Electron spin resonance and microwave photoconductivity in carbynoid films

Electron spin resonance and microwave photoconductivity in carbynoid films

D P Ertchak†, Yu P Kudryavtsev‡, M B Guseva§, A F Alexandrov§,
S E Evsyukov‖, V G Babaev§, L M Krechko§, Yu A Koksharov§,
A N Tichonov§, L A Blumenfeld§ and H J v Bardeleben¶

† Physics Department, Byelorussian State University, F Scornya Avenue 4, 220080 Minsk,
Belarus
‡ A N Nesmeyanov Institute of Organo-Element Compounds, RAS, Moscow 117813, Russia
§ Physics Department, M V Lomonosov State University, Vorobyovy Gory, Moscow 119899,
Russia
‖ BASF Aktiengesellschaft, Polymer Laboratory ZKS/A-B1, 67056 Ludwigshafen, Germany
¶ GPS, Universités Paris 6 et 7, Tour 23/24, 2 Place Jussieu 75251, Paris Cédex 5, France

Abstract. First ESR studies are reported on oriented carbynoid samples prepared by chemical dehydrofluorination of poly(vinylidene fluoride) films. Two types of paramagnetic centres (PC), denoted as C-M1 and C-M2, and an anisotropic broad line were detected. The spectra of the PC C-M1 are isotropic with a g-value of 2.0045 ± 0.0003. The absorption by given PC is well saturated at room temperature and the PC C-M1 can be attributed either to free radical states or pinned quasi-particles similar to topological Su–Schrieffer–Heeger solitons.

The ESR and microwave photoconductivity results obtained confirm the quasi-1D nature of the carbon chains, being the structural elements of the samples studied, and agree with the assumption that the ground state of carbon chains is a state with a spin density wave (SDW) realized at room temperature.

The ESR spectrum of the PC C-M2 consisting of a series of unsaturated lines is anisotropic both in relation to the static magnetic field and in relation to the magnetic component of the microwave field. The study of the interaction dynamics of the microwave field with PC C-M2, the absorption dependence with increase of the microwave field and the temperature dependence allow us to attribute the PC C-M2 to mobile quasi-particles, being domain walls in the alternated spin density distribution, tentatively solitons in the SDW.

It has been found that spin waves associated with the PC C-M2 can be observed in samples treated thermally at $120\,^{\circ}$C for 2 hours (the samples contained fluorine with atomic ratio $F/C = 3/7$ and oxygen at 20 at.%).

It has been proven that the spin waves' excitation and the formation of quasi-particles like solitons can represent the same process.

1. Introduction

Low-dimensional systems possess a number of remarkable properties in comparison with corresponding three-dimensional (3D) analogues. Carbynes are an example of the simplest quasi-one-dimensional (1D) system since they contain only carbon atoms i.e. the atoms of only one periodic table element. Consequently, carbynes can serve as model substances to study the physics in low-dimensional systems in comparison with other 1D organic polymers. At the same time, the 1D structure of carbynes suggests promising potentials for their practical use, e.g. in electronics, in medicine etc [1].

According to theoretical predictions [2], carbynes show a fourfold degeneration of the π-electronic system instead of the twofold degeneration found in most conjugated quasi-1D-systems, e.g. *trans*-polyacetylene (*trans*-PA). According to [2] they appear to possess a rich spectrum of quasi-particles, i.e. topological solitons, polarons, polarexcitons or breathers either in the ground state or as elementary excitations by various external effects. The quasi-particles are the domain walls in the alternating structure of chemical bonds in the atomic chain or, in other words, the domain walls in the coupling-order wave (COW). However, in carbynes the possible spectra of the quasi-particles and elementary excitations are expected to be richer in a number of possible kinds in comparison with the quasi-particle family predicted theoretically in [2]. Indeed, recently a new type of elementary excitation, namely spin waves, has been found in related quasi-1D-carbon systems [3–5] formed as a result of ion-beam modification of diamond films and single crystals and presenting presumably a superlattice of quasi-1D spatially ordered nanotubes in the 3D diamond matrix [3–7]. Furthermore, according to Chugreev and Misurkin [8] the total energy minimum of the carbon chain can be realized as the result of the alternation in both the distributions of bond lengths and the spin or charge density. It depends on the ratio between the magnitude of the Coulomb interactions of π-electrons of a given atom and those of the neighbouring atoms, i.e. on the ratio between π-electron–electron correlation parameters. In other words, the states of a chain with a spin density wave (SDW) and a charge density wave (CDW) as well as mixed states e.g. with CDW/SDW, SDW/COW etc can also be in principle realized. Then the formation and the motion of domain walls in SDW and CDW can be realized similar to those predicted for COW and therefore the number of possible kinds of quasi-particle can be increased. Since the parameters characterizing the electron–electron correlation can be controlled by the method applied to synthesize carbyne chains (e.g., by controlling the doping level, conditions of thermal treatment etc), in principle the carbyne chains with various electronic structures, i.e. those with COW, SDW, CDW and mixed structure, can be obtained.

We have also to note that a discussion started at the time of discovery of carbynes in 1960 [9] concerning the principle possibility of the existence of the carbon in 1D allotrope form (representing in fact an example of pure 1D solids). The cause of the sureness of some authors in considering the existence of the carbynes as impossible in principle is based evidently on the famous theoretical works of Peierls [10] and Landau [11] according to which there is the well known infra-red divergence for mean square of atomic displacements u_i^2 at the wave vector value $k = 0$ for 1D solids. However the mean square deviation of the lattice constant $(u_i - u_j)^2$ (i, j are atomic site numbers) is finite indicating the existence of 1D solids including the carbynes in a dynamical state [12].

The experience gained simultaneously in studies of the physical properties of a number of quasi-1D organic polymers e.g. *trans*-PA showed that crucial physical information on the properties of the quasi-particles and the chain state in general can be obtained predominantly from magnetic resonance studies (for a review see e.g. [13]). The first ESR and microwave conductivity studies of carbynoids (being in fact the doped carbynes, as will be classified in section 2) aiming at obtaining the experimental confirmation of the ideas stated above are described below.

2. Experimental technique

Both unoriented and uniaxially oriented samples were prepared by chemical dehydrofluorination of poly(vinylidene fluoride) (PVDF) films. The starting films for oriented sample production were cast from a solution of PVDF in N,N-dimethylformamide at $\sim$70 °C. After being uni-axially drawn up to a degree of elongation of 500%, the films were fixed in a stainless steel holder in order to prevent shrinkage and to retain the orientation, and were dehydrofluorinated

in the stretched state. The dehydrofluorination reaction was carried out by treating the oriented or unoriented PVDF films with a mixture of saturated KOH solution in ethanol with acetone at room temperature for one hour, i.e. in the way described in [14]. Then the samples were washed with ethanol and water, and dried in vacuum.

The samples contained a rather high concentration of residual fluorine and oxygen atoms. Three sample series were studied. The first series of samples were the samples with an F/C ratio equal to 3/10. They contained 10% oxygen. The second series of samples, being the samples with an F/C ratio equal to 3/7, were thermally treated at $120\,^\circ$C for 2 hours. They contained 20% oxygen after thermal treatment. The contents of F and O in the third series were intermediate between the former ones though not determined exactly. According to the classification proposed for doped PA [13], the samples studied can be referred both to doped carbynes with doping levels >11 mol% and to carbynoids i.e. materials including a wide range of carbyne-like structures, e.g. those with 2D or 3D cross-linking of the chains, resulting in the appearance of carbon chains in directions lateral to the main chains with an essential contamination of impurity atoms incorporated in the lateral carbon chain atomic structure.

