The Structural Studies of Phase Transitions in the Graphite Intercalation Compounds with Iodine Chloride and Bromine

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The paper presents the results of investigation of phase transitions in the intercalation compounds based on fine crystalline anisotropic pyrolytic graphite with iodine chloride and bromine by X-ray diffraction method. As a source for intercalation, the fine crystalline pyrolytic anisotropic graphite with a distance between neighboring graphite layers of 0.340 nm and a crystallite size of 20 nm was used. The intercalation reaction was carried out by standard two-temperature gas-phase method. The stability of graphite intercalation compounds under normal conditions is investigated. It is found that the exposure of graphite intercalation compound with iodine chloride under normal conditions during 20 days has not led to significant changes in the structure of compound while such exposure for graphite intercalation compound with bromine causes some changes in the structure. In particular, transition from the second stage compound to the third stage compound is observed. The coefficient of linear thermal expansion for graphite intercalation compounds with iodine chloride in different temperature intervals is estimated. It is revealed that at a temperature of 260 K there is a significant reduction of the value of the coefficient of linear temperature expansion. It is shown that such a sharp change of the coefficient of linear temperature expansion is related to the phase transition in the intercalate layers from quasicrystalline" state to "quasiliquid" state. For the first time, by the X-ray diffraction method the phase transition of the "disorder – order" type in the intercalate layers is found for graphite intercalation compounds with iodine chloride.

Keywords: Graphite intercalation compound, X-ray diffraction method, Phase transition, Intercalate layer.

1. INTRODUCTION

Graphite is the thermodynamically stable under usual conditions allotropic modification of carbon, which has a pronounced layered structure. The presence of a weak connection between parallel graphite layers makes it possible to introduce monoatomic or mono-molecular layers of various substances into interlayer space of graphite with the formation of so-called graphite intercalation compounds (GICs). GICs are perfect model structures to study the physical properties of two-dimensional systems. A great number of physical phenomena, in particular, charge carriers phonon drag effect, quantum effects of weak localization and interaction of charge carriers were investigated in GICs [1-3]. Another problem that can be solved in the GICs investigation is to identify features of phase transformations in two-dimensional systems. Two types of phase transformation can be considered for GICs, namely, changing the ordering of intercalate layers and changing the ordering of intercalate molecules in a layer. Interlayer ordering of intercalate layers means periodic alternation of graphite layers and intercalate layers. The intra-layer ordering is determined by the position and orientation of the intercalate molecules in the layer. At the temperature of the GIC synthesis, an intercalate is usually found between graphite layers as two-dimensional "quasiliquid" [4, 5]. The change in thermodynamic conditions, such as temperature and pressure, should lead to a change in the character of the intercalate molecules ordering in the layer. Indeed, the transition from a disordered "quasi-liquid" state to an ordered "quasicrystalline" state with the temperature decrease was found for a number of intercalation

compounds by methods of X-ray diffraction and electron microscopy [6, 7]. The temperature of the phase transition of the intercalate in the interlayer space of graphite does not coincide with the temperature of the phase transition of the intercalate substance in the free state. This is due to the fact that during intercalation there is an interaction between the intercalate molecules and graphite atoms, which differs from the interaction of intercalate molecules with each other. When in graphite nonpolar substances, for example, bromine, are intercalated, a whole cascade of phase transformations of all types is observed. The number of transformations and their types depend on the stage of the compound [8]. There are transitions from a "quasi-liquid" state to an ordered "quasicrystalline" state, from one commensurate with graphite layer lattice to another and from commensurate with graphite layer lattice to uncommensurate lattice. Details of these transitions are described, for example, in [9]. A much simpler situation is observed during the intercalation of polar molecules of iodine chloride. Polar iodine chloride molecules injected into the graphite are converted to anions, which form commensurate with graphite layer lattice. At a temperature of ~350 K for GICs based on high oriented pyrolytic graphite (HOPG), phase transformation of intercalate from "quasiliquid" to "quasicristalline" state occurs [10-12]. This transformation and the formation of "mobile ion liquid" are apparently the cause of the anomalous temperature dependence of the resistivity for GICs with ICl at temperatures above 250 K. However, in the literature there is no data on direct studies on the change in the structure of intercalate layers with temperature changes for GIC with iodine chloride.

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The aim of the present work is to study in detail the peculiarities of thermostimulated phase transitions in intercalate layers for GICs with bromine and iodine chloride by X-ray diffraction method.

