

PROPERTIES OF THE SUPERCONDUCTING FERROMAGNET ZrZn_2 *

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The Laves phase ZrZn_2 exhibits weak ferromagnetism at low temperatures that differs in many ways from the predictions of a weakly spin polarised Fermi liquid. Surprisingly, ZrZn_2 recently was even found to become superconducting in the milli-Kelvin temperature range. Ferromagnetism and superconductivity vanish above the same critical pressure $p_c \approx 21$ kbar, suggesting that itinerant ferromagnetism may be a precondition for the superconductivity.

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1. Introduction

The coexistence of magnetism and superconductivity has attracted scientific interest for many decades. Already by the 1960s numerous studies had shown that tiny amounts of magnetic impurities may suppress superconductivity. Extensive investigations of a coexistence of long-range local-moment antiferromagnetic order in the superconducting state of the Chevrel phases were carried out in the 1970s and 80s [1]. Motivated by this work materials were discovered, which even undergo local moment ferromagnetic order at low temperatures so that superconductivity is suppressed again below the magnetic transition temperature. More recently, the ruthenium cuprates and the Borocarbides have been identified as new examples of superconductors that undergo magnetic order in the superconducting state.

All of these systems have in common that magnetic order and superconductivity arise as microscopically well distinguishable phenomena. This contrasts superconductivity on the border of itinerant antiferromagnetism recently reported for lanthanide and actinide based heavy fermion metals [2]. It has been argued that the latter class of materials includes examples of

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magnetically mediated superconductivity. A true coexistence of superconductivity and itinerant magnetism were, in contrast, long believed to be impossible as they were regarded competing forms of electronic order.

The focus of the work described here are itinerant ferromagnets that become superconducting at low temperatures, *i.e.*, deep in the ferromagnetic state. As a first representative exhibiting this behaviour superconductivity was discovered in the uniaxial ferromagnet UGe₂ [3] and recently in the isostructural sibling URhGe [4]. However, the f-orbitals in U-based compounds overlap little, rendering the magnetic state a difficult problem. This is contrasted by the first *d*-electron system exhibiting superconductivity in the ferromagnetic state, ZrZn₂ [5], which will be of interest in this paper.

The paper is structured as follows. In section two special features of the weak ferromagnetism of ZrZn₂ are reviewed. In section three properties of the superconducting state are addressed with particular emphasis on the properties of the a.c. susceptibility and d.c. magnetisation at low temperatures. The paper concludes with a brief summary of important questions raised by the superconductivity of itinerant ferromagnets.

2. The weak ferromagnetism of ZrZn₂

The compound ZrZn₂ was first investigated by Matthias and Bozorth in the 1950s [6], who discovered that it is ferromagnetic despite being composed of nonmagnetic, superconducting constituents. ZrZn₂ crystallises in the C15 cubic Laves structure and the magnetic properties derive from the Zr *4d* orbitals, which have a significant direct overlap [7]. Ferromagnetism develops below the Curie temperature $T_c = 28.5$ K (figure 1) with a small ordered moment $\mu_s = 0.17\mu_B$ per formula unit. The normal metallic state above T_c is characterised by a Curie–Weiss T dependence of the susceptibility of an effective moment $\mu_{\text{eff}} \approx 2\mu_B/\text{f.u.}$

The large Curie–Weiss moment as compared with the small ordered moment shows that ZrZn₂ is special among stoichiometric ferromagnetic metals, because weak long range order develops in a background of strongly enhanced spin density fluctuations. At $T = 1.75$ K a relatively small field $B = 0.05$ T is required to form a single ferromagnetic domain. On further increasing the field, the ordered moment is rapidly increased, with a field of 12 T causing nearly a doubling (Fig. 2). M remains unsaturated up to 35 T, the highest field applied [8]. This behavior contrasts strongly with the elemental ferromagnets Fe, Ni and Co where, after a single domain is formed, fields applied parallel to the easy axis only have a small effect on the ordered moment.

