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Carrier transport in polyacetylene with intermediate doping

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By use of a modified version of Naarmann's method, we have synthesized polyacetylene $(CH)_x$. The doping was carried out in liquid phases of iodine and iron chloride, and the samples obtained were $[CH(I_3)_y]_x$ and $[CH(FeCl_4)_y]_x$, respectively. The dopant concentration y is between 0.01 and 0.05, and belongs to the intermediate doping region. The temperature dependence of the dc conductivity for the different dopant concentrations is measured. In doped *trans*-polyacetylene, charged and neutral soliton pairs are produced in the chains. The conduction mechanism, which is based on the intersoliton hopping of electrons, is the same for polyacetylene with intermediate or light doping. For this reason, Kivelson's model of the average hopping rate, the Hamiltonian of *trans*-polyacetylene explored by Su, Schrieffer, and Heeger, and the method of Ambegaokar, Halperin, and Langer, which is related to the average transition rate, are used and the relation between the average hopping rate and the transition rate obtained. Finally, in the light of percolation theory and the variable-range-hopping model, the formula for conductivity is derived. The theory is in good agreement with the experiments.

I. INTRODUCTION

In 1974, polyacetylene was made from acetylene gas with a Ziegler-Natta catalyst by Shirakawa, Ito, and Ikeda.[1] When the polyacetylene films were doped, the relatively insulating thin films yielded conductivities about $10^3\ \Omega^{-1}\,\text{cm}^{-1}$. The fibers in that type of film are relatively short and the density is low (0.3–$0.4\ \text{g/cm}^3$). In 1987, Naarmann improved the method of Shirakawa, Ito, and Ikeda,[2] and polyacetylene films were synthesized by taking silicone oil as a solvent, the fibers in this type of film are bigger and longer than in the earlier film, and the density is high (0.85–$0.90\ \text{g/cm}^3$). The films can be stretched. After being doped, the samples had conductivities as high as 10^4–$10^5\ \Omega^{-1}\,\text{cm}^{-1}$.

We have modified Naarmann's method. The polyacetylene films synthesized have properties similar to those of Naarmann. The samples are doped with iodine and iron chloride, respectively. The temperature dependence of dc conductivities for different dopant concentrations are measured. Since in doped polyacetylene, the charged and neutral soliton pairs are produced in the chains by dopants, the conductance resulting from electrons hop between the pairs is identical with that in the lightly doped system. Therefore, Kivelson's model on the average hopping rate from site i to site j, $\bar{\nu}_{ij}=\xi^2(R)\gamma(T)(1/N)$ can be introduced. Using the Hamiltonian of Su, Schrieffer, and Heeger (SSH), we found the probability of phonon-assisted hopping $\gamma(T)$, and the relation between the transition rate from site i to site j, Γ_{ij} and $\bar{\nu}_{ij}$ was obtained by the method of Ambegaokar, Halperin, and Langer (AHL), and the relation between the conductance and $\bar{\nu}_{ij}$ was also derived. Finally, according to the percolation theory and the variable-range-hopping (VRH) model, the conductivity formula was obtained. The theory was fitted well with experiments.

II. EXPERIMENTS AND RESULTS

5 ml of silicone oil was injected into a polymerizing bottle. After air in the bottle was drawn out, 3 ml $Al(C_2H_5)_3$ and 3 ml $Ti(OC_4H_9)_4$ were injected into the bottle under a weak nitrogen gas current. Then, the catalyst was heated by oil bath to 115–120 °C for 2 h. After that, the bottle was cooled off. Purified acetylene gas was pumped into the bottle at room temperature, and polymerized for ~ 6 h, and the thin film was synthesized. After the film was washed by purified methylbenzene several times, it was immersed into a solution of 10% HCl in methylalcohol for ~ 20 h. Finally, the film was washed by methylalcohol several times. The polyacetylene film showed a silver-grey gloss. Its thickness was $\sim 90\ \mu\text{m}$, and density was $\sim 0.85\ \text{g/cm}^3$. The contents of *trans*- and *cis*-polyacetylene were determined by infrared-absorption spectrum, the *trans*-$(CH)_x$ content was $\sim 56\%$. The conductivity of the undoped film was $\sim 3.2\times 10^{-7}\ \Omega^{-1}\,\text{cm}^{-1}$.