The ESR measurements were performed using Varian E-Line, Radiopan, Varian E-4 and Bruker spectrometers with a TE_{102} cavity. The absorption of Cr^{3+} ions of a ruby standard sample permanently located in the cavity was used for fine tuning of the phase of the modulation field, for the calibration of the relative values of the magnetic component H_1 of the microwave field and for the calibration of the absorption intensity dependence on the modulation frequency.

For microwave photoconductivity measurements the samples were placed in the node of the electrical component E_1 of the microwave field in the cavity of the Varian E-Line ESR spectrometer. The exciting IR and visible illumination was modulated at a frequency of 10^3 Hz. The spectral dependence of the microwave photoconductivity was normalized for the intensity of the light source. A halogen quartz lamp of 600 W power was used as a light source. Lock-in detection of both microwave and 1 kHz frequency signals was employed. It should be noted that the lock-in detection of the microwave signals, controlling the microwave phase, allows determination of the sign of the current carriers by comparison of the signal polarity of the sample measured with a standard sample of known type of conductivity. Indeed, the microwave power P absorbed by the sample per unit surface area is determined by the following relation:

$$P = (c/4\pi)\mathrm{Re}[\vec{E}_1 \times \vec{H}_1^*]|_{z=z(0)} \tag{1}$$

where c is the light velocity, $\vec{E}_1$ is a component of the electric microwave field, $\vec{H}_1$ is a component of the magnetic microwave field and $z = z(0)$ is the co-ordinate of the sample surface in the microwave propagation direction. Since $\vec{E}_1 = \vec{j}/\sigma$ and $\sigma = en\mu$, equation (1) can be transformed as follows:

$$P = (c/4\pi en\mu)\mathrm{Re}[\vec{j} \times \vec{H}_1^*]|_{z=z(0)}. \tag{2}$$

Here σ is the conductivity, e, n and μ are the charge, concentration and mobility of the current carriers, respectively, and $\vec{j}$ is the current density. It is obvious that the sign of the current carriers will determine the sign of the absorption signal. This means that in the case of microwave phase-sensitive detection the response signal of photocarriers of opposite sign is equivalent to the response signal of photocarriers of the same sign (in comparison to a standard sample) registered 180° out of phase. We note that there is an analogue in the given result with the recently established change of sign of the phase in the electrostatic Aharonov–Bohm effect with change of the carrier sign [15].

3. Results

The spectra of the samples from different series exhibit both common features and some distinguishing traits depending on the amount of the main impurities, *viz.*, fluorine, oxygen, hydrogen, and on the subsequent thermal treatment. Two types of paramagnetic centres (PC) designated as C-M1, C-M2 and a broad line with a linewidth $\Delta H \approx 600$ G (in the samples of the second series) were observed (figures 1, 2).
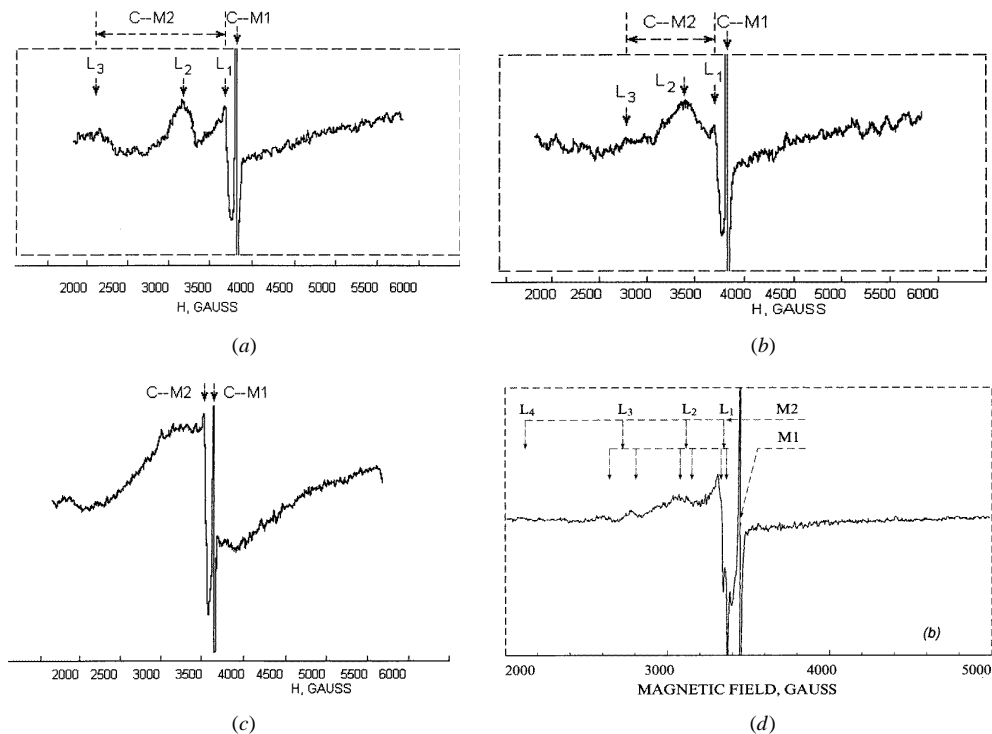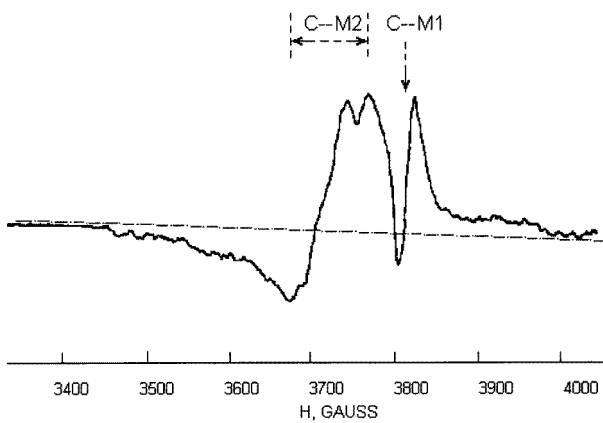

Figure 1. ESR spectra of an oriented carbynoid sample of the second series: (*a*) the sample plane is perpendicular to the microwave magnetic field $\vec{H}_1$, the static magnetic field $\vec{H}$ is parallel to the chain orientation axis, microwave frequency $\nu = 10\,732.4$ MHz; (*b*) the sample plane is perpendicular to the microwave magnetic field $\vec{H}_1$, the static magnetic field $\vec{H}$ is perpendicular to the chain orientation axis, $\nu = 10\,744.0$ MHz; (*c*) the sample plane is parallel to the microwave magnetic field $\vec{H}_1$, the static magnetic field $\vec{H}$ is parallel to the chain orientation axis, $\nu = 10\,262.0$ MHz; (*d*) ESR spectra measured 1.8 years after sample preparation. The sample plane is perpendicular to the magnetic field $\vec{H}_1$, the static magnetic field $\vec{H}$ is parallel to the chain orientation axis, $\nu = 9644.70$ MHz. Top arrows indicate positions of the centre of gravity of the spectral distribution in the groups of lines L_1 ($n = 0$, 1), L_2 ($n = 3$) and L_3 ($n = 5$) and the possible position of the seventh mode. Bottom arrows indicate positions of the two dominating lines in groups L_1, L_2, L_3.

