

Thermally Excited Multiplet States in Macerals Separated from Bituminous Coal

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Electron paramagnetic resonance searches of thermally excited multiplet states in macerals, exinite, vitrinite, and inertinite of Polish medium-rank coal (85.6 wt% C), were performed. Numerical analysis of lineshape indicates a multicomponent structure of the EPR spectra of macerals heated at 300° and 650°C. EPR spectra of exinite and vitrinite are a superposition of broad Gauss, broad Lorentz (Lorentz 1), and narrow Lorentz (Lorentz 3) lines. Two narrow Lorentz (Lorentz 2 and Lorentz 3) lines were observed in the resonance absorption curves of inertinite. The influence of the measuring temperature (100–300 K) on the EPR lines of the macerals was also studied. The experimentally obtained temperature dependence of the EPR line intensities were fitted by the theoretical functions characteristic for paramagnetic centers with ground doublet state ($S = \frac{1}{2}$) and paramagnetic centers with thermally excited triplet ($S = 1$) and quadruplet ($S = \frac{3}{2}$) states. Thermally excited multiplet states were found in exinite and vitrinite. Both paramagnetic centers with doublet ground state ($S = \frac{1}{2}$) and paramagnetic centers with thermally excited states, probably quadruplet states ($S = \frac{3}{2}$), exist in the group of paramagnetic centers of exinite and vitrinite with the broad Lorentz 1 lines. Intensities (I) of the broad Gauss and the narrow Lorentz 3 lines of exinite and vitrinite changes with temperature according to the Curie law ($I = C/T$). The existence of thermally excited multiplet states was not stated for inertinite. The two groups of paramagnetic centers of inertinite with Lorentz 2 and Lorentz 3 lines obey the Curie law. © 2000 Academic Press

Key Words: paramagnetic centers; multiplet states; electron paramagnetic resonance; EPR/ESR; macerals; thermal decomposition.

INTRODUCTION

In our earlier study we found that in bituminous coal thermally excited triplet states exist ($I-4$). There is a controversy between our measurements and the results obtained by Rothenberger *et al.* (5). By studying the changes of the total EPR signal of different coals with the measuring temperature, Rothenberger *et al.* have stated that no excited triplet states exist in bituminous coal. The changes of the intensities of the component lines of the complex EPR spectra of the coals were

not discussed (5). In the works of Smirnova, *et al.* (6, 7), a suggestion was made on the existence of quadruplet states with $S = \frac{3}{2}$ in fusinite and in chars carbonized at 720°C.

The aim of this work is to search thermally excited multiplet states in the heated petrographic constituents of medium-rank coal. Medium coalificated macerals were chosen for study because of the content of the major molecular units in them. Earlier, we studied the evolution of paramagnetic centers during thermal decomposition of these macerals at 300–650°C. Thermal decomposition influenced the concentrations of paramagnetic centers in macerals and their physical behavior (spin–spin and spin–lattice interactions, interactions of maceral paramagnetic centers with oxygen molecules). Different behavior and activity were observed for individual groups of paramagnetic centers existing in these samples. In this work, we compare the results of searching thermally excited multiplet states in individual groups of paramagnetic centers in macerals and their activity during thermal decomposition. Temperature dependence of line intensity for the components of the EPR spectra of the macerals was measured. Both numerical analysis of multicomponent lineshape of the EPR spectra (8) of exinite, vitrinite, and inertinite and numerical analysis of the experimental data for the intensities at the measuring temperature 100–300 K (9) were used.

RESULTS

EPR spectra of the studied macerals reveal complex characteristics resulting from the existence of several groups of paramagnetic centers in these samples. Resonance absorption curves of the individual groups of paramagnetic centers differ in linewidths, but similar values of g factor (2.0027–2.0030) were measured. The low g values indicate that paramagnetic centers with unpaired electrons located on carbon (C) atoms mainly exist in the studied macerals and that heteroatom (N, O) free radicals are absent in these samples. EPR spectra of exinite and vitrinite are superpositions of three lines: broad Gauss, broad Lorentz 1, and narrow Lorentz 3 component. Experi-

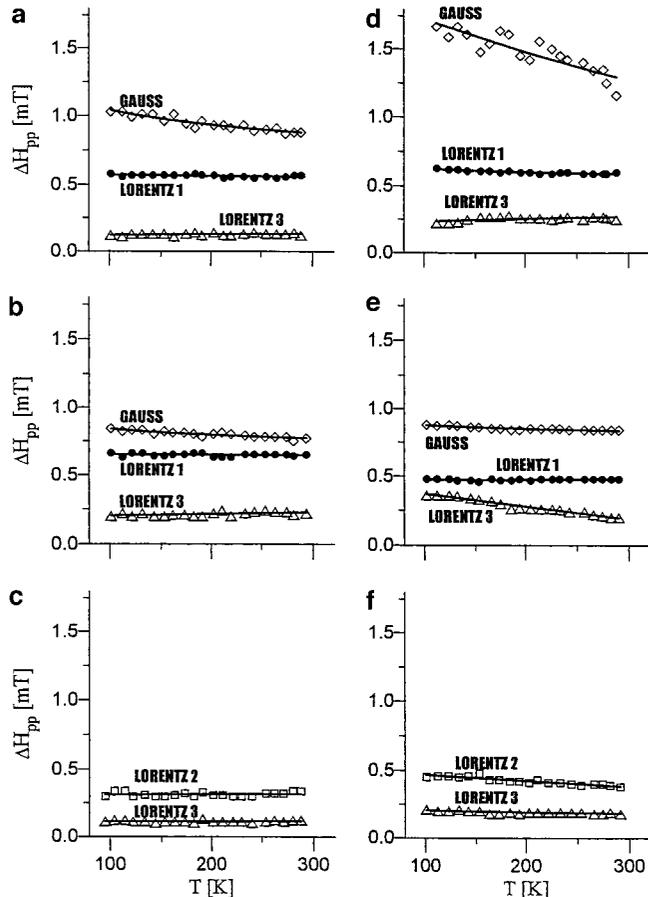


FIG. 1. Temperature dependence of linewidths (ΔH_{pp}) for the EPR components of (a) and (d) exinite, (b) and (e) vitrinite, and (c) and (f) inertinite heated at (a)–(c) 300°C and (d)–(f) 650°C.

mental EPR spectra of inertinite are approximated by the curve being a sum of two narrow Lorentz (Lorentz 2 and Lorentz 3) lines. Linewidths of the components of the EPR spectra of the studied macerals at 100–300 K are presented in Fig. 1. Narrowing of the EPR line with temperature was observed for Gauss lines of exinite and vitrinite (for the samples heated at 300° and 650°C, Figs. 1a, 1b, 1d, and 1e), Lorentz 3 line of vitrinite (for the sample heated at 650°C, Fig. 1e), and Lorentz 2 line of inertinite (for the sample heated at 650°C, Fig. 1f). For the other components of the analyzed EPR spectra, only insignificant changes of linewidths with the measuring temperature were observed (Figs. 1a–1f).

