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X-Ray spectroscopic study of graphite fluoride $(C_2F)_n$ intercalated with benzene

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Samples of intercalated graphite fluoride of the $C_2F \cdot zR$ type (R is C_6H_6) before and after heating to 150 °C in a spectrometer vacuum chamber were studied by X-ray fluorescence spectroscopy. The C-Kα differential spectra of the samples mainly characterizes the electron state of carbon atoms in the benzene molecule inside the C_2F matrix. The differential spectrum is distinct from the spectrum of solid benzene by additional maxima, which indicate the interaction between the benzene molecules and the graphite fluoride matrix. Comparative analysis of the spectrum of the heated sample and those of graphite and graphite fluoride $(CF)_n$ suggests that the layers of the C_2F matrix contain considerable regions of both completely fluorinated and graphite-like regions.

Key words: graphite fluoride, intercalated compounds, X-ray fluorescence spectroscopy, electronic structure.

The treatment of graphite at room temperature with halogen fluorides (BrF_3, ClF_3) affords intercalated compounds of graphite fluoride (ICGF) C_nHalF_m (Hal = Br, Cl). Along with fluorination, some molecules are incorporated between the layers of oxidized graphite; therefore, the composition of the resulting product corresponds to the formula $C_xFHal_y \cdot zR$, where $x \approx 2$, $y \approx 0.1$ (0.02) for Hal = Cl (Br), and R are molecules of various intercalating agents.[1,2] Then the R molecules are easily substituted by other organic and inorganic molecules[3] that may be present for a long time in the matrix structure, providing a very low vapor pressure (~10^{-4}—10^{-5} Torr) even for highly volatile compounds.[4]

According to the data of NMR and X-ray electron and IR spectroscopies,[5,6] regardless of the donor-acceptor properties of intercalating agents, the "guest—host" interaction in $C_2F \cdot zR$ has a van der Waals character. As for the distribution of fluorine atoms in the layers, the model, in which the fluorocarbon network is the alternation of chains of completely fluorinated hexagons and aromatic carbon hexagons, is one of the most developed models.[7] The measured shifts of the C1s levels of the $C_2F \cdot zR$ compounds with various incorporated components also suggest the presence of graphite-like regions inside the graphite fluoride layers.[8]

In this work, we used X-ray fluorescence spectroscopy to study ICGF with benzene. The procedure for the excitation and detection of C-Kα spectra applied by us previously made it possible to obtain the highly resolved spectra of $(CF_x)_n$ (x = 1.12, 0.88, 1.33) without noticeable destruction of the samples and to interpret the spectral peculiarities.[9,10]

Experimental

The $C_2F_{0.9} \cdot 0.09C_6H_6$ compound was synthesized by the previously described procedure.[3]

The C-Kα X-ray fluorescence spectra of this compound, graphite, and solid benzene were recorded on a Stearat X-ray spectrometer. The sample of the starting $C_2F_{0.9} \cdot 0.09C_6H_6$ (~50 mg) was supported on a copper plate and cooled to the temperature of liquid nitrogen in the vacuum chamber of an X-ray tube. The vacuum in the spectrometer chamber was ~10^{-4} Pa. After the C-Kα spectrum of this compound (**1**) was detected, the sample was heated to 150 °C directly in the X-ray tube vacuum chamber for 45 min. The benzene molecules began to leave the graphite fluoride matrix (being monitored by an MX-7304 mass spectrometer) at 70—80 °C, and this process almost completely ceased when the sample was heated to 130—150 °C. Then the heated sample (**2**) was cooled to the temperature of liquid nitrogen, and its X-ray spectrum was measured.

The sample of solid benzene was obtained by the deposition of benzene vapor on a cooled support by a known procedure.[11] The X-ray spectrum of non-textured polycrystalline graphite (grain size ~50 μm) was also measured for the sample cooled to the temperature of liquid nitrogen. All spectra were obtained without rearrangement of the spectroscopic part of the spectrometer. The working regime of the X-ray tube with a copper anode: voltage (U) 6 kV, current (I) 0.5 A. A proportional gas counter with methane filling at ~0.1 atm was used for the detection of radiation. The spectra were obtained with a resolution of ~0.4 eV.

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A single crystal of ammonium biphthalate NH_4AP was used as the crystal-analyzer. The efficiency of reflection of the X-ray radiation of this crystal-analyzer near the C-K adsorption edge increases by 30—40 times within the energy interval of 275—285 eV over the X-ray emission spectrum. Therefore, special mathematical processing is required for correction of the spectrum.[12] The spectrum was recorded by multiple scanning of the specified energy interval. The stored intensity of the spectrum in the maximum was ~2000 pulse s^{-1}.

