^{13}C NMR Study of Layered Organic Superconductors Based on BEDT-TTF Molecules

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The normal state of the layered organic superconductors κ-(BEDT-TTF)$_2X$ (X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br) has been studied by ^{13}C NMR for the first time. The nuclear spin-lattice relaxation rate, T_1^{-1}, is greatly enhanced over the value expected from the Korringa relation and shows an anomalous peak around 50 K for both compounds. This is the first experimental evidence of strong antiferromagnetic spin fluctuations in these materials. The depression of the spin fluctuations observed below 50 K coincides with an appearance of Fermi liquid behavior in the charge transport.

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Bis(ethylenedithio)tetrathiafulvalene, abbreviated as BEDT-TTF, is an electron-donor molecule, which has afforded many organic charge-transfer salts with various types of counteranions. Among them, the κ-phase family of BEDT-TTF salts, κ-(BEDT-TTF)$_2X$, has two-dimensional character in the electronic state, due to a layered structure consisting of conducting BEDT-TTF sheets and insulating anion (X) sheets. It is remarkable that they include a variety of electronic phases such as metallic, superconducting, and insulating ones in spite of their structural similarity [1]. κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl is an insulator at ambient pressure [2]. Under pressure above 0.2 kbar, however, this salt undergoes a superconducting transition at 13 K, above which a very broad resistivity hump manifests itself around 100 K with nonmetallic temperature dependence at the higher temperature side [3]. Such a state with high transition temperature and the peculiarity in the charge transport in the normal state is realized at ambient pressure for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ [4] and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br [5]. Further pressure leads to suppression of the superconductivity and the resistivity hump [6]. The successive appearance of the various electronic phases in this family makes an appeal for a comprehensive understanding of them as a phase diagram inherent in quasi-two-dimensional electronic systems with electron correlation.

NMR is a distinctive probe of the statics and dynamics of the electron spins. NMR study on these compounds has so far been performed at ^{1}H sites [7]. However, the spin density at the hydrogen, which is located at the edges of the molecule, is so small that the Knight shift cannot be resolved and that quantitative analysis is not available. One way to overcome this difficulty is substitution of the ^{13}C isotope at the central double-bonded carbon sites, where the dominant contribution to the highest occupied molecular orbit (HOMO) is well known to be a $2p_z$ orbital with far larger spin density. In the present work, we have applied the ^{13}C NMR method to ^{13}C-labeled samples in order to examine the nature of the electronic phases of κ-(BEDT-TTF)$_2X$ (X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br) in the normal state at ambient pressure. The ^{13}C NMR spectra reflecting the anisotropic shift tensor and the nuclear spin-lattice relaxation rate T_1^{-1} are presented for the first time.

The BEDT-TTF molecules with selective substitution of ^{13}C isotope have been synthesized from ^{13}CS$_2$ according to the method by Larsen and Lenoir [8] with slight modification. Examination of the mass spectrum of the product ensured the successful substitution. The salts of κ-(BEDT-TTF)$_2X$ (X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br) were prepared by electrochemical oxidation. The crystals obtained were ground into powders to avoid the skin effect of metallic samples in the NMR measurements. Prior to the NMR experiments, we measured the static magnetic susceptibility χ_{dc} in order to extract the uniform spin susceptibility and characterize the sample quality. Figure 1 shows the susceptibility of the two salts measured at a magnetic field of 1 T. As seen in the figure, both samples are free from paramagnetic impurity and exhibit similar behaviors; χ_{dc} remains constant [$(0-0.2) \times 10^{-4}$ emu/mol f.u.] above ~100 K but decreases gradually at lower temperatures. These results are in agreement

