Spin-1/2 soliton states in crystalline polyacetylene

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Soliton states in polyacetylene crystals have been studied by the ESR method. Analysis of the ESR spectra of crystalline polyacetylene of various modifications suggests that topological and dynamic solitons exist in the system. The dynamic solitons have ESR spectra similar to those found in the adiabatic fast passage of resonance lines. The spin states of doped samples of crystalline polyacetylene have been analyzed. The relationship between the spin states and the number of current carriers in the case of a slight acceptor doping is discussed.

1. INTRODUCTION

Various localized states of the soliton-excitation type can exist in polyacetylene, depending on the dimerization parameter ρ. These may be either neutral topological solitons which separate domains and carry a sign of 1/2 or charged but spinless solitons.[1–4] Numerous attempts have been made to study soliton states by the ESR method.[5–8] Unfortunately, the interpretation of most of these studies has not been unambiguous, as was pointed out in a review by Zhuravleva.[9] The net result is that today we do not have a unified understanding of the nature of the spin resonance in conducting systems of the polyacetylene type. The main reason for the difficulty is the strong influence of impurities and defects of the chains on the shape of the signal and the magnitude of the dynamic magnetic susceptibility $\chi(\pm) = \chi'(\pm) + i_\chi''(\omega)$. A careful isolation of the samples from oxygen does not improve the situation, since this measure does not eliminate the chain defects which arise in the synthesis process. Existing methods are incapable of compensating for these defects.

In crystalline polyacetylene the situation is different. Here there is a long-range order in the packing of the chains when they are relatively long, ~500–1000 Å, so that all the observed effects are quite reproducible (this is the most important point) and independent of the conditions under which the polyacetylene is synthesized.[10] Here, in contrast with polyacetylene synthesized by the Shirakawa method, the classical ESR method is very effective. We have accordingly carried out a study of the topological and dynamic soliton states in polyacetylene crystals by the ESR method, and we have attempted to refine the degree of charge delocalization of these solitons.

Generally speaking, the very structure of polyacetylene allows effective use of the ESR method to determine the charge density carried by a spin-1/2 soliton. If the soliton mobility is low, the shape of the ESR line is determined by the interaction of the soliton with the nuclear magnetic moments of protons; i.e., a hyperfine structure should be seen in the spectra. If the solitons are highly mobile, this hyperfine structure will be washed out, and information about the degree of delocalization of an electron will be contained with the width of the ESR line. Estimates of this type were first made by McConnell[11] for aromatic compounds. Note that during delocalization of an unpaired electron a partial "depairing" of electrons occurs. In this case the projection of the effective electron spin onto the external field has different signs at different sites of the polymer system, while the total splitting is

$$\sum_i |S_i|\ |a_{s_i}|^2,$$

where $|a_{s_i}|^2$ is the charge density, and S_i is the spin density at the sites. In all cases we have

$$\sum_i S_i = 1.$$

Note that the splitting of an ESR line due to protons in the case of immobile radicals is ~22.5 Oe. The effective width ΔH_{eff} of isolated lines with a washed-out hyperfine structure is determined by the number of protons with which the electron interacts. The width of such a line is

$$\Delta H_{\text{eff}} = \Delta H_0 (n-1)^{-1/2},$$

where n is the number of sites among which the electron is delocalized, and $\Delta H_0 = 22.5$ Oe. In the present study we have used these considerations to determine the effective charge of solitons localized at the sites of polyacetylene chains. We have attempted to use the shape of the ESR lines to estimate the velocity of the solitons.

The ESR spectra were measured with the help of RÉ 1306 ($\lambda = 3$ cm) and RÉ 1308 ($\lambda = 0.8$ cm) spectrometers. Measurements of the temperature dependence (carried out in order to determine the activation energy of the spin states) were carried out in a low-temperature attachment with a maximum cooling to 4.2 K.

