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# Electron localization in the strongly correlated organic system $\kappa$-(BEDT-TTF)$_2X$ probed with nuclear magnetic resonance $^{13}$C-NMR

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$\kappa$-(BEDT-TTF)$_2X$ salts exhibit a wide range of properties from superconductivity to magnetic ordering. The phase diagram of this system has been understood as the competition between anti-ferromagnetic insulating behavior and superconductivity. The $\kappa$-(BEDT-TTF)$_2X$ system has been well explained using a parameter, U/W, as well as the high $T_c$ cuprates. $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, however, behaved as an insulator without magnetic ordering. This salt cannot be described by the phase diagram described by the competition between superconductivity and magnetism. It is interesting to explore the nature of this insulating phase with an eye toward understanding the universal phase diagram of the $\kappa$-(BEDT-TTF)$_2X$ system. Magnetic frustration due to the triangular spin lattice has recently been reported for $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ from $^1$H-nuclear magnetic resonance (NMR) study. To investigate the insulating properties of this salt, we characterized it using $^{13}$C-NMR. In contrast to previous $^1$H-NMR studies, at low temperatures, we observed line broadenings that were proportional to the hyperfine coupling constants, which suggested inhomogeous electron localization. We also observed antiferromagnetic fluctuations which, as is the case with other salts, intensified with decreasing temperature. To understand the electronic properties of $\kappa$-(BEDT-TTF)$_2X$ system, in addition to the U/W, the electron localization effect from the relatively narrow bandwidth is important.

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The electronic behavior of the $\kappa$-(BEDT-TTF)$_2X$ system ranges from antiferromagnetic insulating (AFI) to superconducting (SC). The phase diagram of this system is interpreted as the competition between AFI and SC as well as the high $T_c$ cuprates. Since $\kappa$-(BEDT-TTF)$_2X$ is a half filled electron system, many experiments on $\kappa$-(BEDT-TTF)$_2X$ have been well explained by the universal phase diagram using a parameter, U/W, where U is the effective onsite Coulomb repulsion and W is the bandwidth.[1–3] Recently the salt, which is an exceptional salt with respect to the phase diagram, was found. $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is insulating at ambient pressure, however, it is also known to exhibit superconductivity under high pressure,[4,5] just like $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.[6] While $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl shows a clear antiferromagnetic (AF) transition with a sharp $(T_1T)^{-1}$ peak at ambient pressure,[7,8] there has been no evidence of AF transition in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$. In this sense, this salt is a nonmagnetic insulator. The existence of the nonmagnetic insulator phase requires one to modify the phase diagram. To explain the nature of the insulating phase in this salt and elucidate the universality for the phase diagram of the $\kappa$-(BEDT-TTF)$_2$X family, additional scenario or parameters of the phase diagram are needed. These parameters or scenario not only modify the phase diagram but also give a information on the distinctive feature of the organic system. The spin frustration scenario is presented by Shimizu *et al.*[9] In this scenario, the ratio of the nearest ($t'$) and second nearest ($t$) neighbor overlap integrals between dimers shown in Fig. 1(a) is important. If $t'/t \sim 1$, from the spin frustration effects of this isotropic triangular lattice, a quantum spin liquid state without AF transition could be proposed. They favored the spin frustration scenario based on their results of $^1$H-NMR measurement in which $^1$H-nuclear magnetic resonance (NMR) spectra and the spin lattice relaxation rate showed no indication of AF transition down to 32 mK, and the spin lattice relaxation rate exhibited complex behavior at low temperature. Alternative scenario involves Anderson localization effect due to the relatively narrow bandwidth (W).[4] Indeed, as there were no interdimer S-S contacts within the van der Waals radii (3.7 Å), a narrow bandwidth is expected in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ To reveal the addtional scenario or parameters of the phase diagram, more quantitative studies are needed. Because of the small hyperfine coupling constant between the $^1$H nucleus and electrons, quantitative studies are quite difficult by $^1$H-NMR. $^{13}$C-NMR overcomes these difficulties and yields more detailed information,[7,10–12] because the central C=C site has large electron density of the conduction band and the large hyperfine coupling constant is expected. Thus, we opted to probe $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ using $^{13}$C-NMR.

