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Photoconductivity in *trans*-polyacetylene: Transport and recombination of photogenerated charged excitations

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Photoconductivity in unoriented Shirakawa-type polyacetylene as well as in highly oriented Durham-Graz-type polyacetylene has been measured. Both cw and transient experiments on different time scales have been carried out. The existence and the behavior of a fast and a slow component of the photoconductivity have been investigated in detail and the relationship between the two components has been elucidated. For the fast component we have observed a relaxation time of $\tau_{1/2} \approx 100$ ps, a migration distance of the carriers up to 400 Å, and a mobility of $\mu \approx 2$ cm^2/V s. The mobility of the slow component is 2 orders of magnitude lower. In the oriented samples two kinds of anisotropy of the photocurrent have been found, one with respect to the direction of the applied electric field with a value of $\sigma_{\parallel}/\sigma_{\perp}=50$, and the other with respect to the polarization of the incident light. From a comparison of these data with those of photoinduced absorption measurements, we attribute the fast component mainly to polarons and the slow component to a hopping transport of charged solitonlike defects.

I. INTRODUCTION

Among the conducting polymers, polyacetylene $(\mathrm{CH})_x$ is considered as a prototype of this class of materials.[1-3] Experimentalists and theoreticians are interested in the unusual combination of electrical, magnetic, and optical properties. This interest has been stimulated largely by the development of an elegant theory[4-6] for the nature of the electronic excitations in this material. For the electrical transport properties, which are, of course, the most important properties of a conducting polymer, the question arises whether charge transport is influenced by nonlinear excitations like solitons[4-6] and/or polarons.[7] The dark conductivity of doped polyacetylene seems to be mainly governed by the large amount of disorder present in the samples, leading to a predominance of tunneling between inhomogeneities and hopping between localized states.[8] There have been attempts to identify these localized states as solitons,[9,10] but an unambiguous assignment is not possible, because the measured conductivity is not very specific to the microscopic nature of the hopping sites.

Photoconductivity (PC) is expected to give more information on transport mechanisms than dark conductivity, since it can be studied in undoped samples. Doping unavoidably increases the disorder in the polymer. In addition, photoconductivity is a local probe and also provides information on the mobility and lifetime of photoexcited carriers.

In this paper we report on the photoconductivity of conventional (unaligned Shirakawa-type) *trans*-polyacetylene[11] and of fully oriented Durham-Graz polyacetylene.[12,13] Undoped *trans*-$(\mathrm{CH})_x$ is—independent of the method of synthesis—a 1D semiconductor with a band gap of about 1.7 eV.[14] Photoexcitation across this gap leads to the generation of charged carriers, as in conventional semiconductors. Due to the strong electron-phonon coupling in one-dimensional (1D) systems, however, these carriers distort the underlying lattice. As mentioned above, they are therefore often regarded as new quasiparticles with solitonlike or polaronlike properties. These charged excitations can be observed in PC experiments. The PC in *trans*-$(\mathrm{CH})_x$ (Shirakawa-type as well as Durham-Graz material) consists of two components: a fast component with relaxation times in the picosecond regime[15-19] and a slow component with carrier lifetimes up to seconds.[17-24] With time-dependent measurements we show that these two time constants are not in contradiction with each other, but form a consistent picture of photoexcitations in $(\mathrm{CH})_x$. Temperature-, field-, and intensity-dependent measurements clearly demonstrate the similarity of the electronic properties of Shirakawa-type and Durham-Graz polyacetylenes. With highly oriented samples we obtain additional information on the anisotropic (1D) properties of $(\mathrm{CH})_x$. Two types of anisotropy are observed, one with respect to the direction of the applied electric field, demonstrating anisotropic transport, and another due to the polarization of the incident light, demonstrating anisotropic recombination.

In Sec. II we present the experimental results of the fast PC component which have partially been published in Refs. 17 and 18. In Sec. III we report on the behavior of the slow-PC component and in Sec. IV on the anisotropic features of the highly oriented samples. Finally in Sec. V we discuss the transport and recombination kinetics of the charged excitations resulting from all these data and compare it with conclusions obtained from photoinduced absorption measurements published by other groups.

II. EXPERIMENTAL RESULTS OF THE FAST-PC COMPONENT

The experimental setup for measuring the photocurrent is shown schematically in Fig. 1. For the experiments with the highest time resolution we used 25-ps pulses of a frequency-doubled actively-passively mode-locked Nd-YAG (YAG denotes yttrium-aluminum-garnet) laser operating at 5 Hz with an excitation energy of 2.3 eV. The PC signal was recorded by a PAR 4400 boxcar system fitted with a Tektronix S4 sampling head. The electronic resolution of this system was about 50–60 ps. This value represents a convolution of the laser-pulse rise time (15 ps), the trigger jitter of the boxcar system (15 ps), and the sampling head response time (25 ps). Measurements on a longer time scale were carried out with 500-ps pulses of a nitrogen-laser-pumped dye laser (PRA LN1000/LN107) with a tunable range from 1.2 to 3.2 eV, and a Tektronix 7912 AD (bandwidth, 700 MHz) or a Lecroy 9400 digital oscilloscope (125 MHz).

