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)₂FeCl₄. 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 Fe³⁺ ions. We further argue that the Fe³⁺ moments are essential to stabilize the resulting singlet, two-dimensional superconducting state.

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 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]. Nevertheless, and despite these well known physical limitations, S. Uji et al. [2] have recently reported the observation of a magnetic-field induced superconducting phase (FISC) in the quasi-two-dimensional organic conductor λ-(BETS)₂FeCl₄ for fields exceeding 18 tesla, applied parallel to the conducting layers. This is particularly remarkable since this compound, at zero field, is an antiferromagnetic insulator (AI) below $T_p \approx 8.5$ K [1]. The AI state is suppressed by the application of magnetic fields above 10 tesla at low temperatures [3].

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 Fe³⁺ 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)₂FeCl₄ compound at low temperatures in steady, tilted magnetic fields up to 42 tesla. 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 [4]. This implies that the Cooper pairs condense into a spin-singlet state. We argue further that the Fe³⁺ magnetic state is indeed necessary to stabilize the singlet superconducting state by suppression of diamagnetic currents in the associated in-plane high magnetic fields.

λ-(BETS)₂FeCl₄ (where BETS stands for Bis(ethylenedithio)tetraselenafulvalene) 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 FeCl₄⁻ magnetic anions, hence the b-axis is the least conducting direction. Spin interactions between localized Fe³⁺ 3d electrons and π conducting electrons are expected due to the short interatomic distance between the BETS molecules and the FeCl₄⁻ anions.

Single crystals of λ-(BETS)₂FeCl₄ were obtained by electro-crystallization [5]. Annealed (low strain) gold wires (φ = 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)₂FeCl₄ 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 tesla, 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
$m^* \sim 4m_0$ for the 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 resistance is of order of $10^{-4}$ $\Omega$ cm in the metallic state near 15 T. We estimate $k_F \ell \sim 20$ (where $k_F$ is the Fermi wave vector and $\ell$ is the mean free path) and thus, despite the low scale of $\varepsilon_F$, 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 $B_{th} = 18$ tesla, the onset of this transition increases with magnetic field, reaching a maximum $T_c \cong 4$ K at $B^* = 33$ tesla. Above $B^*$ 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 expect, given the very small, delicate nature of the samples, that the presence of strain, sample quality, or sample mis-alignment may cause some inhomogeneity (percolation) in the superconducting fraction at the onset of the FISC.

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 non-trivial experiment in the present case. This is due to the fact that the magnetic flux may be trapped between two-dimensional superconducting layers. However, as torque magnetization measurements show [3], there is a bulk phase transition at $B_{th}(T)$ from the metallic to the FISC state.

The present work provides two additional, independent pieces of evidence that the FISC is superconducting. The first is that the state is re-entrant 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. The second observation is the effect of the transverse magnetic field (i.e. field perpendicular to the layers) on the FISC state. This behavior is illustrated in Fig. 2(a), where we show results from a systematic variation of the magnetic field away from the in-plane orientation at the lowest temperature of our investigation. The essential detail here is that the zero resistance state begins to vanish for a transverse field $B_{\perp}$ greater than 3.5 T. This observation is elucidated in Fig. 2(b) by plotting the resistance for a constant in-plane field $B_{\parallel} = B\sin(\theta)$ of about 33 T (i.e. $B_{\parallel} = B^*$) vs. the transverse field $B_{\perp} = B\cos(\theta)$. Hence the FISC state is removed when orbital components appear. The most striking observation is that the critical field $B_{\perp}$ for the FISC state is essentially identical to that of the non-magnetic, isostructural material $\lambda$-(BETS)$_2$GaCl$_4$ [9], and by comparison, this suggests that the FISC is also a singlet superconducting state.

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 inter-layer coupling. Our model is as 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 will 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, $J S \cdot \vec{S}$. Thus, the effective field $H_{eff}$ acting on the electron spin is:

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

Eq. (1) is at the heart of the Jaccarino-Peter effect [1]: for $J < 0$ the two contributions will compensate each other to restore superconductivity. For our experiments with $B \cong 20 - 40$ tesla and $T < 5$ K, the iron moments are saturated: $\langle S \rangle = 5/2$. Following Refs. [1,6], the restoration of superconductivity (at $T = 0$) will occur in the field interval $|I(B)| < 0.755\Delta(0)$, where $\Delta(0)$ is the superconducting gap at $T = 0$ (in the absence of the field). The situation, however, is more complicated by the fact that the phase transitions separating normal and superconducting states in the $(T, I(B))$ - plane, may be either 1st or 2nd order [1]. The phase diagram has recently been revised by two of us in [2] (see also [3]); we plot in Fig. 3 the theoretical results, together with the experimental data in the $(T, B)$-plane. Experiments suggest $I(B^*) = 0$ at $B^* = 33$ tesla, $T_c \cong 4.2$ K, and these parameters were used in the theoretical plots in Fig. 3. In Fig. 3 the solid line is the 2nd order transition line. At lower temperatures, transitions from the normal to the
superconducting states begin with a 2nd order transition into the inhomogeneous LOFF-state (shaded area), rapidly followed by a 1st order transition (dashed curve) into the homogeneous state. The branching points are at \(T_1 \approx 2.3 \, \text{K}\). The range of existence of the LOFF state is rather narrow: we estimate the width (at \(T = 0\)) as only \(\Delta B \approx 0.72 \, \text{T}\). (In addition, this state is very sensitive to defects). 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 \(\lambda\)-(BETS)\(_2\)FeCl\(_4\) and its relation to the “conventional” SC state in \(\lambda\)-(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 \(\lambda\)-(BETS)\(_2\)GaCl\(_4\), as is evidenced in the finite upper critical field \(H_c(0) = 12 - 15\) tesla, which is well below the field where the FISC is stable. To restore superconductivity in \(\lambda\)-(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 \(\lambda\)-(BETS)\(_2\)GaCl\(_4\) there is no spin selective process, and hence a correspondingly smaller upper critical field is observed.

Finally, we consider why \(T_c^* \approx 4.2 \, \text{K}\) in \(\lambda\)-(BETS)\(_2\)FeCl\(_4\) is less than \(T_c^* \approx 5.5 \, \text{K}\) for \(\lambda\)-(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. \(\Delta(0)_{Fe} \approx \Delta(0)_{Ga} = 1.76T_c^{Ga}\). \(T_c^* = T_c^{Fe}\) 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 \(\lambda\)-(BETS)\(_2\)FeCl\(_4\) (along with the non-magnetic analog \(\lambda\)-(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 paper 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 \(B_{c1}\) 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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FIG. 1. (a) Resistance $R$ as a function of magnetic field $B$, applied along the in-plane c-axis ($\pm 0.3$ degrees) of a $\lambda$-(BETS)$_2$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 tesla. (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 tesla, while the field of the insert coil was ramped between 0 and and 31.5 tesla). (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 tesla.

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

FIG. 3. Temperature-magnetic field phase diagram showing the AFI, metallic, and FISC states for a $\lambda$-(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. 1A), while solid circles indicate the middle point of the resistive transition as a function of $T$ (from Fig. 1B). Open triangles and circles indicate the region where the resistance vanishes at the level of sensitivity of our instrumentation. 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.