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Classification

Physics Abstracts

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NMR study of transport properties in pure and irradiated Qn TCNQ₂

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Résumé. — A l'aide de mesures de relaxation nucléaire des protons nous déterminons les coefficients de diffusion de spin parallèle et transverse dans des échantillons purs et irradiés par neutrons du conducteur organique Qn TCNQ₂. Une comparaison avec la conductivité montre que les propriétés de transport sont dominées par la dépendance thermique de la mobilité. A partir des mesures de RMN, nous donnons une estimation de l'anisotropie de la conductivité et nous discutons les mécanismes de conduction, ainsi que les effets des défauts créés par irradiation.

Abstract. — From proton nuclear relaxation measurements, we deduce the parallel and perpendicular spin diffusion coefficients in pure and neutron-irradiated 1D organic conductor Qn TCNQ₂. Comparison with conductivity data shows that the transport properties are determined by the temperature-dependent mobility. From our NMR results, we estimate the conductivity anisotropy, discuss the conduction mechanisms and the effects of irradiation induced defects.

1. Introduction. — Quinolinium di-tetracyanoquinodimethanide (Qn TCNQ₂) is one of the oldest known one-dimensional (1D) organic conductors [1]. With a parallel conductivity of $100 (\Omega \cdot \text{cm})^{-1}$ it is just under the borderline of metallic conduction at room temperature. Below a broad maximum around 250 K, the conductivity displays a semi-conducting behaviour at low temperature. Two factors could be responsible for this temperature dependence: the density of the charge carriers, or their mobility. Our previous proton nuclear relaxation studies [2-4] strongly favour the latter hypothesis by showing that the NMR-determined spin diffusion coefficient displays the same variation as the conductivity as a function of both temperature and irradiation-controlled defect concentration. Meanwhile, these results, as well as similar studies [5-8], established nuclear relaxation as an original method for the study of transport properties in these kinds of

materials. In this communication, we present new results concerning the anisotropy and the temperature dependence of the spin diffusion in pure and irradiated samples. These measurements provide an estimate of the anisotropy of the conductivity and give further information about the conduction mechanisms.

The determination of the spin diffusion coefficients is based upon the frequency dependence of the nuclear relaxation rate, which is given by [9]:

$$T_1^{-1} = \frac{3}{5} d^2 F(\omega_n) + (a^2 + \frac{7}{5} d^2) F(\omega_e) \quad (1)$$

$$F(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \langle s^z(t) s^z(0) \rangle$$

where d and a are the anisotropic and isotropic parts of the hyperfine coupling, and ω_n and ω_e the nuclear and electronic Larmor frequencies. The local spin correlation can be expressed as [2, 3]:

$$F(\omega) = kT\chi(f_1(\omega) + f_2) \quad (2)$$

where $kT\chi$ is the effective number of spins per molecule, which is related to the molar susceptibility

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χ_m by : $\chi_m = N(g\mu_B)^2 \chi$, f_2 is the frequency independent part of the normalized spin correlation function and $f_1(\omega)$ is the frequency-dependent contribution of the long wavelength diffusive modes. For an anisotropic diffusion with equivalent perpendicular directions, one has [2, 3] :

$$f_1(\omega) = (2 D_{\parallel} \omega)^{-1/2} \quad (3a)$$

in the 1D regime ($D_{\parallel} > \omega > D_{\perp}$) and :

$$f_1(\omega) = f_1(0) = (4 D_{\parallel} D_{\perp})^{-1/2} \quad (3b)$$

in the 3D regime ($\omega < D_{\perp}$). The diffusion rates D_i ($i = \parallel$ or \perp) are related to the corresponding diffusion coefficients by $\mathcal{D}_i = D_i a_i^2$, with a_i being the intersite distance in the i direction.