A singlet ESR line ascribed to the PC C-M1 has an isotropic *g*-value of 2.0045 ± 0.0003, an isotropic linewidth ΔH (equal to 6.8 ± 0.2 G in samples of the first series) and an isotropic intensity Y corresponding to PC concentration 5.3×10^{17} cm^{-3} (in the samples of given series). The paramagnetic centres C-M1 have longer relaxation times compared to PC C-M2. This conclusion follows from the character of the absorption intensity dependences on the microwave power level (figure 3). Dependencies similar to those presented in figure 3(*a*) are often observed in polymer systems in which paramagnetic centres belong to free radical states.
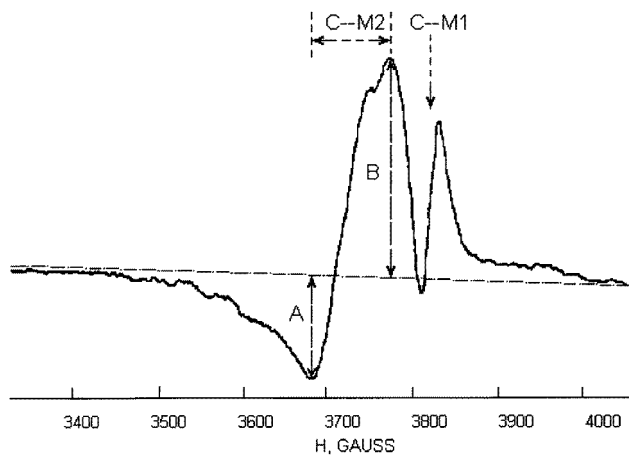
(*a*)

(*b*)
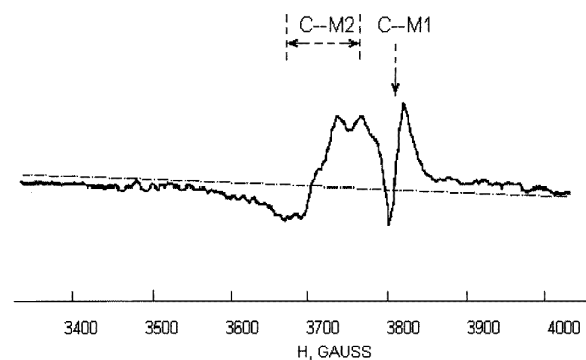
(*c*)

Figure 2. Detailed view of ESR spectra of an oriented carbynoid sample of the third series in the magnetic field range of 3400–4000 G. The microwave magnetic field $\bar{H}_1$ is parallel to the sample plane, the angles θ between the static magnetic field $\bar{H}$ and the normal $\bar{n}$ to the sample plane are 90° (*a*), 30° (*b*) and 0° (*c*). The ratios of the cavity quality Q-factors for the sample orientations characterized by θ equal to 90°, 30°, 0° are as follows: Q (90°):Q (30°):Q (0°) $= 1.37:1.25:1$, $\nu = 10\,685.1$ MHz.
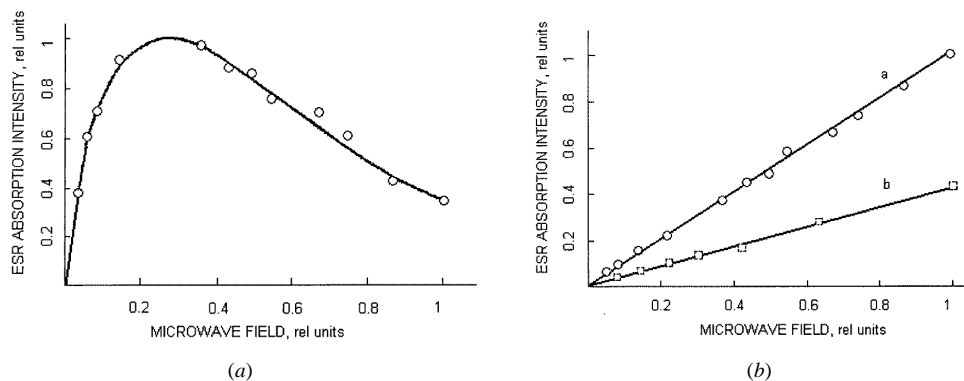
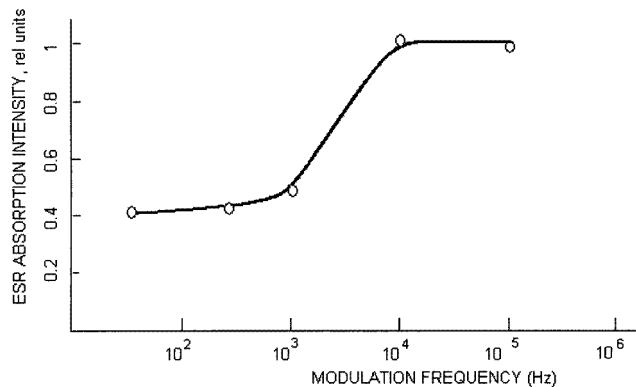**Figure 3.** (*a*) dependence of the intensity of the ESR spectrum of PC C-M1 on the magnitude of the microwave magnetic field H_1 ($f_m = 100$ kHz) in the sample belonging to the first series. (*b*) Paramagnetic absorption intensity of PC C-M2 in dependence on the microwave magnetic field H_1: a, $f_m = 100$ kHz, b, $f_m = 270$ Hz in the sample presented in figure 3(*a*).

However, some quasi-particles, for example topological solitons, can be stable for a long time in pinned states. The resonance absorption kinetics for pinned paramagnetic quasi-particles is also expected to be saturating, i.e., similar to that presented in figure 3(*a*). Consequently, the PC C-M1 can be tentatively assigned to pinned paramagnetic quasi-particles or to localized free radical states.

The spectrum of C-M2 consists of a series of ESR lines whose paramagnetic absorption characteristics including their saturation behaviour differ principally from those of the PC C-M1. The spectrum of C-M2 (figures 1, 2) consists of several groups of lines designated as L_1, L_2, L_3, each of which is a superposition of comparatively narrow lines. Note that the group L_1-lines with an effective width of their envelope of about 100 G are observed in all samples. The groups L_2 and L_3 were only detected in the samples of the second series.