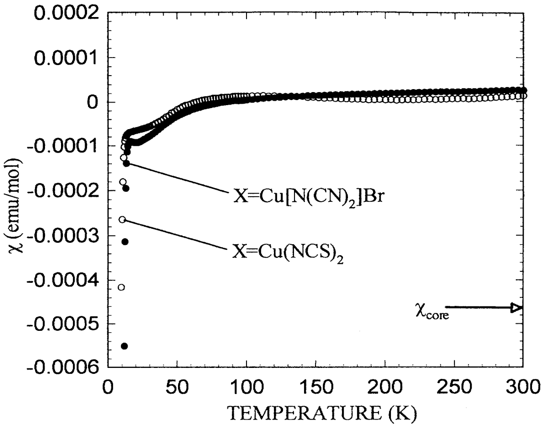

FIG. 1. Static magnetic susceptibility per mole of the formula unit. Core contribution, which is nearly the same for both salts, is shown by the arrow.

with a previous report on the Cu(NCS)$_2$ salt [9]. By subtracting the core diamagnetism (-4.7×10^{-4} and -4.6×10^{-4} emu/mol f.u. for the Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts, respectively) show in the figure, the paramagnetic susceptibility turns out to be 5×10^{-4} emu/mol f.u. in the constant region for both salts. Since the EPR susceptibility gives the same value [10] and χ_{dc} is almost isotropic [9], the paramagnetic part of χ_{dc} is considered as the isotropic spin susceptibility without appreciable orbital contribution.

The ^{13}C NMR experiments were performed for powdered samples at a magnetic field of 8 T. The spectra at room temperature are shown in the inset of Fig. 2. Neutral BEDT-TTF has a central shift of 100 ppm and an asymmetric line shape of apparently uniaxial symmetry due to the anisotropy of the chemical shift convoluted by the $^{13}\mathrm{C}{=}^{13}\mathrm{C}$ Pake doublet. The width is about 120 ppm. The Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts show nearly identical spectra, which are broadened with a central shift of 60 ppm from those of the neutral BEDT-TTF powders. This asymmetrical broadening comes from the anisotropy of the Knight shift.

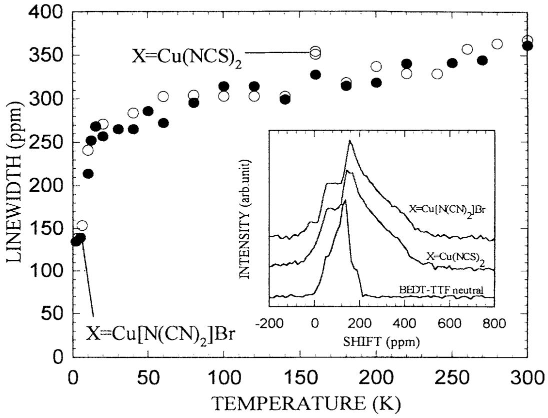

FIG. 2. Linewidth ^{13}C NMR spectra for powdered samples as a function of temperature. Inset shows the spectra where the scale of shift is relative to the line position of TMS.

The hyperfine field at the central carbon nuclei consists of the isotropic Fermi contact field due to the core polarization, the on-site $2p_z$ dipole field, and the off-site dipole field from adjacent one carbon and two sulfur sites. Then, the hyperfine field tensor A defined for one electron spin on the BEDT-TTF molecule is described as

$$A = \sigma_{\mathrm{C}} \begin{pmatrix} \alpha - \beta_{2p_z} & 0 & 0 \\ 0 & \alpha - \beta_{2p_z} & 0 \\ 0 & 0 & \alpha + 2\beta_{2p_z} \end{pmatrix} + \sigma_{\mathrm{C}} \begin{pmatrix} 2\beta_{\mathrm{C}} & 0 & 0 \\ 0 & -\beta_{\mathrm{C}} & 0 \\ 0 & 0 & -\beta_{\mathrm{C}} \end{pmatrix} + 2\sigma_{\mathrm{S}} \begin{pmatrix} (1 + 3\cos\delta)\beta_{\mathrm{S}}/2 & 0 & 0 \\ 0 & (1 - 3\cos\delta)\beta_{\mathrm{S}}/2 & 0 \\ 0 & 0 & -\beta_{\mathrm{S}} \end{pmatrix}, \tag{1}$$

