Crossover between SC states in an unconventional superconductor UCoGe driven by ferromagnetic spin fluctuations

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(Dated: June 22, 2008)

UCoGe is reported as a weak ferromagnetic (FM) two-band superconductor (SC) with the critical temperature, \( T_{SC} \sim 0.7 \) K and the Curie temperature, \( T_{C} \sim 3 \) K at ambient pressure. We report exotic attributes of the SC and FM state in moderate magnetic fields. The observed phenomena clearly demonstrate that the SC regime is superior to the paramagnetic state in the vicinity of \( T_{SC} \). Above \( T_{SC} \), the zero-field state is characterized by a regime with strong FM spin fluctuations, suggesting proximity of the FM quantum critical point (FM-QCP). In addition, we observed that the robust SC regime develops independently on the existence or lack of the long-range FM ordering.

A delicate interplay between the quantum criticality and superconductivity (SC), explicitly in the vicinity of the ferromagnetic quantum critical point (FM-QCP) represents the decisive factor in the magnetically driven superconductivity \([1, 2, 3, 4, 5, 6]\). Recently, Huy et al. reported on UCoGe, which is typified as a weak ferromagnet undergoing a subsequent transition into the coexistence of FM and SC below the critical temperature, \( T_{SC} = 0.8 \) K \([7]\). The magnitude and anisotropy of the upper critical field suggest the \( p \)-wave type of SC and points to an axial SC state with nodes along the easy magnetization direction (c-axis), interpreted in terms of an unusual two-band SC state \([8]\). UCoGe is in fact unique because of its extremely low \( T_{C} \) and small spontaneous magnetic moment, indicating proximity of the FM instability. The UCoGe case has been anticipated as the first example of an unconventional SC (USC) stimulated by critical fluctuations associated with a FM-QCP. In other words, the FM spin fluctuations (FM-SF), sensitively tuned by an external magnetic field serve as a coupled control parameter mediating the onset of SC.

According to Doniach \([8]\), the phonon-induced \( s \)-wave SC in an exchange-enhanced transition metals is generally suppressed by FM-SF, in the neighborhood of the \( T_{C} \). In contrast, the FFLO theory \([10]\) revealed a SC state with a spatially modulated order parameter (OP) coexisting with a long-range FM order in metallic systems with the magnetic-impurity-induced FM. The spin-correlation theory of the FM state, based on the interactions mediated by SF between the fermions proposes an enhancement of the pairing correlations through the FM-SF \([11]\). The SC phase diagram based on this approach comprises two SC phases. The \( s \)-wave type (generalized FFLO) is established in the FM state, however the \( p \)-wave state exists in the paramagnetic region on the border of the FM instability, and is expected to vanish at the QCP. On the microscopic scale, the critical temperature of the SC transition depends on the difference of the pairing interaction and density of states on the Fermi level, respectively, for the particles with the opposite orientation of the corresponding pseudospins. In principle, the competition of the stimulating and suppressing effects on \( T_{SC} \) in FM-SCs determine phase diagrams of these unique materials.

In this Letter, we report exotic features observed in low magnetic fields on a series of polycrystalline and single-crystalline samples of UCoGe. First, we inspected in detail the proposed zero-field ferromagnetism below the \( T_{C} \). However, it was not straightforwardly evidenced from our experimental results, even on the annealed single-crystalline sample. Further, we focused on the anomalous behavior of the critical SC temperature, \( T_{SC} \) in moderate magnetic fields indicated by detailed electrical resistivity and magnetoresistance measurements.

