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_c=0.12. The non-Fermi-liquid temperature variation in the electrical resistivity near x_c 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 \(T_c=0.8\) 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\(_2\) (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 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\(^8\) (0.3\% of \(R\ln2\)) associated with the magnetic transition. More recently, the magnetic and SC properties were determined for a single-crystalline sample.\(^9\) Magnetization data reveal that UCoGe is a uniaxial ferromagnet with the ordered moment \(m_0=0.07\mu_B=2m_0^{0.75}\) 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 signifying the Curie temperature \(T_C=2.8\) K. The temperature variation of the resistivity\(^10,11\) 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\(^3,4,13,14\), 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 isostructural Si. Ferromagnetic UCoGe and paramagnetic\(^15\) UCoSi are isostructural.\(^8,9\) The unit cell volume of UCoSi is \(\sim3.5\)% 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 \(x_c=0.12\). 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 \(0\leq x\leq0.20\) 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 \(\Omega\) 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 interference device magnetometer in magnetic fields up to 5 T and temperatures down to 2 K. The low-field (\(B=10^{-5}\) T) ac susceptibility \(\chi_{ac}\) was measured us-

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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 $\chi_0 = 10^{-8}$ m$^3$/mol and an effective moment $p_{eff} = 1.6 \pm 0.1 \mu_B$/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 $B\geq1$ T is related to the itinerant nature of the magnetic state. The spontaneous magnetization $M_s(0)$ 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

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

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 $B \geq 1$ 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 $B<1$ T are due to the finite temperature at which the data are taken (the ordered moment is not fully developed yet). For $x=0.00$, $M_s(0)=0.029 \mu_B$ ($T \to 0$), in agreement with previous results, while for $x=0.02$, $M_s(0)=0.022 \mu_B$. For the samples with $x=0.05, 0.08$, and 0.10, the data have been taken at $T$
we show the low-temperature part of the resistivity data in a plot of $\rho$ versus $T^\alpha$. 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 ($x \approx 0.10$), the exponent shows a quasilinear decrease from $n = 2$ for $x = 0.00$ to the non-Fermi-liquid value $n = 1$ 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 $x \approx 0.14$, 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 $T_s(x) \rightarrow 0$, 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 $x_{cr}^{FM} = 0.12$. $T_s$, 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 $T_s(x) \rightarrow 0$, we obtain a critical Si concentration for the suppression of SC $x_{cr}^{SC} = 0.12$. The $T_s(x)$ values measured by $\chi_m(T)$ for $x \leq 0.06$ signal the onset of bulk 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 $T_s(x)$.

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 $\kappa = 10^{-11}$ 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$^3$ via the Ehrenfest relation.
phase of an orthorhombic FMSC. On the other hand, it is recognized\textsuperscript{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 \( \pm 12 \) at. % Si. For our polycrystalline UCoGe samples, with RRR \( \approx 30 \), we calculate\textsuperscript{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 \( \ell \). Unconventional SC therefore would require a strong doping-induced reduction in \( \xi \) as well. The depression of non-\( s \)\textsubscript{v} wave SC by nonmagnetic impurities can be modeled 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 \( p \)\textsubscript{v} wave SC in the paramagnet \( \text{Sr}_2\text{RuO}_4 \).\textsuperscript{27} In the case of the UCoGe\textsubscript{1−x}Si\textsubscript{x} alloys, however, the defect-driven depression of \( T_c \) is partly compensated by \( T_c \) 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 \( T_c \).

In summary, magnetic and transport measurements on a series of polycrystalline UCoGe\textsubscript{1−x}Si\textsubscript{x} samples show that ferromagnetic order and superconductivity are both depressed and vanish at the same critical concentration \( x_{cr}=0.12 \). 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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17. This value corrects the estimate \( dT_c/dp=0.048 \) K/kbar given in Ref. 1.


