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Photoexcitation in Durham-route polyacetylene: Self-localization and charge transport

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We have measured the photoinduced absorption and photoconductivity which arises from long-lived photocarriers in unoriented films of polyacetylene prepared by the Durham synthetic route. The spectrally resolved photoinduced absorption shows induced absorption at 0.55 eV and photobleaching at 2.0 eV associated with charged photoexcitations, and induced absorption at 1.5 eV associated with a neutral photoexcitation. Above 200 K the mobility of the charge carriers exhibits an activated temperature dependence ($E_a = 0.31$ eV), and at 290 K we obtain a mobility value of 5×10^{-5} cm^2/V s. These results are interpreted in terms of an interchain-hopping mechanism for bipolaron-like charged-soliton pairs.

I. INTRODUCTION

Conjugated polymers form a class of semiconductors with properties very different from three-dimensionally bonded materials. The conjugation path along the polymer backbone allows ready charge transport along the chain, but as a consequence of the quasi-one-dimensional character of the electronic structure, charges added to the chain cause the chain to relax locally to form soliton-like localized states for polyacetylene[1,2] and polaron-bipolaron states for other polymers.[3,4] This self-localization of added charges (within a region of 10 to 20 carbon-carbon bonds on the chain) confines the excitation to a single polymer chain, and motion past the polymer chain ends or motion to adjacent chains is expected to be inherently difficult. Thus, the motion of charged solitons (or polarons) is strongly affected by the anisotropic electronic structure, and also by the nature of disorder, in the arrangement of polymer chains, etc. Solitons and polarons formed around added charges have associated electronic states deep in the semiconductor gap together with localized vibrational excitations. Both the electronic excitations between the gaps states and the band edges, and the vibrational modes are accessible spectroscopically, and this has allowed a very detailed investigation of these self-localized states.[5,6]

Charge can be added to the polymer chains in various ways: chemical doping provided the first evidence for high electronic mobilities,[7,8] photoexcitation can allow charge separation,[6] and charge injection into accumulation or inversion layers in device structures has recently been demonstrated.[9] Chemical doping introduces further disorder into the structure, though the accommodation of the associated counterions within the structure and the associated Coulomb potentials. Photoexcitation and charge injection provide cleaner means of introducing charge onto the chains, and there is direct experimental evidence for this in the lower frequencies of the ir vibrational modes associated with translation of the soliton along the polymer chain following photoexcitation, which indicates that the charges are less strongly pinned.[10,11]

Investigations of the charge-transport processes in polyacetylene have been made for charge carriers introduced by the three methods reviewed above. Whereas the determination of the charge concentration is simply made for chemical doping (dopant concentration) and accumulation and/or inversion layer formation (electric field in dielectric layer), for photoexcited carriers this is less straightforward. However, in this paper we make use of the fact that the photocarriers in polyacetylene are spectroscopically accessible and can therefore be investigated both by means of the transient optical absorption to which they give rise, and also by the photoconductivity (PC) which results from their mobility. By applying photoinduced-absorption (PA) and photoconductivity measurements to the same samples we obtain information on both the nature of the long-lived charged photoexcitations in the material, and on the transport mechanism by which these carriers move under the influence of an applied electric field.

A. Mechanisms for stabilization of long-lived photoexcited charged solitons

The response of a single polyacetylene chain following photoexcitation was first considered by Su and Schrieffer,[12] whose dynamical simulations show that the photogenerated electron and hole rapidly separate and relax to form isolated positively and negatively charged solitons (S^+ and S^-) within a few periods of the optic phonon modulating the bond dimerization. Measurements of photoinduced absorption under quasistatic conditions of band-gap illumination do show the expected absorption from $S^{\pm}$ states, with an induced absorption feature peaked near 0.43 eV and with a tail to high energies, as expected from the joint optical density states between the soliton level and the band-edges.[10,13–15] However, the $S^{\pm}$ detected under the experimental conditions used[10,13–15] are known to have lifetimes on the order of milliseconds. It is unlikely that $S^{+}S^{-}$ pairs formed on one chain can avoid geminate recombination for this length of time, and there is evidence for a recombination time of no more than a few picoseconds.[16] Orenstein *et al.*[17] suggested that interchain charge transfer is necessary to allow separation of the photogenerated charge pairs; the possibility for three-dimensional diffusion greatly reduces the probability of geminate recombination. Polarization-dependent measurements of PA on highly oriented Durham polyacetylene films show direct evidence for interchain charge transfer, with a higher quantum yield for $S^{\pm}$ photogeneration with the pump beam polarized perpendicular to the chains.[6] Charges separated between chains are expected to relax to form polarons, P^{+} and P^{-},[3,12] but the appearance of a single midgap electronic transition indicates that these polarons are subsequently converted to charged solitons. There are two proposed mechanisms for this.

