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Percolative aspects in photoconductivity

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We present transient photocurrent measurements on samples containing a benztriazole derivative embedded in polycarbonate matrices and we obtain the effective carrier mobilities and their dependence on concentration. This dependence can be viewed in terms of a critical concentration p_c and a critical exponent $\bar{t}$. Our values of $p_c=0.1$ and $\bar{t}=2.5$ are similar to recent findings on continuum percolation. In contrast to simple percolation, the mobility is also field and temperature dependent, obeying a Poole-Frenkel behavior.

I. INTRODUCTION

Photoconductivity measurements are traditionally viewed in the context of dispersive versus normal (nondispersive) transport.[1-4] In the dispersive case the data are often interpreted within the continuous-time random-walk (CTRW) models[1-6] or multiple-trapping (MT) variants.[7,8] Both approaches are mathematically rooted in the scaling properties of the waiting- or detrapping-time distributions $\psi(t)$, and are based on self-similarity in the temporal domain (time fractals).[9,10] On the other hand, scaling is not necessarily restricted to the time domain: Geometric self-similarity, such as that encountered in percolation problems,[11,12] and even energetic self-similarity, as nowadays envisaged for relaxation in glasses,[13] lead to dispersive transport. In general all aspects contribute,[13] and thus it is difficult to establish the main cause for the transport behavior found experimentally.

Based on these considerations, we found it interesting to investigate the geometric aspects of disorder, and to check whether percolative aspects may also be of importance in photoconductivity. We note that, in the related field of energy transport, percolation and fractal models are in common use.[14-16] Furthermore, model experiments for continuum percolation, such as conducting spheres embedded in nonconducting materials (and vice versa)[17-19] nowadays attract much attention. It is therefore interesting[20] to investigate amorphous photoconducting materials which, while less modellike, are of broader impact as far as applications are concerned. As substances we chose a benztriazole derivative embedded in a polycarbonate matrix, and we varied the concentration p of the derivative in a wide range (1%–30%) around the expected critical value.

II. EXPERIMENT

The samples were prepared from the benztriazole derivative (BTA) and from bisphenol-*A*-polycarbonate (Makrolon 2800, Bayer). The concentrations p were determined by weight. The films were cast from tetrahydrofuran solution and spread on a Mylar substrate coated with a thin Al layer by moving a spatula parallel to a precision surface. All samples had a thickness of 10 μm and an area of about 450 mm^2. As a second electrode, a thin layer of semitransparent Al was evaporated onto the sample.

The photocurrents were measured by the time-of-flight (TOF) technique. The charge carriers (holes) were generated near the surface by an N_2-laser pulse ($\lambda=337$ nm, duration 10 ns). To avoid space-charge effects,[3] the light intensity was chosen such that the total injected charge Q was smaller than $0.05\,CU$ (where C is the capacity of the sample). The applied voltage U varied from 100 to 600 V and the temperature from 250 to 355 K. After illumination, the photocurrent was monitored in the time range from 10 μs to 10 s. We used a transient digitizer (Kemo AM-1024) with an externally controllable sampling rate, and we changed both gain and clock frequencies three times for each measurement. The experiment was controlled by a Hewlett-Packard HP-1000 computer.

At low concentrations p(1%–10%), the penetration depth of the laser light might be rather large because the light is absorbed by the BTA chromophore; this impairs the TOF conditions. At these p values we used samples coated with a charge-carrier-injecting Se layer of 1 μm thickness. In order to rule out weak photocurrents at very low concentrations, we also measured the dc currents with a very sensitive electrometer (Keithley 617-E). The dc irradiation of the samples was achieved with a strong uv line ($\lambda=365$ nm) from a high-pressure mercury arc lamp.

