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Physicochemical Properties of Layered Compounds of Graphite

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The results of studies carried out in recent years on certain physicochemical properties (heat capacities, enthalpies of formation, compressibilities, thermal expansions, and thermal stabilities) of layered compounds of graphite are surveyed. The bibliography includes 126 references.

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I. INTRODUCTION

Many compounds with anisotropic layered structures (typical representatives of which are graphite and transition metal dichalcogenides), in which the bonding forces between the species within the layer are much stronger than between the layers, are able to form compounds of a new type as a result of the insertion of various substances in the interlayer space. Among compounds of this kind, those of graphite occupy the principal place, which is in many respects due to the possibility of their extensive application in various fields.

Many substances (metals, alloys, metal halides, oxides, acids, etc.) capable of being inserted in the graphite lattice with formation of new compounds are now known. However, despite the fact that the synthesis of such compounds was described as early as the first half of the past century, their systematic investigation began only about 40 years ago and such research has developed on a wide scale only in the last 25 years.

We may note that hitherto there has been no single terminology in the naming of compounds of this kind. Thus in the Soviet literature they are usually referred to as layered compounds of graphite, graphite interstitial compounds, graphite occlusion compounds, graphite clathrate compounds, graphite intercalation compounds, intercalated graphites, or simply graphitides. In foreign literature they are called "graphite intercalation compounds", "graphite lamellar compounds", intercalated graphites", and "graphitides", although according to the recommendations of the latest International Conference on these compounds[1] it is recommended that the term "graphite intercalation compounds" (abbreviated to GICs) be used.

We shall henceforth employ mainly the term "graphite layered compounds" (GLC), because in our view it emphasises the layered character of the structure of these compounds. The term "graphite interstitial compound" (GISC) appears to be less apt, since the term "interstitial phases" is usually employed, for example in the metallurgical literature, for the

designation of completely different substances. The term "graphitides" can be applied only to compounds of graphite with metals or alloys, because it emphasises the difference between compounds of this class and the carbides and acetylides of the corresponding metals.

As mentioned above, the growing interest in GLC is in many respects due to the constantly expanding fields of their practical application. Thus GLC catalyse various processes (for example, the synthesis of ammonia, artificial diamonds, etc.[2,3]); they are good conductors of electricity and can be used as cathodic materials in chemical current generators.[4] The use of GLC in systems designed for the storage of "thermal" energy,[5] as additives for the improvement of the physicomechanical properties of certain types of abrasive materials and powdered alloyed steels, and also as the raw material for the preparation of a new variety of carbon materials with regulated physicochemical properties, the so-called thermally cleaved graphite,[6] is promising. The increasing interest in GLC is indicated by the establishment in the USA of the Intercal Company specialising in the practical application of these compounds.

In order to be able to predict the behaviour of GLC under operating conditions and for the optimisation of their preparation processes, it is essential to have information about their physicochemical properties. Such information also makes it possible to understand the nature and characteristic features of the interspecies interaction in GLC, which is of considerable practical interest. However, hitherto there have been comparatively few data in the literature on the thermodynamic properties, compressibilities, thermal expansion, and thermal stability of GLC;[7-27] some of the individual properties of the GLC listed above have been subjected to a critical examination in early review publications.[28-35]

In recent years there has been a sharp growth of studies of the properties of GLC (see, for example, Refs.36–42). Regular international conferences on GLC are being held and the international scientific journal "Synthetic Metals", specialising to a large extent in the publication of data on GLC, has been organised. Numerous papers presenting the results of studies on certain physicochemical properties of GLC have been published.

The aim of the present review is to give a systematic critical account and a survey of the literature data of recent years obtained in studies of the heat capacities enthalpies of formation, the influence of high pressure on the properties, thermal expansion, and thermal stabilities of GLC.

II. THERMODYNAMIC PROPERTIES

Hitherto there have been few systematic studies designed to determine experimentally the thermodynamic properties of GLC† (see, for example, Refs.7–13), although in recent years several attempts have been made to carry out such investigations by a calorimetric method.

The heat capacity C_p of the lithium graphitide C_6Li has been investigated[43] in the range 4–300 K and a small anomaly was observed in the heat capacity at ~200 K which, according to the authors,[43] can be related to a structural phase transformation of the compound. The heat capacities of GLC with bromine, containing 0.5, 2.2, and 9.6 at.% of bromine, have been measured in the temperature range 1.5–6 K and the electronic component of the heat capacity as well as the Debye temperatures were calculated.[44] It was shown that the bromine atoms are insignificantly ionised (~1%) in all the GLC.

With the aid of differential scanning calorimetry (DSC), Wu and Vogel[45] investigated stage 1 GLC with antimony pentafluoride in the range 4.2–300 K; a phase transformation of the "order–disorder" type was observed near 185 K. Unfortunately the above authors[45] do not quote either the composition of the GLC investigated or any numerical values of its thermodynamic functions. The heat capacities C_p and magnetic susceptibilities of the GLC $C_{6.2}FeCl_3$, $C_{17}FeCl_3$, and $C_{11.3}NiCl_2$ have been measured.[46] An anomalous behaviour of the heat capacities of the compounds was observed in the vicinity of 4, 1.7, and 20 K respectively and the authors[46] attributed them to the occurrence in the compounds investigated of transitions to states of the "spin glass" type. In the study of stage 2 GLC with $NiCl_2$, Suzuki et al.[47] observed two regions of anomalous behaviour of the magnetic susceptibility at 18.0 and 21.3 K. However, heat capacity measurements revealed an anomaly only in the vicinity of the second temperature but no appreciable changes in heat capacity were observed at the first temperature. Murakami et al.[51] investigated stage 2 GLC with $CoCl_2$ and observed two magnetic transitions at 8.0 and 9.1 K. The temperature variation of the heat capacity of this compound revealed an anomaly only at the second temperature.

A low-temperature DSC study of GLC with titanium(IV)[48] and tin(IV)[49] chlorides showed that the decomposition of the compound with $TiCl_4$ is observed at 247 ± 1 K (the melting point of $TiCl_4$ is T_m = 249 K[48]) and that of the compound with $SnCl_4$ occurs at 237 ± 1 K (T_m = 240 K for $SnCl_4$[49]) regardless of the stage of the compound, i.e. the GLC decompose at temperatures close to the melting points of the intercalants. A DSC study of the products of the reduction of GLC with $SnCl_4$ by potassium showed[50] that the enthalpy of decomposition of the compounds (with fusion of the intercalated tin) is close to the enthalpy of fusion of pure tin, which indicates a weak interaction of the latter with the graphite lattice. Unfortunately none of the past studies[48-50] quote numerical values of C_p for the GLC.

A DSC investigation of the C_p of the unsaturated stage 1 GLC $C_{32}SbCl_{4.7}$[52] revealed a phase transition to the vitreous state at 210 K; on the other hand, the transition did not occur for the saturated stage 1 compound. In a DSC study of the stage 1 GLC C_8Cs, Ubbelohde and Drummond[53] observed a phase transformation at ~250 K whose form depended to a large extent on the type of graphite used for the synthesis. They also estimated the enthalpy and entropy of the observed phase transformation, amounting to ~111.7 J g-atom^{-1} and 0.4 J g-atom^{-1} K^{-1} respectively.

