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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 $x_{cr} \simeq 0.12$. 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[1] that the intermetallic compound UCoGe belongs to the small group of ferromagnetic superconductors (FMSCs): superconductivity with a transition temperature T_s=0.8 K coexists with weak itinerant ferromagnetic (FM) order with a Curie temperature T_C=3 K. Ferromagnetic superconductors attract much interest because in the standard BCS scenario, superconductivity (SC) and FM are incompatible.[2] This is due to the strong depairing effect of the ferromagnetic exchange interaction, which thwarts phonon mediated formation of singlet Cooper pairs. However, an alternative route is offered by spin fluctuation models,[3,4] 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 (under pressure),[5] UIr (under pressure),[6] URhGe,[7] and UCoGe.[1] 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[8,9] 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[1] on polycrystalline samples. The low T_C =3 K and the small value of the ordered moment m_0 $=0.03\mu_B$ reveal that magnetism is weak. Itinerant magnetism is corroborated by the small value of the magnetic entropy[1] (0.3% of $R\ln 2$) associated with the magnetic transition. More recently, the magnetic and SC properties were determined for a single-crystalline sample.[10] Magnetization data reveal that UCoGe is a uniaxial ferromagnet with the ordered moment $m_0=0.07\mu_B \simeq 2m_0^{poly}$ pointing along the c axis. The electrical resistivity $\rho(T)$ measured for a current $I \parallel a$ shows SC below 0.6 K and a sharp kink signaling the Curie temperature T_C=2.8 K. The temperature variation of the resistivity[10,11] is characteristic[12] 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[3,4,13,14] 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 (Ref. 5) and UIr (Ref. 6) under pressure. In the case of UCoGe,[1] 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 isoelectronic Si. Ferromagnetic UCoGe and paramagnetic[15] UCoSi are isostructural.[8,9] The unit cell volume of UCoSi is ~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 simultaneously vanish at a critical concentration $x_{cr} \simeq 0.12$. 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 was 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 $U_{1.02}Co_{1.02}Ge_{1-x}Si_x$ 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 microanalysis (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 ratio, and in the following, x is the nominal concentration. Powder x-ray diffraction patterns at T=300 K for x=0.0, 0.1, 0.2, and 1.0 confirmed the TiNiSi structure. The measured lattice constants are a=6.864 Å, b=4.196 Å, and c=7.261 Å for UCoGe and a=6.876 Å, b=4.108 Å, and c=7.154 Å for UCoSi, in good agreement with the literature.[8,9] The unit cell volume Ω linearly decreases from 209.5 (x=0) to 202.1 Å^3 (x=1), with the main contraction along the b and c axes.

The dc magnetization, $M(T,B)$, was measured in a superconducting quantum inference device magnetometer in magnetic fields up to 5 T and temperatures down to 2 K. The low-field ($B=10^{-5}$ T) ac susceptibility χ_{ac} was measured us-

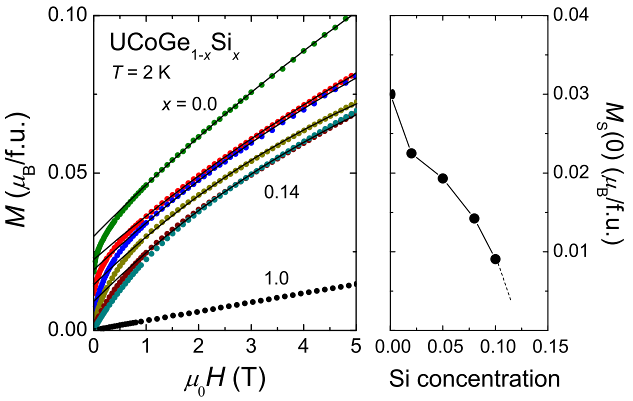

FIG. 1. (Color online) Left panel: magnetization as a function of field for UCoGe$_{1-x}$Si$_x$ alloys at T=2 K. Si concentrations are (from top to bottom) x=0, 0.02, 0.05, 0.08, 0.10, 0.14, and 1.0. The solid lines represent fits to Eq. (1) for $x \leq 0.10$. Right panel: spontaneous magnetization $M_s(0)$ as a function of Si content.

