

Charge disproportionation and inversion symmetry breaking in organic conductor α -(BEDT-TTF)₂RbHg(SCN)₄

Takuma Kawai and Atsushi Kawamoto*

Division of Physics, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060-0810, Japan

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The quasi-two-dimensional organic conductor α -(BEDT-TTF)₂RbHg(SCN)₄ has been investigated by ¹³C-NMR using a field parallel to the ac plane of 9.4 T. We observed no enhancement of $(T_1T)^{-1}$ at 12 K or isotropic reduction of spin susceptibility below 12 K, indicating that spin-density wave formation did not occur at 12 K. Above 100 K, a decrease of spin susceptibility was observed at the C site and a complementary increase was observed at the A and A' sites, suggesting charge disproportionation due to off-site Coulomb interactions. Below 12 K, the spectrum showed broadening and splitting of peaks. These findings indicate that inversion symmetry breaking in charge-density wave instability occurs at low temperatures.

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I. INTRODUCTION

The α -(BEDT-TTF)₂MHg(SCN)₄ (M =Rb, K, NH₄) compounds have a structure consisting of alternating conducting sheets of BEDT-TTF (bis-ethylenedithio-tetrathiafulvalene) and insulating sheets of anion along the b axis, resulting in a pair of one-dimensional open Fermi surfaces and a two-dimensional closed Fermi surface.¹ While these salts have the same structure, their electrical properties differ depending on the anion. The M =K and M =Rb salts remain metallic at all temperatures, whereas the M =NH₄ salt shows superconductivity below 1.1 K.² The title compound, the M =Rb salt, and the M =NH₄ salt, have been reported to show density waves in the ground state at temperatures below 12 and 8 K, respectively. Moreover, several anomalies have been observed below T_{DW} , including the anisotropy of susceptibility,³ steplike electrical resistance,⁴ and an increase in the Hall coefficient.⁵ Hence, a correlation between these anomalies and superconductivity was expected. These anomalous properties may be due to the nesting instability of one-dimensional open Fermi surfaces. The likelihood of a spin-density wave (SDW) state is suggested by studies of the anisotropy of magnetic susceptibility,³ muon spin rotation (μ SR),⁶ torque measurements,⁷ and millimeter-wave magnetoabsorption.⁸ In contrast, the likelihood of a charge-density wave (CDW) state is suggested by NMR (nuclear magnetic resonance),⁹ high-field measurements,¹⁰⁻¹³ and x rays.¹⁴ In a typical CDW, the coherence length of the modulation is enhanced at the transition temperature. In this material, however, the only enhancement of intensity of reflection occurs below 12 K, whereas, at 50 K, the coherence length increases to at most twice its value at room temperature, but it is not enhanced around 12 K.¹⁴ Moreover, in the low-temperature phase, the occurrence of the quantum Hall effect was suggested by magnetization measurements.¹⁵ In the salt α -(BEDT-TTF)₂I₃, which has the same sheet structure as α -(BEDT-TTF)₂MHg(SCN)₄, the charge ordering (CO) state due to off-site Coulomb interaction was proposed theoretically¹⁶ and confirmed by Raman scattering¹⁷ and x-ray studies,¹⁸ and breaking inversion symmetry was indicated by second harmonic generation (SHG) measurements.¹⁹ In α -(BEDT-TTF)₂MHg(SCN)₄, the possi-

bility of charge disproportionation (CD) in the high-temperature phase is indicated by infrared spectra.^{20,21} However, the relationship between CD and CDW is not so clear. It is therefore of interest to determine the contribution of the off-site Coulomb interaction to the α -(BEDT-TTF)₂MHg(SCN)₄ system and assess the relationship between CDW and CO.