The influence of the measuring temperature (100–300 K) on the intensities of the components of the EPR spectra of macerals is shown in Figs. 2 and 3. The intensities of the EPR lines of exinite, vitrinite, and inertinite decrease with the measuring temperature. Graphs of function $IT = f(T)$ are shown (Figs. 4 and 5) for thermally excited multiplet states in macerals. For paramagnetic centers which obey the Curie law with doublet ground states ($S = \frac{1}{2}$), correlations between IT and the measuring temperature (T) are shown as straight lines parallel to

the axis of abscissa ($IT = C$). Thermally excited multiplet states do not fulfil the Curie law. As one can see from Figs. 4 and 5, paramagnetic centers of exinite and vitrinite with Gauss and Lorentz 3 lines and the two groups of paramagnetic centers of inertinite with Lorentz 2 and Lorentz 3 lines fulfil the Curie law. Paramagnetic centers of exinite and vitrinite with broad Lorentz 1 lines do not fulfil the Curie law (Figs. 4a, 4b, 4d, and 4e), because the IT curves as functions of the measuring temperature for Lorentz 1 lines are sloped to the axis of abscissa (Figs. 4a, 4b, 4d, and 4e).

The dependencies of the intensities of the EPR components on the measuring temperature were numerically fitted according to the quasi-Newton method (9) by the functions characteristic for ground doublet ($S = \frac{1}{2}$) states and for both thermally excited triplet ($S = 1$) and quadruplet ($S = \frac{3}{2}$) states (10):

$$\text{I: } I = C/T \quad (\text{ground doublet states}), \quad [1]$$

$$\text{II a: } I = B/(T(3 + \exp(A/T))) \quad (\text{thermally excited triplet states}), \quad [2]$$

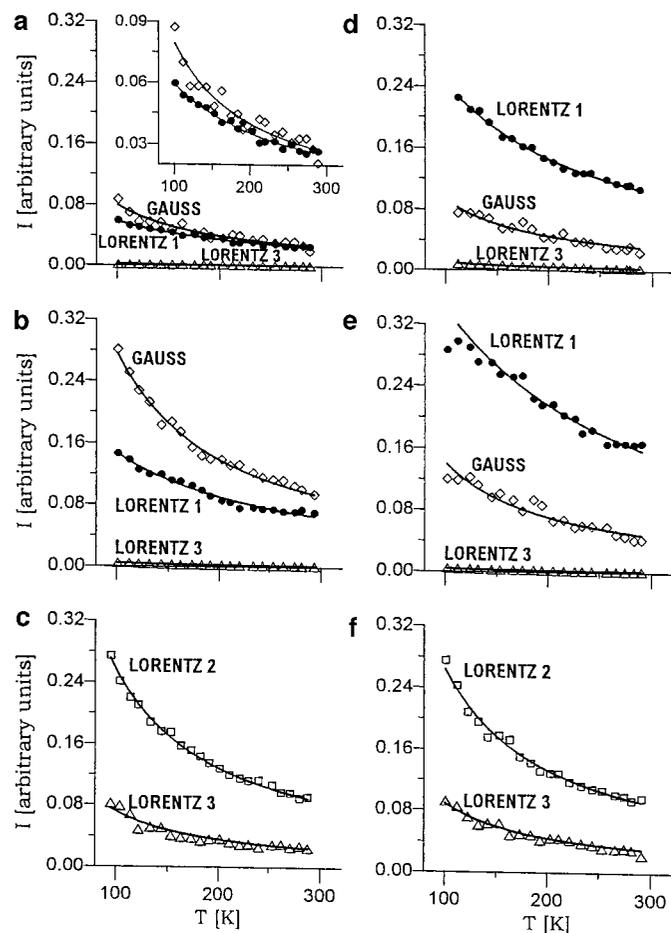


FIG. 2. Temperature dependence of intensities (I) for the EPR components of (a) and (d) exinite, (b) and (e) vitrinite, and (c) and (f) inertinite heated at (a)–(c) 300°C and (d)–(f) 650°C.

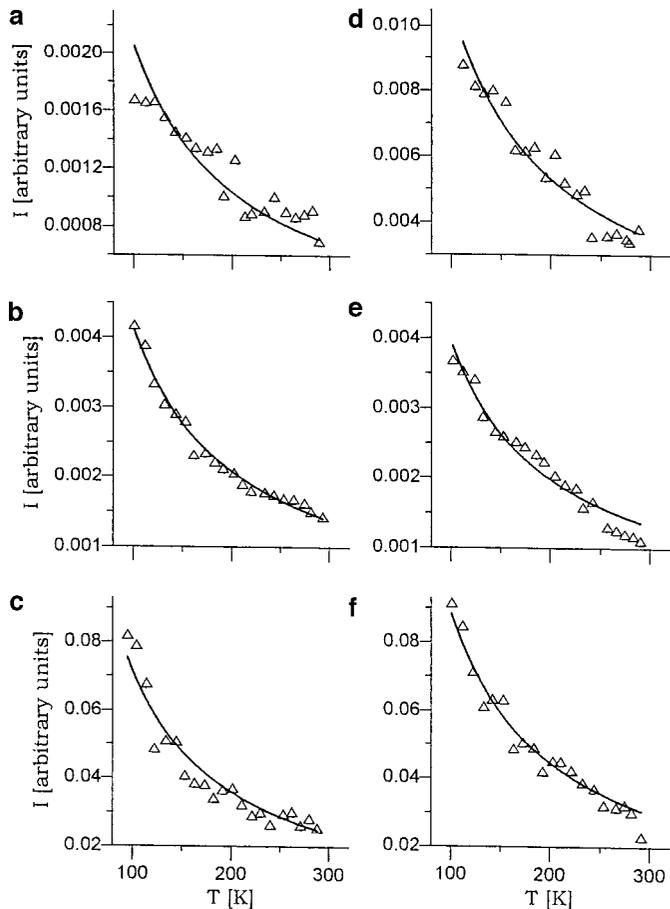


FIG. 3. Temperature dependence of Lorentz 3 line intensity (I) for (a) and (d) exinite, (b) and (e) vitrinite, and (c) and (f) inertinite heated at (a)–(c) 300°C and (d)–(f) 650°C.

$$\text{II b: } I = (B(5 + 3\exp(2A/T)))/(T(5 + 9\exp(2A/T) + 2\exp(3A/T)))$$

(thermally excited quadruplet states). [3]

The values of the constant parameters A ($A = J/k$ [K], where J is the energy of excitation, k is the Boltzmann constant), B , and C were determined.