Orenstein *et al.*,[17] suggested that the neutral, spin-$\frac{1}{2}$ soliton-like defects, S^{0}, present in *trans*-polyacetylene in a concentration of typically 10^{19} cm^{-3}, act as traps for the photogenerated charges, so that the net reaction is $2S^{0} \rightarrow S^{+}+S^{-}$. This process can be tested in two ways. Firstly, the removal of S^{0} states should give a negative light-induced electron-spin resonance (LESR) signal. However, at present there is, in general, no direct experimental evidence for a LESR signal associated with the charged solitons.[18,19] (There is evidence for a negative LESR sample in some samples which from other characterizations contain more defects than samples which do not show a LESR response.)[18] Secondly, associated with the appearance of photoinduced absorption at 0.43 eV from charged solitons, there should be a corresponding photoinduced bleaching (PB) of the optical transitions from the S^{0} states removed. Vardeny and Tauc[20] show that the effect of an on-site Coulomb repulsion, U, is to shift optical transitions associated with $S^{\pm}$ below midgap (PA at 0.43 eV) and transitions from S^{0} to above midgap. They report that at a temperature high enough to suppress the PA at 1.35 eV due to a neutral excited state,[15] typically 200 K, they find PB at 1.4 eV, and they attribute this to the bleaching of absorption due to band-to-S^{0} transitions. However, not all samples of polyacetylene show the same behavior, even if ostensibly made by the same recipe, and Colaneri *et al.*[21] found no evidence for PB at this energy, but instead a broad PB feature at the bandedge and above, which they associate with bleaching of band states.

The alternative route for interchain-separated charges to form solitons is the energetically favored conversion of a like-charge pair of polarons present on the same chain to a like-charge pair of solitons on that chain, e.g., $P^{+}+P^{+} \rightarrow S^{+}+S^{+}$.[18] Motion of this soliton pair to an adjacent chain requires transfer of both charges together with a relatively large-amplitude lattice distortion, and as for bipolaron hopping this will be very much slower than motion of single charges.[22] Soliton states thus stabilized are generated from band states, and PB is expected at the π-π^{*} band edge. No LESR signal is expected, and the saturation PA signal will correspond to a density of order one soliton pair per conjugated length of chain. For *trans*-polyacetylene about one-half of these will have an odd number of carbon atoms, and thus possess an S^{0} level. The saturation PA signal will therefore correspond to a density of photoinduced charged solitons comparable to the density of "extrinsic" S^{0} states, and be the same as for the mechanism involving the ionization of the S^{0} states discussed above. This is the model for the stabilization of long-lived photoexcited charged solitons that is supported by Colaneri *et al.*, on the basis of their measurements on polyacetylene prepared by the Shirakawa synthetic route,[21] and is consistent also with the behavior of polyacetylene prepared by the Durham synthetic route.[6]

B. Photoconductivity in polyacetylene

The photoconductivity (PC) edge in polyacetylene broadly matches the absorption edge,[23–28] and also follows the excitation profile for PA from charged solitons.[10] The PC can be resolved into two components, a temperature-independent "fast" component, and a slower component which can be correlated with the PA due to "long-lived" charged solitons and which decreases with falling temperature. PC anisotropy with polarization of the excitation source has been reported.[23,26–28] The "fast" component shows a small anisotropy after correction for sample reflectivity, with a slightly larger response for perpendicularly polarization, whereas the "slow" component is strongly anisotropic, and is also preferentially excited by perpendicularly polarized excitation (ratio of about 4 to 1). This polarization dependence follows that observed for the "midgap" PA.[6]

The origin of the "fast" component of the PC is not at present well understood, not least because it is not resolved in the transient measurements reported (resolution of about 50 psec).[25–28] It is very likely that the carriers responsible for the phototransport are "hot" and are not self-localized on particular chains, and it is possible that the "fast" photocurrent is turned off when the photocarriers do self-localize as solitons on particular chains.[29]

The "slow" component of the PC is well identified as tracking with time response and light intensity with the PA feature associated with charged solitons.[5,10] Although it has been established that the PC falls as the temperature is lowered, the measurements reported here are the first quantitative set of results for the temperature dependence of the mobility of the photocarriers.

