$^{13}$C NMR study of the chemical pressure effect in (TMTTF)$_2$[(AsF$_6$)$_x$(SbF$_6$)$_{1-x}$] ($x \sim 0.5$)

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Abstract. $^{13}$C NMR measurements of (TMTTF)$_2$[(AsF$_6$)$_x$(SbF$_6$)$_{1-x}$] ($x \sim 0.5$) alloy were performed in order to understand the chemical pressure effect and the electronic state at low temperatures. The charge-ordering transition temperature is the intermediate value between those of SbF$_6$ and AsF$_6$ salts. The broadening of NMR spectra and the weak temperature dependence of the spin-lattice relaxation rate at low temperatures indicate that this salt is situated in the vicinity of the phase boundary between the spin-Peierls and antiferromagnetic phases.

1. Introduction
Quasi-one-dimensional organic charge-transfer salts are important candidates for the researches of the many-body electronic correlation in materials, which are attractive topics in the recent condensed matter physics [1, 2]. A family of (TMTTF)$_2$X salts, where TMTTF is tetramethyltetrathiafulvalen, shows various phases such as antiferromagnetic, spin-Peierls, charge-ordering, ferroelectric, and superconducting by lowering temperature and applying pressure. A modification of the anion, X, is considered to be equivalent to applying a pressure. The ground state of SbF$_6$ salt is an antiferromagnetic at ambient pressure [3]. In contrast, AsF$_6$ salt, which is located at higher pressure region than SbF$_6$ salt, shows a spin-Peierls transition [4]. These two salts undergo the charge-ordering (CO) transition at higher temperatures [5, 6, 7].

In this paper, we report a NMR investigation of the electronic states in (TMTTF)$_2$[(AsF$_6$)$_x$(SbF$_6$)$_{1-x}$] ($x \sim 0.5$) alloy in order to understand the physical property at low temperatures and the chemical pressure effect from the microscopic point of view. The NMR spectrum is sensitive to the CO transition [5] and the nature of the ground state [8, 9]. The information of the spin dynamics at NMR frequencies is provided by the measurements of the nuclear spin-lattice relaxation rate, $1/T_1$.

2. Experimental
We performed $^{13}$C NMR measurements on a single crystal of (TMTTF)$_2$[(AsF$_6$)$_x$(SbF$_6$)$_{1-x}$] ($x \sim 0.5$). Two central C=C double-bonded carbons in a TMTTF molecule are $^{13}$C-enriched as shown in Fig. 1(a). An external magnetic field of 8 T was applied perpendicular to the molecular stacking axis ($a$-axis). The nuclear dipolar splitting of $^{13}$C NMR lines originated from the central C=C double-bonded carbon was canceled by setting the crystal in the configuration of so-called magic angle. The $1/T_1$ was measured by a saturation recovery method.
Figure 1. (a) Molecular structure of $^{13}$C-labeled TMTTF. (b) $^{13}$C NMR spectra of $(TMTTF)_2[(AsF_6)_x(SbF_6)_{1-x}]$ ($x \sim 0.5$). The shift origin is TMS.

3. Results and discussion

Figure 1 (b) shows the temperature dependence of the $^{13}$C NMR spectra. At high temperatures, the observation of two signals, whose intensities are almost equal, is consistent with the presence of two inequivalent $^{13}$C sites in a TMTTF molecule. We labeled these signals as “inner” for the higher frequency signal and “outer” for the lower frequency signal. Below $\sim 125$ K, each spectrum becomes asymmetric and are composed of two lines. This behavior indicates that two TMTTF molecular environments in a unit cell become inequivalent due to the charge-ordering (CO) as discussed in $(TMTTF)_2SbF_6$ and $(TMTTF)_2AsF_6$. The chemical pressure effect is confirmed as a variation of the phase transition temperature $T_{CO}$, which is the intermediate value between $T_{CO}=155$ K ($SbF_6$) [10] and $T_{CO}=100$ K ($AsF_6$) [5]. Below about 30 K, these spectra exhibit a substantial broadening. Here we confirmed that the signal intensity is conserved considering Curie’s law of the nuclear magnetization. The line broadening is probably originated from the inhomogeneity and/or low frequency dynamics of the local moment near the spin-Peierls transition as observed in AsF$_6$ and PF$_6$ salts [11, 12].

