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Organic Conductors

Photoconductivity and Junction Properties of Polyacetylene Films.* T. TANI,† W.D. GILL, P.M. GRANT, T.C. CLARKE and G.B. STREET, IBM Research Lab, San Jose, CA 95193.--Photoconductivity and photovoltaic effects of AsF_5-doped and undoped trans-$(CH)_x$ films have been measured at room temperature in the wavelength region from 0.3μm to 3.5μm. For undoped $(CH)_x$ similar photoconductivity spectra are observed for metal-$(CH)_x$-metal sandwich cells and for symmetric cells with both electrodes on one surface. Typical spectra consist of one main peak at 0.93μm and a comparatively steep rise at wavelengths shorter than 0.6μm. In the photovoltaic effect experiments, designed to measure the intrinsic band gap, we have measured photovoltages from both doped and undoped $(CH)_x$ on which In or Al is evaporated to form Schottky barriers. Typical spectra of lightly-doped samples show an edge at about 0.9μm of a broad band which peaks at about 0.4μm. Interpretation of these features together with I-V and C-V characteristics of the junctions will be discussed.

*Research supported in part by ONRC Contract N00014-76-C-0658.
†IBM World Trade Postdoctoral Fellow, Japan.

( ) Prefer Poster Session
(x) Prefer Standard Session
( ) No preference

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within a stack, and the stacking repeat distance. In this paper we report on physical studies of polymeric materials consisting of conjugated cyclic metal-organic molecules linked by various bridging atoms (X):

—(M—X—(M—X—(M— (M = metal-organic unit

The electrical conductivities of these materials can be varied over a wide range by suitable selection of metal-organic unit, bridging atom, or halogen dopant. Studies of electronic structure and degree of charge transfer by magnetic susceptibility, resonance Raman spectroscopy, and ^{129}I Mössbauer spectroscopy will also be discussed.

*Submitted by C.R. KANNEWURF.

**Supported by the NSF-MRL program under grant No. DMR76-80847 and by the Office of Naval Research.

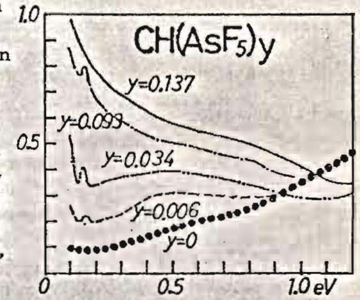
EE 5 Optical Transitions in Trans-$(CH)_x$. P.M. GRANT, IBM Research Lab.--A theoretical model based on one-electron band theory is proposed for interband transitions between the valence and conduction bands of trans-$(CH)_x$. It is shown that these transitions have a strong crystal momentum dependence which results in a much lower optical absorption at the band gap than expected from joint density of states considerations alone. We interpret our experimental results as being in accord with this conclusion. The model applies generally to all chain systems possessing the symmetry properties of trans-$(CH)_x$, such as $(SN)_x$, for example, and explains the low photoemissive yield observed near the Fermi surface in the latter material.

EE 6 Band Structure and Electronic Properties of Pure and Heavily Doped Polyacetylene. C. R. FINCHER, L. LAUCHLAN, M. OZAKI, D. PEEBLES, M. TANAKA, A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- The band structure and electronic properties of pure and heavily doped polyacetylene (both as-grown and stretch oriented) have been investigated by a combination of optical absorption and reflection measurements in the frequency range from the far ir through the visible. The absorption data are consistent with a direct gap of approximately 1.4 eV in the trans-$(CH)_x$. A Kramers-Kronig analysis of the reflection data has been carried out to obtain $\sigma(\omega)$ and $\epsilon(\omega)$. We find that for the undoped semiconducting polymer, the strong transition observed in the visible exhausts the oscillator strength sum rule for π-electrons consistent with an interband transition. The frequency conductivity obtained from Kramers-Kronig analysis of the metallic polymer reflection data suggests "interrupted strand" behavior.

EE 7 Resonance Raman Scattering in Oriented $(CH)_x$ *. L.S. LICHTMANN & D.B. FITCHEN, Cornell U., Ithaca, N.Y., and H. TEMKIN, Bell Labs, Murray Hill, N.J.-- We have investigated resonance Raman scattering at 77K in the organic semiconducting polymer $(CH)_x$ for two different types of samples. One is home-grown films of unoriented polyacetylene in either cis or trans form; the other is Type K Polaroid sheets of highly-oriented polyvinylene. The Raman spectra of the latter correspond closely to those of the trans $(CH)_x$ films. The most interesting features are two broad, structured bands near 1100 and 1500 cm^{-1}, due to backbone stretches, which show dispersion in shape and position for different laser excitation wavelengths. For red excitation, the bands are peaked near 1070 and 1460 cm^{-1}; for shorter wavelengths, higher vibrational frequencies appear. The band shapes, and the selective enhancement of the different components, suggest a distribution of conjugated chain lengths, with somewhat longer chains in the Polaroid samples. We have doped both types of samples by exposure to iodine vapor. The iodine-induced Raman features seen are similar in frequency (110 and 150 cm^{-1}) and in resonance behavior.

*Cornell work supported in part by the NSF.

