Fermi- and non-Fermi-liquid ground states in $M_{1-x}U_xPd_3$ ($M = Sc, Y, La, Pr, Zr, Th$) systems

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Abstract

A growing number of chemically substituted intermetallic compounds of Ce and U exhibit non-Fermi-liquid (NFL) behavior in their low temperature physical properties and apparently constitute a new class of strongly correlated f-electron materials. In this paper, we update the experimental situation for the archetypal NFL f-electron system $Y_{1-x}U_xPd_3$ and briefly describe recent experiments on the related systems $M_{1-x}U_xPd_3$ ($M = Sc, La, Pr, Zr, Th$).

1. Introduction

A new class of strongly correlated f-electron materials whose low temperature physical properties display non-Fermi-liquid (NFL) behavior has emerged during the past several years [1, 2]. The presently known materials that belong to this group are Ce and U intermetallic compounds containing nonmagnetic elemental substituents. The physical properties of these materials exhibit weak power law or logarithmic divergences in temperature that scale with a characteristic temperature $T_0$. This suggests the existence of a quantum critical point at $T = 0$ K, possible origins of which include an unconventional moment screening process, such as a multichannel Kondo effect [3], and fluctuations of an order parameter in the vicinity of a second-order phase transition at $T = 0$ K [4].

In this paper, we update the experimental situation for the $Y_{1-x}U_xPd_3$ system, the first f-electron system in which NFL behavior was discovered [5], and present some recent experimental results on the related systems $M_{1-x}U_xPd_3$ ($M = Sc, Y, La, Pr, Zr, Th$).

2. The $Y_{1-x}U_xPd_3$ system – an update

The most recent version of the low temperature $T$–$U$ concentration $x$ phase diagram of the $Y_{1-x}U_xPd_3$ system is shown in Fig. 1 [6]. Of particular interest are the physical properties of $Y_{1-x}U_xPd_3$ in the cubic Cu$_3$Au phase that extends from $x = 0$ to $x \approx 0.55$. Magnetization $M(T)$ measurements, performed under field-cooling and zero-field cooling conditions on $Y_{1-x}U_xPd_3$ samples in the range $0.2 \leq x \leq 0.55$, exhibit irreversible behavior below an irreversibility temperature $T_{irr}$, reminiscent of spin-glass freezing. A plot of $T_{irr}$ versus $x$ in Fig. 1 delineates a region in which spin-glass and/or antiferromagnetic (AFM) ordering occurs. The kink in the $T_{irr}$ versus
$x$ curve at $x \approx 0.42$ may reflect a change from spin-glass ordering at lower values of $x$ to long-range AFM ordering at higher values of $x$ (long-range AFM ordering of the $U$ moments has recently been observed by neutron scattering experiments on a sample with $x = 0.45$ [7]).

Transport, thermal, and magnetic measurements have revealed the existence of an unconventional Kondo effect in the region $0 < x < 0.55$ [5, 8]. As indicated in Fig. 1, the Kondo temperature $T_K$ decreases rapidly with $x$. This can be explained in terms of a phenomenon, discovered in photoemission studies of $Y_{1-x}U_xPd_3$ and referred to as “Fermi level tuning” [9], in which the U$^{4+}$ 5f binding energy $\varepsilon_{5f} = E_F - E_{5f}$, where $E_F$ is the Fermi energy and $E_{5f}$ is the energy of the U$^{4+}$ 5f state, increases by ~1 eV as $x$ increases from 0 to 1 [1, 8]. The increase of $\varepsilon_{5f}$ with $x$ can be understood in terms of increase of $E_F$ with $x$ as tetravalent U is substituted for trivalent Y. The nearly linear increase of $\varepsilon_{5f}$ with $x$ should cause a rapid decrease in $T_K$ since

$$T_K \sim T_F \exp \left[ -1/N(E_F) \varepsilon_{5f} \right]$$

(1)

$$\sim T_F \exp \left[ -\varepsilon_{5f} / \langle V^2 \rangle \right] N(E_F)$$

where $T_F$ is the Fermi temperature, $N(E_F)$ is the density of states at $E_F$, $\varepsilon_{5f} = -\langle V^2 \rangle / \varepsilon_{5f}$ is the exchange interaction parameter, and $V_{ij}$ is the hybridization matrix element. From this result, it is evident that a decrease in $\langle V^2 \rangle$ or $N(E_F)$ will also cause a decrease in $T_K$ for $x$ as tetravalent $U$ is substituted for trivalent Y. The nearly linear increase of $\varepsilon_{5f}$ with $x$ should cause a rapid decrease in $T_K$ since