As a rule, we recorded the time-dependent photocurrents $I(t)$ four times for each temperature setting and field strength. A typical experimental curve is displayed in Fig. 1 ($p=0.2$, $T=333$ K, $U=300$ V). After an initial period of dispersive transport, the current enters an almost time-independent regime; subsequently the bulk of the charge carriers arrives at the rear electrode, which shows

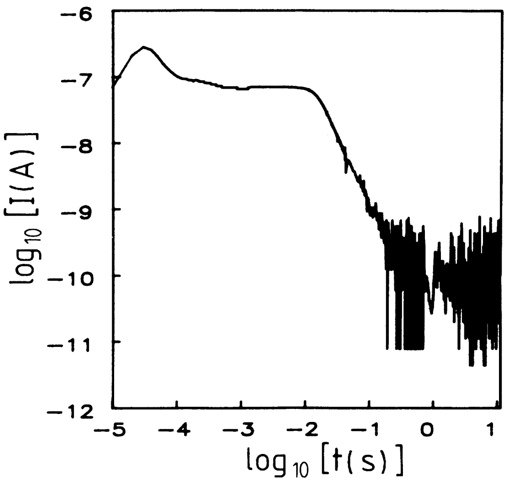

FIG. 1. The transient photocurrent of a sample made from a benztriazole derivative (20 wt.%) and bisphenol-A-polycarbonate, measured by the time-of-flight technique (sample thickness $d=10$ μm, applied voltage $U=300$ V, temperature $T=333$ K).

up as a dramatic break in the photocurrent. The location of this break was determined by a least-squares linear fit to the data in the two regimes. The intersection point of the two straight lines marks the effective transit time t_T. From t_T the effective mobility μ_T was determined as

$$\mu_T = d/t_T E = d^2/t_T U \ .$$

III. RESULTS

The measured effective mobilities μ_T are displayed in Fig. 2 for the concentration range $0.1 \leqq p \leqq 0.3$. The data points correspond to five samples measured at two temperatures ($T=293$ and 333 K). The applied field was varied from 600 to 400 V and from 600 to 200 V, respectively. Below $p=0.1$ no photocurrent was detectable, even under continuous illumination conditions (see Sec. II); hence, at these concentrations μ_T is practically zero.

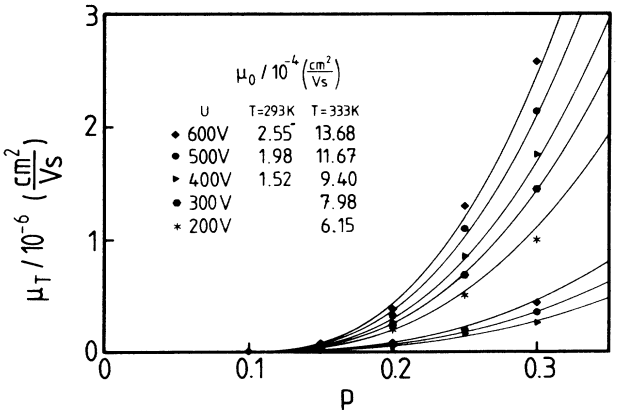

FIG. 2. The effective mobilities μ_T as a function of the benztriazole concentration p. The μ_T data were measured at the U and T values given in the inset. All curves are fits to the percolation model, Eq. (1), with $p_c=0.1$ and $\bar{t}=2.5$. The resulting μ_0 values are listed in the inset.

It is tempting to rationalize the findings of Fig. 2 using a percolation approach. Under percolation conditions, for p above the critical concentration p_c, the conductance and, hence, also the mobility scale in the vicinity of p_c:

$$\mu_T \simeq \mu_0 (p-p_c)^{\bar{t}}, \ (p > p_c) \ . \tag{1}$$

Here $\bar{t}$, the conductivity exponent, is a universal quantity (independent of geometrical and dynamical details). Nevertheless, up until now the connection between $\bar{t}$ and the other static, critical exponents has not yet been fully settled.[21] From computer experiments on three-dimensional (3D) lattices, values for $\bar{t}$ ranging from 1.9 to 2.2 were reported. For continuum percolation in the "Swiss-cheese" geometry (realized for instance in experiments using glass-indium composites)[18] $\bar{t}$ should be higher by 0.5;[22–26] the measurements yield values up to $\bar{t}=3.1$.[18] The critical concentration p_c is, as opposed to $\bar{t}$, not universal in that it depends on the details of the particular geometry and interactions. For nearest-neighbor site interactions p_c varies between 0.198 and 0.312 in going from the fcc to the simple cubic lattice.[21] This spread in p_c values is reduced when one uses the effective occupied volume. In this case all cubic lattices have a critical concentration of $p_c=0.155 \pm 0.01$.[27] Experimentally one finds p_c to vary from 0.04 to 0.1 for the glass-indium system and to be around 0.17 for composites of Ag-coated glass in Teflon.[18]

