Local Spin Susceptibility of $\alpha$-D$_2$I$_3$ ($D = \text{bis(ethylenedithio)}$tetraselenafulvalene (BETS) and bis(ethylenedithio)dithiadiselenafulvalene (BEDT-STF))

Studied by $^{77}$Se NMR

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We performed static susceptibility and $^{77}$Se NMR measurements on $\alpha$-(BETS)$_2$I$_3$ and $\alpha$-(BEDT-STF)$_2$I$_3$ which are analogues of the “zero gap” system, $\alpha$-(BEDT-TTF)$_2$I$_3$ to systematically compare the electronic properties of the $\alpha$-type I$_3$ systems, where BETS, BEDT-STF, and BEDT-TTF are bis(ethylenedithio)tetraselenafulvalene, bis(ethylenedithio)dithiadiselenafulvalene, and bis(ethylenedithio)tetraethiafulvalene, respectively. From the analysis of the NMR lineshape for a polycrystalline sample at high temperatures, which are explained as an admixture of several powder patterns, we found that the local spin susceptibility is not uniform but at least one of the molecular sites has very small susceptibility. It was confirmed from single crystal data that there are three kinds of molecules with different local susceptibilities in a unit cell. The analysis of the angular dependence on a single crystal clarified that the relative magnitude of the local susceptibilities of A, B, and C molecules, $\chi_A^{loc}$, $\chi_B^{loc}$, and $\chi_C^{loc}$, are similar to those of the BEDT-TTF salt: $\chi_C^{loc} > \chi_A^{loc} > \chi_B^{loc}$. On the contrary, the temperature dependence of spin susceptibility and relaxation rate suggested a gap opening well above the metal–insulator transition, whereas no indication of symmetry breaking of the lattice was detected.

KEYWORDS: charge disproportionation, $\alpha$-D$_2$I$_3$, NMR

1. Introduction

$\alpha$-(BEDT-TTF)$_2$I$_3$ is a cation radical salt between an organic BEDT-TTF donor molecule and monovalent I$_3$ anion, where BEDT-TTF (abbreviated as ET, hereafter) is bis(ethylenedithio)tetraethiafulvalene, C$_{10}$H$_8$S$_4$.$^{1,2}$ The symbol $\alpha$ indicates the pattern of donor packing in a two-dimensional conducting layer; there are four ET molecules in a unit cell, and two A, B, and C molecules. The two A molecules are crystallographically equivalent. This salt behaves as a metal with a small temperature variation of resistivity and it undergoes a metal–insulator transition (MIT) at 135 K. At the MIT, spin susceptibility exhibits a sharp drop simultaneously.$^{1-4}$ The mechanism of the MIT in $\alpha$-(ET)$_2$I$_3$ has been a mystery for a long time. Kino and Fukuyama systematically investigated possible ground states of the ET-based molecular compounds by considering the anisotropy of transfer integrals and Coulomb repulsion.$^5$ They pointed out the possibility of charge ordering (CO) in the donor layer. Seo and Fukuyama extended that work by taking into account intermolecular Coulomb repulsion, $V$, and found various types of CO in a wide parameter range.$^6$ The CO in $\alpha$-ET$_2$I$_3$ below the MIT was confirmed experimentally.$^7,9$

It was reported that the insulating state is suppressed under pressure above 1.4 GPa and an extremely narrow-gap semiconducting state appears.$^{10}$ Recently, this anomalous electronic state of $\alpha$-(ET)$_2$I$_3$ under pressure was explained in terms of the “zero-gap state” (ZGS) in which conduction and valence bands come into contact at points.$^{11,12}$ While the ZGS was first confirmed in graphite, a single sheet of graphite, $\alpha$-(ET)$_2$I$_3$ was the first bulk material found to exhibit the ZGS. The relationship between the charge disproportionation (CD) at ambient pressure and the ZGS under pressure has been intensively studied theoretically and experimentally.$^{13-15}$

There are several fundamental issues concerning the ZGS. Is $\alpha$-(ET)$_2$I$_3$ the only material that exhibits a bulk ZGS? Is it possible to find a bulk ZGS at ambient pressure? What is the role of pressure in stabilizing ZGS in $\alpha$-(ET)$_2$I$_3$? To address these issues, we are trying to investigate the electronic state in $\alpha$-ET$_2$I$_3$ by applying conventional hydrostatic pressure (namely, physical pressure)$^{16}$ as well as chemical pressure.

