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HIGH-σ POLYACETYLENE: DC CONDUCTIVITY BETWEEN 14 mK AND 300 K

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ABSTRACT

Highly stretch-oriented polyacetylene (6.5:1) yields conductivities σ of typically 20 000 - 100 000 $\Omega^{-1}cm^{-1}$ at room temperature when highly doped with iodine. Between T = 300 K and T = 14 mK, σ decreases monotonically by about a factor of 5 for fresh samples. Above 400 mK the temperature dependence for fresh samples is fitted by the SHENG formula and can be interpreted within a phenomenological model . On fresh samples, MONTGOMERY measurements of the conductivities parallel ($\sigma_\parallel$) and perpendicular ($\sigma_\perp$) to the stretching axis show a temperature independent anisotropy $A=\sigma_\parallel/\sigma_\perp$ of about 25 indicating a common limiting mechanism for both, $\sigma_\parallel$ and $\sigma_\perp$. Deliberate oxygen ageing drastically changes σ(T) and results in a temperature dependence of A.

INTRODUCTION

Very recently, the synthesis of highly conducting polyacetylene with conductivities well above 20 000 $\Omega^{-1}cm^{-1}$ has aroused considerable interest [1-4]. A study of σ(T) between 3 K and 300 K of fresh samples highly doped with iodine showed that most of the standard models are not able to explain the temperature dependence [4]. A good fit to the high precision experimental data, however, is the SHENG formula (equ. 1). Fresh samples showed an almost temperature independent conductivity anisotropy $A=\sigma_\parallel/\sigma_\perp$, indicating a common limiting mechanism for both, $\sigma_\parallel$ and $\sigma_\perp$ [4].

The experiments presented below are directed towards the following questions: does the SHENG formula describe σ(T) at

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temperatures below 3 K? Can we extract a consistent set of microscopic data from the fit to the SHENG formula? Is there a correlation between the temperature dependence of σ of fresh samples and its room temperature value? And finally: what is the effect of ageing on the conductivity anisotropy A?

EXPERIMENTAL

$(CH)_x$ was obtained by the polymerization technique described elsewhere [1]. We used films of 1 - 5 μm thickness grown on polypropylene as substrate and aligned by 6.5-fold mechanical stretching. The samples were doped in a saturated solution of iodine in dried CCl_4. Platinum contacts were mechanically pressed on the films, resulting in contact resistances of typically 0.5 Ω. The setup for the experiments above 3 K, described elsewhere [4,5], allowed sweep times as long as 50 hours for one single temperature sweep from 300 K to 3 K. Within this range, we obtained typically several thousand data points. Each curve was measured as a temperature cycle. The relative accuracy of $\sigma(T)$ is about 0.01 % ; the accuracy of the absolute value is limited to about a factor of 1.5 by the SEM determination of the sample thickness. For the low temperature range from 14 mK - 4.2 K we used a $^3He/^4He$ dilution cryostat, and the conductivity was measured via an 18 Hz ac resistance bridge method. Above 3 K, we performed measurements with more than 15 different samples, all of which had values of $\sigma(300\ K) > 20\ 000\ \Omega^{-1}cm^{-1}$. We used both, standard four-probe and MONTGOMERY techniques [6,7], leading to consistent results. Below 3 K, we applied the standard four-probe technique. All experiments were performed within the ohmic regime.

EXPERIMENTAL RESULTS

a) Temperature Dependence

Fig. 1a shows the temperature dependence of $\sigma_\parallel$ and $\sigma_\perp$ for a fresh sample as determined via MONTGOMERY technique. The absolute values of $\sigma_\parallel$ of fresh samples at room temperature vary from sample to sample between 20 000 - 100 000 $\Omega^{-1}cm^{-1}$. σ decreases monotonically with decreasing temperature. The reduction factor of $\sigma_\parallel$ by cooling fresh samples from 300 K to 3 K varies between 2.8 and 4, depending on the sample. Fig. 2 shows the temperature dependence of $\sigma_\parallel$ of a fresh sample within the range from 4 K to 14 mK. The conductivity is still decreasing monotonically down to

14 mK by about a factor of 1.34 in this temperature range. Thus, the total reduction factor of $\sigma_\parallel$ by cooling from 300 K to 14 mK varies from 3.7 to 5.4 for these highly conducting samples. No correlation, however, could be observed between the individual values of σ(300 K) and the reduction factor, respectively, for the samples examined.

