Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Semiconductor-Metal Transition of $[Ch(Fec14)_y]_x$; a Magnetic Impurity Doped Polyacetylene

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Version of record first published: 17 Oct 2011.

To cite this article: Y. W. Park , S. I. Lee , W. Rang & H. Shirakawa (1985): Semiconductor-Metal Transition of $[Ch(Fec14)_y]_x$; a Magnetic Impurity Doped Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 167-171

To link to this article: http://dx.doi.org/10.1080/00268948508074617

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 167-171
0026-8941/85/1174-0167/$10.00/0

Printed in the United States of America

SEMICONDUCTOR-METAL TRANSITION OF $[CH(FeCl_4)_y]_x$; A MAGNETIC IMPURITY DOPED POLYACETYLENE

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Abstract Results of electrical conductivity and thermopower measurement on $[CH(FeCl_4)_y]_x$ are presented, where y covers the full doping range. The semiconductor-metal transition is evident and leads to a qualitative change in temperature dependence of the conductivity and thermopower. The analysis of the metallic thermopower data indicates the Kondo-like effect originated from the coupling between the $(CH)_x$ chain and the dopant located near the chain. As a consistent interpretation of our data, we propose a mechanism of the semiconductor-metal transition in doped $(CH)_x$; the one dimensional intersoliton electron tunneling model.

INTRODUCTION

Many studies on the nonmagnetic impurity doped polyacetylene derivatives have been done and the semiconductor-metal transition was observed in all of these polyacetylene derivatives.[1] In this paper, we have studied the semiconductor-metal transition of a magnetic impurity doped polyacetylene; $[CH(FeCl_4)_y]_x$.

EXPERIMENTAL

Doping was done by immersing the $(CH)_x$ film into a solution of the $FeCl_3$ in nitromethane.[2] Mössbauer spectroscopy, EXAFS and ESR studies identify that the chemical composition of the dopant in $(CH)_x$ is $(FeCl_4)^-$.

Samples for thermopower measurements were cooled from room

temperature to 10 K using a Displex system. Techniques for thermopower and conductivity measurements were the same as were described in detail in an earlier publication.[1]

RESULTS AND DISCUSSIONS

We have studied the temperature dependence of conductivity and thermopower of $[CH(FeCl_4)_y]_x$ for y = 0.0025, 0.0086, 0.0217 and 0.0286. The results are similar to those of the nonmagnetic impurity doped $(CH)_x$.[1] The semiconductor-metal transition starts at y ~ 0.001. In the metallic region, however, the data tend to approach to two straight lines matching smoothly around 50 K as shown in Figure 1. In our early study on the heavily doped $(CH)_x$[3],