Single crystals were prepared electrochemically with Geiser's method[4] using an isotope enriched BEDT-TTF-$^{13}$C

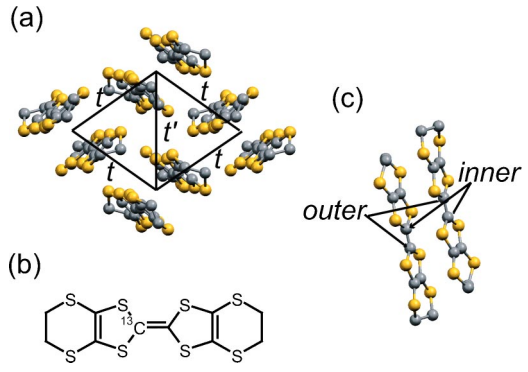


FIG. 1. (Color online) (a) Dimer network sheet in $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$, $t,t'$: Transfer integrals between dimers. (b) Single site $^{13}$C-enriched BEDT-TTF molecule. (c) Dimer structure of BEDT-TTF molecule.

 

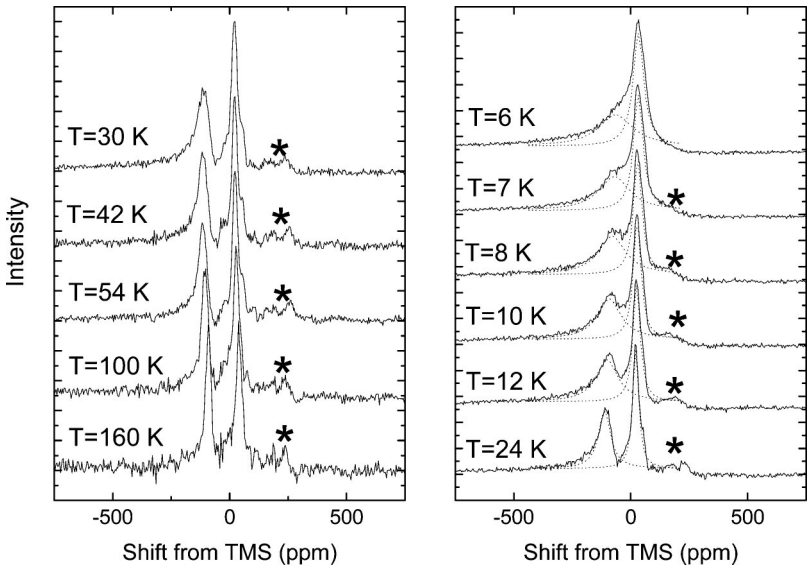


FIG. 2. $^{13}$C-NMR spectra of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$. The dotted lines represent the least-squares fitting with two Lorentzians. (The small additional peaks, *, are due to the misalignment pieces of the stacked sample.)

molecule shown in Fig. 1(b), which helps avoid Pake doublet splitting.[13] Black crystals were well grown on (1,0,0) plane; no polymorphism was observed in our batch. The cell constants and electronic conductivity of our samples under ambient pressure are in good agreement with the results of previous reports.[4,5] The magnetic susceptibility was measured by a superconducting quantum interference device (SQUID) magnetometer. NMR measurements were performed on 15 crystal specimens (about 0.1 mg for each) stacked on the (1,0,0) plane. An external field of 9.4 T was applied perpendicular to (1,0,0). Each unit cell contains two dimers of BEDT-TTF molecules.[4] As the two dimers are magnetically equivalent under the present conditions, only two $^{13}$C-NMR signals, one from the inner, the other from the outer site of the BEDT-TTF dimer shown in Fig. 1(c), are expected.

