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Localization and charge state of metal ions in carbon nanostructures of europium bis-phthalocyanine pyrolysed derivatives

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In the experiments of Mössbauer spectroscopy, transmission electron microscopy (TEM) and atomic force microscopy (AFM) the morphology and structurization of the carbon phase, the charge state of europium and the dynamic properties of europium bis-phthalocyanine pyrolysed derivatives, including the Debye temperature, were revealed. It was found that the pyrolysis of europium bis-pthalocyanine resulted in the amorphous carbon matrix and nanoscaled graphene clusters both forming turbostratic carbon phase. The europium ions in the charge state Eu^{3+}/Eu^{2+} were detected. The data indicated that localization of Eu ions took place between layers of graphenes similar to graphite intercalation compounds. It was shown that an isomeric shift, linewidths and the magnitude of the resonant absorption are essential characteristics of structural transformations at the pyrolysis of rare earth bis-phthalocyanines.

Keywords: pyrolysis, bis-pthalocyanine, carbon nanocomposite, graphene clusters, intercalation, Mössbauer spectroscopy.

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Introduction

It is known that the pyrolytic destruction of carbon compounds with the subsequent formation of polycrystalline graphite proceeds through the formation of a number of carbon phases, including the turbostratic structure of carbon [1]. Turbostratic carbon consists of partially ordered crystalline regions of graphene clusters surrounded by amorphous carbon [2]. Intercalation of alkali and alkaline earth metal ions into graphene clusters of turbostratic carbon is a subject of increased interest [3–6].

The problem of finding effective ways to introduce rare earth elements (REE) into nanoscale carbon shells in order to create new functional materials for a variety of scientific, technical, biomedical and industrial applications remains relevant. One of the ways to solve this problem can be the pyrolysis of molecular precursors with REE atoms coordinated with organic ligands, for example, double-decker diphthalocyanines.

The possibility of intercalation of REE metals into turbostratic carbon during the pyrolysis of diphthalocyanines was specified in the paper [7]. According to the authors, pyrolysis resulted in the formation of amorphous carbon phase and crystallites $\sim 2-3$ nm, while the metal ions were in the chemically bound state. In subsequent publications X-ray scattering and small-angle neutron scattering revealed small carbon clusters, in which the metal can present as an interstitial impurity [8,9]. However, there are very few data on the study of the short-range order of coordination of the REE atom, visualization of carbon structuring at the atomic level, which can be achieved by the methods of Mössbauer spectroscopy and transmission electron microscopy (TEM) [10].

In this paper, using Mössbauer spectroscopy, X-ray diffraction analysis, TEM, and atomic force microscopy (AFM) we studied the phase transformation of europium diphthalocyanine during high-temperature vacuum pyrolysis in order to reveal the features of the morphology and structure of the carbon phase, the local environment and charge state of Eu, and also to compare the dynamic properties of the initial diphthalocyanine and its pyrolyzate.

1. Materials and methods

europium diphthalocyanine ($EuPc_2$) was synthesized By famous method [11] by fusion *o*- of phthalonitrile and Eu acetate at 290−300°C. The $EuPc_2$ formation reaction proceeded for 1 h, after which the temperature was sharply increased to 340−350°C and maintained for 30−40 min to remove excess unreacted *o*-phthalonitrile. The resulting diphthalocyanine was purified by dissolving in dimethyl sulfoxide containing 2% hydrazine hydrate, filtered, titrated in 30% HCl until neutral medium. The resulting precipitate of dark green crystals was washed with distilled water on a Schott filter and dried. Pyrolysis was carried out in a fore-vacuum setup by quick heating to 800°C followed by annealing for 1 h.