Numerical analysis of $I = f(T)$, $IT = f(T)$, $I = f(1/T)$ and $IT = f(1/T)$ curves for broad Lorentz 1 lines of exinite and vitrinite (Figs. 6–13) demonstrated that both paramagnetic centers with doublet ground state ($S = \frac{1}{2}$) and thermally excited multiplet state are present in the paramagnetic centers system responsible for these lines. Experimental intensities (I) of Lorentz 1 lines are the sum of the intensities of the signal from paramagnetic centers with doublet ground state (**I**) and thermally excited paramagnetic centers (**II**), (**I** + **II**). Thermally excited paramagnetic centers can be the centers with the lowest excited triplet states ($S = 1$) or quadruplet states ($S = \frac{3}{2}$). The dependencies of the intensities of the two types of

thermally excited multiplet states on temperature are described by different functions. The functions characteristic of ground doublet ($S = \frac{1}{2}$) states and for both thermally excited triplet ($S = 1$) and quadruplet ($S = \frac{3}{2}$) states are given in Eqs. [1]–[3].

Temperature dependences of total intensity $I = (\mathbf{I} + \mathbf{II}) = f(T)$ and the component intensities (**I**, **II**) for Lorentz 1 lines of exinite and vitrinite on the assumption of the existence of triplet states are presented in Fig. 6. The correlations $IT = (\mathbf{I} + \mathbf{II})T = f(T)$, $I = (\mathbf{I} + \mathbf{II}) = f(1/T)$, $IT = (\mathbf{I} + \mathbf{II})T = f(1/T)$ on the assumption of the existence of paramagnetic centers with excited triplet states are presented in Figs. 7–9. Similar correlations ($I = (\mathbf{I} + \mathbf{II}) = f(T)$, $IT = (\mathbf{I} + \mathbf{II})T = f(T)$, $I = (\mathbf{I} + \mathbf{II}) = f(1/T)$, $IT = (\mathbf{I} + \mathbf{II})T = f(1/T)$) for the total intensity (**I** + **II**) and the component intensities (**I**, **II**) for Lorentz 1 lines of exinite and vitrinite on the assumption of the existence of quadruplet states are shown in Figs. 10–13.

The numerically determined values of the A , B , and C parameters of the functions $I = f(T)$, $IT = f(T)$, $I = f(1/T)$, and $IT = f(1/T)$ for Lorentz 1 lines of exinite and vitrinite on the assumption of the existence of thermally excited triplet and

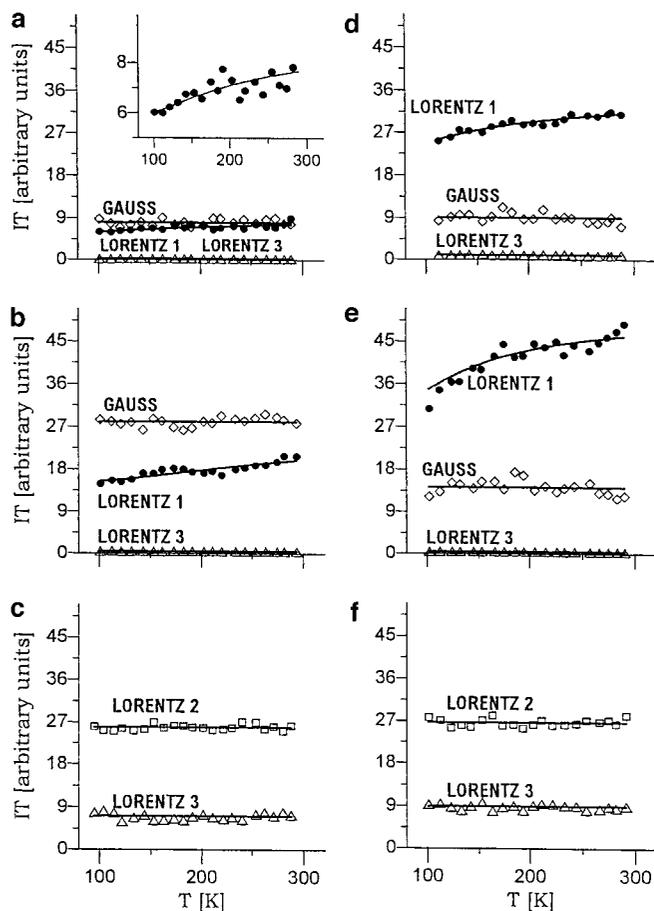


FIG. 4. Intensity–temperature product (IT) versus temperature for the EPR components of (a) and (d) exinite, (b) and (e) vitrinite, and (c) and (f) inertinite heated at (a)–(c) 300°C and (d)–(f) 650°C.