Inspection of Fig. 2 suggests a p_c around 0.1. Taking for simplicity the fairly round values $p_c=0.1$ and $\bar{t}=2.5$, we fitted *each* of the curves in Fig. 2 by an appropriate choice of the μ_0 parameter in Eq. (1). Since the equality holds exactly only at p_c, we used the logarithmic version of Eq. (1) in the mean-square fit, in order to give more weight to the data near p_c. The μ_0 values are given in the inset of Fig. 2. (The best overall fit to the data is $p_c=0.095$ and $\bar{t}=2.46$.)

There are, of course, other possibilities for envisaging

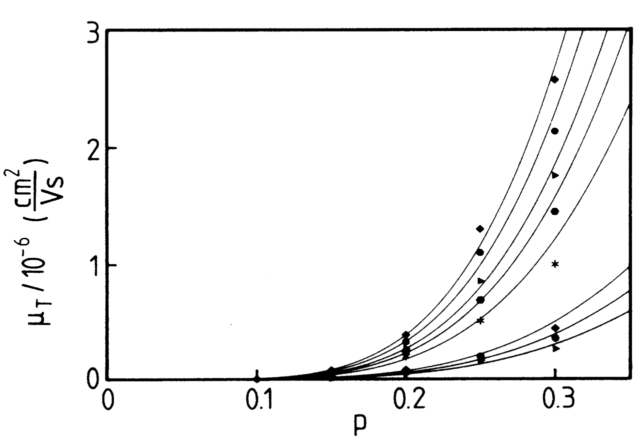

FIG. 3. Same as Fig. 2, only that the theoretical analysis is in terms of the continuum model, Eq. (2), with $k=9$.

the geometric p dependence of μ_T. In a continuous model for disorder, changes of p can be viewed as a rescaling of the length by $a = p^{-1/3}$. If we assume the microscopic processes to be dominated by exchange, the overall mobility obeys

$$\mu_T \simeq (\mu_0 a)\exp(-ka) \sim M\exp(-kp^{-1/3}) \; , \tag{2}$$

where we neglected $\ln a$ compared to a.

A fit to μ_T using Eq. (2) is given in Fig. 3. The one-parameter fit (k was set to $k=9$) again reproduces the overall findings, but is not as good as the percolative approach.

However, geometry alone is unable, as noted in the Introduction, to tell the whole story, as borne out by the dependence of μ_0 on the temperature T and on the applied voltage U. If all disorder were geometric, μ_0 would have to be the same for all curves in Fig. 2. Hence, we conclude that energetic aspects also enter the picture. The μ_0 dependences are consistent with a Poole-Frenkel relation of the form[28]

$$\mu_0 = C\exp[(qU^{1/2} - e_0)/kT] \; , \tag{3}$$

with $q = 2.6\times10^{-3} e\sqrt{V}$, $e_0 = 0.459\,\text{eV}$, and $C = 151\ \text{cm}^2/\text{V s}$. To validate the activated behavior, we have measured μ_0 for the $p=0.25$ sample using 12 different temperatures in the range from 250 to 355 K, and found very good agreement with Eq. (3). [An additional problematic[29] $1/T_0$ term in Eq. (3)—as originally suggested[28]—is not necessary here.]

In summary, photoconductivity in substitutionally disordered media is strongly influenced by geometrical aspects, which may be viewed in the framework of percolation. Indeed, our results are consistent with the recent theoretical[19,21–26] and experimental[17,18] findings on continuum percolation in 3D, to which they provide an example of great importance in applications. Furthermore, the influence of the energetic disorder is also evident, which can, in our case, be attributed to Poole-Frenkel behavior.

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