EE 8 Infrared Reflection Spectra of Doped Polyacetylene: The Semiconductor-Metal Transition. M. TANAKA, C. R. FINCHER, JR., A. J. HEEGER, M. A. DRUY and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- Infrared reflection spectra were taken on polyacetylene stretched films of varying concentrations of iodine and AsF_5. The results show the appearance of free carrier reflection upon doping. The spectra polarized parallel to the stretching direction for a series of AsF_5 doped samples are shown in the figure for the dopant concentration y = 0.0, 0.6, 3.4, 9.3 and 13.7%. The IR reflection data thus imply a semiconductor-metal transition as a function of dopant concentration, with a critical concen- in the range (1-3)%.



Similar results have been obtained with iodine.

EE 9 Donor and Acceptor States in Lightly Doped Polyacetylene, $(CH)_x$. C. R. FINCHER, JR., M. OZAKI, A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- The results of an experimental study of the infrared absorption of the $(CH)_x$ system, lightly doped (< 0.1%) with acceptors and donors, are presented. Additional absorptions are observed near 1370 cm^{-1} (width ~ 50 cm^{-1}) and 900 cm^{-1} (width ~400 cm^{-1}) upon doping with iodine, AsF_5 and sodium. The two additional absorption maxima appear to be general features of lightly doped $(CH)_x$ independent of specific dopant or of cis/trans content. Measurements on stretch-oriented films demonstrate that these absorption maxima are polarized primarily along the polymer chains. We include an experimental determination of the room temperature dielectric constant in undoped $(CH)_x$: $\epsilon_{\parallel}$ = 10 - 12, with uncertainty arising from the incomplete orientation of the $(CH)_x$ films.

EE 10 Hall Effect in AsF_5-Doped $(CH)_x$ Films.* W.D. GILL, T.C. CLARKE and G.B. STREET, IBM Research Lab., San Jose, CA 95193.--Previously reported Hall measurements in heavily AsF_5-doped $(CH)_x$ films[1] yielded an anomalously small, p-type Hall coefficient, R_H. In this paper we report Hall measurements as a function of temperature (4K to 300K) for AsF_5 dopant concentrations such that conductivity σ ranges from metallic behavior at high concentration to semiconducting behavior at low concentrations. As expected, R_H increases as the resistivity increases, however, the product $R_H\sigma$ corresponding to the Hall mobility is very small (2×10^{-2} cm^2/v-sec at ~10 at.% AsF_5) and decreases further as the dopant level decreases. These results will be discussed in terms of possible transport mechanisms in both the metallic and semiconducting regimes.

*Research supported in part by ONR Contract N00014-76-C-0658.

1. K. Seeger, W. D. Gill, T. C. Clarke and G. B. Street, Solid State Commun. 28, 1978 (in press).

EE 11 Photoconductivity and Junction Properties of Polyacetylene Films.* T. TANI,† W.D. GILL, P.M. GRANT, T.C. CLARKE and G.B. STREET, IBM Research Lab, San Jose, CA 95193.--Photoconductivity and photovoltaic effects of AsF_5-doped and undoped trans-$(CH)_x$ films have been measured at room temperature in the wavelength region from 0.3μm to 3.5μm. For undoped $(CH)_x$ similar photoconductivity spectra are observed for metal-$(CH)_x$-metal sandwich cells and for symmetric cells with both electrodes on one surface. Typical spectra consist of one main peak at 0.93μm and a comparatively steep rise at wavelengths shorter than 0.6μm. In the photovoltaic effect experiments, designed to measure the intrinsic band gap, we have measured photovoltages from both doped and undoped $(CH)_x$ on which In or Al is evaporated to form Schottky barriers. Typical spectra of lightly-doped samples show an edge at about 0.9μm of a broad band which peaks at about 0.4μm. Interpretation of these features together with I-V and C-V characteristics of the junctions will be discussed.

*Research supported in part by ONRC Contract N00014-76-C-0658.
†IBM World Trade Postdoctoral Fellow, Japan.

EE 12 Thermopower of Doped $(CH)_x$: The Semiconductor-Metal Transition. Y. W. PARK, A. M. DENENSTEIN, C. K. CHIANG†, A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- Thermopower studies of doped polyacetylene have been carried out as a function of dopant concentration (c) and temperature. The thermo power of pure trans-$(CH)_x$ is large (S = +850 μV/°K) and positive consistent with p-type material. With iodine doping, the thermopower remains positive over the full range of concentration 0 < c 22 mole%. The semiconducto metal transition is clearly observed at $c_t \simeq 3\%$; S falls dramatically from S = +850 μV/°K at c = 0.3% to S = +30 μV/°K at c = 3%. At higher concentrations, S remains nearly constant saturating at +18 μV/°K in the heavily doped metallic polymer. Temperature dependences are consistent with metallic behavior at the highest dopant concentrations and hopping transport through localized states in the undoped polymer.

