Crystalline polyacetylene: Structure, optical properties and photo-induced spin states

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We report on the successful growth of crystalline polyacetylene $(CH)_x$ in three crystal forms, possessing rhombic, hexagonal and monoclinic symmetries, in which the number of chains $x \approx 10^4–10^5$. We measured gaps in the optical spectrum with energies $\Delta_S \approx 2.2$ and 1.7 eV. We find that the spin state with charge equal to one electron charge and spin $S = 1/2$ can occur only in crystalline polyacetylene.

Interest in one-dimensional systems like polyacetylene (PA) centers on the possibility of observing unusual relationships between spin and charge in such systems, as predicted by the soliton model.[1–3] In crystalline polyacetylene, depending on its degree of alloying, it is possible to observe a multiplicity of different effects connected with electronic excitations.[1–6] When the PA crystal ground state is degenerate, excited electronic states are found to be either charged and spinless or uncharged with spins 0, ± 1. However, in the absence of this degeneracy, the dominant excited states of PA are similar to strong-coupled polaron states. With spin $S = 1/2$ and charge equal to the electron charge e; a description of these states is best given in terms of the Peierls model.[4,5] In this system, the fundamental quantity is the interaction of π-electrons with the PA lattice deformation, which consists of distinct contributions from the polymer skeleton Δ_e and the spontaneous molecular deformation Δ_i.[5] Because of this, it is possible to verify the conclusions of Refs. 4, 5 by investigating both the characteristics of individual polyene molecules and the structures of crystals formed from these molecules. In the present report we will discuss the results of such investigations of the properties of crystalline polyacetylene, along with the structure of individual polyene molecules for PA chains with up to 10^5 elementary (–CH–) links.

EXPERIMENTAL METHODS

(a) Method of obtaining crystalline polyacetylene

The standard method of obtaining crystalline polyacetylene is based on the process of epitaxial orientation of PA molecules at the surface of a solution of potassium hydroxide (KOH) in the presence of dehydroxylated polyvinyl chloride (PVC), mediated by liquid catalysts. Examples of catalysts and solvents for PVC are described e.g., in Ref. 7. The mechanism of the crystallization process can be described as follows: molecules of PVC exist in solution in the form of coils of dimensions 500–800 Å; upon approaching the surface of the KOH, these molecules are dehydroxylated in the presence of the catalyst, forming rigid one-dimensional chains of PA. When a critical concentration of chains is attained at the phase boundary, crystals of PA form spontaneously in various polymorphic modifications. The maximum size of the crystals is 2–3 mm. The geometric structure of these modifications corresponds to optically uniaxial hexagonal crystals, along with optically biaxial crystals of rhombic and monoclinic symmetries. We note that use of the technique of interphase dehydroxylation of PVC molecules makes it possible to synthesize crystals consisting only of trans-isomers, whereas in the case of fully-mixed phases, notably for molecules of PVC catalyzed in KOH solution, there is no such constraint. Thus, the synthesis of PA as described in Ref. 7 makes it possible to obtain a mixture of isomers and, as a rule, results in a polymer with amorphous structure.

To compare properties of PA crystals and individual polyene molecules, we used polyenes precipitated chromatographically from heavy residues of cracking oils, or obtained by thermal dehydroxylation of PVC. The molecular mass of these polyenes is about 1600, corresponding to ~100 (–CH) links.

(b) Method of investigating the structure of PA crystals

The structure of crystals obtained by the above methods was investigated by conventional electron-diffraction techniques.[8] The monoclinic crystals were high quality, and their dimensions were suitable for electro-optic measurements; this allowed us to use the method of Kikuchi patterns, which yields an unambiguous result for the Peierls dimerization in the ground state ($\rho = 1$) of PA, that is, it revealed the presence of alternating single and double molecular bonds in this state. The appearance of the Kikuchi patterns is explained by effects due to multiple scattering of electrons. In contrast to traditional Bragg reflection, this phenomenon involves second-order diffraction, in which each reflection gives rise to a pair of Kikuchi lines hkl and $\bar{h}\overline{kl}$, whose intensities depend on crystallinity. From the spacing between parallel dark and light Kikuchi lines, we identify the hkl reflection with the help of the relation $h_i = 2\theta_i k$, where h_i is the spacing between lines, θ_i is the Bragg angle, and k is a constant of the measuring device. The symmetries of Kikuchi lines allows the most precise determination of crystal symmetry, since the two symmetries coincide as a rule; the sharpness of the Kikuchi lines makes it possible to determine with high accuracy the crystal parameters (up to 0.01 Å) and angular orientations (~0.1°) of the crystal. Because Kikuchi patterns contain components due to all the reflection planes, they can be used directly to set up a stereographic projection corresponding to the crystal, i.e., to the stacking pattern of

