UDC 544.23.022 DOI: 10.18698/1812-3368-2020-6-80-92

SPECIFIC FEATURES OF THE STRUCTURE OF VARIOUS COAL RANKS AT THE NANO LEVEL

E.V. Ulyanova ekaterina-ulyanova@yandex.ru
O.N. Malinnikova olga_malinnikova@mail.ru
A.V. Shlyapin shlyapin@mail.ru
B.N. Pashichev borisnik-pa@yandex.ru

Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences, Moscow, Russian Federation

Abstract

Structural factors and functions of radial distribution of atoms of different coal ranks have been calculated by X-ray diffraction analysis. This made it possible to establish that the main structural component is the clusters with graphite-like packing of atoms. The predominant size of these clusters (calculated from the peaks of small-angle X-ray scattering at 5° in CoK_α-radiation) for coals with a carbon content of 83–95 % is within 2–3 nm. Fossil coal is an amorphous carbonaceous substance consisting of polymorphic modifications in the sp^2- and sp^3-states. According to the results obtained using Raman scattering spectroscopy, the physical properties of amorphous natural coals are strongly dependent on the ratio of sp^2- and sp^3-hybridization of atomic orbitals. Moreover, studies have shown that the carbon atoms of the coal matrix in the sp^2-state are represented by both aromatic and aliphatic conjugated chain fragments. It was found that the degree of ordering in rank LF coals is higher than in coals of a higher stage of metamorphism. This is possible if the hydrocarbon matrix in rank LF coals can be represented as a polymer consisting of conjugated chains with periodicity. With an increase in the stage of coal metamorphism, starting with coal rank G, the transformation of the coal structure occurs with a violation of the periodicity of the conjugated fragments of the polymer matrix connecting graphite-like clusters, a decrease in their length, and an increase in randomness in their arrangement

Keywords

Fossil coal, structure models, X-ray diffraction analysis, Raman scattering spectroscopy

Received 26.03.2020
Accepted 26.04.2020

Introduction. Carbon has been known to mankind since ancient times. Relatively recently, only three main allotropic forms of carbon were known: diamond, graphite, and carbyne. The discovery of nanomodification of carbon — fullerenes

and carbon nanotubes — has been made recently. However, it would be a misconception to think that research on carbon-based nanomaterials began with them. Leadership in this matter belongs to bituminous coals, which is a natural nanocomposite consisting of graphite-like carbon clusters, aliphatic hydrocarbon fragments, and mineral inclusions. At the molecular (nano-) level, the structure of the coal substance is a two-component system consisting of carbon in sp^2- and sp^3-states with varying hydrogen content in the form of CH-, CH_2-, CH_3- and OH-groups.

The coal structure issue due to the complexity of its molecular structure has been discussed since the middle of the last century. This led to the existence of a large number of coal structure models. Most of the models were created based on the results of X-ray diffraction analysis (XRD) [1–4]. The currently existing coal structure models suggest the following. It is believed that the macromolecular network at the initial stage of metamorphism is built of randomly distributed carbon lattices. With an increase in the stage of metamorphism, their orientation becomes more ordered, and the forming structure may contain 2–4 aromatic layers. The distance between the aromatic layers varies from 4.5 to 3.5 Å with an increase in the stage of metamorphism. Collections of aromatic planes (clusters) are connected with a variety of aliphatic and hydroxoaromatic fragments, which are crosslinked into irregular macromolecules by various bridges. As in the first [3, 4], and in the subsequent models of the carbon structure [5–10], it is assumed that in the carbon structure carbon atoms with sp^2-hybridization of valence electrons exist only in the form of aromatic compounds (closed poly-conjugated system). Aliphatic fragments crosslinking aromatic clusters contain carbon only with sp^3-hybridization of valence electrons.

At the end of the 20th century, a polyene model that was fundamentally different from the aromatic model appeared. Using the data obtained using IR spectroscopy, the authors of [11–13] proposed to abandon the view of coal as an aromatic substance. The carbon structure is based on a linear poly-conjugated chain system. At the same time, highly-metamorphic coals — anthracites and superanthracites — have the most developed poly-conjugated chain system. It turns out that the opinions of numerous researchers differ not only in assessing the characteristics of graphite-like regions but also in the fact of their existence, as well as in views on the spatial orientation of ordered regions in the hydrocarbon matrix.