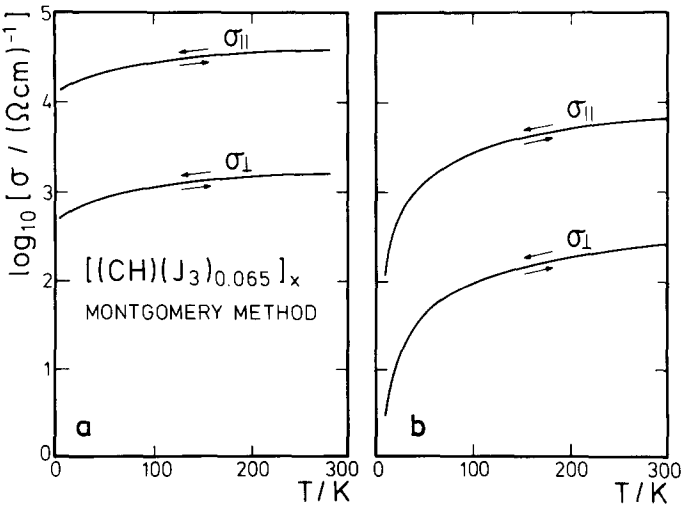

Fig. 1: $\sigma_\parallel(T)$ and $\sigma_\perp(T)$ of stretch-aligned (6.5:1) $[(CH)(J_3)_{0.065}]_x$ (one temperature cycle). a) fresh sample; b) the same sample after O_2-ageing.

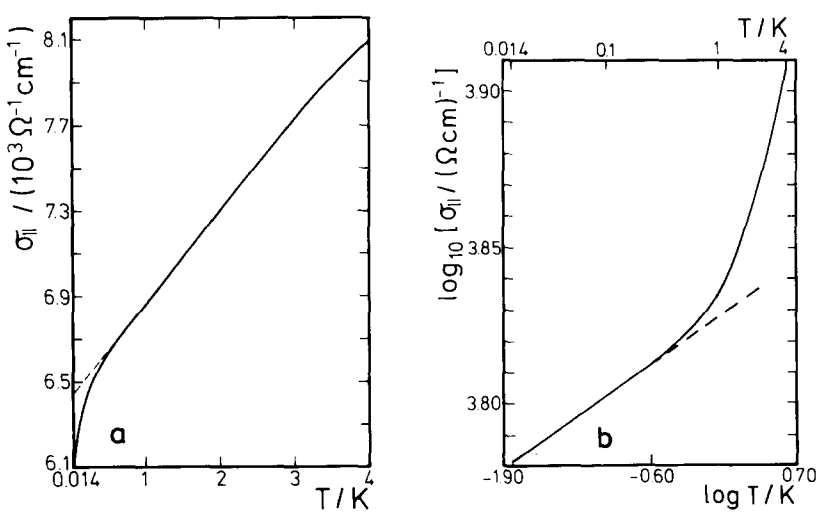

Fig. 2: $\sigma_\parallel(T)$ between 14 mK and 4 K in two different plots. The dotted line in a) is the SHENG fit, the dotted line in b) the fit to a power law.