2. Intrachain diffusion. — In our previous work we measured the spin diffusion coefficient of pure samples as a function of the temperature [2, 3] and that of irradiated samples at room temperature only [4]. Furthermore, the study was limited to small irradiation doses. Here we extend the results by measurements on samples with higher irradiation doses and by studying the temperature dependence of their diffusion coefficient. Neutron irradiation was performed at the KFKI reactor in Budapest with a neutron flux of 3×10^{12} neutrons/cm².s for times of 5, 10, 15 and 20 h. Frequency dependence of T_1 was measured in the range 1-80 kG using conventional pulse NMR techniques for all samples at room temperature and as a function of the temperature for the pure and 20 h irradiated samples. The room temperature results are shown in figure 1. We observe a large increase in the relaxation rate with irradiation. As the room temperature susceptibility is not affected by irradiation [10, 11], this indicates a considerable slowing down of the spin motion. In figure 1, the nuclear relaxation rate has been plotted as a function of $H^{-1/2}$ to exhibit the 1D diffusion. In each case an almost straight line is obtained. However, the results display a slight downward curvature at high fields, especially for the more irradiated samples. From the slopes the parallel diffusion rate is calculated using equations (1) to (3) and assuming, as previously, that the observed frequency dependence arises from the $F(\omega_c)$ contribution. We take 2.6 emu/mole for the susceptibility per TCNQ mole [12], 1.2 G for the isotropic contact coupling of the TCNQ protons and 0.6 and 0.3 G for the anisotropic dipolar coupling of the TCNQ and Qn protons, respectively [13]. The values of the parallel spin diffusion coefficient are given in table I as a function of the defect concentration c , which has been estimated from the irradiation dose, according to reference [14].

To make a quantitative comparison between conductivity and NMR data, we have calculated the conductivity expected from our spin diffusion coefficient using the Einstein formula $\sigma = ne^2 \mathcal{D}/kT$ and taking for the effective carrier density $n = 4 kT\chi/V$,

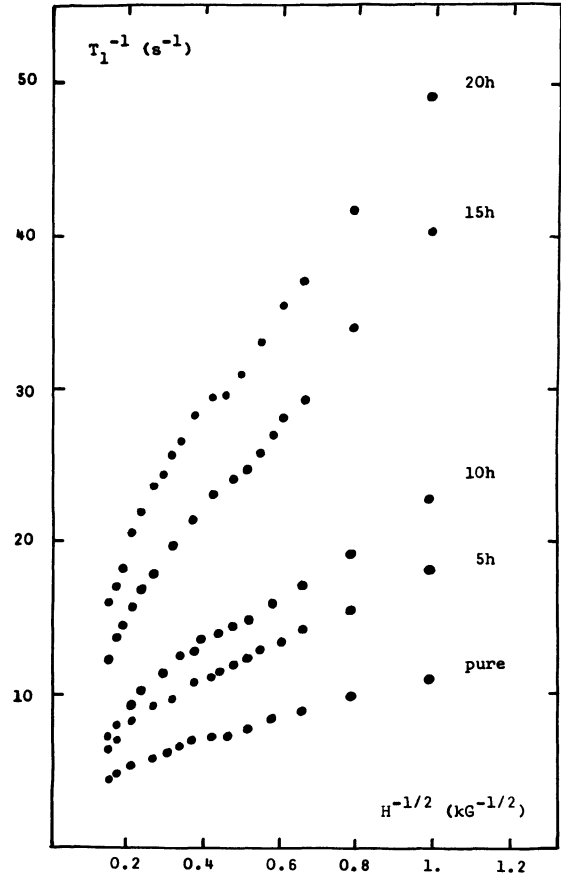


Fig. 1. — Proton nuclear relaxation rate as a function of the inverse square root of the magnetic field in pure and irradiated Qn TCNQ₂ samples at room temperature.

Table I. — Nuclear relaxation rate in the rotating frame and spin diffusion coefficients in pure and irradiated Qn TCNQ₂ at room temperature. $T_{1\rho}$ has been measured at 53.2 MHz.

