PHASE TRANSITIONS OF INTERCALATION INCLUSION

COMPOUNDS $C_2F_{0.92}Br_{0.01}yCH_3CN$ IN THE

TEMPERATURE RANGE 20-260°C

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X-ray phase analysis (XRPA), differential thermal analysis (DTA), and IR spectroscopy studies were performed to investigate stepwise transitions of the fluorographite intercalation inclusion compound (host) with acetonitrile (guest). When heated in a guest atmosphere to 260(±8)°C, the compound of the first stage of saturation with a spacing of $I_c = 9.47 \text{ \AA}$ undergoes sequential disproportionation into gaseous acetonitrile, a compound of the second stage ($I_c = 15.52 \text{ \AA}$), a compound of the fourth stage of occupation ($I_c = 27.77 \text{ \AA}$), and solid solutions based on the fluorographite matrix ($I_c = 6.05 \text{ \AA}$) that form “residual compounds.” In air the “residual compound” of graphite fluoride is formed at lower temperatures. Conditions of mutual transitions and formation of metastable states have been determined for which the domain model with coexisting microphases of different stages of occupation is discussed.

Keywords: intercalation compounds, graphite fluoride, X-ray phase analysis, thermolysis, phase transitions, orientated layers.

INTRODUCTION

Investigation of the properties of fluorinated graphite intercalation compounds (FGICs) having the general formula $(C_2F_xR_z \cdot yA)_n$ and constructed as guest (A)–host ($C_2F_xR_z$) complexes, where $x \approx 0.9$ –1.0 and $z = 0$ –0.03 [1–6] for $R = Br$; $z = 0.07$ –0.20 for $R = Cl$ [7–9]; $z = 0.02$ for $R = SO_3F$ [10]; and $z = 0.25$ for $R = I$ [11], is important from the viewpoint of selective synthesis of new materials including nanocomposite functional materials of carbon-metal and fluorographite-metal types, containing ultradisperse particles [12–14]. The ability of $C_2F_xR_z$ fluorinated matrices to accommodate guest molecules of varying nature, size, and configuration between layers was noted [15] to be of interest for theoretical analysis of the models of low-dimensional clathrate compounds.

In contrast to phase transitions in graphite host–guest systems for which conditions and effects (pressure, temperature, and composition effects of guest inclusions [16–20]) are well known, stepwise transitions in FGICs are difficult to investigate because an “empty” $C_2F_xR_z$ matrix, i.e., the starting α modification of the guest is generally not realized in the course of low-temperature synthesis (graphite fluorination by known procedures [1–10, 21–23]); an inclusion compound with a given guest is obtained by exchange reactions [2, 4–6, 9, 10, 24–26]. Replacement of the components of the oxidative medium of the guest subsystem by an indifferent guest terminates graphite oxidation; in subsequent exchange reactions, the fixed composition of the matrix (C/F ratio) remains constant [24, 25, 27]. The stages of graphite oxidation and replacement of

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one guest by another are readily realizable with FGICs of the first degree of occupation (FGIC-1, regular alternation of matrix and guest layers); after some part of the guest has been removed until an air-dry state is reached, the second stage is realized (FGIC-2) with guest molecules occupying each second layer of the matrix [2, 4, 6, 9, 10, 15]. Evacuation and (or) keeping FGIC-2 in air at elevated temperatures (120-280°C for 1-4 h [4, 9, 28], 15 h [29]) leads to mass loss and to a series of reflections with the maximal value of $d/n = 6.05\text{--}6.35$ Å [4] or a single reflection at $5.8\text{--}5.9$ Å [9], $5.6\text{--}5.8$ Å [28] on the diffractograms of thermolysis products. The single reflection on the diffractograms of the thermolysis products of FGIC with CCl_4 , C_6F_6 , and GeCl_4 was interpreted as d_{004} for FGIC-3 (with the guest occupying each third layer of the matrix) [28]. No publications are available on stepwise transitions of FGICs within the framework of a host–guest binary system. Low-temperature methods for the preparation of $(\text{C}_4\text{F})_n$, $(\text{C}_{3.65\text{--}3.97}\text{F})_n$, and $(\text{C}_{4.04\text{--}4.35}\text{F})_n$ “empty” matrices are described in [30–32]; synthesis of $(\text{C}_2\text{F}_x\text{Cl}_z)_n$ matrixes, where $x \approx 0.9\text{--}1.1$, $z \approx 0.07\text{--}0.10$, is described in [33–35]. It was noted [32] that the “empty” matrix with $x \approx 1$ loses its ability to accept an inclusion this being a considerable hindrance to investigation of guest–host systems. It was admitted [36] that small crystallites (the size of soot) can completely lose the guest; as shown in [37, 38], mechanical grinding of fluorocarbon materials leads to an increased role of surface effects (hydrolysis that forms HF), which decompose the starting sample, and is accompanied by changes in the composition and structure and hence properties of the sample.

