Spin Gap in Perchlorate-Doped *Trans*-Polyacetylene

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Transition to a spin-gap state in a doped conducting polymer is reported for the first time. A decrease in the ESR spin susceptibility was observed near 200 K in *trans*-polyacetylene doped with perchloric ion (ClO_4^-). The thermoelectric power did not show any corresponding anomaly, while the activation energy of the resistivity was decreased slightly on the spin-gap formation. These results suggest that the electronic state undergoes a spin-charge separation and the carriers are actuated by lower energy. It was also shown, by the lattice heat capacity measurement, that the lattice structure, connected to the framework for the soliton lattice, is changed remarkably at the initial stage of doping. [S0031-9007(99)08659-7]

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Trans-polyacetylene, $(CH)_x$, the simplest quasi-one-dimensional conductor, is a Peierls band-gap insulator at half-filling, which can be transformed into an electrical conductor with doping. In undoped *trans*-$(CH)_x$, a domain boundary of two degenerate dimerization phases called topological soliton can be generated as an elementary excitation [1]. In the dilutely doped case with a dopant concentration of less than 1% in the CH units, the electrical charge can be carried by the hopping of the soliton that possesses a charge but no spin [2]. On the other hand, with the doping concentration exceeding 10%, a high electrical conductivity can be maintained over a wide temperature range from room temperature to mK-temperature with only weak temperature dependence [3,4]. The measurement of the spin susceptibility for the metallic state indicates that the charged carrier is not solitonlike. Instead it is electron or holelike, it possesses an electronic charge and $1/2$ spin. As a result, the charge transport in the heavily doped polyacetylene can be described as being similar to that in an anisotropic three-dimensional conductor mediated by interchain transfer [5]. A great deal of interest has been generated in illuminating the crossover from the solitonlike state to the electron or polaronlike state that occurs in the intermediate dopant concentration region [6,7].

We have approached the subject by using a refined polyacetylene called ν-polyacetylene [8], which can provide very high electrical conductivity with doping. Perchloric ion (ClO_4^-) was adopted for the dopant species [9], since the π electrons in the conjugating polymer can be detected via an ESR signal. It is advantageous that the dopant by itself does not create an ESR signal. This contrasts with iodine-doped $(CH)_x$, in which the ESR signal becomes too broad to detect due to a fast relaxation of the conduction electrons by the large spin-orbit coupling [10]. In order to investigate the charged state, the thermoelectric power and the electrical resistivity were measured. In addition, the heat capacity was investigated at low temperature in order to determine the electronic state [11]. As will be shown, however, the heat capacity data revealed an unexpected feature of the lattice or chain arrangement in relation to the doping which provides an opportune basis for considering the intermediately doped state.

Pristine films were prepared by using a refined catalyst and purified acetylene gas [12]. Thin films with a thickness of less than 10 μm were used in order to dope as uniformly as possible. The films were *trans*-isomerized by heating at 200 °C in a vacuum for 1 hour. The doping was then carried out by immersing film in a $Cu(ClO_4)_2$-acetonitrile solution [9]. The dopant concentration was controlled by changing the concentration of the solution and the immersion time, and it was determined by weight uptake. Since the property of the intermediately doped samples is delicately changed by the doping procedure as well as the structural property of the pristine film, pieces cut out of one film were used for the ESR, thermoelectric power, and resistivity measurements described below.

The ESR measurement was carried out in the X-band frequency region. The line shape was symmetric. This is consistent with the resistivity higher than 10^{-3} ohm · cm, giving the skin depth longer than the used sample thickness. The integrated intensity of the ESR signal corresponding to the spin susceptibility of the lightly doped sample with ClO_4^- concentration of 0.9% showed Curie-like temperature dependence, as shown in Fig. 1. In contrast, the integrated intensity of the ESR signal for the heavily doped with 9.9% showed a Pauli-like temperature dependence down to 150 K; this was followed successively by a slight decrease and then a rapid increase below 60 K. The Curie-like part for the lightly doped case can be ascribed to the neutral solitons, which are characterized by a spin-charge separation, through the temperature dependencies of both susceptibility and peak-to-peak width [6,10]. On the other hand, the rapid increase for the heavily doped sample can be ascribed to the strong electron correlation or partial localization of conduction electrons [10]. For the intermediately doped cases with dopant concentrations of 2.6% and 6.6% in Fig. 1, the decrease was

