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PICOSECOND PHOTOINDUCED OPTICAL ANISOTROPY IN TRANS - $(CH)_x$: DIRECT MEASUREMENT OF SOLITON DIFFUSION

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Résumé - Le dichroïsme photoinduit produit par la décoloration de la transition interbande dans le trans-$(CH)_x$ a été observé pour des temps dans le domaine picoseconde. La décoloration est induite instantanément et décroît avec le temps comme $t^{-1/2}$, passant à une loi de puissance plus faible après ~ 50ps. Si la décoloration photoinduite persiste après des temps longs, la mémoire de la polarisation est perdue après ~ 10^{-9} s. Les résultats permettent de déduire le coefficient de diffusion des excitations chargées, D ≃ 2 x 10^{-2} cm^2 s^{-1} à 300K et 80K.

Abstract - Photoinduced dichroism caused by bleaching of the interband transition in trans - $(CH)_x$ was observed in the picosecond time domain. The bleaching is induced instantaneously and decays with time as $t^{-1/2}$, changing to a lower power after ~ 50 ps. Although the photoinduced bleaching persists to long times, polarization memory is lost after ~ 10^{-9}s. The results provide a measurement of the diffusion constant of the charged excitations; D ≃ 2 x 10^{-2} cm^2 s^{-1} at 300K and 80K.

Soliton-anisoliton (S-$\bar{S}$) pairs can be generated in trans - $(CH)_x$ either by charge transfer doping or by photoexcitation. Dynamical calculations which follow the time evolution of a $(CH)_x$ chain after injection of an electron-hole (e-h) pair, have been carried out by Su and Schrieffer /1/. They found that the photoinjected e-h pair evolves to S-$\bar{S}$ in a time of the order of ~ 10^{-13} sec. Because of e-h symmetry, the formation of a soliton causes the formation of a localized electronic state at mid-gap /2/. The resulting soliton can be neutral with spin 1/2 or charged + or - with spin zero.

Initial confirmation of these ideas came from photoexcitation experiments /3/. The photoproduction of S-$\bar{S}$ pairs implies the

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photogeneration of states in the gap, as observed experimentally /4,5/. The reversed spin-charge relation has been verified through a series of ESR experiments /6/ which demonstrated that the quantum efficiency (QE) for photoproduction of spins is orders of magnitude below the QE for photoproduction of charge carriers. Therefore, the photogenerated charge carriers are spinless and are identified as charged S-$\overline{S}$ pairs.

We have investigated /7/ the time evolution of the photoexcited carriers in the picosecond time domain using the pump and probe technique (both polarized) with sub-picosecond resolution. We find photo-induced bleaching ($\Delta\alpha < 0$) in the interband transition region at 2 eV. The bleaching is generated instantaneously and decays with time as $t^{-1/2}$ followed by a slower decay /8/.

We observe photoinduced optical anisotropy for the first time in a macroscopically isotropic solid, $\Delta\alpha_{\parallel} \neq \Delta\alpha_{\perp}$, where // and $\perp$ refer to the polarization of the probe being parallel or perpendicular, respectively, to that of the pump.

In a traditional semiconductor, the photoexcited carriers are delocalized and consequently lose polarization memory in times as short as 10^{-14}s. Even in amorphous silicon, where the band edge states are localized, photoinduced anisotropy is not observed. Our observations in <u>trans</u> - $(CH)_x$ of the photoinduced optical anisotropy therefore imply that the electronic structure is quasi-one-dimensional and that <u>localization</u> of the photoexcited carriers takes place in time less than 2×10^{-13} s. This is consistent with S-$\overline{S}$ pair production.

The photoinduced anisotropy is lost in the nanosecond time range. The polarization memory results from the photogeneration of localized states in regions of the polymer where the $(CH)_x$ chains are parallel to the pump polarization. The eventual loss of photoinduced anisotropy at later times results from diffusion of the solitons over sufficiently large distances ($\sim 10^3$Å) that the excited $(CH)_x$ chains are random with respect to the pump polarization. This effect directly measures the diffusion coefficient; $D \simeq 2 \times 10^{-2}$ cm^2 s^{-1} at 300K and 80K.

Kivelson /9/ described the diffusion of charged solitons in trans-$(CH)_x$ in terms of inter-soliton electron hopping among the localized mid-gap states. The interchain diffusion of photogenerated solitons over large distances may be limited by a similar mechanism. In this case,

however, since the charged solitons are not bound (to ions), phonon assisted hopping would be less important implying a weaker temperature dependence, similar to that of neutral solitons. The values quoted above for D are, in fact, comparable to those obtained for neutral solitons from magnetic measurements /10/.

In summary, the band-to-band transition in trans - $(CH)_x$ is bleached instantaneously within our resolution of 0.2 ps, in agreement with S-$\bar{S}$ pair production. Analysis of the decay of the photo-induced anisotropy indicates soliton diffusion over distances $\simeq 10^3$Å with diffusion coefficient of about 0.02 $cm^2\ s^{-1}$.

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