REDIOSPECTROSCOPIC FEATURES OF LOW-DIMENSIONAL SYSTEMS

Hussien Ali Noor

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Ah2008@mail.ru

Abstract:-This work presents the experimental conditions leading to changing of the line form in electron paramagnetic resonance (EPR) spectra when the extreme properties (line width and intensity) of the object diagnosed are combined with different spectrum recording modes. A change in the line form on recording in the standard mode with the automatic control of a microwave oscillator over the measuring cavity is characteristic for samples with high concentrations of the paramagnetic centers. As the EPR signal intensity is growing, first the line width and symmetry is varying monotonically with a transition to the "dips"«the disruption», and then a hysteresis is revealed for the spectral lines recorded on increasing and decreasing of a magnetic field.

Keywords:-EPR(electron paramagnetic resonance) ، AFC (automatic frequency control) ،PMC(para magnetic centers)

Phisiology Classification QC 170-197

Introduction:-Asarule in the case of EPR spectroscopy the measuring mode sarerealized with the automatic frequency control (AFA) of amicrowaveoscillatorrelativetothefrequency-ofameasuringcavityincombination with high-frequencymodulationandlinearsweepofamag-neticfieldtoproviderecordingofthefirstderivative-fortheparamagneticsignalabsorption. As this takes place, it is usually preferable that matching of the measuring cavity in a microwave unit be effected by means of a circulator at the coupling factor K ≤ 1 [1]. Typical for EPR spectroscopy is the situation when the diagnosed samples, as distinct from FMR, are characterized by low concentrations of the paramagnetic centers leading to much lower values of the microwave power absorption than those of the measuring cavity itself, whereas the typical widths ΔH of spectral lines are generally above 0.1 T [2].

But diagnostication of the properties for novel materials, e.g. heterogeneous and composite systems, systems based on low-dimensional elements, spin glasses, and radiation physics objects, is often associated with the necessity for correct registration of high-intensity signals of absorption by the paramagnetic centers (PMC) of high concentrations ($>10^{20}$ spin/g) at ΔH < 0.1 T [3]. Moreover, the indicated conditions may be combined with a significant non-resonance power absorption of a microwave oscillator by the delocalized charge carriers and with the dielectric losses introduced into the measuring cavity by the sample [4].

Combination of the extreme properties of the diagnosed sample and conventional recording modes may result in the situations liable to cause distortion and loss of the information about the properties of an object under study, incorrect recording of the principal PMC characteristics (g-factor, spectral line width and intensity) and, finally,— erroneous interpretation of the experimental data.

With due regard for the instrumental and physical factors in EPR spectroscopy which affect spectral data, one can eliminate errors and even obtain additional information concerning the physical properties of an object studied (e.g. spatial-temporal localization and delocalization of charges in low-dimensional systems) or develop nondestructive diagnostic techniques.

The principal aim of this work is to reveal the experimental conditions leading to changes in the EPR line form when the extreme properties of a sample under study are combine with the conventional modes of spectral recording.

In this study the model object is represented by samples of coal at the ultimate stage of metamorphization — anthracite. Being widely common, anthracite

- is a representative of the important class of heterogeneous carbonic (low-dimensional) systems for which the modification and development of the magnetic spectroscopy method is of particular significance[4];
- offers the possibility to create various and controlled spectroscopic situations associated with the number of PMC, range of a singlet EPR line width, different combinations of the concentrations of localized spins and delocalized carriers, etc.

Besides, many properties of PMC in anthracite and its analogues still remain inadequately established despite a great number of the relevant publications presenting studies into their paramagnetic properties and structure [5]. Revealing of the peculiarities in the paramagnetic properties of anthracite at different stages of metamorphism provides the basis for the development of new effective techniques to predict shock resistance (dangerous bursts) of coal banks in mines [6].

Experimental method:-EPR studies of coals are usually conducted after their crushing to powder [2, 7]. Naturally, such a comminution is associated with the structural modifications, with the effects of physical and chemical sorption, etc. Because of this, the paramagnetic absorption parameters of the powdered coal and of monolithic samples may be rather different due to the physical and chemical destruction processes proceeding within carbonic materials.

This work presents comparison of the EPR spectral parameters for powdered and monolithic samples of anthracite, namely: width and form of spectral lines. The samples were cut off from anthracite blocks and cut out in the form of a parallelepiped. The parameters of paramagnetic absorption were measured using a SE/X-2544 (RadioPAN) spectrometer and a homodyne variant of SE/X-2543 (RadioPAN) with high-frequency modulation at 100 khz, 25 kHz, and at 80 Hz. Selection of the modulation amplitude and response time was determined by the requirements for undistorted recording of the first derivative of the absorption line [1]. Spectra were recorded both in the standard mode (with the automatically controlled frequency of a clystron over the measuring cavity) and in the mode with the de-energized AFC unit.