2. STUDY OF UNDOPED CRYSTALLINE POLYACETYLENE

Let us consider the manifestations of chain defects with a spin $S = 1/2$ in ESR experiments. Such defects should apparently be associated with topological solitons within chains and at their ends. Generally speaking, the shape of the signals will be determined to a large extent by the short-range order in the packing of chains. For crystals of hexagonal and monoclinic modifications, for example, the typical signal would consist of a doublet and a triplet, respectively. The width of the fundamental line would vary from 15 to 22 Oe. In an amorphous modification, an ESR line would always be a singlet with a width of 7–11 Oe. Figure 1 shows some typical spectra. In the monoclinic modification it was also found possible to observe mobile solitons with a charac-

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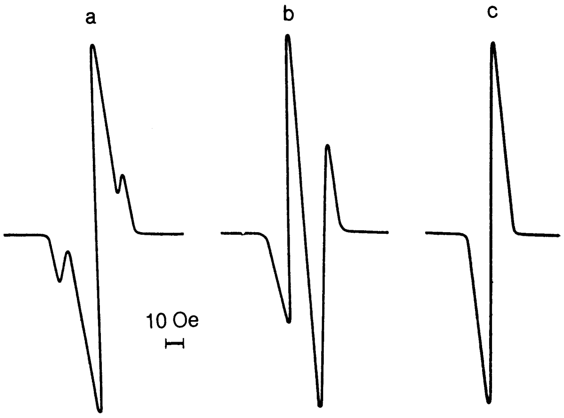

FIG. 1. ESR line shape of crystalline polyacetylene of various modifications: a) monoclinic; b) hexagonal; c) orthorhombic.

teristic linewidth 0.2–1.0 Oe, which corresponds to a very pronounced delocalization of an electron. We will discuss each situation in more detail.

In the monoclinic modification we typically find an ESR spectrum in the form of a triplet, which arises from an interaction of the spin with two protons. This mechanism for the appearance of a triplet is confirmed by an ESR study at a wavelength 0.8 cm, since the splitting remains the same, ~22.5 Oe. Since there is only a single hydrogen atom at each site of the polyacetylene chain, the nature of the triplet must be associated exclusively with solitons with a spin $S = 1/2$ which are fixed at the ends of polyacetylene chains terminating in CH_2 groups. Soliton states of this sort were postulated in studies by Brazovskiĭ[12,13] and are a consequence of a confinement of the bonds in the crystal lattice of polyacetylene. In this case a topological soliton which arises in a chain, e.g., a thermally activated topological soliton, is displaced to the end groups. Pinning of the solitons, however, occurs only if the chain terminates in CH_2 groups. If there is a CH_2 group on one side of the chain, while on the other side there is a CH_3 group, the soliton is pinned only on the side of the CH_2 group. The other soliton "is reflected" from the end of the chain with the CH_3 group; as it moves toward the opposite end of the chain it annihilates with the end soliton, in a process accompanied by the formation of a bond. If there are CH_3 groups at the ends of the chains, the situation is one in which only dynamic solitons exist.

The hexagonal modification of polyacetylene corresponds to a rotation of the chains at the sites of the hexagonal lattice.[4] In the absence of a confinement of bonds, there thus cannot be a displacement of solitons to the ends of the chains, and it becomes possible to observe topological solitons within chains. Information about such states is found from the hyperfine structure involving protons, and the ESR signal is a doublet with a maximum splitting ~23 Oe. The magnitude of the splitting, however, depends on the length and shape of the chains. If, for example, the molecular weight is high, and the chains are in a parallel packing, the splitting is frequently ~16 Oe. Methods for calculating such lines are examined in detail in the monograph by Wertz and Bolton[14] and the paper by McConnell.[11] The distances between the centers of lines calculated on the basis of those recommendations are 16 Oe. A splitting of this magnitude for a proton line corresponds to a slight delocalization of the charge of the electron at a soliton wall. A calculation of the effective charge density by this method shows that the soliton itself carries a charge $\sim(1/3)e$, while the rest of the charge, $(2/3)e$, is "smeared over" the neighboring sites. The number of such sites is $n \geqslant 3$, i.e., as a soliton moves, an unshared electron is delocalized among more than three sites of a polyacetylene chain.

