Local Spin Susceptibility Characteristic of Zero-Gap State of $\alpha$-(BEDT-TTF)$_2$I$_3$ under Pressure

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We performed $^{13}$C-NMR measurements in the metallic state of $\alpha$-(BEDT-TTF)$_2$I$_3$ under pressure to determine the local spin susceptibility at each BEDT-TTF molecular site. We found that the local susceptibility becomes quite different from molecule to molecule in a unit cell with approach to the zero-gap state (ZGS) under pressure. This is related to the charge disproportionation among molecular sites named A (A'), B, and C. We confirmed that the most/least positively charged site, the B/C molecule, carries the smallest/largest local susceptibility. We also confirmed the linear temperature dependence of the local susceptibility at low temperatures. These results are consistent with the theoretical calculation [Eur. Phys. J. B 67 (2009) 139] and should be considered as the characteristics of the ZGS.

KEYWORDS: zero-gap state, charge order, $\alpha$-(BEDT-TTF)$_2$I$_3$, NMR

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1. Introduction

$\alpha$-(BEDT-TTF)$_2$I$_3$, abbreviated as $\alpha$-ET$_2$I$_3$, is a quasi-two-dimensional molecular conductor$^{[1,2]}$ that shows a rich variety of phenomena such as charge ordering (CO),$^{[3,4]}$ superconductivity (SC),$^{[5]}$ and zero-gap state (ZGS).$^{[6]}$ It has layered conducting planes with 4 ET molecules called A, A', B, and C, in a unit cell (see Fig. 1).$^{[1,2]}$ Resistivity at ambient pressure is almost temperature independent until a sharp metal-to-insulator transition occurs at 135 K.$^{[1,3]}$ The application of pressure stabilizes this “metallic” state and, above 1.5 GPa of hydrostatic pressure or 1 GPa of uniaxial compression along $a$-axis, the transition is suppressed down to the lowest temperatures.$^{[5,7,8]}$ Recent theoretical analyses by Katayama and coworkers have indicated that the electronic state under pressure can be understood as the ZGS with a Dirac-cone type dispersion relation for massless fermions.$^{[9-13]}$ Tajima et al. have accumulated experimental evidence of the ZGS through precise transport measurements.$^{[14]}$

On the other hand, it was confirmed that the insulating state at ambient pressure below 135 K is accompanied by charge ordering with horizontal charge stripes by $^{13}$C-NMR measurement$^{[9]}$ and Raman spectroscopy,$^{[4]}$ as predicted theoretically.$^{[15,16]}$ We reported that charge disproportionation exists above the transition, which is enhanced as temperature decreases.$^{[17]}$ The existence of small charge disproportionation is also reported by the Raman measurement.$^{[4]}$ Since the high-temperature phase is continuously connected to the ZGS under pressure, we wanted to know how the charge disproportionation occurs in the ZGS and its relation to the stabilization of the ZGS in this salt.

In our previous work, we suggested that the symmetry between the A and A' molecule is already lost above the transition.$^{[17]}$ However, recent synchrotron X-ray structural analysis$^{[18]}$ and $^{13}$C-NMR measurements$^{[9]}$ confirmed that a horizontal stripe charge pattern, accompanied by the disappearance of inversion symmetry, appears only below the transition and that a small charge disproportionation above the transition does not break the lattice symmetry of $PI$. A second-harmonics generation (SHG) experiment also indicates that there is no symmetry breaking in the high-temperature phase.$^{[20]}$ These contradict the results of our previous NMR analysis. In addition, the synchrotron X-ray measurement suggests that the charge-rich/poor site is the B/C molecule,$^{[18]}$ whereas our NMR results indicate the opposite.$^{[17]}$ Our basic assumption for the NMR analysis was that the Knight shift is proportional to the local density of states and thus to the molecular charge. However, we noted that what we could measure from the NMR Knight shift was not the molecular charge but the local spin susceptibility. These quantities should reflect the band structure in different manners and should not necessarily be proportional to each other. The spin susceptibility is one of the fundamental physical quantities that reflect the intrinsic electronic properties of ZGS.