In the present study, we report the results of static susceptibility and $^{77}$Se NMR measurements on Se analogues of $\alpha$-(ET)$_2$I$_3$: $\alpha$-(BETS)$_2$I$_3$ and $\alpha$-(BEDT-STF)$_2$I$_3$,$^{17}$ where BETS [bis(ethylenedithio)tetraselenafulvalene: C$_{10}$S$_2$Se$_2$H$_4$] and BEDT-STF [bis(ethylenedithio)dithiadiselenafulvalene: C$_{10}$S$_2$Se$_2$H$_3$] are the molecules in which the S sites in the inner five membered ring of the ET are fully and partially replaced by Se, as shown in the Fig. 1. We call these salts BETS and STF salts, hereafter, respectively. A chemical pressure effect may be expected because these salts have larger transverse transfer integrals than the sulfur based ET salt. The BETS and the STF salts show nearly temperature-independent resistance at high temperatures and undergo a MIT, as the ET salt does. The MIT temperatures are lower than that of the ET salt (50 and 80 K for the BETS and the STF salts, respectively) at ambient pressure.$^{18}$

2. Experimental Details

A single-crystal sample of the STF salt with the size of $3 \times 1 \times 0.02 \text{mm}^3$ and polycrystalline samples of the BETS and the STF salts were used. The single crystal was so thin that we estimated the thickness from the sample weight. The relationship between crystallographical axes and sample shape was determined by X-ray measurement. The Se sites of the BETS molecule was enriched with the $^{77}$Se isotope to

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improve the signal-to-noise ratio. \(^{77}\)Se-substituted BETS molecules were synthesized using \(^{77}\)Se metal powder (labeled 95.8% atom, Nippon Sanso).\(^{19,20}\) Polycrystalline samples of several mg in weight were randomly packed in a glass tube and placed inside the NMR coil for polycrystalline measurements.

Static susceptibilities of the same samples that we used in the NMR measurements were measured using the Quantum Design MPMS SQUID magnetometer. Contributions of core diamagnetism were calculated by Pascal’s law.

NMR measurements were performed at an applied field \((H_0)\) of 9 T, which corresponds to a radio frequency (rf) of 73.1 MHz (\(= \gamma H_0\), where \(\gamma\) is the gyromagnetic ratio of \(^{77}\)Se; 8.13 MHz/T). Magnetic field strength was calibrated with the \(^{13}\)C NMR signal of a standard sample of tetramethylsilan.\(^{21}\) The NMR spectrum was obtained by the fast Fourier transformation of the spin echo signal following a \(\pi/2-\pi\) rf pulse sequence when the linewidth was narrower than the rf strength, \(\gamma H_1\), in frequency. Since the \(4p_z\) orbital is considered to give a dominant contribution to the hyperfine coupling with \(^{77}\)Se nuclei, uniaxial hyperfine anisotropy was expected. In the case of the polycrystalline sample, the main contribution to spectral width comes from the anisotropy of Knight shift, i.e., the hyperfine coupling constant multiplied by spin susceptibility. The expected spectrum should be of a characteristic asymmetric shape with a shift of center of gravity owing to the isotropic component of hyperfine coupling. A typical rf strength was \(\gamma H_1 \sim 100\) kHz in frequency, which corresponds \(\sim 0.1\) % in shift; this is not large enough to excite all nuclei, since the spectral width exceeds \(\sim 0.5\%\) at high temperatures. In order to observe such a broad spectrum, we applied the frequency-stepped-spectroscopy method at a fixed field strength, developed by Clark et al.\(^{22}\)

The spin lattice relaxation rate, \(1/T_1\), was measured on a polycrystalline sample of BETS salt. \(T_1\) was determined by the recovery of nuclear magnetization after an inversion \(\pi\) pulse (or saturation comb pulses).