The individual lines of the groups corresponding to C-M2 centres were only partly resolved by X-band measurements immediately after sample preparation. A good resolution into two components has been achieved in the samples of the second series (samples 2.2) measured 1.8 years after their preparation, figure 1(*d*). The field positions of the lines of the group L_1, isotropic in unoriented samples, are weakly anisotropic in oriented samples. In samples of the first series the *g*-values for the group L_1-lines ranged from 2.0233 to 2.0851 (± 0.0005) when the $\vec{H}$-direction was along the chain and the $\vec{H_1}$-direction was perpendicular to the sample plane, respectively. It should be noted that the envelope of the group of lines has essentially asymmetrical shape, e.g. the B/A ratio is ~ 2 for the group L_1 in the samples of the third series, figure 2. The dependence of the intensity of the PC C-M2 lines on the microwave magnetic field is linear, figure 3(*b*), i.e. it is different compared with the analogous dependence for PC C-M1, figure 3(*a*). The dependence is linear for both high and low modulation frequencies f_m, figure 3(*b*), and is identical for all individual line groups since the shapes of superposition remain without visible change with the changes of the microwave power. Studies of the interaction dynamics of the microwave field with the PC C-M2 were performed in a manner analogous to that reported by Ertchak *et al* [4–7].

The feasibility of using a stationary ESR spectrometer for some dynamic studies can be briefly explained as follows. The sinusoidal modulation of the static magnetic field can be represented as a sequence of the impulses of the corresponding effective time duration. Therefore the effective interaction time of a PC with the microwave field is determined by

(*a*)
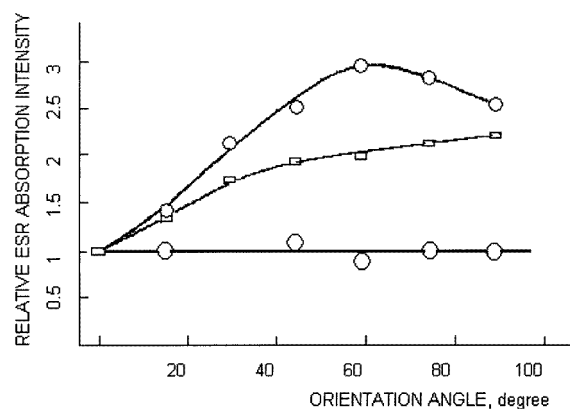
(*b*)

Figure 4. (*a*) Dependence of the intensity of ESR lines of PC C-M2 on the modulation frequency f_m (of the static magnetic field H) in the sample belonging to the first series at relative microwave field $H_1/H_1^0 = 3.6$, where H_1^0 is a microwave field corresponding to microwave power in 100 mW, $H_m = 5$ G. (*b*) Dependencies of the intensity of the spectra of PC C-M1 (bottom line), PC C-M2 (intermediate curve) and the broad line (top curve) on the angle between the static magnetic field $\vec{H}$ and the normal $\vec{n}$ to the sample plane in the sample belonging to the third series. The microwave magnetic field $\vec{H}_1$ is parallel to the sample plane.

the impulse duration, i.e. the modulation frequency. The interaction dynamics has shown a considerable increase of the paramagnetic absorption intensity with increasing modulation frequency f_m (figure 4(*a*)). The values of the modulation amplitude H_m and the magnetic microwave field H_1 were constant during the measurements. As evident from the figure, the modulation frequency dependence has an almost steplike shape, i.e. first the line intensity change is small in the frequency range from 35 Hz up to 10^3 Hz, then the intensity increases drastically in the range of 10^3–10^4 Hz and finally remains almost constant in the range of 10^4–10^5 Hz. It should be noted that this dependence differs in principle from the known modulation frequency dependencies of common unsaturated magnetic systems obeying well known unmodified Bloch equations for which the f_m-dependence coincides with the lower frequency filter characteristics [16]. Likewise the character of the observed f_m-dependence

resembles that for PCs of quasi-one-dimensional tracklike modified structures (nanotubes) produced in diamond single crystals and diamond films upon ion implantation [3–7].

For all oriented samples an anisotropy was found of the PC C-M2 spectrum in relation to the magnetic component of the microwave field. However, the details of this dependence are very sensitive to the level of impurities and to the thermal treatment. This property is demonstrated for samples of the second series, figure 1, where the spectra are presented for identical $\vec{H}$-orientation parallel to the chain axis but for different sample plane orientations to the $\vec{H}_1$-direction, i.e. perpendicular, figure 1(a), and parallel, figure 1(c). The spectrum C-M2 consists of three groups of lines L_1, L_2 and L_3, figure 1, when $\vec{H}_1$ is perpendicular to the sample plane. The positions of the two dominating well resolved lines in the samples 2.2 of the series 2 are correlated for both L_1 and L_3 groups, figure 1(d). Consequently, the group L_3 (as well as L_2) belongs to the same PC as the group L_1. The identical dependencies of the resonance absorption on the modulation frequency and on the microwave field H_1 for the groups L_1, L_2 and L_3 further confirm this conclusion. The lines of the groups L_2 and L_3, figure 1, show also considerable anisotropy in relation to the static $\vec{H}$-field as is evident from the comparison of the spectra with $\vec{H}$-orientation parallel, figure 1(a), and perpendicular, figure 1(b), to the chain axis. The picture observed is characteristic for spin waves. Actually, the group L_1 of lines can be considered an analogue of $n = 0$ and $n = 1$ modes of spin wave resonance in thin ferromagnetic compounds [17]. The groups of lines L_2 and L_3 appearing as left sidebands of the resonance line L_1 correspond to, respectively, $n = 3$ and $n = 5$ modes of the main resonance line. As already stated above, a qualitatively similar picture has recently been observed in related spatially ordered quasi-1D-carbon systems, i.e. nanotubes incorporated in a diamond matrix as the result of ion beam modification of diamond films and diamond single crystals [3–5]. If the $\vec{H}_1$-component of the microwave field is parallel to the sample plane, the spectrum of PC C-M2 is almost isotropic, and consists of the group L_1 only, i.e., spin waves are not excited when the sample plane orientation is parallel to $\vec{H}_1$. Instead of spin wave resonance, an additional broad line ($\Delta H \sim 600$ G) is well registered at a given orientation (figure 1(c)).

In the samples of the first and the third series the characteristic spectral absorption distribution, like to that which takes place with the appearance of L_2 and L_3 groups, is not observed. However, in these samples additional peculiarities have been observed. In particular a broad line which has also appeared simultaneously with the C-M1 and C-M2 spectra when the sample plane orientation was parallel to $\vec{H}_1$ is much broader when compared with that observed in samples of the second series. The line is registered only partly in the field scan range accessible to the Varian E-4 and Radiopan spectrometers. It is characteristic that the amplitudes of envelope of the broad line and of the PC C-M2 both have an angular dependence in contrast to that of PC-M1 (figure 4(b)). It is noteworthy that the asymmetry ratio A/B of an enveloping line of PC C-M2 (figure 2) is also practically isotropic.

The study of additional peculiarities, observed in the first series' samples, is in progress.

The spectral distribution of the microwave photoconductivity was studied in unoriented samples of the first series, figure 5. The distribution is characterized by a rather sharp maximum at ~1.86 eV, a shoulder at ~1.66 eV, some features in a range of 2.15–2.20 eV and the long tail spread to larger wavelengths. The comparison of the polarity of the photoconductivity signal of the samples studied with a standard sample of a known conductivity type allows to conclude that the photoconductivity is of n-type.