The uncertainty in the answers to these questions is since the existing physical methods are good for studying the structures of highly ordered systems, which give clear peaks on spectra and diffractograms. In disordered,

amorphous solids, a strongly weakened atomic order produces broad spectral and diffraction peaks that contain less information than the spectra of crystalline substances. This complicates the analysis of the data obtained since in this case, the experimental results can be consistent with many models. It should be taken into account that the physical properties of amorphous carbon materials, in particular coal, are strongly dependent on the ratio of carbon compounds with sp^2- and sp^3-hybridization of atomic orbitals.

X-ray diffraction studies of coals. Samples of fossil coals of the Donetsk coal basin were examined. Data on chemical analysis of coal samples of different ranks are given in Table 1.

Table 1

Chemical analysis data of coal samples of various ranks

Coal rank	Amount of volatile components per 1 g of coal matter V^{daf}, %	Content of, %			Ash content*, %
		carbon C,	hydrogen H	water W	
Long flaming coal (LF)	42.9	81.9	5.6	11.5	2.87
Gas (G)	35.6	85.0	5.5	7.4	1.35
Fat (F)	34.1	86.1	5.4	1.0	1.9
Skinny (S)	11.2	91.8	4.55	1.7	3.5
Anthracite (A)	7.0	95.4	2.2	4.0	1.0
Superintracite (SA)	2.3	97.5	1.3	2.0	1.0

*The amount of dry residue after coal combustion.

To determine the number of volatile components there is a standard method: 1 g of coal is annealed at 850 °C without air access. The weighting method determines the evaporated part of the coal. The yield of the volatile components is denoted by the symbol V (*volativ*), the yield of dry and ash-free substance — by V^{daf}. This characteristic is important for assessing the thermal stability of structures that make up the organic mass of coal. The yield of volatile components of V^{daf} decreases in some fossil coals with an increasing degree of metamorphism. The coals of ranks LF and G belong to bituminous coals of a low stage of metamorphism; of ranks F and S belong to bituminous coals of a medium stage of metamorphism; A and SA belong to anthracites, i.e., they are separated into a separate high stage of metamorphism.

The nature of the dependence of the intensity of scattered X-rays on the scattering angle for coals and low-temperature cokes has all the features of the diffraction curves of liquids and glasses, which to a certain extent justifies the use of the term amorphous carbons for coals. The difficulty in studying amorphous disordered materials lies in the fact that in this case, the diffraction pattern is very simple — a continuous curve on which only three "diffuse" maximumis observed. The angular position of the maximum is by the lines on the XRD pattern of graphite; the first maximum corresponds to the position of the graphite line (002), the second to (100), and the third to (110); only one, the first, is most clear.

The XRD patterns of the coals of all ranks presented here were taken using X-ray tubes with a molybdenum anode (MoK_α) according to the method described in [14]. XRD patterns were taken in the range of values of the scattering angle $2\theta = 3–90°$. Structural factors $i(s)$ and radial distribution functions of atoms (RDFA) were calculated from the diffraction patterns. The radial distribution function of atoms $g(r)$ provides statistical information on the distribution of atoms in space. The first maximum corresponds to the first coordination sphere, the second — to the second coordination sphere, and so on. The first maximum determines the distance to the nearest atom.

Diffraction patterns of four coal ranks are shown in Fig. 1 *a*, the intensity functions for coals of different ranks differ quite significantly from each other. In the experimentally obtained intensity functions, the necessary corrections are made taking into account atomic factors and incoherent scattering. For better comparison, the intensity functions are reduced to electronic units [14].

The calculated structural factors $i(s)$ also differ from each other (Fig. 1 *b*). The height and shape of the first maximum of structural factors and their position differ most significantly.

