

## TEMPERATURE DEPENDENCE AND ANISOTROPY OF THE HOLE DRIFT MOBILITY IN MONOCLINIC TETRACYANOETHYLENE

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The tensor of the hole drift mobility is determined in monoclinic tetracyanoethylene by the transient photoconductivity technique. The principal tensor components amount to  $\mu_1 = 0.21$ ,  $\mu_2 = 0.10$  and  $\mu_3 = 0.15$  cm<sup>2</sup>/V s at room temperature. Above 250 K the mobility is a decreasing function of temperature and follows an  $\exp(E/kT)$  dependence ( $E = 0.08$  eV) which is inconsistent with both band and hopping models. Below 250 K the mobility is controlled by a hole trapping level of 0.28 eV deep. The photogeneration efficiency is found to be independent of temperature and proportional to the light intensity.

### 1. Introduction

The understanding of charge transport in molecular crystals is still incomplete despite of a number of both experimental and theoretical studies hitherto reported. Much of the theoretical interest has been the temperature dependence of the charge carrier mobility in those materials. The scarcity of reliable mobility data measured over a wide temperature range renders it difficult to test the validity of different theoretical models.

The most extensively studied organic crystals have been polyacenes and their derivatives, especially anthracene and naphthalene. It is only recently that a careful study of the electron mobility in naphthalene [1] revealed an unexpected behaviour at low temperatures giving an impetus to theoretical speculations [2, 3]. In order to get further insight into the problem of charge transport in molecular crystals, extensive studies of a wider range of substances are needed.

The measurements of the mobility are hindered as a rule by the predominance of trapping effects which may drastically reduce the value of the observed mobility and alter its temperature dependence or even render the measurement

impossible. Unfortunately, it is not always clear whether the observed temperature dependence of the mobility is an intrinsic property of the crystal or is affected by trapping states.

The aim of the present paper is to report on the transport of holes in monoclinic tetracyanoethylene (TCNE) studied by the transit time technique. TCNE is known as one of the strongest acceptors forming numerous molecular complexes with various organic donors, little is known, however, about the electrical properties of TCNE itself. It should be noted that the relative simplicity of the TCNE molecule makes it a promising object of theoretical studies.

Two crystallographic modifications of TCNE have been reported; the high temperature phase is monoclinic [4], P<sub>2</sub><sub>1</sub>/n with two molecules per unit cell whereas the low temperature phase is cubic [5], Im3 with six molecules per unit cell. The transition between these two phases is extremely sluggish so that cubic crystals may be easily overheated well above the transition temperature – 292 K and monoclinic crystals can be supercooled down to 77 K without any discernible change in perfection of the crystal [6].

## 2. Experimental

Commercial TCNE was purified by a multiple vacuum sublimation through a layer of activated carbon. Faceted single crystals of monoclinic TCNE were grown by a slow sublimation at ca. 330 K. The crystals were large enough to cut several differently oriented plates with a wire saw. Typical dimensions of the samples were 0.3–1 cm<sup>2</sup> in area and 1 mm in thickness. The crystal plates were polished using various solvents, usually ethyl acetate. It has been found that the mobility values were not affected by this treatment whereas both the magnitudes and shapes of photocurrent pulses depended on the solvent applied.

The mobility measurements were carried out employing the standard "time-of-flight" technique. The sample was mounted between a transparent (SnO<sub>2</sub> coated quartz) front electrode and a brass plate which served as the rear electrode. Short polychromatic light pulses (ca. 1 μs) were generated by a discharge of a 44 nF capacitor through a quartz capillary tube. The exciting light was passed by a cut-off filter to eliminate radiation of energy higher than 4.7 eV which could give rise to spurious photocurrents due to photoemission from electrodes. Current pulses were fed into a wide band preamplifier (input resistance 200 kΩ, overall time constant ≈ 0.6 μs, noise less than 1 × 10<sup>-9</sup> A) and displayed on an oscilloscope screen.

Photocurrents could be observed for both the positively and negatively biased front electrodes. The shapes of the oscilloscope traces (cf. fig. 1) and observed transit times for both polarities were practically the same. This put in doubt our initial conjecture that hole and electron currents were observed. The shapes of the transients suggest the surface generation of the charge carriers, whereas, on the other hand, it is known [7] that TCNE is transparent to the light used in our experiment. Thus, it was necessary to establish which type of charge carriers was involved.

