PHYSICAL REVIEW B VOLUME 52, NUMBER 21 1 DECEMBER 1995-I

Electron correlation in the κ-phase family of BEDT-TTF compounds studied by ^{13}C NMR, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene

A. Kawamoto
Department of Physics, Ochanomizu University, Bunkyo-ku, Tokyo 112, Japan

K. Miyagawa, Y. Nakazawa, and K. Kanoda
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

(Received 19 May 1995; revised manuscript received 31 July 1995)

A ^{13}C NMR study on κ=(BEDT-TTF)$_2X$ (X=Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, and Cu[N(CN)$_2$]Cl) is reported, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene. The superconducting salts of X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br show anamalous enhancement in nuclear spin-lattice relaxation rate T_1^{-1} around 50 K, in spite of monotonic temperature dependence of the anisotropic Knight shift. On the other hand, the insulating salt of X=Cu[N(CN)$_2$]Cl exhibits a divergent peak in $(T_1T)^{-1}$ at 26–27 K, which is confirmed as a manifestation of an antiferromagnetic transition by broadening of the NMR line. Above 27 K, T_1^{-1} shows a temperature dependence typical of critical magnetic fluctuations. The $(T_1T)^{-1}$ and the line shape showed nearly the same profile for these three salts above 60 K, that gives experimental evidence for a correspondence between the anomalous enhancement of $(T_1T)^{-1}$ in the superconducting salts and antiferromagnetic fluctuations established in the insulating salt of κ type. The present results demonstrate the presence of strong electron correlation in both superconducting and insulating salts. Analytical expressions of T_1 and the Knight shift of the ^{13}C NMR for κ-(BEDT-TTF)$_2X$ are given, which are general formulas applicable to other $p\pi$ electronic systems.

I. INTRODUCTION

Bis(ethylenedithio)tetrathiafulvalene, abbreviated as BEDT-TTF, is an electron-donor molecule which has afforded many organic conductors with various types of counter anions. Many of these conducting salts, which consist of quasi-two-dimensional BEDT-TTF layers separated by insulating anion layers, give typical examples of a two-dimensional electronic system. Among them, the κ-(BEDT-TTF)$_2X$ (X=Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, and Cu[N(CN)$_2$]Cl) family are the most attractive in the study of metal-insulator transitions and competition between superconductivity and magnetic ordering.[1] The salts of X=Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br are well-known superconductors with transition temperatures of 10 and 11.6 K, respectively.[1] In spite of a similar crystal structure and electronic band structure, the Cu[N(CN)$_2$]Cl salt is insulating, and undergoes a magnetic transition at a low temperature.[2,3] The ^{13}C NMR study on the ^{13}C-enriched Cu(NCS)$_2$ (Ref. 4) and Cu[N(CN)$_2$]Br salts,[4,5] suggested existence of magnetic fluctuations in a wide temperature range of the normal metallic phase. Its possible relationship to magnetic ordering was also discussed.[4]

In order to confirm these speculations and obtain a comprehensive picture of various electronic phases in the κ-phase family, it is important to clarify the magnetism of the insulating Cu[N(CN)$_2$]Cl salt situated in the vicinity of the above superconductors, and to compare systematically the magnetic fluctuations in these salts. Our recent measurements of magnetization and ^{1}H NMR on a single crystal of the Cu[N(CN)$_2$]Cl salt revealed that the low-temperature magnetic ordering is antiferromagnetic with a moment of 0.4–1.0 of μ_B/dimer.[3] In this connection, further NMR studies are required to characterize the paramagnetic states of these salts.

NMR studies on BEDT-TTF systems have so far been performed mainly with the ^{1}H nuclear probe. However, the ^{1}H sites in BEDT-TTF have so small a hyperfine coupling with conduction electrons that the Knight shift cannot be resolved. Moreover, the dynamics of the ethylene groups[6] containing hydrogens overwhelms the electronic contribution to the relaxation rate at high temperatures. Therefore, ^{1}H is not an ideal NMR probe for BEDT-TTF compounds in spite of the high sensitivity. In the study of correlated electronic systems, a quantitative estimation of the relationship between the dynamic and static susceptibility is important. The difficulties in the ^{1}H probe are overcome by ^{13}C NMR at the central carbon sites, where the $2p_z$ orbital is known to be a main contribution with large spin density to the highest occupied molecular orbital (HOMO). Owing to the sp^2 hybrid orbital, the angular momentum is quenched and the higher-order mixing between $2p_z$ and other $2p$ orbitals must be small. Therefore, unlike transition metals, we can neglect the orbital term in the hyperfine coupling tensor. Thus it consists of the dipole field mainly from the on-site $2p_z$ orbital (and secondarily from off-site orbitals on neighboring carbon and sulfur atoms), and a core polarization of $1s$ and $2s$ orbitals (caused by the on-site $2p_z$ spins and the off-site spins through bonding orbitals), which can be estimated by measurements of shift or calculation of the HOMO. In this paper, we give formulations of ^{13}C nuclear spin-lattice relaxation rate T_1^{-1} and Knight shift K for BEDT-TTF compounds. The experimental results on κ-(BEDT-TTF)$_2X$, including insulating and superconducting salts, are analyzed and discussed in terms of electron correlation.

0163-1829/95/52(21)/15522(12)/$06.00

© 1995 The American Physical Society

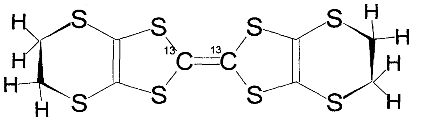

FIG. 1. Molecular structure of the isotope labeled BEDT-TTF.

II. EXPERIMENT

The ^{13}C-isotope-labeled BEDT-TTF molecules shown in Fig. 1 were synthesized according to the method of Larsen and Lenoir.[7] However, we could not reproduce a step of the cyclization using H_2SO_4, as was pointed out by others.[8] The reaction was promoted with the use of HBF_4 instead of H_2SO_4. Isotope labeling was checked by a mass spectrometer, and successful substitution of ^{13}C was confirmed. The κ-(BEDT-TTF)$_2X$ radical salts ($X=\mathrm{Cu(NCS)_2}$, $\mathrm{Cu[N(CN)_2]Br}$, and $\mathrm{Cu[N(CN)_2]Cl}$) were prepared by the electrochemical oxidation method[9] using conventional H-type cells and cylindrical cells. For the $\mathrm{Cu[N(CN)_2]Cl}$ salt, two morphisms of crystals were encountered. Therefore we separated κ-type crystals from non-κ-type needlelike crystals under a microscope.

To avoid the skin effect in metallic state, samples for NMR measurements were ground. Magnetic-susceptibility measurements of these samples showed no sign of paramagnetic impurities and damage by grinding, where the measurements were performed with a commercially available superconducting quantum interference device (SQUID) magnetometer.

The ^{13}C NMR measurements were made for powdered samples under a magnetic field of 8.0 T. ^{13}C NMR spectra were obtained by the fast Fourier transformation (FFT) of a quadrature-detected spin-echo signal. The width of the $\pi/2$ pulse was 2.5–4 μs, which corresponds to a spectral range of 100–150 kHz. This value covered the anisotropic Knight shift in the normal metallic phase, but did not cover the line broadened in the magnetically ordered state of the $\mathrm{Cu[N(CN)_2]Cl}$ salt. The NMR relaxation curves were obtained by the saturation recovery method with a phase-cycling technique of the spin-echo pulse sequence.

III. FORMULATION OF KNIGHT SHIFT AND SPIN-LATTICE RELAXATION RATE ON ^{13}C SITE IN BEDT-TTF

A. Hyperfine coupling field on central ^{13}C atom in BEDT-TTF molecule

The hyperfine field at ^{13}C nuclei is mainly a dipole field caused by the $2p_z$ orbital on the ^{13}C atom and Fermi contact field by core-polarized $1s$ and $2s$ orbitals. In π-organic radicals, owing to the sp^2 hybrid orbital, the angular momentum is quenched, and the higher-order mixing between $2p_z$ and other $2p$ orbitals, which make σ bonds must be small. Indeed, the EPR susceptibility[10] gives the same value as the static susceptibility, which is almost isotropic.[11] Therefore we neglect a contribution of the angular momentum to hyperfine tensor. Then the hyperfine tensor $\mathbf{T}$ is described as

$$\mathbf{T}=A\mathbf{E}-\gamma_e\hbar\left(\frac{\mathbf{E}}{|\mathbf{r}|^3}-\frac{3(\mathbf{r}\cdot\tilde{\mathbf{r}})}{|\mathbf{r}|^5}\right)=A\mathbf{E}+\mathbf{B}, \tag{1}$$

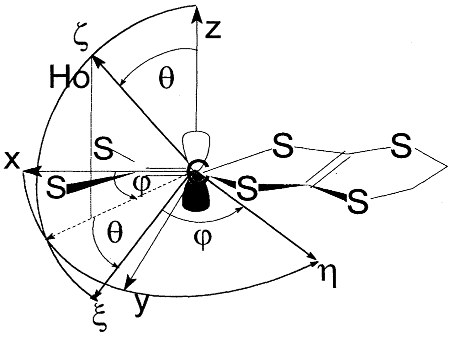

FIG. 2. Polar coordinate in the BEDT-TTF molecule.

where $\mathbf{E}$ is a unit tensor, $\mathbf{r}$ is a vector from a nuclei to an unpaired electron, $\tilde{\mathbf{r}}$ is a transpose vector of $\mathbf{r}$, and γ_e is the gyromagnetic ratio of an electron. Here the tensor is expressed in the xyz coordinate in Fig. 2, where the $2p_z$ orbital and the $^{13}\mathrm{C}{=}^{13}\mathrm{C}$ bond direction are set to the z and x axes, respectively. A is an isotropic core-polarization term, and the second term is a dipole field from the $2p_z$ orbital.

