Simultaneous suppression of ferromagnetism and superconductivity in UCoGe by Si substitution

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We investigate the effect of substituting Si for Ge in the ferromagnetic superconductor UCoGe. Dc-magnetization, ac-susceptibility and electrical resistivity measurements on polycrystalline UCoGe$_{1-x}$Si$_x$ samples show that ferromagnetic order and superconductivity are progressively depressed with increasing Si content and simultaneously vanish at a critical concentration $x_{cr} \approx 0.12$. The non-Fermi liquid temperature variation in the electrical resistivity near $x_{cr}$ and the smooth depression of the ordered moment point to a continuous ferromagnetic quantum phase transition. Superconductivity is confined to the ferromagnetic phase, which provides further evidence for magnetically mediated superconductivity.

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Recently, it was discovered that the intermetallic compound UCoGe belongs to the small group of ferromagnetic superconductors (FMSCs): superconductivity with a transition temperature $T_c = 0.8$ K coexists with weak itinerant FM order with a Curie temperature $T_C = 3$ K. Ferromagnetic superconductors attract much interest, because in the standard BCS scenario superconductivity is due to the strong depairing effect of the ferromagnetic quantum critical point. Evidence for the proximity to a FM QCP has been extracted from magnetization and specific heat data, using the Ehrenfest relation, which thwarts phonon mediated formation of singlet Cooper pairs. However, an alternative route is offered by spin fluctuation models, in which critical magnetic fluctuations associated with a ferromagnetic quantum critical point (FM QCP) mediate SC by pairing the electrons in triplet states. The FMSCs discovered so far are UGe$_2$, UIr$_2$ (under pressure), URhGe$_2$ and UCoGe$_2$. The latter two compounds offer the advantage that SC occurs at ambient pressure, which facilitates the use of a wide range of experimental techniques to probe magnetically mediated SC.

UCoGe crystallizes in the orthorhombic TiNiSi structure (space group $P_{nma}$). Evidence for the proximity to a FM QCP has been extracted from magnetization and specific heat measurements on polycrystalline samples. The low $T_C = 3$ K and the small value of the ordered moment $m_0 = 0.03 \mu_B$ reveal magnetism is weak. Itinerant magnetism is corroborated by the small value of the magnetic entropy ($0.3\%$ of $\ln2$) associated with the magnetic transition. More recently, the magnetic and SC properties were determined for a single-crystalline sample. Magnetization data reveal UCoGe is a uniaxial ferromagnet with the ordered moment $m_0 = 0.07 \mu_B \approx 2m_0^{polg}$ pointing along the c axis. The electrical resistivity $\rho(T)$ measured for a current $I || a$ shows SC below 0.6 K and a sharp kink signaling the Curie temperature $T_C = 2.8$ K. The non-Fermi liquid temperature variation of the resistivity is characteristic for a weak itinerant FM near a critical point, i.e. a Fermi liquid $\rho \propto T^2$ dependence below $T_C$ and scattering at critical FM fluctuations $\rho \propto T^{5/3}$ there above.

In the generic pressure-temperature phase diagram for FMSCs the superconducting phase (the dome) is confined to the magnetic phase and $T_C$ and $T_s$ vanish at the same critical pressure. Such a phase diagram has been reported for UGe$_2$ and UIr$_2$ under pressure. In the case of UCoGe, the analysis of the thermal expansion and specific heat data, using the Ehrenfest relation, shows that $T_C$ decreases with pressure, whereas $T_s$ increases. This places UCoGe on the far side of the superconducting dome with respect to the magnetic quantum critical point. Concurrently, under hydrostatic mechanical pressure $T_s$ is predicted to go through a maximum, before vanishing at the critical point. In this work we use an alternative route to study the evolution of FM and SC, namely chemical pressure exerted by replacing Ge by isostructural Si. Ferromagnetic UCoGe and paramagnetic UCoSi are isostructural. The unit cell volume of UCoSi is $\sim 3.5\%$ smaller than the one of UCoGe, so chemical pressure is relatively weak. By means of magnetic and transport measurements we find that FM order and SC are gradually depressed and vanish simultaneously at a critical concentration $x_{cr} \approx 0.12$. SC is confined to the FM phase in agreement with the generic phase diagram. This yields further support for magnetically mediated superconductivity.

