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Electrical conductivity of SbF$_5$ doped polyacetylene

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Résumé. — Nous avons dopé des films de polyacétylène au pentafluorure d'antimoine, et étudié leur conductivité électrique en fonction de la concentration en dopant. Des énergies d'activation en sont déduites et comparées avec celles obtenues par dopage à l'iode et au pentafluorure d'arsenic. Les résultats sont discutés sur la base d'un modèle de localisation du dopant dans le système.

Abstract. — Conductivity measurements are reported for polyacetylene films with various SbF$_5$ doping concentration. The activation energy behaviour is deduced and compared with previous results obtained with iodine and AsF$_5$ doping. The results are discussed in terms of a qualitative model of the dopant ordering in the system.

1. **Introduction.** — Although acetylene has been polymerized for a long time [1], only these last few years polyacetylene films were synthetized by Shirakawa *et al.* [2], and those films showed very interesting physical properties when doped with halogens and many others dopants [3, 4]. The electrical conductivity in particular increases by at least twelve orders of magnitude from the insulator to metal state. Such a property leads to a considerable development in studies of (CH)$_x$ transport properties. Iodine, bromine and AsF$_5$ are well known dopants, and the electrical properties of the corresponding doped (CH)$_x$ were largely studied [3, 4]. Park [5] and Kwak [6] measured the temperature dependence of the thermoelectric power of doped (CH)$_x$ and explained their experimental results by a degenerate semiconductor to metal transition near 1 to 3 % dopant concentration. We must also note that these films could be stretched by thermal and mechanical treatments giving oriented films and yielding electrical anisotropy with a longitudinal to transverse conductivity ratio roughly

equal to ten [7]. These very peculiar electrical properties of doped (CH)$_x$ could result in a useful development of low cost device technology : n-p type junctions were realized by Chiang *et al.* [8] as well as compensation upon doping, solar cells were obtained from (CH)$_x$-silicium junctions [9], and photo conductivity and Schottky barriers were studied by Tani *et al.* [10].

However, only a good knowledge of (CH)$_x$ transport mechanisms will allow us to improve the (CH)$_x$ device technology.

Until now there has been no satisfactory model which could explain the overall experimental results. Partial interpretation was obtained using the theory of solid inorganic semiconductors [11, 12] and charge transfer theory [4, 13] already successfully used for others conducting materials such as TTF-TCNQ and (SN)$_x$. Some theoretical calculations have been performed using a soliton wave model [14, 15]. Electrical conductivity stands out as one of the most characteristic properties of doped (CH)$_x$ for transport phenomena studies as well as for device technology improvement. We present here some electrical conductivity results obtained with a new dopant,

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SbF_5, and compare them with results obtained previously on iodine and AsF_5 doped samples. We shall discuss the electrical properties of these similar systems.

2. Samples preparation and experimental techniques.

— Polyacetylene films were obtained using the method described in [2]. The polymerization was performed at -78 °C in order to obtain a cis-rich isomer [16]. We used the $Ti(OBu)_4$-$Al(Et)_3$ homogeneous catalytic system in toluene with a molar ratio $[Al]/[Ti] = 4$.

In order to reduce the catalytic residuals in $(CH)_x$ films, we used only the films grown on the reactor surfaces wetted with the catalytic solution. The films were washed in toluene, dried under vacuum and kept under vacuum at -25 °C. The trans-isomer was obtained by heating the sample at 200 °C during one hour. Most films were 100 μm thick. Before doping the samples were characterized by infra-red, conductivity and E.S.R. measurements [17]. Cis-rich $(CH)_x$ films were doped by contact with SbF_5 vapour in equilibrium with its liquid phase. The vapour pressure was controlled by the temperature of the system which ranges between 0 °C and 20 °C. In order to obtain a homogeneous light doping (< 1 %) we proceeded with thin films (< 50 μ). The absence of SbF_5 macroscopic concentration gradient was verified by observing a constant conductivity when etching the sample surfaces. The kinetics of doping process were observed *in situ* by measuring the increase in conductivity. The SbF_5 concentration was determined by the weight increase of the samples.

