Preprint: Phys. Rev. Lett. 93, 186401 (1-4) (2004)

Magnetic Properties of (BEDT-TTF)(ClMeTCNQ) Studied by ESR under Pressure: A Neutral-Ionic Crossover and Thermoinduced Mesophase

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(Dated: September 6, 2004)

The neutral-ionic (N-I) phase transition in (BEDT-TTF)(ClMeTCNQ) is studied with ESR under pressure to tune the transition temperature. Broad peak structures observed in the spin susceptibility around $T_{\rm NI}$ are analyzed with the assumption of spin-Peierls gap of 1100 K, which demonstrates the continuous evolution of ionic domain fraction through $T_{\rm NI}$ over the extent $T_{\rm W} \propto T_{\rm NI}$. An unexpected feature is the presence of sizable ionic droplets even at $T \gg T_{\rm NI}$, which is ascribed to the tiny energy difference between the two phases.

PACS numbers: 71.30.+h, 72.80.Le, 76.30.-v

Mixed-stack charge-transfer (CT) compounds contain one-dimensional columns consisting of donor (D) and acceptor (A) molecules stacked alternately. There exist two major electronic phases in such materials: the neutral (N) phase composed of neutral donors and acceptors and the ionic (I) phase with cation and anion radicals.[1] Each radical molecule in the ionic phase has single 1/2-spin, which usually leads to the Peierls-type lattice distortion to form spin singlet pairs with few exceptions.[2] Some mixed-stack compounds undergo neutral to ionic (N-I) phase transition due to the valence instability with changing of temperature or pressure.[3] It has been reported that the N-I phase transition is accompanied by a variety of critical phenomena including the quantum critical behavior.[4, 5] For example, the compounds exhibit pronounced enhancement in electrical conductivity with approaching the N-I transition pressure. As observed both in (TTF)(CA)[6] and (BEDT-TTF)(ClMeTCNQ),[7] the conductivity exponentially increases over $4 \sim 5$ orders of magnitude with application of pressure below 1 GPa at room temperature. It has been proposed that novel elementary excitations, such as domain walls or charged soliton pairs, play major roles in such peculiar properties of the N-I phase transition,[8, 9] although their conducting mechanism is still unclear yet.

In this letter we directly demonstrate how the fraction of the ionic domain behaves in the N-I phase transition in (BEDT-TTF)(ClMeTCNQ) by virtue of magnetic probe sensitive to the appearance of cation and anion radical 1/2-spins. The pressure-temperature ($P-T$) phase diagram of (BEDT-TTF)(ClMeTCNQ) obtained from the electrical resistivity[7] demonstrates that one can investigate the critical phenomena with controlling the critical temperature $T_{\rm NI}$ by pressure from room temperature to the quantum critical point. At room temperature the N-I phase transition pressure $P_{\rm NI}^{\rm RT}$ is around 1.0 GPa, which is confirmed by uv-visible and infrared optical spectra.[7] Vibrational spectra also indicate that the dimeric lattice distortion takes place simultaneously with the transition.[7] The characteristic findings of this report in the electronic spin susceptibility $\chi_{\rm e}$ in (BEDT-TTF)(ClMeTCNQ) are as follows: 1) a drastic increase of $\chi_{\rm e}$ above 0.7 GPa at room temperature with application of pressure, and 2) a broad continuous peak feature around the N-I phase transition in the respective curves of the temperature dependence. The former correlating closely to the electrical conductivity is ascribable to the evolution of ionic fractions excited thermally with approaching the N-I transition. On the other hand, the latter is analyzed to give the temperature dependence of ionic fractions going through the N-I transition. Surprisingly, this analysis shows that the ionic domains are persistently present even at much higher temperatures than the N-I transition in the neutral phase. This feature is discussed in terms of a double-well potential model with a small barrier potential whose energy is in the same order as the N-I phase transition temperature. This model gives rise to a thermoinduced N-I coexisting phase at $T > T_{\rm NI}$ which is consistent with the results of the experiments.