The samples [about 5-μm-thick Shirakawa-type $(CH)_x$ and 1.7-μm-thick Durham-Graz-type polyacetylene] were mounted on a quartz substrate, onto which two gold electrodes had been evaporated, separated by a gap of 200 μm. Details of the contact geometry have already been reported in Ref. 19. With this setup a static electric field up to 1.5×10^4 V/cm could be applied. The isomerization of the Shirakawa samples have been carried out by heating of 180 °C for 15 min under vacuum. The Durham-Graz-type polyacetylene has been isomerized during the elimination reaction (and stretching) from the precursor to the final polymer.[25] The samples were mounted in a vacuum chamber. All sample handling was carried out in an argon glovebox to avoid oxygen contamination. The photocurrent was recorded by the voltage drop across the series resistance R_M (see Fig. 1), which was, in most cases, the 50-Ω input resistance of the electronic detection system. To investigate the fast component at very short times we illuminated the sample with 25-ps pulses. The observed PC decay is shown in Fig. 2 on a linear plot. We determined a relaxation time for the fast component of $\tau_{1/2}\approx 100$ ps, which is independent of the strength of the applied electric field, the light intensity, and the temperature. In unoriented and oriented samples $\tau_{1/2}$ is also independent of the polarization of the incident light. The signal amplitude is constant with the sample temperature varying from 300 K down to 10 K as also reported by Sinclair *et al.*[16]

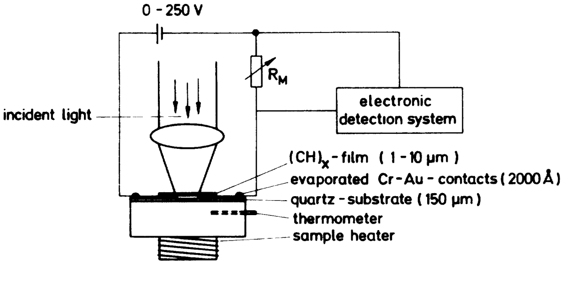

FIG. 1. Schematic setup for measuring the photocurrent. The resistance R_M is in most cases the input resistance of the electronic detection system.

We can estimate the migration distance l of the photocarriers by the following simple relationship:

$$\frac{N_e}{N_{\rm ph}}=\eta\phi\frac{l}{d}\ , \tag{1}$$

where N_e is the number of electronic charges collected in the detection system, $N_{\rm ph}$ the number of absorbed photons, $\eta\phi$ the product of the quantum efficiency and the probability of escaping fast recombination (mainly geminate recombination), and d the distance between the electrodes. Assuming $\eta\phi=0.01$,[26–28] we obtain, for the data shown in Fig. 2 (oriented sample), a migration distance $l_{\parallel}=120$ Å. It should be noted, that the above value of $\eta\phi$ was not obtained from the decay of the photoinduced absorption peak at 1.4 eV as in Ref. 16 but from measurements of the 0.45-eV peak,[27] and from a comparison of photoinduced and doping-induced absorption features.[26]

The number of absorbed photons was determined by measuring the exact profile of the incident light beam to obtain only that part of the intensity which illuminates the "active" sample area between the contacts. Loss of intensity due to reflection (and in some cases weak transmission, depending on the excitation energy, the sample thickness, and the polarization) has also been taken into account.

With $\mu=l/E\tau$, where E is the applied electric field, we

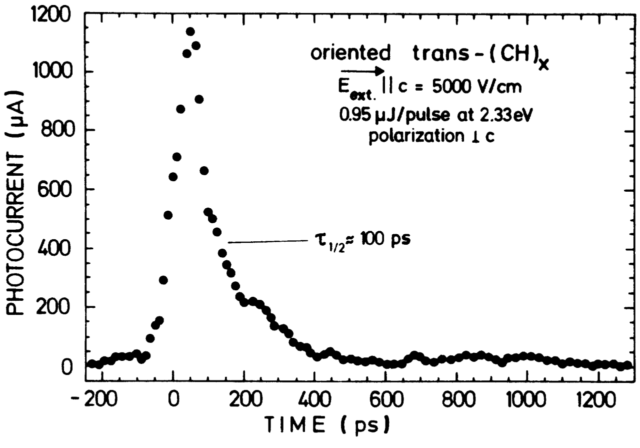

FIG. 2. Fast component of the photocurrent in *trans*-$(CH)_x$ excited with 25-ps laser pulses; $T=300$ K. The energy of the incident light pulses is 0.95 μJ at a sample area of 200 μm $\times$ 330 μm. The integral under the peak corresponds to 1.5×10^6 electronic charges.

get a mobility $\mu_{\parallel} \approx 2$ cm^2/V s, setting $\tau = \tau_{1/2} = 100$ ps. The highest value of $l_{\parallel}$ which we have obtained so far is 400 Å, at an applied field of 1.5×10^4 V/cm. In unoriented Shirakawa material the values of l and μ are lower by a factor of 2.5–3 consistent with geometrical averaging. The dependence of the peak photocurrent (being proportional to the collected charge) on the absorbed light intensity and the applied electric field is shown in Figs. 3 and 4. The peak photocurrent is directly proportional to the light intensity, but is slightly nonlinear with the applied electric field ($I_{\text{ph}} \sim E^{1.1}$). These results correct preliminary data published in Ref. 17, where a later inspection has shown that illumination of the contacts and some sample damage at the highest light intensities had occurred. The superlinear behavior of the field dependence might be explained by an increased probability to escape geminate recombination with increasing electric field. In the framework of the Onsager theory for geminate recombination[29] one would expect only a slight field dependence of the escape factor ϕ for low fields in the 3D case and a strong field dependence for high fields in 3D and all fields in 1D. For polyacetylene with a dielectric constant of $\epsilon \approx 10$ the characteristic field is estimated to $E = E_1 \approx 1.5 \times 10^4$ V/cm (see Ref. 29, Fig. 1). Therefore the results of the low-field regime in Fig. 4 suggest a 3D geminate recombination mechanism. Some measurements in fields up to 10^5 V/cm show a slightly increased slope of the photocurrent versus field curves (also consistent with 3D recombination), but a detailed investigation is difficult since such high field values are already close to the limit of dielectric breakdown.

