\textbf{\textit{\textsuperscript{77}Se-NMR study of quasi-one dimensional organic conductor (TMTSF)\textsubscript{2}X}}

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\textbf{Abstract.} Quasi-one dimensional organic conductor (TMTSF)\textsubscript{2}X with octahedral anions X = PF\textsubscript{6}, AsF\textsubscript{6}, and SbF\textsubscript{6} have been studied by NMR measurements at the Se-sites which are substantially responsible for conductivity in this system. Close resemblances in the temperature dependence of the spin-lattice relaxation rate \(1/T_1\) and the evolution of internal field in the SDW state were observed in the three measured compounds. The existence of the sub-phases in the SDW phase of all these compounds, which is evidenced by \(T_1\) but not from spectrum measurements, indicates that this is a common feature among (TMTSF)\textsubscript{2}X system with an incommensurate SDW wave number and is associated with dynamic property rather than static one.

1. Introduction
The first organic superconductor (TMTSF)\textsubscript{2}X (X = PF\textsubscript{6}, AsF\textsubscript{6}, SbF\textsubscript{6}, ClO\textsubscript{4}, etc.) has been a topic of interest for three decades. Intensive studies have been carried out on this family, however, there still remain several basic problems to be clarified, including nature of the unconventional superconducting phase adjacent to the spin density wave (SDW) ordered state \cite{1}. Besides, the existence of sub-phases in the SDW phase was pointed out by \textsuperscript{1}H-NMR studies \cite{2, 3}, whose mechanism remains unsolved as well. Nuclear magnetic resonance (NMR) is a powerful experimental technique to probe static and dynamic magnetic properties. In contrast to detailed \textsuperscript{1}H-NMR studies on these compounds, there are only few \textsuperscript{77}Se-NMR reports using single crystals in the SDW state \cite{4}, although Se-4s and -4p orbitals mainly contribute to the conduction bands \cite{5}. We have therefore carried out \textsuperscript{77}Se-NMR measurements on single crystal samples of (TMTSF)\textsubscript{2}X with octahedral anions X = PF\textsubscript{6}, AsF\textsubscript{6}, and SbF\textsubscript{6}. Such a systematic study over several isostructural analogues will enable one to conduct comprehensive investigations on this system. The SDW phase of X = PF\textsubscript{6} is characterized by an incommensurate wave vector of \(Q_{\text{SDW}} = (0.5, 0.24 \pm 0.03, -0.06 \pm 0.20)\) from \textsuperscript{1}H-NMR study \cite{6}, and SDW transition temperature \(T_{\text{SDW}}\) is 12 K for X = PF\textsubscript{6} and AsF\textsubscript{6}. Regarding X = SbF\textsubscript{6}, while \(T_{\text{SDW}}\) was first reported as 17 K \cite{7}, another reference indicates \(T_{\text{SDW}} = 12\) K \cite{8}.
2. Experimental details

Single crystals were grown by the standard electro-chemical method. The $^{77}$Se-NMR measurements were carried out using the spin echo technique with a phase-coherent pulsed spectrometer. NMR lines were obtained by sweeping magnetic field, and the spin lattice relaxation time $T_1$ was measured with a single rf-pulse saturation method. All the NMR measurements were performed around the magnetic field of 11.2 T using a commercial superconducting magnet, with magnetic field direction parallel to the crystal $c$-axis.

3. Results and Discussion

![Figure 1](image)

Figure 1. Representative $T_1$ recovery curves (a) above and (b) below $T_{SDW}$ for present (TMTSF)$_2X$ samples. The presented data were obtained for $X = \text{SbF}_6$ at the frequency of 92.680 MHz corresponding to the field of $\sim$ 11.4 T. While $T_1$ was uniquely determined in the paramagnetic state, we evaluated $T_1$ with short and long components below $T_{SDW}$ (see text). The short and long components were temporally obtained by fitting the data of $0.1 \leq (M(\infty) - M(t))/M(\infty) \leq 1$ and $(M(\infty) - M(t))/M(\infty) \leq 0.1$ to the single exponential function, respectively. Here, $M(\infty)$ and $M(t)$ are the nuclear magnetization in the thermal equilibrium and at a time $t$ after a saturation pulse, respectively.