The *trans*-isomer was obtained by thermal annealing at 150 °C for 20 min in a vacuum. The samples were doped in a saturated solution of iodine in CCl_4 or $FeCl_3$ in nitromethane. Afterwards, the samples were washed in CCl_4 or nitromethane and dried in vacua. Finally, the doping level was determined by weight uptake. In the samples doped with iodine $[CH(I_3)_y]_x$, $y=0.014$ and 0.046, and in the samples doped with iron chloride $[CH(FeCl_4)_y]_x$, $y=0.015$ and 0.043. They belong to the intermediate-doping region.

The samples were set on a detecting head which was inserted into liquid nitrogen. The dc conductivities were measured by a conventional four-point method from 77 to 300 K. To form good Ohmic contact between the samples and electrodes, the electrodes were made of gold. The temperature dependence of dc conductivity in the intermediate-doping region was in agreement with the

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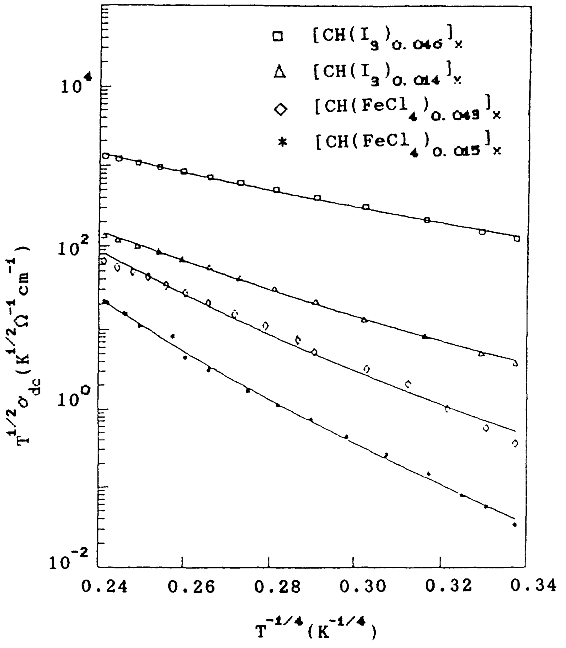

FIG. 1. Logarithm of $T^{1/2}\sigma_{dc}$ versus $T^{-1/4}$ for $[CH(I_3)_y]_x$ and $[CH(FeCl_4)_y]_x$.

VRH mode,[3]

$$\sigma_{dc}=AT^{-1/2}\exp[-(T_0/T)^{1/4}]\ , \quad (1)$$

where σ_{dc} is dc conductivity, T is the temperature, and A and T_0 are constants. Taking the logarithm, Eq. (1) is written as

$$\ln(T^{1/2}\sigma_{dc})=-(T_0^{1/4})T^{-1/4}+\ln A\ . \quad (2)$$

Data from experiments are shown as the solid line for each sample in Fig. 1. The experimental curves are straight with different slopes as shown in Fig. 1. The experimental results were in good agreement with Eq. (2). According to the value of σ_{dc} measured from experiment as $T=295$ K, A and T_0 were determined by solving the equations. A and T_0 were given in Table I. These results showed that in the intermediate-doping region the temperature dependence of dc conductivities for iodine- and iron chloride-doped polacetylene were consistent with the VRH mode.

TABLE I. Experimental values of σ_{dc} (295 K) and parameters for $[CH(I_3)_y]_x$ and $[CH(FeCl_4)_y]_x$.

Samples	σ_{dc} (295 K) ($\Omega^{-1}cm^{-1}$)	A ($K^{1/2}\ \Omega^{-1}cm^{-1}$)	T_0 (K)
$[CH(I_3)_{0.046}]_x$	75.92	4.85×10^5	3.62×10^5
$[CH(I_3)_{0.014}]_x$	7.86	1.10×10^6	1.94×10^6
$[CH(FeCl_4)_{0.043}]_x$	3.77	3.63×10^7	9.06×10^6
$[CH(FeCl_4)_{0.015}]_x$	1.26	2.54×10^8	2.07×10^7

III. MECHANISM OF CONDUCTION

For polyacetylene with intermediate doping, the VRH conductivity formula used above is always empirical. It cannot illustrate the mechanism of conduction of the doped *trans*-polyacetylene.