where the x and z axes are taken to be the directions of the $^{13}\mathrm{C}{=}^{13}\mathrm{C}$ and the $2p_z$ orbital, respectively. The first term is the on-site contribution, and the second and third are the off-site contributions from carbon and sulfur atoms. α is an isotropic core-polarization term. The dipole term, $\beta_{2p_z} = \frac{2}{5}\langle \mu_B/r^3 \rangle_{^{13}\mathrm{C},2p_z}$, is known to be 43 kOe. Under the point dipole approximation, $\beta_{\mathrm{C}} = \mu_B/r^3_{^{13}\mathrm{C}=^{13}\mathrm{C}}$ and $\beta_{\mathrm{S}} = \mu_B/r^3_{^{13}\mathrm{C}=\mathrm{S}}$ are estimated at 3.8 and 1.8 kOe with the use of the bond lengths in the BEDT-TTF molecule [11]. δ is the bond angle of S-^{13}C-S. σ_{C} and σ_{S} are the spin densities of carbon and sulfur atoms for one spin on the BEDT-TTF molecule. According to a MO calculation, the charge densities of the HOMO at the carbon and sulfur sites in question are 0.06 and 0.17 [12], which can be reasonably used as the values of σ_{C} and σ_{S}. Thus, numerical substitution in Eq. (1) happens to yield a form of almost uniaxial symmetry,

$$A = \begin{pmatrix} a - B & 0 & 0 \\ 0 & a - B & 0 \\ 0 & 0 & a + 2B \end{pmatrix}, \tag{2}$$

with $B = 2.1$ kOe$/\mu_B$. The isotropic term a is estimated at 1.3 kOe$/\mu_B$ from the observed central shift of 60 ppm and the spin susceptibility per BEDT-TTF molecule, χ_{spin}, of 2.5×10^{-4} emu/mol. The anisotropy of the shift, ΔK, is given by the relation $\Delta K = (A_{zz} - A_{xx})\chi_{\mathrm{spin}}/\mu_B N$, with N the Avogadro number, and substitution of these values predicts $\Delta K = 290$ ppm.

The observed line shapes for the two salts have characteristics of uniaxial symmetry except for the apparent splitting of the peak (around 100 ppm), which may be attributable to the anisotropy of the superposed chemical shift and/or to possible inequivalent sites of BEDT-TTF. Taking this ambiguity into account, the anisotropy of the Knight shift is in the range of 350 ± 120 ppm. This is consistent with the above estimation. The width is well characterized by the peak-to-peak width of the dispersion curve, which is plotted as a function of temperature in Fig. 2. The temperature dependence is similar to that of the spin susceptibility in Fig. 1, implying that the Knight shift is scaled to the uniform spin susceptibility.

Next, we proceed to the nuclear spin-lattice relaxation rate, T_1^{-1}. Given a hyperfine tensor of the form (2), fluctuations of the hyperfine field perpendicular to the external magnetic field are expressed as

$$\langle \delta H_\perp(\tau)\delta H_\perp(0)\rangle_{\theta,\phi} = \sum_q \frac{4a_q a_{-q} - (1 + 3\cos 2\theta)(a_q B_{-q} + a_{-q}B_q) + (7 - 3\cos 2\theta)B_q B_{-q}}{4} \langle \sigma_q(\tau)\sigma_{-q}(0)\rangle, \qquad (3)$$

