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CONTROL OF ELECTRONIC MAGNETIC AND OPTICAL PROPERTIES
OF DOPED POLYACETYL. (U) CALIFORNIA UNIV SANTA BARBARA
DEPT OF PHYSICS A J HEEGER 15 NOV 84 ARO-19775.3-M5
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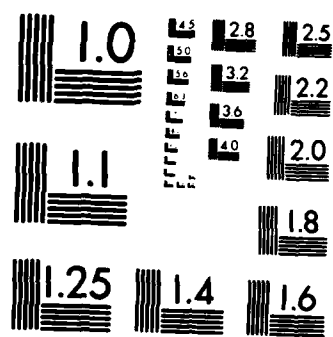
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Final Report

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Title: CONTROL OF ELECTRONIC, MAGNETIC AND OPTICAL PROPERTIES
OF DOPED POLYACETYLENE CONDUCTORS

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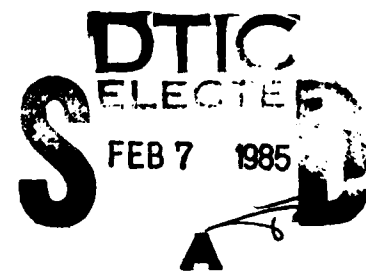
Author and Principal Investigator: A. J. Heeger

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The electronic properties of the novel class of conducting polymers have been investigated using a variety of techniques. Studies during the period of this grant focused on polyacetylene (a conjugated polymer with a degenerate ground state) and polythiophene (an analogous polymer in which the ground state degeneracy has been lifted). Photoinduced absorption and photoinduced ESR studies were carried out on these polymers. In addition an extensive study of the effects of radiation damage on (CH) _x and (CD) _x was completed. The (continued on reverse side)		

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20. (continued)

-construction of a versatile x-ray scattering apparatus was completed and the instrument was used to study the charge density wave state in a quasi-one-dimensional conductor. *Originator furnished Keynotes include:-*

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Statement of the Problem Studied

Polyacetylene has been the center of considerable attention, because of the novel fundamental physics which governs its properties and because of its potential usefulness in technology as an electronic and electrochemical material. As an electrochemical active material, $(CH)_x$ electrodes have been used to fabricate high energy density, high power density electrochemical cells. As an electronic material, the energy gap and large bandwidth of polyacetylene are comparable to those of other potentially useful large scale thin film semiconductors such as amorphous silicon.

The coupling of electronic excitations to nonlinear conformational changes is an intrinsic and important feature of polyacetylene and other conducting polymers. In the presence of a degenerate ground state, this coupling leads to the novel soliton excitations studied extensively in trans- $(CH)_x$. Generalization of these concepts and application to the larger class of (non-degenerate ground state) conjugated polymers has been an obvious goal of the field. Polymers such as poly(thiophene) are therefore of current interest since the two possible structures are not energetically equivalent. As a result, polarons and bipolarons are expected to be the dominant charged species.

Information on the intrinsic properties of the nonlinear soliton excitations has been obtained from a series of photoinduced absorption experiments. These studies were

stimulated by the calculations of Su and Schrieffer which showed that solitons could be photogenerated. Their results demonstrated that in trans-(CH)_x an e-h pair should evolve into a pair of solitons within an optical phonon period, or about 10^{-13} sec. The subsequent experimental results on the photoinduced (PI) change in optical absorption confirmed the predictions of Su and Schrieffer and established the reversed spin-charge relation of the soliton model.

Summary of Most Important Results

I. Photoinduced Absorption Studies of Polyacetylene (G. B. Blanchet et al., Phys. Rev. Lett. 51, 2132 (1983)).

The photogeneration process considered by Su and Schrieffer is indirect and occurs via an electron-hole excitation as an intermediate step. The incident photon generates an e-h pair ($\hbar\omega > 2\Delta$), and the lattice then distorts around the photogenerated charge carriers leading to a soliton-antisoliton (S^+S^- pair. We earlier proposed the direct photogeneration of S^+S^- pairs, which would onset at $2E_S = (4/\pi)\Delta$ where E_S is the soliton creation energy. The effects of nonlinear ground state quantum fluctuations must necessarily be included in such a process since the direct photogeneration of a soliton pair requires a significant lattice distortion simultaneous with the electronic transition. Consequently the quantum efficiency is predicted to be small near threshold and to increase exponentially as $\hbar\omega$ approaches 2Δ . Thus, measurements of the excitation profile for soliton photoproduction can be

expected to give detailed information about the direct and indirect photogeneration processes.

