

Non-Fermi-liquid behavior of the organic superconductor κ -(BEDT-TTF)₄Hg_{2.89}Br₈ probed by ¹³C NMR

Yoshihiro Eto, Megumi Itaya, and Atsushi Kawamoto*

Department of Quantum and Condensed Matter Physics, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

(Received 19 February 2010; revised manuscript received 13 April 2010; published 21 June 2010)

An organic salt, κ -(BEDT-TTF)₄Hg_{2.89}Br₈ exhibits superconductivity at 4.3 K under ambient pressure suggesting non-Fermi-liquid (NFL) behavior just above T_c . Whereas most organic superconductors are controlled by the bandwidth in the half-filled electron system, this salt realizes a carrier doping away from the half-filled electron system as well as high- T_c cuprates. In order to investigate the origin of NFL behavior, we assessed ¹³C-NMR measurements in this salt and observed the antiferromagnetic fluctuation as same as in an organic antiferromagnet κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl with the gap structure. Application of pressure suppresses $(T_1T)^{-1}$ and shifts its maximum to lower temperatures with $(T_1T)^{-1}$ becoming constant above 2 GPa. These results suggest that applying pressure alters the electron system from NFL to FL state and that antiferromagnetic fluctuations contribute to the origin of NFL behavior.

DOI: 10.1103/PhysRevB.81.212503

PACS number(s): 74.70.Kn, 82.80.Gk, 76.60.-k

The physics of organic conductors involve a strongly correlated electron system, similar to that of high- T_c cuprates and heavy-fermion systems.¹ For example, bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), together with inorganic ions, forms many conducting salts, which have various crystal structures. Although the conducting layers of all of these salts consist of the same molecule, these salts show a variety of behavior, from superconductivity to high-resistance insulator.² These salts can also be classified by the arrangement and the electronic properties being closely related. In κ -(BEDT-TTF)₂X, two BEDT-TTF molecules form a dimer and constitute a two-dimensional conducting sheet, with one electron per dimer.³ Hence κ -(BEDT-TTF)₂X is regarded as a two-dimensional half-filled electron system.⁴ Many κ -(BEDT-TTF)₂X salts act as superconductors with the superconducting and antiferromagnetic insulating phases being adjacent to or coexisting at low temperatures.^{5,6} Therefore, these salts are ideal for investigating the relationship between superconductivity and antiferromagnetism.

Carrier doping and applying pressure are complementary methods for research on the phase diagram. Whereas high- T_c cuprates showed superconductivity after carrier doping, many organic superconductors showed superconductivity after applying pressure.⁷ Cuprates and κ -(BEDT-TTF)₂X show both similarities and dissimilarities. Despite differences in their ionic and molecular crystals, cuprates and κ -(BEDT-TTF)₂X have similar properties, in that their superconductive and antiferromagnetic phases are neighboring, and the order parameter of the superconductivity has d -wave symmetry.⁸⁻¹³ Just above T_c , κ -type salts show Fermi-liquid (FL) behavior, as shown by their conductivity, spin susceptibility and $(T_1T)^{-1}$,^{5,14,15} whereas high- T_c cuprates show non-Fermi-liquid (NFL) behavior just above T_c . To investigate the origin of those similarities and dissimilarities, it is important to assess the material that connects cuprates and κ -(BEDT-TTF)₂X. Since carrier doping to organic conductors may occur, Taniguchi *et al.*¹⁶ have focused on κ -(BEDT-TTF)₄Hg_{2.89}Br₈ which was reported by

