

## Deuterated $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br: A system on the border of the superconductor–magnetic-insulator transition

A. Kawamoto

*Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan*

K. Miyagawa and K. Kanoda

*Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*

(Received 25 November 1996)

The electronic state of the deuterated salt of the organic system  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br, has been investigated by dc/ac susceptibility and <sup>1</sup>H/<sup>13</sup>C NMR measurements. We found that the system is situated in the critical region of the transition between a superconducting phase with a  $T_C$  of  $\sim 11.5$  K and an antiferromagnetic phase with a  $T_N$  of 14–15 K. It was also found that the rapid cooling through 80 K drives the superconducting phase into the magnetic phase, that is discussed in the light of the role of disorder near the Mott transition. [S0163-1829(97)08221-0]

Among many BEDT-TTF compounds, a family of  $\kappa$ -(BEDT-TTF)<sub>2</sub>X provide quasi-two-dimensional  $\pi$  electron systems exhibiting metallic, superconducting, and insulating phases. At ambient pressure, the salts with  $X = \text{Cu}(\text{NCS})_2$  (Ref. 1) and  $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  (Ref. 2) have superconducting ground states, while the  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$  salt<sup>3</sup> is an insulator with antiferromagnetic ordering.<sup>4</sup> The latter compound, when pressurized, converts suddenly into a superconducting phase with a transition temperature,  $T_C$ , of 13 K, which is the highest among the organic superconductors.<sup>3,5</sup> Under further pressure,  $T_C$  decreases gradually.<sup>5</sup> Thus, this family covers the critical region of a superconductor–magnetic-insulator transition. The <sup>13</sup>C-NMR study of these salts revealed enhancement of antiferromagnetic spin fluctuations even in the superconducting salts.<sup>6–9</sup> This fact and a more detailed characterization of the magnetic phase<sup>4</sup> supported that the electron correlation is a driving force of the metal-insulator transition and led us to view it as the Mott transition; the difference of an anion gives a slight change of the BEDT-TTF arrangement within the layer and results in a variation of the bandwidth through modification of the transfer integral.<sup>10</sup> Theoretical investigations indicate the important role of electron correlation in the metal-insulator transition in this family of compounds.<sup>11,12</sup>

In the meantime, the deuterated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br has been investigated by several researchers<sup>13–17</sup> with particular attention to the superconducting properties such as the isotope effect on  $T_C$ . However, the reproducibility and bulky nature of the results remain unclear. As for resistivity, a serious sample dependence, which ranges from a nonmetal to a superconductor,<sup>13</sup> including the apparently semiconductor-metal-semiconductor-superconductor transition with decreasing temperatures,<sup>14,15</sup> was reported. A small diamagnetic magnetization observed in the superconducting state<sup>13,16</sup> implies imperfect superconducting phase. (Other works gave only the onset of  $T_C$  (Ref. 17) or magnetization data in an arbitrary unit<sup>15</sup>). A naive interpretation of these observations may be in terms of deterioration of the sample quality. On

the other hand, the system is suggested to be on the boundary between superconductor and insulator.<sup>13</sup>

To clarify the above problem experimentally, we have prepared crystals of the deuterated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br (abbreviated to  $d_8$ -Cu[N(CN)<sub>2</sub>]Br hereafter) in several separate batches and measured dc and ac susceptibility to characterize the normal and superconducting properties, respectively. In addition, we performed <sup>1</sup>H and <sup>13</sup>C NMR measurements for microscopic characterization of the electronic state. It is found that every crystal contains superconducting and nonsuperconducting components with a comparable volume fraction and that the latter phase has a magnetic character similar to  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl; antiferromagnetic ordering with spin canting. These findings demonstrate that this system is situated just in the critical region of the superconductor–magnetic-insulator transition in  $\kappa$ -(BEDT-TTF)<sub>2</sub>X. A drastic effect of the rapid cooling on the superconducting and magnetic phases is also found. These results give a solution to something mysterious so far on this salt.