Figure 2 shows NMR spectra between 160 and 6 K. We observed two peaks from the inner (low frequency) and outer (high frequency) sites, as expected in the present experimental condition. Below 70 K, a broadening of the spectrum was observed. The broadening was larger in the case of the inner site, as compared to that of the outer site. The two spectra overlap each other at low temperature. To estimate NMR shift, $\delta$ and spectrum width, full width at half maximum (FWHM), we fitted the spectrum with two Lorentzians for phenomenalism. From the $\delta$-$\chi$ plot shown in the inset of Fig. 3, we evaluated the hyperfine coupling constants as −2.7 and −0.7 kOe/$\mu_B$ and the chemical shifts as 207 and 100 ppm for the inner and outer sites, respectively. These chemical shift values are comparable to those of neutral BEDT-TTF molecule reported in the literature.[14] To subtract chemical shifts from the observed data, we evaluated the Knight shifts on both sites, as shown in Fig. 3. The spin susceptibility evaluated from the Knight shift increases slightly as the temperature drops from 200 to 50 K, and begins to decrease at around 50 K; below 10 K, it decreases sharply. In this salt, the spin susceptibility from magnetometer in the low temperature region depends on the substation of magnetic impurities (e.g., $Cu^{2+}$) in the individual sample. The spin of the $Cu^{2+}$ ions would exist in the anion layers, which is far from the central $^{13}$C site in the BEDT-TTF molecules, and the additional local field on $^{13}$C nuclei from $Cu^{2+}$ spins is expected to be small. Thus the Knight shift in the central $^{13}$C site reflects the intrinsic spin susceptibility without the contribution of Curie impurities. The temperature dependence of FWHM of the spectrum is shown in Fig. 4. Above 70 K, the FWHM of the both sites is expressed as the phenomenological linewidth by $T_2$ process, the inhomogeneity of the external field and/or misalignment of the stacked samples. Line broadening becomes large below 70 K. The line of the inner site, which has a larger hyperfine constant, is more broadened than that of the outer site. The amplitudes of the broadening are enhanced with decreasing temperature and tend to be saturated below 6 K. Since the inhomogeneity of the electrons makes inhomogeous local field on $^{13}$C site through the

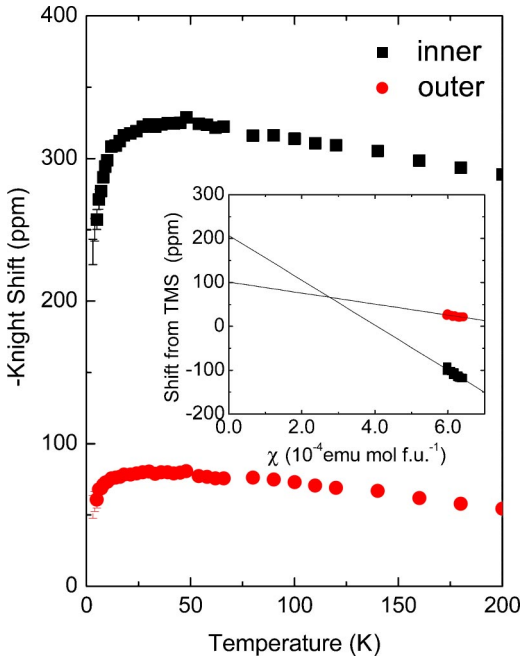


FIG. 3. (Color online) Temperature dependence of Knight shift of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$. Inset: The $\delta$-$\chi$ plot of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$.

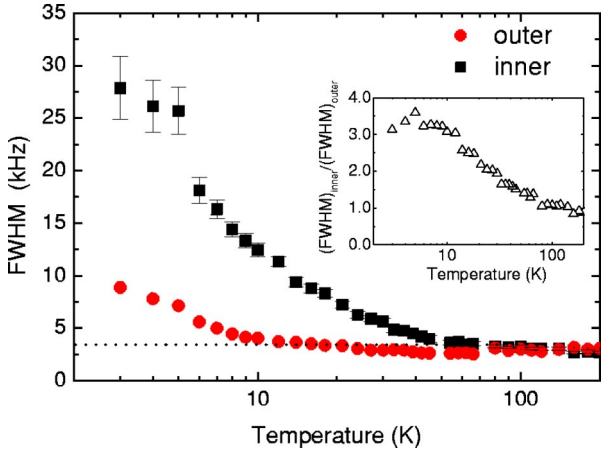


FIG. 4. (Color online) Temperature dependence of FWHM of $^{13}$C-NMR spectra of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$. Inset: Temperature dependence of the ratio of FWHM.

