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NMR in spin-density wave phase of $(\text{TMTSF})_2\text{ClO}_4$

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The spin-density wave (SDW) phase of quenched $(\text{TMTSF})_2\text{ClO}_4$ was investigated by both measurements of narrow band noise and ^1H NMR relaxation rate. In the rapidly quenched phase, the sharp peak of narrow band voltage noise associated with the sliding motion of SDW is abruptly broadened in the narrow temperature range around 1.7 K much lower than the SDW transition temperature (5.7 K) and becomes undetectable at high temperature. This indicates that the spatial coherence of sliding motion is decreasing above this temperature. The divergent behavior in NMR relaxation rate is also observed at 1.7 K in the rapidly quenched phase. These results suggest that another phase transition occurs in the SDW phase. The temperature of this phase boundary decreases proportionally with the SDW transition temperature controlled by the anion quenching rate. The mechanism of this transition is closely related with that of the SDW transition.

1. INTRODUCTION

The spin-density wave (SDW) phase have been widely investigated in organic conductors of $(\text{TMTSF})_2\text{X}$ salts. Although the metal-insulator transition observed around 10 K for several kinds of anion X^- had suggested the occurrence of charge-density wave, successive magnetic measurements proved that the SDW transition occurs in the insulating phase. The static magnetization measurement showed the anti-ferromagnetically ordered spin state [1]. The amplitude and the incommensurate [1] wave vector of SDW was determined from the fitting of NMR line shape structure [2,3]. Most of static properties in the SDW phase were explained by the standard mean field theory on the nesting of the Fermi surface in quasi-two dimensional electronic band which is formed in the stacking of TMTSF column.

The collective mode of SDW condensate was also investigated with various methods. Tomić et al. [4] have measured the non-linear conductivity with the threshold electric field associated with the depinning of SDW condensate in $(\text{TMTSF})_2\text{NO}_3$ at first. After that, similar non-linear conductivity was observed in quenched $(\text{TMTSF})_2\text{ClO}_4$ [5] and $(\text{TMTSF})_2\text{PF}_6$ [6] in succession. The narrow band voltage noise, whose frequency is proportional to the sliding velocity, was successfully detected in anion-quenched SDW phase of ClO_4 salt [7] as in the case of the charge-density wave. The narrowing of NMR line provided by the sliding motion of SDW was also observed in ClO_4 salt [8]. These experiments have established the collective sliding mode of SDW. Especially, latter two measurements could examine the sliding velocity directly. However, the sharp narrow band noise peak was observable only in the low temperature. Moreover, the narrowing of NMR line became unclear with increasing temperature. These suggest that the dynamics of SDW is somewhat different between low and high temperature.

In order to clarify such behaviors related to the SDW dynamics, we carried out the detailed measurement of the narrow band noise with varying the temperature in anion-quenched SDW phase of $(\text{TMTSF})_2\text{ClO}_4$. We also investigated the ^1H NMR relaxation rate with changing the quenching rate. From the results of these experiments, we propose the new phase transition which divides the SDW

phase.

2. EXPERIMENTAL

Single crystal of $(\text{TMTSF})_2\text{ClO}_4$ was synthesized by the standard electro-chemical method. In the course of the present experiments, the sample was cooled slowly down to 77 K to avoid any destruction of sample in the pre-cooling stage. The SDW phase was induced in $(\text{TMTSF})_2\text{ClO}_4$ by the quenching of directional order of anion ClO_4^- . We controlled the anion ordering by the cooling rate (quenching rate R) at the anion ordering temperature 24 K. The quenching was done by immersing the sample into liquid helium directly.

Electric transport properties were measured by the conventional 4-terminal method. The SDW transition temperature was determined from $d(\ln\rho)/d(1/T)$, where ρ is the ohmic resistivity. In the narrow band noise measurement, the voltage signal amplified with the home-made pre-amplifier was analyzed under a constant current with use of a analog spectrum analyzer.

The NMR measurement was carried out with use of the single-coil pulse NMR spectrometer, which operates at 14 MHz. For investigation of ^1H nuclei in methyl group of TMTSF molecule, the proton free coil was used. We confirmed no signal without the sample crystal. The static magnetic field of 0.32 T was applied along the c^* -axis and the rf field is parallel to the a -axis. The spin-lattice relaxation rate T_1^{-1} was determined from the relaxation curve obtained with π - $\pi/2$ pulse sequence.

3. NARROW BAND NOISE

We could observe the non-linear conductivity with the clear threshold electric field in the wide

Fig. 1 Typical voltage noise spectra in the rapidly quenched phase with $T_{\text{SDW}} = 5.7$ K. The sharp narrow band noise appears for a bias current above the threshold.