DC measurements were performed using the usual four probe techniques. Gold wires were fastened with gold paste. For each measurement Ohm's law was checked by graphing the *I.V.* relation. The temperature was varied from 5 K to 350 K. The molar concentration on doped samples is given below by y in the formula $[CH(SbF_5)_y]_x$.

3. Experimental results.

— Figure 1 exhibits the whole behaviour of Log ρ versus $10^3/T$, where ρ is the measured resistivity, between liquid helium and room temperature, for $y = 0.04$. It is evident that the dependence is not linear for the whole range, but activation energies of 15 meV and 1 meV can be defined in the range 100-300 K and at the lowest temperatures respectively.

On figure 2 is plotted Log ρ versus $10^3/T$ for transpolyacetylene and SbF_5 doped cis-polyacetylene in the range 77 K $< T <$ 300 K with $0.001 < y < 0.06$. We observe a large effect of the SbF_5 doping on the conductivity which reaches 50 $(\Omega cm)^{-1}$ at room temperature for $y = 0.06$. A large decrease in conductivity occurs when the temperature is decreased. Looking at the temperature range

$$150 \text{ K} < T < 300 \text{ K}$$
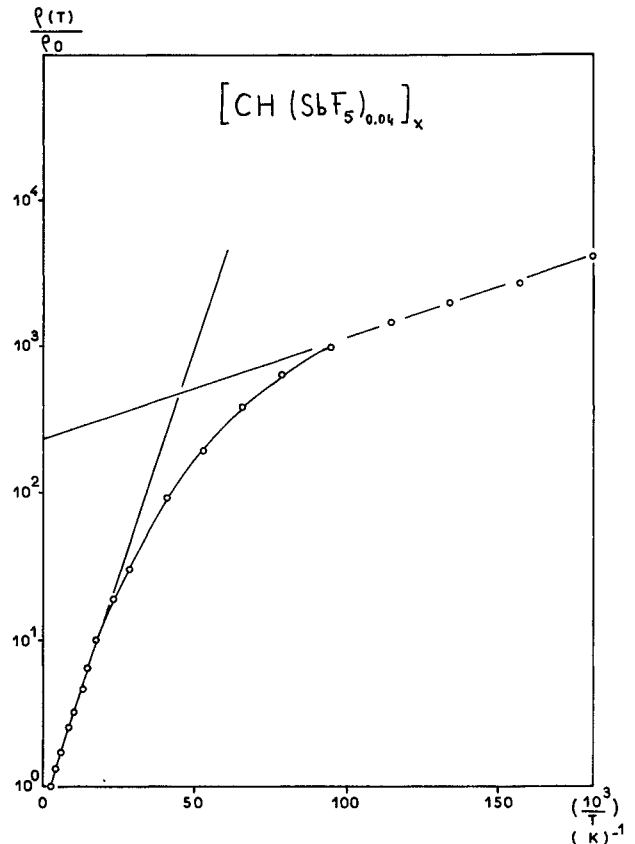
Fig. 1. — Inverse temperature dependence of the resistivity normalized to the room temperature value, for 0.04 SbF_5 doping between 300 K and 5 K. A general linear law is not observed. Nevertheless we define an activation energy in the high temperature range 100 K $< T <$ 300 K, while the one which can be deduced at the lowest temperatures is roughly ten times smaller.

Fig. 2. — Inverse temperature dependence of the resistivity for $[CH(SbF_5)_y]_x$ with $0 < y < 0.06$, in the range 77 K $< T <$ 300 K.