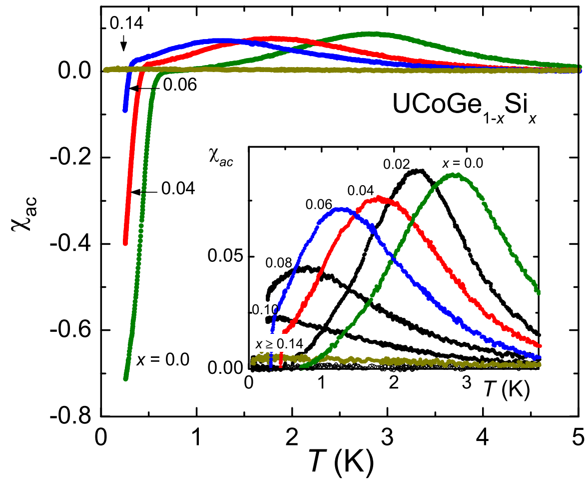

FIG. 2. (Color online) Temperature variation of the ac susceptibility (SI units) of UCoGe$_{1-x}$Si$_x$ alloys for x=0.00, 0.04, 0.06, and 0.14. The inset shows χ_{ac} around the ferromagnetic transition for $0.00 \leq x \leq 0.20$. The data for x=0.20 fall on the horizontal axis.

ing a mutual inductance coil and a phase-sensitive bridge in a ^{3}He system with base temperature of 0.23 K or in a dilution refrigerator with base temperature of 0.02 K. Electrical resistivity data $\rho(T)$ were taken by 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 of 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 $\chi_0 \simeq 10^{-8}$ m^3/mol and an effective moment $p_{eff} \simeq 1.6 \pm 0.1 \mu_B$/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 T) show that upon Si doping, the FM transition is rapidly suppressed to below the low temperature limit of our dc magnetometer (2 K). For x=0.00 and 0.02, we find T_C=3.0 and 2.5 K, respectively. In Fig. 1, we show the field dependence of the magnetization $M(H)$ measured at T=2 K. The gradual increase in $M(H)$ observed for $B \gtrsim 1$ T is related to the itinerant nature of the magnetic state. The spontaneous magnetization $M_s(H=0)$ rapidly drops with increasing Si content. For the ordered compounds, an estimate of $M_s(0)$ can be made by fitting the data to the empirical expression

$$M(H) = M_s(0) + \Delta M(1 - e^{-\mu_0 H/B_0}), \tag{1}$$

where the parameter B_0 probes the magnetic interaction strength of the fluctuating moments. In the high-field limit $M(H=\infty)=M_s(H=0)+\Delta M$, Eq. (1) describes the experimental data well for $B \gtrsim 1$ T (solid lines in Fig. 1). The intercepts of the fits with the vertical axis yield the fit parameters $M_s(H=0)$ in the limit $T \rightarrow 0$. The deviations for $B < 1$ 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, $M_s(0) \simeq 0.029\mu_B$ ($T \rightarrow 0$), in agreement with previous results,[1] while for x=0.02, $M_s(0) \simeq 0.022\mu_B$. 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 $B > 1$ T. The resulting values of $M_s(0)$ are traced in the right panel of Fig. 1. We conclude that $M_s(0)$ 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 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 χ_{ac} locates the Curie temperature, which equals 2.8 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 and broadens (see inset of Fig. 2) and for $x \geq 0.14$, a maximum in χ_{ac} can no longer be identified. This confirms that magnetism vanishes in the concentration range $0.10 < x < 0.14$. The large diamagnetic signal measured for x=0.00,[1] 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 of 0.23–10 K for $x \leq 0.08$ and in the range of 0.02–10 K for $0.10 \leq x \leq 0.20$. For x=0.00, the residual resistivity ρ_0=26 $\mu\Omega$ cm. Upon alloying, ρ_0 linearly increases at least up to x=0.08 at the fast rate of 12 $\mu\Omega$ cm/at. % Si. This shows all Si substitutes for Ge. Concurrently, the residual resistance ratio (RRR)=R(300 K)/R(1 K), which amounts to 27 for x=0, drops to ~5 for x=0.08. For $x \geq 0.10$, however, the RRR levels off at a value of ~4. The strong doping sensitivity of ρ_0 is possibly related to an enhanced site inversion Ge,Si$\leftrightarrow$Co. Notice that the TiNiSi structure is an ordered variant of the CeCu$_2$ structure[16] (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.[1] Upon alloying, the hump shifts to lower temperatures at the same rate as the maximum in χ_{ac}. In Fig. 3,

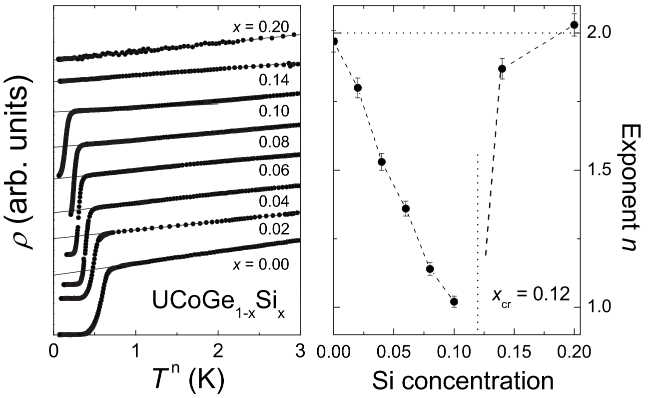

FIG. 3. Left panel: the electrical resistivity ρ (arbitrary units) plotted versus T^n of $UCoGe_{1-x}Si_x$ alloys for x as indicated. The curves are shifted along the vertical axis for clarity. The straight solid lines represent fits $\rho \sim T^n$ (see text). Right panel: exponent n versus Si concentration. The dashed line serves as a guide for the eyes. The vertical dotted line locates x_{cr}. The horizontal dotted line indicates $n=2$.