2. OBJECTS AND METHODS

As a source for intercalation, fine crystalline pyrolytic anisotropic graphite (FPAG) was chosen (the distance between neighboring graphite layers $d_{002} = 0.340$ nm, the crystallite size $L_b = 20$ nm, the parameter of preferred crystallite orientation $\eta = 10^3$).

The specimens of GICs with Br_2 and ICl were obtained by standard two-temperature gas-phase method. Intercalation process parameters (temperatures of graphite T_{gr} and intercalate T_{int} and intercalation time t) are shown in Table 1.

Table 1 – Synthesis temperature, time and stage of GICs

No	Intercalate	T_{gr}, K	T_{int}, K	t, hrs
1	Br_2	318	318	48
2	ICl	300	300	48
3	ICl	297	297	48

The X-ray diffraction patterns of the GICs specimens were obtained by using a diffractometer DRON-4-07 in cobalt radiation (the wave length λ is 0.1791556 nm) with a single-crystal goniometer head GP-15. The regime of the BSV-29 cobalt X-ray tube was 30 kV (voltage) and 30 mA (current). The characteristic K_α-lines of Co were allocated by a pyrolytic graphite monochromator. The diameter of the X-ray beam on the specimen surface was equal to 1.4 mm. The specimens were mounted in a low-temperature chamber and were cooled by two nitrogen gas streams. The test temperature was maintained with an accuracy of 0.5 K (taking into account possible temperature gradients along the specimens) by a VRT-2 temperature controller. At setup, the X-ray beam was oriented along the *00l* plane of specimen. Depending on the region of the reciprocal space, the scanning was performed with steps $\Delta\chi = 0.05\text{-}0.10°$, $\Delta(2\theta) = 0.03\text{-}0.08°$, the accumulation time was equal to 3-10 s. During the measurements, the monochromator and K_β filter were not used in order to obtain the maximum possible intensity of the primary X-ray beam. The details of the measurements in a low-temperature X-ray chamber are described in [13].

The molar concentration of intercalate C in the obtained compounds was estimated by changing the mass of source specimen after intercalation:

$$C = \frac{100(\%)}{\dfrac{M_{int}}{M_{gr}} \cdot \dfrac{m_0}{\Delta m} + 1}, \qquad (1)$$

where M_{int} and M_{gr} are respectively molar mass of intercalate and graphite, $\Delta m/m_0$ is the relative change in mass of the specimen after intercalation. From the molar concentration of intercalate C, the stage of compound S (the number of graphite layers between two layers of intercalate) can be determined using the following formula:

$$S = \frac{100 - 2}{C p^*} \qquad (2)$$

where p^* is the stoichiometric index in the compound formula $C_{p*}X$ (X is intercalate). For investigated compounds $p^* = 7$.

The compound stage S can also be estimated by changing the thickness of the source specimen after intercalation:

$$\frac{\Delta d}{d_0} = \frac{d_i}{S d_{002}}, \qquad (3)$$

where d_0 is the specimen thickness before intercalation, Δd is the change of specimen thickness after intercalation and d_i is the thickness of intercalate layer, for Br_2 $d_i = 0.360$ nm and for ICl $d_i = 0.364$ nm.

Identity period I_s of graphite intercalation compound (I_s is the distance between the subsequent intercalate layers separated by S graphite layers) is determined from *00l* X-ray diffraction patterns according to Wulff-Bragg equation:

$$2 I_s \sin\theta = l\lambda \qquad (4)$$

where 2θ is the angle, at which the corresponding band is observed in the diffraction pattern. Identity period I_s and stage of compounds S are related by the equation:

$$I_s = d_s + (s - 1) \cdot d_{002} \qquad (5)$$

where d_{002} is the interlayer distance in the source for intercalation FPAG, d_s is the distance between two graphite layers that contain intercalate layer, $d_s = d_i + d_{002}$.

Table 2 presents the stage number S calculated from change in mass (Δm) and thickness (Δd) of investigated specimens after intercalation and from X-ray diffraction data.

As can be seen from Table 2, for all intercalation compounds there is a complete correlation between the values of the stage number, calculated from the change of mass and thickness of specimens and from X-ray diffraction data. The insignificant differences between the numbers of compound stage determined by various methods are explained by the fact, that during the intercalation process the part of the intercalate substance is deposited on the specimen surface. This leads to an additional increase of the specimen mass after intercalation. Also, intercalation can lead to an additional stratification of source specimen that causes an increase of the thickness of the specimen.

