## Molecular motion and high-temperature paramagnetic phase in $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl

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The organic conductor  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl has been studied for the examination of the conducting mechanism of the semiconducting behavior at high temperatures by <sup>13</sup>C-NMR spectroscopy. We found that the temperature dependence of the linewidths and the spin-spin relaxation rate  $T_2^{-1}$  showed a peak structure characterized by the hyperfine coupling constant in this region, suggesting a connection between ethylene motion and conducting electrons similar to that observed in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt was thought to be an insulator at high temperature, our findings suggest that all  $\kappa$ -type salts at high temperatures could be in the same phase where the scattering caused by ethylene motion is added to bad metal.

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### I. INTRODUCTION

Organic quasi-two-dimensional salts of general formula  $\kappa$ -(BEDT-TTF)<sub>2</sub>X, where BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene and X is a monovalent anion, are among the best known organic conductor systems [1,2]. Each pair of BEDT-TTF molecules forms a dimer in the conduction sheet, resulting in a half-filled electron system. The electronic phases of the  $\kappa$ -(BEDT-TTF)<sub>2</sub>X salts vary widely with physical or chemical pressures, and these compounds are regarded as strongly correlated electron systems [3].

Both  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>  $Cu[N(CN)_2]Br$  show superconductivity (SC) [2,4] and Fermi-liquid behavior at temperatures just above the superconducting transition temperature  $T_c$ , a property well described by the itinerant electron picture. In contrast,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is semiconducting over the entire temperature range [3], transitioning to a commensurate antiferromagnetic (AF) state at low temperatures [5], suggesting a localized electron picture. In addition, applying physical or chemical pressure to  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl can induce a metallic state and result in SC, as observed for the superconducting  $\kappa$ -(BEDT-TTF)<sub>2</sub>X salts [5]. Although the conducting behavior of these three salts differs markedly, their spin susceptibility and spin-lattice relaxation rate,  $T_1^{-1}$ , are almost the same above 60 K [6]. Despite the  $\kappa$ -(BEDT-TTF)<sub>2</sub>X compounds being the most highly investigated organic superconductors, the nature of their hightemperature phase has not yet been determined. Determining whether  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is an intrinsic insulator at high temperatures is therefore of great interest.

The electrical conductivity of superconducting  $\kappa$ -type salts located in the itinerant region were found to display semiconducting behavior at high temperatures with strong sample dependence [7,8].  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br was observed to form a superlattice below 200 K [9]. As the ethylene group ordered at low temperatures [10], the superlattice is perhaps due to anion layers. The static modification may be associated with its small anomalous or semiconducting resistivity, as observed for the salts

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[12]. However,  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, which does not induce this lattice modulation, but demonstrates the ethylene group ordering at low temperatures, showed similar resistivity behavior [10]. The NMR spectrum was found to be broadened due to a static incommensurate superlattice below 150 K in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br [13]. Although the increased NMR linewidth of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br at lower temperatures due to the superlattice would be expected to increase its electron scattering and reduce its conductivity, its conductivity was observed to increase below 70 K. The mechanism underlying the semiconducting behavior of superconducting  $\kappa$ -type salts was therefore unclear.

 $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [11] and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]I