In *trans*-polyacetylene with intermediate doping, the dopants produce pairs of charged and neutral solitons in the chains,charged solitons are Coulombically bound to dopant ions, and in their potential wells. Negatively charged solitons on the other hand have their electron in a different energy level in the potential well. In three dimensions, transport is essentially due to electrons in charged solitons under phonon-assisted hopping onto the nearby neutral solitons on the chains or on the nearby chains. In view of the fact that electronic function overlap in the intrachain is made up of π bonds, and that in the interchain is made up of Van der Waals's bonds, the two hopping processes of electrons mentioned above are different. In the three-dimensional situation, because the doped polyacetylene is isotropic, we can take the average of the electronic wave-function overlap.

From the analysis above, the conduction mechanism of polyacetylene with intermediate doping can be described by electrons making the transition between charged and neutral solitons, which is identical with that in the lightly doped polyacetylene that Kivelson had proposed.[4] The difference is that in intermediate-doped samples, there are many chains on which the charged and neutral soliton pairs are produced by many dopants. The dopant ions between chains are also plentiful, so the neutral solitons near the ions are plentiful, which is favorable to the hopping conduction of electrons, and the conductivity is also high.

In the hopping conduction, the important quantity is the average hopping rate from site i to site j, i.e., $\bar{\nu}_{ij}$. It depends on the electronic wave-function overlap $\zeta^2(R)$, and the thermal activation probability of electrons to make a phonon-assisted transition $\gamma(T)$, and the site probability $(1/N)$ that electrons may hop in the factor N, which is the total number of sites on a chain. So according to Kivelson's model, the average hopping rate of a electron from site i to site j is[3,4]

$$\bar{\nu}_{ij}=\zeta^2(R)\gamma(T)(1/N)\ . \quad (3)$$

Because the electronic function on the soliton is proportional to $\mathrm{sech}(x/\xi)$, thus falling off at large x as $\exp(-x/\xi)$, we may take the overlap to be given by

$$\zeta^2(R)=\exp(-2R/\xi)\ , \quad (4)$$

where R is the distance between sites i and site j. $R=(R_\parallel^2+R_\perp^2)^{1/2}$, $R_\parallel$ is the component of R along the chain direction, and $R_\perp$ is the distance perpendicular to the chain. ξ is the three-dimensional averaged electronic decay length, $\xi=(\xi_\parallel\xi_\perp^2)^{1/3}$; $\xi_\parallel$ and $\xi_\perp$ are parallel and perpendicular decay length, respectively.

$\gamma(T)$ reflects the probability that electrons are activated by electron-phonon interaction. We can find it by considering the situation of electron-phonon interaction on one of the chains.

A. The calculation of $\gamma(T)$

The SSH Hamiltonian on an electron-lattice coupling system for polyacetylene proposed by Su, Shrieffer, and Heeger is written as[5]

$$\begin{aligned} H=&\sum_n[\varepsilon_0C_n^+C_n-t_0(C_{n+1}^+C_n+C_n^+C_{n+1})]\\ &+\alpha\sum_n(u_{n+1}-u_n)(C_{n+1}^+C_n+C_n^+C_{n+1})\\ &+\frac{K}{2}\sum_n(u_{n+1}-u_n)^2+\frac{1}{2}\sum_n M\dot{u}_n^2\ , \end{aligned} \tag{5}$$

where C_n^+ and C_n creates and annihilates an electron on the nth site, respectively. u_n is a configuration coordinate for displacement of the nth site. t_0 is the hopping integral for the undimerized chain. α is the electron-lattice displacement coupling constant, K is the effective spring constant, and M is the mass of the CH group. It can be seen that energy ε_0 of an electron on site n is retained.[3] By reasonable approximations, the Hamiltonian can be written as (as derived in the Appendix)

$$\begin{aligned} H=&\sum_n\varepsilon_0C_n^+C_n-t_0\sum_{np}C_{n+\rho}^+C_n\\ &+\sum_{qn}\exp(iqna)D_q(a_q^++a_{-q}^{\pm})C_n^+C_n\\ &+\sum_q\hbar\omega_q(a_q^+a_q+1/2)\ . \end{aligned} \tag{6}$$

For Eq. (6), let

$$\begin{aligned} H_0=&\sum_n\varepsilon_0C_n^+C_n+\sum_{qn}\exp(iqna)D_q(a_q+a_{-q}^{\pm})C_n^+C_n\\ &+\sum_q\hbar\omega_q(a_q^+a_q+1/2)\ , \end{aligned} \tag{7}$$

and

$$H_1=-t_0\sum_{np}C_{n+\rho}^+C_n\ . \tag{8}$$

We make a transformation as follows

$$\overline{H}=e^{-S}He^{S}=\overline{H}_0+\overline{H}_1\ , \tag{9}$$

where S is taken to be

$$S=-\sum_{qn}(D_q/\hbar\omega_q)\exp(iqna)C_n^+C_n(a_q-a_{-q}^{\pm})\ . \tag{10}$$