Fig. 2 Frequency of narrow band noise F_{NBN} vs. excess current density J_{SDW} carried by the SDW

temperature range in the SDW phase of quenched $(\text{TMTSF})_2\text{ClO}_4$, when we cooled the sample carefully in the pre-cooling stage down to 77 K and suppressed the resistance jump. In non-linear conduction region, we could also observe the sharp peak of narrow band voltage noise in the low temperature. In Fig. 1, we show typical noise spectra observed at the lowest temperature 1.17 K. The peak appears in the spectra for a bias current above the threshold and its frequency increases with increasing bias current. In Fig. 2, the peak frequency of narrow band noise F_{NBN} is shown against the excess current density J_{SDW} carried by the SDW condensate estimated from the non-linear conductivity curve in the usual manner. As shown in Fig. 2, F_{NBN} is proportional to J_{SDW} with the slope $F_{\text{NBN}}/J_{\text{SDW}}=1010 \text{ kHz/Acm}^{-2}$. This proportionality was confirmed commonly in almost all samples investigated, but the slope value was ranging from 150 to 1010 kHz/Acm^{-2} depending on each sample. Similarly to the charge-density wave case, this linear relation between F_{NBN} and J_{SDW} is described in the wash-board model as

$$F_{\text{NBN}}/J_{\text{SDW}}=1/(en_{\text{SDW}}\lambda_{\text{pin}}), \quad (1)$$

where n_{SDW} is the electron density condensed to the SDW and λ_{pin} represents the effective pinning length. The pinning of SDW by non-magnetic impurities is of second order, because the spatial charge is uniform in the SDW state. Accordingly, it is expected that λ_{pin} is half of the SDW wave length λ_{SDW} . However, the obtained value for λ_{pin} from the narrow band noise is much smaller. The reason of such small value is probably that the SDW is moving only through the partial area of sample.

Fig. 3 Temperature variation of voltage noise spectra.

Although the narrow band noise was clearly observed in the low temperature as shown in Fig. 1, it was not detectable above 1.7 K. We investigated the voltage noise spectra in detail with varying temperature. In Fig. 3, we show the noise spectra observed in another sample than Fig. 1 at three different temperatures for the same excess current density of 0.26 Acm^{-2} . We find the peak at the same frequency position in all spectral curves. We also confirmed that the frequency and the excess current satisfy the linear relation with the slope of 280 kHz/Acm^{-2} in this sample over the temperature range lower than 1.7 K, where the narrow band noise peak could be detected. This indicates that the condensate density is nearly independent of temperature in this low temperature range. As clear from Fig. 3, however, the width of voltage noise peak shows an abrupt increase in the narrow temperature range around 1.7 K. This temperature dependent behavior of narrow band noise was also observed commonly in all samples investigated. The frequency of narrow band noise F_{NBN} is simply related with the sliding velocity v as

$$F_{\text{NBN}} = v/\lambda_{\text{pin}} \quad (2)$$

Accordingly the width of narrow band noise represents the distribution of sliding velocity in space. The observed broadening of narrow band noise width indicates that the velocity correlation over the sample volume is decreasing above this temperature.

It is deduced that the dynamics of SDW suffers a considerable change at this narrow temperature range. However, the non-linear conductivity curve was not very different between low and high temperature. The threshold electric field value is almost continuous through this temperature range. The pinning mechanism is likely to be common between low and high temperature.

4. ^1H NMR

The NMR measurement was performed in order to clarify the origin of the abrupt broadening of narrow band noise. We obtained the relaxation curve by π - $\pi/2$ pulse method and confirmed that the relaxation curve is described by a single-exponential curve in the whole temperature range. The temperature dependence of the spin-lattice relaxation rate T_1^{-1} for the rapid quenching ($R > 50 \text{ K/s}$) is shown in Fig. 4. The relaxation rate shows a sharp peak at 5.7 K. As this peak temperature is almost equal to the SDW transition temperature T_{SDW} determined from the resistivity measurement, this peak behavior is properly assigned to the critical fluctuation due to the SDW phase transition. It is understood that the transition temperature is almost unaffected by the magnetic field of 0.32 T. We find another peak around 1.7 K. This temperature is much lower than T_{SDW} . From the mean field theory, it is expected that most of electrons condense in the SDW state and there is no special excitation in such low temperature. However, the observed peak indicates that the magnetic field fluctuation on ^1H nucleus site becomes larger at this temperature. Its divergent behavior is similar to that at T_{SDW} and strongly suggests another phase transition.