When investigating the photocurrent decay on a longer time scale, the fast- *and* the slow-PC components can be seen. Figure 5 shows the decay of the PC over 8 orders of magnitude in time on a log-log plot. Both from the time and the temperature dependence the two components can be clearly distinguished, the fast component decaying nearly linearly in time and the slow component with $t^{-1/2}$. At room temperature the fast component is only observable up to 1 μs, from then on the slow component dominates. Upon cooling, the slow component decreases in intensity, as will be shown in Sec. III (Fig. 7) and at 100 K (dotted curve) it can no longer be observed, within our experimental sensitivity. The temperature-independent fast component, however, remains

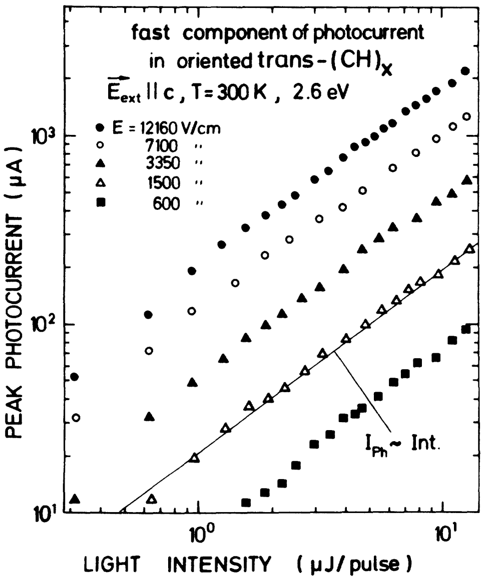

FIG. 3. Intensity dependence of the fast-PC component on a log-log plot at different electric fields. The slope of 1.0 clearly demonstrates the linear behavior between the peak photocurrent and the light intensity.

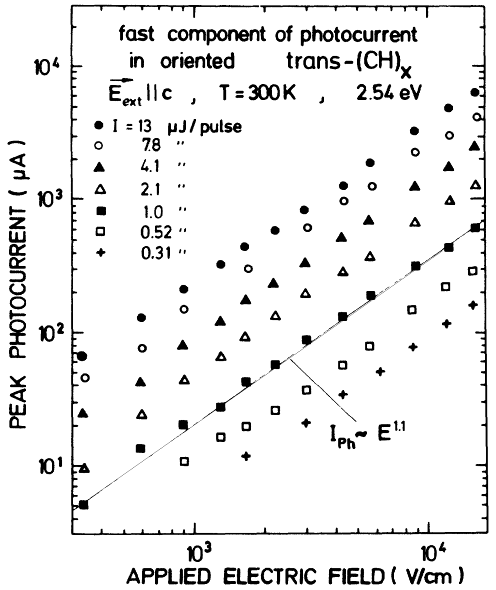

FIG. 4. Field dependence of the fast-PC component on a log-log plot at different intensities. The peak photocurrent I_{ph} is proportional to $E^{1.1}$.

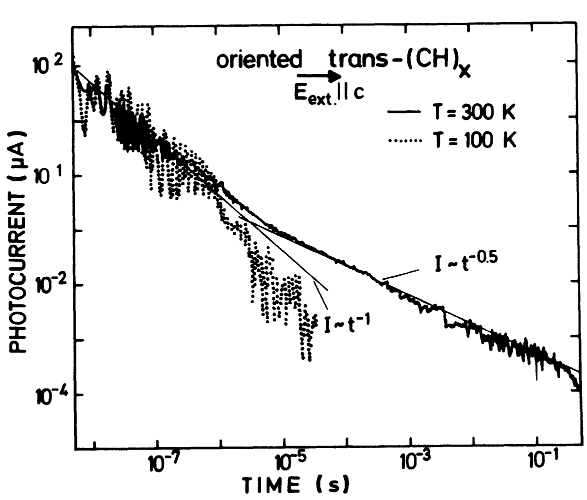

FIG. 5. Decay of the photocurrent after 500-ps excitation investigated from nanoseconds to seconds at 300 K (solid line) and at 100 K (dotted line).

unaffected. The "long-time" decay of Fig. 5 is also included in the tail of the decay in Fig. 2, but cannot be resolved within the sensitivity of the sampling-head detector. However, the curves fit to each other with the restrictions that in the case of 500-ps excitation the observed PC partially relaxes during the illumination, and that—due to the limited bandwidth of 125 MHz (in Fig. 5)—the initial peak is broadened. Therefore these results are only valid for times greater than several nanoseconds. Extrapolating the slow component in Fig. 5 at 300 K to a time of 10^{-10} s (where the mobility and migration distance of the fast component have been estimated) the initial values of the components differ by about 2 orders of magnitude. Therefore the mobility of the slow component can be estimated to be 2 orders of magnitude lower than that of the fast component. The other properties of the slow component will be discussed in the following section.

III. EXPERIMENTAL RESULTS OF THE SLOW-PC COMPONENT

For the measurements of the slow component a chopped cw light source (He-Ne laser or a mercury-xenon lamp) with chopper frequencies around 10 Hz was used in connection with lock-in detection.