C. Durham-route polyacetylene

In the present work we have used polyacetylene prepared by the Durham precursor route.[30] This synthetic route utilizes a solution-processible "precursor" polymer, poly{5,6-bis (trifluoromethyl)-bicyclo[2.2.2]octa-5,7-diene-2,3-diyl) -1,2-ethenediyl}, which can be converted by thermal elimination of hexafluoroorthoxylene to give a fully dense and nonfibrous form of *trans*-polyacetylene.[30] By varying the conditions under which this conversion reaction is carried out it is possible to obtain polyacetylene products with a wide range of morphological and electronic properties.[23,31–35] In particular, if the precursor polymer is stretched during the thermal conversion to polyacetylene, very highly oriented films can be obtained. We have previously shown that these stretch oriented films show properties similar to "high-quality" Shirakawa-route samples, and characteristic of a material in which the straight chain sequences are significantly longer than the typical width of soliton-like excitations. This is evident from the position and dispersion of the resonance Raman spectra.[23,34]

In contrast in unoriented films the Raman frequencies are shifted to higher frequencies and the peak in the π-π^* optical-absorption band is shifted from just below 2 to 2.4 eV.[32] We consider that this is due to the presence of conformational defects such as chain bends or twists, which limit the straight-chain sequences in unoriented films to no more than 20–30 carbon atoms,[34] and which can be removed (at least partially) by the stretch alignment process. In spite of the apparently short "conjugation lengths" in the unoriented Durham-route polyacetylene films, the material still supports soliton-like excitations, and the same vibrational and electronic optical excitations are measured as in the "long-chain" oriented samples.[11] There are frequency shifts in the PA features, the electronic midgap absorption is shifted up from 0.46 to 0.55 eV, and the vibrational excitations of the soliton indicate that its effective mass is considerably enhanced over the value for the oriented films.[11]

While we have put some considerable effort into the investigation of the properties of oriented films,[6] these are only readily obtained as free-standing films, and are usually prepared with thicknesses of a few micrometers. They are thus optically dense above the band edge, and are also difficult to thermally anchor. The latter problem is particularly acute for the PC measurements as we discuss below. Unoriented films are readily cast on appropriate substrates by spin coating the precursor polymer from solution, and we have considerable experience of this technique for the production of semiconductor devices.[9] In the present work, films were spin coated onto sapphire substrates for maximum thermal anchoring. Experiments were performed in an Oxford Instruments helium cryostat with helium exchange gas around the sample.

II. EXPERIMENTAL RESULTS

A. Optical absorption and reflectivity

The optical transmission spectrum obtained from a thin (78 nm) unoriented sample is shown in Fig. 1. The solid curve represents data obtained at 295 K, and shows an extended absorption edge with an onset near 1.5 eV which rises to a broad peak centered at about 2.4–2.5 eV. This is about 0.5 eV higher in energy than for Shirakawa-route and oriented Durham-route samples,[36,37] and is due to the conformational disorder in unoriented films. In order to interpret photoexcitation measurements correctly, we need values for the optical coefficients of the material at the laser pump energy (2.7 eV), and also the temperature dependence of the absorption edge. The results of transmission measurements carried out at different temperatures are illustrated in Fig. 1. The data shown in the inset give values for the fractional transmission change $\Delta T/T$ per degree Kelvin [i.e., $T^{-1}dT/d\Theta$, where Θ is the temperature] of 6.1×10^{-4} K^{-1} and 3.6×10^{-4} K^{-1} at 1.5 and 2.0 eV, respectively. These values are used below to demonstrate that the measured sample photocurrents do not arise from bolometric effects. The absolute reflectance R of the samples was also measured by comparing the light intensity reflected at near-normal incidence with that from a mirror placed in the sample position. At 2.7 eV we obtain values of $R=0.29\pm0.04$ and $T/T_0=(9.6\pm0.5)\times10^{-2}$, which with the measured sample thickness of 78±1 nm leads to a value for the absorption coefficient of $(2.15\pm0.2)\times10^{-5}$ cm^{-1}. This can be compared to the peak values of absorption coefficient of 3×10^5 (Ref. 37) and 1.5×10^5 (Ref. 38) which have been reported for Shirakawa-route polyacetylene.

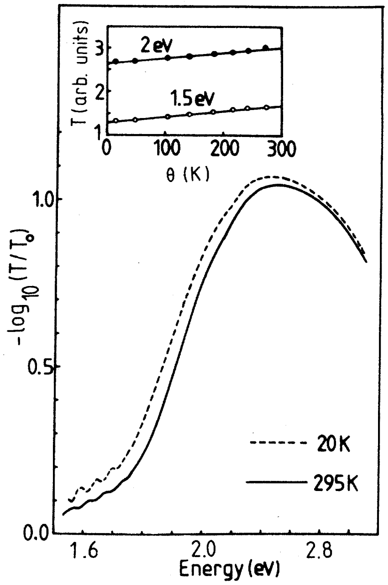

FIG. 1. Optical transmission T for unoriented Durham-route polyacetylene measured at 20 and 300 K (T_0 is the transmission without the sample present). Inset shows the variation of transmission through the sample at 1.5 and 2.0 eV as a function of temperature.

