



^{77}Se NMR evidence for the Jaccarino-Peter mechanism in the field induced superconductor, $\lambda(\text{BETS})_2\text{FeCl}_4$

K. Hiraki, H. Mayaffre, M. Horvatic, C. Berthier, S. Uji, T. Yamaguchi, H. Tanaka, A. Kobayashi, H. Kobayashi, T. Takahashi

► To cite this version:

K. Hiraki, H. Mayaffre, M. Horvatic, C. Berthier, S. Uji, et al.. ^{77}Se NMR evidence for the Jaccarino-Peter mechanism in the field induced superconductor, $\lambda(\text{BETS})_2\text{FeCl}_4$. Journal of the Physical Society of Japan, 2007, 76 (12), pp.124708-1. 10.1143/JPSJ.76124708. hal-00167413

HAL Id: hal-00167413

<https://hal.science/hal-00167413>

Submitted on 20 Aug 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

^{77}Se NMR evidence for the Jaccarino-Peter mechanism in the field induced superconductor, $\lambda(\text{BETS})_2\text{FeCl}_4$

Ko-ichi HIRAKI^{1,7*}, Hadrien MAYAFFRE¹, Mladen HORVATIĆ², Claude BERTHIER^{1,2}, Shinya UJI³, Takahide YAMAGUCHI³, Hisashi TANAKA⁴, Akiko KOBAYASHI⁵, Hayao KOBAYASHI^{6†} and Toshihiro TAKAHASHI⁷

¹*Laboratoire de Spectrométrie Physique, BP87, 38402 St. Martin d'Hères, France*

²*Grenoble High Magnetic Field Laboratory, BP166, 38042 Grenoble, France*

³*National Research Institute for Metals, Tsukuba, Ibaraki, 305-0003*

⁴*National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki 305-8561*

⁵*Department of Humanities and Sciences, Nihon University, Tokyo 156-8550*

⁶*Institute for Molecular Sciences, Aichi 444-8585*

⁷*Department of Physics, Gakushuin University, Tokyo 171-8588*

(Received August 20, 2007)

We have performed ^{77}Se NMR on a single crystal sample of the field induced superconductor $\lambda(\text{BETS})_2\text{FeCl}_4$. Our results obtained in the paramagnetic state provide a microscopic insight on the exchange interaction J between the spins \mathbf{s} of the BETS π conduction electrons and the Fe localized d spins \mathbf{S} . The absolute value of the Knight shift \mathbf{K} decreases when the polarization of the Fe spins increases. This reflects the “negative” spin polarization of the π electrons through the exchange interaction J . The value of J has been estimated from the temperature and the magnetic field dependence of \mathbf{K} and found in good agreement with that deduced from transport measurements (L. Balicas *et al.* Phys. Rev. Lett. **87**, 067002 (2001)). This provides a direct microscopic evidence that the field induced superconductivity is due to the compensation effect predicted by Jaccarino and Peter (Phys. Rev. Lett. **9**, 290 (1962)). Furthermore, an anomalous broadening of the NMR line has been observed at low temperature, which suggests the existence of charge disproportionation in the metallic state neighboring the superconducting phase.

KEYWORDS: Field Induced Superconductivity, Exchange interaction, NMR

1. Introduction

Charge transfer complexes based on organic molecules have attracted a huge amount of interest in the last twenty years due to their low dimensionality and the possibility to control their electronic properties by modification of base molecules or pressure.¹ In the case of 2D complexes, a lot of attention has been paid to superconductivity and its interplay with electron-electron correlations. In particular, a large number of ET (where ET stands for

*E-mail address: ko-ichi.hiraki@gakushuin.ac.jp

†Present address: Department of Humanities and Sciences, Nihon University, Tokyo

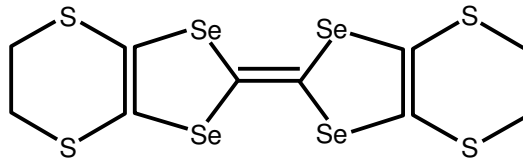


Fig. 1. BETS molecule. One of two Se (at random) in each inner five-membered ring is enriched by NMR active ^{77}Se to nearly 100 %.

the $\text{C}_{10}\text{S}_8\text{H}_8$ (bisethylenedithiotetrathiafulvalene) molecule based superconductors have been extensively studied.² Later on, having in mind magnetic properties of these charge transfer complexes, new materials have been synthesized offering the possibility of an interaction of the conduction electrons of the π band with d localized electrons.³ One of these strongly π - d interacting system is λ -(BETS) $_2\text{FeCl}_4$, which is a charge transfer complex composed of the organic BETS ($\text{C}_{10}\text{S}_4\text{Se}_4\text{H}_8$, bisethylenedithiotetraselenafulvalene, see Fig. 1) donor molecule and magnetic FeCl_4 (Fe^{3+} , $S = 5/2$) counter ion.^{4,5} The two-dimensional conducting sheets are parallel to the crystallographic ac plane and consist of a λ type arrangement of BETS molecules. These sheets are sandwiched by the insulating FeCl_4 layers. It turned out that, in addition to its magnetic properties, the most fascinating property of this compound was again due to its superconducting properties which appear only in the presence of a strong applied magnetic field.^{6,7}

In zero external magnetic field (H_0) the system behaves as a metal below 90 K and undergoes a metal-insulator transition around 10 K, accompanied with an antiferromagnetic ordering.^{4,8} The metal insulator transition temperature decreases with increasing field and above 11 T the system behaves metallic down to lowest temperature. ESR, magnetization measurements and theoretical studies reported that the coupling between delocalized π electron having $s=1/2$ spin and the high spin state of Fe $3d$ spin ($S=5/2$) plays a crucial role in the stabilization of the antiferromagnetic ordering.⁸⁻¹⁰

The most remarkable property of λ -(BETS) $_2\text{FeCl}_4$ is the existence of Field Induced Superconductivity (FISC).^{6,7} When the magnetic field is applied parallel to the ac plane, the system becomes superconductor for $H_0 \geq 18$ T. On increasing H_0 the transition temperature T_c grows up to its maximal value $T_c^{\text{max}} = 4.2$ K at 33 T, and then decreases and falls down to zero at $H_0 = 45$ T. To explain this FISC, the ‘‘compensation’’ mechanism predicted by Jaccarino and Peter¹¹ (JP) has been proposed. The strong applied magnetic field polarizes the Fe spins, and the polarized Fe moments $g\mu_B\mathbf{S}$ produce an extra magnetic field on the conduction electron spins \mathbf{s} through the exchange coupling J . For antiferromagnetic J this exchange field is antiparallel (i.e., opposed) to the applied field, so that the total effective magnetic field can be put to zero for a certain value of the applied (external) magnetic field. In λ -(BETS) $_2\text{FeCl}_4$ such complete compensation seems to happen at 33 T, where T_c^{max} is

reached. This interpretation in terms of the “JP effect” is reinforced by the observation that the isostructural GaCl_4 salt, in which the anion is non-magnetic so that there can be no exchange field, undergoes a superconducting transition under *zero* field at nearly the same T_c^{max} value.¹² The JP mechanism has also been experimentally supported by the transport measurements of Uji *et al.*, who carried out systematic transport studies on the alloy system, $\lambda\text{-(BETS)}_2\text{Ga}_{1-x}\text{Fe}_x\text{Cl}_4$.^{13,14} From analysis of the Shubnikov-de Haas oscillations, they have estimated the exchange field of the $x = 1$ (FeCl_4) salt to 32 T and found it decreasing with x .