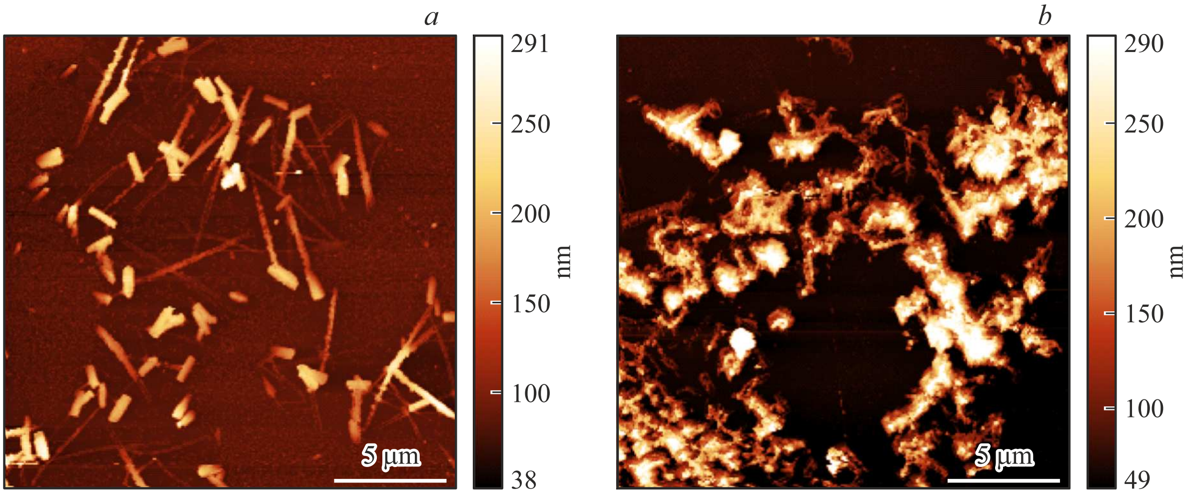

Figure 1. ACM image of morphology of EuPc$_2$ (a) and its pyrolyzate (b) at 800°C.

The Mössbauer spectra of europium diphthalocyanine and its pyrolyzate were recorded on an electrodynamic spectrometer MC−1 −003 in the constant acceleration mode with a source ^{151}Sm $_2$O $_3$ at an absorber temperature of 80 and 300 K. Isomeric shifts are given relative to the Eu$_2$O$_3$ spectrum at 300 K. The velocity scale was calibrated relative to the generally accepted standard α-Fe. The Mössbauer spectra were processed using the MOSSFIT program under the assumption of a Lorentzian line shape. The samples were prepared by pressing a certain amount of the test substance with a neutral filler (powdered sugar) in the form of tablets 0.8mm thick.

The samples were studied by TEM using a Titan80−300 electron microscope (FEI, USA) at an accelerating voltage of 300 kV. The sample weight was suspended in 1 mL Milli-Q, placed in an ultrasonic bath and dispersed for 20 min. A droplet 5 μl of the dispersed sample was deposited on a carbon mesh (Lacey Carbon) acting as a substrate. The images were processed using Gatan DigitalMicrograph v. 2.31.734.0 program.

X-ray diffraction analysis completed on device Rigaku SmartLab 3 kW, cobalt radiation ($\mathrm{Co}K_\alpha = 1.78919\,\text{Å}$), K-betta filter And two-dimensional detector HyPix-3000. To consider the resolution curve of the device, the shape of the peaks of the X-ray tube radiation spectrum was calibrated against a standard silicon polycrystal manufactured by Rigaku. The instrumental resolution (width at half maximum of the peak at small angles) did not exceed 0.03 deg. The measurement was carried out at room temperature in the range of angles of 20 to 90 deg with a step of 0.01 deg in the Bragg−Brentano geometry. Full-profile analysis and calculation of parameters were carried out by the Profex/BGMN program using the Rietveld method [12]. The initial crystal structure for fitting was taken from [13]. The background was adjusted by the 4th order Lagrangian, the Gaussian peak shape convolved with the peaks of the X-ray tube spectrum and the mathematical model of the instrument was used. The preferred orientation was taken into account by decomposing the scale factor of different reflections into spherical harmonics.

Samples for AFM studies were obtained by EuPc$_2$ deposition at the sublimation temperature ($\sim$ 500°C) onto a heat-resistant sapphire glass substrate. The substrate with the sputtered sample was placed in a pyrolysis unit, and pyrolysis was carried out as described above. The measurements were carried out on a SMENA microscope (MT-MDT, Russia) in the semi-contact scanning mode, using NSG03 probes with a curvature radius of 10 nm and a stiffness constant of 1.4 N/m. The probe oscillation amplitude and scanning speed were 30 nm and 0.8Hz, respectively. The images were processed in Gwyddion v. 2.61 program.