B. Photoinduced absorption measurements

Photoinduced absorption measurements were carried out using the 457.9-nm line of a continuous-wave argon-ion laser as a pump beam, and a tungsten lamp and grating monochromator which provided a variable-wavelength probe beam. The probe intensity, T transmitted by the sample and its modulation ΔT were measured using solid-state detectors and a lock-in amplifier which was phase referenced to a mechanical chopper.

The PA spectrum of an unoriented film at 20 K is illustrated in Fig. 2, for a pump intensity of approximately

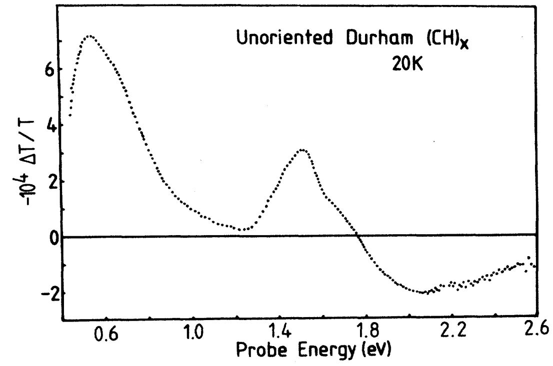

FIG. 2. Photoinduced absorption spectrum for unoriented Durham-route polyacetylene.

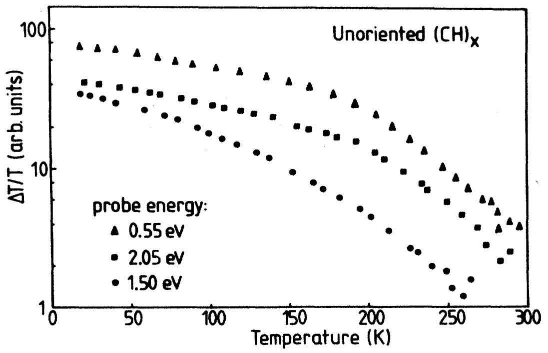

FIG. 3. Temperature dependence of the modulus of the photoinduced absorption signal at energies of 0.55, 2.05, and 1.50 eV.

1 W/cm^{-2} and chop frequency of 79 Hz. The spectrum shows the usual pair of absorption features,[13–17,39,40] with a low-energy (LE) peak at 0.55 eV due to charged soliton-like excitations, and a high-energy (HE) peak at 1.5 eV associated with overall neutral excitations. Above 1.75 eV there is a crossover to photoinduced bleaching of the interband transition, with a peak at 2.05 eV. The energies of all these features[11,39,40] are higher than found in either oriented Durham- or Shirakawa-route polyacetylene, and this is due to the larger π-π^* band gaps on the disordered polymer chains in the unoriented Durham-route material.

The strength of the HE feature is similar here to that measured in Shirakawa-route material,[13,15] but considerably larger than found in oriented Durham-route samples.[40] The contrast in behavior for unoriented and oriented samples, which are in other respects prepared similarly, points to the role of a conformational defect (removed on orientation) in the stabilization of the excitation.[40] We have found that the intensity of the HE feature in unoriented samples is reduced for films which have been held at higher temperatures during isomerization (100 °C rather than 80 °C), and this correlates with the greater degree of local ordering of the chains obtained by the higher-temperature isomerization.[32]

The disorder present in unoriented Durham-route samples strongly affects the recombination kinetics of both the charged and neutral photoexcitations. This is evident from the temperature dependence of the PA features illustrated in Fig. 3, which are much weaker than those measured for oriented Durham-route or Shirakawa-route samples. For example, the "knee" in the LE-feature data which is observed here at about 200 K occurs at around 150 K for oriented samples.[39] The HE peak is even more strongly affected: $\Delta T/T$ has fallen by an order of magnitude from its low-temperature value at 210 K for unoriented films, whereas for oriented films this point is reached at only 85 K.[40] Differences are also observed in the dependence of the PA features with pump intensity, as shown in Fig. 4. All three features exhibit an approximately linear variation with intensity, suggesting monomolecular recombination kinetics, with saturation at high intensities for both the LE and PB peaks. In contrast, with chopped pump beams, the LE features in oriented samples shows a sublinear dependence at low intensity and a more marked saturation. The variation of the PA and PB responses with chopper frequency at 20 K is shown in Fig. 5. Again the LE and HE features are not well differentiated, and typical response times of order 1 msec are obtained.

