Spin-Peierls transition in carbynoid conductors: infrared absorption study

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The results of IR-studies in quasi-1D carbynoid films produced by dehydrohalogenation of poly(vinilidene fluoride) are in good agreement with the assumption that carbynoid films studied are generalized spin-Peierls conductors, the metal to insulator transition in which can be described in the frame of t-J model. Residual atoms of fluorine, hydrogen and atoms of main technological impurity oxygen in the form of various complexes in interchain space are suggested to be spin- (or joint spin- and electrical) conductivity dopants. Antiferroelectric spin wave resonance (AFESWR) being to be optical analogue of antiferromagnetic spin wave resonance has been identified for the first time. Electric spin-Peierls polaron lattice in C-C-bonds is proposed to be responsible for the observed AFESWR both in starting PWDF films and in carbynoid B-films (the samples with the least impurity content). Electric spin moment with pure imaginary value predicted by Dirac as early as 1928 was identified for the first time. Electric spin-Peierls polarones are proposed to be electric spin moment carriers. It has been established that topological solitons, earlier called spin-Peierls solitons (SPS), are simultaneously active, unlike to topological solitons with nonzero spin in \textit{trans}-polyacetylene, in both optical and magnetic resonance spectra. It is explained in suggestion that SPS possess by both electric and magnetic spin moments which can be considered as two components of complex electromagnetic spin vector as a single whole. SPS proposed to be consisting of two coupled domain walls in both magnetic and electric generalized spin density wave (GSDW), produced by electromagnetic spin-Peierls transition in its generalized form in \(\pi\) - and \(\sigma\)-subsystems of carbynoids.

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I. INTRODUCTION AND BACKGROUND

The main feature of carbynoids which distinguishes advantageously carbynoids from all known organic conductors including the most studied organic conductor \textit{trans}-polyacetylene \((t\text{-PA})\) as well as intensively studied at present carbon nanotubes and fullerenes is availability of two \(\pi\)-electronic subsystems. This feature along with the possibility to produce the materials with various kink size in their chain-kinked structure open a multiplicity of very interesting physical properties. So, ESR studies of carbynoid films produced by dehydrofluorination of poly(vinilidene fluoride) have shown that they can be described by quasi-1D spin-Peierls conductor model with spin-Peierls transition in generalized form \[1\]. It is understandable that \(\pi\)-electronic subsystems have to be in carbynoids rather strongly correlated. Consequently, spin-Peierls transition has to be accompanied by spin-charge separation effect in accordance with general quantum field analysis of 1D strongly correlated electronic systems, see for instance \[2\]. Note that spin-charge separation effect was established in 1D conductors for the first time in pioneering works of Su, Schrieffer, and Heeger (SSH) \[3, 4\]. Su, Schrieffer, Heeger identified by analysis of, mainly, ESR and IR absorption data on the base of theoretical model, which is well known at present as SSH-model, the existence in \textit{trans}-polyacetylene of topological solitons, which carry electronic spins without electric charge and \textit{vice versa}. Topological solitons in \(t\)-PA as it is argued in \[5\] produce a class in soliton family, SSH-solitons. Their properties in \(t\text{-PA}\) and consequently spin-charge separation effect which accompanies in \(t\text{-PA}\) the usual \textit{Peierls} transition are studied rather well. At the same time the effect of spin-charge separation did not studied (to our knowledge) in spin-Peierls conductors although there are to be known at present a number of spin-Peierls conductors. There is some progress in this direction the only in carbynoids. Really a mechanism of spin-charge separation in 1D strongly correlated electronic systems has to be topological in its nature and has to be realized by topological solitons’ formation \[2\]. Topological solitons were identified in carbynoids by ESR-study \((\text{C-M2 spectrum})\) \[1, 6\]. From mathematical point of view they can be referred to SSH class, but physically they represent a new kind of solitons. These quasiparticles, according to \[1, 6\] are domain walls in dimerised spin density distribution in distinction from SSH-solitons in \(t\text{-PA}\), which are domain walls in dimerised bond patterns. Topological solitons in carbynoids were called spin-Peierls solitons (SPS). The view on the nature of SPS will be developed in this paper. Especially interesting that preliminary results of IR absorption study, reported very briefly in \[7, 8, 9\], have been shown, that spin-Peierls solitons simultaneously with ESR activity are optically active. It means that mechanism of spin-charge separation has the peculiarities in carbynoids. The aim of presented work is to understand this phenomenon and therefore to grasp in mechanism of spin-charge separation as well as in related phenomena accompanying spin-Peierls transition.

It should take in mind some background details, which
can help to achieve the aim. They are as follows. The magnetic spin wave patterns, obeying to \( k^2 \)-dispersion law (like to that one observed in ferromagnetic thin films) and indicating on new mechanism of room temperature (RT) ferromagnetic ordering of carbon atoms in carbynoid chains, have been observed. Carbynoid films seem to be therefore the first substance among free organic conductors at all with RT-ferromagnetic ordering. Note that ratio of magnetic spin exchange constants \( J \) in carbynoids \([6]\) and in cobalt films obtained by comparison the results presented in \([6]\) and \([11]\) is about 0.63 and 0.76 for two magnetic spin wave resonance patterns registered in carbynoid samples in 1.8 \( T \) after their production. Here the values of lattice parameter \( a \), equaled to 0.128 \( nm \) and 0.3537 \( nm \), were used for carbynoids and cobalt correspondingly. It allows to evaluate the Curie temperature (suggested to be simple average of values corresponding to two ratios of exchange constants \( J \)) \( \sim 777^\circ C \). It is interesting that stability of ferromagnetic ordering in carbynoids is much higher in comparison with the stability of all other magnetically ordered organic conductors. For instance in known organic antiferromagnetically ordered spin density wave (SDW) conductors (DMET, MDTTF, TMTSF-salts, etc) SDW-transition takes place at \( \sim 20K \) or even lower \([11, 12, 13]\). Note that ordering in carbynoids is formed in outer shell in distinction from that one produced by unpaired spins in inner atomic shells of transition metal or rare earth elements. Consequently the properties of ordered state in both cases should be quite different.

Second detail is concerned the generalization of both Peierls and spin-Peierls transitions. It should be noted that representation of pure carbynes as Peierls systems, was established in fact by Heimann et al in \([14, 15]\), where it was proposed that the starting linear atomic chain with equidistant interatomic distance becomes kinked (in fact angle and/or bond dimerized) with \( C_n \)-linear-atomic fragments (kinks), \( n \) equal to 6 - 12, being to be dimer-azation units, Fig.1

This idea was developed on a language of Peierls transition in generalized form in \([1]\). The kink size, interkink angles and, consequently, resulting electronic and geometrical chain structure are determined by the value of electron-electron interatomic interaction along chain, which in its turn is dependent, to definite extent, on production conditions. This circumstance means, that physical properties of carbynes and carbynoids can be varied in very wide range. It seems to be substantial for their practical use. It is interesting to try to predict the possible carbon structures, for which Peierls transition should also be realized in its generalized form. Quasi-1D-carbon clusters, “claimed” to be dimerization units, have to be evidently stable. The linear carbon clusters are the most stable up to \( C_{12} \) \([16]\) in a full accordance with carbynes' structure \([16]\). From \( C_{13} \) to \( C_{25} \) the monocyclic ring clusters are preferable in the absence of the terminal groups \([16]\), although the monocyclic ring clusters can exist according to \([17]\) from \( n =7 \) to \( n =40 \). Note, however, that in the stability interval of monocyclic rings the linear isomers with 8 to 28 atoms were also synthesized by the addition of nonreactive terminal groups \([18]\). Starting from \( n =21 \) the polycycle structures are possible \([12]\) and starting from \( n =32 \) the fullerene structures were found to be the most stable \([19, 20]\). Consequently all listed above stable clusters can be “claimed” in the capacity of dimerization units of corresponding 1D-carbon materials. For instance, if quasi-1D carbon chain is formed from the carbon units with number of atoms nequaled 32 or more pro unit the preferable geometrical structure for the separate unit should be fullerene structure. Indeed in accordance with experimental data in \([21]\) the second known quasi-1D system, where the generalized Peierls transition was experimentally observed, is the quasi-1D-phase of \( KC_{60} \) in which the \( C_{60} \) ions form chains with alternating longer and shorter center to center separation. Center to center separation between \( KC_{60} \)-dimers according to \([21]\) is 9.34 \( A \).

**FIG. 1:** Some Peierls transition schemes for carbyne chain: a) Peierls transition accompanying by bond length dimerization; b) generalized Peierls transition accompanying by kink bond angle alternation (trans-configuration); c) generalized Peierls transition accompanying by kink bond angle alternation (cis-configuration); d) mixed state in result of simultaneous Peierls transition accompanying by bond length dimerization and generalized Peierls transition accompanying by kink bond angle alternation (cis-configuration); e) mixed state in result of simultaneous Peierls transition accompanying by bond length dimerization and generalized Peierls transition accompanying by kink bond angle alternation (trans-configuration).

Therefore it reasonably to suggest that the dimerisation units with more than 12 atoms by generalized Peierls transition in carbon quasi-1D chains will possess by non-linear geometric structure.

The paper is organized as follows. In Sec.II the experimental technique and some details of ESR- and IR-measurements are described. In Sec.III the experimental data of IR studies in carbynoids are presented. The data of IR studies are compared with ESR-data. It is
shown that IR- and ESR-data correlate well and can be explained in the frames of the same model. In Sec.IV the summary and conclusions are represented.

II. EXPERIMENTAL TECHNIQUE

IR absorption studies have been fulfilled on unoriented and uniaxially oriented carbynoid film samples prepared by chemical dehydrohalogenation of poly(vinylidene fluoride) (PVDF). Preparation details were described in [6]. Due to strong absorption in the most interesting spectral range IR-measurements have been done repeatedly on the same samples but grinded and compressed into pellet with KBr. IR measurements have also been done for comparison on starting unoriented and uniaxially oriented PVDF-films as well as on grinded PVDF-films and compressed into pellet with KBr. Uniaxial orientation of PVDF-films was provided by the procedure which was identical to the procedure used by the production of oriented carbynoid films. Among the IR studied sets of samples there were two sets (designated A and B) which have been earlier studied by electron spin resonance (ESR) [6]. We report now infrared (IR)-study results in comparison with ESR results that is those ones obtained only on these two sets of samples. Carbynoid samples contained a rather high concentration of residual fluorine and technological oxygen atoms. The samples of A set (hereinafter A-samples, they were designated as the second series samples in [6]) were with F/C ratio equal to 3/7, their oxygen contamination O/C was 1 to 5. A-samples were thermally treated at 120°C for 2 hours. The contamination of fluorine and oxygen atoms in the samples of B series (hereinafter B-samples, they were designated as third series samples in [6]) was intermediate between 3/10 and 3/7 for the F/C ratio and between 1 to 10 and 1 to 5 for O/C ratio (however O and F content was not determined exactly). Like to the classification proposed for doped t-PA [22], the samples studied can be attributed both to doped carbynes and to carbynoids that is to materials including a wide range of carbyne-like structures.

III. RESULTS AND DISCUSSION

A. IR spectra in carbynoid samples

1. Film samples

Difference between the spectra which belong to the samples of the same sets was negligible. Therefore data the only on two (A and B) unoriented, two (A and B) oriented and two (A and B) grinded samples are presented. General view of IR spectra, registered on oriented carbynoid A- and B-films and on the same samples, but being to be grinded and compressed into pellet with KBr after measurements in film form, is presented in Figures 3 correspondingly. General view of IR spectra, registered subsequently on oriented PVDF-film and then in the same sample, being to be grinded and compressed into pellet with KBr, is presented in Figure 4. Detailed data concerning the positions of observed absorption bands and their relative amplitudes are summarized in Tables I. Main difference of IR spectra of carbynoid films from IR spectra of starting PVDF-films is, as it is seen from Figures, the appearance of IR-activity in the range near 1600 - 1800 cm\(^{-1}\) and the emergence at higher frequencies of broad asymmetric line (BAL) extending in rather wide range for both oriented and unoriented samples (for instance, in the range of 2000 to 3760 cm\(^{-1}\) in unoriented B-sample). Maximum positions of BAL are equal to \(\sim 3467\) and \(\sim 3425\) cm\(^{-1}\) for A- and B-samples correspondingly. Qualitatively the same picture was observed in a number of carbynoids produced by other methods, see for review, e.g. [23]. Especially interesting is that the asymmetry character of BAL, that is, the ratio of effective values of extension of left and right parts of intensity distribution curve relatively the maximal value, is being to be opposite in comparison with that one registered for analogous broad line, which was observed and well studied in \(\text{trans-polyacetylene} [24]\). Effective values of BAL width and relative amplitudes are \(\Delta \nu_{\text{BAL}}^A \approx 840\) cm\(^{-1}\), \(a_{\text{BAL}} = 0.60\) and \(\Delta \nu_{\text{BAL}}^B \approx 820\) cm\(^{-1}\), \(a_{\text{BAL}} = 0.32\) in A- and B-films correspondingly. Therefore the width of BAL and its relative amplitude are increasing in the sequence of B- to A-films. Given increase seems to be correlating with the total impurity increase.

