NQR Study of Neutral-Ionic Transition on TTF-QCl₄

Masayuki Hosoda¹, Kazuya Miyagawa¹, Kazushi Kanoda¹, Fumitatsu Iwase², Hiroshi Okamoto³

¹Department of Applied Physics, University of Tokyo, Japan
²Institute for Molecular Science, Japan
³Department of Advanced Materials Science, University of Tokyo, Japan.

Email: hoppy.de.beber@gmail.com

The quasi-one-dimensional mixed-stack charge transfer complex, tetrathiafulvalene-p-chloranil (TTF-QCl₄), is known to exhibit the temperature- and pressure-induced neutral-ionic phase transition. [1] In the ionic phase, tetrathiafulvalene (TTF) and p-chloranil (QCl₄) are dimerized and a ferroelectric behavior is observed. This transition is characterized by the degree of charge transfer \( \rho \) between the electron donor molecule, TTF, and the electron acceptor molecule, QCl₄, and by their dimerization. Pressure-Temperature phase diagram, where the 1st order phase transition line divides the states with a critical end point around 0.7 GPa is suggested. [2]

We report the results of \(^{35}\)Cl NQR studies on TTF-QCl₄ under pressures. Fig. 1 shows the temperature dependence of NQR frequency under various pressures. At ambient pressure (not shown here), the frequency of resonance line increases with decreasing temperature, and a line splitting, which indicates dimerization, occurs at the transition temperature. The averaged frequency of the split lines has a discontinuous drop at the transition temperature. This shows that a charge transfer suddenly occurs at the transition. Under 0.5 GPa, however, the resonance frequency starts to decrease with temperature before the line splitting occurs at \( T_D \), where the dimerized phase appears. This indicates the continuous development of charge transfer above \( T_D \). With increasing pressure, the line splitting at \( T_D \) becomes moderate.

These results suggest that an ionic phase without dimerization, i.e. ionic paraelectric phase, is more developed at higher pressures.


![Fig. 1: Temperature dependence of the NQR frequency under various pressures.](image)