II. EXPERIMENT

We therefore utilized ¹³C-NMR to investigate the ground state of the M =Rb salt in the low-temperature phase. ¹³C-NMR spectra were determined using a single crystal, which was enriched with ¹³C isotopes on only one side of the central double-bonded carbon sites of BEDT-TTF to prevent spectrum splitting from the Pake doublet. A magnetic field of about 9.4 T (corresponding to a resonance frequency of 100.7 MHz) was applied parallel to the conducting layer. The spectra and spin-lattice relaxation rate T_1 were measured using a spin-echo method and a saturation recovery method. The NMR shift was evaluated relative to tetramethylsilane (TMS). To clarify the characteristic features of the density wave, measurements were performed under slow cooling conditions (1 K/min) because physical properties significantly depend on cooling rate.¹⁴

III. RESULT AND DISCUSSION

Previous ¹³C-NMR spectra of this salt were determined only below 100 K.⁹ As these spectra were determined using a molecule enriched on both sides of the central C=C bond under a field perpendicular to the ac plane, the assignment of peaks was unclear. As shown in Fig. 1, α -(BEDT-TTF)₂RbHg(SCN)₄ has four BEDT-TTF molecules (A, A', B, C) in a unit cell. The A and A' molecules are in a relationship of inversion symmetry, while the B and C molecules are present at the inversion center. Therefore, three of these molecules, A, B, and C, are crystallographic and magnetically independent. Since the A molecule is not present on the inversion center, the two carbon sites on the central double bond are nonequivalent, and the two peaks, A-a and A-b, are expected from molecule A. In contrast,

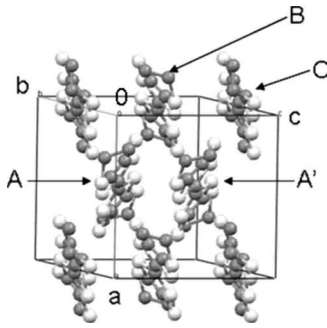


FIG. 1. Crystal structure of α -(BEDT-TTF) $_2$ RbHg(SCN) $_4$.

molecules B and C are on an inversion center, so the two central C=C atoms are equivalent. As a result, there are four independent ^{13}C sites, A-a, A-b, B, and C, in this crystal and four peaks should be observed in NMR spectra.

As shown in Fig. 2, NMR measurements performed under the same conditions as previously used confirmed the decrease in spin susceptibility. However, only two peaks were observed, as shown in Fig. 2(a). Peak assignment in Fig. 2 was decided by rotating the field from the parallel direction to the direction vertical to the ac plane and comparing these results with the results of the in-plane experiment described below.

In another configuration, however, four peaks were observed at room temperature [Fig. 3(b)]. In order to assign peaks, we measured the angular dependence of the NMR shift in the ac plane using the $M=\text{NH}_4$ salt, which gave the same spectrum at room temperature as the $M=\text{Rb}$ salt. The $M=\text{NH}_4$ salt was used because its crystal size is larger than that of the Rb salt, thus reducing the measuring time. Under conditions in which the field was parallel to the ac plane, due to the large contribution of $2p_z$ to the Knight shift, we can easily assign peaks. As the A-a and A-b sites are in the same molecule A and the p_z direction of the two sites are parallel to each other, the angular dependence of A-a and A-b were found to vary with the same phase. Therefore, the open

circles in Fig. 3(a) can be assigned to the A-a sites and the solid circles to the A-b sites. The two remaining sites, B and C, could be assigned by calculating the phase between the direction of the p_z orbital of each molecule and the magnetic field. When the field was parallel to the p_z orbital, the NMR shift was maximized, whereas when the external magnetic field was perpendicular to the direction of the p_z orbital, the NMR shift was minimized. The projection of the angle between the p_z orbitals of molecules A and B to the ac plane and A and C to the ac plane were 77.00° and 70.55° , respectively. Therefore, the phase difference of the NMR shift in the B site should be about 7 greater than the shift in the C site. Thus, we could assign the solid squares and open pentacles in Fig. 3(a) to sites B and C, respectively.

