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## One-Dimensional Wide Energy Bands in a Polydiacetylene Revealed by Electroreflectance

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Above a region of excitonic transitions the polydiacetylene DCHD [poly(1,6-di(N-carbazolyl)-2,4-hexadiyne)] shows at the photoconduction edge a large electroreflectance response for fields parallel to the polymer. The signal broadens with field strength indicating a high-field limit for electroreflectance. Evaluation yields  $E_g = 2.335$  eV,  $m^* = 0.05m_0$ , and  $\mu = 2800$  cm<sup>2</sup>/V sec. The influence of a field perpendicular to the polymer chain is 3 orders of magnitude smaller. This unique anisotropy indicates that delocalization of the electrons occurs only along the polymer.

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Electroreflectance has provided a sensitive tool to study the band structure of inorganic semiconductors. Transitions at singularities of the joint density of states respond particularly sensitively to an external field and are therefore lifted from the broad background reflectance. This sensitivity, however, decreases with decreasing dispersion of the energy bands, which apparently has prevented the application of this technique to organic solids, where the energy bands are usually narrow. Wider bands can be expected when  $\pi$  orbitals overlap in certain crystal directions, as in the polydiacetylenes where single crystals of good quality are available by solid-state polymerization.<sup>1</sup>

This paper presents transverse electroreflectance spectra of the polydiacetylene DCHD [poly(1,6-di(N-carbazolyl)-2,4-hexadiyne)], the structure of which is shown in the inset in Fig. 1. Alternating triple-, double-, and single-carbon bonds form the repeat unit of the polymer chains, which are oriented parallel to the  $b$  axis of the monoclinic crystals.<sup>1</sup> The unit cell along  $b$  is very short, only 4.91 Å. Therefore, it appears possible that translationally equivalent  $\pi$  bonds

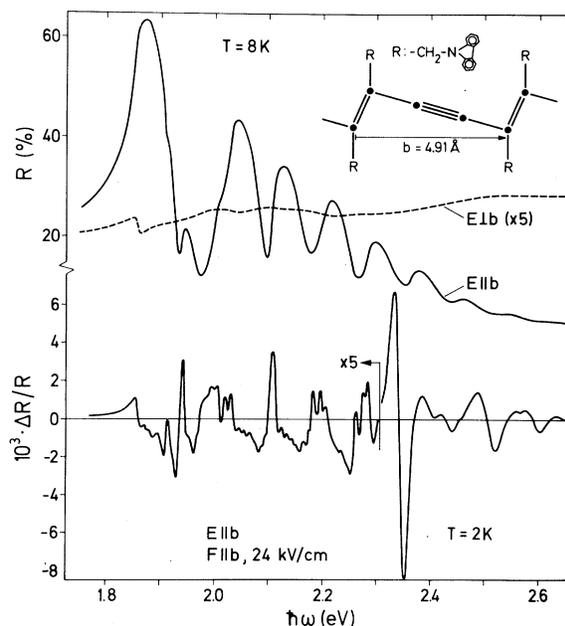


FIG. 1. Comparison of reflectance and electroreflectance spectra of DCHD for polarization of light parallel and perpendicular to the polymer chain. The inset shows the short repeat unit of the polymer.

have sufficient overlap for delocalization of the electrons along  $b$ . Since the interaction between different polymer chains is small, this would result in a one-dimensional band for the  $\pi$  electrons.

The excitation of the  $\pi$ -electron system of the chain gives rise to a strong excitonic peak in reflectance followed by vibronic satellites (Fig. 1). The spectrum is strongly polarized. Coupling to light occurs predominantly for the polarization ( $\vec{E} \parallel \vec{b}$ ) parallel to the polymer chain, pointing to a one-dimensional character of the electron system. Similar spectra are obtained for other polydiacetylenes different only by the side group  $R$  which is a carbazole group in DCHD.