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PA chains. We note here that using this technique to investigate PA crystals with hexagonal symmetry does not yield good results, since the usual (first-order) Bragg diffraction turns out to be the dominant effect; this is because of the large number of defects in that particular modification of crystalline PA.

(c) Method of investigating optical properties of PA

Our basic approach to determining the optical characteristics of PA was implemented using an "Amplival Pol. U" microscope, equipped with a photometric attachment with an engraved microsonde which was capable of studying sections of monocrystals of diameters up to 10 microns; this instrument allowed us to make measurements in the 200–800 nanometer wavelength band both for transmitted and reflected light. For the reflection etalon we used the standard aluminum-silicon-aluminum oxide configuration.

In order to study the absorption coefficient and index of refraction, we used a polarization interferometer, a Mach-Zehnder interferometer and an ellipsometer. The polarization interferometer was built around a Berek compensator operating between 0 and 6 λ and between 0 and 130 λ, while the ellipsometer, also mounted on the base of the "Amplival Pol. U." microscope, was equipped with achromatic layers with wavelength-independent optical path differences. Our method of calculating the anisotropy in the index of refraction and absorption coefficient was similar to standard methods.[9] For determining the absolute value of the index of refraction, we used a Mach-Zehnder "Interpako" interferometer in this work.[10] At the same time, the construction of this interferometer provided us with an analysis of the display of the section under study, with the help of the microscope. The minimum value of the index of refraction that could be determined by this method was 10^{-7}. To study the anisotropy of the absorption coefficient of polyene molecules, we oriented them in a liquid-crystal matrix, taking advantage of the "guest-host" effect.[11]

(d) Methods for investigating the kinetics of the spin states

In the present work we have investigated the kinetics of the spin states excited by light of various wavelengths, as a function of illumination time and for various donor (I_2) concentrations in crystalline PA. The spin states, in particular the number of spins and the size of the g-factor, were analyzed by using an RE1306 radio-spectrometer. In order to photo-excite electrons we used an LT-IPCh-8 YAG laser running quasi-CW, at a power of 60 kW and at a single-mode wavelength of 1.06 microns. A lithium niobate element was used to convert the frequency of the output radiation to 532 nanometers. The laser emission repetition rate was synchronized with the frequency of a low-frequency (50 Hz modulation of the signal from an EPR spectrometer. Samples of polyacetylene were placed in a Dewar and cooled to 77 K. We note that it was the use of this powerful laser for illuminating PA which enabled us to observe the various effects which were predicted in the work of Brazovski and Kirova.[4]

STRUCTURE OF CRYSTALLINE PA

Detailed investigations using X-ray structural analysis, micro-electron diffraction and small-angle scatter of X-rays indicate, in agreement with optical polarization investigations, that there are three symmetry classes of PA crystal: hexagonal, rhombic and monoclinic. A typical electron-diffraction pattern which illustrates this conclusion is shown in Fig. 1. The assumed structures, taking into account the van der Waals radii of the atoms corrsponding to hexagonal and rhombic crystals, are displayed in Figs. 1b, 1d. The multiplicity of structures is present only if we "pin" the rotation of molecules in their hexagonal stacking. This stacking pattern increases the intermolecular spacing up to 5.2 Å and can be obtained by introducing impurities, e.g., potassium ions, into the monoclinic crystal form. In this case, the detailed nature of the "pinning" mechanism of the molecular states remains obscure; however, it can be viewed as an average static orientation of the PA molecules due to rotation of the different $(-\mathrm{CH}-)_y$ links with $y \geqslant 1$ around their equilibrium positions.