Irradiation time	Pure	5h	10h	15h	20h
c (%)	0	1	2	3	4
$T_{1\rho}^{-1}$ (s ⁻¹)	123	109	91	56	42
\mathcal{D}_{\parallel} (10 ⁻² cm ² /s)	16	6.9	4.3	1.2	0.9
\mathcal{D}_{\perp} (10 ⁻⁵ cm ² /s)	{ 6 (from T_1) 8 (from $T_{1\rho}$)	4	3	1	0.5
$\mathcal{D}_{\parallel}/\mathcal{D}_{\perp}$	2 300	1 800	1 400	1 200	1 900

where χ is the previously defined reduced susceptibility and V the volume per TCNQ molecule. This corresponds to the degenerate Fermi gas model which is suggested by the parallel variation of σ and \mathcal{D} with temperature. However it should be noticed that the same relation applies to a correlated system within the mean field approximation since, in this case, the susceptibility is enhanced by the Stoner factor with respect to that of the non-correlated system $\chi = \chi_0/(1 - \alpha)$, while the spin diffusion coefficient is reduced by the same factor $\mathcal{D} = \mathcal{D}_0(1 - \alpha)$ [15]. Figure 2 shows the conductivity deduced from the NMR spin diffusion coefficient and the actually mea-

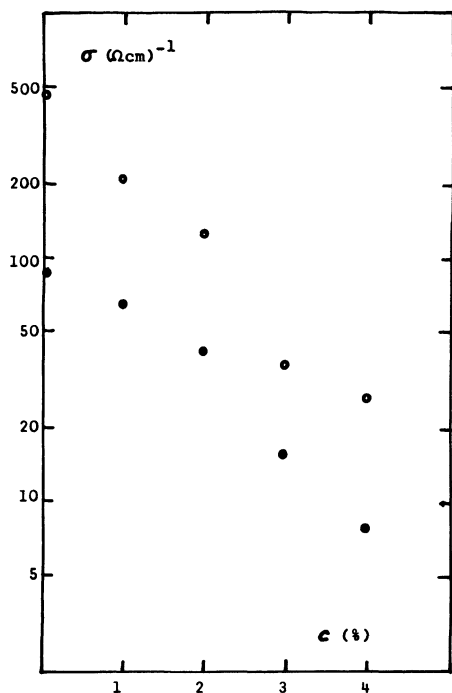


Fig. 2. — Comparison of the conductivity deduced from the NMR determined spin diffusion coefficient (○) and of the actually measured conductivity (●) as a function of the irradiation-controlled defect concentration in Qn TCNQ₂ at room temperature.

sured conductivity as a function of the defect concentration at room temperature. The conductivity has been measured on single crystals chosen in the samples which have been used for T_1 measurements. The impurity dependence of both quantities is similar. However the « NMR conductivity » is systematically about three times larger than the directly measured conductivity. This difference is even larger for the pure sample. Although the uncertainties are quite large for the measurement of the conductivity and for the determination of the spin diffusion coefficient from T_1 , the observed deviation is thought to be significant. It is *a priori* surprising that the « NMR conductivity » turns out to be the largest, because there exist interactions, such as the electron-electron coulombic repulsion, which contribute to the spin, but not to the charge momentum scattering [3, 16], so that they should result in a smaller diffusion rate for the spin than for the conducting charge. On the other hand, it has been suggested [3] that the difference could be accounted for by the fact that the conductivity is a macroscopic measurement, while T_1 is a local measurement, which would be expected to be less sensitive to dilute defects. This explanation is ruled out by the absence of frequency dependence of the conductivity at room temperature [14]. Thus it seems that our calculation of the conductivity from the spin diffusion coefficient overestimates the charge carrier density. This may be related to correlation effects, which are not fully taken into account within the mean field approximation.