The main difference between the fast- and the slow-PC component is, of course, the relaxation time of the carriers contributing to the particular components. In the fast component the relaxation time has a value of 100 ps, as discussed above, whereas in the slow component carriers can be observed which persist for the order of seconds. This is shown in Fig. 6, where the photocurrent is plotted versus the chopper frequency at four different temperatures. Even at the lowest chopper frequency of 2 Hz the photocurrent still increases with decreasing frequency. The number of carriers, however, contributing to the photocurrent decreases continuously with increasing time as shown in Fig. 5. The temperature independence of this decrease with increasing chopper frequency from 300 down to 225 K demonstrates that this effect is not due to a thermal modulation of the dark current, but due to the lifetime of the photocarriers. This becomes evident when comparing the temperature dependence of the slow-PC component with that of the dark current (Fig. 7). In the temperature range from 180 to 300 K the slow-PC component changes by 2 orders of magnitude; the dark current however, changes by more than 4 orders of magnitude. The absolute value of the slow-PC component is influenced by a thermal modulation of the dark conductivity due to the incident light. This influence increases with increasing temperature. All features of the slow-PC component presented in this paper, however, have also been measured at low temperature (about 200 K) and did not show any change in their general behavior (except that the signal amplitudes are much lower than at room temperature). Therefore, we conclude that the slow-PC component at room temperature is influenced, but not masked, by a thermal modulation of the dark conductivity, as argued by Townsend *et al.*[24]

The data in Fig. 7 were all taken on the same sample. In a semilog plot all three curves—fast-PC component, slow-PC component, and dark current—can be approximated by straight lines. As already discussed, the fast-PC component is independent of temperature. For the slow-PC component an activation energy of 0.22 eV is calculated and for the dark current the activation energy

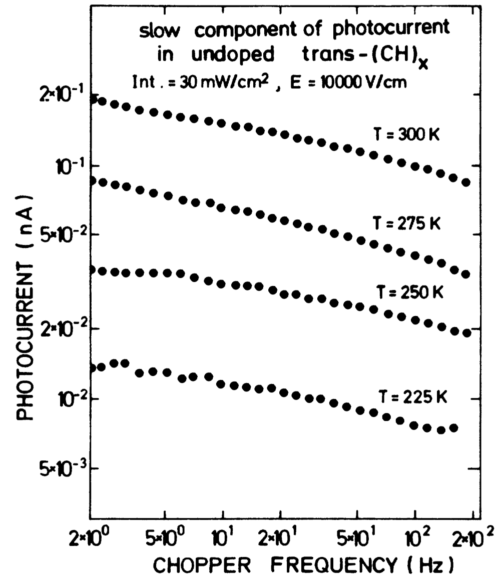

FIG. 6. The slow-PC component as function of the chopper frequency at four different temperatures on a log-log plot.

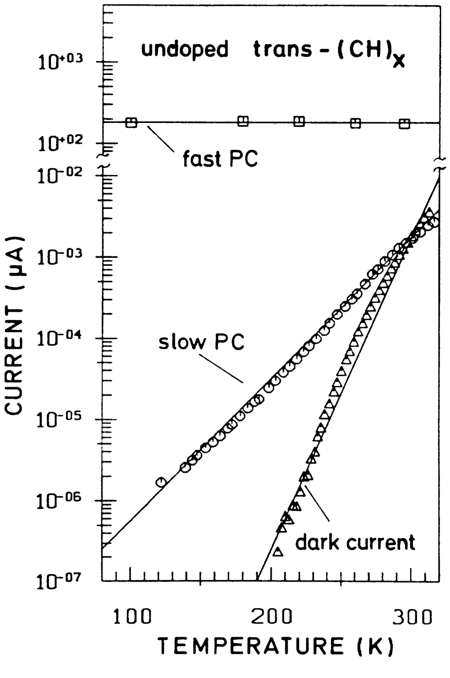

FIG. 7. Temperature dependence of the fast- and slow-PC component and of the dark current. The fast component is temperature independent down to about 10 K. The room-temperature value of the dark conductivity is 7×10^{-7} S/cm.

is found to be 0.45 eV. It should be noted, however, that the temperature range of Fig. 7 is not large enough to decide whether there is really activated behavior. The dark conductivity, for example, can also be fitted by $\ln\sigma \sim (T_0/T)^{1/\gamma}$. This corresponds to Mott's variable range hopping with $\gamma = 1 + d$, where d is the dimensionality of the conductor. The experimental values do not allow us to distinguish clearly between $\gamma = 2$, 3, or 4. (In the case of $\gamma = 4$ one obtains a value of $T_0 = 7 \times 10^9$ K.) Therefore there is no reason to propose another mechanism for the slow-PC component than hopping transport, which is generally accepted for the dark conductivity in polyacetylene. A detailed discussion of the different models to explain the hopping conductivity in polyacetylene is given in Refs. 8 and 10.