Very surprisingly, the excitations respond quite sensitively to an external field. Moderate fields of 20 kV/cm change the reflectivity by more than  $10^{-4}$ , comparable to the response in many semiconductors. This requires, however, that the field is applied parallel to the polymer ( $\vec{F} \parallel \vec{b}$ ). The response to a perpendicular field  $\vec{F} \perp \vec{b}$  is 3 orders of magnitude smaller, hardly noticeable in an experiment. Such anisotropy is unique and has never been observed in semiconductors. Even for the highly anisotropic trigonal Se, the anisotropy of the electroreflectance sig-

nal with respect to field orientation is only 3–4.<sup>2</sup> This anisotropy fits perfectly with the view of a one-dimensional electron system where the electrons are delocalized only along the polymer.

The electroreflectance response of the excitons can be explained as a field-induced energy shift due to a large charge-transfer component of the exciton.<sup>3,4</sup> This part of the spectra will be discussed in a separate paper. Here we intend to discuss only the striking signal found at 2.3 eV. This signal is 10 times larger than the response of the exciton and its satellites, which has been enlarged in Fig. 1 by a factor of 5. A field of 24 kV/cm alters the reflectivity by almost 1%, comparable to the response of the band edge of Ge.<sup>5</sup> The reflectivity does not reveal any peculiarity at this energy. The photoconductivity, however, rises strongly above this point, which has been interpreted as the onset of interband transitions creating free carriers.<sup>6</sup> A similar strong electroreflectance signal has been observed at the photoconduction edge of another polydiacetylene crystal PTS.<sup>7</sup>

Figure 2 shows the electroreflectance spectrum near 2.3 eV at various field strengths. Figure 3 gives the dependence of the amplitude on the field, including results of different samples and at 77 K

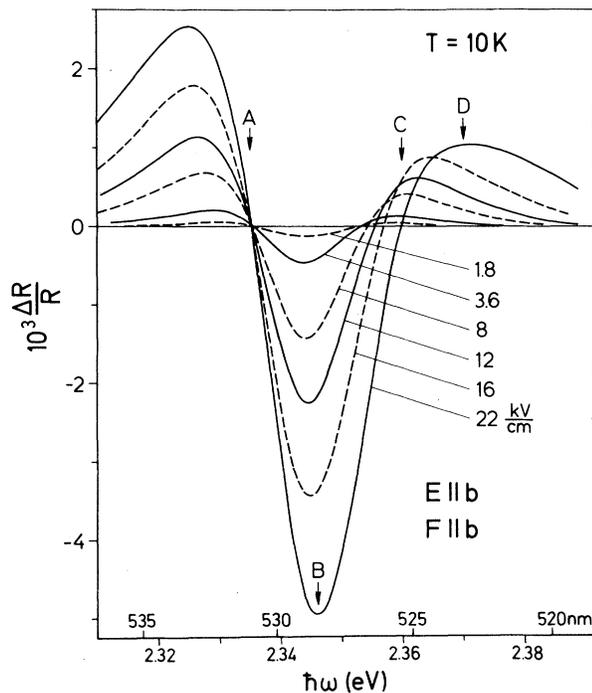


FIG. 2. Field broadening of the band-gap signal in DCHD.

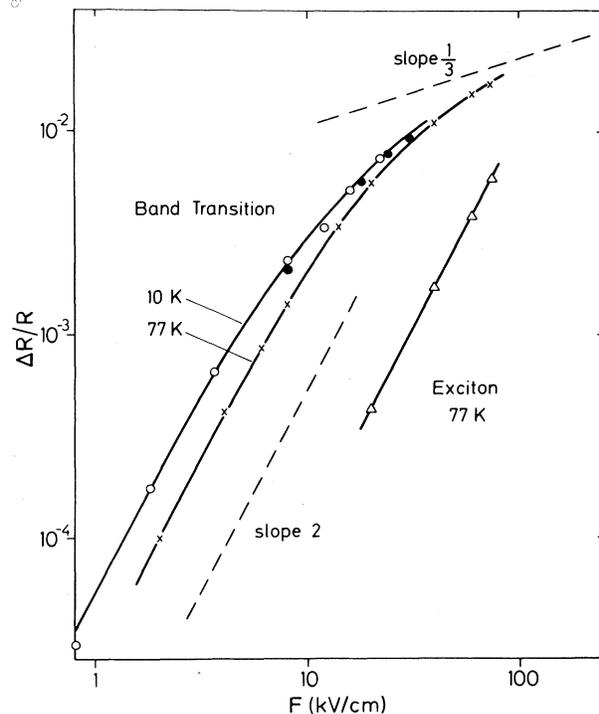


FIG. 3. Field-strength dependence of the amplitude of the band-edge signal and of an excitonic response.