Figure 4 shows the temperature dependence of the NMR shift in a magnetic field parallel to the $[\bar{1}01]$ direction which corresponds to the angle of $\theta=0^\circ$ in Fig. 3(a). In this direction, the four peaks were well separated and we could clearly assess the properties of each peak. Below 100 K, our findings were consistent with those reported previously.⁹ Molecular properties were almost temperature independent from 100 to 12 K, and the NMR shift at all sites decreased below 12 K. The NMR shift (δ) is described by the sum of the Knight shift (K) due to spin susceptibility and the chemical shift (σ) due to the charge on the orbit and can be expressed using the equation $\delta=K+\sigma$. If the chemical shift is about 100 ppm,²² the spin susceptibility below 12 K was reduced 40%. Together with the result from Fig. 2, these findings suggest that the Knight shift and spin susceptibility were almost isotropic. In contrast, static susceptibility, as measured by the superconducting quantum interference device (SQUID) magnetometer, showed strong anisotropy.³ Therefore we must consider the difference between the Knight shift and the static susceptibility. Static susceptibility χ_{static} can be expressed as the sum of spin susceptibility χ_{spin} and the orbital part χ_{orb} , i.e., $\chi_{\text{static}}=\chi_{\text{spin}}+\chi_{\text{orb}}$. Because there was no anisotropy in spin susceptibility, the anisotropy of static susceptibility is thought to be due to the anisotropy of the

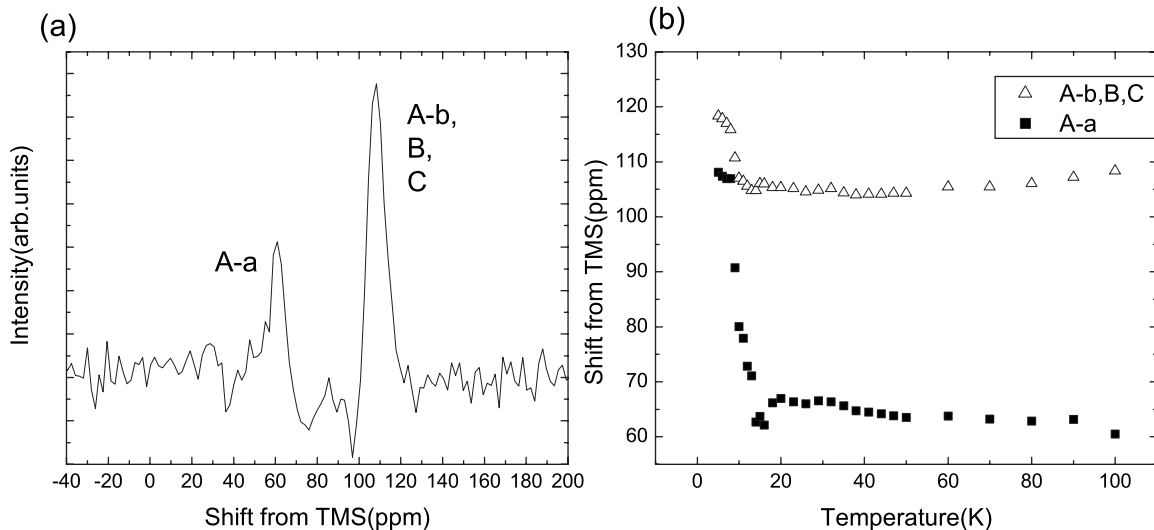


FIG. 2. (a) ^{13}C -NMR spectra at 100 K. (b) Temperature dependence of the NMR shift in the field perpendicular to the ac plane [the shift from tetramethylsilane (TMS) is shown].

