First observation of a magnetic-resonance change in the resistance of an organic semiconductor (weakly doped polyacetylene)

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The resistance of a polymer semiconductor—weakly doped polyacetylene—has been observed to decrease under the influence of a microwave magnetic field under electron-spin-resonance conditions. The effect is related to a change in the probability for the hopping of an electron in a short-lived pair consisting of two paramagnetic centers while hopping is forbidden in the triplet state of the pair.

Polyacetylene is a polymer semiconductor in which the electrical conductivity is very sensitive to the presence of acceptor or donor impurities. This sensitivity makes it possible to vary the resistivity of the sample from $\rho = 10^{10}$ to 10^{-3} Ω·cm (Refs. 1 and 2). If the doping is weak, i. e., if the number of ligand ions (e.g., I_3^- ions) per -CH- group is small, charge transfer between the ligand and the polymer chain gives rise to charge carriers $\dot{h}^+$, the so-called polarons $\text{-CH=CH-}\overset{+}{\dot{\text{C}}}\text{H-CH-CH=}$. We know that the polymer also contains a large number (up to 2×10^{19} g^{-1}) of neutral paramagnetic centers $\dot{S}$, which are regarded as defects of the electronic structure of the $(\text{CH})_X$ chain and which are described as solitons in the dimerized chain[3] $\text{-CH = CH-}\dot{\text{C}}\text{H-CH = CH-}$. A reversible transfer of charge between the $\dot{h}^+$ and the $\dot{S}$ should be manifested in the electrical conductivity of the sample, because of the relation $\rho \sim \nu^{-1}$, where ν is the frequency of charge hops. It is important to demonstrate this point experimentally, since the conductivity of weakly doped polyacetylene is linked to $\overset{+}{S}$ states: spinless charged solitons. Since the hopping of a charge in the process $\dot{h}^+ + \dot{S} \rightarrow h^0 + \overset{+}{S}$ is allowed by spin conservation only for singlet pairs $^1(\dot{h}^+\dot{S})$, there is the hope that the charge hopping frequency can be changed by changing the spin state of the $(\dot{h}^+\dot{S})$ pair. This would be done by arranging resonant Zeeman transitions to the triplet state of this pair over a time shorter than the spin-lattice relaxation time T_1, as in the method[4] of detecting a magnetic resonance from a change in the yield of reaction products (the RYDMR method).

Plane samples of cis- or trans-$(\text{CH})_X$, fabricated by the method of Ref. 5, with a thickness of about 10 μm and with two aluminum electrodes on one surface, were placed in a quartz ampoule in the resonator of the RYDMR spectrometer. This spectrometer was operated in the X range at room temperature. The samples were doped in the ampoule by admitting iodine vapor. The resistance of the samples was varied over the R range (R is roughly equal to ρ) from 10^9 to 10^4 Ω by means of the doping. The electric circuit containing the sample was a series connection of the sample resistance

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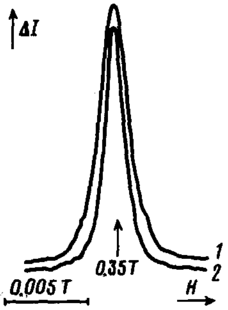

FIG. 1. Spectra of the resonant change in the dark current through a polyacetylene sample at room temperature. 1—Undoped $(CH)_X$ after exposure to air for a month, $R = 3\times 10^8\ \Omega$; 2—trans-$(CH)_X$ weakly doped with iodine, $R = 10^6\ \Omega$.