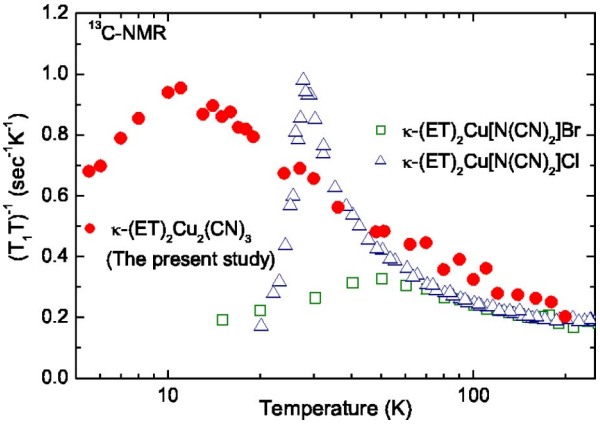


FIG. 5. (Color online) Temperature dependence of $(T_1T)^{-1}$ at the outer site of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$, shown alongside the curves of $\kappa$-(BEDT-TTF)$_2X$ salts for comparison.

hyperfine coupling constant, the spectrum with large hyperfine coupling constants should be broad. As shown in the inset of Fig. 4, below 10 K we can detect the broadening on both sites, and the linewidth ratio between the two sites is almost temperature independent and approximately equal to 3.2. This value is comparable to the ratio of the hyperfine coupling constants, i.e., 3.85. Thus these results suggest the inhomogeneity of the electron density progresses with decreasing temperature. In the case of small inhomogeneity, the broadening is too small to make the spectrum broader than its phenomenological width. Since no anomalies or phase transitions are observed in the electronic conductivity around 70 K, the inhomogeneity presumably starts at room temperature, progresses with decreasing temperature and becomes detectable below 70 K.

Geiser *et al.* suggested that the bandwidth of this salt is four times smaller than those of other $\kappa$-(BEDT-TTF)$_2X$ salts,[4] while other researchers predicted a bandwidth comparable to those of other $\kappa$-(BEDT-TTF)$_2X$ salts.[5] The band structure calculation depends on an arbitrariness of the wave function and parameters. The narrow bandwidth is, however, consistent with the finding that there are no interdimer S-S contacts within van der Waals radii (3.7 Å). The spin susceptibility is proportional to the density of state at Fermi energy, N($E_F$). Since the density of state is approximately proportional to the inverse of the bandwidth, the spin susceptibility is proportional to the inverse of the bandwidth. The spin susceptibility of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ was 10–20% higher than those of other salts at room temperature. This indicated that the bandwidth of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ is comparatively narrow. The ideal one-dimensional (1D) and two-dimensional (2D) electron systems tend to be localized and the large I/W readily causes inhomogeneity of the electrons on a Fermi surface; here I is the strength of the potential of disorder.[15] Because of the narrow bandwidth, in contrast to other $\kappa$-(BEDT-TTF)$_2X$ salts, $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ spontaneously localizes electrons and this line broadening is interpreted as an evidence of the progress of electron localization in this system.

The spin lattice relaxation rate $T_1^{-1}$also provides important information about the spin fluctuation. $T_1^{-1}$ of $^1$H nuclei in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, differs notably from those of other salts: it remains almost temperature independent above 50 K as expected for localized spins, and exhibits complex behavior in the low temperature region,[9] while AF fluctuations appear above 50 K in other $\kappa$-(BEDT-TTF)$_2X$ salts. Our $^{13}$C-NMR study, however, does not reproduce the results of $^1$H-NMR. The temperature dependence of the relaxation rate of $^{13}$C-NMR does not show constant behavior but decreases monotonically with decreasing temperature. Temperature dependence of $(T_1T)^{-1}$ of the outer site in the field perpendicular to the conducting plane is shown in Fig. 5, along with those of other $\kappa$-(BEDT-TTF)$_2X$ salts.[11,13] Since the degree of the localization is small above 70 K from FWHM analysis, the spin fluctuation of this salt is expected to show the same manner as in other $\kappa$-(BEDT-TTF)$_2X$ salts. Indeed, the value of $(T_1T)^{-1}$ is comparable to those of $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X, (X=Br and Cl) at 200 K and increases with decreasing temperature, as does in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]X. The increase of $(T_1T)^{-1}$ is considered as the development of AF fluctuation. Compared with $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, below 70 K, the increase in $(T_1T)^{-1}$ is suppressed, presumably due to suppression of the AF fluctuations by the inhomogeneity of electrons. $(T_1T)^{-1}$ in $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ also shows a broad maximum at around 10 K, which is reminiscent of the critical fluctuations of AF ordering. However, since there is no additional signal from the internal field and the fractional weight of the observed signal does not decrease below 10 K, this anomaly cannot be due to AF ordering.

