Interplay of Nuclear Magnetism and Superconductivity in $AuIn_2$

S. Rehmann, T. Herrmannsdörfer,* and F. Pobell†
Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany
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We report on a new type of magnetic superconductor investigated by susceptibility measurements of $AuIn_2$ at 25 μK $\leq T \leq$ 207 mK and 0.01 mT $\leq B \leq$ 2.00 mT. These experiments have been performed to study the interplay between *nuclear* ferromagnetism and type-I superconductivity. We observe a decrease of the critical field B_s and a broadening of the superconducting transition of the type-I superconductor $AuIn_2$ [$T_s(B = 0) = 207$ mK] caused by the *coexisting* nuclear ferromagnetic state starting at $T_c = 37$ μK. This is the first study on the interplay of nuclear magnetism and superconductivity. [S0031-9007(97)02378-8]

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Studies on the interplay between magnetism and superconductivity during the past decades have led to an understanding of many effects associated with the interaction of these two phenomena. Most of these studies were concerned with the coexistence of antiferromagnetism and superconductivity, whereas the coexistence of long-range ferromagnetism and superconductivity has never been observed [1,2]. The destruction of superconductivity at a critical temperature T_{s2} due to the onset of electronic ferromagnetism below the temperature T_{s1}, where superconductivity appears, was discovered in $ErRh_4B_4$ [3] and $HoMo_6S_8$ [4]. For these materials it was found that oscillatory magnetic order can coexist with superconductivity in a very narrow temperature range just above T_{s2} [1,2]. For $HoMo_6Se_8$ it was observed that superconductivity may coexist with an oscillatory magnetic state with ferromagnetic tendency down to lowest temperatures [5]. However, it was not possible until now to investigate the interplay of *nuclear* magnetic ordering and superconductivity, because until recently spontaneous nuclear magnetic ordering in metals had been reported only for the nonsuperconducting metals Ag, Cu [6], $PrCu_6$, $PrNi_5$, and $Pr_{1-x}Y_xNi_5$ [7]. Recently, we have reported on the observation of nuclear ferromagnetic ordering of In nuclei in $AuIn_2$ at $T_c = 35$ μK [8]. This compound is a type-I superconductor with $T_s(B = 0) = 207$ mK and $B_s(T = 0) = 1.45$ mT [8,9]. The nuclear magnetic ordering is caused by dominantly ferromagnetic indirect exchange interaction of RKKY type between the nuclear magnetic moments $\mu(\mathrm{In}) = 5.50$ μ_n. The good thermal coupling of these nuclear magnetic moments to the conduction electrons (Korringa constant $\kappa = 0.11$ Ksec) enabled measurements of nuclear specific heat, nuclear ac susceptibility, and nuclear magnetic resonance in thermal equilibrium to $T^{\mathrm{nuc}} = T^{\mathrm{el}} \simeq 30$ μK [8]. All these measurements were performed in static fields $B \geq 2.00$ mT to suppress the superconducting state of $AuIn_2$.

In the present work we investigate the field range $B \leq 2.00$ mT to study the interplay between nuclear ferromagnetism and superconductivity in $AuIn_2$. Our data show for the first time the coexistence of nuclear ferromagnetism and superconductivity, and, more generally, we find that $AuIn_2$ is the first type-I superconductor where coexistence with magnetic ordering occurs. We observe a strong decrease of the critical field B_s of the superconducting state and a broadening of this transition at temperatures below the onset of nuclear ferromagnetic ordering of In in $AuIn_2$. B_s remains finite and approximately constant in the nuclear ferromagnetic regime in the investigated temperature and nuclear polarization ranges.

The experimental setup mounted in a copper nuclear refrigerator [10] and the sample preparation are described in detail in our previous publications [8]. The high-purity $AuIn_2$ single crystal of CaF_2 structure contains less than 1 ppm electronic magnetic impurities and has a residual resistivity ratio of 550 [8]. The 8.33 mmol cylindrical sample (5.0 mm diam, 17.2 mm length) was mounted in a calorimetric setup located inside of a mutual inductance coil pair [8]. Inductance changes on a coarse scale are used to sense the transition from the normal state to superconductivity. On a high sensitive scale they are used to measure the nuclear ac susceptibility. The nuclear refrigerator precools the sample in 115 mT to 80 μK. The magnetic field is applied parallel to the z axis of the cylindrical crystal. For an identically treated reference sample of the same batch it was found by neutron diffraction that the z axis is identical with its [111] direction. The calorimetric design of the experiment allows a thermal decoupling of the sample to demagnetize to a chosen magnetic field in the nuclear magnetically ordered state. The temperature difference between the sample and the pulsed Pt wire NMR thermometer on it is at most 20% at lowest temperatures and decreases rapidly with increasing temperature. After precooling, we thermally isolated the sample from the nuclear refrigerator and finally demagnetized it to a minimum temperature of 25 μK from where we started the warm-up stepwise. The normal to superconducting transition of $AuIn_2$ was determined before each temperature step by driving the magnetic field from $B = 2.00$ mT to zero and watching the ac susceptibility. Before further

