Hybridization driven quantum critical behavior in weakly-itinerant ferromagnets

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(Dated: January 19, 2013; Received in ...) arXiv:1104.2287v1 [cond-mat.str-el] 12 Apr 2011

We investigate the unusual magnetic properties of nearly-critical, weakly-itinerant ferromagnets with general formula UTX, where T=Rh,Co and X=Ge, Si. As a unique feature about these systems, we show that changes in the Vd hybridization control their proximity to a ferromagnetic instability, and determine the evolution of: the ground state magnetization, M0, the Curie Temperature, TC, the density of states at the Fermi level, N(EF), the T2 resistivity coefficient, A, and the specific heat coefficient, γ. The universal aspect of our findings comes from the dependence on only two parameters: the Td bandwidth, Wd, and the distance between Td and Uf band centers, CTd − CUf.

PACS numbers:

In the past few years, a new class of materials has attracted significant attention due to their ability to sustain coexisting ferromagnetism and superconductivity at ambient pressure. These are ternary U compounds of general formula UTX, where T=Rh,Co and X=Ge[1, 2]. Together with UGe2, where superconductivity with TC = 0.8 K is obtained under applied pressure in a regime where ferromagnetism is still robust, TC = 35 K[3], and possibly Uhr[4], these materials have joined the special family of spin-triplet, weakly-itinerant ferromagnetic superconductors. Furthermore, the observation that both superconductivity and ferromagnetism are very susceptible to applied pressure, indicates that the Cooper pairing is being induced by the proximity to a ferromagnetic quantum critical point (QCP)[5].

The search for a ferromagnetic QCP has thus encountered a natural candidate, URhGe. Here the QCP could be reached through the chemical substitution of the transition metal element, Rh, since other isostructural compounds are either paramagnets, as URuGe, or even closer to the ferromagnetic instability, as UCoGe. Thus it seemed natural to investigate the evolution of the ferromagnetism and/or superconductivity in URh1−xTxeGe, for T=Ru or Co[6]. This was considered by Sakarya et al. in[6], but, although the suppression of the ferromagnetism went according to expectations in the case of Ru, at xe = 0.38, for the case of Co, instead, a huge and unexpected enhancement of TC (larger than 100%) was observed in TC, before it dropped down to less than 3 K, as xe → 1. The unexpected aspect of this finding comes from the fact that the isovalent doping in URh1−xCo2Ge does not introduce or remove carriers and the enhancement of TC is much larger than what would be expected from volume compressibility effects (less than 30%)[6].

In this letter we describe the mechanism behind such unusual behavior of TC as a function of isovalent disorder, x, in URh1−xCo2Ge, and we explain why a similar behavior is not observed in URhGe1−xSi2. We show that the evolution of TC(x) is governed by changes in the hybridization, Vdf, between the transition metal T=Rh,Co d-band and the actinide U f-level, which influences also other quantities such as density of states at the Fermi level, N(EF), the T2 resistivity coefficient, A, and the specific heat coefficient, γ. As we shall demonstrate, hybridization ultimately controls the proximity to the ferromagnetic instability, or QCP, where marked changes of behavior are observed for different ground state properties in such weakly-itinerant ferromagnetic systems.

The ternary URhGe and UCoGe compounds crystalize in the TiNiSi orthorhombic crystal structure with P(1ma) space group. There are 4 chemical formula units per unit cell and each of the 4 U, Rh/Co, or Ge atoms occupy one of the 4(c) crystallographic positions (x,1/4,z), (1/2−x,3/4,1/2+z), (1/2+x,1/4,1/2−z), and (−x,3/4,−z), resulting in a primitive lattice. The relative positions of the U, Rh/Co and Ge atoms in the unit cell were determined by X-ray (300 K) and neutrons (20 K)[7]: xU=0.9959(9), zU=0.2038(05), xRh/Co=0.5716(7), zRh/Co=0.5730(17), xGe=0.6103(9), zGe=0.5898(10), each of these quantities being measured in units of the lattice parameters a = 6.8552 Å, b = 4.3274 Å, and c = 7.5010 Å for URhGe, and a = 6.8450 Å, b = 4.2060 Å, and c = 7.2220 Å for UCoGe. Samples of URh1−xCo2Ge with x = 0.0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 were prepared by arc-melting the constituent elements (depleted U from Los Alamos National Laboratory, 99.9% purity, Rh/Co/Ge from Johnson Matthey Aesar, 99.95%/99.999%/99.9999% purity) under a purified Ar atmosphere. Samples were x-rayed using powder diffractometry in the University of Florida Major Analysis Instrumentation Center.