In order to give analytical formulations for a powdered sample, we have to generalize the expression of the tensor in Eq. (1) to that in an arbitrary coordinate. An arbitrary frame of coordinates ξ, η, ζ with a magnetic field parallel to the ζ axis is generated by two sequential rotations from the xyz frame fixed at the BEDT-TTF molecule by the so-called Euler angles (θ, φ, ϕ). The third rotation ϕ, which is near the ζ axis, does not need to be considered, because the Hamiltonian in question is degenerate against the rotation around the field. Thus we set $\phi=0$, and the $\xi\eta\zeta$ frame is characterized by θ and φ as shown in Fig. 2. [Note that setting angles (θ, φ) are also polar coordinates of the field (ζ axis) in the xyz frame.] Then the tensor in this frame can be expressed, using the rotation matrix $\mathbf{U}(\theta,\varphi)$, as

$$\mathbf{T}(\theta,\varphi)=\mathbf{U}^{-1}(\theta,\varphi)\cdot\mathbf{T}\cdot\mathbf{U}(\theta,\varphi), \tag{2}$$

where

$$\mathbf{U}(\theta,\varphi)=\begin{pmatrix}\cos\varphi & -\sin\varphi & 0\\ \sin\varphi & \cos\varphi & 0\\ 0 & 0 & 1\end{pmatrix}\times\begin{pmatrix}\cos\theta & 0 & \sin\theta\\ 0 & 1 & 0\\ -\sin\theta & 0 & \cos\theta\end{pmatrix}. \tag{3}$$

In the general spin Hamiltonian of organic free radicals, the Zeeman coordinates of the electron and nucleus are not necessarily parallel to each other.[12] In the organic conductors, the g tensor is almost isotropic, and the hyperfine field from the Pauli paramagnetic spin density of the $2p_z$ orbital on the ^{13}C atom is much smaller than that of the organic free radicals. Hence we can set the same Zeeman coordinate for the nuclei and the electron, and the hyperfine contribution H_{hf}, to the Hamiltonian is simplified as

$$H_{\mathrm{hf}}=\gamma_I\hbar\mathbf{S}\cdot\mathbf{T}(\theta,\varphi)\cdot\mathbf{I}=\gamma_I\hbar\mathbf{S}\cdot\begin{pmatrix}T_{11} & T_{12} & T_{13}\\ T_{21} & T_{22} & T_{23}\\ T_{31} & T_{32} & T_{33}\end{pmatrix}\cdot\mathbf{I},\tag{4}$$

where $\mathbf{I}$ and $\mathbf{S}$ are a ^{13}C nuclear-spin operator and an electron-spin operator, respectively, and γ_I is the gyromagnetic ratio of the ^{13}C nucleus.

Now we can write field operators $\psi_s^+(\mathbf{r})$ and $\psi_s(\mathbf{r})$ in terms of $\Psi_{\mathbf{k}}(\mathbf{r})$ the wave function of conduction band with wave vector k, as follows:

$$\psi_\sigma(\mathbf{r})=\sum_{\mathbf{k}}\Psi_{\mathbf{k}}(\mathbf{r})a_{\mathbf{k},\sigma},\psi_\sigma^+(\mathbf{r})=\sum_{k}\Psi^*_{\mathbf{k}}(\mathbf{r})a^+_{\mathbf{k},\sigma},\tag{5}$$

$$\hat{\mathbf{S}}=\sum_{\sigma,\sigma'}\int\int\int\psi_\sigma^+(\mathbf{r})\mathbf{S}\psi_{\sigma'}(\mathbf{r})dr.\tag{6}$$

Then the hyperfine field $\mathbf{H}_{\mathrm{hf}}$ is expressed as

$$\begin{aligned}\mathbf{H}_{\mathrm{hf}}&=\hat{\mathbf{S}}\cdot\mathbf{T}(\theta,\varphi)\\&=\sum_{k'k}(T_e^{\mathbf{k}',\mathbf{k}}S^{\zeta}_{\mathbf{k}',\mathbf{k}}+\mathbf{T}^{\mathbf{k}',\mathbf{k}}_{\mathbf{c},+}S^-_{\mathbf{k}',\mathbf{k}}+T^{\mathbf{k}',\mathbf{k}}_{c,-}S^+_{\mathbf{k}',\mathbf{k}})\zeta+(T^{\mathbf{k}',\mathbf{k}}_{b,+}S^+_{\mathbf{k}',\mathbf{k}}\\&\quad+T^{\mathbf{k}',\mathbf{k}}_{a,-}S^-_{\mathbf{k}',\mathbf{k}}+T^{\mathbf{k}',\mathbf{k}}_{d,-}S^{\zeta}_{\mathbf{k}',\mathbf{k}})(\xi-i\eta)+(T^{\mathbf{k}',\mathbf{k}}_{a,+}S^-_{\mathbf{k}',\mathbf{k}}\\&\quad+T^{\mathbf{k}',\mathbf{k}}_{b,-}S^+_{\mathbf{k}',\mathbf{k}}+T^{\mathbf{k}',\mathbf{k}}_{d,+}S^{\zeta}_{\mathbf{k}',\mathbf{k}})(\xi+i\eta),\end{aligned}\tag{7}$$

where

$$\begin{aligned}T^{\mathbf{k}',\mathbf{k}}_{a,\pm}&=\frac{(T^{\mathbf{k}',\mathbf{k}}_{11}-T^{\mathbf{k}',\mathbf{k}}_{22})\pm i(T^{\mathbf{k}',\mathbf{k}}_{21}+T^{\mathbf{k}',\mathbf{k}}_{12})}{4},\\T^{\mathbf{k}',\mathbf{k}}_{b,\pm}&=\frac{(T^{\mathbf{k}',\mathbf{k}}_{11}+T^{\mathbf{k}',\mathbf{k}}_{22})\pm i(T^{\mathbf{k}',\mathbf{k}}_{21}-T^{\mathbf{k}',\mathbf{k}}_{12})}{4},\\T^{\mathbf{k}',\mathbf{k}}_{c,\pm}&=\frac{T^{\mathbf{k}',\mathbf{k}}_{13}\pm iT^{\mathbf{k}',\mathbf{k}}_{23}}{2},\\T^{\mathbf{k}',\mathbf{k}}_{d,\pm}&=\frac{T^{\mathbf{k}',\mathbf{k}}_{31}\pm iT^{\mathbf{k}',\mathbf{k}}_{32}}{2},\\T^{\mathbf{k}',\mathbf{k}}_{e}&=T^{\mathbf{k}',\mathbf{k}}_{33},\\T^{\mathbf{k}',\mathbf{k}}_{nm}&=(U^{-1}(\theta,\varphi)\langle\Psi_{\mathbf{k}'}|\mathbf{T}|\Psi_{\mathbf{k}}\rangle U(\theta,\varphi))_{nm}\end{aligned}\tag{8}$$

and

$$\begin{aligned}S^{\zeta}_{\mathbf{k}',\mathbf{k}}&=\tfrac{1}{2}(a^+_{\mathbf{k}',\uparrow}a_{\mathbf{k},\uparrow}-a^+_{\mathbf{k}',\downarrow}a_{\mathbf{k},\downarrow}),\\S^{+}_{\mathbf{k}',\mathbf{k}}&=a^+_{\mathbf{k}',\uparrow}a_{\mathbf{k},\downarrow},\\S^{-}_{\mathbf{k}',\mathbf{k}}&=a^+_{\mathbf{k}',\downarrow}a_{\mathbf{k},\uparrow}.\end{aligned}\tag{9}$$

B. Spin state of central ^{13}C pair in BEDT-TTF

The isotope labeled ^{13}C nuclei at central double-bonded sites in BEDT-TTF make a nuclear dipole coupling with each other. Hereafter, we consider a general formulation where the two ^{13}C nuclei have different shift tensors. As is well known as Pake doublet,[13] the spin states of ^{13}C$=$^{13}C are expressed by one singletlike and three tripletlike states as follows:

$$\begin{aligned}&|1\rangle=|\uparrow\uparrow\rangle,\\&E_1=-\gamma_I\hbar\left\{1+\tfrac{1}{2}\sum_{i=1}^{2}\{{}^iK(\theta,\varphi)+{}^i\sigma(\theta,\varphi)\}\right\}H_0+\frac{D}{4},\\&|2\rangle=\sin\Theta|\uparrow\downarrow\rangle+\cos\Theta|\downarrow\uparrow\rangle,\\&E_2=-\frac{D+\sqrt{D^2-4\delta^2}}{4},\\&|3\rangle=-\cos\Theta|\uparrow\downarrow\rangle+\sin\Theta|\downarrow\uparrow\rangle,\\&E_3=-\frac{D-\sqrt{D^2-4\delta^2}}{4},\\&|4\rangle=|\downarrow\downarrow\rangle,\\&E_4=\gamma_I\hbar\left\{1+\tfrac{1}{2}\sum_{i=1}^{2}\{{}^iK(\theta,\varphi)+{}^i\sigma(\theta,\varphi)\}\right\}H_0+\frac{D}{4},\end{aligned}\tag{10}$$

where

$$D=\frac{\gamma_I^2\hbar^2}{r^3}(1-3\cos^2\vartheta),\quad\vartheta=\cos^{-1}(-\cos\varphi\sin\theta),$$

$$\delta=\gamma_I\hbar\{{}^1K(\theta,\varphi)+{}^1\sigma(\theta,\varphi)-{}^2K(\theta,\varphi)-{}^2\sigma(\theta,\varphi)\}H_0,$$

$$\sin2\Theta=\frac{D}{\sqrt{D^2+4\delta^2}},$$

and H_0 is an external field, ↑ and ↓ denote two Zeeman states of $I=\frac{1}{2}$ spin, r is a distance between ^{13}C$=$^{13}C, and $K(\theta,\varphi)$ is the Knight shift term, which is discussed below. $\sigma(\theta,\varphi)$ is a chemical shift term with the polar angles of θ, φ defined in Fig. 2, and i denotes the ^{13}C site in ^{13}C$=$^{13}C. From the NMR selection rule, $\Delta m=\pm1$, we will observe quartet spectrum of

$$\begin{aligned}&\Delta E_{1\rightarrow2}=\Delta E_0-(2D+\sqrt{D^2+4\delta^2})/4,\\&F_{1\rightarrow2}=1+\sin2\Theta,\\&\Delta E_{2\rightarrow4}=\Delta E_0+(2D+\sqrt{D^2+4\delta^2})/4,\\&F_{2\rightarrow4}=1+\sin2\Theta,\\&\Delta E_{1\rightarrow3}=\Delta E_0-(2D+\sqrt{D^2+4\delta^2})/4,\\&F_{1\rightarrow3}=1-\sin2\Theta,\\&\Delta E_{3\rightarrow4}=\Delta E_0+(2D-\sqrt{D^2+4\delta^2})/4,\\&F_{3\rightarrow4}=1-\sin2\Theta,\end{aligned}\tag{11}$$

where

$$\Delta E_0=\gamma\hbar\left\{1+\tfrac{1}{2}\sum_{i}^{2}\{{}^iK(\theta,\varphi)+{}^i\sigma(\theta,\varphi)\}\right\}H_0,$$

and F represents the absorption intensity.