As the magnitude of the photocurrent depends strongly on the way the sample surface has been prepared, we have performed a series of experiments in which the surface was treated with solutions of various complexing agents (aromatic hydrocarbons, amines etc.). When one of the crystal faces was

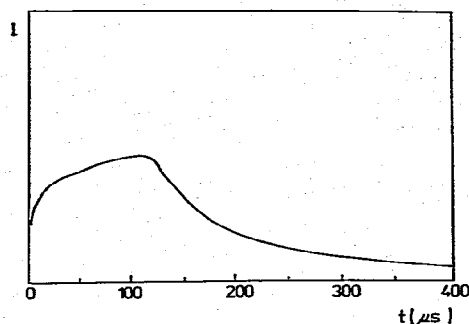


Fig. 1. Typical example of a photocurrent transient. Sample thickness = 0.96 mm,  $T = 271$  K, voltage applied = 350 V.

treated with a cyclohexane solution of pyridine a dark, non-transparent layer of the reaction product was formed. With this surface illuminated only positive photocurrents could be observed, the transit times being identical to those recorded for the non-treated sample. Hence, we infer that the charge carriers involved are holes, the generation of which is enhanced by the presence of surface reaction products. Apparently, electrons cannot be injected from this layer. The negative photocurrents could have been produced by holes photogenerated at the rear surface, as it is the case for non-treated samples, if it were not for the complete absorption of light in the dark surface layer.

On the other hand, the treatment with a cyclohexane solution of fluorene made it possible to see a kink in the tail of the dominant hole signal. This kink has been attributed to the transit of electrons generated at the rear sensitized surface. The mobility of electrons has been estimated to be about half of that of holes.

## 3. Results and discussion

### 3.1. Charge-carrier generation

To the best of our knowledge, the energetic structure of the TCNE crystal is unknown; therefore it is difficult to arrive at any definite conclusions concerning the charge generation mechanism. In order to get some insight into the processes involved

we have made a study of the light intensity, electric field and temperature dependences of the generation efficiency.

The collected charge is proportional to the light intensity (fig. 2) which precludes biphotonic and/or bimolecular generation paths. A typical example of the electric field dependence is shown in fig. 3. At low fields the dependence is sublinear whereas it becomes superlinear at higher fields, the magnitude of the electric field at which the transition occurs varying from sample to sample. Similar behaviour is predicted by the Onsager theory of charge separation [8–10]. However, our results do not comply with the universality of the “slope-to-intercept” ratio as expected by the theory.

The photogeneration efficiency has been found to be practically temperature independent (fig. 4). Such behaviour is uncommon for organic materials in which, as a rule, the photogeneration of charges involves activation steps.

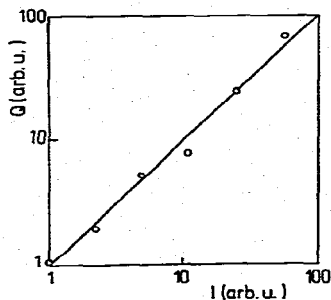


Fig. 2. Light intensity dependence of the collected charge. Sample thickness = 0.76 mm, voltage applied = 1600 V.

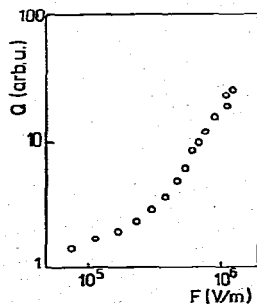


Fig. 3. Electric field dependence of the collected charge. Sample thickness = 0.76 mm.

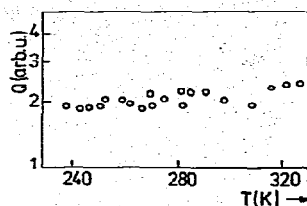


Fig. 4. Temperature dependence of the collected charge. Sample thickness = 0.76 mm, voltage applied = 500 V.

As can be seen from fig. 1 there is a delay in the generation of holes reflected by a relatively slow increase of the initial current. This delay has been found to be almost independent of temperature. Hence, the following mechanism can be suggested. The exciting light is absorbed either by impurities or by TCNE molecules due to the forbidden singlet-triplet transition. Subsequent creation of electron-hole pairs results from interactions between excited molecules and surface impurities which act as electron traps. The delay is due to the migration of triplet excitons to the surface. One should note that shallow trapping of holes in the surface region may also lead to a slow build-up of the current signal [11, 12], however, in this case a strong temperature dependence of the current rise should be observed.