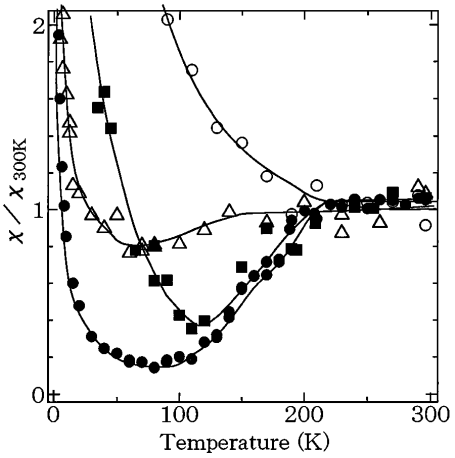

FIG. 1. Temperature dependence of the spin susceptibility χ for four samples; $(CH(ClO_4)_{0.009})_x$ (represented with open circles), $(CH(ClO_4)_{0.026})_x$ (closed squares), $(CH(ClO_4)_{0.066})_x$ (closed circles), and $(CH(ClO_4)_{0.099})_x$ (open triangles). The electric field component of the microwave was applied perpendicularly to the stretched direction. The spin susceptibility is normalized by the value at 300 K. The lines are guide for the eyes.

more pronounced, suggesting the dominance of the spin-gap state, the decrease started near 200 K and was followed by a rapid increase at a lower temperature. It should be noted that the line shape changed in concert with the emergence of the spin gap, as shown in Fig. 2. This suggests the occurrence of the change in spin dynamics. The line shape, which fitted with a Lorentzian with the peak-to-peak width of 1.8 Oe at room temperature, was modified so that it was decomposed into two parts with a broad line (reaching the half-width of 6.5 Oe at 180 K) and a narrow line (1.8 Oe) in the spin gap formation. A similar broad line was reported in the soliton state [13], while the narrow one was formed in the metallic sample.

In contrast, the thermoelectric power of $(CH(ClO_4)_{0.066})_x$ with linear temperature dependence, as commonly found in doped $(CH)_x$, did not exhibit any corresponding anomaly, as shown in Fig. 3. A similar result was obtained for $(CH(ClO_4)_{0.026})_x$ with the larger slopes being consistent with previous reports [14]. The absence of an anomaly corresponding to the spin gap implies that the charged state did not change significantly. Incidentally, the inverse-temperature dependence of the resistivity represented in the logarithmic scale exhibited a change in the slope in the fitted straight line, as shown in Fig. 4. This implies that the spin-charge-separated carriers that appear in the low temperature phase can be actuated with lower energy.

The low-temperature heat capacity for the various dopant concentrations was also measured as a function of temperature T in order to improve the information on the electronic ground state of the intermediately doped sample. The low-temperature heat capacity C was analyzed with $C = \gamma T + aT^3$, where the linear term represents the contribution from the electronic part and the disorder, while the cubic term arises from the chain lattice. Figure 5 shows the dopant concentration dependence for the values of γ and a. For the doped cases, γ represents the electronic contribution [11], the electronic density of states increases with the dopant concentration rather smoothly. On the other hand, the value of a for the doped sample increases remarkably at the initial stage of doping and stays at an almost constant level during the process of the doping. The increase in a indicates that the lattice is softened, this is presumably due to the expansion of the interchain spacing to form channels for accommodation of the dopants. This leads to the conclusion that the chain configuration for a doped $(CH)_x$ is mostly accomplished

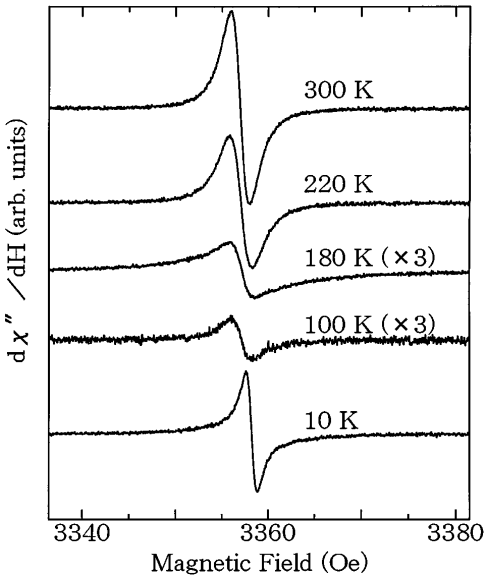

FIG. 2. Temperature dependence of the ESR spectra for $(CH(ClO_4)_{0.066})_x$. The microwave frequency used was 9.4 GHz.