The aim of the present work is to detect mutual transitions of different degrees of occupation for FGICs with acetonitrile and to determine conditions at which they can occur; in order to reduce surface effects on the physicochemical properties of inclusion compounds, the “primary” FGIC-2 was synthesized from the natural graphite fraction with large crystallites ($0.4 \times 0.3 \times 0.02$ mm). The choice of acetonitrile as a guest is dictated by its thermal and chemical stability, as well as its “opening” property [2, 4, 6, 28], and also by the possibility for monitoring sample composition by element analysis and IR spectroscopy. The simple molecular structure of CH_3CN facilitates the modeling of the packing mode of guest molecules in matrix layers and alternation of guest and host layers in the resulting phases.

EXPERIMENTAL

Synthesis and analysis of the starting compounds. The inclusion compound of the second stage with acetonitrile (FGIC-2) was prepared by the procedure of [22], which is described in detail in [36, 39]; the procedure employed natural graphite (particle size $0.4 \times 0.3 \times 0.02$ mm), which was treated by the procedure using acids [40] and calcinated at 700°C (ash content of purified graphite ≈ 0.13 mass %). For oxidative media, we used 10–14% bromine solutions of BrF_3 and then performed exchange reactions of the guest subsystem by bromine and acetonitrile and dried in a flow of dry nitrogen [22, 36, 39]. According to the results of analysis, the product had a composition $\text{C}_2\text{F}_{0.92 \pm 0.01}\text{Br}_{0.010 \pm 0.008} \cdot (0.136 \pm 0.009)\text{CH}_3\text{CN}$ and contained 88.35 mass % matrix. The amount of carbon in the matrix ($\text{C} = 50.018 \pm 0.005$ mass %) was determined gravimetrically using the procedure of [41]; fluorine, nitrogen, and bromine contents were determined by the procedure of [42] at the Analytical Laboratory of the Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences ($\text{F} = 36.24 \pm 0.30$ mass %, $\text{Br} = 1.65 \pm 0.30$ mass %, $\text{N} = 3.98 \pm 0.30$ mass %; the results of analyses are given with an absolute error. Acetonitrile was used as a guest component; during synthesis of primary FGIC-2 and after bidistillation by the known procedure of [43] it had $T_m = -41.4 \pm 0.4^\circ\text{C}$ and $T_b = 82.2 \pm 0.4^\circ\text{C}$. For synthesis of FGIC-1 and composition analysis we used the isopiestic method, which is well established for the synthesis and investigation of the stoichiometry of unstable inclusion compounds of channel [44–46], cell [44, 46], and layer [6, 10, 47] types of host cavity. An FGIC-2 sample (150–500 mg) was kept for at least one day (for FGIC-1 to be formed) and then placed into a thermostatted ($\pm 0.1^\circ\text{C}$) cell over the mixture ($\approx 1:1$ v/v) of FGIC-2 and liquid acetonitrile; saturation with acetonitrile was monitored by weighing the sample until its weight ceased to change. According to statistical treatment of 18 independent analyses, the weighted mean of the matrix content in FGIC-1 was 78.39 ± 0.17 mass %, which corresponded to the composition $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01} \cdot (0.285 \pm 0.003)\text{CH}_3\text{CN}$. After evaluation of the limiting relative error based on the laws of motion with “evaluation for maximum” [48], the final guest to host ratio was

Fig. 1. Diffractograms of FGIC with acetonitrile: *a* — $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01} \cdot 0.136\text{CH}_3\text{CN}$ product of synthesis, *b* — the same after 5 years of storage in a closed weighing bottle in a desiccator.

$\text{C}_2\text{F}_{0.92}\text{Br}_{0.01} \cdot (0.285 \pm 0.012)\text{CH}_3\text{CN}$. The weighted mean of the composition of FGIC-1 is close to the doubled guest content compared to FGIC-2, which was confirmed by the monolayer structure of the guest subsystem in FGIC-1 with acetonitrile [4, 6, 28].

