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Formation of a surface graphite monolayer and intercalationlike compound in the La/graphite system under thermal annealing

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Formation of a graphite monolayer and an intercalationlike compound at the surface of the La/graphite system annealed at temperatures between 180 °C and 900 °C was studied by C 1*s* photoemission, high-resolution electron energy loss spectroscopy as well as by low energy electron diffraction. After annealing at temperatures above 600 °C an accumulation of C at the surface takes place in the form of ''zig-zag'' chains with atomic arrangement similar to that in cis- and trans-polyacetylene molecules. With increasing temperatures, these chains are transformed, first into chains of closed hexagons and then into a complete graphite monolayer on the top of the underlying La carbide. At elevated temperatures above 850–900 °C, formation of a thin surface layer of a La-derived intercalationlike compound occurs.

I. INTRODUCTION

Recently it has been shown by a series of PE (photoemission),[1–9] AES (Auger electron spectroscopy),[1–3,8] and HREELS (high resolution electron energy loss spectroscopy)[10,11] experiments that the deposition of rare-earth (RE) metals onto (0001) surface of graphite with subsequent annealing at certain temperatures (T_{anneal}) in the region of 300–1100 °C leads to formation of chemical phases with electronic and crystalline structures similar to those observed for alkali-graphite intercalation compounds (GIC's).[12,13] Annealing of the RE/graphite systems based on divalent RE metals (Yb, Eu) at temperatures of 300–400 °C is followed by diffusion of RE atoms into the graphite matrix and formation of conventional GIC's.[8] Contrary to that, annealing of the RE/graphite systems involving trivalent RE metals (La, Dy, Gd) up to temperatures of 600–800 °C leads to destruction of the graphite chemical bonds and formation of carbide phases on underlying bulk graphite.[3,6,9] Only annealing of the above systems at elevated temperatures (900–1100 °C) results in recovering of the graphitelike chemical bonds at the surfaces and formation of surface phases with GIC-like valence-band electronic structure.[1–6,9] Detailed analysis of the high-temperature annealed La/graphite system by valence-band[6] and C 1*s* core-level[5] PE as well as by HREELS[10,11] showed that this system has a layered arrangement, which can be described as a thin layer with GIC-like structure [or even one monolayer of graphite (MG)] on the top of (111) surface of La dicarbide.[5] In other words, for the La/graphite system (as well as for Gd/graphite and Dy/graphite structures) growth of the surface GIC-like phase undergoes a stage of carbide formation.

We are interested now in studying a way of formation of this GIC-like surface phase or graphite monolayer on the top of La carbide, in particular, how the transition of the system from the carbide phase to the GIC(MG)/$\mathrm{LaC_2}$(111) occurs. In order to get insight into this problem, in the present work we investigate changes of C 1*s* PE and HREELS spectra as well as modifications of LEED (low energy electron diffraction) patterns of the La/graphite system in a wide range of annealing temperatures.

As a result we derive the following sequence of the La-carbon phases transitions: Step-by-step annealing of the system at temperatures up to 550–600 °C leads to strong intermixing of carbon and lanthanum atoms and, finally, to formation of La-carbide phase terminated by La atoms with hexagonal surface structure and stoichiometry close to LaC. At annealing temperatures above 600 °C accumulation of carbon atoms on the surface takes place in a chemical state different from that both in graphite and carbide phases. We conclude that the segregated carbon forms ''zig-zag'' chains with an arrangement of atoms similar to that in cis- and trans-polyacetylene molecules. Upon further increase of annealing temperatures concentration of the carbon atoms on the surface increases. Thereby, the ''zig-zag'' chains are transformed continuously into chains of closed C hexagons and, then, into a net of such hexagons. This stage is finished at $T_{\mathrm{anneal}} = 800\,^{\circ}\mathrm{C}$ by formation of a complete graphite monolayer on the top of underlying La carbide. At annealing temperatures above 850 °C a transition from the MG to a thin layer of La-GIC takes place at the surface of the system.

