13C NMR Investigation of Low-temperature States in One-dimensional Organic Cation Radical Salt, (TMTTF)$_2$SbF$_6$, under High Pressures

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Abstract.

$^{13}$C nuclear magnetic resonance (NMR) measurements under the application of hydrostatic pressure were carried out on the one-dimensional organic conductor, (TMTTF)$_2$SbF$_6$, to investigate the competed antiferromagnetic and spin-singlet ground states. The charge-ordering (CO) transition temperature, $T_{CO}$, (155 K at ambient pressure), decreased to 100 K under a pressure of 5 kbar, and was suppressed above 8 kbar. Under pressures between 5 kbar and 14 kbar, the low-pressure side antiferromagnetic state (AF-I) was suppressed. At the same time, a spin-gap phase was stabilized. Above 17 kbar, another antiferromagnetic phase appeared below approximately 15 $\sim$ 20 K. A possible reentrant antiferromagnetic phase diagram is discussed from a microscopic point-of-view.

1. Introduction

The (TMTCF)$_2X$ family of salts ($C$=S, Se), which are one-dimensional conductors, possess various ground states including the spin-Peierls, antiferromagnetic state, incommensurate spin density wave and superconductivity. The generalized $P$-$T$ phase diagram of (TMTTF)$_2$SbF$_6$ was first proposed by Jérome. [1] We have also investigated the competed ground states and CO phenomena observed in the intermediated temperature region from the viewpoint of magnetic resonance. [2] The title salt, (TMTTF)$_2$SbF$_6$, is considered to be located at the most negative pressure side in the generalized $P$-$T$ phase diagram mentioned above among the established (TMTCF)$_2X$ salts. Based on recent systematic transport measurements for (TMTTF)$_2$AsF$_6$ and (TMTTF)$_2$SbF$_6$ salts under ultra-high pressures, a possible modified generalized $P$-$T$ phase diagram, as shown in Fig. 1, was proposed. [3, 4] According to this modified phase diagram, the spin-Peierls phase, which is a quantum one-dimensional phase, is sandwiched between two antiferromagnetic phases. In a general sense, however, antiferromagnetic phases are stabilized with finite inter-chain interactions by the application of pressure for conventional systems. Hence, we carried out $^{13}$C NMR measurements for (TMTTF)$_2$SbF$_6$ under the application of hydrostatic pressure to investigate the competed ground states. In this paper, we discuss the justification for the modified 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 were $^{13}$C-enriched, using a pulsed-NMR spectrometer operating under a magnetic field of about 8 T. Hydrostatic pressure was applied using a NiCrAl-BeCu double clamp cell pressure system. We used Daphne No. 7373 oil as a pressure-transmitting medium in the range up to 2 GPa. Above 2 GPa, a recently developed transmitting medium, Daphne No. 7474 oil, was adopted to maintain good hydrostatic pressure. $^{13}$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

(TMTTF)$_2$SbF$_6$ shows a variety of electronic phases with the application of pressure. Hereafter, we show the experimental results under typical pressures (11 kbar and 17 kbar) because of space limitations, and discuss the actual $P$-$T$ phase diagram of (TMTTF)$_2$SbF$_6$. The temperature dependence of the $^{13}$C NMR spectra for (TMTTF)$_2$SbF$_6$ under 11 kbar 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 and outer positions. At ambient pressure, (TMTTF)$_2$SbF$_6$ undergoes a charge-ordering (CO) transition below 155 K. Since the TMTTF molecules are not all equivalent in the CO phase, the NMR spectrum is split into four distinct lines, which originate from the two inequivalent TMTTF molecules. $T_{CO}$ was shifted down to 100 K under 5 kbar, and was suppressed above 8 kbar. Also, the $^{13}$C NMR spectra under 11 kbar remains one doublet in the whole paramagnetic region (down to 10 K).