The field dependence of the slow-PC component is the same as for the fast component. Again the photocurrent is proportional to $E^{1.1}$ (see Fig. 8). This result is not surprising and is the consequence of the higher number of carriers, which have survived already in the fast component when the electric field has been increased. The intensity dependence of the slow component is different from that of the fast component. As shown in Fig. 9 the photocurrent depends sublinearly on light intensity. The power of this sublinearity changes with the penetration depth of the light and hence the carrier density and has a value of 0.6–0.7 in Shirakawa samples and for parallel polarization in Durham-Graz $(CH)_x$. For perpendicular polarization of the incident light the exponent increases to about 0.8. This result is consistent with the intensity dependence of the photoinduced absorption at 0.45 eV observed by Vardeny *et al.*[26] who obtained an initial value of 0.65 with a strong tendency to saturation above an intensity of 100 mW/cm^2 [in Shirakawa-type $(CH)_x$]. The intensity dependence of the fast PC and the field dependence of both components do not change with the polarization of the light.

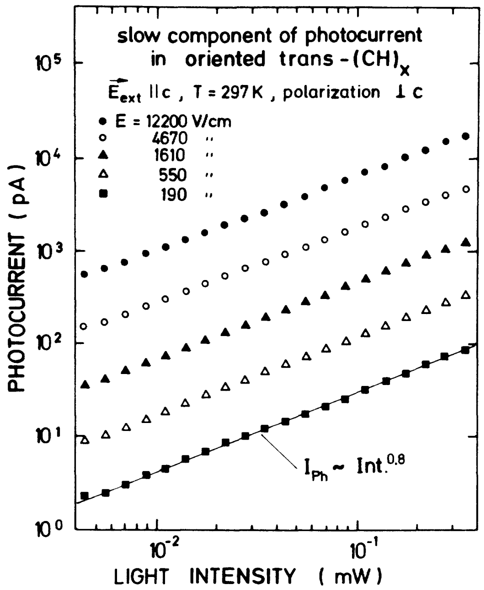

FIG. 9. Intensity dependence of the slow-PC component on a log-log plot. In the case of a polarization perpendicular to the chain direction (in oriented samples) the photocurrent goes with (intensity$^{0.8}$); in other cases [parallel polarization or Shirakawa-type $(CH)_x$] the exponent has a value of 0.6–0.7.

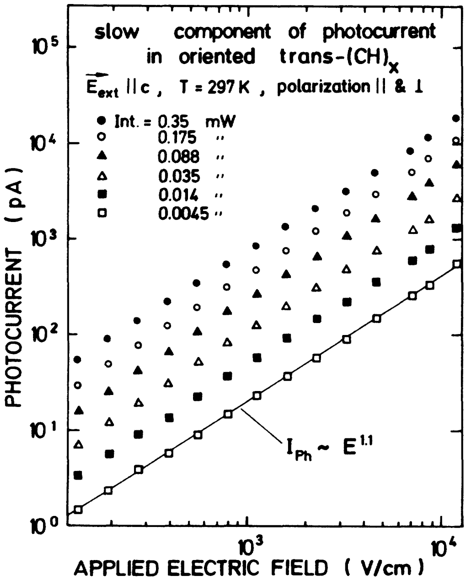

FIG. 8. Field dependence of the slow-PC component on a log-log plot at different light intensities. The photocurrent is proportional to $E^{1.1}$ similar to the behavior of the fast component.

IV. ANISOTROPIC PROPERTIES OF HIGHLY ORIENTED DURHAM-GRAZ-TYPE POLYACETYLENE

As mentioned in the last paragraph of Sec. III, the penetration depth of the light in highly oriented $(CH)_x$ is different for parallel and perpendicular polarization. This arises from the strongly anisotropic optical absorption in this material.[30–32] Figure 10 shows the absorption and reflection for both polarizations. These data were obtained by ir-optical experiments[31] and by measurements of the dielectric function using electron-energy-loss spectroscopy[32] and are important for the evaluation of the polarization dependence of the photocurrent.

Firstly, we shall discuss the effect of the orientation of the applied electric field. When changing the field direction from parallel to the chains to perpendicular, the photocurrent decreases by a factor of 50 for both the slow- and the fast-PC component. Consequently the ratio in the migration distance l and the mobility μ is $l_{\parallel}/l_{\perp} = \mu_{\parallel}/\mu_{\perp} \approx 50$. This strong anisotropy clearly demonstrates that carrier motion is predominantly in chain direction and not perpendicular to it.

The photocurrent shows a significant difference between parallel and perpendicular polarization of the illuminating light (Fig. 11). The direction of the polariza-

