^{13}C NMR Study of Superconductivity near Charge Instability Realized in β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$

Yoshihiko IHARA, Harumi SEKI, and Atsushi KAWAMOTO

Department of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

To investigate the superconducting (SC) state near a charge instability, we performed ^{13}C NMR experiments on the molecular superconductor β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$ [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene], in which charge disproportionation was reported from Raman spectroscopy at 100 K. We found an NMR spectral splitting at $T_{\text{CD}} = 12$ K, which is ascribed to the low-temperature charge instability. Measurements of nuclear spin–lattice relaxation time revealed enhanced fluctuations at T_{CD}. We suggest the relationship between the enhanced fluctuations and superconductivity, which emerges slightly below T_{CD}. In the SC state, we observed a decrease in the Knight shift, which leads us to suggest a spin-singlet SC state. The possibility of an unconventional SC state is discussed.

KEYWORDS: organic superconductor, charge order, NMR

Superconductivity appearing in close proximity to magnetism has fascinated researchers because of its unconventional superconducting (SC) pairing mechanisms. For example, in the Ce-based heavy-fermion superconductor CeCu$_2$Si$_2$, Cooper pairs are mediated by magnetic fluctuations that are enhanced near the magnetic quantum critical point (QCP).[1,2] A similar scenario has been applied to the interpretation of the SC state in a high-SC-transition-temperature cuprate, pnictide, as well as in organic superconductors such as (TMTSF)$_2$PF$_6$[3] (TMTSF: tetramethyltetraselenafulvalene) and κ-(BEDT-TTF)$_2$X[4,5] [BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene], and it has successfully explained the physical properties. Holmes et al.[6] have suggested a novel mechanism that is triggered by an increase in the SC transition temperature T_c of CeCu$_2$Si$_2$ at pressures greater than 3 GPa, at which the system approaches the second critical point ascribed to a valence instability. Theory indicates that enhanced charge fluctuations near an *electric* QCP increase T_c. Thus an experimental study that investigates superconductivity near charge instability is required.

Charge ordering is observed in several BEDT-TTF salts with α- and θ-type structures,[7,8] some of which undergo SC transition in the charge-ordered state.[9,10] A theoretical study shows that an unconventional SC state can be realized in these compounds near charge instability,[11–13] as expected for other superconductors observed near magnetic QCPs. Since optical experiments in BEDT-TTF salts have clearly revealed charge instability and indicated the connection between superconductivity and charge fluctuation,[14,15] investigations of electronic properties in both the normal and SC states by various experimental techniques are essential.

Superconductivity was observed at rather high temperatures reaching 9 K in the β''-type structures β''-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]·Y with M = Ga, Fe, or Cr and Y = C$_6$H$_5$NO$_2$ or C$_6$H$_5$CN.[16–19] These compounds consist of alternating BEDT-TTF and anion block layers. The metallic conductivity is governed by the positive carriers injected into the two-dimensional BEDT-TTF layers. Magnetic anomaly is absent in these β''-family compounds, whereas the anomaly associated with charge ordering has been observed at approximately 100 K by Raman spectroscopy and electric transport measurements.[19] Superconductivity in these salts must be investigated to determine the nature of superconductivity in the vicinity of charge instability.

In addition to the interplay between charge ordering and superconductivity, the extremely high upper critical field H_{c2} of 33 T, which is almost three times the Pauli–Clogston limit, piques our interest.[19] In a magnetic field, superconductivity is suppressed by the Pauli depairing effect.[20] To sustain superconductivity in high magnetic fields, an unconventional SC state was introduced by Fulde and Ferrel and Larkin and Ovchinnikov (hereafter the FFLO state).[21,22] In the FFLO state, the Pauli depairing effect is suppressed by allowing the real-space modulation of the SC gap. Whereas for the spin-triplet SC state, the Pauli depairing is irrelevant because Cooper pairs can preserve their spin degrees of freedom. To comprehend the high-field SC state, SC pairing symmetry must be determined from low-field experiments. NMR spectroscopy is a powerful technique for microscopically investigating the spin symmetry of Cooper pairs. We have carried out the Knight shift (K) measurement in the SC state to determine the SC symmetry.