The crystals of the  $d_8$ -Cu[N(CN)<sub>2</sub>]Br salt were grown by the conventional electrochemical oxidation with use of the deuterated BEDT-TTF molecules. For the purpose of <sup>13</sup>C-NMR, we also synthesized BEDT-TTF molecules where 99% of the central double-bonded carbon sites and 98% of the hydrogen sites are simultaneously substituted by <sup>13</sup>C and deuterium, respectively. The dc and ac susceptibility was measured for five single crystals and two powdered samples with a SQUID magnetometer. The <sup>13</sup>C and <sup>1</sup>H NMR spectra and nuclear spin-lattice relaxation rate,  $T_1^{-1}$ , were measured for one powdered sample; <sup>1</sup>H-NMR were observable at the remaining hydrogen sites of 2%. The spectra were obtained by FFT of the quadrature-detected echo signals.

Figure 1 shows the dc susceptibility of the powdered sample of a slowly cooled ( $\sim 0.2$  K/min)  $d_8$ -Cu[N(CN)<sub>2</sub>]Br salt along with the data of the nondeuterated Cu[N(CN)<sub>2</sub>]Br salt ( $h_8$ -Cu[N(CN)<sub>2</sub>]Br and the Cu[N(CN)<sub>2</sub>]Cl salt at a field of 1 T. Above  $\sim 35$  K, the three

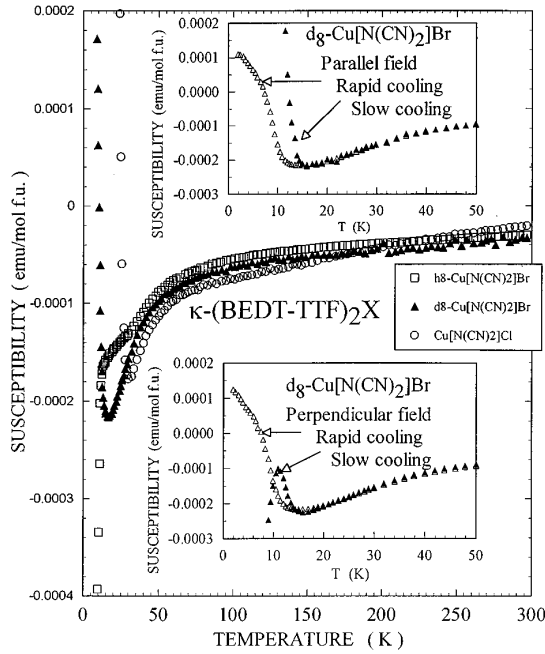


FIG. 1. Temperature dependence of the dc susceptibility of  $\kappa$ -(BEDT-TTF) $_2$ X. The diamagnetic core-contribution is  $-4.7 \times 10^{-4}$  emu/mol f.u. for the three salts. The upper and lower insets show the results of deuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br in a field parallel and perpendicular to the layer, respectively.

systems trace nearly the same susceptibility curve, which is characterized by the steep decrease at lower temperatures. The metallic  $h_8$ -Cu[N(CN) $_2$ ]Br salt has a kink at 35 K, while the nonmetallic Cu[N(CN) $_2$ ]Cl salt exhibits a huge increase above 30 K,<sup>4,18</sup> which is attributed to spin canting in the antiferromagnetically ordered state. The  $d_8$ -Cu[N(CN) $_2$ ]Br salt shows a similar behavior to the Cu[N(CN) $_2$ ]Cl salt except that the increase occurs around 16 K. Therefore it is reasonable to consider that the  $d_8$ -Cu[N(CN) $_2$ ]Br salt contains a considerable fraction of the electronic phase with the same magnetic character as in the Cu[N(CN) $_2$ ]Cl salt.

The dc susceptibility of the  $d_8$ -Cu[N(CN) $_2$ ]Br salt after slow (0.2 K/min) and rapid (100 K/min) cooling is shown in the insets of Fig. 1, where the field was applied parallel (upper inset) or perpendicular (lower inset) to the layer. In both field orientations, the cooling condition influences seriously the susceptibility. After the slow cooling, susceptibility shows a minimum at 15–16 K, below which a sharp increase occurs in both field orientations. The decrease of susceptibility below 11 K in the perpendicular field is due to the diamagnetism of the superconducting component. In the parallel field geometry, diamagnetic shielding is not effective because of the long out-of-plane (Josephson-like) penetration depth [0.2 mm for  $h_8$ -Cu[N(CN) $_2$ ]Br salt (Ref. 19) and possible realization of the vortex lock-in state.<sup>20</sup> This explains why the superconducting diamagnetism does not manifest itself clearly in this field configuration. The absence of decrease of the weak ferromagnetism down to 5 K (the data below 10 K are out of range of the inset) in the parallel configuration suggests that the apparently subsequent transitions in the perpendicular configuration result from a superposition of the magnetic transition and the superconducting one in separate portions of the sample volume. After the