From bulk measurements it is difficult to get direct information on the magnetic behavior of the π conduction electrons, since the contribution of Fe $S = 5/2$ spins to the bulk susceptibility is much larger. Only local probes, like NMR, can provide information on the spin polarization of the π conduction electron band. The first reported NMR results on this material have been obtained on ^1H nuclei.^{15,16} Since the coupling of ^1H nuclei to π conduction band is small, while the direct dipolar coupling to the Fe moments is large, details on the electronic state of the system could not be obtained. As compared to protons, the Se sites have larger coupling constant and relatively smaller gyromagnetic ratio. Therefore, ^{77}Se NMR measurements at high magnetic field are apparently the best way to clarify the role of π conduction electrons spins in the system. Up to now, two NMR studies have been performed on the temperature dependence of the ^{77}Se shift, and interpreted as a proof of the Jaccarino Peter mechanism.^{17,18} However, a direct measurement of the effective field experienced by the conduction electrons when the magnetic field is increased is still missing in $\lambda\text{-(BETS)}_2\text{FeCl}_4$. One should notice that such a Se NMR evidence for the JP mechanism has been found in the parent compound $\kappa\text{-(BETS)}_2\text{FeBr}_4$ by Fujiyama *et al.*¹⁹ However, this system is different, since superconductivity is also present in zero field.²⁰

Here we report ^{77}Se NMR measurements on a single crystal of $\lambda\text{-(BETS)}_2\text{FeCl}_4$, which allowed us to detect the spin polarization of the π electrons through the hyperfine coupling to ^{77}Se nuclei in the field range 13 - 28 T. We found that the spin polarization decreases as H_0 increases, giving a microscopic evidence that the Jaccarino-Peter compensation mechanism occurs in this compound. We also evaluate the coupling constant J between π and d spins.

The paper is organized as follows. Experimental details, and characterization of the sample are described in section 2. In section 3, we discuss the NMR shift in presence of an exchange interaction between the localized spins \mathbf{S} and the π conduction electrons spins \mathbf{s} . The results and discussion are given in section 4. In subsections 4.1 and 4.2 we discuss the π - d interaction in the $\lambda\text{-(BETS)}_2\text{FeCl}_4$ from field and temperature dependence of the NMR shift. The anomalous line broadening observed at low temperature is discussed in section 4.3, where we point out the possibility of charge disproportionation (CD) in the BETS sheets.

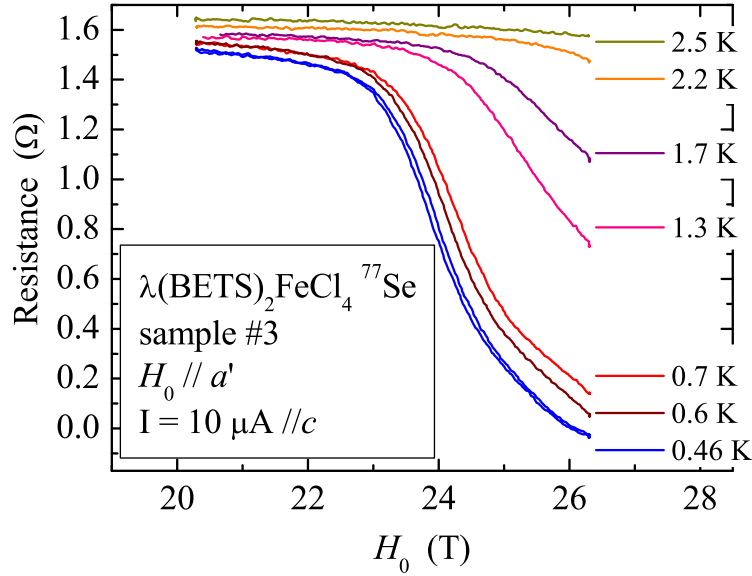


Fig. 2. Resistivity as a function of the magnetic field at various temperature. The sample and that used for NMR measurement sample are part of the same batch.

2. Experimental Details

Experiments were performed on a $\sim 3 \times 0.05 \times \sim 0.01$ mm³ single crystal, enriched with ⁷⁷Se isotope to $\simeq 50$ % (see caption to Fig. 1). The group symmetry of λ -(BETS)₂FeCl₄ is $P\bar{1}$ (triclinic). The detailed synthesis procedure is described elsewhere.^{21,22} Since the natural abundance of ⁷⁷Se isotope is only ~ 7 %, in the absence of isotopic enrichment the number of observable nuclei would be $\sim 10^{15}$, which is a very small number. The enrichment was thus a key ingredient to improve the signal to noise (S/N) ratio to a level compatible with the time-limited experiments in the high-field resistive magnets. Another key ingredient was to optimize the filling factor of the NMR coil by making a microcoil wound using 13 μ m insulated Cu wire to obtain the inner coil diameter of only 75 μ m.

Our crystal was a needle along the c axis, the largest face being the ac plane (*i.e.*, perpendicular to b^*). The sample and the NMR coil were mounted on a goniometer with the rotation axis along c , allowing the possibility to vary the direction of H_0 within the a^*b^* plane and to align it along the axis a' which is the intersection of this a^*b^* plane and the superconducting ac plane. We tried to obtain the initial orientation such that $H_0 \parallel a'$ axis, however, the sample being very small, a precise alignment was very difficult.

The field dependence of NMR spectra were measured in the field range between 13 T and 28 T. The NMR spectra were recorded in a superconducting magnet up to 17 T, while in the field range 16-28 T measurements were performed (at 1.5 K) in a 20 MW resistive magnet of Grenoble High Magnetic Field Laboratory. Spectra were obtained by the Fourier Transform (FFT) of the spin echo signal at fixed magnetic field. The linewidths at low temperature

were broader than the typical *rf* (radio frequency) excitation width (of ~ 0.4 MHz for the pulse of ~ 1.2 μ s). In this case the “frequency sweep” spectra were constructed by summing several individual spectra taken at regular frequency step intervals.²³ The value of the applied magnetic field H_0 was calibrated using the ^{63}Cu NMR signal of the NMR coil and the bare Larmor frequency of ^{77}Se was taken to be $f_0 = \gamma H_0$, with $\gamma = 8.127296$ MHz/T, which is equivalent to take neutral TMTSF as the reference.²⁴ All experiments were carried out in the metallic state. While we have not detected any superconducting transition while rotating the sample at 1.5 K, superconducting phase has been observed on samples of the same batch by transport measurements in the High Field Laboratory at Tsukuba. However, one can see on Fig. 2 that the decrease of the resistivity at 1.5 K is weak, so that the effect on the NMR spectra is expected to be negligible.