The small angle x-ray scattering (SAXS) pattern of dehydrofluorinated oriented films revealed two diffraction maxima thus confirming the uniaxial orientation of the carbon chains and allowing us to determine a unit cell size of 505 pm in the samples of the first series. The x-ray diffraction data are described in detail in [18].
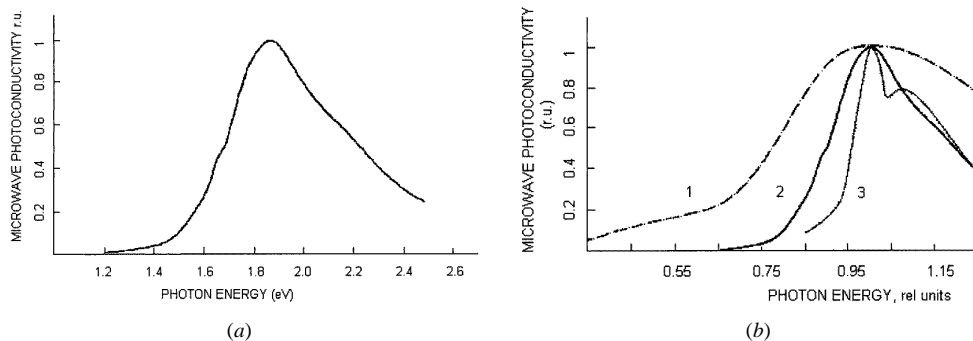
Figure 5. (*a*) Spectral distribution of the microwave photoconductivity in the carbynoid sample of the first series. (*b*) Rescaled spectral distribution of the microwave photoconductivity for given sample: solid line (2) compared with the rescaled absorption coefficients for *trans*-PA and polydiacetylene: dashed (1) and dotted (3) lines correspondingly, taken from [13].

4. Discussion

The results of kinetic and dynamic studies presented in figures 3 and 4(*a*) can be explained by assuming that the PC C-M2 are mobile quasi-particles. Recently, a mechanism was proposed by Ertchak *et al* [3–7] allowing us to explain the observed increase of paramagnetic absorption for higher modulation frequencies by simultaneous unsaturated kinetics. The main idea is as follows. The mechanism of rapid transfer with characteristic times $\tau \ll T_1$ (T_1 is the time of spin–lattice relaxation in a matrix 3D volume) of the energy absorbed by the spin system into the kinetic energy of the motion of the quasi-particles is realized by the resonance in a system of paramagnetic quasi-particles with a low activation energy level for the motion. The possibility of a rapid direct conversion of the energy absorbed by spins of the quasi-particles into kinetic energy is realized because of the coupling of their spin and mechanical momentum under the conditions of a very small activation energy threshold for the motion of quasi-particles. The value of the activation energy in the samples studied for the quasi-particle motion is expected to be comparable to the activation energy for the motion of solitons in *trans*-PA, being equal to ∼0.002 eV [13, 19]. As argued previously [3], the time scale of the τ-process can yield values comparable with the relaxation time of the kinetic energy of electrons, i.e. ∼10^{-13} s [20]. The time scale predicted for a τ-process agrees well with the experimentally observed time of ∼10^{-13} s [21] for 1D energy transfer of the spin system of solitons in *trans*-PA. Note that the time scale for the relaxation processes determined by interactions, having magnetic nature, can achieve values of only ∼10^{-10} s [20]. Note also that the appearance of two spin–lattice relaxation times T_1 and τ is a general consequence of the quasi-one-dimensionality of the paramagnetic systems. In fact, all physical properties, e.g. electrical conductivity, band gap value etc, are quite different in one dimension and in three dimensions [13] for the quasi-one-dimensional systems. In other words, for the quasi-one-dimensional (oriented or unoriented) carbyne or carbynoid systems representing an ensembles of 1D elements with a weak (however non-zero) 3D interaction, the 3D properties should be taken into consideration too. This conclusion agrees well with results obtained by Kirtman *et al* [22] when comparing theoretical magnetic resonance properties of topological solitons in a single *trans*-PA chain with experimental data. Therefore an increase of the ESR absorption intensity with the increase of the modulation frequency can be explained by fast passage conditions relative to a T_1-relaxation process if $f_m^{-1} < T_1$. The data obtained allow us to

estimate the 3D spin–lattice relaxation time T_1 as the inverse value of the modulation frequency at half-height of an intensity increase (figure 4(a)). The value of $\sim 5 \times 10^{-4}$ s was obtained at the measurement conditions indicated above (figure 4(a)) for PC C-M2 in the samples of the first series.

Thus the C-M2 ESR absorption agrees well with absorption characteristics by mobile quasi-particles and naturally cannot be ascribed to any spatially localized PC including all the possible impurities.

The mobile quasi-particles in ion-modified diamond single crystals and diamond films are suggested to be topological solitons [3–7] similar to those observed in *trans*-polyacetylene [13], which, as argued in [4], present an individual class in the soliton family and can be considered Su–Schrieffer–Heeger solitons (SSH solitons). Similar absorption dynamics like those presented in figure 4(a) together with unsaturating H_1-dependence of the resonance absorption intensity on the microwave magnetic field were observed both for PC C-M2 in the samples studied and for moving quasiparticles formed in ion-modified diamond single crystals and diamond films [3–7]. Consequently we can suggest that the PC C-M2 are also solitons. The measurements at 125 K testify in favour of this suggestion. Indeed, the experimental ratio of the absorption intensities at 300 K and 125 K corresponds to that expected from Curie's law. This result means that deep states correspond to the observed paramagnetic centres. As deviations from Curie's law are considerable for the magnetic resonance absorption by such moving spin carriers as e.g. free electrons in the conduction band of solids, the Curie law is violated for electrons in the conduction band as well as for the resonance absorption associated with a known type of magnetic order. At the same time the solitons [13, 19] are known to be quasi-particles with deep levels in the band gap and a low excitation energy for motion. The estimation of the PC C-M2 concentration yields a value of $\sim 6.5 \times 10^{19}$ cm^{-3} for samples of the first series. This value is comparable with the concentration of paramagnetic solitons observed in *trans*-polyacetylene [13], and hence provides some additional support to the soliton concept of the PC C-M2 absorption in the samples studied.

The mechanism of soliton formation seems to be different in the samples studied compared with that in polyacetylene [13, 19] or predicted for polyyne-type chains in [2], that is argued below in (i) to (iv).

(i) Indeed the presence of a band gap in samples studied can be explained as the result of a Mott–Hubbard metal–insulator transition accompanied by the formation of spin density waves or charge density waves in the electronic π-system of carbynoid chains [8, 23, 24]. A study of the spectral distribution of the microwave photoconductivity (figure 5(a)) agrees with this conclusion, revealing that the samples studied have actually a 1D gap of 1.86 eV. This statement is further confirmed by the peaklike shape of the spectral distribution of the intensity of photoconductivity. Moreover, the character of this distribution implies that the value of the electron–electron interactions is considerable. Really, if the correlation interactions are weak the optical properties will be determined to the zeroth order by a single parameter, the gap value [13]. Then the rescaled optical absorption as well as the photoconductivity will be positioned on a universal curve [13]. This universal dependence taken from [13] and presented in figure 5(b) (dashed line) describes the optical absorption of many conducting (quasi-) 1D polymers. The deviation from this universal dependence observed in the samples studied (figure 5(b), solid line) is similar to that observed in polydiacetylene (figure 5(b), dotted line) which, according to Heeger *et al* [13], can be explained by rather strong π-electron–electron interactions. The presence of the strong π-electron–electron interactions speaks in favour of a Mott–Hubbard metal-insulator transition with SDW (CDW) or mixed SDW/CDW formation rather than the usual Peierls transition. Consequently the quasiparticles like solitons, being

domain walls in the alternating distribution of the corresponding density parameter i.e. spin (or charge) in a given case, can be formed.