Then Eq. (9) is written as[8]

$$\overline{H}_0=\sum_n(\varepsilon_0-\Delta)C_n^+C_n+\sum_q\hbar\omega_q(a_q^+a_q+\tfrac{1}{2})\ , \tag{11}$$

$$\overline{H}_1=-t_0\sum_{np}C_{n+\rho}^+C_nX_{n+\rho}^+X_n\ , \tag{12}$$

where $\Delta=\sum_q|D_q|^2/\hbar\omega_q$, and

$$X_n=\exp[\sum_q(D_q/\hbar\omega_q)e^{iqna}(a_q-a_{-q}^{\pm})]\ , \tag{13}$$

where $\overline{H}_1$ describes the hopping of phonon-assisted electrons.

The electron-phonon coupling states on site i can be written as

$$|1_i\rangle\prod_q|n_q\rangle\equiv|1_i\rangle|\{n_q\}\rangle\ . \tag{14}$$

Using Eqs. (12) and (14), we obtain the transition matrix elements of electrons, i.e.,

$$\langle\{n_q'\}|\langle 1_{n+p}|\overline{H}_1|1_n\rangle|\{n_q\}\rangle=-t_0\langle j|X_{n+\rho}^+X_n|i\rangle\ , \tag{15}$$

where $|i\rangle=|\{n_q\}\rangle$ and $|j\rangle=|\{n_q'\}\rangle$ are the phonon states before and after the transition, respectively. When electrons make the transition, the numbers of phonon follow to change, i.e., $|i\rangle\neq|j\rangle$. According to time-dependent disturbance theory,[9] we obtain the transition probability of electrons w, i.e.,

$$w=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\ W(t)\ , \tag{16}$$

where

$$\begin{aligned} W(t)=&t_0^2\sum_{j\neq i}\langle i|X_n^+(t)X_{n+\rho}(t)|j\rangle\langle j|X_{n+\rho}^+X_n|i\rangle\\ =&t_0^2[\langle i|X_n^+(t)X_{n+\rho}(t)X_{n+\rho}^+X_n|i\rangle\\ &-|\langle i|X_{n+\rho}^+X_n|i\rangle|^2]\ , \end{aligned} \tag{17}$$

and

$$X_n(t)=e^{i\overline{H}_0t/\hbar}X_ne^{-i\overline{H}_0t/\hbar}\ . \tag{18}$$

The statistical average value of the time-dependent correlation function of the first term in $W(t)$ is[8]

$$\langle i|X_n^+(t)X_{n+\rho}(t)X_{n+\rho}^+X_n|i\rangle_T=\exp[\varphi(t)-2S_T]\ , \tag{19}$$

where

$$S_T=\sum_q(D_q/\hbar\omega_q)^2(N_q+1/2)|1-e^{iqa}|^2\ , \tag{20}$$

$$\begin{aligned} \varphi(t)=&\sum_q(|D_q|^2/\hbar\omega_q)|1-e^{iqa}|^2\\ &\times[(N_q+1)e^{-i\omega_qt}+N_qe^{i\omega_qt}]\ , \end{aligned} \tag{21}$$

and

$$N_q=(e^{\beta\hbar\omega_q}-1)^{-1},\quad \beta=1/k_BT\ .$$

Similarly one has

$$\langle i|X_{n+\rho}^+X_n|i\rangle_T=\exp(-S_T)\ . \tag{22}$$

Thus $W(t)$ is written as

$$W(t)=t_0^2e^{-2S_T}(e^{\varphi(t)}-1)\ . \tag{23}$$

Inserting Eq. (23) into (16), we find the statistical average value of w, i.e.,

$$w_T=(t_0/\hbar)^2\int_{-\infty}^{\infty}dt(e^{\varphi(t)}-1)e^{-2S_T}\ , \tag{24}$$

and then evaluating w_T, we gain[8]