Suematsu et al.[54] investigated the heat capacity of the graphitide $C_{24}Rb$ below room temperature and observed four anomalies in the heat capacity at 48, 103, 162, and 210–220 K, which are associated with phase (including structural) transformations. However, no numerical values of the corresponding thermodynamic functions are quoted in the above study.[54] The heat capacity of the stage 1 compound $C_{10}Al.Cl_{3.3}$ has been investigated by DSC in the range 120–300 K[55] and an anomaly has been found in C_p near 226 K, associated with a transformation of the "order–disorder" type, whose enthalpy was 900 ± 50 J mol^{-1}, which is within the same limits as for other GLC; the entropy of this transformation has been estimated as 4.0 ± 0.5 J mol^{-1} K^{-1} (Fig.1). However,

†Depending on how many carbon layers separate two nearest layers of the intercalant, GLC are subdivided into compounds with stage 1, stage 2, etc. intercalation.[1] Depending on the degree of filling of the intercalant, GLC are subdivided into saturated (with the limiting content of the adduct) and unsaturated (for which the content of the adduct is less than the limiting value).

no anomalies have been observed in the experimental temperature range for stage 4 GLC with $AlCl_3$ of the type $C_{50}Al.Cl_{3.3}$.[55]

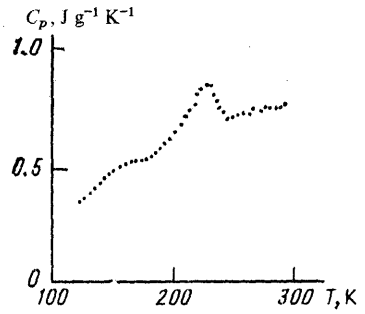


Figure 1. Temperature variation of the heat capacity of the compound $C_{10}AlCl_{3.3}$.[55]

The heat capacities of the compound C_6FeCl_3 (stage 1) and $C_{12}FeCl_3$ (stage 2) have been measured[56] by the DSC method in the range 298–570 K with an error of ±2.8%; the temperature dependence of the heat capacity (J mol^{-1} K^{-1}) of the compounds investigated is described by the equations

$$C_p(C_6FeCl_3) = 141.7 + 0.037T$$
$$C_p(C_{12}FeCl_3) = 176.0 + 0.277T.$$

We may note that, according to a number of data,[27,57–61] the decomposition of the GLC with $FeCl_3$ begins at ~573 K to which should correspond an anomalous change in Cp near 573 K. However, the authors[56] observed no anomalies in the $Cp(T)$ relation. Such discrepancy between the data of different investigations can be explained, in particular, by the different methods of synthesis of the compounds and the different composition and type of graphite used in the synthesis.

The heat capacities of GLC with certain 3*d* metal chlorides, namely $C_{4.68}CuCl_2$ (stage 1), $C_{6.35}CuCl_2$ (stage 1), $C_{7.73}CuCl_2$ (stage 1 with an admixture of stage 2),[62,63] $C_{6.97}CoCl_2$ (stage 1), $C_{16.8}CoCl_2$ (stage 2),[63] $C_{7.7}FeCl_3$ (stage 1),[58,59] $C_{11.83}FeCl_3$ (stage 2),[58] $C_{16.2}NiCl_2$ (stage 2), and $C_{5.5-6.5}.MnCl_2$ (stage 1),[64] have been investigated[58,59,62–64] by the triple thermal bridge method (with an error ≤ 3%). The experimental results are presented in Figs.2 and 3. Least squares treatment of the results yielded the coefficients *a*, *b*, and *c* in the equations relating the heat capacities of the GLC investigated to temperature (Table 1). For the compounds $C_{7.7}FeCl_3$, $C_{11.83}FeCl_3$, and $C_{5.5-6.5}$-$MnCl_2$, the authors[58,59,64] observed anomalies in the heat capacity with maxima at 455 ± 5, 445 ± 5, and 450 ± 2 K respectively, associated with reversible solid-phase transformations of the GLC. The enthalpies of the above transformations were found to be 0.13 ± 0.03 kJ mol^{-1}, 2.78 ± 0.41 kJ mol^{-1}, and 1.33 J g^{-1}.

We may note that no anomalies in the heat capacities of the saturated GLC with $FeCl_3$, having the compositions C_6FeCl_3 and $C_{12}FeCl_3$, have been observed.[56] One of the causes of the discrepancy between the result of the studies of Skoropanov and co-workers[58,59] and Solozhenko et al.[56] for the GLC $C_{7.7}FeCl_3$ and C_6FeCl_3 may be the fact that, as in the case of the GLC with $SbCl_5$,[52] in the unsaturated compound, in contrast to saturated compounds, the transition within the layer involving a change in the structure of the intercalated component are sterically unhindered. Account should also be taken of the different methods of synthesis of the compounds by Skoropanov and co-workers[58,59] and Solozhenko et al.[56] and also of the differences in the type of graphite matrix.

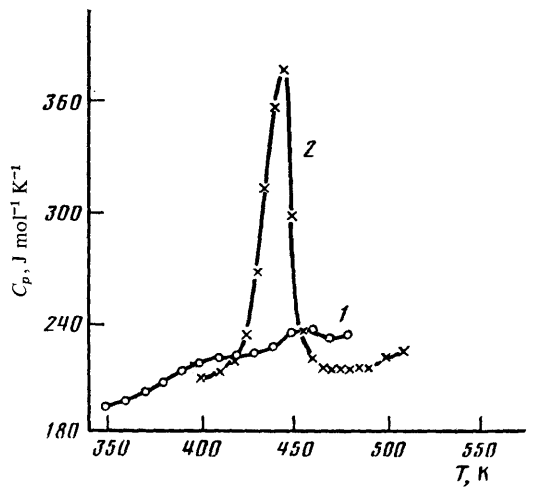


Figure 2. Temperature variation of the heat capacity of the GLC with $FeCl_3$:[58,59,62–64] 1) stage 1; 2) stage 2.

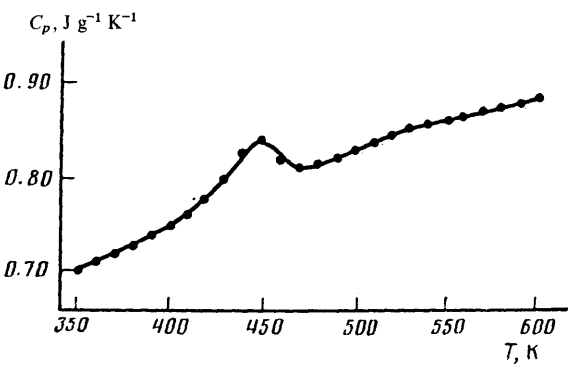


Figure 3. Temperature variation of the heat capacity of the compound $C_{5.5-6.5}MnCl_2$.[64]

The enthalpy of the reaction

$$16C_{graphite}(cryst.) + Br_2(liq) \rightleftarrows C_{16\pm0.3}Br_2(cryst.)$$

has been determined at 308.0 ± 0.5 K[65] and the enthalpy of formation of the compound $C_{16\pm0.3}Br_2$ has been calculated as −16.43 ± 0.76 kJ mol^{-1}.

On the basis of isobaric-thermoanalytical studies, Solozhenko et al.[56] calculated the standard enthalpies of formation of stage 1 and stage 2 GLC with $FeCl_3$:

$$\Delta H^\circ_{f,298}(C_6FeCl_3) = -(491 \pm 13) \text{ kJ mol}^{-1};$$
$$\Delta H^\circ_{f,298}(C_{12}FeCl_3) = -(456 \pm 10) \text{ kJ mol}^{-1}.$$

III. THE INFLUENCE OF HIGH PRESSURES

The study of GLC at high pressures is of considerable theoretical and practical interest, especially in connection with the possibility of employing GLC in the synthesis of artifician diamonds.[3] However, the majority of studies have been devoted to the investigation of the influence of pressure on the electronic or electrical properties of GLC and also on their structure. At the same time data on the compressibilities and phase transformations of GLC under the influence of high pressures are of significant interest.

