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EPR and NRM Investigation on TMTTF–TCNQ†

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We present in this communication, new data obtained on the charge-transfer complex TMTTF–TCNQ. After the discovery of the conducting properties of the quasi one-dimensional charge-transfer complex TTF–TCNQ,[1–4] it was appealing to study the electronic properties of the salt in which the protons of the donor molecule are substituted by four methyl groups which may bring about some disorder in the electronic states.

The resemblance between the electronic structures of TMTTF–TCNQ and TTF–TCNQ has been established from the static susceptibility,[5] the optical and the microwave properties.[6,7]

Substitution of methyl groups to the hydrogen atoms of TTF does introduce modifications to the crystal structure.[8] It is probable that we can discuss the electronic properties of TMTTF–TCNQ within the framework of anisotropic organic metals.

Four leads measurements on compactions show that the electrical conductivities at room temperature of these two materials are quite similar

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within the uncertainties inherent in this method ($\sigma = 15\ \Omega^{-1}\ cm^{-1}$ for TMTTF–TCNQ and $50\ \Omega^{-1}\ cm^{-1}$ for TTF–TCNQ) (see also Ref. 9).

We first summarize the EPR results obtained on polycrystalline TMTTF–TCNQ. The experiment was performed at low frequency ($\nu_s = 40$ MHz) by using a CW crossed-coils spectrometer working down to 5 K with a gas flow cryostat located inside the receiving coil.

The line observed at $g = 2$ was fitted with a lorentzian shape with good accuracy from 300 to 5 K (deviation being within the noise level, i.e. less than 2% of the signal amplitude). The EPR line width decreases continuously from 2.5 gauss at 300 K to 150 milligauss at 15 K (Figure 1). The rise of linewidth below 10 K is due to the existence of a small concentration of paramagnetic centers. The best fitted derivative absorption curves were integrated twice to determine the EPR spin susceptibility.[10] Figure 1 shows the temperature variation of spin susceptibility and linewidth. It is illuminating to compare the EPR spin susceptibility with the static susceptibility obtained by the Faraday method.[5] Since the absolute calibration of the spin susceptibility has not been performed in our experiment, Figure 2 shows the normalized static susceptibility after correction for diamagnetism[5] $\chi_s(T)/\chi_s(300)$ versus the normalized EPR susceptibility $\chi_{EPR}(T)/\chi_{EPR}(300)$. All the static spin susceptibility is included in the single lorentzian resonance line down to 30 K within 3% which is the accuracy of the room temperature susceptibility. It is interesting to stress that the same conclusion was reported recently for TTF–TCNQ by comparing the X-band EPR spin susceptibility with the static susceptibility.[11] We emphasize that the EPR line broadening

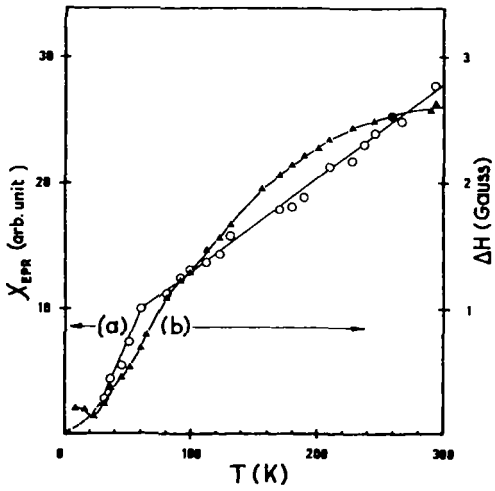

FIGURE 1 (a) The spin susceptibility obtained by EPR.
(b) Peak-to-peak linewidth of the absorption derivative.

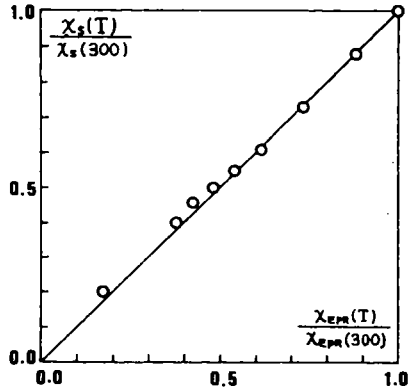

FIGURE 2 EPR normalized spin susceptibility versus normalized static susceptibility.[5]

at 80 K above the metal–insulator transition for TTF–TCNQ[12] is totally missing in TMTTF–TCNQ. (See note added in proofs).