Examining the <sup>13</sup>C-NMR spectrum of  $\kappa$ -(BEDT-TTF)<sub>2</sub>  $Cu(NCS)_2$  showed a strong connection between ethylene motion and conductivity [14]. Although the dynamics of ethylene motion was previously reported [15,16], it was unclear whether the motion couples with the conduction electron. The temperature dependence of the spin-spin relaxation rate  $T_2^{-1}$ , corresponding to ethylene motion, was proportional to the square of the hyperfine coupling constants between the nucleus and conducting electrons. The result is evidence that the ethylene motion is strongly coupled to these electrons.  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br also showed a similar  $T_2^{-1}$  anomaly [17]. The coupling between paramagnetic electrons and ethylene motion was also confirmed by x-ray irradiation. X-ray irradiation may induce disorder in ethylene motion. Irradiation of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> salt suppressed the semiconducting behavior at approximately 100 K, while inducing metallic or temperature independent behavior [18]. Assessment of  $T_2$  by <sup>13</sup>C-NMR suggested that a local structural disorder induced by irradiation inhibited the scattering of conducting electrons by ethylene motion in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>; the  $T_2^{-1}$  for one of <sup>13</sup>C sites, which had the larger hyperfine coupling constant, was reduced, and the site dependence of  $T_2^{-1}$  was weakened after irradiation [19]. This reduction of the coupling, which corresponds to the semiconducting behavior at approximately 100 K, could explain the monotonous metallic or temperature-independent conductivity by irradiation in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> salt. These findings suggested experimentally that the semiconducting behavior of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> at high temperatures is not intrinsic but is due to the incoherent

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dynamic scattering of electrons caused by ethylene motion. Although the strong sample dependence was reported, some samples showed resistivity maximum around 100 K and other samples showed almost temperature-independent behavior around 100 K; all samples showed metallic behavior below 70 K. The ethylene motion is sensitive to cooling rates and defects [20]. The semiconducting behavior with strong sample dependence might be explained by the degree of the defects in crystal. This is one speculation and should be confirmed by the comprehensive transport works for sample dependence.

Transformation of the ethylene group between eclipsed and staggered conformations modifies the symmetry of the molecular orbitals. The difference in orbital energy between two stable conformations is about 20 meV, equivalent to about 5% of the bandwidth, and this dynamic modulation could interact with conducting electrons [14]. Similar connections between a local lattice motion, a so-called "rattling," and conducting electron were recently reported for the inorganic systems of  $PrOs_4Sb_{12}$  [21] and  $\beta$ -pyrochlore oxides [22,23], where the rattling mode is coupled to nonlinearity of harmonic phonon mode. Unlike in the case of lattice phonons, the time scale of the ethylene dynamics drastically slows down from  $10^{-12}$  at 300 K to almost static at glass transition temperature of 70-80 K. The ethylene dynamics contribute to the additional resistivity at some temperatures, whereas the ethylene group ordered and could not contribute to the electron scattering below the glass transition temperature.

X-ray irradiation of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> salt was found to suppress ethylene dynamics, and metallic conductivity was observed. Similarly, irradiation of  $\kappa$ -(BEDT-TTF)<sub>2</sub> Cu[N(CN)<sub>2</sub>]Cl salt resulted in metallic conductivity at high temperatures [24]. If  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is a simple insulator with an energy gap, the mechanism by which irradiation induces metallic conductivity would be very complicated. Previous studies have suggested slight (0.04%) charge doping of the Mott insulator [24–26] or a Mott-Anderson transition induced by disorder [27].

The ethylene motion of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl was also observed in a measurement of thermal expansion [15], <sup>1</sup>H – NMR [5], and specific heat [16]. The high-temperature phase of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl may be identical to that in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl; may be identical to that in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl; in both, ethylene motion contributes significantly to the paramagnetic electrons via the modulation of the highest occupied molecular orbital (HOMO). This possibility can be confirmed by determining whether the electrons in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl are coupled to ethylene motion at high temperatures. Previous NMR studies of this salt did not focus on the high-temperature electronic state [28,29]. We therefore measured the <sup>13</sup>C-NMR spectral linewidths and  $T_2^{-1}$  of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl.

