

A MÖSSBAUER SPECTROSCOPIC STUDY FeCl_3 -DOPED POLYACETYLENE

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Mössbauer spectra of FeCl_3 -doped polyacetylenes $[\text{CH}(\text{FeCl}_3)_y]_x$ ($y=0.010, 0.057$) have been measured at temperatures of 300, 243, 208, 143, 108 and 80K, respectively. For the sample for $y=0.010$, only two doublets were observed at Room Temperature (RT) and a third doublet appeared when temperature decreased to 208K. However the RT spectrum of sample $y=0.057$ consisted of three quadruple-split doublets. The relative intensities of these three doublets, especially for the light doped sample, corresponding to charge transfer, changed with temperature.

1. INTRODUCTION

The electrical conductivity will increase more than several magnitude orders by doping with electron acceptor molecules, such as AsF_5 , Br_2 and I_2 , or electron donors such as Na and K in polyacetylene/1/. Currently much interest is focused on doping different type of donor or acceptor impurities to make p-n junction or heavy doping to make conductors. One of the unresolved problems is the stability of the electrical performance of doped-polyacetylene. Therefore it seems that much work remains to be done to fully understand the fundamental conducting mechanism. After Pron/2/ reported that high electrical conductivity was exhibited on FeCl_3 -doped polyacetylene, immense work has been done in the field, such as studying the dopant structure, the doping mechanism and the electro-magnetic performance of the doped-polyacetylene. But some results reported by various authors are controversial.

We here report the dependence of the dopant state on temperature in FeCl_3 -doped polyacetylene studied by Mössbauer spectroscopy. The dopant concentration is 1.0at% and 5.7at%. The experimental results indicate that the dopant state in the FeCl_3 -doped polyacetylene at room temperature depends on dopant concentration. The FeCl_4^{-2} is formed in addition to FeCl_4^{-1} and $\text{FeCl}_4^{-\Delta}$ ($1 < \Delta < 2$) for heavy doping while for light doping only FeCl_4^{-1} and $\text{FeCl}_4^{-\Delta}$ were formed. The transformation among these complexes was observed when temperature changed from RT to 208K.

2. EXPERIMENTAL

cis-Polyacetylene films were synthesized using the methods of

R-(CH) $_x$ /3/ and Naarmann/4/, respectively. $FeCl_3$ -doping was carried out by immersing the *cis*-(CH) $_x$ film in a saturated $FeCl_3$ solution in dry nitromethane. The film was then vacuum-dried and was kept in a container filled with nitrogen. Mössbauer measurements were performed on both the sample 1# [CH($FeCl_4$) $_{0.010}$] $_x$ and sample 2# [CH($FeCl_4$) $_{0.057}$] $_x$ at temperatures of 300K, 243K, 208K, 143K, 108K and 80K, respectively. The spectra were analyzed by the least square fitting and the values of isomer shift were given relative to that of α -Fe.

3. EXPERIMENTAL RESULTS

The Mössbauer spectra of both samples at temperatures from RT to 80K are shown in fig.1 and fig.2. In this temperature range, the spectra consist of three quadruple-split doublets ((A),(B) and (C)), as indicated in the figures. The Mössbauer parameters for [CH($FeCl_4$) $_{0.010}$] $_x$ and [CH($FeCl_4$) $_{0.057}$] $_x$ are summarized in Table 1 and 2, respectively. The error of these data is less than 0.02 mm/s. For the sample 1#, the intensity of subspectrum A decreased dramatically and the intensity of subspectrum B decreased from 56% to 35% with the decrease of temperature from RT to 208K. The subspectrum C, which did not appear at room temperature, amounted to approximately 50% at 208K. The further temperature decrease from 208K to 80K did not significantly induce changes in the relative intensities of three sub-spectra in the sample 1#. On the other hand, in the sample 2#, the intensity of subspectrum C was already 60% at RT and changed only slightly with the decrease of temperature. Obviously there are big differences between the sample 1# and 2#, based on Mössbauer spectra.

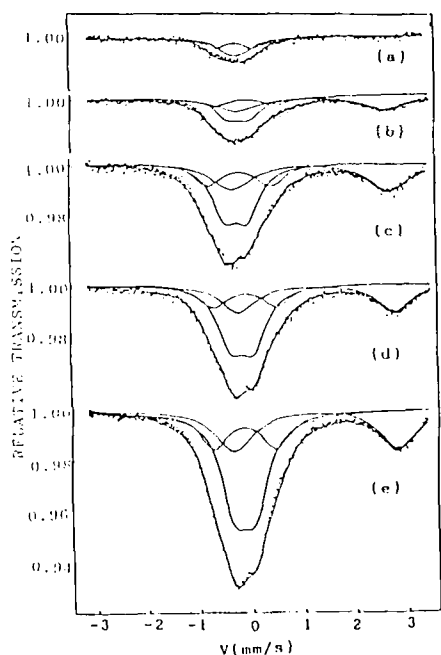
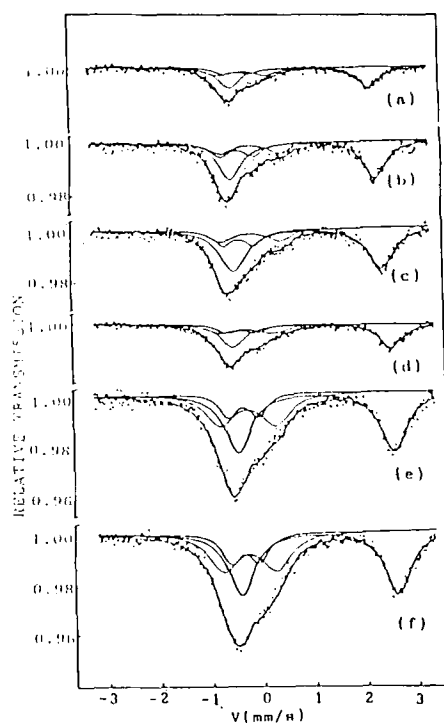
Table 1
Mössbauer parameters of [CH($FeCl_4$) $_{0.010}$] $_x$ at various temperatures.

