ture, and magnetic field intensity.

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Charge Transport in the Organic Conductor Quinolinium Ditetracyanoquinodimethanide [Qn(TCNO)$_2$]

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Proton spin-lattice relaxation-time (T_1) measurements are reported in pure and in neutron-irradiated organic conductor Qn(TCNQ)$_2$. The diffusion constant D (evaluated from T_1) and conductivity σ have the same dependence on the irradiation-induced impurity concentration, showing that charge propagation is responsible for the relaxation time. The temperature dependence of D, when compared with $\sigma(T)$, suggests that the conductivity is determined by the temperature-dependent mobility.

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In spite of considerable effort, charge transport in organic, highly anisotropic conductors is only poorly understood, and various models have been proposed to account for the temperature dependence of the conductivity $\sigma(T)$ in various materials. Qn(TCNQ)$_2$ is a member of the TCNQ salts,[1] which show metalliclike conductivity at high temperatures, followed by a broad maximum and decreasing σ with decreasing temperatures. This behavior was suggested to be due to a smeared metal-to-insulator transition,[2] to a small-band-gap semiconductor type of behavior[3] where $\sigma = \mu n e$ with the number of carriers n increasing exponentially with temperature and μ strongly decreasing with increasing T. A model based on the effect of disorder[4] accounts for $\sigma(T)$ through a temperature-dependent mobility.

In this paper we discuss proton NMR relaxation experiments, T_1, in pure and also in neutron-irradiated Qn(TCNQ)$_2$. We argue that T_1 is determined by the charge diffusion, and is thus directly related to the conductivity. We also show that σ and the diffusion constant have a similar temperature dependence, strongly suggesting that the carrier concentration is only weakly dependent on temperature.

The proton spin-lattice relaxation rate is given by[5]

$$T_1^{-1} = \Omega^z F(\omega_N) + \Omega^+ F(\omega_e),$$
$$F(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle s^z(t) s^z(0) \rangle, \tag{1}$$

where $\Omega^z = \frac{3}{5} d^2$ and $\Omega^+ = a^2 + \frac{7}{5} d^2$ are coupling constants, reflecting hyperfine, a, and dipolar, d, electron-nuclear coupling; ω_N and ω_e are the nuclear and electronic frequencies. The spin correlation function $\langle s^z(t) s^z(0)\rangle$ depends on the dimensionality of the diffusion. For one-dimensional (1D) diffusion, $\langle s^z(t) s^z(0)\rangle \sim (Dt)^{-1/2}$, where D is the diffusion constant, while for 3D diffusion $\langle s^z(t) s^z(0)\rangle \simeq (Dt)^{-3/2}$. This leads, through Eq. (1), to a strongly frequency-dependent T_1 for 1D diffusion,[5,6] and T_1 nearly independent of ω for a 3D diffusion process. The spin-lattice relaxation rate samples the propagation of spins, times the effective number of spins, and can be rewritten as

$$[kT\chi(T)T_1(\omega_e)]^{-1} = (\Omega^z + \Omega^+)f_2 + \Omega^z f_1(0) + \Omega^+ f_1(\omega_e), \qquad (2)$$

where the normalized susceptibility $\chi(T)$ can be obtained from the measured susceptibility χ_m by

$$\chi(T) = \chi_m(T)/Ng^2\mu_B^2.$$

f_2 is independent of ω, and for 1D diffusion $f_1(\omega) = a_0(2D\omega)^{-1/2}$, where a_0 is the lattice constant, while $f_1(0)$ reflects the 3D cutoff effects.[6,7] In Qn(TCNQ)$_2$ charge transfer is complete[8]; the Qn molecules have closed electron shells; therefore all contribution to spin magnetism comes from electrons on the TCNQ chains. The frequency dependence of T_1 was shown to be well described by Eq. (2) between $\omega_N = 340$ and 4 MHz at room temperature.[7] The diffusion constant D may reflect charge diffusion and this is related to the conductivity, or spin diffusion determined by exchange coupling between localized spins. Also, when nuclear relaxation is caused by paramagnetic impurity spins[9] T_1 is proportional to $\omega^{-1/2}$. Available experiments on Qn(TCNQ)$_2$ and on other low-dimensional conductors[7] are not able to distinguish between these possibilities. Impurities introduced by neutron irradiation have a drastic influence on the conductivity[10] of Qn(TCNQ)$_2$ while the high-temperature susceptibility[11,12] remains unaffected. The correlation of the diffusion constant D with transport or magnetic properties therefore allows the main contribution to the diffusion to be evaluated.

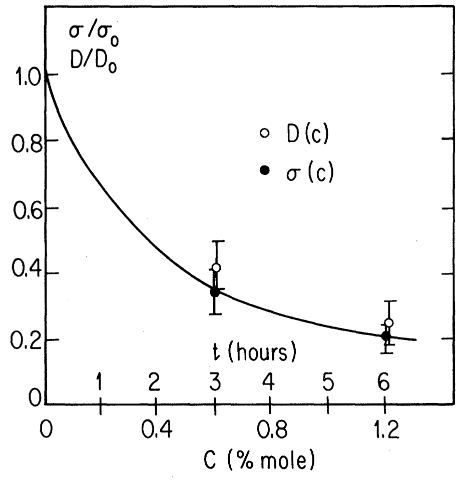

FIG. 1. Frequency dependence of the proton spin-lattice relaxation time at room temperature on pure and irradiated Qn(TCNQ)$_2$. The full lines represent Eq. (2) with $f_1(\omega) \simeq a_0/(2D\omega)^{1/2}$ characteristic to 1D diffusion.

