energy-level structure, charge densities, and collective interactions can be studied and understood with inelastic light-scattering spectroscopy. Somewhat surprisingly, we find that the energy-level structure remains unchanged by photoexcitation, indicating that for densities as high as $\sim 3 \times 10^{12}$ cm^{-2} (equivalent to $\sim 10^{18}$ cm^{-3}) there is no spatial separation between electrons and holes. Such measurements also provide a means to determine directly the electron energy-level structure in quantum wells. The collective excitations display a complex behavior due to coupling among different quantum-well excitations and also with LO phonons. The spectra presented here are broadened by the varying plasma density in different wells. Extension of these studies to single quantum wells should allow one to obtain more quantitative information from spectra.

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[12]Their effect on collective-mode energies is anticipated to be relatively minor because hole subband spacings and effective plasma energies are much smaller.

Electron Hopping Conduction in the Soliton Model of Polyacetylene

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It is shown that at low temperatures, phonon-assisted electron hopping between soliton bound states may be the dominant conduction process in a lightly doped, one-dimensional Peierls system such as polyacetylene. The presence of disorder, as represented by a spatially random distribution of charged dopant molecules, causes the hopping-conduction pathways to be essentially three dimensional. Calculated values of the conductivity, thermopower, and transverse spin diffusion constant compare favorably with experiment.

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Recently, considerable theoretical[1-4] and experimental[5-10] interest has been focused on the properties of *trans*-polyacetylene, $(CH)_x$. Probably the most successful theoretical model of $(CH)_x$ to date is the soliton model of Su, Schrieffer, and Heeger[1] (SSH), and others.[2] In this paper, certain effects of the presence of disorder on the properties of the soliton model are considered. The results provide a satisfactory explanation of the transport properties of lightly doped polyacetylene. In addition, some novel aspects of the

conduction mechanism, electron hopping between dynamical defects, make the problem quite interesting in its own right. In a forthcoming paper (Ref. 3, hereafter called paper II) a microscopic model of polyacetylene is considered, and the present phenomenological results are made quantitative.

According to the model of SSH, undoped polyacetylene is a semiconductor due to a commensurate Peierls distortion which doubles the unit cell (dimerization) and opens a band gap at the Fermi

energy E_F. The soliton is the boundary between regions of the two different senses of the dimerization. Associated with each soliton is a midgap, localized electronic state. In the neutral soliton, this state is singly occupied, and the soliton has spin $\frac{1}{2}$. If the state is doubly occupied or unoccupied, the soliton is charged and spinless. According to SSH, the width of the soliton, $\xi_\parallel$, is about $7a$ where a is the in-chain lattice constant, and the soliton effective mass, $m^* \approx 6m_e$, is surprisingly small.

Upon doping, charged solitons are formed which are bound to the oppositely charged impurity with a binding energy $E_b > 0.3$ eV. One possible conduction mechanism[4,5] involves the thermal liberation of bound charged solitons, followed by free charged-soliton conduction. At low impurity concentrations, such a mechanism leads to a simply activated conductivity, σ, and a strongly temperature-dependent thermopower, S, similar to those found in doped semiconductors,

$$\sigma = \sigma_f \exp\left(-\frac{E_b}{kT}\right), \quad S = \frac{k}{e}\left(\frac{E_b}{kT} + \text{const}\right), \quad (1)$$

where the exponential factor reflects the population of free solitons. Because of the large binding energy, E_b, at reasonable temperatures this population is extremely small.

Another less strongly activated conduction mechanism, electron hopping between solitons, will be dominant at low temperatures. To understand this mechanism simply, consider a negatively charged soliton bound to a positively charged impurity on one chain and a neutral soliton on another, nearby chain. It is always possible for the electron to make a phonon-assisted transition, or hop, from the charged solition to the neutral soliton. If the neutral soliton happens to be near another impurity, the activation energy is small. In fact, as the temperature approaches zero, the activation energy for hopping tends to zero.

To explore the consequences of the hopping picture and compare them with experiment in a consistent fashion, we will consider a phenomenological Hamiltonian appropriate to solitons in polyacetylene.