In this Letter, we focus on the β''-salt with M = Ga and Y = C$_6$H$_5$NO$_2$, which exhibits superconductivity at 7.5 K. Single-crystal samples of this salt were grown using the electrocrystallization technique described in Ref. 17. We obtained two single-crystal phases: plate and needle crystals. The crystalline parameters of the needle crystals are consistent with those reported for the SC samples.[17] Magnetization and resistivity measurements of the needle crystals detected SC transition at $T_c = 7.5$ K, in accordance with a previous report,[17] and the SC fraction estimated from magnetization data is the same as that in Ref. 17. The typical dimensions of the SC needle samples are $1 \times 0.1 \times 0.2$ mm^3. The single-crystal X-ray diffraction revealed that the longest axis is parallel to the crystalline a-axis. For the NMR experiment reported in this Letter, external magnetic fields were applied along the b-axis, which is the second-longest axis of the crystal. To reduce spectral broadening due to sample misalignment, ^{13}C NMR spectra were acquired for
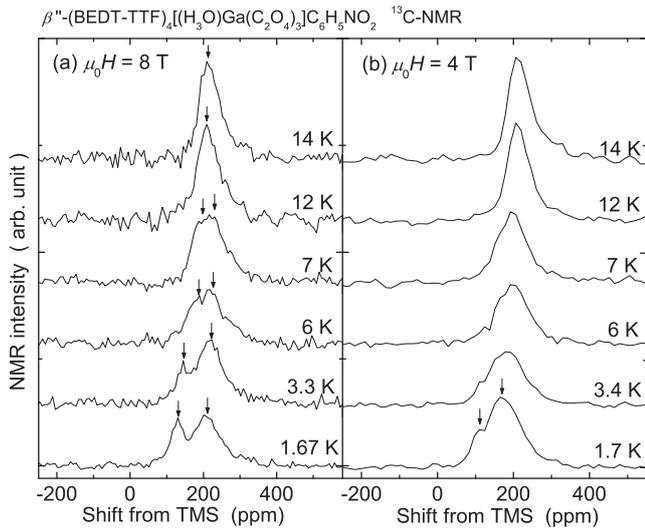
Fig. 1. ^{13}C NMR spectra of β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$ at magnetic fields of (a) 8 T and (b) 4 T along the b-axis. The NMR shift is measured from tetramethylsilane (TMS). The spectral splitting observed below 12 K is ascribed to static charge instability.

Fig. 2. (Color online) (a) Temperature dependence of NMR shift in 8 T. The peak positions were determined by fitting spectra with Lorentzians. The results of the two-peak fit below 9 K are plotted as solid and open circles. The spectrum becomes a single peak above 10 K. The results of the single-peak fit above 10 K are shown as solid triangles. (b) Full widths at half maximum (FWHMs) measured at 4 and 8 T. An abrupt increase was observed below $T_{CD} = 12$ K. The field independent FWHM indicates a charge instability for the anomaly at T_{CD}. (c) In-plane resistivity measured at $H_{\parallel b}$ of 0, 4, and 7 T. T_c is determined as $T_c(0\,T) = 6.7$ K, $T_c(4\,T) = 3.5$ K, and $T_c(7\,T) = 2.8$ K from the midpoint. The inset shows the temperature dependence of $\Delta\rho/\Delta T$. A change in slope was observed below T_{CD}.

one single crystal. To measure the spin–lattice relaxation time T_1, which does not require high frequency resolution, we aligned 30 single crystals on a flat sample holder to improve the signal-to-noise ratio. For the resistivity measurement, we utilized a sample synthesized by the same process as those for the NMR experiment, and applied magnetic fields along the b-axis.