### **II. EXPERIMENT**

One side of the central C=C bond of BEDT-TTF molecule was replaced by  $^{13}$ C nuclei using the cross-coupling method [30,31], preventing the Pake doublet effect and

allowing measurements of  $T_2^{-1}$  at each site. Single crystals of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl were obtained by electrochemical oxidation [3]. The typical crystal size is  $1.5 \text{ mm} \times$  $1.2 \text{ mm} \times 1.0 \text{ mm}$ . To assess the effects of irradiation, the crystals were irradiated with a mean dose of 92.2 MGy at room temperature using a nonfiltered copper target (Philips PW 2243/20) at 40 kV and 20 mA. Uniform damage was attained by irradiating both sides of the crystals. <sup>13</sup>C-NMR measurements were performed in an external magnetic field of 8.5 T, parallel to the *a* axis, and an external magnetic field of 9.4 T, parallel to the b and c axes. The spectra were obtained by fast Fourier transformation (FFT) of echo signals with a  $\pi/2$ - $\pi$  pulse sequence. The NMR shift relative to the tetramethylsilane (TMS) signals and the linewidths (full widths at half maximum) were evaluated by fitting peaks to the Lorentz function, with  $T_2^{-1}$  defined as the rate corresponding to Lorentz decay.  $T_2^{-1}$  was measured during the cooling process, which took about 14 h at each temperature.

## **III. RESULTS AND DISCUSSION**

### A. Linewidth anomaly

In  $\kappa$ -type salts, BEDT-TTF dimers form a corrugated network arrangement in the conducting sheet [2]. Because  $\kappa$ -(BEDT – TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl belongs to the space group *Pnma* and BEDT-TTF dimers have inversion symmetry, all dimers are crystallographically and magnetically equivalent, with the external field parallel to the *a*, *b*, and *c* axes, resulting in two peaks of inner and outer sites in all directions (Fig. 1). The linewidth increased as temperature decreased from 150 to 130 K. The shift and the linewidth for the outer site was altered significantly in the  $H_0 \parallel c$  field.

Figure 2(a) shows the temperature dependence of linewidths in the  $H_0 \parallel a$ ,  $H_0 \parallel b$ , and  $H_0 \parallel c$  fields. These linewidths showed an anomaly at approximately 120 K, especially at the outer site  $(H_0 \parallel c)$ , a behavior similar to that of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [14], with all showing an increase as temperatures decreased below 60 K. The increase at low temperatures was likely due to AF fluctuations. To clarify the connection between linewidths and paramagnetic electrons, it was necessary to estimate the hyperfine coupling constant A of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. This constant can be calculated using the equation  $\delta = A\chi_s + \sigma$ , where  $\delta$ is the NMR shift,  $\chi_s$  is the spin susceptibility, and  $\sigma$  is the chemical shift. Anomalous line broadening in ESR [32] and an anomalous NMR shift not proportional to spin susceptibility below 50 K due to a magnetic fluctuation [29] have been reported. To avoid the influence of magnetic fluctuations, we used the NMR shift at 150 K, together with the chemical shift tensor [33] and spin susceptibility [6], and the results were  $A_{\parallel a, \text{in}} = -0.71 \text{ kOe}/\mu_B, \ A_{\parallel a, \text{out}} = 2.44 \text{ kOe}/\mu_B, \ A_{\parallel b, \text{in}} =$  $-1.06 \,\mathrm{kOe}/\mu_B$  $A_{\parallel b, \text{out}} = 1.55 \text{ kOe}/\mu_B$  $A_{\parallel c, \text{in}} =$ 1.56 kOe/ $\mu_B$ , and  $A_{\parallel c, \text{out}} = 4.18 \text{ kOe}/\mu_B$ . As with  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, the linewidth depended on the hyperfine coupling constant. The linewidth of the outer site is large in the  $H_0 \parallel a$  and the  $H_0 \parallel b$  fields, and much larger in the  $H_0 \parallel c$  field, suggesting coupling between the linewidth anomaly and the paramagnetic electrons.



FIG. 1. Temperature dependence of the <sup>13</sup>C-NMR spectrum of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl in fields of (a)  $H_0 \parallel a$ , (b)  $H_0 \parallel b$ , and (c)  $H_0 \parallel c$ . The low-frequency peaks correspond to the inner site and the high-frequency peaks correspond to the outer site [17].