Lyubovskaya *et al.*¹⁷ As shown in Fig. 1(a), BEDT-TTF molecules in this salt have the same molecular arrangement as in κ -(BEDT-TTF)₂X. This salt belongs to a monoclinic system and BEDT-TTF molecules and Br atoms form a monoclinic system with the orthorhombic sublattice of Hg atoms.¹⁸ Therefore unlike other κ -(BEDT-TTF)₂X salts, the formal charge on each BEDT-TTF molecule is greater than $+0.5e$, due to nonstoichiometry, and hole doping is realized.¹⁹ Moreover this salt shows superconductivity at 4.3 K at ambient pressure.²⁰ From electrical resistivity measurements under pressure, a superconductive transition was observed up to 3 GPa.¹⁶ In addition, electrical resistivity just above T_c showed T -linear behavior under low-pressure region and T^2 behavior under high pressure. Whereas many other κ -(BEDT-TTF)₂X salts show FL behavior just above T_c , these findings indicate that this salt shows NFL behavior under low pressure but shows FL behavior under greater pressure.¹⁶ Magnetic fluctuation has been regarded as the origin of NFL behavior in high- T_c cuprates and heavy-fermions systems. It is unclear, however, whether is the NFL behavior observed in κ -(BEDT-TTF)₄Hg_{2.89}Br₈ is the same as that in high- T_c cuprates and heavy-fermion systems. This question has important ramifications regarding the universal-

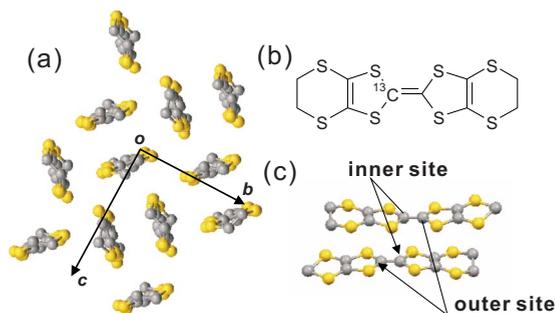


FIG. 1. (Color online) (a) Conducting sheet structure of κ -(BEDT-TTF)₄Hg_{2.89}Br₈ (b) BEDT-TTF molecules enriched with ¹³C isotopes on only one side of the central carbon sites (c) Dimeric structure with site definition of central C=C carbons.

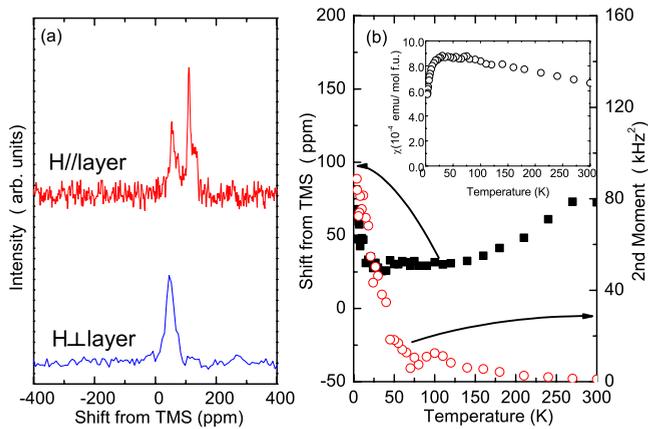


FIG. 2. (Color online) (a) NMR spectrum of κ -(BEDT-TTF) $_4$ Hg $_{2.89}$ Br $_8$ at ambient pressure ($T=210$ K) (b) Temperature dependence of the linewidth and NMR shift at ambient pressure; inset: spin susceptibility at ambient pressure (Ref. 22).

ity between organics and the other systems. Nuclear magnetic resonance (NMR) is the most suitable tool for this purpose. NMR has several advantages over other methods, including its ability to measure spin susceptibility under pressure as Knight shift and to observe the magnetic fluctuations from $(T_1T)^{-1}$. We therefore utilized ^{13}C NMR to assess the electronic state of this salt at ambient pressure and under pressure, and to investigate the existence of magnetic fluctuations and their pressure dependence.

For most ^{13}C -NMR measurements in BEDT-TTF-based organic conductors, the molecules are enriched with ^{13}C isotopes on both sides of the central $^{13}\text{C}=^{13}\text{C}$ sites. The dipole-dipole interaction from $^{13}\text{C}=^{13}\text{C}$, the so-called Pake doublet, complicates the spectrum. To avoid Pake doublet difficulties, we used a BEDT-TTF molecule enriched with ^{13}C isotopes on only one side of the central carbon sites [Fig. 1(b)].²¹ Single crystals were prepared electrochemically.^{16,17} Temperature-dependent NMR measurements were performed at decreasing temperatures under a magnetic field of 9.4 T and the spectra were obtained by fast Fourier transformation of the echo signal with a $\pi/2-\pi$ pulse sequence. Spin-lattice relaxation time was determined by the saturation recovery method. ^{13}C NMR was performed under ambient pressure and at 0.45, 0.65, 0.9, 1.2, 1.6, 2.0, and 2.4 GPa, with external fields perpendicular and parallel to the conduction layer at ambient pressure and perpendicular to the conduction layer under pressure using a clamp cell made of NiCrAl alloy. Daphni oil 7373 was used as pressure medium.