For X-ray phase analysis, the diffractograms of the samples were recorded at room temperature on a DRON-SEIFERT-RM4 diffractometer (CuK_α radiation, graphite monochromator on a reflected beam, scintillation detector with amplitude discrimination). The diagrams were recorded in a stepwise mode in the 2θ range from 4° to 55° . The cells with FGIC-1 were isolated with a teflon film; thermolysis products were applied to a support of silicon single crystal to separate the background from the cell material. In all cases, the planes of the textured particles of the samples were orientated in parallel to the cell plane. The diffractograms of the products contained broadened reflections of FGIC-2 (Fig. 1*a*) and narrow reflections of FGIC-1 whose positions (Table 1, Nos. 1 and 2) almost coincided with the values given in [4] for compounds with CH_3CN based on the $(\text{C}_2\text{F}_{0.9})_n$ matrix: $7.5 \text{ \AA}$ (002) and $5.2 \text{ \AA}$ (003) for FGIC-2; $9.52 \text{ \AA}$ (001) and $4.76 \text{ \AA}$ (002) for FGIC-1 [4]. The size of the unoccupied layer (guest layer) obtained from the spacings of FGIC-2 ($I_{\text{calc}} = 15.52 \text{ \AA}$, calculation performed with d_{00l} values of six reflections, Table 1, No. 1) and FGIC-1 ($I_{\text{calc}} = 9.47 \text{ \AA}$ for four reflections, Table 1, No. 2) was $6.05 \text{ \AA}$, which agreed with literature data for the given type of matrix [4, 6, 47, 49, 50].

IR absorption spectra were recorded on a Scimitar FTS 2000 Fourier spectrometer. The samples were prepared for measurements by the standard procedure of molding 3 mg samples into KBr pellets and grinding the samples in fluorinated and vaseline oils whose spectra did not contain any valence and deformation absorption bands of water. The spectrum of the FGIC-2 product contained bands in the absorption region of the C–F bond (1123.1 cm^{-1} and 1229.7 cm^{-1}) characteristic of graphite inclusion compounds [4, 15], as well as absorption bands nearly coinciding with the fundamental absorption bands of acetonitrile 743.6 cm^{-1} , 918.7 cm^{-1} , 1373.5 cm^{-1} , 1431.2 cm^{-1} , 2253.4 cm^{-1} , and 2293 cm^{-1} [51] (Fig. 2*a, b*). The IR spectra of the same samples obtained in fluorinated and vaseline oils did not contain the λ_{OH} and δ_{HOH} bands, but this did not preclude the presence of some amount of moisture in the samples. The slightly underestimated balance, 99.66 mass % (according to the data of analysis, the total content of the “matrix carbon”, CH_3CN , F, and Br is 99.57%; the ash content is 0.09 mass %), may be the consequence of the presence of oxygen-containing groups along with water; these groups were detected [37, 38] in samples with a developed surface in fluorocarbon materials of varying nature.

The curves of product heating in the temperature range from RT to $300\text{--}320^\circ\text{C}$ were recorded on a DTA apparatus described in [52, 53] ($\approx 30 \text{ mg}$ samples in ampules with a hollow for a thermocouple in the bottom, bottleneck, and extended capillary) at a linear heating rate of $0.6\text{--}9.0 \text{ deg/min}$. When the product was heated from room temperature to 150°C , mass loss (FGIC-2) was up to 0.05 mass %. The heating curve of FGIC-2 showed a small endo effect ($157 \pm 2^\circ\text{C}$) and an extended exo

TABLE 1. Experimental Values of d_{001} and Spacings (I_c) along the c Axis for FGICs with Acetonitrile and for Their Thermolysis Products

No.	Conditions of thermolysis			d_{001} , Å										I_c , Å (±0.02)
	T , °C (±2)	Time, h	Medium	001	002	003	004	005	007	008	009	013	014	
1*	20	—	In air	15.8	7.56	5.24	—	3.09	2.20	1.94	—	—	—	15.51
2*	20	—	L, “guest”	9.50	4.75	—	2.36	1.88	—	—	—	—	—	9.46
3	80	2	Gas, “guest”	15.8	7.50	5.28	—	3.09	2.20	1.95	—	—	—	15.52
4	130	4	In air	16.0	7.53	5.28	—	3.08	2.18	1.95	—	—	—	15.53
5	155	7	The same	15.8	7.56	5.28	—	3.08	2.20	1.95	—	—	—	15.53
6	155	7	Gas, “guest”	16.0	7.53	5.28	—	3.08	2.18	1.94	—	—	—	15.51
7	162	2	In air	6.07 (9.40)**	—	2.00	—	—	—	—	—	—	—	6.04 (9.40)
8	162	1	Gas, “guest”	— (9.41)	(14.0) (4.72)	—	(6.7) —	—	—	—	—	—	(1.97) —	(27.46) (9.43)
9	162	3	The same	— (9.41)	(4.72)	—	(6.97) —	(5.23) —	—	—	(3.10) —	—	(1.97) —	(27.38) (9.43)
10	162	5	The same	— (9.41)	(14.0) (4.72)	—	(7.03) —	(5.61) —	—	—	(3.06) —	—	(1.96) —	(27.83) (9.43)
11	162	7	The same	—	14.0	—	7.03	5.61	—	—	3.06	—	1.96	(27.83)
12	250	1	The same	— 6.07	—	—	7.3 —	—	—	—	3.18 —	2.13 —	1.98 —	28.31 6.07
13	250	2	The same	6.05	—	—	—	—	—	—	—	—	—	6.05
14***	300	2	Gas, “guest” (+ HF)	6.03	—	—	—	—	—	—	—	—	—	6.03
					—	—	—	—	—	—	—	2.14	—	27.82
15***	320	2	The same	5.9 (9.41)	—	—	—	—	—	—	—	—	—	5.9 (9.41)
				—	—	—	—	—	—	—	—	(2.13)	—	(27.69)