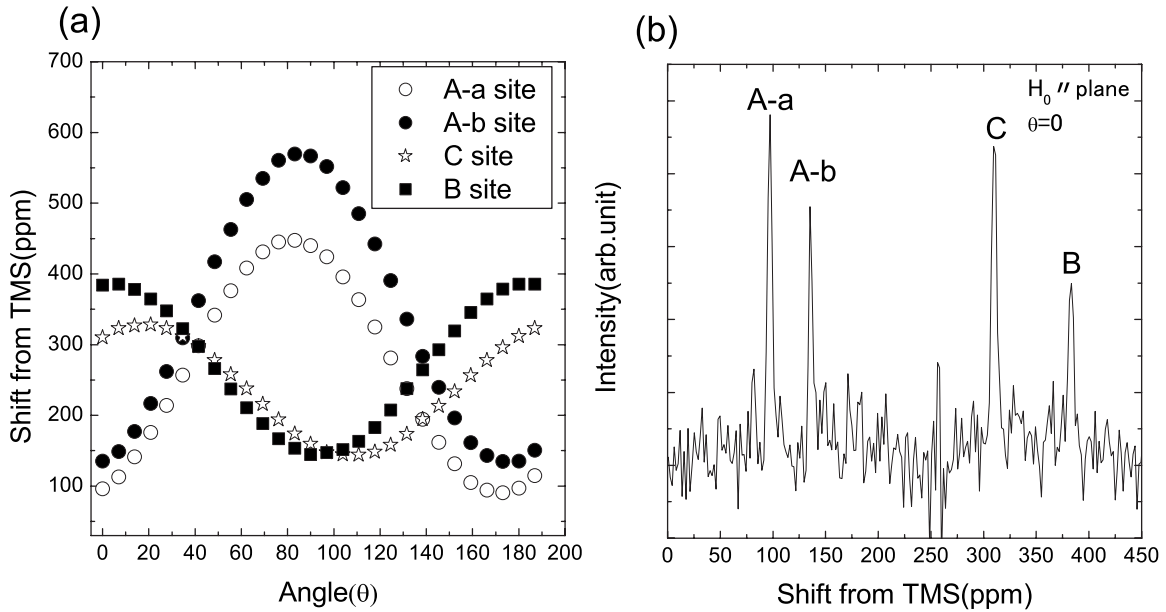


FIG. 3. (a) Angular dependence of the NMR shift of α -(BEDT-TTF)₂NH₄Hg(SCN)₄ in the ac plane. (b) The spectrum with a field applied to $[\bar{1}01]$ of 9.4 T which corresponds to the angle of $\theta=0^\circ$.

orbital part. The isotropic reduction of the Knight shift suggests the formation of a partial spin singlet structure below 12 K and indicates that the Fermi surface may be a reconstructed surface due to CDW. However, at 12 K, an increase of three-dimensional coherency was not observed.¹⁴ The temperature dependence of $(T_1T)^{-1}$ is shown in Fig. 5. Temperature independent properties were observed from 100 to 12 K, but were reduced below 12 K. This reduction is comparable to the results of the NMR shift. The absence of enhancement at 12 K was also confirmed in the magnetic field perpendicular to the ac plane. These results indicate that second-order phase transition due to SDW formation does not occur.

There was another important, as yet unreported, NMR anomaly above 100 K. The shift at the C site obviously dif-

fered from that at the other sites. As shown in Fig. 4, the shift at the C site showed a temperature dependent decrease from room temperature to 100 K. This decreased NMR shift at the C site indicates a decrease in local spin susceptibility at the same site. Assuming that σ is about 100 ppm, we evaluated K using the equation $K = \delta - \sigma$. The decreased NMR shift at the C site suggested that the local spin susceptibility at this site was reduced to 1/3 of its original value at room temperature. The T variation of the NMR shift at the C site from room temperature down to 100 K is about -200 ppm, that of the B site is about $+30$ ppm, and that of A-a is about -30 ppm. Because the ratio of the hyperfine coupling constants of the B and C sites and that of the A-a site is $-3:1$, the reduction at the A-a site corresponds to a shift of $-3 \times -30 = +90$ ppm in the C site. Since the A and A' molecules are equivalent, this shift corresponds to an increase of $+90$

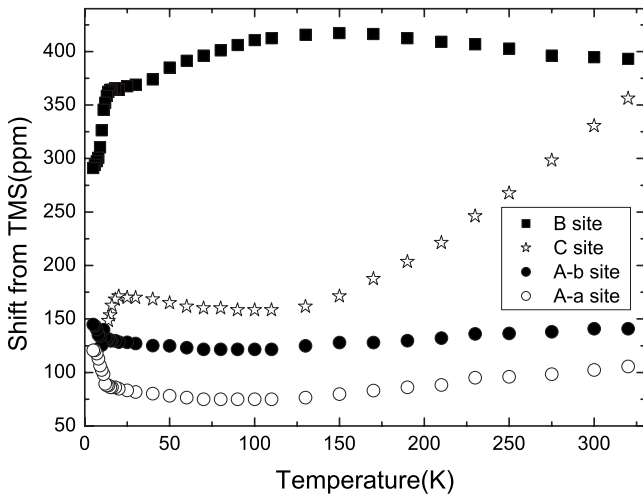


FIG. 4. Temperature dependence of the NMR shift of α -(BEDT-TTF)₂RbHg(SCN)₄ in a field parallel to the $[\bar{1}01]$ direction.