A series of polycrystalline UCoGe$_{1-x}$Si$_x$ samples were prepared with $0 \leq x \leq 0.20$ and $x = 1$. The constituents (natural U 3N, Co 4N, Ge 5N and Si 5N) were weighed according to the nominal composition $U_{1+0.02}Co_{1+0.02}Ge_{1-x}Si_x$ and arc melted together under a high-purity argon atmosphere in a water-cooled copper crucible. The as-cast samples were annealed for ten days at 875 °C. Samples were cut by spark erosion in a bar-shape for transport and magnetic measurements. The phase homogeneity of the annealed samples was investigated by Electron Probe Micro Analysis (EPMA). The matrix had the 1:1:1 composition and all samples contained a small amount (2%) of impurity phases. The EPMA technique did however not allow for a precise determination of the Ge and Si
The dc-magnetization, \( M(T, B) \), was measured in a SQUID magnetometer in magnetic fields up to 5 T and temperatures down to 2 K. The low-field \( (B = 10^{-5} \text{ T}) \) ac-susceptibility, \( \chi_{ac} \), was measured using a mutual inductance coil and a phase-sensitive bridge in a \(^3\)He system with base temperature 0.23 K or in a dilute refrigerator with base temperature 0.02 K. Electrical resistivity data, \( \rho(T) \), were taken using a low-frequency ac-brIDGE in a four-point configuration in the same temperature range.

The dc-magnetic susceptibility \( \chi_{dc}(T) \) of the UCoGe\(_{1-x}\)Si\(_x\) alloys was measured in an applied field of 1 T in the temperature range 2 - 300 K. The effect of doping small amounts of Si on \( \chi_{dc}(T) \) is weak. For all \( x \leq 0.20 \) the data for \( T = 50 \) - 300 K are described by a modified Curie-Weiss law, with a temperature independent susceptibility \( \chi_0 \approx 10^{-8} \text{ m}^3/\text{mol} \) and an effective moment \( p_{eff} \approx 1.6 \pm 0.1 \mu_B/\text{f.u.} \). On the contrary, the effect of doping on the FM transition is large. Measurements of the dc-magnetization in a small field \( (B = 0.01 \text{ T}) \) show that upon Si doping the FM transition is rapidly suppressed to below the low temperature limit of our dc-magnetometer \( (2 \text{ K}) \). For \( x = 0.00 \) and 0.02 we find \( T_C = 3.0 \text{ K} \) and 2.5 K, respectively. In Fig. 1 we show the field dependence of the magnetization \( M(H) \) measured at \( T = 2 \text{ K} \). The gradual increase of \( M(H) \) observed for \( B \geq 1 \text{ T} \) is related to the

\[ M(H) = M_s(0) + \Delta M(1 - e^{-\mu_B H/B_0}) \]

(1)

where the parameter \( B_0 \) probes the magnetic interaction strength of the fluctuating moments. In the high-field limit \( M(H = \infty) = M_s(0) + \Delta M \). Eq. 1 describes the experimental data well for \( B \geq 1 \text{ T} \) (solid lines in Fig. 1). The intercepts of the fits with the vertical axis yield the fit parameters \( M_s(0) \) in the limit \( T \to 0 \). The deviations for \( B < 1 \text{ T} \) are due to the finite temperature at which the data are taken (the ordered moment is not fully developed yet). For \( x = 0.00 \) \( M_s(0) \approx 0.029 \mu_B \) \( (T \to 0) \) in agreement with previous results, while for \( x = 0.02 \) \( M_s(0) \approx 0.022 \mu_B \). For the samples with \( x = 0.05, 0.08 \) and 0.10 the data have been taken at \( T > T_C \). Nevertheless, a rough estimate of \( M_s(0) \) can be obtained, as the magnetic transition shows a large temperature broadening in applied fields \( B > 1 \text{ T} \). The resulting values of \( M_s(0) \) are traced in the right panel of Fig. 1. We conclude \( M_s(0) \) smoothly goes to zero in the concentration range \( 0.10 < x < 0.14 \).

The suppression of \( T_C \) was studied in more detail by the ac-susceptibility technique. The data, taken down to \( 0.23 \text{ K} \) \( (0.00 \leq x \leq 0.10) \) and down to 0.02 K \( (0.14 \leq x \leq 0.20) \), are shown in Fig. 2. The maximum in \( \chi_{ac} \) locates the Curie temperature, which equals 2.8 K and 2.3 K, for \( x = 0.00 \) and 0.02 respectively. These values compare well with those extracted from the dc-magnetization. With increasing Si content the transition becomes weaker, broadens (see inset in Fig. 2) and for \( x \geq 0.14 \) a maximum in \( \chi_{ac} \) no longer can be identified. This confirms magnetism vanishes in the concentration range \( 0.10 < x < 0.14 \). The large diamagnetic signal
FIG. 3: Left panel: The electrical resistivity $\rho$ (arbitrary units) plotted versus $T^n$ of UCoGe$_{1-x}$Si$_x$ alloys for $x$ as indicated. The curves are shifted along the vertical axis for clarity. The straight solid lines represent fits $\rho \sim T^n$ (see text). Right panel: Exponent $n$ versus Si concentration. The dashed line serves to guide the eye. The vertical dotted line locates $x_{cr}$. The horizontal dotted line indicates $n = 2$.

measured for $x = 0.00$, 0.04 and 0.06 down to 0.23 K signals bulk SC. SC is progressively depressed and is no longer observed for $x = 0.14$ (at least down to 0.02 K).