In a previous work on the effect of disorder on TC[8], we found that sizable variations in the electronic mean free path, ℓ, could drive the system from a clean towards...
a diffusive regime, where $T_C$ was found to be enhanced. We thus wanted to compare the evolution of $T_C(x)$ with the variation, with $x$, of disorder in URh$_{1-x}$Co$_x$Ge and URhGe$_{1-x}$Si$_x$, using, as straightforward measures of the disorder, the residual resistivity $\rho_0$ or the inverse of the residual resistivity ratio, $\rho_0/\rho(300K)$. As shown in Fig. 1, the Curie temperatures measured via magnetic susceptibility for the as-melted chunks and the resistivity bars (formed by sucking the molten material into a water-cooled mold, see [8]) agree well. However, as Fig. 1 also shows, the measures of disorder (either $\rho(0)$ or $\rho(0)/\rho(300K)$) did not appear to vary as $T_C(x)$, where the peak at $x = 0.6$ is quite marked. The conclusion is that, for URh$_{1-x}$Co$_x$Ge, the electronic mean free path, $\ell$, is always large enough, $k_F\ell \gg 1$, such that the system is always in the clean limit, and thus the variation in $T_C$ must be controlled by a different mechanism.

The magnetic properties of ternary actinide compounds with general formula UT(Si,Ge), are determined by the $5f$-$nd$-hybridization, $V_{df}$, with $n = 3, 4, 5$ [9]. Quite generally, as one goes down a fixed column in the periodic table (isovalent elements), the 3$d$, 4$d$ and 5$d$ bands of the transition metals become broader, as well as lower in energy with respect to the position of the $f$-level of the U ion [9]. This is in fact observed for the UCoAl, URhAl, UIrAl series [9], as well as for the UCoGe and URhGe compounds here under study [10][11]. As a consequence, the $V_{df}$ hybridization can be written as [12]

$$V_{df} = \frac{W_d W_f}{C_T - C_U},$$  

(1)

where $W_d, W_f$ are the transition metal and $f$-level bandwidths, and $C_T$ and $C_U$ are the centers of the T$d$ and U$f$ bands respectively. In terms of the muffin-tin orbital (MTO) theory by Andersen [13], the above formula becomes $V_{df} = (\eta_d \hbar^2/m^*)\sqrt{r_d^2/r_f^2}$, where $m^*$ is the conduction band effective mass, $\eta_d$ are dimensionless angular momentum dependent coefficients, $r_d$ and $r_f$ are the atomic radii of the $nd$ and $5f$ elements, and $d$ is the interatomic distance [14].

According to density functional theory (DFT) calculations, for URhGe the 4$d$-band of Rh starts at about $-6$ eV, relative to the Fermi level, and extends beyond 2 eV above the Fermi level [14], thus being very broad. Furthermore, the Fermi level is located in a region of high DOS with $5f$-character, see Fig. 2. The Stoner criterion is satisfied and URhGe exhibits ferromagnetic order with $T_C \approx 9.5$ K. This is also consistent with the high electronic contribution to the specific heat for URhGe, which has been estimated as $\gamma \approx 115$ mJ/mol K$^2$ [7] (after subtraction of the magnetic contribution). The results from DFT for URhGe also agree quite well with LSDA+U calculations [15]. For UCoGe, DFT shows that the 3$d$-band of Co starts at about $-4.5$ eV and extends up to approximately 1.6 eV, being, as such, much sharper [11]. Here, instead, the Fermi level is located in a region of much smaller $5f$ DOS, see Fig. 2 and the Stoner criterion is barely satisfied. In this case, UCoGe is very close to the Stoner instability and is thus a nearly critical ferromagnet with $T_C \approx 3$ K. Again this is consistent with the smaller electronic contribution to the specific heat for UCoGe, given by $\gamma \approx 65$ mJ/mol K$^2$ [4].

