# Low magnetic field phase diagram of UCoGe

J. Vejpravová-Poltierová,[1] J. Pospíšil,[1,*] J. Prokleška,[1] K. Prokeš,[2] A. Stunault,[3] and V. Sechovský[1]

[1]*Charles University, Faculty of Mathematics and Physics, DCMP, Ke Karlovu 5, CZ-12116 Praha 2, Czech Republic*
[2]*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner Platz 1, D-14109 Berlin, Germany*
[3]*Institut Laue Langevin, 6 rue Jules Horowitz, BP 156, F-38042 Grenoble Cedex 9, France*

We propose an alternate scenario for the relation between ferromagnetism (FM) and superconductivity (SC) in UCoGe at ambient pressure. On the basis of neutron polarimetry measurement performed in strictly zero field on a single crystal at ambient pressure, we claim that the SC phase does exist in spite of lack of long-range FM order. Moreover, the SC regime dominates to the paramagnetic state in small external magnetic fields. Above the critical SC temperature, $T_{SC}=0.64$ K, the zero-field state is characterized by a regime with strong FM spin fluctuations, suggesting the proximity of the FM quantum-critical point.

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 magnetically driven SC.[1–4] Recently, Huy *et al.*[5,6] reported on UCoGe, which is typified as a weak ferromagnet that undergoes a subsequent transition at the critical temperature, $T_{SC}=0.8$ K into a FM-SC coexistence regime. The magnitude and anisotropy of the upper critical field suggest $p$-wave SC. UCoGe is unique among other FM superconductors because of its low $T_C=2.5$ K and a very small spontaneous magnetic moment of $\sim 0.07$ $\mu_B$,[6] indicating the proximity of FM instability. Although *ab initio* calculations[7] suggested the existence of an appreciable moment on Co atoms in zero field, polarized neutron-diffraction (PND) experiments carried out on a single-crystalline sample show that magnetism is predominantly due to $5f$ electron states and Co moments exist only at high magnetic fields.[8] The UCoGe case has been anticipated as the first example of material with 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 control parameter mediating the onset of SC.

According to Doniach[9] and Berk and Schrieffer,[10] the phonon-induced $s$-wave SC in an exchange-enhanced transition metals is suppressed by FM-SF in the neighborhood of the $T_C$, generally. In contrast, the Fulde-Furrel-Larkin-Ovchinnikov theory[11,12] allows for a SC state with a spatially modulated order parameter (OP) coexisting with a long-range FM order in metallic systems induced by FM impurities. 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.[13] The SC phase diagram based on this approach comprises two SC phases. The $s$-type is established in the FM state, however, the $p$-type 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 at the Fermi level, respectively, for the particles with the opposite orientation of the corresponding pseudospin. In principle, the competition of the stimulating and suppressing effects on $T_{SC}$ in FM-SCs determines the phase diagrams of these unique materials.

The crucial point for the nature of the SC state controlled by FM-SFs that is relevant for UCoGe is the nature of the zero-field (ZF) state just above $T_{SC}$. The question is whether the ZF ground state in UCoGe is indeed a uniform long-range FM or whether UCoGe represents a system with critical FM-SFs.

Although a few scientists groups found UCoGe as a material where SC can coexists with long-range FM we will report on the lack of zero-field FM order in high-quality superconducting single crystal of UCoGe, probed by bulk measurements and confirmed on the microscopic level using strictly zero-field neutron polarimetry (ZFNP). Further, we discuss the anomalous behavior of $T_{SC}$ in moderate magnetic fields as indicated by detailed electrical resistivity and magnetoresistance (MR) measurements. We conclude that the SC in our UCoGe sample can develop in spite of lack of the long-range uniform FM order.

Our single crystal of UCoGe was isolated from a large polycrystalline button as a plate of dimensions: $2 \times 1 \times 0.5$ mm$^3$. The crystal was wrapped in Tantalum foil (99.95%) sealed in vacuum $10^{-7}$ mbar in a quartz tube and annealed at 900 °C for 10 days. X-ray powder diffraction of small piece of the crystal found orthorhombic crystal structure (*Pnma* space group[14]) with lattice parameters $a=684.71$ nm, $b=420.81$ nm, and $c=722.63$ nm. Energy dispersive x-ray analysis (EDX) confirmed chemical composition of the crystal in the elements ratio 1:1:1. We have observed moment $\sim 0.055$ $\mu_B$/f.u. at temperature 0 K and magnetic field 0.01 T, which is comparable with Ref. 6. The magnetization did not saturate with increasing magnetic field. The value of the magnetic moment at temperature 1.8 K and magnetic field 7 T was 0.17 $\mu_B$/f.u.. These results together with indirect parameter $RRR=20$ assured us of the high quality of the studied crystal.

