Superconductivity in an Organic Insulator at Very High Magnetic Fields

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We investigate by electrical transport the field-induced superconducting state (FISC) in the organic conductor λ-(BETS)$_2$FeCl$_4$. Below 4 K, antiferromagnetic-insulator, metallic, and eventually superconducting (FISC) ground states are observed with increasing in-plane magnetic field. The FISC state survives between 18 and 41 T and can be interpreted in terms of the Jaccarino-Peter effect, where the external magnetic field *compensates* the exchange field of aligned Fe^{3+} ions. We further argue that the Fe^{3+} moments are essential to stabilize the resulting singlet, two-dimensional superconducting state.

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Superconductivity is usually destroyed by diamagnetic currents induced in the presence of strong magnetic fields. This effect has orbital character and prevails in most conventional "*s*-wave" superconductors that involve the singlet state of the Cooper pairs. In addition, superconductivity can also be suppressed by the Pauli pair breaking mechanism: here the external field destroys the spin-singlet state of the Cooper pair, imposing the so-called Clogston-Chandrasekhar paramagnetic limit [1,2]. Nevertheless, and despite these well known physical limitations, Uji *et al.* [3] have recently reported the observation of a magnetic-field induced superconducting phase (FISC) in the quasi-two-dimensional organic conductor λ-(BETS)$_2$FeCl$_4$ [where BETS stands for Bis(ethylenedithio)tetraselenafulvalene] for fields exceeding 18 T, applied parallel to the conducting layers. This is particularly remarkable since this compound, at zero field, is an antiferromagnetic insulator (AI) below $T_p \cong 8.5$ K [4]. The AI state is suppressed by the application of magnetic fields above 10 T at low temperatures [5].

The present work was motivated by the apparent increase in the critical temperature of the FISC above 18 T with increasing magnetic field (Ref. [3]). Here, for instance, in the case of spin-triplet superconductivity, there would be, in principle, no limit on the upper critical field. The presence of Fe^{3+} magnetic moments, which coexist with the FISC state, adds further appeal to the triplet state model. To clarify the nature of the FISC, we have studied the λ-(BETS)$_2$FeCl$_4$ compound at low temperatures in steady, tilted magnetic fields up to 42 T. Our main result is the observation of reentrance towards the metallic state at a temperature-dependent critical field. We obtain a temperature-magnetic field phase diagram for the FISC state, which we interpret in terms of the Jaccarino-Peter (JP) field compensation effect [6], which was previously mentioned in Ref. [3] as one possible explanation for the observed phase transition. We argue further that the Fe^{3+} magnetic state is indeed necessary to stabilize the singlet superconducting state by suppression of interplane diamagnetic currents in the associated in-plane high magnetic fields.

λ-(BETS)$_2$FeCl$_4$ crystallizes in a triclinic unit cell. The BETS planar molecules are stacked along the crystallographic *a* axis and constitute conducting planes parallel to the *a*-*c* plane. These conducting layers alternate along the *b* axis with layers containing linear chains of FeCl$_4^-$ magnetic anions; hence the *b* axis is the least conducting direction. Spin interactions between localized Fe^{3+} 3*d* electrons and π conducting electrons are expected due to the short interatomic distance between the BETS molecules and the FeCl$_4$ anions.

Single crystals of λ-(BETS)$_2$FeCl$_4$ were obtained by electrocrystallization [7]. Annealed (low strain) gold wires ($\phi = 12.5$ μm) were attached with graphite paint in a four-terminal arrangement along the *c* axis. An ac current (10 to 100 μA) was used, and the voltage was measured by a conventional lock-in amplifier technique. Samples were mounted in a rotating sample holder in a ^{3}He refrigerator. The measurements were carried out in the Hybrid magnet at the DC Field Facility of the National High Magnetic Field Laboratory.

Our magnetic field dependent resistance of a λ-(BETS)$_2$FeCl$_4$ single crystal is shown in Fig. 1(a) for different temperatures. Here the magnetic field B is applied along the in-plane *c* axis. The main characteristic of the data is that between 18 and 41 T, the resistance of the material drops with decreasing temperature, reaching zero within experimental uncertainties below 2 K in a field range centered near 33 T. It is important to mention that in this part of the (B-T) phase diagram, the material behaves as a good metal. We find Shubnikov–de Haas oscillations (of order 700 T with effective mass $m^\star \sim 4m_0$) for the