There is also essential increase, equal to 1.8, of relative amplitude of the line with position near 2200 cm\(^{-1}\) in the sequence of B- to A-films. It is interesting that this ratio is almost coinciding with corresponding ratio of relative amplitudes for BAL, which is equal \(~1.9\). The line near 2200 cm\(^{-1}\) is characteristic line for polyyne type of carbyne and carbynoid electronic structure [23]. Note that there is some red shift from 2210 cm\(^{-1}\) in B-film to 2195 cm\(^{-1}\) in A-film for the position of the band indicated. Note also that the band near 2200 cm\(^{-1}\) is relatively week pronounced in the samples obtained by dehydrohalogenation of PVDF in comparison with those ones obtained for instance by dehydrohalogenation of poly(vinylidenechlorides) in the agreement with previous observations described in [25].

The structure of IR-absorption bands in the range 400 - 1000 cm\(^{-1}\) is almost coinciding in both oriented and unoriented B-film samples, Table I. Especially interesting that absorption structure is very similar to that one observed in starting PVDF film, compare Fig 2 with Fig 4. The absorption in the range 400 - 590 cm\(^{-1}\) represents itself the single transition band with fine structure. Absorption counter has a resemblance to absorption derivative shape or dispersion shape, although it is asymmetric to some extent. It is especially clear seen in Fig 4 for PVDF sample. If it so, then one should consider dip positions in the range 400 - 470 cm\(^{-1}\) to be signal peaks. In this suggestion the observed fine struc-
FIG. 2: Spectral distribution of IR absorption intensity in carbynoid B-film sample (a) top picture: uniaxially oriented carbynoid film, (b) bottom picture: B-film was grinded and compressed into pellet with KBr.

The structured band becomes clear interpretation. It is typical vibration-rotation band corresponding to vibration transition at 475, 475.5, 477 cm\(^{-1}\) in PVDF-, B-unoriented, B-oriented films correspondingly. Really, peaks at 495, 517, 538 cm\(^{-1}\), shoulder at 557 cm\(^{-1}\), weak peak at 577 cm\(^{-1}\) in B-unoriented film, peaks at 497, 517, 538 cm\(^{-1}\), shoulder at 555 cm\(^{-1}\), weakly pronounced peak in the range 575 - 580 cm\(^{-1}\) in B-oriented film and peaks at 495, 514, 537 cm\(^{-1}\), shoulder in the range 555 - 560 cm\(^{-1}\), weakly pronounced peak at 575 cm\(^{-1}\) in PVDF-film are almost equidistant lines with subsequent addition of \(\sim 20\) cm\(^{-1}\) to the line center at 475 - 477 cm\(^{-1}\), that is all these 5 lines represents well known R-branch. To P-branch one should refer the lines with positions at 456, 423 cm\(^{-1}\) in B-unoriented film, 457, 424 cm\(^{-1}\) in B-oriented film and the lines at 455, 423, 398 cm\(^{-1}\) in PVDF-film. The rotation transition at the center of band, that is at 475 - 477 cm\(^{-1}\), is absent (as usually). Note that the observation of P-branch at dip positions in its turn testifies the correctness of the conclusion that signal from the absorption centers which are responsible for the fine-structured band is registered in dispersion mode. The nature of this band will be discussed in Sec.G.

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FIG. 3: Spectral distribution of IR-absorption intensity in carbynoid A-film sample (a) top picture: uniaxially oriented carbynoid film, (b) bottom picture: A-film was grinded and compressed into pellet with KBr.

The width of this band is also decreasing from \(\sim 100\) cm\(^{-1}\) in PVDF and B-carbynoids to \(\sim 60\) cm\(^{-1}\) in A-carbynoids. Taking into account slightly different off-scale values (scaling factor is 1.3) and the shape of registered signal we obtain then for intensity decrease the value of 8.3. It is also substantial that shape and intensity of the band near 3000 cm\(^{-1}\) with peaks at 3038, 2998 cm\(^{-1}\) and dip at 3013 cm\(^{-1}\), registered in
FIG. 4: General view of spectral distribution of IR absorption intensity in PVDF: (a) top picture: uniaxially oriented PVDF-film, (b) bottom picture: PVDF-film was grinded and compressed into pellet with KBr.

B-sample, are also changed drastically in A-film, compare Fig.2 and Fig.3. Evaluations, which were carried out analogously to those ones for fine-structured band, give the factor $\sim 8.6$ for intensity decrease of the band near 3000 cm$^{-1}$ in A-sample. The band near 3000 cm$^{-1}$ was also observed in starting PVDF-film with the same dip position at 3013 cm$^{-1}$ like to that one in B-sample. At the same time the band has two peaks at 2992, 3033 in oriented PVDF-sample and two peaks at 2990, 3034 cm$^{-1}$, in PVDF-unoriented sample, that is, they are at different positions, shifted to low frequencies, in comparison with those ones in carbynoid B-sample. It seems to be natural to attribute the band near 3000 cm$^{-1}$, registered both in B-sample and in PVDF to C-H vibration mode. However, observed shift of band peaks seems to be indicating on different surrounding of vibration centers. The result agrees well with the suggestion that C-H bonds in carbynoid samples belong to some interchain complexes mainly, but in PVDF-sample the band near 3000 cm$^{-1}$ is vibration mode of lateral valence C-H bonds in chain structure. The shift to low frequencies in PVDF is explained in a natural way, being to be well known shift, taking place by polymerization process including the same C-H units, see for instance [26]. It can be shown that the same conclusion follows from shape analysis of the band near 3000 cm$^{-1}$ both in PVDF and in carbynoid B-sample]. In favour of this suggestion can also indicate the presence of many shoulders near 3000 cm$^{-1}$, that is, shoulders at 3190, 3140, 3108, 3090, 2985, 2950, 2850 cm$^{-1}$ which are detected in oriented B-sample, but they...
FIG. 6: ESR-spectrum in A-film sample, measured in 1.8 year after sample preparation. The sample plane is perpendicular to magnetic field vector of microwave field, the static magnetic field is parallel to the chain orientation axis, resonance frequency $\nu = 9644.70$ MHz. The spectrum is reproduced from 6.

are absent in both oriented and unoriented PVDF films. Consequently the above listed shoulders cannot belong to C-H lateral bonds of polymer carbonyl chain. Especially interesting that shoulders near 3108 and at 2950 cm$^{-1}$ are also presenting in unoriented B-sample, but they are less pronounced and the first shoulder has slightly different frequency, 3100 cm$^{-1}$. At the same time the shoulders at 3190, 3140, 3090, 2985, 2850 cm$^{-1}$ as well as the shoulder at 3538 cm$^{-1}$ are also absent in unoriented B-film. The situation is very similar to averaging-out of spectra for various configurations of nonisotropic point centers in any single crystal by its grinding. The role of such point centers can play the simple molecules which have finite discrete set of possible orientation of C-H bonds in interchain space of uniaxially ordered film with slightly different resonance frequencies. Therefore it seems to be reasonable to ascribe the observed shoulders, observed in oriented carbonyl B-sample, along with main two peaks near 3000 cm$^{-1}$ to C-H bonds in simple molecules or molecular complexes which include C-H bond or several C-H bonds and which are localized in interchain space in some set of energetically slightly different configurations. Note, that the decrease of C-H lateral bonds corresponds by dehydrohalogenation process to equal decrease of C-F lateral bonds 23. Then we obtain in fact the proof that the number of hydrogen and fluorine atoms, which are considered to be responsible in their lateral to carbon backbone valence C-H and C-F configurations is much less (if they are existing at all) in carbonyl B-sample in comparison with those ones in PVDF-sample. It is interesting that in the films of A-set even the number of IR-active complexes with C-H vibration mode is also substantially less (by foregoing factor $\sim 8.6$) in comparison with those ones in B-set. Thus hydrogen, fluorine (and evidently oxygen) atoms form more effectively the interchain molecules and/or complexes in both B- and A-samples. There is clear tendency to decrease of concentration of optically active complexes (at least of those ones including C-H-bonds) in B- to A-sample sequence.

TABLE I: Spectral positions and amplitudes of the lines registered in carbonyl film samples. Here wpp means “weakly pronounced peak”, designations (p) ↔ (d) and (p) ↔ (p) are differences between amplitudes of concrete peak and neighbour dip or peak correspondingly. Amplitude was determined relatively to off-scale value between 1750–1600 cm$^{-1}$.

| Unoriented B-sample | Oriented B-sample | Oriented A-sample |
|---------------------|------------------|------------------|
| Frequency, cm$^{-1}$ | Amplitude | Frequency, cm$^{-1}$ | Amplitude | Frequency, cm$^{-1}$ | Amplitude |
| $\sim 3425$, BAL max. | 0.32 | $\sim 3830$, min | 0.31 | $\sim 3467$, BAL max. | 0.60 |
| 3100, shoulder | 0.20 | 3358, shoulder | 0.31 | 3110, wpp | 0.19 |
| 3014, dip | $\sim 3425$, BAL max. | 0.31 | 2960–3012, almost plateou | 0.37 |
| 3037, peak | 0.41 | 3190, shoulder | 0.22 | 2860, wpp | 0.22 |
| 2997, peak | 0.39 | 3140, shoulder | 0.22 | 2625, wpp | 0.08 |
| 2950, shoulder | 0.20 | 3108, shoulder | 0.22 | 2540, wpp | 0.08 |
| 2865, wpp | 0.08 | 3090, shoulder | 0.22 | 2195, peak | 0.14 |
| 2520, shoulder | 0.03 | 3038, peak | 0.44 | 1080–1750, offscale | 1.0 |
| 2335 | 0.05 | 3013, dip | 0.44 | 937, dip | 1.0 |
| 2210 | 0.08 | 2998, peak | 0.42 | 880, peak | 1.0 |
| 1900, dip | 2985, shoulder | 0.03 | 870, narrow line | 1.0 |
| $\sim 1705$, shoulder | $\sim 2950$, shoulder | 0.22 | 772, shoulder | 1.0 |
| 1570, shoulder | $\sim 2850$, shoulder | 0.07 | 688, dip | 1.0 |
| 1512, dip | 2210, peak | 0.03 | 620, peak | 0.08 |
| 1630–1670 off-scale range | 1600–1710, off-scale range | 1.0 | 540, peak | 1.0 |
| 1040–1440 off-scale range | 1.0 | 1510, dip | 1.0 | 520, peak | 1.0 |
| 990, wpp | 1170 | 1080–1440, off-scale range | 1.0 | 500, peak | 1.0 |
| 3100, shoulder | 0.03 | 3038, peak | 0.44 | 1080–1750, offscale | 1.0 |
2. Grinded samples

The off-scale was absent in grinded samples and a number of additional bands were resolved. Almost the same absorption structure was observed both in oriented and unoriented samples after grinding, compare for instance peak and dip positions in B-oriented and unoriented samples, Table II.
TABLE II: Spectral positions and amplitudes of the lines registered in grinded carbynoid samples and compressed into pellet with KBr. Amplitude was determined relatively the peak at 1068 cm$^{-1}$ in A-samples and relatively the peaks at 1080 cm$^{-1}$ and 1085 cm$^{-1}$ in B-oriented and unoriented samples correspondingly.

| Unoriented B-sample | Oriented B-sample | Oriented A-sample |
|---------------------|-------------------|-------------------|
| Frequency, cm$^{-1}$ | Amplitude        | Frequency, cm$^{-1}$ | Amplitude        | Frequency, cm$^{-1}$ | Amplitude        |
| ~ 3450, BAL max.    | 0.39              | ~ 3452, BAL max.   | 0.80              | ~ 3450, BAL max.    | 0.78              |
| 3290, shoulder      | 3290, shoulder    | 2905, dip          | 2910, shoulder    | 0.23               |
| 3100, wpp           | 3032, peak        | 2863, peak         | 0.14              | 2863, peak         | 0.25              |
| 2963, shoulder      | 2970, peak        | 1750, shoulder     | 0.35              | 1750, shoulder     | 0.22              |
| 2942, peak          | 0.27              | 1650, peak         | 0.46              | 1630, peak         | 1.14              |
| 2895, dip           | 2933, peak        | 1465, shoulder     | 0.42              | 1470, shoulder     | 0.57              |
| 1085, peak          | 1                 | 1438, shoulder     | 0.62              | 1440, shoulder     | 0.66              |
| ~ 1040 wp sh-r      | 1040, should      | 1410, peak         | 0.98              | 1410, peak         | 0.88              |
| 1283, peak          | 0.79              | 1287, peak         | 1                 | 1346, peak         | 0.66              |
| 1230-1260, sh-r     | 1250, shoulder    | 1290, shoulder     | 0.71              | 1                 | 0.13              |
| 1202, peak          | 1.14              | 1200, peak         | 0.93              | 1198, peak         | 1                 |
| 1170, shoulder      | 0.91              | 1170, shoulder     | 0.84              | 1167, peak         | 1                 |
| 1085, peak          | 1                 | 1080, peak         | 1                 | 1068, peak         | 1                 |
| ~ 1040 wp sh-r      | 1040, shoulder    | 1055, shoulder     | 0.80              | 1                  |
| 888, peak           | 0.83              | 888, peak          | 0.60              | 888, peak          | 0.34              |
| 848, peak           | 0.60              | 848, peak          | 0.40              | 850, peak          | 0.22              |
| 750, peak           | 0.12              | 750, wpp (?        | 0.71              | 887, wpp (?       | 1                 |
| ~ 620 wpp           | 0.11              | 623, peak          | 1                 | 1120, shoulder     | 0.84              |
| 605, peak           | 0.12              | 602, peak          | 0.24              | 612, peak          | 0.17              |
| 570, shoulder       | 0.37              | 565, wpp           | 0.44              | 515, wpp           | 1                 |
| 525, wp sh-r (?)    | 0.37              | 515, wpp           | 0.44              | 515, wpp           | 1                 |
| 492, shoulder       | 0.37              | 493, wpp           | 0.49              | 494, peak          | 0.36              |
| 445, wp sh-r (?)    | 0.47              | 478, wpp           | 0.47              | 465, shoulder      | 0.21              |
| 455, shoulder       | 0.48              | 437, dip           | 427, wpp          | 408, peak          | 0.22              |
| 420, dip            | 415, dip          | 408, peak          | 0.22              | 408, peak          | 0.09              |