The polycrystalline UCoGe samples were prepared by arc melting of stoichiometric amounts of high-purity constituents (U - 2N, Co - 3N, Ge - 5N) in the stoichiometric ratio (1:1:1). The samples were annealed at 800 and 900 °C, respectively, for 10 days. The reported single crystal of UCoGe has been isolated from a large polycrystalline button as a plate of dimensions 2 x 1 x 0.5 mm. We want to point out, that the quality of this single-crystalline grain was by far better then any of the attempts to grow a crystal by Czochralski technique in a tri-arc furnace. The single crystal was investigated as cast, and additionally annealed at 900 °C for 10 days. The phase composition of the prepared materials was checked by microprobe analysis and X-ray powder diffraction (XRD). The single crystal was further oriented by Laue method in back-scattering geometry; the proper crystallinity and orientation were carefully checked from both sides of the sample plate. All samples (including the as cast polycrystal with a considerable amount of foreign phases) clearly manifest the transition to the SC state at \( T_{SC} \), but the proposed FM features were much disputable. The typical residual resistivity ratio (\( RRR \)) of polycrystalline materials reached 10; the \( RRR \) of the single-crystal (along the c axis) was about 20. The XRD data can be reliably described by two structure types CeCu\(_2\) and TiNiSi, represented by the space groups \( \text{Imma} \) and \( \text{Pnma} \), respectively. In order to keep our work transparent, we have chosen the \( \text{Pnma} \) scheme, preferred in actual works.

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In order to eliminate the effect of remnant field in the SC reproduced all the low-field experiments several times in order to obtain the lowest remnant field possible. We procedure using the oscillate mode in the SC magnets (ZFC) experiment, respectively, we applied the standard shape. Before each zero-field (ZF) and zero-field-cooled (ZF) sample was studied in magnetic fields applied along the principal crystallographic directions. The electrical resistivity experiments were carried out in applied along the principal axes of the single-crystal) results of identical experiments performed on our annealed polycrystalline samples reflect clearly a subdued character of the easy axis response, suggesting a dominant character of the c-axis contribution (if we ignore any potential texture, which is expected to be negligible in a randomly-fixed powder).

The static $M$ vs. $\mu_0H$ measurements for fields applied along the $b$ and $a$ axis, respectively, revealed results in agreement with [8]. The signal of the corresponding a.c. loops was more then 10 times lower in comparison to the easy axis response; however, the maximum was observed at $H \sim H_m$ on the virgin curve and both branches of the loop, respectively, for both hard directions. The results of identical experiments performed on our annealed polycrystalline samples reflect clearly a subdued character of the easy axis response, suggesting a dominant character of the c-axis contribution (if we ignore any potential texture, which is expected to be negligible in a randomly-fixed powder).

In the pilot paper by Huy et al. [7], the formation of the FM state was proved by appearance of a maximum at around 2.5 K on the temperature dependence of the a.c. susceptibility, recorded at ZF. In our identical experiments (with the strictly kept ZF regime), we lacked the maximum for all polycrystalline samples, however when applying an external magnetic field of 4 mT, the corresponding maximum was observed. Surprisingly, the measurements of the a.c. susceptibility (with the a.c. magnetic field, $H_{ac} = 0.3$ mT, and the external d.c. field applied along the principal axes of the single-crystal) revealed the $T_c$-related maximum already in ZF for the $a$ and $b$ axes, respectively. In contrast, the easy axis ($c$-axis) behavior reflected that of the polycrystalline samples.

The results are shown in Figure 2. In the easy axis, no clear anomaly occurs in ZF-dependence of the real part of the a.c. susceptibility ($\chi'$), but in a d.c. magnetic field of 2 mT an abrupt enhancement of the c-axis-related signal together with a symmetric maximum is observed. When increasing field up to 4 mT the signal is lowered, the maximum vanishes to re-appear at 6 mT while the signal becomes continuously suppressed. When increasing the d.c. magnetic field up to 2 T, the maximum becomes broader and continuously extends to higher temperatures. If we excite the system with an a.c. field applied along the $b$-axis (Figure 3b), the peak appears already in ZF, but is completely inert to the d.c.