### 3.2. Temperature dependence of hole mobility

The temperature dependences of the mobility of holes have been determined for eleven differently oriented samples cut from two large single crystals. Some typical results are presented in fig. 5. At low temperatures the mobility is an increasing function of temperature exhibiting a maximum at about 230 K and falling off for higher temperatures. The same data are replotted on a log-log scale in fig. 5b. It is seen that the high temperature mobility values do not follow a simple  $T^{-n}$  relationship.

A mobility versus temperature dependence exhibiting a maximum can be explained in terms of a hopping model leading to a  $\mu \propto T^{-n} \exp(-E/kT)$  relationship (for a review see ref. [13]). However, hopping models cannot rationalize the steep decrease of the mobility with increasing temperature, as the value of  $n$  should not exceed 1.5. Moreover, the temperature at which the maximum occurs is somewhat different for the two examined crystals.

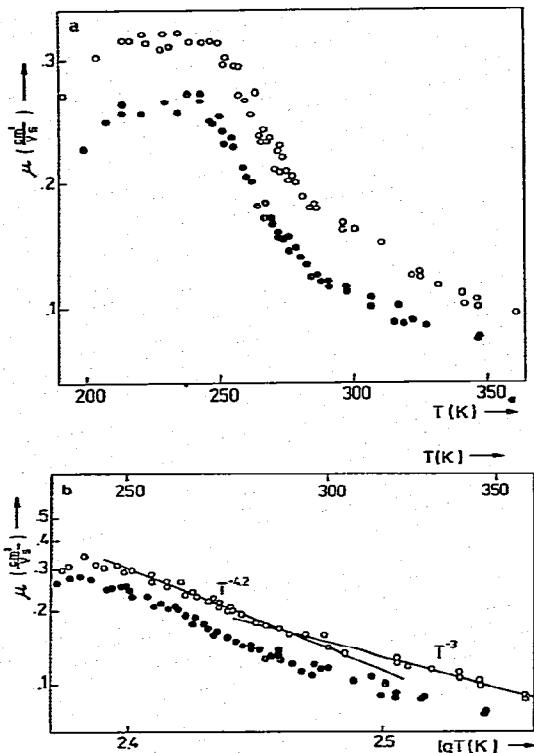


Fig. 5. Examples of temperature dependences of the hole mobility in two differently oriented TCNE samples. (a) Results plotted in linear coordinates. (b) Descending part of the dependences plotted on a log-log scale.

Hence, we conclude that transport of holes in TCNE crystals is trap-controlled at low temperatures.

For multiple trapping at a discrete level the following relation holds

$$\mu^0/\mu_{\text{eff}} = 1 + (N_t/N_c) \exp(E_t/kT), \quad (1)$$

where  $\mu^0$  and  $\mu_{\text{eff}}$  are the lattice and effective mobility, respectively,  $N_t$  and  $N_c$  denote the concentrations of trapping and conducting states, respectively and  $E_t$  is the trap depth.

This formula allows us to evaluate trapping parameters employing extrapolated values for  $\mu^0$  as shown in fig. 6.  $E_t$  has been found to amount to ca. 0.28 eV and  $N_t/N_c = 3 \times 10^{-7}$ . For such a low concentration of traps the average number of trapping events occurring during the transit of a

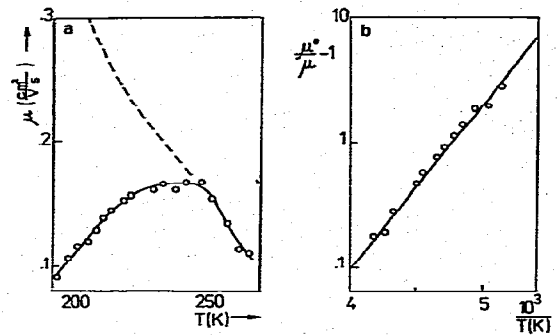


Fig. 6. Illustration of derivation of trap parameters from the activated part of the  $\mu$  versus  $T$  dependence. (a) Experimental data – circles (mobilities were measured in the  $b$  direction), broken line shows the extrapolation of the lattice mobility  $\mu^0$  from the high temperature region. (b) Semi-logarithmic plot of the low temperature data arranged according to eq. (1).

