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Abstract. — The high frequencies properties of (CH)₂ are fundamental in magnetism. Applications of (CH)₂ in junctions or electrode materials require the knowledge of the low frequencies properties. The depolarization thermocurrents allow the ultra low frequency range to be attained and the correspondence between depolarization thermocurrents and frequency dependence of conductivity in Durham (CH)₂ has been studied. The nature and distribution of the traps are well-defined in surface and bulk ; the nature and distribution of the traps in the bulk are shown to be the same in Durham and in trans Shirakawa samples, the only difference being a higher traps density in Durham : consequently the effect of chain ends is pointed out.

1. Introduction.

The two most important methods of synthesis of polyacetylene presented in literature are the synthesis with Shirakawa catalyst [1] (« S » samples) from gaseous acetylene, and the synthesis by the Durham method [2] (« D » samples).

The conduction properties of « S » cis or trans samples have been the subject of numerous works [3-10]. However, most of the experimental measurements were made in a relatively narrow frequency range, and very scarcely by several joined methods. The conductivity mechanisms are not very clear as several parameters are involved such as : the isomerization process, the inhomogeneities, the degree of crystallinity, the surface nature, the chain orientation. A single model is inefficient to explain the conductivity in the whole frequency range.

In a former paper [11], we studied the dielectric properties of undoped cis and trans « S » samples, carefully synthetized with a low catalyst percentage. DC, AC in a large frequency range and thermodepolarization currents (TDC) measurements have been simultaneously done, and some important conclusions have been obtained from this complete set of data. It is the reason why, in the present work, the same methods were also used with unstretched « D » samples where some parameters are very different : chain lengths, impurities from catalyst, density.
2. Experimental results.

The samples were from the Max Planck Institute at Mainz and were prepared by Wegner and Weitzenhöfer. The films were 34 μm thick and electrode areas were about 20 to 25 mm². They were stored in vacuum before use. Gold or aluminium electrodes are deposited in a vacuum near 10⁻⁶ Torr.

The AC measurements (parallel equivalent conductance G and parallel equivalent capacity C) were made, in the range 10⁴ to 10 Hz with a General Radio bridge, and in the ultra low frequency range (1 Hz-10⁻⁴ Hz), by an apparatus previously described [12]. The series equivalent resistance Rₘ and the series equivalent capacity Cₘ were derived from G and C through the usual relations:

\[ Cₘ = C \frac{1}{\text{tg}^2 \delta} \]
\[ Rₘ = \frac{1}{G \left( \frac{\text{tg}^2 \delta}{1 + \text{tg}^2 \delta} \right)} \text{ and } \text{tg} \delta = \frac{G}{\omega C}. \]

The impedance diagrams (1/ω Cₘ versus Rₘ) were used to determine the different relaxations time distributions [11].

The TDC measurements were recorded with different heating rates (between 0.025 and 0.1 °C/s) and polarization voltages (between 1 and 10 V).

The AC or DC measurements give different results according to the electrode nature.

2.1 Au/(CH₃)₂Au CELLS.

2.1.1 DC measurements. — DC conductivity \( \sigma_{\text{DC}} \) is somewhat higher for low voltages (cf. Tab. I) than that observed on « S » samples. On the other hand, the behaviour is non ohmic, the curve Log I versus Log V has a slope lower than 2. The interpretation in terms of space charge limited current is then unlikely.

In a Log I versus V¹² plot, two linear parts of the I(V) characteristics are seen: with \( V < 6 \text{ V} \) and with \( V > 6 \text{ V} \) (Fig. 1).

Therefore, we can admit the occurrence of two Poole Frenkel [13] successive effects or a Schottky effect followed by a Poole Frenkel effect [14] when the voltage is increased: for low voltages, a superficial layer having a greater resistance than the bulk appears. Most of the voltage drops in this surface layer.