Electronic spin susceptibility $\chi_{\rm e}$ was measured as functions of pressure and temperature at about 50 MHz with a home-built ESR spectrometer.[10] A coil over a Teflon tube filled with 20 mg of small single crystals was immersed in the pressure medium, Daphne 7373 oil. A clamp-type high-pressure cell was used for applying pressure. The observed ESR line shapes were well reproduced by a least squares fit to single Lorentzian. Then the $\chi_{\rm e}$ was obtained by calibrating the ESR intensity with $in-situ$ ^{19}F NMR signal from the Teflon sample tube.[11]

The pressure dependence of $\chi_{\rm e}$ at room temperature is shown with closed circles in Fig. 1. It is found that the $\chi_{\rm e}$ increases drastically around $0.7 \sim 1.0$ GPa by two orders of magnitude, and then saturates above 1.0 GPa. It is most probable that this remarkable feature would correspond to the evolution of the ionic fraction

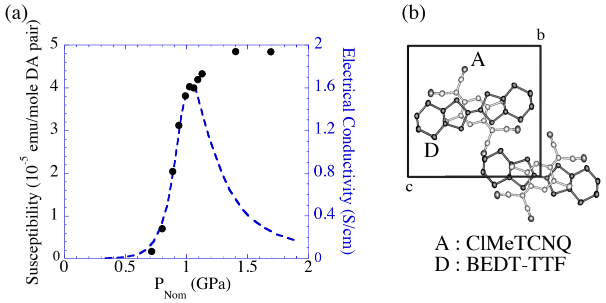

FIG. 1: (a) The pressure dependence of the electronic spin susceptibility in (BEDT-TTF)(ClMeTCNQ) is shown by closed circles along with the electrical conductivity at room temperature (broken line). The abscissa shows a nominal pressure $P_{\rm Nom}$ when clamped. (b) The crystal structure of (BEDT-TTF)(ClMeTCNQ) viewed along the stacking axis.

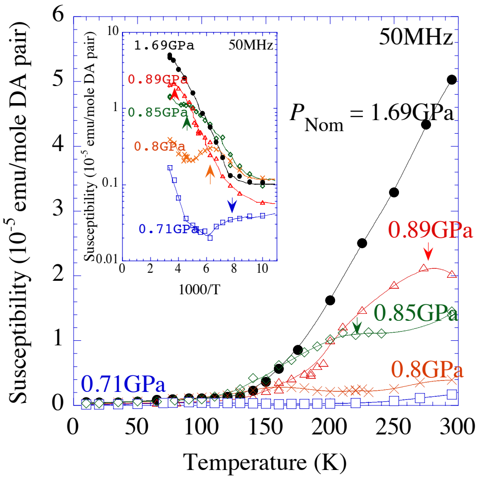

FIG. 2: The temperature dependence of the electronic spin susceptibility under pressure. Inset: Arrhenius plot above100 K. The arrows indicate the peaks, where $\chi_{\rm e}$ without the impurity contributions is used. Each pressure is a nominal value when clamped. Solid curves are guides to the eyes.

around the N-I transition pressure $P_{\rm NI}^{\rm RT} = 1.0$ GPa. The pressure dependence of the electrical conductivity σ is also shown with a broken line in Fig. 1.[7] Note that the feature of $\chi_{\rm e}$ exhibits a strong similarity to that of σ below $P_{\rm NI}^{\rm RT}$, while they obviously deviate from each other above $P_{\rm NI}^{\rm RT}$. Considering that only the ionic radicals carry the spins in semiconducting molecular compounds, the drastic increase of $\chi_{\rm e}$ below $P_{\rm NI}^{\rm RT}$ provides a direct evidence for the growth of ionic radicals in the neutral phase with approaching the transition pressure. It is also important to point out that no discontinuity is observed in the pressure dependence of $\chi_{\rm e}$, implying that the coexistence of the neutral and ionic phases should be continuous through $P_{\rm NI}$. From the saturated $\chi_{\rm e}$ value ($\sim 5 \times 10^{-5}$ emu/mole) under the highest pressure, we estimate the effective number of spins in the ionic phase to be only 0.04 per DA pair. We note that this value is significantly smaller than the nominal number of spins in the ionic phase (2 spins per DA pair).