In amorphous polyacetylene the situation is no different from the known situation for polyacetylene synthesized by the Shirakawa method, so there is no point in going into a detailed discussion of the shape of the ESR signal here.

Let us examine the temperature dependence of the number of spin-1/2 states in various modifications of crystalline polyacetylene. For monoclinic polyacetylene the behavior of χ'' as a function of the temperature adheres strictly to the Curie law, providing solid support for the suggestion that solitons are pinned at the ends of chains. In the amorphous modification of polyacetylene the line shape does not change as the temperature is lowered, while the intensity increases slightly. The activation energy W_{1S} in this case is ~0.016 eV. An increase in the number of spins apparently corresponds to a depairing of spins due to a decrease in the number of electrons in the level with an energy W_{1S}; i.e., this energy corresponds to an activation of electrons to a steady-state level and to a compensation for some of the soliton spins through the formation of new states with a zero spin and with a charge equal to the electron charge e. The corresponding temperature dependence is shown in Fig. 2.

A narrowing of an ESR line upon the doping of polyacetylene is regarded as direct evidence for the existence of dynamic solitons with a spin $S = 1/2$ and a zero charge. Estimates show that an electron is localized among 50–100 carbon atoms. Below we consider a different situation, involving the motion of a particle localized at a single site. We will accordingly take a more detailed look at the effect of a moving soliton without a charge but with spin 1/2 on the resonant absorption of a microwave signal in a magnetic field. It is assumed that the spin-lattice relaxation time of the spins is long and that the orientation of a spin does not change as a soliton passes through an individual chain. The concentration of spins is low, and they interact with each other only slightly.

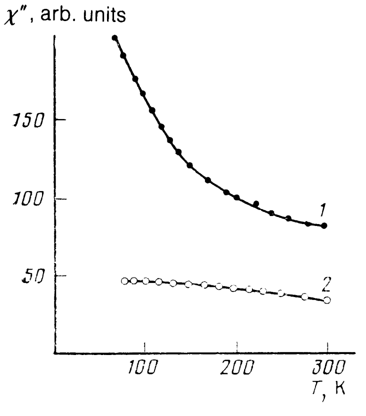

FIG. 2. Temperature dependence of the magnetic susceptibility χ'' in monoclinic (1) and orthorhombic (2) crystalline polyacetylene.

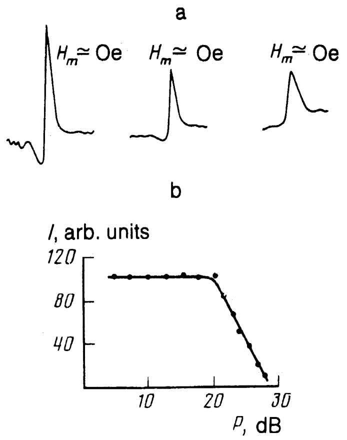

FIG. 3. a—Shape of the ESR signals of crystalline polyacetylene for various amplitudes of the modulating field H_m; b—intensity of the absorption signal I of crystalline polyacetylene versus the power P of the microwave field.

In this situation the behavior of ESR signals is typical of effects associated with the adiabatic passage of resonance lines (Fig. 3). The simplest passage effects for the case of a single spin packet were studied many years ago by Bloch[15]; Bugaĭ[16] carried out research on lines with inhomogeneous broadening. The adiabatic condition for magnetic fields $H = H_0(t) + H_m \cos \omega t$ is satisfied if

