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Global Phase Diagram of the Magnetic Field-Induced Organic Superconductors λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$

Shinya UJI, Taichi TERASHIMA, Chieko TERAKURA, Taro YAKABE, Yoshikazu TERAI, Syuma YASUZUKA, Yasutaka IMANAKA, Madoka TOKUMOTO[1], Akiko KOBAYASHI[2], Fumiko SAKAI[3], Hisashi TANAKA[4*], Hayao KOBAYASHI[4], Luis BALICAS[5] and James S. BROOKS[5]

National Institute for Materials Science, Tsukuba, Ibaraki 305-0003
[1]*National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568*
[2]*Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033*
[3]*Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581*
[4]*Institute for Molecular Science, Okazaki, Aichi 444-8585*
[5]*National High Magnetic Field Laboratory, Florida State University, Tallahassee FL 32306, U.S.A.*

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Organic alloys λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ show superconductivity only under very high magnetic fields parallel to the conducting layer for $x \geq 0.47$. As x decreases, the field induced superconducting phase shifts towards lower fields and a striking field-induced insulator to superconductor transition is observed below 4 T for $x = 0.45$. We show that the overall features of the global phase diagram are well understood in terms of Jaccarino-Peter compensation mechanism. These results provide a new road map for the future design of high magnetic field superconductors.

KEYWORDS: Organic conductor, superconductivity, Jaccarino-Peter effect, high magnetic field
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1. Introduction

Synthesis of new superconductors and understanding of the mechanism of superconductivity have been outstanding challenges in modern physics. For conventional superconductors, Cooper pairs are destabilized under magnetic fields by both the Zeeman and orbital effects. However, it was recently found that a magnetic two dimensional (2D) organic conductor λ-$(BETS)_2FeCl_4$, where BETS is bis(ethylenedithio)tetraselenafulvalene, shows a superconducting phase only under high magnetic fields.[1,2] At zero magnetic field, λ-$(BETS)_2FeCl_4$ shows a metal-insulator transition around 8 K, which is associated to the antiferromagnetic order of the Fe^{+3} spins ($S = 5/2$).[3] This transition has been theoretically discussed in terms of a strong on-site Coulomb repulsion and the exchange interaction between the moments of the localized Fe^{+3} ions and those of the conduction electrons.[5–7] The antiferromagnetic insulating (AFI) phase is removed by the application of a field of the order of 10 T which stabilizes a paramagnetic metallic (PM) phase due to the gain of Zeeman energy of Fe^{+3} moments. Below 1 K, and when a magnetic field is applied parallel to the conducting planes, superconductivity (S) is induced above 17 T and then destroyed above 42 T.[1,2] This field-induced S phase does not appear for fields applied perpendicularly to the 2D conducting layers. The recent observation of Shubnikov de-Haas (SdH) and angular dependent magnetoresistance oscillations[8] reveals the 2D character of its Fermi surface in close agreement with band calculations.[4] In contrast, the iso-structural non-magnetic salt λ-$(BETS)_2GaCl_4$, which has a similar Fermi surface, remains metallic and shows a superconducting transition at $T_c \sim 6$ K. The superconductivity is destroyed under a magnetic field of 13 T (3 T) parallel (perpendicular) to the conduction layers.[9,10] The above facts suggest that both the presence of the Fe moments and the low dimensionality of the electronic state are the key factors in the emergence of the field induced superconductivity in λ-$(BETS)_2FeCl_4$.

In the λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ alloys, the PM–AFI transition is suppressed as x decreases, and then the ground state changes to a S phase for $x \leq 0.35$ (see Fig. 1).[11] A remarkable feature is that two successive phase transitions PM–S–AFI take place for $0.35 \leq x \leq 0.5$ with decreasing temperature. This variety of the magnetic phases apparently