When neighboring ^{13}C nuclear spins are magnetically coupled, the NMR shift of the ^{13}C resonance cannot be correctly determined, because the nuclear spin–spin coupling splits the ^{13}C NMR spectrum into two peaks (Pake doublet[23]). For BEDT-TTF molecules, the coupling of ^{13}C nuclei at the central C=C bond is sufficiently strong to result in this Pake-doublet problem.[24] Therefore, we eliminated the Pake doublet by the selective enrichment of one side of the central C=C bond with ^{13}C using the cross-coupling method[25] between non-enriched ketone and ^{13}C-enriched thio-ketone forms.

β''-salts possess two nonequivalent BEDT-TTF molecules, each of which possesses two nonequivalent ^{13}C sites at the central C=C bond. The four nonequivalent ^{13}C sites should result in four NMR peaks in a field applied exactly along the glide plane ($\parallel b$). However, as shown in Fig. 1, we observed a single-peak NMR spectrum at 14 K, because the NMR spectrum broadening starting from 100 K, where charge ordering was detected by Raman spectroscopy, led to the merging of the split peaks. The absence of resolved spectral splitting is due to the similarity in crystallographic sites between two nonequivalent molecules, which is evident from the crystal structure.[17] We found a clear peak splitting at low temperatures, as indicated by downward arrows in Fig. 1(a). The spectral splitting indicates static ^{13}C-site doubling caused either by the crystallographic symmetry breaking or by the increase in disproportionation between two nonequivalent molecules. Spectral broadening below 12 K and splitting at 1.7 K were also observed at 4 T, although the broader linewidth gives rise to a broad spectrum with a shoulder structure, as indicated by arrows

in Fig. 1(b). The double-peak structure is well resolved only in high fields, because the high NMR frequency (f_0) used in high-field experiments improves the shift resolution.

The temperature dependences of the NMR shift and full width at the half maximum (FWHM) are shown in Figs. 2(a) and 2(b), respectively. The spectral splitting was observed below approximately 9 K, as shown in Fig. 2(a). To determin the onset temperature, however, we adopted the FWHM data, because the splitting is detected as the spectral broadening when the separation of the two split peaks is smaller than the linewidth. Judging from the abrupt increase in FWHM, we determined the onset temperature of the spectral splitting to be 12 K. At the same temperature, an anomaly was also found in resistivity. Figure 2(c) shows the in-plane resistivity measured at 0, 4, and 7 T ($\parallel b$-axis). As shown in the inset of Fig. 2(c), a gradual change in $\Delta\rho/\Delta T$ was observed at approximately 12 K. This behavior is independent of the applied magnetic field. The similar temperature dependences of FWHM and resistivity indicate that the anomaly that induces spectral splitting does reflect electronic properties.

The field-dependent decrease in resistivity at low temperatures was assigned to SC transition. It is noteworthy that superconductivity sets in from a semiconducting state.
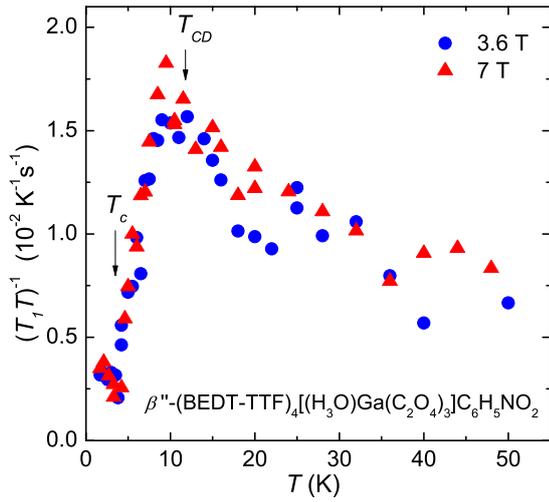
Fig. 3. (Color online) Temperature dependences of $(T_1T)^{-1}$ measured at 3.6 and 7 T. The peak at $(T_1T)^{-1}$ was found at T_{CD} in both fields. The anomaly associated with SC transition was suppressed by the non-Fermi liquid behavior below T_{CD}.