Form and width of EPR line:-The powdered samples of anthracite having the grain size from 70 to 80 mkm are characterized by a symmetric form of the spectral line. Its width, when measured in the air, was about 15 mT, 0.14 mT – after evacuation, and 0.45 mT when the ampoule was filled with toluene [4]. For the samples with a volume of 0.5 mm^3, whose line width comes to 0.018 mT, one can observe a practically symmetric line, the ratio of the low-field A to the high-field B components for the line intensity being (A/B) = 1.03. In this case the spectra recorded in the standard mode and in the mode with the de-energized AFC unit are coincident (Fig. 1, a, curves1 and 2).

The EPR line width correlates with the sample conduction. To illustrate, for the samples with the volume ~0.5 mm^3 cut out of a single piece, ΔH was within the range from 0.018 to 0.11 mT and conduction was from 0.09 to 0.25 Ω^{-1} cm^{-1}. After annealing in the vacuum at 950 °C during a period of 30 minutes, the conduction was 28 $Ом^{-1}см^{-1}$, and ΔH — 2.2 mT.

Fig. 1, b demonstrates spectra of the sample measuring (**X** = 7)x2x3 mm^3. The spectra are recorded with the long edge orientation $\mathbf{X} \perp \mathbf{H_0}$ (or $\mathbf{X} \perp \mathbf{E_1} \perp \mathbf{H_1}$), where $\mathbf{H_0}$ — stationary magnetic field vector, $\mathbf{E_1}$and $\mathbf{H_1}$ — microwave field vector components. The spectrum recorded with the de-energized AFC unit is similar to the dispersion curve (curve 2). The spectra recorded in the standard mode when scanning was performed with increasing (curve 1) and decreasing (curve 1′) of the magnetic induction are nearly coincident.

Figs. 2 and 3 show the spectra of anthracite samples characterized by drastic changes of the intensity, featuring hysteresis. Fig. 2 gives the spectra of the samples with the dimensions (**X** = 7)x3x3 mm^3 measured at the boiling temperature of liquid nitrogen taking different modes of matching the measuring cavity to the microwave line. The long edge **X** of the sample is oriented within the cavity so that **X**||**H$_1$**. The sample is positioned at the center of the cavity. Curves 1 correspond to spectral recording in the standard mode with the increased magnetic field, curve 2 — with the decreased field, and curve 3 — in the mode without the automatic frequency control.

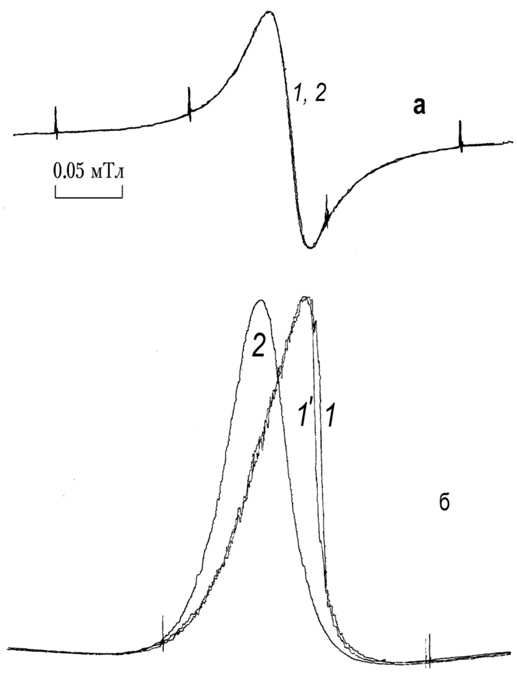

Fig 1. Spectra for the sample of the volume 0.5 mm^3 (a) and (**X** = 7)x2x3 mm^3 (b) recorded in the standard mode (1) and in the mode with the de-energized AFC unit (2), curve 1′ is associated with scanning when the magnetic induction is decreased. Orientation is **X**⊥**H$_0$**, the marks are given every 0.1 mT