C. Calculation of hyperfine field

The conducting two-dimensional layers consist of BEDT-TTF radical dimer units, $(\text{BEDT-TTF})_2{}^+$, which are associated by symmetry operators.[14,15] In the tight-binding approximation, the wave function of the conduction band with wave vector $\mathbf{k}$ and symmetry Γ is expressed as

$$\Psi_{\mathbf{k}}^{\Gamma}(\mathbf{r})=\frac{1}{\sqrt{NM}}\sum_{n=1}^{N}\sum_{m=1}^{M}e^{i\mathbf{k}\cdot\mathbf{R}_\mathbf{n}}D_m^{\Gamma,\mathbf{k}}\phi(\mathbf{r}-\mathbf{R}_\mathbf{n}),\tag{12}$$

where $\mathbf{R}_\mathbf{n}$ is a primitive translation vector, ϕ is a conducting orbital of BEDT-TTF dimer, and $D_m^{\Gamma,\mathbf{k}}$ are characters of the mth symmetry operator with the $\mathbf{k}$ vector in Γ expression.

ϕ is expressed in the framework of the LCAO (linear combination of atomic orbitals) approximation as follows:

$$\phi(r)=\sum_{j=1}^{L}c_j\rho_j(\mathbf{r}-\mathbf{r}_\mathbf{j}),\tag{13}$$

where ρ_j is an atomic orbital of the jth atom in the BEDT-TTF dimer.

Substitution of Eq. (8) with Eqs. (12) and (13) gives

$$\langle\Psi_{\mathbf{k}'}|\mathbf{T}|\Psi_{\mathbf{k}}\rangle=\frac{1}{NM}\sum_{n',n}^{N,N}e^{i(\mathbf{k}\cdot\mathbf{R}_\mathbf{n}-\mathbf{k}'\mathbf{R}_{\mathbf{n}'})}\sum_{m'm}^{M,M}D_{m'}^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}\times\sum_{j',j}^{L,L}c_{j'}^{*}c_j\langle\rho_{n'm'j'}|\mathbf{T}|\rho_{n,m,j}\rangle.\tag{14}$$

For the $A\mathbf{E}$ term in Eq. (1), using the orthogonality of the HOMO, we can calculate

$$\langle\Psi_{\mathbf{k}'}|A|\Psi_{\mathbf{k}}\rangle=\frac{A}{NM}\sum_{n}^{N}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\mathbf{n}}\sum_{m}^{M}\chi_m^{\Gamma,\mathbf{k}'^*}\chi_m^{\Gamma,\mathbf{k}}.\tag{15}$$

If we neglect integrals between different sites, the $\mathbf{B}$ term yields

$$\langle\Psi_{\mathbf{k}'}|\mathbf{B}|\Psi_{\mathbf{k}}\rangle=\frac{1}{NM}\sum_{n}^{N}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\mathbf{n}}\sum_{m}^{M}D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}|c_{13C}|^2\times\langle\rho_{13C}|\mathbf{B}|\rho_{13C}\rangle,\tag{16}$$

where $|c_{13C}|^2$ is an electron population on the central ^{13}C atom, and ρ_{13C} is a $2p_z$ orbital on the C atom in question. (See the Appendix for the contribution of the dipole field on neighboring nuclei.) When we defined $B_{\mathbf{k}',\mathbf{k}}$ and $A_{\mathbf{k}',\mathbf{k}}$ as

$$B_{\mathbf{k}',\mathbf{k}}=\frac{2\gamma_e\hbar}{5NM}\sum_{n}^{N}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\mathbf{n}}\sum_{m}^{M}D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}|c_{13C}|^2\left\langle\frac{1}{r^3}\right\rangle_{2pz},\tag{17}$$

$$A_{\mathbf{k}',\mathbf{k}}=\frac{A}{NM}\sum_{n}^{N}e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_\mathbf{n}}\sum_{m}^{M}D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}},$$

$\langle\Psi_{\mathbf{k}'}|\mathbf{T}|\Psi_{\mathbf{k}}\rangle$ is expressed as

$$\langle\Psi_{\mathbf{k}'}|\mathbf{T}|\Psi_{\mathbf{k}}\rangle=\begin{pmatrix}A_{\mathbf{k}',\mathbf{k}}-B_{\mathbf{k}',\mathbf{k}} & 0 & 0\\ 0 & A_{\mathbf{k}',\mathbf{k}}-B_{\mathbf{k}',\mathbf{k}} & 0\\ 0 & 0 & A_{\mathbf{k}',\mathbf{k}}+2B_{\mathbf{k}',\mathbf{k}}\end{pmatrix}.\tag{18}$$

As the space groups of the κ phase belong to monoclinic C_{2h} (Ref. 14) or orthorhombic D_{2h}, (Ref. 15) $|D_m^{\Gamma}|^2=1$ and therefore

$$D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}=|D_m^{\Gamma}|^2e^{i(\mathbf{k}-\mathbf{k}')\tau_\mathbf{m}}=e^{i(\mathbf{k}-\mathbf{k}')\tau_\mathbf{m}},\tag{19}$$

where τ_m is a nonprimitive translation bector with the mth symmetry operator, and D_m^{Γ} is a character of the factor group with the mth symmetry operator in the Γ expression.

Finally we obtain the following expression:

$$A_{\mathbf{k}',\mathbf{k}}=A_{\mathbf{k}'-\mathbf{k}}=\frac{A}{NM}\sum_{n}^{N}\sum_{m}^{M}e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{R}_\mathbf{n}+\tau_\mathbf{m})},\tag{20}$$

$$B_{\mathbf{k}',\mathbf{k}}=B_{\mathbf{k}'-\mathbf{k}}=\frac{2\gamma_e\hbar}{5NM}\sum_{n}^{N}\sum_{m}^{M}e^{i(\mathbf{k}-\mathbf{k}')(\mathbf{R}_\mathbf{n}+\tau_\mathbf{m})}\rho_{13C}\left\langle\frac{1}{r^3}\right\rangle_{2pz}.\tag{21}$$

Using $A_{\mathbf{k}',\mathbf{k}}$ and $B_{\mathbf{k}',\mathbf{k}}$, the hyperfine field can be written as

$$\begin{aligned}H_{\text{hf}}=\sum_{\mathbf{k}',\mathbf{k}}&\left\{[A_{\mathbf{k}',\mathbf{k}}+B_{\mathbf{k}',\mathbf{k}}(3\cos^2\theta-1)]S_{\mathbf{k}',\mathbf{k}}^{\zeta}+\frac{3i}{4}B_{\mathbf{k}',\mathbf{k}}\sin2\theta(S_{\mathbf{k}',\mathbf{k}}^{-}-S_{\mathbf{k}',\mathbf{k}}^{+})\right\}\zeta\\&+\left[-\frac{3i}{4}B_{\mathbf{k}',\mathbf{k}}\sin^2\theta S_{\mathbf{k}',\mathbf{k}}^{-}+\left(\frac{A_{\mathbf{k}',\mathbf{k}}}{2}-\frac{B_{\mathbf{k}',\mathbf{k}}(3\cos^2\theta-1)}{4}\right)S_{\mathbf{k}',\mathbf{k}}^{+}+\frac{3i}{4}B_{\mathbf{k}',\mathbf{k}}\sin2\theta S_{\mathbf{k}',\mathbf{k}}^{\zeta}\right](\xi+i\eta)\\&+\left[\frac{3i}{4}B_{\mathbf{k}',\mathbf{k}}\sin^2\theta S_{\mathbf{k}',\mathbf{k}}^{+}+\left(\frac{A_{\mathbf{k}',\mathbf{k}}}{2}-\frac{B_{\mathbf{k}',\mathbf{k}}(3\cos^2\theta-1)}{4}\right.S_{\mathbf{k}',\mathbf{k}}^{-}-\frac{3i}{4}B_{\mathbf{k}',\mathbf{k}}\sin2\theta S_{\mathbf{k}',\mathbf{k}}^{\zeta}\right](\xi-i\eta).\end{aligned}\tag{22}$$

