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ABSTRACT

Results of dc and microwave conductivities and dielectric constant measurements on iodine doped $(CH)_x$ are reported. The gradual variation of the transport properties as a function of the iodine concentration indicates that no sharp phase-transition occurs with increasing doping levels. Charged π-phase kinks localized around I_3^- discribe qualitatively the dielectric properties in the lightly doped range.

АННОТАЦИЯ

Излагаются результаты измерения проводимости при постоянном и микроволновом поле и диэлектрической проницаемости на пленке $/CH/_x$, легированной иодом. Постепенное изменение транспортных свойств в зависимости от содержания иода указывает на то, что увеличение содержания примести не приводит к резкому фазовому переходу. Возможно качественное описание диэлектрических свойств с помощью заряженных и локализованных на ионах I_3^- солитонов в слабо легированной области.

KIVONAT

Jóddal szennyezett $(CH)_x$ filmen végzett egyenáramu és mikrohullámu vezetőképesség, valamint dielektromos állandó mérések eredményeit közöljük. A transzport tulajdonságok fokozatos változása a jód tartalom függvényében arra utal, hogy nem történik éles fázisátalakulás ahogy a dopolási szint növekszik. A I_3^- ionok környezetében lokalizált, töltött szolitonok segitségével a dielektromos tulajdonságok kvalitativ leiása adható a gyengén szennyezett tartományban.

INTRODUCTION

Polyacetylene, $(CH)_x$, has been the subject of intense experimental and theoretical work since it was shown to exhibit metallic conductivity when treated by various dopants. Its room temperature conductivity can be varied over twelve orders of magnitude by doping with e.g. halogens.[1,2] The most common view is that pure polyacetylene is a simple semiconductor with relatively unimportant correlation effects, while at high doping levels its behaviour is characteristic of a metal. Though the conductivity of the undoped material is determined by impurities and in the highly doped case it is affected by intrachain hopping, optical studies[3], the temperature dependence of the thermoelectric power[4], magnetic susceptibility[5] as well as that of the conductivity[1] are strong evidences for this picture. The effect of doping is believed to create impurity states, which overlap at higher doping levels. It was claimed[1-5] that at an iodine concentration of about 2 atomic percents a semiconductor-metal phase-transition takes place.

In this paper we report on measurements of transport properties of iodine doped polyacetylene. We have performed d.c. and microwave conductivities and dielectric constant measurements on the $(CHI_y)_x$ system in the range of iodine content of $0 < y < 0.25$. Our aim is to have an insight into the mechanism of the insulator-metal transition taking place during the doping process.

Sample preparation, experimental techniques

$(CH)_x$ films were prepared by the method of Shirakowa et al[6] with titanium tetrabutoxide and triethylaluminium catalic system in tuluene. Polymerization was performed at -78°C using an acetylene pressure of àbout 1 atm. Flexible, shiny films were obtained after ~ 90 minutes on the surface of the solvent with a thickness of 0.05-0.2 mm. Samples were washed in hexane and tuluene to remove the remaining catalyst, then kept in vacuum for hours and, before measurements, were cleaned mechanically. Optical[7] investigations showed that at least 80 % of the as grown film was in the <u>cis</u> isomer form. The bulk density of the $(CH)_x$ films was about 0.4 g/cm^3, slightly depending on the sample preparation.

Iodine treatment was carried out at room temperature by direct contact with I_2 vapour of pressure of 0.03 torr to obtain low doping levels and 0.3 torr for doping levels above 5 atomic percents. The d.c. conductivity was measured <u>in-situ</u>, by four--probe method, using pressed copper contacts. The iodine content was determined also <u>in-situ</u>, by measuring the weight increase of a reference sample in the same surroundings. The reference sample (initial weight: 5-30 mg) cut from the same film as that for the transport measurements was placed on the end of a 0.2 mm thick, 20 cm long quarz fibre. The bending of the quarz fibre was measured optically and recorded continuously. In this arrangement we were able to determine the iodine content <u>in-situ</u> with an accuracy of $2x10^{-4}$ (0.02 atomic percent).