Table 2 – Stage number S for GICs calculated from mass change (Δm), thickness change (Δd) and X-ray diffraction pattern (X-R)

No	Intercalate	S (Δd)	S (Δm)	S (X-R)
1	Br_2	1.96	1.83	2
2	ICl	1.97	1.87	2
3	ICl	2.84	2.55	3

3. EXPERIMENT AND DISCUSSION

3.1 Stability of Graphite Intercalation Compounds with Bromine and Iodine Chloride

To investigate the stability of the intercalation compounds with bromine and iodide chloride, 00*l*-diffracto-

grams were obtained for freshly prepared GICs specimens and for the same specimens exposed under normal conditions during 10 days and 20 days.

Fig. 1 and Fig. 2 present the parts of the X-ray diffraction patterns for GICs with ICl (Fig. 1) and for GICs with Br$_2$ (Fig. 2). For comparison, the fragment of X-ray diffraction pattern for source FPAG is also presented in the figures.
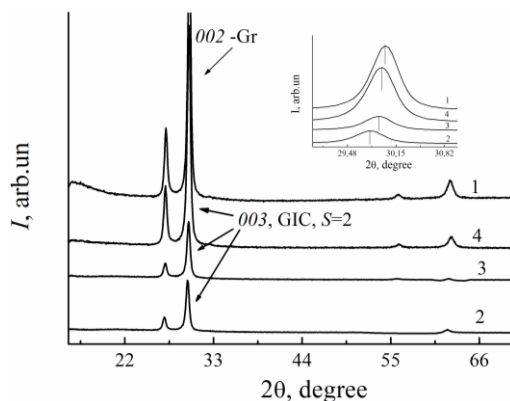

Fig. 1 – X-ray diffraction patterns for source FPAG (1) and for GIC with iodine chloride: 2 – freshly prepared specimen, 3 – specimen after 10 days, 4 – specimen after 20 days. Inset: the band in the range from 29° to 31° for corresponding specimens
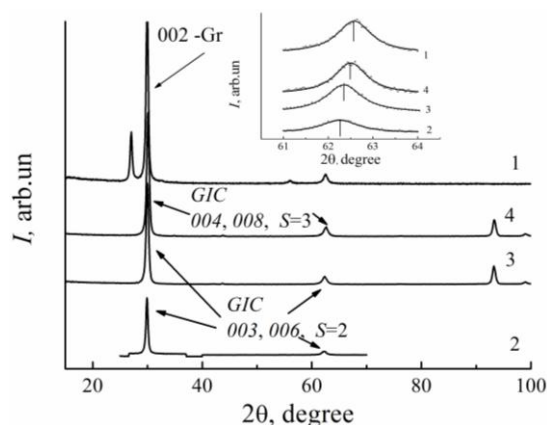

Fig. 2 – X-ray diffraction patterns for source FPAG (1) and for GIC with bromine: 2 – freshly prepared specimen, 3 – specimen after 10 days, 4 – specimen after 20 days. Inset: the band in the range from 61° to 64° for corresponding specimens

As it is easily seen from Fig. 1 and Fig. 2, the X-ray diffraction patterns for GICs contain some new bands, and two the most intensive bands are shifted somewhat compared to the source graphite. Let us note that the distance between intercalate layers (Br$_2$ or ICl) and adjacent layers of graphite is about 0.35-0.36 nm, and the interlayer distance d_{002} for FAPG is 0.34 nm. Therefore identity periods for intercalate layers are nearly multiples d_{002} and position of intercalate 00l-lines is very close to the position of graphite 002- and 004 - bands. However, as can be seen from Fig. 1 and Fig. 2 and the insets, the bands on the X-ray diffraction patterns obtained for the freshly prepared specimens are mostly shifted to the small angels. As the specimens age, the position of the bands is shifted to the right and approaches the position of the bands in the source FPAG.

The calculated according to (5) values of the identity

parameters I_{sc} for different stage compounds and identity parameters I_s determined from X-ray diffraction data (equation (4)) as well as the difference Δ between the calculated values of I_{sc} and I_s ($\Delta = |I_{sc} - I_s|$) for GIC with iodine chloride are given in Table 3. For calculation, the position of the most intensive band is used.