D. Knight shift K

The angular-dependent Knight shift ${}^{i}K(\theta,\varphi)$ can be expressed, in terms of the uniform ζ component of hyperfine field, as

$$\begin{aligned}
{}^{i}K(\theta,\varphi)&=\sum_{\mathbf{k}}\frac{\langle {}^{i}T_{e}^{kk}\hat{S}_{\mathbf{k},\mathbf{k}}^{\zeta}+{}^{i}T_{c,+}^{kk}\hat{S}_{\mathbf{k},\mathbf{k}}^{-}+{}^{i}T_{c,-}^{kk}\hat{S}_{\mathbf{k},\mathbf{k}}^{+}\rangle}{H_0}\\
&\cong\sum_{\mathbf{k}}\frac{\langle {}^{i}T_{e}^{kk}\hat{S}_{\mathbf{k},\mathbf{k}}^{\zeta}\rangle}{H_0}\\
&=\sum_{\mathbf{k}}\left({}^{i}A_{\mathbf{k},\mathbf{k}}+\frac{{}^{i}B_{\mathbf{k},\mathbf{k}}+3\,{}^{i}B_{\mathbf{k},\mathbf{k}}\cos 2\theta}{2}\right)\frac{\langle \hat{S}_{\mathbf{k},\mathbf{k}}^{\zeta}\rangle}{H_0}\\
&=\sum_{\mathbf{k}}\left({}^{i}A+\frac{|{}^{i}c_{13c}|^{2}\gamma_e\hbar(1+3\cos 2\theta)}{5}\left\langle\frac{1}{r^3}\right\rangle_{2pz}\right)\\
&\quad\times\frac{\langle \hat{S}_{\mathbf{k},\mathbf{k}}^{\zeta}\rangle}{H_0}.
\end{aligned}\tag{23}$$

In this paper, the uniform static spin susceptibility χ_e is defined per dimer unit. Then we obtain

$${}^{i}K(\theta,\varphi)=\left\{\frac{{}^{i}A}{\gamma_e\hbar}+\left|{}^{i}c_{13c}\right|^{2}\frac{(1+3\cos 2\theta)}{5}\left\langle\frac{1}{r^3}\right\rangle_{2pz}\right\}\chi_e.\tag{24}$$

A more general formula for hyperfine coupling tensor of nonuniaxial symmetry is given in the Appendix.

E. Spin-lattice relaxation time T_1

The nuclear-spin-lattice relaxation curve of a coupled-spin system may not be described as a single-exponential function of time. In the case that the nuclear relaxation in a system can be described by a spin temperature, however, the nuclear-spin-lattice relaxation rate $1/T_1$ is defined as[16]

$$\frac{1}{T_1}=\frac{1}{2}\frac{\sum_{m\neq n}(E_m-E_n)^2W_{m,n}}{\sum_{m}E_m^2},\tag{25}$$

where $W_{n,m}$ is a transition probability from state m to state n or n to m. In the metallic state, relaxation through electron-nucleus hyperfine coupling is dominant and allowed only for $\Delta m=\pm 1$ by electron-spin fluctuations. Assuming $(D\pm\sqrt{D^2/4+\delta^2})/2\ll\hbar\omega$, Eq. (25) reduces to a form of $1/T_1=(W_{1,2}+W_{1,3}+W_{2,4}+W_{3,4})/2$. Using the formula

$$W_{1,2}=\frac{\sin^2\Theta\;{}^{1}W_{\pm}+\cos^2\Theta\;{}^{2}W_{\pm}+2\gamma_I^2\sin\Theta\cos\Theta\int_{-\infty}^{\infty}\langle\delta^{1}H_{\mathrm{hf}}^{+}(t)\,\delta^{2}H_{\mathrm{hf}}^{-}(0)+\mathrm{c.c.}\rangle\cos\omega t\,dt}{2},\tag{26}$$

we obtained

$$\frac{1}{T_1}=\sum_{i=1}^{2}{}^{i}W_{\pm},\tag{27}$$

where ${}^{i}W_{\pm}$ is a transition probability from $-1/2$ to $1/2$ in a spin system of $I=\frac{1}{2}$ on site i. Consequently, the expression of T_1^{-1} for a pair of dipolar-coupled spins is identical to an average of T_1^{-1} for isolated spins of $I=\frac{1}{2}$. Using Eqs. (20), (21), and (22), and the momentum conservation, we express ${}^{i}W_{+}$ as

$$\begin{aligned}
{}^{i}W_{+}&=\gamma_I^2\int_{-\infty}^{\infty}dt\langle\delta^{i}H_{\mathrm{hf}}^{+}(t)\,\delta^{i}H_{\mathrm{hf}}^{-}(0)\rangle_{\mathrm{AV}}\cos\omega t\\
&=\gamma_I^2\sum_{\mathbf{q}}\left[\frac{9}{16}{}^{i}B_{\mathbf{q}}\,{}^{i}B_{-\mathbf{q}}\sin^2 2\theta\int_{-\infty}^{\infty}dt\langle S_{\mathbf{q}}^{\zeta}(t)S_{-\mathbf{q}}^{\zeta}(0)\rangle_{\mathrm{AV}}\cos\omega t+\frac{9}{16}{}^{i}B_{q}\,{}^{i}B_{-\mathbf{q}}\sin^4\theta\int_{-\infty}^{\infty}dt\langle S_{\mathbf{q}}^{-}(t)S_{-\mathbf{q}}^{+}(0)\rangle_{\mathrm{AV}}\cos\omega t\right.\\
&\quad\left.+\frac{1}{16}[2\,{}^{i}A_{\mathbf{q}}-{}^{i}B_{\mathbf{q}}(3\cos^2\theta-1)][2\,{}^{i}A_{-\mathbf{q}}-{}^{i}B_{-\mathbf{q}}(3\cos^2\theta-1)]\int_{-\infty}^{\infty}dt\langle S_{\mathbf{q}}^{+}(t)S_{-\mathbf{q}}^{-}(0)\rangle_{\mathrm{AV}}\cos\omega t,\right.
\end{aligned}\tag{28}$$

where

$$\begin{aligned}
S_{\mathbf{q}}^{\zeta}&=\tfrac{1}{2}(a_{\mathbf{k}+\mathbf{q},\uparrow}^{+}a_{\mathbf{k},\uparrow}-a_{\mathbf{k}+\mathbf{q},\downarrow}^{+}a_{\mathbf{k},\downarrow}),\\
S_{\mathbf{q}}^{+}&=a_{\mathbf{k}+\mathbf{q},\uparrow}^{+}a_{\mathbf{k},\downarrow},\\
S_{\mathbf{q}}^{-}&=a_{\mathbf{k}+\mathbf{q},\downarrow}^{+}a_{\mathbf{k},\uparrow}.
\end{aligned}\tag{29}$$

By fluctuation-dissipation theory, the dynamic susceptibility is given as

$$\chi''_{\perp}(q,\omega)=\frac{\gamma_e^2\hbar^2\omega}{4k_BT}\int_{-\infty}^{\infty}\langle S_{\mathbf{q}}^{+}(t)S_{-\mathbf{q}}^{-}(0)\rangle_{\mathrm{AV}}\cos\omega t\,dt$$
$$=\frac{\gamma_e^2\hbar^2\omega}{4k_BT}\int_{-\infty}^{\infty}\langle S_{\mathbf{q}}^{-}(t)S_{-\mathbf{q}}^{+}(0)\rangle_{\mathrm{AV}}\cos\omega t\,dt. \tag{30}$$

Assuming that magnetic fluctuation is isotropic, namely

$$\int_{-\infty}^{\infty}\langle S_{\mathbf{q}}^{\zeta}(t)S_{-\mathbf{q}}^{\zeta}(0)\rangle_{\mathrm{AV}}\cos\omega t\,dt=\frac{1}{2}\int_{-\infty}^{\infty}\langle S_{\mathbf{q}}^{+}(t)S_{-\mathbf{q}}^{-}(0)\rangle_{\mathrm{AV}}\cos\omega t\,dt, \tag{31}$$

we obtain a final form of $1/T_1$;

$$\frac{1}{T_1}=\sum_{i=1}^{2}W_{\pm}^{i}$$
$$=\frac{\gamma_I^2k_BT}{\gamma_e^2\hbar^2}\sum_{i,\mathbf{q}}\frac{4\,{}^{i}A_{\mathbf{q}}{}^{i}A_{-\mathbf{q}}-({}^{i}A_{\mathbf{q}}{}^{i}B_{-\mathbf{q}}+{}^{i}A_{-\mathbf{q}}{}^{i}B_{\mathbf{q}})(1+3\cos2\theta)+{}^{i}B_{\mathbf{q}}{}^{i}B_{-\mathbf{q}}(7-3\cos2\theta)}{4}\frac{\chi''_{\perp}(\mathbf{q},\omega)}{\omega}. \tag{32}$$

In the case of an isotropic tensor, namely $B_{\mathbf{q}}=0$, this formula falls into the well-known form applied to the usual metals. A more general formula for the hyperfine coupling tensor of nonuniaxial symmetry is given in the Appendix.