$$T_K \sim (T_K)_0 \exp \left[ -ax \right]$$

(2)

where $(T_K)_0$ is the value of $T_K$ for $x = 0$ and $a = \varepsilon_1 / \langle V^2 \rangle N(E_F)$. The electrical resistivity $\rho(T)$, specific heat $C(T)$, and magnetic susceptibility $\chi(T)$ of the $Y_{1-x}U_xPd_3$ system exhibit NFL behavior at low temperatures $T \ll T_K$ and scale with $T_K$, where the value of $T_K$ has been inferred from the high temperature $T \geq T_K$ behavior of $\rho(T)$ and $\chi(T)$ [1, 5, 8]. The U 5f electron contributions to these properties, $\Delta\rho(T)$, $\Delta C(T)$ and $\Delta\chi(T)$, in the limit $T \ll T_K$ are described well by the following expressions:

$$\Delta\rho(T)/\Delta\rho(0) = 1 - a(T/T_K)$$

(3)

$$\Delta C(T)/T = (-bR/T_K) \ln[b(T/T_K)]$$

(4)

and

$$\Delta\chi(T)/\Delta\chi(0) = 1 - c(T/T_K)^{1/2}$$

(5)

Eq. (4) has the same form as the two-channel spin-½ Kondo formula in which $b = 0.25$ and $b' = 2.4$ [10]. We have used these values of $b$ and $b'$ in Eq. (4) to analyze the $C(T)/T$ data for a sample with $x = 0.2$ since it yielded a value of 42 K for $T_K$ which is close to the value inferred from the electrical resistivity at higher temperatures according to the criterion $\Delta\rho(T_K)/\Delta\rho(0) = 0.8$ ($T_K$ is the temperature where $\Delta\rho(T)$ starts to deviate from a ln $T$ dependence). The values $a = 0.23$ and $c = 0.36$ in Eqs. (3) and (5) were determined from the low temperature $\Delta\rho(T)$ and $\Delta\chi(T)$ data for the specimen with $x = 0.2$ by setting $T_K$ in Eqs. (3) and (5) equal to 42 K.

In the range $100 \leq T \leq 300$ K, $\Delta\chi(T)$ can be described by a Curie-Weiss law

$$\Delta\chi(T) = \chi(T) - \chi_0 = N\mu_{eff}^2/3k_B(T - \theta_p)$$

(6)

where $\chi_0$ is a temperature-independent contribution, $N$ is the number of U ions, $\mu_{eff}$ is the effective magnetic moment per U ion, and $\theta_p$ is the Curie-Weiss temperature. The effective moment $\mu_{eff} \approx 3.1\mu_B$ is smaller than the free ion value of $3.58\mu_B$ for tetravalent U and the Curie-Weiss temperature $\theta_p$ is large and negative. The reduced value of $\mu_{eff}$ and the large value of $|\theta_p|$ are both characteristic of systems which exhibit the Kondo effect where $-\theta_p = \beta T_K$ with $\beta \approx 3-4$. Since $|\theta_p|$ tends to saturate to a constant value of ~100 K for large values of $x \approx 0.5$, we assume that this value represents a non-Kondo contribution that is due to CEF effects and the spin glass and/or antiferromagnetic ordering that occurs for $x \geq 0.2$. Therefore, we set $T_K = (-\theta_p - 100 K)/3$, which gives a value consistent with the values of $T_K$ inferred from the other measurements described above. The behavior of $T_K$ as a function of $x$ is shown in Fig. 2. The decrease of $T_K$ with $x$ is consistent with the “Fermi-level tuning” scenario and the expected exponential form given by Eq. (2). We reached similar conclusions in a previous investigation of the
The measurements extend down to ~80 mK. A similar deviation of $\Delta C(T)/T$ from a logarithmic $T$-dependence at low temperatures was reported by Ott et al. [12]. Within the context of a two-channel spin-$\frac{1}{2}$ Kondo model, this upturn in $\Delta C(T)/T$ could be due to a lifting of the degeneracy of a $U^{4+}$ doublet ground state by magnetic or quadrupolar interactions between $U$ ions which would remove the residual $(R/2)\ln(2)$ entropy. The $\Delta\chi(T)$ data can be described by Eq. (5) below 0.3 and 40 K with parameter values $\chi(0) = 5.9 \times 10^{-3}$ emu/mol $U$, $c = 0.36$, and $T_K = 42$ K for $x = 0.2$. The $\chi(T)$ data were extracted from magnetization $M(H, T)$ data by decomposing the nonlinear $M$ versus $H$ isotherm at 0.6 K into a linear contribution $M_1(H, T) = \chi(T)H$, assumed to be intrinsic, and a nonlinear contribution $M_{nl}(H, T)$, assumed to be due to magnetic impurities, which scales with $H/(T + \theta)$, where $\theta = 0.235$ K, and can be approximated by a Brillouin function. The nonlinear contribution, which could be accounted for by magnetic impurities equivalent to 0.1% Ho, was subtracted from the $M(H, T)$ data to determine $\chi(T)$.