$$H_1/\omega_m H_m \ll (T_1 T_2)^{1/2}, \quad \omega_m H_m \ll \gamma H_1^2,$$

where T_1 and T_2 are the spin-lattice and spin-spin relaxation times, H_0 is the static field, H_m and ω_m are the strength and frequency of the modulating field, and H_1 is the microwave field. Denoting by ΔH the width of a spin packet, we see that in the case $H_m > \Delta H$ a change in the field leads to a passage through the resonance, and the particle distribution among spin levels is inverted. Under the condition $H_m < \Delta H$, there is no passage through the resonance. We can thus estimate the width of a spin packet on the basis of the presence of a region in which the signal intensity depends only weakly on H near $H_m \sim \Delta H$. Figure 4 shows a dependence of this type. We find the value $\Delta H \sim 0.2$ Oe, which corresponds to a pronounced delocalization of a spin along a chain as the spin moves in the case of long spin-lattice relaxation times. Taking into account the proton hyperfine structure, ~ 23 Oe, we find that an electron is delocalized among 150–200 carbon atoms. The latter result corresponds to the appearance in the system of spins that interact weakly with acoustic phonons.

In view of the discussion above, we see that the microwave absorption is uniform over the entire range of magnetic fields up to H_0, and that the derivative of the absorbed power has a peak at $H \sim H_0$. Generally speaking, if there is a strong correlation in the orientation of the spins due to an exchange interaction in the polyacetylene chain a magnetostatic soliton mode may arise, and the absorption spectrum itself will have several peaks at fields $H < H_0$, which are determined by the dimensions of the chain.

The ESR signals which are characteristic of adiabatic fast passage and which have the shape described above are always observed in the spectra of the monoclinic modification in very pure samples. The mechanism for the appearance of dynamic solitons in this crystalline modification was discussed above. Experimentally, one usually observes a triplet, which is significantly more intense than the peak of the dynamic-soliton resonance at high microwave power levels. The reason lies in the very rapid saturation of a line due to the long spin-lattice relaxation time ($\sim 10^{-5}$ s; Fig. 3b). Very low amplitudes of the modulation of the magnetic field were accordingly used in order to distinguish and quench the triplet. Figure 3a shows the shapes of the signals during the selection of a dynamic-soliton absorption line.

Let us examine the temperature dependence of the number of dynamic solitons, which we calculate from the area under the absorption curve in the interval $0 < H < H_0$. In these estimates we need to recognize that the peak observed on the differential absorption curve depends on the steepness of the absorption curve at H_0 and on the number of solitons. To distinguish these contributions it is thus necessary to carry out a careful analysis of the shape and width of the peak. Analysis of the widths of the curves at various temperatures indicates a change in the number of solitons due to their scattering. Figure 5 shows the temperature dependence of the areas under the curves; analysis of these results shows that the number of dynamic spin states decreases linearly with increasing temperature and vanishes in the interval 373–423 K. This effect is reversible; a repeated cycling of the temperature dependence reveals that it is reproducible highly accurately. Since the spin-lattice relaxation time for the signal representing adiabatic fast passage depends only weakly on the temperature, the change in the

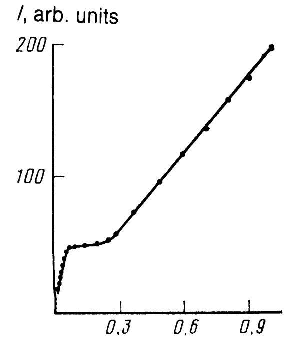

FIG. 4. Intensity I of the absorption signal of crystalline polyacetylene versus the amplitude H_m of the modulating field.

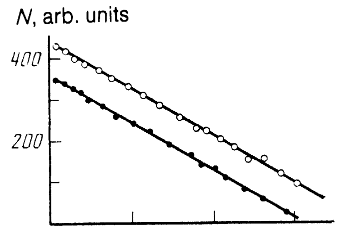

FIG. 5. Temperature dependence of the spin-state density N in monoclinic crystalline polyacetylene for two samples with different degrees of crystallinity.

magnetic susceptibility χ'' cannot be attributed to an interaction of vibrations of the chain and localized spin states. This interpretation would fail to explain the rapid increase in the number of spins with increasing temperature, which amounts to $\sim 3\cdot 10^{17}$ cm^{-3}/deg. On the other hand, no adiabatic-fast-passage signal is observed for the hexagonal modification of crystalline polyacetylene. We can thus attribute the formation of the adiabatic-fast-passage signal to a slight trimerization of the monoclinic modification; i.e., the disappearance of the adiabatic-fast-passage signal is attributed to a polymorphic phase transition of the polyacetylene from the monoclinic modification to the hexagonal modification. This interpretation is also indicated by the suppression of the dynamic-soliton signal by slight acceptor doping, in the course of which the transition of detected by structural methods.