For these reasons, we decided to examine the field orientation dependence of NMR spectra under pressure. We found that our previous analysis was not correct. The site
dependence of the local spin susceptibility does exist but the
symmetry of the inequality was found to be consistent with
P1 symmetry. We also determined the temperature depend-
ce of the local spin susceptibility at each molecular site.
Unfortunately, the maximum pressure available in the
present work was a hydrostatic pressure of 1.1 GPa, which
was slightly smaller than the critical pressure of 1.5 GPa
required to stabilize the ZGS at absolute zero. However, we
found that the temperature dependence of the local spin
susceptibility above 60 K could be compared with the results
of theoretical calculation and revealed the characteristic
features of the ZGS.

2. Experimental Details

The sample used in the present experiments was a single
crystal of α-ET$_2$I$_3$ of 1 mg in weight, where the central
double-bonded carbon of the ET molecule was 99% $^{13}$C-
enriched. Hydrostatic pressure was applied to the crystal
with a BeCu clamp-type cell. The pressure transmitting
medium was Daphne 7373, which solidifies at low temper-
atures, e.g., below 230 K at 1.1 GPa. Pressure reduction
was estimated to be about 0.15 GPa. The values of pressure in
the figures and text are those at low temperatures.

NMR measurements were performed in a field of 7 T,
which corresponds to the resonance frequency of 75 MHz
for the $^{13}$C nuclear spin ($\gamma/2\pi = 10.705$ MHz/T). The field
strength was calibrated with a $^{63}$Cu signal of the NMR coil as
$H_0 = 2\pi f / (\gamma(1 + 63 K))$ where $^{63}f$, $^{63}\gamma$, and $63 K$
are the resonance frequency of $^{63}$Cu, the gyromagnetic ratio
of $^{63}$Cu nuclear spin (11.285 MHz/T), and the Knight shift
of metallic Cu ($\approx 0.232\%$).

An NMR spectrum was obtained by the fast Fourier
transformation of the spin echo signal induced by a $\pi/2-\tau-\pi$
pulse sequence. We rotated the sample in the magnetic field
about the $c^*$ axis so as to rotate the applied field in the
conducting $ab$ plane. Since the external field was always
parallel to the two-dimensional conducting plane, there
should be no serious effect on the orbital motion of the
 carriers. This is essential when we consider the character-
istics of the ZGS.

3. Results and Discussion

3.1 Angular dependence of $^{13}$C NMR line shape

Figure 2 shows the angular dependence of the line shape
at 1.1 GPa. We obtained four peaks of pairs showing large
sinusoidal angular dependences, and an angle-independent
broad line appeared at about 50 ppm. The former are
signals from ET molecules and the latter comes from the
naturally abundant $^{13}$C nuclei in the pressure medium.
The pair structure of the $^{13}$C-NMR spectrum from the ET
molecule is simply explained to be due to the nuclear
dipole-dipole interaction between the central carbon sites
of ET. This is known as the Pake doublet for coupled
equivalent spins and the distance of the split lines is given by

$$ d = \frac{3\gamma^2 h}{2\pi^3} (1 - 3 \cos^2 \theta), $$

where $r$, $\theta$, $\gamma$, and $h$ are the $^{13}$C=$^{13}$C distance, the angle
between the magnetic field and the $^{13}$C=$^{13}$C vector, the
gyromagnetic ratio of the $^{13}$C nucleus, and the Planck
constant, respectively. The large angular dependence of the
center of gravity of each pair reflects the strong anisotropy
of the Knight shift. Since the main contribution to the
resonance shift comes from the hyperfine coupling with the
on-site $\pi$ orbital at the central $^{13}$C-sites, it should reflect
the symmetry of the molecule, and thus the arrangement of
ET molecules in the conducting layer. The Knight shift is
proportional to the spin susceptibility, so that we can obtain
the information on the local spin susceptibility on each
ET molecule, by assigning the observed signals to each
molecule and analyzing the amplitudes of the angular
dependences. We call the observed sinusoids 1, 2, 3, and 4,
as indicated in Fig. 2.

