

shapes of f_d purely from the numerical data, we may consider the present results as an *a posteriori* justification of the assumptions of continuity and monotonicity of $\beta(g)$ in Ref. 2 and as supporting the existence of a single scaling variable. Since the conductivity of a macroscopically large system is a meaningful quantity, and the analysis of Eqs. (4) to (7) does not depend on the *assumption* of only one dominant channel, the number of contributing channels must not depend on M for a very large square or cube; i.e., the number of channels for which $\lambda(W, M) \sim M^2$ must become independent of M when $M \rightarrow \infty$. This strongly supports the assumption of only one dominant channel and therefore the use of the Landauer formula for G also in the case of a multichannel system.¹⁵

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Anomalous Frequency-Dependent Conductivity of Polyacetylene

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The frequency (f) and temperature (T) dependent conductivity (σ) is reported for *cis*-(CH)_x, *trans*-(CH)_x, and ammonia-compensated (CH)_x. A strongly T -dependent dc σ together with a weakly T -dependent ac σ were observed for predominantly *cis*-(CH)_x and for NH₃-compensated samples, similar to $\sigma(f, T)$ of many semiconductors. The *trans*-(CH)_x has a larger "weakly" T -dependent dc σ and anomalous strongly T -dependent ac σ . The latter results are in good agreement with Kivelson's theory of charge transport via intersoliton electron hopping.

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Recently, considerable experimental^{1,2} and theoretical^{3,4} interest has focused on the two isomers of polyacetylene,⁵ *trans*-(CH)_x and *cis*-(CH)_x. According to the soliton model,^{3,4} undoped (CH)_x is a semiconductor due to a commensurate Peierls distortion. For the *trans* isomer, the two possible phases of the dimerization are degenerate in energy, and a soliton is the boundary between regions of the two phases. The energy level associated with the soliton is at midgap. When singly occupied the soliton is neu-

tral with spin $\frac{1}{2}$. If the state is doubly occupied or empty the soliton is charged and spinless. For the *cis*-(CH)_x the two possible phases of dimerization (*cis-transoid* and *trans-cisoid*) are not degenerate in energy. Hence the formation of solitons is not favored energetically in *cis*-(CH)_x. Magnetic,⁶⁻⁸ infrared,⁹ luminescence,¹⁰ and photoconductivity¹¹ studies have been interpreted as evidence for the presence of solitons in the *trans* isomer and their absence in the *cis* isomer.

In this Letter we report the results of an exten-

sive series of measurements of the f and T dependence of the conductivity ($\sigma = \sigma_{dc} + \sigma_{ac}$) of $trans$ -(CH) $_x$, predominantly cis -(CH) $_x$, and NH $_3$ -compensated (CH) $_x$. The results reveal that both the ac and dc component of σ of the $trans$ isomer are larger than those of the cis and the NH $_3$ -compensated $trans$ isomers. The $\sigma(f, T)$ of the cis and NH $_3$ -compensated $trans$ materials are very similar to the well-known behavior of many amorphous and insulating materials.¹² The results for $trans$ -(CH) $_x$ are unique, in that a large, very strongly T -dependent σ_{ac} is observed. Detailed analysis shows this behavior to be inconsistent with usual models for σ_{ac} . In contrast, this $\sigma_{ac}(f, T)$ is in good agreement with the model of phonon-assisted hopping of electrons between solitons recently proposed by Kivelson.¹³

Polyacetylene was prepared by the Shirakawa technique.⁵ The conductivity was measured in a sandwich cell configuration as well as along the length of the film. These films had the previously characterized morphology,¹⁴ transport,¹⁵ and magnetic⁸ properties. The $\sigma(f)$ was obtained at fixed temperature with use of a General Radio capacitance-conductance bridge in a three-terminal configuration. Care was taken to assure that contact sheet resistance effects were not leading to spurious behavior.¹⁶

The experimental results¹⁷ for σ of cis -(CH) $_x$ revealed $\sigma_{dc}(294\text{ K}) = 10^{-10} \Omega^{-1} \text{ cm}^{-1}$. The $\sigma(f)$

showed a marked frequency dependence even at 100 Hz with $\sigma_{ac} \propto f^{0.8}$. As T is decreased σ_{dc} decreases rapidly while σ_{ac} changes very slowly with temperature. This behavior in $\sigma(f, T)$ is very similar to that common to a broad class of disordered semiconductors and insulators. (e.g., Se,¹⁸ anthracene,¹⁶ and impurity conduction in Si¹⁹).

