Soliton Conduction in Polyacetylene $(CH)_x$

S. Ikehata

Department of Physics, University of Tokyo

Bunkyo-ku, Tokyo, Japan 113

Linear polyacetylene is the simplest conjugated organic polymer and has two isomers.(Fig.1)

The ground state energy of cis-structure is greater than that of trans-structure. Therefore the cis-form is thermally isomerized to the trans-form even at room temperature. The ground state of trans-$(CH)_x$ is degenerated because of the symmetry of the bond alternation direction.

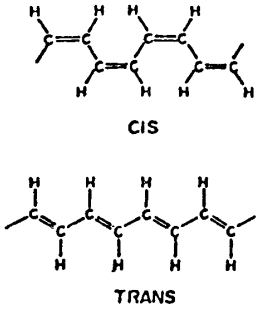

Fig.1 Molecular structure of cis and trans isomers of polyacetylene

Pure polyacetylene is a semiconductor. The energy gap measured by the optical absorption is approximately 1.5eV and 2.1eV for trans- and cis-$(CH)_x$, respectively. Optical absorption data for trans- and cis-$(CH)_x$ are shown in Fig.2.[1)]
These energy gaps are regarded as so-called Peierls gaps due to the bond alternation.

The room temperature conductivity of pristine polyacetylene is approximately $10^{-6}\Omega^{-1}cm^{-1}$ and increases sharply upon doping. The concentration dependence of the room temperature conductivity, shown in Fig.3, suggests a change in the electrical property of doped polyacetylene at dopant level ∿1%.[2)] In fact the thermoelectric power also shows the abrupt change in magnitude at dopant level ∿1%.(Fig.4).[3)] Below this critical concentration, thermoelectric power is large and almost independent of temperature. At higher dopant level such as 10%,thermoelectric power is small and linear in temperature, which is expected for the degenerated electron liquid.(Fig.5) These transport studies suggest that the semiconductor-metal transition takes place at dopant level ∿1%.

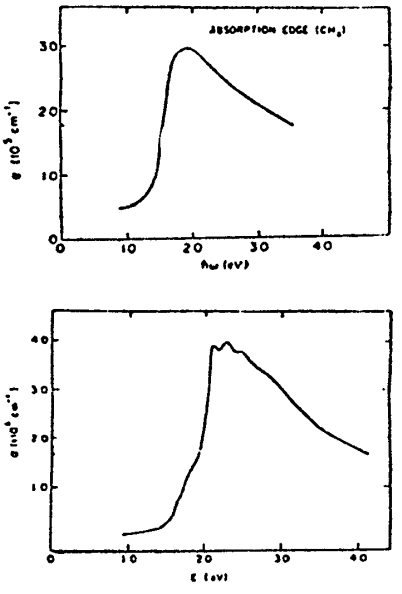

Fig.2 Absorption coefficient a) trans- b) cis-$(CH)_x$

Magnetic susceptibility is a fundamental physical quantity. Especially the Pauli susceptibility is important, because it gives us the density of states at the Fermi energy. Pure cis-$(CH)_x$ has a small Curie type spin susceptibility, presumably coming from the residual magnetic impurities. As shown in Fig.6, the Curie type spin susceptibility increases over ten times in magnitude by the isomerization from cis- to trans-$(CH)_x$.

The Curie susceptibility of pure trans-$(CH)_x$ decreases upon doping.(Fig.7) On the other hand, the Pauli susceptibility stays almost zero well into the highly conducting region and shows an abrupt increase at dopant level 7% to a typical value for a simple metal $\sim 3\times10^{-6}$emu/Cmole.(Fig.8)[4)] The Knight shift measurement of ^{13}C NMR in AsF_5 doped polyacetylene has demonstrated the same behavior of the

Pauli susceptibility.