The thin samples used in this study show no sign of the thermal modulation features seen near the band edge in the PA spectra of micrometer-thick oriented samples.[39,40] At 300 K no PA signal is observable above the noise limit of the experiment, and this allows us to set an upper limit for any pump-induced modulation $\Delta\Theta$, of the sample temperature, Θ. The "worst case" is at 2 eV, where the noise-limited value of $|\Delta T/T| = 1.5\times10^{-5}$ and the temperature-dependent transmission value $T^{-1}dT/d\Theta = 3.6\times10^{-4}\ \mathrm{K}^{-1}$, set a limit of $|\Delta\Theta| < 0.04$ K.

It is now recognized that the metastable charged photoexcitations measured here are not present as the S^+S^- pairs which are produced initially. Of the two models

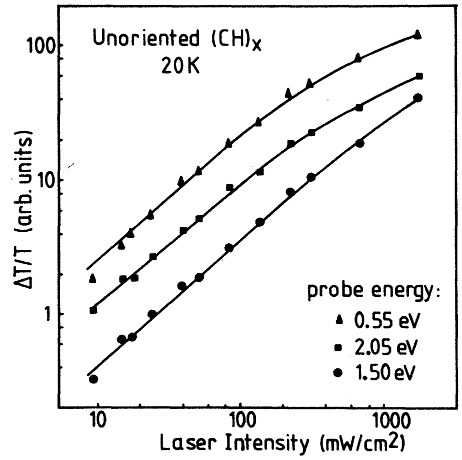

FIG. 4. Pump beam intensity dependence of the modulus of the photoinduced absorption signal, measured at 0.55, 2.05, and 1.50 eV.

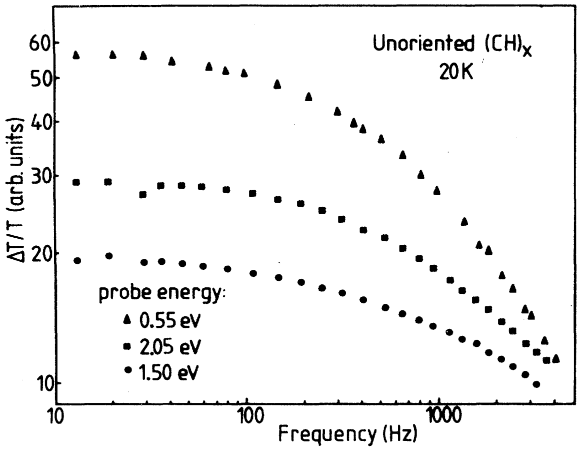

FIG. 5. Frequency dependence of the modulus of the photoinduced absorption signal measured at 20 K, at photon energies of 0.55, 2.05, and 1.50 eV.

put forward for the stabilization of "long-lived" charged solitons that we discuss in Sec. I A, we consider that the model in which there is formation of pairs of like-charge solitons on single chains is appropriate for our results on the unoriented Durham-route polyacetylene. In this model the soliton states are created from band states and the bleaching associated with the midgap absorption should be in the region of the interband transitions. The identical temperature and pump-intensity dependences of the LE and PB peaks illustrated in Figs. 3 and 4 show that this correlation is indeed observed experimentally. Furthermore, the requirement of conservation of area under the $\Delta T/T$ curve (oscillator-strength sum rule) extends the bleaching shown in Fig. 2 to well above 3 eV, well into the interband region.

C. Photoconductivity measurements

After carrying out PA measurements, gold interdigitated electrodes with a gap of 0.04 cm and effective length of 6.3 cm were shadow-mask evaporated onto the surface of the samples. Photoconductivity could then be measured under the same conditions as for the PA experiments; sample photocurrents were measured with a lock-in amplifier referenced to the frequency of the chopper in the path of the continuous-wave laser beam.

The dark current I_d obtained with an applied voltage of 50 V is illustrated by curve A in Fig. 6 and shows an activated temperature dependence with an activation energy E_a of 0.37 ± 0.04 eV. The strongly temperature-dependent dark current can limit the measurement of photoconductivity, since any periodic change in sample temperature, $\Delta\Theta$, produced by the chopped pump beam will give rise to a change in I_d which would be detected along with the ac photocurrent. In order to test for such an effect we note that since I_d is activated, the thermal modulation current ΔI_d, is given by