Table 1. The coefficients a, b, and c in the equation for the temperature variation of the heat capacity: C_p (kJ mol^{-1} K^{-1}) = $a + 10^{-3}bT + 10^{6}cT^{-2}$.[58,59,62-64]

Compound	a	b	c	T, K**
$C_{6.68}CuCl_2$	104.729	95.1342	−2.01471	350—550
$C_{6.83}CuCl_2$	72.9829	121.622	1.00163	370—520
$C_{7.73}CuCl_2$	190.694	−37.0157	−5.68839	370—500
$C_{6.97}CoCl_2$	130.236	97.2574	−2.23586	350—600
$C_{16.8}CoCl_2$	244.854	209.482	−8.54369	350—600
$C_{7.7}FeCl_3$	−157.539	815.818	7.94588	350—410
$C_{16.2}NiCl_2$*	0.721254	0.561208	−0.0226657	350—600
$C_{5.5+6.5}MnCl_2$*	−0.323501	2.18667	0.0315135	350—400
	0.969003	0.0680034	−0.0426992	480—600

*For $C_{16.2}NiCl_2$ and $C_{5.5-6.5}MnCl_2$, C_p was expressed in J g^{-1} K^{-1}; for $C_{5.5-6.5}MnCl_2$, the coefficients a, b, and c were calculated by ourselves from the data of Petrov et al.[64]
**Temperature range.

Table 2. The compressibilities of the GLC with HNO_3 and $SbCl_5$.[66,67]

Compound	Stage	$10^{-3}K_c$, kbar^{-1}	$10^{-3}K_a$, kbar^{-1}
Graphite	—	2.9±0.3	0.1±0.3
GLC with HNO_3	3	5.0±0.7	0.0±0.3
GLC with $SbCl_5$	2	2.0±0.5	0.0±0.5

Notation: $K_c = (d/d)/c$ and $K_a = (da/dp)a$, where a and c are the unit cell parameters and p is the pressure.

Thus the influence of hydrostatic pressure up to 0.8 GPa on the properties of GLC with HNO_3 (stage 3) and $SbCl_5$ (stage 2) has been investigated.[66,67] Table 2 presents the compressibilities along the c and a axes for the test compounds as well as the graphite from which the GLC have been synthesised. It is seen from the Table that the compressibility along the c axis for the GLC with HNO_3 is greater by a factor of ~1.7 than for the initial graphite, while the compressibility along the a axis is much smaller in both cases than along the c axis. At the same time, the pressure dependence of the electrical resistance of the GLC with HNO_3 shows an anomaly at 0.5 GPa, which can be related, according to the authors,[66,67] to a structural transition of the compound (however, the nature of this transition is not explained[66,67]). Unfortunately the exact compositions of the compounds investigated are not given in the two studies.[66,67]

The compounds C_8Cs and $C_{36}Cs$ have been investigated by X-ray diffraction at a high hydrostatic pressure (up to 1.2 GPa) and room temperature.[68] The compressibility of C_8Cs along the c axis was determined as $K_c = (dc/dp)_{p=0}/c = (1.57 \pm 0.05) \times 10^{-12}$ cm^2 dyn^{-1}, which is much less than the corresponding values for the compounds C_8K (2.1×10^{-12} cm^2 dyn^{-1}) and C_8Rb (2.25×10^{-12} cm^2 dyn^{-1}). The greater "rigidity" of the caesium compound compared with the analogous potassium and rubidium compounds implies, according to the authors,[68] that in this GLC there is marked overlapping of the wavefunctions of the 6s electrons of caesium and the π electrons of graphite along the c axis. No pressure-initiated structural transformation was observed for the compound C_8Cs. A reversible phase transformation (with formation of a stage 4 GLC), i.e. a transformation with a change in the stage index of the GLC, was observed[68] in the compound $C_{36}Cs$.

The potassium graphitide C_8K (stage 3) has been studied by neutron diffraction[69] at hydrostatic pressures up to 2 GPa. A reversible phase transition was observed in the pressure range 1.5—1.9 GPa, which leads to the formation of GLC with a non-integral stage index (3/2).

The behaviour of the graphitides C_8M and $C_{12n}M$ (M = Rb or Cs; n = 2, 3, 4) has been investigated with the aid of X-ray diffraction and changes in Raman spectra at hydrostatic pressures up to 1 GPa.[70] Pressure-initiated phase transformations with a change in stage index, characterised by reversibility, hysteresis, and a dependence on the nature of the specimen, were observed for all the GLC with $n \geq 2$. The following transitions were noted: GLC (stage 2) → GLC (stage 3); GLC (stage 3) → GLC (stage 4) +GLC (stage 5); GLC (stage 4) → GLC (stage 4) + GLC (stage 5) → GLC (stage 6). It was also observed that the pressure of the transition involving a change in stage index is higher for $C_{24}Cs$ than for $C_{24}K$ and $C_{24}Rb$, which implies, according to the authors,[70] that the repulsive intralamellar interactions are more intense for caesium than for potassium and rubidium (possibly as a consequence of the greater size of the caesium ions). In addition, the compressibilities $K_d = (\partial d/\partial p)_{p=0}/d_0$ where d is the packing thickness at a pressure p and d_0 the packing thickness at $p = 0$) of the compounds C_8Cs and C_8Rb were measured as $(1.56 \pm 0.05) \times 10^{-12}$ and $(2.42 \pm 0.12) \times 10^{-12}$ cm^2 dyn^{-1} respectively [$K_d = (2.73 \pm 0.09) \times 10^{-12}$ cm^2 dyn^{-1} for the initial graphite and $K_d = (2.13 \pm 0.09) \times 10^{-12}$ cm^2 dyn^{-1} for the analogous potassium compound C_8K].

The compressibility of the stage 1 graphitide C_4KHg has been measured along the c axis[71] and has been found to be $(4.4 \pm 0.1) \times 10^{-12}$ cm^{2}dyn^{-1}, which is approximately twice as large as for the analogous stage 1 GLC C_8K, i.e. the compound C_4KHg is much "softer" in the direction of the c axis than C_8K. According to Kim et al.,[71] the ternary compound can therefore allow a significant decrease of volume without the formation of ultradense islands of the intercalant and also "corridors", which is the driving force of the pressure-initiated transformations with change of stage index in the compound C_8K.

The stage 1 GLC C_6Li has been investigated by NMR at 232 and 293 K and external pressures $p \leq 0.5$ GPa.[72] It was shown that the quadrupole interaction constant for the graphitide is independent of temperature, but increases linearly (at a rate of 1.5 kHz bar^{-1}) with increase of pressure. The degree of charge transfer to each carbon atom estimated by the authors[72] was $-e/12$, which agrees with the results of band calculations. The compressibility of the compound C_6Li along the c axis, estimated in the above study,[72] was $K_c = 1.7 \times 10^{-12}$ cm^{2}dyn^{-1}, which agrees with the analogous values for the graphitides C_8M (M = K, Rb, or Cs).

A thermodynamic model permitting a satisfactory explanation of, in particular, transitions involving a change in stage index under the influence of high pressure by the formation of GLC with a non-integral stage index at high pressures, and also certain other experimental effects in alkali metal graphitides has been proposed.[73]

A phase transition with a change (non-multiple) in the stage index from two to three has been observed by studying the Shubnikov–de Haas effect for the stage 2 GLC $C_{16}ICl$ at room temperature and a hydrostatic pressure of ~1.2 GPa.[74] A characteristic feature of this transition was a monotonic (in all probability non-threshold as regards pressure) increase of the content of stage 3 regions (having the composition $C_{24}ICl$) and a decrease of the content of the stage 2 regions (having the composition $C_{16}ICl$) with retention of the single crystal nature of the corresponding regions. This transition was explained[74] on the basis of the domain model of the GLC.

The influence of high hydrostatic pressures (up to 2.2 GPa) on the electrical properties of the graphitides C_4KHg (stage 1) and also C_8KHg and C_8RbHg (stage 2) has been investigated.[75–77] Transitions to the superconducting state were observed at atmospheric pressure and temperatures of 1.88 and 1.41 K for the stage 2 GLC C_8KHg and C_8RbHg respectively. The application of hydrostatic pressure lowers the temperature of the transition to the superconducting state at rates of -6.3×10^{-5} and -5.3×10^{-5} K bar^{-1} for the potassium and rubidium compounds respectively.[77]

Results of measurements of the pressure dependence of the temperatures of the transition to the superconducting state for the graphitides C_4MHg and C_8MHg (M = K or Rb) as well as the compounds $C_4KCl_{1.5}$, C_8K, and $C_{24}K$ have been surveyed and discussed.[78–80] It was shown that the electrons in the intercalant zone and not those in the graphite zone play the main role in the superconductivity of materials of the given class and that the two-dimensional anisotropy of the properties of the GLC investigated is important under these conditions.