![Graph](image-url)  
**FIG. 1:** Hysteresis loop and virgin magnetization curve measured by a.c. susceptibility (a) and common (d.c.) magnetization (b) measurements at 1.8 K. The panel (a) depicts the butterfly a.c. loop (open circles) together with the virgin a.c. curve (black circles). The derivative of the d.c. virgin curve clearly shows an inflex point almost coinciding with the maximum on the corresponding a.c. branch.

Peculiar details of the UCoGe metallurgy and crystal structure investigation will be simultaneously published elsewhere [13]. The magnetic measurements were performed in a commercial SQUID magnetometer (longitudinal geometry) down to 1.8 K and magnetic fields up to 7 T. As a reference an analogous data series was recorded in a PPMS device using vibration and extraction magnetometers within the same conditions. To verify the fully ordered FM state proposed in [7], we used the a.c. susceptibility butterfly method [14]. The polycrystalline samples were measured as randomly fixed powders; the single crystal was studied in magnetic fields applied along the principal crystallographic directions. The electrical resistivity experiments were carried out in a PPMS device using the $^3$He option with the current applied along the $c$-axis; other geometries were prevented by the sample shape. Before each zero-field (ZF) and zero-field-cooled (ZFC) experiment, respectively, we applied the standard procedure using the oscillate mode in the SC magnets in order to obtain the lowest remnant field possible. We reproduced all the low-field experiments several times in order to eliminate the effect of remnant field in the SC coils.

The crucial point in controlling the SC state by the FM-SF is the nature of the ZF state above the critical SC temperature. Assuming a nearly perfect material (from the structural point of view), the question is whether the UCoGe is a long-range FM or a system with critical FM-SF. A representative easy-axis ($\mu_0H \parallel c$) hysteresis loop and a virgin curve recorded at 1.8 K on the single-crystal is depicted in Figure 1. The Figure 1a shows a typical a.c. butterfly loop with the two maxima at fields, which can be attributed to the coercivity field, $H_c$ in the d.c. loop [14]. However, the virgin curve does not follow the maximum-free trend expected for ferromagnets, because the coercivity and remanence build up after the first field sweep [14]. In principle, the maximum can be ascribed to a crossover between reversible and irreversible dynamic of FM domains, or a kind of field-induced metamagnetic transition [14]. The common d.c. loop in Figure 1b corresponds well to the data presented by Huy et al. [7], the virgin curve clearly shows an inflex point almost coinciding with the maximum on the corresponding a.c. branch.
field of 2 mT. With increasing the d.c. magnetic field, the anomaly is smoothly suppressed but peaks almost at the same temperature. Moreover, the signal at the hard axes is approximately 10 times lower than that in the easy direction (in consistency with the butterfly loop experiments). When we focus on the imaginary part ($\chi''$), we clearly see no anomaly, which usually demonstrates FM ordering. Although there is a clear maximum on the $\chi'$-curve for the measurements along the hard directions, the imaginary part lacks any trend to saturation at low temperatures. Based on magnetization and a.c. susceptibility results, we propose a scenario for UCoGe, which considers that in ZF at temperatures lower than the proposed $T_C \sim 3$ K a paramagnetic state with strong critical anisotropic FM-SF is established, contrary to the FM state reported by Huy et al. [7].

The coexistence of the FM-SF and the USC state was subsequently explored by detailed measurements of the electrical resistivity and magnetoresistance (MR) as shown for the single-crystalline sample in Figure 3. The principal observation is a transient increase of the $T_{SC}$ under applied magnetic field. First, the $T_{SC}$ (determined as the inflection of the jump on the $R(T)$ curve) moves from 0.64 K to 0.66 K at $\mu_0 H = 0$ T and $\mu_0 H = 2$ mT, respectively. It further decreases down to the initial ZF value up to 10 mT, and finally monotonously decays with increasing magnetic field applied, as expected for a SC system. The unusual feature is supported by the MR measurements at temperatures in the vicinity of the $T_{SC}$ (Figure 3b). The curves exhibit a clear dip in the field of 10 mT, which becomes continuously smeared out with increasing temperature. The data recorded on polycrystalline samples are nearly identical. However, the absolute values of the observed effects are naturally reduced.