3. NMR background

The purpose of this work is to determine the polarization of the π -band conduction electrons and to relate it to localized spins polarization. Before describing the experimental results, we shall first discuss the origin of the local field at the Se nuclei, and how we can relate it to the quantities of interest. The minimum starting Hamiltonian describing the interactions between the nuclear spins I^i , the conduction electron spins \mathbf{s}^k and the localized spins \mathbf{S}^j at the Fe sites j can be written as

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{I_s} + \mathcal{H}_{IS} + \mathcal{H}_{\text{exch}} . \quad (1)$$

The first term is the Zeeman interaction for the three types of spins

$$\mathcal{H}_Z = \sum_i -\gamma \hbar I_z^i (1 + K_c^i) H_0 + \sum_j g_{\text{Fe}} \mu_B S_z^j H_0 + \sum_k g_\pi \mu_B s_z^k H_0 , \quad (2)$$

in which K_c^i is the chemical shift. The last term of Eq. 1 corresponds to the exchange interaction between the localized and the itinerant spins

$$\mathcal{H}_{\text{exch}} = \sum_{j,k} g_\pi g_{\text{Fe}} \mu_B^2 J_{k,j} \mathbf{s}^k \mathbf{S}^j . \quad (3)$$

We shall assume that its effect can be expressed as a uniform exchange field $H_{\text{exch}} = g_{\text{Fe}} \mu_B J \langle S_z \rangle$ acting on the π band conduction electrons, that is $\mathcal{H}_{\text{exch}} \approx \sum_k g_\pi \mu_B s_z^k H_{\text{exch}}$. This term is then of the same form as the Zeeman term for π electrons (the last term of Eq. 2), so that their magnetization $-g_\pi \mu_B \langle s_z \rangle = \chi_\pi H_{\text{eff}}$ is determined by their susceptibility χ_π and the *total* effective magnetic field $H_{\text{eff}} = H_0 + H_{\text{exch}}$. We note that the Zeeman interaction polarizes Fe spins antiparallel (negative) to H_0 (i.e., for positive H_0 , $\langle S_z \rangle = -|\langle S_z \rangle|$). Therefore, due to the antiferromagnetic character of the exchange interaction ($J > 0$), H_{exch} is also negative, opposed to H_0 .

The second term in Eq. 1 is the hyperfine interaction between the (polarized) π electrons

and Se nuclei

$$\mathcal{H}_{Is} = \sum_i \gamma \hbar I_z^i A_\pi^i(\theta) g_\pi \mu_B \langle s_z \rangle = \sum_i -\gamma \hbar I_z^i A_\pi^i(\theta) \chi_\pi H_{\text{eff}} , \quad (4)$$

where $A_\pi^i(\theta)$ is the corresponding hyperfine coupling which depends on the direction in which the field is applied. In our case we will denote this direction by the angle θ measuring the rotation of the sample around the c axis.²⁵

The third term is the dipolar interaction between the localized spins at the Fe sites and the Se nuclei

$$\mathcal{H}_{IS} = \sum_{i,j} -\gamma \hbar g_{\text{Fe}} \mu_B I_z^i D_{zz}^{ij} S_z^j = \sum_i -\gamma \hbar I_z^i H_{\text{dip}}^i(\theta) , \quad (5)$$

where D_{zz}^{ij} is the dipolar coupling tensor and $H_{\text{dip}}^i(\theta)$ the corresponding local dipolar field, which can be computed exactly since the structure is known.

Putting together all the terms involving nuclear spins, their resonance frequency f^i will be shifted from the reference by

$$\Delta f^i \equiv f^i - \gamma H_0 = \gamma [A_\pi(\theta)^i \chi_\pi H_{\text{eff}} + H_{\text{dip}}^i(\theta) + K_c^i H_0] , \quad (6)$$

where by index i we distinguish 8 Se sites within the unit cell. As in the low temperature spectra these sites are not resolved, in the following we consider the average values over i and omit the index. By subtracting the dipolar and the chemical shift we focus on the hyperfine contribution of π electrons

$$\delta f(H_0, T) \equiv f - \gamma [H_{\text{dip}}(\theta, M_d(H_0, T)) + (1 + K_c) H_0] = \gamma A_\pi(\theta) \chi_\pi [H_0 - J M_d(H_0, T)] , \quad (7)$$

where the exchange field is explicitly written in terms of the Fe moments $M_d = -g_{\text{Fe}} \mu_B \langle S_z \rangle$, whose field and temperature dependence are given by the (modified) Brillouin function.¹⁸ From this equation it is obvious that plotting $\delta f(H_0 = \text{const.}, T)$ as a function of $M_d(H_0 = \text{const.}, T)$, with T being implicit parameter, one obtains a linear dependence which enables the determination of the J and $A_\pi(\theta) \chi_\pi$ parameters. This procedure, which has been used in the previously published work,^{17,18} relies on the predicted temperature dependence of Fe moments. A more “robust” approach is to exploit the field dependence of this equation in the low temperature limit, where Fe moments are fully polarized, $M_d(H_0, T \sim 0) = 5\mu_B$, and thus field independent. The same parameters are obtained from the linear H_0 dependence of $\delta f(H_0, T \sim 0)$. Furthermore, by going to high enough field we can explicitly reach the point where the applied field cancels the exchange field, that is where the hyperfine shift goes to zero, $\delta f(H_0 = 5\mu_B J, T \sim 0) = 0$.