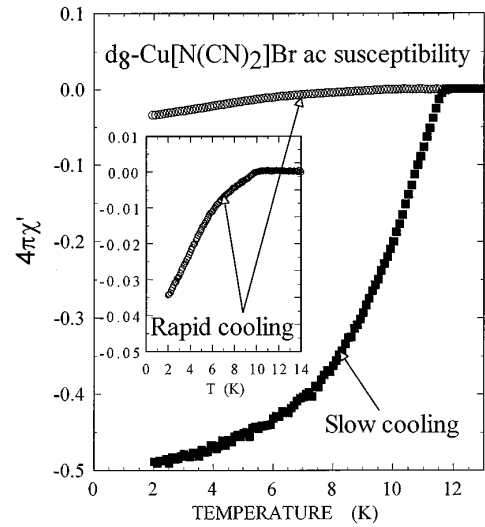


FIG. 2. ac susceptibility of a deuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br crystal after slow or rapid cooling. The ac field is applied perpendicular to the layer. The results after rapid cooling are expanded in the inset.

rapid cooling, the weak ferromagnetism is diminished. At first sight this may be interpreted as a sign of decreased fraction of the magnetic phase. However, this is not the case, as is discussed below.

The ac susceptibility of the  $d_8$ -Cu[N(CN) $_2$ ]Br salt is presented in Fig. 2, where an ac field of 0.1 Oe and 1 Hz is applied perpendicular to the conducting layer. Taking into account the demagnetization effect coming from the disc shape of the sample, the perfect diamagnetism corresponds to a value around 2.5 in the vertical axis in the figure. In the case of the slow cooling, the onset of superconductivity occurs at 11.5 K, which is not so different from the  $T_C$  of the  $h_8$ -Cu[N(CN) $_2$ ]Br salt, while the gradual transition toward low temperatures implies the inhomogeneous nature of the superconductivity. The low-temperature saturation value means a superconducting volume fraction of 20% at most. By the rapid cooling, the fraction diminishes to 1–2% and the onset decreases down to 10 K, as seen in the inset. Considering that the electronic specific heat of the rapidly cooled  $d_8$ -Cu[N(CN) $_2$ ]Br salt does not have any finite  $\gamma$  value,<sup>21</sup> the missing part of the superconducting phase is considered to convert to the insulating magnetic phase, not to normal metallic phase. This is consistent with the  $^{13}\text{C}$ -NMR results described below. From these results, the observed depression of the weak ferromagnetism by rapid cooling should be taken as a negative effect of cooling on the spin canting and/or the antiferromagnetically ordered moment instead of decrease of the magnetic phase fraction.

The above results of the dc/ac susceptibility including the cooling rate dependence were essentially reproducible in all the crystals measured although the volume fraction of the two phases was sample dependent.

The implication that a magnetic phase is present with the superconducting phase in the  $d_8$ -Cu[N(CN) $_2$ ]Br salt was further explored by the  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements. Figure 3 shows the  $^1\text{H}$  NMR spectra of the powdered sample, which is slowly cooled at a rate of the order of 0.1 K/min, at a field of 2.8 T. At high temperatures above 14 K, the spectra

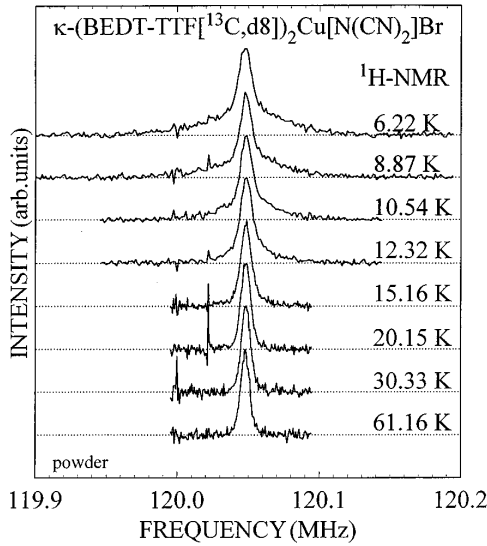


FIG. 3.  $^1\text{H}$ -NMR spectra of deuterated  $\kappa$ -(BEDT-TTF) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  powder after slow cooling.