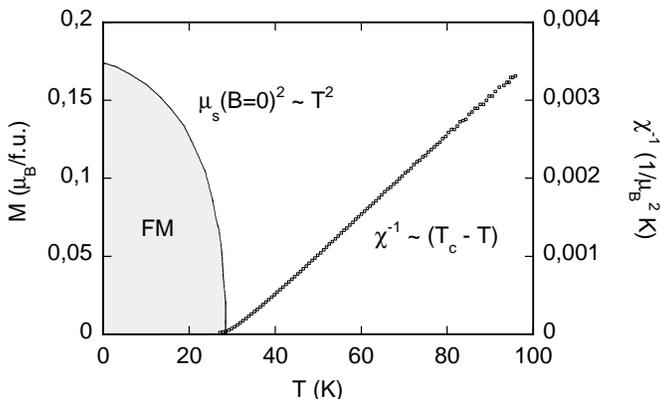


Fig. 1. Temperature dependence of the ordered magnetic moment μ_s and the paramagnetic susceptibility χ in ZrZn_2 . The fluctuating Curie–Weiss moment, $\mu_{CW} \approx 2 \mu_B$ is an order of magnitude larger than the ordered moment $\mu_s \approx 0.17 \mu_B/\text{f.u.}$, where the ferromagnetic transition temperature is $T_c \approx 28.5 \text{ K}$.

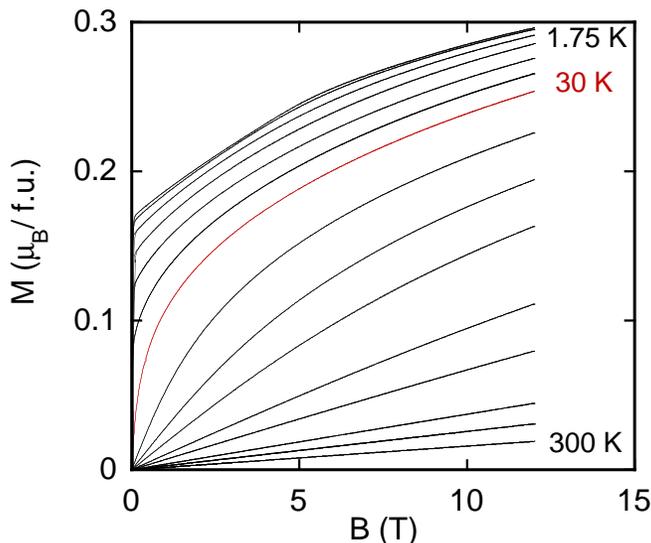


Fig. 2. Magnetic field dependence of the ordered moment at selected temperatures between room temperature and 1.75 K. At the lowest T the ordered moment is highly unsaturated and nearly doubles up to 12 T.

NMR studies and polarized neutron diffraction are consistent with a purely ferromagnetic state of ZrZn_2 [9, 10]. Neutron scattering studies moreover show that transverse excitations in the ordered state are well-developed

ferromagnetic spin waves [11]. The small ordered moment and the magnetic field induced increase of the magnetization, however, are evidence of an exceptionally large *longitudinal* susceptibility. This makes ZrZn_2 an excellent candidate for magnetically mediated superconductive pairing.

The samples studied in the work reviewed here are different from those investigated in previous decades which were grown by sintering the starting materials. Use of a Tantalum container allowed to suppress Zn evaporation losses (for details on the method see Ref. [12]). Moreover, in the high pressure Zn environment ZrZn_2 melts congruently and large single crystals form. The high sample quality is evident, for instance, in low residual resistivities $< 1 \mu\Omega\text{cm}$ and the large charge carrier mean free paths necessary for the observed de Haas–van Alphen quantum oscillations [13]. The deepest probe, however, are low field d.c. magnetisation measurements shown in Fig. 3. For fields less than the coercive field of order 0.002 T the onset of order, measured directly by coupling the signal into a RF-SQUID using a superconducting flux transformer, is very sharply defined in both zero-field-cooled/field-heated (zfc/fh) and field-cooled/field-heated (fc/fh) temperature sweeps. This is not the case for lower quality samples, where large variations are observed [14]. Moreover, the ferromagnetic transition as determined from the high field magnetisation and low field T sweeps agree very well.