It is interesting that the long-wavelength edge of the photoconductivity is well described by the quadratic dependence

$$\sigma h\nu = B(h\nu - E_g)^2 \tag{3}$$

yielding the second energy threshold of 1.13 ± 0.06 eV [18]. Here σ is the conductivity, $h\nu$ is the energy of photoexcitation quantum, B is a factor characterizing the photoconductivity efficiency and E_g is the band gap value. The presence of this threshold as well as a shoulder at 1.66 eV and a feature in a range 2.15–2.20 eV can be explained by several reasons, the most probable of which is that the energy threshold at 1.13 ± 0.06 eV is a 3D-gap value emerging due to interchain charge transfer. The shoulder at 1.66 eV and a feature in the range 2.15–2.20 eV can be associated with a 1D quantum fluctuation effect connected with the main photoconductivity peak (or with the presence of a polaron or exciton state). Given details have to be clarified in subsequent studies.

Note that the dominating 1D peak in an integral sample characteristic such as photoconductivity demonstrates a preponderance of the contribution of the 1D carbyne matrix to the photoelectrical properties in comparison with contribution of the 3D impurity superstructure. The present results are in agreement with ESR results presented above which show a clear preponderance of the contribution of the 1D carbyne matrix to magnetic resonance characteristics. As concerned the samples' classification, this conclusion enables us to classify the samples studied as doped quasi-1D systems, i.e. doped carbynes structures rather than composite carbon/fluorine/oxygen systems.

(ii) Furthermore, since the band gap values due to a Peierls transition in *trans*-PA and a Mott–Hubbard transitions in carbyne (carbynoid) samples appear to be comparable, the energy states of quasi-particles such as solitons in alternating spin density distributions and alternating chemical bond length distributions, in particular in COWs and in SDWs (CDWs) are expected to be *a priori* similar, *viz.*, deep states in a gap. The distinction of the origin of quasi-particles from those observed in *trans*-PA is supported by the deviation of the g-value range of the PC C-M2 from a g-value of 2.0026 which is characteristic of solitons in polyacetylene [25, 26]. Indeed, since the spin–orbital interaction parameter λ for carbon has a relatively low value (e.g., compared to silicon and germanium), the range of the g-changes $\Delta g = g - 2.0023$ for all known intrinsic PC in pure carbon materials is also relatively narrow ($\Delta g < 10^{-2}$). Then it should be expected that the g-value of the solitons predicted to be in the (bond-length alternating) polyyne chains [2] should be close to that in *trans*-polyacetylene ($g = 2.0026$), i.e. should possess other values in comparison with the g-values observed for PC C-M2 for which the Δg-value, ranging from 2.1×10^{-2} to $\sim 8.3 \times 10^{-2}$, is relatively large. The alternated spin (and charge) distribution can essentially change the orbital motion of the spin carriers and, consequently, can considerably change the g-values. Thus, the large Δg-values (of $\sim(2–8) \times 10^{-2}$) observed for PC C-M2 agree well with the assumption of an alternating spin or charge density distribution for the ground state of the chains.

(iii) The observation of the anisotropy of the ESR spectra (figure 1) related to the magnetic component of the microwave field, and the absence of a similar anisotropy related to the electric component of the microwave field, is a manifestation of the resonance absorption effect on the quasiparticles associated with SDW rather than CDW. (The analogous quasiparticles in CDW, if CDW is formed simultaneously, can be spinless and not observable by ESR.) The effect of the anisotropy of the ESR spectra related to the magnetic component of the microwave field can be explained by an anisotropy of the spin wave excitation, and indicates that the samples studied are systems of oriented 1D elements. As inferred from figure 1, the positions of the

spin-wave modes satisfy the quadratic dispersion relation established previously [3] that is similar to the Kittel relation for thin ferromagnetic films [17], i.e.

$$\omega = Ak^2 + \omega_0 \tag{4}$$

$$k = n\pi/d \tag{5}$$

where d is an effective thickness of the 1D elements, and A is a coefficient characterizing the strength of electron–electron correlations. Naturally, the value of the electron–electron correlations strength is anisotropic in terms of the static magnetic field. For example, the ratio of A/d^2 is $\sim 2 \times 10^8$ s^{-1} and 9×10^7 s^{-1} when H is directed along the chains and perpendicular to the chains, respectively. The positions of $n = 0$ and $n = 1$ modes nearly coincide, i.e., deviation from equations (4) and (5) takes place, and the even modes are not observed. The given deviation as well as the absence of even modes are similar to those observed by spin-wave resonance studies in ferromagnetic films and discussed by Seavey and Tannenwald [17]. The appearance of the deviation indicated is explained by the facts that the Kittel approximation is not fulfilled for $n = 1$ and that the even modes cannot be excited as a rule in the homogeneous microwave field applied [17]. In the more complete theory proposed by Wolf [27] and developed by Frait *et al* [28] the calculation of the microwave absorption is realized by means of solving the Maxwell equations (for nonzero electroconductivity σ) and the equation of the magnetization motion (in Gilbert or Landau–Lifshitz formulation) by including the effect of the surface magnetization energy. The substantial moment is the appearance of the surface spin wave modes additionally to the volume spin wave modes. Given modes can have positions to the right of the Kittel resonance field position (i.e. to the right of the main resonance mode in the absence of surface magnetization effect) and were observed in the fourth series of samples (the detailed study of given samples is planned). It is essential also that the mode positions as well widths of the modes and relative mode intensities are dependent on the number of parameters: sample conductivity, magnetic saturation value, exchange (electron–electron correlation) parameter, damping parameter (e.g. Landau–Lifshitz damping constant by Landau–Lifshitz approximation). The given theory allows us to understand also the qualitative difference in relative intensity distribution among spin wave resonance modes observed in implanted diamonds and diamond films [3–7] in comparison with the carbynoid samples studied.

It should be kept in mind that the spectral distribution of the spin wave resonance absorption for the group modes with a high mode number follows the spectral distribution of the mode with $n = 0$ (figure 1). On the other hand, the mode with $n = 0$ is assigned to mobile quasi-particles and is always observed, i.e., with and without spin waves. Consequently, we obtain confirmation that two different types of elementary excitation, *viz.*, spin waves and a system of mobile quasi-particles such as solitons, are actually connected to each other. Hence the system of mobile quasi-particles can be a source of spin waves at appropriate conditions determined by the strength of π-electron–electron correlations between atoms in the chains. The given conclusion can be understood mathematically when we take into account that for example for the nonlinear Korteweg de Vries equation (the nonlinear equation describing the soliton propagation in the samples studied should be similar to the KdV equation as well as the equation describing the soliton propagation in *trans*-PA) the localized starting disturbance is divided into two parts: the solitary wave part and the part with an oscillating wave having an amplitude damping with time [29, 30].