# **B.** Slow dynamics detected by $T_2^{-1}$

In Fourier transform (FT)-NMR, the linewidth can generally be described as  $\Delta \omega = 2\pi/T_2 + \gamma \Delta H$ , where  $\gamma$  is the nuclear gyromagnetic ratio and  $\Delta H$  is the inhomogeneity of the local magnetic field at the corresponding nuclei. Measurement of  $T_2^{-1}$  can clarify whether the increase in linewidths was due to statical or dynamical contribution.

The temperature dependence of  $T_2^{-1}$  may quantitatively explain the peak behavior of the linewidths [Fig. 2(b)]. Since  $T_2^{-1}$  can detect slow magnetic fluctuations at <sup>13</sup>C sites below approximately 10 kHz, the anomaly of the linewidths observed at approximately 130 K was due to a slow magnetic fluctuation.

In thermal expansion measurement [15], the glass transition temperature of the ethylene motion between eclipsed and staggered configurations [Fig. 2(b), inset], 50 ~ 70 K for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, was well explained by the Arrhenius plot of the activation energy of <sup>1</sup>H-NMR. In a parallel manner we confirmed that the time scale of ethylene motion decreases to approximately 10 kHz at approximately 100 K for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [14]. The  $T_2^{-1}$  anomaly is expected to be about 40 K higher than the glass transition temperature. Since the glass transition temperature in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is about 70 ~75 K [15], the  $T_2^{-1}$  anomaly at around 125 K could be due to the ethylene dynamics.

The linewidth in the ESR studies reported the anisotropy within plane and the authors of ESR studies discussed antiferromagnetic correlations/fluctuations as one of the possible reasons for broadening [32]. This effect is caused by a distribution of local fields and can be observed at NMR frequencies. The peak anomaly at around 125 K was, however, observed only in  $T_2^{-1}$ , not in  $T_1^{-1}$  which can detect the fluctuation at NMR frequency. The difference behavior between the NMR and the ESR is not clear. More detailed ESR measurements, for example,  $T_1^{-1}$  and  $T_2^{-1}$  may present more information about the anomalous line broadening in ESR spectrum. We focused on the site-dependent behavior of  $T_2^{-1}$ . Using the spectral density function of ethylene motion,  $J(\omega)$ , the  $T_2^{-1}$ on  $\alpha$  site can be described as

$$(1/T_2)_{\alpha} = (1/T_2)_{\alpha,\mathrm{D}} + (1/T_2)_{\alpha,\mathrm{I}}$$
$$= \int_0^{\Delta} d\omega \{ D_{\alpha}^2 J(\omega) + A_{\alpha}^2 \lambda J(\omega) \}, \qquad (1)$$

where  $\Delta \simeq 2\pi \times 10$  kHz.

The first term in the equation is caused by a direct fluctuation originating from the dipole field of <sup>1</sup>H nuclei and the electron spin, resulting in the displacement of surrounding molecules caused by ethylene motion.  $D_{\alpha}$  is the coupling constant of the dipole field. The second term is a result of indirect fluctuations via HOMO of BEDT-TTF. The reorientational motion modulates HOMO symmetry (between  $C_s$  and  $D_2$ ) and induces fluctuations at the <sup>13</sup>C sites via the hyperfine coupling constant  $A_{\alpha}$  [14]. Here  $\lambda$  is defined as a coupling parameter between ethylene motion and the paramagnetic electrons. The  $T_2^{-1}$  value of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> is proportional to the square of the hyperfine coupling constants, providing experimental evidence of the coupling between molecular motion and the conducting electrons [14]. It is important to examine whether the  $T_2^{-1}$  of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is characterized by the hyperfine coupling constant.