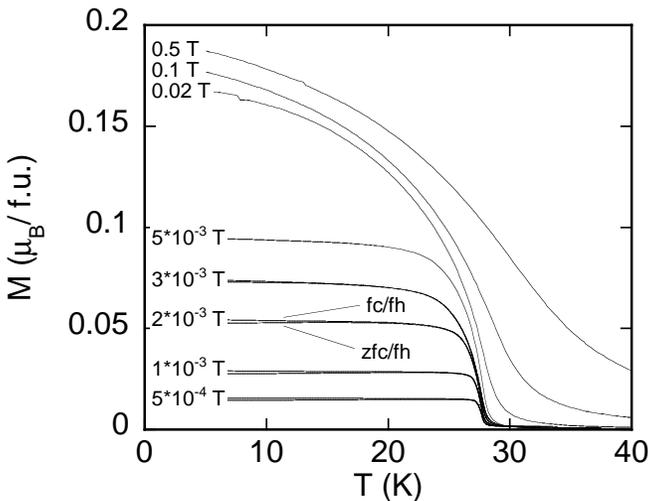


Fig. 3. Temperature dependence of the magnetisation in the reversible and irreversible regime for high quality single crystals. The coercive field in hysteresis loops is found to be 0.002 T.

The development of a phenomenological quantitative framework taking into account self-consistently the effects of thermal spin fluctuations in the 1970s and 80s, provides much of our present day understanding of weakly ferromagnetic metals [15,16]. The underlying concepts have also been transferred to more complicated materials, such as the class of heavy fermion compounds. In fact, these models even provide much of the description of quantum critical phenomena in itinerant magnets in general [17]. A careful quantitative and qualitative comparison of simple materials such as the cubic ferromagnet ZrZn_2 with theory represent therefore a crucial test.

Even though the spin fluctuation models accounts for the low transition temperature and small ordered moment of ZrZn_2 , there are a number of qualitative differences. For instance, the electrical resistivity in the ferromagnetic state does not exhibit the conventional quadratic T dependence of a Fermi liquid. Instead a $T^{3/2}$ dependence is observed over a certain T interval below T_c that is at present unexplained [19]. The inverse susceptibility does not follow the predicted mean-field $T^{4/3}$ dependence, but remains very nearly linear in T . These features may be taken as evidence for the presence of soft spin fluctuations in the ordered regime with a different wavevector q and frequency ω dependence, than the Lorentzian behaviour expected of a ferromagnetic Fermi liquid outside the usual spin wave contributions.

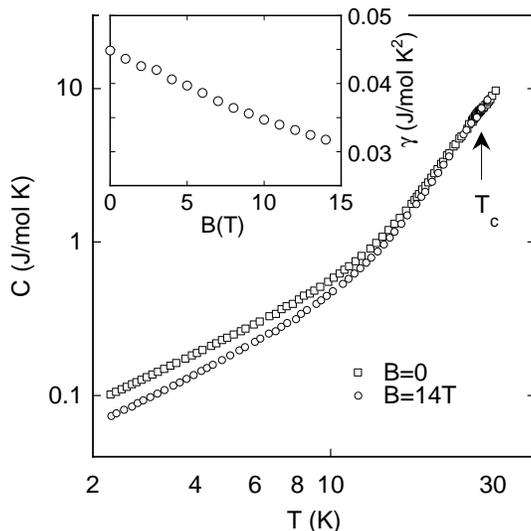


Fig. 4. Temperature dependence of the specific heat at high magnetic field [20]. High magnetic field induces a rapid suppression of the linear T dependence γ as shown in the inset. The ferromagnetic transition temperature at $T_c \approx 28.5$ K is marked by an arrow and may barely be resolved.

