

# Dynamic solitons with a spin $S = 1/2$ and zero charge in a crystalline polyacetylene

A. N. Chuvyrov, L. A. Kosykh, and G. V. Leplyanin

*Physics and Mathematics Division, Bashkir Branch of the Academy of Sciences of the USSR, Ufa*

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The presence of dynamic soliton states characterized by a spin of  $1/2$  and zero charge in a crystalline polyacetylene is reported.

In the case of polyacetylene (PA) various soliton-excitation type localized states are known to be possible, depending on the dimerization parameter  $\rho$ . The ESR method has been used extensively to study the soliton states.<sup>1-4</sup> There has unfortunately been no unanimity in interpreting most of the results of these studies,<sup>5</sup> principally because of the strong effect of impurities and chain defects on the signal shape and the dynamic susceptibility. Insulating the samples from oxygen does not improve the situation, since this measure does not eliminate the chain defects that arise during the synthesis. The situation is different in crystalline polyacetylene: In contrast with polyacetylene, which was obtained on the basis of Shirakawa's method, the chain arrangement of crystalline polyacetylene has long-range order and the degree of structure imperfection in it is low. As a result, the ESR method can be used effectively to study the topological and dynamic soliton states in polyacetylene crystals. Our goal was to study the dynamic soliton states with a spin  $S = 1/2$  and zero charge in crystalline polyacetylene.

The ESR spectra were measured with a PÉ-1306 spectrometer with a wavelength  $\lambda = 3$  and with a digital scanning of the magnetic field. The temperature measurements to determine the activation energy of the spin states were carried out using a low-temperature attachment cooled down to 4.2 K.

The narrowing of the ESR line as a result of PA doping is direct proof that dynamic solitons with a spin  $S = 1/2$  and zero charge exist. Estimates show the degree of electron delocalization at 50–100 carbon atoms. We will consider below a different situation, in which the particle localized at one site is in motion. Let us therefore consider in more detail 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. We assume that the spin-lattice relaxation time of the spin is long and that the spin orientation of a soliton during the time it takes the soliton to pass through a single chain remains constant. The spin density is low and the spins interact with each other slightly. The behavior of the ESR signals in this case is typical of the adiabatic crossing of resonance lines. A simple crossing of a single spin packet was considered by Bloch.<sup>6</sup> Bugaï<sup>7</sup> considered the same situation in the case of nonuniform line broadening. The condition for the adiabatic state in magnetic fields  $H = H_0(t) + H_m \cos(\omega_m t)$  is satisfied when

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

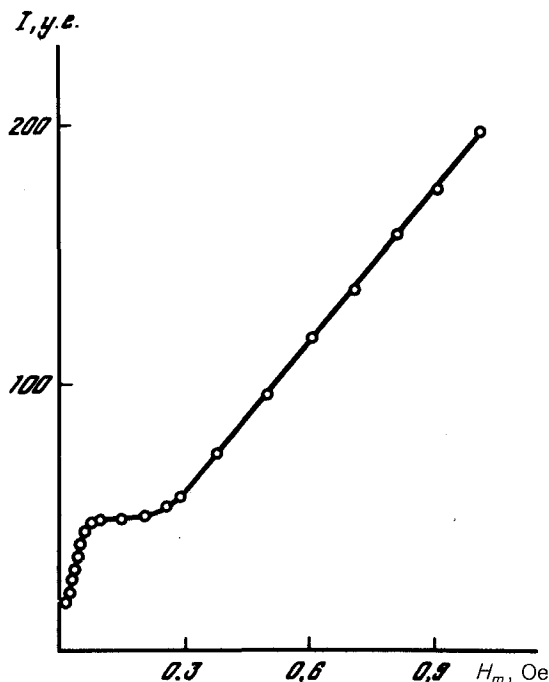


FIG. 1. Intensity of the absorption signal,  $I$ , of crystalline polyacetylene versus the amplitude of the modulating field  $H_m$ .