At low doping levels extreme care was taken to avoid inhomogeneities. For this purpose below 2 % the iodine doping was performed in several steps; at each doping level we determined the steady state value. To indicate the importance of inhomogeneities, we mention that for example at a doping level of $y=10^{-3}$ using a continuous iodinization rate as slow as 0.01 percent/min we found a conductivity 1-1.5 orders of magnitude higher than the steady state value. For this doping rate at 1 % the deviation is about a factor of 2, above 3 % the error is negligible.

It is to be noted that the σ vs y curves slightly depend on the preparation circumstances, the most important factor being probably the density of the $(CH)_x$ films. All the results published in this paper were obtained on samples cut from the same film.

Microwave conductivity and dielectric permeability was measured at 9×10^9 Hz using the cavity perturbation method described by Buravov and Shchegolev[8]. The sample was turned in and out of a strongly undercoupled high quality resonant cavity and the relative changes of the resonance frequency and absorption width were recorded. Doping was carried out in the same way as for the d.c. measurement. In order to determine the iodine content of the samples measured at microwaves the d.c. conductivity of a reference sample was monitored, for which identical circumstances were maintained throughout the measuring cycle.

Experimental results

Figs 1 and 2 shows the concentration dependence of the d.c. conductivity in the $(CHI_y)_x$ system. The conductivity of the undoped sample is less than $10^{-8}\ \Omega^{-1}cm^{-1}$, indicating that the material is sufficiently pure and is mainly in the cis form[9]. The value of $60\Omega^{-1}cm^{-1}$ of the highly doped film is somewhat less than reported by Chiang et al[1]. The conductivity rises rapidly with the dopant content, however there is no doping level where any abrupt change is observable. That the increase is gradual is better visible on the log-log scales (insert of Fig. 2). The straight line corresponds to a $\sigma \propto y^\alpha$ concentration dependence. Such a fit serves only to underline the gradual nature of the transition, we shall not attempt to give a specific meaning to the parameters.

There is a large dispersion between the microwave and d.c. conductivity in the undoped $(CH)_x$. As it is seen in Fig. 3 for $y=0$ the a.c. conductivity is 3 orders of magnitude higher than the d.c. one. This difference decreases continuously with increasing iodine content and above 3 atomic percents it is less than the uncertainity in the absolute values. To emphasize the gradual variation of the dispersion the insert displays the microwave conductivity as a function of the d.c. conductivity.

The dielectric constant of the pure <u>cis</u> $(CH)_x$ is $\varepsilon = 3.5 \pm 0.2$. Since the density of the as grown film is not really characteristic of the fibrous material we evaluated the dielectric constant as for an "ideal" material with density of 1.16 g/cm^3.[10] Thus the volume of samples was calculated from their weight and the ideal material density. This ε value is roughly three times smaller than that obtained by Fincher at al[11] on an aligned film along the chain direction. The concentration dependence of the dielectric constant is shown on Fig. 4. At low doping levels ε varies linearly with iodine content, at higher levels its increase becomes stronger. The temperature dependence of ε measured on a sample containing $y = 0.04$ iodine is plotted on Fig. 5.

Discussion

Low temperature Raman measurements on iodine doped polyacetylene samples indicated[12] that the dopant was present dominantly in the form of I_3^-. A probable description of the impurity state created on the $(CH)_x$ chain by the charge transfer to iodine is the positively charged π-kink model[13,14]. In this model the double bond-single bond sequence of the polymer chains is supposed to be interrupted by two subsequent single bonds, i.e. a π-kink with a positive charge remaining on the carbon atom. No unpaired electrons are linked with π-kinks (which during the reaction with iodine must be created in pairs) thus it explains the unusually low susceptibility observed in the whole doping range[5]. Based on thermoelectric power measurements[4] these states were suggested to be localized in undoped and lightly doped $(CH)_x$ while at high doping levels a metallic behaviour was found.