Temp. (K)	Component A			Component B			Component C		
	IS mm/s	QS mm/s	Inten. %	IS mm/s	QS mm/s	Inten. %	IS mm/s	QS mm/s	Inten. %
300	0.21	0.61	44.2	0.23	0.22	55.8	-	-	-
208	0.32	1.01	17.6	0.23	0.35	34.9	1.38	2.42	47.5
143	0.29	1.02	21.9	0.24	0.36	41.3	1.42	2.52	36.7
108	0.30	1.03	20.7	0.25	0.38	46.6	1.46	2.53	32.6
80	0.29	1.00	20.9	0.28	0.34	45.6	1.44	2.66	33.5
108	0.31	1.13	17.7	0.27	0.38	50.7	1.48	2.57	31.6
143	0.30	1.10	16.6	0.25	0.38	49.4	1.47	2.53	34.0
208	0.21	0.85	16.2	0.26	0.34	43.1	1.27	2.48	40.7
243	0.26	0.85	18.2	0.23	0.32	45.6	1.22	2.48	36.2
300	0.23	0.81	18.5	0.24	0.31	53.9	1.16	2.51	27.6

Table 2

Mössbauer parameters of $[\text{CH}(\text{FeCl}_4)_{0.057}]_x$ at various temperatures.

Temp. (K)	Component A			Component B			Component C		
	IS mm/s	QS mm/s	Inten. %	IS mm/s	QS mm/s	Inten. %	IS mm/s	QS mm/s	Inten. %
300	0.28	0.74	24.8	0.19	0.40	14.6	1.20	2.28	60.5
243	0.37	0.95	18.0	0.16	0.54	18.8	1.23	2.38	63.1
208	0.34	0.96	17.3	0.15	0.51	17.1	1.27	2.42	65.6
143	0.23	0.83	26.1	0.16	0.46	17.3	1.30	2.58	56.5
108	0.25	0.91	31.6	0.17	0.48	13.6	1.35	2.55	54.8
80	0.23	0.43	32.5	0.16	0.46	16.6	1.37	2.57	50.9

Fig. 1 Mössbauer spectra of $[\text{CH}(\text{FeCl}_4)_{0.010}]_x$ at temperature of (a) 300K (b) 208K (c) 143K (d) 108K (e) 80K.Fig. 2 Mössbauer spectra of $[\text{CH}(\text{FeCl}_4)_{0.057}]_x$ at temperature of (a) 300K (b) 243K (c) 208K (d) 143K (e) 108K (f) 80K.

4. DISCUSSION

According to the values of the isomer shift (IS) and quadruple splitting (QS) listed in Table 1 and 2, the component B is the high spin state of Fe(III) which most possibly exists as tetrahedral FeCl_4^- .

The component C is high spin state of Fe(II). Based on the RBS analysis, which showed that the ratio of the amounts of Fe and Cl atoms was near 1:4, and the fact that the component C can be

transformed from the component B, the component C can be considered as tetrahedral FeCl_4^{2-} . The QS of subspectrum A is larger than that of the high spin state of Fe(III) but smaller than that of the low spin state of Fe(II) . We considered the component A as $\text{FeCl}_4^{\Delta-}$ ($1 < \Delta < 2$), or FeCl_4^- with a different geometrical surrounding from the component A.

As is well known, light doping can charge the already existing neutral solitons in the polyacetylene, whereas heavy doping breaks double bonds and creates new solitons. For polyacetylene, 5at% of dopant concentration is the transition point/5/. Therefore for heavy doping the dopant can catch more electrons from the C-chain than for light doping, because of this more FeCl_4^{2-} was formed in sample 2# than in sample 1#. But it is difficult to understand why the charge transfer took place with decreasing temperature in the light doping case. Probably the slight distortion of the polyacetylene crystals could induce some π bonds breaking down, and this process is partly reversible with the temperature reversing.

5. CONCLUSIONS

The temperature dependence of dopant state in various concentration in FeCl_3 -doped polyacetylene has been extensively studied using Mössbauer spectroscopy. In the sample where the dopant concentration was much smaller than 6at%, only FeCl_4^- and $\text{FeCl}_4^{\Delta-}$ ($1 < \Delta < 2$) were observed at RT. The FeCl_4^{2-} appeared at RT in the sample where the dopant concentration was near 6at%. The three components transformed from one to another when temperature changed from RT to 208K for light doping.

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