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EE 13 Magnetic Susceptibility of Doped Polyacetylene. B. R. WEINBERGER, J. KAUFER, A. PRON, A. J. HEEGER, and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- Initial magnetic susceptibility results for AsF_6 doped polyacetylene are reported. Faraday balance measurements of the static magnetic susceptibility were performed on $[CH(AsF_6)_y]_x$ samples with dopant concentrations in the range $0 < y < 0.13$ over the range of temperatures 77K to 295K. For all doping levels total susceptibilities were negative indicating dominance of diamagnetic core contributions over both local moment and conduction electron spin paramagnetism. Results for the heavily doped samples were temperature independent while at the lightest doping level a small Curie law term was observed with magnitude consistent with previous ESR results from the pure polymer. The diamagnetic contributions were subtracted using Pascal's constants, leaving a temperature independent paramagnetic susceptibility consistent with a conduction electron Pauli spin term with $N(E_F) \simeq 0.2$ state/eV - C atom. The existence of the Pauli spin susceptibility has been confirmed and studied in more detail with ESR and Schumacher-Slichter measurements.

EE 14 Degradation Processes in Thin Films of Polyacetylene* S.P.S. Yen, A. Rembaum, S. K. Khanna, and R. B. Somoano, Jet Propulsion Laboratory, California Institute of Technol- We discuss some properties of polyacetylene films that are importance for its future use in practical applications. have carried out accelerated radiation and thermal exposur tests in order to elucidate those processes which adversel affect the usefulness of the material. We report on the effect of these exposure tests on the chemical, electrical, and optical properties. Emphasis is given to those materi properties which are involved in the use of polyacetylene thermal control or as an antistatic coating.
* This paper represents one phase of research performed by the Jet Propulsion Laboraotry, California Institute of Technology, sponsored by NASA Contract NAS7-100.

SESSION EF: NONEQUILIBRIUM SUPERCONDUCTIVITY
Tuesday afternoon, 20 March 1979
Chicago Ballroom Room C at 2:00 P.M.
Charles Falco, presiding

EF 1 Measurement of the Branch Imbalance Relaxation Time in a Superconductor with Magnetic Impurities. Thomas R. Lemberger* and John Clarke**, University of California at Berkeley, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory†--Measurements have been made of the branch imbalance relaxation time, τ_Q, as a function of the energy gap, Δ, in superconducting Al-Er alloys, in which the Er is a magnetic impurity. In these alloys the branch imbalance is able to relax through spin-flip scattering, a mechanism which is not present in either pure Al, or in Al doped with non-magnetic impurities. Typical Er concentrations are ~0.01 at. %. At this impurity concentration, the estimated spin-flip scattering time, τ_S, is about 0.66 nS. Preliminary measurements of τ_Q, interpreted by using the theory of Schmid and Schön[1], yield values for τ_S of 0.72 and 0.91 nS. In view of the uncertainties in both the estimated and measured values of τ_S, this is considered good agreement.
*IBM Fellow
**Guggenheim Fellow
†Work supported by the Division of Materials Science, Office of Basic Energy Sciences, U. S. Dept. of Energy
[1]A. Schmid and G. Schön, J. Low Temp. Phys. 20, 207(1975)

EF 2 The Distribution Function for Superconductors with Charge Imbalance.* K. E. GRAY and H. W. WILLEMSEN, Argonne National Lab., -- We have measured the energy distribution, f, on each branch of the quasiparticle spectrum for superconductors in which a large charge (or branch) imbalance has been created by intense tunnel injection. A double tunnel junction is used along with the techniques of Ref. 1. From the differences in $f_>$ and $f_<$ (which can be as large as 4), the charge imbalance Q^* can be directly determined. Independently we make the traditional determination of Q^* by measuring the quasiparticle-pair potential difference in the middle film. Thus for the first time, these can be directly related, verifying the theoretical interpretation of previous charge imbalance experiments. Details of τ_Q^* measurement and surprising features of $f_>$ and $f_<$ will be discussed.

1. H. W. Willemsen and K. E. Gray, PRL 41, 812 (1978).

EF 3 Dynamical Behavior of a Weak Link Considering Chemical Potential Differences at the Boundaries.†* I. OPPENHEIM and S. FROTA-PESSÔA, Universidade de São Paulo, São Paulo, Brazil and J.A. BLACKBURN, Wilfrid Laurier University,** Waterloo, Ontario, Canada.- We numerically solve the time dependent Ginzburg-Landau equation for a unidimensional weak link, operating above its critical current. The difference between the chemical potentials for the pairs (μ_p) and quasiparticles (μ), which is usually disregarded when applying boundary conditions for the link, is shown to be of importance when determining the space/time behavior of quantities inside the link. We present results for the space/time dependence of μ, μ_p, order parameter, normal current and supercurrent. We also discuss the effect of the boundary conditions on the I-V curves.
† Submitted by S. FROTA-PESSÔA
* Supported by CNPq and FAPESP
** Supported by National Research Council of Canada

EF 4 Temperature-Dependent Resistance of Superconductor-Normal Metal-Superconductor Sandwiches and Charge Relaxation Times of Superconductors.* T. Y. HSIANG† and JOHN CLARKE, Dept. of Physics, University of Calif., Berkeley, and MMRD, LBL, Berkeley, Calif.--The resistance of SNS sandwiches was measured with a dc SQUID voltmeter. As the