Besides, the concentration dependence of the diffusion coefficient is much faster than the linear behaviour previously asserted from measurements in less irradiated samples [4]. This breakdown of Mattiessen's rule had been noticed long ago in 1D organic conductor studies [17]. Results in figure 2 are consistent with an exponential behaviour ($\sigma \propto \exp(-c/c_0)$ with $c_0 \simeq 1.6\%$), which has been observed in a number of 1D organic conductors by Zuppiroli *et al.* [18]. However other fits are possible, such as power laws ($\sigma \propto c^{-n}$ with $n \simeq 3$). The limited precision of our data does not allow us to decide between these different fits.

In figure 3 the temperature dependence of the spin diffusion coefficient is compared to the thermal variation of both continuous (d.c.) and microwave (mw) conductivity for the pure and 20h irradiated samples. The mw conductivity has been measured [14] at 9.1 GHz using the cavity perturbation method of Burarov and Shchegolev [19]. The similarity between the thermal variations of σ and \mathcal{D} has already been noticed [2-4]. It proves that the charge and the spin motion are closely related and suggests that there remains a finite, almost temperature-independent density of states at the Fermi level giving rise to an effective charge carrier density proportional to kT . As the microwave conductivity becomes markedly larger than the d.c. conductivity at low temperature, it is seen in figure 3 that the spin diffusion coefficient

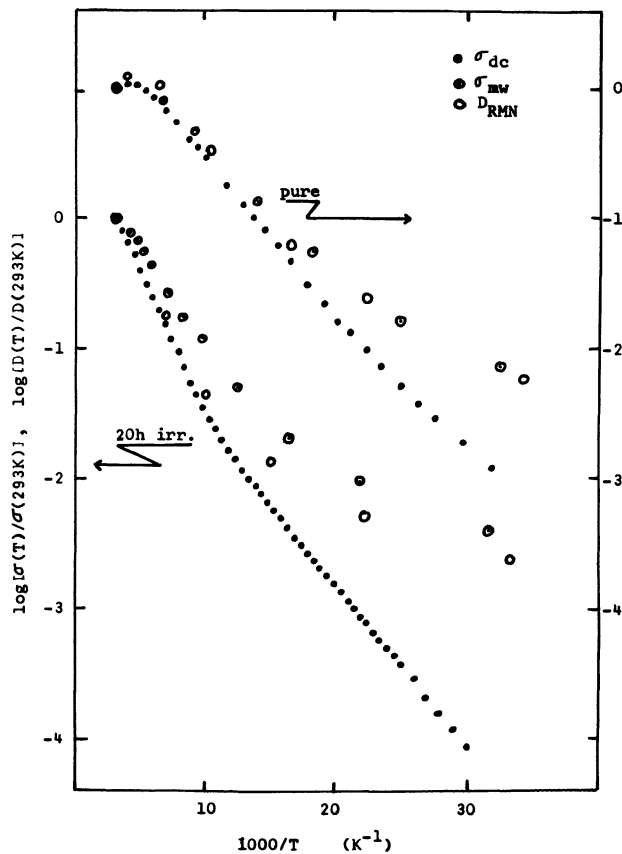


Fig. 3. — Temperature dependence of the spin diffusion coefficient and of the d.c. and mw conductivity in pure and 20h irradiated Qn TCNQ₂.

follows the mw conductivity rather than the d.c. This is consistent with the fact that the nuclear relaxation is a finite frequency measurement, namely, our measurement frequency is $\omega_c/2\pi$, which covers the 2.5-220 GHz range. This should be related to the frequency-dependent conductivity measurements by Holczer and Janossy [20] and by Alexander *et al.* [21], which show that, at low temperature, the conductivity increases from the d.c. value and tends to saturate above 100 MHz.