The microscopic mechanism for the unusual behavior for the Curie temperature in the URh$_{1-x}$Co$_x$Ge series can now be described. As Rh $\rightarrow$ Co, the $d$-bandwidth $W_d$ becomes smaller as it changes its character from 4$d$ $\rightarrow$ 3$d$ (we consider $W_f$ fixed, for simplicity). The smaller $W_d$ reduces the hybridization, $V_{df}$, which causes a large increase of the $f$-DOS at the Fermi level. Now, within the usual approach to itinerant ferromagnetism, one writes $T_C \propto \frac{N(E_F)}{(E_F)^{1/2} + 1}$, where $I$ is the so called Stoner integral and $z = 3$ for a clean itinerant ferromagnet [16]. Thus, we see that an increase of $N(E_F)$ leads to an enhancement of $T_C$. On the other hand, as doping further increases, the bottom of the $d$-band is shifted to
higher energies, \(C_{T,\sigma}\) moves towards \(C_{U,\sigma}\), since the 3d-band is closer to the \(f\)-level than 4d-band. The closeness between the \(d\) and \(f\) bands increases the hybridization, \(V_{df}\), which reduces the 5f-DOS at the Fermi level, reducing \(T_C\) considerably. Thus, the non-monotonic behavior observed experimentally in the \(T_C(x)\) phase diagram of URh1-xCoGe results from the combination of the two effects on \(V_{df}\) (or \(N(E_F)\)) when taken simultaneously.

The stabilization of weakly-itinerant ferromagnetism in the periodic Anderson model has been studied in [17]

\[
H = -t \sum_{\langle i,j \rangle} (d_{i,\sigma}^T d_{j,\sigma} + h.c.) + \varepsilon_d^0 \sum_i n_{i,\sigma}^d + \varepsilon_f^0 \sum_i n_{i,\sigma}^f + V_{df} \sum_i (f_{i,\sigma}^T d_{i,\sigma} + d_{i,\sigma}^T f_{i,\sigma}) + U \sum_i n_{i,\sigma}^d n_{i,\sigma}^f,
\]

where \(t\) is the nearest neighbor hopping integral for the dispersing \(d\)-band, \(\varepsilon_d^0, \varepsilon_f^0\) are the position of the \(d, f\)-states, \(V_{df}\) is the hybridization matrix element between the two, and \(U\) is the on-site Coulomb repulsion for the \(f\)-level, with \(n_{i,\sigma}^f = f_{i,\sigma}^T f_{i,\sigma}\). For large enough \(U \gg V_{df}\), a Hartree-Fock mean field decoupling can be justified, \(\sum_i n_{i,\sigma}^d n_{i,\sigma}^f = \sum_i \langle n_{i,\sigma}^d \rangle \langle n_{i,\sigma}^f \rangle + \sum_i n_{i,\sigma}^d \langle n_{i,\sigma}^f \rangle - \sum_i \langle n_{i,\sigma}^d \rangle \langle n_{i,\sigma}^f \rangle\), where \(\langle n_{i,\sigma}^f \rangle\) gives the average occupation for the \(f\) level at the site \(i\), including the two possible spin projections. We now introduce two Hubbard-Stratonovich fields, \(N_i\) and \(M_i\), associated, respectively, with the total number of \(f\) electrons, and the \(f\) electron magnetization per site, \(N_i = \langle n_{i,\sigma}^f \rangle + \langle n_{i,\sigma}^f \rangle\) and \(M_i = \langle n_{i,\sigma}^f \rangle - \langle n_{i,\sigma}^f \rangle\). We assume the system as homogeneous and replace \(N_i = n_f = N_f/N\), where \(N_f\) is the number of \(f\) electrons and \(N\) is the total number of sites. After this assumption we end up with

\[
H = \sum_k \varepsilon_d(k) d_{k,\sigma}^T d_{k,\sigma} + \varepsilon_f(k) f_{k,\sigma}^T f_{k,\sigma} + \frac{U}{2} \sum_i M_i^2
\]

\[
+ V_{df} \sum_k (f_{k,\sigma}^T d_{k,\sigma} + d_{k,\sigma}^T f_{k,\sigma}) - \frac{U}{2} \sum_i (n_{i,\sigma}^d - n_{i,\sigma}^f),
\]

where \(\varepsilon_c(k) = \varepsilon_d^0 - 2t \sum_{\alpha=1}^d \cos(k,\alpha)\) is the dispersion, and the renormalized \(f\)-level is shifted to \(\varepsilon_f = \varepsilon_f + \mu + U n_f / 2\).