Most of the peaks in oriented and unoriented grinded B-samples were coinciding in their positions. To visible differences between oriented and unoriented grinded B-samples should be referred the very pronounced shoulders at 1040 and 1120 cm$^{-1}$ in oriented sample in comparison with those ones in unoriented sample, shift of 1085 cm$^{-1}$ - band in unoriented sample to 1080 cm$^{-1}$ in oriented sample and the presence of a dip at 2895 cm$^{-1}$ the only in unoriented sample. BAL-maximum is observed in oriented grinded B-sample at 3452 cm$^{-1}$ and at almost the same position in 3450 cm$^{-1}$ in unoriented sample.

Linewidth $\Delta \nu_{\text{BAL}} = 355 \pm 5$ cm$^{-1}$ in oriented grinded B-sample. Along with BAL there are also in oriented grinded B-sample peak at 2933 cm$^{-1}$, weak shoulder at 2970 cm$^{-1}$, peak at 2860 cm$^{-1}$, shoulder at 1750 cm$^{-1}$, peaks at 1650 cm$^{-1}$, 1410 cm$^{-1}$, 1282 cm$^{-1}$, shoulder at 1250 cm$^{-1}$, peak at 1200 cm$^{-1}$, shoulders at 1110 cm$^{-1}$, 1040 cm$^{-1}$, peak at 1080 cm$^{-1}$, shoulder at 1000 cm$^{-1}$, peaks at 888 cm$^{-1}$, 848 cm$^{-1}$, then the lines with rather good resolution at 778, 675, 620 cm$^{-1}$, shoulder at 580 cm$^{-1}$, peaks at 537, 517, 497, 440 (weak), 415 (weak) cm$^{-1}$. In grinded A-sample BAL has max-
imum at \( \sim 3450 \text{ cm}^{-1} \), that is, in distinction from undamaged A- and B-films, practically at the same value with that one observed in grinded oriented and unoriented B-samples. Linewidth of BAL in oriented grinded A-sample has the value \( \Delta \nu_{B A} = 365 \pm 5 \text{ cm}^{-1} \), which is, like to positions of maximum, is coinciding within accuracy of measurements with linewidth value of BAL in grinded B-sample. Further, there are in oriented grinded A-sample the bands with peak positions at 2940, 2860 cm\(^{-1}\), shoulder at 1730, peaks at 1630, 1410 cm\(^{-1}\), absorption with almost plateau shape in the range 1060–1200 cm\(^{-1}\), peaks at 888, 850 cm\(^{-1}\), peak at 620 cm\(^{-1}\), shoulders at 540 cm\(^{-1}\), 520 cm\(^{-1}\), peak at 500 cm\(^{-1}\). It seems to be interesting, that among the lines, which are observed in grinded A- and B-samples there are two groups. There is the group of lines which have practically identical positions for both the samples (most intensive among them are: \( \sim 3450, \sim 2860, 1470, 1440, 1410, 1200, 888, 848 \text{ cm}^{-1} \)). There is also the second group of the lines undergoing the red shift in B- to A-sample sequence. To second group belong the lines with absorption maximum positions at 1080, 1650, 1750 cm\(^{-1}\) in grinded oriented B-sample. They are observed at 1068, 1630, 1730 cm\(^{-1}\) in grinded A-sample. It is essential that relative value of red shift is approximately the same for each of these three lines: \( (\Delta \nu/\nu \approx 0.012) \). One should consider the same relative value of red shift as a strong indication that all three lines belong to the same vibration center. Note that there is the line near 2200 cm\(^{-1}\) in undamaged films, which also undergoes red shift. It has the position at 2210 cm\(^{-1}\) in B-film, its position in A-film is 2195 cm\(^{-1}\). The relative value of red shift for this line is \( \Delta \nu/\nu \approx 0.007 \). Hence it seems to be evident that the line near 2200 cm\(^{-1}\) should belong to another vibration center. The multicomponent low frequency line with the first rotation peak position at 495 cm\(^{-1}\) undergoes some violet shift \( \Delta \nu/\nu = 0.010 \). So we have at the minimum three different vibration system in the samples studied. The next essential feature of absorption character in the samples studied is broadening of all the lines in A-samples in comparison with B-samples. Table 1 Table 1 (compare also Fig.2 with Fig.3). The spectra, which are presented in Fig.2 and Fig.3 were registered on the same IR-spectrometer with the same spectral resolution. For instance the width of well resolved b-line at 1410 cm\(^{-1}\) is 56 cm\(^{-1}\) and 85 cm\(^{-1}\) in B- and A-samples correspondingly. The widths \( \Delta \nu_a \) for a-line (its maximum frequency position \( \nu_a = 1650 \text{ cm}^{-1} \) in B-sample and \( \nu_a = 1630 \text{ cm}^{-1} \) in A-sample) are equaled to \( \sim 125 \text{ cm}^{-1} \) and \( \sim 185 \text{ cm}^{-1} \) correspondingly. The substantial feature of IR-absorption is also growth and drastic redistribution of intensities of red shifted lines in the samples A in comparison with the samples B. It is convenient to use as a reference amplitude the amplitude of any line from the group of two lines 888 and 848 cm\(^{-1}\), amplitude ratio of which is \( \sim 3 : 2 \) and remains the same in both the series of samples. It was found that amplitudes of red shifted lines are increasing relatively reference line at 888 cm\(^{-1}\) and gain values are \( \sim 6, 3.6, 1.8 \) for lines at 1750, 1650, 1080 cm\(^{-1}\) correspondingly. The relative amplitude ratios in this set are 1: 2.5: 4.5 in B-sample and 1: 1.5: 1.1 in A-sample. It is evident that the amplitude alignment takes place in A sample for this set. This result is additional prove that all three lines belong to the same vibration structure that is to the only one type of vibration centers. This conclusion is in agreement with conclusion obtained early in IR studies of carbynes, where the lines at 1060 cm\(^{-1}\), 1600 cm\(^{-1}\), 1720 cm\(^{-1}\) (1720 cm\(^{-1}\) line is mostly appeared as a shoulder \( \approx 23, 29 \)), (that is the lines with the frequency positions near those ones of red shifted three lines) have been observed and were referred along with line near 2200 cm\(^{-1}\) to carbyne localized vibration modes characterizing own carbyne structure (characteristic carbyne lines). It should be noted that BAL was not interpreted in previous studies and correspondingly not referred to characteristic carbyne lines. The lines in spectral range (920 - 1850) cm\(^{-1}\) (A-sample), (940 - 1820) cm\(^{-1}\) (B-sample) as well as in the range \( \sim 400 - 700 \text{ cm}^{-1} \) seem to be superimposed with background lines: MB-line and LB-line respectively. The conclusion about the spectra imposition is very similar to analogous conclusions of many authors. So Gerasimenko et al.\( \text{[27]} \) observed in Si implanted with 2.5 MeV hydrogen ions in addition to peaks that are clearly resolved the considerable unresolved background absorption in the range of \( \sim 1800 \) to 2100 cm\(^{-1}\). MB-line reveals the red shift of its maximal amplitude position \( \nu_{MB} \) along with the broadening in B- to A-sample sequence like to above described characteristic localized modes. The maximum position of MB-line \( \nu_{MB} \) in B-sample is observed approximately at \( \sim 1100 \text{ cm}^{-1} \) and linewidth \( \Delta \nu_{MB} \) is \( \sim 330 \text{ cm}^{-1} \). In A-sample the maximum position \( \nu_{MB} \) is approximately at \( \sim 1070 \text{ cm}^{-1} \) and \( \Delta \nu_{MB} \) is \( \sim 420 \text{ cm}^{-1} \). There is also the correlation of intensity of MB-line with the impurity increase. However the effective rate of the increase of intensity of MB-line with impurity increase being equal to \( \sim 1.9 \) is coinciding with that one of BAL but is lower in comparison with the rate of intensity increase of red shifted lines at 1650 and 1750 cm\(^{-1}\), registered in the same spectral region. Note that along with unshifted and red shifted lines some new lines have been observed in sample A and some lines have disappeared. So there is shoulder at 2910 cm\(^{-1}\) together with main line at 2940 cm\(^{-1}\) instead of single line at 2933 cm\(^{-1}\) and peaks at 1346, 870 cm\(^{-1}\). At the same time peak at 1287 cm\(^{-1}\), shoulders at 1120, 1250, peak at 515 cm\(^{-1}\) have not been observed. Instead of two peaks at 3033, 3020 cm\(^{-1}\) and instead of two peaks at 623, 607 cm\(^{-1}\) the only single-peak bands with intermediate frequencies at 3027 and 612 cm\(^{-1}\) correspondingly have been observed.

Therefore IR-spectra of carbyonid samples are rather rich and complicated and a number of their peculiarities (for instance detailed structure and shape of band near 3000 cm\(^{-1}\)) are subject of additional study. The most interesting at present study seem to be spectral characteristics of thet lines which have the relevance immediately
to carbonyne structure. As seen, they undergo red shift, intensity redistribution in own set by total intensity increase and broadening (along with all resolved lines) in A- to B-sample sequence. These properties are correlating with the total impurity content increase. Certain interest represents the vibration-rotation band, registered with the total impurity content increase. Certain in-

A- to B-sample sequence. These properties are correlating with the total impurity content increase and broadening (along with all resolved lines) in own set by total intensity increase and broadening (along with all resolved lines) in uniaxially oriented are characterized by quite flat background line in the range 1800 – 3600 cm$^{-1}$ for both type of PVDF-samples, Fig.4. It means as was mentioned above that really broad asymmetric line with maximum near 3450 cm$^{-1}$ is characteristic line the only for carbonyne (or carbynes). (This line cannot belong to possible uncontrolled substances in KBr since it is presenting in both ungrinded carbonyne films and grinded carbonyne samples compressed into pellet). At the same time the band with two peaks near 3000 cm$^{-1}$ (at 2992, 3033 cm$^{-1}$) and dip at 3013 cm$^{-1}$ in oriented sample and two peaks at 2990, 3034 cm$^{-1}$, dip at 3013 cm$^{-1}$ in un-oriented sample is very good pronounced. This band was to some extent discussed in Sec.A. Additionally in un-oriented PVDF-sample the peaks at 1700, 772, 620, 538, 516, 495, 439, 414 cm$^{-1}$ were observed. The range 800–1440 cm$^{-1}$ due to off-scale is the only partly informative and the positions of only some dips can be pointed out. Namely, dipshoulders at 1462, 1330 cm$^{-1}$, dips at 1366, 1000, and 933 cm$^{-1}$ and weak peaks at 990, 958 cm$^{-1}$ were found. The spectral lines in oriented PVDF-sample were registered almost at the same or even strictly at the same positions when comparing with unoriented PVDF-sample. So the peaks at 1708, 772, 618, 537, 514, 494, 438, 415 cm$^{-1}$, weak peak at 989 cm$^{-1}$, shoulders at 960, 1462 cm$^{-1}$, dips at 932, 1000, 1366 cm$^{-1}$, dipshoulders at 960, 1330 cm$^{-1}$ have been observed. It is interesting that any absorption bands are absent in the range of 1490 – 1680 as well as in the range 1730 - 1750 cm$^{-1}$ in both unoriented and oriented PVDF-film samples. Consequently these results are direct proof that the bands in the ranges 1630 - 1650, 1730 - 1750 cm$^{-1}$ in carbonyne samples like to BAL are characteristic bands the only for carbonyne structure in correspondence with conclusion in Sec.A. The oriented PVDF-film was also grinded and pressed into pellet with KBr. Unexpected result has been established: the lines which are characteristic for carbonyne structure were registered, that is broad asymmetric line in the range (2300–3700) cm$^{-1}$ with a maximum at ∼3480 cm$^{-1}$, shoulder at 1750 cm$^{-1}$, and a peak at 1650 cm$^{-1}$. The peaks at 1410, 1290, 1175, 1090, 886, 848, 475 cm$^{-1}$, shoulders at 1050, 1000, 610, 515, 450, 435 cm$^{-1}$ were also observed. The relative amplitudes for lines at 1750, 1650, 1090 cm$^{-1}$ are approximately 1 : 3:

10, that is, the vibration modes at 1750, 1650 cm$^{-1}$ are rather strongly suppressed in comparison with the mode at 1090 cm$^{-1}$. Note that relative amplitudes of low frequency lines with positions at 515 cm$^{-1}$, 474 cm$^{-1}$ in grinded PVDF-sample are essentially stronger than those ones in carbonyne A- and B-samples.