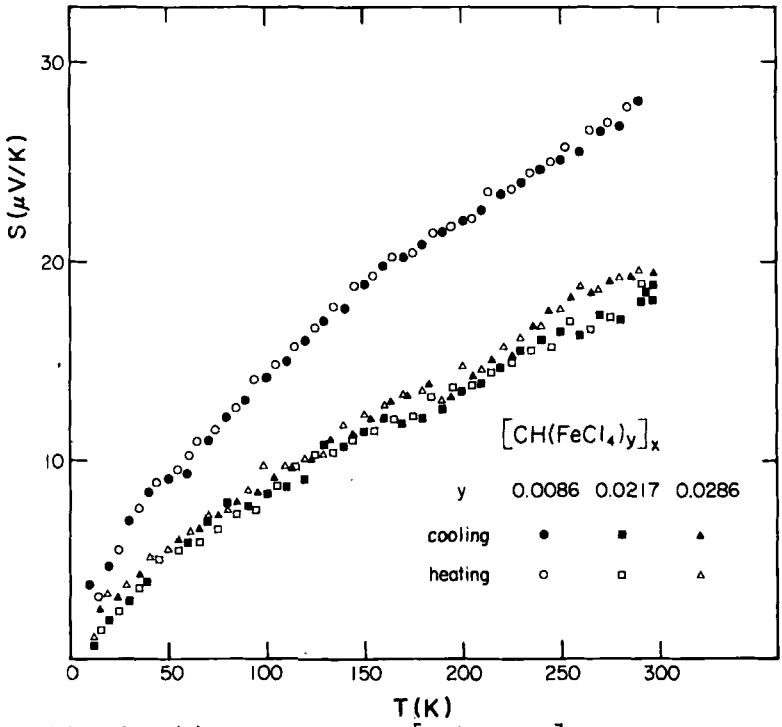

FIGURE 1 S(T) vs. T of Trans-$[CH(FeCl_4)_y]_x$ in linear scale

we found that the $[CH(FeCl_4)_y]_x$ data in the heavily doped limit follow the formula

$$S(T) = AT + \frac{BT}{T + To} \qquad (1)$$

where the second term, $\frac{BT}{T + To}$, is the interpolation formula which Kondo had formulated from the S-d Hamiltonian.[4] The observed data for y = 0.0217 and 0.0286 samples are close to that fitting curve, Eq. (1). This Kondo-like behavior in $[CH(FeCl4)_y]_x$ indicates that there exist a coupling between the localized spin in Fe^{3+} and the charge carriers in the chain. The existence of the coupling with the localized spin suggests that the charge carriers in the chain have spin 1/2. Furthermore, from the analysis of the very broad peak observed in ESR measurement on these samples, we find that for y = 0.0025 sample, the magnetic susceptibility follows Curie law, but for $y \geq 0.0086$ samples, Curie-Weiss type susceptibility are observed with $\theta \simeq + 50$ K. This Curie-Weiss type $\chi(T)$ could also indicate that there exists a coupling between charge carriers in the chain and the localized electrons in $(FeCl4)^-$ dopant located near the chain. And it suggests that the charge carrier in the chain has spin 1/2.

The consistent interpretation we propose is that the doping induced charged solitons are pinned and electrons (or holes) are tunneling between these pinned solitons. The electron injected to the defect free (i.e., perfectly dimerized) portion of the $(CH)_x$ chain from one soliton site may have formed a polaron state (as Su and Schrieffer suggested)[5] until it tunnels to the nearest neighbor soliton sites. However, these tunneling charge carriers are not band type carriers, so that they do not contribute to the Pauli susceptibility even though they carry spin 1/2 to couple with electrons in the $(FeCl_4)^-$ dopant.

The semiquantitative analysis of the above proposal can be given from the extension of the Kivelson's intersoliton electron hopping conduction model[6] in the lightly doped polyacetylene. The

one dimensional intersoliton distance would be $R_1 = (b^2 C_{imp})^{-1}$ where b is the interchain distance and C_{imp} is the impurity concentration. For y = 0.001, $C_{imp} = 8 \times 10^{18}$ and $R_1 = 7800$ Å which is much larger than the three dimensional intersoliton distance. Thus, the three dimensional intersoliton electron hopping mechanism is dominant at this concentration regime. For y = 0.001, $C_{imp} = 8 \times 10^{18}$, $R_1 = 780$ Å and for y = 0.008, $C_{imp} = 6 \times 10^{20}$ and $R_1 = 100$ Å. At this level, the significant one dimensional intersoliton electron tunneling can occur because the charged soliton wave function is spread to about 10 carbon atoms (~ 15 Å) and the mobile neutral soliton's diffusion length is about 35 carbon atoms (~ 50 Å). Finally, for y = 0.05, $C_{imp} = 4 \times 10^{21}$ and $R_1 = 15$ Å and at this intersoliton distance, the soliton wave functions overlap completely. Therefore, the chain becomes a uniform bond length chain equivalent to the single particle band picture.[7]

ACKNOWLEDGMENT

This work was supported by the Korean Science and Engineering Foundation (KOSEF), Korea and by a Grant-in-Aid for Scientific Research No. 56470083 from the Ministry of Education, Science and Culture, Japan.

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