The experimental results for σ of $trans$ -(CH) $_x$ are summarized in Fig. 1. Measurements on six samples produced nearly identical results. At 294 K, σ is independent of f to 10⁶ Hz.²⁰ As T is decreased, σ_{dc} decreases rapidly and a frequency-dependent component is revealed. Both σ_{dc} and σ_{ac} are larger in $trans$ than in cis -(CH) $_x$ at a given temperature. In Fig. 2 the σ_{dc} has been subtracted from the $\sigma(f)$ at each temperature, leaving the frequency- and temperature-dependent σ_{ac} . In general, for constant T , $\sigma_{ac} \propto f^s$ with $s \approx 0.6$. There is some deviation from this simple behavior at higher temperatures.

It is tempting to analyze this behavior in terms of variable range hopping.^{12,15} In fact, the σ_{dc} is well fitted^{15,17} by the predicted behavior, $\sigma_{dc} \propto T^{-13.7}$.

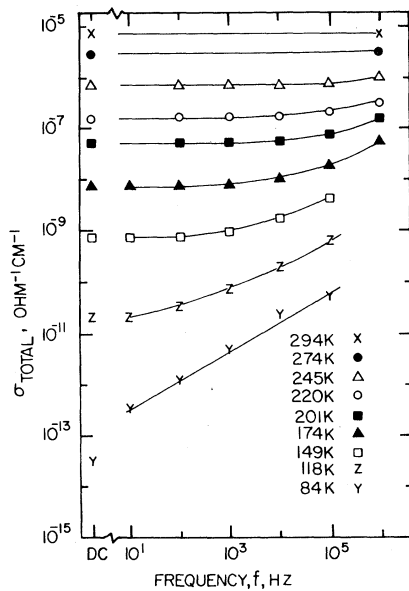


FIG. 1. $\text{Log } \sigma$ vs $\text{log } f$ for $trans$ -(CH) $_x$ at constant temperature. Note the break in the abscissa for dc. The solid lines are drawn as a guide to the eye.

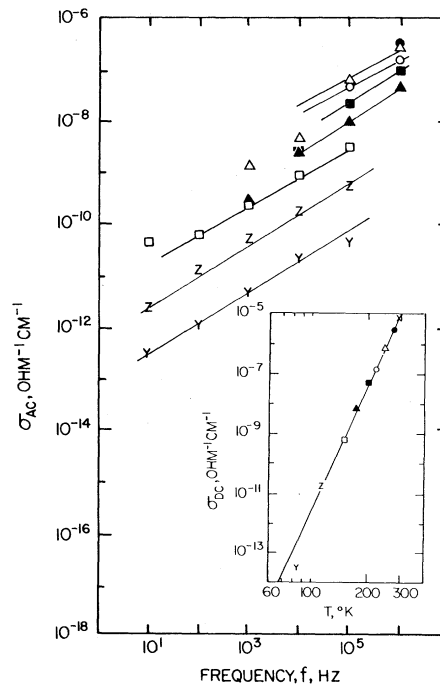


FIG. 2. $\text{Log } \sigma_{ac}$ vs $\text{log } f$ for the data in Fig. 1. The solid lines are drawn as a guide to the eye. The temperatures represented by the different symbols are given in Fig. 1. The inset presents $\text{log } \sigma_{dc}$ vs $\text{log } T$ for the data in Fig. 1. The solid line is the best fit with $\sigma_{dc} \propto T^{-13.7}$.