Table 3 – Calculated identity parameters I_{sc} determined from X-ray diffraction data, identity parameters I_s and difference Δ between them for GIC with ICl

S 00l	I_{sc}, nm	freshly prepared specimen $2\theta = 29.785°$		specimen after 10 days $2\theta = 29.902°$		specimen after 20 days $2\theta = 29.940°$	
		I_s, nm	Δ, nm	I_s, nm	Δ, nm	I_s, nm	Δ, nm
1 002	0.704	0.697	0.007	0.695	0.009	0.694	0.010
2 003	1.044	1.046	0.002	1.042	0.002	1.041	0.003
3 004	1.384	1.395	0.011	1.390	0.006	1.388	0.004
4 005	1.724	1.744	0.020	1.737	0.013	1.735	0.011
5 006	2.064	2.092	0.028	2.083	0.019	2.082	0.018

As seen from Table 3, the smallest difference between the calculated I_{sc} and experimentally determined I_s values of the identity parameters is observed if obtained GIC is the second stage compound. Moreover, despite the slight shift of the band position, GIC remains the second stage compound after 10 days of exposure under the normal conditions and after 20 days.

Analogous calculations for GICs with bromine are presented in Table 4.

Table 4 – Calculated identity parameters I_{sc} determined from X-ray diffraction data, identity parameters I_s and difference Δ between them for GIC with Br$_2$

S 00l	I_{sc}, nm	freshly prepared specimen $2\theta = 62.256°$		specimen after 10 days $2\theta = 62.352°$		specimen after 20 days $2\theta = 62.506°$	
		I_s, nm	Δ, nm	I_s, nm	Δ, nm	I_s, nm	Δ, nm
1 004	0.700	0.693	0.007	0.693	0.007	0.691	0.009
2 006	1.040	1.040	0.000	1.039	0.001	1.036	0.004
3 008	1.380	1.387	0.007	1.385	0.005	1.382	0.002
4 00105	1.720	1.734	0.014	1.731	0.011	1.727	0.007
5 0012	2.060	2.080	0.020	2.077	0.017	2.073	0.013

As can be seen from Table 4, for GIC with bromine there is a somewhat different picture in comparison to GIC with iodine chlorine. The freshly prepared specimen is identified as the second stage compound. It remains the second stage compound after 10 days of exposure under normal conditions. However, after 20 days of exposure, in the GICs there is a transition from the second stage to the third stage.

Thus, the investigated intercalation compounds are sufficiently stable, but according to X-ray diffraction, the

stability of based on FPAG GIC with ICl is somewhat higher than the stability of GIC with bromine.

3.2 Coefficient of Linear Thermal Expansion for Graphite Intercalation Compounds with Iodine Chloride

For source FPAG and for based on it the third stage GIC with ICl, the temperature dependence of the linear thermal expansion coefficient was investigated by X-ray diffraction method. For this, the exact position of the 0014 intercalate band (compound of stage $s = 3$, $2\theta = 101.904°$) was determined in temperature interval from 200 K up to 285 K with step 5 K. This band was chosen because at higher angles the position of the band can be determined more precisely. For comparison, also the change of angular position of 004 graphite band has been investigated.

Fig. 3 presents the temperature dependence of the parameter $C_0 = 2d_{002}$ determined from the angular position of the 004 - band with using the Wulff- Bragg equation for source FPAG.
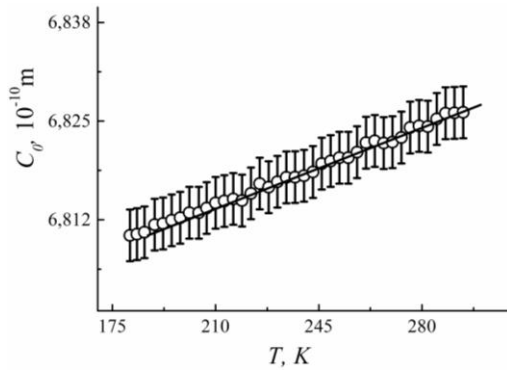
Fig. 3 – Temperature dependence of C_0 for source FPAG

As can be seen from Fig. 3, in the temperature interval from 200 K to 285 K the linear increase of C_0 with constant slope coefficient is observed. Estimated according to the equation

$$\alpha_{TGr} = \frac{1}{C_0}\left(\frac{\partial C_0}{\partial T}\right), \qquad (6)$$

the value of the coefficient of linear thermal expansion α_{TGr} is $2.3 \cdot 10^{-5} K^{-1}$.