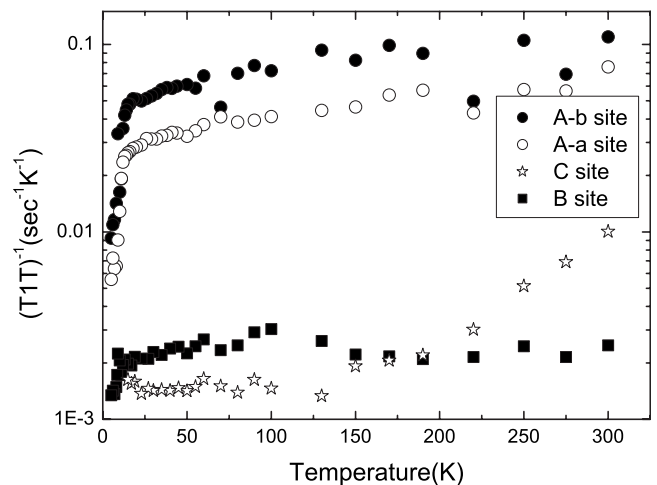


FIG. 5. Temperature dependence of ¹³C nuclear spin-lattice relaxation rate.

$\times 2 = +180$ ppm. Therefore, the spin susceptibility of the C site moves mainly into the A and A' molecules. This disproportionation seems to be consistent with the reflection spectrum in the vicinity of 100 K reported by Dressel *et al.* It is important that CD develops without breaking $P\bar{1}$ symmetry. That is, CD does not occur between A and A' molecules while retaining crystal symmetry. The previous NMR study below 100 K assumed that the B and C sites are equivalent;⁹ however, below 100 K, the spin susceptibility at the B and C sites actually differs by threefold. The reduction of the local spin susceptibility of the C site was also confirmed by $(T_1T)^{-1}$. Considering the Korringa relationship between the relaxation rate T_1 and χ_{spin} , $(T_1T)^{-1} \propto \chi_{\text{spin}}^2$, we could also evaluate the reduction of spin susceptibility from $(T_1T)^{-1}$. As shown in Fig. 5, the $(T_1T)^{-1}$ of the C site decreased from room temperature to 100 K, in agreement with the NMR shift. When we compared the value at 100 K with that at room temperature, we found that the spin susceptibility at 100 K was about 1/3 that at room temperature. This corresponds to a decrease in the NMR shift. We also observed similar properties using the $M=\text{NH}_4$ salt. Therefore, our finding suggests that this is a common property of the $\alpha\text{-(BEDT-TTF)}_2\text{MHg(SCN)}_4$ family. The local field at each site is due to spin magnetization on the Fermi level via the hyperfine coupling constant. This constant depends on structure, which does not change significantly in this salt. Therefore in the framework of the band picture, all sites should show the same temperature dependence, and we must consider the mechanism underlying these properties. The same anomaly was also reported in the metallic phase of the $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ salt,²³ which showed a CO transition with inversion symmetry breakage, indicating a connection between the transition and the anomaly in the metallic phase. In the quarter filled system, the off-site Coulomb interaction enhanced the charge disproportionation between the sites,¹⁶ and spin susceptibility at each site showed different temperature-dependent properties. Therefore the anomaly at each site can be explained by the contribution of charge disproportionation. The metallic phase of $\alpha\text{-(BEDT-TTF)}_2\text{MHg(SCN)}_4$ was thought to be that of the simple metal. However, the anomaly at the C site suggests that charge disproportionation contributes to $\alpha\text{-(BEDT-TTF)}_2\text{MHg(SCN)}_4$ as well as to $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$.