$= \sigma_0 \exp[-(T_0/T)^{1/4}]$, with $T_0 = 2 \times 10^9$ K, for the full T range studied. All treatments of hopping in a manifold of states near the Fermi-level share the common feature of a weakly T -dependent ac conductivity. A classic example is the result of Austin and Mott,²¹ which predicts $\sigma_{ac} \propto f^s T$, with $s \approx 0.8$. However, while the predicted $\sigma_{ac}(T)$ is linear in T , experimentally $\sigma_{ac}(T)$ is observed to change by a factor of 10^3 for a factor of 3 in temperature. Hence the usual Fermi-level hopping models cannot self-consistently model the dc and the ac conductivity. Such a strong T dependence can, in principle, arise from thermal activation of charge carriers from localized states in the gap to the mobility edge.²² The σ_{ac} and σ_{dc} would then both be proportional to $\exp(-E_A/k_B T)$ with E_A the activation energy. However, this functional form is inconsistent with our observed $\sigma_{dc}(T)$.

Recently, Kivelson has proposed¹³ a phenomenological model for hopping conduction based upon

$$\sigma_{dc} = A e^2 [\gamma(T)/k_B T N] (\xi/R_0)^2 y_n y_{ch} (y_n + y_{ch})^{-2} \exp(-2BR_0/\xi). \quad (1)$$

Here $A = 0.45$, $B = 1.39$, k_B is the Boltzmann constant, y_n and y_{ch} are the concentrations 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 where c_{im} is the concentration of impurities, ξ is the dimensionally averaged decay length for a soliton, $(\xi_{\parallel}\xi_{\perp}^2)^{1/3}$, and N is the number of carbon atoms per $(CH)_x$ chain. $\gamma(T)/N$ is then proportional to the fraction of time a pair of solitons are so situated that the initial and final soliton states are within $k_B T$ of each other. Kivelson shows¹³ that band-center optical phonons are most important, leading to $\gamma(T) \propto T^{n+1}$, so that, from Eq. (2), $\sigma(T) \propto T^n$, with $n \sim 10$.

The σ_{dc} of *trans*-(CH)_x shown in Fig. 1 is replotted in the inset in Fig. 2. It is seen that $\sigma_{dc}(T) \propto T^{13.7}$ is a very good fit to the data (reproducible in many samples). The lower measured σ_{dc} for $T = 84$ K may reflect the onset of a decrease in the contribution of acoustic phonons to the hopping in addition to the T dependence of the optical phonons.

The conductivity at finite frequency in a disordered system is always larger than the dc conductivity. Physically, this is due to the presence of pairs or larger clusters of anomalously close sites between which an electron can hop at a rate greater than the rate which characterizes the difficult hops on the percolation network. Kivelson¹³ has used the pair approximation to obtain an approximate analytic expression for the excess conductivity (above σ_{dc}) at finite frequencies:

$$\begin{aligned} \sigma_{ac} &= (e^2/\hbar)(c_{im}^2/384k_B T)n^{(0)}(1-n^{(0)})\xi_{\parallel}^3\xi_{\perp}^2\hbar f \{ \ln[4\pi f N/n^{(0)}(1-n^{(0)})\gamma(T)] \}^4 \\ &= K^1(f/T)[\ln(Df/T^{n+1})]^4 \equiv K^1 x. \end{aligned} \quad (2)$$

Here $n^{(0)}$ is the fraction of solitons that are charged, and K^1 and D are constants. Comparison of this model with experiment is now straightforward. After scaling the σ_{ac} with K^1 , there is only one adjustable parameter (D). The results are sensitive to the choice of D ; even a change of a factor of 2 in D leads to significant differences in the fit to the data. In Fig. 3, we present the σ_{ac} data of Fig. 2 replotted versus x for $D = 1 \times 10^{24}$ sec K^{14.7}. The results demonstrate a linear

