Compensation of Effective Field in the Field-Induced Superconductor κ-(BETS)$_2$FeBr$_4$ Observed by ^{77}Se NMR

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We report results of ^{77}Se NMR frequency shift in the normal state of the organic charge-transfer salt κ-(BETS)$_2$FeBr$_4$ which shows magnetic field-induced superconductivity (FISC). From a simple mean-field analysis, we determined the field and the temperature dependences of the magnetization m_π of the π conduction electrons on BETS molecules. We found that the Fe spins are antiferromagnetically coupled to the π electrons and determined the exchange field to be $J = -2.3$ T$/\mu_B$. The exchange field from the fully saturated Fe moments ($5\mu_B$) is compensated by an external field of 12 T. This is close to the central field of the FISC phase, consistent with the Jaccarino-Peter local field-compensation mechanism for FISC [Phys. Rev. Lett. **9**, 290 (1962)].

There has been considerable interest in the correlation between conduction electrons and local spins in solid state materials. Competition between magnetic ordering due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the formation of a Kondo singlet state accompanied by mass enhancement of conduction electrons is a canonical problem [1]. In the last decades, several organic charge-transfer salts with anions containing magnetic ions have been synthesized [2,3]. It is widely recognized that the physical properties of organic conductors are determined by a single band formed by the highest occupied molecular orbitals (HOMO) consisting of hybridized π orbitals on donor molecules, and simple tight binding approximation works extremely well for the description of the HOMO band. Such simplicity is a significant advantage in the study of correlation between conduction π electrons and local moments.

Recently, field-induced superconductivity (FISC) has been discovered in λ-(BETS)$_2$FeCl$_4$ under magnetic fields between 17 T and 40 T [4,5], where BETS stands for bis(ethylenedithio)tetraselenafulvalene. The FISC occurs only when the external field is applied parallel to the two-dimensional conducting layers for the π electrons. The FISC is rapidly suppressed by tilting the field, indicating onset of the orbital pair breaking.

The FISC in λ-(BETS)$_2$FeCl$_4$ has been proposed to be due to the Jaccarino-Peter (JP) mechanism [6,7] originating from antiferromagnetic coupling between the Fe local moments and the π electrons (π-d interaction). Superconductivity is expected when the external field H_{ext} nearly cancels the exchange field from Fe moments, minimizing the spin-Zeeman pair breaking effect. Indeed, the superconducting transition temperature T_c in λ-(BETS)$_2$FeCl$_4$ shows a maximum at $H_{ext} = 32$ T [5], which agrees well with the exchange field estimated from the Zeeman split-

ting of the Shubnikov–de Haas oscillation [8,9]. Also a nonmagnetic analog λ-(BETS)$_2$GaCl$_4$ shows superconductivity at zero field [10].

A κ-type polymorph of BETS based material, κ-(BETS)$_2$FeBr$_4$, has been also reported to show FISC between 10 T and 15 T with the maximum of $T_c = 0.3$ K at 12.5 T [11,12]. Similar to the λ-type polymorph, two-dimensional conducting BETS layers parallel to the ac plane alternate with the anion layers as shown in Fig. 1. Under zero magnetic field, antiferromagnetic order of Fe moments occurs below $T_N = 2.5$ K where the system remains metallic and superconductivity appears below $T_c = 1.1$ K. This is in contrast to the case of λ-(BETS)$_2$FeCl$_4$, where antiferromagnetic order of Fe spins at zero field at $T_N = 8$ K causes a metal-insulator transition [13].

Nuclear magnetic resonance (NMR) is an excellent probe to measure local spin density; therefore, it can be used to test the validity of the JP mechanism for FISC.
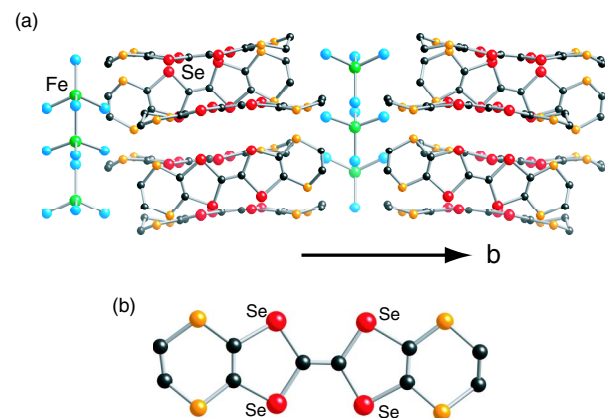

FIG. 1 (color online). (a) Crystal structure of κ-(BETS)$_2$FeBr$_4$. (b) A BETS donor molecule with Se atoms.