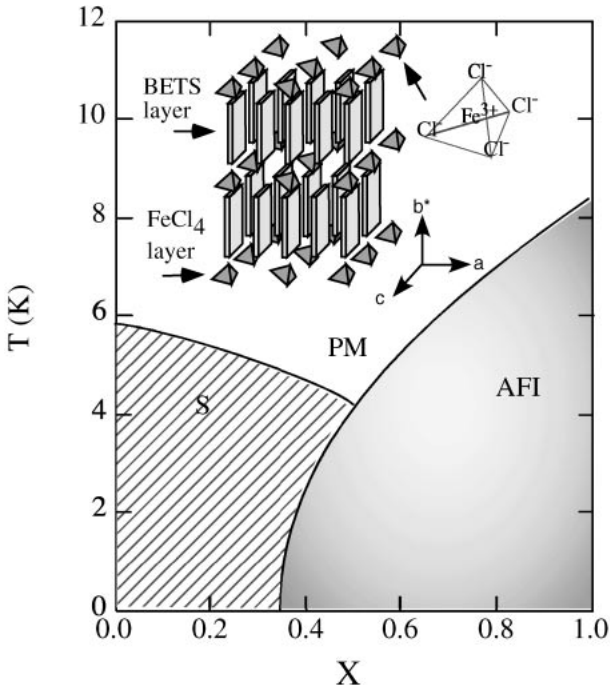

Fig. 1. Phase diagram of the organic alloys λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ in absence of external magnetic field. PM, AFI and S denote paramagnetic metal, antiferromagnetic insulator and superconductor, respectively. Inset: Schematic crystal structure of λ-$(BETS)_2FeCl_4$.

*Present address: National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8568.

originates from the interaction between the Fe magnetic moments and the conduction electrons on the BETS molecules. In order to further investigate the field-induced superconductivity, we have performed a systematic electrical transport study on λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ alloys and determined their global magnetic phase diagram.

2. Experimental

The crystal structure of the series of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ alloys has triclinic symmetry.[4] The planar BETS molecules are stacked along the *a* axis and have fairly strong intermolecular interactions along the *c* axis, forming 2D conducting layers (see inset of Fig. 1). The $FeCl_4$ ion (insulating) layer is intercalated between BETS layers making the *b* axis the least conducting direction. Because of the short inter-atomic distance between BETS and $FeCl_4$, finite exchange interactions between the conduction electrons of the BETS molecules and the Fe^{+3} 3d electrons are expected. Needle-like single crystals of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$, elongating along the *c*-axis, were prepared by electrochemical oxidation in an appropriate solvent.[4] The Fe and Ga concentrations of the λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ crystals were determined by electron probe microanalysis. The error in concentration is ∼10%. The resistance was measured by a conventional four-probe *ac* technique.

3. Results

The resistance as a function of magnetic field H of a λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ single crystal, where $x = 0.47$, is shown in Fig. 2. The inset shows the semi-log plot of the resistance for $T = 0.6$ K and 1.4 K. At 0.6 K, as the field increases, the resistance abruptly decreases by more than eight orders of magnitude around 5 T and then the S phase is stabilized. As the field further increases, the PM phase is recovered above 23 T. At 0.6 K, the resistance shows a small bump at 6 T in the down sweep (inset of Fig. 2). This anomaly may suggest the presence of the PM phase intervening between the AFI and S phases in a narrow field region. Hysteresis is observed only near the transition around 5 T.

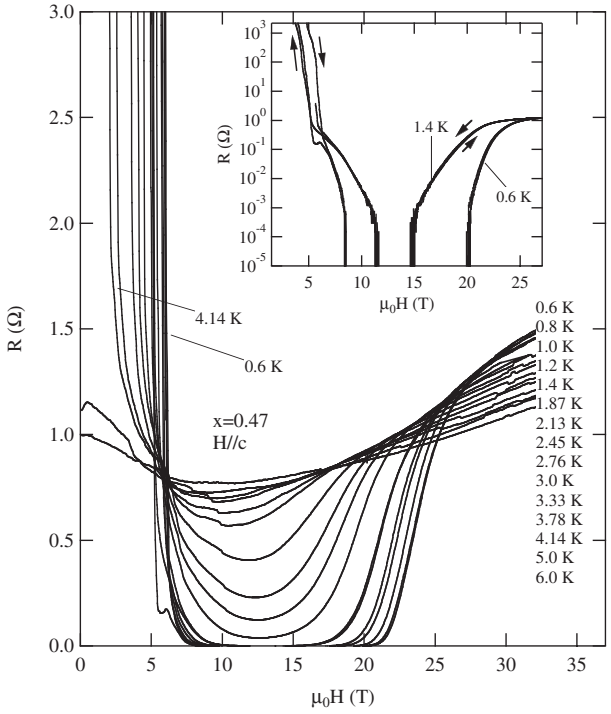

Fig. 2. Resistance as a function of magnetic field in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.47$) Inset: Semi-log plot of the resistance for $T = 0.6$ K and 1.4 K.

