# FULLERENE-LIKE STRUCTURES IN COALS

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**Abstract**
Anthracites are considered as raw materials for the production of fullerenes, and the radiospectroscopy method is proposed for express diagnostics of carbonic materials. In this work the features of the influence exerted by sizes, forms, and structures of anthracite samples on EPR signals are studied. It has been demonstrated that the features of the recorded EPR spectra for the coals exhibiting high degrees of metamorphization are associated with high concentrations of the localized spins at the recording conditions and also with the peculiarities of their spatial-temporal localization within the fullerene-like structures of the coals.

**Key words**:- diamond**,** Anthracite**,** fullerene , EPR, microwave radiation

**Phisiology Classification QC 170-197**

**Introduction:-** Carbon atoms are capable of forming a number of allotropic forms significantly differing in their structure, in physical and chemical properties — from monocrystalline diamond and graphite to the forms with less ordered, quasi-morphic structures. Allotropic forms of carbon have become model objects for several branches of the basic science and applications. The terms «diamond-like», «graphite-like» are the notions widely used for the description of the properties exhibited by the structurally and chemically different solids.Finding of one of the allotropic carbonic forms is of particular importance, being also a stimulus for further development, refinement, and even revision of the concepts, notions, and models associated with the material structure. In other words, we can expect that the terms «fullerene-like elements and structures» will be conventional, similar to the terms «diamond-like and graphite-like». The notion «fullerene-like» is even more adequate for the description of microscopic (nanoscopic) structural features of a material from the viewpoint of its size and form (0-, 1-dimension).Among the fullerene-like elements and structures, we can name not only the closed single-layer and polyatomic 0-dimensional carbonic formations with $n>>60$ but also single- and multilayer 1-dimensional tubelenes, differently ordered multilayer ultra-dispersed clusters, their aggregates. It should be noted that, as distinct from 2-dimensional graphite-like structures, the fullerene-like elements have a lower dimension. Ideal fullerene-like elements have a closed system of σ-bonds, being capable of aggregation by means of π–conjugation.Models for different fullerene-like structures have been discussed broadly in the publications treating the physical structuring features of carbon atoms in the processes of pyrolysis of organic fibres and nets and also path forming (tracking) in monocrystalline diamond on high-energy ion implantation; the structural models of the coals, their metamorphization have been correlated; roles of the structural and physical factors in forming of the critical states in coals liable to cause dangerous gas-dynamic phenomena have been established.As a rule, a commercial-grade graphite is used as a raw material for the industrial production of fullerenes. A search for inexpensive sources of raw materials to be used during a synthesis of fullerenes is still in progress. Thorough studies of anthracite are necessary to elucidate its structure and the possibilities of its use as a raw material for the fullerene production.

**Experimental**:- Studies of EPR in the coals are conventionally performed with the powders [1, 2]. It is natural that comminution of coal should result in breaking of its structure, enhancement of adsorption processes and, possibly, of chemical reactions. Because of this, the paramagnetic absorption parameters of powdered and monolithic samples may be different. This work presents a study into the properties of paramagnetic absorption of, predominantly, monolithic samples with the use of a SE/X-2544 (RadioPAN) spectrometer.Lowering of the cavity quality (Q) factor after positioning of a sample was dependent on its orientation, reaching the highest value for the orientation $\mathbf{X} \perp \mathbf{H_1}$, where $\mathbf{H_1}$ – vector of the magnetic component of a microwave field, and $\mathbf{X}$ – long edge of the sample.EPR spectra for the sample measuring 7x3x3 $mm^3$ are shown in Fig. 1. Curves 2 and 3 are recorded in the nominal mode, i.e. with the automatic frequency control (AFC) of a klystron relative to the frequency of a working cavity for the forward (increasing magnetic field, curve 2) and backward scanning (curve 3). In both cases one can observe the intensity changes, whereas the spectral form is different. There are no frequency changes without the use of AFC (curve1). The width of the observed asymmetric line in this case is ΔH=0.025 mT.

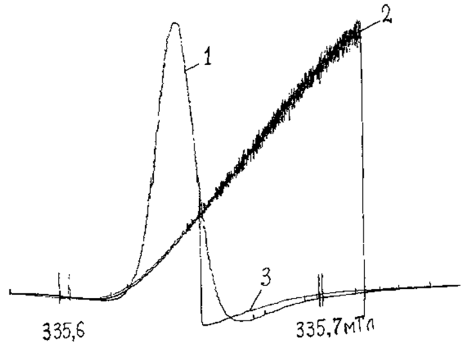


Fig.1. Spectra for the first derivative o an EPR signal of the anthracite sample measuring 7x3x3 $mm^3$, $\mathbf{X} \perp \mathbf{H_1}$ without (1) and with AFC when $\mathbf{H_0}$ is increasing (2) or decreasing (3); $P_1$ = 3 mW, the marks are given every 0.1 mT

A spectral interval between the intensity changes (hysteresis width) is influenced by the power of microwave radiation $P_1$ and by the Q factor of a cavity. With an increase in $P_1$, a width of hysteresis is decreased, whereas in the case of the lowering Q factor (e.g., when the sample size is growing or with the use of an absorber) it is increased. The greatest hysteresis width (0.55 mT) has been obtained for $\mathbf{X} \perp \mathbf{H_1}$. When the sample volume is < 20 $mm^3$, there is no hysteresis. Also, it is not observed for large samples having the EPR line width > 0.1 mT. Depending on its orientation, the sample with a volume of 50 $mm^3$ exhibits three forms of EPR lines: in the form of a dispersion signal and with the low-field A to the high-field B ratio of its amplitude given as A/B>>1 or A/B<<1