Spectra were calibrated by the C-Kα spectrum of solid benzene obtained on a spectrometer with the diffraction lattice.[13] The accuracy of determination of the energy of X-ray lines was ~0.3 eV.

Results and Discussion

The C-Kα spectrum of the heated sample **2** contains information on the electronic structure of the graphite fluoride matrix, which depends on the character of the distribution of fluorine atoms in the layers. When we assume that the layer structure indeed contains large graphite-like regions, the subtraction of half the intensity of the C-Kα spectrum of graphite from the spectrum of sample **2** gives a curve corresponding to the electron state of the carbon atoms linked with the fluorine atoms. The X-ray fluorescence spectrum of sample **2**, the C-Kα spectrum of graphite, and the differential spectrum are presented in Fig. 1. For comparison, the spectrum of graphite fluoride $(CF)_n$ obtained previously[9] is presented in the insert. This spectrum reflects the electron state of the carbon atoms bound to the fluorine atoms.

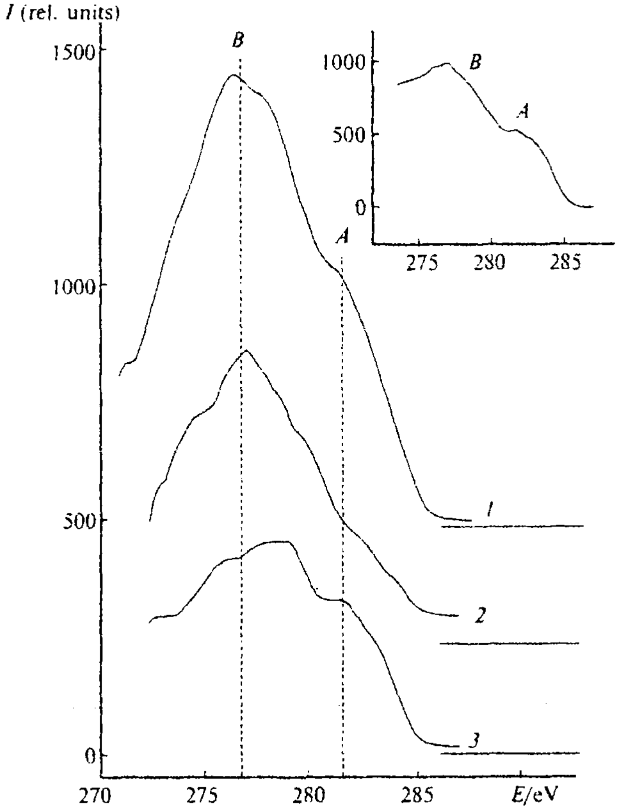

Fig. 1. C-Kα Spectra of the $C_2F_{0.9} \cdot 0.09C_6H_6$ sample heated in the X-ray tube chamber (*1*) and graphite (*2*). The intensity of the presented C-Kα spectrum of graphite is halved as compared to the initial spectrum normed to the maximum of spectrum *1*. Spectrum *3* was obtained by the subtraction of spectrum *2* from spectrum *1*. The previously published[9] C-Kα spectrum of $(CF)_n$ is presented in the insert.

The differential spectrum (see Fig. 1, curve *3*) as well as the spectrum of the CF matrix contains two main bands (*A* and *B*) characterized by the energy positions at 280—285 and 275—280 eV, respectively. The relative intensity of maximum *A* in the differential spectrum is higher, and the position of maximum *B* is shifted toward the short-wave region by ~1 eV. Similarity of the spectrum of $(CF)_n$ and the differential spectrum (*3*) assumes that the layers of the C_2F matrix contain both fluorinated and fluorine-free regions. The marked distinction between the spectra indicates that the structure of the C_2F layer contains carbon atoms whose electron state differs from both graphite and $(CF)_n$. The presence of at least three types of carbon atoms in the structure of graphite fluorides $C_2F \cdot zR$ has previously been established by the X-ray electron study of these compounds.[8]

Both carbon atoms of the benzene molecule and the atoms of the graphite fluoride matrix participate in the formation of the C-Kα spectrum (Fig. 2) of the compound $C_2F_{0.9} \cdot 0.09C_6H_6$. Assuming that almost all incorporated molecules were removed from the matrix by thermal treatment, we may conclude that the difference between the spectra of samples **1** and **2** mainly reflects the electron state of the carbon atoms of the benzene molecules. It can be expected that this differential spectrum is also affected by the change in the electron state of the carbon atoms of the matrix which interacted in any way with the incorporated molecules. In our opinion, the contribution of this component to the differential spectrum should not exceed several percent, because the number of these carbon atoms is the same or, which is more probable, less than that of the carbon atoms of the remote molecule, but these atoms remain in the system and, hence, participate in the formation of the spectra of both compound **1** and sample **2**.

