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TEMPERATURE DEPENDENCE OF NMR $T_1$ AND $\chi$ IN $\text{Br}_3$, $\text{AsF}_6$-DOPED (CH)$_x$


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Résumé - Nous avons mesuré la dépendance en température du temps de relaxation $T_1$ de RMN des protons et de la susceptibilité paramagnétique de Pauli $\chi_p$ dans le polyacétylène (CH)$_x$ dopé avec Br$_3$ et AsF$_6$. Une évaluation de la conductibilité microscopique $\sigma_{\text{NMR}}$ est obtenue à partir de ces résultats et comparée à la conductibilité à courant continu $\sigma_{\text{DC}}$.

Abstract - We have measured the temperature dependence of proton NMR $T_1$ and Pauli paramagnetic susceptibility $\chi_p$ in Br$_3$- and AsF$_6$-doped (CH)$_x$. The microscopic conductivity $\sigma_{\text{NMR}}$ has been calculated from them, and compared with $\sigma_{\text{DC}}$.

It is well known that polyacetylene (CH)$_x$ becomes metallic when doped with acceptor or donor molecules. In this work we have measured the temperature dependence of both proton NMR relaxation time $T_1$ and paramagnetic susceptibility of AsF$_6$- and Br$_3$-doped trans-(CH)$_x$. From the $T$-proportional metallic part of relaxation rates $T_1^{-1}$ and the $T$-independent Pauli part $\chi_p$ of magnetic susceptibility, we have calculated the diffusion constant $D_u$ and the microscopic conductivity $\sigma_{\text{NMR}}$ of metallic electrons along (CH)$_x$ chains.

The formula used to obtain $D_u$ and $\sigma_{\text{NMR}}$ were the same as used by Nechtschein et al in the room temperature proton NMR work on AsF$_6$-doped (CH)$_x$ /1/. In the metallic state the proton NMR relaxation rate $T_1^{-1}$ is connected with the Pauli susceptibility $\chi_p$ through following equation.

$$T_1^{-1} = k_B T \chi_p \left[ -\frac{3}{5} d^2 f(\omega_n) + \left( a^2 + \frac{7}{5} d^2 \right) f(\omega_e) \right],$$

$$f(\omega) = \left( 2 D_u \omega \right)^{-1/2}.$$ (1)

As the isotropic part of hyperfine field $|a/\gamma_E|$ is known as 23.4 Gauss /2/, and the ratio of dipolar part $d$ to isotropic one has been determined as $d^2/a^2 \approx 0.25$ /1,3/ by the Overhauser experiment, we can obtain the diffusion constant $D_u$ from eq. (1). Using this $D_u$, the mean free path $\xi$ and the microscopic conductivity $\sigma_{\text{NMR}}$ are derived through following two equations /4,5/,

$$\xi = 2 \pi \frac{\chi_p D_u c_u}{\Sigma},$$

$$\sigma_{\text{NMR}} = 2 e^2 \xi / (\pi \hbar \Sigma),$$ (2)

where $c_u$ and $\Sigma$ are the lattice constant and the cross-sectional area of a (CH)$_x$ chain, respectively. In following sections the obtained $\sigma_{\text{NMR}}$ will be compared with $\sigma_{\text{DC}}$ which is measured with the usual four-terminal method on the same sample.
I - AsF₆-DOPED (CH)ₓ

Figure 1 shows the experimental result on temperature dependence of proton NMR relaxation rate $T_1^{-1}$ in AsF₆-doped trans-(CH)ₓ. The result is interpreted as a superposition of two contributions. The first is a $T$-proportional one due to metallic origin. This contribution becomes dominant at temperatures above 200 K. The second is a hump of Bloembergen type below 200 K. That is considered to be due to the modulation of proton magnetic dipolar interaction, which is caused by the molecular motion of (CH)x chains. The peak position was found to shift towards the low temperature side, as lowering the NMR Larmor frequency down to 5.0 MHz.

The proton magnetization decay curve from which the above $T_1$ of metallic state was determined, was single-exponential except a small initial drop. In samples of semiconducting state of dopant concentrations below AsF₆/C ≈ 0.03, the decay curve was non-single-exponential. This means that the low concentration samples are inhomogeneous. The degree of deviation from single-exponential was heavier in cis-started sample than in trans-started one. Because of those non-single-exponential decay curves the $T_1$ result for low concentration samples is not shown in Fig. 1.

The spin paramagnetic susceptibility was measured with the Schumacher-Slichter ESR method /6/ on the same sample as NMR. The $T$-independent Pauli part $\chi_p$ was obtained from a temperature dependence experiment. The result is shown in Fig. 2 as a function of dopant AsF₆ concentration, which was determined by a $^{19}$F NMR experiment. The measured $\chi_p$ was found to change in order of $(T_1 T)^{-1}$, as naturally expected. The $\chi_p$ obtained in this experiment was similar to those reported earlier /7,8/.

The microscopic conductivity $\sigma_{\text{NMR}}$ was calculated through eqs. (1), (2) and (3) and listed in Table I. In this Table it is also shown $\sigma_{\text{DC}}$ measured with the usual four-terminal method. The reason why $\sigma_{\text{NMR}}$ is substantially larger than $\sigma_{\text{DC}}$, will be due to the fact that the latter is limited by the inter-fibril hopping rate.