The influence (at room temperature) of solid-phase pressures (up to 8.5 GPa) on a series of GLC with *d* elements and their chlorides has been investigated[81] and it has been shown that the structures of the compounds investigated do not undergo appreciable changes after their treatment at a pressure up to 8.5 GPa.

We may note that in all the studies discussed above, the influence of high pressures on the properties of various GLC was investigated at room temperature or below room temperature, while the behaviour of the GLC at high pressures and temperatures was not considered, although such data are extremely important and necessary, in particular, in considering the possibilities of the synthesis of artificial diamonds from GLC. The behaviour of a stage 1 GLC with $FeCl_3$ has been investigated under the conditions of quasi-hydrostatic pressures (2–8 GPa) and high temperatures (up to 2000 K) in only one study.[82] It was shown that at $T <$ 700 K the test compound undergoes no changes over the entire experimental pressure range, but it does decompose as the temperature rises with formation of a mixture of higher stage GLC and iron(II) and iron(III) chlorides. On the other hand, the formation of diamonds from the GLC investigated was not observed under the experimental conditions.[82]

IV. THERMAL EXPANSION

The coefficients of thermal expansion (CTE), whose knowledge is especially necessary when the possibility of obtaining artificial diamonds from the corresponding GLC is considered, have been determined in recent years for certain GLC.

The CTE have been measured along the *a* and *c* axes in certain alkali metal graphitides by X-ray diffraction in the temperature range 10–300 K.[83,84] It was shown that the thermal expansion along the *c* axis depends greatly on the density of the arrangement of alkali metal atoms in the interplanar spaces within the GLC and also on the stage index of the compound, being greatest for the potassium graphitide C_8K. It has also been observed that the thermal expansion along the *a* axis of the potassium compounds C_8K and $C_{24}K$ and also of the highly oriented pyrolytic graphite is negative in the experimental temperature range. The results obtained[83,84] are listed in Table 3.

Table 3. The coefficients of thermal expansion along the *a* ($\alpha_\parallel$) and c ($\alpha_\perp$) axes of graphite and the GLC with alkali metals.[83,84]

Compound	$\alpha_\parallel \cdot 10^6$, K^{-1}	T, K	$\alpha_\perp \cdot 10^6$, K^{-1}	T, K
Graphite	0.20	200–280	2.4±0.4	200–300
C_8K	0.40	170–285	4.5±0.8	250–300
$C_{24}K$	0.40	165–280	3.6±0.4	250–300
$C_{36}K$	—	—	3.0±0.6	230–300
C_8Rb	—	—	3.0±0.7	250–300
$C_{24}Rb$	—	—	3.3±0.5	240–300
C_8Cs	—	—	2.8±0.6	240–300

Table 4. The coefficients of thermal expansion of the GLC with sulphuric acid and of graphite.[85]

Stage index*	$10^6\alpha$, K^{-1}	
	83–173 K	223–303 K
1	48.1±1.1	64.7±1.1
2	37.8±0.2	72.3±2.9
3	30.7±0.8	55.3±0.8
4	27.6±1.4	47.7±1.4
Graphite	19.14	25.6

*Only the stage indices of the compounds are indicated in the original communication, but their chemical compositions are not given.

The temperature variation of the repeat period of the GLC with sulphuric acid having four stage indices (from 1 to 4) has been measured by X-ray diffraction in the temperature range 83–303 K.[85] For all the compounds, an anomalous thermal expansion was observed at temperatures from 173 to 213 K, its value gradually diminishing (from 0.097 Å for the stage 1 compound to 0.040 Å for the stage 4 compound). The coefficients of linear thermal expansion α for all the GLC investigated, which proved to be 1.5–3 times greater than the corresponding values for the initial graphite, have been published[85] for two temperature ranges (83–173 and 223 to 303 K). Some of the data obtained[85] are compiled in Table 4 (we may note that, unfortunately, the above communication[85] contains no information about the chemical composition of the test compounds, which to some extent hinders the interpretation of the results).

Vangelisti et al.[86] determined by X-ray diffraction the value of α_1 for the stage 1 GLC with $AlCl_3$ and $GaCl_3$ and highly oriented pyrolytic graphite and obtained α_1 (K^{-1}) = 38.0×10^{-6}

(in the range ~0–300 K), 29.4×10^{-6} in the range ~0–100 K), and 26.5×10^{-6} (in the range ~100–300 K).

The structure of the stage 2 GLC $C_{11.3}NiCl_{2.13}$ has been investigated by neutron diffraction and it was found that, when the temperature is raised from 5 to 300 K, the repeat period along the *c* axis increases by 0.078 Å compared with the analogous value (0.071 Å) for the stage 1 GLC with $FeCl_3$. The authors[87] found that at room temperature the CTE of the compound $C_{11.3}NiCl_{2.13}$ is ~4×10^{-5} K^{-1}.

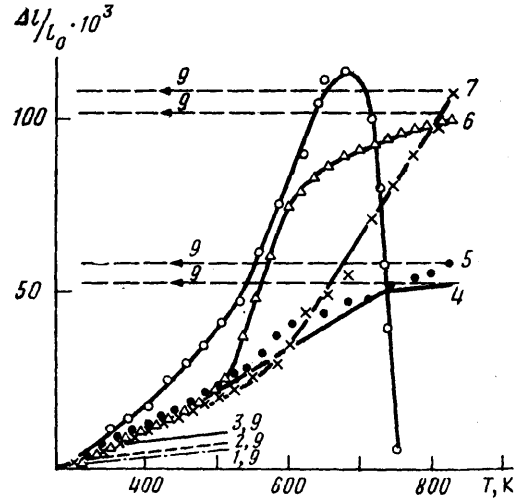


Figure 4. Temperature variation of the relative elongation in the axial direction ($\Delta l/l_0$) of pressed cylindrical specimens of the graphite from the Zaval'evsk deposit (curve *1*), cobalt (curve *2*) and (curve *3*) dichlorides, and the compounds $C_{9.5}CuCl$ (curve *4*), $C_{6.97}CoCl_2$ (curve *5*), $C_{6.35}CuCl_2$ (curve *6*), $C_{16.8}CoCl_2$ (curve *7*), and $C_{7.7}FeCl_3$ (curve *8*) on heating (curves *1–8*) and cooling (curve *9*).[58,59,63,88,89]

Table 5. The coefficients of thermal expansion (α) of certain GLC with metal chlorids.[58,59,63,88,89]

Compound	Stage	$\alpha \cdot 10^6$, K^{-1}	*T*, K
$C_{6.35}CuCl_2$	1	9.9	290–440
ditto	1	13.5	450–520
»	1	70.0	530–590
»	1	19.7	600–820
$C_{6.97}CoCl_2$	1	11.7	290–540
ditto	1	26.5	550–590
»	1	8.0	600–800
$C_{16.8}CoCl_2$	2	10.2	300–580
ditto	2	31.1	590–820
$C_{9.5}CuCl$	1	7.2	300–370
ditto	1	14.0	380–715
»	1	1.5	725–820
$C_{7.7}FeCl_3$	1	20.7	310–540
ditto	1	66.7	560–640

We may note that the above studies[83–87] were performed below room temperature and that CTE data in the range above room temperature appeared for the GLC only recently. The results of studies of the characteristic features of the thermal expansion at temperatures up to 820 K for pressed cylindrical specimens of certain GLC (obtained using graphite from the Zaval'evsk deposit) with cobalt(II), copper(II), copper(I), and iron(III) chlorides have been published[58,59,63,88,89] and are summariesed in Fig. 4 and Table 5. It is shown that the CTE of the GLC are significantly greater than for the corresponding graphite–salt mixtures, depend on the type of intercalated salt and the stage index of the GLC and are characterised by anisotropy and the possibility of hysteresis. It has been shown[63] that the application of cyclic cold pressing (up to 0.2 GPa) in the formation of cylindrical specimens of the GLC with $Co(Cu)Cl_2$ leads to an increase of the linear CTE and that the influence of such pressing on the stage 1 and 2 GLC is tentative (Fig. 5). With increase of the number of the "heating to 523 K–cooling to 300 K–pressing of the specimen until attainment of the initial dimensions" cycle, the linear CTE of the stage 1 GLC diminishes and that of the stage 2 compound increases.