We remark that it is also easy to study the angular dependence of hyperfine coupling by comparing the line positions taken at two well separated field values H_1 and H_2 . As in the low temperature limit both H_{dip} and H_{exch} are field independent, from Eq. 6 we get that

$$[\Delta f(H_2) - \Delta f(H_1)] / \gamma (H_2 - H_1) - K_c = A_\pi(\theta) \chi_\pi . \quad (8)$$

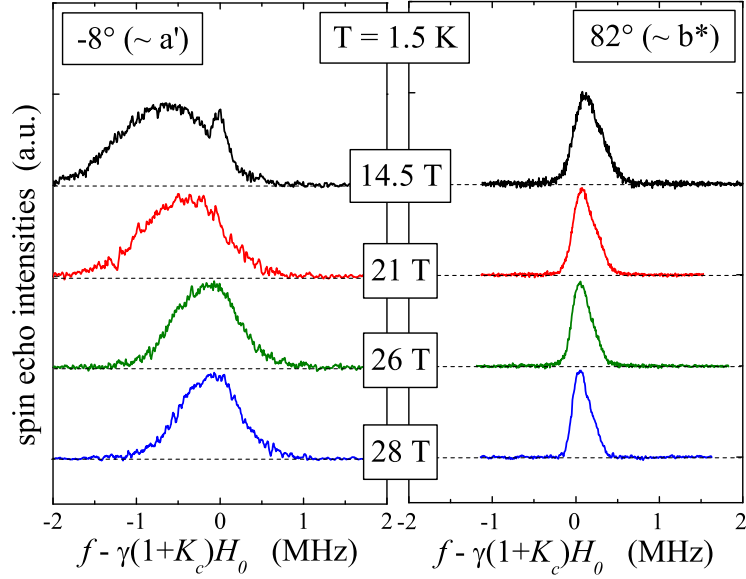


Fig. 3. ^{77}Se NMR spectra recorded at four different fixed values of the applied field H_0 , pointing to two different orientations²⁵ in the $a'b^*$ plane. The difference in the shift and linewidth behavior is due to the anisotropy of the hyperfine coupling A_π of the conduction electrons. The decrease of the linewidth on increasing the magnetic field is due to the decrease of the effective field $H_{\text{eff}} = |H_0 + H_{\text{exch}}|$.

Note that the hyperfine coupling $A_\pi(\theta)$ is expected to have uniaxial symmetry reflecting the Se $4p_z$ orbital.

We have seen that the essential prerequisite to discuss the hyperfine shift is the calculation of the dipolar contribution, including demagnetization effects. We use the Lorentz method²⁶ in which we first divide the volume of the sample into two parts. The first part is a sphere with a radius much larger than interatomic distance, for which we sum all the individual dipolar fields assuming a point dipole M_d at each Fe site, to obtain the so called dipolar field H'_{dip} . The contribution of the rest of the sample outside the “Lorentz sphere”, the so called demagnetization contribution $H''_{\text{dip}} = 4\pi M_z(\frac{1}{3} - N)$, is obtained assuming uniform magnetization M_z ²⁷ and the effects of the sample shape are taken into account by the “demagnetization factor” N .²⁸ The total H_{dip} is the sum of the two terms $H'_{\text{dip}} + H''_{\text{dip}}$. Finally, the chemical shift K^c was taken equal to that measured in $\lambda\text{-(BETS)}_2\text{GaCl}_4$,²⁴ $K^c = -0.0116\%$.

4. Results and discussions

4.1 Low temperature field dependence of the line shift

Fig. 3 shows ^{77}Se NMR spectra at four values of the external field from 14.5 to 28 T for two different orientations of the crystal. For the first orientation (close to a') one clearly observes that on increasing H_0 not only the spectrum shifts, but also gets narrower. Such a decrease of the linewidth is expected if part of it is of magnetic origin and proportional to

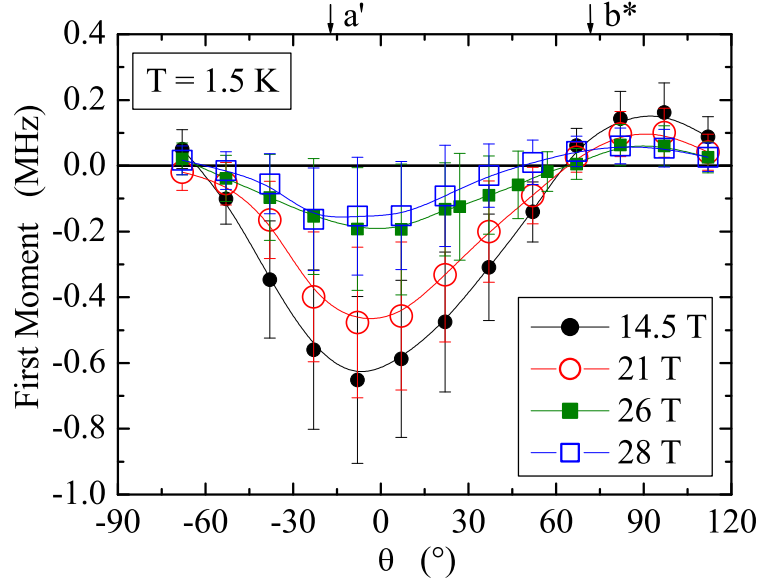


Fig. 4. Angular dependence²⁵ of the first moment of the ^{77}Se NMR lines at four different values of H_0 . These data are not corrected from the dipolar and demagnetization contribution. The vertical bars accompanying the symbols are not the error bars, but correspond to the width of the lines.

H_{eff} which decreases as H_0 increases. This means that the linewidth is due to a distribution of $A_\pi\chi_\pi$, pointing to a possible modulation of $\chi_\pi(\mathbf{R})$. For the second orientation (close to b^*) the variation of shift and the widths of the lines are much smaller. This difference in the width and shift behavior is actually due to the anisotropy of the hyperfine coupling $A_\pi(\theta)$, as expected for π electrons.

Fig. 4 shows the angular dependence of the shift at four field values, 14.5, 21, 26 and 28 T. These raw data include the angular dependence of dipolar contribution which, because of the demagnetization factor, is somewhat difficult to obtain exactly, since the shape of the crystal is not perfectly known. However, it is quite reasonable to assume that for these field values the Fe moments are fully saturated at 1.5 K, so that the dipolar contribution is independent of H_0 . We can thus use Eq. 8 to obtain directly $A_\pi(\theta)\chi_\pi$. From four available field values, we have created three differential ($H_i - 14.5 \text{ T}$) sets of data, and plotted in Fig. 5 their average $A_\pi(\theta)\chi_\pi$ value for each value of θ . The experimental angle dependence is fitted²⁵ to the theoretically expected one, $\chi_\pi[A_{\text{iso}} + A_{\text{ax}}(3\cos^2\theta\cos^2\psi - 1)]$, where $\psi = 13.6^\circ$ is the (average) minimum angle between the π orbitals and the a^*b^* plane (or $H_0(\theta = 0)$ direction²⁵). From the fit, we found $\chi_\pi A_{\text{iso}} = 0.092 \%$ and $\chi_\pi A_{\text{ax}} = 0.193 \%$. To further determine the value of A_π we need an estimate for χ_π . We will assume that χ_π in $\lambda(\text{BETS})_2\text{FeCl}_4$ is the same as in $\lambda(\text{BETS})_2\text{GaCl}_4$ where $\chi_\pi = 4.5 \times 10^{-4}$ emu/mole at room temperature and 6.3×10^{-4} emu/mole at low temperature.²⁹ Retaining the low temperature value of χ_π , we find $A_{\text{ax}} = 35 \text{ kOe}/\mu_B$. This value should be compared to a theoretical prediction for the

