Pressure-induced enhancement of the transition temperature of the magnetic-field-induced superconducting state in λ-$(BETS)_2FeCl_4$

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The effect of a small hydrostatic pressure $p \simeq 1.4$ kbar on the temperature-magnetic field phase diagram of the organic conductor λ-$(BETS)_2FeCl_4$ is reported. At zero field a hysteretic superconducting ($T_c \simeq 5.6$ K) to antiferromagnetic insulator transition ($T_N \simeq 4$ K) is found. Furthermore, the transition temperature to the field-induced superconducting (FISC) state, as well as its concomitant upper critical field, is found to increase by ~33%. The phase diagram of the FISC state for both pressures is well described in terms of the Jaccarino-Peter effect if the interactions among quasiparticles is taken into account.

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The complex interplay between magnetism and superconductivity is a central topic in condensed matter physics due to the vast amount of evidence suggesting that unconventional superconductivity (SC) occurs in the proximity of magnetically ordered states.[1] This proximity to,[2] or the coexistence with,[3] magnetism has been taken as evidence for a magnetically mediated SC pairing mechanism. Nevertheless according to our current understanding of SC, local magnetic moments, similarly to an external magnetic field, are expected to suppress SC via two mechanisms: The Pauli[4] and the orbital effects. This commonly accepted scenario has been seriously challenged by the discovery of a series of ferromagnetic superconductors such as UGe_2,[5] $ZrZn_2$,[6] and the borocarbides.[7] In this context, the recent report of magnetic field-induced superconductivity (FISC) in the magnetic organic conductor λ-$(BETS)_2FeCl_4$ (Refs. 8 and 9) constitutes, perhaps, an unique example of a cooperative interaction between both types of orderings, where field-induced ferromagnetism becomes the essential ingredient for stabilizing SC at very high magnetic fields ($B=\mu_B H_0$) and low temperatures (T) in an otherwise antiferromagnetic insulator. In fact, according to Refs. 9–11, the measured dependence of the FISC's phase diagram on T and on B can be explained in terms of the so-called Jaccarino-Peter (JP) compensation[12] effect: An external field orients the $S=5/2$ spin of the Fe^{+3} ions which, in turn, exert an exchange field $J\langle S\rangle$ on the spins s of the conduction electrons via the exchange interaction, $J\vec{s}\cdot\vec{S}$. Thus, the effective field $H_{\rm eff}$ acting on the conduction electron spin is

$$\mu_B H_{\rm eff} = \mu_B H_0 + J\langle S\rangle. \quad (1)$$

If $J<0$, i.e., the coupling between localized and itinerant spins is antiferromagnetic, a certain external field $\mu_B H_0$ can *compensate* the exchange field $J\langle S\rangle$, which in presence of an attractive pairing mechanism allows the condensation of Cooper pairs. The JP scenario has been confirmed by studying the evolution of the phase diagram[13] in the λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ alloys as well as through measurements of Shubnikov de Haas (SdH) oscillations.[14] However, a few aspects of the phase diagram of the λ-$(BETS)_2FeCl_4$ compound still remain unclear. Namely, the nature of the AFI ground state, the reason for the absence of SC at zero field and, more particularly, an explanation for the inexact fit to the simple JP description, as seen in Ref. 9. This last aspect was treated in Ref. 15 and the authors concluded that the experimental data of Ref. 9 can be well fitted to the JP description only if a nonuniform SC subphase, the so-called FFLO state,[16] is included into the phase diagram assuming a rather *anisotropic* 2D electron spectrum.

Here, we report the T-B phase diagram of the organic conductor λ-$(BETS)_2FeCl_4$ under a moderate value of hydrostatic pressure: $p \simeq 1.4$ kbar. The antiferromagnetic insulating (AFI) ground state is quickly suppressed by the application of pressure and, at $B=0$, superconductivity is stabilized at $T_c \simeq 5.6$ K followed by an unusual SC to AFI transition at $T_N \simeq 4$ K that displays substantial hysteresis. Also p increases considerably the transition temperature (and the associated critical fields) to the field-induced superconducting state. If we take into account the interactions among quasiparticles, we can improve our previously reported fit[9] to the Jaccarino-Peter description for the FISC state. Finally, for both pressures an excellent description of the FISC phase boundary can be attained by including a FFLO superconducting subphase assuming an isotropic two-dimensional electronic dispersion.