where  $T_1$  and  $T_2$  are the spin-lattice and spin-spin relaxation times,  $H_0$  is the static field,  $H_m$  and  $\omega_m$  are the magnitude and frequency of the modulating field, and  $H_1$  is the microwave field. If the width of the spin packet is  $\Delta H$ , a change in the field at  $H_m > \Delta H$  causes a crossing of the resonance and the particle distribution over the spin levels is reversed. When  $H_m < \Delta H$ , there is no crossing of the resonance. This behavior allows us to estimate the width of the spin packet from the weak  $H$  dependence of the signal near  $H_m \sim \Delta H$ . This dependence is illustrated in Fig. 1, from which we see that  $\Delta H \sim 0.2$  Oe. This corresponds to a strong delocalization of the spin along the chain, which moves if the spin-lattice relaxation time is long,  $T_1 \sim 10^{-4}$  s. Since proton hfs is  $\sim 23$  Oe, the delocalization is equal to 150–200 carbon atoms. The latter situation corresponds to the appearance in the system of weakly interacting spins with acoustic phonons.

Taking the foregoing arguments into account, we see that microwave absorption is uniform over the entire range of magnetic fields to  $H_0$  and that the derivative of the absorbed power has a peak in fields  $H \sim H_0$ . In general, if there is a strong correlation of spin orientations due to the exchange interaction, a polyacetylene chain may generate a magnetostatic soliton mode and the absorption spectrum will have several peaks at  $H < H_0$  which are governed by the chain size.

The ESR lines with the shape described above are always observed in the spectra of a monoclinic modification in very pure samples. The mechanism for the appearance of dynamic solitons in this crystal modification was discussed above. A triplet can generally be observed experimentally. At high microwave power levels this triplet is

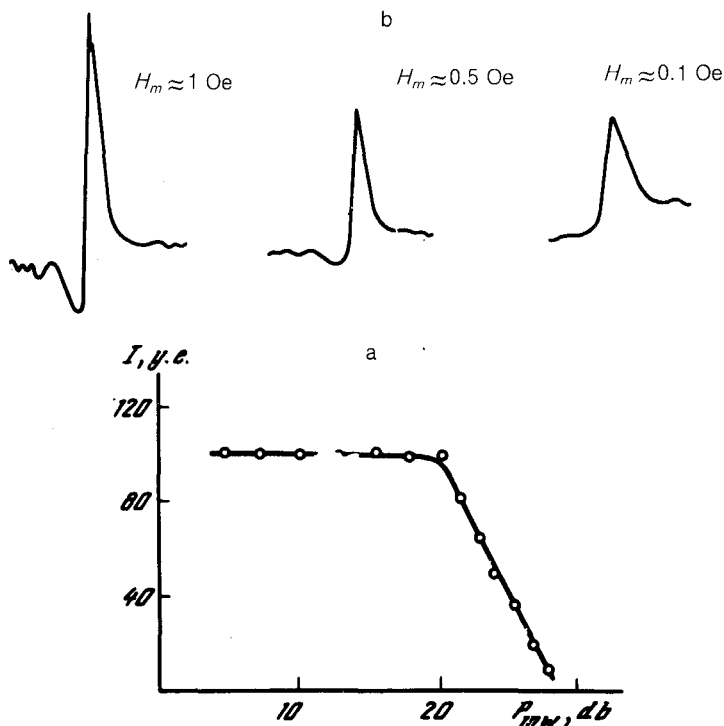


FIG. 2. (a) Intensity of the absorption signal,  $I$ , of the crystalline polyacetylene versus the microwave field power level,  $P_{mw}$ ; (b) shape of the ESR signals of crystalline polyacetylene versus the amplitude of the modulating field,  $H_m$ .

much more intense than the dynamic-soliton resonance peak because of the very fast saturation of the line due to the long ( $\sim 10^{-4}$  s) spin-lattice relaxation time (Fig. 2a). To isolate and suppress the triplet, we have accordingly used very small modulation amplitudes of the magnetic field. The signal shape of an isolated dynamic-soliton absorption line is shown in Fig. 2b.