Our main purpose was to determine what occurred in the 12 K anomaly. The contribution of charge disproportionation suggests a relationship between DW transition and inversion symmetry. The spectra with a different field direction in the ac plane from 16 to 6 K are shown in Fig. 6. Four peaks, of A-a, A-b, B, and C, were observed at 14 K, whereas each of A-b, B, and C peaks split into two peaks below 10 K. The splitting of peak A-b indicates that the A and A' molecules became crystallographically nonequivalent, i.e., the inversion symmetry between A and A' is broken below 10 K. The splitting of peaks B and C indicates that the inversion symmetry on B and C molecules is broken. In addition, peaks B and C broadened after the transition due to the increase of modulation amplitude. In incommensurate CDW, the line-width of each site is proportional to the hyperfine coupling

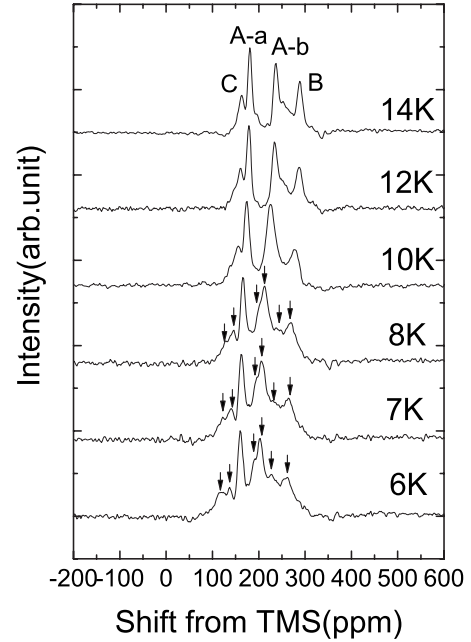


FIG. 6. ^{13}C NMR spectra with a field applied to the angle of $\theta=30^\circ$ at the temperature from 14 to 6 K.

constant. Since the hyperfine coupling constants at sites B and C are larger than at site A, peaks B and C are broader than peak A. This broadening of the NMR spectra is consistent with the incommensurate structural modulation due to CDW instability.

The inversion symmetry breaking in the unit cell was expected to be due to off-site Coulomb interactions and coexistent with the CDW instability. From metallic behavior in the low-temperature phase, the CO state with large charge separation such as $\alpha\text{-(BEDT-TTF)}_2\text{I}_3$ is unlikely and small CD within the band picture is suitable. X-ray results suggested that the unconventional features of the transition are not related to a magnetic component in the density wave modulation because the modulation is already present in the high-temperature metallic phase. Moreover, although the increase of the modulation amplitude was observed, there was no increase of coherency.¹⁴ These may be related to a breakage of symmetry. Without long-range superstructure, the inversion symmetry breaking did not change the translational symmetry and the crystal system. Therefore it modified the transfer integrals between molecules and changed the Fermi surface slightly. As a result, the nesting instability might be enhanced. Electronic states and superconductivity without inversion symmetry have become topics of great interest. Pure triplet superconductivity rarely occurs and the asymmetric Hamiltonian makes a large LS coupling.^{24,25} This disappearance of symmetry may be connected to the anomalous properties of the $M=\text{K}$ and Rb salts in the low-temperature phase and to the superconductivity of the $M=\text{NH}_4$ salt. Assessment of the latter under conditions of superconductivity is now in progress. Further progress in determining the electronic properties of organic conductors in an acentrosymmetric system is desired.

IV. SUMMARY

We performed NMR measurements of α -(BEDT-TTF)₂RbHg(SCN)₄ using a magnetic field parallel to the ac plane. Our findings, together with results of the measurements under two field directions, indicate an isotropic reduction of spin susceptibility below 12 K. In contrast, above 100 K, a decrease in spin susceptibility was observed at the C site and increases were observed at the A, A', and B sites. This redistribution may be due to the contribution of charge disproportionation. However, this behavior does not break the symmetry of the crystal. Moreover, because similar

properties were observed using the $M=\text{NH}_4$ salt, this may be a common property of the α -(BEDT-TTF)₂MHg(SCN)₄ family. Below 12 K, it was suggested that the inversion symmetry in the unit cell was broken from the splitting of peaks and there was broadening of the spectrum due to the development of modulation. Considering that incommensurate structural modulation was observed above 12 K, the anomaly at 12 K is likely to be a phase transition with breakage of symmetry, which enhanced the modulation.

This result suggested that the T_{DW} anomaly was not the crossover behavior but the phase transition with the inversion symmetry breaking.