The volume of the superconductivity at ambient pressure has been found not to be bulk whereas bulk superconductivity was observed at pressures over 0.4 GPa.¹⁶ First, to determine the properties of this salt at ambient pressure, we determined its NMR spectrum and T_1 . Since BEDT-TTF molecules form dimers in the conducting layers, and since there are two nonequivalent sites, two peaks, one each from the inner and outer sites, are expected [Fig. 1(c)]. For $\text{H}\perp$ layer, however, only one peak was observed at all temperatures [Fig. 2(a)], suggesting that the inner and outer sites have almost the same hyperfine coupling constant in this configuration. Indeed, two peaks are observed for the

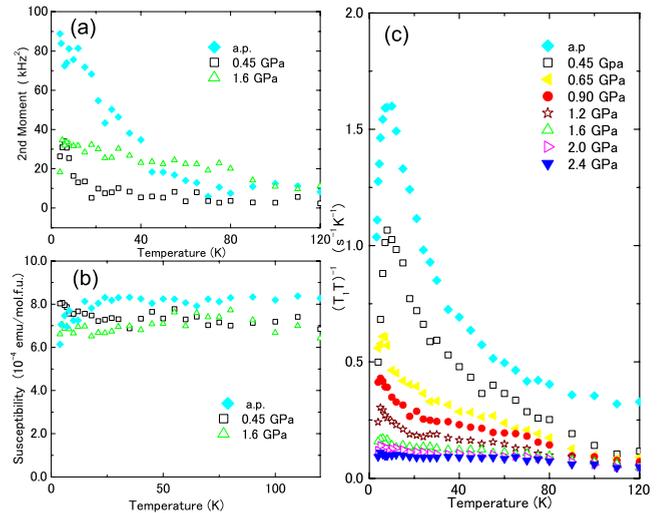


FIG. 3. (Color online) Temperature dependence under pressure of the (a) second moment, (b) spin susceptibility, (c) and $(T_1T)^{-1}$.

$\text{H}\parallel$ layer. We found that the NMR shift, δ , was proportional to spin susceptibility, χ , with a negative hyperfine coupling constant [Fig. 2(b)]. From the χ - δ plot, we determined that the hyperfine coupling constant A was -1.58 kOe/ μ_B and the chemical shift σ was 263 ppm.

As shown in Fig. 2(b), the linewidth of the peak, evaluated as second moment, increases rapidly with decreasing temperature. Since the spin-spin relaxation time, T_2 , is almost constant at 0.79 ms, the increase in linewidth is due to the inhomogeneity of the spin susceptibility. As the Raman spectrum of this salt, which is sensitive to the charge on the molecule, did not broaden at all temperatures, this was not an inhomogeneity of charge. Hence this broadening was likely due to the inhomogeneity of the spin magnetization. This salt acquires a random potential from its sublattice of Hg atoms. Therefore, the random potential causes an inhomogeneity of the conducting electrons. Considering the temperature dependence of the linewidth, we hypothesize that broadening of the linewidth may be due to the formation of an inhomogeneity by impurities. The inhomogeneity of the spin prevents the emergence of bulk superconductivity at ambient pressure. The effect of this inhomogeneity must be considered when assessing the anomalous behavior of this salt under ambient pressure.

This inhomogeneity causes by the competition between the random potential and the band width. The presence of this inhomogeneity may prevent bulk superconductivity. Figure 3(a) shows the temperature dependence of the linewidth under pressure. We found that the increase in inhomogeneity is suppressed at pressures above 0.45 GPa, suggesting that the application of pressure causes the inhomogeneity of the spin susceptibility to disappear. Since this salt shows bulk superconductivity above 0.4 GPa,¹⁶ the suppression of the inhomogeneity and bulk superconductivity are likely related.