II. EXPERIMENTAL DETAILS

The experiments were conducted in two different ultrahigh vacuum (UHV) chambers with CLAM and ELS 22 HREELS spectrometers allowing one to carry out measurements of C 1*s* core-level PE and vibrational excitations spectra, respectively.

The HREELS experiments were performed with an ELS

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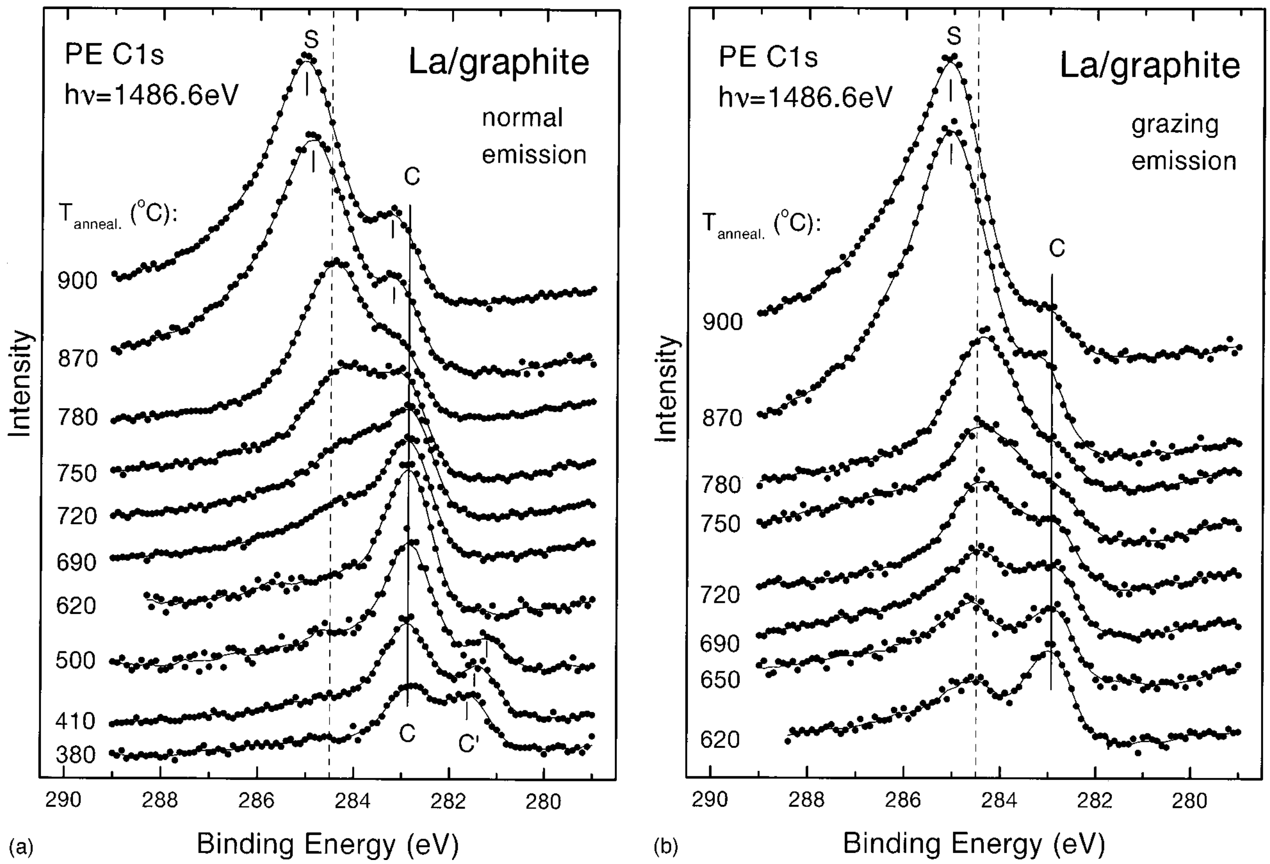

FIG. 1. C 1*s* spectra of the La/graphite system measured in the normal (a) and grazing (b) emission geometry after annealing at different temperatures. Energy positions of different components (**S**, **C**, and **C**′) are marked by solid lines. Energy position of the C 1*s* peak for pristine graphite is shown by a dashed line.

