博士論文（要約）

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}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}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}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}C and ^{1}H-NMR and ^{35}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}Cl-NQR and ^{1}H-NMR under pressures.

[Results and Discussions]

1. Magnetic excitations in TTF-CA

First, the pressure dependences of ^{13}C-NMR shift and $1/T_1$ were measured at 285 K. Both increase with applied pressure, indicating that the spin degrees of freedom become vital under pressures. We compared the spin shift and $1/T_1$ at 14 kbar in the I_{para} region with the calculated values on the basis of the uniform 1D Heisenberg model using the estimated exchange interaction, J = 2400 K, and the hyperfine field tensors of analogous materials, $(TMTTF)_2Br$ and $(TMTTF)_2AsF_6$. However, the experimental spin shift value at 14 kbar is less than the half of the calculated value, whereas the $1/T_1$ at 14 kbar is 16 times larger than the calculated value. This contradiction suggests that the uniform 1D Heisenberg model is not appropriate for describing the present spin state and an alternative picture should be invoked such as the mobile soliton picture.

Next, to inquire further whether the picture of mobile spin soliton is valid or not, we investigated the frequency dependence of ^{1}H-NMR $1/T_1$ at 300 K under 14 kbar in the I_{para} region. $1/T_1$ shows prominent frequency dependence in a range between 50 and 300 MHz and a saturation at lower frequencies. This behavior is well fitted by the formula for the diffusive spin motion situated in the 1D-3D crossover region, which indicates that the spin solitons move diffusively along 1D chains with weak inter-chain interactions.

Finally, to see how the dimer liquid state with the spin solitons changes into the ferroelectric state with the long-range order of dimerization, we performed ^{13}C-NMR and ^{35}Cl-NQR measurements under temperature variation at 14 kbar. Both the ^{13}C-NMR spin shift and $1/T_1$ decrease exponentially below T_c = 272 K, indicating the non-magnetic nature of the ground state with a finite excitation gap. In the ferroelectric state, the excited spins should be in the form of triplets (or bound soliton pairs) to hold the long-range order. However, the gap energies deduced from spin shift and $1/T_1$ for 200 K < T < T_c are remarkably different (Δ_{shift} = 3240 K, $\Delta_{1/T1}$ = 1270 K), suggesting unconventional magnetic excitations below T_c. As a conceivable scenario, we proposed that the motion of the thermally excited triplets (or bound soliton pairs) along the 1D chains contributes to $1/T_1$ even below T_c. In this case, the local lattice deformations can be dynamical associated with the travelling of the excited spins. Indeed, ^{35}Cl-NQR $1/T_1$, which

probes the lattice fluctuations, exhibits nearly similar temperature dependence to that of ^{13}C-NMR $1/T_1$ for 140 K < T < 250 K, supporting the existence of the spin-lattice coupled excitations even below T_c.

2. Mechanism of phase transition in DMTTF-CA

It was suggested that the spin degrees of freedom aren't involved in the dimerization transition by the previous ^{35}Cl-NQR measurements at ambient pressure. We propose that the electronic energy gain is acquired by the modulations in the transfer integrals (the Peierls mechanism) or the Madelung energy gain with the lattice dimerization. Around T_c, where ρ is as small as 0.3, the Madelung energy gain is not significant and thus the Peierls mechanism is more likely for the dimerization at ambient pressure.

As pressure is applied, the ^{35}Cl-NQR frequency is reduced and the system comes close to the ionic state around 9 kbar. ^{1}H-NMR $1/T_1$ at 9 and 11 kbar captures the thermally activated spin excitations. Therefore, the spin degrees of freedom can be involved in the dimerization transition at high pressures. Also, ^{35}Cl-NQR $1/T_1$ at 9 kbar exhibits the T^2-dependence up to 200 K and then a weak enhancement appears with a less prominent shoulder structure than observed in TTF-CA at 14 kbar, which is likely the manifestation of the spin-lattice coupled excitations such as the travelling of the excited spins. Thus, the excited spins have more difficulty in travelling in DMTTF-CA at 9 kbar than in TTF-CA at 14 kbar.

Finally, we found a new phase at high pressures above 11 kbar. ^{35}Cl-NQR and X-ray diffraction measurements revealed that this phase has the cell doubling along the *a*-axis differently from the *b*-axis in the ionic state below 11 kbar and is likely in an antiferroelectric state with the electric dipole moments in the 1D chain staggered along the *a*-axis.

[Concluding remarks]

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}C and ^{1}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}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}C-NMR and ^{35}Cl-NQR. For the mechanism of the phase transition in DMTTF-CA, ^{35}Cl-NQR measurements showed that the spin degrees of freedom are not significant in the dimerization transition at low pressures. Under high pressures, ^{35}Cl-NQR and ^{1}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.

The present study demonstrated that the exotic magnetic excitations such as the mobile spin solitons emerge by the coupling between the spin and lattice. The presence of such spin excitations promise novel magnetoelectric effects due to the entanglement between charge, spin, and lattice, different from those derived from the spin-orbit interactions in inorganic systems. We believe that this study offers a new field of research in charge-spin-lattice coupled systems.

[References]

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