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# Magnetic-field-induced superconductivity in the antiferromagnetic organic superconductor $\kappa$-(BETS)$_2$FeBr$_4$

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The high magnetic field electronic state of the quasi-two-dimensional organic superconductor, $\kappa$-(BETS)$_2$FeBr$_4$ was investigated by the resistance measurements. At very low temperatures, magnetic-field-induced superconductivity (FISC) was observed under high magnetic field parallel to the conducting layers. The obtained magnetic phase diagrams are well reproduced by Fisher's theory based on the Jaccarino-Peter compensation mechanism, where the external field and internal field caused by the magnetic moments are canceled out. The analyses of the phase diagram show that the orbital effect is not so small in this compound, which makes the Fulde-Ferrell-Larkin-Ovchinnikov state less likely.

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## I. INTRODUCTION

One of the recent greatest concerns in the field of strongly correlated electron systems is the study of the interplay between magnetism and electric conduction. In most of the organic layered systems, which is the typically strongly correlated system, magnetic moments are introduced in insulating layers and electric conduction is dominated by $\pi$-electrons on donor molecules, forming conducting layers. Strong interaction between the magnetic moments and the $\pi$-electrons is realized if the overlap integrals between the molecular orbitals of the anion and $\pi$-orbitals of the donor molecules are fairly large. In general, such a $\pi$-$d$ interaction destabilizes the superconductivity because the internal field caused by the magnetic ions has a tendency to destroy the Cooper pairs by the Zeeman effect. However, unexpectedly, the superconductivity stabilized only under high magnetic field was recently discovered in the organic conductor with magnetic anion, $\lambda$-(BETS)$_2$FeCl$_4$ (BETS=*bis*(ethylenedithio)tetraselenafulvalene) (Refs. 1–3) and a series of alloys $\lambda$-(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$.[4] So far, only a few compounds have been reported to show magnetic-field-induced superconductivity (FISC).[5,6]

The FISC observed in these materials is explained as follows. In general, conventional $s$-wave superconductivity is destroyed under magnetic fields by two effects, orbital effect and Zeeman effect. In the case of two-dimensional (2D) conductors like $\lambda$-(BETS)$_2$FeCl$_4$, the orbital effect is strongly suppressed even at high magnetic fields as long as the field is applied exactly parallel to the 2D layers. The other one, Zeeman effect can be suppressed by the compensation mechanism proposed by Jaccarino and Peter.[7] When the external field is applied, the large localized magnetic moments are aligned in the same direction. If the negative exchange interaction $J$ between the magnetic moments and the $\pi$-electrons is present, the $\pi$-electrons feel the internal field antiparallel to the external field. In this way, the external field and internal field can be compensated. It means that the Zeeman effect does not work at all when the both fields are canceled out completely. This mechanism is called the Jaccarino-Peter (J-P) effect. Consequently, the superconductivity can be stabilized in high field parallel to the 2D layers. To conclude that the FISC induced by the J-P effect is a universal phenomenon in layered magnetic systems under some conditions, we need to perform systematic studies of layered magnetic materials.

The quasi-2D organic conductor, $\kappa$-(BETS)$_2$FeBr$_4$ is composed of conducting layers with BETS molecules and insulating layers with anions FeBr$_4$ containing Fe ions in high spin state, $S=5/2$. The alternate stack of these layers makes the electronic state 2D with the closed Fermi surface predicted from the band calculation.[8] This salt undergoes antiferromagnetic (AF) order of the Fe$^{3+}$ spins at 2.5 K, with the magnetic easy axis along the $a$-axis, and then shows the superconductivity below 1.4 K.[8]

Because the crystal structure of this salt is very similar to that of $\lambda$-(BETS)$_2$FeCl$_4$, $\kappa$-(BETS)$_2$FeBr$_4$ has been expected to be another material showing FISC.[9,10] Actually, slight decrease of the resistance[11] and thermal conductivity[12] suggesting the presence of FISC have been reported under high magnetic field. Moreover, because the zero field ground state is superconducting, the phase diagram could be directly compared with Fisher's theoretical model based on the J-P effect.

In this paper, we report the systematic resistance measurements under the magnetic field at temperatures down to 25 mK. We show the clear evidence of the FISC in this salt and discuss the magnetic phase diagram.

