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

S. Fujiyama,1, 2 M. Takigawa,3 J. Kikuchi,3 H-B. Cui,4, 2 H. Fujiwara,4, 2 and H. Kobayashi4, 2

1Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan
2CREST-JST, Kawaguchi, Saitama 332-0012, Japan
3Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
4Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

(Dated: November 10, 2018)

PACS numbers: 74.70.Kn, 75.20.Hr, 76.60.-k

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 Kondo singlet state accompanied by mass enhancement of conduction electrons is a canonical problem. In the last decades, several organic charge-transfer-salts with anions containing magnetic ions have been synthesized and. It is widely recognized that physical properties of organic conductors are determined by a single band formed by the HOMO (highest occupied molecular orbitals) consisting of hybridized $\pi$-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 $\pi$-electrons and local moments.

Recently, field-induced superconductivity (FISC) has been discovered in $\kappa$-(BETS)$_2$FeBr$_4$, which shows magnetic field-induced superconductivity (FISC). From a simple mean field analysis, we determined the field and the temperature dependencies of the magnetization $m_{\sigma}$ of the $\pi$ conduction electrons on BETS molecules. We found that the Fe spins are antiferromagnetically coupled to the $\pi$ electrons and determined the exchange field to be $J = -2.3 \, \text{T}/\mu_B$. 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)).

A $\kappa$-type polymorph of BETS based material, $\kappa$-(BETS)$_2$FeCl$_4$ has been also reported to show FISC between 10 T and 15 T with the maximum of $T_c = 0.3 \, \text{K}$ at 12.5 T. Similar to the $\kappa$-type polymorph, two dimensional conducting BETS layers parallel to the ac-plane alternate with the anion layers as shown in Fig. 4. Under zero magnetic field, antiferromagnetic order of Fe moments occurs below $T_N = 2.5 \, \text{K}$ where the system remains metallic and superconductivity appears below $T_c = 1.1 \, \text{K}$. This is in contrast to the case of $\kappa$-(BETS)$_2$FeCl$_4$, where antiferromagnetic order of Fe spins at zero field at $T_N = 8 \, \text{K}$ causes a metal-insulator transition.

Nuclear magnetic resonance (NMR) is an excellent probe to measure local spin density, therefore, can be used to test the validity of the JP mechanism for FISC. Measurements of Mo NMR frequency shift was reported in a Shevrel phase intermetallic FISC compound (Eu,Sn)Mo$_6$(S,Se)$_8$ for which the JP mechanism was proposed between conduction electrons and doped Eu.

![FIG. 1: (a) Crystal structure of $\kappa$-(BETS)$_2$FeBr$_4$. (b) A BETS donor molecule with Se atoms.](image-url)
spins \[\{15\}^{10}\]. 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 \(^{77}\text{Se}\) NMR in \(\kappa\)-(BETS)\(_2\)FeBr\(_4\), both as a function of \(H_{\text{ext}}\) at a constant temperature (1.5 K) and as a function of temperature at a constant field (15.5 T). The results shows that the spin polarization of \(\pi\) electrons is determined as the product of effective field, which is the sum of \(H_{\text{ext}}\) and the antiferromagnetic exchange field from Fe spins, and the local susceptibility of \(\pi\) 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 \(^{77}\text{Se}\) NMR experiments were performed using a rectangular plate-like single crystal of \(\kappa\)-(BETS)\(_2\)FeBr\(_4\) 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-emu/mol. The Curie constant is close to the value expected for the localized high spin state of Fe\(^{3+}\) \([16]\).

The first term is the contribution from the magnetization \(m_d\) through the hyperfine coupling \(A_{i,\alpha}^{\pi}\). The second term is the contribution from the Fe magnetization \(m_d\) through the direct dipolar coupling \(A_{i,\alpha}^{\text{dip}}\) and the transferred hyperfine coupling \(B_i\). While the coupling constant \(A_{i,\alpha}^{\pi}\) 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 outer-most 4\(p\) states, we expect \(B_i\) to be nearly isotropic.