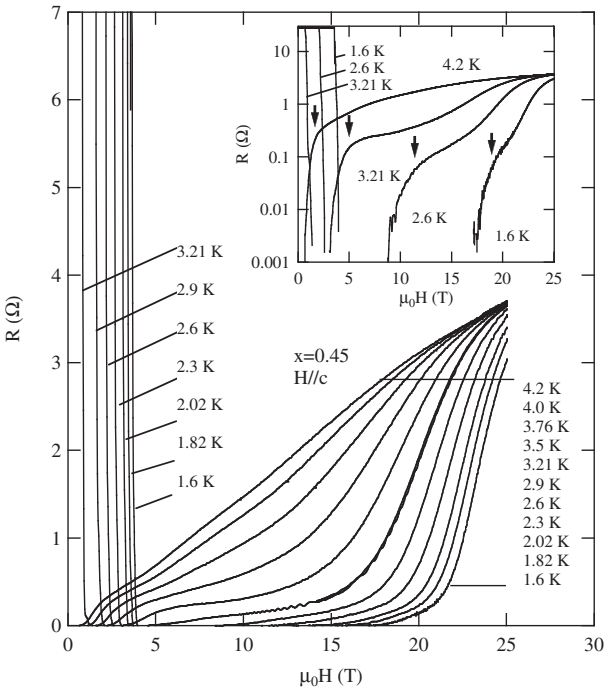

Fig. 3. Resistance under magnetic fields in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ ($x = 0.45$). Inset: Semi-log plot of the resistance. The arrows indicate the steep change in the resistive transitions.

The resistance as a function of field for $x = 0.45$ is shown in Fig. 3. In spite of the small difference in x, the resistive transition has drastically changed respect to $x = 0.47$. At 1.6 K, the resistance decreases by more than 10 orders of magnitude at 4 T, which is ascribed to the AFI–S transition. To our knowledge, this is the first report of a magnetic field-induced insulator–superconductor transition. As the field further increases, the resistance in a linear scale shows a kink at ∼22 T and then a steep increase. Above 3.3 K, the field induced S transition no longer occurs. In the semi-log plot, we can see a kink like behavior similar to that of $x = 0.47$, as indicated by arrows. The AFI–S and S–PM transition fields decrease with increasing temperature.

We have performed resistance measurements for several alloys, and obtained a global phase diagram for $H \parallel c$ (Fig. 4). In these phase diagrams, we define the midpoints of the resistive transition (closed circles) as the PM–S critical field. The PM–AFI and AFI–S transition fields are obtained from the onset of the sharp increase in the resistance (triangles). The former and the latter transition are of the first and of the second order, respectively. For $x = 0.45$, the S–PM transition at high fields seems to be very anomalous with a not well defined midpoint, consequently, and for comparison, the onset of the steep change in the resistance in the semi-log plot is also plotted by opened circles.

As x decreases, the AFI phase shrinks, which is simply

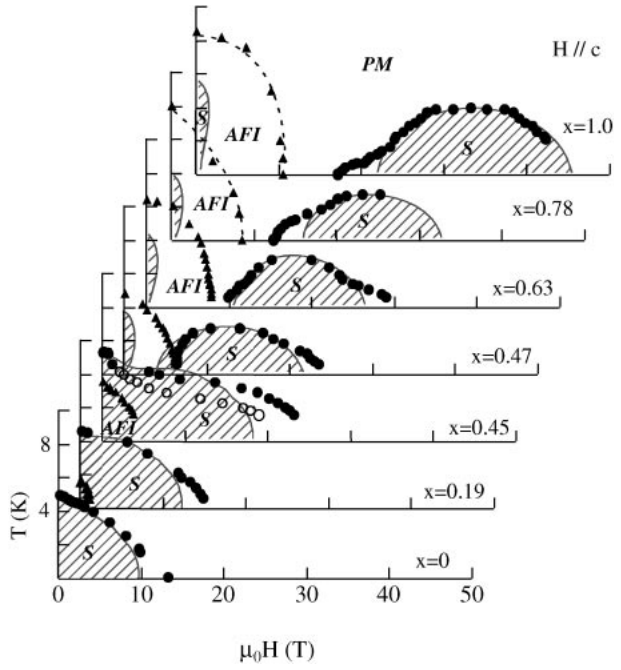

Fig. 4. Global magnetic phase diagram of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ under fields applied parallel to the *c* axis. The PM–S transition fields are defined as the midpoints of the resistive transitions (closed circles), and the AFI–PM or AFI–S transition fields are given by the onset of a sharp change in resistance (triangles). For $x = 0.45$, the onset of the steep change in the PM–S transition is also plotted by opened circles for comparison. The phase boundaries shown by circles and triangles are second and first order transitions, respectively. The shaded areas show the superconducting phases calculated with the parameters listed in Table I.

