

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

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

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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 a 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 (NI) phase transition due to the valence instability with changing temperature or pressure [3]. It has been reported that the NI 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 when approaching the NI transition pressure. As observed both in tetrathiafulvalene-chloranil (TTF) (CA) [6] and bis(ethylenedithio)tetrathiafulvalene-2-chloro-5-methyltetracyanoquinodimethane (BEDT-TTF) (CIME TCNQ) [7], the conductivity exponentially increases over 4–5 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 NI phase transition [8,9], although their conducting mechanism is unclear yet.

In this Letter we directly demonstrate how the fraction of the ionic domain behaves in the NI phase transition in (BEDT-TTF)(CIME TCNQ) by virtue of a magnetic probe sensitive to the appearance of cation and anion radical $1/2$ spins. The pressure-temperature (P - T) phase diagram of (BEDT-TTF)(CIME TCNQ) obtained from the electrical resistivity [7] demonstrates that one can investigate the critical phenomena by controlling the critical temperature T_{NI} by pressure from room temperature to the quantum critical point. At room temperature

the NI phase transition pressure $P_{\text{NI}}^{\text{RT}}$ 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 χ_e in (BEDT-TTF)(CIME TCNQ) are as follows: (i) a drastic increase of χ_e above 0.7 GPa at room temperature with application of pressure; (ii) a broad continuous peak feature around the NI 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 when approaching the NI transition. On the other hand, the latter is analyzed to give the temperature dependence of ionic fractions going through the NI transition. Surprisingly, this analysis shows that the ionic domains are persistently present even at much higher temperatures than the NI 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 NI phase transition temperature. This model gives rise to a thermoinduced NI coexisting phase at $T > T_{\text{NI}}$, which is consistent with the results of the experiments.

Electronic spin susceptibility χ_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 a single Lorentzian. Then the χ_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 χ_e at room temperature is shown with solid circles in Fig. 1(a). It is found that the χ_e

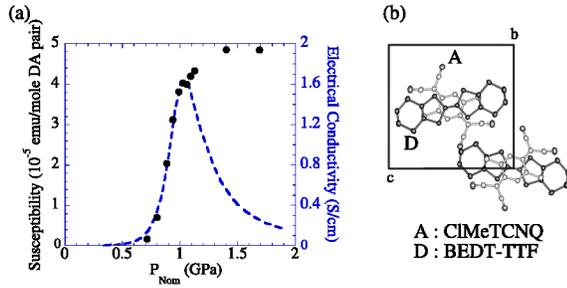


FIG. 1 (color online). (a) The pressure dependence of the electronic spin susceptibility in (BEDT-TTF)(ClMeTCNQ) is shown by solid circles along with the electrical conductivity at room temperature (dashed line). The abscissa shows a nominal pressure P_{Nom} when clamped. (b) The crystal structure of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

increases drastically around 0.7–1.0 GPa by 2 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 around the NI transition pressure $P_{\text{NI}}^{\text{RT}} = 1.0$ GPa. The pressure dependence of the electrical conductivity σ is shown with a dashed line also in Fig. 1(a) [7]. Note that the feature of χ_e exhibits a strong similarity to that of σ below $P_{\text{NI}}^{\text{RT}}$, while they obviously deviate from each other above $P_{\text{NI}}^{\text{RT}}$. Considering that only the ionic radicals carry the spins in semiconducting molecular compounds, the drastic increase of χ_e below $P_{\text{NI}}^{\text{RT}}$ provides direct evidence for the growth of ionic radicals in the neutral phase when approaching the transition pressure. It is also important to point out that no discontinuity is observed in the pressure dependence of χ_e , implying that the coexistence of the neutral and ionic phases should be continuous through P_{NI} . From the saturated χ_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 χ_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 χ_e continuously increases with increasing temperature up to 300 K. In contrast, below 1 GPa, broad peak features are found at T_{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_{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 NI phase boundary obtained from the electrical resistivity [7] shown by a solid curve in Fig. 3, we conclude that the T_{Peak} roughly corresponds to

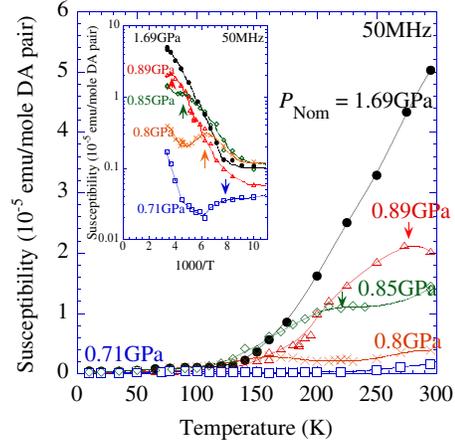


FIG. 2 (color online). The temperature dependence of the electronic spin susceptibility under pressure. Inset: Arrhenius plot above 100 K. The arrows indicate the peaks, where χ_e without the impurity contributions is used. Each pressure is a nominal value when clamped. Solid curves are guides to the eyes.