Let us consider the temperature dependence of the dynamic solitons which was calculated from the area under the absorption curve in the interval  $0 < H < H_0$ . In such estimates it is essential to take into account that the peak on the differential absorption curve depends on the slope of the absorption curve at  $H_0$  and on the number of solitons. To distinguish between these contributions, we must therefore thoroughly analyze the shape and width of the peak. Analysis of the width of the peaks at various temperatures shows that the number of solitons changes as a result of scattering. The temperature dependences of the areas under the curves are shown in Fig. 3. It follows from the analysis of these curves that the number of dynamic spin states changes linearly with increasing temperature and they vanish at temperatures 373–423 K. This effect is reversible: Multiple cycling of the temperature dependences makes it possible to reproduce them very accurately. Since the variation in the number of centers, say, as a result of a one-degree change in temperature amounts to  $3 \times 10^{17} \text{ cm}^{-3}$ , it cannot

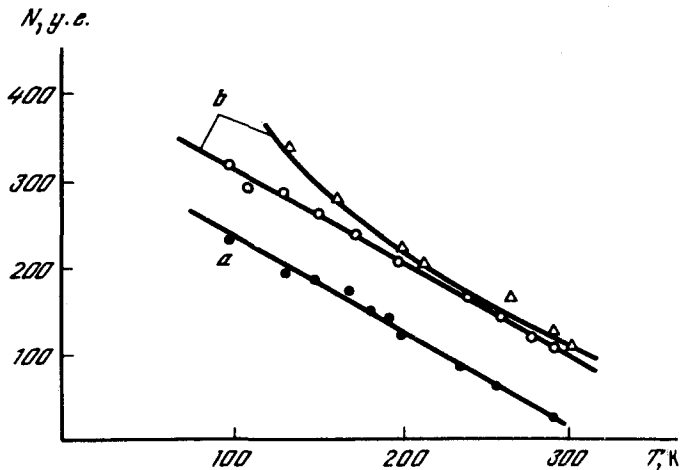


FIG. 3. Temperature dependence of the spin state density,  $N$ , of crystalline polyacetylene of (a) monoclinic modification and (b) hexagonal modification.

be explained strictly in terms of linear interaction of the spins with the lattice vibrations of the chain. The nature of the ESR signal clearly can be found from the change in the ESR line shape: Above the transition point and the point at which the dynamic soliton absorption signal disappears the topological-soliton signal has the shape of a doublet. The latter result is attributable to the formation of a hexagonal phase. In other words, the nature of  $T_c$  is determined exclusively by the structural transition in the case of chain retardation in the monoclinic or orthorhombic polyacetylene modification. The suppression of the dynamic-soliton signal due to a slight doping, at which the transition indicated above is detected by the structural methods, also points to this conclusion.

Experiments in which a very slight doping is introduced before the transition to the hexagonal modification have made it possible to observe a strong exchange interaction and the appearance of a magnetostatic mode at low temperatures. The study of this mode is, however, of interest in itself. For this reason, it has not been considered in this study.

<sup>1</sup>M. Nechtschein, F. Devreux, M. Guglielmi, and K. Holczer, *Phys. Rev.* **B27**, 61 (1983).

<sup>2</sup>N. Kinoshita, M. Tokumoto, and H. Shirakawa, *Mol. Cryst.* **83**, 1099 (1982).

<sup>3</sup>K. Holczer, J. P. Boucher, F. Devreux, and M. Nechtschein, *Phys. Rev.* **B23**, 1051 (1981).

<sup>4</sup>P. Bernier, M. Rolland, C. Linaya, and M. Disi, *Polymer* **21**, 7 (1980).

<sup>5</sup>T. S. Zhuravleva, *Usp. Khimii* **56**, 128 (1987).

<sup>6</sup>F. Bloch, *Phys. Rev.* **70**, 460 (1946).

<sup>7</sup>A. A. Bugaï, *Fiz. Tverd. Tela* **4**, 11 (1962) (sic).

Translated by S. J. Amoretty