First, we consider the phase differences in these sinusoidal
curves, and assign each signal to a molecular site. Sinusoids
1 and 2 have a coherent phase. They obviously come from
A (A') molecules because of the symmetry of the α-phase
molecule in the high-temperature phase. The relative phase
differences from sinusoids 1 and 2 to sinusoids 3 and 4 at
200 K are about 50 and 70°, respectively. Considering that
the dihedral angles between A (A') and B/C are reported as
59/70°, respectively, it seems reasonable to assign line 3
to molecule B and line 4 to molecule C.

3.2 Spectrum for A and A' molecules

The next question is whether or not A and A' mole-
cules are equivalent. At first sight, it seems that sinusoids
1 and 2 correspond to A and A' molecules, respectively,
suggesting different local susceptibilities between them.
However, the A (A') molecules are not centro-symmetric,
so that the two carbons on the central double bond are not
equivalent to each other. This is in contrast to that is the
cases of the B and C molecules, on which an inversion
center is located. When coupled nuclear spins are not
equivalent, one generally expects a quartet, instead of a
Pake doublet, with the following frequencies and relative intensities:

$$
\begin{align*}
\omega_{outer}^n &= \omega \pm \left[ \frac{d}{3} + \sqrt{d^2/9 + (\Delta\omega)^2} \right] \\
\omega_{inner}^n &= \omega \pm \left[ \frac{d}{3} - \sqrt{d^2/9 + (\Delta\omega)^2} \right] \\
I_{outer}^n &= 1 + (d/3)\sqrt{d^2/9 + (\Delta\omega)^2} \\
I_{inner}^n &= 1 - (d/3)\sqrt{d^2/9 + (\Delta\omega)^2}.
\end{align*}
$$

Here, $d$ and $\Delta\omega$ are the dipolar splitting for the Pake
doublet and the difference in the resonance frequency
between the coupled nuclear sites, respectively. Since we
have observed four peaks for A and A' molecules, there
are two possibilities: they are either two Pake doublets or
a single quartet. We found that the best criterion for
answering this question is to measure the splitting of pairs
precisely. In the case of the quartet, the splitting width of
each doublet should be 2/3 that of a Pake doublet, as
clearly shown by calculating, for instance, $\omega_{outer}^n - \omega_{inner}^n$.

Figure 3 shows the distance between peaks for each pair
at 200 K obtained from Fig. 2(a). The splitting for sinusoids
1 and 2 is close to 2/3 of the others. This is clear evidence
of a quartet structure for A and A' molecules. Furthermore,
since we observed only a single quartet, A and A' must have
the same environment, which means that the charge density
on the A and A' molecules should also be the same in the
high-temperature phase.
3.3 Amplitude of the sinusoids

Now, we focus on the amplitude of the sinusoidal curves of the resonance shift in Fig. 2. We expect it to be proportional to the local spin susceptibility of each molecular site. The resonance shift itself is proportional to the susceptibility but the amplitude is a better probe than the shift, since the amplitude is free of ambiguity in determining the zero shift position. It is easily seen that the amplitude of the sinusoids, that is, the local spin susceptibility is quite different from molecule to molecule even at 200 K. Denoting the local spin susceptibility at the \( \text{C}_{11} \) molecular site by \( \chi_{\text{C}_{11}} \), where \( \chi_{\text{A}}, \chi_{\text{A}'} \), \( \chi_{\text{B}}, \) and \( \chi_{\text{C}} \), we obtain \( \chi_{\text{C}} > \chi_{\text{A}(\text{A'})} > \chi_{\text{B}} \). Here, we considered the average amplitude of sinusoids 1 and 2 for \( \text{A} \) and \( \text{A}' \) molecules. As temperature decreases, the amplitude is reduced but the reduction in sinusoid 3 is the most marked. At 40 K, the 4 sinusoids shrink in a certain shift range so that it becomes difficult to deduce any reliable sinusoids from the spectrum. We consider that the system has become a non-magnetic charge ordered state where only chemical shifts are dominant. A similar tendency is also
observed when we apply pressure, as is plotted in Fig. 4. The amplitude of sinusoid 4 at both temperatures seems to be pressure-independent, whereas the others tend to decrease continuously as pressure increases, particularly, for sinusoid 3. We claim that the inequality of the local spin susceptibility from molecule to molecule is enhanced as temperature decreases and also as pressure increases.