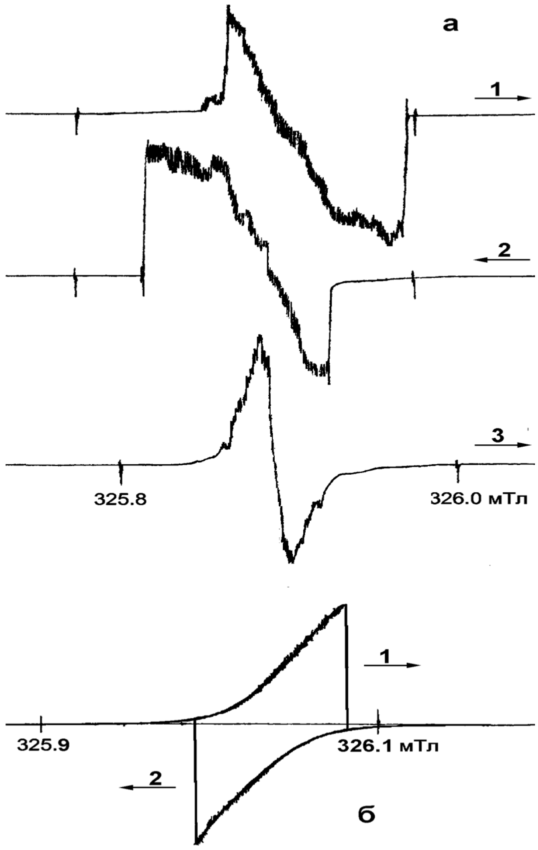

Fig. 2. Spectra for the sample of the volume (X = 7)x3x3 mm^3 with the orientation X||H$_1$: at the center of the cavity in the liquid nitrogen filled ampoule using different modes for matching of the measuring cavity to the microwave line; recording in the standard mode when scanning is performed with the increased (1) or decreased (2) magnetic induction and with de-energized AFC unit (3); P_1 = mW, the marks are given every 0.1 mT, the arrows are in the scanning direction

As seen in Fig. 2, the symmetric spectral line 3 (derivative of the absorption signal) recorded at the conditions with a lowered non-resonance absorption of the microwave oscillator power (the sample conduction at T = 77 K was decreased; activation energy was 0.04 eV) reveals qualitative changes when recording is performed with the de-energized AFC unit.

Fig. 3, a shows EPR spectra of the sample measuring (X = 7)x3x3 mm^3. The long edge X of the sample is oriented in the cavity so that X||H_1. The center of the sample is about 5 mm higher than that of the cavity. Curves 1 and 2 are recorded in the standard mode using the forward (with the increasing magnetic induction, curve 1) and backward (with the decreasing magnetic induction) scanning procedure (curve 2). In both spectra one can observe drastic changes of the intensity with the characteristic hysteresis. A width of the hysteresis (spectral interval between the changes) is equal to 0.006 mT.

There are no changes of the intensity when spectra are recorded with the de-energized AFC (Fig. 2, curve 3, Fig. 3, a, curve 3). In this case the line form is similar to the first derivative of the dispersion curve.

The EPR spectra and changes in the intensity of the microwave oscillator measured for the sample of the volume (X = 7)x2.2x3 mm^3 at X||H_0 are given in Fig. 3, b and Fig. 3, c, respectively. The intensity changes for this sample are also observed in the standard working mode of a spectrometer (Fig 3, b, curves 1, 2). A width of the hysteresis is 0.3 mT. The EPR spectral line of the sample recorded with the de-energized AFC unit is characterized by the ratio *(A/B)* = 3.5 (Fig. 3, b, curve 3). In the process of recording a frequency of the microwave oscillator is chnaging, exhibiting both its monotonic variation in the process of spectral scanning and the changes associated with hysteresis dips (Fg. 3). A maximal change of the intensity was recorded with the hysteresis 0.55 mT in width (about10 MHz).

The hysteresis width measured at the sample orientation X||H_0 was invariable (0.16 mT) for the magnetic field modulation frequencies 100 kHz (standard mode), 25 kHz, and 80 Hz. When the power P_1 of microwave radiation within the cavity is increased with the help of an attenuator, a width of the hysteresis is, as a rule, monotonically decreasing, whereas with the use of an absorber it is increased. At the orientation X||H_1 of the sample with the volume (X = 7)x3x3 mm^3 the hysteresis width was recorded as a function of the power as a curve with a maximum.

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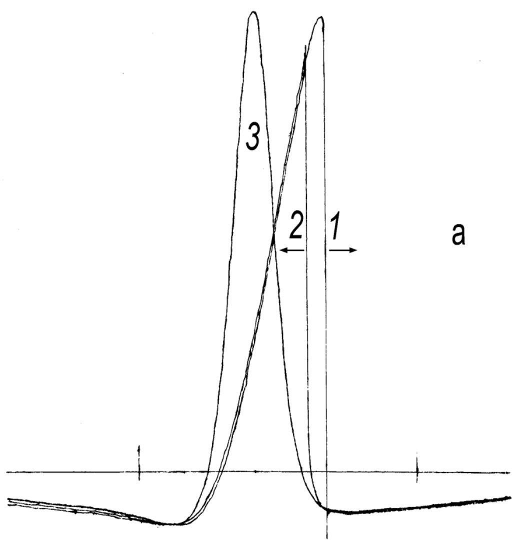