IV. RESULTS AND DISCUSSION

A. Line-shape analysis

The NMR spectra for powders of the κ salts and neutral BEDT-TTF at room temperature are shown in Fig. 3. The neutral BEDT-TTF has a central shift of about 110 ppm from TMS (tetramethylsilane). This value is consistent with that in the previous work.[17] The observed line shapes for the three salts have nearly the same central shift and uniaxial symmetry, except for the apparent splitting of the peak around a 100-ppm position. The qualitative resemblance indicates that the electronic characters of the three salts are nearly the same, at least at room temperature. The line shape of the powdered samples is expressed as

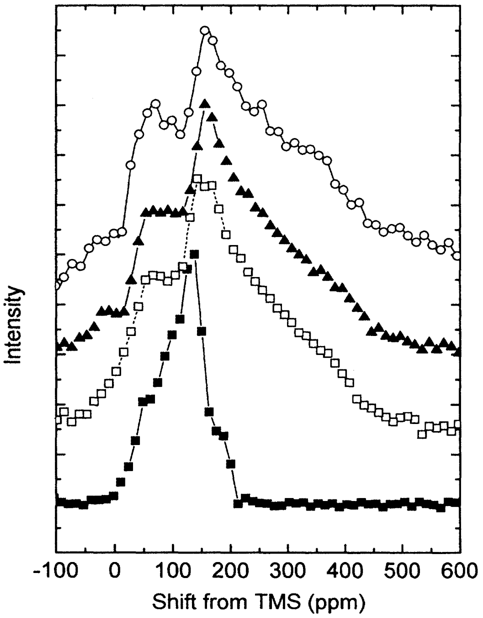

FIG. 3. ^{13}C-NMR spectra of κ salts and neutral BEDT-TTF at room temperature, where the scale of the shift is relative to the line position of TMS per mole of the formula unit ▲: Cu[N(CN)$_2$]Br; □: Cu(NCS)$_2$; ○: Cu[N(CN)$_2$]Cl; ■: neutral BEDT-TTF.

$$F(\nu)=\frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}f_{\theta,\varphi}[\nu-\sigma(\theta,\varphi)$$
$$-K(\theta\varphi)]\sin\theta\,d\theta, \tag{33}$$

where $f_{\theta,\varphi}(\nu)$ is a line shape of doublet structure due to ^{13}C$=^{13}$C nuclear dipole interaction. Assuming that $f_{\theta,\varphi}(\nu)$ is composed of two Lorentzians separated at both sides of a total shift of a uniaxial Knight shift $K(\theta,\varphi)$ and an isotropic chemical shift σ of 110 ppm for simplicity, Eq. (33) yields

$$F(\nu)=\frac{1}{4\pi}\int_0^{2\pi}d\varphi\int_0^{\pi}f_{\theta,\varphi}(\nu-\sigma-K_{\parallel}\cos^2\theta$$
$$-K_{\perp}\sin^2\theta)\sin\theta\,d\theta, \tag{34}$$

where

$$f_{\theta,\varphi}(x)=\frac{\Omega}{[x-3D_{\mathrm{ppm}}(1-3\cos^2\vartheta)/4]^2+\Delta^2}$$
$$+\frac{\Omega}{[x+3D_{\mathrm{ppm}}(1-3\cos^2\vartheta)/4]^2+\Delta^2},$$

where $D_{\mathrm{ppm}}=(\gamma_I\hbar/r^3)(1/H_0)$, and Ω is a normalization factor. The value of D_{ppm}, which characterizes the doublet, is 36 ppm in the present case of $H_0=8.03$ T and $r=1.35$ Å. We obtain $K_{\perp}=-5$ ppm, $K_{\parallel}=340$ ppm, and Δ as fitting parameters of 31 ppm (see Fig. 4). Then the isotropic and anisotropic parts of K, defined as

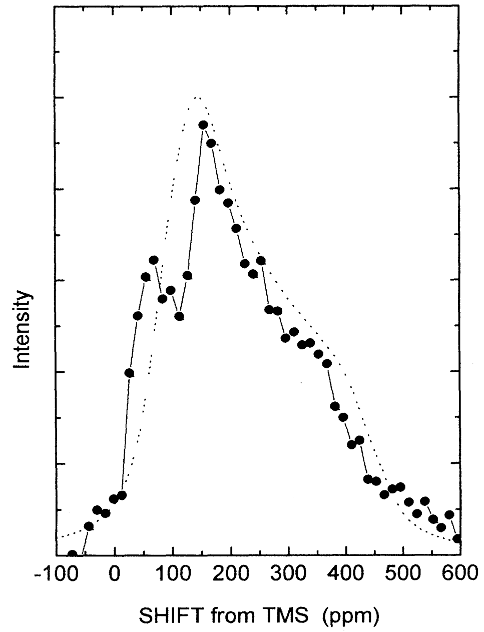

FIG. 4. ^{13}C NMR spectrum of Cu[N(CN)$_2$]Cl salt, and a sumulation curve based on Eq. (34).

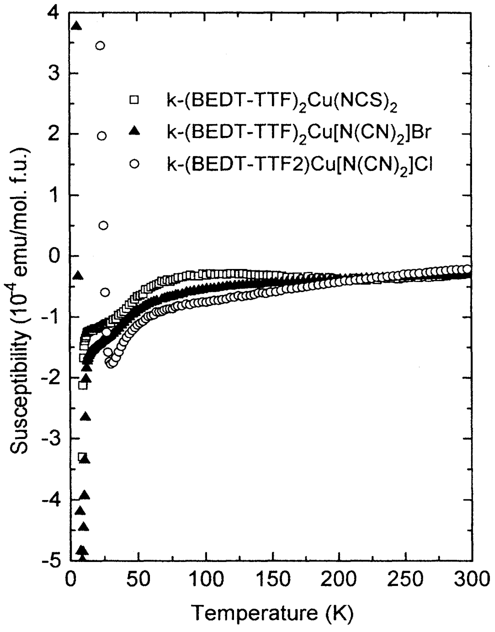

FIG. 5. Static magnetic susceptibility of κ salts per mole of the formula unit. ▲: Cu[N(CN)$_2$]Br; □: Cu(NCS)$_2$; ○: Cu[N(CN)$_2$]Cl. The core diamagnetism is about -4.7×10^{-4} emu/mol for the three salts.

$$K_{\text{iso}}=\frac{2K_{\perp}+K_{\parallel}}{3} \quad \text{and} \quad K_{\text{aniso}}=\frac{K_{\parallel}-K_{\perp}}{3}, \tag{35}$$

are 110 and 115 ppm, respectively. On the other hand, Eq. (24) gives a relationship between the anisotropic Knight shift and spin susceptibility,

$$K_{\text{aniso}}=\frac{2|c_{13c}|^2}{5}\left\langle\frac{1}{r^3}\right\rangle_{2pz}\chi_e. \tag{36}$$

Using 0.03,[18] which is obtained from the extended Huckel calculation as $|c_{13C}|^2$ normalized to the dimer, 1.17 $\times 10^{25}$ cm^{-3} as $\langle 1/r^3\rangle_{2p_z}$ and an experimental value of 4.5 $\times 10^{-4}$ emu/mol dimer as χ_e at room temperature, K_{aniso} is estimated to 105 ppm, which is in good agreement with the value deduced from the line-shape analysis.

However, the splitting structure with a separation of 90 ppm observed around a 100-ppm position cannot be reproduced by Eq. (34), as seen in Fig. 4. Since every molecule in the Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]Cl salts[15] and every dimer unit in the Cu(NCS)$_2$ salt[14] are crystallographically equivalent, it is unlikely that there exist plural BEDT-TTF sites with different shift tensors. Therefore the splitting structure around the 100-ppm position may come from the inequivalence of Knight shift tensors at two central carbon sites within a BEDT-TTF molecule. Indeed, Mayaffre *et al.* reported two different tensors with isotropic terms of 183 and 10 ppm, and anisotropic terms ($B1$ and $B2$), of (202 and 163 ppm) and (190 and 120 ppm), respectively,[5] which were determined from single-crystal measurements for the Cu[N(CN)$_2$]Br salt. The large difference of the isotropic terms between the two sites is in strong contrast with nearly the same values of the anisotropic terms. If the isotropic terms are determined by the subtle balance of one on-site and three off-site polarizations with different signs, only the isotropic term is likely to be altered by a small modification of the spin-density profile around the carbon site. Another possible origin of the large difference of the isotropic term is a slight mixing of the $2s$ orbital to the HOMO ($2p_z$) caused by the breakdown of the planar atomic coordination around the ^{13}C atom. In a crystallographic study, however, such a deformation of the molecule is not clear.

The temperature dependence of the magnetic susceptibility is shown in Fig. 5, where the diamagnetic core contribution is $\approx 4.7\times 10^{-4}$ emu/mol dimer for the three salts. The magnitude and temperature dependence are similar for all three salts, except for the weak ferromagnetic behavior below 30 K for the Cu[N(CN)$_2$]Cl salt. The ferromagnetism is due to spin canting in an antiferromagnetic order.[3] As shown in Fig. 6, the overall temperature dependence of K_{aniso} for three κ salts is similar to those of the spin susceptibility in Fig. 5. Therefore, we conclude that the anisotropic Knight shift K_{aniso} is scaled to the uniform spin susceptibility except for the Cu[N(CN)$_2$]Cl salt below 60 K. This confirms that the ^{13}C nucleus probes the local field due to paramagnetic conducting electron spins. The temperature dependence of the line shape for the Cu[N(CN)$_2$]Cl salt is shown in Fig. 7. Above 60 K, the line shape is nearly the same as in other κ salts. As the magnetic transition is approached, however, the width of the spectra broadens in spite of a gradual decrease of the spin susceptibility in Fig. 5, indicating an antiferromagnetic (AF) nature.