Measurements of Mo NMR frequency shift were reported in a Shevrel phase intermetallic FISC compound $(Eu, Sn)Mo_6(S, Se)_8$ [14], for which the JP mechanism was proposed between conduction electrons and doped Eu spins [15,16]. Although the results support partial cancellation of external field by the exchange field from the Eu spins, quantitative analysis was hindered by complication of the states near the Fermi level with both the s and the d bands.

In this Letter, we report the frequency shift of ^{77}Se NMR in κ-$(BETS)_2FeBr_4$, both as a function of H_{ext} at a constant temperature (1.5 K) and as a function of temperature at a constant field (15.5 T). The results show that the spin polarization of π electrons is determined as the product of effective field, which is the sum of H_{ext} and the antiferromagnetic exchange field from Fe spins, and the local susceptibility of π electrons, which is independent of magnetization of Fe spins, m_d. The exchange field is estimated to be in the range 10–12 T for the saturated Fe magnetization of $5\mu_B$/Fe. This agrees well with the field for the highest T_c in the FISC phase, thus supporting the JP mechanism.

The ^{77}Se NMR experiments were performed using a rectangular platelike single crystal of κ-$(BETS)_2FeBr_4$ grown by the standard electrochemical oxidation method. The magnetic susceptibility follows a Curie-Weiss law $\chi(T) = C/(T - \theta)$ with $\theta = -5.5$ K and $C = 4.70$ K $\cdot$ emu/mol. The Curie constant is close to the value expected for the localized high spin state of Fe^{3+} (4.4 K $\cdot$ emu/mol for $S = 5/2$ and $g = 2$) and the negative value of θ indicates antiferromagnetic interactions [17]. A unit cell contains eight BETS molecules, which are related by symmetry operations of the crystal structure (space group $Pnma$). We consider the cases in which the field is directed along the a, b, or c axis of the crystal, which are invariant under all symmetry operations. Then all BETS molecules should yield identical NMR spectrum. We expect ^{77}Se NMR spectrum composed of four distinct lines corresponding to the four inequivalent Se sites in a BETS molecule [Fig. 1(b)].

The ^{77}Se NMR spectra at $T = 1.5$ K obtained for several different values of the external field along the b and c axes are shown in Fig. 2. The horizontal axis represents the

FIG. 2 (color online). ^{77}Se NMR spectra at $T = 1.5$ K for H_{ext} along the b axis (a) and along the c axis (b). The resolved four (two) peaks are denoted as $b1$, $b2$, $b3$, and $b4$ ($c1$ and $c2$).

frequency shift $\delta\nu = \nu - \gamma_N H_{ext}$, where ν is the signal frequency and $\gamma_N = 8.118$ MHz/T is the nuclear gyromagnetic ratio. While four resonance lines are indeed observed for $H_{ext} \parallel b$ [Fig. 2(a)], the spectrum is broader and only two peaks are clearly resolved for $H_{ext} \parallel c$ [Fig. 2(b)].

The hyperfine field acting on a Se nucleus comes from both the π electrons and the Fe spins. Thus the frequency shift at the site i ($i = 1$–4) for the field along the α direction has two terms,

$$\delta\nu_{i,\alpha} = \gamma_N A^\pi_{i,\alpha} m_\pi + \gamma_N (A^{dip}_{i,\alpha} + B_i) m_d. \qquad (1)$$

The first term is the contribution from the magnetization of π electrons (m_π) through the hyperfine coupling $A^\pi_{i,\alpha}$. The second term is the contribution from the Fe magnetization m_d through the direct dipolar coupling $A^{dip}_{i,\alpha}$ and the transferred hyperfine coupling B_i. While the coupling constant $A^\pi_{i,\alpha}$ is determined by the fractional weights of Se atomic orbitals participating in the HOMO of BETS molecules, B_i is due to hybridization between the Fe-d states and the Se atomic orbitals which do not participate in the HOMO. Since the relevant states for B_i are the inner-core states, not the outermost $4p$ states, we expect B_i to be nearly isotropic.