The fragments of X-ray diffraction patterns for third stage GIC with iodine chloride obtained in the temperature interval from 200 K to 285 K are presented in Fig. 4.

As seen from Fig. 4, with increasing temperature, the band shape, the half-width and band intensity are practically unchanged, while the angular position of the band is shifted to smaller angles. From X-ray data, according to equation (4) the identity period I_s was calculated for each temperature.

The temperature dependence of identity period $I_s(T)$ for investigated GIC with iodine chloride is presented in the Fig. 5.

As it follows from Fig. 5, the identity period I_s linearly increases with temperature, as well as the parameter C_0 for the source FPAG. However, at the temperature
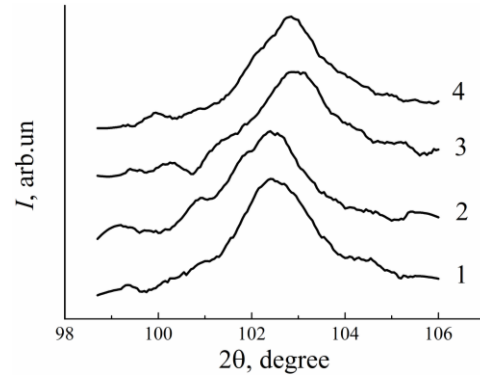
Fig. 4 – The fragments of X-ray diffraction patterns (0014-band) for GIC with iodine chloride at different temperatures: $1 - T = 285$ K, $2 - T = 260$ K, $3 - T = 230$ K, $4 - T = 200$ K
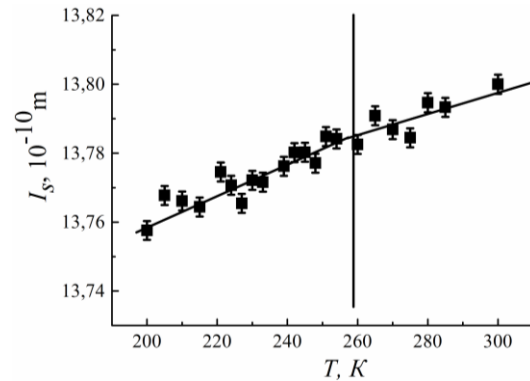
Fig. 5 – Temperature dependence $I_s(T)$ for the third stage GIC with ICl. The solid line denotes the approximation by the least squares method

$T = 260$ K there is a sharp change of the slope coefficient of the $I_s(T)$ dependence. The relative coefficients of linear thermal expansion were determined for two temperature intervals $[200 \div 260]$ K and $[260 \div 285]$ K that is, for temperature intervals, in which the slope coefficients are constant according to equation:

$$\alpha_{TGIC} = \frac{1}{I_s}\left(\frac{\partial I_s}{\partial T}\right). \qquad (7)$$

These coefficients are, respectively, the following: $\alpha_{TGIC} = 4.07 \cdot 10^{-5} K^{-1}$ in the temperature interval $[200 \div 260]$ K and $\alpha_{TGIC} = 2.23 \cdot 10^{-5} K^{-1}$ in the temperature interval $[260 \div 285]$ K. Thus, at the temperature $T = 260$ K, the coefficient of linear thermal expansion decreases almost twice.

The change with the temperature of the identity period I_s is determined by the change with the temperature of the distance d_{002} between the adjacent layers of source graphite and the change with the temperature of the distance d_s between two layers of graphite containing the intercalate layer.

Thus, using the equation (5), as well as the experimentally obtained values of I_s, $d_{002} = C_0/2$, α_{TGr} and α_{TGIC} in the different temperature interval, one can determine the coefficient of linear thermal expansion for the intercalation layer:

$$\alpha_{Ts} = \frac{I_s \alpha_{TGIC} - (s-1)d_{002}\alpha_{TGr}}{d_s}. \tag{8}$$

For the third stage ($s = 3$) GIC, equation (8) can be written as:

$$\alpha_{Ts} = \frac{I_s \alpha_{TGIC} - 2d_{002}\alpha_{TGr}}{d_s}, \tag{9}$$

where $d_s = 0.704$ nm.