The bulk measurements were performed in Magnetic Property Management System and Physical Property Measurement System, respectively, both manufactured by Quantum Design Inc. Before each ZF and zero-field-cooled experiment we applied a standard demagnetization procedure in order to obtain the lowest remanent field possible. Control
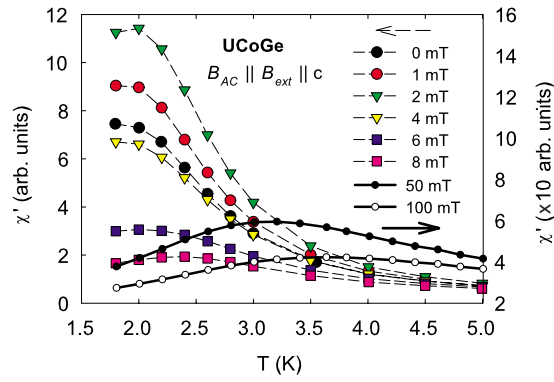
FIG. 1. (Color online) Low-temperature ac susceptibility (real part, $\chi'$) for external dc fields, $B_{\text{ext}}$ applied parallel to the $c$ axis and to the ac-driving field ($B_{\text{ac}}=0.1$ mT).

measurement using pure indium showed that the remanent field was of the order of 0.1 mT.

In order to probe the ZF ground state of UCoGe on a microscopic level we have performed a ZFNP experiment, a special type of PND. In the simplest PND, one records Bragg reflection intensities $I^{\pm}(\mathbf{Q}) \propto |F_N(\mathbf{Q}) \pm F_M(\mathbf{Q})|^2$, where the + and − sign refer to up and down polarization directions of the incoming neutron beam and calculates the so-called flipping ratios (FR) $FR(\mathbf{Q})=I^+(\mathbf{Q})/I^-(\mathbf{Q})$. For Bragg reflections of either pure nuclear or magnetic origin absence of the interference term leads to FR=1.00. From mathematical formula[15] describing the influence of individual nuclear and magnetic contributions to measured FRs, it follows that off-diagonal elements, if different from zero, indicate possibly a complicated noncollinear magnetic order. In the case that UCoGe exhibits FM order, it is expected that the sample would consists from magnetic domains forcing these elements to be close to zero. On the contrary, diagonal elements would be in this case lower than 1.00 due to beam depolarization.

The experiment was carried out using CRYOPAD polarimeter[15] in D3 diffractometer at the ILL with polarized neutrons, $\lambda=0.825$ Å. All the measured data have been consequently corrected for both polarizer and analyzer efficiencies.

The philosophy of the experiment was simple and straightforward—if there is any long-range FM order present in the sample, significant deviations from 1.00 in the diagonal components of the FR matrix below the $T_C$ must be observed. To optimize the resulting statistical error for fixed measurement time we used the approach described in detail in Ref. 16.

In the original paper by Huy *et al.*,[5] the formation of the FM state was manifested by the appearance of a maximum at around 2.5 K on the temperature dependence of the ac susceptibility (see Fig. 1). Our single-crystal experiments under similar conditions (the ac magnetic field, $B_{\text{ac}}=0.1$ mT, and the external dc field applied along the easy axis) revealed no clear anomaly around $T_C$ in the temperature dependence of the real part of the ac susceptibility, $\chi'$ when measured in ZF. However, an abrupt enhancement of the signal with a symmetric maximum with increasing dc magnetic field up to 2 mT is observed. With further increasing field, the signal be-
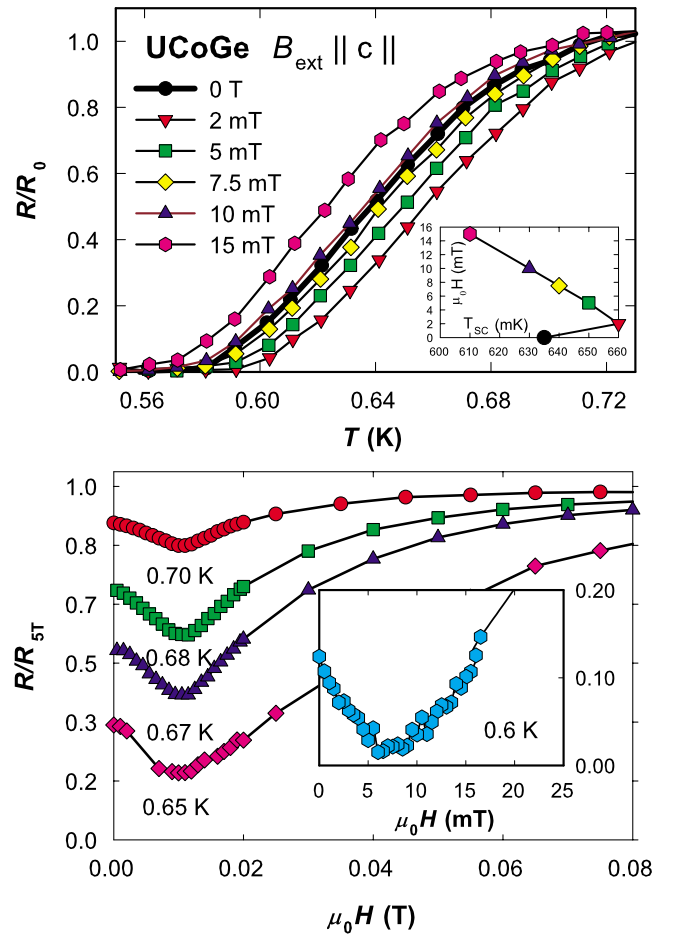