At ambient pressure, (TMTTF)$_2$SbF$_6$ undergoes the antiferromagnetic phase transition below 8 K ($T_N$), which was confirmed by the huge line splitting and the divergent increase in the spin-lattice relaxation rate, $T_1^{-1}$. For pressures between 5 kbar and 14 kbar, the enhancement of $T_1^{-1}$ just above $T_N$ and the huge line splitting below $T_N$ were not observed, indicating that the antiferromagnetic transition was suppressed. The typical temperature dependence of $T_1^{-1}$ (at 11 kbar) is shown in Fig. 3. With the disappearance of the antiferromagnetic phase, a curious electronic phase appeared at low temperatures as described below. Under 11 kbar, $T_1^{-1}$ shows an abrupt decrease below 6 K. It should also be noted that in the $^{13}$C NMR spectra, two distinct lines in the paramagnetic region merged into one line at 2 K. Since the two distinct lines in the high-temperature region originate from two inequivalent inner and outer $^{13}$C sites on the same TMTTF molecule with different hyperfine coupling constants, as mentioned before, the decrease in the line-splitting indicates the disappearance of the hyperfine coupling interaction, i.e., the disappearance of unpaired spins. These observations suggest that (TMTTF)$_2$SbF$_6$
undergoes a spin-gap phase transition under a pressure between 5 kbar and 14 kbar. This spin-gap behavior under pressure seems to be consistent with the spin-Peierls phase proposed in the modified generalized $P$-$T$ phase diagram, as shown in Fig. 1. However, no obvious shift in the center of gravity of the absorption lines was seen down to 2 K. In the case of the typical spin-Peierls system, we can expect a shift of about 150 ppm for the magic-angle configuration. [2] We conclude that the disappearance of the Knight-shift, which is one evidence of the spin-singlet Peierls phase transition, has not been observed. We do not have a clear explanation for this anomaly at present.

Above 17 kbar, the other ground state appeared. Figure 4 shows the $^{13}$C NMR spectra of (TMTTF)$_2$SbF$_6$ under 17 kbar at 2 K. The $^{13}$C NMR spectra at 2 K shows clear line-splitting. (Since the relative intensity of the central line is small compared to the intensities of the side lines, the central line likely originated from small contamination of the residual spin-gap phase or from dislocations). The splitting width gradually increases below 15 $\sim$ 20 K. It is to be noted that the scale of the horizontal axis is extremely large, Since the huge splitting of $^{13}$C NMR cannot be explained by charge separation or charge disproportionation phenomena, it therefore likely originated from internal staggered fields. We therefore conclude that (TMTTF)$_2$SbF$_6$ undergoes an antiferromagnetic phase transition at around 15 $\sim$ 20 K. Considering the modified generalized $P$-$T$ phase diagram (Fig. 1), the antiferromagnetic phase under 17 kbar is possibly AF-II. While it is not clear at present whether AF-I and AF-II have the same origin, it should
be noted that the splitting width of $^{13}$C NMR spectra of AF-II is much larger than that of AF-I (ca. 1000 ppm). [5] Hence, it seems likely that the origins of the antiferromagnetic ground states are different, since the electronic states of the paramagnetic phase (for example, the existence of the clear charge-ordering phase) seem to be quite different.

Recently, a theoretical approach for two different antiferromagnetic phases was considered within the framework of competition between the Wigner crystal and the bond-charge-spin-density wave. [6] Yoshioka also proposed competition between the dimer-Mott phase and two CO phases. [7]. In this scenario, a spin-Peierls (spin-gap) ground state is stabilized in the dimer-Mott state. According to these theoretical approaches, reentrant AF ground states seem likely for $(TMTTF)_2X$ salts.

![Figure 4. $^{13}$C NMR spectra of $(TMTTF)_2SbF_6$ under 17 kbar at 2 K. The scale of the horizontal axis should be noted. The splitting of the side peaks is extremely large.](image)

In conclusion, we carried out $^{13}$C NMR measurements under the application of hydrostatic pressure on $(TMTTF)_2SbF_6$ to clarify the competing ground states. The low-pressure side antiferromagnetic state (AF-I) was suppressed under pressures between 5 kbar and 14 kbar, and the spin-gap phase appeared at the same time. Above 17 kbar, another antiferromagnetic phase transition appeared. These observations prove the justification of the modified generalized P-T phase diagram. However, several unsolved problems remain. The spin-gap phase cannot be explained within the framework of the simple spin-singlet state, because of the remaining finite Knight-shift. It is not clear at present whether the AF-I and AF-II phases have the same origin. Further investigation to understand the detailed electronic state is now under way.

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