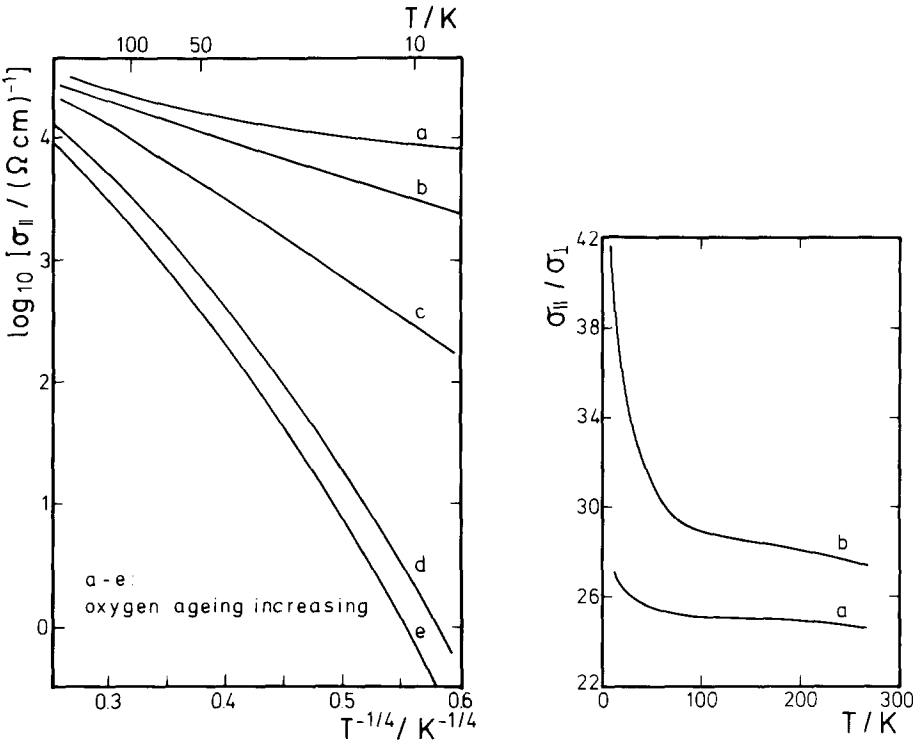

Fig. 3: $\sigma_{\parallel}(T)$ for different stages of ageing of the same sample by 1 at O_2 (standard four-probe measurement). a) fresh sample, b) after 2 hours at 260 K, c) after additional 1 hour at 260 K, d) after additional 1 hour at 320 K and e) after additional 2 hours at 320 K [4].

Fig. 4: Temperature dependence of the conductivity anisotropy $A = \sigma_{\parallel}/\sigma_{\perp}$ for the data of Fig. 1a (fresh sample, curve a) and Fig. 1b (same sample after ageing, curve b).

b) Anisotropy and Ageing

Deliberate ageing of the samples with oxygen results in a drastic change of the temperature dependence of both, $\sigma_{\parallel}$ and $\sigma_{\perp}$, leading to a reduction of the conductivities mainly at low temperatures. Fig. 3 shows $\log(\sigma_{\parallel}(T))$ versus $T^{-0.25}$ between 8 K and 250 K for a fresh sample (curve a) and for different degrees of ageing of the same sample (curves b-e) [4]. While the room temperature value of $\sigma_{\parallel}$ is reduced by less than a factor of 10, the conductivity at 3 K is diminished by more than 5 orders of magnitude. Only strongly aged samples exhibit an almost constant factor of reduction of the conductivity on further ageing (curves d-e).

For fresh samples, $\sigma_{\parallel}$ and $\sigma_{\perp}$ show almost the same temperature dependence: the anisotropy A(T) has values of 20 - 26 and changes by only about 2 - 10 % from 300 K to 3 K. Fig. 4a shows A(T) for the sample of Fig. 1a. Ageing the sample of Fig. 1a for one week at room temperature by 100% oxygen at ambient pressure leads to a reduction of σ(300 K) by a factor of 6 and a change in the temperature dependence, which is shown in Fig. 1b. While σ(300 K)/σ(3 K) = 2.8 for the fresh sample of Fig. 1a, it amounts to more than 100 in Fig. 1b. During this ageing process, the anisotropy increases only slightly by about 8% at room temperature. Its temperature dependence, however, as compared to the fresh sample, changes significantly (Fig. 4 b) showing a pronounced increase of about 60 % towards lower temperatures. This increase of the anisotropy is perfectly reproduced with different samples.

DISCUSSION

Different fresh high-σ samples differing by a factor of 5 in the room temperature conductivity have been investigated. Even for the samples with the highest conductivities of 100 000 $\Omega^{-1}cm^{-1}$, no "metallic" temperature dependence could be observed; even the slope of the σ(T) curves did not decrease with increasing σ(300 K). This may indicate that phonon scattering does not contribute significantly to the sample resistance at room temperature. This is consistent with considerations of PIETRONERO [8] and of KIEVELSON and HEEGER [9], who argued, that phonon scattering should not play an important role in one-dimensional carbon π polymers, and who estimated the ideal value of σ to be higher than that of copper. This also explains that for kT significantly larger than the height of the potential barriers (see below), the conductivity asymptotically approaches a constant value σ_o (see Fig. 1a). Thus, $1/\sigma_o$ could be interpreted as the resistance determined by defect scattering.