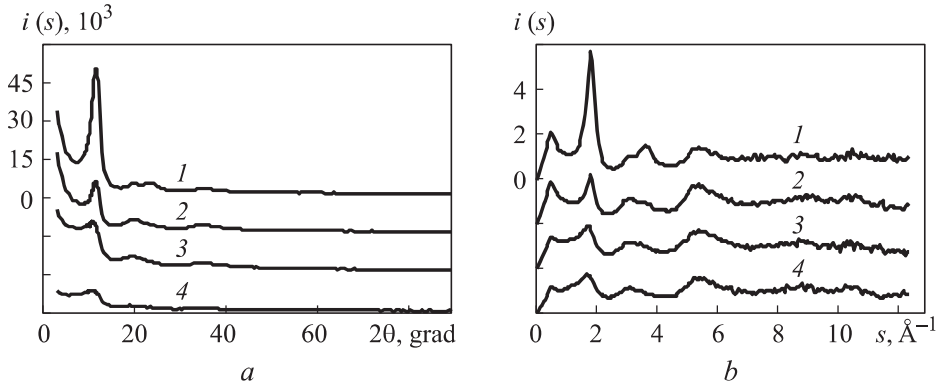

Fig. 1. X-ray diffraction patterns of intensities (*a*) and structural factors (*b*) of coals of ranks A (*1*), S (*2*), F (*3*) and LF (*4*)

Full RDFA were calculated based on structural factors. Despite the noted differences in the intensity functions and structural factors, the total RDFA of all coal ranks have much in common (Fig. 2 *a*). In the above diffraction patterns, the heights and shapes of the first maximums (002) and their positions are most different. However, the calculated and constructed plots of the total RDFA show that the differences between these functions are not as significant as those of the intensity functions, although the studied coal ranks differ significantly in physical nature (see Fig. 1).

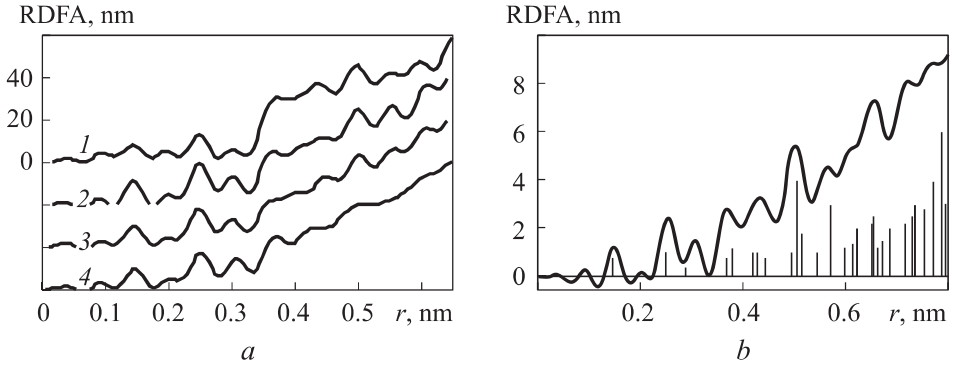

Fig. 2. RDFA of coal of ranks A (*1*), S (*2*), F (*3*) and LF (*4*) (*a*) and rank S coal (*b*)

Considering that the main element of all coal ranks is carbon, spectrally pure graphite has also been investigated. Despite the fundamental differences between these materials, the calculated total RDFA of pure graphite and rank S coal almost coincide in the region of the first coordination spheres (Fig. 2 *a*). This could be seen in Fig. 2 *b*, which shows the RDFA of rank S coal, and the vertical segments show the coordination spheres of crystalline spectrally pure graphite. The graphite lattice is hexagonal; the base of the unit cell is a rhombus. The shortest interatomic spacing between an atom located inside the base and three rhombus atoms is 0.142 nm [15]. The radius of the second coordination sphere is equal to the lattice parameters $a = b = 0.246$ nm, that is, approximately 1.5 times more than the shortest distance between atoms. Despite the fact that the coordination spheres of graphite do not exactly coincide with the first maximum of the distribution function, they describe all the maximums quite completely. The average values of the radii of the first (r_1) and second (r_2) coordination spheres of the four coal ranks and graphite are given below:

Coal rank	LF	F	S	A	Graphite
r_1, nm	81.9	86.1 9	1.8	95.4	100.0
C, %	0.147	0.146	0.145	0.144	0.142
r_2, nm	0.252	0.249	0.250	0.249	0.247

It turns out that diffraction patterns from coals of different ranks differ significantly from each other, and the total functions of the radial distribution of coal atoms differ slightly. According to the above, the main structural constituent of the coal of all ranks is the clusters with atomic packing according to the type of a graphite lattice (graphite-like clusters). The observed difference in the lattice parameters of graphite and coal can be explained by the fact that, in addition to carbon atoms, coals contain hydrogen atoms, which occupy the second place in the concentration of atoms in the coals of all ranks. Presumably, in addition to clusters with graphite-type atomic packing, there is also a certain fraction of clusters with different atomic packing.

