Topological excitations emerge at domain boundaries between degenerate ground states; in particular, their motional degrees of freedom lead to exotic magnetic and transport properties in one-dimensional (1D) systems. The neutral-ionic (NI) phase transition material, TTF-CA, which is a quasi-1D charge-transfer complex, is an ideal system for the emergence of such excitations because multiple states, a neutral (N) state and two degenerate dimerized ionic states with oppositely directed electric polarizations (I_A and I_B) compete with each other due to a strong charge-spin-lattice coupling; thus, NI domain walls and spin/charge solitons with/without spin-1/2 are theoretically suggested to reside between N and I_A (I_B) domains and between I_A and I_B domains, respectively. However, there has been no experimental evidence for mobile topological excitations.

In this work, we demonstrate the contributions of topological excitations to magnetism and conductivity in TTF-CA by performing NMR and electrical resistivity measurements. The \(^{13}\)C-NMR spectral shift and spin-lattice relaxation rate, \(T_1\), measured under elevated pressures at 285 K, are enhanced in the paraelectric ionic (I_para) phase [1] (Fig. 1) where I_A and I_B domains are dynamically fluctuating [2]. In the I_para phase, \(^1\)H-NMR \(T_1\) exhibits a prominent frequency dependence that indicates the diffusive motion of solitonic spin excitations [1]. For the charge excitations, the electrical conductivity shows a maximum at the NI crossover pressure of ~9 kbar (Fig. 1) and the observed activation energy is much smaller than the one-particle excitation gap, indicating that the low-energy excitations such as the NI domain walls carry a charge current [3]. Above ~9 kbar, the conductivity keeps a large value, ~1 S/cm, (Fig. 1), which is attributable to the charge solitons in the I_para phase [3]. As temperature is decreased, the I_para phase transitions to the ferroelectric ionic (I_ferro) phase, in which the motion of topological excitations is restricted by a 3D ferroelectric order. However, we detected unconventional mobile spin excitations and low-energy charge excitations even in the I_ferro phase. We propose that the “bound” solitonic excitations are responsible for the magnetism and conductivity in the I_ferro phase.

References