2. Results and discussion

It is known that diphthalocyanines are typical molecular crystals in which the molecules are bound by a weak Van der Waals interaction, while inside the molecules a stronger covalent bond acts between the atoms. The crystal structure of diphthalocyanines is based on a molecular column composed of diphthalocyanine molecules along the c axis of crystal growth [11]. The AFM image of EuPc$_2$ clearly demonstrates the acicular shape of such crystals (Fig. 1, a). The diphthalocyanine pyrolysis leads to the destruction of crystals with an amorphous phase formation (Fig. 1, b).

Nanoscale morphological features of the pyrolyzate structure were revealed by TEM. Images of the most characteristic areas of the pyrolyzate, observed by dark-field transmission scanning microscopy (TSM), make it possible to unambiguously reveal metal atoms (Fig. 2, a). Analysis by energy dispersive X-ray spectroscopy (EDXS) indicates the predominance of C and Eu, as well as impurity amounts

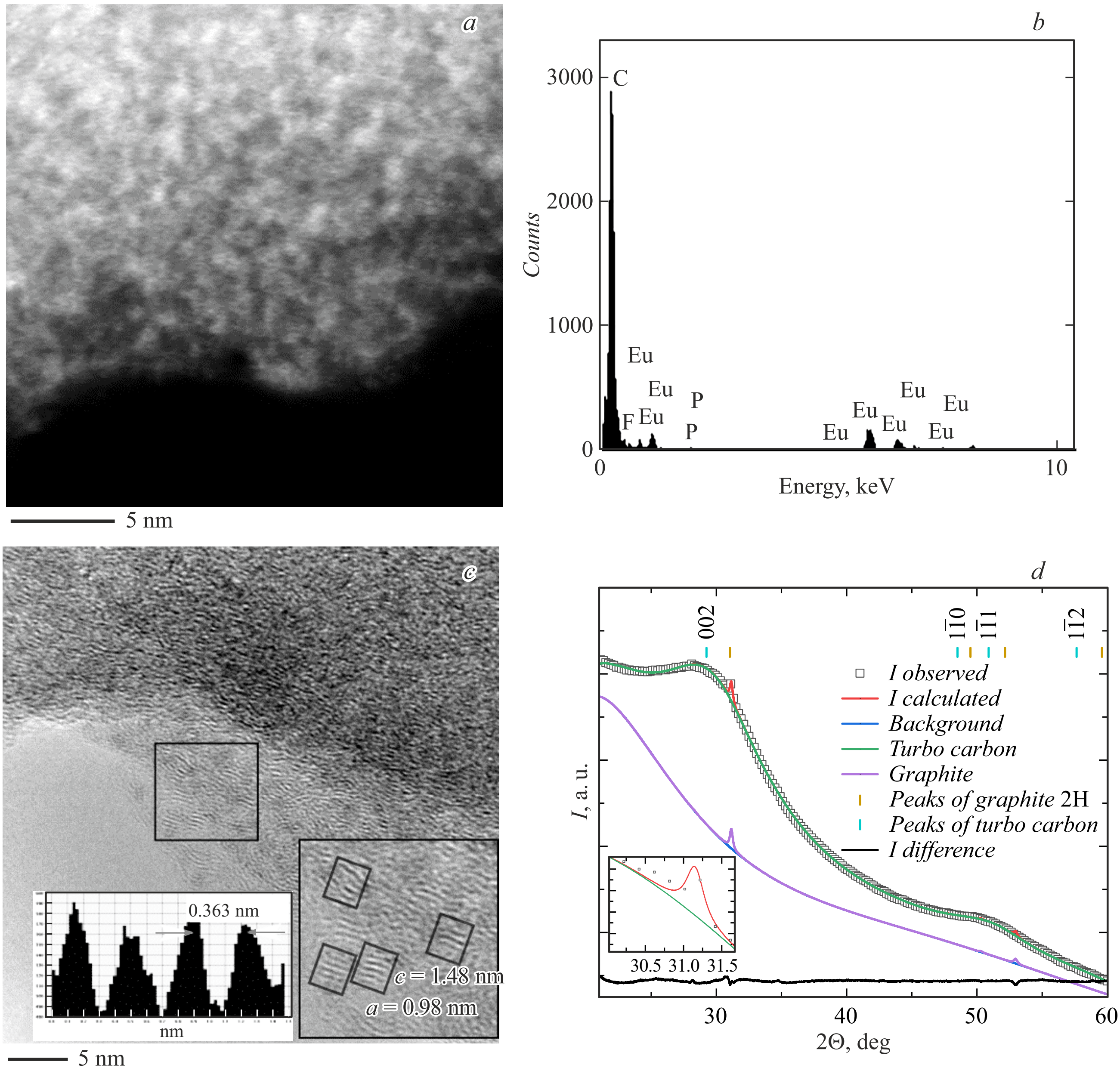

Figure 2. Analysis of pyrolyzed Eu diphthalocyanine by electron microscopy and X-ray diffraction analysis: dark-field mode of TSM (*a*); EDXS data (*b*); TEM bright-field mode (*c*); X-ray diffraction analysis (*d*).

of F and P, which we attribute to sample contamination (Fig. 2, *b*).