3.4 Anomalous behavior of B molecule

The temperature dependence of sinusoid 3, which corresponds to the B molecule, is considerable, as mentioned above. Figure 5 shows the results at several temperatures. The amplitude decreases markedly as temperature decreases, and below 80 K, even the phase is inverted. This clearly indicates a marked reduction in local spin susceptibility in the B molecule, and the phase inversion suggests that it is important to consider the contribution of chemical shift. It was found that the chemical shift tensor for the central $^{13}$C of the ET molecule depends on the molecular charge during the study of the charge-ordered nonmagnetic state in $\theta$-(ET)$_2$RbZn(SCN)$_4$. The reported principal values of the chemical shift tensor are given in Table I. The thin curves in Fig. 5 are the calculated chemical shift for the B molecule with different charges of +0.8, +0.2, and 0 (neutral), when the external field is rotated in the $ab$ plane. It is evident that sinusoid 3 approaches the curve for the molecular charge of +0.8 at low temperatures. This observation indicates that it is necessary to correct the chemical shift contribution when we consider the local susceptibility from the observed amplitude.

We note that the phase difference of sinusoid 3 from sinusoids 1 and 2 at 1.1 GPa.

3-1,2 P = 1.1 GPa

### Table I. Principal values of chemical shift tensor.

<table>
<thead>
<tr>
<th></th>
<th>D$_X$</th>
<th>D$_Y$</th>
<th>D$_Z$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral ET</td>
<td>66</td>
<td>178</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Poor ET (+0.2)</td>
<td>103</td>
<td>198</td>
<td>46</td>
<td>25</td>
</tr>
<tr>
<td>Rich ET (+0.8)</td>
<td>176</td>
<td>242</td>
<td>65</td>
<td>25</td>
</tr>
</tbody>
</table>
sinusoid 4 stays constant at about 70°. This is also related to the large reduction in local susceptibility in the B molecule. We consider that intermolecular hyperfine coupling with neighboring C molecules may break the molecular symmetry, as discussed for a similar ET system.27 Assuming that the principal axis of intermolecular coupling is parallel to the a-axis, the phase shift towards the a-axis, $\delta$, is given by $\tan(2\delta) = \sin(2\phi_0)/[\xi^{-1} + \cos(2\phi_0)]$, where $\phi_0$ is the angle between the a-axis and the projection of the normal axis of the B molecule on the $ab$ plane and $\xi$ is the ratio of the intermolecular hyperfine field to the intramolecular one. Since $\phi_0 = 25.0°$, $\xi$ should be as large as 3.7 to explain $\delta = 20°$ observed at 110 K. Considering the amplitude of 39 ppm observed at this temperature, we obtain 6.8 and 25 ppm for the intra- and intermolecular contributions, respectively. The small value of the intramolecular contribution is due to the cancellation by the chemical shift. At 80 K, the intramolecular contribution is dominated by a large negative chemical shift, which leads to a small phase shift and inversion.

### 3.5 Correction of chemical shift contribution

As mentioned above, the amplitude of sinusoidal resonance shift should be proportional to the local spin susceptibility of each molecular site through the anisotropic contribution of hyperfine coupling. However, it has also been pointed out that the correction of the contribution of chemical shift is important, since the Knight shift becomes small as temperature decreases. It was reported that the chemical shift tensor depends on the molecular charge,24,25) so that the correction may be difficult when the effective charge on each molecular site is unknown. Fortunately, as far as the rotation in the $ab$ plane is concerned, the anisotropy of the chemical shift does not depend so much on the molecular charge. Taking into account the relative orientation of the molecules with respect to the laboratory frame, we obtain $(D_{\text{max}} - D_{\text{min}})/2 = -73, -78$, and $-84$ ppm, for ET$^0$, ET$^0.2$, and ET$^0.8$ molecules, respectively. The differences among A (A’), B, and C molecules are within ±1 ppm. The minus sign is taken for the phase of the chemical shift anisotropy that is opposite to the Knight shift in the present $ab$ plane rotation.

