13C NMR Investigation of Re-entrant Antiferromagnetic States of (TMTTF)$_2$SbF$_6$

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Abstract. $^{13}$C nuclear magnetic resonance (NMR) investigations were performed on the one-dimensional organic conductor (TMTTF)$_2$SbF$_6$ to clarify its electronic properties in the proximity of the ground states. An abrupt broadening of $^{13}$C NMR absorption lines below 8 K ($T_N=8$ K), confirmed a long-range antiferromagnetic phase transition. Below $T_N$, the absorption lines are composed of four distinct broad lines, indicating a commensurate magnetic structure. The amplitude of staggered magnetization, $\rho$, is comparable to (TMTTF)$_2$Br, and on the order of 0.1 $\mu_B$ according to the splitting of $^{13}$C NMR lines at 3 K.

1. Introduction

(TMTTF)$_2X$, are extensively studied materials, and are well-known quasi-one-dimensional organic conductors possessing various ground states such as spin-Peierls, antiferromagnetic and superconductivity states with applied pressures or counter anions, $X$. (TMTTF)$_2$SbF$_6$ is considered to be located at the most negative pressure side in the generalized phase diagram of (TMTCF)$_2X$ proposed by Jérome. [1] Observation of superconductivity in (TMTTF)$_2$AsF$_6$ (at 4.5 GPa) and (TMTTF)$_2$SbF$_6$ (6 GPa) under high pressure is also supporting this scenario. [2, 3] At the same time, this model has produced a new unsolved problem: Another antiferromagnetic phase can be expected on the negative pressure side of the spin-Peierls phase according to ESR measurements for (TMTTF)$_2(\text{AsF}_6)_{x}(\text{SbF}_6)_{1-x}$ [4], and $^{13}$C NMR measurements for (TMTTF)$_2$SbF$_6$ under physical pressure. [5] The modified generalized Pressure-Temperature ($P$-$T$) phase diagram including recent understanding of CO phase transitions is shown in Fig. 1.

However, this phase diagram is based on the preconceived idea that the spin-Peierls phase, which is a quantum one-dimensional phase, is sandwiched by two antiferromagnetic phases. For conventional systems, antiferromagnetic phases are stabilized with finite inter-chain interaction by applying pressure. In addition, it is not clear whether the two antiferromagnetic phases (AF-I and AF-II) are of the same origin or not. To understand the $P$-$T$ phase diagram for these materials, we carried out pulsed $^{13}$C NMR measurements on (TMTTF)$_2$SbF$_6$ below 100 K, and compare the magnetic behavior of (TMTTF)$_2$SbF$_6$ with that of (TMTTF)$_2$Br, which possesses the antiferromagnetic ground state on the high-pressure side of the generalized phase diagram.
2. Experimental

$^{13}$C NMR measurements were carried out on a (TMTTF)$_2$SbF$_6$ single crystal in which the central C=C double-bonded carbons are $^{13}$C-enriched using a pulsed-NMR spectrometer operating at 86.538 MHz. The $^{13}$C NMR spectra were obtained by Fourier transformation of the spin echo signals ($\pi/2-\tau-\pi-\tau$-echo) between 2 and 100 K. For the temperature dependence measurements, we used the so-called magic-angle configuration, satisfying $3\cos^2\theta-1=0$ ($\theta \sim 55^\circ$) to simplify the analysis.

3. Results and Discussion

The temperature dependence of the $^{13}$C NMR spectra for (TMTTF)$_2$SbF$_6$ is shown in Fig. 2. Since the TMTTF molecules stack to form 1D zigzag chains, the central C=C sites are inequivalent and consist of inner (solid large circles in Fig. 2) and outer (small circles in Fig. 2) positions. Below 100 K, (TMTTF)$_2$SbF$_6$ has already undergone the transition to the $4k_F$ (-o-O-o-O along 1D-chains) charge ordering (CO) state ($T_{CO} \sim 155$ K), so the TMTTF molecules are not all equivalent. Hence, the NMR spectrum displays four distinct lines, which originate from the two inequivalent TMTTF molecules. The large splitting (creating two doublets) of 100 ppm, which comes from the difference in the hyperfine coupling between the inner and outer $^{13}$C sites.

The small splitting of 50 ppm is due to the CO state. As seen in Fig. 2, line splitting caused by CO is not clear under several temperatures. It is due to the line splitting width is comparable to the absorption linewidth. Therefore, we performed peak-fitting assuming four Gaussian lines.

Below 8 K, the $^{13}$C NMR spectra abruptly change. The line splitting becomes large, and each of the distinct lines also shows obvious broadening. These observations clearly indicate a long-range antiferromagnetic magnetic transition below 8 K. The fact that the $^{13}$C NMR spectra are composed of four distinct lines indicates that the antiferromagnetic state is commensurate. The maximum splitting is about 1000 ppm at around the $c^*$-axis (vide infra), which is about 1/10th of that of conventional antiferromagnetic states such as in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, [6] but comparable to that of (TMTTF)$_2$Br. [7]

It is an open question whether the two antiferromagnetic phases (AF-I and AF-II) are of the same or not. The magnetic behaviors of the paramagnetic state in (TMTTF)$_2$SbF$_6$ and (TMTTF)$_2$Br seem quite different (existence of CO, magnetic fluctuation, and so on). Relationship of the CO configuration and the wave-vector of the antiferromagnetic phase and also commensurability are important to understand the possible origin of the competition electronic phases. Recent theoretical investigation including inter-chain Coulomb interaction predicted possible crossover between different charge configuration. [8] To estimate the amplitude of the staggered moment is also important for understanding of the dimensionality of the magnetic fluctuation.