Measurements on a single-crystal sample were performed for the STF salt. The angular dependence of the single-crystal NMR spectrum was measured for the external field rotated in the conducting \(ab\) plane. Because of the limitation of the crystal size, we placed the needle-like sample inside a thin NMR coil to improve the filling factor of the coil and mounted them on the goniometer. We rotated the sample together with the NMR coil. Therefore, the effective rf strength depends on the field orientation, and the measurements were limited to angles larger than \(\sim 40^\circ\) from the coil axis.

### 3. Results and Discussion

#### 3.1 Results on polycrystalline samples of BETS and STF salts

Figure 2 shows the temperature dependence of spin susceptibility per formula weight (FW), \(\chi^{\text{spin}}\), of the BETS (closed symbol) and the STF (open symbol) salts, respectively. Our previous data on the BETS salt (batch SM1999) reported in ref. 23 are also plotted as crosses for comparison. Although the data of the present BETS sample scatter because the sample quantity was so small, the Curie-like enhancement below 50 K is much smaller than that observed in the batch SM1999. Considering that the NMR results shown later, the low-temperature enhancement of \(\chi^{\text{spin}}\) in SM1999 does not seem to be intrinsic. As shown in the figure, \(\chi^{\text{spin}}\) of the BETS salt exhibits negative values below about 50 K. This should mean that the estimation of core diamagnetism was not correct. However, the ambiguity in the constant core diamagnetism is not a significant matter so much for the NMR analysis in the present study.

We emphasize that the \(\chi^{\text{spin}}\) for both salts decrease gradually with no anomaly at the MIT, unlike the sharp drop at the 135 K transition in the ET salt. The temperature dependence of susceptibility was found to fit the formula \(\chi^{\text{spin}} = (C/T) \exp(-\Delta/k_B T)\) quite well, as shown by the solid lines in Fig. 2. The data for the BETS salt were fitted by \(\chi^{\text{spin}} = (C/T) \exp(-\Delta/k_B T) + \chi^{\text{offset}}\), where \(\chi^{\text{offset}}\) represents the ambiguities in estimating core diamagnetism and background correction. The gap, \(\Delta/k_B\), and the constant, \(C\), were estimated to be 290 K and 0.29 emu K FW\(^{-1}\) for the BETS salt and 280 K and 0.33 emu K FW\(^{-1}\) for the STF salt, respectively. This strongly suggests that a finite gap of...
\~{3}00 K has already opened at temperatures much higher than the MIT temperature.

Figure 3 shows the NMR spectra of the BETS and the STF salts at several typical temperatures. Characteristic features are very similar to each other: a broad asymmetric spectrum at high temperatures and a sharp single line at lower temperatures were observed. The central shift \( (K) \) and the linewidth (sqrt\( M^2 \)), defined as the square root of the second moment of the spectrum, were found to decrease gradually with cooling and to become almost constant at low temperatures below \~{50} K. The constant value of \( K \) at low temperatures is considered to be the chemical shift of the BETS and the STF molecules.

The spectrum at high temperatures contained a double peak structure (p1 and p2) as shown in Fig. 3. Since the two peaks were found to have different relaxation rates, as mentioned later, we concluded that the spectrum is composed of multiple powder patterns with different widths. The width of a powder pattern is caused by the anisotropy of the hyperfine field, so that the multiple powder pattern structure indicates that the local susceptibility is not uniform within the system. The detailed analysis of the local spin susceptibility is given in the next subsection.