This observation can mean that by grinding a dehydration takes place. In other words the PVDF-sample converts partly to carbonyne structure. Analogous phase transition of carbon materials by grinding has been reported by Kirda et al [28]. They established that the average interatomic distance in anthracite sample which has been milled on vibromill was decreasing from 145 pm to 128 pm. We consider both the cases to be examples of the phase transitions, correspondingly, PVDF → carbonyne, and anthracite → carbonyne, appearing by the grinding.

Beside the lines, being to be characteristic for carbonyne structure there is group of lines in grinded PVDF-sample which have analogues in grinded carbonyne samples, at that they have substantially greater relative amplitudes in carbonyne structure. Peak positions of lines of this group in grinded PVDF are 1410, 1290, 1240 (shoulder), 1175, 1050, 886, 848 cm$^{-1}$. Their analogues for instance in B-sample are 1410, 1283, 1240, band with not pronounced maximum in the range 1230–1260, 1202 (tentatively), 1040 (shoulder), 888, 846 cm$^{-1}$.

Amplitude increase of these lines in the samples sequence: grinded PVDF → grinded carbonyne seems to be meaning that indicated lines can be attributed to carbon backbone, correspondingly, in grinded PVDF and carbonyne chains and cannot be assigned to fluorine, oxygen molecules/molecular ions, their complexes, or carbon-fluorine, oxygen-fluorine bonds.

So, the measurements of IR-absorption in both PVDF-films and grinded PVDF-samples are in agreement with conclusions of Sec.A. Furthermore, these results can be considered as a direct proof that broad line with maximum near 3450 cm$^{-1}$ is characteristic band the only for carbonyne structure like to the bands in the ranges 1630 - 1650, 1730 - 1750 cm$^{-1}$, 1060 - 1090 cm$^{-1}$, as well as the band in the range ∼ 2100 - 2200, which were attributed to characteristic bands for carbonyne structure early in carbonyne studies [23, 27]. The results allow also to suggest that the lines with peak positions in grinded PVDF at 1410, 1290, 1240 (shoulder) 1175, 1050, 886, 848 cm$^{-1}$ can be attributed to vibration modes of carbon backbone, that is, it is suggested that they are not responsible for possible lateral C-F or C-H valence bond vibrations.

C. Nature of red shift and origin of background IR-lines

Although the bands in the ranges 1630 - 1650, 1730 - 1750 cm$^{-1}$ as well as the band in the range 1060 - 1090 cm$^{-1}$ were attributed to characteristic bands for carbonyne structure in a number of previous studies [23]...
and references therein, for instance references [1 - 8, 14 - 29] in [23], nevertheless the detailed origin of these bands was not established unambiguously. Further, any attention was not drawn on the presence of broad background lines LB, MB. The origin of BAL was almost not discussed.

It can be suggested that MB- and LB-lines are the manifestation of the interaction between localized IR-modes. This interaction can be realized both immediately by localized phonon-phonon interaction and by means of spin transfer (and/or charge transfer) through spin-phonon (respectively charge-phonon) interaction. In a result any interaction mentioned can lead to formation of background lines. Note, that formation mechanism of IR LB- and MB-lines seems to be related to formation mechanism of ESR-background lines in neutron-irradiated or ion implanted silicon and in electron-, neutron-irradiated or ion implanted diamond, see, for instance [29, 30].

If spin transfer (or joint spin-charge transfer) is determining mechanism, then it has to lead to the broadening of all resolved IR-bands by spin-dopant (both spin- and charge dopants) concentration increase. Really all IR-lines are essentially broader in the samples with greater fluorine and oxygen content, compare Figures 2 and 3, see also Tables 7 and 7. It testifies in favour of suggestion. Note that this idea has direct experimental confirmation in the case of charge transfer, So broadening of IR-lines was observed by dopant concentration increase due to enhance of charge transfer in a number of organic conductors, for example in alkali-metal-doped polymeric fullerenes [31]. The simplest way for realization of spin transfer in the samples studied is the transfer by means of quasiparticles with nonzero spins. Consequently we can suggest that two sets of the localized IR-modes undergoing red shift with the impurity content increase belong to various quasiparticle kinds with nonzero spins. The most probably, that the bands at 1750, 1650, 1080 cm\(^{-1}\) that is first set modes can be attributed to localized vibration modes of spin-Peierls soliton with ESR-spectrum C-M2, Fig.2. The additional arguments see below in Sec.D).

The spectra presented in Fig.5, Fig.6 are reproduced from [1] and [4], but they need in short comment. Let us remember that PC C-M1 were attributed in [6] to chemical radicals of unknown origin. The point of view on the origin of PC C-M1 can be developed. It is very plausible that C-M1 centers can be attributed to private case of chemical radicals, namely to pinned solitons which belong to the family introduced by Rice et al [32]. Essential difference of Rice-solitons from SSH-solitons is very strong localization of unpaired spins in Rice model. The suggestion that C-M1 centers can be attributed to pinned Rice solitons seems to be correlating with both very pronounced saturation behavior of PC C-M1 by microwave power, reported in [2], and much smaller g-value deviation from g = 2.0023 for PC C-M1 in comparison with that one of PC C-M2. We suggest that the line at 2210 cm\(^{-1}\) can belong to Rice solitons, which are, from other hand, responsible for ESR-spectrum C-M1, Fig.5. The correlation of ratio of intensities of ESR lines of PC C-M1 and C-M2 with ratio of intensity of 2210 cm\(^{-1}\) line to total intensity of 1750, 1650, 1080 cm\(^{-1}\) lines in B-sample and their correlating change in B- to A-sample sequence, see Fig.2 3 5 can testify in favour of this suggestion. (Note that intensity of ESR absorption is determined by means of double integration of resonance spectrum).

With regard to PC C-M2, one can see that their ESR-spectra are more complicated. In the simplest case PC C-M2 spectrum consist of one group of unresolved or partly resolved lines which is observed in both A- and B-samples. In accordance with [1, 6] PC C-M2 represent themselves spin-Peierls solitons. There are additional lines L1, L2, L3 in C-M2 ESR-spectrum of A-samples, Fig.5. They correspond to spin wave resonance (SWR) which seems to be associated (see below) with spin-Peierls soliton lattice formation. The lines L1, L2, L3 are SWR modes with n = 1, n = 3, n = 5 correspondingly. It should be noted that by appearance of spin waves usual PC C-M2 spectrum is in fact simultaneously the mode with n = 0 in SWR-spectrum. The L1-line is therefore the line consisting of 2 overlapped SWR-modes with n = 0 and with n =1. The SWR-modes with n = 0 and with n =1 were resolved in C-M2-spectrum of A-sample registered after 1.8 year storage, owing to splitting of all SWR-modes with n ≠ 0 into 2 components, Fig.6 One can see from Fig.6 that L1-line really consist of 3 components.

Note that the lengths of SWR modes allow to determine carbon chain polyconjugation length. Moreover they in principle all give directly the value of polyconjugation length. Really it should be \(\lambda_1/2\), where \(\lambda_1\) is the length of the first SWR-mode. The vacuum value of \(\lambda_1\) is 3.19 cm in the experiment presented in Fig.6 Refraction coefficient \(n_\lambda\) in X-range of microwave frequencies is unknown for carbynoids. Suggesting \(n_\lambda\) in the range 1.6 - 160 we obtain \(\lambda_1/2 = 1\) cm - 100\(\mu\)m, that is in fact the value up to sample size. In particular if \(n_\lambda = 2.28\) we obtain the value of polycnjugation length strictly equal to the sample size in 0.7 cm. Therefore we are dealing in fact with sufficiently homogeneous system of carbon chains, which are long, their length is comparable with sample size. Direct evaluation of conjugation length corresponds therefore to initial conception on carbyne structure [23].

Note that there is a qualitative similarity in the shape of BAL in IR spectra with the shape of ESR-lines of PC C-M2. They are also asymmetric, see, Fig.5, Fig.6 with like to BAL opposite to usually observed asymmetry extent.

It should be noted that analogous broad asymmetric IR-band with the same maximum position near 3450 cm\(^{-1}\) (0.43 eV) was observed in trans -polycetylene (in photoexcited sample). It is remarkable that it was registered simultaneously (on the same signal gain scale) with a number of strongly IR-active localized vibration modes of charged SSH-soliton. Nevertheless it was attributed to
 electronic transition, namely to transition from a electrically charged SSH-soliton state in the middle of bandgap to the nearest band of quasicontinuum energy levels \[33\]. The fact that vibrational and electronic transitions of SSH-solitons can be displayed on the same scale is very striking. Usually, typical IR-oscillator strengths are, for example, for local impurity modes, as well known, smaller than those ones for electronic transitions by a factor of \(\sim 10^4\).

We believe that broad asymmetric IR-bands at 3425 cm\(^{-1}\) and at 3467 cm\(^{-1}\) in B- and A-films correspondingly, which are also displayed simultaneously with IR-vibration localized modes (Figures 2, 3), can be attributed to electric spin transition of spin-Peierls solitons from their states in bandgap to the nearest electric spin-conductivity band of quasicontinuum energy levels \(E_{sc}\). In other words since SPS due to spin-charge separation have zeroth electric charge and, consequently, zeroth electric dipole moment, they can be optically active, if they possess by nonzero electric spin moment. Electric spin moment, according to Dirac relativistic quantum theory, has pure imaginary value \([34]\). So we suggest that SPS possess by both electric and magnetic spin moments which can be considered as two components of complex electromagnetic spin vector as a single whole. Then the nature of SPS can be developed. They seem to be consisting of two coupled domain walls in both magnetic and electric GSDW, produced by electromagnetic spin-Peierls transition in its generalized form in \(\pi\) - and \(\sigma\) -subsystems of carbynoids respectively. In other words SPS are domain walls in dimerized both electric \(J_E\) - and magnetic \(J_H\) -exchange interaction between kink fragments of carbon chain. Therefore SPS represent themselves a new type of solitons, which can be referred to SSH-soliton class. The energy of BAL-transition gives the energy position of SPS states in bandgap. Therefore the energy position of SPS in bandgap is near \(\sim E_{sc} - 0.43\) eV in both A- and B-samples. Note that energies of these states are strictly coinciding in grinded samples, but they are slightly different (in 0.006 eV) in films. The asymmetry of the shape of IR-0.43 eV-band in t-PA, \([\text{which to our opinion seems to be appeared due to essential electron-charge conductivity on the transition frequency}],\) was the main argument to refer 0.43 eV-band to namely electronic transition but not to vibration mode \([33]\). The same argument seems to be taking place in the case of spin-conductivity, however in contrary to electron-charge transition the pure electron-spin transition (as consequence of the spin-charge separation) corresponds \([\text{how it can be shown}]\) to the line with opposite (mirror) left to right asymmetry character, which is appeared due to high spin-conductivity at transition frequency.

Therefore there is clear correlation of IR-spectra parameters with impurity content which in turn determines the formation of spin carriers, that is spin-Peierls solitons (and, possibly, related quasiparticles) and spin transfer. The charge of SPS has to be zero, since they are products of spin-charge separation but they have accordingly to suggestion the nonzero complex spin moment. Then simultaneous IR and ESR activity can be explained if spin-Peierls solitons possess both magnetic and electric spin moments. From direct analogy with t-PA follows that appearance of BAL with maximum position near 3450 cm\(^{-1}\) in IR spectra can be explained as a result of electric spin-transition from SPS states in band gap \(E_{sc} - 0.43\) eV to electric spin-conductivity band. Results obtained are also in good agreement with proposal that the lines at 1080, 1650, 1750 cm\(^{-1}\) undergoing the same value of relative red shift with impurity increase are SPS vibration modes.

