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Linear high-field magnetoconductivity of doped polyacetylene up to 30 Tesla

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We have studied the high-field (up to $H=30$ T) magnetoconductivity $(\Delta\sigma(H)/\sigma(0)=[\sigma(H)-\sigma(0)]/\sigma(0))$ of highly conducting polyacetylene films heavily doped with ClO_4^-, $FeCl_4^-$, and iodine at the temperature range 0.6–1.4 K. At relatively low fields, their field dependence is different from each other according to the specific properties of the dopant with which the spin state of conduction electrons are coupled. In the high-field region, however, the magnetoconductivity is linearly dependent on the magnetic field irrespective of the type of dopants. The change from the low field $\Delta\sigma(H)/\sigma(0)\propto H^{1/2}$ to the high field $\Delta\sigma(H)/\sigma(0)\propto H$ as well as the effect of dopants is attributed to the competition between the magnetic length L_H and the dopant-specific length scales, both of which are relevant to the delocalization under the magnetic field. The origin of linear dependence of magnetoconductivity at high fields is also discussed.

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I. INTRODUCTION

High room-temperature conductivity is one of the most interesting characteristics of doped high-density polyacetylene (PA).[1,2] From the magnetotransport of PA heavily doped with iodine, it was found that the localization due to the disorder plays an important role in the electrical transport of the bulk film.[3,4] For $FeCl_4^-$ doped PA films, not only the disordered metallic features including the low-energy vibrational excitation[5] but also the magnetic properties of dopant are considered in many ways.[6,7] And the effect of magnetic dopants on the charge transport was studied in comparison with that of nonmagnetic dopants.[8] The ClO_4^- doped films show relatively the higher room-temperature conductivity and the lower resistivity ratio $[\rho(T)/\rho(300\ \text{K})]$ at low temperatures than those doped with other dopants.[9]

In most of the previous reports, the magnetoconductivity (MC) data of highly conducting PA were discussed in terms of the weak localization theory,[3,4,10,11] where the competition between the localization $[\Delta\sigma_L(H,T)]$ and the electron-electron interaction $[\Delta\sigma_I(H,T)]$ makes the variety of changes in the field dependence $[\Delta\sigma(H,T)]$, i.e.,

$$\Delta\sigma(H,T)=\Delta\sigma_L(H,T)+\Delta\sigma_I(H,T). \tag{1}$$

Although this picture explains quite well a number of experimental results for the magnetotransport of the doped PA, the difference in $\Delta\sigma(H,T)$ of PA films doped with different dopants has not been fully taken into account. Moreover, the magnetic field had been limited to $H\leqslant 17$ T in all previous experiments, so that the characteristic behaviors of the MC under high magnetic fields have not been explored yet. In this paper, we report on the MC of PA films heavily doped with ClO_4^-, $FeCl_4^-$, and iodine, respectively, under high magnetic fields up to $H=30$ T. We have studied the role of dopants and the effect of high magnetic fields on the electrical transport by the direct comparison between the MC data of PA films doped with different dopants. The results indicate that the dominant conduction mechanism related to the delocalization of the weakly localized states is strongly dependent on the strength of magnetic fields and the type of dopants.

II. EXPERIMENTAL PROCEDURE

High-density PA films were prepared from stretch-oriented $(l/l_0=3)$ films synthesized following the modified Shirakawa method.[12] The ClO_4^- doping and the $FeCl_4^-$ doping were done up to the saturation level (7–9 mol. % for both cases). The iodine doping was done in the gas phase until the conductivity value starts to be saturated (10–12 mol. %). The conductivity was measured along the stretched direction using a standard dc four-probe method in the temperature range 0.6–300 K. The MC up to $H=30$ T below $T=1.4$ K was measured in the longitudinal configuration $(\mathbf{H}\|\mathbf{J})$ using the resistive magnet at the National High Magnetic Field Laboratory, Tallahassee, Florida. The temperature was fixed within $\Delta T=\pm 0.01$ K during field sweep by controlling the vapor pressure of ^{3}He gas.