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

- ¹H. Mori, S. Tanaka, M. Oshima, G. Saito, T. Mori, Y. Maruyama, and H. Inokuchi, *Bull. Chem. Soc. Jpn.* **63**, 2183 (1990).
- ²H. H. Wang, K. D. Carlson, U. Geiser, W. K. Kwok, M. D. Vashon, J. E. Thompson, N. F. Larsen, G. D. McCabe, R. S. Hulscher, and J. M. Williams, *Physica C* **166**, 57 (1990).
- ³T. Sasaki and N. Toyota, *Synth. Met.* **42**, 2211 (1991).
- ⁴T. Sasaki, N. Toyota, M. Tokumoto, N. Kinoshita, and H. Anzai, *Solid State Commun.* **75**, 93 (1990).
- ⁵T. Sasaki, S. Endo, and N. Toyota, *Phys. Rev. B* **48**, 1928 (1993).
- ⁶F. L. Pratt, T. Sasaki, N. Toyota, and K. Nagamine, *Phys. Rev. Lett.* **74**, 3892 (1995).
- ⁷P. Christ, W. Biberacher, H. Müller, and K. Andres, *Solid State Commun.* **91**, 451 (1994).
- ⁸S. V. Demishev, A. V. Semeno, N. E. Sluchanko, N. A. Samarin, I. B. Voskoboinikov, V. V. Glushkov, J. Singleton, S. J. Blundell, S. O. Hill, W. Hayes, M. V. Kartsovnik, A. E. Kovalev, M. Kurmoo, P. Day, and N. D. Kushch, *Phys. Rev. B* **53**, 12794 (1996).
- ⁹K. Miyagawa, A. Kawamoto, and K. Kanoda, *Phys. Rev. B* **56**, R8487 (1997).
- ¹⁰J. S. Qualls, L. Balicas, J. S. Brooks, N. Harrison, L. K. Montgomery, and M. Tokumoto, *Phys. Rev. B* **62**, 10008 (2000).
- ¹¹P. Christ, W. Biberacher, M. V. Kartsovnik, E. Steep, E. Balthes, H. Weiss, and H. Müller, *JETP Lett.* **71**, 303 (2000).
- ¹²N. Harrison, L. Balicas, J. S. Brooks, and M. Tokumoto, *Phys. Rev. B* **62**, 14212 (2000).
- ¹³Mark V. Kartsovnik, D. Andres, and W. Biberacher, *C. R. Chim.* **10**, 6 (2007).
- ¹⁴P. Foury-Leykian, S. Ravy, J.-P. Pouget, and H. Müller, *Synth. Met.* **137**, 1271 (2003).
- ¹⁵N. Harrison, A. House, M. V. Kartsovnik, A. V. Polisski, J. Singleton, F. Herlach, W. Hayes, and N. D. Kushch, *Phys. Rev. Lett.* **77**, 1576 (1996).
- ¹⁶H. Seo and H. Fukuyama, *J. Phys. Soc. Jpn.* **66**, 1249 (1997).
- ¹⁷R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, and A. Kawamoto, *Phys. Rev. B* **67**, 224105 (2003).
- ¹⁸T. Kakiuchi, Y. Wakabayashi, H. Sawa, T. Takahashi, and T. Nakamura, *J. Phys. Soc. Jpn.* **76**, 113702 (2007).
- ¹⁹K. Yamamoto, S. Iwai, S. Boyko, A. Kashiawazaki, F. Hiramatsu, C. Okabe, N. Nishi, and K. Yakushi, *J. Phys. Soc. Jpn.* **77**, 074709 (2008).
- ²⁰M. Dressel, N. Drichko, J. Schlueter, and J. Merino, *Phys. Rev. Lett.* **90**, 167002 (2003).
- ²¹N. Drichko, M. Dressel, C. A. Kuntscher, A. Pashkin, A. Greco, J. Merino, and J. Schlueter, *Phys. Rev. B* **74**, 235121 (2006).
- ²²R. Chiba, Doctoral thesis, Gakushuin University, 2002.
- ²³S. Moroto, K.-I. Hiraki, Y. Takano, Y. Kubo, T. Takahashi, H. M. Yamamoto, and T. Nakamura, *J. Phys. IV France* **114**, 399 (2004).
- ²⁴P. W. Anderson, *Phys. Rev. B* **30**, 4000 (1984).
- ²⁵L. P. Gor'kov and E. I. Rashba, *Phys. Rev. Lett.* **87**, 037004 (2001).