Based on the results of studies of the small-angle scattering region (the investigated range of 2θ angles started from 2°) on a *Huber* general-purpose diffractometer with monochromatization of the diffracted beam in CoK_{α}-radiation, in [14], clear maximums were obtained in the scattering angle range of 5–7°. This allowed the authors to calculate the diameter of graphite-like clusters for all coal ranks from the equation proposed in [16]. The calculated diameter of clusters for all coals varies in the range 1.97–2.74 nm. The exception is the coals of rank LF, their diameter can be more than 6.0 nm [14]. The XRD studies carried out to allow us to conclude that the main structural component of coals is the clusters with atomic packing similar to graphite and that the carbon structure may contain some other type of packing of carbon atoms associated with hydrogen atoms.

With the subsequent development of such spectroscopic methods as nuclear magnetic resonance (NMR), electron paramagnetic resonance, IR spectroscopy, no answer to the question of what is the main structural unit of coals — graphite crystallites or a linear poly-conjugated chain system — was obtained. The existing works [17–20] proceed only from the aromatic model of the carbon structure, disregarding the possible presence of poly-conjugated chains. To clarify this issue in the study of coals, the method of Raman scattering (RS) was used.

RS spectroscopy is a standard non-destructive tool and is very promising for structural studies of crystalline and nanocrystalline substances, as well as substances that are neither crystalline nor completely amorphous, that is, carbon materials. The bands in the Raman spectra are a consequence of transitions from the ground vibrational sublevel to excited vibrational sublevels. The position of the band maximums is associated with the conformation of the molecule and the local structure of the substance. The study of carbon materials is based on the assumption that the *G*-band is associated with crystalline graphite (graphite, about 1580 cm^{-1}), the appearance of the *D*-band (Raman spectra of a diamond,

about 1350 cm^{-1}) is determined by various kinds of structural disordering of the graphite structure. For the first time, two types of bands in the Raman spectra of coal in the regions of 1575–1620 and 1355–1380 cm^{-1} were described in [21, 22], they are called the *G*-band (graphite) and the *D*-band (disordered). The authors of works [21, 22] linked the existence of *G*- and *D*-bands with graphite structures present in the coals. In subsequent works, for example, [23, 24], the *G*- and *D*-bands were also associated with the presence of only graphite structures in coal. Empirically, the Raman spectra of amorphous carbon in visible light, in addition to two brightly distinguished *G*- and *D*- peaks, exhibit nearby and several small peaks (usually about 1100–1200 and 1400–1500 cm^{-1}) [25]. The graphitization process with the growth of metamorphism does not eliminate the *D*-bands, i.e., defects in the structure are retained, although XRD analysis confirms an increase in the ordering in the graphite networks, which should decrease the intensity and width of the *D*-band. However, the intensity of the *D*-band does not decrease. This is since different thermobaric conditions under which coal seams were formed led to the creation of imperfections in the graphite-like part of the coal substance due to the appearance of bends, twisting, and bending in micrographene grids and an increase in the deformation energy in them [9, 10].

The size of a graphite cluster in the sp^2-state does not exceed 5.0–6.0 nm [5]. Therefore, coal, both in the graphite-like and in the hydrocarbon part, is an amorphous substance containing a mixture of sp^2-, sp^3-states with varying hydrogen content in the form of CH-, CH_2-, CH_3-, and OH-groups.