where a_q and B_q are matrix elements of a and B with a scattering vector of q, $\langle \sigma_q(\tau)\sigma_{-q}(0)\rangle$ is the correlation function of the spin density on BEDT-TTF, θ is the angle between the magnetic field and the symmetry axis, and ϕ is another variable in polar coordinates. As seen in this form, the fluctuations depend on θ, reflecting the strong anisotropy in the hyperfine coupling, and therefore the relaxation rate of the nuclear magnetization also depends on θ. For this reason, the recovery curve of nuclear magnetization for powdered samples as in the present study does not follow a single exponential function of time. Indeed, the experimental profiles of the nuclear relaxation shown in Fig. 3 are well reproduced by a simulation based on Eq. (3), as displayed in the inset of the figure. [Here and in the calculations below, we assume that the correlation function in Eq. (3) is isotropic.] Therefore we define the relaxation time T_1^0 from the initial slope. Thus determined values of $(T_1^0 T)^{-1}$ are shown in Fig. 4. Both salts exhibit similar and anomalous temperature dependence in spite of the flat temperature dependence of the Knight shift and uniform spin susceptibility. $(T_1^0 T)^{-1}$ remains constant (0.09 $\sec^{-1}\,\mathrm{K}^{-1}$) above 200 K, below which it increases gradually and forms a peak at 50–60 K for the Cu(NCS)$_2$ salt and at 40–50 K for the Cu[N(CN)$_2$]Br salt. At lower temperatures, $(T_1^0 T)^{-1}$ is depressed asymptotically to 0.1 $\sec^{-1}\,\mathrm{K}^{-1}$ at 10 K. The sudden decrease below 10 K for the Cu(NCS)$_2$ salt is due to the superconducting transition, which is not discussed here because of ambiguities arising from application of a large magnetic field (8 T) and measurements of a powdered sample.

One can calculate T_1^0 analytically, based on Eq. (3). It is expressed as

$$\begin{aligned}(T_1^0)^{-1} &\equiv -\left(\frac{\partial \ln M_z(t)/M_\infty}{\partial t}\right)_{t=0} \\ &= \frac{\gamma_I^2}{2}\sum_q (a_q a_{-q} + 2B_q B_{-q}) \\ &\quad \times \int d\tau \langle \sigma_q(\tau)\sigma_{-q}(0)\rangle \cos\omega\tau, \end{aligned} \qquad (4)$$

where $M_z(t)$ is the nuclear magnetization. Using the expression of the correlation function in terms of the dynamic susceptibility, $\int d\tau \langle \sigma_q(\tau)\sigma_{-q}(0)\rangle \cos\omega\tau = [4k_B T/(\gamma_e \hbar)^2]\sum_q \chi_q''(\omega)/\omega$, we obtained a relationship between T_1^0 and the dynamic susceptibility of BEDT-TTF as

$$\frac{1}{T_1^0 T} = \frac{k_B \gamma_I^2}{\gamma_e^2 \hbar^2}\sum_q (2a_q a_{-q} + 4B_q B_{-q})\frac{\chi_q''(\omega)}{\omega}. \qquad (5)$$

When only the uniform part is considered in the summation, Eq. (5) turns out to be an extended version of the Korringa relation to the case of anisotropic hyperfine coupling. (Note that this becomes the usual Korringa relation when $B = 0$.) Using the values of a and B evaluated above, the Korringa relation yields $(T_1^0 T)^{-1} = 0.006\ \sec^{-1}\,\mathrm{K}^{-1}$. It is obvious that the experimental values in Fig. 4 are enhanced by more than 1 order of magnitude over the Korringa law. The large enhancement and the anomalous temperature dependence of $(T_1^0 T)^{-1}$ are considered to come from antiferromagnetic spin fluctuations with finite q vector. The present results give NMR evidence for strong electron correlation in these κ-phase superconductors. It is noted that

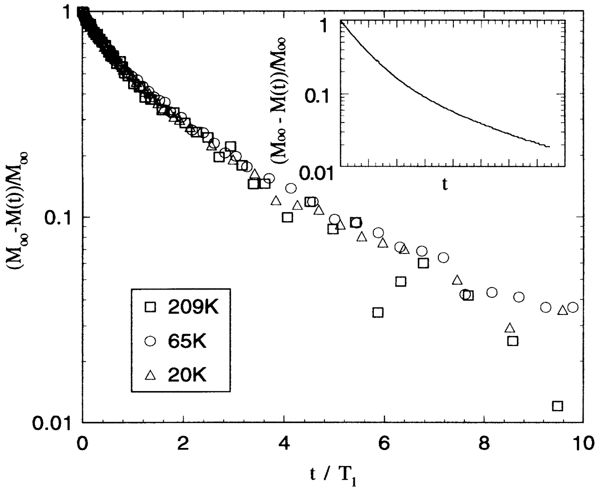

FIG. 3. Recovery curves of the nuclear magnetization at several temperatures. Scale of horizontal axis is normalized to the relaxation rate, T_1^0, determined from the initial slope at each temperature. Inset depicts a simulation curve based on Eq. (3).