The studies of magnetic susceptibility reveal the anomalous charge-spin relations. The increase of the Curie susceptibility by the isomerization from cis- to trans-$(CH)_x$ means that the spin carrier of trans-$(CH)_x$ must have no charge. And the anomalous behavior of the Pauli susceptibility means that in the concentration range less than 7% the charge carrier has no spin. To explain these anomalous charge-spin relations, we must introduce the novel electronic states and/or the electron-phonon states.

Considering the degeneracy of the ground state of trans-$(CH)_x$, there ocurrs the formation of the neutral domain wall(neutra soliton) and/or the charged domain wall(charged soliton) by the isomerization from cis- to trans-$(CH)_x$, which separates two directions of the dimerization.(Fig.9) The neutral soliton has an unpaired electron, which contributes to the Curie susceptibility observed by the isomerization from cis_ to trans-$(CH)_x$. According to Su et al.[5], the domain wall spreads over 15 lattice constants and has the formation energy of $2\Delta/\pi$, where 2Δ is gap energy of pure polyacetylene. The effective mass of soliton is calculated to be $\sim 6m_e$, where m_e is the electron mass. The formation energy of solitons $2\Delta/\pi$ is smaller than that of electrons(holes) in the conduction (vallence) band. Thus, the formation of solitons would be favored upon doping. The charged solitons mentioned here are spin-less chareged carriers and contribute to electrical conduction, but not to the Pauli susceptibility.

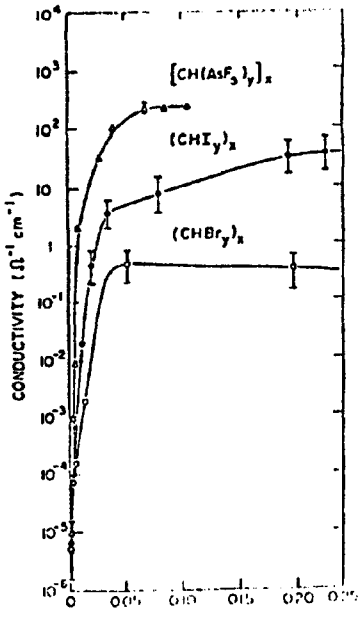

Fig.3 Electrical conductivity at room temperature as a function of dopant concentration

Recently, Kivelson has studied the problem of electrical conduction due to solitons and proposed a novel transport mechanism[6]. He suggested that the phonon assisted electron-hopping between charged and neutral solitons could be the dominant conduction mechanism in pure and lightly doped trans-$(CH)_x$. Kivelson has predicted that the temperature dependence of conductivity follows the power law $\sigma \sim T^n$ and the thermoelectric power is calculated to be as follows, $\pm|k_B/e|\{(n+2)/2+\ln y_n/y_{ch}\}$,