The profiles of the C-Kα spectra of the starting and heating samples (see Fig. 2) are similar. The broad maximum *A* in the region of 281—285 eV and the more intense band *B* that occupies a low-energy interval can be distinguished in both spectra. The points in Fig. 2 correspond to the experimental data. The statistical scatter in the short-wave spectral region (282—285 eV) is ~2%, whereas it is substantially higher in a longer-wave region of the spectrum. The spectral contour was obtained by averaging using the Fourier method, smoothing over five points.

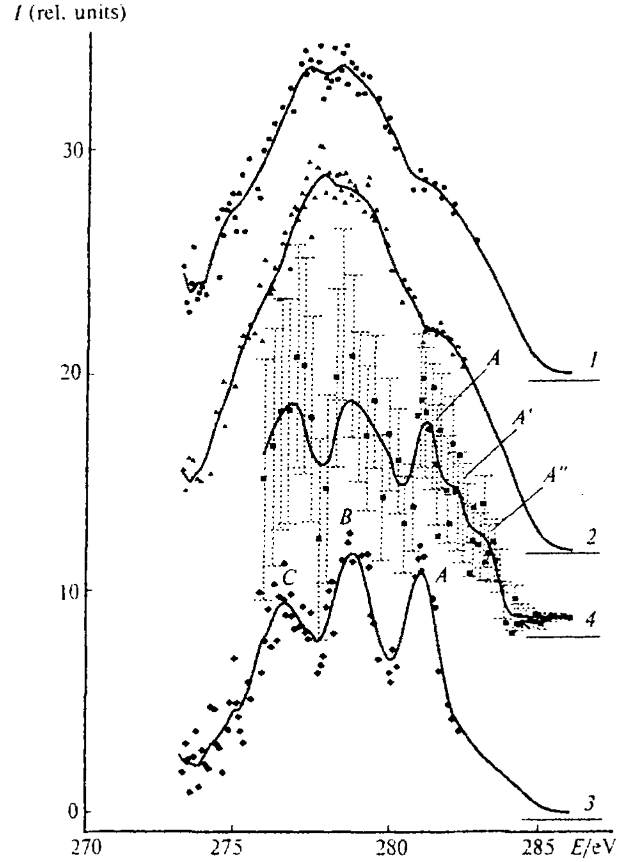

Fig. 2. C-Kα X-ray fluorescence spectrum of compound $C_2F_{0.9}\cdot 0.09C_6H_6$: starting sample (*1*); sample heated to 150 °C (*2*); solid benzene (*3*); and difference of spectra *1* and *2* increased tenfold (*4*). The dotted vertical lines correspond to the doubled root-mean-square deviation.

The difference in the spectra obtained by the subtraction of spectrum *2* from spectrum *1* corresponds to the X-ray spectrum of the benzene molecules inside the C_2F matrix. This difference amplified by a factor of 10 is presented by curve *4*. The vertical lines correspond to the 2σ values obtained by the subtraction of the spectra:

$$\sigma = \sqrt{\sigma_1^2 + \sigma_2^2},$$

where σ_1 and σ_2 are equal to $\sqrt{I_1}$ and $\sqrt{I_2}$, respectively, and I is the intensity of the line. The low statistics in the region of energies lower than 280 eV does not allow us to reliably reproduce the structures of maxima *B* and *C*, whereas the short-wave bands *A*, *A'*, and *A''* are detected rather convincingly.

The β value[14] characterizing the 95% probability of the appearance of the maximum, $\beta = 0.1N/(2\sqrt{N})$, can serve as a criterion of the accuracy of determination of the maxima of intensities of two lines ($I_1 = N$, $I_2 = 0.9\cdot N$) that differ by 10%. To have the β parameter higher than 1, it is necessary that the number of pulses stored in one point is greater than 400. This condition is knowingly fulfilled for maxima *A* ($N = 1000$), *A'* ($N = 1400$), and *A''* ($N = 2000$). In addition, each maximum characterized by a width of 1—1.5 eV consists of 15—20 points, which increases the accuracy of determination of the maximum by 15—20 times.