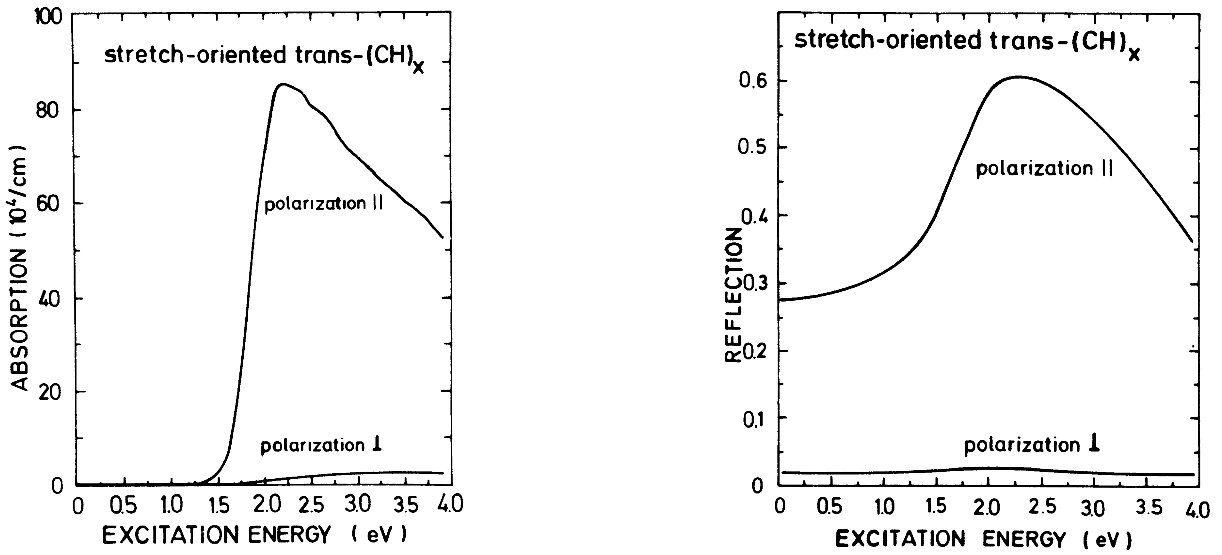

FIG. 10. Absorption and reflection spectra of highly oriented Durham-Graz-type polyacetylene obtained from Refs. 31 and 32.

tion of the linearly polarized light was turned continuously by either a half-wave retardation plate for a fixed wavelength or a Fresnel rhombus[33] for different wavelengths (1.7–3.2 eV). At an excitation energy of 2.6 eV, the amplitude of the fast-PC component is about four times higher when the light is polarized perpendicular to the chains (solid circles). After normalizing these data to a constant number of absorbed photons, the ratio reduces to 1.7 (open circles), since in the case of parallel polarization nearly 60% of the light is reflected (see Fig. 10) compared to 2.5% for perpendicular polarization. This anisotropy ratio of 1.7 for the fast-PC component is independent of the wavelength of the incident light (from 1.7 to 3.2 eV), the applied electric field, and the light intensity, as already discussed in detail in Ref. 19.

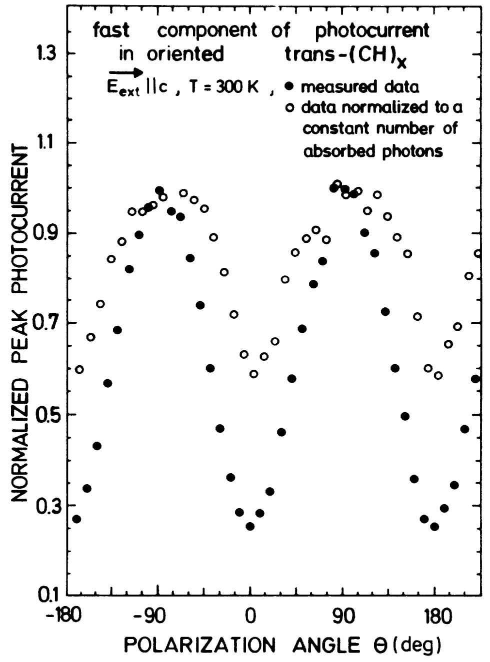

FIG. 11. Anisotropy of the fast-PC component with respect to the polarization of the incident light. θ is the angle between the polarization and the chain direction. Excitation energy is 2.6 eV.

For the slow component this anisotropy is higher and has been reported for the first time by Townsend *et al.*[24] It is slightly intensity dependent and has a value of three to five (Fig. 12). The higher the intensity, the higher the anisotropy as is evident from the different exponents for the intensity dependence for parallel and perpendicular polarized light.

V. DISCUSSION

In this section we shall discuss the mechanisms of transport and recombination of charged excitations in $(CH)_x$. This shall involve also a comparison of our PC results with data obtained from photoinduced absorption (PA) measurements published by other authors.[24,26–28,30,34–45]

The PA spectrum consists of two absorption peaks, the so-called low-energy (LE) peak at 0.45 eV and the high-energy (HE) peak at about 1.4 eV. From the close correlation[38] of the LE peak with the photoinduced infrared-active modes observed below 0.2 eV—a signature of charged defects on a polyene chain—and from the absence of such a correlation[42] for the HE peak, it was deduced that only the LE peak is due to charged excitations (charged solitons) whereas the HE peak is overall neutral. The identification of the bleaching bands associated with these two absorption peaks is still controversial. Vardeny and Tauc[43] and Orenstein[42] have observed a bleaching band around 1.4 eV associated with the LE peak (for

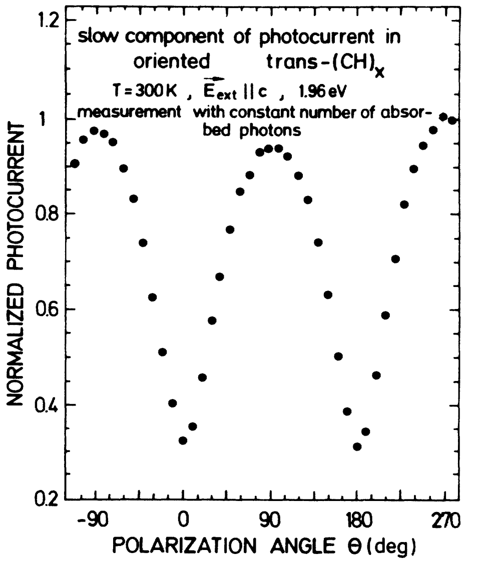

FIG. 12. Polarization anisotropy of the slow-PC component excitation energy is 2.1 eV. In this case the signal amplitudes have been measured directly at a constant number of absorbed photons by changing the intensity of the incident light in a sufficient way (instead of a numerical correction after the measurement as done in Fig. 11).