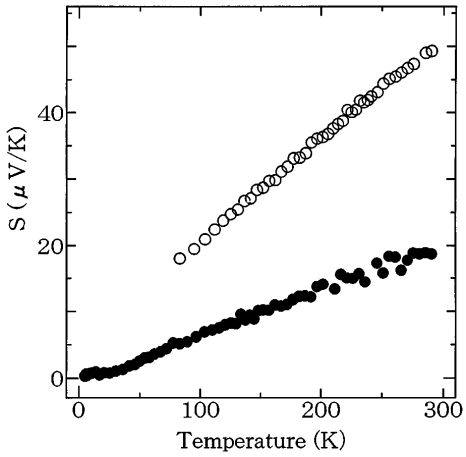

FIG. 3. Temperature dependence of the thermoelectric power S for $(CH(ClO_4)_{0.066})_x$ (represented with closed circles) and $(CH(ClO_4)_{0.026})_x$ (open circles).

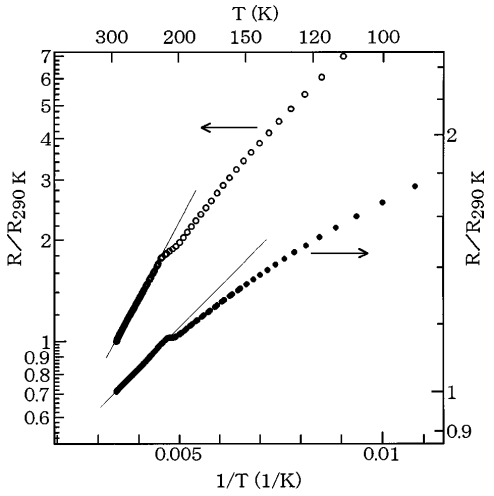

FIG. 4. Temperature dependence of the electrical resistivity R normalized with that at 290 K for $(CH(ClO_4)_{0.066})_x$ (represented with closed circles) and $(CH(ClO_4)_{0.026})_x$ (open circles).

upon the initiation of doping. For the doping of small size alkali metal, it has been thought that the dopants are accommodated into the space between the chains without considerable expansion [15]. In contrast to this, dopants such as AsF_6^- and ClO_4^- which have a larger size than the preexisting channel need an expansion of the space and modification of the structure [16]. Thus, the heat capacity measurement has provided new insight into the chain lattice for doped polyacetylene with ClO_4^--type species.

With regard to the electronic transport in the doped polyacetylene, it is concluded that the charged solitons contribute to the electrical transport in the most diluted doped sample, while the electron or holelike carriers dominate in the heavily doped sample. The elucidation of the electronic phases relevant to the crossover between these states has been a long-standing target of study [17,18]. The present experimental results, which show a transition to the spin-charge separated state in the intermediately doped $(CH)_x$ in response to cooling, demonstrate that the crossover between the polaronlike and solitonlike states appears in the same structural framework. This contrasts a report by Chen and Heeger [13] which states that the crossover was recognized in different samples with a concentration boundary at 6%. The concentration dependence of the spin-gap behavior displayed in Fig. 1 shows that the effect of the gap is maximized near 6%, but exists already at 2.6% and remains even at 9.9%. It is noteworthy that the onset temperature of the spin gap is ~200 K for both the 2.6% doped sample and the 6.6% doped sample, suggesting that the soliton lattice responsible for the spin gap is of a similar structure irrespective of the dopant concentration.

It should be noted that the structural background affects the transition to the spin-gap state which can be observed in a sample. First, the quality of the pristine film is essential. For example, we obtained samples exhibiting the spin-gap transition with the use of the pristine film grown at the wall of the container, but not with use of film grown at the bottom. The difference is ascribed to the quality of the structure of the pristine film: the former could be stretched more than three times, while the latter could not do so. Also, the doping process influences the result significantly. The reason why we could observe the crossover within a sample is due to the refined quality of the pristine ν-$(CH)_x$, probably with fewer cross links and/or fewer chain interruptions, as evidenced by the high conductivity realized in ν-$(CH)_x$ when heavily doped [8]. Furthermore, when the doping was carried out with the use of a pristine *cis*-film, instead of the *trans*-isomerized film, the spin gap was formed in a somewhat different way, as shown in Fig. 6. The decrease in the spin susceptibility appears below 130 K, although the line width started to increase near 200 K. A way of the appearance was somewhat awkward: the

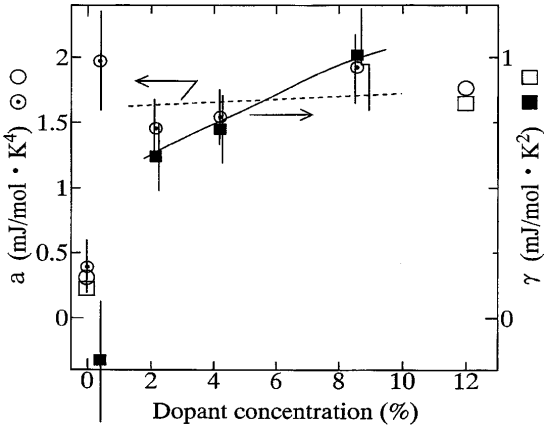

FIG. 5. Dopant concentration dependence of the coefficients of γ (represented with closed squares) and a values (open circles with center dot). Reported data by Moses *et al.* [11] are denoted by open marks.