where in liquid nitrogen larger fields were applicable. Up to 6 kV/cm at 10 K the signal rises quadratically with the field strength. This is typical for the low-field limit of electroreflectance when the field is a small perturbation of the electronic states.<sup>8</sup> The shape of the spectrum is then determined by lifetime broadening. With further increasing fields, however, the signal rises more slowly, differently from the excitonic response which rises quadratically over the full range of fields. Simultaneously, the signal broadens, which is clearly indicated by the shift of the zero  $C$  and the maximum  $D$  in Fig. 2. This behavior is in accordance with the high-field limit of electroreflectance when the perturbation of the electron states by the field exceeds lifetime broadening. At moderate fields this has been achieved only in a few cases<sup>5,9</sup> when, because of a small effective mass, the electro-optical energy  $\hbar\theta = (\hbar^2 e^2 F^2 / 2m^*)^{1/3}$  becomes sufficiently large. If this high-field limit is realized then the signal should only increase with  $F^{1/3}$ ,<sup>5,10</sup> a dependence which is approached in DCHD. Further hints for the high-field limit are seen in the comparison of the band-signal amplitudes at 10 and 77 K in Fig. 3. At low fields the signal at 10 K is about twice as large as at 77 K because of the smaller lifetime broadening. The high-field limit is reached earlier at 10 K and because of the resulting slower increase of the signal with rising fields both curves approach each other. At fields above 20 kV/cm both curves merge, indicating that thermal broadening is no longer dominant. This high-field range is not reached for the excitons where also no field broadening is observed.

Theoretical studies for the high-field limit of electroreflectance<sup>10</sup> show that the external field causes oscillations of the joint density of states around its field-free shape, reflecting the behavior of the Airy functions  $\text{Ai}(x)$ , which are the solutions for a free electron in a uniform field. The field-modulated spectrum should scale with the argument of the Airy function  $x = (E_g - \hbar\omega) / \hbar\theta$ , where  $\hbar\theta$  ( $\sim F^{2/3}$ ) is the electro-optic energy and  $E_g$  the band gap. The band-gap signal in DCHD follows this prediction, as shown in Fig. 4, where the distance between certain points of the spectrum marked in Fig. 2 is plotted versus  $F^{2/3}$ . The curves for 10 and 77 K do not coincide because of different thermal broadening. At high fields, however, at both temperatures the spectrum broadens at the same rate with the predicted field-strength dependence. With the additional information, obtained by Kramers-Kronig analysis,

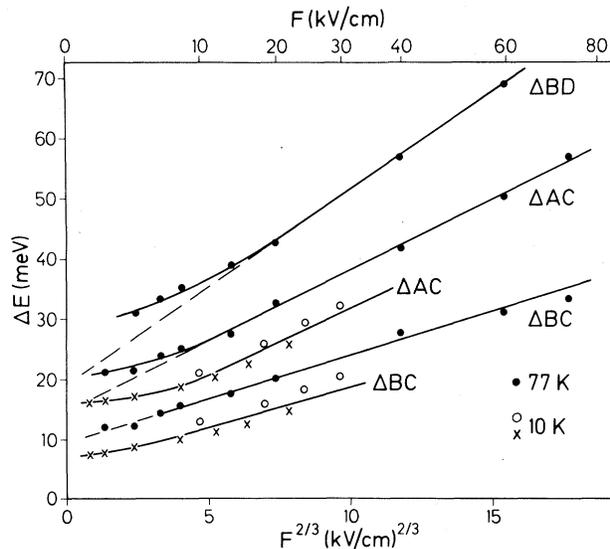


FIG. 4. Scaling of the field broadening of the band-gap signal with  $F^{2/3}$ .