The weak magnetic order is finally barely evident in the specific heat shown in Fig. 4, for which an anomaly at T_c may just be resolved [20]. The very small entropy loss is consistent with the predominant spectrum of spin fluctuations. Here magnetic field induces a substantial reduction of the linear contribution to the specific heat $C/T = \gamma$. The nearly 30% reduction of γ shown in the inset of Fig. 4 may indeed be accounted for within the spin fluctuation model mentioned above [20]. However, for the phenomenological parameters taken from experiment on the same sample, γ is systematically found to be lower than experiment. This difference is particularly striking in high quality samples. It is therefore tempting to speculate on the presence of additional contributions to the specific heat in the limit of high purity [18]. These may also be at the heart of the deviations observed in resistivity and susceptibility.

3. Superconductivity in ZrZn_2

The low value of T_c and small ordered moment indicate that ZrZn_2 is close to a ferromagnetic quantum critical point (QCP), defined as the point where ferromagnetism disappears at zero-temperature [21]. Thus, the high sample quality and the prediction [22] that superconductivity is controlled by the QCP led us to revisit this compound.

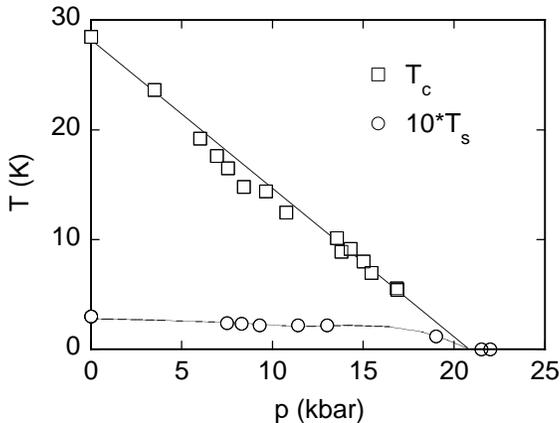


Fig. 5. Pressure dependence of the ferromagnetic ordering temperature T_c and superconducting ordering temperature T_s . The pressure dependence of T_c was determined in d.c. magnetization measurements. The pressure dependence of T_s was determined from the resistivity. Superconductivity disappears for $p > p_c \approx 21$ kbar, in the paramagnetic phase down to the lowest T measured, $T = 15$ mK. Note that, for clarity T_s is magnified by a factor of ten.

Indeed, when releasing the pressure necessary to suppress the ferromagnetic order, we recently found that $ZrZn_2$ develops superconductivity in the ferromagnetic state below $T_s \approx 0.28$ K [5]. Our initial observation of a 30% transition in the resistivity and almost ideal superconductive shielding has now been supplemented by the observation of a full resistive transition with T_s and H_{c2} unchanged [23].

Before addressing remarkable features of the superconductivity, low temperature magnetic properties are reviewed further. Shown in Fig.6 are the real and imaginary part of the low frequency, low amplitude a.c. susceptibility. Very slow field sweeps between a large negative and large positive field are dominated by a pronounced maximum for fields smaller than the coercive fields. In the irreversible regime the imaginary part is also large. In the very soft ferromagnetic state diamagnetic shielding and a large dissipative contribution are observed, indicative of superconductivity. This