The temperature dependences of $\chi_{\rm e}$ under various pressures are shown in Fig. 2. Here the pressure values clamped at room temperature are indicated. The observed features are as follows: At the highest pressure of 1.69 GPa, the $\chi_{\rm e}$ continuously increases with increasing temperature up to 300 K. In contrast, below 1 GPa, broad peak features are found at $T_{\rm Peak}$ marked by arrows in Fig. 2. This peak is followed by the other increase forming a minimum with increasing temperature under the pressures below 0.8 GPa. The obtained $T_{\rm Peak}$'s are plotted with open squares against pressure in Fig. 3. In this plot, thermal contraction of the pressure medium at low temperature was corrected according to the literature.[12] By comparison with the N-I phase boundary obtained from the electrical resistivity[7] shown by a solid curve in Fig. 3, we conclude that the $T_{\rm Peak}$ roughly corresponds to the N-I phase transition temperature $T_{\rm NI}$. Importantly, all the temperature dependences of $\chi_{\rm e}$ are continuous through the $T_{\rm NI}$'s. At the highest pressure of 1.69 GPa where the system is ionic in the whole measured temperature range, the overall temperature variation of $\chi_{\rm e}$ can be reproduced by the double exponentials along with a small Curie term:

$$\chi_{\rm e} = \frac{a}{T}\exp(-\frac{\Delta E_1}{kT}) + \frac{b}{T}\exp(-\frac{\Delta E_2}{kT}) + \frac{C}{T}, \qquad (1)$$

where $a = 0.7$ emuK/mole (2 spins per DA pair), $\Delta E_1/k \approx 1100$ K, $b = 2 \times 10^{-4}$ emuK/mole, $\Delta E_2/k \approx 110$ K, and $C = 5 \times 10^{-6}$ emuK/mole. The observed monotonic increase of $\chi_{\rm e}$ in Fig. 2 is dominated by the first large exponential term with the gap energy of 1100 K. This spin gap is consistent with the small number of spins of 0.04 spins per DA pair at room temperature as described before. It is likely that the spin gap is associated with the singlet pair formation caused by the SP type lattice distortions as detected by the vibrational spectra above 1.0 GPa.[7] We can conclude that the major signals observed in the ESR can be ascribed to the spins activated thermally over the SP gap: $\Delta E_1 = \Delta E_{\rm SP}$. The second exponential term has much smaller contribution than the first one both in magnitude and in gap energy, and then it can be attributed to unknown minor spins. The third Curie term of 10^{-5} spins per DA pair could be ascribed to domain walls or solitons as phase kinks due to defects or impurities.[13] It is also found that the temperature dependence of $\chi_{\rm e}$ for all the other curves measured below 1.69 GPa can also be reproduced by eq. (1) below the $T_{\rm NI}$'s. Interestingly, the activation energy of the major exponential terms for 0.85 and 0.89 GPa are similar to that of 1.69 GPa as confirmed in the inset of Fig. 2, demonstrating similar slopes in the temperatures between 100 and 150 K. This implies that the

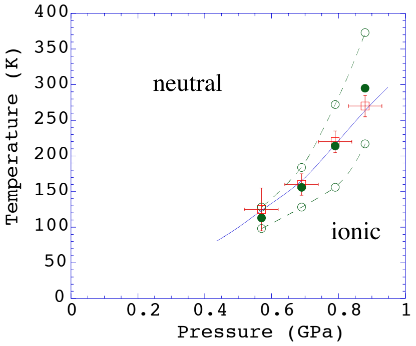

FIG. 3: The pressure-temperature phase diagram of (BEDT-TTF)(ClMeTCNQ). Solid line: The phase boundary between the neutral and the ionic phase determined by the electrical resistivity.[7] Open squares: The peak temperatures for the spin susceptibility obtained with ESR. Closed circles: T_{NI} estimated from $\Delta E(T) = \Delta E_0 \tanh\{(T - T_{\mathrm{NI}})/T_0\}$ in $N_{\mathrm{I}}(T) = N_0/\{1 + \exp(\Delta E/kT)\}$. Open circles: $T_{\mathrm{NI}} \pm T_{\mathrm{W}}$. T_{W} is defined in the text. Note that the pressure in this Figure is not nominal but is estimated at T_{Peak} by correcting thermal contraction of the medium.[12]