3. Interchain diffusion. — All the previously presented proton nuclear relaxation measurements in Qn TCNQ₂ were restricted to the 1-80 kG magnetic field range. Although they show the well-defined 1D $\omega^{-1/2}$ frequency dependence of T_1^{-1} , they fail to show the 3D low-frequency saturation predicted by equation (3b). Therefore, we have extended the frequency range toward low frequencies by using a field cycling method [22]. It consists of polarizing the nuclear spins in a given sufficiently large magnetic field, rapidly reducing the field to any smaller value, letting the spins relax in this field and then raising the field back to the previous value, where the NMR signal is observed. This method allows measurement of the nuclear relaxation in low field with sufficient sensitivity. In our experiment, the polarization and observation field was 4.5 kG and the time to change the field up and down was less than 15 ms [23]. The results for pure Qn TCNQ₂ are shown in figure 4, together with the relaxation rates measured with conventional pulse techniques. The whole field range runs from 100 G to 80 kG. The agreement between both kinds of measurements in the common field range is excellent. When plotted as a function of $H^{-1/2}$ (Fig. 4), the nuclear relaxation rate displays the expected behaviour for an anisotropic diffusion with equivalent perpendicular directions (Eq. 3). The arrangement of the TCNQ molecules in the plane perpendicular to the chain axis [24] is consistent with the absence of preferential direction in this plane. From the cross-over between 1D and 3D regimes, we get the perpendicular diffusion rate $D_{\perp} = 7 \times 10^9$ rad./s, which leads to

$$\mathcal{D}_{\perp} = 6 \times 10^{-5} \text{ cm}^2/\text{s}$$

taking for a_{\perp} the mean distance between TCNQ chains [24]. Thus, one is led to predict for the conductivity anisotropy :

$$\frac{\sigma_{\parallel}}{\sigma_{\perp}} = \frac{\mathcal{D}_{\parallel}}{\mathcal{D}_{\perp}} \simeq 2\,500.$$

This result is in strong disagreement with value published, ten years ago, by Sakai *et al.* [25], who give a room temperature perpendicular conductivity of $10 (\Omega \cdot \text{cm})^{-1}$. However, more recent measurements seem to give a much higher anisotropy [26]. In fact, owing to the thin needle shape morphology of Qn TCNQ₂ crystals, it is probably very difficult to

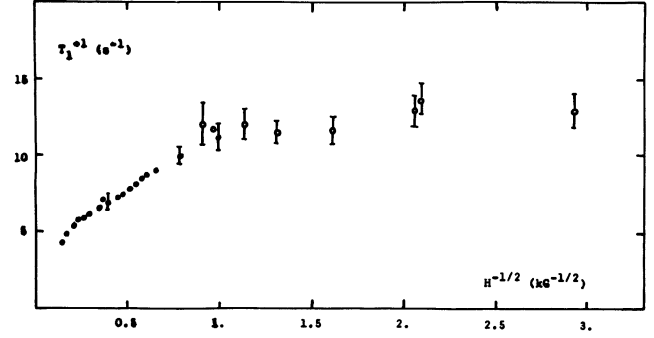


Fig. 4. — Proton nuclear relaxation rate as a function of $H^{-1/2}$ in pure Qn TCNQ₂ at room temperature as measured with conventional pulse technique (●) and field cycling method (○).

measure accurately the transverse conductivity. The proposed $\sigma_{\parallel}/\sigma_{\perp}$ value sets Qn TCNQ₂ as a rather good 1D compound, better than TTF TCNQ but less anisotropic than KCP. This is consistent with the absence of any long range order in Qn TCNQ₂ down to very low temperature [27].

In irradiated samples the nuclear relaxation time cannot be obtained by using the field cycling apparatus because T_1 becomes of the order of the dead time caused by field switching. Therefore, we have measured the proton nuclear relaxation time in the rotating frame $T_{1\rho}$, which gives low-frequency information independent of that given by T_1 . It is expressed as [9] :

$$T_{1\rho}^{-1} = \frac{1}{2}(a^2 + \frac{4}{5}d^2)F(\omega_1) + \frac{3}{10}d^2F(\omega_n) + \frac{1}{2}(a^2 + \frac{13}{5}d^2)F(\omega_c) \quad (4)$$