When localization occurs, the temperature dependence of the conductivity in the insulating regime should be describable by the variable range hopping model.[16] In Fig. 6, we show the temperature dependence of conductivity above 40 K and fitting curves using the 1D ($d$=1), 2D ($d$=2) and three-dimensional ($d$=3) variable range hopping models, the equation $\sigma(T)=\sigma_0 \exp\{A(1/T)^{1/(d+1)}\}$, and the gap model. It is found that the gap model fails to predict the conductivity of this salt; the best fit is obtained using the 2D variable hopping model.

$\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ exhibits superconductivity under a pressure of about 3 kbar.[4,5] Pressures exceeding 1 kbar

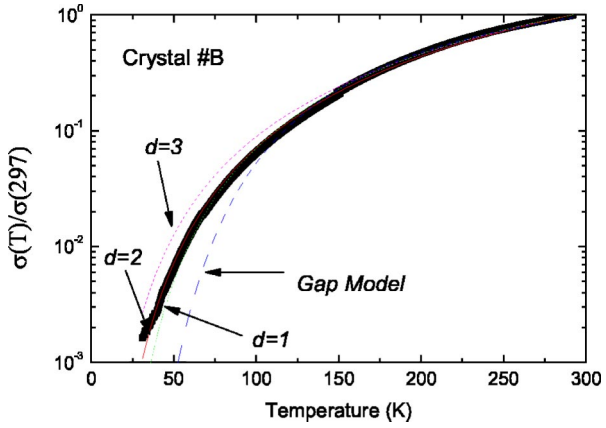


FIG. 6. (Color online) Temperature dependence of the electrical conductivity of $\kappa$-(BEDT-TTF)$_2$Cu(CN)$_3$ using fittings with the variable range hopping ($d=1,2,3$) and gap models. All the values are normalized at $T=297$ K.

sufficiently reduce interdimer distances in organic solids and enlarge the transfer integrals and the bandwidth. Consequently, Anderson localization is suppressed and the electron system is converted to those of $\kappa$-(BEDT-TTF)$_2X$, X =Cu[N(CN)$_2$]Br and Cu(NCS)$_2$. This results in superconductivity at low temperature. Indeed, the temperature dependence of conductivity under pressure resembles those of $\kappa$-(BEDT-TTF)$_2X$, X=Cu[N(CN)$_2$]Br and Cu(NCS)$_2$ with the maximum of resistivity.[17,18] The W of $\kappa$-(BEDT-TTF)$_2X$ is about ten times smaller than those of the high $T_c$ cuprates. The small W readily causes the electron localization on a Fermi surface. Thus, the electronic properties of $\kappa$-(BEDT-TTF)$_2X$ are not only characterized by the U/W, but also the electron localization due to the small bandwidth.

$(T_1T)^{-1}$ of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ shows a broad peak at around 10 K, and the spin susceptibility decreases sharply below this temperature. These results clearly reflect a change in the magnetic state, and may suggest the formation of spin singlet structure with a spin-gap-like behavior or the crossover between bad metal and good metal picture. The mechanism for the behavior of the maximum $(T_1T)^{-1}$ at $T^*$ in X =Cu[N(CN)$_2$]Br and Cu(NCS)$_2$ salts [7,11] is still unclear. It is very interesting to observe how the variation in the gap-like behavior under high pressure correlates to $T^*$.

In conclusion, the present $^{13}$C-NMR is performed successfully to investigate the origin of the insulating behavior of $\kappa$-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, We observed the enhancement of the line broadening of the spectra of inner and outer site. The ratio of linewidth at low temperature is in good agreement with the ratio of the hyperfine coupling constants. This suggests strongly the inhomogeneity of the electron density originated from Anderson localization. In contrast to previous $^1$H-NMR studies, $(T_1T)^{-1}$ showed a broad peak at around 10 K and the spin susceptibility decreased sharply below this temperature. Temperature dependence of the electrical conductivity is best fitted by the 2D-variable hopping model. These results also suggest that the Anderson localization of the conduction band is an origin for the insulating behavior in this salt. To understand the electronic properties of $\kappa$-(BEDT-TTF)$_2$X system, in addition to the U/W, the electron localization effect (I/W) from the relatively narrow bandwidth is important.

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