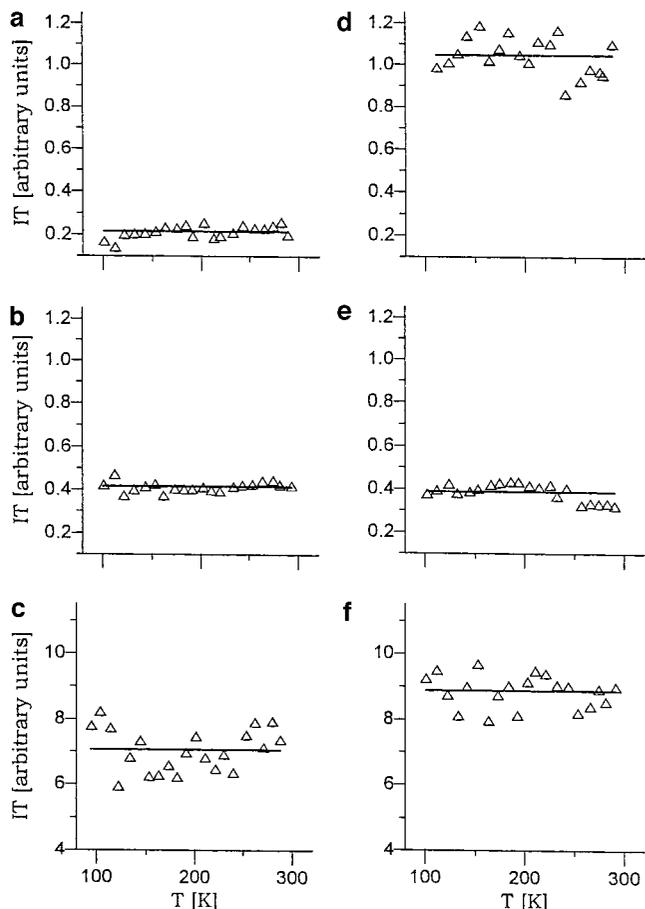


FIG. 5. Intensity-temperature product (IT) versus temperature for Lorentz 3 lines of (a) and (d) exinite, (b) and (e) vitrinite, and (c) and (f) inertinite heated at (a)–(c) 300°C and (d)–(f) 650°C.

quadruplet states are presented in Table 1. The values of A , B , and C parameters obtained by fitting the experimental total curves ($\mathbf{I} + \mathbf{II}$) to the sum of theoretical component curves (\mathbf{I} , \mathbf{II}) depend on the coordinate system. This effect probably results from experimental errors of the analyzed physical values, which require complex procedures to determine. The distinctly lowest differences of the values of the parameters (A , B , C) for different coordinate systems [(I, T) , (IT, T) , $(I, 1/T)$, $(IT, 1/T)$] were obtained on the assumption of the existence of quadruplet states in the studied macerals.

DISCUSSION

A large number of paramagnetic centers ($\sim 10^{17}$ – 10^{21} spin/g) was measured for both macerals and coals (11–19). Macerals are the petrographic constituents of coal differing in physical and chemical properties, because of their different plant origin and metamorphoses (20, 21). The degree of coalification increases from exinite to inertinite, and the value of the atomic H/C ratio decreases from exinite to inertinite. Relatively higher content of oxygen atoms O is observed for exinite and vitrinite

than for inertinite. The values of the aromaticity factor increases as follows: exinite < vitrinite < inertinite. Density and reflectance increases from exinite to inertinite. The above properties of the three types of macerals became more similar for coals with the highest carbon content. Paramagnetic center systems of individual coal macerals reveal a different character. Concentration of paramagnetic centers increases from exinite to inertinite (11, 12).

Our earlier room-temperature studies (17) of the macerals analyzed in this work indicated that paramagnetic centers with strong dipolar interactions located in molecular units consisting of a few aromatic rings are responsible for the broad Gauss and broad Lorentz 1 lines of exinite and vitrinite. The unresolved hyperfine structure of interactions of unpaired electrons and nuclei belonging to simple aromatic units are also responsible for the broadening of these lines. It was proved that paramagnetic centers, having mainly delocalized π electrons, with narrow Lorentz 2 lines of inertinite, and paramagnetic centers with narrow Lorentz 3 lines of exinite, vitrinite, and inertinite exist in large multiring structures (17). Exchange interactions and a superexchange effect are responsible for the narrowing of these lines. Paramagnetic centers responsible for the broad and narrow resonance curves differ in spin-lattice relaxation time. Broad and narrow EPR lines saturate at low and high microwave powers, respectively. The most active interactions with paramagnetic oxygen molecules were detected for paramagnetic centers with the narrowest Lorentz 3 lines (22). Single EPR lines of the four groups of paramagnetic centers (with Gauss and Lorentz 1–3 lines) existing in the medium coalified macerals were measured for pyridine extracts of these macerals (17). Paramagnetic centers responsible for broad Gauss and Lorentz 1 components of the coal EPR spectrum were found in the extracts of exinite and vitrinite. Single broad Gauss lines were measured for extracts of exinite from durain and clarain and for vitrinite from durain. Single broad Lorentz 1 lines were measured for the extracts of vitrinite from vitrain and clarain. Paramagnetic centers responsible for the narrow Lorentz components of the coal EPR spectrum were found in the extracts of inertinite. Single Lorentz 2 lines and single Lorentz 3 lines were measured for extracts of inertinite from clarain and durain, respectively.

Opinion about the localization of paramagnetic centers responsible for broad and narrow lines in simple and in multiring aromatic units was confirmed by earlier EPR analyses of coal samples with different degrees of coalification (18, 19). Paramagnetic centers with broad EPR lines were not detected in anthracites—samples without simple aromatic units (19). Paramagnetic centers with these narrow EPR lines were not observed in macerals (exinite, vitrinite, and inertinite) separated from coal with low carbon content (73.8% C)—samples free from the multiring aromatic structures (18). This view was also confirmed by microwave saturation electron paramagnetic resonance experiments. Application of EPR and FT-IR (16) spectroscopy indicated