Our measurements confirm the existence of localized states at low doping levels. The large dispersion between the a.c. and d.c. conductivities in the lightly doped range indicates a contribution to the microwave conductivity from hopping between localized states in a similar way than that observed in doped and amorphous semiconductors. The randomness in the energy of the available states may arise from structural distortions around the dopants or it is due to the electrostatic field of the randomly packed I_3^-. In the metallic region the states are extended and the dispersion disappears.

The initial increase of the dielectric constant with doping may be qualitatively understand in the framework of the π-kink model. We visualize the transition to the first excited state of a π-kink bound to an acceptor ion as a shift of a double bond by a lattice constant d (Fig. 6). Denoting by W the energy difference and by p the dipole transition matrix element between the ground and excited states the polarizability of a π-kink is $\alpha = 4p^2/W$ at temperatures much less than W. Since a weak increase of ε with temperature is observed around ambient we take $W/k = 1000$ K, furthermore as an order of magnitude estimate we replace p by ed. With these assumptions we find $\alpha_{\pi\text{-kink}} \sim 10^{-21}$ cm^3. At low doping levels the material may be considered as a gas of strongly polarizable particles (bound π-kinks) embeded in a medium of permeability ε_o (CH_x matrix), thus the dielectric constant is: $(\varepsilon-\varepsilon_o)/4\pi = \rho\, \alpha$, where ρ is the density of the π-kinks. From the initial slope of the concentration dependence of ε, assuming one π-kink per I_3^- ions we find $\alpha_{\text{measured}} = 1.6\times10^{-21}$ cm^3 in reasonable agreement wit the bound π-kink model.

The polarizability of the defects induced by iodine is extremaly large and the nearly linear increase of ε for dopant concentrations of several percents is rather surprizing. If the polarizibilities were isotropic a divergence in ε (polarization catastrophe) would occur for $4\pi/3\ \rho\alpha = 1$ according to the Clausius-Mosotti relation. From the above estimation this limit is reached at iodine concentrations of about 0.8 %. It seems that the picture of non-interacting localized defects may be invalid at very low iodine concentrations.

Our findings do not support the assumption of a metal-insulator transition at a well defined dopant concentration[1-5]. We have not found any dividing line between the semiconducting and metallic states as the doping level was increased. Such a phase-transition would be observable in the conductivity or - in a more pronounced way - in the dielectric constant. There is no doubt that electronic states responsible for the conductivity are localized at low dopant concentrations and extended in the metallic region but it seems that the transition between these states is gradual and is far from being completed at a few percents of iodine concentration.

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FIGURE CAPTIONS

1. dc conductivity of $(CHI_y)_x$ is the range of $0 < y < 0.03$

2. dc conductivity of $(CHI_y)_x$ in the range of $0 < y < 0.25$. The insert shows the concentration dependence on logarithmic scales.

3. Concentration dependence of the microwave (x) and dc (●) conductivity of iodine doped polyacetylene. The insert displays the microwave conductivity as a function of the dc conductivity. The dopant concentrations are also indicated.

4. Dielectric constant of $(CHI_y)_x$ in the range of $0 < y < 0.03$.

5. Temperature dependence of the dielectric permeability measured on a $(CHI_{0.04})_x$ sample.

6. Ground and first excited states of a π-phase-kink. The defect is believed to be smeared over several lattice constants.