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increasing the temperature, the field was driven back to 2.00 mT. B_s was defined as the field value where 50% of the normal to superconducting transition is passed.

The critical field measured at 200 μK $< T \leq 207$ mK agrees well with the BCS equation $B_s(T) = 1.45\ \mathrm{mT}\,[1 - (T/207\ \mathrm{mK})^2]$ with known parameters of $AuIn_2$ (see Fig. 1). At $42 \leq T \lesssim 200\ \mu$K the critical field decreases slightly with decreasing temperature to a value $B_s(42\ \mu\mathrm{K}) = 1.41$ mT. However, decreasing the temperature further from 42 to 35 μK, the critical field is strongly reduced from $B_s\,(42\ \mu\mathrm{K}) = 1.41$ mT in the nuclear paramagnetic phase to $B_s\,(35\ \mu\mathrm{K}) = 0.95$ mT in the nuclear ferromagnetic phase (see Figs. 1 and 2). A further decrease of the temperature to 25 μK reduces B_s only weakly to an approximately constant value $B_s(25\ \mu\mathrm{K}) = 0.87$ mT. This means that the main part of the drop of the critical field takes place between $T_c(\chi_{\max}) = 42\ \mu$K, where the maximum of nuclear ac susceptibility occurs and $T_c(C_{\max}) = 35\ \mu$K, where the maximum of the nuclear magnetic specific heat occurs [8]. The value $T_c(\chi_{\max}) = 42\ \mu$K for $1.43 \leq B \leq 2.00$ mT (see Fig. 1) agrees with our former results [8]. The finite and approximately temperature independent B_s at $T \leq 30\ \mu$K could be interpreted as an appearance of a new stable coexistence region of nuclear ferromagnetism and superconductivity. This result is in contrast to the observations made for the electronic ferromagnetic type-II superconductors $ErRh_4B_4$ and $HoMo_6S_8$, where superconductivity vanishes near the onset of electronic ferromagnetic ordering, as indicated by a vanishing critical magnetic field. In these materials, superconductivity and electronic magnetic order of oscillatory type coexist only in the narrow temperature ranges $T_{s2} = 0.75 < T < T_c = 0.9$ K for $ErRh_4B_4$ [11] and $T_{s2} = 0.65 < T < T_c = 0.75$ K for $HoMo_6S_8$ [12], respectively.

The superconducting transition in the magnetically ordered state is strongly broadened compared to its width in the paramagnetic state. In the insets of Fig. 2 we show typical susceptibility versus magnetic field curves of the transition in the nuclear paramagnetic and ferromagnetic regions, respectively. For $T > (37 \pm 1)\ \mu$K the transition width is too small to be detectable with the used field steps of 5 μT. Below $T = (37 \pm 1)\ \mu$K the transition is broadened to a value of (0.20 ± 0.03) mT, using the 90%–10% criterion. The change from a sharp to a broadened transition takes place in a narrow temperature interval of about 1 μK around $T_c = 37\ \mu$K. In comparison with $T_c(C_{\max})$ and $T_c(\chi_{\max})$ this characteristic temperature with its small error bar may define the nuclear magnetic ordering temperature more exactly. Furthermore, from the calibration of our susceptometer we know that at $T < 37\ \mu$K the sample is still fully diamagnetic, $\chi = -1$ at $B = 0$, in the superconducting state. This means that superconductivity occurs in the whole sample even in the ferromagnetic state.