*For n independent determinations, $I_{n=6} = 9.47$ Å for FGIC-1, $I_{n=6} = 15.52$ Å for FGIC-2, and $I_{n=7} = 27.77$ Å for FGIC-4 (Table 1, No. 8-12, 14, 15).

**Here and below the values in parentheses are the interplanar distances and spacings for nonequilibrium states.

***Data for samples with a partially broken matrix.

effect with a maximum whose position depended on the rate at which the temperature was raised: $260 \pm 8^\circ\text{C}$ (3.2 deg/min) and $308 \pm 12^\circ\text{C}$ (7 deg/min). On the heating curve of FGIC-1, another endo effect was observed at $100.4 \pm 0.6^\circ\text{C}$, which corresponded to the temperature of decomposition of FGIC-1 into FGIC-2 (XRD data) and a gaseous guest. Mixtures of guest–host systems containing from 0 mass % to 88.35 mass % guest were prepared by the traditional procedure for binary systems [54, 55]; the FGIC-2 product (3-35 mg) and the guest component (10-50 mg) were placed in glass ampules, which were sealed, after profound cooling, while concurrently extending the capillary; after that the mixtures were kept at room temperature for a

Fig. 2. IR absorption spectra of pure acetonitrile (*a*); freshly isolated product of synthesis (*b*); product stored in a closed ampule for ~15 years (*c*); product of annealing for 2 h at 150 (*d*); the same at 250°C (*e*). The dots denote the absorption bands of the matrix. The IR spectra of the samples in vaseline and fluorinated oils do not show absorption bands in the range 1550-1750 cm^{-1} .

period of time sufficient for an equilibrium to set in (15-20 h). Before the recording of the heating curves, the ampules were opened, and their contents were allowed to contact atmosphere through a capillary hole 0.15-0.20 mm in diameter and 30-35 mm in length. Below 300°C the heating curves of the binary mixtures had three (in the range ≈ 1 -79 mass % host) or two (≈ 80 -88%) (depending on the composition of the mixture) endo effects and one (for the whole range of concentrations under study) extended exo effect whose maximum position depended on the heating rate: 260°C for 3.2 deg/min and 308°C for 7 deg/min. The maxima of the low-temperature endo effects ($82.1 \pm 0.4^\circ\text{C}$) almost coincided with the boiling temperature of the guest; as in the case of heating of the individual FGIC-1, the temperature at which the second endo effect was recorded (100.5°C) was independent (within the limits of the measurement error, $\pm 0.6^\circ\text{C}$) of the composition of the mixture and heating rate (2-9 deg/min). After the product was cooled, pure guest placed in the ampule, and the sample kept at room temperature (for at least 1 day), the heating curves were reproduced many times. For mixtures in the range of compositions with 79-88 mass % matrix, below 140°C the heating curve contained one endo effect at 100.5°C . All samples obtained by heating binary mixtures with 8-87 mass % matrix to 110-130°C had the same mass (within the weighing error) as the FGIC-2 sample taken for their preparation; the diffractograms of all samples contained reflections of the starting FGIC-2 with the same values of hkl (Table 1, No. 1) and intensity ratios. The region of existence of FGIC-1 was determined and its stoichiometry was evaluated (Fig. 3) by constructing Tamman triangles (from the specific heat effects [54, 55]). Part of the diagram with a host content of more than 88.35 mass % was constructed using XRPA data and allowing for IR spectral data of the thermolysis products in acetonitrile.