Note also that the formation of the well resolved structure of PC C-M2 points to a process of self-ordering of the structure. This process resembles the crystallization of amorphous substances (e.g., amorphous SiO_2, common glasses) with time. A possible explanation of this self-ordering effect is as follows. According to Heimann *et al* [31, 32] the carbyne chains

represent a superposition of atomic linear C–C fragments (clusters) of definite lengths. The C–C fragments are connected to each other, producing alternating kinks in chemical bonds. The kink angles and kink-offset distances are proposed to be statistically fluctuating and hence satisfy the concept of a paracrystal [24, 33]. The kinks in the carbon chains terminate the crystallographic identity period and thus define discrete *c*-axis lengths ('conjugation length') [24, 31, 32]. There exists also the concept of a temperature-dependent 'equilibrium' of chain lengths [31, 34]. This concept may lead to a random distribution of the chain lengths around a mean value. It should be expected that immediately after their preparation the oriented carbynoid samples have some distribution in atomic cluster lengths around the length corresponding to the conditions of synthesis. Irregularities in the distribution of impurities, and hence the difference of the chain lengths as well as the presence of other chain defects [35] can lead to an initial set of spin (and charge) density distributions which, presumably, can explain the presence of the superposed paramagnetic absorption lines in groups L_1, L_2, L_3 assigned to PC C-M2. Then, the difference of experimental spectra obtained after a storage time of 1.8 years may correspond to a time-dependent chain 'self-rearrangement' for other conditions fixed, e.g., temperature. This is also well in accord with observations by Kavan and Kastner [36] on carbynoid samples stored up to 14 years that show systematic changes in their physical properties with time.

(iv) The assumption of an SDW formation in carbyne is believed to be confirmed directly by the observation of a broad line. This line may be associated with collective spin absorption by the SDW. The possibility of the collective magnetic absorption by SDWs means that SDWs themselves can move along chains. This suggestion allows us to explain the presence of the angular dependencies of the intensities of the broad line and the PC C-M2 (figure 4(*b*)). The measured angular dependencies (figure 4(*b*)) can be explained by an anisotropy of excitation for the motion both of mobile quasi-particles suggested to be solitons in a SDW (corresponding to the PC C-M2 spectra) and of the SDW itself (corresponding to the broad line). The identity of both the values of the degree of asymmetry and the angular dependencies of the degree of asymmetry for the broad line and PC C-M2 can be naturally explained, since the given values and dependencies are characteristic of systems with related absorption and spin energy transfer properties. The detailed analysis of the line shapes provides additional arguments in favour of the concept of the formation of SDW and of the existence of mobile quasi-particles in SDWs.

The ground state of carbyne (carbynoid) chains with SDWs is presumably a result of the effect of the main residual impurity atoms such as oxygen, fluorine and hydrogen. The doping effect of these impurities can be tentatively associated with their diffusion mobility. High diffusion mobility of the fluorine atoms was observed in Si [37] and is also expected in PVDF-based carbynoids due to the sufficiently large interchain distance since the value equal to 505 pm was obtained for unit cell parameter (from x-ray diffraction data as was stated above) i.e., larger than the interatomic distance of 235 pm in Si. Furthermore the mobility of the impurity atoms which are not included in a main carbon backbone is a general property of 1D organic polymers [38]. Therefore, it is possible that impurity complexes, e.g., FO_4, can be formed during the dehydrohalogenation process. The doping effect of such a complex is expected to be similar to that of ClO_4 complexes in *trans*-PA. Furthermore, the doping of 1D organic polymers with halogens is well known [39]; consequently the residual fluorine atoms themselves can act as dopants.

The fluorine atoms in a comparable (but something less) concentrations (per unit length) with the concentration of carbon atoms can surpassingly stimulate a commensurate or incommensurate transitions in the spin or charge distributions along atomic chains leading correspondingly to formation of SDWs or/and CDWs. Which of these transitions may occur is

probably dependent on the relative concentration of doping atoms and their kind of distribution along the carbon chains. It should be noted that the SDW and CDW in the samples studied can be simultaneously produced similarly to those observed in the perovskite $La_{1-x}Sr_xFeO_3$ structure [40]. However, CDWs cannot evidently be immediately detected by ESR (the charged quasiparticles like charged solitons in *trans*-PA [13] expected to be spinless). In other words, the presence of impurity atoms (F, O) seems to preserve the Peierls bond length and bond angle instability. According to Ung *et al* and Mazumdar *et al* [41, 42], the presence of the elements of two-dimensionality in the interaction is inherent for quasi-1D chains with SDW. Thus, the appearance of the transversal interaction of the main atomic chain with impurity atoms (and with complexes of impurity atoms) localized in bonds lateral to the chain direction seems to favour these conclusions.

The results obtained allow proposal of a stabilization mechanism of the carbon chains in the samples studied. The stabilization can be achieved dynamically by means of the formation of mobile SDWs (and probably CDWs) as well through the formation of mobile quasi-particles in spin density distribution (and probably in charge density distribution) in full correspondence with theoretical predictions of the dynamical stabilization for the pure 1D solids [12]. It is suggested that the commensurate (incommensurate) transitions can take place, i.e. spin density distributions along the atomic chains can have other spatial order in comparison with the chemical bond distribution. The role of impurity atoms affecting the physical properties (charge transport, spin transport etc) can also be taken into account in correspondence with [14, 24, 31, 32, 43–52] as an additional factor stabilizing the carbyne chains. However dynamic stabilization seems to be preferred since the dopants (as well as other impurities, which are not incorporated in the C–C chain immediately) are known [38] as stated above in (quasi-) 1D polymers to be mobile themselves.

5. Conclusions

First ESR studies are described for the dehydrofluorination products of poly(vinylidene fluoride) films i.e. carbynoids classified as doped carbynes. Paramagnetic centres, designated C-M1 and C-M2, and a broad line with a width of $\sim$600 G were found in these materials. The PC C-M1 are isotropic and well saturated by microwave power and are attributable to pinned quasi-particles tentatively assigned to pinned topological solitons or free radical states similar to those observed in a number of organic polymeric systems. The ESR spectrum of the PC C-M2 is anisotropic both in relation to the directions of a static magnetic field and in relation to the magnetic component of a microwave field. The mobile quasi-particles are proposed to be responsible for this spectrum, which follows from the study of (i) the interaction dynamics of the resonance microwave field with the PC C-M2, (ii) the dependence of the absorption intensity on the microwave power level as well as (iii) from the conclusion about the law of the absorption intensity changes with the temperature changes.

The analyses of the anisotropy of the PC C-M2 and the broad line parameters along with data on the g-value deviations from $g = 2.0023$ allows us to propose a chain state with a spin density wave (or SDW/CDW mixed state) as a ground state of carbon chains and to propose the PC C-M2 model associated with domain walls in the spin density distribution, tentatively assigned to solitons in SDW. According to the given proposal a chain state with a spin density wave is realized at room temperature.

It was found that under certain preparation conditions (thermal treatment at 120 °C for 2 hours, fluorine content in atomic ratio F/C = 3/7, oxygen at 20 atomic %) spin waves associated with PC C-M2 can be observed. The excitation of the spin waves seems to be determined by more efficient electron–electron correlations in these samples.

The observed anisotropy of the paramagnetic absorption of C-M2 and of the broad line in relation to the magnetic component of the microwave field is proposed to be associated with an anisotropy of the motion excitation of quasi-particles and SDWs.