The bright-field image (Fig. 2, *c*) makes it possible to visualize the carbon matrix, which is represented by disordered (amorphous) carbon and nanoscale graphenes assembled into clusters, which corresponds to the turbostratic structure of carbon [14]. The observed graphene clusters are characterized by an average size 1−2 nm and a slightly increased (∼ 0.363 nm) interplanar spacing relative to graphite (0.334 nm).

The results of X-ray diffraction analysis (Fig. 2, *d*) revealed the X-ray amorphous structure, which is in good agreement with the data on the study of carbonization and graphitization processes of thermally treated soot carbon [2]. A weak peak at 002 deg, shown in the insert (Fig. 2, *d*), is characteristic for highly textured graphite, while there is a similarity in interplanar spacing along the axis *c* (0.666 and 0.665 nm, respectively). The size of such granules in the test sample is ∼ 42 nm, and the quantitative content is less than 0.01%. For turbostratic carbon the lattice constant parameters are defined as: $a = 0.249$ nm and $c = 0.701$ nm. The average interplanar spacing based on d_{002} diffraction data was 0.351 nm and turned out to be somewhat smaller than that observed by the TEM method. The size of ordered crystalline regions along the axis *a* and *c* 1.582 ± 0.035 nm and 0.852 ± 0.004 nm, respectively. No

Calculated parameters of the Mössbauer spectra of $EuPc_2$ and its pyrolyzate at 300 and 80 K

Sample	T, K	IS, mm/s	W, mm/s	ε, %	Charge state
$EuPc_2$	300	0.86 ± 0.15	2.22 ± 0.53	0.39	+3
	80	0.66 ± 0.04	2.15 ± 0.13	2.9	+3
$EuPc_2$(pyr)	300	-0.26 ± 0.06	3.40 ± 0.20	2.5	+3
		-14.00 ± 0.79	7.43 ± 1.69	0.5	+2
	80	-0.12 ± 0.04	3.63 ± 0.14	7.2	+3
		-12.59 ± 0.30	6.30 ± 1.14	1.5	+2

Note. IS — isomer shift, W — absorption linewidth, ε — value of resonant absorption.

crystalline phases of Eu and its compounds were found, which does not exclude their existence in the nanoscale X-ray amorphous state.

Mössbauer spectroscopy, as tool for studying short-range order, makes it possible to obtain the most reliable data on the valence state and localization of Eu ions in pyrolysis products, as well as on the dynamic properties of the initial diphthalocyanine and its pyrolyzate, which is one of the important tasks of this study. Mössbauer spectra^{151}Eu $EuPc_2$ and pyrolyzate ($EuPc_2$(pyr)) were taken at 300 and 80 K and presented on Fig. 3, the results of their processing are in Table.

In $EuPc_2$ spectra measured at 300 and 80 K (Fig. 3, *a*, *b*, see Table) a single line was observed with close parameters of line width (W) and isomeric shift (IS), which value is typical for Eu^{3+} [15]. Measurements at 300 K showed an extremely low resonant absorption (ε), equal to 0.39%. Low-temperature measurements at 80 K demonstrate the increase by seven times in resonant absorption up to 2.9%. Mössbauer spectrum of EU diphthalocyanine pyrolysate, taken at 300 K, is represented two singlet lines with various intensity of absorption with magnitude of isomeric shift -0.26 and -14.00 mm/s, characteristic For Eu^{3+} and Eu^{2+} [16], and Also value ε, equal to 2.5 and 0.5% respectively.