Neutron irradiation was performed in the reactor Melusine of the Centre d'Etudes Nucléaires de Grenoble (neutron flux 1.4×10^{14} n/sec) for times of 3 and 6 h. Care has been taken to keep the sample temperatures below 60 °C to avoid damage due to excessive heating. The spin-lattice relaxation time T_1 is shown in Fig. 1. for pure and irradiated Qn(TCNQ)$_2$ in the usual, $\omega^{-1/2}$, representation. $T_1(\omega)$ can be represented well by a $\omega^{-1/2}$ behavior in the measured frequency range and we suggest that the major effect of irradiation is to reduce the on-chain diffusion coefficient. A fit of the experimental data by Eq. (2) with $f_1(\omega) = a_0(2D\omega)^{-1/2}$ leads to the concentration dependence of the diffusion constant. Figure 2 shows D/D_0 and σ/σ_0 (the latter measured on a single crystal) as a function of the irradiation time. The relation between irradiation time and impurity concentration c [per formula unit Qn(TCNQ)$_2$] has been derived before[10]; we believe that c values shown in Fig. 2 are accurate within a factor of 2. The full line of Fig. 2 represents a linear increase of the inverse diffusion coefficient, as suggested by studies for spin diffusion in impure Heisenberg chains[13]:

$$D(c)^{-1} = D^{-1}(0) + c\tilde{D}^{-1}, \qquad (3)$$

where $D(0)$ is the diffusion coefficient of the pure sample and $\tilde{D}$ represents an effective diffusion

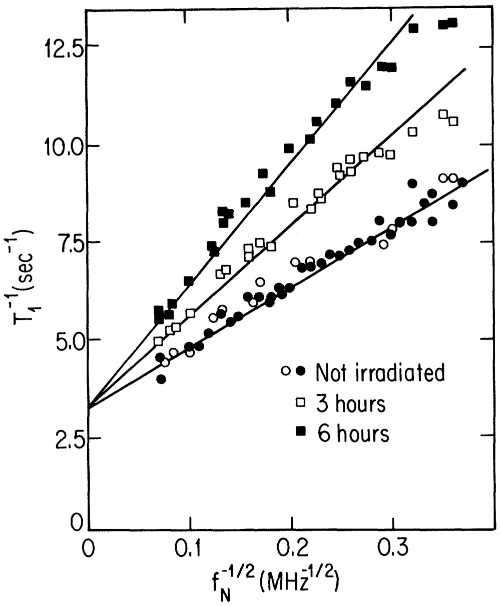

FIG. 2. Concentration dependence of σ and D at room temperature. $\sigma = 100\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and $D = 0.10$ cm^2/sec for the pure sample. The full line is a fit by Eq. (3) with parameters given in the text.

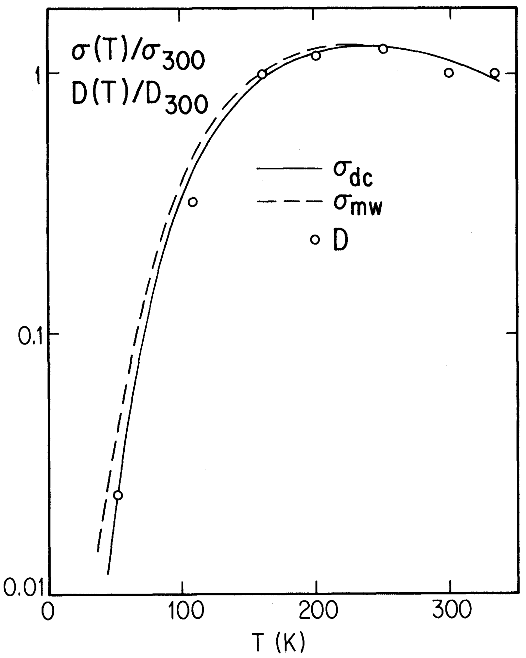

FIG. 3. Temperature dependence of σ and D in pure Qn(TCNQ)$_2$. dc and mw refer to static and microwave conductivity.

constant due to impurities. The full line of Fig. 1 is a fit by Eq. (3) with parameters $D(0) = 0.1$ cm^2/sec (see below) and $\tilde{D} = 2.4\times10^{-4}$ cm^2/sec.