that in this energy range the shape of  $\Delta R/R$  is about the same as that of  $\Delta\epsilon_2$ , the electro-optic energy can be calculated.<sup>10</sup> The band gap is found at 2.335 eV, about 0.48 eV above the first excitonic transition. The resulting reduced effective mass  $m^* = 0.05m_0$  is surprisingly small for an organic solid, but it agrees with the experience from semiconductors that field broadening in electroreflectance is observed only in cases of small effective mass. This value of the mass is an upper limit, uncertain mainly by the question of whether one- or three-dimensional electro-optic functions should be employed. Using the difference between zeros and maxima rather than the argument of the function itself reduces this uncertainty. The extreme anisotropy of the electroreflectance spectrum with respect to field orientation proves that the light mass and the corresponding wide bandwidth is obtained only along the polymer chain. The shape of the spectrum, however, gives no hints for a one-dimensional band edge with a polelike singularity. Theoretical studies indicate that this singularity may be removed by the influence of the deeper-lying strong excitonic transitions.<sup>11</sup>

At about 10 kV/cm the electro-optic energy becomes comparable to lifetime broadening. The corresponding energy  $\hbar\theta = 8.6$  meV can be used to estimate the lifetime  $\tau$  for the electrons to be  $8 \times 10^{-14}$  s. This results in a microscopic mobility  $\mu = 2800$  cm<sup>2</sup>/V s. A high mobility is also in-

licated by transport measurements in polydiacetylenes.<sup>12</sup>

We conclude from the results on DCHD that electroreflectance is a sensitive tool in the study of delocalized states in organic solids. In cases like DCHD, where, as a result of a small length of the unit cell overlap between translationally equivalent  $\pi$  states becomes large, energy bands of considerable dispersion result with correspondingly small mass and high mobility. The electroreflectance signal on the photoconduction edge in DCHD is in excellent accordance with band-structure theory as developed for inorganic semiconductors. The small influence of a field perpendicular to the polymer ( $\vec{F} \perp \vec{D}$ ) reveals the polydiacetylene crystal DCHD as a one-dimensional semiconductor with the electrons delocalized along the polymer but still restrained to a single chain.

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## Role of Dislocations in the Electrical Conductivity of CdS

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A large anisotropy in the electrical conductivity of CdS appearing below 30°K is reported. This anisotropy casts serious doubt on the customary view that impurity hopping supplies the low-temperature conductivity. We present a new model for this conductivity based upon the electronic screening of the piezoelectric polarization around dislocations. Numerical solutions of the highly nonlinear Poisson equation quantitatively justify this model.

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Impurity conduction is the phenomenon which is conventionally invoked to explain the excess conductivity of lightly doped semiconductors at low temperatures.<sup>1</sup> It comes about through phonon-assisted tunneling from filled to empty donors or by thermal excitation of electrons to double occupancy states of donors among which transport can occur. Measurements of Ge and Si with controlled impurity concentrations have justified this model.<sup>2</sup>

Impurity conduction has also been invoked to explain excess low-temperature conductivity in as-grown CdS<sup>3,4</sup> with donor minus acceptor concentrations of  $N_D - N_A \cong 6 \times 10^{15} \text{ cm}^{-3}$ , and Cl-doped CdS<sup>4</sup> with  $N_D - N_A > 2 \times 10^{17} \text{ cm}^{-3}$ . The analysis<sup>4</sup> of these Cl-doped samples in terms of  $r_s$ , the

mean distance between excess donors, agreed with impurity-conduction theory but did not extrapolate to encompass the as-grown sample which had much more conductivity than expected on the basis of its large  $r_s$ . In both of these studies<sup>3,4</sup> the samples were oriented with the current flow along the  $c$  axis.

Here I report an unexpected, large anisotropy of the low-temperature excess conductivity of undoped CdS. This anisotropy will lead us to consider a new mechanism to replace impurity conductivity for these samples. The conductivity for the two bar samples cut from the same as-grown<sup>5</sup> plate is shown in Fig. 1(a). Both samples show excess low-temperature conductivity but the sam-