$T > 200$ K); Colaneri *et al.*,[45] however, have only observed the interband transition bleaching at 1.7 eV. In view of the above-mentioned correlation, it is opportune to compare only the behavior of the LE peak with results obtained by PC experiments, but not the HE peak (as was done in Ref. 16).

A. Transport properties

The PA signal is sensitive only to the number of photoexcited states, whereas PC is proportional to the product of the carrier number and their mobility. The absence of any correlation between the decay of the PA signal at 0.45 eV (attributable to charged solitons), and the decay of the *fast*-PC component in Fig. 5 (as indicated in Fig. 10 of Ref. 42) demonstrates that the fast PC must be either (1) primarily due to the high mobility of photogenerated charged solitons before they get trapped at various defects, or (2) due to a different species of photocarriers, which cannot be observed in the LE peak of PA. In the former case the observed PC decay of Fig. 2 must be a "mobility relaxation time" rather than a carrier lifetime. This loss in mobility is, of course, superimposed on a loss of carriers, which can be estimated by extrapolating the slow component in Fig. 5 ($t > 10$ μs) to short times. The value obtained thereby would give rise to only 1% of the initial PC signal. In the second case, which will be discussed in more detail later, both higher carrier numbers and higher mobility can be responsible for the fast PC.

We conclude from the unusual temperature independence of the fast-PC component (Fig. 7) and from the anisotropy with respect to the direction of the applied electric field that the fast PC is due to "hot" carriers, moving with a high kinetic energy relatively free along the polymer chains. According to calculations of Phillpot *et al.*[46] photoexcited solitons (kinks) and polarons in *trans*-$(CH)_x$ should be reflected (and sometimes transmitted or trapped) at the ends of finite chain segments and at other impurities, which act as potential barriers between different chain segments. (The higher the kinetic energy of these carriers, the higher will be their probability for elastic rather than inelastic scattering.[47]) For this reason, the observed mobility of 2 cm^2/V s is still relatively small compared to theoretical predictions of the ideal conductivity of conjugated polymers.[48] Applying an external field will only cause a net displacement of the charge center. Consequently, the photocarriers of the fast-PC component will have relatively short migration distances up to 400 Å. After the hot carriers have lost their kinetic energy by getting trapped, the further motion can be described by hopping, as in the case of the dark conductivity,[8,49] (already discussed in Sec. III). The alternative mechanism of dispersive transport has been suggested[21] to explain the power-law decay of the slow-PC component, shown in Fig. 5. However, as discussed below, this mechanism has to be ruled out.[40] For dispersive transport the mobility μ decreases with time.[50] This has been observed, for example, in a-As_2Se_3,[51] where the ratio of the photocurrent $i(t)$ and the change in transmission $\Delta T(t)$ results in a time-dependent $\mu(t)$. In *trans*-$(CH)_x$, however, the mobility of the slow-PC component is time independent as shown by Orenstein.[42] The strong similarity in the decay of the slow-PC component and PA consequently demonstrates that carrier recombination determines the decay in this time regime.

B. Recombination mechanisms

The mechanism of bimolecular recombination has been proposed to explain various features of PC and PA in Refs. 37 and 41, but must also be exlcuded. For bimolecular recombination the rate of decay of the slow-PC component should decrease with decreasing intensity, however, this was not observed. No change in the $t^{-1/2}$ decay could be observed even with different light polarization in the oriented samples, where the density of absorbed photons can be varied by three orders of magnitude (high intensity at parallel polarization and low intensity in the perpendicular case). PA experiments also contradict bimolecular recombination.[30,40]

According to Vardeny and Ehrenfreund[40] the power-law decay can be accounted for by a broad distribution of recombination times, but is not specific to any particular recombination or transport mechanism.

The polarization anisotropy has not only been observed in PC, but also in PA measurements[30] at the LE peak. This unambiguously indicates that this anisotropy is due to the number of carriers and not to their mobility. Bimolecular recombination, proposed by Dorsinville *et al.*[41] for the explanation of similar results in modified stretch-oriented Shirakawa-type $(CH)_x$, has to be excluded, as discussed in the previous paragraph. Townsend and Friend[30] have explained this anisotropy by a higher probability of the photoexcited electron-hole pairs immediately separating onto neighboring polymer chains if the absorbed light is polarized perpendicular to the chain direction. Carriers on different chains escape geminate recombination more easily. A higher probability for interchain-carrier creation has recently also been calculated by Danielsen.[52] In addition to this direct process some carriers on the same chain segments should be able to hop to a different chain before they relax into charged solitons on a subpicosecond time scale. This explains the relatively weak anisotropy factor of 1.7. Interchain carriers are not only created by direct interchain excitation but also by initial hopping events. Such carriers are, of course, not affected by the direction of the polarization but contribute in the same way to the observed PC. The large anisotropy of the optical absorption (Fig. 10) favors in addition intrachain absorption much more than interchain absorption. Every lack of chain orientation (±3° in our samples) therefore decreases the polarization anisotropy.[53] In nonoriented samples the opposite behavior can be observed, which is not surprising. The parallel direction shows a higher PC than perpendicular as demonstrated recently by Sinclair *et al.*[54] But even in the case of perfect chain alignment the ratio of interchain to intrachain absorption for light polarized perpendicular remains finite due to the zig-zag structure of the polyacetylene chain.

