Journal of Low Temperature Physics, Vol. 142, Nos. 3/4, February 2006 (© 2007)
DOI: 10.1007/s10909-006-9198-4

EPR Study of the Electronic States of β'-(BEDT-TTF)(TCNQ)

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β'-(BEDT-TTF)(TCNQ) is a compound of BEDT-TTF (=ET) and TCNQ molecules aligned orthogonally with each other, forming two-dimensional sheets and one-dimensional columns of 1/4-filled π band, respectively. It is known that the metal-insulator transition occurs at 330 K at ambient pressure. We have measured the electronic spin susceptibility by means of the EPR-NMR method at 50 MHz, and the angular dependence of g-factor and line width of EPR both at Q (34 GHz) and W (94 GHz) band. We successfully confirmed that the antiferromagnetic transition occurs in ET sheets and TCNQ columns, independently.
PACS numbers: 61.66.Hq, 75.50.Ee, 76.30.-v.

β'-(BEDT-TTF)(TCNQ) is an organic charge transfer complex of BEDT-TTF (=ET) and TCNQ molecules, with the molecular planes orthogonal with each other[1]. Thus, the electronic interaction is very weak between the sheets and the columns. It was reported that 1) the metal-insulator transition occurs at 330 K at ambient pressure[2], 2) the existence of an antiferromagnetic ordering for the TCNQ columns below 3 K is suggested by the SQUID susceptibility[2] and 3) the existence of an antiferromagnetic transition at 20 K is suggested only for the ET sheets[3]. We have measured EPR at high fields; W and Q bands and EPR-NMR at low field to clarify the electronic state of β'-(ET)(TCNQ). The points are that 1) we measured the spin susceptibility (=χ_p) with EPR-NMR method, and 2) we have determined the individual contribution of χ_p(ET) and χ_p(TCNQ) by the angular dependence of EPR, which definitely demonstrates the rapid decrease of EPR intensity relevant to the ET-sheet. We also obtained the electronic hopping rate between the ET sheets and TCNQ columns with the frequency dependence of the *g*-factor and the line width of EPR, as demonstrated by Hiraoka and co-workers[5-8].

First, the electronic spin susceptibility with the EPR-NMR method between 2.8 K and 300 K is shown in Fig. 1. We found the decrease of the spin susceptibility below 4 K as temperature decreases, consistent with Ref. 2: this decrease should correspond to the antiferromagnetic transition in the TCNQ columns.

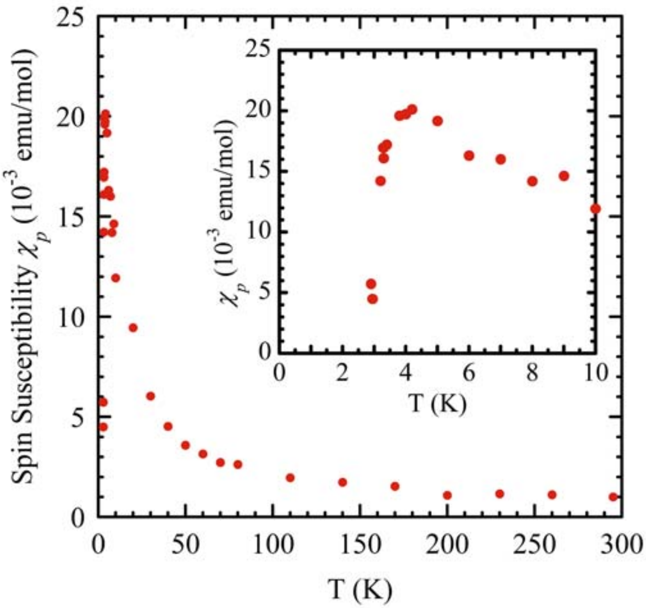

Fig. 1 Temperature dependence of the spin susceptibility χ_p. The inset shows the expanded figure in the low temperature region.

Second, we obtained the angular dependence of the *g*-factor and the line width at Q and W bands between 3 K and 300 K as shown in Fig. 2 (Left). It is reported that the average of *g*-factor can be expressed as follows[2,4]:

$$\overline{g}(T) = \frac{\chi_{p(ET)}(T)}{\chi_{p(ET)}(T) + \chi_{p(TCNQ)}(T)}\overline{g}_{ET} + \frac{\chi_{p(TCNQ)}(T)}{\chi_{p(ET)}(T) + \chi_{p(TCNQ)}(T)}\overline{g}_{TCNQ} \quad (1)$$

Third, we separated the *g*-factor of ET and TCNQ using both the spin susceptibility and the extended form of the eq.(1) that includes the angular variation of the *g*-factor, with assuming $g_{av}(ET) = 2.007$. The result is shown in Fig. 2 (Right).