carrier may be of the order of unity. If this is the case the current pulses display long tails, transit times being poorly resolved (see e.g. ref. [14]). Such disperse transients have been observed for several samples at low temperatures; in some cases two distinct transit times could be distinguished (fig. 7). The first kink corresponds to the arrival of holes which reached the rear electrode without being trapped, the other kink is related to the effective mobility. This corroborates our assumption that hole transport at low temperatures is limited by shallow traps. It is tempting to assess the frequency factor  $\nu$  and the capture-cross-section  $\sigma$  of the traps involved. For transients similar to that shown in fig. 7

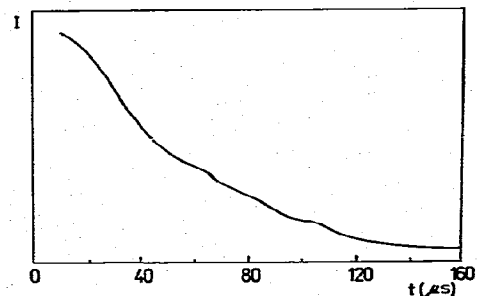


Fig. 7. Example of highly disperse transient observed at low temperatures in some samples. Sample thickness = 0.76 mm, voltage applied = 500 V,  $T = 214$  K.

the trapping time  $\tau$  is approximately equal to the trap-free transit time:  $\tau = t_f$ . From the relation  $\tau = (N_t v_{th} \sigma)^{-1}$ , where  $v_{th}$  is the thermal velocity of charge carriers, one can estimate the capture-cross-section  $\sigma = (t_f N_t v_{th})^{-1}$  and the frequency factor  $\nu = N_c v_{th} \sigma = N_c / N_t t_f$ .

Inserting typical experimental values one obtains  $\nu = 10^{10} - 10^{11} \text{ s}^{-1}$  and, for lack of further knowledge, taking  $v_{th} = 10^5 \text{ cm/s}$  and  $N_c = 4 \times 10^{21} \text{ cm}^{-3}$ ,  $\sigma \approx 10^{-16} \text{ cm}^2$ .

Above 250 K the temperature dependence of the mobility suggests that transport of holes is lattice controlled. Although the mobilities for all crystallographic directions are well below  $1 \text{ cm}^2/\text{V s}$  (which is a generally accepted lower limit of the validity of the band representation) the mobility is a steeply decreasing function of temperature. Such behaviour is in apparent disagreement with any existing models (cf. ref. [13]).

As most coherent transport models predict a  $T^{-n}$  dependence it is common to present mobility as a function of temperature on a log-log scale. Such presentation (fig. 5b) suggests the existence of two temperature regions corresponding to  $n \approx 5$  and  $n \approx 3$  for lower and higher temperatures, respect-

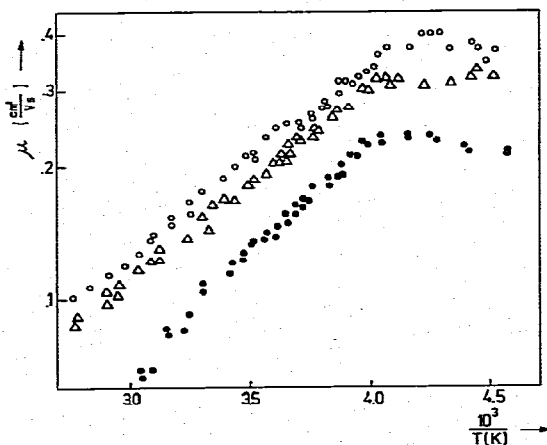


Fig. 8. Temperature dependence of the hole mobility presented on a semi-logarithmic scale. Different symbols refer to differently oriented samples. For only one sample (out of eleven samples studied) the plot deviates significantly from linearity – these results are shown as full circles.

ively. Although a slight anomaly in the temperature dependence of lattice parameters of supercooled monoclinic TCNE at 270–285 K has been reported [6], we feel that the change in the value of  $n$  has probably no physical significance as replotting the same data in  $\log \mu$  versus  $T^{-1}$  coordinates gives linear dependences for the whole lattice controlled mobility region (fig. 8). Hence it follows that the temperature dependence of mobility may be described by  $\mu \propto \exp(E/kT)$ , where  $E \approx 0.08 \text{ eV}$  ( $650 \text{ cm}^{-1}$ ).