Figure 1 shows representative $T_1$ recovery curves obtained above and below $T_{SDW}$ for $X = \text{SbF}_6$. Since $^{77}$Se nucleus has the nuclear spin $I = 1/2$, the recovery curves in the paramagnetic state were fit well to a single exponential function. On the other hand, we could not obtain unique $T_1$ below $T_{SDW}$ for all the three compounds, possibly due to distribution of internal field in the SDW state with incommensurate $Q$-vector. Hence we evaluated the $T_1$ data with short and long $T_1$ components, as shown in Fig. 1(b).

The temperature dependences of $1/T_1$ for the three compounds are summarized in Fig. 2(a)-(c). At high temperatures above 30 K, $1/T_1$ shows rather metallic behavior, namely the Korringa law $1/T_1 \propto T$. At low temperatures, the temperature dependence of $1/T_1$ is analogous with the previous $^{77}$Se-NMR study [4]. $1/T_1$ shows critical slowing down behavior when approaching $T_{SDW}$ from high temperatures. Additionally $1/T_1$ shows a shoulder-like anomaly at $T_X \sim 4$ K in the SDW state. Note that, in the temperature region from $T_X$ to $T_{SDW}$, $1/T_1$ follows rather $T^{1.5}$ than $T$ indicated in Ref. [4]. The difference is possibly associated with the different resonance line shape in the SDW state between our results and that in Ref. [4]. Namely, in the present study, the NMR line significantly broadens and splits into double-peaked lines below $T_{SDW}$, as shown in Fig. 3(b) and (c) (also see Ref. [9]), so that the $T_1$ measurements were performed at
Figure 2. Summary of the temperature dependences of $1/T_1$ for $X = \text{AsF}_6$, $\text{SbF}_6$, and $\text{PF}_6$ compounds. For all these compounds, $T_1$ in the SDW state was evaluated with short and long components as shown in Fig. 1.

the peaks of the split lines. Here we did not see any significant discrepancy between the $T_1$ data measured at the two different peaks. On the other hand, no clear splitting is seen in the NMR spectrum reported in Ref. [4]. The double-peak line shape is reproduced by assuming sinusoidal internal fields at Se nucleus positions having the same incommensurate wave number with the SDW $Q$-vector [9]. The line width at 4.2 K corresponds to $\sim 800$ Oe, larger than the value previously reported [4]. Thus the $T_1$ relaxation process in this anomalous state between $T_X$ and $T_{\text{SDW}}$ is not only attributed to residual free carriers in the SDW state, but also to magnetic mechanism.

NMR spectrum measurement is a useful tool to investigate the evolution of the static SDW state. In Fig. 3(a), we plot the normalized interval of the split NMR lines, $\Delta(T)/\Delta_0$, observed in the SDW state as a function of temperature. $\Delta_0$ was obtained by extrapolating $\Delta(T)$ as $T \to 0$. From this plot, onset temperature for the SDW order is determined to be 12.0–12.5 K for all these compounds. The evolution of the internal field is steeper than the BCS curve just below $T_{\text{SDW}}$, consistent with the report of $^1$H-NMR [2]. Contrary to the remarkable anomaly in $1/T_1$ at $T_X$, NMR line does not show any change in the line shape within the experimental accuracy, indicating that the transfer between the sub-phases at $T_X$ is mainly brought about by dynamic properties [9].

Apparently our results show that the anomaly at the sub-phase boundary $T_X \sim 4$ K observed in $X = \text{PF}_6$ ($^1$H- and $^{77}$Se-NMR) [2, 3, 4] and $\text{AsF}_6$ ($^1$H-NMR) [10] is also seen in $X = \text{SbF}_6$ compound. Because, for (TMTTF)$_2$Br, a corresponding anomaly is not detected in the commensurate SDW state [3], our findings support the view that the existence of the sub-phases in the SDW phase is a common feature among (TMTSF)$_2$X system with an incommensurate SDW wave number. As shown in Table 1, the lattice parameters, as well as the unit cell volume, of $X = \text{PF}_6$ and $\text{AsF}_6$ are close to each other. On the other hand, $X = \text{SbF}_6$ has 2–3 % larger volume than others, which brings an expectation of negative pressure effects on physical properties. The observed close resemblances in $1/T_1$ and $\Delta(T)/\Delta_0$ between $X = \text{SbF}_6$ and others are probably consistent with the regime that the ratio of the strongest electron transfer energy along the $a$–axis and the perturbational transfer along $b'$–direction is responsible for
Figure 3. (a) The normalized interval of the split lines $\Delta(T)/\Delta_0$ as a function of temperature for $X = \text{AsF}_6$, $\text{SbF}_6$, and $\text{PF}_6$ compounds. The dotted line shows a BCS curve. (b) and (c) show representative lines for $X = \text{PF}_6$ and $\text{SbF}_6$, respectively. Both were measured at 1.5 K and at the NMR frequency $f$. The arrows represent $\Delta(T)$.