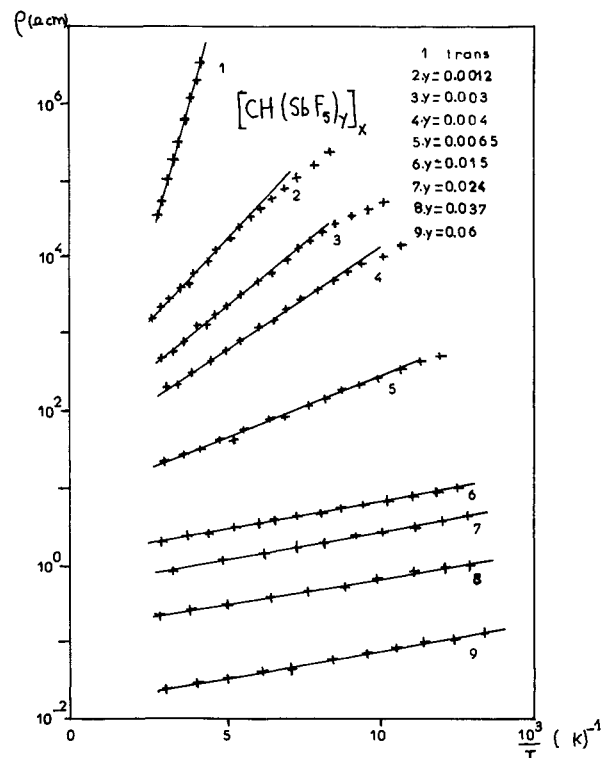where the observed dependence is quite linear, an activation energy E_a can be deduced. For undoped trans-(CH)$_x$ E_a reaches 300 meV. For SbF$_5$ doped cis-(CH)$_x$ E_a decreases from 100 meV ($y = 0.001$) to 15 meV ($y > 0.01$). With higher doping concentrations E_a remains constant.

Figure 3 exhibits the thermal activation energy E_a versus SbF$_5$ concentration. An important change can be observed near $y = 0.01$, which is discussed below.
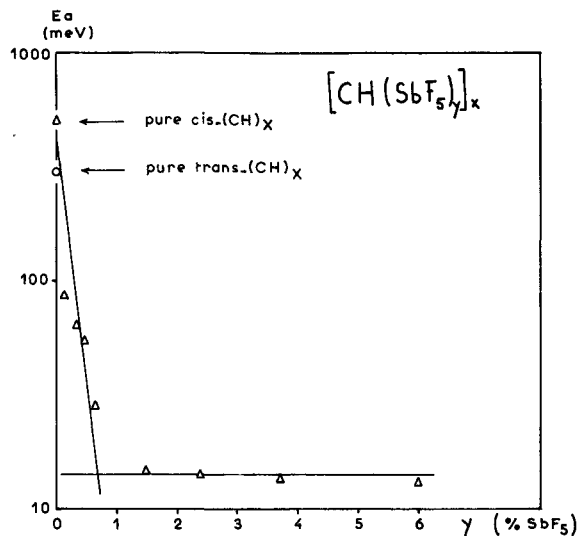

Fig. 3. — Concentration dependence of the activation energy as deduced from the data of figure 2, for [CH(SbF$_5$)$_y$]$_x$, showing two distinct regions $y < 0.8$ % and $y > 0.8$ % corresponding to semiconducting and metallic behaviour respectively.

4. Discussion.

— Obviously the SbF$_5$ doped (CH)$_x$ gives results comparable with those obtained with iodine, bromine and AsF$_5$ doping species as well for the absolute value of the conductivity as for its temperature dependence and the resulting activation energies [3, 4, 5].

We first note an important discrepancy with the semiconductor behaviour : the thermal activation energies of cis-(CH)$_x$ (500 meV) and trans-(CH)$_x$ (300 meV) are smaller than the half optical gap $Eg/2$ which would be obtained with classical semiconductors using the relation

