

ESR studies of (BEDT-TTF)(ClMeTCNQ) under pressure[☆]

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Abstract

(BEDT-TTF)(ClMeTCNQ), one of mixed-stack charge-transfer (CT) compounds located on the boundary of a neutral (N) phase and an ionic (I) phase, shows a pressure or temperature induced NI phase transition. Magnetic properties associated with the transition were investigated using electron spin resonance (ESR) under hydrostatic pressure. The NI phase transition temperature was determined as the peak temperature (T_p) of the electronic spin susceptibility derived from the ESR intensity under several pressures. The susceptibility increases as the temperature goes down near T_p . This increase is interpreted as the growth of the ionic domain in the neutral phase.

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1. Introduction

Mixed-stack charge-transfer (CT) compounds consist of alternating donor (D) and acceptor (A) molecules with a strong one-dimensional (1D) nature due to the DA stacking structure. The neutral–ionic (NI) phase transition was found in TTF-CA [1], accompanied by lattice dimerization by Peierls instability that is characteristic of the 1D systems [2]. On the other hand, (BEDT-TTF)(ClMeTCNQ) is expected to be more 2D since BEDT-TTF molecules have relatively large intercolumnar overlaps. In fact, this 2D nature appears to give rise to more continuous NI phase transition, as deduced from the electrical resistivity measurement [3]. In this study, we performed ESR intensity measurements as a function of temperature and pressure to investigate the phase transition from the magnetic view point.

2. Experiment

ESR intensity under pressure was measured around 50 MHz using a clamp-type cell of CuBe alloy with a

pressure medium Daphne 7373 oil. To obtain absolute value of electronic spin susceptibility (χ_e), the ESR intensity was calibrated with in situ ^{19}F NMR of a tube containing the sample [4].

3. Results and discussion

Fig. 1 shows the temperature dependences of χ_e at various pressures. At 16.9 kbar χ_e decreases with decreasing temperature and its temperature dependence can be reproduced by the sum of two exponential terms and a small Curie-like term. One exponential term, that is much smaller than the other, is attributed to unknown minor spins and neglected in this report. On the other hand the decrease of the major term can be accounted for as the spin-Peierls transition associated with lattice dimerization, since 16.9 kbar is much higher than the critical pressure of the NI transition (Fig. 2). Curie-like spins whose density is about 10^{-5} per site are assigned to spin solitons or domain walls in the ionic phase [6,7]. The temperature dependences under other pressures are similar to each other, that is, χ_e increases as temperature goes down and reaches its peak at T_p , then reduces. Since the decrease at $T < T_p$ can be reproduced with the same formula, it would also correspond to the spin-Peierls transition. In Fig. 2 we plot T_p 's in the pressure–temperature phase diagram determined from the electrical resistivity measurement, taking account of the pressure change due to thermal contraction of the pressure medium using the reported data [5]. It turns out that T_p 's fall on the phase boundary, and consequently, T_p

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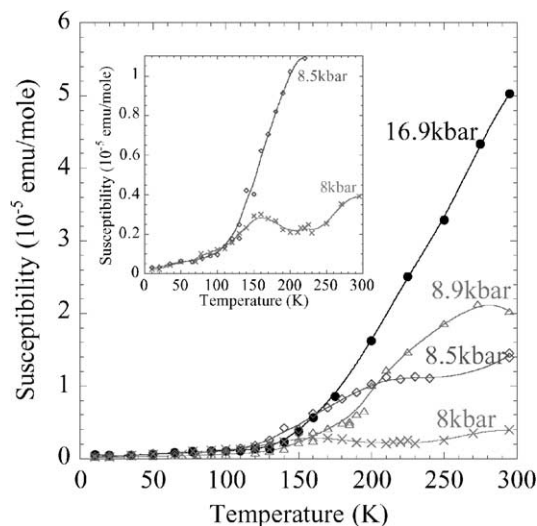


Fig. 1. Temperature dependences of the electronic spin susceptibility. Each pressure value is a nominal one when the pressure was clamped at room temperature. Solid lines are guides for eyes.

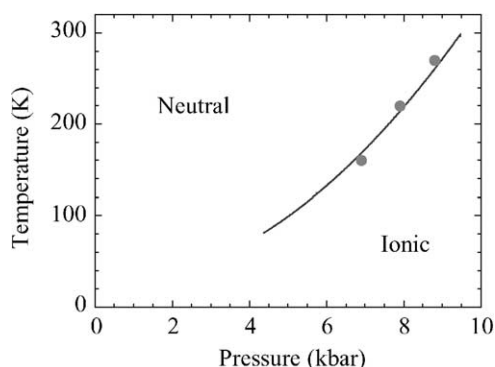


Fig. 2. Peak temperature, T_p , of the spin susceptibility as the function of the pressure (filled circles). Phase boundary between the neutral and the ionic phases obtained from the electrical resistivity measurement [3] (solid line).

should be regarded as the temperature at which the NI phase transition accompanied by the spin-Peierls transition occurs.

It is considered that the ionic domain size increases as the temperature approaches T_p because of the fluctuation near the boundary, giving rise to the increase of χ_e . It is noted that in (BEDT-TTF)(CIME TCNQ) the spin-Peierls transition typical of 1D system and the NI phase transition take place at the same temperature in spite of 2D character caused by the BEDT-TTF molecules.

4. Conclusion

We measured the electronic spin susceptibility in (BEDT-TTF)(CIME TCNQ) as a function of temperature and pressure. The susceptibility peak observed at each pressure corresponds to the NI phase transition accompanied by the spin-Peierls transition. The ionic domain size grows as the temperature approaches the transition. The NI phase transition of (BEDT-TTF)(CIME TCNQ) in the low temperature and pressure range is considered to be more continuous than that of TTF-CA since the former has more 2D nature [3]. However, the spin-Peierls instability is not suppressed in this material in the pressure range used for this experiment.

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