determination of $T_{SDW}$, and the smallest transfer in the $c$--direction is negligible, as indicated in the Ref. [11].

Table 1. Lattice parameters of $X = \text{PF}_6$, $\text{AsF}_6$ from Ref. [7] and of the present $X = \text{SbF}_6$ sample. $V$ is the volume of the triclinic unit cell. The data for the present $X = \text{SbF}_6$ sample is in good agreement with those from Ref. [7].

| $X$     | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
|---------|---------|---------|---------|-------------|
| $\text{PF}_6$ | 7.297   | 7.710   | 13.522  | 714.0       |
| $\text{AsF}_6$ | 7.277   | 7.711   | 13.651  | 719.9       |
| $\text{SbF}_6$ | 7.294   | 7.726   | 13.908  | 737.7       |

4. Conclusion
Systematic $^{77}\text{Se-NMR}$ study have been carried out on single crystal (TMTSF)$_2X$ with octahedral anions $X = \text{PF}_6$, $\text{AsF}_6$, and $\text{SbF}_6$. The anomaly at the sub-phase boundary $T_X \sim 4$ K, which were previously indicated by $^1\text{H}$- and $^{77}\text{Se-NMR}$ on $X = \text{PF}_6$ [2, 3, 4] and $^1\text{H-NMR}$ on $X = \text{AsF}_6$ [10], was almost equally observed in the temperature dependence of $1/T_1$ but not in the spectrum measurements on the three measured compounds. Our results obviously shows that the existence of the sub-phases is common over the (TMTSF)$_2X$ with an incommensurate SDW wave number, and it originates from dynamic features rather than static ones. It is interesting that, in spite of $2 - 3$ % difference in the unit cell volume, close resemblances in the temperature dependence of $1/T_1$ and in the evolution of internal field in the SDW state were observed in
all these compounds. More detail studies, especially NMR measurements with different angle external fields and/or under pressure, are in progress.

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References
[1] Jerome D, Mazaud A, Ribault M and Bechgaard K 1991 J. Physique Lett. 41 95
[2] Takahashi T, Harada T, Kobayashi Y, Kanoda K, Suzuki K, Murata K and Saito G 1991 Synth. Met. 41-43 3985
[3] Nomura K, Kubota H, Kotomizu M, Hanajiri T, Nakatsuji S and Yamada J 2003 Synth. Met. 133-134 19
[4] Valfells S, Kuhns P, Kleinhammes A, Brooks J S, Moulton W, Takasaki S, Yamada J and Anzai H 1997 Phys. Rev. B 56 2585
[5] Azevedo L J, Schirber J E and Engler E M 1984 Phys. Rev. B. 29 464
[6] Takahashi T, Maniwa Y, Kawamura H and Saito G 1986 J. Phys. Soc. Jpn. 55 1364
[7] Parkin S S P, Ribault M, Jerome D and Bechgaard K 1981 J. Phys. C: Solid State Phys. 14 5305
[8] Vignolles D, Ulmet J P, Naughton M J, Binet L and Fabre J M 1998 Phys. Rev. B 58 14 476
[9] Mito T, Nishiyama K, Koyama T, Ueda K, Kohara T, Takenchi K, Akatsu H, Yamada J, Kornilov A, Pudalov V M and Qualls J S 2010 Physica C 470 S592
[10] Nomura K, Hosokawa Y, Matsunaga N, Nagasawa M, Sambongi T and Anzai H 1995 Synth. Met. 70 1295
[11] Yamaji K 1982 J. Phys. Soc. Jpn. 51 2787