Experimental part, sample preparation and spectra analysis results. In the studies, RS-spectra of coal were recorded on an *InVia* (*Renishaw*, Great Britain) setup using a laser with a wavelength of 473 nm. One side of the sample was smoothly polished. Immediately before measurements, an adhesive tape was applied to the sanded side and abruptly torn off. Grains of coal remained on the adhesive tape in an even continuous layer. This approach made it possible to expose the lower layers on the main piece of coal without disturbing its structure. The spectra were recorded from the side of the exposed layers on the main piece of coal. Since the laser wavelength is 473 nm, RS-light from the coal was recorded in the wavelength range of 500–515 nm. The chosen blue laser (473 nm) made it possible to obtain a more intense RS-signal from coal than using long-wavelength lasers. Each spectrum was the result of averaging three accumulations (signal accumulation time was 60 s). To trace the change in the side arms in the *D*-band, the obtained spectra were approximated by Lorentzians. Decomposition into Lorentzian curves and determination of the intensities

of the main peaks of the RS-spectra were performed using the *Origin* 7.0 software. For convenience, all RS-spectra of coals were normalized to the maximum intensity of the *G*-band. The spectra of the three coals ranks are shown in Fig. 3.

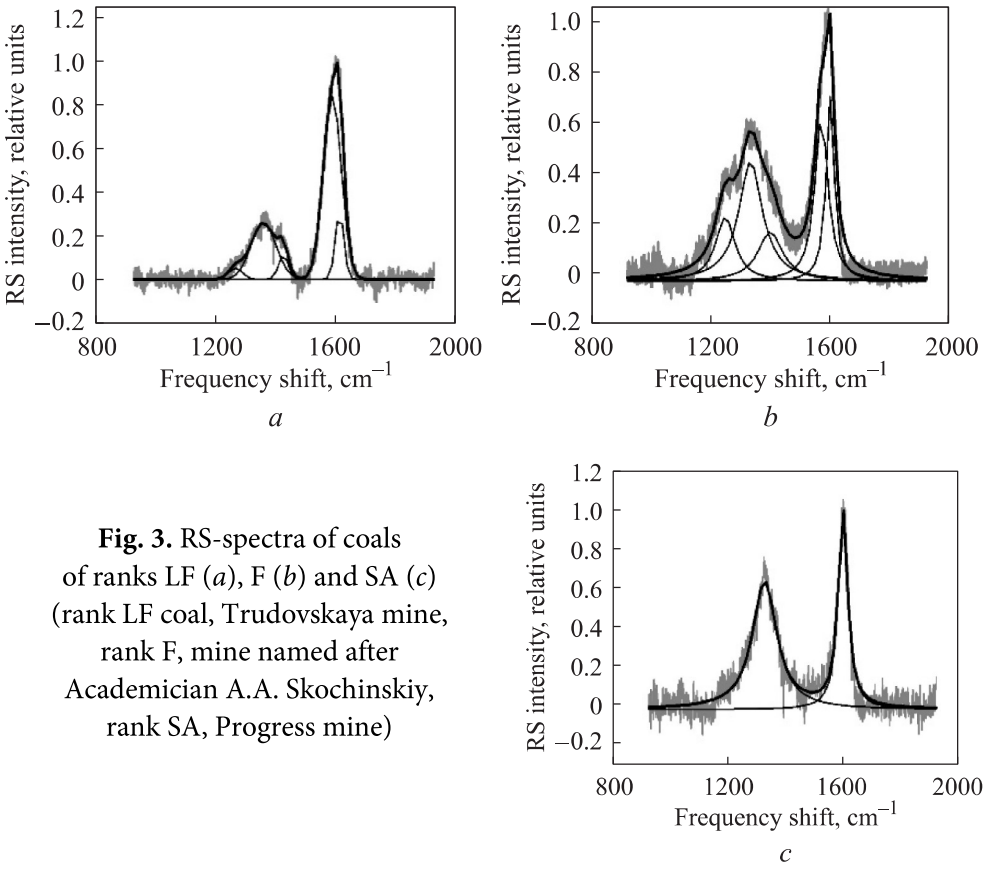

Fig. 3. RS-spectra of coals of ranks LF (*a*), F (*b*) and SA (*c*) (rank LF coal, Trudovskaya mine, rank F, mine named after Academician A.A. Skochinskiy, rank SA, Progress mine)

The results of the analysis show that the RS-spectra of coals of ranks LF, G, F, K can be described by five Lorentzian curves, rank S — by four, A — by three, SA — by two. With an increase in the degree of metamorphism, the structure of the RS-spectra of coals becomes simpler. There is a change in the configuration of the *D*-bands, which for ranks LF-S coals is associated with a decrease in the number of structural groups ($-CH_2$ and $-CH_3$). With an increase in the degree of metamorphism, the number of volatile components in coals decreases from 45 % (rank LF coal) to 2–3 % (rank SA coal). The corresponding changes in the hydrocarbon components were also confirmed by the data of NMR spectroscopy [25, 26].

