ESR studies of mixed-stack charge-transfer compounds of (BEDT-TTF) analogs under pressure

H. Sakamoto [a] *, K. Mizoguchi [a], and T. Hasegawa [b]

[a] Dept. of Phys., Tokyo Metropolitan Univ., Hachioji, Tokyo, 192-0397, Japan

[b] RIES, Hokkaido Univ., Hokkaido, 060-0812, Japan

Abstract

Electron spin susceptibility of mixed-stack charge-transfer compounds, (BEDT-TTF)(ClMeTCNQ) and (BEDO-TTF)(Cl$_2$TCNQ), was measured by ESR under several hydrostatic pressures. In (BEDT-TTF)(ClMeTCNQ) the temperature dependence of the susceptibility at each pressure has a peak structure at the temperature where neutral-ionic phase transition and spin-Peierls transition take place simultaneously. The phase diagram was obtained from the peak temperatures and pressures, consistent with that determined by transport measurement. The susceptibility of the second compound (BEDO-TTF)(Cl$_2$TCNQ) was extremely sensitive to pressure change. With increasing pressure, the jump at 120 K at ambient pressure disappeared and the one-dimensional Bonner-Fisher type susceptibility emerged.

Keywords: Electron spin resonance, Magnetic phase transition, Other phase transition

1. Introduction

Mixed-stack charge-transfer compounds have one-dimensional structure with donor and acceptor molecules stacked alternately. They are in either a neutral (N) or an ionic (I) phase. Compounds near NI phase boundary such as TTF-CA show N-I phase transition induced by pressure or by lowering temperature [1,2]. In general it has been known that N-I phase transition is accompanied by lattice dimerization due to the Peierls instability [3]. In contrast to that, recently synthesized (BEDT-TTF) analogs are thought to have strong two dimensional character because of interaction between BEDT-TTF molecules on adjacent columns [4]. Thus in these materials it is expected that magnetic properties in ionic phase can be observed without Peierls instability. In fact, it has been reported that in (BEDO-TTF)(Cl$_2$TCNQ) at ambient pressure, spins on ionized molecules at room temperature remain alive down to 4.2K [4]. It has also been suggested that in (BEDT-TTF)(ClMeTCNQ), its relatively strong two-dimensionality causes the NI phase transition in the low temperature and low pressure range to be more continuous than that of TTF-CA [5]. In the present report we will demonstrate the electronic spin susceptibility (χ_e) observed by ESR under hydrostatic pressures to discuss the magnetic properties and the phase transition of (BEDT-TTF)(ClMeTCNQ) and (BEDO-TTF)(Cl$_2$TCNQ).

* E-mail: sakamoto@phys.metro-u.ac.jp

2. Experimental

ESR was measured around 50 MHz between ambient pressure and 16.9 kbar. A clamp-type cell of CuBe alloy was used for applying pressure with Daphne 7373. Absolute value of susceptibility was obtained by calibrating ESR intensity with in-situ ^{19}F NMR of a sample tube.
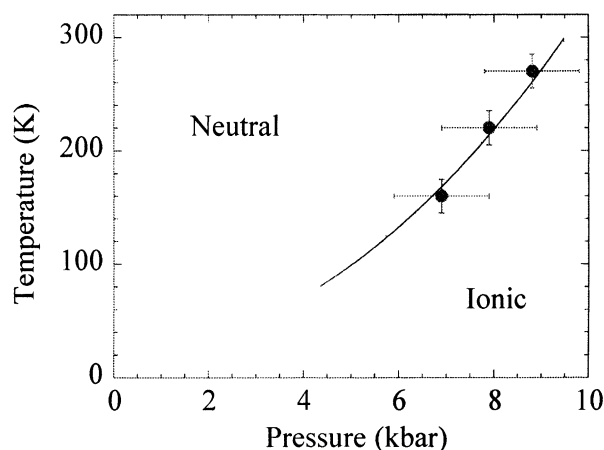

Fig. 1. P - T phase diagram of (BEDT-TTF)(ClMeTCNQ). The solid curve is the border line determined from the electrical transport measurement. The solid circles are obtained from the susceptibility peak.
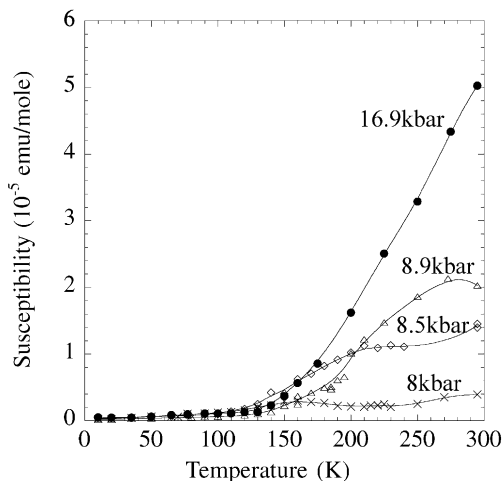
Fig. 2. The temperature dependences of the electronic spin susceptibility for (BEDT-TTF)(ClMeTCNQ) under various pressures. The solid lines are guids for eyes.
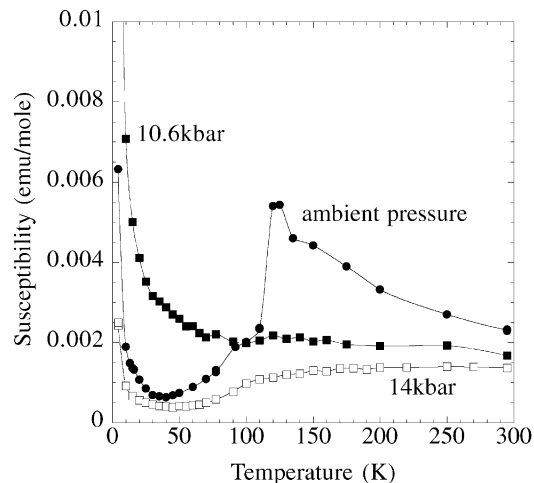