22 HREELS spectrometer consisting of two double cylindrical 127° deflectors. HREELS spectra were taken with a primary electron energy (E_p) of 20 eV and an energy width of the elastically reflected beam of about 8–10 meV. Further description of experimental details of the HREELS experiments can be found in Ref. 10. The C 1*s* PE spectra were measured at the normal emission and grazing emission angle of 70° relative to the normal surface using a standard CLAM analyzer and a x-ray tube as a source of photons with $h\upsilon = 1486.6$ eV (Al K_α line). Base pressure in the experimental setups during measurements was better than 5×10^{-11} mbar. Both experiments were conducted under same conditions of the sample preparation. A correlation between results of the PE and HREELS studies was established on the basis of characteristic line shapes of C(KVV) Auger signals (as in Ref. 3) and structure of LEED patterns measured in both cases.

Deposition of La onto graphite substrates were performed by evaporation from pieces of La metal welded onto a W-Re wire (HREELS setup) or inserted in a Mo crucible that was heated by electron bombardment (CLAM setup). Thickness of the deposited La films as monitored using quartz microbalances. In both experiments thickness of the deposited La overlayers was in the range of 300 Å.

Substrates for the experiments were natural flakes of graphite with high degree of crystallinity as it was seen from the measured sharp (1×1) hexagonal LEED patterns characteristic for (0001) surface of graphite. They were cleaved using adhesive type in ambient atmosphere and heated in UHV to 1200 °C for several hours. Temperature of the samples in the HREELS chamber was controlled by a Ni-NiCr thermocouple. In the CLAM setup the sample temperature was determined by an optical infrared pyrometer corrected for the emission brightness of graphite. As a result of this correction characteristic temperatures determined in this work are lower by approximately 100 °C than those reported in some of our earlier publications.[1–4]

III. EXPERIMENTAL RESULTS

A. C 1*s* spectra

Figure 1 displays the C 1*s* photoemission spectra for the La/graphite system after annealing at different temperatures between 380 °C and 900 °C measured in the normal (a) and grazing (b) emission geometry. In the figure the energy position of the C 1*s* peak for pristine graphite is indicated by a dashed lines. Almost all C 1*s* spectra shown in Fig. 1 display two-component line shapes. The individual components are marked as **C**, **C**′, and **S**. Changes of their intensities for the normal emission geometry and characteristic values of binding energies (BE's) are presented in Fig. 2(a) and Table I, respectively. Corresponding variations of the intensity ratio between C1*s* and La 4*d* PE signals defined as amplitude of the peaks ($I_{\mathrm{C}\,1s}/I_{\mathrm{La}\,4d}$) are shown in logarithmic scale in Fig. 2(b). As it can be seen from the analysis of the C 1*s* spectra (Fig. 1), three distinct regions of annealing temperatures can be distinguished.