In Fig. 7, we plot the temperature dependence of the amplitude, that is, half of the Knight shift anisotropy, $(K_{\text{max}} - K_{\text{min}})/2$, measured at 1.1 GPa. We added 78 ppm to the observed values as the correction for the chemical shift. The ambiguity due to the charge dependence of the chemical shift should be within ±5 ppm. To find the Knight shift anisotropy as $(K_i - K_j)/2$, one should simply multiply its values plotted in Fig. 7 by a factor of $1/\cos^2 \theta = 1.04$, where $\theta$ is the angle of the $\pi$-orbital (the normal axis of the ET molecule) from the $ab$ plane. $(\theta = -11.4, +10.5, and +13.6°$, for A (A’), B, and C molecule.)

### 3.6 Analysis of spectra observed at 40 K

Before discussing the temperature dependence of the local spin susceptibility, we tried to analyze the $^{13}$C-NMR spectra at 40 K. They are composed of several well-resolved sharp peaks, but they shrink in a narrow frequency range of 80–260 ppm, as mentioned previously. It is not possible to determine any sinusoidal behaviors of peak shifts as before. We thus tried another approach to analyze the observed spectra. Using available experimental data as much as possible, we tried to reproduce the observed angular dependence of the NMR spectrum.

We found that the reported data of the chemical shift tensor given in Table I for neutral, ET$^0$, and ET$^{0.8}$ molecules suggest a linear dependence of the principal value on the effective charge, $\rho$, as $(D_X, D_Y, D_Z) = (134\rho + 70, 78\rho + 180, 45\rho + 31)$ ppm. For example, for ET$^{0.5}$, we obtained (137, 219, 53) ppm. We used this relation to estimate the chemical shift for a given molecular charge. We assumed that the hyperfine coupling tensor for the central $^{13}$C nuclei does not depend on molecular charge, so that the Knight shift tensor is merely scaled to the local spin susceptibility. We used the shift tensor determined for ET-$(\text{ET}:\text{CsZn(\text{SCN})})_2$ (abbreviated as $\theta$-CsZn) at RT as reference: $(K_X, K_Y, K_Z) = (94, 107, 577)$ ppm.25) After correcting the chemical shift tensor for ET$^{0.5}$, i.e., $(D_X, D_Y, D_Z) = (137, 219, 53)$ ppm given above, we obtained a pure Knight shift tensor, $(K_X, K_Y, K_Z) = (-43, -112, 524)$ ppm. It should be noted that the Knight shift tensor well approximate uniaxial symmetry along the normal axis of the molecule. This is consistent with the fact that the dominant contribution for the Knight shift comes from the $\pi$ ($p_\pi$) orbital of the carbon site.28) This should be compared with the measured spin susceptibility of this salt, $6.0 \times 10^{-6}$ emu/mol,29) to deduce the hyperfine coupling tensor.

Our adjustable parameters are molecular charges $\rho_i$ for the chemical shift, local susceptibilities normalized to that of the $\theta$-CsZn salt, $\chi_i = \chi_i/K_{\text{CsZn}}$, at 4 different molecular sites, $i = A(A'), B$, and C, and an offset shift to take into account a possible ambiguity in determining the zero shift position. We use the crystallographic data22) obtained at RT for molecular orientations. Since the system is considered to be in a CO state at 40 K,12) the A and A’ molecules should no longer be equivalent but should carry different charges. We consider the peak separation of Pake doublets due to nuclear dipolar coupling. Even the A/A’ molecules should give a Pake doublet instead of a quartet, since the difference in the resonance shift, $\Delta\omega$, between the coupled...
0.17,19) In the previous work, we claimed that the local susceptibility has already been noted at ambient positions taking the adjusting parameters. Susceptibilities remain finite and partially compensate for than the observed one. We considered that the local molecules are nonmagnetic with zero spin susceptibility. This assumption failed to explain the observed spectra, since central carbon sites should be much smaller than nuclear dipolar coupling d.