## II. EXPERIMENT

Single crystals of $\kappa$-(BETS)$_2$FeBr$_4$ were obtained by electrochemical oxidation described elsewhere.[13] Samples used in the measurements were black plate-like crystals, and the typical size is about $0.5\times0.4\times0.03$ mm$^3$. Gold wires of 10 $\mu$m in diameter were attached with carbon paint in a con-

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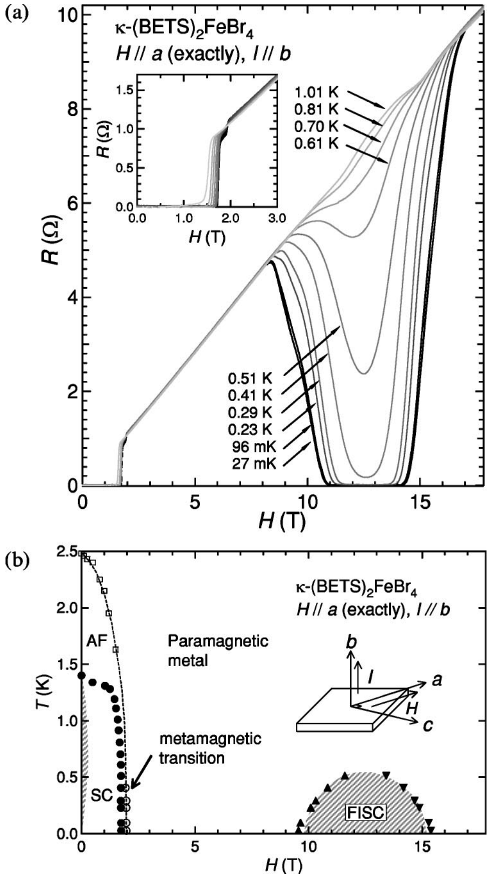

FIG. 1. (a) Field dependence of the interlayer resistance at various temperatures for $H \| a$. Inset shows the data in low field region. (b) Magnetic phase diagram for $H \| a$. Closed circles, open circles, and closed triangles shows the superconducting, metamagnetic and the field induced superconducting transitions, respectively. Open squares shows the metamagnetic transition determined from the SQUID and transport measurements (Ref. 8). Dotted line is the guide to the eyes. Shaded areas show the calculated superconducting phases by using Fisher's theory (Ref. 14).

figuration for interlayer resistance measurements. The resistance was measured by a conventional four-terminal ac technique. The measurement was carried out by using a dilution refrigerator with a 20 T superconducting magnet down to 25 mK at NIMS. The samples were aligned in the field by a specially designed rotator with 0.03° precision.

## III. RESULTS

Figure 1(a) shows the field dependence of the resistance at various temperatures for the magnetic field exactly parallel to the *a*-axis. As the magnetic field increases, superconductivity is broken at 1.8 T, and then a steplike increase corresponding to the metamagnetic transition of the Fe$^{3+}$ spins, is observed (inset of Fig. 1).[8] At 27 mK, the resistance increases almost linearly with field above 2 T, and then shows an abrupt drop by three orders of magnitude at about 8 T. In the region between 11 T and 14 T, the resistance is zero within the instrumental resolution. This behavior gives us a clear evidence of the FISC in this salt. At higher fields above 17 T, the FISC seems to be completely removed. As the temperature increases, the FISC becomes unstable and almost suppressed at 0.81 K. The zero resistance is observed only in very low temperature region below about 0.3 K. At 1 K, a small hump is observed around 12.6 T, the reason of which is not clear.