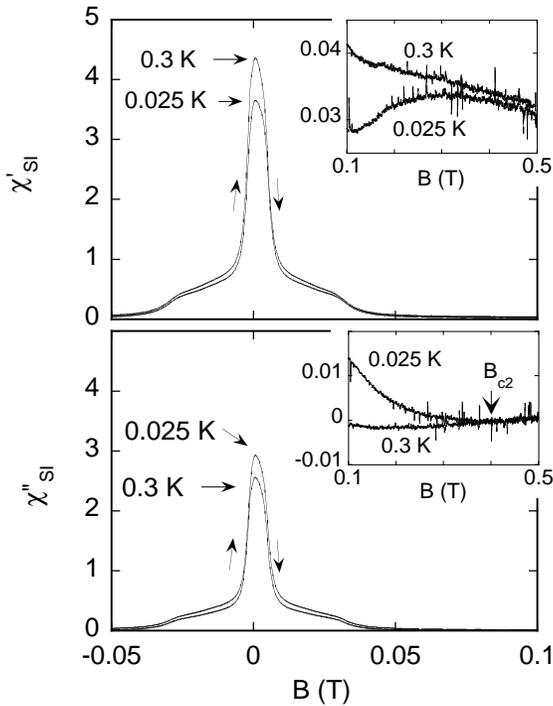


Fig.6. Real and imaginary part of the low frequency, low amplitude a.c. susceptibility as measured in slow field cycles. The susceptibility develops a large diamagnetic signal contribution on a ferromagnetic background as shown in Fig. 7. The large contribution to the imaginary part when entering the superconducting state is typical of superconductivity.

behaviour persists, though weak, even at fields well above the coercive field of 0.002 T, suggesting that the superconductivity does not exist only in the ferromagnetic domain walls. Further, it is not surprising that on an absolute scale we do not observe diamagnetic shielding, since the superconductivity develops in the ferromagnetic state and will be subject to spontaneous flux formation. After subtraction of an essentially T independent background well above T_s the susceptibility is seen to display nearly perfect diamagnetic shielding as shown in Fig. 7.

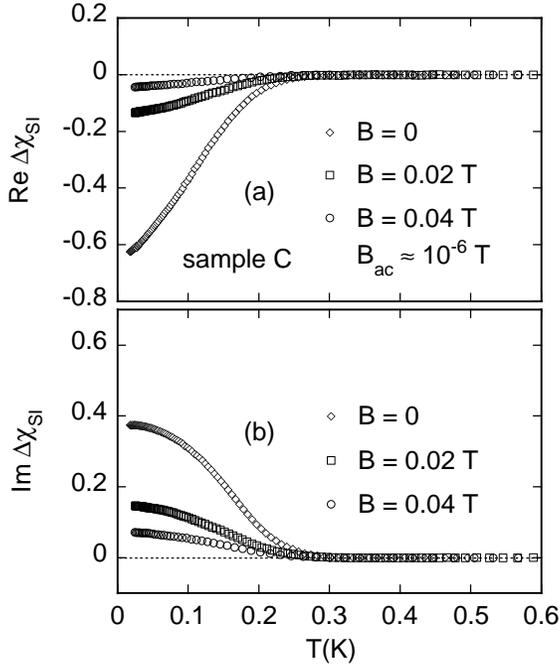


Fig. 7. Temperature dependence of the real and imaginary part of the a.c. susceptibility in selected magnetic fields after subtraction of a ferromagnetic background as explained in the text and illustrated in Fig. 6.

We have also tried to observe Meissner flux expulsion in the d.c. magnetisation. Shown in Fig. 8 are zfc/fh and fc/fh field sweeps at very low fields well below the coercive field [24]. The d.c. field amplitude is similarly small than the a.c. amplitude used in the a.c. susceptibility measurements. Here we observe quantitative agreement of the a.c. and d.c. measurements, but a flux expulsion is absent.

The superconductivity in $ZrZn_2$ has a number of remarkable features. First, it only appears to occur in high-purity single-crystal samples. Unconventional or non s -wave forms of superconductivity generally require the

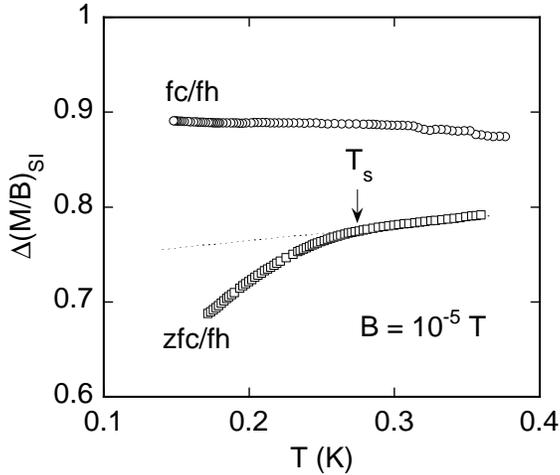


Fig. 8. Low temperature, low field change of the d.c. magnetisation as measured directly with a SQUID. No Meissner flux expulsion is observed, but the drop in the zfc/fh behaviour corresponds quantitatively with the a.c. susceptibility.