A sensitive parameter of structural transformations and the charge state of the Mssbauer atom is the magnitude of the isomeric shift. The change in the nearest environmentEu^{3+} during pyrolysis is accompanied by a IS decrease from $+0.66$ mm/s for $EuPc_2$ to -0.12 mm/s in the spectrum of the pyrolyzate (see Table). The paper [15] shows significant variations in the IS value depending on the coordination number and chemical bond length for various Eu^{3+} compounds. These structural parameters undergo significant changes during the pyrolysis of the initial europium diphthalocyanine. We think that the aforementioned decrease in the isomeric shift can be due to the total effect of changes in the interatomic spacing of Eu−ligands, coordination number, and the relative contribution of the degree of ionic or covalent bond in the pyrolysis product.

It is known that the value of resonant absorptionε and the width of the absorption line W are parameters associated with the dynamics of vibrational motions of atoms in the crystal lattice. The decrease in the effect magnitude is observed when the resonant atom is located on the sample surface or in compounds belonging to the class of molecular crystals. This influence of vibrational properties on the magnitude of the effect of recoilless absorption of γ-quanta was well studied on the example of ^{119}Sn and ^{151}Eu atoms, and is shown in [17–19].

In the diphthalocyanine macrocycle (Fig. 4) the Eu ion is located between two phthalocyanine ligands at an almost equal distance (0.243 nm) from the eight intracyclic N atoms surrounding it, which form two planes of almost equal squares with sides of 0.275 nm [20]. As noted above, $EuPc_2$ is a typical molecular crystal in which the molecules are bound by a weak Van der Waals interaction, while a stronger covalent bond acts between the atoms inside the molecules. Therefore, the probability of the Mssbauer effect can be represented as: $f_a = f_{\text{at}} f_{\text{mol}}$ [19]. For the molecular crystal of europium diphthalocyanine ($EuPc_2$), the weak Van der Waals interaction between molecules seems to be the determining factor for the low resonant absorption ε in the Mössbauer spectrum at 300 K. This is a consequence of the high degree of freedom associated with thermal vibrations of the molecule in the crystal structure. „Freezing" of thermal vibrations at 80 K leads to a significant increase in resonant absorption up to 2.9%.

A comparative analysis of the Mössbauer parameters of the precursor and pyrolyzate at 80 K provides information on structural changes during pyrolysis. The increase in resonant absorption in the pyrolyzate (see Table) may indicate a fundamental change in the geometry and chemical composition of the nearest environment of europium. Comparison of the AFM, TEM, and XDA data indicates the absence of long-range order in Eu compounds. The observed Mössbauer parameters characterizing the short-range order cannot be attributed to the X-ray amorphous states of the known Eu compounds [16,21]. Consequently, the localization of Eu ions can take place both on fragments of amorphous carbon and in the interplanar space of graphene clusters. In the latter case, for Eu ions of different valence a more rigid Eu−ligand bond shall be observed, which correlates well with the observed increase in the resonant absorption ($\varepsilon = 7.2\%$).

The noticeable broadening of the resonance absorption lineEu^{3+}/Eu^{2+} in the pyrolyzate (compared to the structure of crystalline $EuPc_2$) we attribute to the increase in the imperfection and defect rate of graphene base layers, leading to variations in the local environment of the europium ion. As a result, a superposition of spectral components with different IS values can be observed, leading to a noticeable broadening of the absorption line.

It is known that Mössbauer spectroscopy is a convenient tool for studying charge transfer and lattice dynamics