Recent experiments on irradiated Qn(TCNQ)$_2$ show that the magnetic susceptibility does not change upon irradiation at high temperatures.[11,12] This gives direct evidence that localized spins are not created by irradiation and the concentration dependence of T_1 is not due to relaxation caused by localized spins. When D is determined by spin diffusion the decrease of D occurs through decreased exchange couplings I between spins and this in turn would lead to a susceptibility which increases with irradiation. In the strong-coupling limit $D = I/\hbar$ (Ref. 7) and the magnetic susceptibility is given by the Bonner-Fisher expression with y on the order of 300 K for the pure sample.[14] The observed change in D, when related to a decrease of the average exchange constant I, would lead to an approximately 20% increase of the high-temperature susceptibility for 6-h irradiation, in contrast to what is observed. D, however, has the same concentration dependence as the conductivity, as expected for charge diffusion (see below). We conclude, therefore, that D measured by T_1 is determined by charge diffusion in Qn(TCNQ)$_2$.

To determine the temperature dependence of the charge diffusion, we have measured $T_1(\omega)$ at different temperatures in pure Qn(TCNQ)$_2$. At temperatures between 50 and 300 K, the relaxation time can be represented by $T_1^{-1} = A + B\omega^{-1/2}$, as given by Eq. (2), between 200 and 6 MHz.[7] D evaluated by use of Eq. (2) and the measured susceptibility[12] is shown in Fig. 3 together with the dc and microwave conductivity.[15] The main feature of Fig. 3 is clear: The temperature dependence of D and σ is similar, suggesting strongly that $\sigma(T)$ is determined mainly by a temperature-dependent diffusion; the temperature dependence of the number of carriers does not play a significant role. The behavior of the diffusion constant is in clear contrast to that predicted by a semiconductor model.[3] The conductivity when fitted by $\sigma(T) = \mu(T)\exp(\Delta/kT)$ leads to $\Delta/k = 600$ K and $\mu(T) = AT^{-2.5}$. This predicts a mobility which *increases* by a factor of 90 when temperature is lowered from 300 to 50 K while the diffusion constant *decreases* by more than an order of magnitude in this temperature range. In case of a gradual metal-insulator transition,[2] accompanied by a gap opening at the Fermi level, $\sigma(T)$ reflects mainly the decrease of the number of carriers and consequently the mobility has a temperature dependence different from that of the conductivity. We suggest therefore that these models are not appropriate to describe the charge transport in Qn(TCNQ)$_2$ and similar organic conductors. On the other hand, the temperature dependence of the diffusion coefficient leads to a natural explanation of earlier findings: In the temperature range 150–300 K the slight maxima of the susceptibility of χ_m and diffusion coefficient D cancel each other giving rise to a pseudo-Korringa law, while the strong decrease of D below 150 K leads to an increase in T_1^{-1} originally attributed to impurities.[16] We note that the above relation between T_1 and σ is expected to break down at low temperatures where T_1 is determined by spin diffusion between localized spins.[17]

A detailed comparison of D and σ depends on the particular model by which the charge transport is described, and also on the underlying electron-electron and electron-phonon interactions. We can, however, evaluate an effective mean free path both from the diffusion constant and from the conductivity. For a 1D electron gas with weak Coulomb correlations the diffusion constant is given by[18,19]

$$D = V_F l^*(1-\alpha) \tag{4}$$

where $\alpha = Un(\epsilon_F)$, with U the on-site Coulomb interaction, V_F the Fermi velocity, and l^* the mean free path. The same approximation leads to the susceptibility $\chi = a_0/2\pi h V_F(1-\alpha)$. Thus,

$$l^*/a_0 = 2\pi h \chi D a_0^2 . \qquad (5)$$

While Eq. (5) is expected to be modified for strong Coulomb correlations, the magnetic susceptibility suggests that the intermediate-coupling limit is appropriate. As the enhancement factor α drops out of the expression, Eq. (5) provides an adequate initial basis to include the phase-space reduction of diffusing electrons due to interactions. With the coupling constants $a = 1.2$ G and $d = 0.6$ G,[20] and susceptibility $\chi_m(300) = 5.2\times10^{-4}$ emu/mole,[1] the diffusion constant is $D = 0.1$ cm^2/sec. With $a_0 = 3.3$ Å, Eq. (5) leads to an effective mean free path $l^* = 0.6a_0$ at room temperature. The conductivity leads to a mean free path

$$\frac{l}{a_0} = \frac{\pi h}{2e^2 a_0^2 N_c}\sigma , \qquad (6)$$

where N_c is the number of chains per unit volume, and $\sigma(300\text{ K}) = 10^2\ \Omega^{-1}\text{ cm}^{-1}$ leads to $l = 0.3a_0$. The good agreement between l^* and l further supports the close relation between D and σ.

In conclusion, we have shown that the proton nuclear spin-lattice relaxation time T_1 is determined by the charge diffusion of electrons of the TCNQ chains. Impurities depress the charge diffusion and conductivity, with barrier effects important only at low frequencies. The temperature dependence of the conductivity is determined mainly by the temperature-dependent mobility, with temperature-dependent carrier concentration playing only a secondary role. The origin of the temperature dependence of the mobility, shown in Fig. 3, is unclear. It may reflect disorder-induced localization with decreasing temperature[4,21] and also a Brownian motion of strongly interacting electrons in periodic potentials.[22] The strong frequency dependence of the conductivity[15] observed at low temperatures suggests that disorder effects are important, but further investigations are required to establish whether this effect is dominant also at temperatures around and above the conductivity maximum.

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