Calculated according to (9) coefficient of linear thermal expansion α_{TGIC} in the temperature interval [200÷260] K is $5.8 \cdot 10^{-5}$ K^{-1} and in the temperature interval [260÷285] K α_{TGIC} is $2.16 \cdot 10^{-5}$ K^{-1}. So, at $T = 260$ K the relative coefficient of linear thermal expansion for intercalate layers decreases by 2.5 times.

The reason for the sharp change in the relative linear thermal expansion coefficient is obviously the phase transition in the intercalate layers from quasicrystalline" state to "quasiliquid" state.

As it is known, there is a phase transition from quasicrystalline" state to "quasiliquid" state in the based on HOPG GIC with ICl at $T = 350$ K. As shown in the paper [14], the temperature at which this transition takes place in the GIC based on fine crystalline graphite decreases to 260 K. The use of the fine crystalline graphite with a relatively weak interaction between graphite layers as a source of graphite for intercalation leads to the formation of GICs with greater identity parameter I_s. This is equivalent, in a first approximation, to reducing pressure along the *C*-axis. Estimation of temperature shift is carried out under the assumption that increase in the distance between the graphite layers in the FPAG is equivalent to decrease in the external pressure, gives the value ~ 90 K. This value corresponds well with the experimentally obtained value of the phase transition temperature in the GIC based on FPAG: 350 K - 90 K = 260 K.

3.3 Thermostimulated Phase Transitions in Graphite Intercalation Compounds with Iodine Chloride

To establish the ordering of intercalate molecules in a layer, the studies of X-ray $hk0$ diffraction patterns for the third stage GIC with ICl in temperature range from 160 K to up 300 K were performed. Fig. 6 presents the part of $hk0$ X-ray diffraction patterns for GIC with ICl at temperature $T = 300$ K.

As can be seen from Fig. 6, there is a group of weak maxima in the region $2\theta = 44° \div 56°$. These maxima correspond to $hk0$-reflections from graphite matrix. Other bands were not observed for this GIC in the whole angular range $15° \div 110°$ at $T = 300$ K.

The parts of $hk0$ X-ray diffraction patterns for GIC with ICl at low temperatures are presented in Fig. 7a for a freshly prepared specimen and in Fig. 7b for a specimen after 8 days of exposure under normal conditions.

As shown in Fig. 7, with decreasing temperature for both a freshly prepared specimen of GIC with ICl and a specimen after 8 days of exposure under normal conditions in the angular interval $2\theta = 30^0 \div 38^0$, a new band appears. The intensity of this band increases with a decrease in temperature.
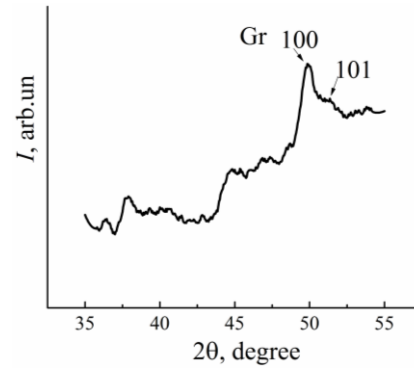

Fig. 6 – The part of $hk0$ X-ray diffraction pattern for GIC with ICl, $T = 300$ K
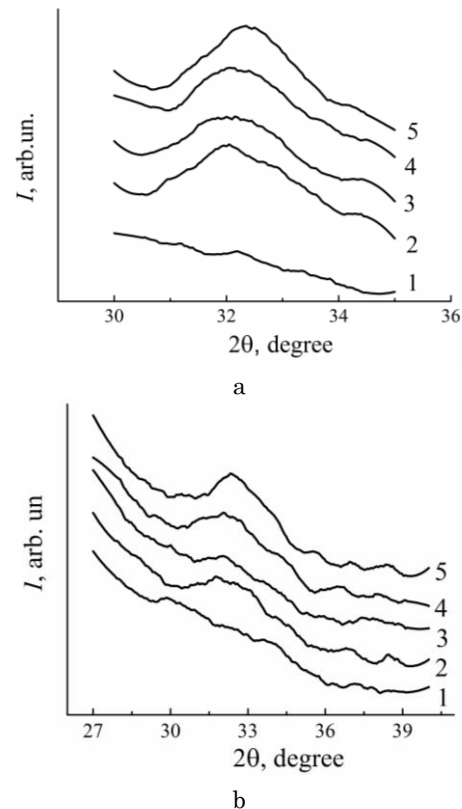

a

b

Fig. 7 – The parts of $hk0$ X-ray diffraction patterns for GIC with ICl: (a) a freshly prepared specimen, 1 – 200 K, 2 – 190 K, 3 – 180 K, 4 – 170 K, 5 – 160 K; (b) a specimen after 8 days, 1 – 300 K, 2 – 184 K, 3 – 180 K, 4 – 177 K, 5 – 173 K