FIG. 2. (Color online) (a) Low-temperature electrical resistivity normalized to the value at 0.75 K measured with electrical current and magnetic fields applied along the $c$ axis. (b) Low-temperature magnetoresistance measured along the $c$ axis normalized to values obtained at field of 5 T applied along the $c$ axis. In the inset, measurement at 0.6 K is shown.

comes continuously depressed, the maximum becomes broader and continuously extends to higher temperatures. The ac susceptibility results suggest, that in ZF, at temperature $T \sim 2.0$ K, a paramagnetic state with strong critical anisotropic FM fluctuations is established in our sample.

The coexistence of the FM-SF and the USC state was subsequently explored by detailed measurements of the electrical resistivity and MR as shown in Fig. 2(a). The bulk SC state has been confirmed by measuring of the Meissner effect, as well. The principal observation is a transient increase of the $T_{\text{SC}}$ under applied magnetic field in low fields. First, the $T_{\text{SC}}$ (determined as the inflection point on the resistivity curve) moves from 0.64 to 0.66 K as the field is increased from $B=0$ T to $B=2$ mT, respectively. It moves down, to the initial zero-field value, for a field of 10 mT, and finally monotonously decreases with increasing magnetic field applied, as expected for any SC system. This unusual field dependence is supported by the MR measurements at temperatures in the vicinity of the $T_{\text{SC}}$. The MR curve exhibits a clear minimum in a field of 10 mT, which becomes continuously smeared out with increasing temperature. Although all

TABLE I. The list of flipping ratios for (202) and (301) Bragg reflections measured on UCoGe single crystal above and below the suggested ferromagnetic phase transition $T_C \sim 2.5$ K. In parenthesis the statistical errors according to Ref. 16 are shown.

| $T$ (K) | $hkl$ | $P_{in}$ | $P_{out}$ | | | $hkl$ | $P_{out}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $+(x)$ | $+(y)$ | $+(z)$ | | $+(x)$ | $+(y)$ | $+(z)$ |
| 15.0 | 202 | $+(x)$ | 1.018(9) | −0.002(11) | −0.005(11) | 301 | 0.97(2) | −0.05(2) | −0.04(2) |
| 15.0 | | $+(y)$ | −0.030(11) | 1.007(9) | 0.024(11) | | 0.00(2) | 1.02(2) | Not measured |
| 15.0 | | $+(z)$ | 0.005(11) | 0.013(12) | 0.999(11) | | 0.01(2) | Not measured | 1.00(2) |
| 1.15 | 202 | $+(x)$ | 1.009(11) | 0.033(13) | 0.002(13) | 301 | 1.00(2) | −0.01(2) | −0.01(3) |
| 1.15 | | $+(y)$ | −0.007(14) | 1.019(12) | 0.011(15) | | −0.02(3) | 0.98(2) | 0.01(3) |
| 1.15 | | $+(z)$ | 0.012(15) | 0.01(2) | 1.002(13) | | −0.03(3) | 0.02(3) | 1.05(3) |

these data support the idea that in the absence of a magnetic field UCoGe does not posses static long-range FM order; it does not prove unambiguously that the FM is really missing. Other order types that include even ferrimagnetism as suggested by *ab initio* calculations[7] cannot be principally excluded. The crucial proof, however, is provided by the above described ZFNP experiment.