$$\Delta I_d = (\Delta\Theta E_a / k_B \Theta^2) I_d \tag{1}$$

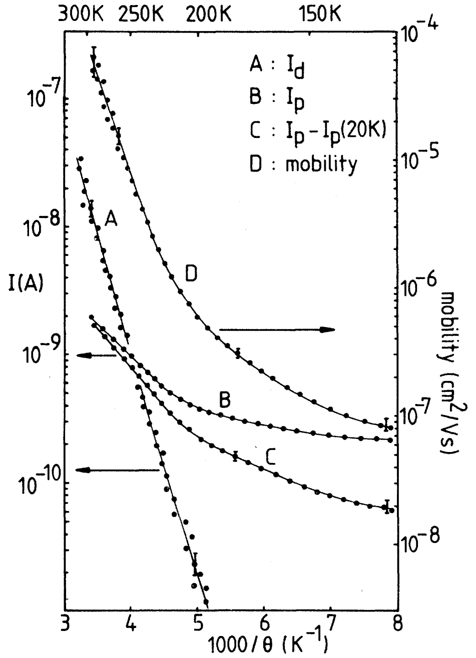

FIG. 6. Photoconductivity results. Plotted against reciprocal temperature are A, the dark current I_d; B, the photocurrent I_p; C, I_p minus its value at 20 K; D, the photocarrier mobility calculated using Eq. (4).

(for $\Delta\Theta \ll \Theta$). At $\Theta = 300$ K, using the measured value of $I_d = 2 \times 10^{-8}$ A and the upper limit for $\Delta\Theta$ set by the PA data (0.04 K), we obtain $\Delta I_d = 4 \times 10^{-11}$ A. This value is a factor of 100 smaller than the photocurrent I_p measured under the same conditions.

The temperature dependence of the photocurrent is illustrated by curve B in Fig. 6. Above about 200 K, I_p appears activated (activation energy 0.1 eV) and below this temperature tends to a constant value of 1.5×10^{-10} A. At high temperatures the photoconductivity is dominated by a temperature-dependent "slow" component which is due to the motion of the charged solitons observed in PA experiments. This correlation has previously been demonstrated by Blanchet *et al.*,[10] who showed that the excitation spectra for the PA and the photoconductivity are the same, and by Orenstein,[5] who showed that the two quantities exhibit the same time decay after pulsed excitation. A smaller fraction of the photocurrent is due to a temperature-independent fast component which exhibits a decay time of less than a few hundred picoseconds,[25–28] and which eventually dominates the response at sufficiently low temperature. This was established here by comparison of the chop frequency and intensity dependence of I_p and $\Delta T/T$.

Curve C in Fig. 6 shows the "slow" PC obtained from curve B by subtracting the value of I_p at low temperatures (1.5×10^{-10} A). The temperature dependence of the photocurrent can arise from both the carrier concentration and the mobility, as seen from the expression for the steady-state photocurrent,

$$I_p(\Theta)=N(\Theta)\mu(\Theta)eEw \ , \tag{2}$$

where N and μ are the areal carrier concentration and mobility, respectively, e is the electronic charge, E the applied field, and w the sample width. In contrast, the temperature dependence of the PA signal due to the same carriers arises only from the change in the steady-state areal carrier concentration, and is independent of the mobility, i.e.,

$$\Delta T/T(\Theta)=N(\Theta)\sigma \ , \tag{3}$$

where σ is the absorption cross section of a photocarrier, which we take to be 8×10^{-16} cm^{-2}.[5] We can therefore use the temperature variation of the PA response to obtain the temperature dependence of the mobility. Dividing Eq. (2) by Eq. (3) gives the following expression for the carrier mobility,

$$\mu(\Theta)=I_p(\Theta)\sigma[\Delta T/T(\Theta)eEw] \ . \tag{4}$$

We use Eq. (4) to calculate the photocarrier mobility from the data for the LE PA shown in Fig. 3, and the data for the slow component of the photocurrent in Fig. 6. The results of this calculation are shown as curve D in Fig. 6. AT 290 K we obtain a mobility value of 5×10^{-5} cm^2/Vs, which is low, and typical of a conduction mechanism involving phonon-assisted hopping. Above about 200 K the mobility is activated with an activation energy of 0.31 ± 0.03 eV, and at lower temperatures shows a deviation to a non-Arrhenius type of behavior. A marked increase of the mobility above 200 K is highly plausible, since such an effect would enhance the collision rate between photocarriers leading to a reduction in lifetime and a decrease in the steady-state PA, as observed experimentally.

III. DISCUSSION

A. Mobility of long-lived photocarriers

If we are to be able to learn about the mechanism for the transport of the charged photoexcitations in polyacetylene, we must start by establishing what these photoexcitations are. We know that the photocarriers that we measure have lifetimes of the order of milliseconds. The two models we have to choose between in the literature stabilize the excitations either through pinning to extrinsic defects (the neutral soliton ionization model) or through self-trapping as like-charge pairs of solitons (the bipolaron model).