![FIG. 2: Low-temperature a.c. susceptibility (real part, $\chi'$ and imaginary part, $\chi''$) for external d.c. fields applied parallel to the c and b axes. The plots demonstrate the anisotropic behavior of the FM-SF under moderate magnetic fields.](image1)

![FIG. 3: Results of electrical resistivity measurements on the UCoGe single crystal (I $\parallel$ c $\parallel$ $\mu_0 H$). The panel (a) demonstrates the anomalous evolution of the relative electrical resistivity, $R/R_0$ ($R_0$ was obtained from the fit to the normal-state data: $AT^2 + R_0$) SC state in the vicinity of the $T_{SC}$ under various external magnetic fields. The panel (b) shows the in-field dependence of the relative electrical resistivity, $R/R_{ST}$ at temperatures in the vicinity of the $T_{SC}$. The minimum at $\sim 0.01$ T, attributed to the crossover is enhanced when approaching the homogeneous SC state at $\sim 0.6$ K in our sample (shown in the inset of the Figure 3b).](image2)
order, the magnetic field stabilizes the FM-SF, and the proper \( p \)-wave spin-triplet SC state is established within one of the pairs of the two allowed symmetry classes.

In conclusion, we have investigated low-field phenomena in UCoGe stimulated by the interplay of FM-SF and superconductivity in the vicinity of the FM-QCP. We observed two unique features: 1. unusual enhancement of \( T_{SC} \) under applied magnetic fields, and 2. evidence of FM-SF in zero magnetic field, contrary to the claimed zero-field FM order. We constructed a tentative phase diagram considering the critical phenomena on the border of the SC region. Finally, our observations propose a crossover between two SC phases, with potentially different symmetries of the OP. However, the nature of the phase II is so far speculative. Fine experiment, typically angle-dependent in-field measurements on a well-defined single-crystal, in order to determine the corresponding symmetry of the SC gap in the II and III phases, respectively, would help to discriminate between the above-discussed scenarios.

This work is a part of the research plan MSM 0021620834 that is financed by the Ministry of Education of the Czech Republic.

\[ \text{FIG. 4: The detail of the tentative FM-SC phase diagram.} \]

The phase I corresponds to the state below the critical field \( H_{cr} \), characterized with FM-SF. The phase II represents the SC state with the anomalous evolution of the \( T_{SC} \). The phase III is attributed to the previously reported USC state with the proposed \( p \)-wave SC state coexisting with FM, and the phase IV is ascribed to the FM state, which is provoked by applied magnetic field from the FM-SF.

veloped and the unconventional \( p \)-wave spin-triplet state can be formed. The proposed mechanism can be reflected in theories of Blagoev and Fay [11, 16], which claim, that for weakly FM metals the coexistence of longitudinal SF and a gapless Goldstone mode allows formation of the two SC states with a generally different symmetry of the OP. For an orthorhombic system with uniaxial FM, four symmetry classes are allowed, which can be split in two pairs comprising two equivalent co-representations; in general, each of them may have a different \( T_{SC} \). Within one of the pairs, the sub-states in magnetic domains with the magnetic moments oriented parallel or antiparallel to the magnetic field can be expressed by the two co-representations. Within the above-described picture, either a crossover between the two sub-states of the two co-representations, or between the two pairs of states may occur. In general, there is no straightforward proof for the competition of the two analogous pairs of the SC classes in the vicinity of QCP. Therefore we propose, that the anomalous behavior of the \( T_{SC} \) in phase II is probably not due to the crossover between the two different pairs of classes, but the applied magnetic field rather influences the critical FM-SF as the governing factor conditioning the phase line of the SC state. Considering the previous scenario of ZF dis-

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