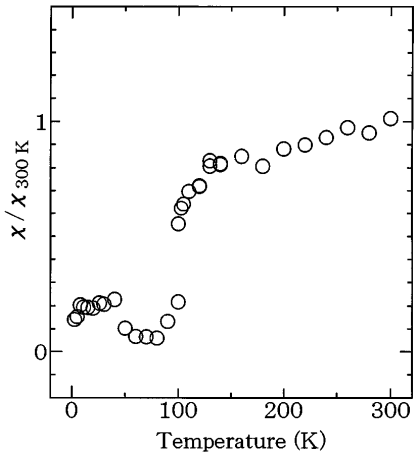

FIG. 6. Temperature dependence of the spin susceptibility χ normalized with that at 300 K for $(CH(ClO_4)_{0.073})_x$ prepared by doping to *cis*-$(CH)_x$.

transition to the spin-gap state occurred rather abruptly and the behavior varied from one case to another. This means that the transmuting process from *cis* to *trans* may affect the resultant structure. We are reminded of the structural property of undoped $(CH)_x$, which is reported to undergo a structural transition in the temperature region between 200 and 100 K, according to the dilatometric measurement [19]. This suggests that the involvement of structural change cannot be ruled out on formation of the soliton lattice in such a quasi-one-dimensional system, although it was claimed that the transition is genuinely electronic [13].

In doped $(CH)_x$, the structural inhomogeneity cannot be ruled out. Nevertheless, as is obvious through the temperature dependence of spin susceptibility, a simple inhomogeneity cannot explain the spin gap. It should be noted also that the ESR line shapes at higher temperatures than the transition temperature were well fitted with a single Lorentzian. Consequently, we recall a dilute phase in potassium-doped $(CH)_x$ with dopant concentrations of $\sim 2\%-5\%$, where the metallic portion exists in diluted fashion and carriers are quasimetallic [20]. In the present case, the dilute phase is likely formed above the transition temperature. On the other hand, the system is phase separated below the transition temperature as demonstrated by the decomposition of the ESR line shape, probably due to correlations between charged carriers [7]. Since the phase separation is considered to relate to structural nature, the occurrence is influenced not only by the intercalation process during doping but also by pristine structure of the film.

In order to explain the crossover in relation to the dopant concentration, Kivelson and Heeger [17] proposed a model of first-order transition to a metallic state with an increase in the dopant concentration, resulting in a strong-coupling polaronic metal in the heavily doped $(CH)_x$. Based upon an exact periodic solution of the continuum version of the Su-Schrieffer-Heeger model, however, Takahashi [18] concluded that the charged soliton lattice has the lowest formation energy and that the polaron band is not probable. Cruz and Phillips examined the role of the on-site, nearest neighbor, and bond-repulsion Coulomb interactions, but they found that it was difficult to stabilize the polaronic metal [21]. To explain the metallic conductance, a contribution of defects in the soliton lattice, called interstitial soliton and soliton hole, was proposed [22], but questions still remain.

It is noteworthy that the theoretical calculations have been developed based upon a single-chain model. In other words, the interaction between the adjacent chains has been neglected, although interchain interaction is unavoidable, particularly to treat a delicate situation. In the present case, the charged excitations, like solitons on the chain, can interact with dopants existing on the plural numbers of surrounding channels. The unavoidable disorder in the $(CH)_x$ also serves to make the potential field cause the dopant arrays to be incommensurate with each other. Consequently, the soliton lattice, when it is formed via the mutual interaction of charged solitons within a chain, cannot be pinned to the dopant array. Hence a collective charge array becomes mobile with a lower activation energy, as detected through the temperature dependence of the resistivity, as shown in Fig. 4. We should mention, however, that the disorder should be moderate, otherwise the solitons are pinned strongly or cannot be aligned to form the lattice.

The elementary excitation known as a charged soliton, which was found in the dilutely doped $(CH)_x$ in the early 1980s [1] has led studies of the non-Fermi liquid nature of low-dimensional conductors, including transition-metal oxides. By pursuing an investigation, which made use of refined sample synthesis, we have obtained clear-cut results demonstrating the emergence of a spin gap by varying temperature, which is found in current unconventional conductors, in the most historical material.

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