$$w_T=(t_0/\hbar)^2(\pi/\gamma)^{1/2}\exp(-E_a/k_BT)\ , \tag{25}$$

where

$$E_\alpha=(\tfrac{1}{4})\sum_q \frac{|D_q|^2}{\hbar\omega_q}|1-e^{iqa}|^2 ,$$

$$\gamma=\sum_q |D_q|^2|1-e^{iqa}|^2[N_q(N_q+1)]^{1/2} .$$

Because the effective electron-phonon coupling parameter is a simple, smooth, single-peaked function of energy, and it falls at an average optical-phonon frequency, $\hbar\omega_0=0.15$ eV, and the peak is determined by half-width of optical-phonon spectrum $\hbar\Delta\omega=0.05$ eV,[4] i.e., the effective energy of optical phonons is between 0.13–0.18 eV, $e^{\beta\hbar\omega_q}\gg 1$. We can take $\hbar\omega_q=\hbar\omega_0=0.15$ eV in the γ as an approximation, and

$$\gamma=\left[\sum_q |D_q|^2|1-e^{iqa}|^2\right]e^{-\hbar\omega_0/(2k_BT)} ,$$

letting $\gamma_0=\sum_q|D_q|^2|1-e^{iqa}|^2$, then Eq. (25) is given by

$$w_T=(t_0/\hbar)^2(\pi/\gamma_0)^{1/2}\exp(-E_\beta/k_BT) , \tag{26}$$

where $E_\beta=E_\alpha-\hbar\omega_0/2$. Letting $w'=(t_0/\hbar)^2(\pi/\gamma_0)^{1/2}$, Eq. (26) is given by

$$w_T=w'\exp(-E_\beta/k_BT) , \tag{27}$$

where E_β is regarded as an activation energy in a chain. In fact, an electron on a charged soliton at site i is in the energy state E_i of potential well, and the empty site on a neutral soliton at site j is in the energy state E_j. An electron is activated by the phonon and hops from site i to site j, the difference of energy is $\Delta E=E_i+E_\beta-E_j$. We assume that in the situation with intermediate doping, the surroundings of site i and site j are identical, that is to say there are identical actions of soliton and impurity potential for site i and site j. So the actions can be offset for ΔE. Then we obtain the thermal activation probability of electrons by electron-phonon interaction from site i to j,

$$\begin{aligned}\gamma(T)&=w'\exp[-(E_i+E_\beta-E_j)/k_BT]\\&=w'\exp(-\Delta E/k_BT) .\end{aligned} \tag{28}$$

Inserting Eq. (28) and (4) into (3), we obtain the average hopping rate of an electron from site i to site j,

$$\bar{\nu}_{ij}=\nu_0\exp[-(2R/\xi)-(\Delta E/k_BT)] , \tag{29}$$

where $\nu_0=w'/N$. Obviously it depends on the length of chain, i.e., depends on the quality of polyacetylene films.

B. The transition rate and conductance

Using the AHL method[10] and Kivelson's theory,[4] we obtain the electronic average transition rate from site i to site j,

$$\Gamma_{ij}=\langle f_i(1-f_j)\rangle\bar{\nu}_{ij} , \tag{30}$$

where f_i is the probability of an electron being on site i and $(1-f_j)$ is the probability that site j is empty. In thermal equilibrium the net current from site i to site j must vanish, with thermal equilibrium values of quantities denoted by the superscript 0, the condition that the current vanish requires

$$\Gamma_{ij}^0=f_i^0(1-f_i^0)\bar{\nu}_{ij}=\Gamma_{ji}^0 , \tag{31}$$

where f_i^0 is the thermal equilibrium distribution function. At a certain temperature, applying voltage between site i and site j, the net current from site i to site j is[3]

$$\Gamma_{ij}-\Gamma_{ji}=(\Gamma_{ij}^0/k_BT)(\delta E_{Fi}-\delta E_{Fj}+eV_{ij}) , \tag{32}$$

where $E_{Fi}=E_i-E_F$, represents the electric energy on the site i measured from the Fermi energy E_F. δE_{Fi} is the energy change on site i caused by chemical-potential change. $\delta E_{Fi}-\delta E_{Fj}+eV_{ij}$ is the potential-energy difference between site i and site j. From the usual definition of conductance $G_{ij}=e(\Gamma_{ij}-\Gamma_{ji})$, as the ratio of electric current to potential difference (=potential-energy difference/e), we obtain from Eq. (32)

$$\begin{aligned}G_{ij}&=e^2\Gamma_{ij}^0/k_BT\\&=[e^2f_i^0(1-f_j^0)/k_BT]\bar{\nu}_{ij} .\end{aligned} \tag{33}$$