The dipolar coupling tensors are nearly diagonal and calculated as $(A^{dip}_{i,a}, A^{dip}_{i,b}, A^{dip}_{i,c}) = (-4.1, 7.3, -3.2), (-4.4, 7.8, -3.4), (-4.2, 8.7, -4.5), (-4.2, 8.5, -4.3)10^{-3}$ T/μ_B for the four Se sites. Although we have not succeeded in assigning resonance lines to specific sites, the dipolar field is more or less the same for all sites. Taking the values $A^{dip}_{i,c} = -0.004$ and $A^{dip}_{i,b} = 0.0085$ T/μ_B for all sites and subtracting them from the observed shift, we obtain $\delta\nu'_{i,\alpha} = \gamma_N A^\pi_{i,\alpha} m_\pi + \gamma_N B_i m_d$. The H_{ext} dependence of $\delta\nu'$ at $T = 1.5$ K is shown in Fig. 3 for various sites and different field directions. Note that the Fe moments are completely saturated ($m_d = 5\mu_B$) in this field range at 1.5 K.

In all cases, $\delta\nu'$ show linear dependences on H_{ext}. Since the Fe moments are saturated and fluctuations are negligible, we may consider the effects of π-d exchange interaction in a mean-field approximation. The polarization of π electrons is expressed as

$$m_\pi = \chi_\pi(H_{ext} + Jm_d), \qquad (2)$$

where Jm_d is the exchange field acting on the π electrons from the Fe moments and χ_π is the local susceptibility of the π electrons in the absence of π-d exchange interaction. Combining Eqs. (1) and (2), the slope of the lines in Fig. 2 gives the value of $A^\pi_{i,\alpha}\chi_\pi$, which is listed in the upper panel of Table I. These values are within the range of the anisotropic ^{77}Se NMR shift reported in a nonmagnetic analog λ-$(BETS)_2GaCl_4$ at low temperatures, which is between -0.1% and 0.6% [18]. This supports the validity of our mean-field definition of χ_π.
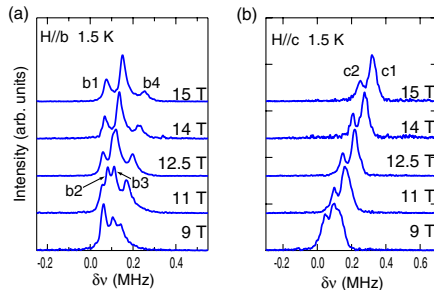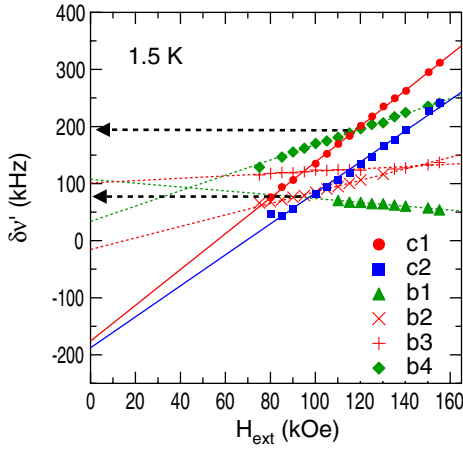
FIG. 3 (color online). H_{ext} dependence of $\delta\nu'$ (defined in the text) at $T = 1.5$ K. The solid (dotted) lines are the fits to straight lines for $H_{ext} \parallel c$ ($H_{ext} \parallel b$). The arrows show the values of $B_i m_d$.

If the JP field-compensation mechanism is valid, we expect m_π to become zero at the central field of the FISC phase. Since B_i is assumed to be isotropic, $\delta\nu'_{i,\alpha}$ is expected to be independent of the field direction when $m_\pi = 0$. Thus the two lines for $H_{ext} \parallel c$ and $H_{ext} \parallel b$ in Fig. 3 corresponding to the same sites should cross at a field where $m_\pi = 0$. By inspecting Fig. 3, we indeed recognize that each line for $H_{ext} \parallel b$ crosses one line for $H_{ext} \parallel c$ in the range 10–12 T. This field range agrees approximately with the field for the highest T_c in the FISC phase (12.5 T).