An approximate value of its thickness can be obtained from the expression of Schottky or Poole Frenkel effect:

\[ J = A \exp\left[ e(\beta E^{1/2} - V_0)kT \right] \]

where \( J \) is the current density, \( e \) the electron charge, \( E \) the applied electric field, \( V_0 \) the surface barrier height, \( k \) the Boltzmann constant, \( T \) the absolute temperature, \( A \) a constant and \( \beta \) a characteristic constant:

\[ \beta_s = 2 \times 10^{-5} \text{ (m. V)}^{1/2} \text{ or } \beta_{PF} = 4 \times 10^{-5} \text{ (m. V)}^{1/2} \]

for a Schottky (\( \beta_s \)) or Poole Frenkel (\( \beta_{PF} \)) effect.

Let \( L' \) be the surface layer thickness, \( L \) the sample thickness and \( V \) the applied voltage: \( E \equiv V/L' \) and if two voltages, \( V_1 \) and \( V_2 \) are successively applied to the sample
Table I.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>$\sigma$DC(RT) (Ohms.cm)$^{-1}$</td>
<td>Au/(CH)$_2$/Au $4 \times 10^{-9}$ (1 V applied)</td>
<td>Au/(CH)$_2$/Au $2 \times 10^{-8}$ (1.5 V applied)</td>
</tr>
<tr>
<td></td>
<td>Au/(CH)$_2$/Al $2 \times 10^{-9}$ (10 V applied)</td>
<td>10$^{-8}$ (10 V applied)</td>
</tr>
<tr>
<td>$\sigma$AC(RT) (Ohms.cm)$^{-1}$</td>
<td>$2 \times 10^{-7}$ (10$^4$ Hz)</td>
<td>$10^{-8}$ (10$^4$ Hz)</td>
</tr>
<tr>
<td></td>
<td>$2 \times 10^{-8}$ (TBF)</td>
<td>$10^{-10}$ (TBF)</td>
</tr>
</tbody>
</table>

Thermocurrents of depolarization

<table>
<thead>
<tr>
<th>applied voltage</th>
<th>$Q = PS(nC)$</th>
<th>Activation energy eV</th>
<th>Mobility $\mu$(cm$^2$/Vs)</th>
<th>$h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 V</td>
<td>10 V</td>
<td>0.30</td>
<td>$10^{-3}$ (high voltages) to $10^{-4}$ (low voltages)</td>
<td>0.33</td>
</tr>
<tr>
<td>150 V</td>
<td>10 V</td>
<td>0.35</td>
<td></td>
<td>0.15</td>
</tr>
</tbody>
</table>

$Q$ is the whole detrapped charge measured by the area of the thermodepolarization peak, $S$ the sample area and $P$ the whole polarization ($P = (\varepsilon_s - \varepsilon_0)/E$) with $E$ the electric field.

$N.B.$: The hypothesis allowing the mobility value are the same as in [11]. $h$ is the parameter of the Cole and Cole distribution of relaxation times.

Fig. 1. — Log $I = f(V^{1/2})$ for a Durham sample Au/(CH)$_2$/Au: thickness 34 $\mu$m, area 25 mm$^2$ at room temperature.
we have:

\[ J_1/J_2 \equiv \exp \left[ \frac{(E_1^2 - E_2^2)}{\beta e/kT} \right] \] (3)

we obtain a value of \( L' \) around 0.4 \( \mu \text{m} \), and thus \( L/L' \approx 85 \). We will see later that \( L' \) is in good agreement with the AC measured capacitance value of the surface layer: this layer is a great deal more resistive than the bulk and probably contains a trap density higher than the bulk trap density.

Naturally it is difficult to distinguish a Schottky effect from a Poole Frenkel effect: however a Schottky effect depends on the nature of electrode metal, and the experiment shows a difference of behaviour between gold and aluminium electrodes: the current is higher with Au electrodes; however the thickness of the surface layer is quite the same in the two cases: it is the reason why a Poole Frenkel effect seems more realistic in spite of a small asymmetry between the curves recorded with opposite polarizations (Fig. 6).

For voltages higher than 6 V the surface layer is short circuited and the whole voltage is applied to the bulk. Using two voltages \( V_3 \) and \( V_4 \geq 6 \text{ V} \), we find a very « good » value of \( \beta_{PF} \) by using, for the evaluation of the electric fields \( E_3 \) and \( E_4 \), the whole sample thickness.

The activation energy depends on the applied voltage, and the measured value varies from 0.38 eV at low voltages, to 0.30 eV for the highest used voltages.