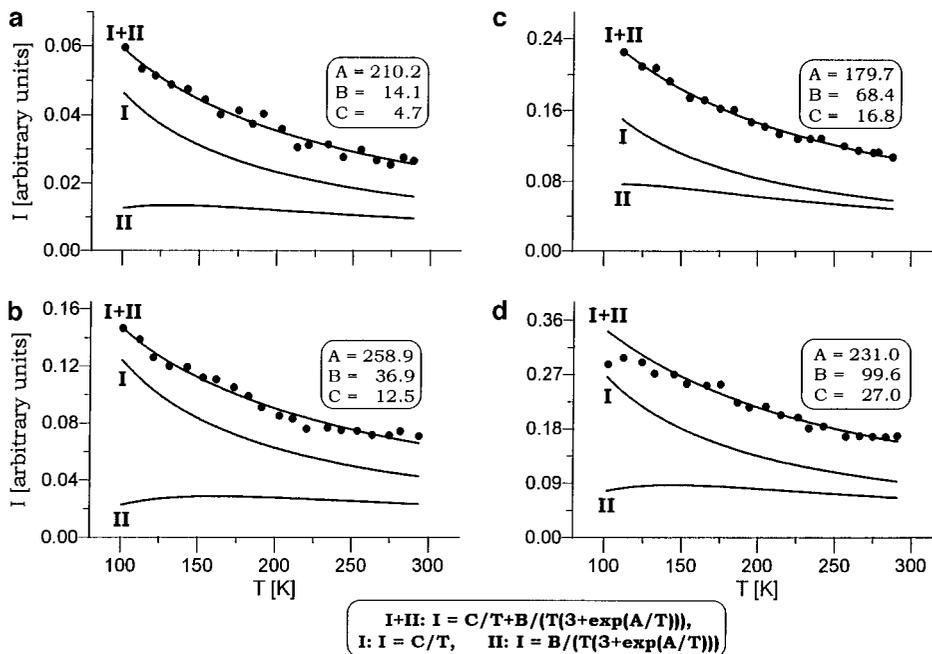


FIG. 6. Temperature dependence of Lorentz 1 line intensity (I) for (a) and (c) exinite, and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of triplet states ($S = 1$). **I**, **II** are the curves for paramagnetic centers with doublet states ($S = \frac{1}{2}$) and thermally excited states ($S = 1$), respectively.

that the long spin–lattice relaxation times were characteristic of coal samples with low content of aromatic structures (the coal fraction with low densities, coal extracts, and peaches). Broad EPR lines of such simple coal structures

saturated at relatively low microwave power. The narrow EPR lines of multiring coal structures with high aromaticity characterized the fast spin–lattice relaxation processes and these lines saturated at higher microwave powers (16).

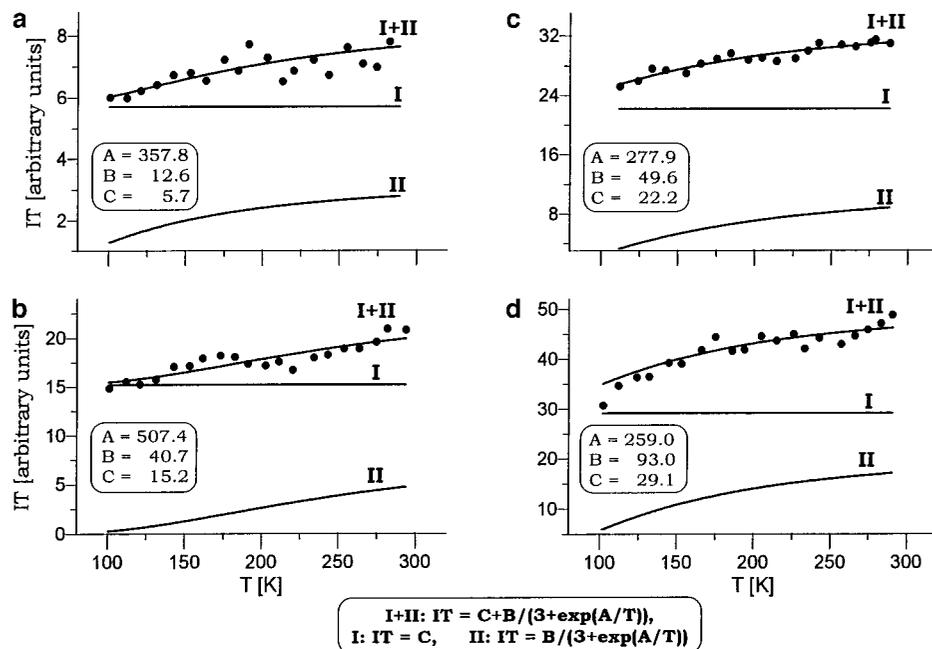


FIG. 7. Intensity–temperature product (IT) versus temperature for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of triplet states ($S = 1$). Notation as in Fig. 6.

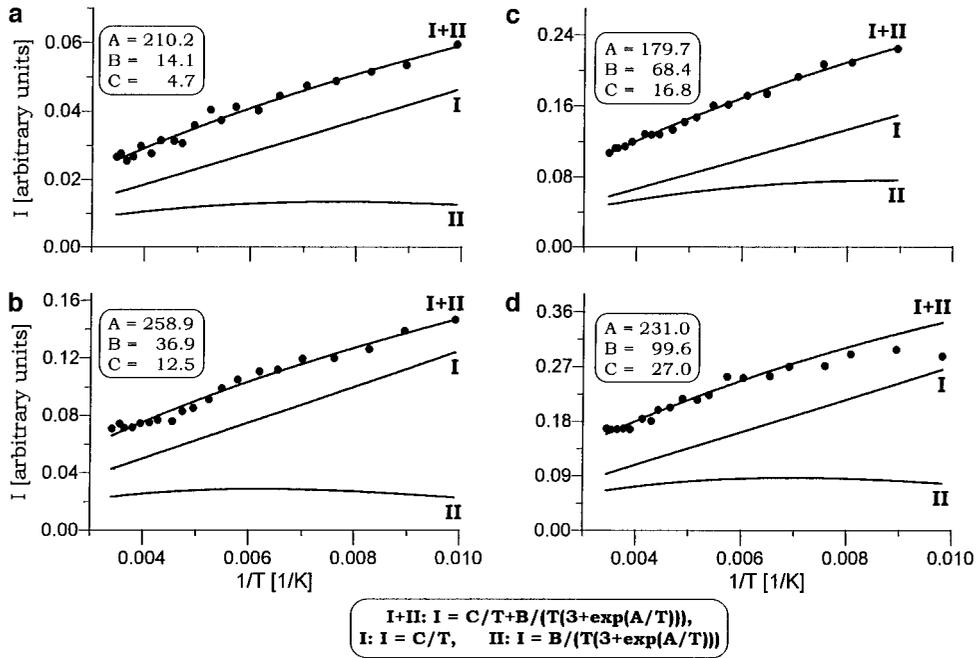


FIG. 8. Intensity (I) versus $1/T$ for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of triplet states ($S = 1$). Notation as in Fig. 6.