3. ESR STUDY OF SPIN STATES WITH IODINE DOPING

Generally speaking, weak acceptor doping (in our case, with small amounts of iodine) will change only the shape of an ESR signal, regardless of the particular modification of the polyacetylene. For example, the monoclinic modification is characterized in the absence of a dopant by a triplet ESR signal. The addition of iodine erases this triplet and gives rise to a symmetric singlet of width $\Delta H_{pp} \sim 7$–11 Oe. In the absence of a dopant the temperature dependence of the magnetic susceptibility χ'' has two components: χ''_0, which is independent of the temperature, and a component which obeys the Curie law (Fig. 2). With increasing dopant concentration the number of spin states decreases, undergoes an essentially total compensation, and then increases again to a certain maximum which corresponds to one spin per 20–30 carbon atoms. The nature of the $\chi''(T)$ dependence does not differ from that of the original undoped monoclinic polyacetylene. These two components can be attributed to the presence of, on the one hand, immobile radical defects and, on the other, particles which obey Fermi statistics. The component of the magnetic susceptibility associated with the latter particles does not depend on the temperature. However, the relative magnitudes of the two components do depend on the doping level (Fig. 6). Let us examine the behavior of χ'' as a function of the doping level. There are two ways to interpret the decrease in χ'' with increasing iodine concentration: On the one hand, it may be a consequence of a compensation for defects in a chain, but in this case it would be difficult to explain the increase in the number of paramagnetic centers at high iodine concentrations ($\geqslant 40\%$). It is thus more plausible to attribute the temperature-dependent component of the magnetic susceptibility to topological solitons or slightly mobile polarons. The temperature-independent part, χ''_0, is determined by a system of fermions, e.g., solitons with $q = 0$ and $S = 1/2$.

In amorphous polyacetylene the slight constant component of the magnetic susceptibility vanishes as the doping level is raised (Fig. 7), and we are left with only the component which obeys the Curie law. This result indicates, in particular, that a disordered folding of polymer chains rules out the appearance of Fermi particles and leads to a pronounced delocalization of defects.

4. RELATIONSHIP BETWEEN THE SPIN STATES AND THE NUMBER OF CURRENT CARRIERS IN SLIGHTLY DOPED CRYSTALLINE POLYACETYLENE

A serious objection to the soliton model of charge transport in polyacetylene is the lack of a correlation between the number of spins and the number of carriers in doped polyacetylene. A low doping level is of interest here, since polyacetylene behaves as a metal at a high doping level. At a low doping level, an increase in the dopant concentration results in a conversion of spin-carrying neutral solitons into charged defects. In this case the magnetic susceptibility tends to a limiting value which corresponds to one spin per isolated chain if the polyacetylene is not uniformly doped. If the doping is instead uniform, only itinerant electrons contribute to the susceptibility, and the susceptibility is independent of the temperature. Unfortunately, this situation cannot always be arranged since polyacetylene contains numerous structural defects.[8] This is the general situation for polyacetylenes synthesized by the Shirakawa method.

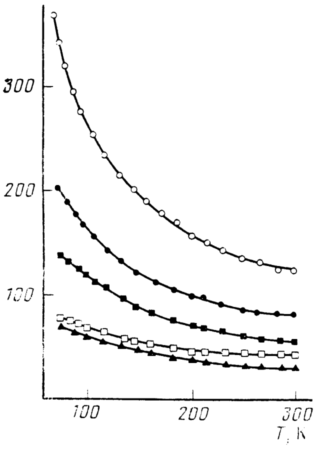

FIG. 6. Temperature dependence of χ'' of monoclinic crystalline polyacetylene at various iodine concentrations: ○—40%; ●—undoped polyacetylene; ■—30%; □—5%; ▲—15%.