Generally, it is difficult to investigate spin susceptibility under pressure, due to background signals from the pressure cell. NMR, however, enables the investigation of these spin susceptibilities without such difficulty. Spin susceptibility can be calculated by dividing the Knight shift by the hyper-

fine coupling constant A . After measuring the NMR shift under pressure, we could calculate spin susceptibility from the hyperfine coupling constant A and the chemical shift σ . Figure 3(b) shows the temperature dependence of the spin susceptibility, as determined by Knight shift under pressure. Application of pressures suppress the decrease in spin susceptibility at low temperature and spin susceptibility shows an almost temperature-independent behavior above 0.45 GPa. Thus these results suggest that this salt shows Pauli susceptibility without inhomogeneity above 0.45 GPa.

Our main purpose is to assess the magnetic properties of this salt under bulk superconductivity conditions. The behavior of this salt in the bulk superconductivity region suggested a connection between NFL behavior and magnetic fluctuation. Figure 3(c) shows the pressure dependence of $(T_1T)^{-1}$. While spin susceptibility became almost constant under pressure, $(T_1T)^{-1}$ increases with decreasing temperature, suggesting the development of antiferromagnetic fluctuation observed in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl salt.²³ $(T_1T)^{-1}$ also shows a gaplike behavior at around 7–9 K under 0.45 GPa and $(T_1T)^{-1}$ is suppressed and its maximum shifts to a lower temperature under greater pressure. Finally $(T_1T)^{-1}$ becomes constant above 2 GPa. Due to the temperature-independent behavior of the spin susceptibility and $(T_1T)^{-1}$ under high pressure, the FL state probably occurs above 2 GPa. These results suggest that the electron system changes from NFL to FL in response to increase pressure and the reduction in antiferromagnetic fluctuations.

Whereas the gap behavior of $(T_1T)^{-1}$ is observed in ambient and low-pressure region, the decrease in spin susceptibility at low temperature is only observed under ambient pressure. Hence the decrease in spin susceptibility under ambient pressure is thought to be connected not with the gap behavior of $(T_1T)^{-1}$ but rather with the inhomogeneity.

Taniguchi *et al.*¹⁶ suggested high- T_c phase in NFL state below 2 GPa and low- T_c phase in FL state above 2 GPa. Our results suggest that this salt is an organic superconductor that shows NFL behavior just above T_c due to antiferromagnetic fluctuations below 2 GPa.

These behaviors are qualitatively different from those of other band width controlled superconducting κ -(BEDT-TTF)₂X salts, wherein the development of magnetic fluctuations is suppressed at characteristic temperatures. The maximum of $(T_1T)^{-1}$ shifts to higher temperature when pressure is applied and spin susceptibility is decreased and the electrical conductivity is significantly increased.^{5,15,24} In contrast, there was no significant anomaly of spin susceptibility and the electrical conductivity at that temperature in this salt.

The NFL behavior of κ -(BEDT-TTF)₄Hg_{2.89}Br₈ suggests the pairing mechanism intermediated by the antiferromagnetic fluctuation with \mathbf{Q} vector observed in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl. In other band width controlled superconducting κ -(BEDT-TTF)₂X salts, the antiferromagnetic fluctuation with \mathbf{Q} observed in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl is suppressed at around 50 K (Refs. 23 and 25) and shows FL behavior just above T_c .^{5,15} Therefore the connection between the superconductivity and

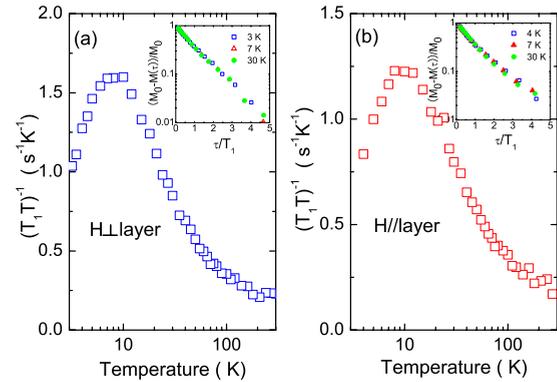


FIG. 4. (Color online) Temperature dependence of $(T_1T)^{-1}$ at (a) $H \perp$ layer and (b) $H \parallel$ layer at ambient pressure; inset: recovery profile of each configuration at several temperatures.

antiferromagnetism is not clear.^{11,12} These noteworthy differences are expected to originate in the difference between the band-width control and carrier-doped control to the antiferromagnetic insulator.