Fig. 4. (Color online) Temperature dependence of NMR shift determined by right peak positions. The decrease in NMR shift below T_c indicates a spin-singlet SC state. The horizontal arrow denotes the chemical shift $\sigma(0.5e)$, which was estimated from the σ of α-(BEDT-TTF)$_2$I$_3$.

We defined T_c as the temperature at which resistivity becomes half of the normal-state values. The actual values are $T_c(7\,T) = 2.8\,K$, $T_c(4\,T) = 3.5\,K$, and $T_c(0\,T) = 6.7\,K$. As T_c for the zero field is much lower than that for the onset of spectral splitting and the splitting is clearly observed even in high fields, SC transition is excluded as the origin of spectral splitting. We can also exclude the magnetic instability by the field-independent FWHM below 12 K. When an internal magnetic field induced by magnetic transition splits the NMR spectrum, the frequency separation (Δf) is independent of the external field. Therefore, when we use the NMR shift ($\delta = \Delta f/f_0$) as the horizontal axis, the separation should decrease in high fields. While in the paramagnetic state, as the magnetization is proportional to the external field, the linewidth in NMR shift is independent of the external field. The field-independent FWHM shown in Fig. 2(b) clearly indicates that the anomaly at 12 K is not caused by the order in spin degrees of freedom. We note that the β''-salt demonstrates two independent charge instabilities at 100 K and $T_{CD} = 12\,K$. As the low-temperature anomaly occurs close to T_c, we suggest a relationship between the SC mechanism and the fluctuations near charge instability.

We investigated the dynamical properties above T_{CD} by measuring T_1 at 3.6 and 7 T. As shown in Fig. 3, $(T_1T)^{-1}$ increases with decreasing temperature, forming a peak at T_{CD}. In general, $(T_1T)^{-1}$ is expressed in terms of the dynamic susceptibility $\chi''(q,\omega)$ as

$$\frac{1}{T_1T} = \frac{2\gamma_n^2 k_B}{(\gamma_e\hbar)^2} \sum_q A_q A_{-q} \frac{\chi''(q,\omega)}{\omega}. \quad (1)$$

In the Fermi liquid state, $(T_1T)^{-1}$ is proportional to the square of the density of states, and is temperature-independent. The temperature dependence of $(T_1T)^{-1}$ is generated by the enhanced magnetic fluctuations in the vicinity of magnetic transition. However, for β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$ with charge instability at T_{CD}, magnetic fluctuations are so weak as they do not induce a strong temperature dependence. Charge fluctuations can be enhanced at T_{CD}, but they cannot be directly detected
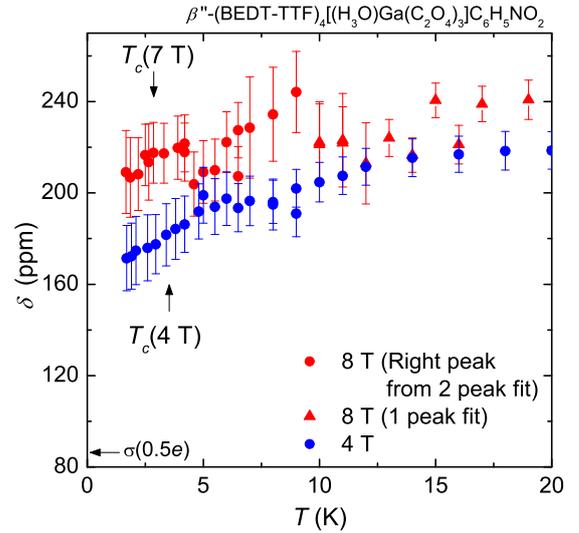
by ^{13}C NMR experiment, because ^{13}C nuclei with a nuclear spin $I = 1/2$ do not have an electric quadrupole moment, which can interact with charge fluctuations. The coupling between charge and magnetic fluctuations is required to increase $(T_1T)^{-1}$ at T_{CD}. One possible interpretation is that the fluctuations in local spin density, which are generated by charge density fluctuations, create fluctuating magnetic fields at the ^{13}C site. Direct observation of charge fluctuations is desired to reveal the mechanisms of spin-charge coupling.