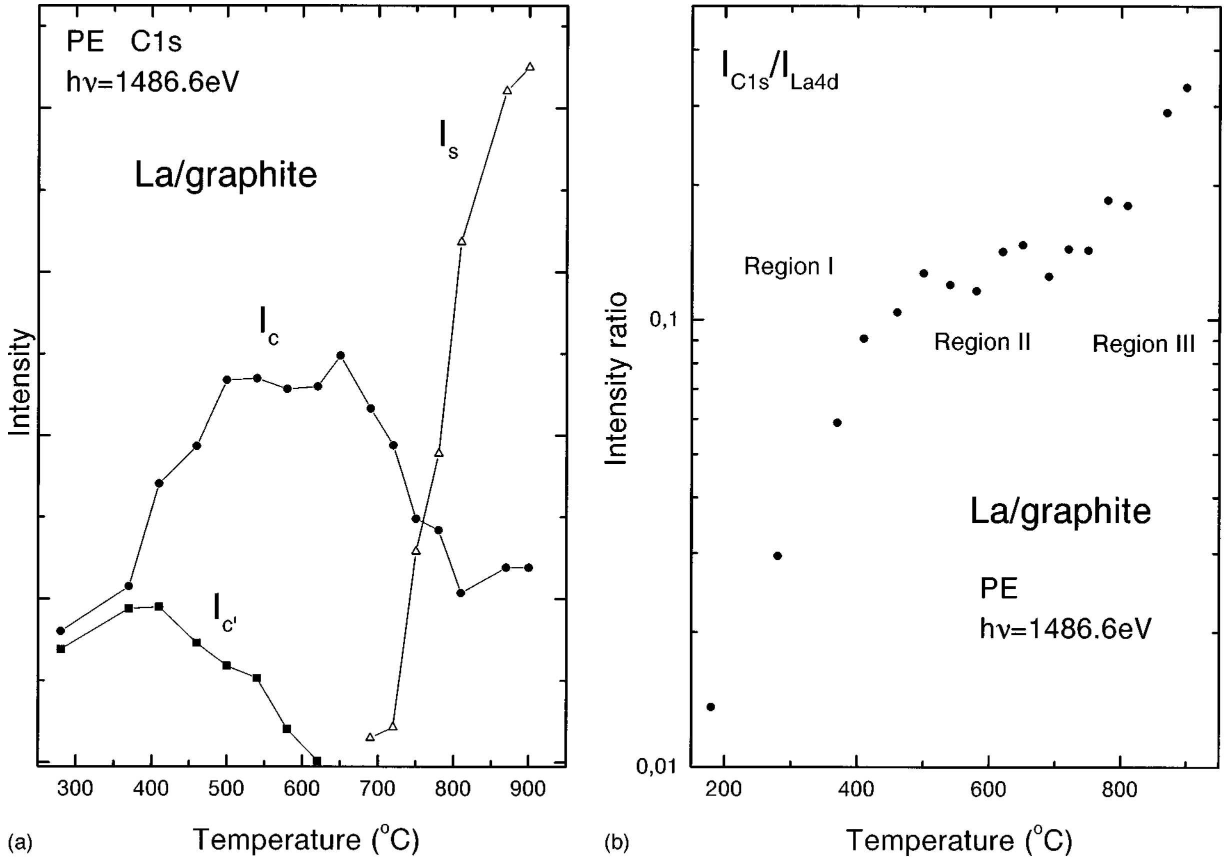

FIG. 2. (a) Intensities (I_C, $I_{C'}$, and I_S) of individual components (**C**, **C**′, and **S**) of the C 1*s* spectra and (b) $I_{C\,1s}/I_{La\,4d}$ intensity ratio depending on annealing temperature of the La/graphite system.

In the region of annealing temperatures (lower than 550–600 °C) the spectra in Fig. 1(a) are characterized by two components (**C** and **C**′) with the BE's of 282.7–282.9 eV and 281.2–281.5 eV, respectively. According to Ref. 6 feature **C**′ is related to the La(M_2VV) Auger peak. Upon increase of annealing temperatures intensity of component **C**, first, continuously increases [Fig. 2(a)]. Thereby, this structure is slightly shifted toward higher BE's. Intensity of the second component (**C**′) decreases beginning from T_{anneal} ~400 °C until it becomes completely quenched at temperatures of 550–600 °C.

After annealing at temperatures of about 600 °C the normal emission spectra are mainly characterized by single pronounced peak **C** at 282.9–283.0 eV BE. As it can be seen in

TABLE I. Energy positions of various structures in C 1*s* PE and HREELS spectra as well as types of LEED patterns for the La/graphite system after annealing at selected temperatures. Asterisk indicates structures of weak intensities.

	Graphite	Region I LaC (La terminated)		Region II LaC (with C chains or MG)			Region III GIC/LaC$_2$
Method	RT	280 °C	550 °C	650 °C	775 °C	800 °C	900 °C
PE		281.5	281.2				
(eV)		282.7	282.9	282.9	283.0	283.0	283.3
	284.5			284.3*	284.4	284.4	285
HREELS				45	45*		
(meV)				65	65*		
	110			110–130			
	195					180	180
				205	205	205	
LEED	(1×1)	$(\sqrt{3}\times\sqrt{3})R30°$ rel. to pattern of graphite		''star''-like $(1\times4)R30°$ rel. to patterns in regions I			$(\sqrt{3}\times\sqrt{3})R30°$ rel. to pattern of graphite