We first calculated the peak positions, assuming that all molecules are nonmagnetic with zero spin susceptibility. This assumption failed to explain the observed spectra, since the calculated spectrum was much more angular dependent than the observed one. We considered that the local susceptibilities remain finite and partially compensate for the angular dependence of the chemical shift. This seems reasonable since the temperature of 40 K is not so low compared with the transition temperature of 60 K.

Figure 8 shows the calculated angular dependence of peak positions taking the adjusting parameters $\rho_A = \rho_B = +0.8$, $\rho_A = \rho_C = +0.2$, $\bar{\chi}_A = \bar{\chi}_N = 0.29$, $\bar{\chi}_B = 0.07$, and $\bar{\chi}_C = 0.39$ and the offset shift of $-21$ ppm. (All observed peaks have shifted to the higher frequency side by 21 ppm to obtain better agreement with the calculation.) The agreement seems fairly good. However, considering the large number of adjusting parameters, we only claim the following: (i) the B molecule carries very little susceptibility even though it is rich in charges; (ii) the charges at the A and A' molecules are no longer equivalent to each other; (iii) the local susceptibilities at the A, A', and C sites remain finite at this temperature. We claim neither that the charge ratio $\rho_A/\rho_N$ should be equal to $\rho_B/\rho_C$, nor that $\bar{\chi}_A$ should be equal to $\bar{\chi}_N$.

The values of the anisotropic part of the Knight shift, $(K_{\text{max}} - K_{\text{min}})/2$, may be rather reliable. They are calculated as 89, 23, and 117 ppm, for the A/A', B, and C molecules, respectively. We have plotted these data in Fig. 7.

### 3.7 Estimation of spin susceptibility

It is clearly seen that the local spin susceptibility differs from site to site: $\chi_C > \chi_{A(A'A)} > \chi_B$. The susceptibility decreases as temperature decreases for all sites. $\chi_C$ and $\chi_{A(A'A)}$ show a T-linear behavior below about 100 K, while $\chi_B$ decreases more rapidly. A similar site dependence of the local susceptibility has already been noted at ambient pressure.17,19 In the previous work, we claimed that the B/C molecule should be a charge-poor/charge-rich site, respectively, by assuming that the local susceptibility might be proportional to the local charge.17 This statement was wrong, since sinusoid 3 corresponding to the B molecule approaches the curve of the chemical shift for the charge-rich site with a charge of $\sim 0.8$, as seen above. This is consistent with the results of synchrotron X-ray structural analysis18 and recent $^{13}$C-NMR19 at ambient pressure. It has been shown theoretically that there is no reason for the proportionality between the local susceptibility and the local charge.13 We will discuss this issue later.

Using the Knight shift tensor derived for $\theta$-(ET)$_2$-CsZn(SCN)$_4$ at RT,24,25 the Knight shift anisotropy $(K_{\text{max}} - K_{\text{min}})/2$ in the ab plane rotation calculated as 304 ppm. The measured spin susceptibility of the $\theta$-CsZn salt is $6.0 \times 10^{-4}$ emu/mol at RT.29 Since the average observed value of the Knight shift anisotropy at 200 K is $(371 \times 2 + 273 + 439)/4 \sim 363$ ppm, we obtain $7.2 \times 10^{-4}$ emu/mol for this salt. The measured susceptibility at ambient pressure and RT is $6.8 \times 10^{-4}$ emu/mol.30 The agreement between the results is fairly good.

