Effect of a weak magnetic field on the electrical conductivity of polyacetylene films

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A decrease in the electrical conductivity of polyacetylene films when an external magnetic field is switched on, saturating in fields $H \gtrsim 100$ Oe, is observed. The effect is explained by the dependence of the hopping probability of current carriers along soliton levels on the spin state of polaron-soliton paramagnetic particle pairs.

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The semiconducting properties of polyacetylene $(CH)_x$ films have been widely studied in recent years. An interest in these properties is attributable to the discovery of a strong dependence of the electrical conductivity of $(CH)_x$ on the donor or acceptor impurities: doping can change it by 12 orders of magnitude.[1] A characteristic of the energy spectrum of states in $(CH)_x$ is the presence of local states, solitons, in the middle of the forbidden band, whose width is 1.5 eV.[2] These states occur as a result of the presence of defects in the structure of polymer molecules, namely, a breakdown of alternation of single and double bonds. The model proposed by Kivelson[3] attributes all of the conductivity of weakly doped $(CH)_x$ to hopping conductivity over the soliton levels. A different conductivity mechanism is described in Ref. 4, wherein it is assumed that electron transitions occur between regions of metallic conductivity formed by doping. In order to clarify the mechanism of conductivity in $(CH)_x$ films, it is necessary to perform experiments that are directly concerned with the motion of current carriers in these films.

In our work we investigated film specimens of $(CH)_x$ obtained by Shirakawa's[5] and Wegner's[6] methods; the experimental results for both types of films were identical. The starting specimens contained $\sim 90\%$ of the cis-isomer of $(CH)_x$. We prepared the specimens on quartz substrates with preliminary deposition of aluminum or tin dioxide electrodes. We measured the electrical conductivity of $(CH)_x$ at constant current using an electrometric amplifier; in so doing the specimens were placed in a vacuum $\sim 10^{-6}$ mm Hg or in an atmosphere of the doping gases (O_2, I_2, NH_3). The specific resistance of the starting specimens at room temperature was 109–1011 Ω cm. The cis-transisomerization due to heating of the specimens in a vacuum at 200 °C for two hours decreased the resistance by two to three orders of magnitude. Placing the specimens in an oxygen or iodine atmosphere increased their conductivity due to doping of $(CH)_x$ by acceptor molecules. The temperature dependence of the conductivity of $(CH)_x$ specimens, weakly doped with iodine, had the form $i \sim T$.[13,7] The results obtained show that the specimens of $(CH)_x$ studied by us have equivalent properties, described in the literature.

We obtained new results while studying the sensitivity of the electrical conductivity of polyacetylene films to an external field. Figure 1 shows the relative change in

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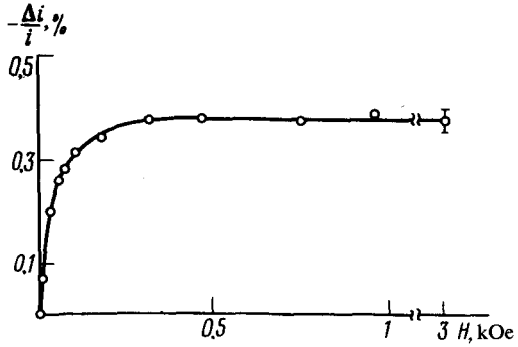


FIG. 1. Dependence of the relative change in current $\Delta i/i$ through a $(CH)_x$ specimen on the magnetic field intensity H. $T = 295$ K.

current through a surface type specimen when a constant magnetic field is switched on, $\Delta i/i = [i(H) - i(0)]/i(0)$, as a function of the magnetic field intensity H. In this case, the current followed Ohm's law; the quantity $\Delta i/i$ (magnetic effect) did not depend on the mutual orientation of the current and magnetic field and on the intensity of the electric field applied to the specimen for fields in the range $(10–3)\times 10^3$ V/cm. The electrical conductivity of the specimens did not change in magnitude for a long time (more than 10^2 h), which indicates the absence of any nonequilibrium processes related to chemical or structural transformations in the specimens. Figure 2 shows the tem-