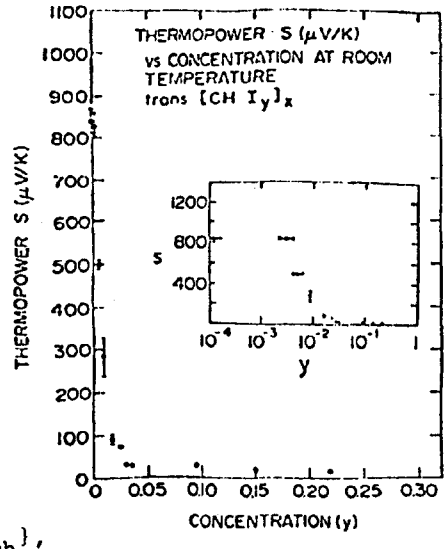

Fig.4 Thermoelectric power as a function of iodine concentration

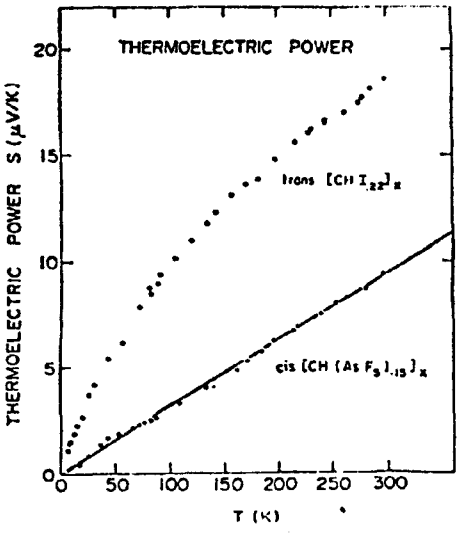

Fig.5 Temperature dependence of thermoelectric power for heavily doped $(CH)_x$

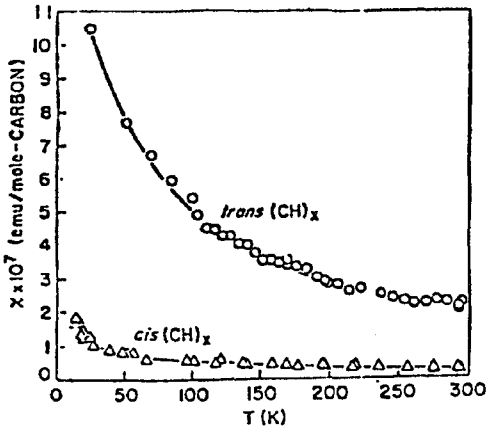

Fig.6 Spin susceptibility of pure cis- and trans-$(CH)_x$

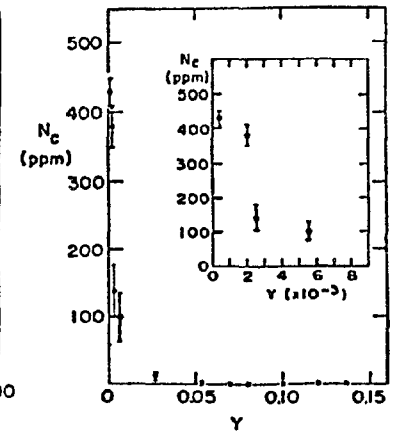

Fig.7 Curie constant as a function of dopant concentration

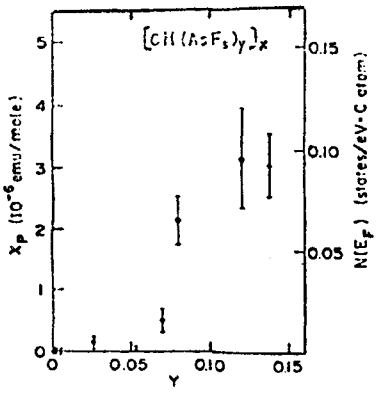

Fig.8 Pauli susceptibility and density of states at the Fermi energy as a function of dopant concentration

where y_n and y_{ch} are the concentrations of neutral and charged solitons, respectively. Recently, Moses et al.[7] have found a power law dependence of temperature in the electrical conductivity, $\sigma \sim T^n$ with $n \sim 13$. Substitution of $n \sim 13$ into the theoretical expression for S yields $S \simeq 850 \mu V.K^{-1}$ using the appropriate value of $\ln y_n/y_{ch} \simeq 2.5$. Thus, the temperature dependence of the electrical conductivity and the value of thermoelectric power are in good agreement with Kivelson's results.

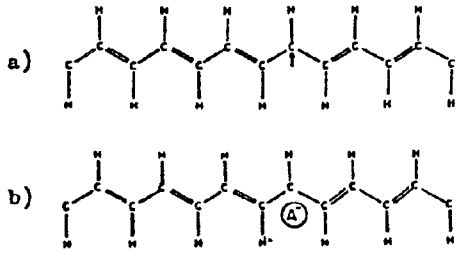

Fig.9 a) Neutral and b) charged soliton defect in trans-$(CH)_x$

The magnetic properties and the transport properties are well explained by the picture of charged and neutral solitons, at least in the pure and lightly doped trans-$(CH)_x$. The problem of soliton conduction in highly conducting regime is very interesting, but it needs further theoretical studies.

References

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