III. RESULTS AND DISCUSSION

A. Metallic nature with the effect of localization

Figure 1 shows the MC of highly conducting PA films doped with (a) ClO_4^-, (b) $FeCl_4^-$, and (c) iodine measured

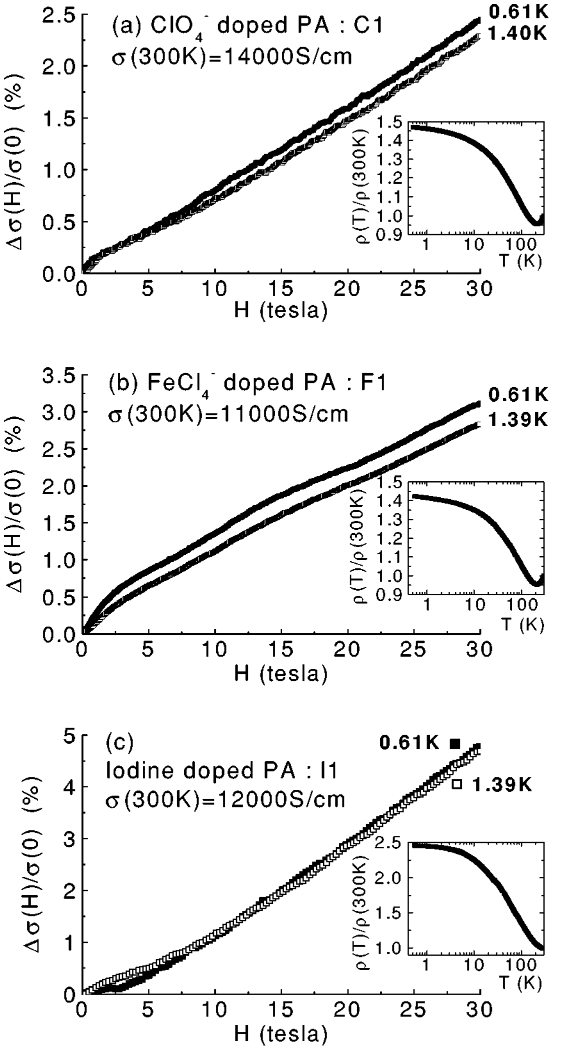

FIG. 1. Temperature dependence of normalized resistivity and magnetoconductivity up to $H=30$ T for (a) the ClO_4^- doped, (b) the $FeCl_4^-$ doped, and (c) the iodine doped polyacetylene films.

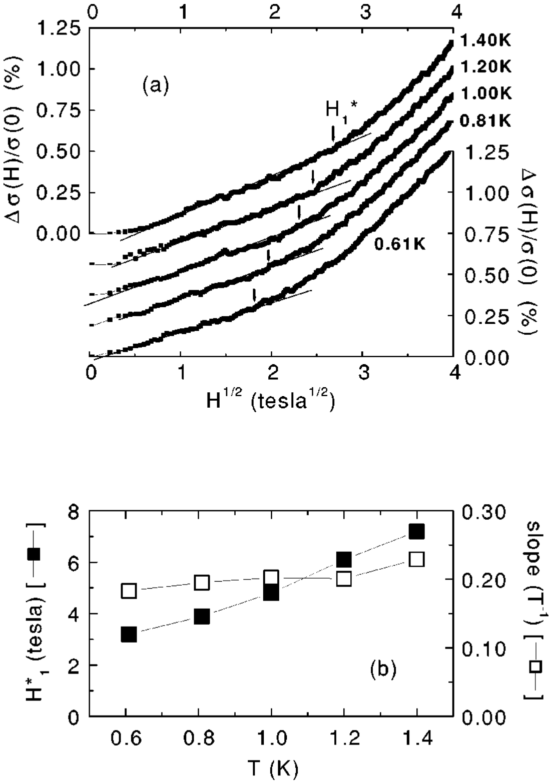

FIG. 2. (a) $\Delta\sigma(H)/\sigma(0)\propto H^{1/2}$ of ClO_4^- doped polyacetylene at different temperatures in the low-field region. H_1^* indicates the characteristic field at which $\Delta\sigma(H)/\sigma(0)$ starts to deviate from the $H^{1/2}$ dependence. (b) Temperature dependence of H_1^* and the slope of the linear part plotted in (a).