In Table I we list as an example FR matrices determined for the (202) and (301) Bragg reflections at two different temperatures, one well above and the other well below the suggested ferromagnetic phase transition $T_C \sim 2.5$ K. First we note that all off-diagonal elements are negligible and within error bars equal to zero. Second, all diagonal elements are close to 1.00. This is not surprising for data taken at 15 K as at this temperature is UCoGe not magnetically ordered. However, diagonal elements are equal to 1.00 below the proposed $T_C$ and even below $T_{SC}$ (not shown). The same observation has been made also for all other measured Bragg reflections suggesting that the ZF conditions that are necessary prerequisite for conservation of the neutron polarization within the CRYOPAD zero-field chamber are fulfilled in our case at all temperatures. This is possible only if UCoGe is not ferromagnetic in the whole temperature range. This result is in clear contrast to ($\mu$-SR) experimental results by de Visser *et al.*[17] for a polycrystalline sample. To explain the apparent controversy we recall that polycrystalline UCoGe samples have often larger magnetization than single crystals that need to be carefully heat treated. Moreover, positive muons sense local moments on another time window than neutrons and other local probes. The $^{59}$Co nuclear quadrupole resonance (Ref. 18) measurements also on polycrystalline sample led to conclusion that UCoGe is in self-induced vortex state having about 30% of the volume superconducting. Let us also note that the internal field ($B_{loc}$) deduced from $\mu$-SR (Ref. 17) is 15 mT. This field is about four orders of magnitude larger than the residual field inside the CRYOPAD chamber. So even if the sample would consist from FM domains, resulting stray field would destroy the neutron polarization. When considering the values of the relaxation rate $(\Delta) \sim 0.3$ ms$^{-1}$ and internal field $B_{loc} \sim 15$ mT in UCoGe,[17] the specific $\mu$-SR time window ranges from $10^{-7}$ to $10^{-6}$ s, which fairly covers that of the PN scattering. Therefore, the sample aggregation state and/or interference of the probe with the sample, respectively, play an important role in interplay of FM-SC.

On the basis of our experimental results, we propose an approximate low-temperature magnetic phase diagram in Fig. 3. There are two essential questions about the proposed phase diagram. The first is a competition of FM-SF against the robust FM state. The second point is the classification of the two generally different SC states related to the phase SF-SC and FM-SC, respectively. The major controversy points to the nature of the low-field SC state related to the phase SC-SF. Let us propose two fundamentally diverse scenarios. In the first, the two SC states are of different symmetries. In zero-field, the order parameter is expected to be isotropic resulting in the only allowed *s*-type SC, but when we reach the robust FM state, the anisotropy of the Fermi surface is fully developed and the unconventional *p*-type can be formed. The proposed mechanism can be supported by the theory of Blagoev,[13] which claims, that for weakly FM metals the coexistence of longitudinal SF and a gapless Goldstone mode allows formation of both the *s*-wave and the *p*-wave-type[19] SC. The crucial discrepancy is, that the *p*-type should occur in the paramagnetic limit and the *s*-type in the FM. On the other hand, we have observed significant changes in the FM-related ac susceptibility, which can be explained by a change in the anisotropy and dynamics of the SF. Isotropic SF in the vicinity of the crossover point (potential QCP) therefore suggest possibility of the two SC states with a different symmetry. We can also consider the effect of
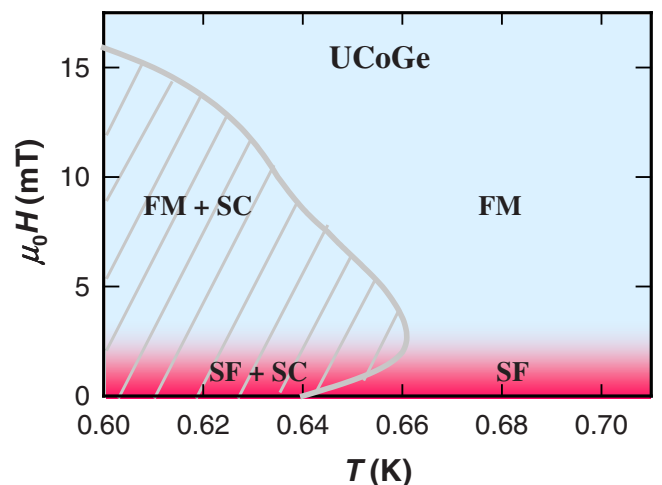


FIG. 3. (Color online) Suggested magnetic phase diagram of UCoGe single crystal for magnetic field applied along the *c* axis.