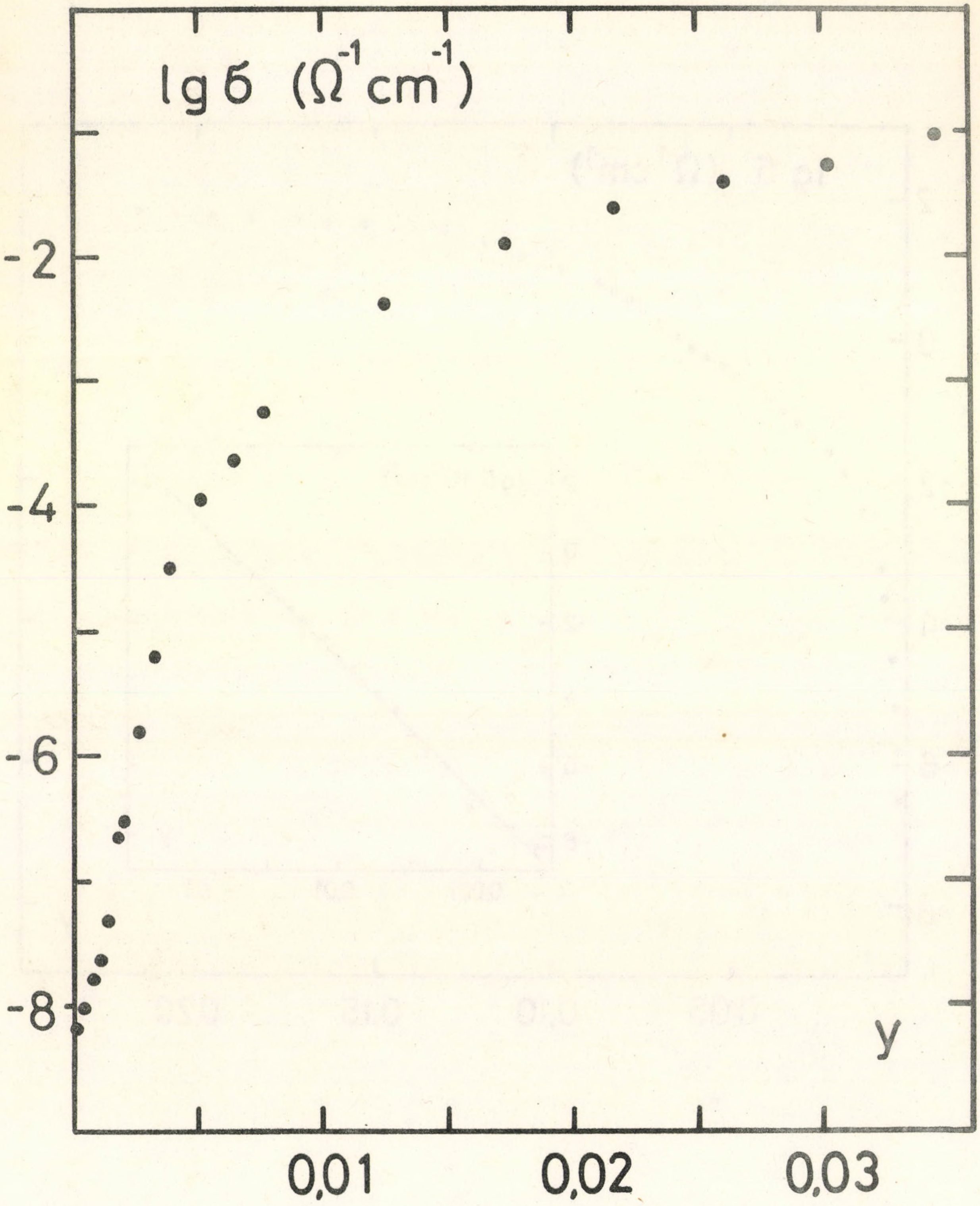