The electrical resistivity was measured in the temperature interval 0.23 – 10 K for $x \leq 0.08$ and in the range 0.02 – 10 K for 0.10 $\leq x \leq 0.20$. For $x = 0.00$ the residual resistivity $\rho_0 = 26 \mu\Omega cm$. Upon alloying $\rho_0$ increases linearly at least up to $x = 0.08$ at the fastest rate of 12 $\mu\Omega cm$ per at.% Si. This shows all Si substitutes for Ge. Concurrently, the residual resistance ratio $\text{RRR} = R(300\text{K})/R(1\text{K})$, which amounts to 27 for $x = 0$, drops to $\sim 5$ for $x = 0.08$. For $x \geq 0.10$, however, the $\text{RRR}$ levels off at a value $\sim 4$. The strong doping sensitivity of $\rho_0$ is possibly related to an enhanced site inversion Ge,Si ↔ Co. Notice the TiNiSi structure is an ordered variant of the CeCu$_2$ structure (for UTX compounds crystallizing in the latter structure the transition metal atoms T and group IV atoms X are randomly distributed over the 8h Cu sites).

The FM transition appears as a broad hump in $\rho(T)$ for pure UCoGe. Upon alloying, the hump shifts to lower temperatures at the same rate as the maximum in $\chi_{ac}$. In Fig. 3 we show the low-temperature part of the resistivity data in a plot of $\rho$ versus $T^n$. Here $n$ is determined by fitting $\rho \sim T^n$ for $T_s < T < T_C$. For each $x$ the best value of $n$ was obtained by fitting over a larger and larger temperature range, while keeping $n$ constant and the error small. In the magnetic phase ($x \leq 0.10$) the exponent shows a quasi-linear decrease from $n = 2$ for $x = 0.00$ to the non-Fermi-liquid value $n \approx 1$ for $x = 0.10$ (see Fig. 3). Close to the critical point the temperature range for the fit becomes very small and the values of $n$ should be interpreted with care. Nevertheless, the decreasing trend is evident. For $x \geq 0.14$ the Fermi liquid value $n = 2$ is recovered. The SC transition is depressed with increasing Si content and no SC has been observed down to 0.02 K for $x = 0.14$.

Having determined the evolution of the FM and SC phases in the UCoGe$_{1-x}$Si$_x$ alloys by magnetic and transport measurements, we construct the phase diagram shown in Fig. 4. $T_C$ is depressed quasi-linearly, at least with $x = 0.08$, at a rate $dT_C/dx = -0.25 K/\text{at.}\% \text{Si}$. By extrapolating $T_C(x) \to 0$ we arrive at a critical Si concentration for the suppression of FM order $x_{cr} = 0.11$. For $x > 0.08$ a tail appears, and the data extrapolate to $x_{cr}^\text{FM} \approx 0.12$. $T_s$, determined resistively by the midpoint of the transition, is depressed somewhat faster than linear, initially at a rate $dT_s/dx = -0.06 K/\text{at.}\% \text{Si}$. By smoothly extrapolating $T_s(x) \to 0$ we obtain a critical Si concentration for the suppression of SC $x_{cr}^\text{SC} \approx 0.12$. The $T_s(x)$ values measured by $\chi_{ac}(T)$ for $x \leq 0.06$, signal the onset of bulk SC and follow the same trend. Notice $T_s(x)$ bulk extrapolates to a slightly lower $x_{cr}$, i.e. close to the value $x_{cr} = 0.11$ obtained by the linear extrapolation of $T_C(x)$.