A good fit of the temperature dependence for the fresh sample is obtained with the SHENG formula [10,12].

$$\sigma(T) = \sigma_o \cdot \exp[- T_1/(T + T_o)] \qquad (1)$$

Equ. 1 fits the experimental data (Figs. 1a, 2a) in the temperature range from 0.4 K to 300 K (i.e. for almost three orders of magnitude in the temperature). The parameters σ_o, T_1 and T_o are

given in Table 1 for the data of Fig. 1. The values of T_1 and T_o differ from sample to sample by not more than a factor of 1.5, for fresh samples. For the sample, the temperature dependence of which we published recently [4], the fit between 3 K and 300 K was perfect within the graphical line width. For the sample of Fig 1a, which was the sample with the most shallow temperature dependence, the average deviation is about 3%. Severe deviations arise below a temperature T_{loc}, which for the fresh sample of Fig. 2 is 400 mK. For aged samples T_{loc} is much higher, up to 50 K.

sample		σ_o / $\Omega^{-1}cm^{-1}$	T_o / K	T_1 / K	ΔE /meV	w / Å
fresh	$\sigma_{\|\|}$	53500	76	112	9.6	14.7
	$\sigma_\perp$	2180	71	113	9.7	15.8
aged	$\sigma_{\|\|}$	12900	50	240	21	32.6
	$\sigma_\perp$	519	55	274	24	31.7

Table 1: Parameters of equ. 1 and 2 ($\Delta E = k \cdot T_1$).

The SHENG model has been applied to doped polyacetylene by different groups in the past [4,12-16]. It describes $\sigma(T)$ assuming highly conducting regions separated by potential barriers of width w and height V_o. The charge transfer is caused by tunneling, enhanced by thermal voltage fluctuations. For parabolic barriers, SHENG derived equ. 1. The applicability of the SHENG model to polyacetylene, however, is not quite obvious [17]: SHENG introduced a parameter λ in his theory, which is a measure for the amount of image force correction, and which, for λ=0.07 gives a parabolic barrier. λ is given by $\lambda = 0.795 \cdot e^2/(16\pi\varepsilon\varepsilon_o w V_o)$ where ε is the dielectric constant of the barrier [12]. The values of w and V_o resulting from our experimental data of T_o and T_1 (see Table 1), however, are not consistent with λ in SHENG's theory.

However, in a phenomenological model, an interpretation of the data is possible, independent of the applicability of the SHENG model: in the low temperature limit of equ. 1, the conductivity approaches a finite value $\sigma(T=0) = \sigma_o \cdot \exp(-T_1/T_o)$; in the high temperature limit $T >> T_o$, $\sigma(T)$ becomes $\sigma = \sigma_o \cdot \exp(-T_1/T)$ being a thermally activated conductivity with an activation energy

$\Delta E = kT_1$. Thus, the SHENG formula (equ. 1) may be regarded just as a formula which correctly describes the high and low temperature limits and which, in accordance with the experimental data, interpolates between these limits. The interpretation of $\sigma(T=0)$ as a tunneling conductivity yields the width w of the potential barriers:

$$T_1/T_o = \sqrt{2m \cdot \Delta E} \cdot w \cdot 2/\hbar \qquad (2)$$

(rectangular barriers). The values of ΔE and w resulting from the data of Fig. 1 are shown in Table 1. Thus, reasonable microscopic parameters of the barriers can be derived.

For very low temperatures ($T<0.4$ K), a different, much steeper temperature dependence is observed, which indicates a change in the dominating transport mechanism. Contrary to other experiments on less conducting polyacetylene samples [18], $\sigma(T)$ cannot be fitted with $\sigma(T) = a + b \cdot T^{0.5}$ in this temperature range, but obeys a power law $\sigma(T) = \alpha \cdot T^{\beta}$, ($\alpha$ = 6716 $\Omega^{-1}cm^{-1}K^{-\beta}$, β = 0.0247), i.e. $\log(\sigma(T)) \sim \log(T) + \text{const.}$, see Fig. 2b.

$\sigma(T)$ of the aged samples can only be fitted to equ. 1 for higher temperatures (e. g. for T > 50 K in Fig. 1b). As to be expected, ageing leads to an increase in the average values of w and ΔE. For strong ageing (e.g. Fig. 3, curves d-e), no such fit is possible.

CONCLUSIONS

For fresh samples of high-σ polyacetylene we conclude from our experiments, that the temperature dependence of σ for 400 mK < T < 300 K is determined by barriers between highly conducting regions. For $T < T_{loc}$ = 400 mK, the temperature dependence becomes much stronger, which may be due to localization effects, causing an additional resistivity. For aged samples, T_{loc} increases with increasing degree of ageing.

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