The structural layout for monoclinic crystals is shown in Fig. 1f. Its distinctive feature is that molecules of PA lie in parallel regions spaced at a distance of about 3.4 Å. However, the spacing between axes of molecules lying in one plane is also 3.4 Å. This number is 0.2 Å smaller than that

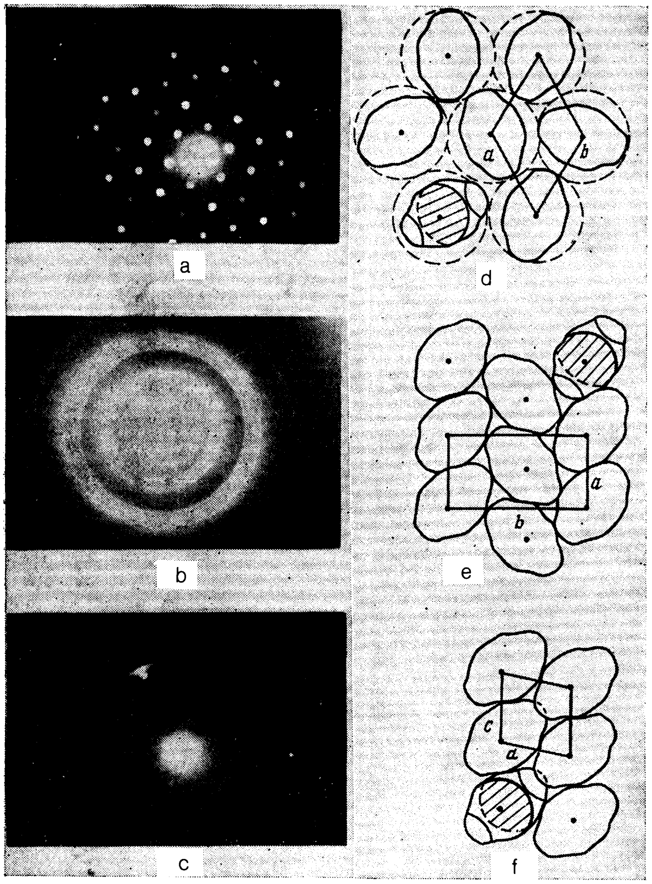

FIG. 1. Structural layout (b, d, f) and electron diffraction pattern (a, c, e) of polyacetylene for various crystal modifications: a, b are hexagonal with a = b = 5.2 Å, c = 2.52 Å; c, d are rhombic with a = 4.0 Å, b = 7.9 Å; e, f are monoclinic with Kikuchi lines: a = c = 3.9 Å, b = 2.52 Å.

calculated from the values of the van der Waals radii of the atoms of carbon and hydrogen, and indicates the presence of an exchange interaction between molecules in neighboring lattice sites. The existence of such an interaction leads to the formation of a perfect, defectless crystal structure which is characterized by the presence of Kikuchi lines in the electron-diffraction pattern (Fig. 1e).

An answer to the question of what is the periodicity of the PA crystals along the *c*-axis parallel to the PA molecules was obtained from small-angle X-ray experiments. Here it was established that both polymorphic modifications of PA are made up of stiff chains of molecules with a length greater than 10^3 Å. However, we have not succeeded in establishing whether the dimensions of sections of PA chains coincide with those of the original PVC molecules ($\sim 10^{-4}$ cm), or whether "folds" occur in the trans-isomer links in the structures under study.

A more detailed analysis of the electron-diffraction patterns of the various modifications of PA allows us to address the question of the presence of alternating bonds. In the absence of impurities, the periodicity of crystals along the molecular axis (perpendicular to the planes of Figs. 1b, 1d and 1f) for all the modifications was about 2.52 Å. Introducing iodine impurities or doping with potassium increases this value to 2.61 Å, which can be related to the destruction of the Peierls dielectric.

We point out that in the polyene compounds precipitated from cracking residues of oils or from thermo-dehydroxylation of polyvinyl chloride, we observe only two structural modifications of the crystal, namely the rhombic and hexagonal, where the second predominates in low-purity samples. Removal of impurities in the form of light hydrocarbons by thermal cracking results in fine crystals (300–500 Å) with rhombic symmetry.