This striking difference in behaviour of electron spin dynamics between the two compounds provided the original motivation for an analysis of the local electron spin susceptibility by NMR proton spin–lattice relaxation measurements. The experiments have been conducted at 18 MHz, watching the recovery of the magnetization by 90° pulse, following the saturation of the NMR signal by a comb of 90° pulses. The results for TMTTF–TCNQ (D_4) with a deuteration level of 95% are shown in Figure 3. Similar experiment performed on non-deuterated material indicates that the T_1 of TCNQ

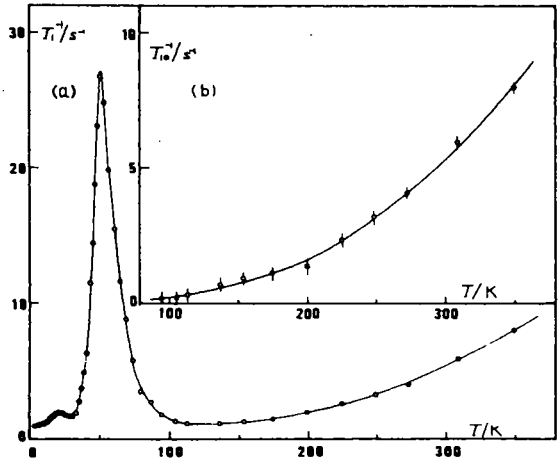

FIGURE 3 (a) Observed nuclear relaxation rate T_1^{-1} of protons in TMTTF–TCNQ (D_4) at 18 MHz.
(b) Electronic contribution to the relaxation rate T_{1e}^{-1} from 95 to 350 K.

protons cannot be much shorter than that of TMTTF protons. The 52 K peak is attributed to the classical reorientation of the CH_3 groups in the three-nodal potential, while the 22 K peak is due to the modulation of the tunneling splitting through the transitions of CH_3 group between the ground and first excited torsional states.[13,14] When both peaks of the relaxation rates are analyzed in terms of the BPP type spectral density functions,[15] a barrier height of 800 cal/mole (400 K) for the hindering potential and a torsional splitting energy of 130 cal/mole (65 K) are derived. These values are very similar to those of CH_3 rotation in *p*-tert-butyltoluene determined by the joint work of NMR and infrared spectroscopy.[14]

Once the contribution of CH_3 reorientation to the spin-lattice relaxation is substracted from the observed relaxation rate of Figure 3a, the electronic contribution to the relaxation rate is derived and is shown in Figure 3b between 95 and 350 K. We note the close similarity between Figure 3b and the temperature variation of T_1^{-1} in TTF–TCNQ (D_4).[16]

The experimental results presented in this note for χ_{EPR}, linewidth of EPR and T_1^{-1} of PMR in TMTTF–TCNQ are interesting when they are examined in the frame work of the results of TTF–TCNQ. We may suggest from the results of relaxation rates that the local dynamic properties of the electron spin susceptibility as well as its static and uniform components are the same in both systems. Moreover the phase transition indicated by a kink of $\chi(T)$ at 60 K in TTF–TCNQ exists in TMTTF–TCNQ as well (Figure 1a).

In conclusion the experimental results presented here show that the behaviour observed for the spin susceptibility and spin-lattice relaxation of TTF–TCNQ is not necessarily related to the broadening of the EPR line width above 60 K. Thus far the magnetic properties have been analyzed in terms of a two-chains model by the Pennsylvania group,[5] one chain being in the Lee–Rice–Anderson intermediate state[17] characteristic of quasi one dimensional systems and the other behaving as Pauli metal above 60 K.

The experimental features of TMTTF–TCNQ provide hints that the magnetic properties of the TTF–TCNQ family should now be reexamined in details.

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Note added in proofs

After this communication has been submitted a linewidth analysis has been performed on the powder spectrum of different TMTTF–TCNQ samples. On some samples this analysis has revealed a strong line width anisotropy and therefore a temperature dependence of the line width qualitatively similar (although less pronounced) to the behaviour noticed for TTF–TCNQ.[12] These results will be published in a forthcoming publication by D. Jerome *et. al.*