times R \ln 2$.

U_2Ni_2Sn orders below T_N=25 K. In the paramagnetic range, μ_{eff} can be described by Eq. (1) yielding μ_{eff}=2.3 μ_B/U, Θ_p=−110 K, and $\chi_0=1.8\times10^{-8}$ m^3/mol. We are aware that the presence of the χ_0 term can be an artifact due to the averaging the anisotropic χ values in polycrystal.

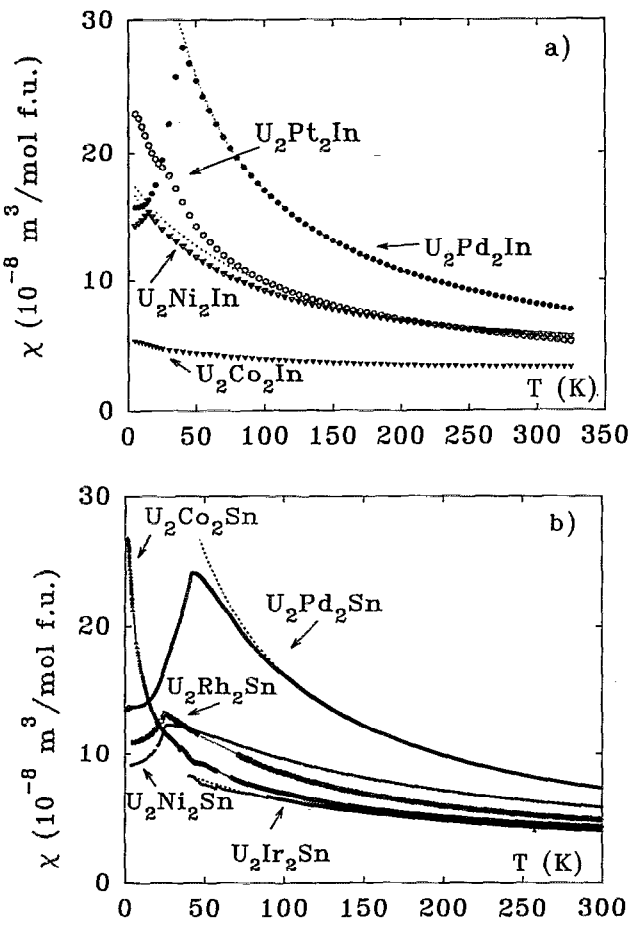

FIG. 1. Temperature dependence of magnetic susceptibility of (a) U_2T_2In and (b) U_2T_2Sn. The dotted lines shown in some cases are the MCW fits.

Regarding other compounds, we have found magnetic ordering in **U_2Rh_2Sn** with T_N=24 K. A weak magnetic entropy of $0.4\times$R ln 2 is again indicative of a strongly itinerant $5f$ magnetism, but the γ value is rather low (131 mJ/mol K^2).

Besides U_2Pt_2In, some other nonmagnetic compounds exhibit spin-fluctuation features: **U_2Co_2Sn**, **U_2Rh_2In**, and **U_2Ir_2Sn**. They display γ values ranging from 130 (U_2Ir_2Sn) to 280 mJ/mol K^2 (U_2Rh_2In) (a strong upturn in C/T is found in U_2Co_2Sn and a weaker one in U_2Rh_2In). Finally, the presumably most itinerant $5f$ states cause a weak itinerant paramagnetism in **U_2Co_2In** (γ=32 mJ/mol K^2) and **U_2Ru_2Sn** (20 mJ/mol K^2).

Assessing variations of properties in the group of U_2T_2X compounds, we can deduce the following trends: (i) The $5f$ localization increases within each transition metal series towards the right end of the periodic table. This is similar to findings in other groups of light actinide compounds. (ii) The U_2T_2In compounds have a weaker tendency to magnetic ordering than their U_2T_2Sn counterparts.

III. ELECTRONIC STRUCTURE CALCULATIONS

To follow electronic structure variations in the system of U_2T_2In compounds, we performed calculations using the optimized HLCAO[5] method in a fully relativistic version.[6]

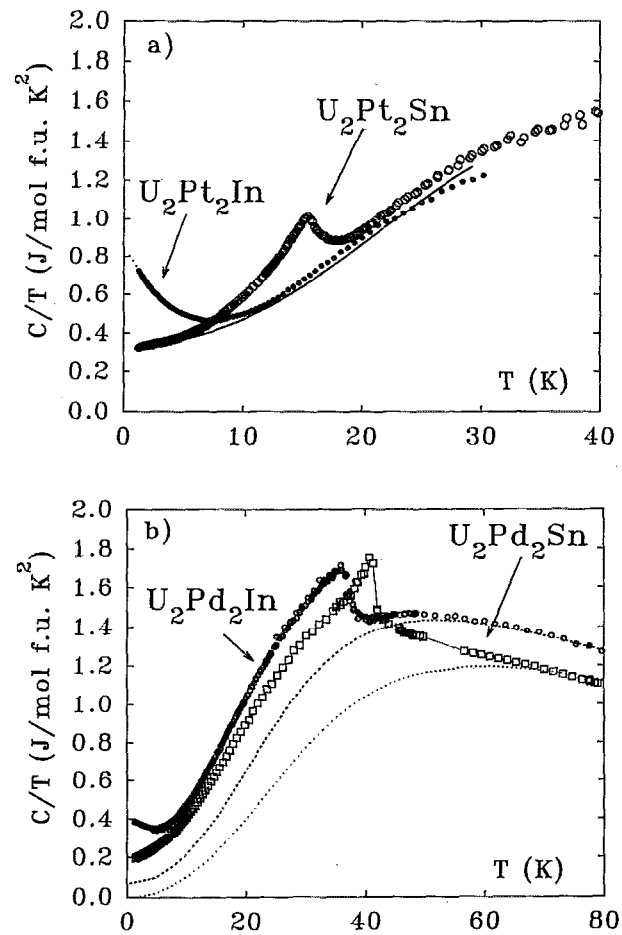

FIG. 2. C/T vs T plots of (a) U_2Pt_2X and (b) U_2Pd_2X. The dotted lines show the Debye background approximating the high-temperature specific heat. For U_2Pt_2Sn (full line) it is shifted down to fit to the low-temperature γ.