up to $H=30$ T. The temperature dependence of resistivity data without magnetic fields are plotted in the inset figures. There are resistivity minima around $T^*\simeq 215$ K for ClO_4^- and $FeCl_4^-$ doped films. At low temperatures the resistivity increases as temperature decreases [i.e., negative temperature coefficient of resistivity (TCR)], but the resistivity ratio $[\rho_r=\rho(0.5\ \mathrm{K})/\rho(300\ \mathrm{K})]$ in the low temperature region reaches only to $\simeq 1.4$–1.5 for the ClO_4^- doped and the $FeCl_4^-$ doped films, and $\simeq 2.4$ for the iodine doped one. The conductivity data could be well fitted to the heterogeneous model,[13] and the metallic nature of these samples are confirmed from this zero-field results as well as the room-temperature conductivity values.

By comparing samples doped with three different dopants, we can find out that the MC is positive and shows a linear behavior in the wide range of the magnetic field. The positive MC (i.e., negative magnetoresistance) and the negative TCR at low temperatures could be understood as the results of weak localization effects, in which the breaking of the time reversal symmetry under magnetic fields results in the breaking of the localized states. As shown in Eq. (1), the weak localization picture predicts the MC as a combination of the localization and the electron-electron interaction contributions. In general the former gives the positive MC, and the latter gives the negative one (when the Hartree term is larger than the exchange term).[11] Therefore the positive MC in Fig. 1 implies that the localization effect is more important in the magnetotransport of highly conducting polyaceytlene.

In the above discussion, it looks contradictory that the localization effects occur at such highly conducting films. From the heterogeneous model,[13] however, we can argue that the presence of highly conducting region inside a film increases the absolute magnitude of the conductivity, but still includes the weak localization term due to the poorly conducting part, which is called, the barrier.

B. $H^{1/2}$ dependence of MC at low fields

The MC at very low fields ($H\ll 1$ T) was discussed elsewhere.[14] Therefore, hereafter the field range denoted by "low fields" corresponds to approximately $H\simeq 1-8$ T throughout this paper, because the maximum field is $H=30$ T.

The MC of the ClO_4^- doped PA at different temperatures is plotted in Fig. 2. As in Fig. 2 (a), the MC at low fields shows the $H^{1/2}$ dependence up to $H=H_1^*$. Figure 2(b) shows the temperature dependence of the characteristic field H_1^*

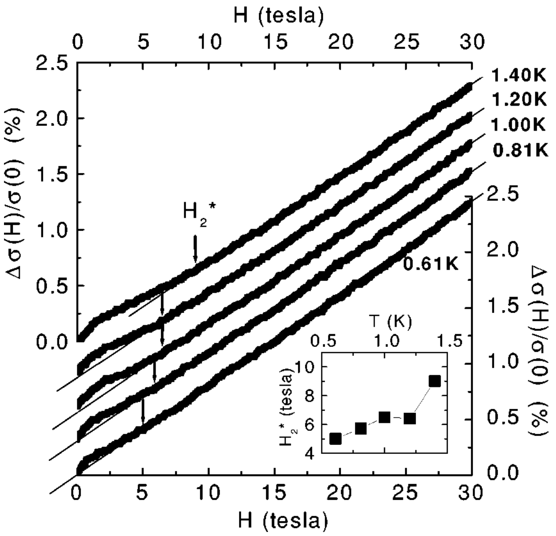

FIG. 3. $\Delta\sigma(H)/\sigma(0)\propto H$ of ClO_4^- doped polyacetylene at different temperatures in the high-field region. H_2^* indicates the field at which $\Delta\sigma(H)/\sigma(0)$ starts to show the linear behavior. The inset shows the temperature dependence of H_2^*.

and the slope of the linear part in (a). The results indicate that the $H^{1/2}$ dependence reaches up to the higher fields with small change of the slope as the temperature increases.