Each of our many measurements of the temperature dependent critical field was performed during a warm-up

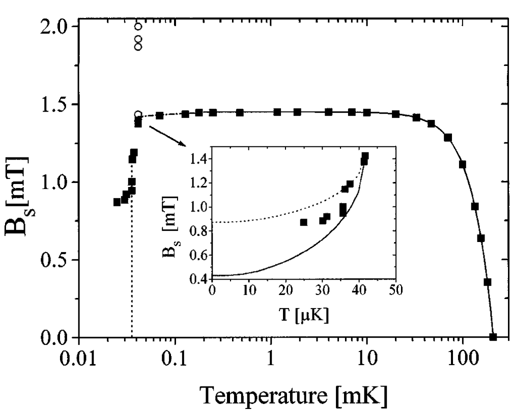

FIG. 1. Critical field B_s of the superconducting transition of $AuIn_2$ (closed squares) as a function of temperature. The solid line represents the $B_s(T)$ behavior according to BCS theory. The dash-dotted line is the fit of the data at $T \geq 42\ \mu$K as discussed in the text. The dotted line indicates the change from sharp superconducting transitions ($\Delta B_s < 5\ \mu$T) to broadened transitions ($\Delta B_s = 0.2$ mT) (see Fig. 2). The open circles indicate the temperatures $T_c(\chi_{\max})$ of the maximum of the nuclear magnetic susceptibility χ. The inset shows the calculations $\Delta B_s \propto M$ for $T < 42\ \mu$K [dotted line for $B_s(T = 0) \equiv 0.87$ mT and solid line for $B_s(T = 0) \equiv 0.44$ mT], see text.

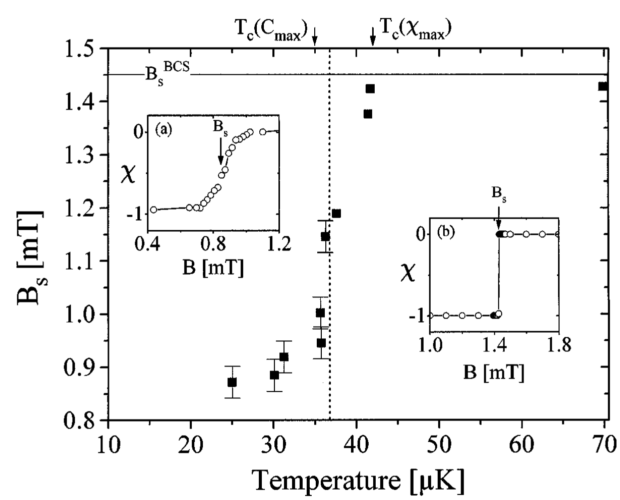

FIG. 2. Critical field B_s of the superconducting transition of $AuIn_2$ as a function of temperature. The solid line represents the critical field $B_s = 1.45$ mT. The dotted line indicates the nuclear ferromagnetic phase transition obtained from the broadening of the superconducting transition, $T_c = (37 \pm 1)\ \mu$K (see text). The error bar of B_s is ± 0.03 mT at $T < 37\ \mu$K. For $T > 37\ \mu$K the error bar is $< 5\ \mu$T. Insets (a) and (b) show typical susceptibility versus magnetic field curves of the superconducting transition in the nuclear ferromagnetic and paramagnetic regimes, respectively. For comparison, the "critical" temperatures where the nuclear heat capacity and the nuclear magnetic susceptibility, respectively, show their maxima are indicated on top.

starting after demagnetizing the sample starting from different precooling conditions. According to these precooling conditions of $70 \leq B \leq 115$ mT and $T \geq 80$ μK before demagnetizing the sample, entropy reductions $\Delta S_{\mathrm{prec}}/S_{\infty}$ up to 29% were obtained [$S_{\infty} = 2R\ln(2I + 1)$ with $I = \frac{9}{2}$, the high temperature entropy of the nuclear spin system]. These precooling entropy reductions are almost conserved during demagnetization because the increase of the entropy of the sample is only a few percent [8]. Some representative $B_s(T)$ curves with different $\Delta S_{\mathrm{prec}}/S_{\infty}$ values are shown in Fig. 3. For $T > 42$ μK the critical field is independent from the precooling conditions. But below this temperature, the reduction of B_s seems to be the stronger the larger the entropy reduction was. $B_s(T)$ approaches constant minimum values of $0.87\ \mathrm{mT} \leq B_{s,\min} \leq 1.25$ mT depending on the precooling conditions. The maximum reduction $\Delta B_{s,\max} = 1.45\ \mathrm{mT} - B_{s,\min}$ seems to be proportional to the reduction of nuclear entropy and to the square of the nuclear polarization (see inset of Fig. 3). Assuming this dependence of $\Delta B_{s,\max}$ on $\Delta S_{\mathrm{prec}}/S_{\infty}$ to be valid also at higher entropy reductions, one would expect the full depression of B_s after an entropy reduction of 70%. This would yield reentrant superconductivity.