Conversion of chemical structure during thermal decomposition of macerals and coals was accompanied by changes of the amount and properties of their paramagnetic centers (11, 12, 23–33). The strongest changes of concentration of paramagnetic centers in the studied macerals heated at 300–

650°C occurred above 550°C (28–33). The concentration of paramagnetic centers in exinite increased up to 600°C and decreased at higher temperature. The increase and decrease of concentration of paramagnetic centers were measured for vitrinite and inertinite, respectively. Thermal decomposition of

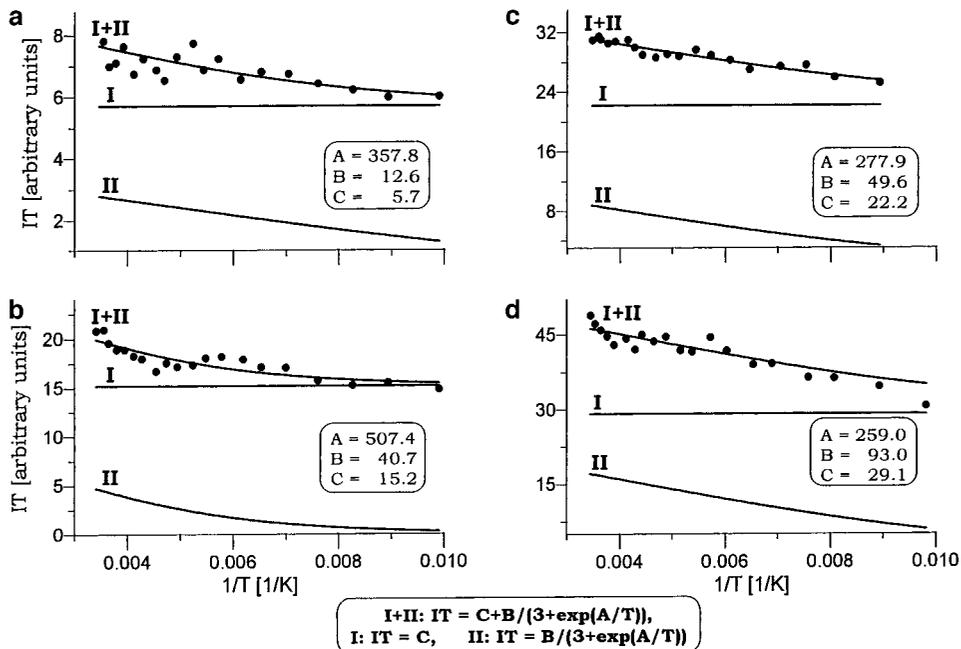


FIG. 9. Intensity–temperature product (IT) versus $1/T$ for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of triplet states ($S = 1$). Notation as in Fig. 6.

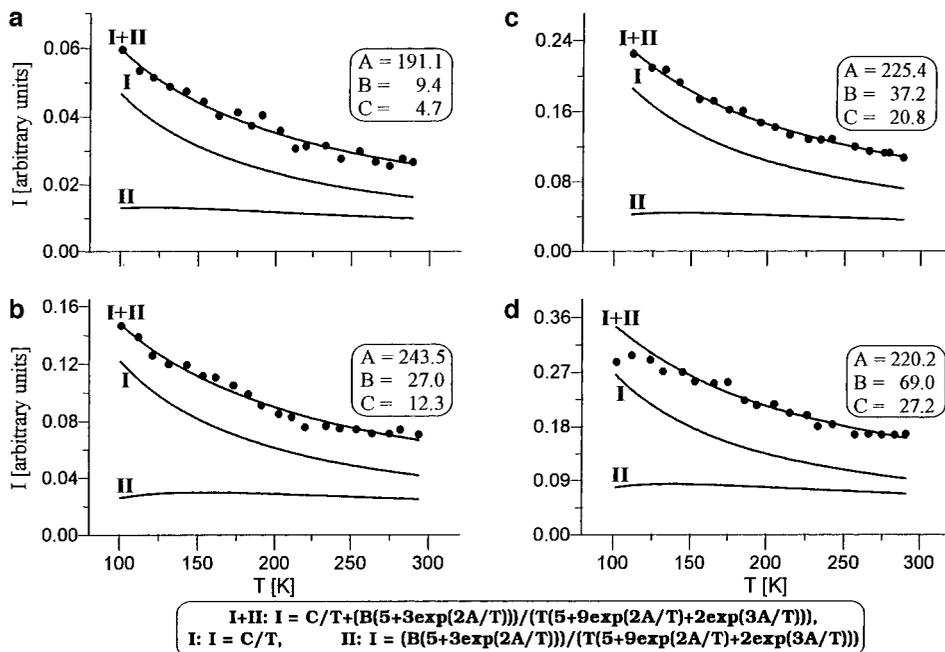


FIG. 10. Temperature dependence of Lorentz 1 line intensity (I) for (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of quadruplet states ($S = \frac{3}{2}$). Notation as in Fig. 6.

macerals influenced the spin–spin and spin–lattice interactions of unpaired electrons in the samples. The modification of interactions of maceral paramagnetic centers with oxygen during thermal decomposition was observed. Paramagnetic centers responsible for broad Lorentz 1 lines were the most active

during thermal decomposition of exinite and vitrinite. Considerable increases and decreases of concentration of those paramagnetic centers in the heating samples were detected. The present work points out that paramagnetic centers of exinite and vitrinite with broad Lorentz 1 lines also differ from the

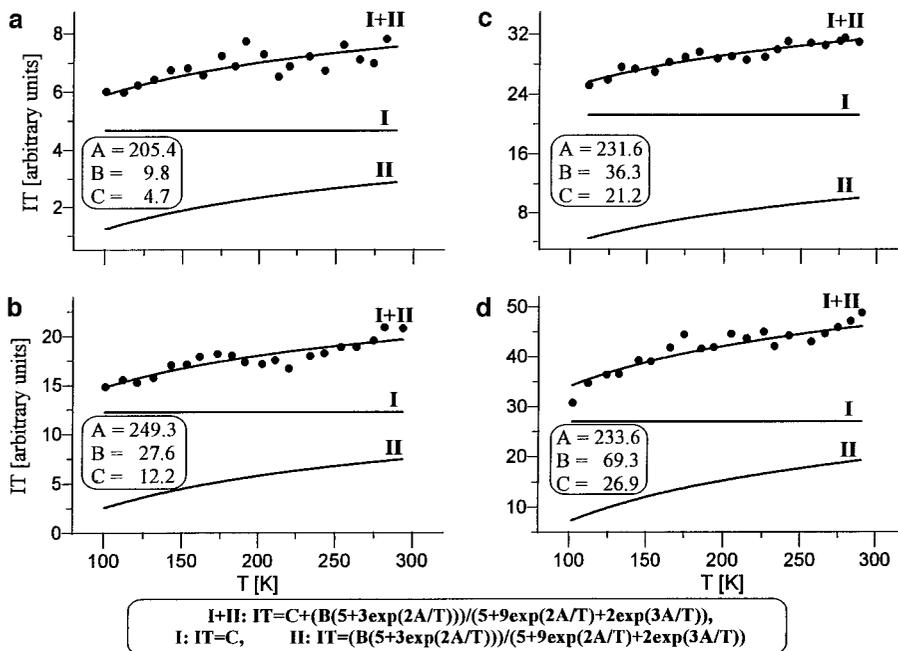


FIG. 11. Intensity–temperature product (IT) versus temperature for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of quadruplet states ($S = \frac{3}{2}$). Notation as in Fig. 6.