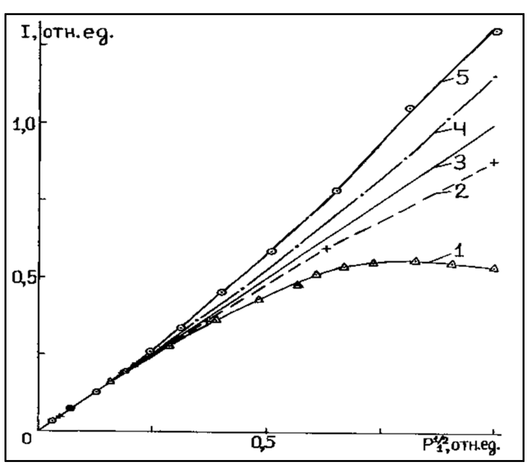

**Fig.2. Intensity I of the EPR line as a function of the microwave radiation power $P_1^{1/2}$ for the anthracite sample with the volume 0.5 mm$^3$ (1), for ruby (2), linear dependence of I on $P_1^{1/2}$ (3) for the spectral carbon powder (4), for the anthracite powder in toluene(5)**

A width of the EPR line correlates well with the sample conduction. To illustrate, for samples with the volume ~0.5 mm$^3$ chipped out of a single piece, ΔH was varying within the limits from 0.018 to 0.11 mT, and the conduction measured for the samples 7 mm in length was varying from 0.09 to 0.25 $\Omega^{-1}$ cm$^{-1}$. After the annealing procedure in the vacuum at 950°C for a period of 30 minutes, the conduction was 28 $\Omega^{-1}$ cm$^{-1}$, ΔH – 2.2 mT. A width of a practically symmetric line for the anthracite powder in the air was 15 mT; on evacuation down to the pressure $5\cdot10^{-2}$ mm Hg – 0.145 mT, and when the ampoule was filled with toluene – 0.45 mT.

Fig. 2 shows the results obtained in a study of the paramagnetic absorption intensity depending on the microwave radiation $P_1^{1/2}$. Curve 2 in Fig. 2 reveals a change in the absorption intensity of ruby positioned at the cavity center as a function of $P_1^{1/2}$. This function has a weak tendency for saturation. For the monolithic sample with the volume 0.5 mm$^3$ exhibiting a symmetric EPR line, the function of $P_1^{1/2}$ represents a bell-shaped curve with a maximum at $P_1$ = 34 mW (Fig. 2, curve 1). A similar form of the function has been observed for monolithic samples with the volume 8, 27, 32, and 63 mm$^3$, whose absorption line exhibits the Dyson-type asymmetry [3] or dispersion signal curve.The superlinear dependence similar to that for the implanted diamond [4] is observed for anthracite powders (curve 5) and for the carbon rod used during spectral analysis (curve 4). Curve 5 was measured for the anthracite powder wetted with toluene. A similar form of the function is associated with the powder within the evacuated ampoule.

**Conclusions**:- The hysteresis phenomenon in EPR spectra for anthracites, changes in their intensities are revealed when the three following conditions are combined: high absolute concentration of the paramagnetic centres within a sample; short width of spectral lines; significant dielectric losses introduced by the sample in the cavity. This combination of sample's properties results in the formation of a complex microwave system «working cavity — sample», just this system affords a nonstandard operation mode of the AFC unit – locking of the microwave oscillator frequency by a «high Q cavity of the sample», with the frequency varying under the magnetic field effect, rather than by the working one.Unusual combination of the paramagnetic properties characteristic for anthracite (irregular narrow width of an EPR line, line form, and g-factor with the marked electrical conduction and heterogeneous structure of the material) in turn necessitates that their interpretation be realized using mechanisms of the spatiotemporal electrons delocalization in a special structural environment with the fullerene-like elements and structures present in anthracite. The formation of such structures is determined by the metamorphization processes of, predominantly, one-dimensional carbonic systems. Petrographic studies of the coals are in line with this model [5].

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## هياكل الشباه الفوليرين في الفحم الحجري

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الخلاصة:-

أنثراسايت يعتبر كمادة خام لإنتاج الفلورين، وطريقة التحليل الطيفي الراديوي كوسيلة من وسائل التشخيص السريع لمواد الكربون .في هذا العمل دراسة تأثيرات الحجوم والاشكال وهياكل لعينات الانثراسيت على اشارة الرنين الكهرومغناطيسي . واثبت من تسجيل مجموعة الاطياف الخاصة للرنين الكهرومغناطيسي للفحم عالي الجودة والتحول يرتبط بتأثيرات التركيزات العالية وان التحول يعتمد على شروط التسجيل ، فضلا عن خصوصيات بهم المكانية والزمانية من الفوليرين مثل الهياكل في الفحم.

الكلمات المفتاحية :- الماس ، أنثراسايت ، فوليرن ، الرنين الكهرومغناطيسي

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