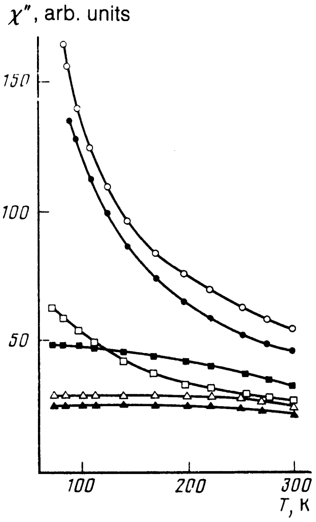

FIG. 7. Temperature dependence of χ'' of orthorhombic crystalline polyacetylene at various iodine concentrations: ○—40%; ●—30%; ■—undoped polyacetylene; □ = 5%; △—1%; ▲—$\lesssim 1\%$.

Let us examine the interrelation between the conductivity and the magnetic properties of polyacetylene crystals. Here, by analogy with the polyacetylene synthesized by the Shirakawa method, the conductivity can range over more than 10–12 orders of magnitude, from $\sigma \sim 10^{-14}\ \Omega^{-1}/\text{cm}$ to $10^{-2}\ \Omega^{-1}/\text{cm}$, depending on the particular dopant. The highest conductivity is reached at molar concentrations of the dopant (e.g., iodine) corresponding to values of 10–12%. A further increase in the dopant concentration results in an instability of the *trans* isomer and its conversion into the *cis* modification, as detected by IR spectroscopy. We will accordingly not discuss dopant concentrations above 12%.

Up to this critical concentration, however, crystalline polyacetylene is a typical semiconductor having an activation mechanism for conductivity. This assertion is illustrated by Fig. 8, which shows $\ln\sigma^{-1}$ versus the reciprocal temperature. For crystals of the monoclinic and hexagonal symmetries the values of the activation energy are 1.3 and 0.8 eV, respectively, at high temperatures. At low temperatures, however, the carrier activation energy is 0.12 eV, independent of the type of crystal. The values 1.3 and 0.8 eV correlate well with the size of the optical gap, found from the absorption spectra; these gaps are 2.6 and 1.8 eV for the monoclinic and hexagonal polyacetylene, respectively.[10] In Shirakawa polyacetylene the carrier activation energy is 0.3 eV at a low doping level and does not correlate with the size of the energy gap found from optical measurements, 1.6 eV.

We have already discussed the situation with a high dopant concentration. In this case the high-frequency magnetic susceptibility consists of two components: one which is independent of the temperature and one which obeys a Curie law. The T-dependent component is determined by the doping level and is apparently a contribution from polarons localized near I_3^- anions. The linewidth determines the degree of delocalization of this polaron, which ranges from 3 to 10 carbon atoms. These polarons, however, apparently do not contribute strongly to the conductivity, since their number does not change with the temperature and is affected only by the doping level. Also independent of the temperature is the degree of delocalization of the spins.

A correlation between the number of spins and the conductivity was first detected in crystalline polyacetylene at a low dopant concentration, below 1%. In this situation the magnetic susceptibility obeys an activation law with an activation energy ~0.12 eV (Fig. 8). Analysis of the results in Fig. 8 shows that localized states with an energy of 0.12 eV are indeed neutralized at temperatures below 200 K. Above this temperature, however, we find the usual activation-law conductivity, similar to that of a semiconductor. Although the activation of neutral spin states at temperatures above 200 K does occur, it does not determine the nature of the conductivity. This result leads to an explanation of the nature of the current carriers in crystalline polyacetylene at low temperatures. The "inversion" of the number of carriers and the number of spins which we described above can occur only if the carriers corresponding to the 0.12-eV level have a charge $+e$. Only the randomization of localized states of this sort would lead to neutral localized states with a spin 1/2. These states, however, are not mobile since the ESR linewidth is ~7–8 Oe, i.e., the properties of these states are similar to those of kinks.