Thermolysis of FGIC in air was conducted in open glass ampules. FGIC-2 (30-50 mg) samples were heated from RT to the specified temperature at a rate of 10-20 deg/min and kept for 1-2 h at a fixed temperature ($\pm 2^\circ$). Thermolysis in a guest

Fig. 3. Phase diagram of the $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01}$ – CH_3CN binary system. Figurative points: 1 — boiling of the guest, 2 — equilibrium FGIC-1 + liquid + vapor, 3 — equilibrium FGIC-1 + FGIC-2 + vapor, 4 — equilibrium FGIC-4 + solid solution + vapor, 5 — X-ray diffraction data, 6 — specific heat effects, 7 — equilibrium FGIC-2 + FGIC-4 + vapor. The left part of the diagram is considerably shifted toward the host component (FGIC is virtually insoluble in acetonitrile). The prime marks the metastable states (below 250°C) and regions with a violated component structure of the binary system (above 260°C).

medium was performed in ampules with a bottleneck and an extended capillary (length 70–75 mm, diameter 0.3–0.5 mm, sample to ampule volume ratio 80–100) for samples of guest–host binary mixtures, which contained 50–60 mass % matrix. In this run, the gas phase above the boiling point of acetonitrile (82.2°C) was an almost pure guest component at a pressure of vapor of ≈ 1 atm. Since in the high-temperature range DTA data revealed a considerable effect of the heating rate on solid-phase processes, the temperature of the binary mixtures was raised slowly (at a rate of ≈ 0.6 deg/min) in order to obtain data that reflected the equilibrium (or nearly equilibrium) state of the system. After the given temperature was achieved, the samples were kept at this temperature for 2–7 h and then cooled in ice water; then X-ray phase analysis was carried out.

Heating the samples to $\approx 160^\circ\text{C}$ did not change the general IR spectrum pattern characteristic of the product of synthesis; the number of absorption bands, the intensity ratio, and the wave numbers were almost the same as for the starting freshly prepared FGIC-2 sample (Fig. 2d) and for the sample that was kept in a sealed ampule at room temperature or over P_2O_5 in a closed weighing bottle in a desiccator. When the temperature of annealing in the atmosphere of the guest was increased to 260°C , the band intensities of acetonitrile decreased, and the wavenumbers remained unchanged for the components of both subsystems (Fig. 2e). After the sample was heated to 320°C , the IR spectra showed pronounced changes: new medium-intensity bands appeared, and the wavenumber of the C–F bond decreased to 1118 cm^{-1} , indicating that the amount of fluorine in the host matrix decreased [56]. When exposure time increased to 7–9 h, weak bands appeared at lower temperatures (270–280°C). From IR and DTA data obtained at low heating rates it followed that the components of the

system persisted to ≈ 250 – 260°C — the temperature limit below which interpretation of the results of the procedures used for the guest–host system yields most reliable data.

RESULTS AND DISCUSSION

XRPA data (Fig. 1*a*; Fig. 4*a-d*; Table 1, Nos. 1, 3-6) combined with DTA and IR spectroscopy data indicate that the structure of FGIC-2 is constant over a wide range of temperatures and persists (within the measurement error of interplanar distances — Table 1, Nos. 1, 3-6) irrespective of thermolysis conditions (air or guest atmosphere) and of storage time at elevated temperatures (to $\sim 160^\circ\text{C}$) or room temperature (prolonged storage, Fig. 1*b*).

When the annealing temperature was raised above 160 – 162°C , the picture changed drastically and depended on the above-mentioned conditions. Thermolysis in air led to the formation of a mixture of microphases with $I_c = 6.05\text{ \AA}$ and FGIC-1 with $d_{001} \sim 9.40\text{ \AA}$ (Fig. 4*e*; Table 1, No. 7), while in acetonitrile thermolysis gave FGIC-1 and a new microphase (Figs. 3 and 5) with $I_c = 27.77\text{ \AA}$ (Table 1, Nos. 8-11). The value of $I_c = 27.77\text{ \AA}$ almost coincided with the calculated spacing for the inclusion compound of the fourth stage of occupation (FGIC-4): $I_{\text{calc}} = (6.05 \cdot 4 + 3.42) = 27.62\text{ \AA}$, where $6.05\text{ \AA}$ is the thickness of the unoccupied layer of the matrix, and $3.42\text{ \AA}$ is the thickness of the guest layer, whose values follow from the experimental values of spacings for FGIC-1 ($9.47\text{ \AA}$) and FGIC-2 ($15.52\text{ \AA}$). The structural rearrangements of FGIC under isothermal conditions ($162 \pm 2^\circ\text{C}$) and under the guest atmosphere at different exposure times may be traced using the data of Table 1, Nos. 8-11 and in Fig. 5*a-d*. Thus after annealing for 1-2 h, the diffractograms showed a mixed-layer state (Fig. 5*a*) with dominant hkl reflections corresponding to a microphase at the first stage of occupation; as the exposure time increased and the system approached equilibrium (or a nearly equilibrium state), the contribution from FGIC-1 microphases to the total diffraction pattern decreased, while the contribution of FGIC-4 increased (Fig. 5*b, c*). After 7 h of annealing, the diffraction pattern contained only reflections of FGIC-4 (Table 1, No. 11; Fig. 5*d*); a small shoulder in the region of low angles ($2\theta \approx 10^\circ$) might be a consequence of the presence of a certain amount of FGIC-1. Indeed, if we compare the composition $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01} \cdot 0.07\text{CH}_3\text{CN}$ of the compound of the fourth degree of occupation obtained by calculation from the stoichiometry of FGIC-1 (Table 2) and the composition $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01} \cdot 0.08\text{CH}_3\text{CN}$ obtained from experiment (according to element analysis