form a sharp single line with a width of 10 kHz. At room temperature, the line becomes further narrower due to the ethylene vibrations. Below 14 K, a part of the spectra becomes broadened, being superposed on the line remaining narrow. The broadening indicates generation of inhomogeneous local field. The broadening due to the vortex structure is expected to be negligible in the temperature range reported here ( $>6$  K in Fig. 3) because of the motional narrowing due to thermal fluctuations of vortices such as melting. Indeed, our single-crystal measurements on hydrogenated  $\kappa$ -(BEDT-TTF) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  at 1.5 T showed no practical broadening (less than 5 kHz) at least down to 6 K. Our observation of broadening in the deuterated salt is of the order of 100 kHz, which is nearly equal to the line splitting in the single crystal of the antiferromagnetic material  $\kappa$ -(BEDT-TTF) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ .<sup>4</sup> Thus, it is concluded that the line remaining narrow is from the superconducting phase and the broader line is from the antiferromagnetic phase. The decomposition of the spectral intensity into the two lines at the lowest temperature suggests that about 75% of the sample volume is occupied by the magnetic phase. The broadening of spectra was also observed in  $^{13}\text{C}$  NMR.

Next, the  $^{13}\text{C}$  nuclear spin-lattice relaxation rate,  $T_1^{-1}$ , is presented. The hyperfine coupling tensor of the central carbon sites in the BEDT-TTF molecule has anisotropic terms comparable or larger than the isotropic terms.<sup>6–9</sup> Since the former gives the angular dependence of the nuclear relaxation rate against the applied field and the two sites of  $^{13}\text{C} = ^{13}\text{C}$  in the BEDT-TTF molecule have different hyperfine coupling tensors, the nuclear relaxation curve in the powdered sample does not follow a single exponential function, as was observed in the previous and present experiments. as in a previous study,<sup>6,7</sup> we define the nuclear relaxation rate by the initial slope of the relaxation curve, which corresponds to the solid angle average of the relaxation rate. In Fig. 4, we show  $^{13}\text{C}$  NMR  $(T_1T)^{-1}$  of the powdered sample of the  $d_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt as well as the data of the  $h_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  and  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$  salts obtained previously.<sup>7</sup> From room temperature down to 60 K, the data

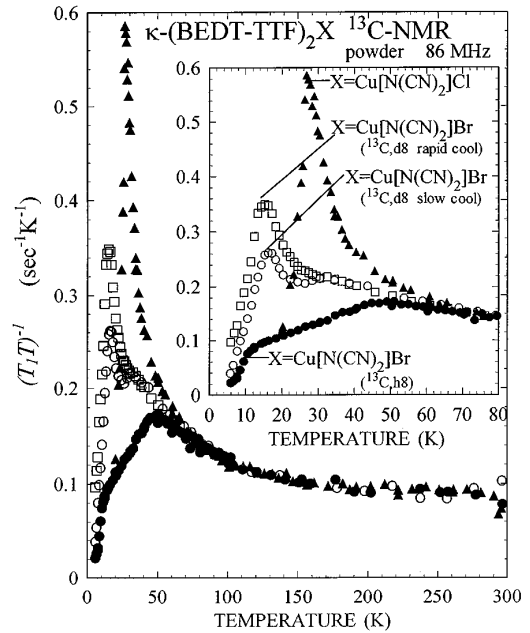


FIG. 4.  $^{13}\text{C}$  nuclear spin-lattice relaxation rate of  $\kappa$ -(BEDT-TTF) $_2\text{X}$ . The low-temperature region is expanded in the inset.