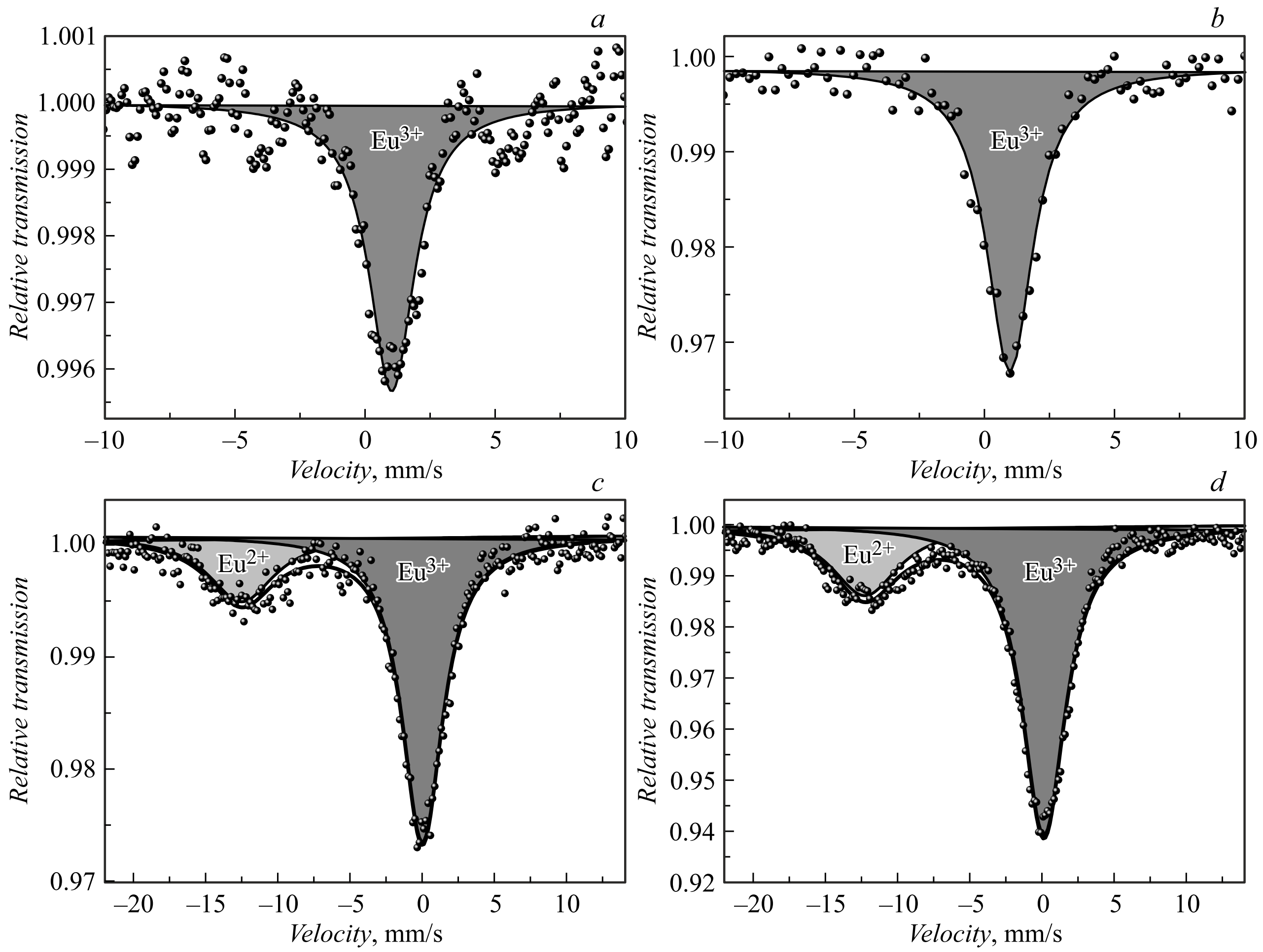

Figure 3. Mössbauer spectra of $EuPc_2$ (a, b) and its pyrolyzate $EuPc_2(pyr)$ (c, d) at 300 and 80 K, respectively.

in graphite-intercalated compounds [22,23]. Apparently, turbostratic carbon, in which metal ions are introduced into the interlayer space of graphene clusters, can be considered as a metal carbon nanocomposite similar to macrostructural formations of graphite-intercalated compounds. Appeal to the results of these publications is possible if one takes into account some difference between the processes of metal intercalation into crystalline graphite compounds from the pyrolysis of the precursor ($EuPc_2$), which already contains the metal ion. Graphite behaves in insertion reactions as an amphoteric compound capable of accepting electrons from donors and donating electrons to acceptors. It is known that intercalation of lanthanides is possible in various ways, for example, by direct action of metal vapors on graphite in metal tubes sealed under vacuum, or by heating the compressed mixture of metal powders (metal salts) and graphite [24]. Eu intercalation into graphite by the first method and subsequent study by Mössbauer spectroscopy [23] revealed only Eu^{2+} in the resulting compound, which indicates a noticeable amount of *s* electron density transferred from Eu ions to graphite layers. An opposite example of the acceptor system was demonstrated in [25] for the intercalated compound formed as a result of the reaction of graphite with $EuCl_3$ in the presence of Cl_2. In the Mössbauer spectrum, only the Eu^{3+} singlet was observed with parameters characteristic for typical europium chloride. In the opinion of the authors, this means that intercalation of the initial europium chloride is possible with concomitant chlorination of graphite, when the excess of chloride ions acts as electron acceptor.