OPTICAL PROPERTIES OF CRYSTALLINE POLYACETYLENE

In investigating the properties of conducting polymers, an important role is played by the effects of absorption and refraction of light for various electron concentrations.[12] A general theoretical calculation of the optical constants of these materials was performed by Brazovski and Matveenko.[13] In their original states, the crystals described above are Peierls dielectrics with a specific resistivity of up to 10^{14} ohm-cm, in which the number of electrons ρ coincides with the number of carbon atoms ($\rho = 1$). Alloying them with iodine allows one to change the electron concentration within broad limits and to decrease the specific resistivity down to 1–10 ohm-cm. Thus, it is possible to test the basic conclusions presented in the work of Brazovski and Matveenko;[13] we have carried out such tests in the present work.

Let us examine the basic properties of the changes in absorption and index of refraction of PA for the various crystal modifications, and compare them to properties of individual polyene molecules. We will not discuss the monoclinic crystal form in any depth, because its small dimensions (no larger than 10 microns) preclude a detailed investigation of its optical constants. We remark only that maximum absorption of light for this form occurs in the wavelength region 650–700 nanometers (2–1.8 eV), while the absolute value of the absorption amounts to 3×10^4 cm^{-1}.

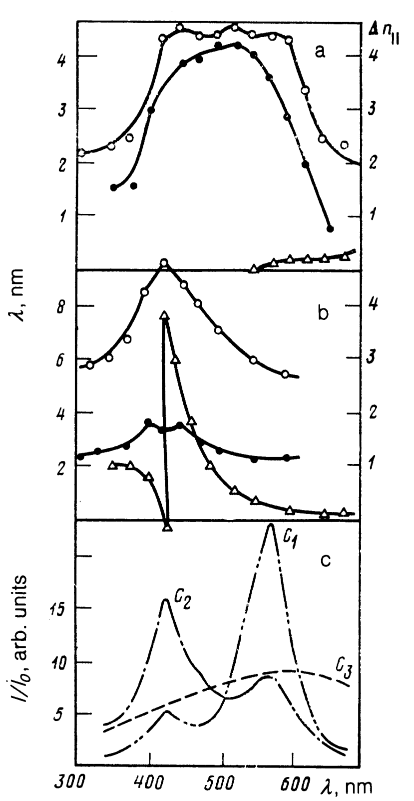

FIG. 2. Dispersion dependence of the absorption coefficient (○, ●) and index of refraction (△) for the rhombic (a) and hexagonal (b) modifications of polyacetylene; for orientation of the plane of polarization along (○, △) and perpendicular (●) to the PA chains. Graph (c) shows the change in the absorption spectrum of polyacetylene when it is doped with iodine for various concentrations of the latter: $C_1 \approx 0.1\%$, $C_2 \approx 1\%$, $C_3 \approx 5\%$.

A typical absorption spectrum and characteristic variation in index of refraction for the rhombic crystal form is shown in Fig. 2a. Apparently, the dependence of absorption on wavelength has three weakly-resolved maxima when the plane of polarization of the light waves is oriented along the long axis of the molecules. The characteristic variation of the index of refraction is significantly anisotropic in the long-wavelength region of the spectrum, although this assertion could not be tested for wavelengths smaller than 550 nanometers (2.6 eV). A small donor concentration (I_z, less than 0.01%), leads to substantial changes in the absorption spectra; for constant iodine concentration these features are unstable and take a form typical of hexagonal crystal forms (Fig. 2b). An intermediate spectrum which occurs during the transition is shown in Fig. 2c. More investigations of the structure of weakly-doped PA reveal changes in crystal structure, along with a transition from the monoclinic and rhombic modifications to hexagonal. This modification is distinguished by the presence of a sharp absorption maximum in the wavelength region ≈415 nanometers (Fig. 2b). In this case, the dependences of the absorption coefficient and index of refraction have the form typical of one-dimensional oscillators with a sharply-expressed maximum in the absorption coefficient, along with positive and negative values of the dispersion of the index of refraction for waves polarized along the direction in which the molecules are oriented. When the energy of the light quanta increases above 4 eV, the absorption coefficient increases, and at 5 eV it attains a value of $\sim 10^4$ cm^{-1}.