D. Hamiltonian of vibronic system of carbynoids

SPS, representing the new type of solitons, electromagnetic solitons, were introduced in \([1, 6]\) as magnetic solitons. Here the notion "magnetic soliton", as well as the notions "electric soliton", "electromagnetic soliton" mean correspondingly the solitons, which are formed in magnetically ordered, ferro(antiferro)electrically ordered or simultaneously magnetically and ferro(antiferro)electrically ordered media. Note, that in separate pure ESR or pure optical experiments SPS behave as magnetic or electric solitons, that is, their dual nature seems to be not becoming apparent. Therefore their properties can be compared with the properties of known magnetic and optical solitons separately. Electric solitons, determined in such a way, are, to our knowledge, unknown at all at present. SPS in magnetic "hypostasis" belong, as it was mentioned above, to SSH-soliton class. At the same time the known magnetic solitons belong to sine-Gordon class \([35]\). The conclusion relatively the SPS type is in accordance with the structure of Hamiltonian (see below) which is proposed for theoretical description of interacting electronic and vibration subsystems in spin-Peierls compounds. We cannot use the SSH-model for carbynoids immediately since in the SSH-model the equality in "rights" of the part of total wave function, which depend on spin variables is ignored. It restricts naturally the application of SSH-model in the case of strong electron-electron interaction, taking place in the samples studied (see Sec.E). The tradition way to take into account the role of spin variables is indirect. It is realized with symmetry requirement to total wave function, which leads to appearance of exchange term, characterized by constant \(J\), in Coulomb interaction. Consequently to restore the role of spin variables we have to add to SSH-Hamiltonian J-dependent terms. The corresponding model is well known t-J model, in which both spin-phonon and charge-phonon interaction are taken into account. This model was proposed by Terai \([36]\). The model, used by Terai, can be developed by including of additional terms, taking into consideration the interaction between the solitons themselves on the one hand and with impurities on the other hand (like to known extension of SSH-model). Then the Hamilto-
nian is:
\[
\hat{H}_{i-J} = -\sum_{i,\sigma} t[1 - \alpha(u_{i+1} - u_i)](\hat{c}_{i,\sigma}^+ \hat{c}_{i+1,\sigma} + \hat{c}_{i+1,\sigma}^+ \hat{c}_{i,\sigma}) \\
+ \sum_{i=1}^{N} J[1 - \lambda(u_{i+1} - u_i)](\hat{S}_i \hat{S}_{i+1} - \frac{1}{4} \hat{n}_i \hat{n}_{i+1}) \\
+ \sum_{i=1}^{N} \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i=1}^{N} k(u_{i+1} - u_i)^2 + \sum_{j=1}^{N} k'(\delta \theta_j)^2 \\
+ \sum_{q=1}^{N} V_{q}^{imp} \hat{c}_{q,\sigma}^+ \hat{c}_{q,\sigma} + \sum_{q=1}^{N} V_{q}^{sol} \hat{c}_{q,\sigma}^+ \hat{c}_{q,\sigma},
\]
where \( t \) is hopping integral, \( J \) is exchange constant, which is equal to \( J_H \) or \( J_E \) in the case of ferromagnetic or ferroelectric ordering respectively, \( \hat{c}_{q,\sigma}^+ \) and \( \hat{c}_{q,\sigma} \) are creation and annihilation operators of a particle with spin \( \sigma \) on the \( q \)-th unit site, \( \hat{S}_q \) is spin operator, \( \hat{n}_q \) is number particle operator, \( u_q \) is the displacement of the \( i \)-th atomic unit in the lattice, \( p_q \) is the momentum conjugate to \( u_q \), \( \alpha \) and \( \lambda \) are charge-phonon and spin-phonon coupling constants respectively, \( V_{q}^{imp}, V_{q}^{sol} \) characterize the interaction at \( q \)-th atomic unit site of the solitons with counter impurity complexes and with the solitons on surrounding chains respectively, \( k \) and \( k' \) are spring constants, which characterize the vibration along the chain axis and perpendicular to the chain axis respectively. It can be seen from the expression (1) (without even solution) that along with bond alternation like to SSH-model there is analogous alternation of exchange interaction between spin-localizing units. We take for possible the predominance in (1) of \( J \)-dependent term in the samples studied. Then, \textit{a priori}, it becomes to be evident that the SPS solution will have mathematically the form, which is similar to well known soliton solution of SSH-Hamiltonian and as a result the appearance of purely magnetic solitons (in the case when \( J \) is equal to \( J_H \) belonging to SSH-family in distinction from the known sine-Gordon magnetic solitons. Therefore modified t-J model above proposed seems to be reasonable and necessary generalization of SSH-model for organic conductors in the case of the systems undergoing the spin-Peierls or generalized spin-Peierls transitions, that is for the systems for which the electron-electron interaction is rather strong. Really it is known that the SSH-model is inapplicable immediately for the case when on-site Coulomb interaction \( U \) is \( > 4.68 \) eV \([37]\). The fact that \( t - J \) model proposed can be considered in its kernel as a SSH-model generalization follows from Hamiltonian (1) since if \( J = 0 \) we have the extended SSH-model \([38]\) in which the possibility of soliton-lattice formation is taken into account (by last term).

E. Evaluation of U-value and comparison with quantum field theory predictions

According to Horovitz \([39]\) the number of IR active modes of topological soliton in polymer chain is deter-
mained by the number of degrees of freedom of elementary monomer unit of the chain. It seems to be the most probably that three above mentioned red shifted IR-lines in the samples studied are the modes associated with three degrees of freedom which don’t bring out the atoms of elementary unit from the chain direction. Consequently it can mean that at least \( n = 4 \), that is 4 carbon atoms belong to the single linear atomic unit, taking part in spin-bond alternation process during spin-Peierls transition. In fact the number \( n \) can be \( > 4 \), since, first, not all the modes were resolved well in rather complicated IR-spectrum, second, several modes can be strongly coupled and be displayed by a single line in a spectrum and, third, not all IR active modes can be localized modes \[38\]. Actually the resolution in carbyne characteristic spectral range was achieved in the spectra of third set of samples (which are not reported in this work). Along with peak at 1086 cm\(^{-1}\) the peaks at 1655, 1730, 1789 cm\(^{-1}\), shoulders at 1620 and 1700 cm\(^{-1}\) were observed. According to Horovitz criterion the number of carbon atoms in dimerization unit in this sample is \( \geq 7 \). Note that the present result is in fact the additional proof of Heimann et al suggestion on the kinked shape of carbyne chain \[14, 15\]. On other hand it means, that spin-Peierls transition should be namely in generalized form discussed in \[1\], that in its turn indicates that electron-electron correlations in carbyne chain are really strong. Additional argument to this conclusion is very large shift \( \Delta E \) of SPS energetic states in the gap from midgap position, which can be simply evaluated if one takes into account that gap value is 1.86 eV \[6\], consequently \( \Delta E \) equals to 0.5 eV. The value of shift \( \Delta E \) indicates directly according to \[22\] that electron-electron correlations are rather strong. This result can be considered to be experimental proof of necessity of J-term inclusion in equation \[11\] for description of vibronic states in carbynoids.

Above proposed modified t-J model is equivalent to some extent to Hubbard model, for instance at small J values t-J model is strictly equivalent to large U-values Hubbard model \[40\]. Consequently we can use for the evaluation of U the approach of Kivelson and Heim \[41\] and simple expression for U derived there:

\[
U \sim 2\xi \Delta E, \tag{2}
\]

where \( 2\xi \) is the width of the soliton in relative interatomic distance units. For evaluation of U we have used the same value of relative width of free spin-Peierls solitons in B-samples equaled to \( 2\xi = 15 \) like the width of SSH-soliton in t-PA. The value of \( U = 7.5 \) eV obtained in that way agrees in principle with conclusion of Subbaswamy, Grabowski that the ground state in organic conductors at large U (at \( U > 4.69 \) eV in the case of t-PA) is the state with SDW, where distribution of spin density is harmonic (further it will be designated as HSDW) \[37\]. Note that ground state of samples studied identified to be also spin density wave with periodic but nonharmonic density distribution, it is designated GSDW, see Fig.1. From mathematical point of view the difference between these states is minimal since GSDW can be represented as superposition of HSDWs, where amplitude of main harmonic is strongly exceed the others. Actually the expansion of GSDW (GCDW) profile in Fourier series is:

\[
f(x') = A(2L_0 + L_1) \sum_{m=0}^{\infty} \left\{ \frac{2(2L_0 + L_1)}{2L_1 \pi^2 m^2} \left( \cos \frac{\pi m L_0}{2L_0 + L_1} - \cos \frac{\pi m L_0 + L_1}{2L_0 + L_1} \right) - \pi L_1 m \sin m\pi \right\} \cos \frac{2\pi mx'}{L}, \tag{3}
\]

\[
f(x) = A(2L_0 + L_1) \left[ \frac{1}{4} + (2L_0 + L_1) \sum_{m=1}^{\infty} \left( \cos \frac{\pi m L_0}{2L_0 + L_1} - \cos \frac{\pi m L_0 + L_1}{2L_0 + L_1} \right) \cos \frac{2\pi mx}{L} \right]. \tag{4}
\]

The sense of the parameters \( L_0, L_1, L \) is seen from Fig.8. The functions \( f(x), f(x') \) denote spin density distributions \( S(x), S(x') \) in the case of GSDW and charge density distributions \( \rho(x), \rho(x') \) in the case of GCDW. Expression \( f(x') \) corresponds to position of chain atoms along \( X' \)-direction, Fig.8 that is like to that one presented in top schema of Fig.7. Expression \( f(x) \) corresponds to position of chain atoms along \( X \)-direction, Fig.8. We see in this case, that is, by asymmetric deviation of spin (or charge) density relatively the chain direction, that the constant component is appeared. It can lead in the case of GSDW to ferromagnetic ordering if spin distribution is magnetic spin distribution and to ferroelectric ordering by electric spin distribution. One can also see from \( f(x) \) and \( f(x') \) that the amplitude of components with \( m > 1 \) is inversely proportional to \( m^2 \), that is, it diminishes rather quickly when number \( m \) increases. In the first order approximation the relations \( f(x) \) and \( f(x') \) can be represented by:

\[
f(x') = A(2L_0 + L_1) \alpha \cos \frac{2\pi x'}{L} + o \left( \frac{1}{m^2} \right), \tag{5}
\]
parameters, characterizing the spin liquid. They showed that the separate spin and charge excitations of strongly interacting electronic system are topological solitons in a Luttinger liquid, that is, in other words, the separation of spin and charge in the 1D t-J model is determined by topological mechanism in agreement with our data.

The experimentally observed ordering is also agreed with [2] and can be explained in the frame of quantum field model used in [2] as a second order phase transition. According to [2] it can be induced from gapless Luttinger spin liquid due to frustrations and leads to long-range spatial order, in particular to dimerization or other types of order.

So our results allow to conclude that spin-Peierls-solitons are elementary excitations in carbynoid conductors, obtained by dehydrohalogenation of polyvinylidene fluoride. We can conclude on example of carbynoid samples studied that in spin-Peierls systems the role of spin-carriers seems to be predominating in comparison with the role of electric charge carriers by interaction with external electromagnetic field in both the radiofrequency and optical ranges that is both magnetic and electric spin-carriers determine main features in IR- and ESR-spectra.

