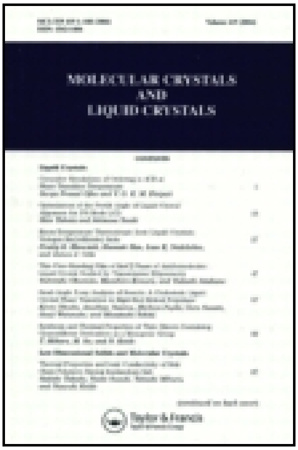

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Electron Mobility and Field Induced Trapping in the Charge-Transfer Crystal Phenanthrene-PMDA

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Electron Mobility and Field Induced Trapping in the Charge-Transfer Crystal Phenanthrene-PMDA.

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Photoconduction experiments have been performed on single crystals of the 1 : 1 charge-transfer complex phenanthrene-PMDA (pyromellitic-acid-dianhydride). This material belongs to that class of donor-acceptor-complexes which exhibit little charge transfer in the ground state but almost complete electron transfer in the lowest excited singlet state. The crystalline complex is an insulator consisting of one-dimensional stacks of alternating donor and acceptor molecules. The molecular planes are almost parallel and have a spacing of about 3.4 Å.[1] The dense packing along the stack axis give rise to an anisotropy of those physical properties which are governed by the overlap of molecular wave functions.

Drift mobility experiments were undertaken by using the standard time-of-flight method of Kepler and LeBlanc.[2] Special care was taken to obtain transients which were not distorted by space charge effects.

Figure 1 shows the temperature dependence of the electron drift mobility for different orientations of the crystal. For each orientation one obtains a thermally activated mobility with an activation energy ΔE of about 1000 cm^{-1}. This temperature dependence can be explained in two different ways:

a) The mobility is trap limited and ΔE corresponds to the trap depth.

b) The mobility can be described by a small polaron hopping model and ΔE yields the polaron binding energy.

One can show[3] that shallow traps with a depth of 1000 cm^{-1} can only affect the mobility, if their concentration exceeds 10^{-2} mol/mol. It is unlikely that in these zone refined crystals the concentration of chemical impurities is as high as 1%. However, the kind and the number of physical impurities in our samples has not been determined.

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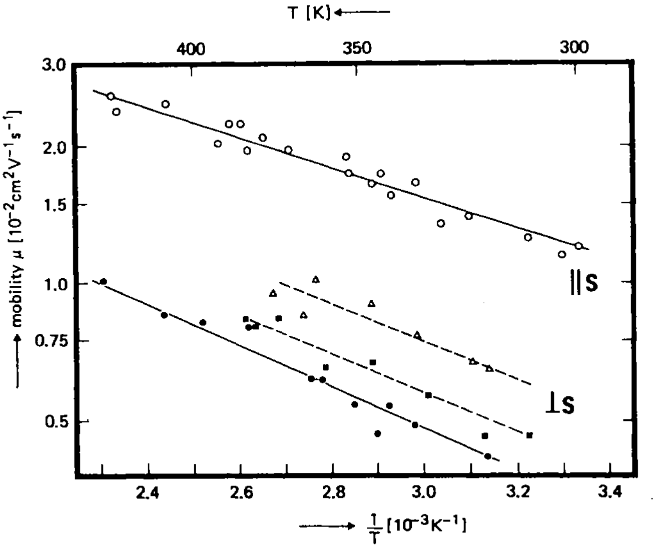

FIGURE 1 Temperature dependence of the electron drift mobility for different orientations of the electric field. The measurements with the applied field perpendicular to the stack axis were performed at three orientations, which were different by an angle of 45°.

It seems more probable to describe the mobility by a small polaron hopping model. This is also supported by the similarity of ΔE with the activation energy that was found for the triplet exciton mobility in crystals of weak charge transfer complexes. One knows that the exciton motion in these crystals can be described as a polaron motion.[4,5]

Figure 1 further shows that the mobility along the stack axis is larger by about a factor of three than perpendicular to it. This reveals that the free electron is not confined to the acceptors, but that the electron wave function is partially delocalized over the donors in order to account for the higher mobility along the stack axis. Qualitatively the same anisotropy of the mobility was also found for the crystal anthracene-PMDA.[6] Due to the close molecular packing along the stack axis this corresponds to an anisotropy of about 1 : 20 in the charge carrier jumping rate along and perpendicular to the stack axis. In that respect we have a nearly one-dimensional system, and in the following we will report a unique trapping mechanism that we can explain only by a one-dimensional charge carrier hopping model.

The transients also yield the trapping time τ, the lifetime of a free charge carrier. The upper curve in Figure 2 shows that for the electric field perpendicular to the stack axis, τ is field independent. This is the common situation in organic solids where the trapping is determined by the random carrier

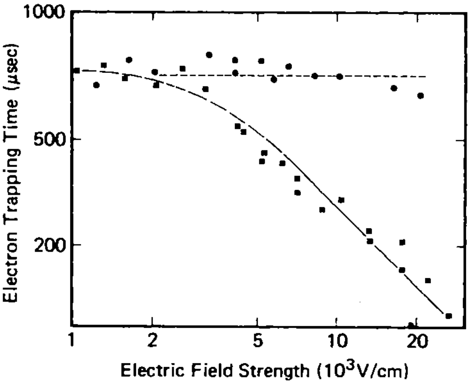

FIGURE 2 Electron trapping time as a function of the electric field for the electric field parallel (lower curve) and perpendicular to the stack axis (upper curve).

diffusion. However, the lower trace in Figure 2, obtained for the electric field parallel to the stack axis, reveals a field dependence of the trapping time. At field strengths higher than $5 \cdot 10^3$ V/cm τ is inversely proportional to the electric field. We refer to this as field induced trapping and explain it subsequently.

It is reasonable to assume within the frame of a hopping model that the trapping velocity is proportional to the rate at which charge carriers sample new sites. The measurements then indicate that when an electric field is applied, the rate of encountering new sites is increased. At first sight this is very puzzling since for the applied field strengths the thermal velocity of the charge carriers is much larger than their drift velocity. However, if one takes into account the dimensionality of the charge carrier diffusion, one can derive the following conclusions: In higher dimensional systems many of the diffusive jumps lead the charge carrier to a previously unsampled molecule, whereas in one dimension the diffusion very often leads the charge carrier to already encountered sites. This results in a drastic reduction of the trapping rate in a one-dimensional conductor.

A "critical field strength" E_c will be calculated, above which the drift term dominates the diffusion term in determining the trapping rate. One finds $E_c \sim 10^6$ V/cm for two- and three-dimensional systems and $E_c = 1$ V/cm for a one-dimensional photoconductor.

Experiments at field strengths as high as 10^6 V/cm have not been reported on organic crystals. Therefore a field dependent trapping time has not been observed for two- and three-dimensional systems. In one-dimensional conductors, however, one should find a field dependent trapping time at extremely low field strengths.

The fact that in our experiment the trapping time is field dependent only at field strengths above 10^3 V/cm shows that the system is not ideally one-dimensional. Therefore higher field strengths are necessary so that the drift term affects the trapping rate. Furthermore the results show that measurements of the trapping time may yield another method to determine the anisotropy of the charge carrier mobility.

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