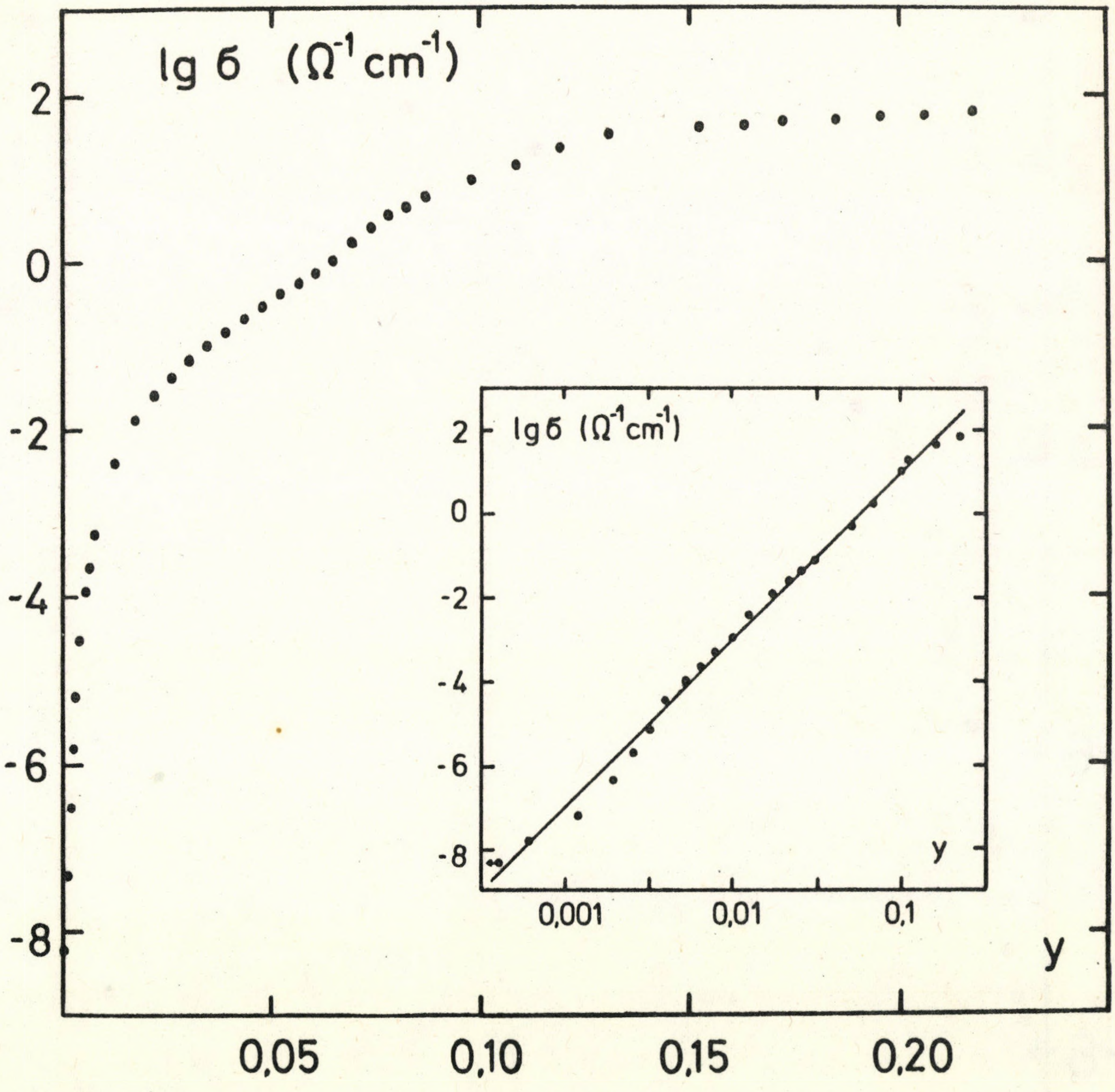