The $H^{1/2}$ dependence of the MC could be ascribed to the effect of localization, where $\Delta\sigma_L(H,T)$ in Eq. (1) for the three-dimensional system can be given as[11]

$$\Delta\sigma_{L,3\mathrm{D}}(H,T)\simeq 0.605\frac{e^2}{2\pi^2\hbar}\left(\frac{eH}{\hbar c}\right)^{1/2} \tag{2}$$

when

$$L_H \ll L_{\mathrm{in}}=(D\tau_{\mathrm{in}})^{1/2}. \tag{3}$$

Here L_H is the length scale within which charge carriers have the diffusive motion under magnetic fields and start to lose their phase coherence due to the magnetic flux, and L_{in} (τ_{in}) is the inelastic scattering length (time) within which the localized states become delocalized due to the phonon scattering. Because L_H is typically the same as the Landau orbit size $(eH/\hbar c)^{-1/2}$ and τ_{in} is proportional to T^{-p} where p is determined by the system dimensionality or the dominant dephasing mechanism,[11] Eq. (3) gives $H \gg \hbar c/eD\tau_{\mathrm{in}}$, which means the high magnetic field and low-temperature region. At fixed temperature, τ_{in} is also fixed and roughly 10^{-10} sec at $T\simeq 1$ K.[4,10,14] Because $L_H \propto H^{-1/2}$, L_{in} is less than L_H at extremely low fields (which usually results in the H^2 dependence of the MC). But it changes to $L_H < L_{\mathrm{in}}$ as the magnetic field increases, where the most relevant length scale for the breaking of the localized states is L_H.

C. Linear magnetoconductivity at high fields

The main interesting point of this report is the linear MC of heavily doped, highly conducting PA irrespective of the type of dopants in the high field region. Figure 3 for the ClO_4^- doped sample shows that the $H^{1/2}$ dependence of the MC reaches up to H_1^* and it changes to be linear $\Delta\sigma(H)/\sigma(0)\propto H$ at high fields. (Such a linear behavior were found in a few figures of some previous literatures,[3,15] but only for iodine doped films with $H < 17$ T.) The small arrow points out the starting field (H_2^*) of the linear behavior at each temperatures. It also increases with increasing temperature as H_1^* does. The tendency of the linear MC is almost the same for other dopants at high fields as in Fig. 1.

This result is completely different than the prediction of the three-dimensional weak localization picture in Eq. (2) at high fields. As shown in the previous section, the magnetic length L_H was considered as the dominant length scale from the $H^{1/2}$ dependence of the MC. When we estimate its magnitude, $L_H=(eH/\hbar c)^{-1/2}=25.66H^{-1/2}(\mathrm{nm})$. Therefore at the characteristic field such as H_1^* or H_2^*, the magnetic length L_H^* is around 8–15 nm. Because those characteristic fields are related to the change of the MC from $\Delta\sigma(H)/\sigma(0)\propto H^{1/2}$ to $\Delta\sigma(H)/\sigma(0)\propto H$, we could suppose the existence of another length scale which is comparable to L_H^*. Then the change of the MC could be ascribed to the change from $L_H > L_H^*$ to $L_H < L_H^*$ as the field increases. One possible suggestion is that the magnetic length scale at the characteristic fields is comparable to the diameter of fibrils of high density PA film.[12] The diffusive motion of charge carriers in the interfibrillar conduction could be modified in different ways as the magnetic length gets shorter than the diameter of fibrils.