Schein et al. [1] have observed a similar dependence of the electron mobility in naphthalene crystals (the value of  $E$  was  $47 \text{ cm}^{-1}$ ) and attributed it to the scattering by optical phonons. However, Efrima and Metiu claim in ref. [3] that “the theory gives no physical significance to this exponential behavior” which “is probably accidental”.

### 3.4. Anisotropy of the hole mobility

The tensor of the hole mobility in TCNE has been determined using a least-squares fit for mobility values obtained for ten differently oriented crystal plates. The principal tensor components  $\mu_1, \mu_2, \mu_3$  as well as the angle  $\varphi$  (taken from  $a$  to  $c$ ) which makes the tensor  $x_1$  axis with the crystallographic  $a$  axis are shown in table 1. As the  $b$  axis is a twofold symmetry axis it coincides with the tensor  $x_2$  axis [15]. The lowest hole mobility corresponds to the  $b$  direction, the highest mobility direction is close to the  $a$  axis.

A comparison of the experimental data with theoretical calculations carried out by Jodkowski and Chojnacki [16] is shown in table 2. The calculations of the anisotropy have been based on the tight-

Table 1  
Principal components of the hole mobility tensor

Temperature (K)	$\mu_1$ ( $\text{cm}^2/\text{V s}$ )	$\mu_2$ ( $\text{cm}^2/\text{V s}$ )	$\mu_3$ ( $\text{cm}^2/\text{V s}$ )	$\varphi$ (deg)
273	0.26	0.14	0.19	-24
293	0.21	0.10	0.15	-15
313	0.16	0.084	0.13	-37
333	0.13	0.066	0.11	-38
average error	0.01	0.01	0.01	10

Table 2  
Comparison of theoretical and experimentally determined anisotropy of the hole mobility

	Theoretical ref. [16]	Experimental
$\mu_{aa}/\mu_{bb}$	2.52	1.85
$\mu_{cd}/\mu_{bb}$	2.37	1.36

binding model within the  $\pi$ -electronic approximation (for details of the method see ref. [16]). Although the theoretical approach does not take into account the anisotropy of phonon interactions it leads to good agreement with the experimental values. As the calculations reflect the anisotropy of the overlap of molecular wavefunctions one can infer that the overlap is a decisive factor in electronic transport in TCNE.

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#### References

- [1] L.B. Schein, C.B. Duke and A.R. McGhie, *Phys. Rev. Letters* 40 (1978) 197.
- [2] H. Sumi, *Solid State Commun.* 28 (1978) 309; *J. Chem. Phys.* 70 (1979) 3775.
- [3] S. Efrima and H. Metiu, *Chem. Phys. Letters* 60 (1979) 226.
- [4] D.A. Bekoe and K.N. Trueblood, *Z. Kristallogr.* 113 (1960) 1.
- [5] R.G. Little, D. Pautler and P. Coppens, *Acta Cryst.* B27 (1971) 1493.
- [6] J. Świątkiewicz, *Sci. Papers Inst. Org. Phys. Chem., Wrocław Techn. Univ. No. 16, Ser. Conf. 3* (1978) 305.
- [7] C.E. Looney and J.R. Downing, *J. Am. Chem. Soc.* 80 (1958) 2775.
- [8] L. Onsager, *Phys. Rev.* 54 (1938) 554.
- [9] R.R. Chance and C.L. Braun, *J. Chem. Phys.* 64 (1976) 3753.
- [10] J. Mort and D. Pai eds., *Photoconductivity and related phenomena* (Elsevier, Amsterdam, 1976).
- [11] M. Silver, K.S. Dy and I.L. Huang, *Phys. Rev. Letters* 27 (1971) 21.
- [12] M. Samoć and Z. Zboiński, *Phys. Stat. Sol. A* 46 (1978) 251.
- [13] L.B. Schein, *Chem. Phys. Letters* 48 (1977) 571; *Phys. Rev. B* 15 (1977) 1024.
- [14] F.W. Schmidlin, *Phys. Rev. B* 16 (1977) 2362.
- [15] J.F. Nye, *Physical properties of crystals* (Clarendon Press, Oxford, 1957).
- [16] J.T. Jodkowski and H. Chojnacki, *Sci. Papers Inst. Org. Phys. Chem., Wrocław Techn. Univ. No. 16, Ser. Conf. 3* (1978) 179.