We introduce ferromagnetic order by writing \(M_i = M_0\). The Hamiltonian becomes \(H = NU^2 / 4 + \sum_k C^T \mathcal{H} C\), where we have defined \(C^T = \sum_{\uparrow,\downarrow} (c_{k,\uparrow} c_{k,\downarrow} f_{k,\uparrow} f_{k,\downarrow})\) and

\[
\mathcal{H} = \begin{pmatrix}
\varepsilon_c(k) & 0 & V_{df} & 0 \\
0 & \varepsilon_c(k) & 0 & V_{df} \\
V_{df} & 0 & -\varepsilon_f - h & 0 \\
0 & V_{df} & 0 & -\varepsilon_f + h
\end{pmatrix}.
\]

The above Hamiltonian is quadratic in the fermion operators and can be easily diagonalized. The new eigenvalues are \((l = \text{lower}, u = \text{upper branches})\)

\[
E_{u,\pm}(k) = \frac{1}{2} \left[ (\varepsilon_c(k) + \varepsilon_f \pm h) + \sqrt{\varepsilon_c^2(k) + (\varepsilon_f \mp h)^2 + 4V_{df}^2} \right],
\]

\[
E_{l,\pm}(k) = \frac{1}{2} \left[ (\varepsilon_c(k) + \varepsilon_f \pm h) - \sqrt{\varepsilon_c^2(k) + (\varepsilon_f - h)^2 + 4V_{df}^2} \right],
\]

where \(h = U M_0 / 2\). The self-consistency equations for \(M_0\) and \(n_f\) are given by \(M_0 = (1/N) \sum_k \{ \langle n_{k,\uparrow} \rangle - \langle n_{k,\downarrow} \rangle \}\) and \(n_f = (1/N) \sum_k \{ \langle n_{k,\uparrow}^f \rangle + \langle n_{k,\downarrow}^f \rangle \}\) or explicitly as

\[
M_0 = \frac{1}{N} \sum_k \sum_{\sigma=\pm} \text{sign}(\sigma) \left[ \frac{E_{u,\sigma}(k) - \varepsilon_c(k)}{E_{u,\sigma}(k) - E_{l,\sigma}(k)} n_{FD}(E_{u,\sigma}(k) - \mu) + \frac{E_{l,\sigma}(k) - \varepsilon_c(k)}{E_{l,\sigma}(k) - E_{u,\sigma}(k)} n_{FD}(E_{l,\sigma}(k) - \mu) \right],
\]

\[
n_f = \frac{1}{N} \sum_k \sum_{\sigma=\pm} \left[ \frac{E_{u,\sigma}(k) - \varepsilon_c(k)}{E_{u,\sigma}(k) - E_{l,\sigma}(k)} n_{FD}(E_{u,\sigma}(k) - \mu) + \frac{E_{l,\sigma}(k) - \varepsilon_c(k)}{E_{l,\sigma}(k) - E_{u,\sigma}(k)} n_{FD}(E_{l,\sigma}(k) - \mu) \right],
\]

where \(n_{FD}(E - \mu) = (\varepsilon_c^\beta(E - \mu) + 1)^{-1}\), with \(\beta = 1/k_B T\). We find \(M_0(x = 0) = 0.22 \mu_B / \text{U-atom}\), for URhGe, and \(M_0(x = 1) = 0.06 \mu_B / \text{U-atom}\), for UCoGe, in very good agreement with experiments [18], showing that in UCoGe \(V_{df}\) is indeed much larger, see Fig. [3]. We have also calculated the total density of states for the above band structure using Eqs. [4] with \(n_f = 0.4 [9]\) and \(U = 9\) (in units of \(t\)). The results in Fig. [2] are in very good agree-
ment with LSDA+U \cite{[15]} and DFT data \cite{[11]}. Notice that the splitting between + and − states near $E_F$ is proportional to $h = U M_0$ /2, being thus much larger for URhGe than for UCoGe, see Fig. 2. The change in behavior of $M_0(V_{df})$ occurs exactly when $V_{df}$ becomes larger than such splitting, and $M_0$ decreases linearly as a function of $V_{df}$, before it vanishes for $V_{df} \approx 1.9$ (in units of $t$), at the ferromagnetic QCP.