FM domains in USC, so the SC phases have the same symmetry of the OP. For an orthorhombic system, there are four classes, and two pairs of equivalent corepresentations, which in general have a different $T_{SC}$. The equivalent corepresentations correspond to the same SC phase but each of them describes the substate in magnetic domains[20] with the magnetic moment with orientation parallel or perpendicular to the magnetic field direction. We may observe either a crossover between the two states of the two corepresentations, or homogenize the FM state by the applied magnetic field, so the proper *p*-type SC state[21] is established within one of the corepresentations. In general, there is no reason for competition between the two in general analogs SC phases. Therefore we propose, that the anomalous behavior of $T_{SC}$ in the SF-SC phase is not due to the crossover between two different corepresentations of the same group, but rather due to the magnetic field influences on the critical FM-SF, which is the governing factor conditioning the phase line of the SC state.

In conclusion, we have investigated relation of SC and FM in UCoGe in strictly zero-field conditions. We have observed: (1) fully robust SC state in spite of no long-range FM order in zero magnetic field and ambient pressure, which is in good agreement with our work on polycrystal[22] and (2) enhancement of the $T_{SC}$ under applied small magnetic fields in the vicinity of the SC and FM phase lines. We propose a *B-T* phase diagram comprising the critical phenomena in low magnetic fields on the border of the SC region. Finally, our results suggest a crossover between two SC phases, in analogy to the observations at elevated pressures by Slooten *et al.*[23]

*jiri.pospisil@centrum.cz

[1] F. Lévy, I. Sheikin, B. Grenier, and A. Huxley, Science **309**, 1343 (2005).

[2] F. Hardy and A. D. Huxley, Phys. Rev. Lett. **94**, 247006 (2005).

[3] D. Aoki, A. D. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J. P. Brison, L. Lhotel, and C. Paulsen, Nature (London) **413**, 613 (2001).

[4] F. Lévy, I. Sheikin, and A. Huxley, Nat. Phys. **3**, 460 (2007).

[5] N. T. Huy, A. Gasparini, D. E. de Nijs, Y. K. Huang, J. C. P. Klaasse, T. Gortenmulder, A. de Visser, A. Hamann, T. Görlach, and H. v. Löhneysen, Phys. Rev. Lett. **99**, 067006 (2007).

[6] N. T. Huy, D. E. de Nijs, Y. K. Huang, and A. de Visser, Phys. Rev. Lett. **100**, 077002 (2008).

[7] M. Diviš, Physica B **403**, 2505 (2008).

[8] K. Prokeš, A. de Visser, Y. K. Huang, B. Fåk and E. Ressouche, Phys. Rev. B **81**, 180407(R) (2010).

[9] S. Doniach, Proceedings of the Manchester Many Body Conference, 1964 (unpublished).

[10] N. F. Berk and J. R. Schrieffer, Phys. Rev. Lett. **17**, 433 (1966).

[11] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).

[12] A. I. Larkin and Y. N. Ovchinnikov, Sov. Phys. JETP **20**, 762 (1965).

[13] K. B. Blagoev, J. R. Engelbrecht, and K. S. Bedell, Phys. Rev. Lett. **82**, 133 (1999).

[14] F. Canepa, P. Manfrinetti, M. Pani, and A. Palenzona, J. Alloys Compd. **234**, 225 (1996).

[15] F. Leliévre-Berna, P. J. Brown, F. Tasset, K. Kakurai, M. Takeda, and L.-P. Regnault, Physica B **397**, 120 (2007).

[16] F. Leliévre-Berna, P. J. Brown, and F. Tasset, Physica B **397**, 138 (2007).

[17] A. de Visser, N. T. Huy, A. Gasparini, D. E. de Nijs, D. Andreica, C. Baines, and A. Amato, Phys. Rev. Lett. **102**, 167003 (2009).

[18] T. Ohta, T. Hattori, K. Ishida, Y. Nakai, E. Osaki, K. Deguchi, K. Sato, and I. Satoh, J. Phys. Soc. Jpn. **79**, 023707 (2010).

[19] R. Roussev and A. J. Millis, Phys. Rev. B **63**, 140504 (2001).

[20] V. P. Mineev, Phys. Rev. B **66**, 134504 (2002).

[21] K. Scharnberg and R. A. Klemm, Phys. Rev. Lett. **54**, 2445 (1985).

[22] J. Pospíšil, J. Vejpravová-Poltierová, and V. Sechovský, J. Magn. Magn. Mater. **322**, 1137 (2010).

[23] E. Slooten, T. Naka, A. Gasparini, Y. K. Huang, and A. de Visser, Phys. Rev. Lett. **103**, 097003 (2009).