Fig. 4. Diffractograms of the samples maintained for 2-7 h in a guest atmosphere: *a* — at 80°C , *b* — 155°C , *c* — in air at 130°C , *d* — 155°C , *e* — 162°C ; Table 1 (Nos. 1, 3-7).

Fig. 5. Diffractograms of the products of thermolysis under acetonitrile after annealing at $162 \pm 2^\circ\text{C}$ for 1 (*a*), 3 (*b*), 5 (*c*), and 7 h (*d*); Table 1, Nos. 8-11.

TABLE 2. Characteristics of Solid $C_2F_{0.92}Br_{0.01} \cdot yCH_3CN$ in the $C_2F_{0.92}Br_{0.01}-CH_3CN$ System

Phase	I_c , Å (± 0.02)	T_{dec} , °C	y
FGIC-1	9.47	100.5 $\pm$ 0.6	0.287 $\pm$ 0.012
FGIC-2	15.52	157 $\pm$ 2	0.136 $\pm$ 0.009
FGIC-4	27.77 (27.62)*	250 $\pm$ 8	<0.07**
Solid solution	6.05	—	<0.07**

*Spacing obtained from I_c for FGIC-1 and FGIC-2.

**The values of y : $y \approx 0.08$ (experimental), $y = 0.070$ (calculated from the stoichiometry of FGIC-1), $y = 0.068$ (calculated from the stoichiometry of FGIC-2).

Fig. 6. Scheme of the structure of the “mesophase” — a nonequilibrium transition state of the clathrate system at the moment at which FGIC-1 + FGIC-2 + FGIC-4 coexist. The guest to host layer thickness ratio is 1:2.

data, C = 56.9 mass %, F = 38.4 mass %, N = 2.5 mass %, Br = 1.8 mass %), we can see that the guest content is slightly overestimated. The 001 reflection typical of the FGIC-1 microphase (the presence of which should naturally lead to an overestimated guest content in the total volume of the product of annealing being analyzed) was revealed on the diffractograms of the samples heated in air at 200°C for 1-2 h (Fig. 4e; Table 1, No. 7). One can assume that higher exposure times and isothermal conditions in a current of gaseous guest at the temperature of the sample being annealed will favor synthesis of pure FGIC-4 and formation of microphases (and possibly individual phases) of compounds of higher degrees of occupation. Mixed-layer structure of FGIC was previously observed at room temperature under conditions of a $C_2F \cdot yBrF_3 - BrF_3$ binary system [47], or in FGIC-1 dried with guests of varying nature [4], or in the course of drying an FGIC-2 sample in air and heating it to 80-100°C with benzene, acetone, and *n*-heptane based on a fluorochlorographite matrix [9]. A simple scheme that represents the 2D structure of the general clathrate system in a transition (nonequilibrium) state and reflects the coexistence of the FGIC-1, FGIC-2, and FGIC-4 microphases is given in Fig. 6. The model admits that idealized host layers are flexible due to the presence of a matrix of sp^3 -hybridized carbon atoms in the fluorographite layers of macromolecules. The scheme reveals that the ratio of the (FGIC-1, FGIC-2, and FGIC-4) microphases may be substantially changed by varying the length of any microdomain I-V and/or increasing the number of layers similar to 1-2, 5-6, and 9-10, all of these being factors that depend on the background of the sample and equilibrium conditions (for example, the temperature gradient of the external medium and sample); in this case, the plane-parallel orientation of layers does not change.