The non linearity of \( I(V) \) curves appears in the « D » samples, but not in the « S » ones, in relation to a much higher trap density.

2.1.2 AC measurements. — In figure 2, some results of AC measurements in a large frequency range (\( 10^{-3} \) to \( 10^5 \) Hz; voltage amplitude 0.1 V) are given. In figure 3 a

![Graphs showing conductance and capacity vs. frequency](image)

Fig. 2. — Log \( G \) (conductance) and Log \( C \) (capacity) versus Log \( f \) for \( \text{Au/(CH}_2\text{)}_2/\text{Au} \) sample: (1) 294 K, (2) 244 K, (3) 203 K, (4) 173 K.
comparison between high frequency conductivity \( \sigma (HF) \), very low frequency conductivity \( \sigma (TBF) \) and \( \sigma (DC) \) are given versus \( 1000/T \). Examples of impedance diagrams are shown figure 4. Two successive relaxations can clearly be seen on these diagrams: a bulk relaxation for high frequencies, and a surface relaxation for low frequencies; the characteristic

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**Fig. 3.** — Conductivity \( \sigma \) versus \( 1000/T \): (1) HF plateau (2) \( \sigma (DC) \) \( (V = 1.5 \, V) \) (3) \( \sigma (TBF) \) plateau \( (10^{-3} \, Hz) \), (4) from [15].

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**Fig. 4.** — a) Impedance diagram at \( T = 294 \, K \). Two circle arcs are seen: a bulk relaxation for high frequencies \( (f > 3 \times 10^3 \, Hz) \) and a surface relaxation for low frequencies \( (f < 3 \times 10^3 \, Hz) \). b) Impedance diagram for high frequencies relaxation with lower \( R_s \) and \( 1/C_s \omega \) is shown.
frequencies of the relaxation time corresponding to the maximum of the impedance circle can be obtained: the activation energy of the slow relaxation is about 0.38 eV and of the fast relaxation 0.3 eV.

Impedance circles are off-centered, due to a relatively small dispersion of the relaxation times.

2.1.3 Thermodepolarization current measurements (TDC). — Figure 5 shows an example of depolarization thermocurrents using « D » samples. Two unresolved peaks are seen, corresponding to the two preceding relaxations: the lower temperature peak is due to the bulk relaxation, and the higher temperature peak, to the surface layer and (or) contact relaxation.

The non linearity of the recorded current versus the polarization voltage is in relation with the preceding Poole Frenkel effects on $I(V)$ curves, and the equivalence of TDC and AC measurements is only valuable for the lowest applied voltages ($< 1$ V) (this is very different from the « S » samples).

![Fig. 5. — Thermodepolarization current (rate of temperature rise : 0.09 K/s) Au/(CH)$_x$/Au cell (tension of polarization 15 V).](image)

2.2 Al/(CH)$_x$/Au CELLS.

2.2.1 DC measurements. — Log $I$ vs. $V^{1/2}$ curves are plotted in figure 6. We still observe two distinct slopes corresponding to surface and bulk effects. The surface layer thickness is of the same order of magnitude with Al as with Au electrodes.
The bulk effect corresponding to high polarization voltages, gives a correct value for the coefficient $\beta_{PF}$. However a difference can be observed between the two polarization directions, particularly in the presence of oxygen. Hence the surface effect is not merely of the Poole Frenkel type. On the other hand, the surface layer is more resistant for a given voltage than in the case of gold electrodes, and the current is much lower for low applied voltages. The electrode nature is important, even for high voltages: for a given $V$, the current is lower than with gold electrodes.

2.2.2 AC measurements. — Dielectric spectra at various temperatures (Fig. 7) and impedance diagrams (Fig. 8) for 293 K are plotted.

The electrode effect is larger and the circle corresponding to contact is apparent on the figure, with a very large radius, but the bulk circle does not appear because the corresponding radius is much smaller.

2.2.3 TDC measurements. — Thermodepolarization currents are plotted in figure 9. For high voltages, a large peak spread, corresponding to the bulk effect can be noticed. For lower voltages, the bulk and contact effect can be distinguished, and the contact relaxation becomes relatively more pronounced when the voltage decreases. As with Au contacts, the behaviour is non linear versus voltage, and the correspondence between TDC and AC measurements cannot be pointed out, except in the low (< 1 V) voltage range.