the NI phase transition temperature T_{NI} . Importantly, all the temperature dependences of χ_e are continuous through the T_{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 χ_e can be reproduced by the double exponentials along with a small Curie term:

$$\chi_e = \frac{a}{T} \exp\left(-\frac{\Delta E_1}{kT}\right) + \frac{b}{T} \exp\left(-\frac{\Delta E_2}{kT}\right) + \frac{C}{T}, \quad (1)$$

where $a = 0.7$ emu K/mole (2 spins per DA pair),

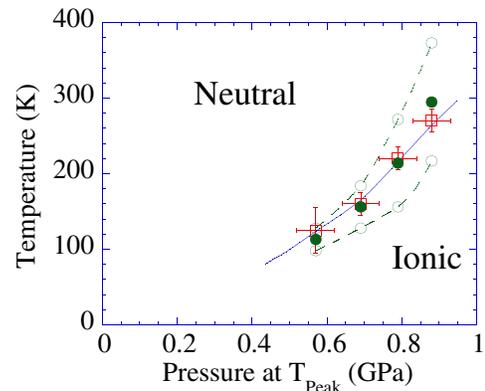


FIG. 3 (color online). The pressure-temperature phase diagram of (BEDT-TTF)(ClMeTCNQ). Solid line: The phase boundary between the neutral and the ionic phase determined by the electrical resistivity [7]. Open squares: The peak temperatures for the spin susceptibility obtained with ESR. Solid circles: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

$\Delta E_1/k \approx 1100$ K, $b = 2 \times 10^{-4}$ emu K/mole, $\Delta E_2/k \approx 110$ K, and $C = 5 \times 10^{-6}$ emu K/mole. The observed monotonic increase of χ_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 spin-Peierls (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: $\Delta E_1 = \Delta E_{SP}$. The second exponential term has a 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 χ_e for all the other curves measured below 1.69 GPa can also be reproduced by Eq. (1) below the T_{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 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 reasons are as follows: (i) the continuous variation of χ_e from the SP-type ionic phase to the neutral phase across T_{NI} and (ii) the higher T_{SP} than T_{NI} . Then, the number of ionic radicals $N_I(T)$ can be extracted from χ_e with the constant SP gap of 1100 K. With $N_I(T)$, the intrinsic part of χ_e , namely, the first term of Eq. (1), can be modified as follows:

$$\chi_e = a' \frac{N_I(T)}{T} \exp\left(-\frac{\Delta E_1}{kT}\right). \quad (2)$$

The intrinsic χ_e together with the $N_I(T)$ deduced from Eq. (2) for 0.8 GPa are shown in Fig. 4. $N_I(T)/N_0$ provides a temperature evolution of the ionic fraction demonstrated in the inset of Fig. 4, where N_0 is the total number of molecules. A remarkable observation is that $N_I(T)/N_0$ shows a continuous and gradual decrease with the increase of temperature, which is contradictory to the expected first order nature in the NI transition, and also that the sizable ionic fraction still survives in the neutral phase at $T \gg T_{NI}$. 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 quasicrossover transition. Figure 5 shows

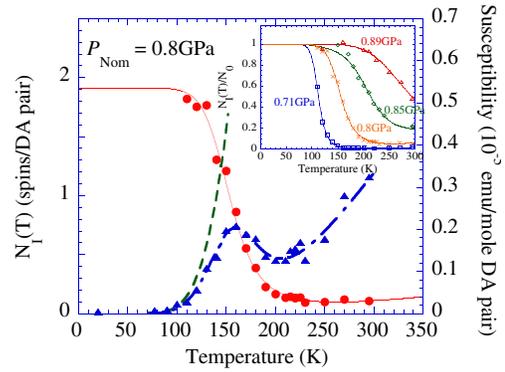


FIG. 4 (color online). The temperature variation of the intrinsic spin susceptibility (solid triangles) and the number of ionic radicals $N_I(T)$ (solid circles) at 0.8 GPa, obtained from Eq. (2). $N_I(T)$ below 100 K are discarded because of significant scattering by the small exponential factor. The solid line shows the estimated $N_I(T)$ with Eq. (3). The dashed 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.

schematic views of the double-well potentials at the three different temperature regions: $T < T_{NI}$, $T = T_{NI}$, and $T > T_{NI}$. 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

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

To reproduce the temperature evolution of the ionic fraction $N_I(T)/N_0$ 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 $T = T_{NI}$ 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 $\Delta T = T_{NI} - T$ 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 $T \gg T_{NI}$, as demonstrated by the solid lines in the inset of

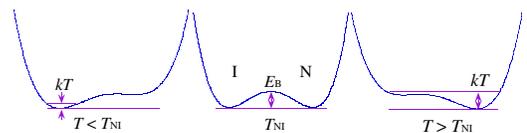


FIG. 5 (color online). Schematic representation of the potential energies at the three temperature regions. The horizontal direction corresponds to an order parameter.

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 $T \gg T_{\text{NI}}$. The appearance of the residual ionic fraction could be due to the tiny energy barrier separation between the neutral and ionic phases. From the above discussion the ionic fraction should be called a thermoinduced NI mesophase. As expected, the reproduced $N_i(T)$ tends to be about two 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 an 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 $P < P_{\text{NI}}^{\text{RT}}$. In this context, with the change of the ground states at $P > P_{\text{NI}}^{\text{RT}}$, the carriers should switch to the neutral fraction with an odd number of neutral molecules. This gives a consistent picture of the observed deviation of χ_e and σ at $P > P_{\text{NI}}^{\text{RT}}$, 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 NI 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. These 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 $T_{\text{NI}}/T_{\text{SP}}$; if T_{NI} is much smaller than T_{SP} , quite a 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 NI phase transitions with the 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 when approaching the NI 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 NI transition as the continuous switch from the ionic to the neutral phase. This novel type of phase transformation is interpreted as the crossover between the neutral and the ionic phase by the double-well potential model. This model also reproduced the thermoinduced NI mesophase, where ionic radicals survive even at $T \gg T_{\text{NI}}$. 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.

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