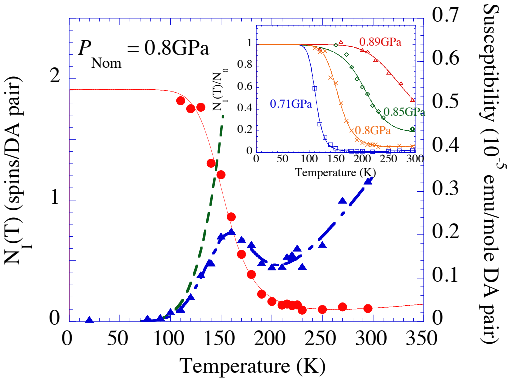

FIG. 4: The temperature variation of the intrinsic spin susceptibility (closed triangles) and the number of ionic radicals $N_{\mathrm{I}}(T)$ (closed circles) at 0.8 GPa, obtained from eq. (2). $N_{\mathrm{I}}(T)$ below 100 K are discarded because of significant scattering by the small exponential factor. The solid line shows the estimated $N_{\mathrm{I}}(T)$ with eq. (3). The broken line indicates $\exp(-\Delta E_1/kT)/T$. The inset shows the temperature dependence of the ionic fraction. Pressure indicates a nominal value when clamped.

ΔE_{SP} is almost independent of pressure. This pressure-independent nature is also consistent with the saturated behavior above 1 GPa in Fig. 1.

It is most likely that the thermally excited ionic domains in the neutral phase above T_{NI} have also the dimerized structure. The reason is as follows: 1) the continuous variation of χ_{e} from the SP-type ionic phase to the neutral phase across T_{NI}, and 2) the higher T_{SP} than T_{NI}. Then, the number of ionic radicals $N_{\mathrm{I}}(T)$ can be extracted from χ_{e} with the constant SP gap of 1100K. With $N_{\mathrm{I}}(T)$, the intrinsic part of χ_{e}, namely, the first term of eq. (1) can be modified as follows:

$$\chi_{\mathrm{e}} = a' \frac{N_I(T)}{T} \exp(-\frac{\Delta E_1}{kT}). \tag{2}$$

The intrinsic χ_{e} together with the $N_{\mathrm{I}}(T)$ deduced from eq. (2) for 0.8 GPa are shown in Fig. 4. $N_{\mathrm{I}}(T)/N_0$ provides a temperature evolution of the ionic fraction demonstrated in the inset of Fig. 4, where N_0 is the total number of molecules. Remarkable observation is that $N_{\mathrm{I}}(T)/N_0$ shows continuous and gradual decrease with the increase of temperature, which is contradictory to the expected first order nature in the N-I transition, and also that the sizable ionic fraction still survives in the neutral phase at $T \gg T_{\mathrm{NI}}$. This residual ionic fraction is a direct consequence of the increase of χ_{e} above the minimum, e.g., above 200 K at 0.8 GPa as shown in Fig. 4.

Here, we demonstrate that this system is a special case of the first order transition with a unique parameter set, resulting in the quasi-crossover transition. Figure 5 shows schematic views of the double-well potentials at the three different temperature regions: $T < T_{\mathrm{NI}}$, $T = T_{\mathrm{NI}}$, and $T > T_{\mathrm{NI}}$. The horizontal direction represents an order parameter such as the charge transfer or the spin density. In this situation, the predicted ionic fraction is expressed with a simple relation by the Boltzmann factor, as follows:

$$\frac{N_I(T)}{N_0} = \frac{1}{1 + \exp(\frac{\Delta E}{kT})}. \tag{3}$$

To reproduce the temperature evolution of the ionic fraction $N_{\mathrm{I}}(T)/N_0$ in Fig. 4, the following conditions are required. The first is that the height of the energy barrier, E_{B}, between the two phases at $T = T_{\mathrm{NI}}$ should be of the order of kT_{NI}. This ensures rapid thermal equilibration between the wells, which meets the experimental missing of hysteresis in the electrical resistivity.[7] The next is that the energy difference ΔE between the N and I phases is proportional to $\Delta T = T_{\mathrm{NI}} - T$ and saturates, as well represented by the empirical formula of $\Delta E = \Delta E_0 \tanh(\Delta T/T_0)$ with $T_0 \approx 80$ K and ΔE_0 of the order of 0.1 eV. With this relationship eq. (3) reproduces the variation of the ionic fraction very well, including the presence of the residual ionic fraction observed at $T \gg T_{\mathrm{NI}}$, as demonstrated by the solid lines in the inset of Fig. 4. Here, notice that the transition width becomes broader as the pressure increases as seen in the inset of Fig. 4. This fact implies that ΔE_0 is suppressed by the pressure, which enhances the residual ionic fraction at $T \gg T_{\mathrm{NI}}$. The appearance of the residual ionic fraction could be due to the tiny energy barrier separation between the neutral and the ionic phases. From the above discussion the ionic fraction should be called a thermoinduced N-I mesophase. As expected, the