The appearance of this extended maximum in the $hk0$ X-ray diffraction patterns directly indicates that at a temperature below 300 K a phase transition in the intercalate layer occurs, which is accompanied by a change of ICl ions ordering in the layer. In other words, there is a phase transition of iodine chloride ions in the interlayer distance of graphite from a two-dimensional "qusiliquid" disordered state (complete absence of any reflexes on the diffraction pattern) to an ordered two-dimensional "quasicrystalline" state (the appearance and growth of the diffraction maximum). This transition is not one-time and occurs in a wide temperature range. The temperature, at which this phase transition takes place, completely correlates with the temperature of the phase transition, which is determined in GIC with ICl by

changing the coefficient of linear thermal expansion, and also with the phase transition temperature that is determined for this GIC in the investigation of its transport properties [10].

4. CONCLUSIONS

Thus, the carried out structural investigations by X-ray diffraction method have allowed to establish some peculiarities of phase transitions in GICs with chloride iodine and bromine. In particular, it has been found that GICs with iodine chloride and bromine are fairly stable compounds. The exposure of GIC with iodine chloride under normal conditions during 20 days did not lead to significant changes in the identity parameter for this compound. For GICs with bromine, only after 20 days of exposure under normal conditions the transition from the second stage to the third stage was observed.

The temperature dependence of the identity parameter for GIC with iodine chloride has been experimentally investigated. Based on this dependence, the temperature dependence of the relative coefficient of linear temperature expansion of the intercalate layer is determined. It was found that at temperature 260 K, there is a significant reduction of the coefficient of linear temperature expansion (~ 2.5 times). It has been shown that such a sharp change in the coefficient of linear temperature expansion is related with the phase transition in the intercalation layers from quasicrystalline" state to "quasiliquid" state.

For the first time by the X-ray *hkl*-diffraction method, the phase transition in intercalate layers for GIC with iodine chloride in the temperature region from 160 K up to 300 K is directly investigated. It has been found that this is the transition of iodine chloride anions from two-dimensional "qusiliquid" disordered state to an ordered two-dimensional "quasicrystalline" state. It is shown that the temperature interval, in which this phase transition takes place, completely coincides with the temperature interval, in which the features of the temperature dependence of transport properties such as resistivity and thermopower take place.

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Структурні дослідження фазових переходів в інтеркальованих сполуках графіту з хлоридом йоду та бромом

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У статті наведені результати досліджень методом рентгенівської дифракції фазових переходів в інтеркальованих сполуках на основі дрібнокристалічного анізотропного піролітичного графіту з хлоридом йоду та бромом. Як вихідний для інтеркалювання був використаний дрібнокристалічний анізотропний піролітичний графіт з відстанню між сусідніми шарами 0.340 нм та розмірами кристалітів 20 нм. Інтеркалювання проводилося стандартним двотемпературним газофазним методом. Досліджена стабільність інтеркальованих сполук графіту при нормальних умовах. Виявлено, що витримка інтеркальованої сполуки графіту з хлоридом йоду при нормальних умовах протягом 20 діб не приводить до суттєвої зміни структури сполуки, в той час як аналогічна витримка для інтеркальованої сполуки з бромом спричинює незначні зміни в структурі. Зокрема, спостерігається перехід від сполуки другої стадії до сполуки третьої стадії. Для інтеркальованих сполук з хлоридом йоду в різних температурних інтервалах оцінений коефіцієнт лінійного теплового розширення. Виявлено, що при температурі 260 К спостерігається суттєва зміна коефіцієнту лінійного теплового розширення. Показано, що така істотна зміна коефіцієнту лінійного теплового розширення пов'язана з фазовим переходом в шарах інтеркалянта з «квазікристалічного» е «квазірідкий» стан. Вперше методом рентгенівської дифракції в інтеркальованих сполуках з хлоридом йоду виявлений в шарі інтеркалянта фазовий перехід типу «безпорядок-порядок».

Ключові слова: Інтеркальована сполука графіту, Метод рентгенівської дифракції, Питомий опір, Фазовий перехід, Шар інтеркалянту.