In the charge-disproportionate state, where the NMR spectrum splits, T_1 was obtained using the integrated intensity of two peaks. We also measured T_1 using the right and left halves of the split spectrum, which results in the same value within experimental error. The uniform T_1 values over the entire NMR spectrum allow us to confirm that the spectrum splitting is not caused by macroscopic phase separation, but by the intrinsic instability of the electronic state. Below T_{CD}, the Fermi liquid behavior in $(T_1T)^{-1}$ is absent until the SC state emerges. The non-Fermi liquid behavior is consistent with the semiconducting resistivity just above T_c. Since $(T_1T)^{-1}$ decreases below T_{CD} following a power law close to T^2, a clear anomaly associated with SC transition was not observed at T_c. Note that $(T_1T)^{-1}$ keeps following a power-law behavior even in the SC state, which is suggestive of unconventional superconductivity.

The spin symmetry of Cooper pairs is studied by measuring the spin susceptibility χ_s in the SC state. We determined χ_s from the NMR shift measurement, as the NMR shift is the sum of the Knight shift, which is proportional to χ_s, and the constant chemical shift σ ($\delta = K + \sigma = A\chi_s + \sigma$). The Knight shift is obtained by subtracting σ from the NMR shift. Because σ is specific to the BEDT-TTF molecule and dependent only on the valence of the molecule, we employed a chemical-shift tensor for α-(BEDT-TTF)$_2$I$_3$[26] to evaluate σ for β''-(BEDT-TTF)$_4$-[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$. For the field $H \parallel b$, we find $\sigma(0.5e)$ to be approximately 85 ppm. Figure 4 shows the

temperature dependence of the NMR shift determined by the peak position. Below T_{CD}, we used right-peak positions because the NMR shift variation associated with charge disproportionation is small for this peak. At 4 T, the reduction in NMR shift was observed below 4 K. At 7 T, only a tiny reduction was detected below 2.5 K, because T_c was suppressed by magnetic fields. The extrapolation of the NMR shift toward 0 K does not reach $\sigma(0.5e) = 85$ ppm even at low fields. This is ascribed to the modification of σ in the charge-disproportionate state. A singlet spin state is suggested for Cooper pairs, as χ_s decreases in the SC state. For a spin-singlet superconductivity, an unconventional SC state, such as the FFLO state, is required to account for the extremely high H_{c2}. NMR spectrum measurements in high magnetic fields are essential to unravel the SC state in high fields.

In β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$, electron–electron correlations become strong at low temperatures so that the conventional Fermi liquid state is violated, and a charge-disproportionate state is realized. At T_{CD}, we observed enhanced magnetic fluctuations possibly induced by charge fluctuations in addition to the semiconducting resistivity. If charge fluctuations are enhanced near T_c, a charge-fluctuation-induced superconductivity can be addressed for β''-(BEDT-TTF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]·C$_6$H$_5$NO$_2$, as theoretically predicted for α- and θ-salts.[11,13] In α-salts, charge instability is observed at rather high temperatures exceeding 50 K, while superconductivity occurs at $T_c \simeq 1$ K. Contrastingly, in β''-salts, T_{CD} is suppressed to 12 K, which is close to T_c. Low-energy charge fluctuations may induce a high T_c in β''-salts.

In conclusion, the origin of NMR spectral splitting at T_{CD} was ascribed to a charge instability, because FWHM is independent of the external field. Although $(T_1T)^{-1}$ measurements at the ^{13}C site can detect only magnetic fluctuations, the observed increase in $(T_1T)^{-1}$ is associated with charge fluctuations as $(T_1T)^{-1}$ shows a maximum at T_{CD}. Below T_{CD}, the non-Fermi liquid behavior is observed and superconductivity sets in at $T_c \simeq 7$ K, where the fluctuations were still enhanced. We propose a relationship between charge fluctuations and superconductivity. The NMR shift decreases in the SC state, which is suggestive of a spin-singlet SC state. In order to understand the extremely high H_{c2}, an unconventional SC state, such as the FFLO state, should be taken into account.