The dipolar coupling tensors are nearly diagonal and calculated as \((A_{i,\alpha}^{\text{dip}}, A_{i,\beta}^{\text{dip}}, A_{i,\gamma}^{\text{dip}})\)\(=\)(-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/\(\mu_B\) 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 \(A_{i,\alpha}^{\text{dip}}\)\(=\)0.004 and \(A_{i,\beta}^{\text{dip}}\)\(=\)0.0085 T/\(\mu_B\) for all sites and subtracting them from the observed shift, we obtain \(\delta \nu' = \gamma_N A_{i,\alpha}^{\pi} m_{\pi} + \gamma_N B_i m_d\). The \(H_{\text{ext}}\) dependence of \(\delta \nu'\) at \(T\)\(=\)1.5 K is shown in Fig. 2 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 \(H_{\text{ext}}\). Since the Fe moments are saturated and fluctuations are negligible, we may consider the effects of \(\pi-d\) exchange interaction in a mean-field approximation. The polarization of \(\pi\) electrons is expressed as

\[m_{\pi} = \chi_{\pi}(H_{\text{ext}} + J m_d),\]

where \(J m_d\) is the exchange field acting on the \(\pi\)-electrons from the Fe moments and \(\chi_{\pi}\) is the local susceptibility of the \(\pi\) electrons in the absence of \(\pi-d\) exchange interaction. Combining Eqs. 11 and 12, the given value of \(A_{i,\alpha}^{\pi} m_{\pi}\), which is listed in the upper part of Table I. These values are within the range of the anisotropic \(^{77}\text{Se}\) NMR shift reported in a non-magnetic analog \(\kappa\)-(BETS)\(_2\)GaCl\(_4\) at low temperatures, which is between -0.1\% and 0.6\% \[18\]. This supports the validity of our mean-field definition of \(\chi_{\pi}\).

If the JP field-compensation mechanism is valid, we...
expect $m_{\pi}$ 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 $H \parallel c$ and $H \parallel b$ 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 $H \parallel b$ crosses one line for $H \parallel c$ 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 line-width 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 $H \parallel b$ to a specific line for $H \parallel c$. Since there are only two peaks for $H \parallel c$, 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.

By subtracting $\gamma_N B m_d$ from $\delta \nu'_{i,\alpha}$, we obtain $\gamma_N A_{i,\pi m}^T$ and 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 (1) nearly the same for all four Se sites and (2) independent of the directions of $H_{ext}$. A small distribution in the estimated value of $J$ could be due to insufficient spectral resolution for $H \parallel c$ 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.

An independent support for the validity of our mean-field analysis was obtained from the temperature dependence of the shift measured 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 $\gamma_N (A_{i,\pi}^{dip} + B_i)m_d$ from the measured shift, we obtained the shifts due to $m_{\pi}$ ($A_{i,\pi}^{\pi} m_{\pi}/H_{ext}$), which is plotted against $m_{\pi}$ in Fig. 5. The plot yields a straight line again for all sites and field directions. If we assume no $T$-dependence for $\chi_{\pi}$ as supported by nearly $T$-independent NMR shift in $\kappa$-(BETS)$_2$GaCl$_4$, the slope and the intercept at $m_{\pi}=0$ give the values of $A_{i,\pi}^{\pi}\chi_{\pi} J$ and $A_{i,\alpha}^{\pi}\chi_{\alpha} J$, respectively. The values of $A_{i,\pi}^{\pi}\chi_{\pi}$ and $J$ thus obtained are listed in the lower panel of Table I. The independent sets of data for the $H_{ext}$-dependence and the $T$-

![FIG. 3: $H_{ext}$ dependence of $\delta \nu'$ at $T=1.5$ K. The solid (dotted) lines are the fits to straight lines for $H \parallel c$ ($H \parallel b$). The arrows show the values of $B_i m_d$.](image)

![FIG. 4: Frequency shifts due to magnetization of $\pi$ electrons at 1.5 K.](image)

### TABLE I: Estimated values of $A_{i,\alpha}^{\pi}\chi_{\pi}$ and $J$ by the $H_{ext}$ (top) and $T$ (bottom) dependences of the frequency shifts.