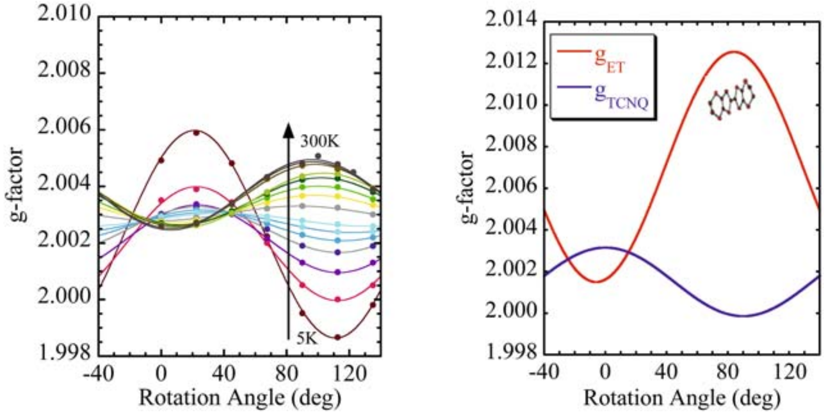

Fig.2. Left: Angular dependence of the *g*-factor for *β'*-(ET)(TCNQ) between 3 K and 300 K. Right: Angular dependences of the *g*-factor, g_{ET} and g_{TCNQ} inherent in the ET and TCNQ molecules, respectively, assumed under the configuration studied.

Fourth, in Fig. 3 we demonstrate χ_p(ET) and χ_p(TCNQ) obtained from Fig. 2 and eq. (1), together with the total susceptibility, SQUID(χ_p+χ_{AF}), where χ_{AF} is the antiferromagnetic susceptibility. Note that SQUID(χ_p+χ_{AF}) is much larger than χ_p(EPR) below 20 K. This observation can be attributed

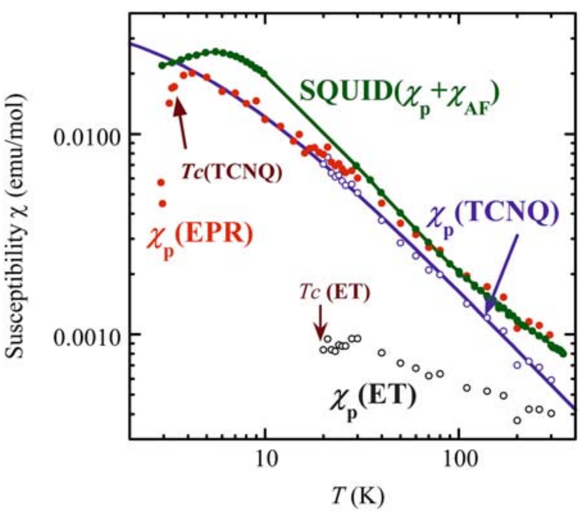

Fig.3. Temperature dependence of the susceptibility. SQUID(χ_p+χ_{AF}) is the total susceptibility by Iwasa *et al.*[2].

to the antiferromagnetic transition in the ET-sheets at 20 K, since χ_p(EPR) gives only the paramagnetic susceptibility. This conclusion is consistent with the present separation of χ_p(ET) and χ_p(TCNQ). It is also stressed that χ_p(TCNQ) is reasonably reproduced by the Curie-Weiss law with $\Theta = -4$ K and one spin per each pair of TCNQ molecules.

We clearly demonstrated the independent contribution of χ_p(ET) and χ_p(TCNQ) to the magnetic ordering, suggesting a very weak interaction between ET and TCNQ. The exchange interaction within the TCNQ column is also weak, as demonstrated by the Curie-Weiss temperature as low as - 4 K, resulting in a very narrow bandwidth of TCNQ of the order of 10 meV. The ET should have a wider bandwidth as expected from the almost temperature independent χ_p(ET). We presume that the metallic state at higher temperatures above 330 K might be attributed to the ET-sheet not to the TCNQ-column, as pointed out by Iwasa and co-workers[2].

ACKNOWLEDGEMENTS

This work was supported by Grant-in-Aid for Scientific Research on the Priority Areas “Super-Hierarchical Structures”, and “Molecular Conductors” by the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and by Grant-in-Aid for Scientific Research C, No. 17540334, and No.17540332 by Japan Society for the Promotion of Science.

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