Fig. 6. — Log $I = f (V^{1/2})$ with Al/(CH)$_x$/Au cell: a) forward polarization, b) backward polarization.
Fig. 7. — Log $G$ (conductance) and Log $C$ (capacity) versus frequency for a cell Al/(CH)$_2$/Au at three temperatures: 1) 315 K, 2) 306 K, 3) 273 K. The conductivity is lower than with Au electrodes, but the capacity is of the same order of magnitude.

Fig. 8. — Impedance diagram of Al/(CH)$_2$/Au cell. The impedance circle corresponding to the bulk is not seen because the order of magnitude of the DC and AC resistances is not the same (the Al contact is very resistant).
Fig. 9. — Thermodepolarization current of Al/(CH)$_x$/Au cell: 1) polarization voltage 6 V, 2) 3 V, 3) 1.5 V. Rate of temperature rise: 0.05 K/s.

Table I compiles the experimental data (the corresponding data for « S » (CH)$_x$ [11] are also recalled). As in Shirakawa samples, the detrapped carrier density could be, in a first approximation, assumed as the free carrier density, the « D » (CH)$_x$ being a disordered solid. This density is much higher than in « S » samples. The mobility is voltage dependent in « D » (CH)$_x$. With a value for low voltages of the same order of magnitude as in « S » (CH)$_x$.

3. Discussion.

« D » (CH)$_x$ was studied by several workers [15, 16, 22-24]. They have compared « D » and « S » polyacetylene samples. Particularly, spectroscopic Raman studies enable one to determine the conjugation sequence length distributions, although the underlying phenomenon is not clear [17-19]. The crystal structure and string lengths are likely to be related. The Raman spectra show dominance of short sequences.

On the other hand, EPR studies have led to higher line spreading than in « S » (CH)$_x$ indicating a much weaker spin mobility.
Our measurements show several important features, particularly by comparison with previous results in "S" cis and trans samples [11].

While the TDC curves are analogous between cis and trans (CH)₂ "S" isomers, being only transferred in the temperature scale, but with the same area and consequently the same trapping distribution and density, the TDC curves with «D» samples correspond to a much higher trap density.

However, the activation energies are very near in «D» and «S» polymers. It is the reason why the same mechanism can be inferred in both samples: the difficult hops which determine the macroscopic conductivity are, in the two cases, the hops between chains, and likely to be between the chain ends. However in «D» isomers, the chains are much shorter, and consequently the density of trapped carriers is much higher than in «S» isomers. With the hypothesis that trapped carriers at low temperature are those which ensure the peak depolarization current and the direct current (being then detrapped), the carrier density is then much higher in «D» samples than in «S» samples: we then find a carrier density $N \approx 1.5 \times 10^{12}/\text{cm}^2$, about 60 times higher than in «S» undoped and «pure» (CH)₂ (that is to say, prepared in the best conditions).

Our results on AC conductance and capacitance measurements are obtained over eight decades.

In the very low frequency range and with a low voltage amplitude (0.1 V) a «plateau» of conductance is seen, much lower than in the higher frequency range. On the other hand, corresponding to this «plateau», an important rise of capacity is seen: this capacity plateau corresponds to the resistive surface layer effect (thickness 0.4 μm) determined by the low voltage part of the DC $I(V)$ characteristics (Poole-Frenkel effect). This resistive layer corresponds to a low mobility: and the reason of this low mobility and somewhat higher activation energy is not clear. This low mobility can be obtained from TDC measurements: a value $\mu \approx 10^{-4}$ cm²/V.s can be approximately given. In this work we have used thick films (typically 34 μ) so as to minimize the contact effects, like the Schottky-barrier in diode device (thickness about 1 μ) reported by Burroughs et al. [25]. However our results are close to those found with thin films [22]. The contact effects are not at present well resolved.

The bulk, although thicker, is less resistive, with a mobility around room temperature of about $10^{-3}$ cm²/V.s. The DC conductivity is limited in «D» samples by the surface layer, even with Au electrodes. On the other hand, in both «S» and «D» samples the same order of magnitude of the activation energy involves the same trap nature: most of these traps are likely chain ends in «D» samples and it is the reason why the distribution of relaxation times is narrower in these samples than in «S» samples where other impurities, as catalyst or chemical impurities can play a relatively high part.