Fig. 1.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-4
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0,10
0,15
0,20
y
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0,001
0,01
0,1
y

Fig. 2.

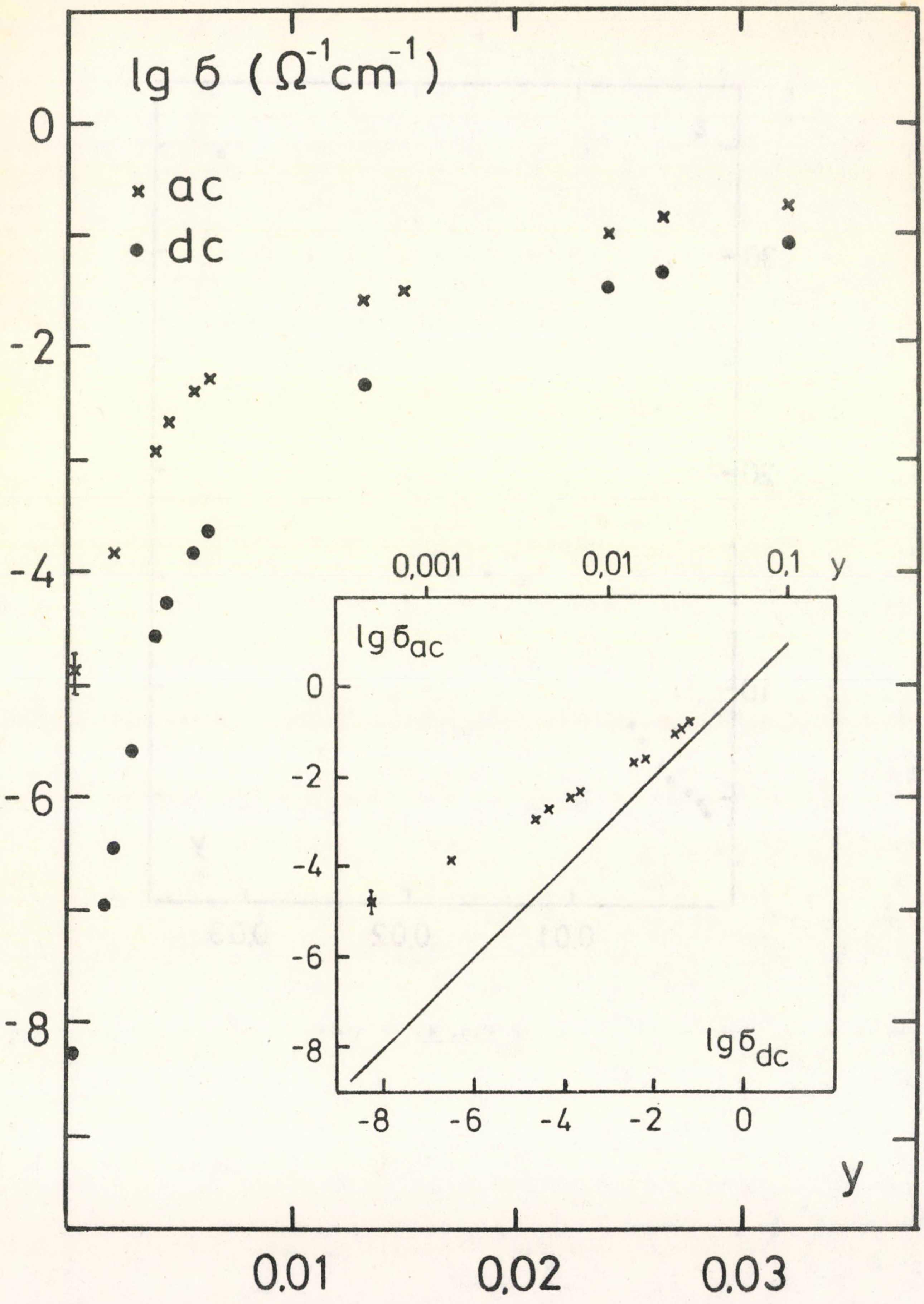
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Fig. 3.