due to a reduction of the exchange coupling between Fe moments produced by the substitution with non-magnetic Ga ions. However, the S phase shifts towards lower fields without significant change in the maximum T_c. For $x \geq 0.63$, the AFI and S phases are separated by the PM phase, but both phases almost adjoin each other for $x = 0.47$. For $x = 0.45$, the AFI phase is completely surrounded by the S phase. For $x = 0.19$, the AFI phase is only observable in a very small region. For $x = 0$, the AFI phase does not exist and only the S phase is observed, which is consistent with previously reported results.[9] Recently, Mielke *et al.* argue a dimensional crossover in the superconducting state for $x = 0$ under fields perpendicular to the conducting layers.[10]

4. Discussion

The possibility of Jaccarino and Peter (J–P) effect[12] has been proposed as the mechanism responsible for the field induced S phase in λ-$(BETS)_2FeCl_4$.[1,2] In the PM phase of λ-$(BETS)_2FeCl_4$, the localized Fe moments are aligned along the external field (H). In the presence of a strong negative exchange interaction J between the Fe 3d and the conduction electrons spins, the conduction electron spins experience a strong internal magnetic field (H_J) created by the Fe moments, whose direction is antiparallel to H. Therefore, the resulting field experienced by the conduction electron spins approach zero when $H \approx H_J$.[13] Under these conditions the Zeeman effect, one of two destructive mechanisms against superconductivity, is completely absent. As long as H is parallel to the conducing layers, the orbital effect, which is the other of two destructive mechanisms against superconductivity, is virtually suppressed. Therefore, superconductivity can be induced by high parallel fields H in the order of $\sim H_J$.

After the initial idea of the compensation mechanism proposed by Jaccarino and Peter, Fisher gave a full description for H_{c2} in the case of 2D system with fields aligned along the conducting layers,[13]

$$\ln\frac{1}{t} = \left(\frac{1}{2} + \frac{i(\lambda_{so}-\lambda_m)}{4\gamma}\right)\Psi\left(\frac{1}{2} + \frac{h^2+\lambda_m+i(\lambda_{so}-\lambda_m)/2+i\gamma}{2t}\right) \tag{4.1}$$

$$+\left(\frac{1}{2} - \frac{i(\lambda_{so}-\lambda_m)}{4\gamma}\right)\Psi\left(\frac{1}{2} + \frac{h^2+\lambda_m+i(\lambda_{so}-\lambda_m)/2-i\gamma}{2t}\right) - \Psi\left(\frac{1}{2}\right), \tag{4.2}$$

$$\gamma = \left[\alpha^2(h+h_J)^2 - (\lambda_{so}-\lambda_m)^2\right]^{1/2}. \tag{4.3}$$

In this theory, reduced units are used: $t = T/T_c$, $h = H_{c2}/H^*_{c2}$ where T_c and H^*_{c2} are respectively, the critical temperature and the orbital critical field for $T = 0$ in the absence of magnetic impurities. The internal field H_J due to the Fe moments is given by $\sum_i J\langle S_i\rangle/g\mu_B$, where $\langle S_i\rangle$ is the statistical average of the Fe spin, described by the Brillouin function. Ψ is the digamma function. The dimensionless scattering parameters are

$$\lambda_{so} = \frac{2\hbar}{3\pi k T_c \tau_{so}}, \tag{4.4}$$

and

$$\lambda_m = \frac{\hbar}{\pi k T_c \tau_m}, \tag{4.5}$$

where τ_{so} and τ_m are the spin–orbit scattering time and magnetic scattering time due to the magnetic impurities, respectively. The so-called Maki parameter is defined as $\alpha = \sqrt{2}H^*_{c2}/H_{Pauli}$, where H_{Pauli} is the Pauli paramagnetic limit.[14,15]

There are five adjustable parameters, T_c, H^*_{c2}, H_J, λ_{so}, and λ_m. The experimental results for all the concentrations can be well fitted by Fisher's theory as shown by the shaded areas in Fig. 4. Here we take $\lambda_m = 0$ for simplicity. The obtained parameters are listed in Table I. The critical temperature T_c is somewhat scattered. This is probably due to the fact that T_c for these salts depends significantly on sample quality and on stress upon cooling. The scattering parameter λ_{so} ranges from 3.6 to 4.8, which gives $\tau_{so} = (0.8\text{–}1.1) \times 10^{-12}$ s. The saturated value of the internal field $\mu_0 H^*_J$ is 36 T for $x = 1.0$ and decreases with decreasing temperature. According to recent measurements of SdH