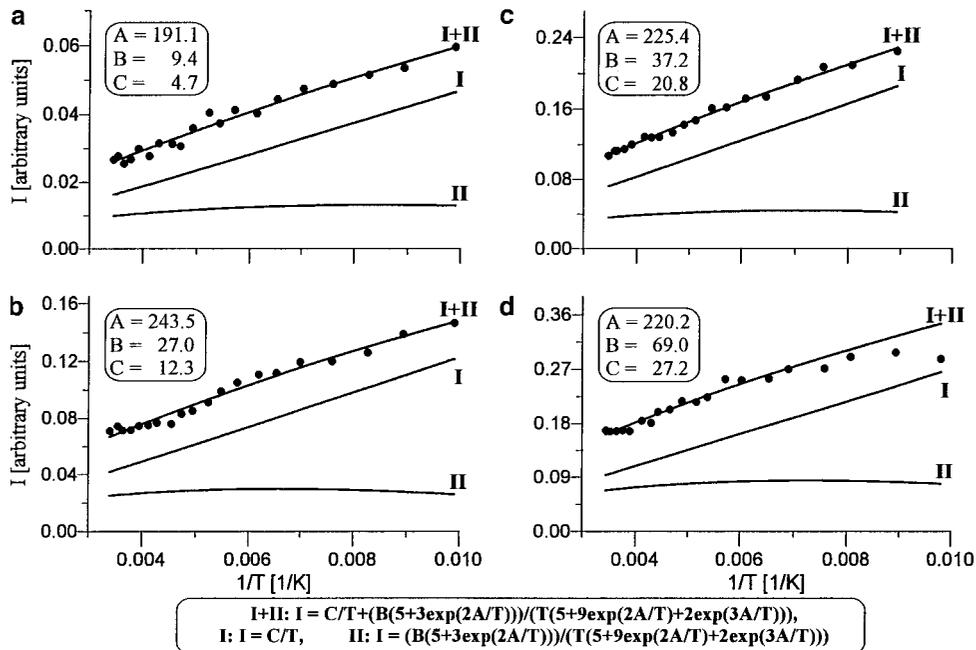


FIG. 12. Intensity (I) versus $1/T$ for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of quadruplet states ($S = \frac{3}{2}$). Notation as in Fig. 6.

other groups by the existence of thermally excited multiplet states.

Studies of the influence of the measuring temperature (100–300 K) on the intensities of the component lines of the EPR spectra of macerals heated at 300° and 650°C indicate that not

all paramagnetic centers of those samples fulfil the Curie law (Figs. 2–13). The ground state of paramagnetic centers responsible for Gauss, Lorentz 2, and Lorentz 3 components of the heated exinite, vitrinite, and inertinite is doublet type ($S = \frac{1}{2}$), and these paramagnetic centers fulfil the Curie law (Figs. 2–5).

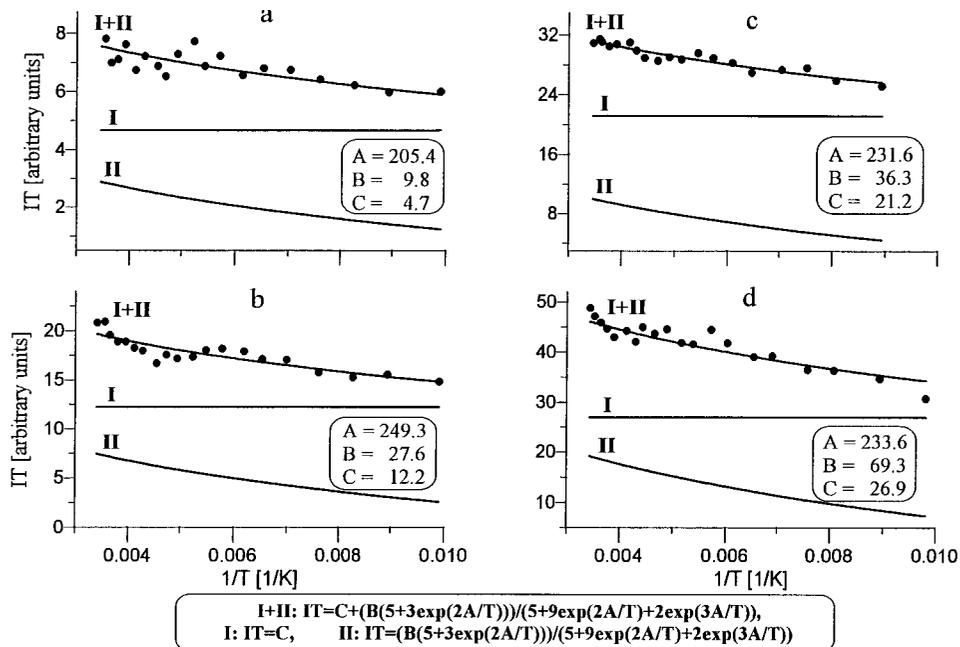


FIG. 13. Intensity–temperature product (IT) versus $1/T$ for Lorentz 1 lines of (a) and (c) exinite and (b) and (d) vitrinite heated at (a) and (b) 300°C and (c) and (d) 650°C on the assumption of the existence of quadruplet states ($S = \frac{3}{2}$). Notation as in Fig. 6.