λ-$(BETS)_2FeCl_4$ single crystals were obtained by electrocrystallization.[17] Samples were mounted in a CuBe piston cylinder pressure cell and inserted in a ^{3}He refrigerator. All samples were aligned inside the cell in order to keep $B \| c$ axis. No pressure was applied at room temperature, a $p \simeq 1.4$ kbar, monitored through an InSb gauge is induced by

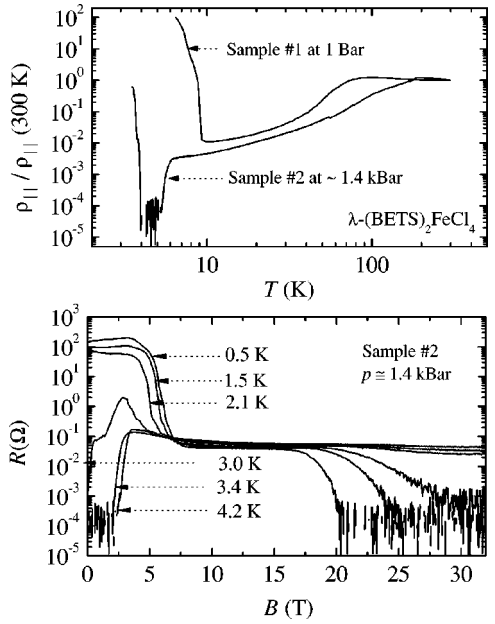

FIG. 1. Upper panel: In-plane resistivity $\rho_{\|}$ of a λ-$(BETS)_2FeCl_4$ single crystal as a function of temperature T at 1 bar and under 1.4 kbar of hydrostatic pressure. An abrupt increase in resistivity is observed at the transition from metallic to the AFI ground state. Notice that under 1.4 kbar, superconductivity precedes the AFI state. Lower panel: Resistance as a function of field at several temperatures and under 1.4 kbar.

the solidification of the pressure medium, i.e., Fluorinert. The temperature was stabilized by regulating the pressure of both ^{4}He and ^{3}He baths. The upper (u) panel of Fig. 1 shows the in-plane resistivity $\rho_{\|}$, normalized respect to its value at $T=300$ K, as a function of T for both values of pressure $p=1$ bar and 1.4 kbar and for two λ-$(BETS)_2FeCl_4$ single crystals. The abrupt upturn at $T_N \simeq 8.5$ K indicates a phase transition towards the AFI ground state[18] characterized by the antiferromagnetic order of the localized $S=5/2$ spins of Fe^{+3}. The application of 1.4 kbar decreases the resistivity by a factor of ~ 3 for 10 K$\leqslant T \leqslant$100 K while the onset of metallic behavior ($dR/dT>0$) is displaced from $T \leqslant 70$ K up to nearly to $T \geqslant 200$ K. These observations can be explained in terms of an increase of overlap between Se π orbitals resulting from the pressure-induced unit cell reduction. At low T an abrupt drop in $\rho_{\|}$, by nearly two orders of magnitude, precedes the AFI state which is displaced to $T_N \simeq 4$ K. The lower (l) panel of Fig. 1 shows the B dependence of the in-plane resistance R for several temperatures as indicated in the figure. As seen, at higher T this highly conducting state is suppressed by the application of an external field $B_{c2} \simeq 2.5$ T, confirming the SC nature of this phase. This value of B_{c2} is much lower than what is obtained for the isostructural SC compound λ-$(BETS)_2GaCl_4$,[19] indicating that in our case SC is destroyed by the polarization of the Fe^{+3} moments. Thus, similarly to the λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ (Ref. 20) compound for $x \leqslant 0.43$, under pressure the $x=1$ system also presents an uncommon SC to insulator transition upon cooling. A considerable amount of hysteresis is associated to this transition as can be seen,

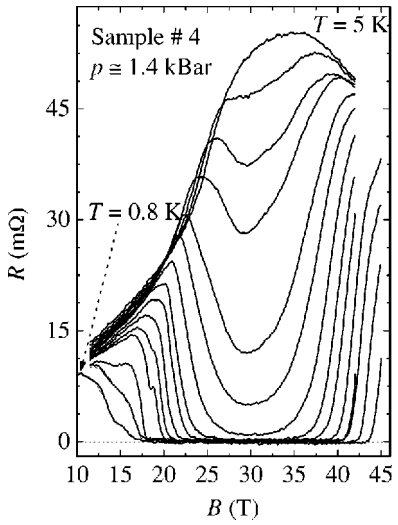

FIG. 2. Resistance as a function of the external magnetic field for various temperatures, at $p=1.4$ kbar. (Since the hybrid magnet is composed of a superconducting outsert coil in combination with a Bitter-type resistive insert coil, the field generated by the outsert is kept constant at approximately 11.5 T, while the field of the insert coil is ramped between 0 and and 31.5 T). The interval in T between traces is approximately 0.25 K.

for example, by comparing u and l panels: In the u panel the AFI state appears at $T_N \simeq 4.0$ K while in the l panel the same sample still is in the SC state at 3.4 K. This hysteresis or metastability is most likely due to a phase transition of the first order.