Because of the large size of the band gap, $2\Delta_0 \approx 1.4$ eV, compared to both the temperature and the phonon energies, excitations of the valence and conduction bands play a relatively minor role in determining the transport properties of lightly doped $(CH)_x$. Thus we consider a reduced Hilbert space with one electronic state (the midgap localized state) per soliton. The Hamiltonian of the soliton-impurity system is then

$$H = e\sum_{\vec{R}} Q_{\vec{R}} V_{\text{imp}}(\vec{R}) + \sum_{\vec{R}} \tfrac{1}{2}m^*(\dot{\vec{R}})^2$$

$$+ H_{\text{ph}} + H_{\text{el-ph}}, \quad (2)$$

where the set $\{\vec{R}\}$ labels the positions of the solitons, $a_{\vec{R}s}^\dagger$ is the creation operator of an electron with spin s in the bound state of the soliton at $\vec{R}$, $eQ_{\vec{R}} = e(\sum_s a_{\vec{R}s}^\dagger a_{\vec{R}s} - 1)$ is the charge on the soliton, $V_{\text{imp}}(\vec{R})$ is the electrostatic potential due to the charged impurities acting on the soliton at $\vec{R}$, and H_{ph} and $H_{\text{el-ph}}$ are, respectively, the phonon energy and the electron-phonon interaction. Each soliton is confined to a single chain. Within the Born-Oppenheimer approximation the effect of the full valence band is incorporated in the model solely in the values of the phonon energies, and of the soliton effective mass since the valence-band electrons follow the ionic motion adiabatically. The important term in $H_{\text{el-ph}}$ is the off-diagonal term which causes electronic transitions from one soliton bound state to another,

$$H_{\text{el-ph}} = \sum_{\substack{\vec{R}\neq\vec{R}'\\s}} \sum_\alpha \hbar\omega_\alpha \lambda_\alpha(\vec{R},\vec{R}')$$

$$\times (a_{\vec{R}s}^\dagger a_{\vec{R}'s} - a_{\vec{R}'s}^\dagger a_{\vec{R}s})(b_\alpha^\dagger - b_\alpha), \quad (3)$$

where α labels a phonon state with energy $\hbar\omega_\alpha$, and $b_\alpha^\dagger$ is the corresponding phonon creation operator. Additional terms that might appear in the reduced Hamiltonian are discussed in paper II.

The hopping conductivity is determined by the rate at which an electron hops between a pair of solitons. Such a hop is only energetically feasible (at low temperatures) if each soliton is near an impurity. Consider two solitons in the vicinity of the impurities at $\vec{R}$ and $\vec{R}'$, respectively. When an electron hops, both solitons change their charge state so that the interaction energy between the two solitons and the impurities necessarily changes. If E_i and E_f denote, respectively, the initial and final energies of the two-soliton system, then the energy $E_f - E_i$ must be provided by the absorption (or emission) of a phonon. The rate at which this transition occurs is given by Fermi's golden rule:

$$\nu_{\vec{R}\vec{R}'}(E_i - E_f) = 2\pi\hbar^{-1}(E_i - E_f)^2\{n(E_f - E_i)g(E_f - E_i)$$

$$+ [1 + n(E_i - E_f)]g(E_i - E_f)\},$$

$$g(E) = \theta(E)\sum_\alpha |\lambda_\alpha(\vec{R},\vec{R}')|^2 \delta(E - \hbar\omega_\alpha), \quad (4)$$

where $\bar{n}(E)$ is the average Bose occupation number. This rate must be averaged over a thermal distribution of initial and final soliton energies:

$$\bar{\nu}_{\vec{R}\vec{R}'} = \int dE_i \, dE_f \frac{\rho(E_i)}{Z(T)} \frac{\rho(E_f)}{Z(\infty)} \exp\left(-\frac{E_i}{kT}\right)$$

$$\times \nu_{\vec{R}\vec{R}'}(E_i - E_f), \qquad (5)$$

where $\rho(E)$ is the density of states of the charged soliton and $Z(T) = \int dE \, \rho(E) e^{-E/kT}$. The most important $\vec{R}$ dependence of ν arises from the overlap factor $S(\vec{R} - \vec{R}')$ between the electronic bound states on the two solitons. Thus

$$\bar{\nu}_{\vec{R}\vec{R}'} \approx [\gamma(T)/N] S^2(\vec{R} - \vec{R}'), \qquad (6)$$

where $N = Z(\infty)$ is the number of carbons per $(CH)_x$ chain. The seemingly strange factor of $1/N$ reflects the fraction of the time that a neutral soliton is in the vicinity of the impurity at $\vec{R}'$. $S(\vec{R})$ falls off exponentially with distance and is highly anisotropic as a result of the quasi-one-dimensional nature of polyacetylene:

$$\ln[S(R)] \approx -[(R_\parallel/\xi_\parallel)^2 + (R_\perp/\xi_\perp)^2]^{1/2}, \qquad (7)$$

where $R_\parallel$ $(R_\perp)$ is the component of $\vec{R}$ parallel to (perpendicular to) the chain direction, and $\xi_\parallel$ and $\xi_\perp$ are the appropriate wave function decay lengths $(\xi_\perp < \xi_\parallel)$.