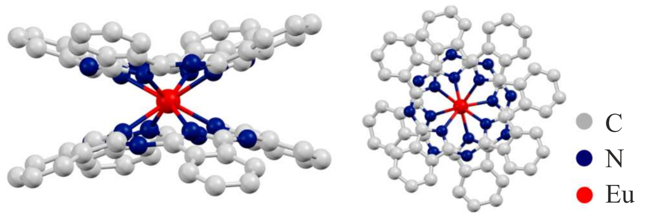

Figure 4. Schematic representation of the double-decker structure of $EuPc_2$ [20].

In our case, in the original $EuPc_2$, the europium ion has a charge 3+, and during pyrolysis graphene clusters are formed with the charge state of europium 3+ and, to a lesser extent, 2+. The appearance of Eu $^{2+}$ may indicate the acceptance of one electron from graphene to the ion Eu^{3+}, by analogy with graphite-intercalated compounds of donor type studied in papers [22,26,27]. This process is apparently characterized by the reaction kinetics depending on the temperature and duration of annealing, which is confirmed by the data of the paper [7], in which a gradual change in the charge state of europium from 3+ to 2+ was observed during the pyrolysis of $EuPc_2$ in the temperature range 800−1000°C. However, to determine the mechanism of charge transfer during the pyrolysis of europium diphthalocyanine or the influence of other factors, apparently, a number of additional studies will be required.

As for the dynamic properties of $EuPc_2$ lattice and its pyrolyzate, then based on the available data on the structure of REE diphthalocyanines [11,20] and nanoscale graphenes, it can be assumed that such compounds, as a rule, can be characterized by a low Debye temperature. Indeed, the analysis of the Mössbauer spectra of the precursor and pyrolyzate at temperatures of 300 and 80 K in accordance with the method [28] made it possible to determine the estimated values of the Debye temperature (T_D) for $EuPc_2$, which turned out to be equal to 123 ± 5 K. A similar calculation for the pyrolyzate spectra showed the values $T_D = 152 \pm 5$ K and 156 ± 5 K for the Eu ions $^{2+}$ and Eu^{3+}, respectively. Insignificant differences in the value of T_D for Eu ions of different valences suggest that their local environment in graphene clusters has a similar configuration.

The totality of data on the pyrolysis of REE diphthalocyanines radically differ from the data on the pyrolysis of monophthalocyanines of transition elements. In particular, for Fe monophthalocyanine Mössbauer spectroscopy and TEM revealed metallic nanoclusters α-Fe up to 100 nm in size in the form of inclusions in the carbon matrix [10]. The reason for the differences may be the structure of the precursors. In the case of one-deck molecules, the metal is coordinated with one ligand; in the case of double-decker molecules the metal is coordinated and isolated between two ligands.

Conclusion

Mössbauer spectroscopy, X-ray diffraction analysis, TEM, and AFM were used to study the phase transformation of europium diphthalocyanine during high-temperature vacuum pyrolysis. Analysis of TEM images and EDXS data of the pyrolyzate indicates the predominance of C and Eu. The carbon matrix is represented by turbostratic carbon, in which graphene clusters with a characteristic size ∼ 1−2 nm and an average interplanar spacing between graphenes of 0.351 nm were revealed by direct visualization and based on X-ray diffraction analysis data. The study by Mössbauer spectroscopy at 300 and 80 K made it possible to determine the charge state in europium diphthalocyanine and its pyrolyzate Eu^{3+} and Eu^{3+}/Eu^{2+}, respectively. It is shown that the isomeric shift, absorption linewidth, and resonant absorption are sensitive characteristics of structural transformations during the pyrolysis of REE diphthalocyanines. The comparison of the Mössbauer and TEM data ensures the conclusion that, as a result of pyrolysis the localization of Eu ions can be most preferable between the layers of graphene clusters. In pyrolyzate of europium diphthalocyanine the distribution of Eu was found mainly in the atomic form without the formation of phase of carbides, nitrides or aggregation into metal clusters of Eu. The data obtained made it possible to reveal previously unknown features of the structuring of the metal−carbon phase during the pyrolysis of REE diphthalocyanines.

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Conflict of interest

The authors declare that they have no conflict of interest.

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