Unfortunately, we could not follow evolution of the NMR peak frequencies as the field is rotated in the bc plane due to broad linewidth and additional line splitting for the field away from the b or c direction. Therefore, we have to make a best guess to assign each line for $H_{ext} \parallel b$ to a specific line for $H_{ext} \parallel c$. Since there are only two peaks for $H_{ext} \parallel c$, at least one of these corresponds to more than one site. Crossing of three lines ($c2$, $b1$, $b2$) at nearly the same field (9.7 T and 10.0 T) strongly suggests that the $b1$ and the $b2$ peaks evolve into the $c2$ peak upon field rotation. We then obtain $\gamma_N B m_d = 85$ kHz for these sites. Similarly, the $b4$ and the $c1$ lines crossing at 11.8 T are assigned to a common site with $\gamma_N B m_d = 190$ kHz. There is small ambiguity about the $b3$ line, which crosses the $c1$ line at 9.5 T and the $c2$ line at 11.5 T. However, both cases lead to a similar value of $\gamma_N B m_d = 120$ kHz because of very small slope of the $b3$ line.

TABLE I.   Estimated values of $A^\pi_{i,\alpha}\chi_\pi$ and J by the H_{ext} (top) and T (bottom) dependences of the frequency shifts. $c2'$ denotes the line resolved in the temperature dependence, but not at 1.5 K.

Lines	$c1$	$c2$	$c2'$	$b1$	$b2$	$b3$	$b4$
$A^\pi_{i,\alpha}\chi_\pi[\%]$	0.39	0.35		−0.04	0.12	0.02	0.17
$J[\mathrm{T}/\mu_B]$	−2.33	−2.03		−1.93	−2.04	−2.35	−2.32
$A^\pi_{i,\alpha}\chi_\pi[\%]$	0.53	0.43	0.44	−0.05	0.14	0.004	0.17
$J[\mathrm{T}/\mu_B]$	−2.48	−2.19	−1.83	−2.39	−2.25	−1.88	−2.16

By subtracting $\gamma_N B_i m_d$ from $\delta\nu'_{i,\alpha}$, we obtain $\gamma_N A^\pi_{i,\alpha} m_\pi$ as plotted in Fig. 4. The compensation fields $H_{ext} = -J m_d$ obtained from the condition $m_\pi = 0$ are in the range 10–12 T, in agreement with the center of the FISC phase. Thus our results support the JP mechanism. The values of J are listed in the upper panel of Table I. The estimated values of J are nearly the same for all four Se sites, which is consistent with our mean-field analysis. A small distribution in the estimated value of J could be due to insufficient spectral resolution for $H_{ext} \parallel c$ and/or possible small anisotropy of B_i. Our microscopic estimate of the compensation field agrees well with the earlier estimate of the exchange field (12 T) based on the analysis of the Schubnikov–de Haas oscillations [8,19].

An independent support for the validity of our mean-field analysis was obtained from the temperature dependence of the shift measured between 5 K and 80 K at a constant field of 15.5 T. At this field, m_d is well represented by the Brillouin function $B_{5/2}(5\mu_B H_{ext}/k_B T)$. By subtracting $\gamma_N(A^{dip}_{i,\alpha} + B_i)m_d$ from the measured shift, we obtained the shifts due to m_π ($A^\pi_{i,\alpha} m_\pi/H_{ext}$), which is plotted against m_d in Fig. 5. The plot yields a straight line again for all sites and field directions. If we assume no T dependence for χ_π as supported by nearly T-independent NMR shift in λ-$(BETS)_2GaCl_4$ [18], the slope and the intercept at $m_d = 0$ give the values of $A^\pi_{i,\alpha}\chi_\pi J$ and $A^\pi_{i,\alpha}\chi_\pi$, respectively. The values of $A^\pi_{i,\alpha}\chi_\pi$ and J thus obtained are listed in the lower panel of Table I. The fact that the independent sets of data for H_{ext} dependence and the T dependence of the shift lead to similar values of the parameters supports validity of the mean-field analysis of Eqs. (1) and (2). We notice that the values of $A^\pi_{i,c}\chi_\pi$ determined from two sets of data differ by about 30%. Although overlap of NMR lines for $H_{ext} \parallel c$
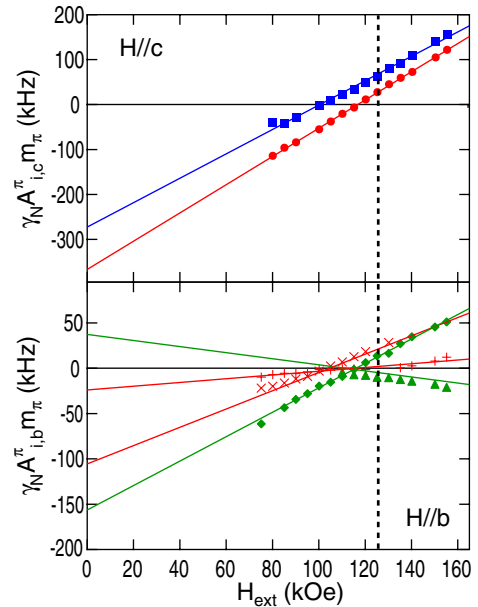