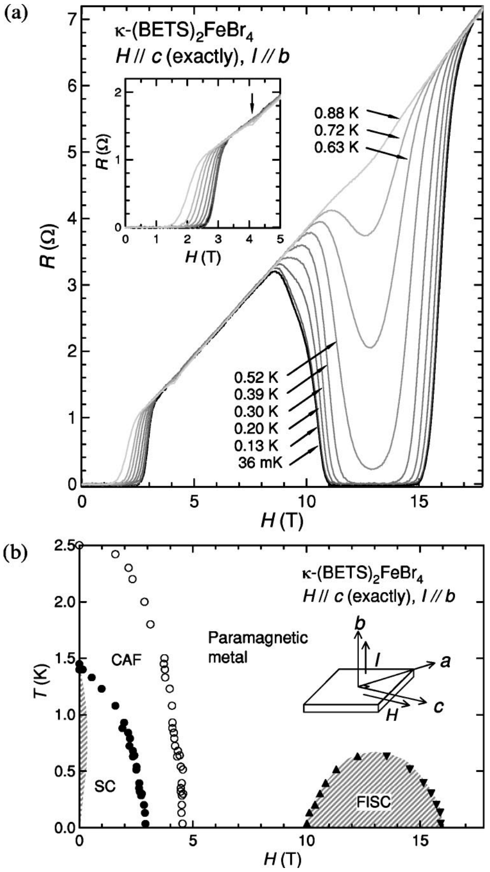

FIG. 2. (a) Field dependence of the interlayer resistance at various temperatures for $H \| c$. Inset shows the data in low field region. (b) Magnetic phase diagram for $H \| c$. Closed circle, open circle, and closed triangle shows the superconducting, canted antiferromagnetic and the field induced superconducting transitions, respectively. Shaded areas show the calculated superconducting phases by using Fisher's theory (Ref. 14).

Figure 1(b) shows the magnetic phase diagram for $H \| a$ constructed from the data in Fig. 1(a). The superconducting critical field is defined as the middle point of the resistive transition. The low field superconducting phase is surrounded by the AF phase, where the AF phase boundary corresponds to the metamagnetic transition field. The FISC has the maximum $T_c (\sim 0.5\text{ K})$ at 12.6 T.

The field dependence of the resistance at various temperatures and the magnetic phase diagram for $H \| c$ are shown in Fig. 2. The overall feature is similar to the case for $H \| a$, but the low field superconducting phase is more stable in this field direction. The anomaly in the resistance corresponding to the transition from the canted AF state (CAF) to the paramagnetic state is seen as indicated by the arrow in the inset of Fig. 2(a), but not so clear. The FISC is also observed in this field direction in almost the same temperature-field region for $H \| a$.

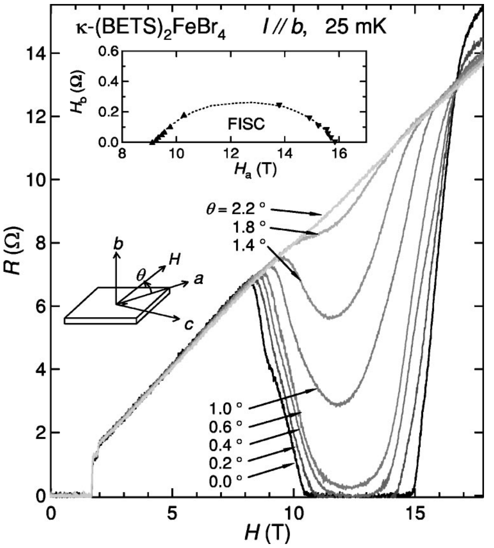

FIG. 3. Interlayer resistance as a function of the magnetic field for various field angles tilted from the *a*-axis. Inset shows the $H_b$-$H_a$ phase diagram at 25 mK.

Figure 3 shows the resistance as a function of the magnetic field for various field angles from the *a*-axis. As the field is inclined from the conducting layers, the FISC is suppressed immediately, which is accompanied with the shift of the minimum position to the lower field because of the increase of the orbital effect. At the field angles higher than $\theta=2.2°$, the FISC completely disappears. By decomposing the critical field into two components along the *a*- and *b*-axis, we can obtain the $H_b$-$H_a$ phase diagram as shown in the inset of Fig. 3 (Ref.15). We note that the critical field is very anisotropic reflecting the low dimensionality of this salt. The FISC is completely suppressed by the perpendicular field of $H_b=0.26$ T, which corresponds to $\theta=1.2°$.

## IV. DISCUSSION

In this study, we obtained the first certain evidence of the FISC in $\kappa$-(BETS)$_2$FeBr$_4$. This is the second example showing FISC in organic conductors following the λ-type BETS based salts.[1–4] The full description giving the superconducting critical field in the presence of the internal field is obtained by Fisher based on the J-P effect.[4,14] In the model, five parameters are contained: $T_c$, $H_{c2}^*$, $H_J$, $\lambda_{so}$, and $\lambda_m$, where $H_{c2}^*$ is the orbital critical field for $T=0$ in the absence of magnetic impurities, $H_J$ is the exchange field due to the Fe moments, and $\lambda_{so}$ or $\lambda_m$ represents the spin-orbit or magnetic scattering parameter. The internal field is a function of $H_J$, which is given by the Brillouin function. In general, internal field is slightly smaller than $H_J$ because of the interlayer coupling effect.[16]