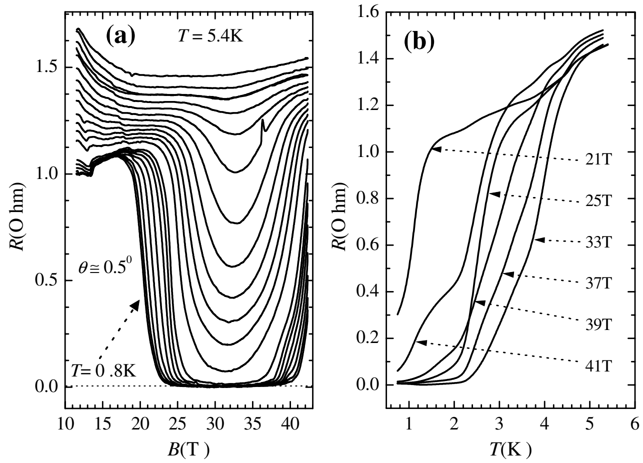

FIG. 1. (a) Resistance R as a function of magnetic field B, applied along the in-plane c axis ($\pm 0.3°$) of a λ-$(\mathrm{BETS})_2\mathrm{FeCl}_4$ single crystal for temperature intervals of approximately 0.25 K, between 5.4 and 0.8 K. The superconducting state develops progressively with decreasing temperature but is suppressed for fields sufficiently away from (above or below) 33 T. (We note that 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 was ramped between 0 and and 31.5 T.) (b) Resistance as a function of temperature T for several values of B obtained from the field scans shown in (a). The FISC transition has a maximum transition temperature $T_c \simeq 4.2$ K near 33 T.

magnetic field perpendicular to the conducting planes [8], which for an isotropic model would give a Fermi energy $\varepsilon_F \sim 200$ K. The normal state resistivity is of order of $10^{-4}\ \Omega \cdot \mathrm{cm}$ in the metallic state near 15 T. We estimate $k_F \ell \sim 20$ (where k_F is the Fermi wave vector and ℓ is the mean free path) and thus, despite the low scale of ε_F, the standard metallic conditions are fulfilled.

In the FISC state at higher fields, the resistivity drops typically by 2 to 4 orders of magnitude, putting it at or below the conductivity of copper, and beyond our ability to measure by standard ac lock-in methods. From the isothermal field scans we can extract the temperature dependence of the resistance at fixed values of the field; see Fig. 1(b). For fields between 18 and 37 T, the resistance shows a phase transition from the metallic phase (above 4.2 K) to the full superconducting state. Above a certain threshold field $B_{\mathrm{th}} = 18$ T, the onset of this transition *increases* with magnetic field, reaching a maximum $T_c \cong 4$ K at $B^{\star} = 33$ T. Above $B^{\star}$ the onset *decreases* in temperature with increasing field, and above 41 T the FISC is suppressed rapidly. We note that the experimental resistance does not fall immediately to zero below T_c. We interpret this as an evidence for complex magnetic flux penetration and trapping in our sample. Evidence for this is also provided by the hysteretic behavior observed in torque magnetization measurements shown in Ref. [3] and which was interpreted by the authors as evidence for flux pinning.

We next discuss a central question concerning the interpretation of the FISC state as "truly" superconducting, beyond the observation of zero resistance within experimental uncertainties. The Meissner effect—the standard test for the onset of superconductivity—where magnetic flux is excluded when a sample enters the superconducting state, may become a nontrivial experiment in the present case. This is due to the fact that the penetration of the magnetic field, which compensates the internal exchange field, is essential for the stabilization of the FISC state. Furthermore, the magnetic flux may penetrate and be trapped in between two-dimensional superconducting layers. And, in fact, torque magnetization measurements, which give thermodynamic evidence for a phase transition at $B_{\mathrm{th}}(T)$, indicate that the magnetic field remains pinned between the conduction layers producing a large hysteresis in the torque signal [3].

The present work provides an additional, independent piece of evidence that the FISC is superconducting: The FISC state is reentrant to a metallic state above 41 T, which excludes triplet pairing. This observation also rules out field-induced low-resistance models. When magnetic scattering or some other form of higher resistance state is removed by magnetic fields, restoration of disorder-related, inelastic processes at higher fields is very unlikely. Furthermore, and as is pointed out in Ref. [3], the application of a transverse magnetic field, i.e., perpendicular to the conducting layers, produces a dramatic effect on the FISC state. This behavior is quantitatively illustrated in Fig. 2(a), where we show results from a variation of the magnetic field away from the in-plane orientation at the lowest temperature of our investigation. The zero resistance state begins to vanish for a *transverse field* $B_{c\perp}$ greater than 3.5 T. This observation is elucidated in Fig. 2(b) by plotting the resistance for a *constant in-plane field* $B_{c\|} = B\sin(\theta)$ of about 33 T (i.e., $B_{c\|} = B^{\star}$) vs the transverse field $B_{c\perp} = B\cos(\theta)$. Hence the FISC state is removed when orbital components appear. Note that the critical field $B_{c\perp}$ for the FISC state is essentially identical to that of the nonmagnetic, isostructural material λ-$(\mathrm{BETS})_2\mathrm{GaCl}_4$ [9]. The approximately linear increase in resistivity $\rho \propto (B_{c\perp} - B_{c\perp\mathrm{out}})$ may also be ascribed to trapped flux. A full explanation of this effect will require a further study (now being planned) involving a systematic experimental comparison of $B_{c\perp}$ for both Fe- and Ga-based compounds.