When the annealing temperature was increased further to 220-230°C, the diffractograms of the samples contained

When thermolysis was conducted according to Scheme 1, the primary color of the compound persisted to a temperature of 250–260°C; in the case of Scheme II, to a temperature of $\approx 190^\circ\text{C}$. When the temperature was raised above the stated temperatures and the exposure time increased to 7–10 h, or when the temperature was abruptly raised from RT to ≈ 500 – 600°C in the thermal impact mode, this led to an irreversible change in color from light yellow to black and to dispersion of FGIC; bulk volume of the sample increased dozen-fold, crystallites changed their plane-parallel orientation, and hence the number of components in the system changed (IR spectral data). The sharp change in the properties of FGIC at elevated temperatures and under authentically nonequilibrium conditions may be caused by a number of interrelated factors such as matrix fluorine elimination and accelerated formation of bulky oxygen-containing functional groups on the surface of the sample [37, 38], which “close” the clathrate system, blocking the way out for guest molecules; this leads either to dispersion or to droplike structure formation, which depends on the reaction time [4]. This is facilitated by slow diffusion of guest molecules lying between bent layers (Fig. 6), which have a rather well developed rough surface relief. This property is useful for seeking optimal conditions for the synthesis of guest–carbon and guest–fluorocarbon nanocomposites or metal–carbon and metal–fluorocarbon materials in the case of metal-containing guests, which hold promise for use as sorbents and catalysts [12–14]. Synthesis of materials may be made controllable by varying grain size of fluorographite, heating rate, thermal impact mode, the nature of the guest component, and the solvent in which thermolysis is to be carried out. The effect of any of these parameters on the course of synthesis of a composite with a given property naturally demands profound investigations.

At the temperature of matrix destruction with evolution of HF (270–320°C), i.e., when the number of components in the system changed, the spacing decreased to 5.9–5.8 Å; this was consistent with the conclusions of [6, 56, 57], which revealed a relationship between the fluorine content in the matrix and the interlayer distances. IR spectroscopy data and element analysis for nitrogen ($N \approx 2.1$ mass %) indicated that the products have a guest component whose complete removal from the matrix layers is virtually unattainable as in the case of graphite [18, 58, 59–61]. The foregoing indicated that there is a homogeneity region near the matrix composition, namely, a region of “residual compounds” of fluorographite (Fig. 3), typically characterized by the presence of a reflection with $d_{00l} \approx 6.05$ Å on the diffractograms. For samples whose diffractograms had a single reflection at 5.8–5.9 Å after annealing (i.e., for samples heated at 260–270°C in a guest atmosphere or for those heated at 190–200°C in air for 3–4 h), the FGIC-1 and/or FGIC-2 structure was not restored after prolonged (up to six months) contact with liquid or gaseous acetonitrile: the diffractograms acquired diffuse bands characteristic of amorphous carbon materials. It may be assumed that the “empty” matrix at an oxidation level of $x \approx 0.9$ – 1.0 will be indifferent with respect to clathrate formation because of the dominant host–host interactions during low-temperature synthesis (if conditions of realization at normal temperatures are found). It should be added that our numerous experiments on structure identification of FGIC thermolysis products in $\text{C}_2\text{F}_{0.92}\text{Br}_{0.01}\text{--CH}_3\text{CN}$ in the temperature range 20–260°C did not reveal any reflections corresponding to FGIC-3 with $I_{\text{calc}} = (6.05 \cdot 3 + 3.42) = 21.57$ Å. For guests whose molecules differ from the acetonitrile molecule in size and internal symmetry, the possibility of an FGIC-3 structure is not absolutely ruled out under certain conditions because under nonequilibrium conditions, a metastable FGIC-1 microphase can arise at high probability (Fig. 3).

It is noteworthy that despite weak matrix–guest interactions (IR data), layer thickness of the guest 3.42 Å and host 6.05 Å remains constant (within the measurement error; Table 1, Nos. 3–6) within the whole region of existence of FGIC-2 (Fig. 3). In our opinion, this constancy is the consequence of the operation of the known principle of closest packing [62] (site occupancy [63]) of guest molecules in the host matrix, working within the whole temperature range of existence (below $160 \pm 2^\circ\text{C}$) for FGIC-2. Previously, the classical (Fig. 8a) [16, 19, 49] and Daumas–Herold models (Fig. 8b) were suggested for graphite inclusion compounds [64] and employed for structure description of FGIC-2 [4] and FGIC-3 [28] and discussed in the literature as two variations of layered structure for these compounds [4, 11, 16, 19, 28, 49, 64, 65]; however, one can also consider an idealized variation (Fig. 8c), in which the shift of the boundaries of pair contacts between adjacent host layers by a half-spacing of the guest layer leads to the same type of configuration of the bent matrix layers throughout the