From the conductivity measurement under pressure, T_c showed a maximum at around 0.6 GPa and decreased with further pressure.¹⁶ The correlation between T_c and the gap temperature is expected. The decrease in $(T_1T)^{-1}$ might be due to fluctuations of superconductivity, even in a high magnetic field of 9.4 T. In a quasi-two-dimensional electron system, the parameters of the superconductivity, λ and ξ should differ greatly in the $H \parallel$ and \perp layers. If the fluctuation arises from the superconductivity of this material, we should expect different behavior of $(T_1T)^{-1}$ in the $H \parallel$ layer. Indeed the large anisotropy were observed as $-dH_{c2}^{\parallel}/dT=100$ kOe/K and $-dH_{c2}^{\perp}/dT=18$ kOe/K.²⁰ Figure 4 shows the results in the $H \perp$ layer and $H \parallel$ layer. The result in the $H \perp$ layer [Fig. 4(a)] is similar to that in the $H \parallel$ layer [Fig. 4(b)]. These results suggest that the fluctuation of superconductivity is unlikely and the gap behavior in $(T_1T)^{-1}$ is expected to be due to the magnetism of the conducting electrons. Applying pressures up to 2 GPa, the gap temperature in $(T_1T)^{-1}$ shifts to 0 K and FL state is realized. The relationship between FL behavior and the superconductivity is important. While in strongly overdoped cuprates, FL state emerges and the superconductivity is absent,^{26,27} this salt shows the superconductivity above 2 GPa. However, the contactless T_c measurement by LC -tank circuit suggested that T_c is rapidly decreasing with applying pressure.²⁸ To confirm low- T_c phase above 2 GPa, and clarify similarities and dissimilarities between organics and cuprates, reliable T_c measurements are desired. Recently, NFL to FL crossover behavior in quasi-one-dimensional organic superconductors, (TMTSF)₂X has been reported from resistivity measurements under pressure and discussed the comparison with inorganic systems.²⁹

In summary, we performed ¹³C-NMR measurements on κ -(BEDT-TTF)₄Hg_{2.89}Br₈. We observed that, as the temperature was decreased, the linewidth of peak increased due to spin inhomogeneity. This inhomogeneity prevents the emergence of bulk superconductivity at ambient pressure. Above 0.45 GPa, at which the inhomogeneity is suppressed, a temperature-independent Pauli susceptibility is observed.

However $(T_1T)^{-1}$ shows large antiferromagnetic fluctuations just above T_c with a gaplike behavior. When pressure is increased, $(T_1T)^{-1}$ is suppressed and its maximum shifts to lower temperatures. Finally $(T_1T)^{-1}$ becomes constant above 2 GPa. These results suggest that the application of pressure changes the electron system from NFL to FL state and that, similar to high- T_c cuprates, antiferromagnetic fluctuations contributes to the origin of this NFL behavior.

The authors wish to thank K. Kumagai and Y. Furukawa of Hokkaido University for stimulating discussions, and H. Taniguchi of Saitama University for his information about the preparation of single crystals and for discussions about transport measurements. This study was supported in part by a Grant-in-Aid for Scientific Research (Grant No. 18540306) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