We could clearly confirm the hyperfine coupling dependent behavior of  $(1/T_2)$  for  $H_0 \parallel a$ . As shown in Fig. 1(a), the peak for the inner site shows very little change suggesting small hyperfine coupling constant and that the second term in Eq. (1) is small for inner site. The  $T_2^{-1}$  for the inner site, which is mainly due to the first term in Eq. (1), is slightly enhanced at around 125 K, whereas the  $T_2^{-1}$  for the outer site with moderate hyperfine coupling constant shows the distinct peak at around 125 K due to the second term in Eq. (1). We also observed the hyperfine coupling dependent behavior of



FIG. 2. (Color online) Temperature dependence of the (a) linewidths and (b)  $T_2^{-1}$  of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl in the fields  $H_0 \parallel a, H_0 \parallel b$ , and  $H_0 \parallel c$ . The dashed lines are guides for the eye. The inset shows the ethylene motion of the BEDT-TTF molecule.

 $(1/T_2)$  for  $H_0 \parallel b$  and  $H_0 \parallel c$ . Since the coupling constant of the dipole field,  $D_{\alpha}$ , mainly depends on steric dimer structure and does not show significant site dependence, the first term of the equation,  $(1/T_2)_D$ , at around 125 K for all can be roughly estimated as  $(1/T_2)_{\parallel a,in}$  of  $1.0 \times 10^3$  s<sup>-1</sup>. Using this value, the second term of each site,  $(1/T_2)_I$ , was estimated as  $(1/T_2)_{\parallel a, \text{out, I}} = 3.0 \times 10^3 \text{ s}^{-1}, (1/T_2)_{\parallel b, \text{out, I}} = 4.0 \times 10^3 \text{ s}^{-1}, (1/T_2)_{\parallel b, \text{in, I}} = 2.7 \times 10^3 \text{ s}^{-1}, (1/T_2)_{\parallel c, \text{out, I}} = 11.5 \times 10^3 \text{ s}^{-1}, \text{and } (1/T_2)_{\parallel c, \text{in, I}} = 2.9 \times 10^3 \text{ s}^{-1} \text{ at peak temperature. With}$  $H_0 \parallel c$ , the ratio of  $(1/T_2)_{\rm I}$  for inner to outer sites is about 1:4.0, and is characterized by the ratio of the hyperfine coupling constants at these sites; i.e.,  $A_{\parallel c, \text{out}}/A_{\parallel c, \text{in}} = 2.68$  and  $(A_{\parallel c, \text{out}}/A_{\parallel c, \text{in}})^2 = 7.18$ . The ratios of  $(1/T_2)_I$  are described by the hyperfine coupling constants. The contribution of the indirect term to the  $T_2$  process suggests that the couplings between ethylene motion and the paramagnetic electrons are the same as that in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> [14]. For  $H_0 \parallel b$ , the ratio of  $(1/T_2)_I$  for the inner to the outer site was approximately 1:1.5 and also consistent with the ratio of the hyperfine coupling constants at these sites; i.e.,  $A_{\parallel b, \text{out}} / A_{\parallel b, \text{in}} = 1.46 \text{ and } (A_{\parallel b, \text{out}} / A_{\parallel b, \text{in}})^2 = 2.14.$ 



FIG. 3. (Color online) Temperature dependence of (a) linewidth and (b)  $T_2^{-1}$  of irradiated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl in a  $H_0 \parallel c$  field. The dashed lines are guides for the eye.

In spite of that the weak anisotropy of the *g* value has been reported [32], and  $\lambda$  may also show slight dependence on field direction; the consistency among  $H_0 \parallel a$ ,  $H_0 \parallel b$ , and  $H_0 \parallel c$  could be confirmed semiquantitatively.

### C. Ethylene motion and x-ray irradiation

Figure 3 shows the temperature dependence of linewidth and  $T_2^{-1}$  after irradiation under the field along the *c* axis. Linewidths increased over the entire temperature range due to irradiation-induced disorders. Because irradiation did not increase the value of  $T_2^{-1}$ , the observed linewidth broadening was not due to dynamics but to the inhomogeneity of the local field. Importantly, the anomaly at approximately 130 K at the outer site was suppressed. As with  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>, the  $T_2^{-1}$  value of this site, which has the larger hyperfine coupling constant, was reduced by an amount corresponding to the decrease in the indirect term, suggesting that the scattering of electrons by ethylene motion was suppressed owing to the disorder.

