

## 論文の内容の要旨

論文題目

NMR/NQR studies on magnetic excitations  
in neutral-ionic transition materials  
(中性-イオン性転移物質の磁気励起に関するNMR/NQR研究)

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### [Introduction]

In one-dimensional systems, a variety of phenomena have been observed when electron-electron interactions are entangled with electron-lattice interactions. Among them, a neutral-ionic (NI) transition is often exhibited by quasi one-dimensional mixed stack organic complexes consisting of donor (D) and acceptor (A) molecules. This phenomenon is characterized by charge transfer and lattice dimerization. Decreasing temperature and/or applying pressure induces a charge transfer from D to A due to the increase of the inter-site Coulomb energy so that the system changes from a neutral phase to an ionic one. Moreover, a lattice dimerization follows because of the spin-Peierls instability. In many cases, the dimerization occurs simultaneously with the charge transfer, so the NI transition materials are non-magnetic in both the neutral and ionic phases; the former is regarded as a band insulator, whereas the latter is as a dimerized spin-singlet Mott insulator.

The mixed stacking charge transfer salt, TTF-CA, has long been investigated as the first NI transition material. However, a recent  $^{35}\text{Cl}$ -NQR study suggests that an ionic phase without the lattice dimerization resides above 9 kbar around room temperature [1], which suggests the appearance of paramagnetic spins in this region. Indeed, as pressure is increased at room temperature, the spin-lattice relaxation rate  $1/T_1$  of  $^1\text{H}$ -NMR is enhanced in the high pressures [2]. On the other hand, an apparently contradicting indication of the lattice dimerization was observed by the infrared absorption measurements, which show the activation of  $a_g$  mode [3]. These features are consistently explicable in terms of the time scales specific to the experimental probes, assuming that the dimerization is temporarily fluctuating at a characteristic frequency between the frequency windows of the NQR ( $10^7$ - $10^8$  Hz) and infrared ( $10^{13}$  Hz) probes. In this picture, the paramagnetic state above 9 kbar is not viewed as a homogenous 1D spin-chain system, but possibly as a “dimer liquid” with solitonic and mobile spin excitations. The direct evidence for the solitonic excitations has been awaited and the mechanism of the symmetry-breaking ferroelectric transition from the solitonic states should be clarified.

The conventional picture of the NI transition invokes the spin-Peierls instability as the origin of the lattice dimerization. However, an earlier  $^{35}\text{Cl}$ -NQR work on DMTTF-CA at ambient pressure suggested that the lattice dimerization occurs without charge transfer enough to generate spins on D and A molecules [4], which seems against the spin-Peierls picture of the dimerization. This suggests a possible

variation in the mechanism of the NI transition and thus it is meaningful to investigate a separate NI transition system to know universality and variation in the characteristics of NI transition.

The purpose of the present study is two-fold. One is to clarify the nature of the spin states in the ionic phase of the conventional NI transition material, TTF-CA; more specifically, we aim to demonstrate the possible solitonic excitations at high pressures above 9 kbar and reveal how they condense into the dimerized ferroelectric phase. We employed the  $^{13}\text{C}$  and  $^1\text{H}$ -NMR and  $^{35}\text{Cl}$ -NQR experiments under pressures to tackle these issues. The other is to seek NI transition mechanisms different from the conventional one. Here, we aim to reveal the phase diagram and the spin/charge/lattice states in DMTTF-CA, for which the validity of the conventional picture of the NI transition was questioned, for comparison with TTF-CA. For this purpose, DMTTF-CA has been investigated by  $^{35}\text{Cl}$ -NQR and  $^1\text{H}$ -NMR under pressures.

## [Results and Discussions]

### 1. Magnetic excitations in TTF-CA

First, the pressure dependences of  $^{13}\text{C}$ -NMR shift and  $1/T_1$  were measured at a temperature of 285 K. Both increase with applied pressure, indicating that the spin degrees of freedom become vital under pressures. Assuming the uniform 1D Heisenberg model, the reported band parameters of TTF-CA gives an estimate of the exchange interaction,  $J = 2400$  K. Using the reported hyperfine coupling tensors of an analogous material, the shift and  $1/T_1$  were evaluated; however, the experimental shift value at 14 kbar is less than a half of the calculated value, whereas the  $1/T_1$  at 14 kbar is 16 times larger than the calculated value. These results suggest that the uniform 1D Heisenberg model is not appropriate for describing the present spin states and an alternative picture should be invoked such as the mobile soliton picture.