This result could be directly compared with that of the previous report for helical polyacetylene.[16] The conductivity of iodine doped helical film is much smaller than that of the high-density one in Fig. 1(c), but the similar linear MC in the high-field region could be observed. The helical polyacetylene consists of well-defined fibers and those fibers are twisted to form the ropes. When we compare its structure with that of the stretch-oriented high-density film, the fibrillar structure is common to both types of polyacetylene because the high-density film was synthesized following the modified Shirakawa method.[12] Therefore, the linear MC of iodine doped helical polyacetylene supports the importance of the fibrillar structure in the transport under high magnetic fields.

Because the simple application of the weak localization theory to the experimental results fails as discussed above, the observed $\Delta\sigma(H)/\sigma(0)\propto H$ at high fields requires a more careful explanation in relation to the distinct morphology of polyacetylene system. There are a few works[17–19] dealing with the linear behavior, but all those approaches could not be applicable to the present doped PA case because each physical mechanism is restricted only to the case of variable range hopping conduction, the presence of the strong ferromagnetic interaction, and/or the antiferromagnetic spin fluctuation, respectively. Therefore another explanation for the linear dependence is necessary, and we suggest the starting point of view in understanding the present results by considering the characteristic length scale L_H^* and the weak localization picture on the assumption that L_H^* is comparable to the typical size of polymer fibrils. When the magnetic length L_H is much larger than that of the dimensions of polymer fibrils (i.e., $H<H^*$), lots of interfibrillar contact points are included within every area with the size of L_H. This could be considered as the homogeneously disordered system, and the three-dimensional weak localization picture is applicable. In the high-field region (i.e., $H>H^*$), however, L_H decreases and it becomes smaller than the average distance between contact points of polymer fibers. Therefore some areas with the size of L_H may include one or a few interfibrillar junctions, but others may not. On the basis of the above discussion, the diffusion coefficient of the system could be spatially dependent and the diffusive motions of charge carriers through those interfibrillar junctions could possibly explain the linear MC at high fields.[20] The detailed theoretical model is under investigation.

D. Dopant specific scattering processes at low fields

In order to discuss the dopant effect to the MC in detail, we plot the low field data of all samples with different dopants at various temperatures in Fig. 4. The magnitude of the MC for the ClO_4^- doped film does not change significantly as the temperature changes from 0.6 to 1.4 K as in Fig. 4(a). But it shows the temperature dependence for other dopants. For the $FeCl_4^-$ doped film in Fig. 4(b), the MC at $T = 0.61$ K is the largest one and the magnitude decreases as the temperature increases. On the contrary, the iodine doped film shows the smallest MC at $T = 0.61$ K and the magnitude increases with increasing temperature in Fig. 4 (c), which is just the opposite to the case of the $FeCl_4^-$ doped PA.

Because such a difference in the MC is associated with the different type of dopants, it is so natural that we should think over the physical properties of the dopant itself to explain the dopant dependence in Fig. 4. In Ref. 8, the dopant $FeCl_4^-$ was compared with the dopant ClO_4^- because the structure of those two dopants is identical but the former has the magnetic moment.[7] In such a case, the spin state of a charge carrier is coupled with the localized magnetic moment of a nearby dopant, which could be expressed as an additional term in the Hamiltonian by $J\vec{\sigma}\cdot\vec{S}$ where J is the coupling constant and $\vec{\sigma}(\vec{S})$ indicates the spin state of the charge carrier (the magnetic dopant). This spin-flip Hamiltonian gives delocalization of weakly localized states due to the destruction of time-reversal symmetry.[11] Because the average distance between dopants is less than 1 nm, the length scale L_s, which corresponds to the magnetic scattering described above, could be dominant compared with L_{in} and/or L_H. Under magnetic fields, the suppression of the spin-flip scattering reduces the resistance, which results in the positive MC, but its effect gets weakened as the temperature increases as shown in Fig. 4(b).