Let us compare the results obtained here with the results of investigations of individual polyene molecules in solution. Such a comparison reveals the important fact that the absorption maximum ($\approx$415 nanometers) of the hexagonal form coincides with that of the low-concentration solution ($C < 0.1\%$). As the polyene concentration in the solutions increases, the maximum in absorption shifts over to occupy a position characteristic of the PA rhombic modification ($C > 1\%$); this is connected with formation of clusters whose dimensions are on the order of the length of separate PA molecules and whose stacking corresponds to the rhombic form. At concentrations below 0.1%, absorption is due only to isolated polyene molecules. The coincidence of the spectra mentioned above with that of hexagonal PA allows us to draw an inference about the weak effect of the crystal field on the optical properties of the crystal: in the notation of Ref. 5, $\Delta_e \approx 0$.

In order to pin down more precisely the mechanism by which light is absorbed, we investigate the effects of high donor concentrations (up to 5%). First of all, a high donor concentration causes the optical anisotropy of PA to disappear and produces a smooth shift of the absorption maximum over to the low-energy region around 1.9 eV (Fig. 2c), where the absolute value of the absorption coefficient amounted to 10^4 cm^{-1}. This result allows us to clarify the nature of the absorption maximum of light both for weakly-doped PA and for separate polyene molecules. In the doped material we have $\rho < 1$, which preserves the ideal periodicity of the PA structure and gives rise to the appearance of a series of thresholds at the edge of the absorption band, given by the relation $\omega - 2\Delta_1 \approx n^2\varkappa_0^2/\Delta_1$, where 2Δ, is the absorption band edge, $\varkappa_0 = \pi/2c$, $c = |\rho - 1|/a$, a is the mean atomic separation, and $n = 0, 1, 2, \ldots$. Because the value of the absorption at its maxima decreases like 1:0.11:0.02: ..., in any real physical experiment it is possible to identify only the $n = 0$ and 1 thresholds. The appearance of such thresholds has a simple physical meaning. They correspond to light absorption by domains with characteristic dimensions $na/|\rho - 1|$. Apparently, the intersection of such thresholds also forms the absorption maximum in the hexagonal form of PA (Fig. 2b). Another possible explanation for the absorption maxima near 415 nm is the presence of polyene molecules in the PA with dimensions of $\approx$38 A. However, as we showed above, small-angle X-ray experiments are not in agreement with the existence of such molecules. We note also that the dispersion of the index of refraction can be estimated theoretically from the Kramers-Kronig relation and the work of Brazovski and Matveenko.[13] The corresponding estimates so obtained coincide with the dependence for the hexagonal crystal shown in Fig. 2b.

Let us compare these results with the work in Ref. 12, where investigations were also conducted on the anisotropy of optical properties of PA films oriented by mechanical stretching in one direction. From the evidence of Fig. 2, such a comparison suggests that the properties of these stretched films are close to those of trans-polyacetylene with fairly large donor concentrations. ($\approx$3–5%). In this case, coincidence of the absorption maxima in the 1.9 to 2 eV range was observed, along with the dependences of the real and imaginary parts of the dielectric permittivity calculated with the Kramers-Kronig relation from the reflection coefficients $R_\parallel$, $R_\perp$. However, for weakly-doped crystals (less than 1%) of various modifications, one obtains only qualitative agreement in the dispersion curves for $n_\parallel$, $n_\perp$, $k_\parallel$, $k_\perp$. The character of these dependences for small doping appears to be general, which points to the presence of one-dimensional oscillators excited by the incidence of light waves polarized along the length of the molecular axes.

PHOTO-EXCITATION OF SPIN STATES IN POLYACETYLENE CRYSTALS

Let us examine the results of investigating the kinetics of thermo- and photo-excitation of spin states in polyacetylene crystals as functions of symmetry and degree of alloying with iodine. To begin with, we remark that their presence can be verified only in crystals with rhombic and monoclinic symmetry. Furthermore, a weak I_2 doping, leading to the change of structure described above, quenches the thermal excitation of spin states. In addition, photoexcitation at various wavelengths ($\lambda = 1064$, 532, 367 nm) also does not result in their generation. On the other hand, the energy of the photo-generated spins depends on the degree of alloying of the PA. Thus, for large numbers of donors (up to 3%) these spins can be excited only at the fundamental laser line $\lambda = 1064$ nm, while for rhombic and monoclinic crystals which are in the ground state (i.e., the Peierls dielectric), generation occurs at the wavelength of the first harmonic $\lambda = 532$ nm.