We can consider two possibilities as mechanisms of the line broadening for the Cu[N(CN)$_2$]Cl salt. One is an inhomogeneity of the local field which varies much more slowly

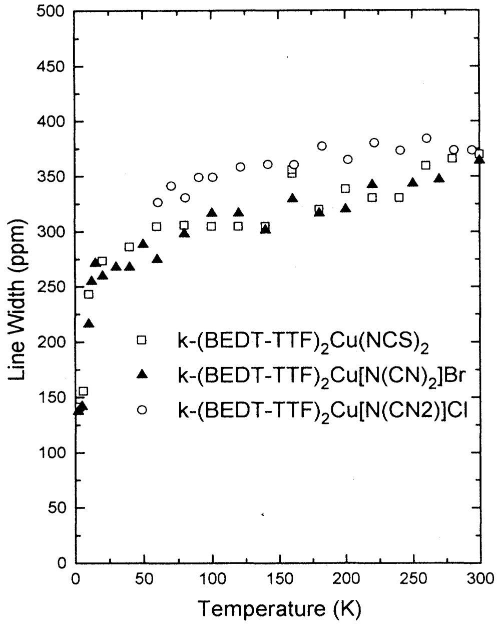

FIG. 6. Temperature dependences of linewidth of ^{13}C NMR spectra in three salts. ▲: Cu[N(CN)$_2$]Br; □: Cu(NCS)$_2$; ○: Cu[N(CN)$_2$]Cl.

than the NMR frequency on the ^{13}C atom. Another is a decrease of the transverse relaxation time T_2. In the line shape of ^{1}H NMR,[3] no broadening or significant change of line shapes were observed above 26–27 K. Since the indirect spin-spin coupling comes from second-order perturbation of the hyperfine tensor, ^{1}H nuclei in BEDT-TTF molecules have only direct spin-spin coupling with negligible indirect coupling. It is possible for ^{13}C nuclei to have an appreciable indirect spin-spin coupling mediated by conduction electrons,

$$H'_d=\sum_{\mathbf{q}}\sum_{(i,j)} a^{\mathbf{q}}_{(i,j)}\tilde{\mathbf{I}}_i\cdot\mathbf{I}_j\chi'(\mathbf{q},\omega)_{\omega\to 0}, \tag{37}$$

in addition to the direct spin-spin coupling, where $\chi'(\mathbf{q},\omega)$ is the real part of dynamic susceptibility with a $\mathbf{q}$ vector. Therefore the observed broadening possibly corresponds to enhancement of the real part of the dynamic susceptibility.

If the indirect spin-spin coupling is responsible for the line broadening, the transverse relaxation rate T_2^{-1} should also be enhanced. In order to specify the mechanism of the line broadening, we measured the transverse nuclear magnetic relaxation curve for powdered samples at 60 and 28 K. As shown in Fig. 8, the relaxation profiles at these temperatures are nearly the same, in contrast to the remarkable difference of line shape in Fig. 7. The characteristic decay time is 100–200 μs, which corresponds to a linewidth of 5–10 kHz. This value does not explain the observed width (~100 kHz) at 33 K, but is in a range of the ^{13}C$=$^{13}C Pake doublet. Thus T_2 is dominated by temperature-independent ^{13}C$=$^{13}C dipolar interaction and not involved in the mechanism of the line broadening. Thus we consider that the line broadening is not due to the indirect spin-spin coupling. A broadening in the Knight shift is reported below 190 K for the Cu[N(CN)$_2$]Br salt by single-crystal measurements.[5] This may have some connection with the present observation for the Cu[N(CN)$_2$]Cl salt. However, we note that the broadening in the Cu[N(CN)$_2$]Cl salt is much larger than that for the Cu[N(CN)$_2$]Br slat, which did not show a clear broadening in the power spectra.

When the magnetic transition occurred at 27 K, the spectra spread over a wide range of frequency, as shown in Fig. 5, and could not be covered by the present rf pulse. Thus we cannot enter into details of the ordered state.

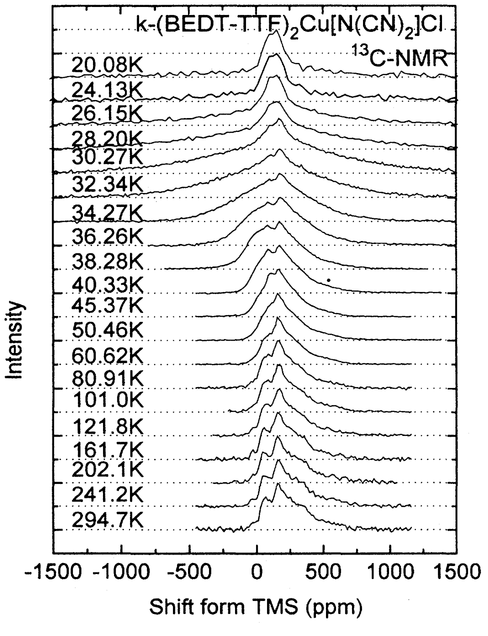

FIG. 7. Temperature dependence of line shape of ^{13}C NMR spectra for the X=Cu[N(CN)$_2$]Cl salt.

B. T_1 and recovery curve of powdered samples

As seen in Eq. (32), the relaxation rate depends on θ, and therefore the recovery curve of the nuclear magnetization in powdered samples does not follow a single-exponential function of time. As shown in Fig. 9, the experimental profile of the recovery curves, of which the time scale is normalized to the initial slope of the curve, T_1^0, shows nonlinear curves but does not depend on temperature. One can simulate the recovery curve, neglecting the $\mathbf{q}$ dependence of the hyperfine coupling tensors $A_{\mathbf{q}}$ and $B_{\mathbf{q}}$, in Eqs. (32) or (A5) (see the Appendix) and spin-spin interaction between interdimer ^{13}C sites, and using Knight shift tensors for evaluation of these. The solid and dotted curves in Fig. 9 are simulated ones with estimated values of K_{iso} and K_{aniso} for both sites of $i=1$ and 2 in Eq. (32), and with reported values of tensors[5] in Eq. (A5), respectively. Hereafter, we define the relaxation time T_1^0 from the initial slope of the curve, in both theoretical calculation and experimental determination of T_1. From Eq. (32), a relationship between T_1^0 and dynamic susceptibility on BEDT-TTF is given for the powder as

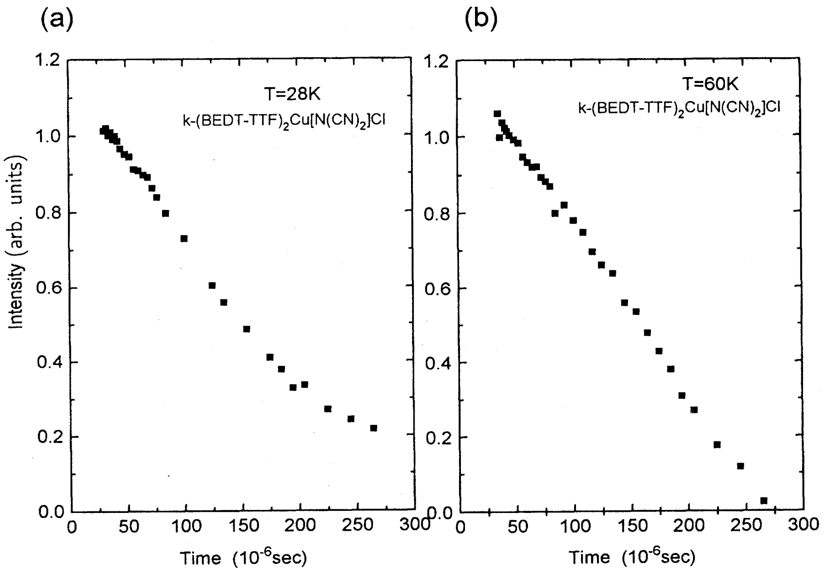

FIG. 8. Transverse nuclear magnetic relaxation curve of the Cu[N(CN)$_2$]Cl salt at (a) 28 K and (b) 60 K.

$$\frac{1}{T_1^0}=\frac{1}{4\pi}\int_0^{2\pi}d\phi\int_0^{\pi}\frac{1}{T_1}|\sin\theta|d\theta$$
$$=\frac{k_B\gamma_I^2T}{2\gamma_e^2\hbar^2}\sum_{i,\mathbf{q}}(2{}^iA_{\mathbf{q}}{}^iA_{-\mathbf{q}}+4{}^iB_{\mathbf{q}}{}^iB_{-\mathbf{q}})\frac{\chi''(\mathbf{q},\omega)}{\omega}, \tag{38}$$

in the case of uniaxial symmetry for both sites. For the general case of nonuniaxial symmetry (see the Appendix), it is expressed by

$$\frac{1}{T_1^0}=\frac{k_B\gamma_I^2T}{2\gamma_e^2\hbar^2}\sum_{i,\mathbf{q}}\left(2{}^iA_{\mathbf{q}}^iA_{-\mathbf{q}}+\frac{2(2{}^iB1_{\mathbf{q}}{}^iB1_{-\mathbf{q}}+{}^iB1_{\mathbf{q}}{}^iB2_{-\mathbf{q}}+{}^iB2_{\mathbf{q}}{}^iB2_{-\mathbf{q}}+2{}^iB2_{\mathbf{q}}{}^iB2_{-\mathbf{q}})}{3}\right)\frac{\chi''(\mathbf{q},\omega)}{\omega}, \tag{39}$$

where i represents two inequivalent carbon atoms.

If the $\mathbf{q}$ dependence of $A_{\mathbf{q}}$, $B_{\mathbf{q}}$, and $\chi''(\mathbf{q},\omega)$ is negligible, these equations turn out to be extended versions of the Korringa relation between the relaxation rate and the anisotropic Knight shift. In the case of Eq. (38) with equivalent sites for $i=1$ and 2, one obtains a simple formula

$$T_1^0TK_{\text{aniso}}^2=\frac{1}{(\beta^2+2)}\left(\frac{\gamma_e}{\gamma_1}\right)^2\left(\frac{\hbar}{4\pi k_B}\right), \tag{40}$$

where $\beta=A/B_0=K_{\text{iso}}/K_{\text{aniso}}$.