II - Br₃-DOPED (CH)ₓ

Figure 3 shows the temperature dependence of proton NMR relaxation rate $T_1^{-1}$ in Br₃-doped trans-(CH)ₓ. The feature of this result is that the hump of Bloembergen type is absent. That is in contrast to other cases such as AsF₆-doped, I₃-doped /9/ or pristine /9/ trans-(CH)ₓ. Because the hump is absent in our Br₃-doped case, the metallic $T_1 T = \text{const}$-behaviour is seen over the entire temperature range between 4.2 K
Fig. 3 - Proton NMR relaxation rate $T_1^{-1}$ in Br$_3$-doped trans-(CH)$_x$ vs temperature $T$. Br$_3$/C: 0.73%.

and 300 K. The finite $T_1^{-1}$ at $T=0$ will be due to fixed paramagnetic impurities. A similar experimental result on a different Br$_3$-doped sample was already reported in our previous paper /10/.

To obtain the Pauli paramagnetic susceptibility $\chi_p$, we first applied the Schumacher-Slichter ESR method. However, the obtained value was as small as $\sim 1 \times 10^{-8}$ emu/mole-carbon. The $\sigma_{\text{NMR}}$ which was calculated from this value was much smaller than $\sigma_{\text{DC}}$.

Next, we applied the method of static Faraday balance. Five samples were prepared, of which concentrations were determined by weight uptake. To prevent the outgoing of dopant Br, the samples were packed in thin polyethylene bags. By separating the inverse-T Curie part from experimental data of temperature dependence, the T-independent part was determined. When the T-independent part was plotted against the concentration, we found a rather abrupt increase in it between the two samples of Br$_3$/C=0.022 and 0.030, besides the steady decrease proportional to the dopant concentration, which was ascribed to diamagnetism of dopants. Between the two samples we noticed a change of colour in dull surface of (CH)$_x$ film. We identified the change as a transition to metallic state. The increase in the susceptibility when the transition is crossed will naturally be ascribed to the appearance of Pauli paramagnetic susceptibility. In Fig. 4 thus obtained $\chi_p$ was plotted. For the sample of Br$_3$/C=0.073, on which NMR $T_1$ was measured, the $\chi_p$ was $4 \times 10^{-6}$ emu/mole-carbon.

The calculated $\sigma_{\text{NMR}}$ using this $\chi_p$ is shown in Table I. It is remarkable that $\sigma_{\text{NMR}}$ is similar in both Br$_3$- and AsF$_6$-doped cases. The $\sigma_{\text{NMR}}$ is substantially larger than $\sigma_{\text{DC}}$ also in this Br$_3$-doped case. The cause will be attributed to inter-fibril hopping rate.

<table>
<thead>
<tr>
<th></th>
<th>AsF$_6$ 4.0 %</th>
<th>AsF$_6$ 5.2 %</th>
<th>AsF$_6$ 7.7 %</th>
<th>Br$_3$ 7.3 %</th>
<th>$\Omega^{-1}\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{NMR}}$</td>
<td>$8 \times 10^{-3}$</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-4}$</td>
<td>$4 \times 10^{-3}$</td>
<td>$\Omega^{-1}\text{cm}^{-1}$</td>
</tr>
<tr>
<td>$\sigma_{\text{DC}}$</td>
<td>$6 \times 10^{-1}$</td>
<td>$4 \times 10^{-2}$</td>
<td>$6 \times 10^{-2}$</td>
<td>$1 \times 10^{-1}$</td>
<td>$\Omega^{-1}\text{cm}^{-1}$</td>
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For the case of I₃-doped (CH)x, Epstein et al has obtained $\chi_p \sim 3 \times 10^{-6}$ emu/mole-carbon with the method of Faraday balance /11/. With the ESR method no detectable $\chi_p$ has been observed /12/. This difference is similar to our Br₃-doped case. The dopant concentration where the transition to metallic state occurs is also similar in the Br₃- and I₃-doped /11/ cases. In the I₃-doped case $\sigma_{NMR}$ can also be calculated with the proton NMR $T_1$ reported by Masin et al /9/. The result is $\sigma_{NMR} \sim 2 \times 10^{3}$ $\Omega^{-1} \text{cm}^{-1}$. This is larger than $\sigma_{DC} \sim 3 \times 10^{13}$.

III - CONCLUDING REMARKS

In this paper we were mainly concerned with $\sigma_{NMR}$ in the metallic state which was calculated from the proton NMR $T_1$ and the Pauli paramagnetic susceptibility $\chi_p$. The obtained $\sigma_{NMR}$ was larger than $\sigma_{DC}$ measured with the usual four-terminal method. The difference was attributed to the fact that the $\sigma_{DC}$ is limited by the interfibril hopping rate.

However, the present experiment has afforded other new remarkable facts to be explained in the future. One of them is that in the Br₃-doped case the $\chi_p$ measured with the resonance method of ESR was smaller than that with the static Faraday method by more than two orders of magnitude. This difference will be explained by the presence of some broad component in ESR spectra. Similar anomaly has also been reported in the I₃-doped case. The other is that the hump of Bloembergen type in the temperature dependence of proton NMR $T_1$ is not observed in the Br₃-doped case. This will be attributed to the difference in doped structure. To solve the above questions further studies will be required.

REFERENCES