Fig. 8. Schemes of the structure of FGIC-2: *a* —classical model, *b* — Daumas–Herold model, *c* — lenslike model with 2D monomolecular clusters of guest molecules.

entire volume of the crystal. Real FGIC-2 samples can obviously contain domains with any of these packing motifs of guest and host layers, which depends on the background of the sample (size of the host macromolecule, degree of its fluorination, conditions of equilibrium, etc.) and leads to reduced crystal symmetry and also to strains in the crystal. The two models are supported by the kinetic (Fig. 1*a, b*) and thermodynamic stability of FGIC-2 (Fig. 3, 4*a-d*; Table 1, Nos. 1, 3-6) for prolonged periods of time and within wide ranges of temperature; other factors that evidence in favor of the two models are as follows: disproportionation of FGIC-2 (under nearly equilibrium conditions above 157°C) into FGIC-4 and a metastable FGIC-1 microphase, but not into a mixture of domain microphases at different stages of occupation; comparison of the stoichiometric coefficients for FGIC-1 and FGIC-2 ($0.285/0.136 = 2.13 > 2$ [6] and this work), for FGIC based on the same matrix with chloroform ($0.204/0.088 \approx 2.3 > 2$ [66]), and for FGIC based on the $(C_2F_{1.0})_n$ matrix with BrF_3 ($0.33/0.13 = 2.5 > 2$) and acetone ($0.22/0.10 = 2.2 > 2$ [50]); and also preserved intensity ratios for *hkl* reflections irrespective of the external conditions (Fig. 4) and after repeated saturation-decomposition cycles [6]. The idealized 2D model (Fig. 8*c*) has a regular alternation of lenslike capsules formed by linkages between adjacent host layers and filled with guest molecules, resulting in 2D molecular clusters; for each type of guest molecule, the size of the cluster depends on host–host and guest–host [67] and, in the general case, guest–guest interactions [68, 69]. The role of guest–guest interactions in the formation of layered clathrate systems is probably much more significant than for inclusion compounds with cell and channel type voids, in which single or chain type guest molecules are dominant and guest–guest interactions are drastically weakened by the spatial factor, namely, by the absence of direct contact between guest molecules. The local weakening of host–host interactions due to the presence of intermediate cluster layers in the model promotes spontaneous incorporation of guest into the interlayer space and full occupation of the latter with guest molecules in FGIC-1 [4, 6, 9, 50, 66]. One can also assume that for guest components whose molecules differ in size and internal symmetry, the pair contacts of adjacent host layers are characterized by a certain equilibrium distance, which depends on the ratio between the three components of intermolecular interaction (*L* in Fig. 8*c*). When this distance is exceeded, the structure collapses into domains with a spacing of ≈ 6 Å, after which the matrix loses, completely or partially, its ability to form clathrates.

Thus physicochemical studies of the phase transitions of fluorographite intercalation compounds with acetonitrile indicated that under equilibrium (or nearly equilibrium) conditions, one can find three individual clathrate compounds and solid solutions based on the fluorographite matrix formed in graphite fluoride–guest systems (Table 2, Fig. 9). It is shown how the system passes from a mixed-layer to equilibrium (or nearly equilibrium) state (the dynamics of this process), and conditions of synthesis of the phase at the fourth stage of occupation, not previously discussed in the literature, are described. Variations of arrangement are discussed for the general clathrate system of second-stage compounds and metastable transition states with coexistent microphases of the first, second, and fourth stages of occupation.

The structural model suggested for FGIC-2, where clusters of guest molecules are isolated in lenslike voids formed by pairwise linkages between adjacent host matrix layers throughout the entire volume of crystal, complies with the definition of the term “clathrate” (inclusion compound), as reflected by the term clathrate intercalate [70], which appeared in discussions on terminology for inclusion compounds. The isolated position of the lenslike clusters of guest molecules ensures certain hydrophobicity of compounds that contain even chemically active substances such as bromine (chlorine) trifluoride as

Fig. 9. Diffractograms of the individual clathrate phases: FGIC-1 (a), FGIC-2 (b), FGIC-4 (c), and solid solution based on the $C_2F_{0.92}Br_{0.01}$ fluorographite matrix (d) (the diffractograms correspond to the data of Table 1; Nos. 2, 1, 11, and 13; the asterisk marks the reflection from the Teflon film).

guests, mentioned in the pioneering work [1]. The isolated position of guest cluster assemblies in bulk crystal provides not only inertness of the guest component with respect to external effects, but also an extremely low vapor pressure under normal conditions [4, 6, 22, 32, 71].

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