The results obtained allow us to propose a mechanism of a dynamic stabilization of carbon chains in carbynoid samples studied. The stabilization can be realized by means of the formation of a moving SDW and by means of the formation of mobile quasi-particles, which seem to be solitons in the spin density distribution along the chains.

Acknowledgments

References

[1] Kudryavtsev Yu P, Heimann R B and Evsyukov S E 1996 *J. Mater. Sci.* **31** 5557–71
[2] Rice M J, Phillpot S R, Bishop A R and Campbell D K 1986 *Phys. Rev.* B **34** 4139–49
[3] Erchak D P, Guseva M B, Aleksandrov A F, Alexander H and Pilar fon Pilchau A 1993 *JETP Lett.* **58** 275–8
[4] Ertchak D P *et al* 1997 *Phys. Status Solidi* **203** 529–48
[5] Ertchak D P, Efimov V G and Stelmakh V F 1997 *J. Appl. Spectrosc.* **64** 433–60
[6] Erchak D P, Efimov V G, Zaitsev A M, Stelmakh V F, Penina N M, Varichenko V S and Tolstykh V P 1992 *Nucl. Instrum. Methods Phys. Res.* B **69** 443–51
[7] Erchak D P *et al* 1993 *Diamond Relat. Mater.* **2** 1164–7
[8] Chugreev A L and Misurkin I A 1989 *J. Struct. Chem.* **30** 377–80
[9] Sladkov A M 1981 *Sov. Sci. Rev.* B **3** 75–110
[10] Peierls R 1934 *Helv. Phys. Acta* **7** (Supplement 2) 81–3
[11] Landau L 1937 *Zh. Exp. Teor. Fiz.* **7** 627–32
Landau L 1937 *Phys. Z. Sowjetunion* **11** 545
[12] Apostol M 1996 *Synth. Met.* **79** 253–7
[13] Heeger A J, Kivelson S, Schrieffer J R and Su W-P 1988 *Rev. Mod. Phys.* **60** 781–850
[14] Kudryavtsev Yu P, Evsyukov S E and Babaev V G 1992 *Izv. Akad. Nauk Ser. Khim.* **1223–1225** (in Russian)
[15] Montambaux G 1996 *Phys. Rev.* B **54** R17 273–R17 275
[16] Boivin C, Jacolin C and Savard J Y 1973 *Rev. Sci. Instrum.* **44** 191–6
[17] Seavey M H and Tannenwald P E 1958 *Phys. Rev. Lett.* **1** 168–9
[18] Krechko L M 1994 Carbyne: the first allotrope crystalline carbon modification *Dissertation* MSU, Moscow
[19] Su W P, Schrieffer J R and Heeger A J 1980 *Phys. Rev.* B **22** 2099–111
[20] Abragam A 1961 *The Principles of Nuclear Magnetism* (London: Oxford University Press)
[21] Nechtschein M, Devreux F, Greene R L, Clarke T C and Street G B 1980 *Phys. Rev. Lett.* **44** 356–9
[22] Kirtman B, Hasan M and Chipman D M 1991 *J. Chem. Phys.* **95** 7698–716
[23] Kertesz M, Koller J and Azman A 1978 *J. Chem. Phys.* **68** 2779–82
[24] Heimann R B 1994 *Diamond Relat. Mater.* **3** 1151–7
[25] Goldberg I B, Crowe H R, Newman P R, Heeger A J and MacDiarmid A G 1979 *J. Chem. Phys.* **70** 1132–6
[26] Weinberger B R, Ehrenfreund E, Pron A, Heeger A J and MacDiarmid A G 1980 *J. Chem. Phys.* **72** 4749–55
[27] Wolf P 1966 *Basic Problems in Thin Film Physics* (Goettingen: Vandenhoeck and Ruprecht) p 392
[28] Frait Z, Fraitova D and Marchal G 1997 *Phys. Status Solidi* b **201** 257–67
[29] Lonngren K and Scott A (eds) 1978 *Solitons in Action* (New York: Academic)
[30] Novikov S P (ed) 1980 *Soliton Theory. Inversal Problem Method* (Moscow: Nauka) pp 320
[31] Heimann R B, Kleiman J and Salansky N M 1983 *Nature* **306** 164–7
[32] Heimann R B, Kleiman J and Salansky N M 1984 *Carbon* **22** 147–56
[33] Heimann R B 1997 *Carbon* **35** 1669
[34] Whittaker A G 1978 *Science* **200** 763–4
[35] Evsyukov S E, Paasch S, Thomas B and Heimann R B 1997 *Ber. Bunsenges. Phys. Chem.* **101** 837–41

[36] Kavan L and Kastner J 1994 *Carbon* 1533–6

[37] Jeng S-P, Ma T-P, Canteri R, Anderle M and Rubloff G W 1992 *Appl. Phys. Lett.* **61** 1310–12

[38] Kirova N and Brazovskii S 1997 *Synth. Met.* **85** 1450–2

[39] Yoshino K, Harada S, Kyokane J, Iwakawa S and Inuishi Y 1980 *J. Appl. Phys.* **51** 2714–17

[40] Li J Q, Matsui Y, Park S K and Tokura Y 1997 *Phys. Rev. Lett.* **79** 297–300

[41] Ung K C, Mazumdar S and Toussaint D 1994 *Phys. Rev. Lett.* **73** 2603–6

[42] Mazumdar S, Lin H Q and Campbell D K 1991 *Synth. Met.* **41–43** 4047–50

[43] Eastmond R, Johnson T R and Walton D R M 1972 *Tetrahedron* **28** 4601–16

[44] Whittaker Q G and Wolten G M 1972 *Science* **178** 54–6

[45] Hay A S 1969 *J. Polym. Sci.* **7** 1625–34

[46] Korshak V V, Kudryavtsev Yu P, Khvostov V V, Guseva M B, Babaev V G and Rylova O Yu 1987 *Carbon* **25** 735–8

[47] Korshak V V, Kudryavtsev, Yu P, Korshak, Yu V, Evsyukov S E, Khvostov V V, Babaev V G and Guseva M B 1988 *Makromol. Chem. Rapid Commun.* **9** 135–40

[48] Berdyugin V V, Kudryavtsev Yu P, Evsyukov S E, Korshak Yu V, Shorygin P P and Korshak V V 1989 *Dokl. Akad. Nauk SSSR* **305** 362–5 (in Russian)

[49] Korshak V V, Kudryavtsev Yu P, Evsyukov S E, Korshak Yu V, Guseva M B, Babaev V G and Kostishko B M 1988 *Dokl. Akad. Nauk SSSR* **298** 1421–4 (in Russian)

[50] Kudryavtsev Yu P, Evsyukov S E, Babaev V G, Guseva M B, Khvostov V V and Krechko L M 1992 *Carbon* **30** 213–21

[51] Kudryavtsev Yu P, Evsyukov S E, Korshak Yu V, Guseva M B, Babaev V G and Khvostov V V 1993 *Izv. Akad. Nauk Ser. Khim.* **N3** 450–63

[52] Udod I A, Shchutic V I, Bulychev B H, Sirotinkin S P, Guseva M B, Babaev V G, Kudryavtsev Yu P and Evsyukov S E 1993 *J. Mater. Chem.* **3** 413–16