An important qualitative question is whether the conduction process is predominantly one or three dimensional. The typical separation between impurities on a given chain is proportional to c_{im}^{-1} where c_{im} is the concentration of impurities, while the typical three-dimensional separation between impurities is proportional to $(c_{im})^{-1/3}$. At low impurity concentrations the typical intrachain hopping distance is much greater than the typical interchain hopping distance, and so interchain hopping dominates despite the wave function anisotropy. Therefore, the percolation problem reduces to the well-known three-dimensional R-percolation network. Thus, the approximation scheme of Butcher, Hauden, and McInnes[6] (see paper II) can be used to calculate the hopping conductivity:

$$\sigma_{hop}$$

$$\approx A \frac{e^2 \gamma(T)}{kTN} \frac{\xi}{R_0^2} \frac{y_n y_{ch}}{(y_n + y_{ch})^2} \exp\left(-\frac{2BR_0}{\xi}\right), \qquad (8)$$

where $A = 0.45$, $B = 1.39$, y_n and y_{ch} are the concentration of neutral and charged solitons per carbon atom, respectively, $R_0 \equiv [(4\pi/3)c_{im}]^{-1/3}$ is the typical separation between impurities with c_{im}

the concentration of charged impurities, and ξ is the dimensionally averaged decay length $\xi = (\xi_\parallel \times \xi_\perp^2)^{1/3}$. σ is a very rapidly increasing function of c_{im} (despite a possible decrease in the number of neutral solitons, y_n, upon doping) because of the exponential dependence in Eq. (8) on R_0. This dependence reflects the electronic overlap between soliton bound states separated by a characteristic distance between impurities BR_0.

Only the magnitude of the conductivity, and not its temperature dependence, is sensitive to the impurity concentration. This is a consequence of the fact that each site is equivalent. The temperature dependence of $\gamma(T)$ is due solely to the dynamic disorder associated with the soliton motion.

The equivalence of the sites also implies that the thermopower, S, is independent of the percolative aspects of the problem. In fact, one might guess that the energy current is zero, as in a molecular crystal, since the two transition rates between a pair of sites, $\nu_{\vec{R}'\vec{R}}(E)$ and $\nu_{\vec{R}\vec{R}'}(E)$, are equally affected by a local temperature change. However, the total transition rate $\bar{\nu}_{\vec{R}\vec{R}'}$ depends on the thermal distribution of soliton excited states at the initially charged site $\vec{R}'$. Thus, the thermopower is

$$S = (k/e)[\bar{\epsilon}/kT + \ln(y_n/y_{ch}) + \ln Z(T)], \qquad (9a)$$

where $\bar{\epsilon}$ is the average energy transported from the charged to the neutral soliton per hop,

$$\bar{\epsilon} \, \bar{\nu}_{\vec{R}\vec{R}'} = \int dE_i \, dE_f E_i \frac{\rho(E_i)}{Z(T)} \frac{\rho(E_f)}{Z(\infty)} \exp\left(-\frac{E_i}{kT}\right)$$

$$\times \nu_{\vec{R}\vec{R}'}(E_i - E_f). \qquad (9b)$$

The first term in Eq. (9a) is independent of impurity concentration; the second is the usual statistical term, $(k/e)(\mu/kT)$, which changes sign depending on whether the soliton band is more or less than half full. Since the first term is typically the larger, Eq. (9a) has the remarkable property that the sign of the thermopower depends only on the type of doping, not on the filling fraction of the soliton band.

In order to evaluate the expressions in Eqs. (7)–(9), values of $g(E)$ and $\xi_\perp$ must be obtained. In paper II it is shown that the electron-phonon coupling is greatest to band-center optical phonons. As the temperature is lowered, these phonons are frozen out, leading to a rapid decrease in $\gamma(T)$. A simple single-peaked model, $g(E) \propto E^x \exp(-xE/\hbar\omega_0)$, is adopted with $\hbar\omega_0 = 0.15$ eV and $x \sim 9$, chosen so that the peak center and width

of $g(E)$ are the same as in the phonon spectrum calculated by Melé and Rice.[2] This model leads to the predictions

$$\gamma(T) \sim \gamma_0 T^{x+2} \text{ and } \sigma(T) \sim T^{(x+1)}. \tag{10}$$