The composition, width, and position of the *D*- and *G*-bands are affected not only by the disorder (the presence of sp^3-bonds) in the graphite structure but also by the presence of sp^2-chains, except for sp^2-rings. These factors affect

the RS-spectra as competing forces, changing their shape [27]. The presence of sp^2-chains increases the FWHM (full width at half maximum) values of the *G*-band. The experimental technique for analyzing carbon materials is very simple and is implemented by determining the relative ratio of the intensities of the I_D / I_G, I_D, I_G bands — the maximum of the intensity of the *D*- and *G*-bands [27], and the L_a size, which in RS spectroscopy corresponds to the width of the ordered cluster:

$$L_a = C(\lambda)\frac{I_G}{I_D},$$

where $C(\lambda)$ = 3.01 nm for λ = 473 nm. The subscript "*a*" indicates that the dimensions are calculated along the crystal direction *a* for an ideal graphite lattice. The results of calculating the sizes of clusters L_a, the parameters of changing the frequency shift of the *G*-band and side arms for the coals of the studied ranks are given in Table 2.

Table 2

Results of calculating the sizes of clusters L_a, the parameters of changing the frequency shift of the *G*-band and side arms for the coals of the studied ranks

Coal rank	Frequency shift of *G*-band, cm^{-1}		I_D / I_G	L_a, nm	*FWHM* of *G*-band, cm^{-1}
	G_1	G_2			
SA	–	1603.6	0.72	4.16	42
A	–	1599.2	0.64	4.65	43
S	–	1600.9	0.50	6.18	49
F	1575.2	1604.5	0.58	5.12	53
G	1577.1	1612.8	0.49	6.02	80
LF	1575.9	1607.3	0.27	11.28	108

In this work, the ratio of the peak heights of the bands is taken as the ratio I_D / I_G. The use of band areas is more justified when the integrated band is associated with vibrations of the same bond, and the peaks associated with vibrations of other bonds do not contribute to the band area. In other words, the bands under study are clear, symmetrical, have no "arms", and do not change their shape when passing from one comparable sample to another. There are arms in the RS-spectra of coals, so the use of the I_D / I_G ratio is legal.

For coals of ranks from LF to SC (skinny caking), the *G*-band is decomposed into two components with a frequency shift of about 1580 and 1600 cm^{-1}.

The bands with similar values of the frequency shift may be conditioned by the nanosized graphite clusters and the presence of conjugated chain structures. The initial peak at 1520 cm^{-1} for sp^2-chains shifts with a decrease in the number of C atoms in the chain towards higher frequencies; therefore, chains with less than 25 C atoms can shift the peak to 1580 cm^{-1} [26]. At the same time, defects in graphite planes at small crystallite sizes shift the peak from 1580 to 1600–1620 cm^{-1}. The position of the *G*-band will depend on the combination of the length of the conjugated chains and the size of the crystallites in the test substance.

In the case of coal of ranks A and SA, the *G*-bands are represented by the same curve; the peak of the bands approximately corresponds to 1600 cm^{-1}. Therefore, it is logical to assume that, in this case, the spectra is due to the nanosize of graphite clusters. It is also known from XRD studies that the structure of anthracites and superanthracites consists of graphite-like nanoclusters [1] and the *G*-band is due only to their small size. The coals of ranks LF, G, and F contain both sp^2-rings and sp^2-chains. Then the band approximately corresponding to 1575 cm^{-1} (rank LF–F) appears due to the presence of conjugated chain structures in these coals.

