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Nuclear Spin-Lattice Relaxation and EPR Studies of TTF–TCNQ and TMTTF–TCNQ Under Hydrostatic Pressure†

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The quasi one-dimensional metallic character of TTF–TCNQ has been established by measurements of electrical conductivity, magnetic susceptibility, thermoelectric power, microwave conductivity and optical reflectivity at ambient pressure.[1] The metallic character of TMTTF–TCNQ is discussed in the preceding report[2] in comparison with that of TTF–TCNQ. The metallic state results from the strong π-orbital overlap along the TCNQ and TTF chains. In TTF–TCNQ both chains are metallic with transfer integrals of order 0.1 eV. The interchain transfer integral is of the order of 1 meV, which shows that the interchain hopping time of electrons is much shorter than the characteristic time scale of electron spin dynamics (ω_s, T_{1s}) and nuclear spin relaxation. Therefore, the ratio of the spin-lattice relaxation times of each chains observed by Rybaczewski *et al.*[3] using deuterated TTF–TCNQ which is nearly independent of the temperature down to 60 K indicates a

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temperature independent ratio of the static susceptibilities of the individual chains. Under these conditions, the nuclear spin relaxation rate T_1^{-1} should be related to the observed spin susceptibility χ_s by the Korringa relation, $(T_1T)^{-1} \propto A^2\chi_s^2K(u, T)$, where K is the Korringa enhancement factor which depends on the electron–electron Coulomb correlation u and temperature T.

Although Rybaczewski *et al.* have concluded that the Coulomb correlation is small $[K(u \cdot T) \simeq 1]$ and $(T_1T)^{-1} \propto \chi_s^2$ in TTF–TCNQ, as can be seen in Figure 1, the log–log plot of $(T_1T)^{-1}$ against χ_s shows that the exponent of α in the relation $(T_1T)^{-1} \propto \chi_s^\alpha$ is not exactly 2.0, but rather 2.2 for both materials, TTF-TCNQ and TMTTF-TCNQ.

The purpose of this pressure investigation is to clarify whether this "Korringa" behaviour is followed when a change of the density of states at Fermi level is induced by means other than a change in the temperature. The experimental procedures for the measurements of relaxation rate are the same as those mentioned in the preceding report.[2] The EPR measurements under pressure were also made at 40 MHz using a different spectrometer sensitive to the dispersive component of χ. Although there is clear evidence for large increases in EPR linewidth under pressure the values of the susceptibility quoted here are subject to the following two limitations: (a) a detailed analysis of the lineshape needs to be carried out, especially for TTF–TCNQ where the linewidth is $\sim 1/3$ of the applied static field; (b) further checks on the sensitivity of the spectrometer under pressure should be made. The pressure equipment will be described elsewhere.

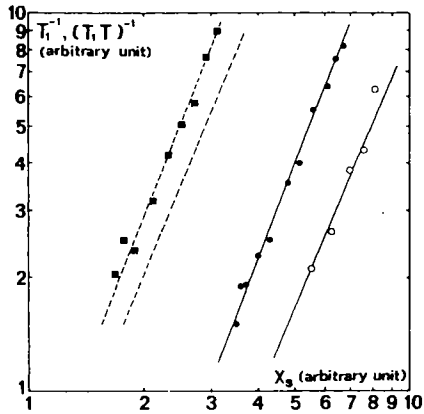

FIGURE 1 Log–log plots of $(T_1T)^{-1}$ versus χ_s
--■-- TMTTF–TCNQ ambient pressure, temperatures from 100–350 K
---- TTF–TCNQ ambient pressure, temperatures from 100–300 K (Refs. 3 and 4)
—●— TMTTF–TCNQ room temperature, pressures up to 10 Kbar
—○— TTF-TCNQ room temperature, pressures up to 4 Kbar.

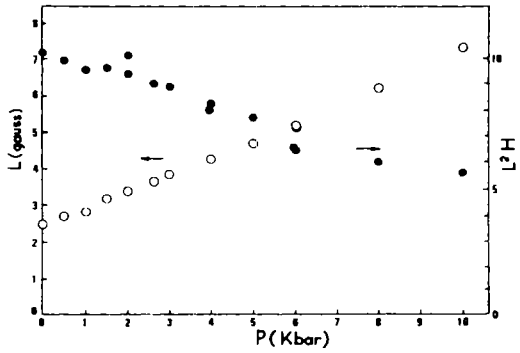

FIGURE 2 EPR results for TMTTF–TCNQ at room temperature
○ Left-hand scale—linewidth L versus pressure
● Right-hand scale—normalized spin susceptibilty (L^2H of derived dispersion curves) versus pressure.