Next, to inquire further whether the picture of mobile solitons is valid or not, we investigated the frequency dependence of  $^1\text{H}$ -NMR  $1/T_1$ , which is a measure of the spectral density function at the NMR resonance frequency, at 300 K under a pressure of 14 kbar. If the spin solitons move around in a diffusive manner, the  $1/T_1$  is expected to exhibit a frequency dependence characteristic of the dimension of the motion, whereas the uniform 1D Heisenberg model would give almost frequency independent  $1/T_1$  for  $T$  ( $= 300$  K)  $\ll J$  ( $= 2400$  K). The  $1/T_1$  shows a prominent frequency dependence in a range between 14 and 300 MHz and a saturation at lower frequencies, as shown in Fig. 1(a). This behavior is well fitted by the formula for the diffusive spin motion situated in the 1D-3D crossover, which indicates that the spin solitons move diffusively along 1D chains with weak inter-chain interactions.

Finally, to see how the dimer liquid with spin solitons changes into the ferroelectric state with a long-range order of dimerization, we performed  $^{13}\text{C}$ -NMR and  $^{35}\text{Cl}$ -NQR measurements under temperature variation at 14 kbar. Both the  $^{13}\text{C}$  Knight shift and  $1/T_1$  show kinks at 272 K ( $= T_c$ ) and decrease exponentially with temperature below  $T_c$ , as shown in Figs. 1(b) and (c), confirming the non-magnetic nature of the ferroelectric state with a finite excitation gap. In the ferroelectric state, the

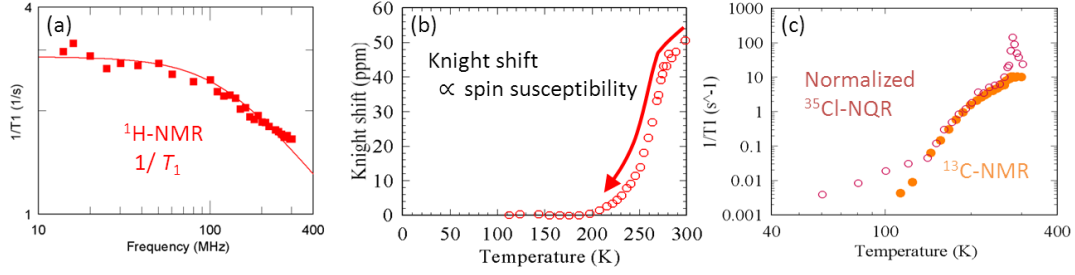


Fig. 1. (a) Frequency dependence of spin-lattice relaxation rate  $1/T_1$  of  $^1\text{H}$ -NMR at 300 K. Solid line is fitted with the formula of  $1/T_1$  by 1D-3D crossover diffusive spin motion. (b) Temperature dependences of Knight shift of  $^{13}\text{C}$ -NMR at 14 kbar. (c) Temperature dependence of  $1/T_1$  of  $^{13}\text{C}$ -NMR and  $^{35}\text{Cl}$ -NQR at 14 kbar.  $1/T_1$  of  $^{35}\text{Cl}$ -NQR is normalized by that of  $^{13}\text{C}$ -NMR at 140 K.

solitons cannot be excited in the same manner as in the paraelectric state above  $T_c$  because it would break the long-range ferroelectric order, but they can be in the form of bound soliton-antisoliton pairs (or the triplets). The temperature dependences of the Knight shift and  $1/T_1$  are of the Arrhenius type in  $200\text{ K} < T < T_c$  (the shift is unmeasurably small in  $T < 200\text{ K}$ ) and the deduced gap energies are  $\Delta_{\text{shift}} = 3140\text{ K}$  and  $\Delta_{1/T_1} = 1270\text{ K}$ ; the large difference suggests unconventional magnetic excitations. As a conceivable mechanism, we propose that the motion of the thermally excited triplets or bound solitons along the 1D chains contributes to  $1/T_1$  even below  $T_c$ . In this case, local lattice deformations are expected to follow the travelling of the spins and to cause lattice fluctuations different from the phonons. Indeed,  $^{35}\text{Cl}$ -NQR  $1/T_1$ , which probes the lattice fluctuation, exhibits nearly the same temperature dependence as  $^{13}\text{C}$ -NMR  $1/T_1$  shows for  $140\text{ K} < T < 230\text{ K}$  ( $< T_c$ ) (Fig. 1(c)), supporting the persistence of the spin-lattice coupled mobile excitations even below  $T_c$ .