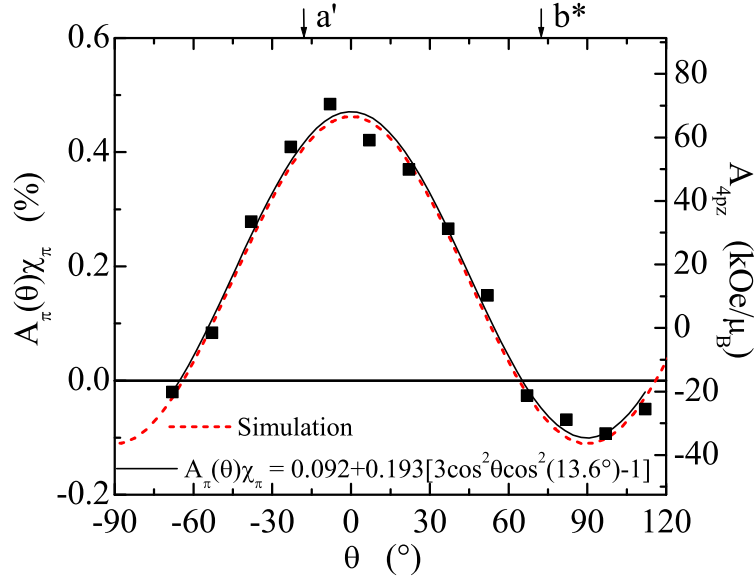


Fig. 5. Experimentally determined $A_\pi(\theta)\chi_\pi$ at 1.5 K (solid squares), simplified fit for the angular dependence²⁵ (line) and more detailed theoretical prediction (dotted line), as explained in the text.

dipolar hyperfine coupling constant of a p -type ($4p_z$) electronic orbitals, $A_{ax} = \frac{2}{5}\langle r^{-3} \rangle \mu_B \sigma$, where for π orbitals of Se in the BETS molecule³⁰ $\langle r^{-3} \rangle = 9.28 a_0^{-3}$ and the spin density²⁴ is $\sigma \sim 0.16$. We find the predicted value $A_{ax} = 37 \text{ kOe}/\mu_B$ in excellent agreement with the experimental value of $35 \text{ kOe}/\mu_B$ estimated above. In the analysis given above we assumed that all the π orbitals point in the same direction in space. As this is only approximately true, we also calculated the predicted angular dependence of the hyperfine coupling considering the exact orientation of orbitals for all 8 Se sites in the molecule. The average hyperfine coupling ($\langle A_\pi^i(\theta) \rangle_i$) obtained in this way, plotted in Fig. 5, is nearly indistinguishable from the simplified fit, confirming excellent agreement with the theory.

We shall now come to the problem of the demagnetization factor. In Fig. 6 is shown the predicted angular dependence of the dipolar contribution to the lineshift from a Lorentz sphere of 35 \AA radius, the demagnetization contribution due to the shape of the crystal, and their sum. As the sum has quite large amplitude, it is expected to play an essential role in the determination of H_{exch} . We also remark that the sum results from a strong compensation of two components which are both very strong. As the shape of the tiny crystal and thus the demagnetization factor is not precisely known, this can introduce some uncertainty in the determination of H_{exch} .

In Fig. 7, is shown the angular variation of the shift of the Se lines after correction from the dipolar and the demagnetization contributions, for the four different magnetic field values. This corrected experimental values correspond to δf defined by Eq. 7. As explained in Section 3

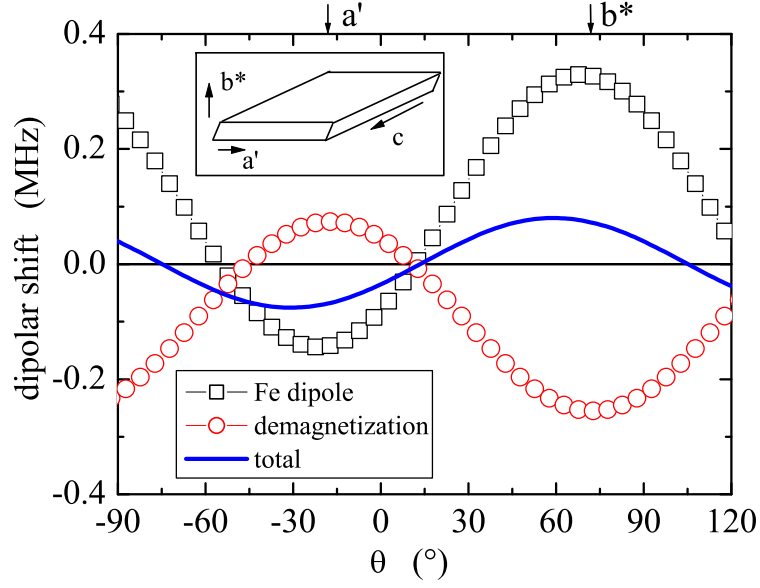


Fig. 6. Contribution of the dipolar interaction and of the demagnetization field ($N_{a'} = 0.2$, $N_{b^*} = 0.8$, $N_c = 0$) as a function of the angle in the $a'b^*$ plane. Inset: shape of the crystal.

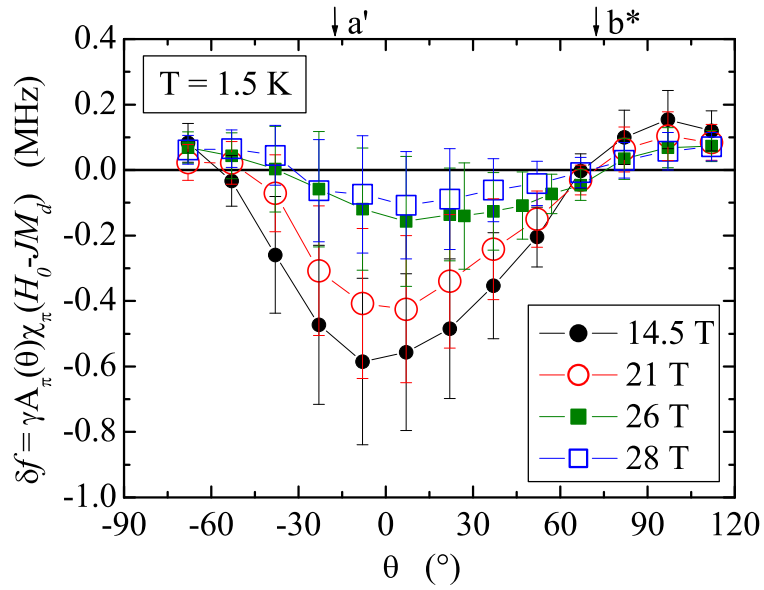


Fig. 7. Angular dependence of the shift of the Se lines at 14.5, 21, 26 and 28 T after subtraction of the dipolar and demagnetization contribution.