Experimental results are summarized as follows.

1) Pressure variation of EPR line-width and spin susceptibility were measured up to 10 Kbar for TMTTF–TCNQ and up to 4 Kbar for TTF–TCNQ. In the latter case the linewidth is so broad that it becomes comparable to the applied static field. In both cases, the linewidth increases approximately linearly with pressure, 0.48 gauss/Kbar (i.e. 18%/Kbar) for TMTTF–TCNQ (Figure 2) and 1.4 gauss/Kbar (i.e. 28%/Kbar) for TTF–TCNQ (Figure 3) at room temperature. It is interesting to note the relative changes in the linewidth of TTF–TCNQ under pressure are independent of temperature in the range studied.

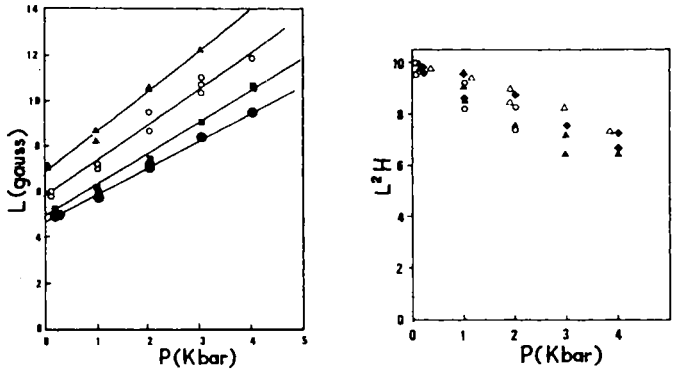

FIGURE 3 EPR results for TTF–TCNQ at several temperatures. (a) Linewidth L versus pressure at 343 K●, 295 K■, 220 K○ and 170 K▲. (b) Normalized spin susceptibility (L^2H of derived dispersion curves) versus pressure at 343 K△, 295 K◆, 220 K▲, 170 K○. The values of L^2H are normalized by the ambient pressure values at each temperature.

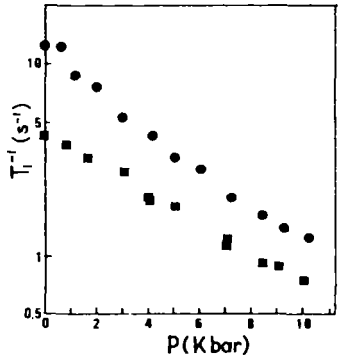

FIGURE 4 Pressure dependence of proton relaxation rate at room temperature, ● TTF-TCNQ, ■ TMTTF-TCNQ.

2) In both materials, χ_s decreases with pressure. The relative decreases under pressure are 5.6%/Kbar for TMTTF-TCNQ and 7% Kbar for TTF-TCNQ at room temperature (Figures 2 and 3b).

3) As shown in Figure 4, the nuclear relaxation rate decreases strongly with pressure in both materials rather more quickly than expected from the pressure variation of χ_s. In Figure 1 the relaxation rates are also plotted against χ_s with pressure as the implicit parameter. This shows that there is also some deviation from a Korringa law, the exponents are ≈ 2.2 for both materials, which is the same as the value derived from the temperature variation. It is easily concluded that the electronic states of both quasi one-dimensional systems resemble each other. The nuclear spin relaxation rate is therefore related to the observed spin susceptibility by the phenomenological equation, $T_1^{-1} \propto A^2 T \chi_s^{2.2}$. The difference of the exponent from 2.0 may be due to the interchain interaction and to the electron correlation. This point needs deeper and more precise consideration.

4) The temperature variation of relaxation rate under pressure shows that at 10 Kbar the maximum of T_1^{-1} due to CH_3 rotation moves to 70 K and the hindering potential increases to twice the value at ambient pressure. But the EPR and NMR results up to 10 Kbar mentioned above make it clear that the dynamical disorder of CH_3 rotation has no effect on the electronic states above 80 K.

1. See the recent review article by A. J. Heeger and A. F. Garito in *Low-Dimensional Cooperative Phenomena* (Ed. by H. J. Keller, Plenum Press, 1975), pp. 89, and references therein.
2. C. Berthier *et al.*, this conference, previous communication.
3. E. F. Rybaczewski, A. F. Garito, and A. J. Heeger; *Phys. Rev. Letters*, **34**, 524 (1975).
4. J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev.*, **B10**, 3131 (1974).