1. Neutral soliton ionization and inter-soliton hopping

During isomerization from *cis* to *trans*, polyacetylene always shows the build up in concentration of spin-$\frac{1}{2}$ defects, whether it is produced by the Shirakawa or Durham synthetic routes. The final concentration is usually a few hundred parts per million carbon atoms. An extensive investigation of these defects has been carried out using magnetic resonance techniques (see Ref. 35 and references therein), and there is some degree of consensus that the region of the polymer chain over which the spin is localized shows many of the characteristics of the neutral soliton, with delocalization over some 10 to 20 carbon atoms. Much attention has been given to their possible role in determining the electronic properties of the material.

Electrical conductivity in polyacetylene in the low-doping regime, where the charged excitations are well spaced, bears some resemblance to that found in amorphous semiconductors[42] in that the carrier mobility falls rapidly with falling temperature. On-chain motion of charged solitons is expected to be easy, and it is well accepted that since straight-chain lengths are very much shorter than sample dimensions, carrier transport must involve interchain motion. Furthermore, since these interchain hops are likely to be slow they will be the rate-determining steps in the transport mechanism. As has previously been noted by Kivelson,[43] the potential barrier for interchain hopping of isolated solitons is very large, due to their topological nature. Kivelson has proposed a model appropriate for low doping concentrations when there are both charged and neutral solitons present, in which the interchain transfer of charged is achieved by transfer of charge from neutral to charged solitons (and vice versa) which may be on adjacent chains. This model of intersoliton hopping gives a strongly temperature-dependent hopping rate (the multiphonon transfer gives a power-law dependence for the mobility of the form T^n with n about equal to 10). Epstein[44] has successfully fitted both the dc and ac conductivities for polyacetylene produced by the Shirakawa synthetic route to this model.

Within the single-particle models for the soliton formation in polyacetylene,[1,2] the neutral soliton has a singly occupied state at midgap and this should always be preferentially charged prior to the formation of new solitons to accommodate added charges. However, on-site Coulomb interactions will raise the energy at which the neutral soliton can accept an electron or hole,[20] and the optical transitions from neutral soliton to band edge is considered to be shifted up from midgap to close to the band edge (1.4 eV). It is important to remember that a polyacetylene chain with a neutral soliton is not in its ground state unless the chain has a odd number of carbon atoms; the role of chain defects in stabilizing the soliton must therefore be considered. Our view is that in Durham-route polyacetylene, the spin-$\frac{1}{2}$ defects that are usually termed as neutral solitons are located in highly disordered regions of the chains, where the local π-π^* gap is higher than average. The energies for charging the defects are thus mostly raised above the energy for interband excitations, so that the defects play no part in the electrical and optical properties of the material. We summarize the evidence for this.

(a) The PB associated with PA due to photoexcited charged solitons is coincident with the π-π^* band, and indicates that the charged solitons are created from band states. This is as observed for Durham-route polyacetylene, and at least some samples of Shirakawa-route polyacetylene[21] (though not for others).[5,20]

(b) Anisotropic measurements of the ESR line due to the spin-$\frac{1}{2}$ defects in oriented samples show a smaller anisotropy (1.5 to 1) than that calculated from the anisotropic hyperfine interaction between electron and proton (2 to 1).[45] We infer that the spin-$\frac{1}{2}$ defects do not reside in the oriented regions of the sample.

(c) We have previously argued that the so-called high-energy PA feature at 1.35 eV is stablized by structural defects. We find that for Durham-route polyacetylene its magnitude falls with an increasing degree of order (from unoriented to oriented). We find also that for the oriented samples, the HE PA is unpolarized with respect to the probe beam (in contrast with the LE feature which is strongly polarized).[40] This indicated that the excitation that is probed in these experiments is either localized to within one carbon-carbon bond, or resides in the disordered regions of the sample, presumably in the regions in between the oriented crystallites. If, as has been suggested on the basis of light-induced ESR data,[19] the HE feature is associated with the neutral spin defects, then we can infer that these reside in disordered regions of the chains.

2. *The bipolaron model and interchain bipolaron motion*

We favor the "bipolaron model" for the stabilization of the charged photoexcitations in Durham-route polyacetylene, for the reasons advanced above, and also because in most respects the behavior of the photoexcitations in other polaron-supporting polymers is very similar (though the PA shows the presence of two midgap states).[6] When we turn to consider the mechanism for the transport of the photocarriers, we must, therefore, reject the intersoliton hopping model due to Kivelson. We consider that the interchain transport process is the hopping of the pairs of like-charge solitons which, in this respect, behave as bipolarons. As discussed by Chance, Brédas, and Silbey,[46] like-charge soliton pairs are analogous to biopolarons and are not topologically restrained from interchain hopping. The process by which they do this will involve an intermediate stage in which one of the two charges has transferred to an adjacent chain, and the instantaneous description is of two polarons on adjacent chains. If the second charge then follows the first, the bipolaron has moved from one chain to another and has surmounted an energy barrier equal to the stabilization energy of the bipolaron (or soliton antisoliton pair). Here, we identify this as the activation energy we find for the mobility of the photocarriers, of 0.31 eV.