of the  $d_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt are on the universal curve followed by other salts and, below 60 K, are in between the  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$  data reflecting the progressive growth of antiferromagnetic fluctuations followed by the freezing at 27 K and the  $h_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  data showing depression of the fluctuations below 50 K. This behavior indicates that the  $d_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt is situated in a critical region between the magnetic insulator,  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$  salt, and the superconductor,  $h_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt. The peak formation around 14–15 K is attributed to the antiferromagnetic transition in the magnetic phase. (It should be noted that the spectra in the ordered state are spread out of a frequency range of  $\pm 150$  kHz covered in the present pulse condition.) Another feature in  $(T_1T)^{-1}$  of the  $d_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt is a hump around 30 K in slow cooling, which becomes less prominent after rapid cooling. (In this experiment, cooling could not be controlled to be as rapid as in the susceptibility measurements; by rapid cooling, we mean the nominal rate of the order of 1 K/min here.) As was seen in the dc/ac susceptibility and  $^1\text{H}$ -NMR spectra, the sample contains magnetic and nonmagnetic (superconducting) phases. Therefore, the determined relaxation rate is the volume average of the values of each phase. With this in mind, the hump can be viewed as a reflection of the  $(T_1T)^{-1}$  profile of the metallic phase, where the depression of  $(T_1T)^{-1}$ , which occurs at 50 K for the  $h_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  salt, is postulated to occur around 30 K. This temperature roughly corresponds to the inflection point of the nonmetal-to-metal crossover in the resistivity behavior observed in Refs. 13–15; the similar correspondence between the crossover in the charge transport and the NMR relaxation anomaly is found in the  $h_8$ - $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  and  $\text{Cu}(\text{NCS})_2$  salts. The appreciable enhancement of  $(T_1T)^{-1}$  with a less prominent hump below 30 K after rapid cooling is reasonably explained by the decreased volume fraction of the metallic (superconducting) phase.

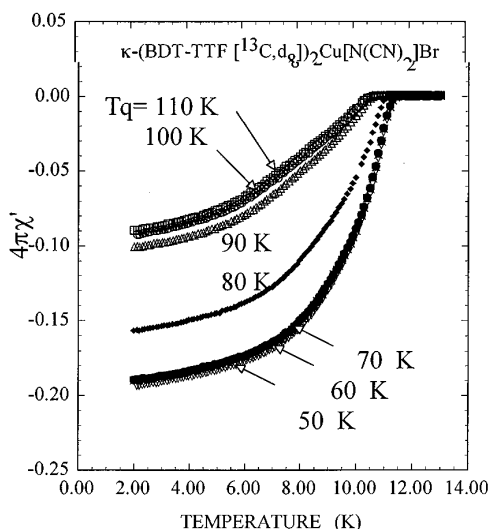


FIG. 5. ac susceptibility of a deuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br crystal after rapid cooling from various  $T_q$ . For details of the process, see text.

Finally, in order to examine what is going on in the process of rapid cooling, we made a series of dc susceptibility measurements for the powdered sample in the following sequence: (i) the sample was cooled slowly at a rate of 0.2 K/min from room temperature down to 13 K so that the slowly cooled state was established as the initial state, (ii) the sample was warmed up to  $T_q$ , followed by rapid cooling from  $T_q$  down to 13 K, and (iii) ac susceptibility was measured to characterize the superconducting volume fraction. The processes of (ii) and (iii) were repeated for elevated  $T_q$  from 20 to 110 K. As seen in Fig. 5, the initial state is kept up to  $T_q$  of 70 K, while it converts into the rapid cooled state if it is quenched from  $T_q$  of higher than 90 K. After this series of quenching experiments, the sample was warmed up to 120 K and then cooled slowly down to 70 K, from which it was rapidly cooled to 6 K. The subsequent ac susceptibility measurement at 6 K reproduced the result of the initial state set by the slow cooling. (In this experiment, the cooling rate from  $T_q$  is limited to  $\sim 20$  K/min at most by the cooling power of the SQUID system and not so fast as the case in Figs. 1 and 2, where the crystal was transferred rapidly from the room-temperature area down to the low-temperature area at a rate of  $\sim 100$  K/min. This is the reason why the superconducting volume fraction in Fig. 5 remains appreciable

compared with the rapid cooling case in Fig. 2.) From these results, it is concluded that the temperature window through which the slow and rapid cooling makes a difference to the ground state of the sample is around 80 K. A similar kind of rapid cooling effect is often encountered in several organic materials and is attributed to the introduction of various kinds of disorder in most cases. Related phenomena at the relevant temperature are reported; a kink in resistivity and a sharp anomaly in the thermal expansion coefficient at 80 K in Ref. 22, in which the thermally induced order-disorder transition in the ethylene conformation is argued to occur at this temperature. There may be a case that the rapid cooling through this temperature window leads the disorder to be frozen even at the lower temperatures. In any case, the issue of the phase transformation from the superconductor to the magnetic insulator by the rapid cooling can be addressed as the effect of some disorder on the superconducting phase. The effect of disorder can be either by itself or through the volume change of the unit cell. It is noteworthy that there is a theoretical suggestion that the disorder in the metallic state near the antiferromagnetic Mott insulator induces staggered moment.<sup>23</sup> The suppression of the spin canting and/or moment by the rapid cooling is not explained by the volume effect alone but may be a manifestation of the effect of disorder itself on the antiferromagnetic phase.