### 3.8 Comparison with theoretical calculation

As mentioned before, $\alpha$-(ET)$_2$I$_3$ was found to be in the ZGS under pressure with a Dirac-cone-type dispersion relation for massless fermions.8-12 The hydrostatic pressure of 1.1 GPa used in the present work is slightly lower than the critical pressure for stabilizing the ZGS at absolute zero. However, it is interesting to compare our experimental results with the expected properties for the ZGS, since the electronic state above the transition temperature of $\sim 60$ K may carry some characteristics of the ZGS. Katayama et al. have calculated the density of states and magnetic response for each molecular site in a unit cell using a set of reasonable band and interaction parameters for this salt.33 They obtained the electron densities, $(n_1, n_2) = 1.460$ for the A and the A' sites, $(n_3) = 1.369$ for the B site, and $(n_4) = 1.711$ for the C site at $T = 0$ by integrating the density of states. Since a neutral molecule should carry $(n = 2$, the molecular charges are $\rho_A = \rho_A = +0.54$, $\rho_B = +0.63$, and $\rho_C = +0.29$. This is consistent with the results of a recent synchrotron X-ray diffraction experiment.

What we can estimate from the Knight shift is not the molecular charge but the local spin susceptibility. The spin susceptibility is determined by the density of states in the vicinity of the Fermi level. Katayama et al. have shown that the density of states $D(\varepsilon)$ has a linear dependence on the energy $\epsilon$, as $D(\varepsilon) = K_\varepsilon |\varepsilon|$, in the vicinity of the Fermi level, because of the Dirac-cone-type dispersion relation, and that the spin susceptibility is given as $\chi_\alpha = 2(\ln 2)K_\alpha T$ at low temperatures, where $\alpha = A$, A', B, and C. With the parameters that they chose, they obtained $K_A/A' \sim 137.1$, $K_B \sim 38.9$, and $K_C \sim 212.9$, or $K_B/K_A/A' \sim 0.284$ and $K_C/K_A/A' \sim 1.55$. They showed that the strong site dependence of $K_\alpha$ comes from the angular dependence of eigenvectors belonging to each site around the contact points and thus the inclination of the Dirac cone plays an essential role in giving the site dependence. The spin susceptibility $\chi_\alpha$ is related to the electron density $(n_\alpha)$ but not to the charge $\rho$. On the other hand, there is no explanation of the proportionality between $\chi_\alpha$ and $(n_\alpha)$.

The temperature dependence of $\chi_\alpha$ calculated by Katayama et al., shown in Fig. 7 in ref. 13, is similar to our result in Fig. 7. The T-linear dependence is well demonstrated.
below 100 K for the A (A') and C molecules. The reduction in $\chi$ at the B molecule is more pronounced than that indicated by the theory: $\chi_B/\chi_{A,A'} \sim 0.19$ and $\chi_C/\chi_{A,A'} \sim 1.37$ at 80 K. However, this ratio is rather sensitive to the choice of the band parameters and the discrepancy should not be considered as a serious problem.\textsuperscript{31} We claim that the observed $T$-linear behavior is the characteristics of the ZGS.

4. Conclusions

We performed $^{13}$C-NMR measurements on the metallic state of $\alpha$-(BEDT-TTF)$_2$I$_3$ under pressure to determine the local spin susceptibility at each ET molecular site. We found that the local susceptibility becomes quite different from molecule to molecule in the unit cell with approach to the ZGS under pressure. We confirmed that the most/least positively charged site, the B/C molecule, carries the smallest/largest local susceptibility. In contrast, A and A' molecules were found to remain equivalent to each other, keeping the lattice symmetry of $P1$. These are consistent with the results of X-ray\textsuperscript{18} and Raman studies.\textsuperscript{4} We also confirmed a linear temperature dependence of the local susceptibility at low temperatures. These behaviors are consistent with the theoretical calculation by Katayama \textit{et al.}\textsuperscript{13} and should be considered as the characteristics of the ZGS.

Since the hydrostatic pressure of 1.1 GPa used in the present work is slightly lower than the critical pressure for stabilizing the ZGS at absolute zero,\textsuperscript{3} the results at 40 K should be considered to be affected by the CO transition. We showed that the angular dependence of the peak shift could be explained by a set of reasonable parameters, assuming CO stabilization. To address the interesting properties of the ZGS predicted by theories,\textsuperscript{12,33} however, it is necessary to investigate the properties at much lower temperatures and higher pressures. $^{13}$C-NMR measurements aimed at clarifying the properties of the ZGS at lower temperatures are now under way.

Acknowledgments

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31) Y. Suzumura: private communication.