C. The percolation theory and dc conductivity

The problem of finding the conductivity is the percolation problem. The case that most resembles the present one is that of the electron hopping within a narrow nondegenerate band, the so-called isoenergetic case, studied by Butcher, Hauden, and McInnes.[11] Inserting Eq. (29) into (33), the dc conductivity[4]

$$\begin{aligned}\sigma_{\mathrm{dc}}&=(A'e^2\nu_0/k_BT)f^0(1-f^0)(\xi/\bar{R}^2)\\&\quad\times\exp[-(2B\bar{R}/\xi)-(\Delta E/k_BT)] ,\end{aligned} \tag{34}$$

where A', B are constants, and B is related to the percolation threshold, $A'=0.45$, $B=1.39$.

In view of the VRH model,[12] the average hopping distance, or range R, increases with decreasing T. Taking the average of spherical surface, $\bar{R}$ in the Eq. (34) is $\bar{R}=\int_0^R r^3dr/\int_0^R r^2dr=\frac{3}{4}R$. Taking one localization state i as a center, within the sphere of radius R, and the energy between E and $E+\Delta E$, the state numbers are $\frac{4}{3}\pi R^3g(E_F)\Delta E$, where $g(E_F)$ is the density of states for Fermi energy. To determine the range at a given T we consider that for the electron to find a site ΔE higher in energy requires on the average a volume around the original site

$$\Delta E=[(4/3)\pi R^3g(E_F)]^{-1} . \tag{35}$$

Let

$$f(R)=-(2B\bar{R}/\xi)-(\Delta E/k_BT) , \tag{36}$$

to maximize the hopping rate we may take the maximum value of $f(R)$, i.e., $df(R)/dR=0$, this leads to

$$\xi=(2/3)[\pi BR^4g(E_F)k_BT] . \tag{37}$$

If y_{ch} and y_{n} express the numbers of charged and neutral solitons per C atom, respectively, $y_{\mathrm{ch}}/(y_{\mathrm{ch}}+y_{\mathrm{n}})$ replaces

f^0, while $y_{\mathrm{n}}/(y_{\mathrm{ch}}+y_{\mathrm{n}})$ replaces $(1-f^0)$, and $f^0(1-f^0)$ is

$$y_{\mathrm{ch}}y_{\mathrm{n}}/(y_{\mathrm{ch}}+y_{\mathrm{n}})^2 \ . \tag{38}$$

This quantity obviously depends on the type of impurity and dopant concentration. Inserting Eqs. (37) and (38) into (34), we obtain

$$\sigma_{\mathrm{dc}}=AT^{-1/2}\exp[-T_0/T)^{1/4}] \ , \tag{39}$$

where

$$\begin{aligned} A&=4(\tfrac{2}{3})^3A'e^2v_0[\pi Bg(E_F)\xi]^{1/2}\\ &\quad\times k_B^{-1/2}y_{\mathrm{ch}}y_{\mathrm{n}}/(y_{\mathrm{ch}}+y_{\mathrm{n}})^2 \ . \end{aligned}$$

$T_0=24(B/\xi)^3/[\pi k_B g(E_F)]$. A depends on the quality of film, the type of impurity, and the dopant concentration, obviously. Equation (39) is the VRH conductivity. It is in agreement with the experimental results.

IV. CONCLUSION

From the experiments we have obtained the temperature dependence of dc conductivities for iodine- and iron chloride-doped samples in the intermediate-doping region, the results are in good agreement with Eq. (1), which is the VRH model. Taking into consideration that in doped *trans*-polyacetylene the charged and neutral soliton are produced by the dopant, the polyacetylene conduction mechanism of the intermediate doping is the intersoliton electron hopping, which is identical with the lightly doped, hence Kivelson model and the average hopping rate can be introduced. Using the SSH Hamiltonian, we found the probability of phonon-assisted hopping. In light of the AHL method, percolation theory, and the VRH model, we obtain the relation of T dependence of the conductivity σ_{dc}, i.e., Eq. (39), which is consistent with the experimental results.