In order to compare the effect of chemical and hydrostatic pressure we calculate from the difference in unit cell volume of UCoGe and UCoSi that 1 at.% Si is equivalent to 0.35 kbar (here we assume the isothermal compressibility $\kappa \approx 10^{-11} \text{ Pa}^{-1}$). Concurrently, the measured doping-induced depression of $T_C$ (Fig. 4) translates to $dT_C/d\rho = -0.71 K/\text{kbar}$, which is about a factor three larger than the value $\sim 0.25 K/\text{kbar}$ calculated via the Ehrenfest relation. This indicates Si does not merely exert chemical pressure. Indeed hybridization phenomena in UTX alloys are in general strongly anisotropic. As regards the SC transition, Si doping obviously has a different effect than hydrostatic pressure. The measured doping-induced depression of $T_s$ (Fig. 4) translates to $dT_s/d\rho = -0.17 K/\text{kbar}$, while the Ehrenfest relation shows $T_s$ increases at a rate $dT_s/d\rho = 0.02 K/\text{kbar}$.
The suppression of magnetic order in the UCoGe$_{1-x}$Si$_x$ alloys can be understood in terms of a simple Doniach picture\textsuperscript{12}: by doping the smaller Si atoms the 5$f$ - 3$d$ hybridization strength increases, which leads to a loss of magnetism. The rapid suppression of FM order provides further evidence that UCoGe is close to a FM QCP. This is corroborated by the steady decrease of the non-Fermi liquid exponent $n$ of the resistivity measured in the FM phase (see Fig. 3). The itinerant nature of the FM state suggests that the critical point is of the Moriya-Hertz-Millis\textsuperscript{12,19,20} type. The extracted exponent $n \approx 1$ near $x_{cr}^{FM}$ is much smaller than the value $n = 5/3$ predicted for a clean FM QCP. A similar observation was made for the doping-induced FM QCP in URh$_{1-x}$Ru$_x$Ge alloys\textsuperscript{21}; at $x_{cr} = 0.38$ $n \approx 1.2$. Clearly, disorder reduces\textsuperscript{22} $n$. The smooth depression of $M_s(0)$ indicates the ferro-to-paramagnetic transition at $T = 0$ $K$ is a continuous phase transition. Additional experiments, e.g. specific heat, are required to put the evidence for a FM QCP at $x_{cr} \approx 0.12$ on firm footing.

The magnetic and SC phase diagram (Fig. 4) presents compelling evidence that superconductivity is confined to the FM phase. Moreover, by smoothly extrapolating $T_C(x)$ and $T_s(x)$ we arrive at a most important conclusion, namely $x_{cr}^{FM} = x_{cr}^{SC} \approx 0.12$. This shows that FM order and SC are closely tied together. The simultaneous suppression of FM order and SC yields strong support for triplet SC mediated by FM spin fluctuations\textsuperscript{22,23,11,14}. Evidence for triplet SC is furnished by the absence of Pauli limiting in the upper critical field $B_{c2}^{UP}$. Moreover, the observed anisotropy in $B_{c2}$ provides evidence for an axial SC gap with nodes along the direction of the ordered moment, as calculated\textsuperscript{23} for the A phase of an orthorhombic FMSC. On the other hand, it is recognized\textsuperscript{12,24} that triplet SC is extremely sensitive to scattering at non-magnetic impurities and defects. Therefore, it is surprising that SC survives till doping concentrations of $\sim$12 at.\% Si. For our polycrystalline UCoGe samples, with $RRR \sim 30$, we calculated\textsuperscript{25} an electron mean free path, $\ell \approx 500$ Å, in excess of the SC coherence length $\xi \approx 150$ Å, a necessary condition for unconventional SC. Upon replacing Ge by Si the residual resistance increases, leading to a corresponding decrease of $\ell$. Unconventional SC therefore would require a strong doping-induced reduction of $\xi$ as well. The depression of non-s wave SC by non-magnetic impurities can be modelled using a generalized form\textsuperscript{25,26} of the Abrikosov-Gor’kov pair-breaking theory. A recent example is provided by the defect-driven depression of $p$-wave SC in the paramagnet Sr$_2$RuO$_4$\textsuperscript{27}. In the case of the UCoGe$_{1-x}$Si$_x$ alloys, however, the defect-driven depression of $T_c$ is partly compensated by $T_s$ increasing due to chemical pressure. Also, one may speculate that upon the approach of the FM QCP, FM fluctuations stimulate triplet SC even stronger. Obviously, more experiments are needed to unravel the different pairing and de-pairing contributions to $T_s$.

In summary, magnetic and transport measurements on a series of polycrystalline UCoGe$_{1-x}$Si$_x$ samples show that ferromagnetic order and superconductivity are both depressed and vanish at the same critical concentration $x_{cr} \approx 0.12$. The non-Fermi liquid exponent in the resistivity near $x_{cr}$ and the smooth depression of the ordered moment point to a continuous FM quantum phase transition. Superconductivity is confined to the ferromagnetic phase, which provides further evidence for magnetically mediated superconductivity. These results offer a unique route to investigate the emergence of superconductivity near a FM QCP at ambient pressure.

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