Fig. 4 Temperature dependence of ^1H spin-lattice relaxation rate T_1^{-1} for the rapid quenching rate $R > 50 \text{ K/s}$. The solid curve is a guide for eye.

We investigated further the temperature dependent behavior of the relaxation rate with varying the anion quenching rate R . In Fig. 5(a) and (b), the relaxation rate is shown against the temperature for the quenching rate $R = 10 \text{ K/s}$ and $R = 0.5 \text{ K/s}$, respectively. The transition temperature is estimated from the resistivity measurement as 5 K and 4 K. As clear from Fig. 5, the peak temperature associated with the SDW transition decreases showing the decreasing T_{SDW} with decreasing quenching rate. For $R = 10 \text{ K/s}$, we find the low temperature peak at 1.4 K. For $R = 0.5 \text{ K/s}$, the low temperature peak is not observed in the present temperature range, but T_1^{-1} shows only the increasing behavior toward

the low temperature. However, we naturally deduce that it has a peak at slightly lower temperature.

Fig. 5 Temperature dependence of T_1^{-1} ; (a) $R=10$ K/s. (b) $R=0.5$ K/s

The number of electrons thermally excited across the SDW gap is decreasing exponentially in such low temperature region and it gives negligible contribution to the NMR relaxation. Accordingly, the observed peak in T_1^{-1} is probably related with the spin structure of the SDW. The change in the amplitude or the wave number is expected. We examined the NMR line width which is closely related to the spin structure. However, we had no detectable change in the NMR width at the temperature where the peak was observed in T_1^{-1} . Previous NMR experiments [2,3] also reported the absence of drastic change in the NMR line shape. It is deduced that the change in spin structure is very small, if it is present. However, the local field fluctuation is clearly not small. We need to find some kind of degree of freedom which provides the magnetic fluctuation in the low temperature SDW phase.

5. DISCUSSION

The divergent peak in the NMR relaxation rate is observed at the temperature much lower than T_{SDW} . This temperature is very near the narrow temperature range where the abrupt broadening occurs in the narrow band noise peak. These suggest that another phase transition occurs in the SDW phase. The SDW phase is divided by this phase transition into two-sub phases. In Fig. 6, we add this new phase boundary determined from Fig. 4 and Fig. 5 to the phase diagram for the anion quenching rate. As we observe no peak but only the increasing T_1^{-1} toward the low temperature for $R=0.5$ K/s, we show the deduced temperature from Fig. 6(b) as an open circle.

The new phase transition temperature T^* is nearly proportional to T_{SDW} with $T_{SDW}/T^* \sim 3.5$ over the whole investigated region of the quenching rate. It is understood that the mechanism responsible to this new transition is closely related with that of the SDW transition. Takahashi et al. [9] have reported similar anomalous behavior in NMR relaxation rate on $(TMTSF)_2PF_6$. Although the observed anomalous temperature dependence of T_1^{-1} in $(TMTSF)_2PF_6$ is somewhat different from the divergent behavior in $(TMTSF)_2ClO_4$, the anomalous temperature T^* is also roughly proportional to T_{SDW} with $T_{SDW}/T^* \sim 3.5$ in $(TMTSF)_2PF_6$. This suggests that the mechanism of this anomaly is common in the SDW phase.

This anomalous behavior is distinguishable in the dynamics of SDW. The narrow band noise shows an abrupt broadening, while the non-linear conductivity curve and the threshold electric field vary continuously with temperature. Delrieu et al. [8] observed the motional narrowing of NMR line provided by the sliding motion of SDW in quenched $(TMTSF)_2ClO_4$. Although the NMR line structure is almost fully narrowed for a bias current exceeding the threshold in the low temperature region, with increasing temperature the narrowing becomes unclear. The NMR line is not narrowed above 2.5

K even in the non-linear conduction region, where the large part of current is carried by the SDW condensate. This behavior also suggests the change in the actual motion of SDW and is probably related to the anomalous behavior observed in the narrow band noise, although the characteristic temperature is slightly higher in the motional narrowing of NMR.

Fig. 6 Phase diagram for the anion quenching rate on $(\text{TMTSF})_2\text{ClO}_4$

Although it is expected that the spatial structure of SDW changes at T^* , the change is not detectable with the static NMR, as described in the previous section. The change of static spin structure is likely to be very small. The discommensuration structure may play some role. Although the discommensuration is not fully understood in the SDW phase, it could give some degree of freedom. However, there is not any evidence for the presence of such structure at present and it is still open problem. We need the accumulation of experimental results to clarify this transition in connection with the dynamics of SDW.

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