Since the $d$-bandwidth, $W_d$, decreases monotonically as Rh is replaced by Co, we parametrize

$$W_{df}(x) = W_{df}^R(1-x) + W_{df}^C x,$$  

(5)

where the values for $W_{df}^R$ and $W_{df}^C$ agree with \cite{[10]} \cite{[11]}, giving $t^R = 1$ eV and $t^C = 0.6$ eV. Analogously, $\epsilon_0^R = C^R_d$ approaches continuously to $\epsilon_0^R = C$, with $C_{H} = -2$ eV, $C_{H} = -1.5$ eV, and $C_{U} = 0$ eV, before hybridization. However, this approach, though monotonic, deviates from linearity \cite{[12]} and thus we write

$$\Delta C_{df}(x) = \Delta C_{df}^R (1-x) + \Delta C_{df}^C x + \delta x(1-x) + \delta \delta x(1-x)^2,$$  

(6)

where $\delta$ and $\delta$ are adjustable parameters. Below we plot $T_C(x)$ for URh$_{1-x}$Co$_x$Ge where the $V_{df}$ hybridization induced, non-monotonic behavior for $T_C$ can be observed.

The nontrivial evolution of $N(E_F)$ governed by $V_{df}$ has also measurable consequences in transport properties. For example, the resistivity of URh$_{1-x}$Co$_x$Ge behaves as $p \sim AT^2$, for all $x$, where $A$, the resistivity coefficient, exhibits also a nonmonotonic behavior as a function of $x$ \cite{[13]}. Although it is generally difficult to separate electronic and magnetic contributions to $A$, for the case of weakly-itinerant ferromagnets, the dominant magnetic scattering contribution to the resistivity is \cite{[10]}

$$\rho_{mag} \sim |IN(E_F) - 1|^{-1/2}T^2 = AT^2.$$  

(7)

In fact, $A$ can be thought of as a direct measure of the proximity to the ferromagnetic QCP, being large for URhGe but even larger for UCoGe, smaller at intermediate doping $0 < x < 1$ \cite{[13]}. Thus $\rho_{mag}$ should have the opposite behavior as $T_C$, see Fig. 4 right panel.

It is interesting to compare the above results for URh$_{1-x}$Co$_x$Ge with the case of another isovalent-disordered compound, URh$_{1-x}$Si$_x$. The substitution Ge $\rightarrow$ Si in URh$_{1-x}$Si$_x$ does not modify the $V_{df}$ hybridization, and causes, at most, a small broadening of the Rh, 4$d$-band, due to substitutional disorder. Such small broadening causes an almost negligible reduction of the 5$f$-DOS at the Fermi level, and thus $T_C$ is expected to be slightly reduced at the point of largest disorder, $x = 0.5$. This is exactly what we measured for URh$_{0.5}$Si$_{0.5}$ where we found $T_C(x = 0.5) = 8.5$ K, only 10% smaller than the endpoints $T_C(x = 0) = T_C(x = 1) = 9.5$ K.

We have shown that in nearly critical, weakly itinerant ferromagnets, such as URh$_{1-x}$Co$_x$Ge, the proximity to a ferromagnetic QCP is controlled by the hybridization, $V_{df}$, between the transition metal and the antinide. Smaller values for $V_{df}$ drive the system away from the QCP, while larger values for $V_{df}$ pushes the system towards the QCP. The unusual behavior observed for $T_C(x)$, $M_0(x)$, and $A(x)$, can all be quantitatively understood from the nontrivial evolution of $V_{df}(x)$ as the 4$d$-band of Rh changes character to the 3$d$-band of Co.

A.H.C.N. acknowledges DOE grant DE-FG02-08ER46512 and ONR grant MURI N00014-08-1-1063. Work at Florida supported by the US DOE, grant no. DE-FG02-86ER45268.