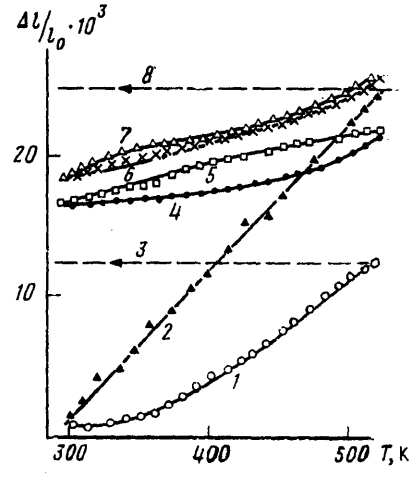


Figure 5. The influence of the previous thermal and baric history on the thermal expansion of the GLC with $CoCl_2$:[63] 1), 2), 4), and 6) heating; 3), 5), 7), and 8) cooling; 1), 3), 6), and 7) $C_{6.97}CoCl_2$; 2), 4), 5), and 8) $C_{16.8}CoCl_2$; "heating–cooling": 6) and 7), 4) and 6) the second and subsequent cycles; "heating–cooling–pressing": 1) and 3), 2) and 8) the fourth cycle.

It has also been established that the process involving the removal from the test compounds of the intercalated components is superimposed on their thermal expansion proper, which in the case of the stage 1 GLC with $FeCl_3$ at a temperature in excess of 660 K leads to the complete breakdown of the initial form of the test specimen.[58,59] It has been suggested that the marked increase in the size of the specimen on heating to 820 K for the stage 2 GLC with $CoCl_2$ compared with the stage 1 compound is probably caused by the preferential alteration of the distances between the carbon networks of the graphite skeleton (in the regions where there is no intercalated component) in the stage 2 GLC as a consequence of the decrease of the electron density caused by the donor–acceptor interaction between the carbon layers and the cobalt chloride (the carbon layers function as electron donors),

while the distance between the carbon layers and the salt in the GLC with $CoCl_2$ corresponding to both stage indices increases to a lesser extent.

V. THERMAL STABILITY

Despite the great practical value of data on the thermal stability of GLC, for the majority of them (even for the compounds with $FeCl_3$ which have been most thoroughly characterised from this standpoint[20-27]), the question of their behaviour on heating has not been finally solved.

The behaviour of GLC with homogeneous (1) and mixed (1 + 2) stage indices having the composition graphite + $FeCl_{3-y}$ (where $0 \leq y \leq 1$) on heating has been investigated by Raman spectroscopy[90] and it was found that after the compounds had been kept at 648 K, a fraction of the stage 3 compound appeared. The increase of y (i.e. of the fraction of intercalated $FeCl_2$) after heating was also confirmed by measuring the Mössbauer effects.

An isobaric thermoanalytical investigation of the decomposition processes in nitrogen, helium, and argon atmospheres of GLC with $FeCl_3$ corresponding to stage 1 (C_6FeCl_3) and 2 ($C_{12}FeCl_3$) has been carried out in the temperature range 298–750 K and in the pressure range 10–700 mmHg.[56] It was shown that the thermal decomposition of these compounds takes place in steps. Thus at a low pressure the stage 1 compound decomposed in two steps:

$$\text{GLC (stage 1)} \rightarrow \text{GLC (stage 2)};$$
$$\text{GLC (stage 2)} \rightarrow \text{graphite} + FeCl_3.$$

At higher pressures the thermograms showed a single peak which the authors assigned[56] to the process

$$\text{GLC (stage 1)} \rightarrow \text{graphite} + FeCl_3.$$

We may note that the formation of GLC with $FeCl_2$ or $FeCl_2$ was not observed[56] in the decomposition of the compounds investigated, which conflicts with the results of other studies.[22,24,57-60,90]

In a DSC study of GLC with titanium(IV) and tin(IV) chlorides corresponding to different stage indices showed that, regardless of composition, these compounds decompose below room temperature—near the melting point of the corresponding pure intercalated component (249 K for $TiCl_4$ and 240 K for $SnCl_4$).[48,49]

The behaviour of the stage 2 GLC with aluminium bromide, having the composition $C_{20.8}AlBr_{3.5}$, has been investigated by differential thermogravimetric analysis (heating to 1173 K at a rate of 10 K min^{-1} in an atmosphere of dry nitrogen and a pressure of 10^5 Pa) (Fig. 6).[91] The specimen lost mass in three stages: 1) initially (at 343–473 K) the excess bromine was probably lost (weight loss 7%); 2) next there was a stepwise transition from the stage 2 compound to one corresponding in terms of its composition to stage 6 (at 693 K the weight loss was 38.5% and the rate of decomposition slowed down sharply); 3) on further heating to 1173 K, the weight loss reached 43–47% (on the other hand in the case of the complete decomposition of the substance, the weight loss of the specimen should be 55%). The authors explained this[91] by the low rate of desorption of the GLC decomposition products, the relatively short decomposition time, and also the formation of a residual graphite compound.

The thermal behaviour of the graphitides C_4KHg and $C_4KTl_{1.5}$ has been studied[92] and proved to be significantly different for the two compounds. Thus the melting points of the pure alloys and the alloys intercalated in graphite and having the same composition were found to be 449 for KHg, ~673 K for KHg in C_4KHg, ~593 K for $KTl_{1.5}$, and ~603 K for $KTl_{1.5}$ in $C_4KTl_{1.5}$. This enabled the authors[92] to assume, in conformity with crystallographic data, that the interaction between the layers of the intercalated "alloy" and the neighbouring layers of the graphite is much weaker for thallium compounds than for mercury compounds.

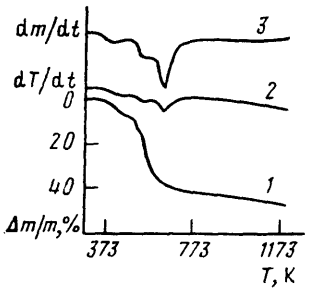


Figure 6. Thermal analysis curves for the compound $C_{20.8}$. $AlBr_{3.5}$: 1) weight loss by the specimens; 2) DTA; 3) DTA.[91]

The results of an investigation of GLC with metal fluorides having the compositions $C_9F(MgF_2)_{0.08}$, $C_{11}F(MgF_2)_{0.14}$, and $C_{11}F(AlF_3)_{0.09}$ and also of the graphite fluoride $(C_2F)_n$ by differential thermal analysis in air have been published.[93] Starting from 463 K, a broad exothermic peak was observed for the compounds $C_x(MgF_2)_y$ (the decrease of the weight of the specimen began at the same temperatures). For the compound $C_{11}F(AlF_3)_{0.09}$, the broad exothermic peak began at 503 K. The authors did not elucidate the nature of these peaks.[93] The peaks near 1103 K, which were observed for all three compounds, were assigned to the oxidation reaction of the graphite residue. For the graphite fluoride, two exothermic peaks were noted at 846 and 970 K, the first corresponding to the decomposition of the compound and the second to the oxidation of the residual carbon.