the separation of the energy (temperature) and spatial dependence of the rate of hopping among sites. The wave function overlap is assumed to vary exponentially with distance while the rate at which the hopping transition occurs is averaged over the thermal distribution of initial- and final-site energies and assumed to be proportional to a power law in temperature, T^{n+1} . Kivelson¹³ associated this formalism with the phonon-assisted hopping of electrons between soliton sites. In this model, charged solitons are Coulombically bound to charged impurity sites. The excess charge on the soliton site makes a phonon-assisted transition to a neutral soliton on another chain. If this neutral soliton is near another charged impurity, the energy of the charged carrier before and after the hop is unchanged. The T dependence of the conductivity is then determined¹³ by the probability, $\gamma(T)$, that the neutral soliton is near the charged impurity and the initial and final energies are within $k_B T$ of each other:

relationship between σ_{ac} and x for over six orders of magnitude in variation of σ_{ac} , f , and x . This self-consistent agreement in the functional form of $\sigma_{ac}(f, T)$ and $\sigma_{dc}(T)$ demonstrates the utility of the Kivelson phenomenological formalism.

The data can now be evaluated for self-consistency without any adjustable parameters. Equation (1) may be solved by using $\xi = 3.56 \times 10^{-8}$ cm

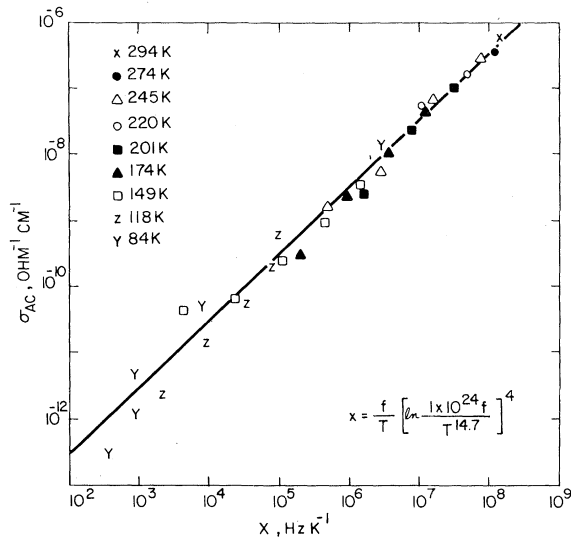


FIG. 3. $\text{Log } \sigma_{ac}$ vs $\text{log } x$, with $x \equiv (f/T) [\ln(10^{24} f/T^{14.7})]^4$ for the data in Fig. 2. The best fit with a slope of 1 is given by the solid line.

(Ref. 13), $y_n = 5 \times 10^{-4}$ (Ref. 8), $N = 2000$ (Refs. 8 and 23), and $\hbar\gamma(T) = (500 \text{ eV})(T/300 \text{ K})^{14.7}$ (Ref. 13), to obtain a value for $c_{im} = y_{ch}\rho$ (ρ is the volume density of carbon atoms) of $1.3 \times 10^{19} \text{ cm}^{-3}$ ($y_{ch} = 2.35 \times 10^{-4}$). This is in good agreement with depletion measurements on heterojunctions.²⁴ Utilizing this, together with¹³ $\xi_{\parallel} \approx 10 \times 10^{-8} \text{ cm}$ and $\xi_{\perp} \approx 2.5 \times 10^{-8} \text{ cm}$, we calculate the constants K^1 and D in Eq. (2), obtaining $K^1 = 6.3 \times 10^{-16} \Omega^{-1} \text{ cm}^{-1} \text{ sec K}$ and $D = 4.0 \times 10^{23} \text{ sec K}^{14.7}$. This compares extremely well with the experimental value of $K^1 = 3 \times 10^{-15} \Omega^{-1} \text{ cm}^{-1} \text{ sec K}$ and $D = 1.0 \times 10^{24} \text{ sec K}^{14.7}$. These small differences between the experimental and calculated K and D are within the uncertainty of the values of the parameters used for input to the calculated K and D .