The development of a model that can account for the NFL behavior in the low temperature physical properties of $Y_{1-x}U_xPd_3$ requires information about the ground state of $U^{4+}$ in the cubic CEF. In a cubic CEF, the nine-fold degenerate $J = 4$ Hund’s rule multiplet of $U^{4+}$ is split into $\Gamma_4$, $\Gamma_5$, triplets, a $\Gamma_1$ singlet, and a $\Gamma_3$ nonmagnetic doublet that carries an electric quadrupole moment. If $\Gamma_3$ were the ground state, then the NFL characteristics in the physical properties at low temperature could be associated with a quadrupolar Kondo effect [12]. The quadrupolar Kondo model maps onto the two-channel spin-$\frac{1}{2}$ Kondo model and is based on an exchange interaction between an $S = \frac{1}{2}$ pseudo spin associated with the electric quadrupole moment of the $\Gamma_3$ ground state, and $\sigma = \frac{1}{2}$ pseudo spins of two time-reversed channels of conduction electrons, one channel corresponding to magnetic spin up and the other to magnetic spin down. According to the quadrupolar Kondo model, the electrical resistivity should vary as $\Delta \rho(T)/\Delta \rho(0) = 1 - a(T/T_K)^{1/2}$ [14], in disagreement with the linear $T$-dependence of Eq. (1) that is observed experimentally, while the specific heat should be given by Eq. (4) [10] and the magnetic susceptibility by Eq. (5) (where $\chi(0)$ is the van Vleck susceptibility for the $\Gamma_3$ ground state and the first CEF excited state) [15], both of which have $T$-dependences that are consistent with experiment. When the NFL behavior of $Y_{1-x}U_xPd_3$ was first reported, the $T^{1.2}$ temperature dependence of $\Delta \rho$ had not yet been calculated and arguments were advanced that $\Delta \rho(T)$ should have a linear $T$-dependence. Also, the value of $\Delta \chi(0)$ in Eq. (5) was consistent with the calculated van Vleck susceptibility between a $\Gamma_3$ ground state and the $\Gamma_5$ first excited state at 7 meV, the CEF...
energy level scheme that Mook et al. [16] inferred from inelastic neutron scattering measurements on \( Y_{0.8} U_{0.2} Pd_3 \). The conclusion that the ground state is the \( \Gamma_3 \) nonmagnetic doublet was based on the small quasielastic line width \( \Delta / 2 < 0.1 \) meV which is significantly smaller than the \( k_B T_K \sim 4 \) meV value expected for a Kondo effect of magnetic origin. Thus, it appeared that the NFL behavior of \( Y_{1-x} U_x Pd_3 \) could be explained in terms of a quadrupolar Kondo effect.

In subsequent inelastic neutron scattering studies on samples with \( x = 0.2 \) and 0.45, McEwen et al. [17] also concluded that the \( \Gamma_3 \) nonmagnetic doublet was the probable ground state, but with the \( \Gamma_4 \) and \( \Gamma_5 \) excited levels at 2.5 and 36 meV, respectively. They attributed the features at 16 meV to phonons and noted that there was dispersion of the \( \Gamma_4 \), \( \Gamma_4 \) excitation from which they inferred the existence of nearest neighbor AFM correlations.