below Eq. 7, a linear fit of δf as a function of H_0 shown in Fig. 8 allows direct determination of H_{exch} since $\delta f = 0$ corresponds to $H_0 + H_{\text{exch}} = 0$. We obtain $|H_{\text{exch}}| = 32 \pm 2$ T, in very good agreement with the value of 33 T corresponding to the maximum of T_c . We underline that this value is obtained without any assumption on the values of the hyperfine field $A_\pi(\theta)$

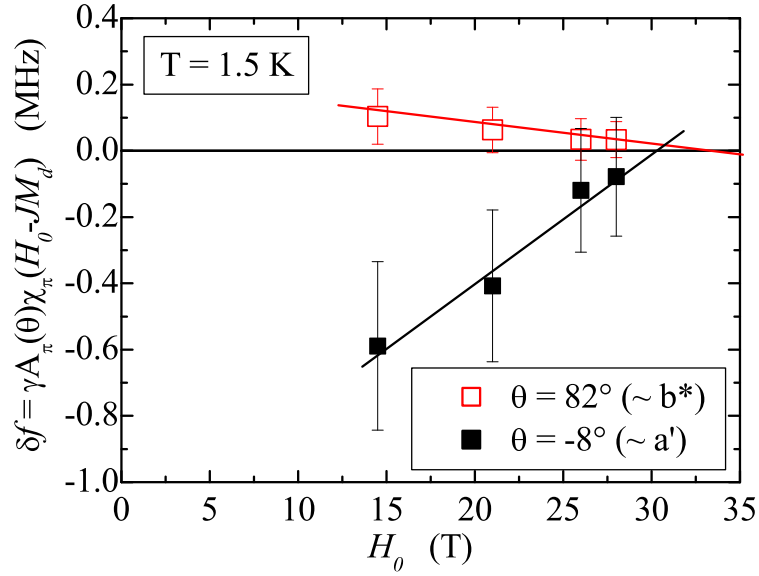


Fig. 8. Determination of the exchange field from the field variation of the shift at two different values of θ . The $|H_{\text{exch}}|$ is given by the intercepts of the shift with the zero value and found equal to 32 ± 2 T.

and the susceptibility χ_π of the π band. The main source of error is the determination of demagnetization contribution. That a small error of that type is possible can be seen in Fig. 7: although the extrema of the shift should appear at the same value of θ whatever is the applied magnetic field, one can observe a slight deviation, which could indicate that our correction for the dipolar contribution is not completely correct.

4.2 Temperature dependence of the line shift

As we have seen in section 3, the value of H_{exch} can also be extracted from the temperature dependence of the shift of the Se line at constant value of the field, provided one knows the temperature dependence of M_d . In a previous paper,¹⁷ we have analyzed in this way our results obtained at 14.5 T. However, for the determination of H_{exch} , we did not take into account the demagnetization factor, and we considered the Brillouin function of independent Fe moments. As shown by Wu *et al.*,¹⁸ this Brillouin function has to be modified to take into account the effect of antiferromagnetic interactions between these Fe moments, through the π conduction electrons. Here we present such complete analysis for two values of the field, $H_0 = 14.5$ and 26 T. In Fig. 9 are shown the temperature dependence of the Se NMR lines with temperature at these two fields. Evaluating the temperature dependence of M_d using the modified Brillouin function mentioned above, and correcting the data for the demagnetization field and dipolar field, one can plot the corrected shift which is proportional to $\gamma A_\pi(\theta)\chi_\pi[H_0 - JM_d]$ as a function of $M_d(T)$ with the temperature as an implicit parameter, as shown in Fig. 10. The intersection of the straight lines on the vertical axis ($M_d = 0$) corresponds to $\gamma A_\pi(\theta)\chi_\pi H_0$,

leading to the estimate $A_\pi(\theta)\chi_\pi = 0.44\%$ close to the value of 0.37% determined in the previous subsection (for the corresponding orientation) by a method which does not depend on any evaluation of demagnetization factor nor on the temperature dependence of M_d . From the slope of the lines in Fig. 10 and the above given two $A_\pi(\theta)\chi_\pi$ values, we obtain $|H_{\text{exch}}| = 30$ and 34 T. The average of these two values, $|H_{\text{exch}}| = 32 \pm 2$ T, is the same as the estimate obtained in the previous subsection, in agreement with the expected value of 33 T corresponding to the maximum of the transition temperature for superconductivity.

4.3 Anomalous broadening of NMR line

As shown in Fig. 9, very broad NMR lines were observed for $H_0 \parallel a'$ at low temperature. This anomalous line broadening was observed only in the low temperature region ($T < 30$ K), while at higher temperatures the linewidth scales to the M_d . To find the mechanism of this low temperature line broadening in the metallic state, we have measured the angular dependence of the NMR spectrum when H_0 is rotated in the $a'b^*$ plane at 1.5 K. Fig. 11 presents both the linewidth (full width at half maximum, FWHM) and the shift data. It turns out that the angular dependence of the width is strongly correlated to that of the shift. The maximum of the width and the (negative) extremum of the shift nearly coincide at $\theta \simeq 0$. Also the minimum of the width is observed for the direction which gives a zero shift, that is $\theta \simeq 64^\circ$. This strongly suggests that the line broadening is not due to defects in the crystals, but is caused by an intrinsic spatial distribution of the spin susceptibility $\chi_\pi(\mathbf{R})$. This is also supported by the field dependence of the linewidth shown in Fig. 3, as already mentioned in the beginning of Section 4.1. Higher H_0 values correspond to a smaller value of H_{eff} and thus to smaller linewidth. Let us call $\Delta\chi_\pi$ the second moment of spin susceptibility distribution. From Fig. 11, $\Delta\chi_\pi$ is comparable to χ_π . As the spectra are just broadened without any appreciable structure, this indicates that the $\Delta\chi_\pi$ is continuously distributed in the crystal. Supposing that the spin density is proportional to the charge density in the paramagnetic state, one possible mechanism for this anomalous broadening is charge disproportionation in the conducting layer which has been proposed to explain microwave conductivity³¹ and X-ray measurements.³² This would indicate that the distribution of the BETS valence is remarkably large. Quite similar line broadening has been observed in the charge ordering system, θ -(BEDT-TTF)₂RbZn(SCN)₄ in the “metallic” state above the metal-insulator transition temperature.³³ Another possible mechanism for the broadening is an oscillation of spin polarization in the conducting layer induced by the magnetic moment of the Fe atoms. This problem should be addressed in more details in the future.