A roughly temperature-independent thermopower $S \approx (k/e)[(x+3)/2 + \ln(y_n/y_{ch})]$ also results. This simple model may be expected to be reliable so long as a substantial range of energies contributes to the integrals in Eqs. (4) and (9). At lower temperatures the hopping rate is sensitive to the detailed behavior of $g(E)$ at small E, and so a more elaborate model is necessary. An additional complication arises at low temperatures as a result of the slight differences in the energetics of different sites which we have ignored. $\xi_\perp$ depends on the interchain spacing b and the interchain hopping matrix $t_\perp$. In paper II a reasonable value of $t_\perp \approx 0.1$ eV is shown to lead to $\xi_\perp \approx \frac{1}{2}b \approx 2.3$ Å.

In a single crystal of $(CH)_x$ a slightly anisotropic conductivity, $(\sigma_{\parallel}/\sigma_\perp) = (\xi_{\parallel}/\xi_\perp)^2$, would result from the fact that the typical hop has a larger component in the parallel direction than in the perpendicular direction. Real polyacetylene, however, is disordered and so an isotropic conductivity, $\sigma = \frac{1}{3}(\sigma_{\parallel} + 2\sigma_\perp)$, is quoted in Eq. (8).

Accompanying the charge motion is spin diffusion. The hopping contribution to the spin diffusion constant, D_{hop}, is related to the conductivity by an Einstein relation:

$$D_{hop} = (1/e^2)(kT/c_{im})\sigma. \tag{11}$$

Because of its light mass, the neutral soliton is likely to have a large diffusion constant[7] D_n. Thus, we expect that the parallel component of the spin diffusion constant is dominated by neutral soliton diffusion $(D_n \gg D_{hop})$, and so the measured parallel spin diffusion constant is not expected to obey Eq. (11). However, solitons cannot move between chains, so that the perpendicular component of spin diffusion must proceed via electron hopping and so must satisfy Eq. (11). This is one of the strongest predictions of the hopping picture.

Experimentally, the thermopower is found to be large, $S \sim k/e$ (10), and roughly independent of temperature.[5] Up to impurity concentrations of a couple tenths of a percent, S is also independent of impurity concentration, as is the functional form of the conductivity, even when the magnitude of the conductivity is changed by almost two orders of magnitude by the incorporation of dopants.[8] The conductivity can be well approximated by a power law [in accordance with Eqs.

(8) and (10)], while it definitely cannot be said to be simply activated. Also, a spin diffusion frequency has been measured in putatively undoped polyacetylene. An extremely large anisotropy has been observed, with $\nu_{\parallel}$, the parallel diffusion frequency, equal to about 6×10^{13} Hz at room temperature and $\nu_\perp \sim 4.5 \times 10^7$ Hz. To obtain an estimate of $D_\perp$, we assume $D_\perp = b^2 \nu_\perp$.

In both its magnitude and its independence of temperature and impurity concentration, the theoretical thermopower is in agreement with the experiments. This is one of the most notable successes of the theory. In paper II, the magnitude of the conductivity is calculated with the use of Eq. (8) and the microscopic model of $(CH)_x$ sketched above. A quantitative comparison between theory and experiment is made there. The qualitative agreement with experiment is excellent, as to both the temperature dependence (subactivated) and the extreme sensitivity to dopant concentration of the magnitude of the conductivity. Finally, although the parallel spin diffusion constant is much larger than would be predicted from the Einstein relation in Eq. (11), the perpendicular component of the spin diffusion constant predicted by Eq. (11) is close to its measured value. A typical value of the room-temperature conductivity in putatively undoped polyacetylene is $2 \times 10^5 \ \Omega^{-1} \ cm^{-1}$ which, according to Eq. (8), corresponds to an accidental doping concentration of $y_{ch} \approx 3 \times 10^{-4}$. If we use these values in Eq. (11), we obtain the result $D_\perp/b^2 \approx 10^7$ Hz, in reasonable agreement with experiment. Further measurements of the temperature and impurity concentration dependence of the perpendicular spin diffusion constant to check the validity of the Einstein relation in Eq. (11) will provide a crucial test of the hopping picture.

It should be noted that another picture of conduction in polyacetylene, which denies the existence of solitons and instead invokes the existence of metallic clusters, has been proposed,[9] but it is hard to reconcile with the spin diffusion data, as well as with other evidence that supports the soliton model.[10]

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