(a) Kinetics of spin states in a Peierls dielectric

In crystals of PA which are in their ground state, illumination generates an ensemble of $S = 1/2$ spin states whose number saturates around 10^{19} cm^{-3}. This result is illustrated in Fig. 3. When the laser radiation is switched off, in the previously illuminated PA the kinetics of the spin states is determined by the degree of alloying and structural integrity. However, in PA which is in its nondegenerate ground state, one first records the disappearance of "fast" states which have time constants $\tau_c \sim 10^{-6}$–10^{-4} s—the segment AB on curve 1. To illustrate the presence of such states, in Fig. 3 we show curves of the modulation of the EPR signal for this particular segment (curve 5). Next, the number of spins grows until it exceeds the level at $t = t_B$ by 1.5 to 3 times. The formation of these states takes place in a time 10–10^2 s, i.e., section BC on curve 1. Finally, there are two segments corresponding to slow exponential decay of the number of spins—segments CD and DE. We point out that photoexcitation of spin states is observed only at low temperatures; for temperatures above 150 K, the generation of spin states is undetectable.

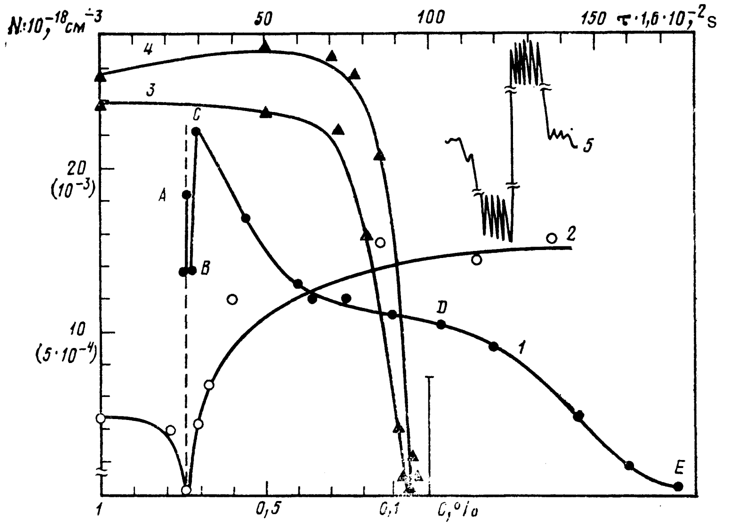

FIG. 3. Spin state kinetics in crystalline polyacetylene: 1—for a nondegenerate ground state, 2—for iodine-doped crystals. The number of spin states per unit volume as a function of polyene concentration in solution is shown for decreasing concentrations (3) and increasing concentrations (4); the scale is shown by the numbers in brackets on the vertical axis. The inset shows the EPR absorption spectrum for modulation of the light at a frequency of 2 gHz with fixed magnetic field (5).

We will now discuss an interpretation of the results obtained here for the dependence of the spin states on photoexcitation, within the framework of Refs. 4 and 5, starting with the ground state of PA. The value 1/2 for the spin and the buildup in the number of such states are explained by the generation of strongly-coupled polarons. By invoking this mechanism, we explain the absence of any noticeable increase in conductivity, despite the generation of a large number of photoelectrons. The most important result of these investigations is the apparent detection of a growth in the number of spin states after the laser is switched off, which may correspond to the decay of bipolarons with spin $S = 0$ into pairs of polarons with spin $S = 1/2$. Segment CD of the curve is characteristic of domain relaxation; its disappearance corresponds to their annihilation. Such domains, whose boundaries are static 180° kinks with spin $S = 1/2$, are possible only in the PA ground state as a consequence of two or three-dimensional confinement of π-bonds inside and outside the domains. The existence of such domains, in particular, can explain the growth of the number of spins on segment BC, since the decay of bipolarons causes the number of domains to grow. It is possible that this mechanism of domain formation is by itself sufficient to explain the phenomena oberved under photoexcitation.

We note here that our point of view with regard to the kinetics of spin excitations is also confirmed by investigating how the number of spin states vary with temperature. Thus, for PA in its single-crystal ground state, the number of excited spins decreases as the temperature decreases, whereas for doped or amorphous PA the number of spins increases. This latter effect is due to the appearance of isolated domain walls which disappear in the presence of thermally excited electrons, transforming into uncharged soliton states; in this case the conductivity also increases. All this data is presented in the table.