Figure 4 shows the temperature dependences of \( K \) (closed symbols) and \( \sqrt{M^2} \) (open symbols), of the spectra for the STF (a) and the BETS (b) salts, respectively. The relationships of \( K \) and \( \sqrt{M^2} \) to \( \chi^{\text{iso}} \) are plotted in the inset of the figures. The slopes of the straight lines give isotropic and anisotropic hyperfine coupling constants, \( A_{\text{iso}} \) and \( A_{\text{an}} \).

Figure 5 shows the typical spectra of the STF and BETS salts in the high-temperature metallic state. The observed asymmetric shape with structures seems to be the admixture of two or more powder patterns with different widths. The dotted lines are the sum of two calculated powder patterns, \( \chi_B \), which appear when the local susceptibilities are the same, but the coefficient depends on their relative magnitudes. Since \( \chi_B \ll \chi_A \sim \chi_C \), as we will see later, we obtain \( \sqrt{M^2} \sim \sqrt{16/15}A_{\text{an}}\chi_A = \sqrt{16/15}A_{\text{an}}\chi^{\text{iso}}/2N_A \).

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Next, we focus on the spin dynamics of the system. Figure 6 shows the temperature dependences of the relaxation rate, $1/T_1$, of the two peaks of the spectrum, p1 and p2, of the BETS salt. As shown in the figure, the relaxation of p1 is much faster than that of p2. This means that the p1 peak has higher local spin density because the relaxation rate is usually proportional to the square of the local spin susceptibility according to the Korringa relation. At low temperatures below 50 K, all components merged into a single peak, so that it became difficult to distinguish each individually. In this case, we defined the shorter and the longer $T_1$'s by fitting the relaxation curve to a double exponential function. Both components of the relaxation decrease exponentially with cooling. This means that there is a spin gap to excite the conduction electron spins. From the slope of the straight line in Fig. 6, the gap energy, $\Delta/k_B$, was estimated to be about 300 K, which is consistent to the gap energy obtained by the susceptibility measurements.

The ratio between the high and low relaxation rates is roughly 10, as shown in Fig. 6. Considering that $1/T_1$ is proportional to the square of $\chi^{loc}$, the ratio between $\chi^{loc}$(rich) and $\chi^{loc}$(poor) is estimated to be at least $\sim 3$. This is consistent with the results of the analysis of the observed powder spectrum.

3.2 Results of single-crystal measurements on STF salt

To analyze the detailed electronic structure, NMR measurements using a single-crystal sample are necessary. Fortunately, we had a high-quality single-crystal sample of the STF salt of relatively large size. We measured the angular dependence of $^{77}$Se-NMR on the single crystal by rotating the external field in the conducting $ab$ plane to determine the local susceptibility on each molecular site, as we did on the ET salt by $^{13}$C NMR. Three well-separated NMR peaks with relative intensities of $1:2:1$ were typically observed at high temperatures as shown in Fig. 7. This is quite natural because there are four molecules in the unit cell, two A, B, and C molecules. The peak positions are plotted in Fig. 8. Peaks were easily assigned because the relative phases of the angular dependence correspond well to the structure. The Knight shift of each site is given by

$$K_{A,B,C} = \frac{A_{iso} + A_{an}[3 \cos^2(\theta - \phi_{A,B,C}) \cos^2 \phi_{A,B,C} - 1]}{\chi_{A,B,C}} \times \chi_{A,B,C}^{loc}$$

in the present geometry, where $\phi_{A,B,C}$ is the angle between the molecular plane and the $a$ axis and $\phi_{A,B,C}$ is the tilt angle of the principal axis of the $p_z$ orbital with respect to the rotating plane. Since we do not know the exact value of chemical shift, it is impossible to determine the local susceptibility from the central shift. Therefore, we focus on the anisotropic components obtained from the amplitude of the angular dependence of the peak position. The anisotropic part of the hyperfine shift was evaluated as listed in Table I; the local susceptibility on the B molecule is the smallest; about one-third of the others at 125 K. It is clear that the...
The local susceptibilities decrease rapidly with temperature. An almost single peak with no shift was observed below the measured temperature range, as far as the NMR properties are concerned. These findings are qualitatively the same as those for the ET salt.