$$\rho = \rho_0 \exp \frac{Eg}{2 k_B T}.$$

Mac Diarmid and Heeger [18] give $Eg \sim 1\,400$-$1\,600$ meV deduced from the visible absorption behaviour. Such a discrepancy can be explained by deep impurity levels in polyacetylene provided by O$_2$,
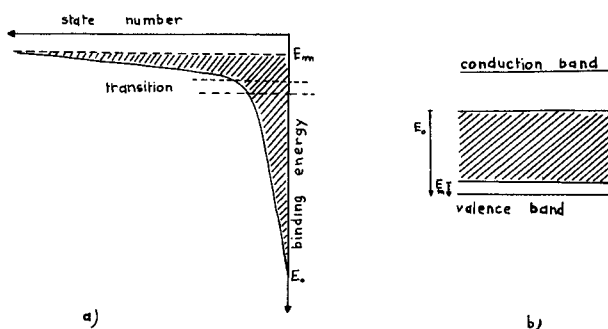
which is probably introduced during the experimental process after polymerization, and act as a dopant which can be compensated [19, 20]. On the other hand, oxygen coming from the catalyst, whose molar ratio [O]/[CH] is of the order of 0.1 % as shown by elementary analysis, leads to the neutral TiO$_2$ specie which doesn't react with the polymeric chains.

On the other hand, figure 3 shows an important change in the activation energy dependence around (0.8 ± 0.2) % doping concentration. The same behaviour occurs with iodine doped samples in the concentration range 2 to 3 %, as evidenced by conductivity [3] and thermoelectric power [5, 6] measurements. Raman studies [21, 22] have identified in this last case the I$_3^-$ chemical species, which assume one transferred electronic charge.

Consequently, the carrier concentration which defines the transition from semiconducting to metallic behaviour is one third of the molar iodine concentration, i.e. of the order of 1 %, which is similar to our experimental value (0.8 ± 0.2) % obtained with SbF$_5$ doping. This suggests one transferred electronic charge per doping molecule, in agreement with results obtained by different authors [23] on the very similar system [CH(AsF$_5$)$_y$]$_x$ where the transition also occurs near 1 % doping concentration. So we can expect that the semiconductor to metal transition only depends on the carrier concentration and not on the dopant nature.

Let us analyse the conductivity as a classical semiconducting process. At room temperature, assuming one carrier per SbF$_5$ molecule, the carrier concentration can be measured by the weight increase of the sample. From the crude formula $\sigma = nq\mu$, where n is the carrier number and q the charge, we can estimate the mobility μ. Results are reported in table I. We note an increase of μ versus dopant concentration. The saturation value 0.3 cm^2 V^{-1} s^{-1} is of the same

Fig. 4. — Qualitative model of dopant ordering in polyacetylene : a) relative population of impurity levels ; b) schematic diagram of impurity band in (CH)$_x$ gap. The activation energy E_a lies in the range E_0 to E_m.

Table I. — Estimated values of carrier number and mobilities for different SbF$_5$ dopant concentrations at T = 293 K.

y (%)	0.12	0.3	0.45	0.65	1.5	2.4	3.7	6
n (10^{+19} cm^{-3})	—	—	—	12	28	45	68	110
μ (cm^2 V^{-1} s^{-1})	—	—	—	2×10^{-3}	10^{-2}	1.6×10^{-2}	3.5×10^{-2}	3×10^{-1}

order of magnitude as previous values obtained from Hall effect measurements [24] or calculations [3].

In the light of the preceding results and starting from the qualitative model proposed by Fincher et al. [12], we suggest that the temperature dependence of the conductivity and the behaviour of the activation energy versus dopant concentration can be interpreted in terms of a distribution of energy levels in the gap. In undoped samples the initial impurities, evidenced by chemical analysis, takes place in the deepest possible states, for instance by a direct chemical binding with the chain. With increasing dopant concentration all the other possible states are successively occupied, located along the chain and invoking only a charge transfer with one or more than one chain. The interchain states are needed to understand the existence of a macroscopic electrical conductivity. At high dopant concentration only the least bound states, such as those near the surface of the fibrils, as suggested by Rice and Timonen [14], are allowed. A large part of those weakly bound molecules can be removed by pumping [4].

5. **Conclusion.** — We have shown that the semiconductor to metal transition only depends on the carrier concentration and not on the dopant nature. In order to explain our experimental results, we have suggested a qualitative model of the dopant ordering in the polyacetylene system. This interpretation points out the importance of both the semiconducting behaviour which appears through the temperature dependence of the electrical conductivity σ and a percolation description suggested by the dopant concentration dependence of σ.

More experimental results are needed to determine the type of chemical binding between the dopant specie and the $(CH)_x$ chains in order to have a better understanding of the transport properties.

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