We next consider how the FISC state is stabilized. While the two anions (Fe^{3+} and Ga^{3+}) have different ground states at $T = 0$ in the low field range of the (B-T) phase diagram, alloying by Ga and external pressure restores superconductivity in the Fe-based material [10]. We expect that the superconducting states, in both cases, are close in energy. We therefore argue that the in-plane physics is similar for both materials, and the differences in the phase diagrams arise from correspondingly small energies related to, for instance, the interlayer coupling. Our model is as

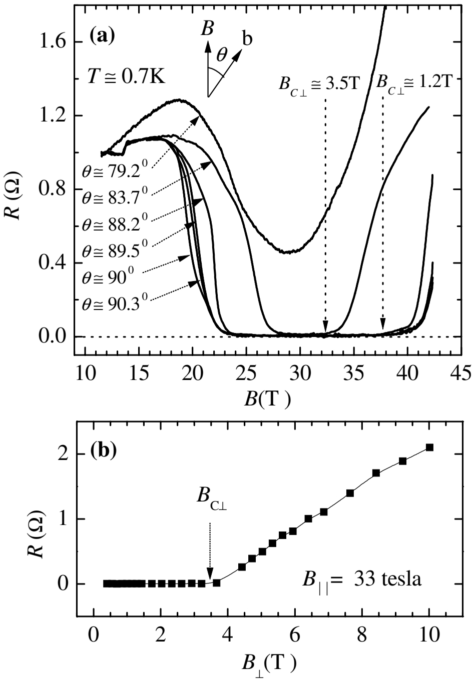

FIG. 2. (a) Resistance as a function of magnetic field at $T = 0.7$ K and for five different angles θ (indicated in the figure) between B and the interplane b axis. Notice that the interplane critical field $B_{c\perp}$, defining the orbital effect, decreases as θ approaches 90°. (b) Resistance for constant in-plane field $B_{c\|}$ vs transverse magnetic field $B_{c\perp}$ at $T = 0.7$ K.

follows. In-plane fields orient the $S = 5/2$ spin of the Fe^{3+} ions, and we assume that this decouples the BETS conducting layers. The problem then becomes two dimensional (2D), with no diamagnetic currents flowing between layers in the presence of a purely in-plane magnetic field (we return to this point later). For the 2D geometry, the in-plane field can destroy singlet superconductivity by means of paramagnetic effects only, i.e., breaking the Cooper pairs [1]. The $S = 5/2$ Fe^{3+} magnetic moments, oriented by magnetic field, exert the 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_{eff} acting on the electron spin is

$$I(B) = \mu_B H_{\mathrm{eff}} = \mu_B B + J\langle S\rangle . \tag{1}$$

(For our experiments with $B \cong 20{-}40$ T and $T < 5$ K, the iron moments are saturated: $\langle S\rangle = 5/2$.) The Jaccarino-Peter effect is the compensation in Eq. (1) of the magnetic field, B, by the exchange field, $J\langle S\rangle$, at $J < 0$, so that the effective field, H_{eff}, may become below the Clogston limit [1,2] at higher B. According to [1], the first order phase transition from the paramagnetic normal metal into the superconducting state at $T = 0$ would occur at $I(B) = \Delta(0)/\sqrt{2}$, where $\Delta(0)$ is the superconducting gap at $T = 0$ (in the absence of the field). The actual situation is more complicated by the fact that the phase transition separating the normal and the superconducting states in the $(T, I(B))$-plane may be either first or second order [11–15]. Thus, at low enough temperatures the first order phase transition is preceded by the second order transition into the inhomogeneous LOFF (Larkin-Ovchinnikov-Fulde-Ferrell) phase [14,15] at $|I(B)| < \Delta(0)$. This phase is highly sensitive to the presence of defects. In the pure limit it would occupy a stripe in the $(T, I(B))$-plane as shown below in Fig. 3: at $T = 0$ $\Delta B \simeq 3.73$ T, which is beyond the resolution of our electrical transport measurements. Our experiments suggest $I(B^\star) = 0$ at $B^\star = 33$ T and $T_c \cong 4.2$ K. These parameters were used in the theoretical plots in Fig. 3. We see from Fig. 3 that the theoretical model discussed above reproduces the main features of the FISC phase diagram very well.