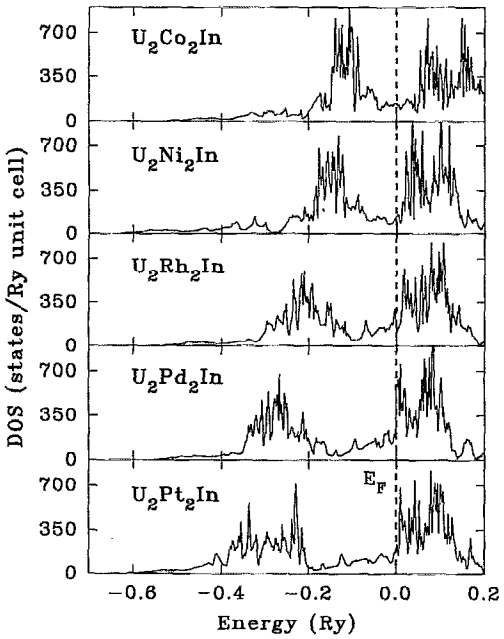

FIG. 3. Calculated total density of states of U_2T_2In.

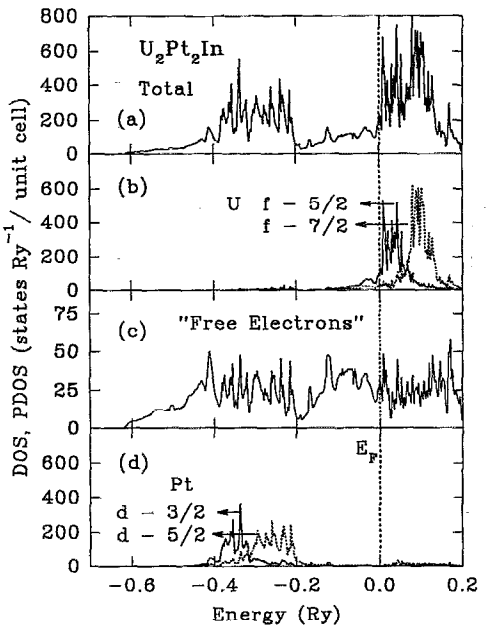

FIG. 4. Calculated total and orbital-projected density of states for U_2Pt_2In.

Self-consistency is treated by the Kohn–Sham density-functional theory in the local-density approximation (LDA).

The total densities of states (DOS) for U_2T_2In (T=Co, Ni, Rh, Pd, Pt) calculated fully relativistically are displayed in Fig. 3. The obtained spectra are characterized by a nearly free-electron background of s-, p-, and uranium $6d$ electrons, which extends to about 0.6 Ry below E_F. In all cases bonding and antibonding band groups are well separated by a broad and deep minimum around E_F. The orbital-projected DOS for the $5f$ and T-d orbitals (see, e.g., U_2Pt_2In shown in Fig. 4) indicate that the bonding (antibonding) states are predominantly T-$d(5f)$. There is, however, an appreciable amount of covalency—the $5f(T$-$d)$ contribution to the bonding and the antibonding states, respectively. The estimate of the contribution of a direct $5f$-$5f$ overlap to the width of the f-projected DOS proved that the $5f$-d hybridization appreciably enhances the $5f$ bandwidth.[6]

Practically no electron transfer from U to T was found in U_2Pd_2In. But it does increase with decreasing population of the d states. As expected, the spin-orbit splitting of Co- and Ni-$3d$ states is small, with moderate spin-orbit splitting in Rh- and Pd-$4d$ states (0.02 Ry), and the largest splitting in Pt-$5d$ and U-$5f$ states (0.1 Ry).

The Fermi level gradually shifts from the top of the bonding band in U_2Co_2In to the bottom of the antibonding band in U_2Ni_2In, U_2Rh_2In, and U_2Pt_2In, and finally into the antibonding band in U_2Pd_2In, which displays much weaker transfer of $5f$ (and $4d$) electrons into free-electron states. This reduced transfer may be understood as the result of shifting down of the Pd-$4d$ states compared to the Ni-$3d$ states or Pt-$5d$ states. The experimentally observed development in the γ values is qualitatively consistent with the trends in the calculated DOS at the Fermi level $N(E_F)$. We have also partitioned the total DOS into different contributions and the change of total DOS at E_F can be mainly ascribed to the variations of $N(E_F)^{U}_{f5/2}$.

Since the width of the covalence gap (>1 eV) exceeds the exchange splitting of elemental Co and Ni, any possible magnetism should arise from $5f$ electrons only. Applying the LDA Stoner theory, we have obtained the Stoner product $I\times N(E_F)$=0.6, 1.3, 2.0, 11.5, and 3.1 for U_2Co_2In, U_2Ni_2In, U_2Rh_2In, U_2Pd_2In, and U_2Pt_2In, respectively. Therefore the observed nonmagnetic ground state of U_2Co_2In and magnetic ground state of U_2Ni_2In and U_2Pd_2In are qualitatively consistent with our calculations. The nonmagnetic heavy fermion behavior of U_2Rh_2In and U_2Pt_2In cannot be described by our LDA calculations, which lead to a Stoner instability.

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