By using the description for three dimensional (3D) case, the reason of which is discussed later, we can fit the obtained magnetic phase diagrams as shown by the shaded areas in Fig. 1(b) and Fig. 2(b). The calculated low field superconducting state is stable only in very limited regions as compared with the experimental results. In the calculation, because a paramagnetic state of the magnetic ions is assumed, the internal field steeply increases with the external field at low temperatures. This is the reason why the calculated low field superconducting phase is destroyed by such low fields. However, the Fe 3*d* spins in this salt are antiferromagnetically ordered in the low field region. Therefore, the internal field remains very small until the metamagnetic transition takes place for $H\|a$, or until the 3*d* spins are sufficiently canted for $H\|c$. As a consequence, the low field superconducting phase can survive up to higher fields than the calculated ones.

TABLE I. Parameters used in the calculation of the superconducting critical fields. The parameters for the λ-(BETS)$_2$FeCl$_4$ are also listed for comparison (Ref. 4).

| | $T_c$ (K) | $\lambda_{so}$ | $H_J^*$ (T) | $H_{c2}^*$ (T) |
|---|---|---|---|---|
| $\kappa$-(BETS)$_2$FeBr$_4$ ($H\|a$) | 1.4 | 2.1 | 13.3 | 16.3 |
| $\kappa$-(BETS)$_2$FeBr$_4$ ($H\|c$) | 1.4 | 1.7 | 13.5 | 18.4 |
| λ-(BETS)$_2$FeCl$_4$[a] | 5.5 | 4.3 | 36 | 55 |

[a] Reference 4.

In this salt, the magnetic easy axis is the *a*-axis, and the magnetization in $H\|a$ becomes larger than that in $H\|c$ for $H>1$ T.[8] It shows the larger internal field in $H\|a$. This is the reason why the low field superconducting phase in $H\|c$ can survive in relatively higher fields than $H\|a$.

The parameters used in the calculation are listed in Table I together with the result in λ-(BETS)$_2$FeCl$_4$.[4] In all cases, $\lambda_m=0$ is assumed for simplicity. The observed FISC phases can be well reproduced by the calculation for both field directions. The obtained saturated exchange field $H_J^*$ is larger than the saturated internal field giving the highest transition temperature, 12.6 T. The value $H_J^*$ is consistent with the saturated exchange field calculated from the intermolecular overlap integrals by Mori *et al.*[10]

The presence of such a large internal field is proved by the Shubnikov-de Haas (SdH) oscillation reported previously[17] as first pointed out by Cepas *et al.*[9] In the presence of a large internal field, it is expected that two frequencies corresponding to the two FS's of up and down spin electrons are observed. The internal field can be directly calculated from the difference of the frequencies, $\delta F=(1/4)\cdot g\cdot(m_{\text{eff}}/m_0\cdot H_J)$, where $m_0$ is the free electron mass, $m_{\text{eff}}$ is the effective mass [$=7.9\ m_0$ (Ref. 17)] and $g$ is the $g$-factor.[9] Assuming $g=2$, we obtain the internal field of 12.7 T. This value is in quite good agreement with the internal field obtained from the present phase diagrams.

These results clearly show that the observed FISC is caused by the J-P compensation mechanism also in this system as in the case of λ-(BETS)$_2$FeCl$_4$. Recently, FISC is observed in the hybrid superconductor/ferromagnet system, where the lattice of magnetic dots (Co/Pd) is formed on the superconducting Pb film.[18] In this system, the dipole stray field between the dots plays an important role for the compensation of the applied field instead of the negative exchange interaction required in the J-P mechanism. In that case, there is no restriction in choosing superconducting film. However, the FISC is achieved in relatively low field because the stray field is not so large and the orbital effect is not quenched in these system because the magnetic field is applied perpendicular to the film.