where ω_1 is the nuclear Larmor frequency in the rotating field. Thus, taking advantage of

$$F(\omega_n) = F(\omega_1) = F(0),$$

a combined measurement of T_1 and $T_{1\rho}$ at a given frequency gives both $F(\omega_c)$ and $F(0)$. From $F(0)$ and D_{\parallel} , it is possible to calculate D_{\perp} . The room temperature values of $T_{1\rho}$ at $\omega_n/2\pi = 53.2$ MHz in pure and irradiated samples and the corresponding perpendicular diffusion coefficient are given in table I. It should be noticed that the uncertainty in $T_{1\rho}$ measurement is rather large (about 30 %), especially for values exceeding 100 ms. Thus, as the determination of \mathcal{D}_{\perp} is rather sensitive to the value of $T_{1\rho}$, the results for \mathcal{D}_{\perp} given in table I should be considered only as giving the order of magnitude. However, the agreement between the two determinations of \mathcal{D}_{\perp} in the pure sample (from $T_{1\rho}$ and from the low-frequency saturation of T_1) is quite good and leads us to have some confidence in the results. It is seen in table I that the perpendicular diffusion decreases with the defect concentration, yielding an almost constant anisotropy within the experimental errors.

4. Discussion. — Let us now discuss the consequences of our findings as they concern the conduction mechanisms in Qn TCNQ₂. Our new results confirm and reinforce our previous observation that the spin diffusion coefficient and the conductivity vary in a similar way with respect to both temperature and defect concentration. It is difficult to imagine that such a similarity is just accidental, more especially taking into account that the spin susceptibility is practically insensitive to temperature and defects in the considered temperature range. One thus concludes that the conductivity is dominated by temperature-dependent mobility and that the mechanisms which limit the spin diffusion are the same as those which limit the charge transport. In particular, this rules out any model in which the temperature dependence of the conductivity is due to an activated number of charge carriers related to a permanent or low-temperature gap [28]. However, the quantitative comparison between the spin diffusion coefficient and the conductivity shows that the simple band model overestimates the charge carrier density. There is no evident explanation for this fact, although it may be related to correlation effects, which have been shown to be important in this material [29].

As concerns the effect of irradiation, there are two major results : the strong dependence of the parallel conductivity and the approximate independence of the anisotropy with respect to defect concentration. These two results have been accounted for in other 1D organic conductors by Zuppiroli *et al.* [18], who assume that both parallel and perpendicular conductivities are controlled in irradiated samples by transverse phonon-assisted fixed range hopping. In that model, the irradiation-induced defects break the chains and modulate the energy of the isolated segments. The width of the energy distribution is proportional to the defect concentration : $\Delta E = \varepsilon c$. The electron diffusion is governed by phonon-assisted hopping between segments of neighbouring chains. This process requires an energy ΔE and gives rise to an activated hopping rate $W = W_{\perp}^0 \exp(-\varepsilon c/kT)$, which explains the exponential variation of the conductivity with respect to both c and T^{-1} in irradiated materials. This model cannot be applied just as it is in Qn TCNQ₂, where our NMR technique measures the intrachain 1D diffusion. However, as Qn TCNQ₂ seems to be a very good 1D system, it can be thought [30] that the dominant process for the parallel conductivity is the phonon-assisted hopping through the damaged molecules within the chains rather than between the weakly coupled neighbouring chains. Using the same arguments as before, this would again give for D_{\parallel} and D_{\perp} an exponential dependence on c and thus an anisotropy independent of the defect concentration.