It is important to examine the applicability of alternative models such as the hopping of polarons^{25,26} to $\text{trans}-(\text{CH})_x$. Although polaron hopping in an ordered lattice can lead to a strongly T -dependent σ_{ac} , σ_{dc} would then be simply activated. This is inconsistent with the experimental results for $\sigma_{dc}(T)$. It remains to be seen if addition of disorder to the polaron model or other approaches could account for the observed data.

Upon compensation with ammonia gas, both σ_{dc} and σ_{ac} are reduced to or below the levels of the $\text{cis}-(\text{CH})_x$.¹⁷ The T dependence in both σ_{dc} and σ_{ac} are now similar to the cis isomer. As the concentration of spins (neutral solitons) is only

weakly dependent upon ammonia compensation,²⁷ this strongly suggests that the ammonia compensates the charged soliton centers, so that only the underlying traditional ac transport mechanisms are observed.

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Specific Heat of the Kondo Model

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The magnetic impurity contribution to the specific heat of metals is calculated as a function of temperature. The calculation, based on the solution of a recently proposed spinless model for the Kondo problem, shows the specific heat as a universal function of the temperature scaled by the Kondo temperature. The universal function is well described by the analytically solvable resonant-level model over the entire temperature range.

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We report the first renormalization-group calculation of the magnetic impurity contribution to the specific heat of metals for the full temperature range $0 < k_B T < D$. The numerical results show that the specific heat is a universal function of the temperature scaled by the Kondo temperature T_K . Over the full temperature range, the universal function is remarkably well described by (the analytical expression for) the specific

heat for the resonant-level model. For $T \ll T_K$, the specific heat is proportional to the temperature and agrees with results previously obtained^{1,2} for this temperature range.

Our calculation is based on a recently proposed^{3,4} spinless Hamiltonian—henceforth referred to as the *VG* Hamiltonian—whose partition function maps onto the partition function for the Kondo Hamiltonian. The *VG* model, depicted in Fig. 1, is defined⁵ by

$$H_{VG} = \sum_k \epsilon_k c_k^\dagger c_k + (G/2)(bb^\dagger - b^\dagger b)(f_0^\dagger f_0 - \frac{1}{2}) + \sqrt{2}V(b^\dagger f_0 + \text{H.c.}), \quad (1)$$

where the (normalized) operator f_0 is $\sum_k c_k / \sqrt{2}$. The conduction energies, measured relative to the Fermi level, lie in a band $-D$ to D and follow a linear dispersion relation $\epsilon_F = V_F k$, where the momenta k are measured from the Fermi momentum.

The G term in (1) is a momentum-independent scattering potential whose sign depends on the occupancy of the impurity level b . From this term alone, each conduction wave function acquires a phase shift δ_G or $-\delta_G$ depending on whether the impurity level is empty ($bb^\dagger = 1$) or full ($b^\dagger b = 1$). Here $\delta_G = -\tan^{-1}(\pi\rho G/4)$, where $\rho = 1/D$ is the density of conduction states.

The V term in (1) couples the impurity level to the conduction states, producing a resonance in the conduction band. In particular, for $G = 0$ the rate of transitions between the impurity level and the conduction band—proportional to the square

of the matrix element of $Vf_0^\dagger b$ between the initial (impurity state filled) and final (impurity state empty) states—is twice the resonance width $\Gamma = \pi\rho V^2$. For $G > 0$, this rate is reduced. To see this, consider the case in which the impurity state is initially filled (i.e., $b^\dagger b = 1$). The conduction states are then subject to a repulsive potential G in the final state (where $bb^\dagger = 1$) so that the conduction wave functions in the vicinity of the impurity site are reduced relative to the case $G = 0$. The matrix element of $Vf_0^\dagger b$ is consequently smaller and the transition rate is reduced⁶ to a value $2\Gamma^* < 2\Gamma$.

This effective width Γ^* sets another energy scale in the problem. For $T \leq \Gamma^*$, the two-parameter *VG* model is identical to a one-parameter (i.e., Γ^*) resonant-level model. In particular the specific heats of the two models are very