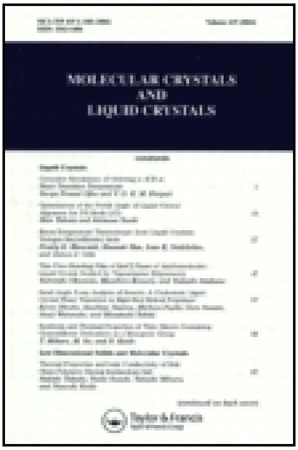

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Nuclear Relaxation in Two Conductive TCNQ Salts

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Nuclear Relaxation in Two Conductive TCNQ Salts

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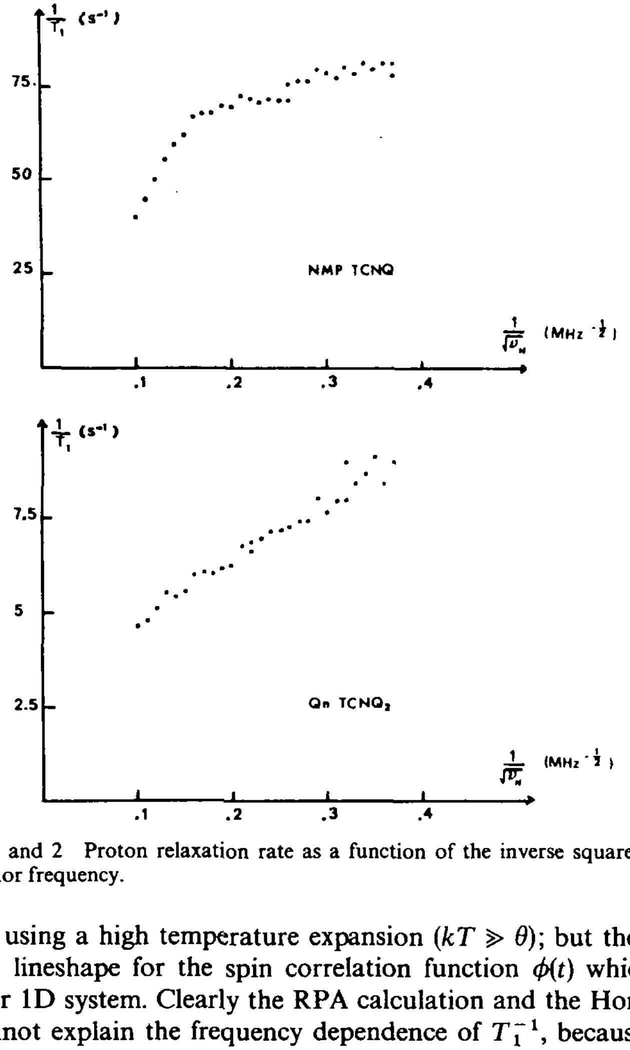
As shown by recent studies[1] the frequency dependence of the nuclear relaxation rate is a sensitive probe of spin dynamics in 1D system. We have investigated by this method the properties of two conductive TCNQ salts: N-Methyl-Phenazinium (NMP) TCNQ and Quinolinium (Qn) $TCNQ_2$. We have measured the proton relaxation time T_1 as a function of the nuclear Larmor frequency ν_N between 7 and 100 MHz. The measurements have been performed at room temperature on polycristalline samples. The nuclear relaxation rates are plotted in Figures 1 and 2 versus $\nu_N^{-1/2}$. We obtain straight lines on the entire frequency range from 7 to 100 MHz for Qn $TCNQ_2$ and only from 40 to 100 MHz for NMP TCNQ. This is the experimental evidence of a 1D diffusive motion for the electronic spins in these compounds. The aim of this paper is to attempt a qualitative explanation of such a behaviour, which was not reported so far in conductive TCNQ salts.

Usually, electronic properties of NMP TCNQ and Qn $TCNQ_2$ are described by the linear Hubbard hamiltonian which can be written as follows.

$$\mathscr{H} = U + \Theta = u \sum_{\lambda} n_{\lambda\uparrow} n_{\lambda\downarrow} - \theta \sum_{\lambda\sigma} (c^{+}_{\lambda\sigma} c_{\lambda+1\sigma} + c^{+}_{\lambda+1\sigma} c_{\lambda\sigma})$$

We defined n as the average number of electrons per site ($n = 1$ for NMP TCNQ and $n = \frac{1}{2}$ for Qn $TCNQ_2$).

Some theories have been proposed to explain the temperature dependence of T_1 in these compounds. In Qn $TCNQ_2$ the results are interpreted in term of Korringa relation.[2] For the NMP salt, Ehrenfreund, *et al.*[3] have attributed the unusually strong absolute value of T_1^{-1} to an enhancement of the Korringa relaxation process due to the coulomb interaction. This interpretation is based upon the RPA calculation of the dynamic susceptibility by Moriya[4] and Izuyama, *et al.*[5] Hone and Pincus[6] have calculated the nuclear relaxation rate in the case of a half-filled band ($n = 1$) with strong interactions



FIGURES 1 and 2 Proton relaxation rate as a function of the inverse square root of the nuclear Larmor frequency.

($u \gg \theta$) by using a high temperature expansion ($kT \gg \theta$); but they assume a gaussian lineshape for the spin correlation function $\phi(t)$ which is very dubious for 1D system. Clearly the RPA calculation and the Hone–Pincus theory cannot explain the frequency dependence of T_1^{-1}, because they do not take into account the dynamic properties of 1D system.