*atkawa@phys.sci.hokudai.ac.jp

- ¹R. H. McKenzie, *Science* **278**, 820 (1997).
- ²J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. H. Whangbo, *Organic Superconductors* (Prentice Hall, Englewood, Cliffs, NJ, 1992).
- ³H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.* **17**, 55 (1988).
- ⁴K. Kanoda, *Physica C* **282-287**, 299 (1997).
- ⁵A. Kawamoto, M. Yamashita, and K. I. Kumagai, *Phys. Rev. B* **70**, 212506 (2004).
- ⁶S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jerome, C. Meziere, M. Fourmigue, and P. Batail, *Phys. Rev. Lett.* **85**, 5420 (2000).
- ⁷J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, and J. M. Kammers, *Inorg. Chem.* **29**, 3272 (1990).
- ⁸S. M. De Soto, C. P. Slichter, A. M. Kini, H. H. Wang, U. Geiser, and J. M. Williams, *Phys. Rev. B* **52**, 10364 (1995).
- ⁹H. Mayaffre, P. Wzietek, D. Jerome, C. Lenoir, and P. Batail, *Phys. Rev. Lett.* **75**, 4122 (1995).
- ¹⁰K. Kanoda, K. Miyagawa, A. Kawamoto, and Y. Nakazawa, *Phys. Rev. B* **54**, 76 (1996).
- ¹¹T. Arai, K. Ichimura, K. Nomura, S. Takasaki, J. Yamada, S. Nakatsuji, and H. Anzai, *Phys. Rev. B* **63**, 104518 (2001).
- ¹²K. Izawa, H. Yamaguchi, T. Sasaki, and Y. Matsuda, *Phys. Rev. Lett.* **88**, 027002 (2001).
- ¹³Y. Nakazawa and K. Kanoda, *Phys. Rev. B* **55**, R8670 (1997).
- ¹⁴T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors*, 2nd ed. (Springer, New York, 1997), p. 150.
- ¹⁵M. Itaya, Y. Eto, A. Kawamoto, and H. Taniguchi, *Phys. Rev. Lett.* **102**, 227003 (2009).
- ¹⁶H. Taniguchi, T. Okuhata, T. Nagai, K. Satoh, N. Mori, Y. Shimizu, M. Hedo, and Y. Uwatoko, *J. Phys. Soc. Jpn.* **76**, 113709 (2007).
- ¹⁷R. N. Lyubovskaya, E. A. Zhilyaeva, A. V. Zvarykina, V. N. Laukhin, R. B. Lyubovskii, and S. I. Pesotskii, *JETP Lett.* **45**, 530 (1987).
- ¹⁸R. Li, V. Petricek, G. Yang, P. Coppens, and M. Naughton, *Chem. Mater.* **10**, 1521 (1998).
- ¹⁹T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, and H. Taniguchi, *J. Phys. Chem. B* **109**, 15226 (2005).
- ²⁰R. N. Lyubovskaya, E. I. Zhilyaeva, S. I. Pesotskii, R. B. Lyubovskii, L. O. Atovmyan, O. A. D'yachenko, and T. G. Takhirov, *JETP Lett.* **46**, 188 (1987).
- ²¹M. Yamashita, A. Kawamoto, and K. Kumagai, *Synth. Met.* **133-134**, 125 (2003).
- ²²A. V. Skripov, A. P. Stepanov, V. A. Merzhanov, R. N. Lyubovskaya, and R. B. Lyubovskii, *JETP Lett.* **49**, 265 (1989).
- ²³A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, *Phys. Rev. B* **52**, 15522 (1995).
- ²⁴H. Taniguchi, A. Kawamoto, and K. Kanoda, *Phys. Rev. B* **59**, 8424 (1999).
- ²⁵A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, *Phys. Rev. Lett.* **74**, 3455 (1995).
- ²⁶A. P. Mackenzie, S. R. Julian, D. C. Sinclair, and C. T. Lin, *Phys. Rev. B* **53**, 5848 (1996).
- ²⁷R. A. Cooper, Y. Wang, B. Vignolle, O. J. Lipscombe, S. M. Hayden, Y. Tanabe, T. Adachi, Y. Koike, M. Nohara, H. Takagi, C. Proust, and N. E. Hussey, *Science* **323**, 603 (2009).
- ²⁸H. Oike, International Symposium on Molecular Conductors, Okazaki, Japan, 2008 (unpublished).
- ²⁹N. Doiron-Leyraud, P. Auban-Senzier, S. René de Cotret, C. Bourbonnais, D. Jérôme, K. Bechgaard, and L. Taillefer, *Phys. Rev. B* **80**, 214531 (2009).