The decomposition in air of mixed GLC with uranium hexafluoride and Freon 113, having the composition $C_n[UF_6 \cdot (\text{Freon 113})]$, has been investigated by thermogravimetric analysis.[94] It was found that the ternary compound decomposed in four stages: (1) at 313–473 K; (2) at 448–523 K; (3) at 473–723 K; (4) at 703–988 K. The graphite fluorination products with intercalated UF_6 molecules are obtained in the first three decomposition stages (analogous products are formed on thermal decomposition of the GLC with UF_6) and uranium is not removed from the compound. During the fourth (exothermic) stage, the residual Freon is evolved with simultaneous loss of carbon, which is proportional to the uranium content. The amount of Freon in the initial GLC and the intermediate products of their decomposition is not correlated with the uranium content but is proportional to the amount of graphite. In the most stable intermediates, formed after the third decomposition stage, there are approximately 12 carbon atoms per Freon 113 molecule.

The removal of ammonia from the ternary GLC $C_{12}M(NH_3)_2$ (where M = lithium, sodium, potassium, rubidium, caesium, calcium, strontium or barium) has been investigated by chemical analysis and X-ray diffraction.[95] In terms of their behaviour as regards the elimination of ammonia, the GLC were classified[95] in three groups: (1) GLC with caesium and rubidium, from which the entire ammonia is removed; (2) GLC with sodium and potassium, which also evolve most of the

ammonia and are themselves converted into new GLC; (3) GLC with lithium and alkaline earth metals, which give rise to amides on decomposition and the decomposition process itself is extremely complex.

It has been shown[96] that the graphite compounds $C_2F.yEFn.zR$ of a new type, which have the cage structure (the molecules of the fluoride in them are, as it were, located in cages formed by the carbon layers and fluorine atoms), exhibit a fairly high (in our view) thermal stability (up to 573–673 K). It has been established by differential thermal analysis (DTA) that the compound $C_2F.0.35BrF_3.0.17SnF_4$ decomposes at 553–623 K in several stages (although the stages themselves have not been described). It has been shown[98] that the GLC $C_{10.3}MoF_6$ is stable up to 523 K and the compound $C_{53.7}.WF_6$ is stable up to 503 K, both GLC decomposing on heating to 823 K with formation of pure graphite.

Studies on the graphite compounds $(CF_{0.97}.0.05HSO_3F)_n$ and $(CF_{1.23-1.25})_m$ showed[99] that their thermal stability depends both on the type of the initial graphite and on the conditions under which the compounds are obtained, varying in the range from 533 to 733 K. It has been shown with the aid of DTA[100] that, on heating to 373 K, hydrogen fluoride is evolved endothermically from the compound $C_xF.yNO_3.zHF$, while in the temperature range 623–673 K the complete exothermic decomposition of the compound takes place. The thermal stability of the compounds $[C_xF_y(NH_2)_z]_n$ and $C_xF_x.Cl_y.zN_2O_4$ has been investigated[101] and it has been shown that the graphite aminofluorides are thermally stable up to 373 K, and that their decomposition involves the formation of carbon, nitrogen, and hydrogen fluoride. When the compound $C_xF_yCl_y.zN_2O_4$ is heated to temperatures in the region of ~473 K, NO_2 is evolved into the gas phase (but the composition of the solid residue was not indicated). A definite correlation has been observed[102] between the thermal stability of graphite fluorides (according to DTA data) and the interplanar spacing in these compounds: the temperatures of the onset of decomposition are higher for compounds with a smaller interplanar spacing.

In a study of the thermal stability of the graphite oxide fluoride $C_8O_{0.8}F_{3.6}$,[103] two exothermic effects were observed on the derivatogram: at 453 K (this peak is characteristic of oxygen-containing graphite compounds) and at 673 K (graphite fluorides normally decompose in this temperature range). The mass spectrum of the gaseous decomposition products of the compound revealed the presence of the ion CF^+, CF_2^+, CF_3^+, COF_2^+, CO^+, and CO_2^+. The thermal stability of GLC with metal fluorides having the composition C_8MoF_5, $C_{22.9}.NbF_5$, and $C_{13.6}TaF_5$ has been investigated[104] and it has been shown that the compound C_8MoF_5 decomposes in the temperature range 443–608 K. The decomposition is accompanied by a large number of superimposed exothermic and endothermic effects, which can be explained, according to the authors,[104] by the disproportionation of the intercalated MoF_5. In the decomposition of other GLC, a smooth weight loss was observed in the temperature ranges 673–763 K (for $C_{22.9}.NbF_5$) and 563–683 K (for $C_{13.6}TaF_5$); in this case there was apparently no disproportionation of NbF_5 and TaF_5.

Lisitsa et al.[105] investigated the amino-derivatives of graphite $C_3O(NH_2)_{1.3}$ and $C_3(NH)_{1.3}$ and found that the former compound is almost fully converted into volatile products in the region of 673 K in an inert atmosphere. According to mass-spectrometric data, the compound $C_3(NH)_{1.3}$ is stable up to 573 K, decomposing in the region of 773 K with evolution of gaseous hydrogen cyanide, ammonia, and hydrogen. It has been demonstrated by ^{19}F NMR[106] that reversible disproportionation of ClF_3 with formation of ClF and ClF_5 takes place within the crystal structure of the compound $C_{3.65}.F_{2.17}Cl_{0.42}$. With the aid of derivatographic studies of the carbon fluorides $(CF_x)_n$, it has been shown[107] that, depending on the fluorine content and the conditions in the preliminary treatment of the specimens, the temperature of the onset of their decomposition is in the range 543–653 K and the maximum rate of decomposition is attained at temperatures in the range 753–833 K. A relation between the structure of the initial carbon material and the thermal stability of fluorocarbon materials has also been noted in another investigation;[108] fluorination of materials with a more ideal structure yielded specimens with a lower thermal stability.

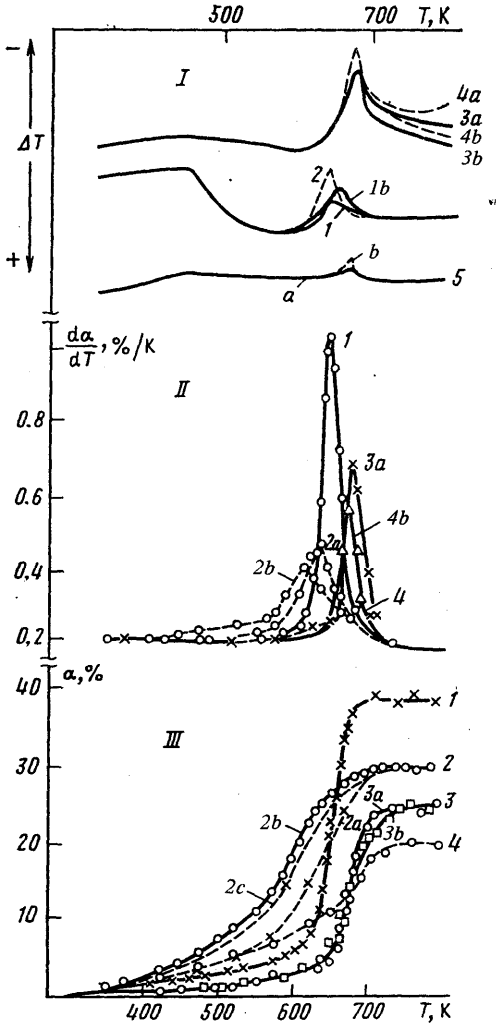


Figure 7. DTA (I), DTG (II), and TG (III) curves for $C_{7.7}FeCl_3$ (curves *1*, *3*, and *5a*) and $C_{11.83}FeCl_3$ (curves *2*, *4*, and *5b*) *in vacuo* (curves *1* and *2*), in air (curves *3a* and *4a*), in argon (curves *3b* and *4b*), and in a sealed tube (curve 5), the specimens (30 mg) having particle sizes ≤0.25 mm curves *1*, *2a*, and *2b*) and 0.25–0.5 mm (curves *1b* and *2b*), at heating rates of 1 K min^{-1} (curves *2b* and *2c*) and 5 K min^{-1} (curves *1*, *2a*, and *3–5*) α is the degree of conversion of the specimen).[58,59]

The thermal decomposition of the compound $C_{16.1}BrF_{9.3}$ has been studied[109] with heating at a rate of 10 K min^{-1} in argon and with the specimen kept for 1 h in nitrogen at 513, 573, and 713 K. It was shown that the decomposition takes place stepwise. Processes involving the oxidative fluorination of the graphite skeleton and leading to the expansion of the lattice in the direction of the c axis take place in the first stage. The new phase is formed in the second stage (at 713 K and above) and decomposes destructively at 833–863 K and above with formation of gaseous fluoro-derivatives of carbon having unsaturated and saturated compositions[110] and also an amorphous carbon residue.