R, a constant voltage source (0–300 V), and a load resistor ($R_0 = 10^5\ \Omega$). The microwave power was amplitude-modulated at a frequency[1)] of 1300 Hz. A signal from the load resistor R_0 was fed to a narrow-band amplifier and a synchronous detector, from which the output signal was fed to a chart recorder. The alternating component of the current through the sample was sought at the frequency of the modulation of the microwave power under electron-spin-resonance conditions by slowly sweeping the static magnetic field H_0. The magnetic component of the microwave field in the resonator was $H_1 \simeq 1$ Oe. Under these conditions we observed a change in the dark resistance of the sample at the resonance. The relative change in the current through the sample at the resonance was $\gtrsim 10^{-5}$. Figure 1 shows some typical spectra found from the resonant change in the dark current through the sample for various samples. The sign of the effect observed in the current is positive: The electrical conductivity of the samples increases at resonance. Proof that the observed effect is not due to a possible heating of the sample during resonant absorption of microwave power by paramagnetic centers in the sample comes from the following observations: a) When the level of the modulated microwave power was increased in some special experiments, we did in fact observe an increase in the current through the sample, at any field H_0, due to a heating of the sample. In these experiments we observed a slow change in the signal from the load resistor R_0 due to the thermal time constant of the sample, $\tau \simeq 3$ s. When, on the other hand, at the higher microwave power level we rapidly arranged resonance conditions by means of the field H_0, we observed an instantaneous change in the current, which implied a nonthermal nature for the observed resonant change in the electrical conductivity. Under ordinary experimental conditions, at the low microwave power level, the nonresonant absorption caused no changes in the temperature of the sample which were detectable in the current ($\Delta T < 1°$). The line width in the spectrum of the observed effect exceeds the line width in the ordinary ESR spectrum, determined from the absorption microwave power, by 8–10 Oe in the same samples.

Figure 2 shows the energy level diagram of the $(\dot{h}\ ^+\dot{S})$ pair in a magnetic field. This diagram explains the observed effect in terms of the theory of magnetic spin effects.[4,6] The ultimate effect of the microwave field is to change the lifetime of the $(\dot{h}\ ^+\dot{S})$ pair, as can be seen in the change in the mobility (and diffusion coefficient) of the charge

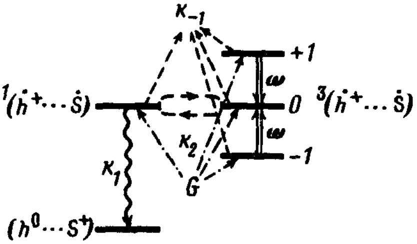

FIG. 2. Resonant transitions in a pair of paramagnetic particles $(\dot{h}^{+}\dot{S})$ in an external magnetic field H_0. The dot-dashed arrows G indicate an equiprobable population of the singlet, $^1(\dot{h}^{+}\dot{S})$, and triplet $^3(\dot{h}^{+}\dot{S})$, states of the pair as a result of random encounters of the $\dot{h}^{+}$ and the $\dot{S}$. k_1—Transition to the purely singlet state $^1(h^0\overset{+}{S})$; k_2—intercombinational transition; k_{-1}—decay of the pair into uncorrelated states $\dot{h}^{+}$ and $\dot{S}$, independent of the spin of the pair.

during its hopping. The magnetically sensitive hops of the charges which occur in the $(\dot{h}^{+}\dot{S})$ pairs are not the only type of hopping. There is apparently also a magnetically insensitive hopping of a charge in the $\dot{h}^{+}h^0$ and $\dot{S}\overset{+}{S}$ pairs. The observed spectra thus demonstrate for the first time that a magnetic-resonance change can occur in the dark resistance of a semiconductor. We attribute this effect to a change in the frequency of the charge hopping in the pairs of paramagnetic particles. The observation of a resonant signal confirms the interpretation of this effect of a static external magnetic field on the resistance of polyacetylene.[6–8] This observation shows that (1) the charge transfer can occur as a result of hopping to paramagnetic centers, (2) one of the states of the pair involved in the charge transfer is a spinless state, and (3) the polarons—the particles carrying the charge and the spin—participate in the current flow through the sample at low doping levels ($10^9 > \rho > 10^5$ Ω·cm). At high doping levels the sensitivity to a magnetic field disappears, apparently because of a competition from charge transfer by other mechanisms, which are insensitive to a magnetic field.

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1)The index of the magnetic modulation of the resistance of the samples was found to increase as the frequency of the external magnetic field was raised to 2 kHz.

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