According to the data given in Table 2, the smallest value of the I_D / I_G ratio and the largest ordered cluster size L_a = 11.28 nm refer to the rank LF coal. The maximums in the diffractograms of rank LF coal are the least pronounced compared to the maximum of the other coals ranks. This discrepancy can be explained by the fact that the low intensity of the *D*-band for rank LF coal (Fig. 3 *a*) may be associated not with the deformation of aromatic rings (deformation increased the I_D / I_G value), but with the presence of conjugated chains (which should decrease the I_D / I_G value). If, in this case, the chains form a conjugated polymer system (i.e., they fit with a certain periodicity), then the RS-spectra will show a sufficiently large degree of ordering. Thus, by analyzing the RS spectroscopy data and comparing them with XRD data, the schematic models of the coal structure can be represented in the form shown in Fig. 4.

Conclusion. According to the proposed model, the structure of the rank LF coal is an ordered polymer matrix consisting of conjugated chain structures and including randomly located graphite-like clusters. For the coals of higher stages of metamorphism, starting from D, in the coal structure there is a violation of the frequency of conjugated fragments of the polymer matrix and reducing their length, as evidenced by the RS-spectra of these coals. With the growth of metamorphism, the number of CH_3-groups in coals increases,

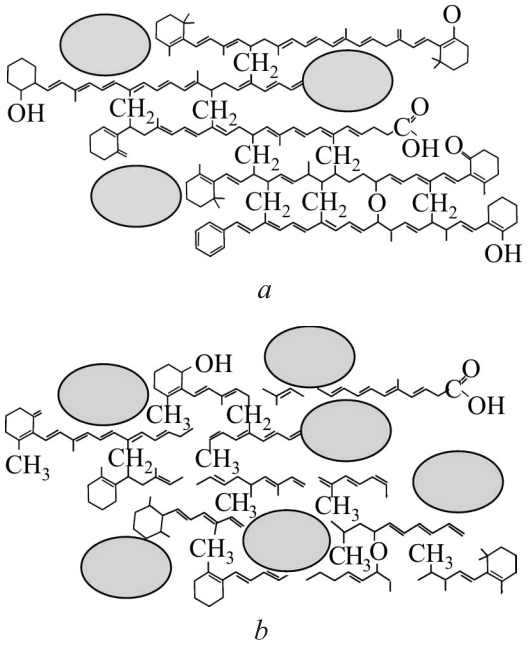

Fig. 4. Schematic models of the structure of coals of ranks LF (*a*) and G–F (*b*): — graphite-like clusters

and the number of graphite-like clusters gradually increases, and their mutual reorientation occurs. The structure of clusters of coals of ranks G–SA is highly ordered, as evidenced by their RLFFA little differing from each other.

Translated by K. Zykova

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Ulyanova E.V. — Dr. Sc. (Eng.), Leading Researcher, Laboratory no. 2.1 Physical-Chemical and Thermodynamic Processes in Rocks, Department no. 2 Center for Methane and Gas Dynamic Phenomena in Coal and Ore Deposits, Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences (Kryukovskiy tupik 4, Moscow, 111020 Russian Federation).

Malinnikova O.N. — Dr. Sc. (Eng.), Head of Laboratory, Laboratory no. 2.1 Physical-Chemical and Thermodynamic Processes in Rocks, Department no. 2 Center for Methane and Gas Dynamic Phenomena in Coal and Ore Deposits, Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences (Kryukovskiy tupik 4, Moscow, 111020 Russian Federation).

Shlyapin A.V. — Cand. Sc. (Eng.), Head of Department no. 2, Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences (Kryukovskiy tupik 4, Moscow, 111020 Russian Federation).

Pashichev B.N. — Leading Engineer, Laboratory no. 2.1 Physical-Chemical and Thermodynamic Processes in Rocks, Department no. 2 Center for Methane and Gas Dynamic Phenomena in Coal and Ore Deposits, Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences (Kryukovskiy tupik 4, Moscow, 111020 Russian Federation).

Please cite this article as:

Ulyanova E.V., Malinnikova O.N., Shlyapin A.V, et al. Specific features of the structure of various coal ranks at the nano level. *Herald of the Bauman Moscow State Technical University, Series Natural Sciences*, 2020, no. 6 (93), pp. 80–92.
DOI: https://doi.org/10.18698/1812-3368-2020-6-80-92