To elucidate the question of whether the electronic structure of the benzene molecule incorporated into the C_2F matrix changes as compared with that of the free molecule or not, we compared its spectrum with the C-Kα spectrum of solid benzene (see Fig. 2) measured under the same experimental conditions. The X-ray spectrum of solid benzene is almost identical to that of the molecules in the gas phase.[11] The C-Kα spectrum of solid benzene is characterized by three maxima *A*, *B*, and *C*. The spectrum of incorporated benzene exhibits the splitting of band *A*, resulting in the appearance of additional maxima at the short-wave side. The effect of decreasing the intensity of maximum *A* as compared to those of *B* and *C* has also been observed in previous experiments.[15,16] We attribute this distinction to change in the electron state of the carbon atoms of the incorporated molecule due to interaction with the graphite fluoride matrix (not necessary to the formation of a chemical bond).

The X-ray emission spectrum appears due to the electron transitions between the upper valent and inner atom-like levels of the molecule. Therefore, the appearance of additional lines in the spectrum (see Fig. 2, curve *4*) can be related to both the splitting of degenerate levels of the benzene molecule and the difference in the energies of the internal 1s levels of the carbon atoms of this molecule. The splitting of valent degenerate orbitals results from a decreased symmetry of the environment (as compared to D_{6h} for free benzene). The splitting of the internal levels can occur due to the differences in the charge state of the carbon atoms in C_6H_6 that appear due to the Coulomb interaction with the neighboring negatively charged fluorine atom.

The last assumption was checked for the simple model consisting of the benzene molecule and the dipole in which the negative charge corresponds to the fluorine atom and the positive charge corresponds to the carbon atom of the graphite fluoride network. The benzene molecule is arranged at an angle of 45° to the dipole axis, and the distance from the negative charge to the nearest atom of the molecule is 1.73 Å. The absolute values of point charges remote from each other at a distance of 1.3 Å, which is characteristic of the covalent C—F bond, were accepted as 0.9. The quantum-chemical calculation of this model has been performed using the 6-311G* basis set of functions in the framework of the self-consistent Hartree—Fock field included in the Jaguar program package.[17] Consideration of this model makes it possible to elucidate the effects of changing the electronic structure of the benzene molecule due to the Coulomb interactions.

The theoretical spectra were calculated in the one-electron approximation of frozen orbitals. The intensity of the X-ray transition is proportional to the sum of the

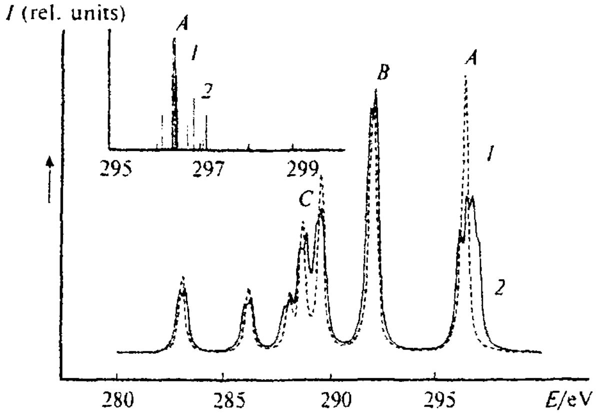

Fig. 3. Comparison of the theoretical C-Kα spectra of the free benzene molecule (*1*) and the molecule interacting with a dipole (*2*). The calculated intensities of the X-ray transitions that form maximum *A* in both spectra are presented in the insert.

squares of the coefficients with which the 1s and 2p basis functions of the given atom enter into the final and initial molecular orbitals (MO). The resulting spectrum is the sum of the Lorentzian lines, taking into account their intensities. The transition energy corresponds to the difference of the one-electron energies of the corresponding MO. The calculated C-Kα spectrum of the model and the theoretical spectrum of the benzene molecule (for comparison) are presented in Fig. 3. The calculated intensities of the transitions that form maximum *A* in both spectra are shown in the insert. Two effects observed in the experiment are clearly seen from consideration of the results of calculation of this model: the decrease in the relative intensity of the first maximum as compared to those of other maxima and its splitting into several lines, in particular, the appearance of two additional lines in the short-wave part of the spectrum (see insert). This effect is explained by the different charge states of the carbon atoms in the benzene molecule, due to which MO are split resulting in the appearance of additional lines in the X-ray spectrum. The change in the charge states of the carbon atoms under the electrostatic field provides a qualitative description of the short-wave part of the spectrum of benzene incorporated in the C_2F matrix.

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