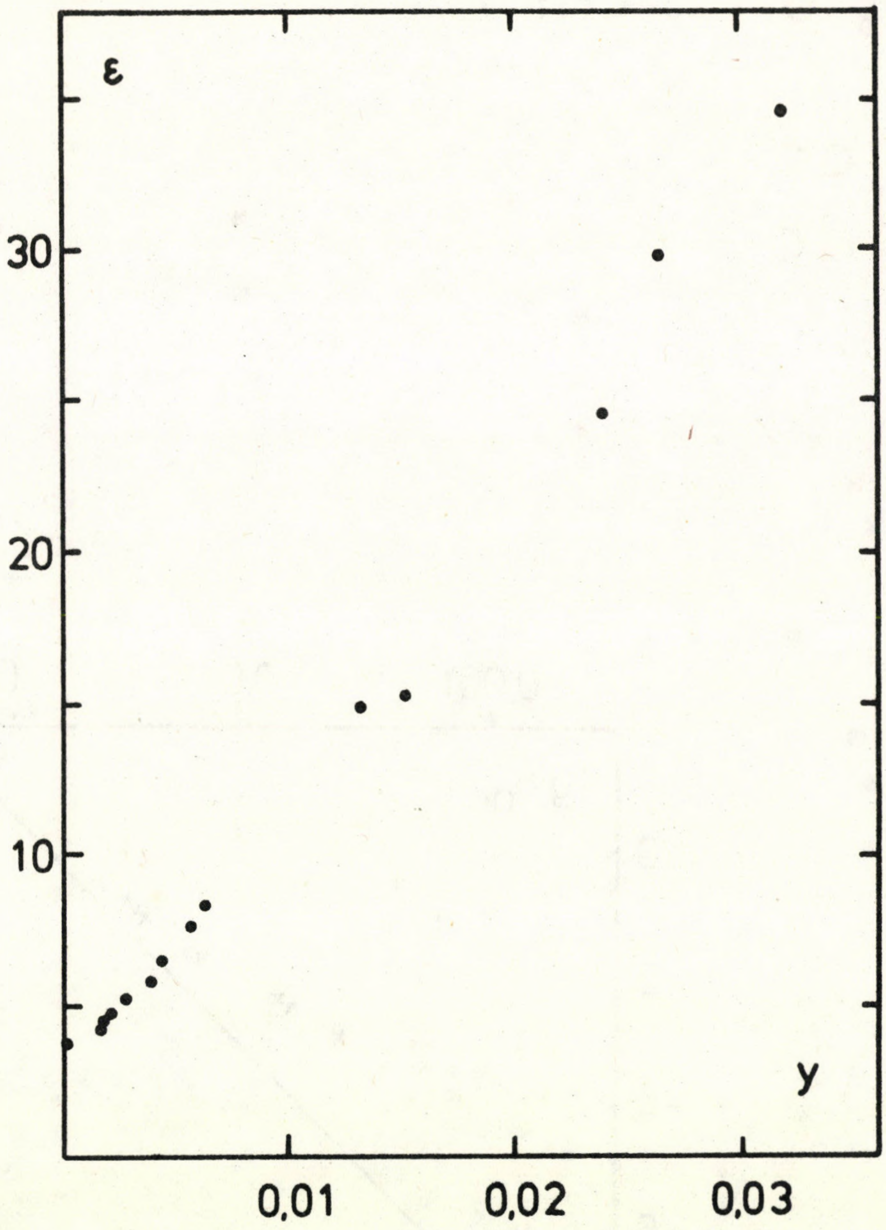

Fig. 4.