Table 6. The energy characteristics (the apparent activation energies E_a, the enthalpies ΔH, and the entropies ΔS) of the solid-phase transformations and the enthalpies of thermal decomposition along the section E–F (ΔH^*) in the thermostimulated processes in GLC.[57–60,111–114]

Compound	Medium	E_a, kJ mol^{-1}		Solid phase transformations		ΔH^*, kJ mol^{-1}
		section C–D	section E–F	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	
$C_{6.8}FeCl_3$ (stage 1)	sealed tube	—	—	—	—	14.4
	air (argon)	—	—	—	—	85
	vacuum	—	—	—	—	93
$C_{7.7}FeCl_3$ (stage 1)	sealed tube	—	—	0.13±0.03	0.3±0.1	—
	vacuum	4.4±0.7	26±4	—	—	—
$C_{11.63}FeCl_3$ (stage 2)	sealed tube	—	—	2.78±0.41	6.1±1.2	19.5
	air (argon)	—	—	—	—	94
	vacuum	12.2±1.8	32.4±4.2	—	—	106
$C_{6.36}CuCl_2$ (stage 1)	vacuum	—	23±1	—	—	—
$C_{7.73}CuCl_2$ (stage 1 and 2)	sealed tube	—	—	—	—	75
	air (argon)	—	—	—	—	115
	vacuum	—	29±2	—	—	170

Note. The sections are indicated in Fig. 8 and have been assigned to definite thermoinitiated processes.

A number of studies[57–60,111–114] have been devoted to the investigation of the kinetics, thermodynamics, and mechanism of the pyrolysis of GLC and layered compounds of carbon fibres (LCCF) with iron(III), copper(II), and other metal chlorides by dynamic thermogravimetric measurements (TG), quantitative DTA combined with X-ray diffraction and chemical analysis, time of flight mass spectrometry, and Mössbauer spectroscopy. It was shown that the GLC with $CuCl_2$ ($FeCl_3$) begin to undergo thermal decomposition at relatively low temperatures (460–500 and 320–350 K respectively) and that the physicochemical parameters of the linear pyrolysis depend on a number of experimental factors: the degree of dispersion of the GLC particles, the mass of the sample, the rate of heating of the specimens, the gaseous environment (vacuum, inert gas, air), the external pressure, and the nature of the carbon matrix [Zaval'evsk graphite, carbon fibres based on cellulose hydrate, polyacrylonitrile (PAN), etc.] (Figs. 7–11 and Table 6). When the GLC are heated, hydrogen chloride and water, present in the materials (at the defects in the graphite skeleton and at the edge molecules of the intercalated chlorides) by virtue of the methodological features of the synthesis,[115] are removed initially (section A–B in Fig. 8 corresponds to this process for the GLC with $FeCl_3$). It was found that the stage 2 GLC have a somewhat higher thermal stability than the stage 1 compounds, but that their main thermal degradation occurs approximately within the same temperature limits as for the pure salts, which indicates a low strength of the bond between the layers of the graphite matrix and the intercalated component. On passing from GLC to LCCF, the thermal stability of the compounds falls somewhat, being lower for the LCCF based on a cellulose hydrate than for the LCCF based on PAN (cf. Figs. 9 and 11). It was established that, when the GLC with $FeCl_3$ is heated to 800 K, $FeCl_3$ ... # from them at T > 370 K (section C–D in Fig. 8), while at higher temperatures $FeCl_3$ dissociates in the interplanar space within the graphite skeleton into $FeCl_2$ and in Cl_2 with formation of a GLC with $FeCl_2$ and the removal of Cl_2 (section E–F in Fig. 8). This conclusion agrees with other data[22,24,90,116,117] but conflicts with the results of Solozhenko et al.[56] The possible causes of the discrepancies between the two sets of data in Refs. 57–60 and 56 may be, in particular, different experimental conditions, different type and degree of dispersion of the initial graphite, etc.

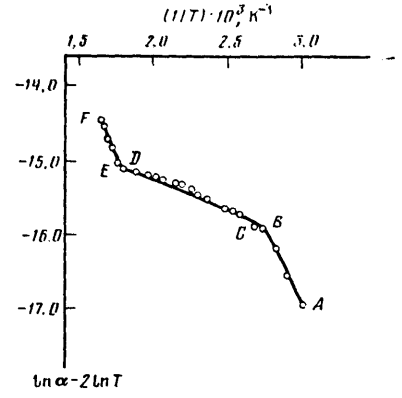


Figure 8. A typical form of the dependence of $\ln \alpha - 2\ln T$ on $1/T$ for the linear pyrolysis *in vacuo* of the GLC with $FeCl_3$ used[58,59] to estimate the apparent activation energies.

Several studies of the properties of LCCF have been published in recent years. Oshima et al.[118] obtained LCCF with $CuCl_2$, consisting of a mixture of stage 1 and 2 compounds, and demonstrated by electrical resistivity measurements that the LCCF with $CuCl_2$ are stable in air up to 450 K.

The compounds formed on interaction of gaseous fluorine and lithium fluoride with graphite materials of different nature (natural and pyrolytic graphite as well as carbon fibres) and having the composition $C_xF(LiF)_y$ (where x and y are 9–13 and 0.1–0.002 respectively for graphite) have been investigated by X-ray diffraction, ^{19}F NMR, thermogravimetric analysis (TGA), and conductimetric measurements.[119] The thermal stability in air was a maximum for the compounds obtained from carbon fibres: the LCCF decomposed at 680 K (a decrease in mass and an endothermic reaction were recorded at this temperature), while the compounds based on natural graphite decomposed at 537 K. We may note that, after

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prolonged exposure to air at room temperature, the specimens obtained from carbon fibres underwent reversible changes (manifested, in particular, by a decrease of their resistivity).

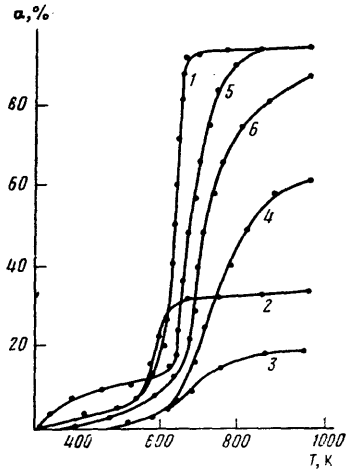


Figure 9. TGE curves for $CuCl_2$ (curve *1*) and LCCF with $CuCl_2$ based on viscose (curves *2* and *5*) and PAN (curves *3–6*) and the compound $C_{6.35}CuCl_2$ (curve *4*) *in vacuo* (curves *1–4*) and in air (curves *5* and *6*); α is the degree of decomposition of the test specimen; heating rate 5 K min^{-2}.[112]