4. Concluding Remarks

We have performed spin susceptibility and $^{77}$Se NMR measurements on polycrystalline and single-crystal samples of the $\alpha$-type I$_3$ salts, $\alpha$-(BETS)$_2$I$_3$ and $\alpha$-(BEDT-STF)$_2$I$_3$, which are analogues of $\alpha$-(ET)$_2$I$_3$. We expected that the electronic properties of the BETS and STF salts at ambient pressure might be similar to that of the ET salt under pressure at, for example, 1.1 GPa, since the transport properties are similar among them. Actually, we observed very similar polycrystalline NMR spectra on the BETS and STF salts in the entire measured temperature range. The analysis of the powder spectra of the BETS and STF salts and the relaxation measurements on the BETS salt consistently revealed that the local susceptibilities are not uniform, but one of the molecular sites carries only one-third of those at the other sites. Single-crystal measurements on the STF salt revealed that the “spin-poor” site is the B molecule, and in addition, that the two A molecules remain equivalent in the entire measured temperature range, as far as the NMR properties are concerned. These results agree well with those of our single-crystal $^{13}$C NMR measurements on the ET salt under pressure.

However, the temperature dependence of spin susceptibility looks quite different. In the ET salt at 1.1 GPa, we reported a $T$-linear behavior of local susceptibilities below 100 K, which is characteristic of the ZGS. On the contrary, the susceptibilities for the BETS and STF salts decrease considerably at temperatures well above the MIT temperature. The temperature dependences of spin susceptibility and relaxation rate suggest that a finite spin gap of ~300 K has already opened at high temperatures around RT. This gap should not be a CO gap, since two A molecules stay equivalent in the measured temperature range, matching the P1 symmetry, which rules out, at least, the formation of CO of a vertical stripe type, as in the ET salt at ambient pressure.

It may be possible that the observed gap is a pseudo gap and a linear density of states characteristic of the ZGS appears only at much lower temperatures. It should be noted, however, that the gap like nature appears only in the spin mode, since the present salts show temperature-independent resistivity at temperatures above MIT. This seems to suggest that the electron correlations are responsible for this gap or pseudo gap opening in the present systems.

The Se substitution may increase the transfer integrals not only along the transverse but also along the vertical direction. Additionally, the spin density in a molecule also should be different from that in the ET molecule. Although the band structures of BETS and STF salts seem to be similar, the BETS/STF salts should not be exactly the same as those for the ET salt.
same as the ET salt under pressure. The difference in the temperature dependence of the spin susceptibilities might come from the slight differences in the band structure and/or the electron correlation between them.

At the moment, we do not have any reasonable explanation for the above behavior. It is clear that the S to Se replacement leads to much more than the chemical pressure effect that we expected. Further investigations are inevitably required. Single-crystal $^{13}$C NMR measurements on BETS salt are in progress to compare the results directly with the results of the ET salt.

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14) A. Kawamoto: private communication.
21) External magnetic field was determined by $^{13}$C resonance frequency ($^{13}$C/T) of tetramethylsilan. $H_0$ was determined as $^{13}$C/T, where $^{13}$C is the gyromagnetic ratio of $^{13}$C, 10.705 MHz/T.
24) The relationship between $\chi^{\text{spin}}$ and $\chi^{\text{loc}}$ is defined as follows: the unit of $\chi^{\text{spin}}$ is emu-FW$^{-1}$. FW means $2N_a$ of donor molecules and $N_b$ of $I_x$. The unit cell of the system contains $2N_a$ of A and $N_a$ of B and C molecules. Therefore 1 FW contains $N_a$ of A, and $N_a/2$ of B and C molecules. Thus, $\chi^{\text{spin}} = N_a\chi^{\text{loc}} + (N_a/2)\chi^{\text{loc}} + (N_a/2)\chi^{\text{loc}}$.