Table I. Superconducting parameters in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$.

x (Fe)	T_c (K)	λ_{so}	$\mu_0 H_J^*$ (T)	$\mu_0 H_{c2}^*$ (T)
1.0	5.5	4.3	36	55
0.78	3.7	4.2	25	40
0.63	4.1	3.6	20	30
0.47	3.7	4.8	15	24
0.45	5.2	3.8	13	20
0.19	4.5	3.8	2	20
0	4.7	3.6	0	16

T_c: critical temperature.
λ_{so}: dimensionless spin–orbit scattering parameter.
H_J^*: saturated internal field due to the Fe moments.
H_{c2}^*: orbital critical field for $T = 0$ in the absence of magnetic impurities.

oscillations in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$,[16] $\mu_0 H_J^*$ is estimated to be 32 T for $x = 1.0$ and decreases with decreasing x. The results shown in Table I are consistent with the previous SdH experiments. For λ-$(BETS)_2FeCl_4$, an internal field of 32 T is estimated from the intermolecular overlap integrals.[17]

The orbital critical field H_{c2}^* monotonically decreases with decreasing x. The quantity H_{c2}^* corresponds to the critical field when the Zeeman effect is absent, i.e. when only the orbital effect works as the destructive mechanism against superconductivity. Therefore, it is a measure of the Josephson coupling between the adjacent superconducting layers. The larger is the value of H_{c2}^* the smaller is the Josephson coupling. A possible explanation is a spin selective mechanism via the counter ions between the conducting layers.[18]

The Fisher's theory predicts that S phases are also present in low field regions for $x \geq 0.47$ because the antiferromagnetic order is not taken into account. In this system, the AFI phase is more stabilized at low fields so that the predicted S phases can not be detected experimentally. For λ-$(BETS)_2FeCl_4$, it is reported that the AFI phase is destabilized at high pressures and then S phase appears.[19] This pressure induced S phase may correspond to the predicted S phase inside the AFI phase.

In Fig. 4, we note that the S phase at low temperatures is broader than what is expected from the theory. For $x = 0.47$, the low field side of the S phase is suppressed because of the competition between the AF order and the superconductivity. In Fisher's theory, conventional BCS superconductivity with a homogeneous energy gap is assumed. However, an inhomogeneous superconducting phase, the so-called Fulde–Ferrell–Larkin–Ovchinnikov (FFLO) phase, whose order parameter oscillates in space, is expected to be stabilized.[20,21] The FFLO phase may be present near the superconducting phase boundaries if the superconductor is in the clean limit and the orbital effect is strongly suppressed. The Dingle temperature extracted from the SdH oscillation is about 1 K, suggesting a mean free path, in the conducting layers, of about 1000 Å at 15 T.[16] This is much longer than that in-plane coherence length 100 Å in λ-$(BETS)_2GaCl_4$ showing that superconductivity is in the clean limit within the conducting layers. Therefore, at low temperatures, the low or high field side of the S phase, which is not reproduced by the theory, may suggest the eventual presence of the FFLO state as theoretically discussed in λ-$(BETS)_2FeCl_4$.[22,23] Quite recently, a possibility of the FFLO state is proposed even in λ-$(BETS)_2GaCl_4$.[24]

5. Conclusions

We have shown that the superconducting phases in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ are understood in terms of the J–P effect. This fact provides material design guiding principles for future high magnetic field superconductors: 1) Highly anisotropic 2D conductors, i.e., compounds composed by two distinct layers, conducting and insulating. 2) Large and dense localized moments within the insulating layers. 3) Large negative exchange coupling between the conduction electrons and the localized moments. 4) A superconducting ground state at zero field, or a magnetically ordered ground state that can be suppressed by an external field which stabilizes a paramagnetic state. By fulfilling these conditions, we may obtain superconductors which are stabilized under much higher magnetic fields applied parallel to the conducting layers.

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18) A possible model is obtained in ref. 2. For the Fe^{3+} ions, all the 3d-levels are fully occupied by the same spins, while the 4s levels are empty for the Ga^{3+} ions. At high magnetic fields, the 3d spins of Fe^{3+} ions are fully polarized, consequently Hunds rule excludes the tunneling of a singlet Cooper pair between superconducting layers

via the 3d levels of the Fe^{3+} ions. However, the Cooper tunneling is possible via the empty 4s levels of the Ga^{3+} ions.
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