The proximity (or competition) between AF and SC orderings, as in the present case, has been observed in many compounds ranging from the cuprates to the organic superconductors and is believed to lead to unconventional superconducting behavior, see, for example, Ref. 21. In any case, the close proximity of SC to a state that has been claimed to be a Mott insulating phase,[11,22] suggests that it should not be treated in the weak coupling limit. Nevertheless, the clarification of the nature of the SC in λ-$(BETS)_2FeCl_4$ will require further systematic studies, particularly thermodynamic and spectroscopic measurements.

At lower T, the AFI is suppressed by an external field of the order of $\simeq 5$ T, and at a T dependent critical field $B_c \geqslant 15$ T the resistance drops by more than 2 orders of magnitude, reaching the level of sensitivity of our experimental setup, due to the entrance into the FISC state. Under pressure the FISC state clearly appears at lower critical fields B_c than those reported in Refs. 8 and 9. In order to study the overall effect of p on the B-T phase diagram, detailed T dependent measurements were performed under field from 11.5 to 45 T using the NHMFL's hybrid magnet. Figure 2 shows the resistance R as a function of B, applied along the in-plane c axis ($\pm 0.3°$ degrees) of a λ-$(BETS)_2FeCl_4$ single crystal at 1.4 kbar and for temperature intervals of approximately 0.25 K, between 5.4 and 0.8 K, from Ref. 9. The FISC state develops progressively with decreasing T, but is suppressed for fields sufficiently away from (above or below) the compensation field $H^{\star} \simeq 32$ T. Here the main observation is the p-induced broadening of the entire B-T diagram of the

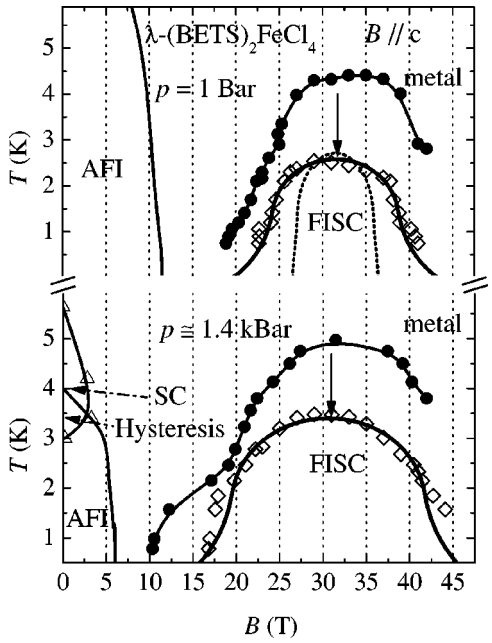

FIG. 3. Upper panel: The resulting B-T phase diagram for fields nearly parallel to the c axis at $p=1$ bar, from the data of Ref. 9 but defining the phase boundary differently (see text). AFI stands for the antiferromagnetic insulator phase and FISC stands for the field-induced superconducting phase. Lower panel: The phase diagram under $p=1.4$ kbar of hydrostatic pressure. In both figures solid circles indicate the onset of the resistive transition while open diamonds indicate the field dependent temperature where the resistance goes to zero. The solid lines represent fits to the Jaccarino-Peter description for a finite value of the Landau parameter F_0^a including a 2D-LOFF subphase (see text). The dotted line is the expected JP fit for $F_0^a=0$ and with no inclusion of subphases (from Ref. 9). Arrows indicate the approximate position of the compensation field $B^\star$.

FISC state: Under pressure, the FISC state also develops progressively with decreasing T but the onset of its maximum transition temperature increases up to $T_c \simeq 5$ K, respect to $T_c \simeq 4.5$ K at 1 bar. Furthermore, at $T=2$ K and $p=1$ bar the metallic to FISC transition takes place $B_c \sim 23.7$ T (middle point of the resistive transition) and is suppressed at an upper critical field $B_{c2} \sim 42$ T. While under 1.4 kbar these transitions take place respectively at $\simeq 18.6$ K and $\simeq 43$ T. This represents a broadening in $\Delta B = B_c - B_{c2}$ of $\sim 35\%$. Notice, that this effect cannot be attributed to a pressure gradient, since this scenario is incompatible with the sharpness of both metal to SC and SC to AFI transitions seen in the u panel of Fig. 1. Also, as seen below, this is incongruent with the observed reduction in the width of the resistive transition to the FISC state under pressure.