| lines  | c1     | c2     | c2'    | b1     | b2     | b3     | b4     |
|--------|--------|--------|--------|--------|--------|--------|--------|
| $A_{i,\alpha}^{\pi}\chi_{\pi}[\%]$ | 0.39   | 0.35   | -0.04  | 0.12   | 0.02   | 0.17   |
| $J [T/\mu_B]$ | -2.33  | -2.03  | -1.93  | -2.04  | -2.35  | -2.32  |
| $A_{i,\alpha}^{\pi}\chi_{\pi}[\%]$ | 0.53   | 0.43   | 0.44   | -0.05  | 0.14   | 0.004  | 0.17   |
| $J [T/\mu_B]$ | -2.48  | -2.19  | -1.83  | -2.39  | -2.25  | -1.88  | -2.16  |
observed (Fig. 5). We also expect significant discrepancy from the linear relation between estimation amounts to $J \equiv \Sigma J_j / g \mu_B = -2.25$ (Hotta [20]), which agrees very well with our estimate $J=-2.3 \, \text{T}/\mu_B$.

For a system with strong $\pi$-$d$ hybridization leading to local screening of $d$ spins by conduction electrons, a gap may be developed in the spin excitation spectrum of the $\pi$ electrons and strong $T$ dependence of $\chi_{\pi}$ would be expected. In such a case, we would expect a deviation from the linear relation between $m_{\pi}$ and $m_d$, which is not observed (Fig. 5). We also expect significant discrepancy in the estimated values of $J$ determined from the $H_{\text{ext}}$ dependence and the $T$ dependence of the shifts, again in contradiction to the observation. We therefore conclude that $\chi_{\pi}$ 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 $\pi$-$d$ exchange interaction, $-(q^2 \mu_B/k_B)J=6$ 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 $\chi_{\pi}$ above 1.5 K.

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

We acknowledge K. Kanoda, C. Hotta, T. Mori and E. Fujinawa for fruitful discussions. This work was supported by the JSPS (No. 17740213) and the MEXT (No. 13NP0201, 13640375, and 16076204).

---

* Electronic address: fujiyama@ap.t.u-tokyo.ac.jp

1 Present address: Dept. of Physics, Meiji University, Kawasaki 214-8571, Japan

2 Present address: Dept. of Chemistry, Osaka Prefecture University, Osaka 599-8570, Japan.

1. H. Tsunetsugu, M. Sigrist, and K. Ueda, Rev. Mod. Phys. 69, 809 (1997).

2. P. Day, et al., J. Am. Chem. Soc. 114, 10772 (1992).

3. E. Coronado et al., Nature 408, 447 (2000).

4. S. Uji et al., Nature 410, 908 (2001).

5. L. Balicas et al., Phys. Rev. Lett. 87, 067002 (2001).

6. V. Jaccarino and M. Peter, Phys. Rev. Lett. 9, 290 (1962).

7. O. Fischer, Helv. Phys. Acta, 45, 331 (1972).

8. O. Cépas, R.H. McKenzie, and J. Merino, Phys. Rev. B 65, 100502 (2002).

9. S. Uji et al., Phys. Rev. B64, 024531 (2001).

10. H. Kobayashi et al., Chem. Lett. 1559 (1993).

11. T. Konoike et al., Phys. Rev. B 70, 094514 (2004).

12. H. Fujinawa et al., J. Am. Chem. Soc. 124, 6816 (2002).

13. H. Kobayashi et al., J. Am. Chem. Soc. 118, 308 (1996).

14. F.Y. Fradin et al., Phys. Rev. Lett. 38, 719 (1977).

15. H.W. Meul, C. Rossel, M. Decroux, and O. Fischer, Phys. Rev. Lett. 53, 497 (1984).

16. O. Fischer et al., J. Phys. C 8, L474 (1975).

17. H. Fujinawa et al., J. Am. Chem. Soc. 123, 306 (2001).

18. S. Takagi et al., J. Phys. Soc. Jpn. 72, 483 (2003).

19. S. Uji et al., Physica B298, 557 (2001).

20. C. Hotta and H. Fukuyama, J. Phys. Soc. Jpn. 69, 2577 (2000).

21. T. Mori and M. Katsuhara, J. Phys. Soc. Jpn. 71, 826 (2002).