The last question concerns the mobility in pure Qn TCNQ₂. Several theories of the conductivity in 1D disordered conductors have been proposed. A calculation by Gogolin *et al.* [31, 32] is based upon a phonon-assisted hopping between localized states; it gives : $\mathcal{D}_{\parallel} = W_{\text{ph}} l^2$ where W_{ph} is the phonon-induced transition probability and l the localization length due to both static (defects, impurities) and dynamic [33] (phonons) disorder. Within the usual kinetic theory one has :

$$W_{\text{ph}} = 2 \pi \lambda kT/\hbar \quad (5)$$

where λ is the dimensionless electron-phonon coupling and $l = v_{\text{F}} \tau$, where v_{F} is the Fermi velocity, and τ the scattering time which results from phonon and impurity scatterings : $\tau^{-1} = \tau_{\text{ph}}^{-1} + \tau_{\text{i}}^{-1}$. The impurity scattering rate is given by :

$$\tau_{\text{i}}^{-1} = 2 \pi c_{\text{i}} \Delta^2 n(E_{\text{F}})/\hbar \quad (6)$$

where c_{i} and Δ are the impurity concentration and potential, respectively, and $n(E_{\text{F}})$ is the density of states at the Fermi level. Moreover Abrikosov and Ryzhkin [34, 35] remarked that only a fraction of these transitions are possible because the phonon energy is generally smaller than the energy distribution of the localized states, which is of the order of $\hbar\tau^{-1}$. Accordingly, they introduce a reduction factor $\omega_{\text{D}} \tau$, where ω_{D} is the Debye frequency, which changes the diffusion coefficient to $\mathcal{D}_{\parallel} = W_{\text{ph}} l^2 (\omega_{\text{D}} \tau)$ when $\omega_{\text{D}} \tau < 1$. This theory has the advantage of reproducing the broad conductivity maximum [36] which occurs for $\tau_{\text{i}} \simeq \tau_{\text{ph}}(T)$, but it fails to explain the thermally activated behaviour at low temperature. However, it should be noticed that the calculation is limited to the weak scattering case ($\hbar\tau^{-1} < kT$). When this condition breaks down, either for large impurity potential or concentration, or at low temperature, the width of the energy distribution of the localized states becomes too large and it is likely that thermally activated phonons are required, as in Zuppiroli's model [18]. It is thus tempting to propose a unified picture for both pure and irradiated Qn TCNQ₂, in which the transport properties are dominated by phonon-assisted hopping between localized states. These hoppings can be activated or non-activated depending on the width of the energy spectrum of the localized states ($\hbar\tau^{-1} = \varepsilon c$) relative to the thermal energy. Activated behaviour is expected at low temperature and for high defect concentration or strong impurity potentials such as those due to irradiation induced defects. In particular, this would explain that the conductivity maximum is displaced toward higher and higher temperatures with increasing irradiation dose until the conductivity becomes activated in the whole temperature range [14].