## 2. Mechanism of phase transition in DMTTF-CA

For DMTTF-CA, we conducted  $^{35}\text{Cl}$ -NQR and  $^1\text{H}$ -NMR experiments under pressure and temperature variations to investigate the mechanism of the phase transition. The charge transfer from DMTTF to CA is determined by the frequency shift of  $^{35}\text{Cl}$ -NQR line whereas the lattice dimerization is known from the line splitting. In TTF-CA, the lattice dimerization follows after the sufficient charge transfer is accomplished as seen in a large decrease in  $^{35}\text{Cl}$ -NQR frequency ( $\nu_Q$ ), whether it is a jump-like or continuous decrease (Fig. 2(a)) [5], which is not inconsistent with the spin-Peierls mechanism. In DMTTF-CA, however, the change of  $\nu_Q$  is a continuous or weak first-order like and, just below the transition, the dimerization occurs even under insufficient charge transfer for the formation of the ionic states under low pressures (Fig. 2(b)). This suggests that the spin degree of freedom plays a secondary role in the dimerization transition under low pressures in DMTTF-CA; instead, the electronic energy gain, if any, may be caused by the modulations in the transfer integrals (the so-called Peierls mechanism) or a increase in the Madelung energy, associated with the lattice modulation. As the pressure is increased, the  $\nu_Q$  decreases down to the values indicative of the ionic phase, although  $\nu_Q$  shows no appreciable change

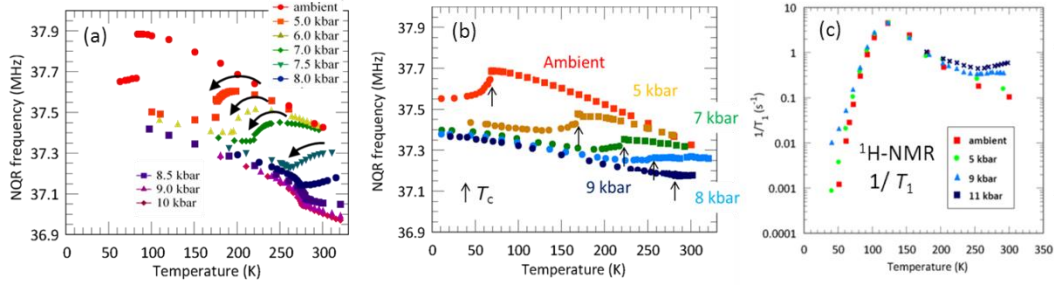


Fig. 2. (a) Temperature dependence of  $^{35}\text{Cl}$ -NQR resonance frequency in TTF-CA [6] and (b) DMTTF-CA. (c) Temperature dependence of  $1/T_1$  of  $^1\text{H}$ -NMR in DMTTF-CA.

around the transition. It is expected that paramagnetic spins emerge at high pressures.

Next, to probe the spin degree of freedom, we performed  $^1\text{H}$ -NMR measurements. As shown in Fig. 2(c), the  $1/T_1$  exhibits a maximum around 120 K irrespectively of the applied pressure. It is well-known that such a behavior arises from molecular motions such as the rotation of methyl groups. In the present case, the DMTTF molecule has two methyl groups, the rotation of which explains the observed behavior. At 9 and 11 kbar, however, an enhancement in  $1/T_1$  is observed around room temperature, suggesting another relaxation mechanism that contributes to  $1/T_1$ , very probably spin fluctuations. The vitalization of the spin degrees of freedom indicates the system comes close to the ionic phase at pressures above 9 kbar and reserves a possibility that the system crosses over into the spin-Peierls regime at the high pressure.

## [Conclusions]

In this thesis, we studied the magnetic excitations in TTF-CA and the mechanism of the NI transition in DMTTF-CA through NMR and NQR measurements under pressures. For the magnetic excitations in TTF-CA,  $^{13}\text{C}$  and  $^1\text{H}$ -NMR experiments revealed that the unbound spin solitons move diffusively along 1D chains in the dimer liquid state. In the dimerized ferroelectric state, the  $^{13}\text{C}$ -NMR experiments confirmed that magnetic excitations are gapped and suggest that the thermally excited spins are in the form of bound soliton-antisoliton pairs (or triplets). In addition, we proposed that the motion of the thermally excited spins contributes to  $1/T_1$  even in the dimerized ferroelectric state, in the light of the results of  $^{13}\text{C}$ -NMR and  $^{35}\text{Cl}$ -NQR. For the mechanism of the phase transition in DMTTF-CA,  $^{35}\text{Cl}$ -NQR measurements showed that the spin degrees of freedom are not significant in the dimerization transition at low pressures. Under high pressures,  $^{35}\text{Cl}$ -NQR and  $^1\text{H}$ -NMR showed that the ionic phase carries paramagnetic spins, suggesting a possible involvement of the spin degrees of freedom in the dimerization transition at high pressures.

## [References]

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