Fig. 3. The temperature dependences of the electronic spin susceptibility for (BEDO-TTF)(Cl2TCNQ) under various pressures.The solid lines are guids for eyes.

3. Results and discussion

It has been indicated by optical spectroscopy that at room temperature the neutral phase of (BEDT-TTF)(ClMeTCNQ) undergoes a transition to the ionic phase with dimeric lattice distortions at 10 kbar [5]. In addition, the pressure-temperature phase diagram shown in Fig. 1 has been obtained by electrical resistivity measurement [5]. The temperature dependence of χ_e at several pressures is indicated in Fig. 2. First, we discuss χ_e at 16.9 kbar. As seen from Fig. 1, at room temperature this system is ionic phase accompanied with the lattice dimerization. Therefore the monotonic decrease of χ_e at 16.9 kbar in Fig. 2 seems to correspond to the disappearance of the spins on the ionized molecules by the spin-Peierls (SP) transition. Next, regarding χ_e below 10 kbar we notice that there are broad peak structures. These peak temperatures (T_p) are plotted on the phase diagram as shown by the closed circles in Fig. 1, where the pressures are corrected at T_p with the reported data to take account of thermal contraction of the pressure medium [6]. From Fig. 1, it is found that T_p are located on the phase boundary, which leads to the following interpretations about the temperature dependence of χ_e above and below T_p. The increase of χ_e with a decrease in temperature to T_p can be understood as the growth of the ionic domain size as the system approaches the N-I phase transition point. On the other hand, the decrease of χ_e with decreasing temperature below T_p is ascribed to the SP transition, similar to the 16.9 kbar case. Thus the observed results support the possibility that the SP state appears simultaneously with the N-I phase transition at T_p, although the two dimensionality is enhanced by BEDT-TTF molecules. In a SP system (DMe-DCNQI)$_2$Li, the pressure change of the SP transition temperature (T_{SP}) has been reported to be about 1 K/kbar in the pressure range close to that of this study [7]. Assuming that this result is applicable to the present case, and considering that at 16.9 kbar T_{SP} should be higher than 300 K as known from Fig. 2, we can expect that for the data below 10 kbar T_{SP} is higher than T_p and is not

so different from T_{SP} at 16.9 kbar. Thus, in the temperature range between T_p and T_{SP}, if spins are present, exchange interaction between donor and acceptor molecules in the neutral phase seems to be strong enough to cuase the SP transition. As mentioned above, T_{SP} at each pressure appears to be close to T_{SP} at 16.9 kbar, which means that the SP gap also does not substantially change under pressure. This may correspond to the similar rising of χ_e with an increase in temperature around 100 K in Fig. 2.

Figure 3 shows χ_e of (BEDO-TTF)(Cl2TCNQ) under pressure as a function of temperature. It has been understood that the abrupt jump near 120 K at ambient pressure is related with a novel transition from weakly interacting to strongly interacting spin states caused by molecular displacement [8]. It turned out that the pressure of 10 kbar suppresses the jump of χ_e and transforms it to the Curie-Weiss behavior except for a steep increase in low temperature range. Under higher pressures, χ_e changes to the Bonner-Fisher type accompanied by decrease probably due to the SP transition below 100 K. This result suggests that one dimensionality is induced by pressure in spite of the presence of BEDO-TTF molecules.

References

[1] J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. 46 (1981) 253.
[2] J. B. Torrance, A. Girlando, J. J. Mayerle, J. L. Crowley, V. Y. Lee, and P. Batail, Phys. Rev. Lett. 47 (1981) 1747.
[3] A. Girlando, F. Marzola, and C. Pecile, J. Chem. Phys. 79 (1983) 1075.
[4] T. Hasegawa, T. Mochida, R. Kondo, S. Kagoshima, Y. Iwasa, T. Akutagawa, T. Nakamura, and G. Saito, Phys. Rev. 62 (2000) 10059.
[5] T. Hasagawa, T. Akutagawa, T. Nakamura, T. Mochida, R. Kondo, S. Kagoshima, and Y. Iwasa, Phys. Rev. 64 (2001) 085106.
[6] K. Murata, H. Yoshino, H. O. Yadav, Y. Honda, and N. Shirakawa, Rev. Sci. Instrum. 68 (1997) 2490.
[7] M. Hiraoka, H. Sakamoto, K. Mizoguchi and R. Kato, Phys. Rev. B65 (2002) 174413.
[8] T. Hasagawa, T. Akutagawa, T. Nakamura, T. Naito, T. Inabe, T. Mochida, R. Kondo, S. Kagoshima, Y. Iwasa, and G. Saito, to be published.