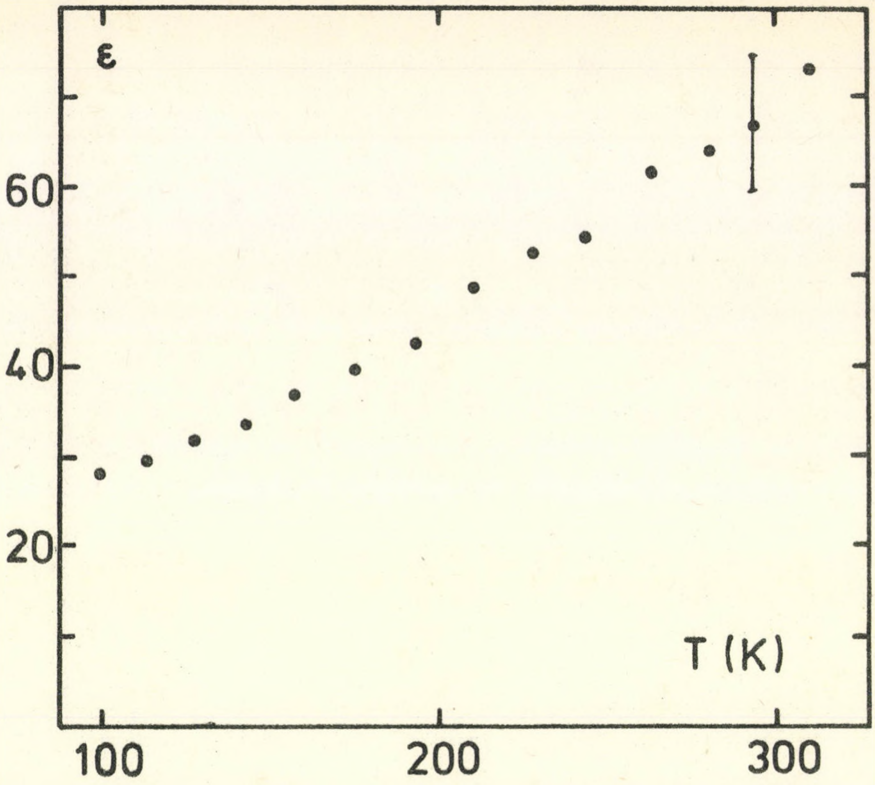

Fig. 5.

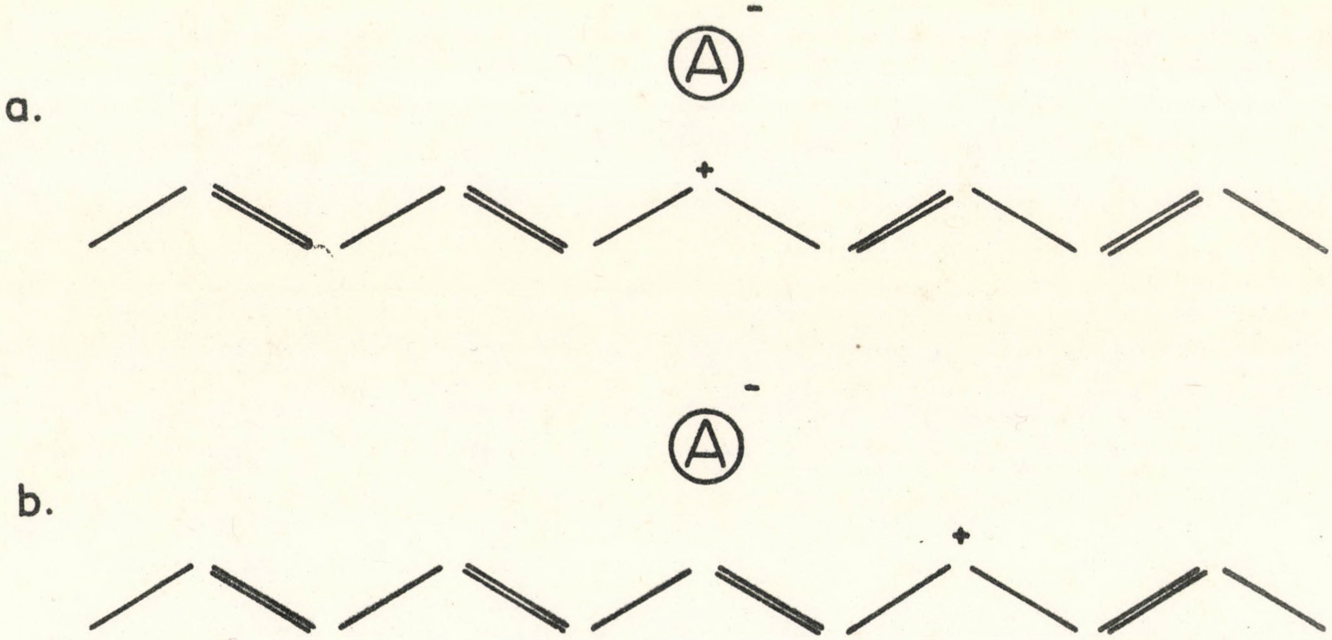

Fig. 6.

Kiadja a Központi Fizikai Kutató Intézet
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