Recently, Dai et al. [7] performed polarized inelastic neutron scattering (INS) as well as elastic neutron scattering measurements on samples with \( x = 0.2 \) and 0.45. The polarized INS measurements indicated that the ground state was the \( \Gamma_3 \) triplet with an excited state \( \Gamma_5 \) nonmagnetic doublet at 5 meV and a \( \Gamma_3 \) triplet at 39 meV. The quasielastic line width \( \Delta / 2 \) was estimated to be \( \leq 1 \) meV, still much smaller than the value \( k_B T_K \sim 4 \) meV expected for a magnetic Kondo effect. However, it is possible that the \( \Gamma_5 \) ground state is split due to local deviations from cubic symmetry at the \( U \) sites by an amount that is smaller than the resolution of the polarized INS measurements (\( \sim 5 \) meV). Elastic scattering measurements on the sample with \( x = 0.45 \) revealed the occurrence of long-range AFM order with a Néel temperature \( T_N = 21 \) K and an ordered moment \( \mu = 0.7 \mu_B \) \( U \). The AFM structure is the same as for the compound \( UPd_3 \), which also has the cubic \( Cu_3 Au \) structure, in which there is a doubling of the chemical unit cell in two directions [7]. The magnetization \( M(T) \) was found to be reversible and to vary as \( [M(T)/M(0)]^2 = (1 - T/T_N)^{0.7} \). The AFM ordering in the \( x = 0.45 \) sample is rather surprising since the magnetization of this sample exhibits irreversible behavior reminiscent of spin glass freezing with \( T_{irr} \) equal to the Néel temperature \( T_N \).

Neutron scattering measurements on the sample with \( x = 0.2 \) did not indicate any magnetic order above 0.2 K. However, critical fluctuations associated with AFM ordering with the same wave vector as the \( \Gamma_5 \) were observed on cooling from 77 to 0.2 K.

A metallurgical study of selected \( Y_{1-x} U_x Pd_3 \) samples in the range \( 0 \leq x \leq 0.2 \) by means of electron probe microanalysis by Stillow et al. [18] revealed local variations of the composition \( x \) on a scale of 10 \( \mu m \) for arc-melted and unannealed samples, such as those used in the present investigation. We have also observed \( U \) concentration fluctuations and changes in microstructure as \( x \) is varied in the \( Y_{1-x} U_x Pd_3 \) system in our ongoing investigation which will be reported on at a later date.

Thus, it would appear that the situation in the \( Y_{1-x} U_x Pd_3 \) system is considerably more complex than originally envisaged, and no single model presently available seems to be able to account for all of the properties of this rich and interesting pseudobinary alloy system. It is possible that a combination of factors including a multichannel Kondo effect, fluctuations of an order parameter above a 0 K second-order phase transition, and chemical disorder will be required to explain the behavior of this system.

3. \( M_{1-x} U_x Pd_3 \) systems based on other \( M \)-elements

We have investigated the properties of systems with the formula \( M_{1-x} U_x Pd_3 \) for \( M = Sc, La, Pr, Zr, \) and \( Th \), in addition to \( Y \) [8,19]. The systems based on trivalent \( M \)-elements (\( Sc, La, Pr \)) crystallize in the cubic \( Cu_3 Au \) structure for \( 0 \leq x < 0.5 \), while those based on the tetravalent \( M \)-elements (\( Zr, Th \)) crystallize in the hexagonal \( Ni_3 Ti \) structure, like pure \( UPd_3 \). No Kondo effect is observed for \( M_{1-x} U_x Pd_3 \) with \( M = La, Pr \) (very low \( T_K \)), while a Kondo effect is observed for \( M_{1-x} U_x Pd_3 \) with \( M = Sc, Y \) with values of \( T_K \) that exhibit Fermi level tuning and are larger for \( Sc \) than the corresponding \( T_K \) values for \( Y \). This follows from Eq. (1) if \( N(E_F) \) and/or \( \langle V^2 / \ell \rangle \) increases with decreasing unit cell volume \( v_c \) of the \( MPd_3 \) host compounds of trivalent \( M \)-elements. The values of \( v_c \) are related in the following way: \( v_c(\text{La}) > v_c(\text{Pr}) > v_c(\text{Y}) > v_c(\text{Sc}) \), yielding the following ordering of \( T_K : T_K(\text{La}) < T_K(\text{Pr}) < T_K(\text{Y}) < T_K(\text{Sc}) \).