References

- [1] KEPLER, R. G., BIERSTEDT, P. E. and MERRIFIELD, R. E., *Phys. Rev. Lett.* **5** (1960) 503.
- [2] DEVREUX, F. and NECHTSCHHEIN, M., *Lecture Notes in Physics* **95** (1979) 145.
- [3] DEVREUX, F., Thesis, Grenoble (1979) unpublished.
- [4] DEVREUX, F., NECHTSCHHEIN, M. and GRUNER, G., *Phys. Rev. Lett.* **45** (1980) 53.
- [5] SODA, G., JÉROME, D., WEGER, M., ALIZON, J., GALLICE, J., ROBERT, H., FABRE, J. M. and GIRAL, L., *J. Physique* **38** (1977) 931.
- [6] EHRENFREUND, E. and HEEGER, A. J., *Solid State Commun.* **24** (1977) 29.
- [7] EHRENFREUND, E. and NIGREY, P. J., *Phys. Rev. B* **21** (1980) 48.
- [8] SHAFFHAUSER, T., ERNST, R. R., HILTI, B. and MAYER, C. W., *Phys. Rev. B* **24** (1981) 76.
- [9] DEVREUX, F., BOUCHER, J. P. and NECHTSCHHEIN, M., *J. Physique* **35** (1974) 271.
- [10] MILZAK, M., KORIN, B., COOPER, J. R., HOLCZER, K., GRUNER, G. and JANOSSY, A., *J. Magn. Magn. Mat.* **15-18** (1980) 215.
- [11] SANNY, J., GRUNER, G. and CLARK, W. G., *Solid State Commun.* **35** (1980) 657.
- [12] BULAEVSKII, L. N., ZVARYKINA, A. V., KARIMOV, Y. S., LYUBOVSKII, R. B. and SHCHEGOLEV, I. F., *Sov. Phys. JETP* **35** (1972) 384.
- [13] DEVREUX, F., JEANDEY, Cl., NECHTSCHHEIN, M., FABRE, J. M. and GIRAL, L., *J. Physique* **40** (1979) 671.
- [14] HOLCZER, K., GRUNER, G., MIHALY, G. and JANOSSY, A., *Solid State Commun.* **31** (1979) 145.
- [15] LUTHER, P. and FULDE, A., *Phys. Rev.* **170** (1968) 570.
- [16] LYO, S. K., *Phys. Rev. B* **24** (1981) 6253.
- [17] CHIANG, C. K., COHEN, M. J., NEWMAN, P. R. and HEEGER, A. J., *Phys. Rev. B* **16** (1977) 5163.
- [18] ZUPPIROLI, L., BOUFFARD, S., BECHGAARD, K., HILTI, C. and MAYER, C. W., *Phys. Rev. B* **22** (1980) 6035.
- [19] BURAROV, L. I. and SHCHEGOLEV, I. F., *Prib. Tek. Eksp.* **4** (1971) 171.
- [20] HOLCZER, K. and JANOSSY, A., *Solid State Commun.* **26** (1978) 689.
- [21] ALEXANDER, S., BERNASCONI, J., SCHNEIDER, W. R., BILLER, R., CLARK, W. G., GRUNER, G., ORBACH, R. and ZETTL, A., *Phys. Rev. B* **24** (1981) 7474.
- [22] ANDERSON, A. G. and REDFIELD, A. G., *Phys. Rev.* **116** (1959) 583.
- [23] ANDREANI, R., Thesis, Grenoble (1975) unpublished.
- [24] KOBAYASHI, H., MARUMO, F. and SAITO, Y., *Acta Crystallogr. B* **27** (1971) 373.
- [25] SAKAI, N., SHIROTANI, I. and MINOMURA, S., *Bull. Chem. Soc. Japan* **45** (1972) 3314.
- [26] GRUNER, G., private communication.
- [27] BOZLER, H. M., GOULD, C. M. and CLARK, W. G., *Phys. Rev. Lett.* **45** (1980) 1303.
- [28] EPSTEIN, A. J. and CONWELL, E. M., *Solid State Commun.* **24** (1977) 627.
- [29] CHAIKIN, P. M., KWAK, J. F. and EPSTEIN, A. J., *Phys. Rev. Lett.* **42** (1979) 1178.
- [30] MIHALY, G., BOUFFARD, S., ZUPPIROLI, L. and BECHGAARD, K., *J. Physique* **41** (1980) 1495.
- [31] GOGOLIN, A. A., MEL'NIKOV, V. I. and RASHBA, E. I., *Sov. Phys. JETP* **42** (1976) 168.
- [32] GOGOLIN, A. A., MEL'NIKOV, V. I. and RASHBA, E. I., *Sov. Phys. JETP* **45** (1977) 330.
- [33] MADHUKAR, A. and COHEN, M. H., *Phys. Rev. Lett.* **38** (1977) 85.
- [34] ABRIKOSOV, A. A. and RYZHKIN, I. A., *Solid State Commun.* **24** (1977) 319.
- [35] ABRIKOSOV, A. A. and RYHKIN, I. A., *Adv. Phys.* **27** (1978) 147.
- [36] GOGOLIN, A. A., ZOLOTUKHIN, S. P., MEL'NIKOV, V. I., RASHBA, E. I. and SHCHEGOLEV, I. F., *JETP Lett.* **22** (1975) 278.
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