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APPENDIX

The total Hamiltonian consists of three parts,[6] i.e.,

$$H=H_e+H_{ep}+H_p \ , \tag{A1}$$

where H_e describes the sum of energy of an electron on site n.

$$H_e=\varepsilon_0\sum_n C_n^+C_n-t_0\sum_n(C_{n+1}^+C_n+C_n^+C_{n+1}) \ .$$

It is given by

$$H_e=\varepsilon_0\sum_n C_n^+C_n-t_0\sum_{n\rho}C_{n+\rho}^+C_n \ , \tag{A2}$$

where $\rho=\pm1$, $-t_0\sum_{n\rho}C_{n+\rho}^+C_n$ describes the hopping of electrons.[6]

H_{ep} is the electron-phonon interaction energy and taken to be

$$H_{ep}=\alpha\sum_n(u_{n+1}-u_n)(C_{n+1}^+C_n+C_n^+C_{n+1}) \ . \tag{A3}$$

With the consideration of[3,6]

$$C_n=N^{-1/2}\sum_k\exp(ikna)C_k \ , \tag{A4}$$

$$\begin{aligned} C_{n+1}&=N^{-1/2}\sum_k\exp[ik(n+1)a]C_k\\ &=N^{-1/2}\sum_k\exp(ikna)C_k\exp(ika)\\ &=N^{-1/2}\sum_k\exp(ikna)C_k(1+ika+\cdots)\\ &\approx C_n+N^{-1/2}\sum_k C_k(ika) \ , \end{aligned} \tag{A5}$$

we have

$$C_{n+1}^+C_n\approx C_n^+C_n+N^{-1}\sum_k\sum_{k'}C_k^+C_{k'}(-ika)\exp[-i(k-k')na] \ , \tag{A6}$$

$$C_n^+C_{n+1}\approx C_n^+C_n+N^{-1}\sum_k\sum_{k'}C_{k'}^+C_k(ika)\exp[-i(k'-k)na] \ . \tag{A7}$$

Because of the Peierls distortion, the chain is distorted so as to change the lattice constant from a to $2a$,[3,6] and give rise to acoustic and optical phonons. u_n and u_{n+1} can be expressed in terms of creation and annihilation operators,[7]

$$u_n=\sum_q(\hbar/NM\omega_q)^{1/2}(a_q+a_{-q}^+)\exp(iqna)=\sum_q B_q[1+(iqna)+\cdots] \ , \tag{A8}$$

$$u_{n+1}=\sum_q B_q\exp[iq(n+1)a]=\sum_q B_q[1+iq(n+1)a+\cdots] \ , \tag{A9}$$

where $B_q=(\hbar/NM\omega_q)^{1/2}(a_q+a_{-q}^+)$ and a_{-q}^+ and a_q are the phonon creation and annihilation operators. q is the wave vector of phonons. ω_q is the frequency. Because we only investigate the optical phonon–electron interaction, the acoustic branch signs are omitted. For simplicity of calculation, inserting Eqs. (A6)–(A9) into (A3), we take the first approximation and obtain

$$H_{ep}=2\alpha\sum_{n}(u_{n+1}-u_{n})C_{n}^{+}C_{n}+\alpha\sum_{n}\sum_{q}\sum_{kk'}B_{q}N^{-1}\{C_{k}^{+}C_{k'}(-ika)(iqa)\exp[-i(k-k')na]$$

$$+C_{k'}^{+}C_{k}(ika)(iqa)\exp[-i(k'-k)na]\}$$

$$=2\alpha\sum_{n}(u_{n+1}-u_{n})C_{n}^{+}C_{n}=\sum_{qn}\exp(iqna)D_{q}(a_{q}+a_{-q}^{+})C_{n}^{+}C_{n}\ , \tag{A10}$$

where $D_q=(e^{iqa}-1)(4\hbar\alpha^2/NM\omega_q)^{1/2}$. Since $\omega_q=\omega_{-q}$,[7] one has $D_{-q}=D_q^{+}$.

H_p represents the phonon energy, $H_p=(K/2)\sum_n(u_{n+1}-u_n)^2+\frac{1}{2}\sum_n M\dot{u}_n^2$. It can be quantized as[7]

$$H_p=\sum_{q}\hbar\omega_q(a_q^{+}a_q+\tfrac{1}{2})\ . \tag{A11}$$

So the SSH model Hamiltonian is written as

$$H=\sum_{n}\varepsilon_0C_n^{+}C_n-t_0\sum_{np}C_{n+p}^{+}C_n+\sum_{qn}\exp(iqna)D_q(a_q+a_{-q}^{+})C_n^{+}C_n+\sum_{q}\hbar\omega_q(a_q^{+}a_q+\tfrac{1}{2})\ , \tag{A12}$$

which is Eq. (6).

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