superconducting coherence length $\xi_s = 290 \text{ \AA}$, derived from the upper critical field $B_{c2} \approx 0.4 \text{ T}$, to be somewhat smaller than the electronic mean free path, which is here of the order 1000 \AA . In view of the sensitivity to sample quality, the superconductivity is likely to be unconventional in nature [25]. The second interesting feature is the lack of an anomaly in the specific heat at the superconducting transition (not shown). If we interpret this literally, it means that the superconducting state is strongly gapless with large portions [26] or even all of the Fermi surface surviving in the superconducting state. The ‘zero-field’ superconducting transition in ZrZn_2 differs fundamentally from that in a conventional superconductor since it occurs in the presence of ferromagnetism. In fact, the transition in ZrZn_2 is similar to the transition in a conventional superconductor for applied fields close to B_{c2} , where the superconducting anomaly is suppressed [27]. The third remarkable feature of the superconductivity in ZrZn_2 is that it is observed within the ferromagnetic phase, which poses the question [9, 28, 29] of the microscopic relationship between ferromagnetism and superconductivity. A macroscopic, *i.e.*, uniform co-existence of the two states throughout the sample is consistent with the magnetic response we observe, *i.e.*, flux expulsion upon cooling the sample through T_s in a small magnetic field is almost negligible. In fact, an incomplete Meissner effect, *i.e.*, imperfect flux expulsion is thought to be a signature [30] of the phase coexistence of superconductivity and ferromagnetism.

We can exclude scenarios in which the superconductivity is due to inclusions of a second phase or a surface impurity based on thorough metallurgical tests [31]. As a further important test we have investigated the interplay of superconductivity and ferromagnetism under hydrostatic pressure shown above. Surprisingly, hydrostatic pressure suppresses both the ferromagnetism and the superconductivity above a critical pressure $p_c = 21$ kbar. Thus, it is not sufficient to be close to the ferromagnetic quantum critical point for superconductivity to occur in ZrZn_2 , it must also be in the ferromagnetic state! This may arise naturally in scenarios where the Cooper pairs are in a parallel-spin (triplet) state, which is already favored in the ferromagnetic state. Such behavior could well be universal for itinerant ferromagnets in the limit of small Curie temperature and long electron mean free path.

4. Summary

Some of the most pressing questions raised by the discovery of superconductivity in coexistence with itinerant ferromagnetism in ZrZn_2 may be summarised as follows:

1. Is the ferromagnetism affected by the superconductivity (an unchanged ferromagnetic state may suggest equal spin pairing of a triplet superconducting state)?
2. Is the superconductivity a bulk phenomenon and hence related to a new thermodynamic state?
3. How important is it to be near a quantum critical point?
4. What is the superconductive pair interaction?

We have recently carried out detailed studies of the d.c. magnetisation under pressure in single crystal UGe_2 [32] and URhGe [33]. In UGe_2 we can rule out the presence of quantum criticality. The zero temperature pressure induced phase changes are instead all first order. For the case of URhGe we do not find any evidence for the vicinity to a zero temperature phase transition. This suggests that quantum criticality is not relevant. Preliminary results in ZrZn_2 [34] show that the ordered moment collapses linearly with pressure suggesting quantum criticality at p_c . Surprisingly, however, the longitudinal susceptibility nevertheless appears to be constant as the critical pressure is approached, suggesting a pronounced deviation from the predicted divergence at a ferromagnetic QCP. This would also suggest that the vicinity to a QCP is not relevant for superconductivity in the ferromagnetic state. On the other hand, the normal state properties

of $ZrZn_2$ deviate from those of a normal Fermi liquid. Even though all superconducting ferromagnets are strong contenders for ferromagnetically mediated pairing, additional features of the spectra of excitations may be instrumental for the occurrence of superconductivity that were so far not considered.

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