Though the crystal structures of $\kappa$-(BETS)$_2$FeBr$_4$ and λ-(BETS)$_2$FeCl$_4$ are very similar, the ground states are quite different. In λ-(BETS)$_2$FeCl$_4$, the $\pi$-$d$ coupled antiferromagnetic state is stabilized below 8 K, and then the system becomes insulating.[19] This transition is explained as a Mott transition induced by the strong $\pi$-$d$ interaction.[20] On the other hand, in $\kappa$-(BETS)$_2$FeBr$_4$, the electronic state remains metallic even below the Néel temperature, and the zero field ground state is superconducting. These features show that the $\pi$-$d$ interaction is not so strong in this salt. The main reason why the $\pi$-$d$ interaction is weaker in $\kappa$-(BETS)$_2$FeBr$_4$ is the absence of the Se-Br contact, while there is the short Se-Cl contact causing strong $\pi$-$d$ interaction in λ-(BETS)$_2$FeCl$_4$.[8] Since the strong $\pi$-$d$ interaction induces large internal field, the FISC is observed at much higher field in λ-(BETS)2FeCl4.

In λ-(BETS)$_2$FeCl$_4$, the observed FISC phase is somewhat broader in low temperature than the result fitted by the Fisher's theory.[2,4] One possible reason to explain the result is the presence of the inhomogeneous superconductivity, Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) state,[21,22] as has been pointed out theoretically.[23–25] The suitable conditions for FFLO state are: (i) Large paramagnetic moments are present, (ii) Superconductivity is in clean limit, and (iii) Orbital effect is quenched. In λ-(BETS)$_2$FeCl$_4$, these conditions are well satisfied, so the FFLO state can be stabilized over the critical fields of the conventional superconducting state. Also in $\kappa$-(BETS)$_2$FeBr$_4$, the first two conditions seemed satisfied. However, the observed FISC phase is almost completely reproduced by Fisher's theory in this salt. This result suggests that the orbital effect is stronger in this compound, which makes the FFLO state less likely.

In Table I, we note that the orbital critical field $H_{c2}^*$ is much smaller in $\kappa$-(BETS)$_2$FeBr$_4$ than that in λ-(BETS)2FeCl4. The value of $H_{c2}^*$ means the critical field when the Zeeman effect is absent and only the orbital effect exists. Thus, the small value of $H_{c2}^*$ shows that the orbital effect is not quenched sufficiently. The orbital critical field can be also estimated from the slope of the $H_{c2}(T)$ near $T_c$ for the low field SC phase; ~11 T, ~8 T for $H \| a, H \| c$, respectively.[26] However, because the low field SC phase is strongly affected by the internal field caused by the ordered Fe 3$d$ spins, this estimation may be inadequate in this case.

For anisotropic 3D superconductors, in-plane and out-of-plane coherence lengths, $\xi_\|$ and $\xi_\perp$ are expressed as

$$H_{c2\|} = \frac{\phi_0}{2\pi\xi_\perp(T)\xi_\|(T)},\ H_{c2\perp} = \frac{\phi_0}{2\pi\xi_\|(T)^2}, \tag{1}$$

where $\phi_0$ is a flux quantum, $H_{c2\|}$ and $H_{c2\perp}$ is the critical field for $H$ parallel and perpendicular to the layers. If we define $H_{c2\perp}$ as the maximum value of $H_b$ in $H_b$-$H_a$ phase diagram (inset of Fig. 3), and $H_{c2\|}$ as the high field boundary of the FISC phase measured from 12.6 T,[16] we can calculate the coherence length in FISC phase; $\xi_\| = 280$ Å, $\xi_\perp = 42$ Å. In $\kappa$-(BETS)$_2$FeBr$_4$, the $\xi_\perp$ is larger than the interlayer spacing (18.3 Å), while these are the same order of magnitude in λ-(BETS)$_2$FeCl$_4$. This result suggests the stronger three dimensionality in $\kappa$-(BETS)$_2$FeBr$_4$, and is consistent with the smaller $H_{c2}^*$ in this compound than that in λ-(BETS)$_2$FeCl$_4$. It also validates that we used the Fisher's theory for the 3D case to fit the phase diagrams.

In summary, we observed the clear evidence of the FISC in $\kappa$-(BETS)$_2$FeBr$_4$ by the resistance measurement. The obtained magnetic phase diagram can be well reproduced by Fisher's theory based on the J-P effect. From the results, we conclude that FISC caused by the J-P effect should be a universal phenomenon if the system has low dimensionality, large magnetic moments, and negative strong exchange interaction between conducting electrons and magnetic moments. The analyses of the phase diagram show that the orbital effect is not so small in this compound, which makes the FFLO state less likely.

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