Electrical resistivity \( \rho \) versus \( T \) data between \( \sim 2 \) K and room temperature for \( M_{1-x} U_x Pd_3 \) systems with \( M = Sc, Y, \) \( Pr, La \) are shown in Fig. 4. At low temperatures, the physical properties of \( M_{1-x} U_x Pd_3 \) exhibit non-Fermi-liquid characteristics for \( M = Sc \) and \( Y \) and Fermi-liquid behavior for \( M = La \) and \( Pr \). The \( \Delta C/T \) versus \( T^2 \) data in the range \( 0.4 \leq T \leq 5 \) K for \( La_{1-x} U_x Pd_3 \) shown in Fig. 5 reveal a large temperature independent enhancement of \( \gamma \) of \( \sim 500 \) mJ/mol \( U K^2 \) for the samples with \( x = 0.025 \) and 0.050, indicative of local Fermi-liquid behavior. This large enhancement of \( \gamma \) implies that there is appreciable hybridization of the localized \( U \) 5f states with the conduction electron states, but the physics is apparently different than in the \( M_{1-x} U_x Pd_3 \) systems with \( M = Sc, Y \) that display local non-Fermi-liquid behavior at low temperatures. Features are observed in the specific heat of the samples with \( x = 0.075 \) and 0.10 that are probably associated with spin-glass or AFM ordering of the \( U \) ions, consistent with the irreversibility observed in low field \( M(T) \) measurements on these
Fig. 4. Electrical resistivity $\rho$ versus temperature $T$ for $M_{1-x}U_xPd_3$ ($M =$ Sc, Y, Pr, La).

samples. For the $M_{1-x}U_xPd_3$ systems with $M =$ Zr and Th, no Kondo effect is observed, presumably because these tetravalent ions result in large values of $\xi_5f$ and correspond to small values of $T_K$.

4. Concluding remarks

The $Y_{1-x}U_xPd_3$ system exhibits a rich variety of behavior in the cubic Cu$_3$Au phase ($0 < x \leq 0.55$) which includes an unconventional Kondo effect, Fermi level tuning of the Kondo temperature, NFL behavior of the low temperature physical properties that scale with $T_K$ ($0 < x \leq 0.2$), and spin-glass and/or long-range AFM order ($0.2 < x \leq 0.55$). No Kondo effect is observed for $M_{1-x}U_xPd_3$ with $M =$ La, Pr (very low $T_K$), while a Kondo effect is observed for $M_{1-x}U_xPd_3$ with $M =$ Sc, Y with values of $T_K$ that exhibit Fermi level tuning and are larger for Sc than the corresponding $T_K$ values for Y. Possible mechanisms for this behavior include a multichannel Kondo effect, of either magnetic or
electric (quadrupolar) origin, and fluctuations of an order parameter above a 0 K second-order phase transition. Chemical disorder may also play an important role. The NFL behavior seems to be a general phenomenon of f-electron systems; more than ten f-electron systems have been found in which the $T$-dependences of $\Delta \rho(T)$, $\Delta C(T)$, and $\Delta \chi(T)$ at low temperatures $T \ll T_0$, where $T_0$ is a characteristic temperature (which can be identified with $T_K$ in many several systems), scale with $T_0$ and are the same as those exhibited by $Y_{1-x}U_xPd_3$, although in some cases the parameter $a$ that appears in the electrical resistivity is negative [1,2]. As we suggested several years ago [1,2], these systematics of NFL behavior appear to be general characteristics of a new class of strongly correlated f-electron materials. Much more work remains to be done to find new f-electron systems that exhibit NFL behavior, characterize the NFL behavior, and establish the underlying microscopic mechanisms that are responsible for the NFL behavior. Further work also needs to be done on the related $M_{1-x}U_xPd_3$ ($M = Sc, La, Pr, Zr, Th$) systems to determine how their physical properties compare to those of the $Y_{1-x}U_xPd_3$ system and explore new physics of these materials.

Acknowledgements

Research at UCSD was supported by the US National Science Foundation under Grant No. DMR-9107698 and the US Department of Energy under Grant No. DE-FG03-86ER45230. Work at ORNL was supported by US Department of Energy Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Work at LANL was performed under the auspices of the US Department of Energy.

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