FIG. 4 (color online).   Frequency shifts due to magnetization of π electrons at 1.5 K.
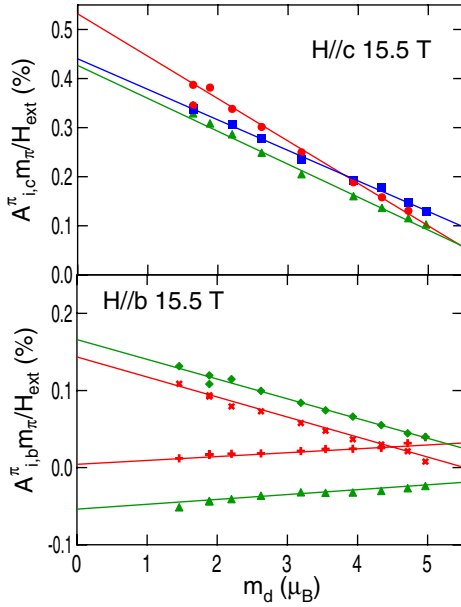
FIG. 5 (color online). Frequency shifts due to the magnetization of π electrons are plotted against the magnetization of Fe moments $m_d \equiv B_{5/2}(5\mu_B H_{\text{ext}}/k_B T)$ at $H_{\text{ext}} = 15.5$ T.

could cause such systematic errors, this may indicate a gradual decrease of χ_π with decreasing temperature. Indeed, in λ-(BETS)$_2$GaCl$_4$, χ_π shows a slight reduction below 20 K [18].

The exchange π-d interaction of this material is estimated theoretically within the second order perturbation by use of the extended Hückel calculation. When d spins are polarized along the field direction, the π-d interactions work simply on each molecule as an exchange field as $H = \Sigma_j \mathcal{J}_j \langle S \rangle$ by neglecting the spin fluctuation. Here $\mathcal{J}_j$ is the π-d interaction between molecules and surrounding d spins with expectation value $\langle S \rangle$. The theoretical estimation amounts to $\mathcal{J} \equiv \Sigma_j \mathcal{J}_j/g\mu_B = -2.25$ [20] or -3.0 T/μ_B [21], which agrees very well with our estimate $J = -2.3$ T/μ_B.

For a system with strong π-d hybridization leading to local screening of d spins by conduction electrons, a gap may be developed in the spin excitation spectrum of the π electrons and strong T dependence of χ_π would be expected [1]. In such a case, we would expect a deviation from the linear relation between m_π and m_d, which is not observed (Fig. 5). We would also expect significant discrepancy in the estimated values of J determined from the H_{ext} dependence and the T dependence of the shifts, again in contradiction to the observation. We therefore conclude that χ_π is nearly independent of temperature showing Pauli-paramagnetic character above 1.5 K.

It should be noted that we are interested mainly in the behavior at high magnetic field, where the Zeeman energy for the large $S = 5/2$ Fe spins is much greater than the π-d

exchange interaction, $-(g^2\mu_B/k_B)J = 6$ K. Hence we do not expect quantum fluctuations or the Kondo screening to be important. This is consistent with no indication of spin-gap behavior in χ_π above 1.5 K.

In summary, the frequency shift of ^{77}Se NMR in the field-induced superconductor κ-(BETS)$_2$FeBr$_4$ was found to depend linearly on H_{ext} at $T = 1.5$ K and the magnetization of Fe spins (m_d) at $H_{\text{ext}} = 15.5$ T. The results are consistent with the molecular field approximation for the π-d exchange interaction. The local susceptibility of the π electrons χ_π is independent of m_d and shows Pauli-paramagnetic behavior above 1.5 K. The exchange field on the π electrons from Fe moments is canceled near 12 T where the FISC occurs. We have determined microscopically the antiferromagnetic π-d interaction $J = -2.3$ T/μ_B that is consistent with the mechanism of local field compensation for FISC first proposed by Jaccarino and Peter.

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