Let us now return to the question regarding the nature of the new FISC state in λ-(BETS)$_2$FeCl$_4$ and its relation to the "conventional" SC state in λ-(BETS)$_2$GaCl$_4$. Here we argue that remarkably, the Fe^{3+} magnetic ions may be essential to stabilize the two-dimensionality of the FISC state produced by the JP effect. Both compounds have similar, anisotropic, layered structure. Nevertheless, there is an inter-plane electronic coupling in the λ-(BETS)$_2$GaCl$_4$, as is evidenced in the finite upper critical field [9] for the in-plane direction,

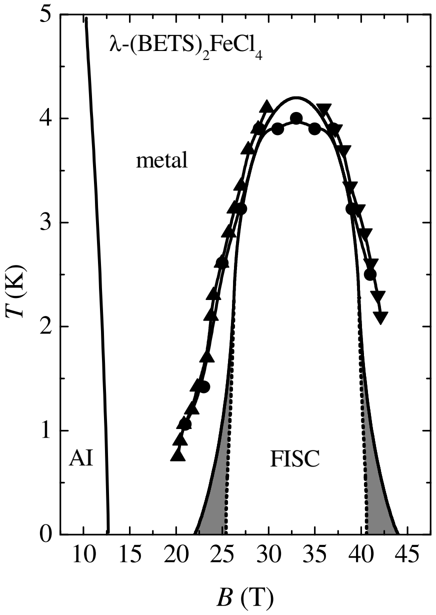

FIG. 3. Temperature-magnetic field phase diagram showing the AI, metallic, and FISC states for a λ-(BETS)$_2$FeCl$_4$ single crystal vs in-plane magnetic field. Solid triangles indicate the middle point of the resistive transition as a function of B [from Fig. 1(a)], while solid circles indicate the middle point of the resistive transition as a function of T [from Fig. 1(b)]. The solid line is a theoretical fit (see text) to a second order phase transition towards the FISC while the dashed line indicates a first order transition from the inhomogeneous LOFF state (shaded area) into the bulk SC state. Our electrical transport measurements do not have sufficient resolution to resolve both the second and the first order phase transitions.

$H_{C2}(0) = 12-15$ T, which is well below the field where the FISC is stable. To restore superconductivity in λ-(BETS)$_2$FeCl$_4$ within the field range of the JP compensation effect, one needs a mechanism to fully eliminate the diamagnetic interlayer currents in this compound. We suggest that the coupling between 2D BETS layers comes about through the bridging of MCl$_4$ tetrahedra, so that in the second order effective tunneling matrix element, the (MCl$_4$)^0 state shows up as the intermediate state in simple perturbation theory. While the p shell is empty for Ga^{3+}, all the "d levels" are occupied in Fe^{3+}, according to Hund's rule. Placing an additional electron at the Fe^{3+} site (with spin antiparallel to $\vec{S}$) is energetically unfavorable; i.e., it costs the Hund coupling energy. Furthermore, when the $S = 5/2$ spins of Fe^{3+} are aligned by the field, an electron with parallel spin has no accessible states on the d shell, and the energy cost inside the FeCl$_4$ complex is expected to increase even further. Therefore, tunneling across magnetically oriented Fe^{3+} tetrahedra becomes a spin selective process; consequently, transport of an s-wave Cooper pair between adjacent planes is excluded. Clearly, in λ-(BETS)$_2$GaCl$_4$ there is no spin selective process, and hence a correspondingly smaller upper critical field is observed [9].

Finally, we consider why $T_c^\star \cong 4.2$ K in λ-(BETS)$_2$FeCl$_4$ is less than $T_c^\star \cong 5.5$ K for λ-(BETS)$_2$GaCl$_4$. Our guess is that both superconducting ground states (due to the two dimensionality) are basically the same at $T = 0$ [i.e., $\Delta(0)_{\mathrm{Fe}} \cong \Delta(0)_{\mathrm{Ga}} = 1.76 T_c^{\mathrm{Ga}}$]. $T_c^\star = T_c^{\mathrm{Fe}}$ seems to be smaller, since at higher temperatures, thermal activation of the Fe^{3+} spins via the exchange interaction J provides a mechanism for pair breaking scattering.

We conclude by noting that λ-(BETS)$_2$FeCl$_4$ [along with the nonmagnetic analog λ-(BETS)$_2$GaCl$_4$] has provided a rich new area for the study of low-dimensional superconductivity and magnetism, where the two mechanisms compete on a very low energy scale. In this Letter we have provided a simple theoretical picture that describes the broader features of the newly discovered high field induced superconducting state. We show experimentally that in-plane diamagnetic currents ($B_{c\perp}$) can destroy the FISC state. We have argued that magnetic ions are actually essential to suppress the coupling between planes in the presence of in-plane magnetic fields. However, there are many unusual features in this system that will require a significant, further level of both experimental and theoretical work. In particular, the mechanism by which the magnetic field penetrates in the bulk of our 2D superconducting samples remains unclear and may produce hysteretic behavior.

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