

Neutral-Ionic Transition of (BEDT-TTF)(ClMeTCNQ) Studied by ESR Under Pressure

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The electron spin susceptibility of (BEDT-TTF)(ClMeTCNQ) was measured by ESR under pressure. Analysis of the susceptibility leads to the temperature dependence of the ionic fraction through the neutral-ionic phase transition, revealing that the transition is broad and continuous. It is demonstrated that this transition is crossover-like between the two phases, which can be understood by the unique double-well potential.

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1. INTRODUCTION

Mixed-stack charge-transfer compounds have been intensively investigated since the discovery of neutral-ionic (NI) phase transition which takes place by lowering temperature and/or applying pressure¹. Usually the spin-Peierls (SP) transition simultaneously occurs with the NI transition². It was also known that the NI transition is accompanied by some critical phenomena such as quantum critical transition³. We have studied the NI transition of (BEDT-TTF)(ClMeTCNQ) by ESR under pressure and obtained the pressure-temperature phase diagram⁴. Moreover we obtained the temperature dependence of the ionic domain fraction through the NI transition. Then, it was demonstrated that this case is the special one of the first order phase transition. In this paper we show that the NI-transition of this system can be interpreted by a double-well potential model with unique parameters.

2. EXPERIMENTAL

Electronic spin susceptibility χ_e was obtained from ESR intensity as a function of temperature and pressure. The pressure was applied using a

CuBe clamp-type pressure cell with Daphne 7373 oil as a pressure medium. Powder samples were prepared by the reported method⁵. The observed ESR line shapes were well reproduced by a single Lorentzian and the intensity was calibrated by *in situ* ¹⁹F NMR signal from a Teflon sample tube.

3. RESULTS AND DISCUSSION

Figure 1 shows temperature variations of χ_e under several pressures⁴. Peaks indicated by arrows correspond to the NI transition temperature T_{NI} at each pressure. The decrease below T_{NI} is due to the SP transition in the I phase. These results suggest that 1) the transition from the Peierls distorted I phase to the N phase is continuous, 2) the SP transition temperature is higher than T_{NI} , and 3) the SP gap ΔE_{SP} is 1100K independent of pressure⁴. Thus it is expected that the thermally excited I phase in the N phase above T_{NI} is dimerized. Then the evolution of the ionic fraction $N_i(T)$ in the whole temperature range can be extracted from the susceptibility using the following formula;

$$\chi_e = a' \frac{N_i(T)}{T} \exp\left(-\frac{\Delta E_{SP}}{kT}\right). \quad (1)$$

Obtained $N_i(T)/N_0$'s are shown in Fig. 2 (left), where N_0 is the number of the whole molecules. One can see the following characteristic features in the figure: 1) continuous and broad variation through T_{NI} in spite of the first

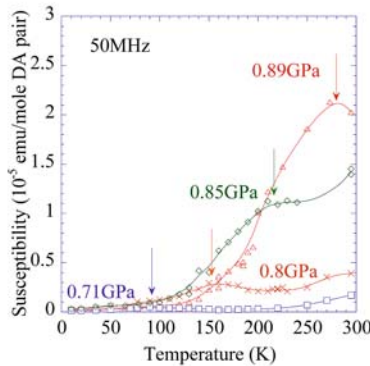


Fig. 1. The temperature dependences of χ_e under pressure. The figures are nominal pressures when clamped. χ_e includes minor spin contribution that is not essential.

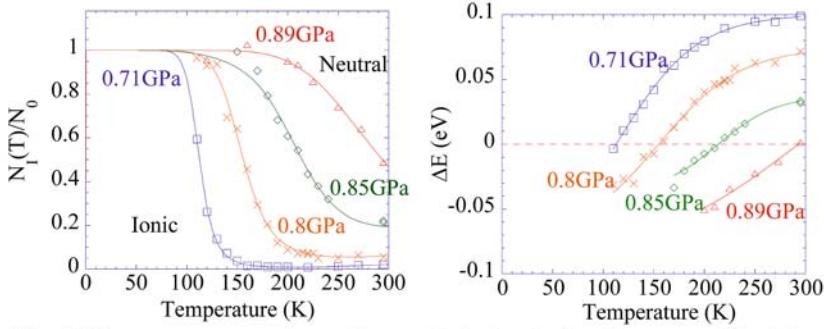


Fig. 2 The temperature dependence of the ionic fraction normalized by the whole molecules (left) and ΔE (right).

order phase transition and 2) finite ionic fraction still survives even in the N phase. Recently the coexistence of the two phases has been confirmed by X ray diffraction⁶. These features can be understood by a double-well potential model with $E_B \sim kT_{NI}$, where E_B is the energy barrier between N and I phases at T_{NI} . The potentials at three different temperature regions are shown schematically in Fig. 3. This small E_B assures a rapid thermal equilibration, that is, the continuous, crossover-like transition.

Considering the Boltzmann factor with the energy gap ΔE between the I and N phases, $N_I(T)/N_0$ is expressed as

$$\frac{N_I(T)}{N_0} = \frac{1}{1 + \exp\left(\frac{\Delta E}{kT}\right)}. \quad (2)$$

ΔE 's obtained by fitting eq. (2) to $N_I(T)/N_0$ in Fig. 2 (left) are shown in Fig. 2 (right), and reproduced by the empirical formula $\Delta E = \Delta E_0 \tanh(\Delta T/T_0)$ as indicated solid lines, where $\Delta T = T_{NI} - T$, $T_0 \sim 80$ K, and $\Delta E_0 \sim 0.1$ eV. Solid lines in Fig. 2 (left) indicate successful reproduction of $N_I(T)/N_0$ by eq. (2)

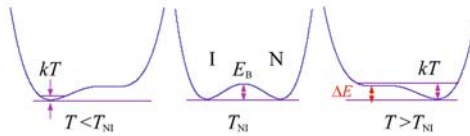


Fig. 3 Schematic illustration of the potential energy between I and N phases at three temperature regions. The horizontal direction represents an order parameter such as the charge transfer.

with this formula. ΔE is proportional to $T_{\text{NI}} - T$ near T_{NI} and saturates, which leads to not only the decrease of χ_e across T_{NI} but also the finite ionic fraction in the N phase.

Thus the novel properties of the NI transition of this system are attributed to the temperature variation of the small energy difference between the N and I phases.

4. CONCLUSIONS

ESR measurements under pressure were performed to observe the electron spin susceptibility of (BEDT-TTF)(CIME TCNQ). By analyzing the susceptibility we demonstrated that the NI phase transition of this system is crossover-like between the N and I phases, the special case of the first order transition, dominated by the double-well potential energy with the particular parameters.

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