In conclusion, the present susceptibility and NMR measurements demonstrated that the deuterated  $\kappa$ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$ ]Br is a material situated just in a critical region of the Mott-like superconductor–magnetic-insulator transition in quasi-two-dimensional  $\pi$  electron systems with the  $\kappa$ -type dimeric arrangement of the molecules. Rapid cooling, which possibly introduces disorder to the electronic system, drives the superconducting phase into the antiferromagnetic phase. More detailed characterization of this antiferromagnetic phase, such as the moment and commensurability of the magnetic order, will give further information on the nature of this superconductor–magnetic-insulator transition.

The authors thank Y. Nakazawa for helpful discussion on thermodynamic aspect. K.K. is grateful to H. Kino, H. Fukuyama, and K. Miyake for enlightening discussion. K. Kato and T. Takayama (IMS) are acknowledged for their technical support in low-temperature experiments. This work was supported by Grant-in-Aid for Scientific Research Nos. 06243102 (Priority Area “Novel Electronic States in Molecular Conductors”) and 06452064 from the Ministry of Education, Science, Sports and Culture, Japan.

<sup>1</sup>H. Urayama *et al.*, Chem. Lett. **1988**, 55 (1988).

<sup>2</sup>A. M. Kini *et al.*, Inorg. Chem. **29**, 2555 (1990).

<sup>3</sup>J. M. Williams *et al.*, Inorg. Chem. **29**, 3272 (1990).

<sup>4</sup>K. Miyagawa *et al.*, Phys. Rev. Lett. **75**, 1174 (1995).

<sup>5</sup>J. E. Schirber *et al.*, Phys. Rev. B **44**, 4666 (1991).

<sup>6</sup>A. Kawamoto *et al.*, Phys. Rev. Lett. **74**, 3455 (1995); **75**, 3587 (1995).

<sup>7</sup>A. Kawamoto *et al.*, Phys. Rev. B **52**, 15 522 (1995).

<sup>8</sup>H. Mayaffre *et al.*, Europhys. Lett. **28**, 205 (1994).

<sup>9</sup>S. M. De Soto *et al.*, Phys. Rev. B **52**, 10 364 (1995).

<sup>10</sup>K. Kanoda, Hyperfine Interact. **104**, 235 (1997)

<sup>11</sup>H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **64**, 2726 (1995); **64**, 4523 (1995); **65**, 2158 (1996).

<sup>12</sup>V. Ivanov and K. Kanoda, Physica C **268**, 205 (1996).

<sup>13</sup>T. Komatsu *et al.*, Phosphorous, Sulfur, and Silicon **67**, 295 (1992).

<sup>14</sup>H. Sato *et al.*, Physica C **185-189**, 2679 (1991).

<sup>15</sup>H. Ito *et al.*, J. Phys. Soc. Jpn. **60**, 3230 (1991).

<sup>16</sup>M. Tokumoto *et al.*, Jpn. J. Appl. Phys. Series 7, 395 (1992).

<sup>17</sup>H. H. Wang *et al.*, Synth. Met. **41-43**, 1983 (1991).

<sup>18</sup>U. Welp *et al.*, Phys. Rev. Lett. **69**, 840 (1992).

<sup>19</sup>K. Kanoda *et al.*, Synth. Met. **55-57**, 2865 (1993).

<sup>20</sup>P. A. Minsky *et al.*, Phys. Rev. Lett. **70**, 1323 (1993); Phys. Rev. B **50**, 15 929 (1994).

<sup>21</sup>Y. Nakazawa and K. Kanoda, Phys. Rev. B **53**, R8875 (1996).

<sup>22</sup>M. Kund *et al.*, Physica B **191**, 274 (1993).

<sup>23</sup>K. Miyake (private communication).