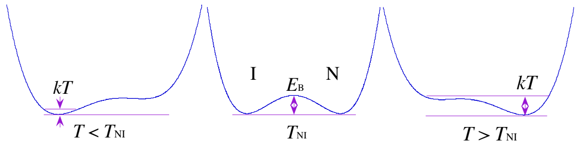

FIG. 5: Schematic representation of the potential energies at the three temperature regions. The horizontal direction corresponds to an order parameter.

reproduced $N_I(T)$ tends to about 2 spins per DA pair below T_{NI}. The obtained T_{NI} is plotted by the open circles in Fig. 3 together with the transition width T_W, defined as the temperature difference between T_{NI} and the point where $N_I(T)/N_0 = 0.9$. Actually, the infrared vibrational spectra at 300 K show the appreciable broadening of the optically-forbidden a_g mode over the transition width T_W.[7] From these analyses we can conclude that the ionic phase transforms gradually and continuously to the neutral phase over the temperature width of T_W without hysteresis typical of the first order phase transition.

How is the domain picture, as discussed above, corresponding to the electrical conductivity? The observed similar pressure dependence of σ and χ_e below 1 GPa shown in Fig. 1 suggests that the charge carriers increase in proportion to the ionic domain fraction. However, the ionic domain with the same number of cations as that of anions would not contribute to the electrical transport. It is probable that the ionic domains with odd number of ions should be thermally produced at some probability, and their diffused motion should carry the electrical charges. We consider that this picture leads to the observation that the electrical conductivity is proportional to the number of ionic fractions at $P < P_{NI}^{RT}$. In this context, with the change of the ground states at $P > P_{NI}^{RT}$, the carriers should switch to the neutral fraction with odd number of neutral molecules. This gives a consistent picture for the observed deviation of χ_e and σ at $P > P_{NI}^{RT}$, where the decrease of σ can be ascribed to the decrease of the neutral phase.

Finally we briefly comment on the magnetic response around the N-I phase transitions in (TTF)(CA), where it is reported that the χ_e at ambient pressure abruptly emerges at T_{NI} and follows the Curie law below T_{NI} with the spin concentration of 1×10^{-4} per molecule. This Curie spins are major spin carriers ascribable to the domain walls of dimerized lattice in the ionic phase.[13] In the present system, the Curie spins of 10^{-5} per DA pair can also be ascribable to the domain wall solitons. However the major part is the spins thermally activated over ΔE_{SP} which is large enough to mask the possible sharp increase of the Curie component at T_{NI}. This difference is reasonably elucidated in terms of T_{NI}/T_{SP}; if T_{NI} is much smaller than T_{SP}, quite few spins are thermally excited, where the Curie spins emerge as in (TTF)(CA). In contrast, if T_{NI} is high enough, sufficient spins are excited thermally, which smears the Curie spins in the ionic phase as in the present case.

In conclusion we investigated the magnetic properties of (BEDT-TTF)(ClMeTCNQ) around the N-I phase transitions with use of ESR under pressure. The abrupt increase of χ_e is observed against pressure, which can be interpreted as the expansion of the thermally excited ionic domain fraction with approaching the N-I transition. From the analyses of the temperature dependence of χ_e, it is found that the ground state of the ionic phase is the spin-Peierls state with the gap energy of about 1100 K that is almost independent of pressure. Moreover the evolution of the ionic fraction is observed through the N-I transition as the continuous switch from the ionic to the neutral phase. This novel type of phase transformations is interpreted as the crossover between the neutral and ionic phase by the double-well potential model. This model also reproduced the thermoinduced N-I mesophase, where ionic radicals survive even at $T \gg T_{NI}$. All these findings demonstrate that the ionic domains in the neutral phase as well as the neutral domains in the ionic phase play essential roles in the observed peculiar magnetic as well as electrical properties in this compound.

This work is partly supported by Grant-in-Aid for Scientific Research on the Priority Area "Molecular conductors" by the Ministry of Education, Science, Sports and Culture of Japan.

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