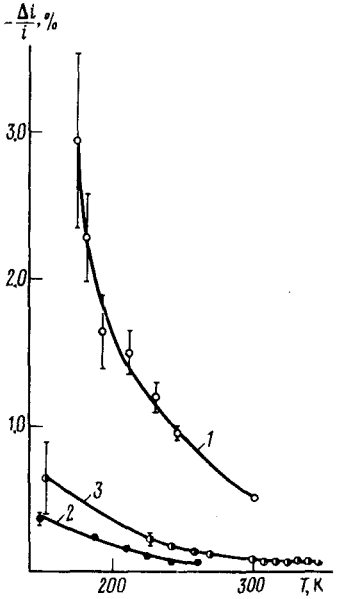
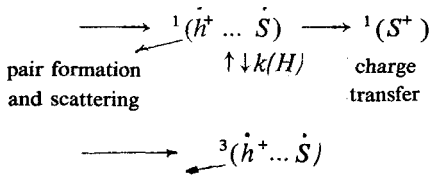


FIG. 2. Temperature dependence of the magnitude of the magnetic effect on the current $\Delta i/i$ measured in a field $H = 2$ kOe on films of starting $(CH)_x$ (10% trans-isomer, $R_{comp} \cong 1\times 10^{11}$ Ω) (1), $(CH)_x$ doped with iodine $R_{comp} \cong 2\times 10^7$ Ω) (2), and isomerized $(CH)_x$ (heating at 73 °C in a vacuum for 2 hours, $R_{comp} \cong 3\times 10^9$ Ω) (3).

perature dependence of $\Delta i/i$ in a saturating magnetic field $H = 2$ kOe for three different specimens of $(CH)_x$: starting specimen (10% trans-cis), isomerized specimen in trans-form, and doped specimen with iodine. For all three specimens the magnitude of the effect increased with decreasing temperature. At a constant temperature the magnetic effect decreases with increasing electrical conductivity of the specimen, irrespective of whether the increase in the electrical conductivity is caused by isomerization or doping. Elimination of the doping acceptor impurity (iodine) when evacuating the specimen or compensating it with a donor impurity (ammonium) led to a reversible increase in the resistance of the specimen and in the magnetic effect on the conductivity. A magnetic effect on the electrical conductivity, whose behavior was analogous to that described above, was also observed on sandwich-type specimens and on surface specimens with a small gap between the electrodes, which, due to injection, have nonlinear current-voltage characteristics of the form $i \sim V^n$, where $1 < n \leqslant 2$. Using a probe method it was shown that the change in electrical conductivity occurs in the entire volume of the specimen and is not related to metal-polymer phenomena occurring on the contact.

For current carriers in polyacetylene having low conductivity ($\mu < 1$ cm^2/V s), the usual magnetoresistance effect in magnetic fields of low intensity is negligibly small ($\Delta\sigma/\sigma \cong 10^{-6}\mu^2 H^2$, where H is in oersteds) and cannot explain the results obtained in our work. However, the dependence of the electrical conductivity of $(CH)_x$ on the external magnetic field and the small acting magnetic fields (Fig. 1) are characteristic for processes involving paramagnetic particle pairs; in addition, the rate of the process depends on the mutual orientation of the particle spins in a pair.[7] This provides a justification for the following explanation of the anomalous effect of the magnetic field on electrical conductivity. One of the mechanisms for charge transfer in $(CH)_x$ is the hopping mechanism. If charge transfer depends on the relative orientation of the spins of the hopping charge $\dot{h}^+$ and of the state $\dot{S}$ to which the hop occurs, then we can expect that the singlet and triplet states will be mixed in the pairs $(\dot{h}^+ \ldots \dot{S})$ if their lifetime is $\sim 10^{-9}$ s. This mixing depends on the hyperfine interaction and on the intensity of the external magnetic field H. Charge transfer on $\dot{S}$ occurs only in the singlet state of such pairs. In polyacetylene the states $\dot{S}$ are apparently paramagnetic solitons, which occur in the polymer in concentrations up to 2×10^{19} cm^{-3}, while the charges $\dot{h}^+$ are holes (polarons), localized near the doping impurity. The following scheme illustrates what we have said:



The second stage of the transfer, just as the magnetically sensitive stage, is the division of the charged soliton S^+ into a pair of paramagnetic particles $\dot{S}$ and $\dot{h}^+$. Charge transfer along the conduction bands competes with the hopping mechanism at room temperature, but at low temperatures the latter mechanism predominates, which increases the magnetic effect (Fig. 2).

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