In the general case of Eq. (39), one obtains a slightly complicated formula

$$\frac{T_1^0T}{2}\sum_i\left({}^iK_{\text{iso}}^2+\frac{2({}^iK_{\text{aniso},11}^2+{}^iK_{\text{aniso},11}{}^iK_{\text{aniso},22}+{}^iK_{\text{aniso},22}^2)}{3}\right)=\left(\frac{\gamma_e}{\gamma_I}\right)^2\left(\frac{\hbar}{4\pi k_B}\right). \tag{41}$$

The experimental results of $(T_1^0T)^{-1}$ is shown in Fig. 10. The Cu[N(CN)$_2$]Cl salt shows a divergent peak of $(T_1^0T)^{-1}$ at 26–27 K, which corresponds to the magnetic ordering. The temperature dependence at higher temperatures is considered to originate from critical magnetic fluctuations. Taking account of a difference in the hyperfine couplings and the gyromagnetic ratios of ^{1}H and ^{13}C, the profile of this divergence in ^{13}C NMR is well scaled to that in the ^{1}H NMR.[3] The most remarkable result in Fig. 10 is the behavior above 60 K, where the three salts have quantitatively the same character, namely a gradual growth of $(T_1^0T)^{-1}$ toward lower temperatures. This gives evidence of magnetic fluctuations even in the superconductors. Using K_{iso} and K_{aniso}, the value of $(T_1^0T)^{-1}$ expected in the uncorrelated case is evaluated as 0.009 s^{-1} K^{-1} from Eq. (40) for the equivalent-site model. [These values of $(T_1^0T)^{-1}$ are somewhat larger than in our previous report,[4] because the shift values obtained in the present analysis are a little larger than by the previous determination.] For the inequivalent-site model, a value of 0.017 s^{-1} K^{-1} is obtained from Eq. (41), with the two shift tensors

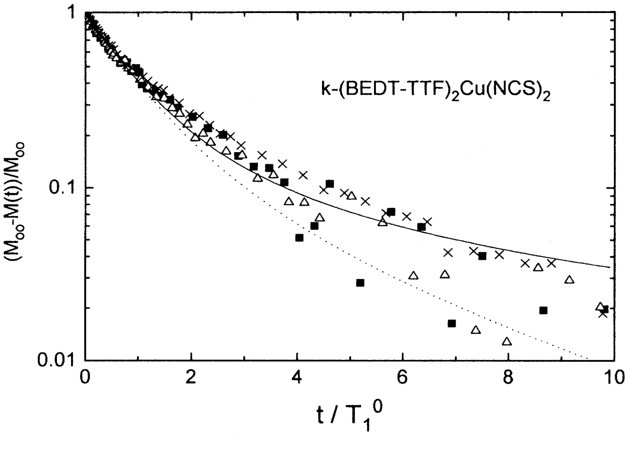

FIG. 9. Profile of recovery curves of the nuclear magnetization for the powder sample at several temperatures, ■: $T=295$ K; △: $T=151$ K; ×: $T=65$ K. The scale of the horizontal axis is normalized to the relaxation rate T_1^0 (see text). The solid curve is simulated with the use of the estimated K_{iso} and K_{aniso} for both sites in Eq. (32). The dotted curve is simulated with the use of the reported values of tensors (Ref. 5) in Eq. (A5).

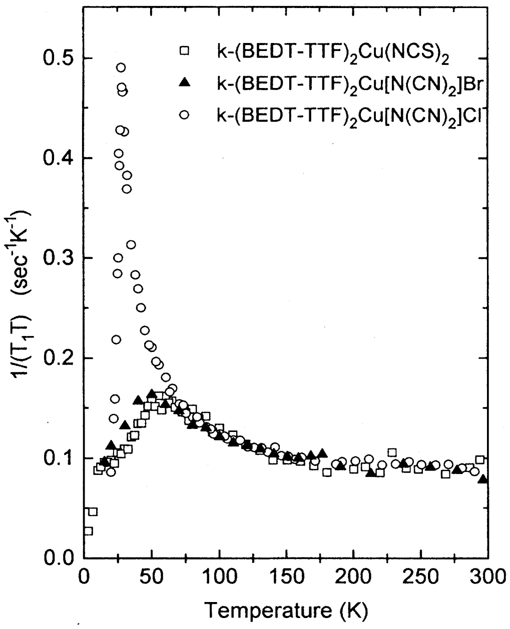

FIG. 10. Temperature dependence of $(T_1^0T)^{-1}$. ▲: Cu[N(CN)$_2$]Br; □: Cu(NCS)$_2$; ○: Cu[N(CN)$_2$]Cl.

given in Ref. 5. It is obvious that the experimental values in Fig. 10 are enhanced by one or one-half order of magnitude than the value expected from the Korringa laws. Therefore we conclude that the anomalous temperature dependence and large enhancement of $(T_1^0T)^{-1}$ around 50 K in the two superconducting salts come from antiferromagnetic spin fluctuations with a finite wave vector Q, which might correspond to the wave vector in AF phase of the Cu[N(CN)$_2$]Cl salt. Then a depression of the fluctuations below 50 K for the two salts leads to the superconducting ground state instead of antiferromagnetic order. However, it is emphasized that a large enhancement in $(T_1^0T)^{-1}$ still remains just above the superconducting transition. It is noted that the mass enhancement in the Shubnikov–de Haas oscillations for the Cu(NCS)$_2$ salt has been discussed in terms of renormalization of electron-electron interactions.[19,20]

The depression of $(T_1T)^{-1}$ below about 50 K for the Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br salts is reminiscent of the spin gap behavior discussed in high-T_c Cu oxides, where a similar depression in $(T_1T)^{-1}$ appears without a marked anomaly in resistivity, characterizing apparent separation of spin and charge degrees of freedom in strongly correlated electrons in two dimensions. In the present materials, however, the resistivity shows an anomalous change from low-temperature metallic behaviors to high-temperature nonmetallic ones with inflection points at the corresponding temperatures: 60 K for the Cu(NCS)$_2$ salt[21] and 40–50 K for the Cu[N(CN)$_2$]Br salt.[22] This may be considered as a crossover from a metallic to a semiconducting state with a very small but finite charge-excitation gap. In this context, the NMR anomaly can be interpreted as a crossover from a Fermi-liquid regime to an antiferromagnetic critical fluctuation regime with the nature of localized spins. Indeed, $(T_1T)^{-1}$ tends to saturate to a finite value at low temperatures in the normal state at least for the Cu(NCS)$_2$ salt, unlike the spin gap behavior. The measurements of $(T_1T)^{-1}$ on the condition that the superconductivity is completely destroyed will give further insight into the nature of the low-temperature magnetism.

These two superconductors ($X=$Cu[N(CN)$_2$]Br and Cu(NCS)$_2$) are situated very close to the antiferromagnetic insulator ($X=$Cu[N(CN)$_2$]Cl). A depression of the anomaly and the value of $(T_1^0T)^{-1}$ by pressure for the Cu[N(CN)$_2$]Br salt was reported by Mayaffre *et al.*[5] These results suggest that pressure tends to suppress the effect of electron correlation and leads the system to a usual metal that obeys the Korringa law.

Concerning the nature of the AF phase of the Cu[N(CN)$_2$]Cl salt, our previous analysis of the ^{1}H NMR line shape of a single crystal suggested that the amplitude of the AF order is large (0.4–1.0 of μ_B/dimer) and Q is commensurate.[3] These two characteristics of the AF states are quite different from those of conventional spin-density wave (SDW) as in the TMTSF compounds. Thus we consider that the origin of the AF transition is not the nesting of open Fermi surfaces, but a strong correlation of electrons.

We make a brief comment on the connection of structural modulation to the $(T_1T)^{-1}$ anomaly around 50 K. From a crystallographic study, the appearance of a superstructure below 200 K for the Cu[N(CN)$_2$]Br salt was reported by Nogami *et al.*[23] Considering that such a structural anomaly is not observed for the other two salts, it is unlikely that the formation of a superstructure is responsible for the present NMR relaxation results.

V. CONCLUSION

So far the two salts, κ-(BEDT-TTF)$_2X$ ($X=$Cu(NCS)$_2$ and Cu[N(CN)$_2$]Br), have been paid particular attention to, partially owing to the highest T_c among the organic superconductors, and since the importance of electron correlation in these materials was often inferred in several experimental results. In the present work, we performed a ^{13}C NMR study on an antiferromagnetic insulator with the same structure, the Cu[N(CN)$_2$]Cl salt, as well as the two superconducting salts. A comparison of results for the three salts and a quantitative analysis of them provided unambiguous evidence of the presence of antiferromagnetic spin fluctuations in this family. We conclude that the κ-phase compounds are strongly correlated electronic systems.

Formulations for the NMR analysis given in this paper are available for general molecular conductors with $p\pi$ electrons.

ACKNOWLEDGMENTS

The authors thank Y. Morita, T. Suzuki, and K. Nakasuji for their teaching of the synthesis of the isotope labeled the BEDT-TTF molecule, N. Yokoi and E. Nomura (Toray Fine Chemicals) for their help in isotope substitution, and H. Anzai for his valuable suggestion on crystal growth. Thanks are also due to K. Kato, T. Takayama, and K. Hayasaka for technical support of the low-temperature experiments. This work was supported in part by a Grant-in-Aid for Scientific Research No. 06452064 and Priority Area "Novel Electronic States in Molecular Conductors" No. 06243102 from the Ministry of Education, Science, and Culture, Japan.