F. Spin-Peierls soliton-lattice formation

The most strong spin-conductivity is observed in the samples of A-group, that is in the samples with a maximal impurity content, since the only in these samples magnetic spin waves can be excited and detected. It seems to be understandable that with spin-Peierls solitons’ concentration increase in result of spin-dopant (molecules and clusters from residual and technological impurities) increase the (quasi)continuous spin medium, which is necessary for spin waves’ propagation, can be created at some spin-Peierls solitons’ concentration value. Note that the process of SPS creation by doping can be considered to be entirely analogous to the process of creation of charged SSH-solitons by electric charge-doping procedure [22], that is, the same type of quasiparticles can be produced by various doping species. The spacing between SPS introduced by doping is naturally decreased by increasing the dopant concentration and it can become to be comparable with the width of a SPS. Coherent interaction of SPSs leads then to the spin-Peierls soliton lattice (SPSL) formation in a manner similar to the topological SSH-soliton lattice formation in trans-polyacetylene discussed for instance in [43, 44]. Accordingly, in bandgap, appearing in result of generalized spin-Peierls transition, the narrow magnetic spin-conductive band should be additionally formed in the samples A instead of deep individual states of SPSs. The presence of spin-conductive narrow band of SPS states in forbidden spin-Peierls gap instead of isolated spin Peierls-soliton energy levels seems to be necessary condition for magnetic spin wave excitation associated with these solitons. It seem to be evidently that the appearance of magnet-
ically ordered condensed state with SPSL has to lead to broadening of BAL, that is IR-line which now correspond to transition of spin carriers from narrow SPS spin-conductive band in forbidden gap into main spin-conductive band and especially to the broadening of SPS vibration modes. Really $\Delta \nu_{BA \parallel}$ changes from $\approx 730 \text{ cm}^{-1}$ to $\approx 840 \text{ cm}^{-1}$ in A to B film sample sequency (a factor of 1.15), the width $\Delta \nu_{a}$ of a-line observed at 1650 before SPSL-formation and at 1630 cm$^{-1}$ after magnetic SPSL-formation increases from $\sim 125 \text{ cm}^{-1}$ to $\sim 185 \text{ cm}^{-1}$ (a factor of 1.48). It should be noted that the appearance of ordering in A-samples of ferromagnetic type $\text{CuFeO}_3$ is agreed well with lattice formation from SPSs, since they have a shape of SSH solitons’ type. Physically it means that in distinction from HSDW, where spin density distribution is harmonic, and from GSDW, where spin density distribution is nonharmonic but symmetric relatively zero line, nonharmonic SPSL is also in fact density wave (DW) with also periodic, but nonsymmetric relatively zero line spin distribution (zero line position is determined by positions of centers of carbon atoms in chain before metal-insulator transition). SPSL has the only positive sign in coordinate distribution of spin density while in HSDW and in GSDW the positive and negative signs are alternating. Nevertheless the term SDW can be kept in principle for DW of these 3 types. The observation of Dyson-like shape of ESR-lines, Fig.6 with the asymmetry of the shape being to be opposite to conventional Dyson effect is [how it can be shown] the direct indication of spin-conductivity effect. It should be noted that identical asymmetry character of ESR-lines was observed in other spin-Peierls conductors, for instance, in inorganic compound $\text{CuGeO}_3$ [14] (see Figure 1 in [15], however the authors of [16] did not present any comments to this result). The conclusion about SPSL formation is also in agreement with calculation in [6] of infrared active localized modes for SSH-soliton lattice in t-PA, where the authors have found that the frequencies of soliton vibration modes are decreased and their localization is weakened when the dopant content is increasing. Qualitatively similar picture has to be taking place for SPSL since SPSs and SSH-solitons belong mathematically to the same class. The picture predicted is really taking place. It is proved by observation in A-samples, respectively, of red shift and broadening of vibration modes of SPSs. It has to pay attention on the following peculiarity of carbynoid conductors studied. The increase of impurity concentration has to be resulting like to 1D-character of the sample properties. Given conclusion was confirmed by Hartree-Fock calculations taking into account 3D-interactions due to Na-superlattice by using of SSH + extended Hubbard model for so heavily doped t-PA. Soliton lattice state with a gap is preserved even if quantum fluctuations of electron and lattice subsystems were completely taken into account. Although in Na-doped t-PA the soliton lattice is formed from starting coupling-order wave (private case of CDW), the situation in the samples studied seems to be $\text{a priori}$ qualitatively similar. In carbynoid A-samples SPSL seems to be formed from GSDW or more strictly from mixed GSDW - GCDW state, which is similar to soliton lattice in Na-doped t-PA in the sense that it is also the state with breakdown translation symmetry. Note that mixed SDW - CDW state is characteristic for the systems described by t-J model [36]. (It is interesting also that t-J model predicts a spin-wave-like excitations in so-called high-frequency limit [52] which were really observed in the samples studied, that is, there isn’t contradiction between the description on t-J model base and SDW - representation of ground state). Let us remember that some mixing of CDW state in its private case of coupling-order wave follows from the observation of weakly pronounced IR band near 2200 cm$^{-1}$ and, probably, ESR CM1-centers, which seem to be indication on the presence of single-triple bond alternation. For our discussion is substantial that in the case of mixed ground state the electrical gap due to CDW and magnetic gap due to SDW (both can be appeared in generalized sense) exist (or not) synchronously. It means that we do in any case the correct conclusion on magnetic gap existence from the results of microwave photoconductivity studies in [6]. It should be noted that effective concentration of impurity centers (impurity centers seem to be presenting the dopant units in the form of molecules or their complexes but not in the form of single impurity atoms) that is effective doping level is essentially lower in correspondence with atomic ratios of number of F and O atoms to number of C atoms. It is interesting to try to establish which impurities are responsible for the spin-doping effect. At present we can suggest the presence in the interchain space of the following formations from residual and technological impurity counteratoms: oxygen molecules, fluorine clusters, fluorine-oxygen complexes and complexes including C-H bond. The presence of hydroden complexes was discussed. The spin-doping effect can tentatively be associated with molecules or complexes which have nonzero spin like to oxygen molecules and probably, fluorine-oxygen complexes. The formation of fluorine-oxygen complexes in interchain space seems to be the consequence of the diffusion mobility of their components. High diffusion mobility of impurity atoms, which aren’t included in a main carbon backbone, is a general property for 1D-organic polymers [38]. Therefore, it is possible that fluorine-oxygen complexes, for instance $\text{FO}_4^-$, can be formed. The spin-doping effect of the complexes with nonzero spin is expected to be analogous
to charge-doping effect of well known charged dopants in 1D-organic polymers, for instance, pure halogen ion groups like to \((J_1)^-\) or \((J_0)^-\) [49, 50] and \((O_2)^-\) ions [51]. We evaluate that doping level in our samples is not exceeding in any case (but can be comparable) with that one in heavily (~11%) sodium doped \(t\)-PA studied in [47]. Hence follows immediately that the only SPSL formation will preserve the transition to "spin-metallic" state. Therefore the assumption on the formation of magnetic SPSL in \(A\)-samples agrees well with ESR, IR-absorption and microwave photoconductivity data. The electric SPSL has even more so to be formed, that it can be expected in both type of the samples. However it cannot be registered immediately in both film and grinded samples studied by means of IR-absorption spectroscopy. It cannot be registered in films owing to off-scale in necessary spectral range. It cannot be registered in grinded samples because of absence of translation invariance in grinded samples, diluted by KBr, since even "polycrystalline" structure on the base of electric SPSL seems to be not taking place (but relatively magnetic SPSL it can be). This conclusion becomes understandable if one takes into account that lattice period of electric SPSL is expected to be much more exceeding lattice period of magnetic SPSL. It is also understandable, that presence of electric SPSL is sufficient for excitation and propagation of electric spin waves, but in general is insufficient for emergence of magnetic spin waves. Although electric SPSL is difficult to detect by IR-absorption methods in the samples studied, nevertheless the magnetic SPSL was experimentally identified. Additional argument in favour of SPSL model gives evaluation of possible relative change of cinematic constant by magnetic SPSL formation from the value of red shift. Actually, the changes in IR-spectra by magnetic SPSL formation can qualitatively be explained taking into account general spectroscopic properties of polymers on the simple model representing the translation-invariant chain consisting of \(N\) oscillators with eigenfrequency \(\nu\) and characterized by cinematic \(\tau\) and force \(k\) coefficients for any pair of neighbouring oscillators. The vibration branch assigned to single soliton mode by soliton lattice formation can be given then by the expression, which is analogous to that one known for polymer chain [26], that is by

\[
\nu_m^2 = \{1 + 2\tau \cos\left(\frac{m\pi}{N} + 1\right)\}\{\nu_0^2 + 2k \cos\left(\frac{m\pi}{N}\right) + 1\}, \tag{8}
\]

where \(m = 1, 2, 3, ..., N\).

For large \(N\)-numbers the frequency shift between \(i\)-th localized mode of free soliton and \(N\)-multiply degenerated mode in soliton lattice is satisfying the expression

\[
\nu_{s,i}^2 - \nu_{0,i}^2 = 2\tau_{s,i}\nu_{0,i}^2 + k_{s,i} + 2k_{s,i}\tau_{s,i}, \tag{9}
\]

that is the frequency shift has really to be taking place. The effect is similar to that one observed always by polymer formation where vibration eigenfrequencies are shifted down relative to eigenfrequencies of monomer-units, from which given polymer is built, even in the case when free monomer structure and structure of corresponding polymer unit are coinciding. To evaluate the contribution in the shift due to soliton lattice formation we take into account the fact, that frequency shift observed (that is, the shift for the origin of which SPSL formation is proposed to be responsible) is small in comparison with starting frequency of soliton modes before SPSL formation. Then the expression for the shift of \(i\)-th soliton vibration mode in common case, when both the cinematic and the force parameters can be changed, will be:

\[
\delta\nu_{s,i} = \frac{(\nu_{0,i}^2 + k_{s,i})\delta\tau_{s,i}}{\nu_{s,i}} + \frac{(1 + 2\tau_{s,i})\delta k_{s,i}}{2\nu_{s,i}}, \tag{10}
\]

where \(\delta\tau_{s,i}\) and \(\delta k_{s,i}\) are the change of the cinematic and the force parameters. Note that the expressions (8) to (10) seem to be valid in the case of the formation of soliton lattice of both the types, that is the lattice from the solitons like to SSH-solitons in \(t\)-PA and the lattice from spin-Peierls solitons identified in the samples studied. In the state with SPSL the electric charge distribution and consequently the force coefficients can be considered to the first order approach to be unchanged like to those ones in conventional SDW-state. Then we have

\[
\delta\tau_{s,i} = \frac{\nu_{s,i}\delta\nu_{s,i}}{(\nu_{0,i}^2 + k_{s,i})}. \tag{11}
\]

The cinematic coefficient seems to be decreasing due to effective soliton mass increase in the soliton lattice state in comparison with soliton mass in free state. Physical explanation of the effective soliton mass increase by soliton lattice formation seems to be consist in the following: to excit the motion of one soliton all the solitons in soliton lattice have to be excited simultaneously in a soliton train. It seems to be reasonable to suggest that to establish the law for the change of cinematic constant \(\delta\tau_{s,i}\) for \(i\)-th soliton mode one should use the functional dependence \(\tau = \tau(M)\) for the simplest carbon compounds, where the carbynoid chain monomer unit is presenting and which has the vibration eigenfrequency near one of the eigenfrequencies of spin-Peierls -soliton modes. Then the simple variation procedure can be used. The most suitable modelling vibration mode seems to be \(C = C\) stretching mode of monomer \(C = C\) unit which is presenting in ethylene or allene, the eigenfrequency of which is near 1650 cm\(^{-1}\), that is, it practically coincides with the eigenfrequency of main spin -Peierls-soliton mode at 1650 cm\(^{-1}\) (which is designated as \(a\)-band, then \(i = a\) in eq. (9) to (11). Taking into account that for modelling \(C = C\) unit the dependence \(\tau = \tau(M)\) is \(\tau = 2/M_0\), where \(M_0\) is carbon atom mass, and believing the mass to be variable, we have the relation

\[
\tau = 2/M. \tag{12}
\]
Then the variation of mass according to eq.12 corresponding to the determined by eq.11 variation of $\tau$ allows to evaluate the change of soliton mass by SPSL formation. Physically it means, that by formation of soliton lattice, parameter $\tau$ will "feel" surrounding. Surrounding can be taken into account if relation $\tau = 2/M_0$ is preserved but $M$ becomes variable near $M_0$ in which turn is determined by experimentally measured $\delta M_{s,a}$. For so a-band $(i = a)$ we have:

$$|\delta M_{s,a}| = \left|\delta \frac{2}{M_0^2}\right|. \quad (13)$$

Consequently, neglecting free SPS mass in comparison with the SPS mass in SPSL we obtain the evaluation value for the SPS mass $m_{sL}$ in SPSL:

$$m_{sL} = |\delta M| = \frac{M^2s,a_\delta \nu_{s,a}}{2(\nu_{0,a} + k_{s,a})}. \quad (14)$$

Using for the force constant $k_{s,a}$ the value in the range between $15.1 \times 10^6$ cm$^{-2}$ and $68$ eV A$^{-2}$ ($71.1 \times 10^6$ cm$^{-2}$) corresponding to allene and carbyne we obtain for the effective value of $s,a$ mass in SPSL the evaluation in $0.11 - 0.13$ a.m.u. We obtain also the evaluation of $\delta \tau/\tau$ which is $\sim 1\%$. Note that this value is coinciding with the evaluation value in $\sim 1\%$ predicted by Mozurkewich et al [54] for changes in ratio of Youngs’ modulus for condensate and underlying lattice by CDW depinning in CDW-conductors. Mozurkewich et al have suggested in their model that the total stiffness of a CDW conductor can be separated into contributions from the CDW condensate and the underlying lattice which are additive for pinned CDW, while for a fully depinned CDW the total stiffness is determined by the stiffness of the underlying lattice. Although this model yields elasticity change within the range of experimentally observed shifts Bourne and Zettl [58] have used for the explanation of elastic properties of CDW conductors TaS$_3$, NbSe$_3$ in the presence of ac, and/or dc electric fields the development of the model [54] proposed in [54] which treats the interaction of deformable CDW with a deformable underlying lattice. Bourne and Zettl have determined for instance the changes in ratio of Youngs’ modulus for condensate and underlying lattice by CDW depinning in TaS$_3$, taking place when ac frequency varies in the range $0 - 10$ MHz. They were equal to $\sim 4 \times 10^{-3}$ and are explained by the model proposed in [59] better. At the same time the model of Mozurkewich et al [54] proposed for interpretation of elastic properties of CDW conductors seems to be more appropriate for changes of optical properties in particular of the centers being to be topological disturbances in CDW itself and becoming to be pinned by CDW pinning. Really from microscopic point of view the changes in Youngs’ modulus established in [54, 58, 59] are equivalent to the changes in spring constants for the stretching vibration modes of topological defects in CDW that is $\delta k/k$ is also $\sim 1\%$ for the vibration modes of these centers in CDW-conductors by depinning. It is substantially that optical transitions are realized for the time which is insufficient for any deformation of underlying lattice, that is model developed in [59] becomes coinciding in limit of undeformable underlying lattice with the model proposed in [54]. The same evaluated values for $\delta \tau/\tau$ in studied SDW-conductor (defined in generalized above sense) by SPSL formation and for $\delta k/k$ in above mentioned CDW-conductors by depinning seems to be understandable if one takes into account that the relative energies of interaction of valence electron condensates with an underlying atomic lattice seem to be comparable for SDW- and CDW-states and they seem to be also comparable with relative energy of SPS condensate formation, that is with the energy of SPSL interaction with the underlying atomic lattice. It is understandable also that the appearance of the spin wave propagation in result of SPSL formation can lead to some effective change $\delta k_{s,i}$ in the force constants however it seems to be necessary to take into account in the second order approach. It seems to be interesting to consider the phase transition GSDW to SPSL from energy conservation law, that is, to which form transform the energy of vibration, corresponding to difference in the frequencies of SPS vibration modes. We suggest that this energy transform directly in the energy of exchange interaction of electric spins of SPS which necessary has to emerge in condensed state with SPSL. If it so we can evaluate the value of exchange interaction from energy conservation law as follows. Since exchange interaction is determined by spin couples then evaluation value in zero approximation for exchange parameter in SPSL is predicted to be equal to double value of red shift, that is, of order $34-40$ cm$^{-1}$. This value will be equal to splitting parameter in electric spin wave resonance. Therefore the reasonable value in $\sim 1\%$ of relative change of cinematic constant $\delta \tau/\tau$ by magnetic SPSL formation obtained from observed value of red shift of main vibration mode of SPSs is strong additional indication in favour of the idea of SPSL formation in A-samples. So above listed arguments seem to be sufficient to insist that the formation of magnetic SPSL in A-samples is actually takes place.