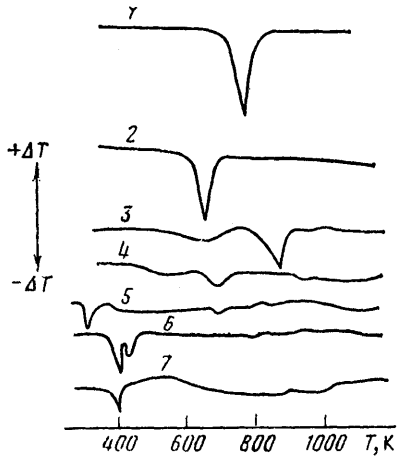


Figure 10. DTA curve for $CuCl_2$ (curves *1* and *2*), the compound $C_{6.35}CuCl_2$ (curves *3* and *4*), and the LCCF with $CuCl_2$ [based on viscose (curves *5* and *7*) and PAN (curve *6*)] *in vacuo* (curves *2*, *4*, and *5*), in argon (curves *1*, *3*, and *6*), and in air (curve *7*); heating rate 5 K min^{-1}.[112]

By measuring the temperature variation of the resistivity of LCCF with $FeCl_3$ and $CuCl_2$ ($4 < T < 600$ K), Endo et al.[120] showed that the desorption of the intercalated component from the compound is not observed up to ~513 K (for $CuCl_2$) and 613 K (for $FeCl_3$). It was also found that both LCCF are stable in air. A LCCF with potassium has been synthesised[121] and its electrical properties have been investigated. The authors[121] established the formation of compounds with different stage indices in the case of the LCCF and also found that the LCCF with potassium undergo the same phase transformations as the layered compouds of potassium with synthetic graphite, although the transition temperature and the rate of transformation can differ for different materials.

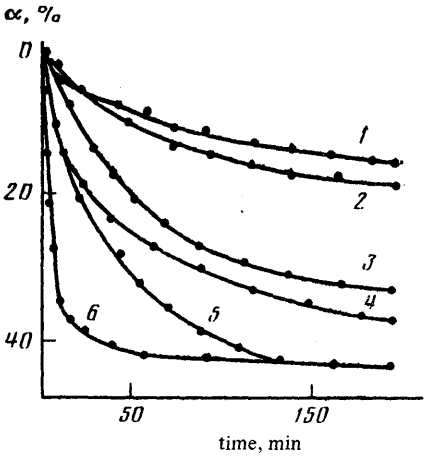


Figure 11. Dependence of the degree of decomposition (α, %) of specimens of the LCCF with $CuCl_2$ based on viscose (curves *1*, *2*, *5*, and *6*) and the compound $C_{6.35}CuCl_2$ (curves *3* and *4*) on the duration of their heat treament *in vacuo* at different temperature (K): 1) 523; 2) 548; 3) and 5) 573; 4) and 6) 623.[112]

The intercalation of certain strong acceptors (AsF_5, SbF_5, SO_3, and HSO_3F) and their mixtures in carbon fibres and the electrical properties of the resulting LCCF have been studied.[122] It was shown that the LCCF with AsF_5, enclosed in a Teflon envelope, retained their thermal stability up to 373 K. Natarajan et al.[123] investigated the electrical properties of LCCF with ICl, Br_2, and $CuCl_2$ and showed that the LCCF with $CuCl_2$, which are stable in air, retain their themal stability up to 373 K. Dziemianowicz and Forman[124] investigated the properties of LCCF with certain acceptors (nitric acid, $AlCl_3$, and $FeCl_3$). It was noted that both chlorides form LCCF with different stage indices. In contrast to the data of Endo et al.,[120] Dziemianowicz and Forman[124] noted that the LCCF with $AlCl_3$ and $FeCl_3$ are extremely unstable in air (they are rapidly and irreversibly hydrated and drying of the hydrated product does not lead to the reformation of the initial LCCF).

In the above studies the compounds were investigated under the usual pressure. Solozhenko and Kalashnikov[82] investigated the behaviour of GLC with $FeCl_3$ at high pressures (2 to 8 GPa) and temperatures (300–2000 K) showed that the observed decomposition reactions of the stage 1 compound can be described by means of the scheme

$$\text{GLC with } FeCl_3 \text{ (stage 1)} \rightarrow \text{GLC with } FeCl_3 \text{ (higher stages)} + FeCl_3$$
$$\downarrow \qquad\qquad \downarrow\uparrow$$
$$FeCl_3 + C(\text{graphite}) \qquad FeCl_2 + 0.5Cl_2.$$

As was in fact suggested by the authors,[82] the decomposition of the GLC with $FeCl_3$ at high static pressures and temperatures then proceeds via a qualitatively different mechanism than in the case of high dynamic pressures.

We may note that, according to a number of data,[61,125,126] the removal of the intercalated components of the GLC does not necessarily require heating and has been observed for a number of compounds even at room temperature. Thus Hwang et al.[125] investigated the behaviour of the stage 1 compound C_8Cs, whilst it was maintained *in vacuo* (10^{-9} mmHg, room temperature) for a week. It was shown that caesium is removed from the GLC, which leads to the appearance of a multiphase structure in which the size of the domains is ~1 μm. By measuring the Mössbauer effect, it was demonstrated[126] that, after prolonged (up to 1 year) exposure to air of the specimens of the GLC with $FeCl_3$ corresponding to stage indices, the following phenomena were observed: an appreciable decrease of the iron content [and hence of iron(III) chloride] in the specimens; in the case of the specimens containing a certain number of vacancies, $FeCl_3$ was converted into the $FeCl_4^-$ ions; after the formation of the $FeCl_4^-$ ions, the GLC specimens with individual stage indices were converted into disordered substances.

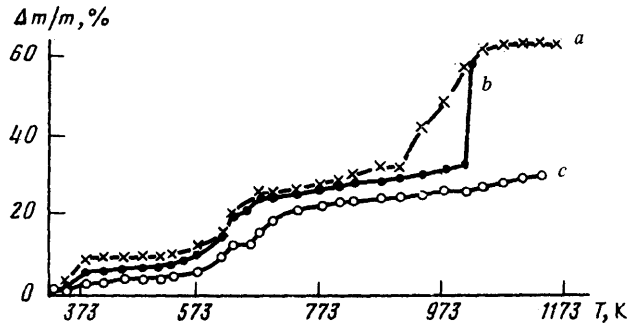


Figure 12. TGA curves for the GLC with $FeCl_3$: *a*) freshly prepared; *b*) after storage in air; *c*) after storage (the maximum weight loss for the stage 1 GLC is 65%).[61]

An extensive study of the behaviour of the GLC with $FeCl_2$ and $FeCl_3$ under different conditions (in particular, during storage, heating, and treatment with water and various solvents) has been carried out[61] by the gravimetric, X-ray diffraction, electron microscope, and Mössbauer spectroscopic methods[61] (Fig.12). Two main types of processes were observed: a gradual conversion of the initial compound into GLC with higher stage indices or direct removal of the component intercalated in the graphite skeleton. A mechanism of the possible reactions occurring when the GLC are kept in air for a long time (up to 40 days) was put forward[61] and it was shown that the products of the decomposition of the compound are iron(II) and iron(III) chloride hydrates and oxide hydrates, disordered graphite, etc.

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It is seen from the results presented above that, despite the apparently large number of data on the physicochemical properties of GLC which have been published in recent years, there are no systematic data of this kind for the majority of the compounds.

A future systematic study of the physicochemical properties of GLC over a wide range of temperatures and pressures will be necessary and it will be desirable to carry out a simultaneous combined study of various properties on identical specimens, since it has been demonstrated that many properties of GLC depend on the previous history of the specimens (in particular, on the duration and conditions of their storage). The latter factor makes it necessary to approach the comparison of data obtained by different investigators with much caution and makes it essential to take into account the form of the graphite matrix in the compound.

Unfortunately, there are very few data on the thermophysical and thermodynamic properties of GLC, the need for which (especially for accurate data) is great. It is desirable that the relevant communications should present the results of the chemical analysis of the compounds (and should not simply indicate the stage index of the GLC, as is being done at the present time in many investigations), because certain properties of GLC depend on whether the given compound is saturated or unsaturated. The lack of information about the formula composition of the test substances frequently makes it difficult to both interpret the data obtained and to compare the results of different investigations with one another. The accumulation of reliable data on the physicochemical properties of GLC will permit further progress in the elucidation of the relation between their structure and properties.

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