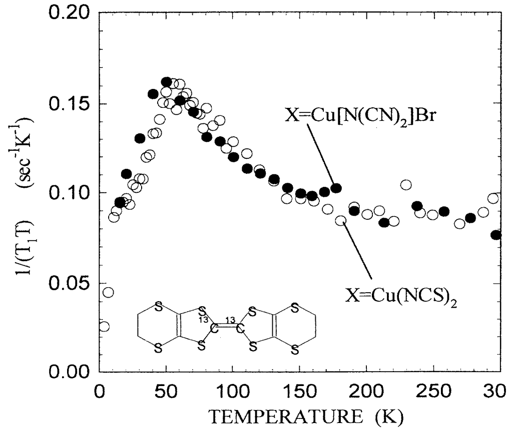

FIG. 4. $(T_1^0 T)^{-1}$ as a function of temperature. For the definition of T_1^0, see text.

the mass enhancement in the Shubnikov–de Hass oscillations for the $Cu(NCS)_2$ salt has been discussed in terms of renormalization of electron-electron interactions [13,14].

It is worth comparing these results with that of the isostructural insulator κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, which was suggested to undergo a magnetic transition [15]. Our recent ^{1}H NMR study has evidenced antiferromagnetic ordering around 26 K, above which $(T_1T)^{-1}$ shows a temperature dependence typical of critical magnetic fluctuations [16]. Taking into account a difference in the hyperfine coupling and gyromagnetic ratio between ^{1}H [7,17] and ^{13}C, the temperature dependence of ^{1}H $(T_1T)^{-1}$ for the Cu[N(CN)$_2$]Cl salt above 70 K [16] implies a similar profile and magnitude of ^{13}C $(T_1T)^{-1}$ to those found in $Cu(NCS)_2$ and Cu[N(CN)$_2$]Br salts. These facts suggest that the increase of $(T_1T)^{-1}$ down to 40–60 K in Fig. 4 is a manifestation of the growth of antiferromagnetic fluctuations. The depression of the fluctuations at lower temperatures for $Cu(NCS)_2$ and Cu[N(NC)$_2$]Br salts leads to the superconducting ground state, while further growth of the fluctuations for Cu[N(CN)$_2$]Cl salt leads to the antiferromagnetic ground state. The present two superconductors are situated very close to the antiferromagnetic insulator. Since the temperature giving a peak of $(T_1T)^{-1}$ is lower for Cu[N(CN)$_2$]Br than for $Cu(NCS)_2$, the former salt may be closer to a superconductor–magnetic-insulator transition, possibly the Mott transition.

It should be noted that 40–60 K coincides with an inflection point of the resistivity vs temperature curve [6], below which a clear Fermi liquid behavior is observed. The appreciable coupling of the spin and charge degrees of freedom means that our systems are not in the strong-U limit regime as in the Cu oxide superconductors.

In conclusion, the ^{13}C NMR study revealed that the organic superconductors κ-(BEDT-TTF)$_2X$ ($X =$ $Cu(NCS)_2$ and Cu[N(CN)$_2$]Br) had strong antiferromagnetic spin fluctuations and were strongly correlated electron systems situated in the vicinity of the metal-insulator transition. A depression of the fluctuations leading to magnetic ordering is deeply related to the transition to a Fermi liquid and possibly to the appearance of superconductivity.

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Note added.—Recently H. Mayaffre *et al.* [Europhys. Lett. **28**, 205 (1994)] have reported the pressure dependence of $(T_1T)^{-1}$ for a single crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The result at ambient pressure was similar to our result in Fig. 4. They found a decrease in the enhancement of $(T_1T)^{-1}$ around 50 K under pressure, suggestive of depression of the antiferromagnetic spin fluctuations.

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