G. Origin of absorption structure in range 395 - 950 cm$^{-1}$ in PVDF- and carbynoyd B-films

Along with fine-structured band at $475 - 477$ cm$^{-1}$, registered in dispersion mode both in PVDF- and carbynoyd B-films (see Sec.A) there are strong intensive bands, which are also observed in PVDF- and carbynoyd B-films, which however are registered in absorption mode. The shape of two well resolved bands is very similar, that can be considered as evidence of the same origin of these bands. Both the bands along with peaks have characteristic shoulders. Peak positions are $618, 620$ cm$^{-1}$ for the first band and they have the same value of 772
cm\(^{-1}\) for the second band accordingly in oriented and unoriented PVDF films. The first band has shoulder at 607 cm\(^{-1}\), and shoulder appears at 750 (±10 cm\(^{-1}\)) in the second band in both oriented and unoriented PVDF films. **Strictly the same values of peak and shoulder positions have been observed in oriented and unoriented carbynoid B-films.** The most probably, that to the structure consisting of these 2 bands one can refer the band with peak near 915 cm\(^{-1}\) (strict peak position and the shape of this band were not established due to partial off-scale and overlapping with other bands), which is observed in oriented and unoriented PVDF- and carbynoid B-films. There is also indication that the bands above described and fine-structured band at 475 - 477 cm\(^{-1}\) produce some united structure (US). It is almost the same spacing with the value near ~150 cm\(^{-1}\). It is evidently that this united structure cannot be attributed in PVDF to valence vibrations of C-H or C-F lateral bonds since all the components of this structure are observed in carbynoids and, that is striking, strictly at the same positions and even with slightly increased (by 5%) relative amplitude. Therefore US-bands can belong the only to some intrinsic disturbances of C-C bonds in PVDF and accordingly the only to some intrinsic disturbances in \(\sigma\)-bond subsystem of carbynoids. Note, that usually \(\sigma\)-bond subsystem is not taking into account by determination of electronic properties of carbyne chains (\(\pi\)-electronic approximation is usually used). The origin of these disturbances should seek in peculiarity of PVDF structure, evidently in alternation of \(\sigma\)-bonded CF\(_2\) and CH\(_2\) groups. Although all carbon atoms form single C-C bond between themselves along the chain in this compound we have to take into account that each of two neighboring carbon atoms interact with two different surrounding atoms in lateral bonds. Then become to be possible the following 2 main variants for ground state: 1) the state with CDW (in the form of HCDW or GCDW) including private case of CDW - the state with bond length alternation as a result of Peierls transition in generalized or conventional form. Then topological defects in corresponding charge distributions will be charged solitons or polarons with zero magnetic spin moment. 2) the state with electric spin moment density wave, ESDW, (in the form of HESDW or EGSDW) including private case of ESDW - the state with alternation of exchange interaction or, on bond language, the state with "J-bond" length alternation as a result of electric spin-Peierls transition in generalized or conventional form. Here we believe in implicit form, that the states with nonzero electric spin have own classification schema, that is \(\sigma\)-state relatively magnetic spin value will be most probably \(\pi\)-state relatively electric spin value. Then topological defects in corresponding electric spin density distributions will be solitons or polarons with nonzero electric spin. Naturally the state with conventional magnetic SDW (in the form of HSDW or GSDW) cannot be produced due to zero magnetic spin moment in \(\sigma\)-state of macromolecule. In suggestion that case 1 takes place it is difficult to explain the appearance of rotational structure in PVDF, since C-H and C-F-lateral bonds should take participation in this rotation (due to interaction between charges of carbon backbone and lateral bonds) which is evidently unreal in solid matrix. It is also incomprehensible the appearance of dispersion mode in absorption spectra. At the same time case 2 allows to explain all the peculiarities in US-band spectrum observed. Let us consider this case in some details. Independently of detailed form of ESDW we obtain as elementary excitations solitons and polarons (that is, soliton and antisoliton pairs) which possess by nonzero electric spin. Formation of ESDW corresponds to antiferroelectrically ordered ground state. Since the interaction in antiferroelectrics has long range order and owing to formation of solitons and polarons the state with continuous electric spin distribution in ESDW -form slightly transforms (like to that one established in A-samples for magnetic GSDW) into soliton or polaron electric spin lattice with substantially more strongly localized electric spins. We suggest that electric spin-Peierls polaron lattice (ESPPL) is formed. So we suggest the formation of antiferroelectrically ordered lattice which consist of 2 sublattices A and B. They correspond to soliton and antisoliton components of polaron correspondingly. Hamilton operator for ESPPL can be represented in a form:

\[
\hat{H} = \mu_n \sum_{n,\alpha} \hat{E}^{E} \hat{S}_n^{E(\alpha)} + \frac{1}{4} \sum_{\bar{n} \neq n, \alpha, \beta} J_{\alpha,\beta}(\bar{n}-\bar{m}) \hat{S}_{\bar{n}}^{E(\alpha)} \hat{S}_{\bar{m}}^{E(\beta)},
\]

(15)
where \( \alpha, \beta = A, B \). Vectors \( \vec{n}, \vec{m} \) are vectors of the lattice, vector \( \vec{E} \) is vortex component of total electric intracrystalline and external field, \( \gamma_{\alpha,\beta}(\vec{n} - \vec{m}) \) is exchange integral, \( J_{\alpha,\beta} < 0, J_{\alpha,\alpha} = J_{B,B} > 0 \), \( \vec{g} \) is electrical analogue of magnetic resonance g-tensor, \( \vec{S}_{\vec{n}} \), \( \vec{S}_{\vec{m}} \) are electric spin operators, corresponding to \( \vec{n} \)-element in sublattice A and \( \vec{m} \)-element in sublattice B, \( \mu^E \) is electrical analogue of Bohr magneton. Mathematically similar Hamiltonian is the Hamiltonian for antiferromagnets, which is well known. So we can write its solution right away, following, for example, (15):

\[
\varepsilon_1(\vec{k}) = \frac{1}{2} \left[ \alpha(\vec{k}) - \beta(\vec{k}) + \sqrt{\alpha(\vec{k})^2 + \beta(\vec{k})^2 - 4\gamma^2(\vec{k})} \right],
\]

\[
\varepsilon_2(\vec{k}) = \frac{1}{2} \left[ \beta(\vec{k}) - \alpha(\vec{k}) + \sqrt{\alpha(\vec{k})^2 + \beta(\vec{k})^2 - 4\gamma^2(\vec{k})} \right].
\] (16)

Here \( \alpha(\vec{k}) = \alpha(-\vec{k}) = L_{AA}(0) - L_{AA}(\vec{k}) + \mu^E_E E + \gamma(0), \beta(\vec{k}) = \beta(-\vec{k}) = L_{AA}(0) - L_{AA}(\vec{k}) - \mu^E_E E + \gamma(0) \). \( \gamma(\vec{k}) = \gamma(-\vec{k}) = -2L_{AB}(\vec{k}) \), \( L_{AB}(\vec{k}) = S^E \sum_{\vec{n}\in A} J^E_{\alpha\beta}(\vec{n})e^{i\vec{k}\vec{n}} \).

\( \alpha, \beta = A, B \), \( S^E \) is value of the spin. Square root in (16) is arithmetic square root. Therefore we have two branches of elementary exitation. In long-wavelength approximation \((ka \ll 1)\) expressions for \( \varepsilon_1(\vec{k}) \) and \( \varepsilon_2(\vec{k}) \) can be simplified and we obtain the following dispersion law:

\[
\varepsilon_{1,2}(\vec{k}) = \pm \mu^E_E E + k\sqrt{\gamma(0)(l_{11} + l_{12})},
\] (17)

where \( g^E \) - tensor is suggested to be isotropic and

\[
l_{11} = \frac{S}{2} \sum_{\vec{n}} \vec{n}^2 J^E_{AA}(\vec{n}), \quad l_{12} = -\frac{S}{4} \sum_{\vec{n}} \vec{n}^2 J^E_{AB}(\vec{n}).
\] (18a-b)

Note, that known solution corresponds to continual limit. However, in the case of the chain of finite length \( L \) the values of \( \vec{k} \) in the first Brillouin zone are discrete. To restore the solution for discrete case one should insert the following boundary conditions:

\[
A_{\vec{n}} = A_{\vec{n}} + \vec{c}_n L, B_{\vec{n}} = B_{\vec{n}} + \vec{c}_n L, i.e. e^{ikL} = 1
\] (19)

Here we have taken into account, that in 1D-case the direction of lattice vector \( \vec{n} \) coincides with chain direction. Then after using of transform to boson operators during derivation of eq.(16) we obtain for \( \varepsilon_k \)

\[
k_m = \frac{2\pi m}{L}
\] (20)

where \( m = 0, 1, 2, \ldots \). Therefore, for the frequencies of antiferroelectric resonance we have

\[
\nu(m) = g^E \mu^E_E E + \frac{2\pi m}{L} \sqrt{\gamma(0)(l_{11} + l_{12})},
\] (21)

It is seen, that the spectrum of antiferroelectric spin wave resonance (AFESWR) of 1D linear chain with length of \( L \) represents in long-wavelength approximation the equaldistant set of AFESWR-modes. It is also seen, that this approximation corresponds to linear resonance of the system on external electromagnetic field. Then the superposition principle is taking place and one can insist that the mode with \( m = 0 \), that is fine-structured band at \( 475 - 477 \) cm\(^{-1} \), is determined by the first part of Hamiltonian, but the modes with \( m \neq 0 \), that is the bands with peaks at 618, 772 and near 915 cm\(^{-1} \) are determined by the second part of Hamiltonian. It is essentially and it allow to explain the difference in registered shapes of \( m = 0 \) mode and \( m \neq 0 \) modes in a natural way. Really, in the work (16) was shown that optical transition dynamics for the ensemble of two-level optical centers can be described by quantum mechanical optical analogue of Landau-Lifshitz (L-L) equation. L-L equation in the case of the ensemble of two-level noninteracting optical centers is:

\[
\frac{\partial \vec{S}^E(z)}{\partial t} = \left[ \vec{S}^E \times \gamma_E \vec{E} \right],
\] (22)

where vector \( \vec{E} \) is:

\[
\vec{E} = E_1 e^{i\omega t} e_+ + E_2 e^{-i\omega t} e_+ + \left( -\frac{\omega}{\gamma_E} \right) e_z.
\] (23)

Two components \( E^+ = E_1 e^{i\omega t}, E^- = E_2 e^{-i\omega t} \) are right- and left-rotatory electric constituents of external electromagnetic field with amplitude \( E_1 \). The third component \( E^z = (\frac{-\omega}{\gamma_E}) \) is intracrystalline electric field, which produces the splitting \( h\omega_0 \) of energy level for each of chain elements into two components. Intracrystalline electric field \( E_0 \) corresponds to the frequency \( \omega_0 \) in accordance with the relation

\[
\omega_0 \longrightarrow \frac{1}{\tau} \mu^E_E E_0 = \gamma_E E_0,
\] (24)

where \( \gamma_E \) is gyromagnetic ratio, that is electrical analogue of gyromagnetic ratio. When proceed in (22) to the observable values and to take into account the relaxation processes, we obtain well known optical analogue of Bloch equations. Their solution for the case of linear response is:

\[
S^E_x = \chi^E_x \frac{(\omega_0 - \omega)E_1}{1 + (\omega_0 - \omega)^2\tau^2},
\] (25)

\[
S^E_y = \chi^E_y \frac{E_1}{1 + (\omega_0 - \omega)^2\tau^2}. \] (26)