One possible mechanism of the x-ray irradiation effect was based on previous discussion of the effects of x rays on  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [20]. Figure 4(a) shows a schematic diagram of ethylene motion in a pure sample [10]. A or B represents the two stable configurations, with eclipsed or staggered conformations. The double minimum potential shows that the modification of HOMO by ethylene motion scatters the



FIG. 4. Schematic potential diagram of ethylene motion of the BEDT-TTF molecule in (a) pure and (b) damaged samples [10,20]. Occupancy of the A or B wall gives rise to the two stable (eclipsed or staggered) configurations of the molecule.

electrons effectively. After irradiation, however, the potential has multiple minima due to disorder, as shown in Fig. 4(b) [20]. The ethylene motion between these multiple minima cannot modify the symmetry and energy level effectively, with the indirect term in Eq. (1) decreasing as a result of irradiation.

### **D.** Ethylene dynamics and the phase diagram in $\kappa$ salts

The *P*-*T* phase diagram of  $\kappa$ -type salts divides the hightemperature region into a paramagnetic insulating (PI) phase as in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt with an intrinsic energy gap and a paramagnetic metallic (PM) phase as in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> salt, with a crossover or phase transition line between them [Fig. 5(a)] [34]. However, this concept was based on semiconducting behavior over the entire temperature range in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt, resulting in an unclear boundary between the PI and PM phases.

The semiconducting behavior in nonirradiated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is divided into two regions from the resistivity measurements [35,36]. Above 50 K, semiconducting behavior is not always observed at high temperatures. Moreover, the salt has been reported to show not insulating but weak metallic behavior above 50 K. Below 50 K, resistivity steeply increased without sample dependence. We found that electron scattering was caused by ethylene motion and that the indirect scattering process was suppressed by irradiation, explaining findings of the metallic conductivity above 50-70 K [24]. The magnetic behavior of the three  $\kappa$ -type salts at high temperatures was identical, both qualitatively and quantitatively [6]. These results indicate that the high-temperature phase of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl above 50-60 K was not an insulator but was rather the same itinerant state as observed for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. Previous suggestions that the emergence of metallic conductivity due to irradiation was caused by slight charge doping [24-26] or a Mott-Anderson transition induced by disorder [27] were based on the assumption that nonirradiated  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl is a small gap insulator at high temperatures based on Fig. 5(a). Although the effects of x-ray irradiation are complicated, the suppression of the indirect term in Eq. (1), representing the qualitative change induced by irradiation, may provide a simple



FIG. 5. (a) Conceptional phase diagram of  $\kappa$ -(BEDT-TTF)<sub>2</sub>X [34]. (b) Modified phase diagram based on our findings. Temperature (vertical axis) is in a logarithmic scale. Cl, Br, and NCS indicate the positions of compounds with different anions  $X = Cu[N(CN)_2]Cl, Cu[N(CN)_2]Br$ , and Cu(NCS)<sub>2</sub>, respectively.

explanation for the strong sample dependence and increase of conductivity after irradiation. From thermal expansion measurements [15], ethylene motion freezes below 70 K in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl. This result is consistent with metallic behavior above about 60 K after irradiation in this material [24].

The Drude edge of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br salts are not clearly observed above 50 K [7], suggesting that the high-temperature phase is not a simple metal but a bad metal, with the mean free path of conducting electrons being shorter than the lattice constant. Scattering by ethylene groups in such bad metal enhances the semiconducting behavior of  $\kappa$  salts. The semiconducting behavior of these salts is not intrinsic, with  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br prepared with tetrahydrofuran showing metallic behavior [7,8]. Fluctuation spectroscopy suggests that ethylene motion of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl also occurs under critical pressure [37]. Resistivity exceeding the Ioffe-Regel-Mott limit under critical pressure [38] may result from electron scattering by ethylene motion in the bad metal state. Transport measurement of the conducting behavior of  $\kappa$ -type salts needs to consider not only a pure electron system but the additional scattering caused by ethylene motion.