The observed dependence $\Delta B_{s,\max}$ on the precooling conditions could be qualitatively explained if domains occur in the nuclear ferromagnetic phase. The polarization of the nuclear spin system in the paramagnetic region due to an external magnetic field possibly gives rise to the growth of those domains magnetized parallel to the applied field when the ferromagnetic state is entered. This would lead to a macroscopic net spontaneous magnetization of the nuclear ferromagnetic system which increases with increasing polarization in the paramagnetic state. Let us note that hints for the appearance of domains were already discussed by us [8].

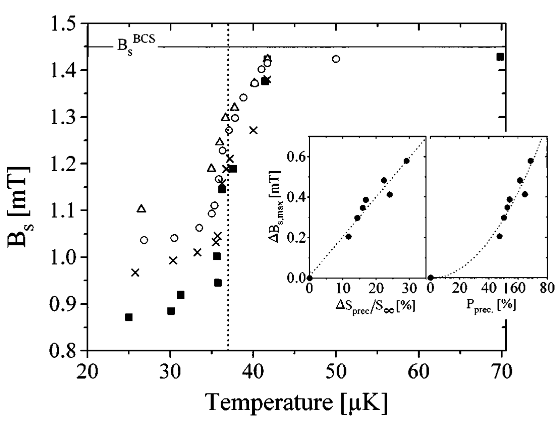

FIG. 3. Critical field B_s of the superconducting transition of AuIn_2 as a function of temperature of four representative measurements with the precooling conditions $\Delta S_{\mathrm{prec}}/S_{\infty} =$ 16%, 24%, 22%, and 29%, resulting in $B_{s,\min} = 1.10$ mT (open triangles), 1.04 mT (open circles), 0.97 mT (crosses), and 0.87 mT (closed squares), respectively. The solid line represents the critical field $B_s = 1.45$ mT. The insets show the reduction $\Delta B_{s,\max} = B_s - B_{s,\min}$ as a function of entropy reduction $\Delta S_{\mathrm{prec}}/S_{\infty}$ and polarization $P_{\mathrm{prec}} = M_{\mathrm{prec}}/M_0$ after precooling. The dotted lines in the insets indicate the behavior $\Delta B_{s,\max} \propto \Delta S_{\mathrm{prec}}/S_{\infty}$ and $\Delta B_{s,\max} \propto P_{\mathrm{prec}}^2$, respectively.

The calculated saturation magnetization of the nuclear spin system in AuIn_2 is $\mu_0 M_0 = \mu_0 N_0 \mu_n g_n I/V_{\mathrm{mol}} = 1.01$ mT at $T = 0$ K, which is smaller than $B_s(T \ll T_s) = 1.45$ mT. Assuming that the reduction of B_s is only due to the saturation magnetization (see below), it follows that the maximum available reduction should be 1.01 mT and therefore $B_{s,\min} = B_s(T \ll T_s) - \mu_0 M_0 = 0.44$ mT. Hence a full suppression of superconductivity seems to be impossible even at lowest temperatures. This might explain the absence of complete destruction of superconductivity by nuclear magnetic order. On the other hand, the above mentioned possibility of complete destruction of superconductivity at $\Delta S_{\mathrm{prec}}/S_{\infty} = 70\%$ (corresponding to a nuclear polarization $P_{\mathrm{prec}} = M_{\mathrm{prec}}/M_0 = 93\%$) contradicts this conclusion. Unfortunately, we cannot clarify this question with our data at present.