The complex-valued function of the response, that is complex electrical susceptibility, is

\[
\chi_E = \chi_E^t + i\chi_E^\nu,
\] (27)

where

\[
\chi_E^t = \frac{S^E_x}{2E_1}, \chi_E^\nu = \frac{S^E_y}{2E_1}.
\] (28)
and

\[ \chi_0 = i|\chi_0| \]

(29)

is pure imaginary quantity, since electric spin vector is a vector with imaginary components \[34\]. Then absorption signal, that is \( Im\chi_E \) will be

\[ Im\chi_E \sim \frac{\omega_0 \tau^2 (\omega_0 - \omega)}{1 + (\omega_0 - \omega)^2 \tau^2} \frac{1}{2} |\chi_0| \epsilon. \]  

(30)

Therefore it really has the dispersion-like shape. Since the signal which is determined by the second part of Hamiltonian (15) is proportional to superposition of products of \( \vec{S}_i \vec{S}_j \), where both the spins are imaginary vectors, it will have an absorption-like shape, but it will be registered \( \pi \) out of phase in comparison with that one detected, for instance, by magnetic resonance absorption. Really, the lines registered in US-spectrum in absorption mode are \( \pi \) out of phase to the signal of dispersion-like mode of the same spectrum. This conclusion follows from comparison of the signal polarities of observed AFESWR modes with \( m \neq 0 \) and \( m = 0 \) in reference to the relative polarities of dispersion and absorption signals in magnetic resonance, see for instance \[57\]. Splitting energy in 150 cm\(^{-1}\) is rather large. It means that electric spin-Peierls polaron lattice in C-C \( \sigma \)-bonds is stable formation and although polaron lattice was emerged owing to alternation of CF\(_2\) and CH\(_2\) monomers in PVDF-polymer structure, it is not needed after its formation in F- and H-atoms for its existence. So the observation of the same US-spectrum in carbonyd B-samples, which evidently can be attributed to electric spin-Peierls polaron lattice in \( \sigma \)-subsystem, becomes natural explanation and confirms in its turn the correctness of conclusion on rather high stability of ESPPL being to be formed in \( \sigma \)-bonds. Therefore, antiferroelectric spin wave resonance being to be optical analogue of antiferromagnetic spin wave resonance has been identified for the first time. Electric spin-Peierls polaron lattice in C-C \( \sigma \)-bonds is deduced to be responsible for observed AFESWR. The observation of antiferroelectric spin wave resonance (owing to its spectroscopic peculiarities) is the most direct proof of observability of imaginary electric spin moment (at least in condensed matter), which was predicted by Dirac as early as 1928. So, electric spin moment was identified for the first time.

H. Incommensurate SDW-phase in carbonyds and incommensurate to commensurate SDW transition

Relatively rapid changes in ESR-spectra with storage time in the B-samples were reported in \[1\] (however, they were not discussed there). The changes observed are determined (how it will be argued below) by the incommensurate to commensurate SDW-transition (designation "SDW" is used in generalized sense). According to \[1,6\] the SDW-formation in carbonyd films is believed to be directly confirming by the observation of a broad ESR-line, which was always observed in A-samples by arbitrary sample orientation and at any storage time, although broad ESR-line was observable in B-samples the only for relatively short time period after their preparation. Broad line is attributed to collective ESR-absorption by SDWs themselves. The possibility of collective magnetic absorption by SDW means that SDW itself can move along underlying chain lattice. SDW-movement can consist in spatial variation of their amplitudes and phases and in sliding as it was mentioned above. The observed very broad ESR line, Fig.5 can be attributed to sliding of corresponding SDW, that is, GSDW in our case. In other words it can be depinned at the excitation by microwave field, which is used by ESR-measurements. This conclusion is in agreement with results described in \[55,59,60\] indicating that characteristic depinning energies for CDW-slicing of the known systems correspond to the range of microwave frequencies. We bear in mind here that depinning energy for SDW will be of the same order with that one for CDW, since SDW ground state can be viewed as two CDW states – one for the spin-up and one for the spin-down sub-bands, Fig.7 ESR peculiarities, observed in B-samples, Fig.5 can be explained in the following way. Substantial relatively short storage time change in ESR-absorption (displaying by the measurements in 12 days) seems to be, predominantly, determined by the changes of spin-phonon interaction, being in its turn a result of the impurity redistribution. Really, some minimal modification of spin-phonon interaction, practically not accompanying by atomic rearrangement, can lead to pinning of SDW as well as to spin-Peierls soliton pinning, however with different efficiency since wave function of SDW-state is delocalized along the chain in distinction from well localized domain-wall wave function of the SPSs. The conclusion is in agreement with experimentally observed 3.75 times smaller average rate for ESR-absorption intensity change by PC C-M2, assigned to spin-Peierls solitons in comparison with the rate of intensity change of very broad ESR-line, Fig.5 assigned with SDW-motion. Fluorine atom groups, fluorine-oxygen complexes, oxygen molecules and a number of complexes with C-H bonds, which are suggested to be formed in interchain space, can be redistributed in some time after the sample production. There seems to be reasonable to propose that this redistribution leads to impurity complexes selfordering, that is, to regularity in their positions along chains. Driving force for the selfordering can be, the most probably the periodic density wave potential. Residual impurity redistribution is the factor, which, in its turn, in self-consistent way can affect SDW parameters. The role of impurity redistribution is especially effective in density wave pinning if density wave state is near incommensurate to commensurate transition. The mechanism is like to the mechanism proposed in \[62\] and consists in the following. Impurities slightly modify the wave vector of SDW (and in principle the lattice constant of the underlying lattice) to get the
commensurate case. On the other hand, when the period of a SDW-modulation becomes commensurate with the lattice period, the interaction between two periodicities becomes also substantial and the resulting commensurate potential can easy pin the SDW. We believe that the case described above takes place in carbynoid B-samples and that the excitation energy for the movement of commensurate GSDW exceeds the energy of X-band microwave photons.

Thus the origin of drastic changes in ESR-spectra in relatively short storage time presented in Fig[4] can be explained by the redistribution of main spin-dopants in the starting periodic SDW-field. SDW-field in turn is modified by a new distribution of the impurities. The processes stated seem to be self-consistent, and they result finally in the incommensurate to commensurate SDW-transition. In its turn the incommensurate to commensurate SDW-transition brings to substantial SDW-pinning which results in the drastic decrease in ESR-absorption. Whether starting SDWs (mixed with CDWs) will be commensurate or incommensurate it depends probably on the ratio of carbon atoms to main dopant impurity atoms complexes per chain length unity that is probably whether is the ratio indicated integer or fractional (the case of the ordered impurity distribution between adjacent carbon chains is keeping in mind). The concrete chain state, that is with commensurate or incommensurate SDWs’, will depend on the relative concentration of doping complexes, on their distribution function along the carbon chains in interchain space and finally on dopant profile after its redistribution during the sample storage. The suggestion on the trend to periodical selfordering of residual impurity complexes in B-samples after their fabrication agrees well with the observation of the formation of the ordered impurity superlattice in highly Na-doped t-PA (that is in the material being related to carbynoids)[21][63]. Consequently, density wave state in carbynoid samples produced by means of PVDF dehydrohalogenation can be spontaneously modified in some time after the sample production. The modification can lead both to quantitative changes consisting in the change of the parameters characterizing the SDW-kind, that is depinning energy, wave vector, etc, and to qualitative changes consisting in the realization of the incommensurate to commensurate transition in density wave state (and vice versa in principle). The result stated seems to be general for all the density wave conductors and in principle can be used to obtain the samples with desirable distribution profile in synthetic conductors’ technology by means of employing of the periodical external fields at the synthesis. Note that observed in A-samples broad ESR-line associated with sliding of modified SDW (the modification consist in SPS lattice formation) as a result of its excitation by microwave field is well registered independently on the storage time period. It can be explained if to suggest that the SPSL period is incommensurate with atomic lattice period of the chain. The possibility of the excitation of SPSL motion or SWR will then depend on direction of dc and ac fields relatively chain direction. At the same time SPSL in A-samples being to be incommensurate with atomic lattice is rather stable formation since it remains incommensurate with storage time. It means that the formation of SPS lattice stabilizes starting incommensurate SDW-phase and the physical properties of the materials. Note that above discussed stability properties are concerned the only π-subsystem of carbynoids and will be correct only in π-approximation. The results discussed in Sec.G show that π-approximation can be not valid. Especially interesting it seems to study the stability of electronic σ-subsystem in both B- and A-samples, in particular the stability of ESPPL in B-samples. Therefore IR- and ESR-absorption data agree well. They indicate on the formation of rather stable SPS lattice in A-samples (that in the samples with rather high impurity content) and the formation of unstable incommensurate GSDW state in B-samples (with lower impurity content) where the incommensurate to commensurate DW-transition is proposed to be taking place in relatively short storage time (12 days) after sample production.

IV. SUMMARY AND CONCLUSIONS

The results of IR studies in quasi-1D carbynoid films produced by dehydrofluorination of poly(vinilidene fluoride) agree well with ESR-results and lead to the conclusion that the carbynoid films produced by dehydrofluorination of poly(vinilidene fluoride) are spin-conductors with spin-Peierls ground state being stable at room temperature. The spin-conductivity increase detected by both IR- and ESR-methods on the same carbynoid samples correlates with the concentration increase of residual fluorine (and maybe hydrogen, which was uncontrolled) and technological oxygen atoms. They tentatively produce in interchain space various complexes between themselves. These complexes in their turn can be attributed to spin-conductivity dopants. The correlation has been established in appearance of red shift of positions of IR lines at 1080, 1650, 1750 cm$^{-1}$, position of maximum of broad background line (MB-line) in the range of 900 -1900 cm$^{-1}$ (all observed in grinded film samples) and 2210 cm$^{-1}$ IR-line (observed in starting ungrinded film) as well as in broadening of all observed resolved IR-lines with the content of above mentioned residual and technological impurities. The lines with the frequencies 1080, 1650, 1750 cm$^{-1}$ undergoing the same value of relative red shift (0.012) in the samples with more high impurity content (A-samples) are attributed to localized vibration modes of solitons of new type, called spin-Peierls solitons. They are characterized simultaneously by earlier reported C-M2 ESR-spectrum. t has therefore been established that spin-Peierls solitons are simultaneously active, unlike to topological solitons with nonzero spin in trans-polyacetylene, in both opti-
cal and magnetic resonance spectra. Simultaneous optical and ESR activity of SPS is explained in suggestion that SPS possess by both electric and magnetic spin moments which can be considered as two components of complex electromagnetic spin vector as a single whole. SPS proposed to be consisting of two coupled domain walls in both magnetic and electric GSDW, produced by electromagnetic spin-Peierls transition in its generalized form in $\pi$ - and $\sigma$ -subsystems of carbynoids respectively. In other words SPS are domain walls in dimerized both electric $J_E$ - and magnetic $J_H$-exchange interaction between short kink fragments of carbon chain and represent themselves a new type of solitons, which can be referred to SSH-soliton class. Real part of electromagnetic spin vector of SPS is proposed to be responsible for magnetic SPS-lattice formation and simultaneous emergence of ferromagnetic-like ordering in A-samples (the samples with the most impurity content of the range used).

IR- and ESR-absorption data indicate that SPS in $\pi$-subsystem of A-samples is incommensurate but rather stable. Starting ground state in B-samples (with lower impurity content) is unstable incommensurate GSDW state and the incommensurate to commensurate DW-transition is proposed to be taking place in relatively short storage time (12 days) after sample production.

The broad asymmetric IR-line with position at the frequency 3450 cm$^{-1}$ is attributed to transition of spin carriers from the SPS localized levels in bandgap ($E_{sc}$ - 0.43 eV) (in B-samples) or from narrow spin-conductivity band in gap, centered near ($E_{sc}$ - 0.43 eV) (in A-samples) to main spin-conductivity band.

Coulomb on-site interaction U is evaluated to be equal 7.5 eV, confirming the necessity for the generalization of SSH-model developed for trans-polyacetylene. The way for the generalization is proposed and it seems to be successful in the frame of modified t-J model, which in private case of $J = 0$ coincides with the approach based on SSH-model.

The IR-and ESR-data agree well with topological nature of spin-charge separation mechanism developed for 1D strongly correlated systems by Mudry and Fradkin in the effective quantum field theory consideration which includes the fluctuations of order parameters, characterizing the spin liquid in contrast to deconfining mechanism of spin-charge separation being the result of mean field approach.

Antiferroelectric spin wave resonance being to be optical analogue of antiferromagnetic spin wave resonance has been identified for the first time. Electric spin-Peierls polaron lattice in C-C $\sigma$-bonds is deduced to be responsible for observed AFESWR both in starting PWDF films and carbynoind B-films. The observation of antiferroelectric spin wave resonance (owing to its spectroscopic peculiarities) is the most direct proof of observability of imaginary electric spin moment (at least in condensed matter), which was predicted by Dirac as early as 1928. So, electric spin moment was identified for the first time.

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