Semiconducting behavior at high temperatures is a characteristic feature of BEDT-TTF. The  $\kappa$ -type organic conductors  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]X (X = Br, Cl) [BMDT-TTF:bis(methylenedithio)tetrathiafulvalene] consist of a rigid donor molecule, with electrical resistivity not showing a maximum behavior, but rather showing a metallic behavior, at all temperatures [39].

 $T_1$  of <sup>13</sup>C-NMR [40] and thermal-expansion measurements [15] of  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br have shown that after ethylene motion stops, these salts show another anomaly at  $T^* \sim 50$  K. The mean free path begins to increase below  $T^*$ , and both these salts become good metals [7].

At low temperatures,  $\kappa$ -type salts can be divided into two phases, with  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl being an antiferromagnetic insulator and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br and  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub> being superconductors. Both phases meet at the critical end point ( $p_0 \sim 200-300$  bars,  $T_0 \sim$ 30–40 K), with a phase transition line below this point [38,41]. Because  $T^*$  decreases when  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br is deuterated [42], the crossover  $T^*$  line seems to connect to this end point, as shown by the dashed line in Fig. 5. As temperatures decrease, superconducting salts transition from a high-temperature to a superconducting phase via the Fermi-liquid state.

For  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt, the metallic behavior was expected below the glass transition temperature,

70-80 K, as in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. As mentioned previously, however, the resistivity rapidly increases without sample dependence below 50 K and the crossover between metal and semiconductor at around 60 K was observed in the irradiated sample [35,36]. The anomaly below 55 K is also observed in the NMR spectrum in  $H_0 \parallel c$  field. Below 55 K, NMR peaks drastically shifted and the shift for the inner site was comparable to that for the outer site. Since the hyperfine coupling constant for the inner site is much smaller than that for the outer site, the comparable shift could not be explained by simple paramagnetic spins. From these results, some crossover or phase transition was expected at this temperature at ambient pressure. The resistivity measurement under pressures suggested the crossover or phase-transition line from 55 K at ambient pressure to the critical end point [38,41]. Hence the phase diagram of the  $\kappa$  phase can be expected by Fig. 5(b) with some crossover or phase transition line between high-temperature and AF phases, not by Fig. 5(a). Recently, a dielectric anomaly was observed in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl below 30 K [43], suggesting the existence of a novel phase between the high-temperature and AF phases. Vibrational spectroscopy, however, ruled out the possibility of charge disproportionation [44], and the nature of this anomaly is still uncertain. Further theoretical and experimental studies may illuminate the association between the high-temperature phase and this phenomenon.

## **IV. CONCLUDING REMARKS**

To conclude, <sup>13</sup>C-NMR spectroscopy of  $\kappa$ -(BEDT-TTF)<sub>2</sub>  $Cu[N(CN)_2]Cl$  showed anomalies in its linewidths and  $T_2^$ at high temperatures. The temperature dependence of  $T_2^{2-1}$ shows a maximum, and the degree of the anomaly depends on the hyperfine coupling constant. The suppression by irradiation of ethylene dynamics verified the coupling between ethylene dynamics and the conducting electrons. These results suggest that the high-temperature phase of the  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl salt is not an insulator but rather is in a state in which ethylene motion is strongly linked to the electrons, as in  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. Our findings provide a simple explanation for the inconsistency between transport and magnetic measurements, the strong sample dependence of conductivity at high temperatures, and the x-ray irradiation effect. Moreover, the connection between the high-temperature phase and the anomaly of the dielectric constant is interesting and requires further investigation.

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