There are two phenomena, electromagnetic and exchange interactions, which are responsible for the interplay of superconductivity and magnetism. Both are interactions between the magnetic moments (or an applied field) on one side and the momentum and spin of the conduction electrons on the other side [1,2]. In $\mathrm{HoMo_6S_8}$ the electromagnetic interaction between the conduction electrons and the magnetization of the magnetic Ho^{3+} dominates the suppression of the critical field, whereas in $\mathrm{ErRh_4B_4}$ the destruction of superconductivity is mainly caused by exchange interactions between the magnetic Er^{3+} ions [1,2]. From the multiple pair-breaking theory of Fulde and Maki [13] the upper critical field of a type-II superconductor B_{s2} influenced by electronic magnetism can be described as $B_{s2}(T) = B_{s2}^{*}(T) - \Delta B_{s2}(T) = B_{s2}^{*}(T) - \mu_0 M(B_{s2}, T)$ in the case of negligible exchange interaction and therefore dominating electromagnetic induction; $B_{s2}^{*}(T)$ is the upper critical field in the absence of magnetic influence, $M(B_{s2}, T)$ is the magnetization. Ginzburg [14] considered this situation already in 1957 for type-I superconductivity influenced by the magnetization of magnetic ions. In order to determine the possible origin of the reduction of the (type-I) superconducting critical field B_s of AuIn_2 we took $B_s \equiv B_{s2}$ and the spontaneous saturation magnetization of the nuclear ferromagnet $M(T) = M_0 B(\alpha) \equiv M(B_{s2}, T)$ in the equation of Fulde and Maki with the Brillouin function $B(\alpha)$, $\alpha = \mu B_i(M(T))/Ik_B T$ and the interaction field $B_i(M(T))$ given in [15] and calculated $B_s(T)$ for $T < 42$ μK. However, taking as parameter either $B_s(T = 0) \equiv B_{s,\min} = 0.87$ mT from the experimental results (see Fig. 1) or $B_s(T = 0) \equiv 1.45\ \mathrm{mT} - \mu_0 M_0 = 0.44$ mT from the saturation magnetization, both simulations with $\Delta B_s \propto M$ deviate clearly from the measured reduction of the critical field (see inset of Fig. 1). Obviously, other effects which might be responsible for the reduction of B_s have to be considered too. For example, in the case of negligible electromagnetic interaction and dominating effective exchange field $H_J \propto \mu_0 M(B_{s2}, T)$, the critical field $B_{s2}(T) = B_{s2}^*(T) - \text{const} \times H_J^2(M,T)$, and therefore $B_{s2}(T) = B_{s2}^*(T) - \text{const} \times \mu_0 M^2(B_{s2}, T)$ [13]. Nevertheless, the equation $\Delta B_s = \mu_0 M_0 B(\alpha)$ describes the slight decrease of B_s at $42 \leq T \lesssim 200$ μK in a field of about 1.45 mT (see Fig. 1).

Up to now we have discussed the influence of magnetic ordering on the superconducting properties. Vice versa the influence of superconductivity on magnetism is considered to be weak, because the superconducting coherence length in $AuIn_2$, $\xi_0 = 4.9$ μm (using $\xi_0 = 2\hbar^2 k_F / \pi m_{\text{eff}} \Delta$ with $k_F^{-1} = 1.448$ Å^{-1}, effective mass $m_{\text{eff}} = 1.00\ m_{e0}$ [8], and gap energy $\Delta \simeq 4 k_B T_s$) is large compared to the characteristic length of the RKKY interaction (of the order of $\simeq$nm [8]) responsible for nuclear magnetic ordering [16]. After a cycle of field sweeps, driving the sample superconducting at a temperature $T < T_c$ and again normal conducting, no increase of the temperature within the error bar of 1 μK occurred, and the nuclear susceptibility was nearly unchanged still showing the characteristic temperature dependence in the ordered state [8]. The observation that the increase of entropy is negligible after driving the sample superconducting starting from the normal conducting and nuclear ordered state and going back to this state means that the nuclear spin arrangement kept its entropy and enthalpy and may have been still ferromagnetically ordered in the superconducting state, even at $B = 0$. Otherwise a significant increase of entropy and a change of the nuclear susceptibility should have occurred (remember that the lattice and electronic contributions to the entropy are negligible in the μK temperature range). This is a very remarkable result taking into account that the nuclear order in $AuIn_2$ is caused by indirect exchange interactions between the nuclear moments mediated by normal conduction electrons.

In summary, we have reported the first observation of the weakening of superconductivity due to long-range nuclear ferromagnetic order and the coexistence of both phenomena. It seems that the nuclear magnetic interactions are not significantly influenced by superconductivity. In addition, $AuIn_2$ is the first system where type-I superconductivity competes with magnetic order. Obviously, more investigations are necessary to understand some of the unexpected observations for this new type of magnetic superconductor. A measurement of the spin polarization and orientation using neutron diffraction, which we intend to do, might be an important step, in particular to prove whether $AuIn_2$ shows a simple ferromagnetic nuclear spin arrangement.

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*Also at Hahn-Meitner-Institut Berlin, Glienicker Str. 100, D-14109 Berlin, Germany.

†New address: Forschungszentrum Rossendorf, D-01314 Dresden, Germany.

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