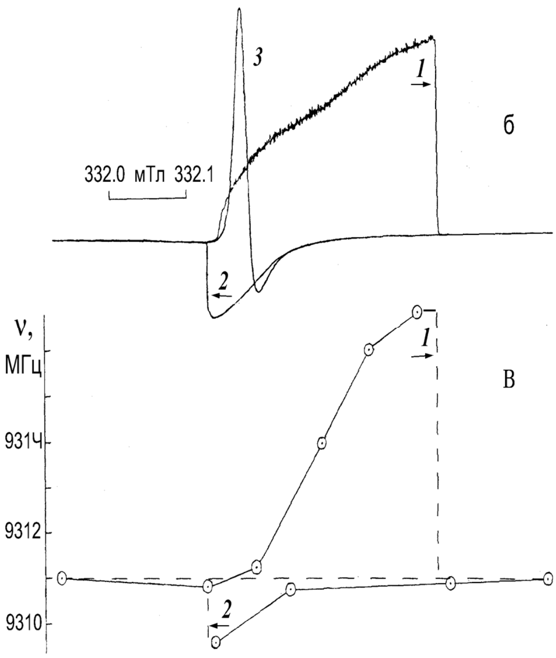

Fig. 3. Spectra for the sample of the volume (**X** = 7)x3x3 mm^3 with the center located higher than that of the cavity by ~5 mm at the orientation **X**||**H$_1$** (a); EPR spectra (b) and frequencies □ of the working cavity (B) recorded for the sample with the volume (**X** = 7)x2.2x3 mm^3 (**X**⊥**H$_0$**). Recording was realized in the standard mode when scanning was performed with the increasing (1) or decreasing (2) magnetic induction and with the de-energized AFC unit (3), P_1 = 3 mW, the marks are given every 0.1 mT

Hysteresis is not exhibited for the samples below 20 mm^3. Also, it is not observed for the samples of a large volume whose width of the EPR line recoded with the de-energized AFC unit is over 0.07 mT.

Discussion:-As demonstrated by analysisof the obtained experimental data, there is a great difference in the parameters of paramagnetic absorption spectra for monolithic and powdered samples of anthracite. A width of the EPR line in monolithic samples is considerably smaller than that of the powder, being invariable upon evacuation of the ampoule or sample wetting with toluene. The indicated differences point to the fact that comminution of anthracite leads to the structural transformation processes in the material and to changes in its conduction [7].

An important feature of the samples under study is the dependence of the line form on the sample size, associated with the volume increases as small as 0.1 — 0.5 mm^3. For samples of the volume up to 70 mm^3, with variations of the spectrum recording conditions and sample orientation within the cavity , one can observe a symmetric line having the form of a dispersion curve and the line with the ratio *(A/B)* that is much greater or lower than1.

Changes in the form of a spectral line on recording in the standard mode with automatic frequency control of a microwave oscillator over the measuring cavity are characteristic for the samples with high concentrations of the paramagnetic centers. As the EPR signal intensity is growing, the spectra first reveal a monotonic increase of the line width and symmetry, then going to the “dips”, and next – to exhibition of the “hysteresis”- form lines recorded upon increasing or decreasing of a magnetic field.

Anomalous changes in the EPR spectral line forms are exhibited to a greater extent on recording of narrow lines and with the increased non-resonance losses in the measuring cavity, a character of the form changing being also dependent on the mode of matching the measuring cavity to the microwave line.

Conclusion:- Based on analysis into the forms of spectral lines and the conditions of their exhibition, it has been inferred that hysteresis distortions of EPR lines are due to a specific concurrence between the selective properties of a measuring cavity and of the measured sample with the use of AFC. The principal spectroscopic features of this concurrence will be considered in future works.

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مميزات الاطياف الراديويه المنخفضة النظم ثلاثية الابعاد

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حسين علي نور

Ah2008@mail.ru

الخلاصة :-

ويعرض هذا العمل الشروط التجريبية التي تؤدي إلى تغيير شكل الخط في أطياف الرنين الكهرومغناطبسبة للإلكترون عندما يتم الجمع بين خصائص الجسم وتشخيص الطوائف المختلفه (عرض الخط والكثافة) مع طرق تسجيل الطيف المختلفة. تغيير شكل الخط في التسجيل في الوضع العادي الموجات المذبذب التحكم التلقائي في تجويف قياس سمة للعينات بتركيزات عالية من مراكزالمغناطيسية. كما تزداد كثافة إشارة الرنين الكهرومغناطيسية ، أولاً بعرض الخط والتناظر وهو متفاوتة إلاخفاق مع انتقال إلى "انخفاض" «تعطل»، ومن ثم كشفت عن التباطؤ للخطوط الطيفية التي سجلت في تزايد ونقصان للمجال المغناطيسي

الكلمات المفتاحيه :- الرنين الكهرومغناطيسي ،التحكم الاوتوماتيكي للتردد ، المراكز المغناطيسيه