The spectrum at 101 K is shown in Fig. 2. The spectrum is composed of four Gaussian spectra, denoted by Line A, B, C and D, which have almost same area. We measured the spin-lattice relaxation rates $1/T_1$ for each spectra by fitting the recovery curve of the nuclear magnetization $M(t)$ to a stretched exponential $((M(\infty) - M(t))/M(\infty) \propto \exp(-(t/T_1)^{\beta}))$. The estimated values of $1/T_1$ for Line A to D are 31.3, 6.64, 64.6, and 14.4 s$^{-1}$. Considering that the $1/T_1$ of the charge-rich spectrum is larger than that of charge-poor, Line C (D) are assigned for the outer (inner) nucleus at the charge-rich molecule and charge-poor molecule, respectively. We also derived $1/T_1$ in discrete frequencies over the spectrum as shown in the same figure. The $1/T_1$ over the spectrum corresponds to the profile of four decomposed spectra. The ratio of the charge occupancy at 101 K is 0.32 : 0.68 (the amplitude is $\rho \sim 0.18$), assuming that the $1/T_1$ is proportional to the square of the charge quantity on the TMTTF molecule. The $\rho$ is also intermediate between the values of $\rho \sim 0.17$ for AsF$_6$ salt [11] and $\rho \sim 0.25$ for SbF$_6$ salt [13].

The temperature dependence of the $1/T_1$ is shown in Fig. 3(a). The $1/T_1$ monotonically decreases with decreasing temperature. The $1/T_1$ of Line A to D at 101 K are plotted in the
Figure 2. $^{13}$C NMR spectrum at 101 K below $T_{CO}$. The spectrum is composed of four Gaussian spectra. The $1/T_1$ measured at discrete frequencies is shown over the spectrum.

Figure 3. (a) Temperature dependence of $1/T_1$. The data of AsF$_6$ salt are plotted after ref. [11]. (b) Recovery curve of the nuclear magnetization at 4.2 K.

figure. Below 100 K, $1/T_1$ is represented by the value for the overlapped spectrum. Before the discussion of temperature dependence of the $1/T_1$ at low temperatures, we mention the distribution of $1/T_1$ at low temperatures. The recovery curve of the nuclear magnetization becomes a non-single exponential at low temperatures. Figure 3(b) is the recovery curve taken at 4.2 K. The $\beta$ in the stretched exponential function is evaluated to be 0.46, indicating that the $1/T_1$ is almost randomly distributed. The most likely cause of the distribution in $1/T_1$ is the CO. Another possibility is the effect of the disorder of the counter anion due to the alloying. It is noticed, however, that the distribution of $1/T_1$ is not observed at high temperatures. Therefore, in this case, the phase boundary of the spin-Peierls state, whose existence is suggested by the broadened spectra, is the source of the distribution.

Around an antiferromagnetic phase transition, $1/T_1$ shows a divergent increase due to the critical slowing down of the antiferro spin-fluctuations. The absence of such kind increase of $1/T_1$
in this salt indicates that the ground state is not the antiferromagnetic. However, the decrease of $1/T_1$, which is the characteristic behavior of spin-Peierls transition, is very weak compared to the data of AsF$_6$ salt as shown in Fig. 3. Moreover, the rapid component in $T_1$ is detected as seen in the recovery curve. The $1/T_1$ value of the initial recovery of the nuclear magnetization at 4.2 K is plotted in Fig. 3(a). These results suggest that the spin-Peierls phase is terminated at extremely low temperatures and is bounded on the other phase such as antiferromagnetic phase. This salt is situated in the vicinity of the phase boundary between these phases. This scenario is not contradict to the distribution of $1/T_1$ discussed above. The detail analysis of $1/T_1$ and the NMR measurements in the other salts in this alloy system are underway.

4. Conclusion
We investigated the chemical pressure effect in $(\text{TMTTF})_2[(\text{AsF}_6)_x(\text{SbF}_6)_{1-x}]$ ($x \approx 0.5$) alloy by means of $^{13}$C NMR technique. The charge-ordering temperature $T_{CO} \sim 125$ K, which was roughly deduced by the spectral analysis, is the intermediate value between the pure compounds, AsF$_6$ and SbF$_6$. At low temperatures, this salt appears to approach the spin-Peierls phase transition. The temperature dependence of $1/T_1$, however, shows anomalous behavior without the rapid reduction expected below the spin-Peierls phase transition. This suggests that this salt is situated in the vicinity of the boundary between the spin-Peierls phase and antiferromagnetic phases.

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