According to the calculations of Danielsen the probability of the direct anisotropic photogeneration should decrease with increasing excitation energy away from the band edge. On the other hand, the probability of the initial hopping processes for intrachain carriers should increase with increasing excitation energy. We have observed that within our experimental resolution and reproducibility of ±5%, there is no change in the anisotropy when varying the excitation energy from 1.7 to 3.2 eV (after correction, as explained in Sec. IV). The uncorrected raw data change significantly as demonstrated in Ref. 19. This can probably be interpreted as a compensation of these two effects.

All carriers remaining on the same chain segment except some few reaching the contacts cannot contribute to PC. They recombine or convert into neutral excitations which are responsible for the HE peak in PA experiments, as proposed by Kivelson and Wu.[55] Even in the case of a certain separation of the intrachain carriers for a short time in the external electric field, the optically excited pairs will mainly recombine by geminate recombination and not by recombination between different pairs. Therefore these carriers will not give any net contribution to the observed PC. The ratio of those few carriers reaching the contacts relative to the total photocurrent can be estimated from the ratio of the migration distance and the distance of the contacts and is found to be about 10^{-4}. This intrachain recombination is, of course, a 1D and not 3D process. The escape probability, however, is mainly determined by the defects acting as potential barriers and not by the influence of the electric field. This explains why the field dependence of the detected PC is characteristic for three-dimensional rather than one-dimensional recombination, as discussed in Sec. III.

Charges separated between different chains (segments) are expected to form initially polarons rather than solitons. Consequently they do not contribute to the LE peak in PA measurements but they are seen in the fast component of the photocurrent. These polarons, however, can convert into charged solitons and give rise to the retarded contribution (after ≈40 ps) in the LE peak in time-resolved PA experiments, as shown by Rothberg *et al.*[27]

There are two mechanisms suggested for this conversion.[45] Orenstein *et al.*[28] have proposed that the neutral soliton defects present in $(CH)_x$ act as traps for the photogenerated polarons and convert them into charged solitons. These solitons will then already be trapped and can therefore only contribute to the slow-PC component. The alternative explanation suggested by Moraes *et al.*[56] is a conversion of like-charged pairs of polarons on the same chain into like-charged soliton pairs. Both models are possibly valid since not in every case will a polaron find another one to form a pair. In the model of Orenstein the fast PC will only be due to polarons before they get trapped; in the other case polarons and also the bisolitons should contribute to the fast PC, since the solitonic states are then created from band states and not by trapping events. The absence of saturation in the intensity dependence of the fast PC (Fig. 3), in contrast to the slow PC (Fig. 9), seems to favor the model of Orenstein, since the polarons created by interchain separation are not expected to show any saturation, whereas the subsequent solitonic states will exhibit saturation in both models. However, the absence of saturation in the fast-PC component should not be seen as definitive evidence for one of these models, as this effect may be due to other mechanisms not discussed here. Jeyadev and Conwell[57] suggested determining the different contributions to the fast PC by measuring the field dependence at very high electric fields (more than 10^6 V/cm), where soliton and polaron heating is expected to become important. As already mentioned in Sec. II we were only able to increase the electric field to values slightly higher than 10^5 V/cm, and even at this limit it is not completely sure that dielectric breakdown does not affect our experimental results. Moreover, the additional effects of a change in the escape factor for geminate recombination would unfortunately complicate the analysis of such an experiment.

The difference in the intensity dependence of the fast and the slow PC allows us in principle to explain the different polarization anisotropies of the two components. For the fast component the photoresponse is linear with intensity for both polarization directions, leading to the observed anisotropy of 1.7. The slow component shows different intensity dependence for parallel and perpendicular polarization as a consequence of the different penetration depths of the light, resulting in different saturation levels for the creation of charged soliton defects. For parallel polarization the intensity dependence is less steep, and therefore the anisotropy increases. We recall here that the sublinear intensity dependence is not caused by bimolecular recombination processes but by an effect of saturation, as mentioned above.

VI. SUMMARY

In summary, we have shown the existence of fast- and slow-PC components by direct measurements and have investigated their dependence on time, temperature, light intensity, electric field, and the polarization of the light and of the electric field in detail. For the fast component we found a relaxation time of $\tau_{1/2}\approx 100$ ps, a migration distance of up to 400 Å, and a mobility of $\mu_{\parallel}\approx 2$ cm/V s. From the temperature independence of the fast PC we infer that the carriers are able to move freely along the polymer chains with a high kinetic energy. The slow component consists of carriers persisting up to seconds with a time-independent mobility, which is by a factor of 100 smaller than that of the fast PC. The transport mechanism of the slow PC is determined by hopping processes in analogy to the dark conductivity. The difference in the intensity dependence of the fast and slow PC demonstrates that only the slow PC tends to saturation. We have established the similarity between electronic properties of unorientated Shirakawa-type $(\mathrm{CH})_x$ and highly oriented Durham-Graz-type samples. The anisotropic properties of these materials can only be investigated in the highly oriented samples. (The Durham-Graz-type samples have in addition the advantage of a well-defined morphology and excellent surface quality, which allows a much better determination of the essential optical constants.) In the oriented samples we have observed a strongly anisotropic mobility of the photocarriers with respect to the applied electric field ($\mu_{\parallel}/\mu_{\perp}\approx 50$). The PC signal amplitude is also anisotropic with respect to the polarization of the incident light. For this reason we conclude that the photogenerated charge, detectable with PC must be attributed to carriers separated on different polymer chains (or chain segements). Therefore they have initially to be polarons. Carriers remaining on the same chain recombine into neutral excitations.

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