The excitation profile for solitons in trans-(CH)_x was determined by measuring the strength of the photoinduced absorption as a function of the photon energy of the photogeneration source. The results demonstrate soliton photoproduction at energies well below the principal interband absorption edge. These data prove that charged soliton-antisoliton pairs are photogenerated directly (threshold $\hbar\omega = 4\Delta/N$) assisted by quantum fluctuations in the ground state, as well as indirectly at higher energies ($\hbar\omega \geq 2\Delta$) via structural relaxation around electron-hole excitations.

II. Photoexcitation in Poly(thiophene): Photoinduced Absorption and Photoinduced ESR (F. Moraes et al., Phys. Rev. B 30, 2948 (1984)).

In a recently completed study we reported the first observation of photoinduced absorption and photoinduced ESR in poly(thiophene). The observation of relatively sharp photoinduced mid-in peaks (at 1020 cm⁻¹, 1120 cm⁻¹, 1200 cm⁻¹ and 1320 cm⁻¹) demonstrates that localized structural distortions are indeed formed, consistent with photogeneration of polarons or bipolarons. The observation of photoinduced spins implies that the dominant photoexcitations are polarons. We find in addition a broad photoinduced absorption peaked at 3600 cm⁻¹ (0.45eV) which we attribute to the lowest energy electronic excitation of the photogenerated polarons.

III. Effect of Energetic C^{+6} Irradiation on Transport Properties of trans-(CH) $_x$ and trans-(CD) $_x$ (J. Kaufer et al., J. Chem. Phys. 78, 7459 (1983)).

A study of the effects of irradiation by energetic carbon ions (56 MeV C^+) on the transport properties of polyacetylene is presented. The in situ monitoring of the resistivity, ρ , shows an initial nonlinear increase by a factor of 10^4 as a function of the integrated flux of particles, ϕ . For trans-(CH) $_x$, the increase in ρ saturates at a plateau starting at $\phi_0 \approx 5 \times 10^{12}$ particles/cm 2 , whereas trans-(CD) $_x$ behaves differently. After a similar (but slower) initial increase, ρ of trans-(CD) $_x$ peaks at ϕ_0 and subsequently decreases for $\phi > \phi_0$. Parallel thermoelectric power data show an increase from $\sim 880 \mu V/K$ to $\sim 1100 \mu V/K$ for $\phi \approx \phi_0$ for both isotopes. Characterization studies of the irradiated film using infrared and Raman spectroscopy show no detectable change in backbone structure; and ESR measurements show no increase in the number of unpaired spins. Moreover, after irradiation the polymer can be doped to the highly conducting metallic regime. We therefore conclude that the conjugated (CH) $_x$ chains remain intact during irradiation; either the deposited energy is rapidly dissipated to avoid bond-breaking or there is a high tendency to self-heal. The increase in ρ is primarily the result of a decrease in the number of carriers. The dramatic differences in trans-(CH) $_x$ and trans-(CD) $_x$ suggest that hydrogen or deuterium is released during irradiation and that these radicals subsequently compensate the residual carriers in the polymer.

Aside from this compensation effect, it is concluded that polyacetylene is relatively immune to damage by irradiation.

IV. Construction of Triple-Axis X-ray Spectrometer for Studying Structural Properties of Conducting Polymers and Related Quasi-one-dimensional Conductors

The construction of this versatile x-ray scattering apparatus was completed. The capital equipment funds ($\sim \$100,000$) were provided by the University of California, Santa Barbara. The construction of the apparatus is complete, and detailed measurements began during the summer of 1984.

V. X-Ray Diffraction Study of the CDW Phase in $(\text{TaSe}_4)_2\text{I}$: Determination of the CDW Modulation Amplitude. (K. B. Lee, D. Davidov and A. J. Heeger, Solid State Commun., in press)

An extensive x-ray diffraction study of the charge density wave (CDW) phase in $(\text{TaSe}_4)_2\text{I}$ is reported. We have observed the superstructure satellites at $2\vec{q}$ in addition to those at $\vec{q}$ reported by Fujishita et al. The results imply a sinusoidal lattice modulation with polarization almost perpendicular to $\vec{q}$ (i.e. transverse) and the existence of CDW domains. At 15K we have extracted an approximate value for the amplitude of the lattice modulation perpendicular to $\vec{q}$ to be $\mu_{\perp} \sim 0.087 \text{ \AA}$.

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