APPENDIX

Considering not only the core polarization and on-site $2p_z$ dipole field but also the off-site dipole field from one neighboring carbon and two neighboring sulfur sites ($S1$ and $S2$), we can approximate Eq. (14) as follows:

$$\begin{aligned}\langle\Psi_{\mathbf{k}'}|\mathbf{T}|\Psi_{\mathbf{k}}\rangle &\cong A_{\mathbf{k},\mathbf{k}'}\mathbf{E}+\frac{1}{NM}\sum_n^N e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_n}\sum_m^M D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}(|c_{13C}|^2\langle\rho_{13C,\mathrm{onsite}}|\mathbf{B}|\rho_{13C,\mathrm{onsite}}\rangle+|c_{13C}|^2\langle\rho_{13C,\mathrm{offsite}}|\mathbf{B}|\rho_{13C,\mathrm{offsite}}\rangle\\ &\quad+|c_S|^2\langle\rho_{S1}|\mathbf{B}|\rho_{S1}\rangle+|c_S|^2\langle\rho_{S2}|\mathbf{B}|\rho_{S2}\rangle)\\ &=\begin{pmatrix} A_{\mathbf{k},\mathbf{k}'}-B1_{\mathbf{k},\mathbf{k}'} & 0 & 0\\ 0 & A_{\mathbf{k},\mathbf{k}'}-B2_{\mathbf{k},\mathbf{k}'} & 0\\ 0 & 0 & A_{k,k'}+B1_{k,k'}+B2_{k,k'}\end{pmatrix},\end{aligned}\tag{A1}$$

$$\begin{aligned}B1_{\mathbf{k}',\mathbf{k}} &= B_{\mathbf{k}',\mathbf{k}}+\frac{\gamma_I\hbar}{NM}\sum_n^N e^{i(\mathbf{k}-\mathbf{k}')\mathbf{R}_n}\sum_m^M D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}\left(|c_{13C}|^2\left\langle\frac{1-\cos^2\theta_x}{r^3}\right\rangle_{2px}^{\mathrm{offsite}-C}+|c_s|^2\left\langle\frac{1-\cos^2\theta_x}{r^3}\right\rangle_{3px}^{S1}\right.\\ &\quad\left.+|c_s|^2\left\langle\frac{1-\cos^2\theta_x}{r^3}\right\rangle_{3px}^{S2}\right)\\ &\equiv B_{\mathbf{k},\mathbf{k}'}+B1'_{\mathbf{k},\mathbf{k}'},\end{aligned}\tag{A2}$$

$$\begin{aligned}B2_{\mathbf{k}',\mathbf{k}} &= B_{\mathbf{k}',\mathbf{k}}+\frac{\gamma_I\hbar}{NM}\sum_n^N e^{i(\mathbf{k}-\mathbf{k}')R_n}\sum_m^M D_m^{\Gamma,\mathbf{k}'^*}D_m^{\Gamma,\mathbf{k}}\left(|C_{13C}|^2\left\langle\frac{1-\cos^2\theta_y}{r^3}\right\rangle_{2pz}^{\mathrm{offsite}-C}+|c_s|^2\left\langle\frac{1-\cos^2\theta_y}{r^3}\right\rangle_{3pz}^{S1}\right.\\ &\quad\left.+|c_s|^2\left\langle\frac{1-\cos^2\theta_y}{r^3}\right\rangle_{3pz}^{S2}\right)\\ &\equiv B_{\mathbf{k},\mathbf{k}'}+B2'_{\mathbf{k},\mathbf{k}'},\end{aligned}\tag{A3}$$

where θ_x and θ_y are angles between r and x, y axes, respectively, and $B1'_{\mathbf{k},\mathbf{k}'}$ and $B2'_{\mathbf{k},\mathbf{k}'}$ are off-site terms.

By numerical integration on the $2p_z$ orbital of C and $3p_z$ orbital of S, and using $|c_s|^2=0.17$ (Ref. 18), we estimate $B1'_{\mathbf{k},\mathbf{k}'}/B_{\mathbf{k},\mathbf{k}'}$ and $B2'_{\mathbf{k},\mathbf{k}'}/B_{\mathbf{k},\mathbf{k}'}$ as -0.08 and -0.11, respectively. Therefore, the hyperfine coupling tensor on the central ^{13}C atom in BEDT-TTF happens to be of nearly uniaxial symmetry.

In general, the anisotropic term in the hyperfine coupling tensor does not have a uniaxial symmetry as described above. The angular-dependent Knight shift $K(\theta,\varphi)$ and the spin-lattice relaxation rate $T_1^{-1}(\theta,\varphi)$ are given

$$K(\theta,\varphi)=\sum_{\mathbf{k}}\,[A_{\mathbf{k},\mathbf{k}}+(B1_{\mathbf{k},\mathbf{k}}+B2_{\mathbf{k},\mathbf{k}})\cos^2 2\theta-(B1_{\mathbf{k},\mathbf{k}}\cos^2\varphi+B2_{\mathbf{k},\mathbf{k}}\sin^2\varphi)\sin^2\theta]\,\frac{\langle S^z_{\mathbf{k},\mathbf{k}}\rangle}{H_0},\tag{A4}$$

$$T_1^{-1}(\theta,\varphi)=\frac{2\gamma_1^2\mathbf{k}_BT}{\gamma_e^2\hbar^2}\sum_{\mathbf{q}}\left(A_{\mathbf{q}}A_{-\mathbf{q}}+\frac{(B1_{\mathbf{q}}B2_{-\mathbf{q}}+B1_{-\mathbf{q}}B2_{\mathbf{q}})(1-\cos 2\theta)}{4}\right.$$
$$-\frac{(A_{\mathbf{q}}B1_{-\mathbf{q}}+A_{-\mathbf{q}}B1_{\mathbf{q}})(1+3\cos2\theta-\cos2\varphi+\cos2\theta\cos2\varphi)}{8}$$
$$-\frac{(A_{\mathbf{q}}B2_{-\mathbf{q}}+A_{-\mathbf{q}}B2_{\mathbf{q}})(1+3\cos2\theta+\cos2\varphi-\cos2\theta\cos2\varphi)}{8}+\frac{B1_{\mathbf{q}}B1_{-\mathbf{q}}(5-\cos2\theta-\cos2\varphi+\cos2\theta\cos2\varphi)}{8}$$
$$\left.+\frac{B2_{\mathbf{q}}B2_{-\mathbf{q}}(5-\cos2\theta+\cos2\varphi-\cos2\theta\cos2\varphi)}{8}\right)\frac{\chi_\perp^{\parallel}(\mathbf{q},\omega)}{\omega}, \tag{A5}$$

respectively. From Eq. (A5), a relationship between T_1^0 and the dynamic susceptibility for the powder is also given as

$$\frac{1}{T_1^0}=\frac{k_B\gamma_I^2T}{\gamma_e^2\hbar^2}\sum_{\mathbf{q}}\left(2A_{\mathbf{q}}A_{-\mathbf{q}}+\frac{2(2B1_{\mathbf{q}}B1_{-\mathbf{q}}+B1_{\mathbf{q}}B2_{-\mathbf{q}}+B2_{\mathbf{q}}B1_{-\mathbf{q}}+2B2_{\mathbf{q}}B2_{-\mathbf{q}})}{3}\right)\frac{\chi''(\mathbf{q},\omega)}{\omega}. \tag{A6}$$

In the case of a pair of dipolar-coupled nuclear spins with different hyperfine coupling tensors, $T_1^{-1}(\theta,\varphi)$ and T_1^0 of the system are given by averages of the above formulas at each site.

---

[1] 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**, 1501 (1991).

[2] U. Welp, S. Fleshler, W. K. Kwok, G. W. Carabtree, K. D. Carlson, H. H. Wang, U. Geiser, J. M. Williams, and V. M. Hitsman, Phys. Rev. Lett. **69**, 840 (1992).

[3] K. Miyagawa, A. Kawamoto, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **75**, 1174 (1995).

[4] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. Lett. **74**, 3455 (1995).

[5] H. Mayaffre, P. Wzietek, C. Lenoir, D. Jerome, and P. Batail, Europhys. Lett. **28**, 205 (1994).

[6] T. Takahashi, T. Tokiwa, K. Kanoda, H. Urayama, H. Yamochi, and G. Saito, Synth. Met. **27**, A319 (1988).

[7] J. Larsen and C. Lenoir, Synthesis, 134 (1989).

[8] H. Muller and Y. Ueda, Synthesis, 853 (1993).

[9] A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. VanderVoort, J. E. Thompson, D. L. Stupka, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 2555 (1990).

[10] T. Nakamura, T. Nobutori, M. Miyamoto, Y. Tsubokura, R. Tsuchiya, T. Takahashi, K. Kanoda, and G. Saito, J. Supercond. **7**, 671 (1994).

[11] N. Toyota, T. Sasaki, H. Sato, and Y. Watanabe, Physica C **178**, 339 (1991).

[12] M. Iwasaki, J. Magn. Res. **16**, 417 (1974).

[13] G. E. Pake, J. Chem. Phys. **16**, 327 (1948).

[14] H. Urayama, H. Yamochi, G. Saito, S. Sato, A. Kawamoto, J. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, Chem. Lett., 463 (1988).

[15] U. Geiser, A. J. Schultz, H. H. Wang, D. M. Watkins, D. L. Stupka, J. M. Williams, J. E. Shirbe, D. L. Qvermyer, D. Jung, J. J. Novoa, and M.-H. Whangbo, Physica C **174**, 475 (1991).

[16] C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed (Springer-Verlag, Berlin, 1990).

[17] A. Vanirub, S. Vija, E. Lippmaa, V. Prigodin, R. Beha, and M. Mehring, Phys. Rev. Lett. **69**, 3116 (1992).

[18] T. Mori (private communication).

[19] N. Toyota, E. W. Fenton, T. Sasaki, and M. Tachiki, Solid State Commun. **72**, 859 (1989).

[20] J. Caufield, W. Lubczynski, F. L. Pratt, J. Singleton, D. Y. K. Ko, W. Hayes, M. Kurmoo, and P. Day, J. Phys. Condens. Matter **6**, 2911 (1994).

[21] K. Murata, M. Ishibashi, Y. Honda, N. A. Fortune, M. Tokumoto, N. Kinoshita, and H. Anzai, Solid State Commun. **76**, 377 (1990).

[22] Yu. V. Sushko, V. A. Bondarenko, R. A. Petrosov, N. D. Kushch, E. B. Yagubskii, M. A. Tanatar, and V. S. Yefanov, Physica C **185-189**, 2681 (1991); L. I. Buravov, N. D. Kushch, V. A. Merzhanov, M. V. Osherov, A. G. Khomenko, and E. B. Yagubskii, J. Phys. (France) I **2**, 1257 (1992).

[23] Y. Nogami, J. P. Pouget, H. Ito, T. Ishiguro, and G. Saito, Solid State Commun. **89**, 113 (1994).