More recently, Villain[7] has considered the case of infinite Coulomb repulsion ($u \gg \theta, kT$) for a non half-filled band ($n \neq 1$). The problem is then reduced to the calculation of the position correlation function for the itinerant electrons. A 1D diffusive low is obtained for the frequency spin correlation function: $\phi(\nu) \propto \nu^{-1/2}$. On the other hand, the limit of electrons without interactions ($u = 0$) can be solved exactly[8] and for a narrow band, one can observe a deviation from Korringa relation and a logarithmic divergence for $\phi(\nu)$ at low frequencies: $\phi(\nu) \propto \ln \nu^{-1}$.

Here we analyzed the case of strong interactions and high temperature ($u, kT \gg \theta$). We calculate the spin correlation function in the Q-space.

$$\phi(t) = \sum_{Q} \langle S_Q^+(t) S_{-Q}^- \rangle \tag{1}$$

Due to the commutation rule $[U, S_Q^+] = 0$, the problem is somewhat similar to the exchange narrowing of the EPR line. Thus by using the same formalism[9] we obtain

$$\langle S_Q^-(t) S_{-Q}^- \rangle = \langle S_Q^+ S_{-Q}^- \rangle \exp\left\{ -|t| \int_0^{+\infty} M_Q(\tau)\, \mathrm{d}\tau \right\} \tag{2}$$

where $M_Q(\tau)$ is the so-called memory function. The basic hypothesis contained in Eq. (2) is the Markoffian assumption, i.e. that the memory function decreases much faster than the function $\langle S_Q^+(t) S_{-Q}^- \rangle$ itself. This condition is fullfilled for small wave number Q which are preponderant at low frequency. The important point in this calculation is that the time evolution of $M_Q(\tau)$ is governed by the effective hamiltonian

$$\overline{\Theta} = \frac{1}{t} \int_0^t \mathrm{d}\tau\, e^{-iU\tau} \Theta\, e^{iU\tau} \qquad t \gg \frac{1}{u}$$

which includes the scattering effects due to the Coulomb repulsion. Thus by assuming a gaussian lineshape for $M_Q(\tau)$, one obtains

$$\int_0^{+\infty} M_Q(\tau)\, \mathrm{d}\tau = DQ^2 \tag{3}$$

where the diffusion coefficient D can be expressed as

$$D = \theta \left(\frac{\pi[1 - n + n^2(x/2)]}{3n[1 - n(x/2)]} \right)^{1/2} \tag{4}$$

x is defined by $\langle n_{\lambda\uparrow} n_{\lambda\downarrow} \rangle = (n^2/4)x$ ($x = 1$ for $u/kT \ll 1$ and $x = 0$ for $u/kT \gg 1$ and $n \leq 1$). It characterizes the thermodynamic properties of the system. Note that in our calculation the density operator is reduced to $\rho = \exp[-(U - \mu N)/kT]$.

The frequency spin correlation function can then be deduced from Eq. (1), (2) and (3)

$$\phi(\nu) = \frac{1}{4\pi} n \left(1 - n \frac{x}{2} \right) (4\pi D \nu)^{-1/2}$$

From the expression of D (4), one can see that the result is not valid in the case $n = 1$ at low temperature ($u/kT \gg 1, x \to 0$). Indeed in this case the real hopping of the electrons from one site to another is no longer possible. As shown by Hone and Pincus,[6] the density operator should be developed as a function of θ/kT to obtain the term of virtual hopping. In fact the Hubbard hamiltonian is reduced in this case to the Heisenberg model and therefore one expect a diffusive behaviour for the spin correlation function with a diffusive constant $D = \sqrt{2\pi}\,\theta^2/u$.

The diffusive behaviour, that we have obtained, is due to the scattering of electrons from a Bloch-state to another one by the Coulomb repulsion. Thus we can infer that this basic result—diffusive behaviour—remains valid for moderate Coulomb interaction ($u \sim \theta$) and at lower temperature ($kT \lesssim \theta$). These conditions roughly correspond to the case of NMP TCNQ and Qn TCNQ_2 at room temperature. However because of the different thermodynamic properties, the quantity $\langle S_Q^+ S_{-Q}^- \rangle$ (Eq. 2) and the diffusion constant D are expected to have a stronger temperature dependence.

References

1. Ahmed-Bakheit, Barjhoux, Ferrieu, Nechtschein, and Boucher, *Solid State Com.*, **15**, 25 (1974); Boucher, Ferrieu, and Nechtschein, *Phys. Rev. B*, **9**, 3871 (1974); Borsa and Mali, *Phys. Rev. B*, **9**, 2215 (1974); Ferrieu, *Phys. Lett.*, **49A**, 253 (1974); Devreux and Nechtschein, *Solid State Com.*, **16**, 275 (1975).
2. Ehrenfreund, Etemad, Coleman, Rybaczewski, Garito, and Heeger, *Phys. Rev. Lett.*, **29**, 269 (1972).
3. Ehrendreund, Rybaczewski, Garito, and Heeger, *Phys. Rev. Lett.*, **28**, 873 (1972).
4. Moriya, *J. Phys. Soc. Jap.*, **18**, 516 (1963).
5. Izuyama, Kim, and Kubo, *J. Phys. Soc. Jap.*, **18**, 1025 (1963).
6. Hone et Pincus, *Phys. Rev. B.*, **7**, 4889 (1973).
7. Villain, to be published in *Solid State Com.*
8. Devreux, *J. Phys. C*, B. L 132 (1975).
9. Kubo and Tomita, *J. Phys. Soc. Jap.*, **9**, 888 (1954); Reiter, *Phys. Rev. B*, **7**, 3325 (1973).