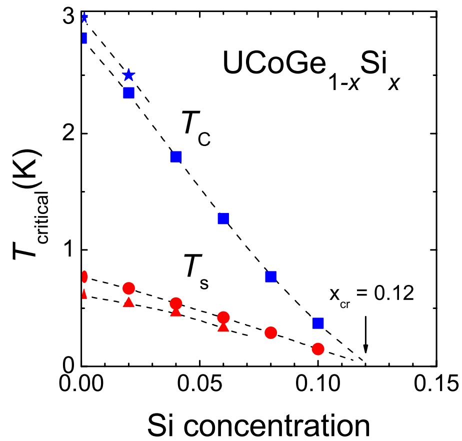

FIG. 4. (Color online) Curie temperature, determined by $M(T)$ (★) and $\chi_{ac}(T)$ (■), and superconducting transition temperature, determined by $\rho(T)$ (●) and $\chi_{ac}(T)$ (▲), as a function of x for $UCoGe_{1-x}Si_x$ alloys. The dashed lines serve as a guide for the eyes. Superconductivity and ferromagnetism both vanish at $x_{cr} \simeq 0.12$.

we show the low-temperature part of the resistivity data in a plot of ρ 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 quasilinear decrease from $n=2$ for $x=0.00$ to the non-Fermi-liquid value $n \simeq 1$ 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 quasilinearly depressed, at least until $x=0.08$, at a rate $dT_C/dx=-0.25$ K/at. % 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 $x_{cr}^{FM} \simeq 0.12$. T_s, resistively determined by the midpoint of the transition, is depressed somewhat faster than linear, initially at a rate $dT_s/dx=-0.06$ K/at. % Si. By smoothly extrapolating $T_s(x) \to 0$, we obtain a critical Si concentration for the suppression of SC $x_{cr}^{SC} \simeq 0.12$. The $T_s(x)$ values measured by $\chi_{ac}(T)$ for $x \leq 0.06$ signal the onset of bulk[1] SC and follow the same trend. Notice that $T_s(x)$ 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 $\kappa \simeq 10^{-11}$ Pa^{-1}). Concurrently, the measured doping-induced depression of T_C (Fig. 4) translates to $dT_C/dp=-0.71$ K/kbar, which is about a factor of 3 larger than the value of -0.25 K/kbar calculated[1] via the Ehrenfest relation. This indicates that Si does not merely exert chemical pressure. Indeed, hybridization phenomena in UTX alloys are, in general, strongly anisotropic.[16] As regards to 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 $dT_s/dp=-0.17$ K/kbar, while the Ehrenfest relation shows that T_s *increases* at a rate of $dT_s/dp=0.02$ K/kbar.[17]

The suppression of magnetic order in the $UCoGe_{1-x}Si_x$ alloys can be understood in terms of a simple Doniach picture:[18] by doping the smaller Si atoms, the $5f$-$3d$ 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 in 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[12,19,20] type. The extracted exponent $n \simeq 1$ 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 $URh_{1-x}Ru_xGe$ alloys:[21] at $x_{cr}=0.38$, $n \simeq 1.2$. Clearly, disorder reduces[22] n. The smooth depression of $M_s(0)$ indicates that the ferromagnetic-to-paramagnetic transition at $T=0$ K is a continuous phase transition. Additional experiments, e.g., specific heat, are required to set the evidence for a FM QCP at $x_{cr} \simeq 0.12$ 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, $x_{cr}^{FM}=x_{cr}^{SC} \simeq 0.12$. 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.[3,4,13,14] Evidence for triplet SC is furnished by the absence of Pauli limiting in the upper critical field B_{c2}.[10] 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[23] for the A

phase of an orthorhombic FMSC. On the other hand, it is recognized[3,24] that triplet SC is extremely sensitive to scattering at nonmagnetic impurities and defects. Therefore, it is surprising that SC survives until doping concentrations of $\sim$12 at. % Si. For our polycrystalline UCoGe samples, with RRR$\sim$30, we calculate[1] 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 in ℓ. Unconventional SC therefore would require a strong doping-induced reduction in ξ as well. The depression of non-*s*-wave SC by nonmagnetic impurities can be modeled using a generalized form[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_2RuO_4.[27] In the case of the $UCoGe_{1-x}Si_x$ alloys, however, the defect-driven depression of T_s 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 depairing 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 $x_{cr} \simeq 0.12$. 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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