In order to quantify the effect of pressure, Fig. 3 shows the T-B phase diagrams for both values of p. Its upper panel contains the data taken at $p=1$ bar, which is included here for comparison. While the lower panel results from the combination of measurements performed in both samples No. 2 ($B<10$ T) and No. 4 ($B>10$ T) under 1.4 kbar. In Fig. 3 solid circles indicate the onset while open diamonds indicate the "foot" of the resistive transition, i.e., the temperature or the field where the resistance reaches zero.

As can be seen in the upper panel of Fig. 3, at $p=1$ bar the width of the resistive transition [defined as $\tau=(T_{\text{onset}}-T_c)/T_c$ where T_{onset} and T_c correspond, respectively, to the onset and the foot temperatures] is remarkably large $\tau=0.8$ in the vicinity of $B^\star \sim 32$ T. Particularly, if we compare with what is seen in the isostructural Ga compound where τ ranges between 0.45 and 0.65 (Ref. 23) or with the transition seen at $B=0$ and $p=1.4$ kbar where $\tau \simeq 0.17$. Notice that T_c as defined here increases by a factor of $\sim 33\%$ under pressure. This is a somewhat surprising result, since the increment in conductivity can be easily understood in terms of an increment in the amplitude of the transfer integrals $t_{a,b,c}$ (and thus of the bandwidth $W \propto 4t_{a,b,c}$) among closest neighbors in a tight binding dispersion. Naively, this is expected to lead to a decrease in the density of states and thus in T_c. In the other hand, as can be seen in the lower panel, around $B^\star\tau$ is found to decrease to a value of 0.44 under $p=1.4$ kbar suggesting again an "improvement" in sample quality/homogeneity. In both cases, the region comprised within τ is quite asymmetric with respect to $B^\star$, increasing with B. In this system the SC layers are weakly or Josephson coupled (otherwise the orbital effect would suppress the FISC for $B \| a$-c plane), thus its effective dimensionality is 2 and consequently the effects of SC fluctuations are relevant and most likely responsible for the width represented by τ. This behavior bears strong similarities with the so-called pseudogap phase seen in the cuprates[24] and also in 2D organic compounds[25] where the slope of the in-plane metallic state resistivity increases below a certain temperature $T^\star > T_c$ upon cooling (the estimated Ginzburg parameter $G_i \simeq 10^{-2}$ is comparable to that observed in cuprates which further justifies this analysis). Consequently, it is possible that p favors the SC phase in detriment of the pseudogap region increasing T_c, or simply it increases the relevant energy scales of the system as in seen in the cuprates.[27] Due to the uncertain nature of the region represented by τ we have chosen only the region below T_c as the actual phase boundary for the FISC state. In Fig. 3 solid lines represent fits of $T_c(p,B)$ to the JP effect where the Landau correction is introduced into the expression relating the Pauli critical field $B_p = \Delta(T=0)/\sqrt{2}\mu_B$ to T_c: $B_p(T) = 1.85\sqrt{1+F_0^a}T_c(\text{K})$.[26] F_0^a is the so-called Landau parameter which in the Fermi-liquid theory describes the spin antisymmetric and spatially isotropic part of the quasiparticle interaction.[28] For both pressures a fairly reasonable fit is obtained for a value $F_0^a \simeq 0.26$ if we also include, as in Refs. 9 and 15, a FFLO subphase for which we assumed a two-dimensional isotropic dispersion. Given the incertitude on the nature of the region comprised within τ and thus on the precise location of the phase boundary, these fits, as those of Ref. 15, cannot be taken as a solid but only as an indirect evidence for the FFLO state. Finally, notice how B^*, indicated by solid arrows, slightly decreases under pressure, what is unexpected since one would expect the reduction of the unit cell volume to increase the number of localized spins per volume and thus J.

In conclusion, the clarification of the mechanism leading to the AFI should provide important clues respect to the nature of SC in λ-(BETS)$_2$FeCl$_4$. Under pressure, the

coexistence of SC with localized magnetic ions in the paramagnetic state, the proximity of the superconducting relevant energy scale to that of a Mott antiferromagnetic phase and the indications of a pseudogap phase could be taken, by analogy with the cuprates, as indirect evidence for unconventional superconductivity. Notice that the Jaccarino-Peter description requires only a singlet superconducting state whose gap symmetry can differ from the standard *s*-wave one. Certainly, this interesting possibility, the role of higher pressures as well as the possible existence of a FFLO sub-phase suggested by our phase-diagrams, deserve further experimental studies.

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