1) F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer: Phys. Rev. Lett. **43** (1979) 1892.
2) N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich: Nature **394** (1998) 39.
3) D. Jérome, A. Mazaud, M. Ribault, and K. Bechgaard: J. Phys. Lett. **41** (1980) 95.
4) J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W.-K. Kwok, M.-H. Whangbo, and J. E. Schirber: Science **252** (1991) 1501.
5) S. Murakami and N. Nagaosa: J. Phys. Soc. Jpn. **69** (2000) 2395.
6) A. T. Holmes, D. Jaccard, and K. Miyake: Phys. Rev. B **69** (2004) 024508.
7) K. Miyagawa, A. Kawamoto, and K. Kanoda: Phys. Rev. B **62** (2000) R7679.
8) Y. Takano, K. Hiraki, H. M. Yamamoto, T. Nakamura, and T. Takahashi: Synth. Met. **120** (2001) 1081.
9) H. Nishikawa, Y. Sato, K. Kikuchi, T. Kodama, I. Ikemoto, J. Yamada, H. Oshio, R. Kondo, and S. Kagoshima: Phys. Rev. B **72** (2005) 052510.
10) N. Morinaka, K. Takahashi, R. Chiba, F. Yoshikane, S. Niizeki, M. Tanaka, K. Yakushi, M. Koeda, M. Hedo, T. Fujiwara, Y. Uwatoko, Y. Nishio, K. Kajita, and H. Mori: Phys. Rev. B **80** (2009) 092508.
11) J. Merino and R. H. McKenzie: Phys. Rev. Lett. **87** (2001) 237002.
12) H. Watanabe and M. Ogata: J. Phys. Soc. Jpn. **74** (2005) 2901.
13) J. Merino, A. Greco, N. Drichko, and M. Dressel: Phys. Rev. Lett. **96** (2006) 216402.
14) M. Tanaka, K. Yamamoto, M. Uruichi, T. Yamamoto, K. Yakushi, S. Kimura, and H. Mori: J. Phys. Soc. Jpn. **77** (2008) 024714.
15) S. Kaiser, M. Dressel, Y. Sun, A. Greco, J. A. Schlueter, G. L. Gard, and N. Drichko: Phys. Rev. Lett. **105** (2010) 206402.
16) M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse, and P. Guionneau: J. Am. Chem. Soc. **117** (1995) 12209.
17) H. Akutsu, A. Akutsu-Sato, S. S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A.-K. Klehe, J. Singleton, D. A. Tocher, M. R. Probert, and J. A. K. Howard: J. Am. Chem. Soc. **124** (2002) 12430.
18) A. I. Coldea, A. F. Bangura, J. Singleton, A. Ardavan, A. Akutsu-Sato, H. Akutsu, S. S. Turner, and P. Day: Phys. Rev. B **69** (2004) 085112.
19) A. F. Bangura, A. I. Coldea, J. Singleton, A. Ardavan, A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, T. Yamamoto, and K. Yakushi: Phys. Rev. B **72** (2005) 014543.
20) A. M. Clogston: Phys. Rev. Lett. **9** (1962) 266.
21) P. Fulde and R. A. Ferrell: Phys. Rev. **135** (1964) A550.
22) A. I. Larkin and Y. N. Ovchinnikov: Zh. Éksp. Teor. Fiz. **47** (1964) 1136 [Sov. Phys JETP **20** (1965) 762].
23) G. E. Pake: J. Chem. Phys. **16** (1948) 327.
24) A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda: Phys. Rev. B **52** (1995) 15522.
25) M. Yamashita, A. Kawamoto, and K. Kumagai: Synth. Met. **133–134** (2003) 125.
26) T. Kawai and A. Kawamoto: J. Phys. Soc. Jpn. **78** (2009) 074711.