What can be said about high frequency conductivity? Two different possibilities were pointed out in detail in the case of «S» samples: variable range hopping, that is to say hopping of charge carriers along a distribution in energy and distance of localized states [20] and Kivelson model which is based on an electron phonon-assisted hopping between solition states [21]. For the first model the DC conductivity must follow Mott's law: $\ln \sigma \sim T^{-1/4}$ (in three dimensional and pair approximations) and the AC conductivity is proportional to $T$. For intersoliton electron hopping (isoenergetic) the DC conductivity varies as a power of temperature, $T^n (n \equiv 14$ for trans polyacetylene), and the AC conductivity varies as:

$$\sigma(\omega, T) \sim \frac{\omega}{T^4} \left[ \ln \left( \frac{T \omega}{T_0^{n+1}} \right) \right]^4$$

$\sigma_{AC}(T)$ is not linear in $T$ and in the $\omega^n$ description, $n$ is increasing with increasing temperature ($s > 0.8$): the different frequency curves for different temperatures do not converge in the high
frequency domain. The similarity observed in our preceding measurements related to cis and trans «S» samples [11] lead us to invoke similar mechanisms to account for the transport properties of cis and trans isomers, according to the model proposed by Epstein et al. [3] for the conductivity in cis (CH)$_2$: hopping of carriers among sites with only a dispersion in site energies and not in site separations: this fact was argued to assimilate charge carriers with bipolaronic defects on cis chains, the main difference between cis and trans isomers being a different temperature dependence of mobility: the topological defects have an easier motion in trans (CH)$_2$ chains.

It will be noticed that the activation energy is quite the same in «D» trans samples as in «S» samples. Due to the very important part played by the traps in «D» polyacetylene, it seems that the preceding theory of bipolaronic defects can be argued also for this isomer: the conjugation sequence length is responsible for the lower mobility on chains, but this fact does not significantly affect the total activation energy, and cannot be detected from the AC conductivity temperature dependence.

However in our measurements, in the high frequency and low temperature range $\sigma$ (AC) ~ $\omega^n$ where $n$ is temperature dependent ($n$ is raised when the temperature is lowered). It is difficult to give the significance of this behaviour, because in the equivalent circuit to the sample, the surface inhomogeneity (similar to a Maxwell-Wagner effect) must be taken into account. What is the reason for this inhomogeneity? Several mechanisms can be argued: contact curvature (but with an Au electrode this effect is not seen in «S» samples), oxygen diffusion in a rather thin layer, or the mechanical effect on the surface layers during the elaboration are the more likely mechanisms.

The TDC measurements gives a maximum temperature peak $T_m$ closed 200 K. This temperature reported by Townsend et al. [22] would be characteristic for the recombination of photoexcited carriers.

Conclusion.

The present paper was the continuation of a preceding work on dielectric properties and depolarization thermocurrents in Shirakawa «S» cis and trans (CH)$_2$. At a low voltage, and as well in «S» samples, there is a good agreement between TDC and AC measurements with low applied voltages. In the preceding work [11], the transport properties in both cis and trans (CH)$_x$ were accounted for by a similar mechanism. This mechanism is also operative in Durham samples. In all cases the results show clearly that the macroscopic inhomogeneities of the samples manage all the electrical properties in the low frequency range. From this type of study no definite conclusion about the choice of the model (variable range hopping or Kivelson model) may be drawn. In Durham samples, the traps are more numerous in the two parts of the samples: surface layer and bulk. These traps are probably associated with catalyst residues (Fluorinated ortho-xylene molecules [22]) present at the chain ends, produced during thermal conversion of the precursor polymer. This has been reported by Townsend et al. [22].

The activation energy corresponding to the bulk (Tab. I) is very near the value obtained with Shirakawa samples. Townsend et al. have found the same value.

The same model can therefore be applied in «S» and «D» samples, and in both, AC and TDC measurements are in a very good agreement. This analogue behaviour points out the importance of the chain ends in the macroscopic conductivity of all the (CH)$_x$ samples.

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