Let us examine the kinetics of the PA spin states in solution. Here the decrease in the number of thermally excited spin states is nonlinear with the decrease in solution concentration, so that below a certain critical concentration ($C_{\rm cr} < 0.05$) the spin excitations are not detectable (Fig. 3). This concentration corresponds to a solution of individual polyene molecules. If we increase the concentration of PA molecules in solution by removing some of the solvent, we observe once again the appearance of a concentration-dependent number of thermally excited spin states, as shown in Fig. 3. These results reveal the connection between the spin excitations in PA and the interaction of molecules with the crystal field Δ_e; they also explain the absence of spin excitations in hexagonal PA crystals, in which the interaction between chains is weak.

(b) Spin state kinetics in the presence of iodine doping

Here, interest centers on investigating PA crystals with high concentrations of iodine ($C > 0.1\%$). In this case, as the donor concentration increases ($C > 0.03\%$), the number

TABLE I. Change in the number of states N with spin 1/2 and resistance per unit volume versus temperature for various iodine concentrations.

T, K	N_c, cm^{-3}		ρ, Ω cm	
	$C = 10^{-4}\%$	$C = 0{,}5\%$	$C = 10^{-4}\%$	$C = 0{,}5\%$
77	$1{,}5 \cdot 10^{15}$	$7{,}6 \cdot 10^{18}$	$7 \cdot 10^{14}$ $(7 \cdot 10^{14})$	10^{12} $(2 \cdot 10^{10})$
300	$7{,}2 \cdot 10^{16}$	$3 \cdot 10^{17}$	$7 \cdot 10^{14}$ $(7 \cdot 10^{14})$	$4{,}5 \cdot 10^{6}$ $(3 \cdot 10^{6})$

Note: The values of the resistance per unit volume in brackets are given for the aggregate of photoexcited states after 100 seconds.

of thermally-excited spin states grows to a certain critical number $N_c \approx 3\times 10^{19}$ cm^{-1} for $C \approx 3\%$ and 300 K. When the concentration of iodine exceeds this value of 3%, the number of $S = 1/2$ spin states decreases and $S = 0$ excited states begin to form. Photoexcitation of PA with less than the critical number of $S = 1/2$ spin states leads to a buildup in the number of $S = 1/2$ spins. However, when the number of such spins is close to critical, further photoexcitation forms $S = 0$ states and the number of $S = 1/2$ spins decreases. In Fig. 3 we show a typical curve characterizing the spin $S = 1/2$ kinetics (curve 2). When the photoexcitation ceases, the number of $S = 1/2$ spins grows to a certain value which need not coincide with the initial number of spins.

At this point, let us note certain features of the structure of PA at high dopings $C > 3\%$. The chief peculiarity is that crystals with hexagonal symmetry undergo polymorphic transformations into crystals of rhombic symmetry. A typical electron diffraction picture of such a PA crystal looks exactly like the picture shown in Fig. 1c; that is, the spin excitations appear here because of the structural transformation, and are not characteristic of strongly-doped hexagonal crystals at all. A more detailed investigation of the above-mentioned polymorphic transformation will be the subject of a separate work.

CONCLUSION

The results we have obtained here allow us to draw definitive conclusions regarding the mechanism by which electronic excitations arise under the action of light and temperature, for various doping levels of crystalline polyacetylene. In the absence of ground state degeneracy, in rhombic and monoclinic crystals spin $S = 1/2$ excitations predominate with the properties of strong-coupling polarons. Under photoexcitation, the number of such states increases. However, doping polyacetylene with iodine quenches the photoexcited $S = 1/2$ states and increases the spinless charge carriers. Freezeout of long chains at crystal lattice sites leads to an analogous effect, as does the transition to the hexagonal modification, i.e., with the appearance of $S = 1/2$ spin states there corresponds a crystal field which leads to an effect similar to two- and three-dimensional confinement of π-bonds. This conclusion is confirmed by an investigation of solutions containing individual polyene molecules.

In conclusion, the authors acknowledge their debt to C. A. Brazovski and N. N. Kirova for discussion of the results obtained here.

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