In addition to the transitions with energies 0.8 and 0.12 eV there can be a transition with energy 0.68 eV. Accordingly, at temperatures at which the conductivity regime changes the W_{2S} level can be filled and additional localized states can be actively formed. These events occur in a very narrow transition region, and the mobility of the solitons increases sharply, leading to a narrowing of the ESR line (see the inset in Fig. 8). The degree of delocalization of the spins reaches 50–60 carbon atoms. At low temperatures, however, only states with a low soliton mobility are realized.

5. CONCLUSION

Of primary interest in a study of crystalline polyacetylene are states with spin $S = 1/2$ and $q = 0$, and the role played by states with $S = 0$ and $q = \pm e$ in the electrical conductivity. A correspondence is observed between the shape of the ESR signals and the crystalline structure: For the monoclinic structure, there is characteristically a triplet, for the hexagonal structure a doublet, and for the amorphous modification a singlet. What is the reason for this? The strong bond confinement in polyacetylene crystals rules out the existence of solitons in a chain. Immediately after a soliton and an antisoliton appear, they either annihilate or

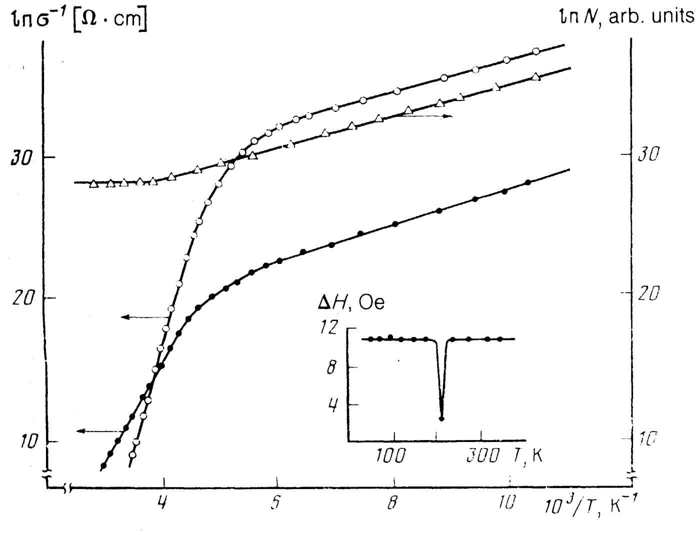

FIG. 8. Spin-state density and $\ln\sigma^{-1}$ versus the reciprocal temperature. ○, △—Monoclinic modification; ●—hexagonal modification. The inset shows the temperature dependence of the ESR linewidth.

are displaced to a boundary of the chain, in a process accompanied by the formation of end solitons. The latter are stable if the number of atoms in the polyacetylene chain is even, or unstable if it is odd. The observed triplet thus corresponds to a localization of a spin at a CH_2 end group. In the hexagonal modification the presence of the doublet corresponds to a pronounced localization of a soliton at a site, and a splitting occurs in the field of a single proton of a CH group. When the spin-lattice relaxation times are long, it is possible to observe a signal whose derivative has a single peak; this can be interpreted as absorption of microwave power by moving solitons with spin $S = 1/2$. A similar absorption occurs during passage effects in two-level systems.[15,16] For that case, however, the sign of the derivative depends on the direction in which the field is scanned.

In crystalline polyacetylene doped lightly with iodine we have managed to observe, for the first time, a correlation between the number of spins and the number of carriers. This result is evidence of a correct choice of the soliton model for this temperature range. At high temperatures, however, polyacetylene is similar to a semiconductor with a band gap ~ 1.3 or 0.8 eV for the monoclinic or hexagonal modification, respectively.

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