5. Concluding remarks

We have performed ⁷⁷Se NMR measurements in the Field Induced Superconductor, λ -(BETS)₂FeCl₄ in the low temperature and high magnetic field metallic regime. Our study allowed a direct microscopic determination of the exchange field H_{exch} induced by the ex-

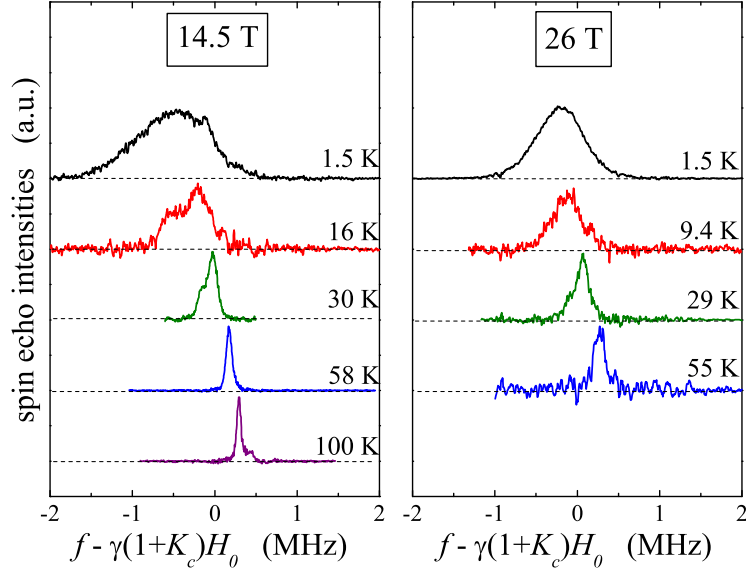


Fig. 9. Se NMR spectra at various temperatures at 14.5 and 26 T. The field direction is close to a' .

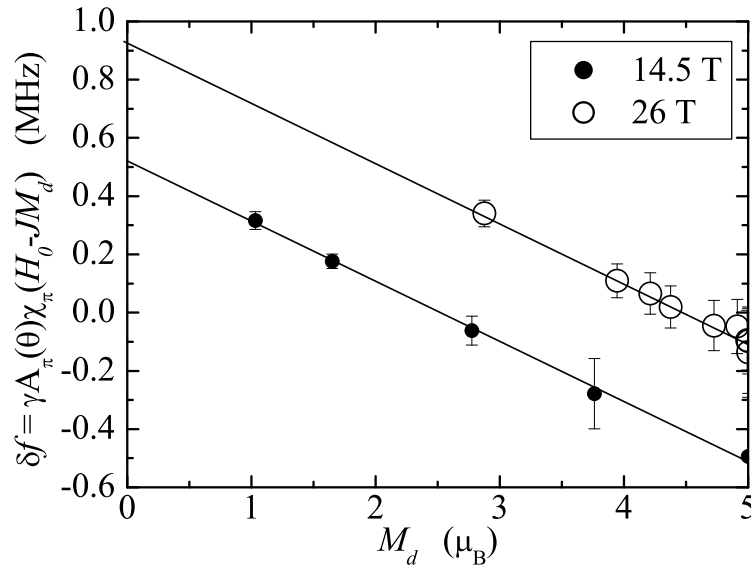


Fig. 10. Resonance shift as a function of the Fe moment M_d which is calculated by a modified Brillouin function taken from.¹⁸

change coupling between the conduction electrons of the π band and the localized spin $S = 5/2$ of the Fe atoms. Two independent ways have been used. One is based on the temperature dependence of the Fe moment and that of the shift of the ^{77}Se NMR line. Another method was to measure at low temperature, so that the Fe moments are saturated, and to record the angular dependence of the shift at (four) different applied field values varying from 14.5 to

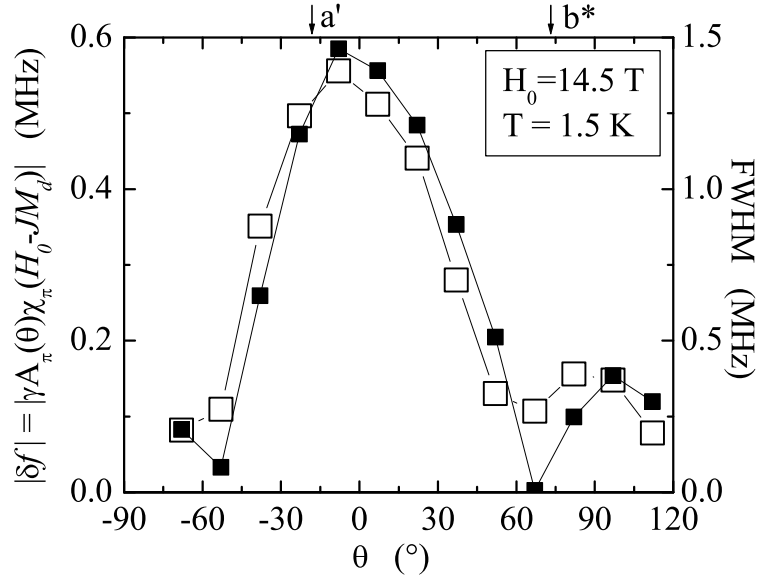


Fig. 11. Absolute value of the shift corrected for the dipolar contribution ($|\delta f|$, closed symbols, left scale) and linewidth (open symbols, right scale) of the ^{77}Se NMR line as a function of the field orientation in the $a'b^*$ plane at 14.5 T and 1.5 K. Note that the angle at which the linewidth is minimum ($\theta \simeq 64^\circ$) is also the one at which $A_\pi(\theta)$ vanishes as determined from Fig. 5.

28 T. This allowed us to determine directly the product of the susceptibility of the π band and the hyperfine coupling, $A_\pi(\theta)$, which contains an isotropic term and one corresponding to the spin polarization of π orbitals at the Se sites. As the external field increases, the amplitude of the angular variation of the shift decreases, since it is proportional to the total effective field $H_0 + H_{\text{exch}}$ in which two components have opposite signs. This is a direct experimental proof of the compensation mechanism proposed by Jaccarino and Peter.¹¹ Both methods led to $|H_{\text{exch}}| = 32 \pm 2$ T, in excellent agreement with the value of 33 T for which the transition temperature of the superconducting phase is maximum. This value is also in agreement with theoretical estimates.^{34,35} The error bars are mainly due to the difficulty to evaluate the demagnetization field in our sample.

In addition to these main findings, an anomalous line broadening has been observed at low temperatures. The linewidth has been found proportional to the hyperfine shift and to have the same angular dependence. One possible interpretation is the occurrence of charge disproportionation in the metallic state neighboring the superconducting phase. The relationship between these two types of order has been recently discussed in the charge ordering system $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$.^{36,37}

6. Acknowledgment

The authors are grateful to Prof. K. Takimiya from Hiroshima University for the ^{77}Se isotope enrichment of the sample and to Prof. W.G. Clark from University of California, Los

Angeles, for advises about tiny NMR coil. This work was partially supported by Japan Society for Promotion of Science, by High Technical Research Center of Gakushuin University, by Grant-in-Aid for Scientific Research on Priority Areas of Molecular Conductors (No. 15073221) from the Japanese Ministry of Education, Culture, Sports, Science and Technology, and by the French ANR grant 06-BLAN-0111.