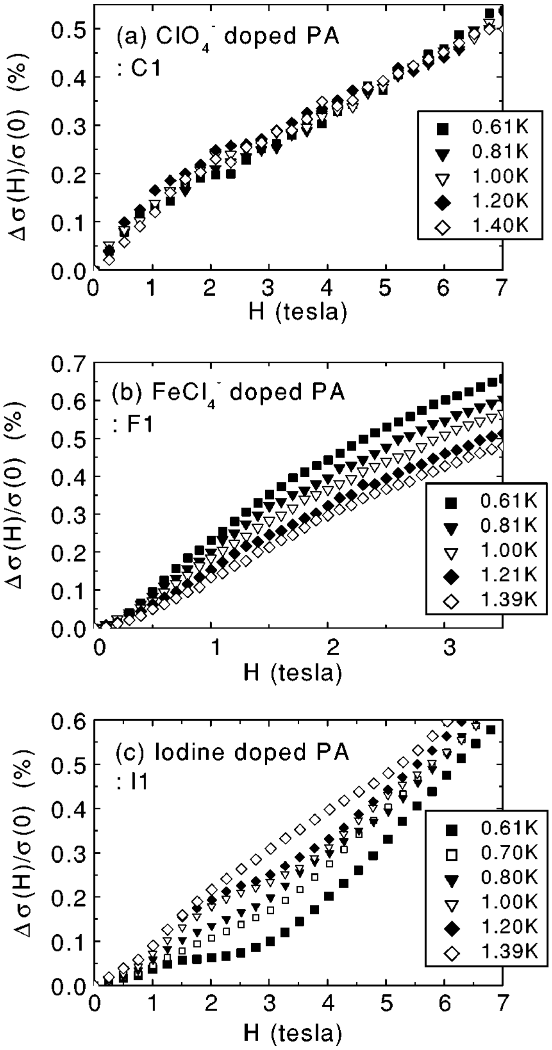

FIG. 4. Dopant dependence of the magnetoconductivity at different temperatures. Note that, as temperature increases, the magnitude of the $FeCl_4^-$ doped PA in (b) decreases but that of the iodine doped PA in (c) increases.

For the iodine doped PA, there are lots of reports for the magnetotransport and the data are discussed thoroughly in terms of the weak localization theory considering anisotropic properties of the system[3] and the importance of the electron-electron interaction.[4] Those reports were quite successful in explaining the obtained results of the iodine doped PA, but they are insufficient to explain the dopant dependence because the proposed explanations could be applicable to all the heavily doped, highly conducting PA irrespective of the type of dopants. When we examine the characteristics of the iodine dopant in comparison with other dopants, we notice that the atomic number of iodine is much bigger than that of any other dopant such as the ClO_4^- ion. Such a heavier element could make a stronger electric field around itself, and it consequently induces not only the potential scattering by the Coulomb interaction but also the spin-orbit scattering by the coupling between the spin state of a charge carrier and its motion under the potential field of an adjacent dopant.[21] Because the magnetic field has an effect on the spin state of a charge carrier, the influence of the weak spin-orbit scattering could be the possible origin of the specific field dependence of iodine doped films in Fig. 4(c). It has already been mentioned that the spin-orbit scattering produces a negative MC.[11,21] Therefore the combination of the positive component of the MC due to the localization effect [which is almost the same without temperature dependence as in Fig. 4(a)] and the negative one due to the moderate strength of the spin-orbit scattering (which decreases as temperature increases) could result in the reduction of the total magnitude of the positive MC at low temperatures.

IV. SUMMARY

We have examined the MC under high magnetic fields up to $H=30$ T for highly conducting PA films doped with different dopants ClO_4^-, FeCl_4^-, and iodine. At relatively low fields, the different temperature and field dependence of the MC for different dopants are discussed on the basis of the weak localization effects with possible influence of the weak spin-orbit and the spin-spin scatterings according to the specific properties of dopants. In the high-field region, the linear MC is observed irrespective of the type of dopants and this change from $\Delta\sigma(H)/\sigma(0)\propto H^{1/2}$ to $\Delta\sigma(H)/\sigma(0)\propto H$ is related to the decrease of the magnetic length (L_H) with increasing magnetic field. The possible physical origin of the linear MC is suggested in connection with the small L_H at high fields and the importance of interfibrillar junctions.

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