TABLE 1

Values of Calculated Parameters A , B , and C as Functions $I = f(T)$, $IT = f(T)$, $I = f(1/T)$, and $IT = f(1/T)$ for the Lorentz 1 Line in the EPR Spectra of Exinite and Vitrinite under the Assumption of the Presence of Thermally Excited Triplet ($S = 1$) or Quadruplet ($S = \frac{3}{2}$) States

Maceral	Temperature of decomposition [°C]	Function	Assumption of					
			Triplet states ($S = 1$)			Quadruplet states ($S = \frac{3}{2}$)		
			A [K]	B	C	A [K]	B	C
Exinite	300	$I = f(T)$	210.2	14.1	4.7	191.1	9.4	4.7
		$I = f(1/T)$						
		$IT = f(T)$	357.8	12.6	5.7	205.4	9.8	4.7
	650	$IT = f(1/T)$						
		$I = f(T)$	179.7	68.4	16.8	225.4	37.2	20.8
		$I = f(1/T)$						
Vitrinite	300	$IT = f(T)$	277.9	49.6	22.2	231.6	36.3	21.2
		$IT = f(1/T)$						
		$I = f(T)$	258.9	36.9	12.5	243.5	27.0	12.3
	650	$I = f(1/T)$						
		$IT = f(T)$	507.4	40.7	15.2	249.3	27.6	12.2
		$IT = f(1/T)$						
Vitrinite	300	$I = f(T)$	231.0	99.6	27.0	220.2	69.0	27.2
		$I = f(1/T)$						
		$IT = f(T)$	259.0	93.0	29.1	233.6	69.3	26.9
	650	$IT = f(1/T)$						

Paramagnetic centers of exinite and vitrinite with broad Lorentz 1 lines do not fulfil the Curie law (Figs. 4a, 4b, 4d, and 4e). This group of paramagnetic centers with Lorentz 1 lines are mainly created by paramagnetic centers with doublet ground state ($S = \frac{1}{2}$) and additionally by thermally excited multiplet states. Intensities of the EPR signals from paramagnetic centers with doublet ground state are considerably higher than those for thermally excited multiplet states (Figs. 6–13).

The existence of paramagnetic centers, which do not fulfil the Curie law in the group of paramagnetic centers responsible for Lorentz 1 lines in the studied macerals is unquestionable (Fig. 4). It is possible to fit the experimental data of temperature dependence of Lorentz 1 line intensities by the theoretical functions characteristic for thermally excited triplet (Figs. 6–9) and quadruplet (Figs. 10–13) states. Unfortunately, the plots of these two functions in the studied temperature range did not differ considerably (Figs. 6–13); however, we obtained the best agreement of the results of fitting the experimental data in different coordinate systems for functions of quadruplet states. We believe that it resulted from the adequate choice of the type of fitting functions. The effect of slight differences between A , B , and C parameters of the functions (Eqs. [1]–[3]) on the assumption of quadruplet states (Table 1) probably points out that quadruplet states ($S = \frac{3}{2}$) rather than triplet states ($S = 1$) exist in exinite and vitrinite. The energy of excitation (J/k , Table 1) for doublet–quadruplet states for paramagnetic centers of exinite (191.1–231.6 K) and vitrinite (220.2–249.3 K) with Lorentz 1 lines is comparable with thermal energy kT .

The existence of quadruplet states in carbonized organic samples was suggested earlier (6, 7).

The performed analysis of the EPR spectra of exinite, vitrinite, and inertinite confirmed the earlier results about the existence of thermally excited multiplet states in coals. Thermally excited multiplet states in the macerals studied in this work were also found in paramagnetic center system with broad Lorentz EPR lines, as was earlier proved for coals (1, 2). Paramagnetic centers with thermally excited multiplet states were not found in groups of paramagnetic centers with narrow EPR signals both in neither the macerals analyzed in this work nor in the earlier studied coals (1, 2).

CONCLUSIONS

The application of electron paramagnetic resonance spectroscopy to the studies of behavior of complex paramagnetic center systems of thermally decomposed macerals from medium-rank coal indicates that:

1. Three different groups of paramagnetic centers exist in the studied exinite and vitrinite. They are responsible for the broad Gauss, broad Lorentz 1, and narrow Lorentz 3 component lines in their EPR spectra. Only two groups of paramagnetic centers with narrow Lorentz 2 and Lorentz 3 lines were observed in inertinite.

2. Paramagnetic centers with ground doublet state ($S = \frac{1}{2}$) obeying the Curie law mainly exist in the studied macerals.

3. It was found that the broad Lorentz 1 line present in the

EPR spectra of exinite and vitrinite is responsible for the temperature dependence of integral line intensity, which does not fulfil the Curie law. This proved the existence of thermally excited multiplet states in exinite and vitrinite. Numerical analysis of the correlations between the intensity of Lorentz 1 lines and the measuring temperature indicated that rather paramagnetic centers with thermally excited quadruplet ($S = \frac{3}{2}$) rather than triplet ($S = 1$) states occur in exinite and vitrinite.

4. Thermally excited multiplet states were not found in inertinite.

EXPERIMENTAL

Samples

Exinite from durain, vitrinite from vitrain, and inertinite from clarain of Polish medium-rank (85.6 wt% C) coal were analyzed. The coal contained 9 vol% exinite, 77 vol% vitrinite, and 14 vol% inertinite. Lithotypes: durain, vitrain, and clarain were hand-picked from original coal. Lithotypes were demineralized using an aqueous solution of hydrochloric and hydrofluoric acids at 50°C. Macerals were separated by centrifugation of the demineralized lithotypes in toluene-carbon tetrachloride mixtures with required density. Exinite (density < 1.24 g/cm³), vitrinite (density 1.28–1.30 g/cm³), and inertinite (density > 1.36 g/cm³) were obtained from durain, vitrain, and clarain, respectively. Purities of the maceral samples were: 75, 97, and 96 vol%, respectively. The macerals were heated in an inert atmosphere of flowing argon at 300° and 650°C per 40 min.

The heated samples were mixed with SiO₂ (1:5) and placed in thin-walled glass tubes. No EPR signal of impurities or defects in glass were observed in empty tubes. The sample tubes were evacuated at 0.01 Pa for 24 h and sealed under vacuum.

EPR Method

The EPR measurements at 100–300 K were performed using an X-band (9.3 GHz) spectrometer with magnetic modulation 100 kHz. The EPR spectra were taken with attenuation of microwave power 20 dB (~0.7 mW) to avoid signal saturation.

The lineshape of the EPR spectra was studied using an algorithm given by Opfermann (8). Attempts were made to approximate the experimental spectra by different superpositions of Gauss and Lorentz curves. The best results of curve fitting were assumed to be those approximations which gave the smallest value of the root-mean-square deviation. The parameters of the best fitted lines, linewidth (ΔH_{pp}), g factor, and integral intensity (I) of the components of the total spectrum, were evaluated. The intensities of the EPR components of the studied macerals were compared to the intensities of EPR signals of a ruby crystal, permanently placed in the resonance cavity, which was used as the inert reference.

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