The angular dependence of the $^{13}$C NMR shift within the $b^*c^*$ plane in the antiferromagnetic phase of (TMTTF)$_2$SbF$_6$ is shown in Fig. 3. Here, we compare the experimental results in
the present study with a previous $^{13}$C NMR investigation of the antiferromagnetic phase in (TMTTF)$_2$Br. [7] As seen in the (TMTTF)$_2$Br, four broad distinct $^{13}$C NMR lines were observed for (TMTTF)$_2$SbF$_6$. The linewidth of (TMTTF)$_2$SbF$_6$ under $T_N$ is much larger than that in the paramagnetic region. The charge separation is now unresolved, and the contribution of the two sites split into four with large shift. The splitting is clearly due to the staggered magnetization. The four broad distinct lines probably originate from the inner and outer $^{13}$C-sites. In previous our study, the magnetic structure of (TMTTF)$_2$Br was clarified by $^1$H NMR as wave-vector, $Q=(1/2, 1/4, *)$, with the -up-0-down-0-up- spin configuration along the stacking axis. [9] The amplitude of the staggered magnetization was evaluated to be $\rho=0.14 \mu_B$. In our measurements, the sample is rotated along the $\alpha$-axis, which is the hard axis. Since the external field (8 T) is much larger than that of the spin-flop field (0.5 T), the staggered moments are always perpendicular to the external field within $b^*c^*$ plane. In the case of antiferromagnetic phases for TMTCF based organic conductors, the intra-molecular contribution is dominant for $^{13}$C NMR shift because of strong hyperfine-coupling, although slight deviation from simple sinusoidal angular-dependence probably comes from the inter-molecular contribution. Hence, the angular dependence of the $^{13}$C-shift, $\Delta H$, is approximately explained by the anisotropy of the Knight shift, $\Delta K$:

$$\Delta H = (\gamma/2\pi\chi)\Delta K \sin \theta \cos \theta M, \quad (1)$$

where $\gamma$, $\chi$ and $M$ are the gyromagnetic ratio, spin susceptibility and electron magnetization,
respectively. The $\Delta K$ is reported as 65 ppm for outer $^{13}$C-site within $b^\prime c^\ast$ plane. [7] Considering that the $\chi$ ($5.5 \times 10^{-4}$ emu/mole) and the spin distribution of outer $^{13}$C-site (0.05) of (TMTTF)$_2$SbF$_6$ salt, the amplitude of the magnetic moment is roughly estimated as (or less than) 0.1$\mu_B$ per 0.5 electron from the maximum splitting of 1000 ppm. Hence, if we assume the charge separation, the amplitude of the staggered magnetization, $\rho$, is about (or less than) 0.15$\mu_B$, which is comparable to that of (TMTTF)$_2$Br. In fact, our preliminary recent $^3$H NMR investigation of (TMTTF)$_2$SbF$_6$ indicates that the amplitude of the staggered magnetization in the antiferromagnetic phase is about $\rho$=0.11$\mu_B$. [10] While NMR relaxation of (TMTTF)$_2$SbF$_6$ shows conventional antiferromagnetic behavior in paramagnetic region, the amplitude of the staggered magnetization is small as seen in 1D system. Although we cannot have clear explanation at present, the gradual suppression of the degree of charge separation might play important role.

There seems to be a slight discrepancy between the (TMTTF)$_2$SbF$_6$ and (TMTTF)$_2$Br salts. In the case of (TMTTF)$_2$SbF$_6$, the angles which give extreme values for the four distinct lines differ. Although we cannot rule out the possibility of experimental error completely, one possible explanation is that different magnetic structures, i.e., different antiferromagnetic wave vectors, $Q$, exist in (TMTTF)$_2$SbF$_6$ and (TMTTF)$_2$Br salts. As discussed in ref. [8], the charge configuration of the CO phase is sensitive to relative intensity between the neighbor and second-neighbor inter-chain Coulomb interactions. Slight difference in crystallographic inter-chain network may be important to understand the difference between (TMTTF)$_2$SbF$_6$ and (TMTTF)$_2$Br.

In conclusion, we confirmed the existence of a long-range commensurate antiferromagnetic state below 8 K. The amplitude of the staggered magnetic moment in the antiferromagnetic state of (TMTTF)$_2$SbF$_6$ seems to be comparable to (TMTTF)$_2$Br. These observations indicate that the possible origin of the ground state of both salts is the same and reentrant AF-sP-AF ground states is likely for (TMTTF)$_2X$ salts, although the wave-vector of the magnetic structure is slightly different. It is also noted that there is a dimer-Mott phase between two CO phase according to ref. [8]. As for the dimer-Mott phase, a spin-Peierls ground state of seems very likely. To understand the origin of the unusual reentrant AF-sP-AF ground states for (TMTTF)$_2X$ salts, $^{13}$C NMR and crystallographic investigations under high pressure are now underway.

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