References

- 1) See for example J. Phys. Soc. Jpn **75** No. 5 (2006) and references therein.
- 2) T. Ishiguro, K. Yamaji and G. Saito, *Organic Superconductors*(Springer-Verlag, Berlin, Heidelberg, 1998).
- 3) E. Coronado and P. Day, Chem. Rev. **104**, 5419 (2004)
- 4) A. Kobayashi, T. Udagawa, H. Tomita, T. Naito and H. Kobayashi, Chem. Lett. **1993**, 2179 (1993)
- 5) H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe and P. Casseux, J. Am. Chem. Soc. **118**, 368 (1996)
- 6) S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka and H. Kobayashi, Nature **410**, 908 (2001)
- 7) L. Balicas, L. S. Brooks, K. Storr, S. Uji, M. Tokumoto, H. Tanaka, H. Kobayashi, A. Kobayashi, V. Barzykin and L. P. Gor'kov, Phys. Rev. Lett. **87**, 067002 (2001)
- 8) M. Tokumoto, T. Naito, H. Kobayashi, A. Kobayashi, V. N. Laukhin, L. Brossard and P. Casseux, Synth. Met. **86**, 2161 (1997)
- 9) L. Brossard, R. Clerac, C. Coulon, M. Tokumoto, T. Ziman, D. K. Petrov, V. N. Laukhin, M. J. Naughton, A. Audouard, F. Goze, A. Kobayashi, H. Kobayashi and P. Cassoux, Eur. Phys. J. B **1**, 439 (1998)
- 10) C. Hotta and H. Fukuyama, J. Phys. Soc. Jpn. **69**, 2577 (2000)
- 11) V. Jaccarino and M. Peter, Phys. Rev. Lett. **9**, 290 (1962)
- 12) H. Kobayashi, H. Akutsu, E. Arai, H. Tanaka and A. Kobayashi, Phys. Rev. B **56**, R8526 (1997)
- 13) S. Uji, C. Terakura, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, F. Sakai, H. Tanaka and H. Kobayashi, Phys. Rev. **65**, 113101 (2002)
- 14) S. Uji, T. Terashima, C. Terakura, T. Yakabe, Y. Terai, S. Yasuzuka, Y. Imanaka, M. Tokumoto, A. Kobayashi, F. Sakai, H. Tanaka, H. Kobayashi, L. Balicas and J. S. Brooks, J. Phys. Soc. Jpn. **72**, 369 (2003)
- 15) S. Endo, T. Goto, T. Fukase, H. Matsui, H. Uozaki, H. Tsuchiya, E. Negishi, Y. Ishizaki, Y. Abe and N. Toyota, J. Phys. Soc. Jpn. **71**, 732 (2002)
- 16) G. Wu, P. Ranin, W. G. Clark, S. E. Brown, L. Balicas and L. K. Montgomery, Phys. Rev. B **74**, 064428 (2006)
- 17) K. Hiraki, H. Mayaffre, M. Horvatić, C. Berthier, H. Tanaka, A. Kobayashi, H. Kobayashi and T. Takahashi, J. Low. Temp. Phys. **142**, 185 (2006).
- 18) Guoqing Wu, W. G. Clark, S. E. Brown, J. S. Brooks, A. Kobayashi and H. Kobayashi, cond-mat/0706.0933
- 19) S. Fujiyama, M. Takigawa, J. Kikuchi, HB. Cui, H. Fujiwara and H. Kobayashi, Phys. Rev. Lett. **96**, 217001 (2006)
- 20) T. Konoike S. Uji, T. Terashima, S. Yasuzuka, H. Fujiwara, B. Zhang and H. Kobayashi, Phys. Rev. B **70**, 094514 (2004)
- 21) K. Takimiya, T. Jigami, M. Kawashima, M. Kodani, Y.o Aso, T. Otsubo, J. Org. Chem., **67** (**12**), 4218 (2002)
- 22) K. Takimiya, Y. Kataoka, N. Niihara, Y. Aso, T. Otsubo, J. Org. Chem., **68** (**13**), 5217 (2003)
- 23) W. G. Clark, M. E. Hanson, F. Lefloch and P. Ségransan, Rev. Sci. Inst. **66**, 2453 (1995)
- 24) S. Takagi, D. Maruta, H. Sasaki, H. Uozaki, H. Tsuchiya, Y. Abe, Y. Ishizaki, E. Negishi, H. Matsui,

- S. Endo and N. Toyota, J. Phys. Sci. Jpn. **72**, 483 (2003)
- 25) The zero reference for the angle θ has been taken to correspond to the maximum of the fit given in Fig. 5. Physically this corresponds to magnetic field being closest to the (average) direction of electronic π orbitals. With respect to this reference a' direction (lying in the ac plane) is at $\theta(a') = -17^\circ$.
- 26) R. M. White, "Quantum Theory of magnetism", Mc Graw Hill (1970)
- 27) Knowing that there are two Fe spins in the unit cell of 1716 \AA^3 (at 10 K),⁵ the $M_z = 54$ Gauss.
- 28) Considering the dimensions of the sample, we found $N_{a'} = 0.2$, $N_{b^*} = 0.8$, $N_c = 0$.
- 29) H. Tanaka, A. Kobayashi, A. Sato, H. Akutsu and H. Kobayashi, J. Am. Chem. Soc. **121**, 760 (1999)
- 30) S. Fraga, J. Karwowski, K.M. Saxena, *Handbook of Atomic data* (Elsevier, Amsterdam, 1976)
- 31) H. Matsui, H. Tsuchiya, E. Negishi, H. Uozaki, Y. Ishizaki, Y. Abe, S. Endo and N. Toyota, J. Phys. Sci. Jpn. **70**, 2501 (2001)
- 32) S. Komiyama, M. Watanabe, Y. Noda, E. Negishi and N. Toyota, J. Phys. Sci. Jpn. **73**, 2385 (2004)
- 33) R. Chiba, K. Hiraki, T. Takahashi, H. M. Yamamoto and T. Nakamura, Phys. Rev. Lett. **93**, 216405 (2004)
- 34) O. Cépas, R. H. McKenzie and J. Merino, Phys. Rev. B **65**, 100502 (2002)
- 35) T. Mori and M. Katsuhara, J. Phys. Soc. Jpn. **71**, 826 (2002)
- 36) N. Tajima, A. Ebina-Tajima, M. Tamura, Y. Nishio and K. Kajita: J. Phys. Soc. Jpn. **71**, (2002) 1832.
- 37) A. Kobayashi, S. Katayama and Y. Suzumura, J. Phys. Soc. Jpn. **74**, 2897 (2005)