A simple calculation can be used to check whether this type of mechanism is consistent with the measured magnitude of the mobility. The general expression for the hop rate of a self-localized carrier is

$$R=\omega \exp(-W_h/k_B\Theta) \tag{5}$$

where W_h is the hop energy and ω is the attempt-to-hop frequency.[42] For three-dimensional hopping, the mobility obtained using the Einstein diffusion relation is

$$\mu=\frac{ea^2\omega}{6k_B\Theta}\exp(-W_h/k_B\Theta) \tag{6}$$

where a is the hop distance.[42] If we take $a=4.2$ Å (the interchain separation), $\omega=3.9\times10^{13}$ Hz (the average frequency of the optic phonons which modulate the chain dimerization), and $W_h=0.31$ eV (the measured activation energy), then at 290 K we obtain a mobility of 1.9×10^{-6} cm^2/V s. This value is lower than the measured value, but is nevertheless of the correct order of magnitude. In fact, the hop-distance parameter a is more correctly interpreted as the average distance that a carrier is able to travel between interchain hops, and this will be considerably higher than the interchain separation if the charge carrier is able to move along the chain. A value of $a=21$ Å is required to adjust the modeled mobility to the experimental value, and we consider that this is a reasonable value for unoriented Durham-route polyacetylene.[32]

Models of "small-polaron" transport give hop rates which change from an activated high-temperature dependence at some fraction of the characteristic phonon temperature (Debye temperature for coupling to acoustic phonons), to a weaker nonactivated behavior at lower temperatures.[47–49] This is due to a change from phonon-assisted hopping over the barrier at high temperatures to tunneling through the barrier at low temperatures. For the results we obtain on the mobility of photocarriers in polyacetylene, we find that the activated behavior present above about 200 K gives over to a weaker temperature dependence at lower temperatures. It is tempting, therefore, to associate this change in behavior to the crossover from hopping to tunneling in the "small-polaron" model.

Like-charge pairs of solitons on long, defect-free chains of polyacetylene are shown in calculations to stay apart; both the potential due to the displacement of atoms on the chain and the Coulomb interaction between the two charges are repulsive.[50] If the two like-charge solitons are able to separate, then the bipolaron hopping rate will be reduced.[46] However, both interchain coupling[51] and the finite extent of conjugation along the chains will act to confine the two solitons, and we consider that it is unnecessary to take account of separated solitons for the unoriented Durham-route polyacetylene.

B. Comparison with mobility of extrinsic carriers

For the case of photocarriers, we are able to identify from spectroscopic measurements that they are present as like-charge pairs of solitons; hence, we must describe the transport in terms of bipolaron motion along and between chains. For carriers introduced through chemical doping the situation is less clear because in general we have less spectroscopic information. It is interesting here to compare the properties of as-made samples of Durham-route polyacetylene. These contain the usual level of spin-$\frac{1}{2}$ defects, as already discussed, and they also contain a low concentration of charges which are responsible for the dc conductivity. Measurements on Schototky-barrier diodes formed between aluminum and the polyacetylene[9] do provide the necessary information to characterize the charges present. From the current-voltage and capacitance-voltage characteristics we know that the charge carriers are p type and present in a concentration of about 10^{16} cm^{-3}. From the differential optical transmission measurements through the depletion regime we also know that these *p*-type carriers show the same midgap optical-absorption signature that we find in PA for the photocarriers, with a peak in absorption at 0.55 eV. This concentration of charge defects is consistent with thermopower measurements,[52] and it is also evident that the carrier concentration does not vary significantly in the temperature range which is accessible to measurements (above 200 K). We do not know the origin of these *p*-type carriers, though we suspect that they are associated with catalyst residues at the chain ends of the Durham precursor polymer.

The transport properties of these extrinsic carriers are now readily established. The dark conductivity is shown in Fig. 6; it shows activated behavior, with energy of activation 0.37 eV. The room-temperature carrier mobility inferred from the conductivity (3×10^{-8} S/cm) and the concentration is about 2×10^{-5} cm^2/V s. These values are rather similar to those we have established for the photocarriers, and we consider that the same model for transport is appropriate for both the extrinsic carriers and the photocarriers. At low temperatures the dark conductivity falls more rapidly than the photocarrier mobility, as seen in Fig. 6. We have not been able to establish whether the concentration of *p*-type carriers remains constant below 200 K, but we suspect the carriers become trapped at the dopant sites, and that this accounts for the discrepancy between the measured dark conductivity and mobility limited by interchain motion of bipolarons.

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