Fig. 2(b), the ratio of C 1*s* to La 4*d* peak intensities enhances continuously upon increase of annealing temperatures. This shows growth of total concentration of carbon and intermixing of carbon and lanthanum atoms close to the surface of the system. The ratio $I_{\mathrm{C}\,1s}/I_{\mathrm{La}\,4d}$ measured at $T_{\mathrm{anneal}}=550-600\,°\mathrm{C}$ and normalized to the corresponding photoionization cross sections[14] amounts to approximately 1 that corresponds to a stoichiometry close to LaC. Carbon 1*s* PE peaks with similar line shapes and BE's as presented for $T_{\mathrm{anneal}}=620\,°\mathrm{C}$ in Fig. 1 are typical for carbides of *d* metals [for instance, TaC and HfC (Refs. 15–17)]. Therefore, we identify component **C** as carbide-derived. This assignment is in agreement with the conclusion derived in our earlier works[1–3] on the basis of PE and AES experiments.

Annealing of the La/graphite system at temperatures between 500 °C and 750 °C [region II in Fig. 2(b)] reveals significantly slower increase of the $I_{\mathrm{C}\,1s}/I_{\mathrm{La}\,4d}$ intensity ratio than that during the previous stage of the thermal treatment. At these annealing temperatures, an additional features (**S**) appears at the high-BE side of the C 1*s* spectra. The intensity of this component sharply increases with annealing temperature and reaches values comparable with that for carbide-derived component **C** at $T_{\mathrm{anneal}}\sim750\,°\mathrm{C}$. Its BE (284.4 eV), that is similar to the BE of the C 1*s* peak in graphite, does not change within the temperature region II. As it can be seen in Fig. 2(a) the absolute intensity of carbide-derived component **C** decreases with the growth of intensity of component **S**. C 1*s* spectra taken at the grazing emission angle [Fig. 1(b)] are characterized by a similar two-component structure located at the same binding energies as that observed in the corresponding C 1*s* normal emission spectra [Fig. 1(a)]. We underline, however, that for any annealing temperature intensity of high energy component **S** relative to intensity of component **C** in the case of the grazing emission geometry is higher than that measured at the normal emission. After annealing at 620 °C feature **S** is already monitored in the grazing emission signal, although it is still not present in the spectrum taken in the normal emission geometry.

Annealing of the La/graphite system at temperatures higher than 750–800 °C leads again to a significant increase of the $I_{\mathrm{C}\,1s}/I_{\mathrm{La}\,4d}$ ratio measured in the normal emission geometry [region III in Fig. 2(b)]. This increase is clearly attributed to the behavior of high-energy component **S** that, in contrast to the previous stages of thermal treatment, provides now a dominant contribution into the PE spectra. Further suppression of the low-energy carbide-derived component is monitored in this temperature region. Besides that, energies of both high- and low-energy components shift toward higher BE's to about 284.9–285.0 eV and 283.2–283.3 eV, respectively (Fig. 1 and Table I).

B. LEED experiment

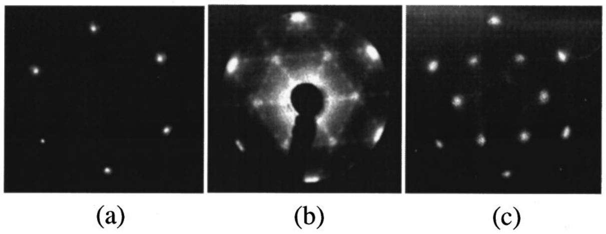
FIG. 3. LEED patterns ($E_p=70$ eV) for (a) pristine graphite, (b) the La/graphite system after annealing at 750–800 °C, and (c) 900 °C.

Figure 3 shows general trend of LEED pattern changes ($E_p=70$ eV) when going from graphite to the intermediate carbide-derived phase ($T_{\mathrm{anneal}}=775-800\,°\mathrm{C}$) and further to the high-temperature phase ($T_{\mathrm{anneal}}=900\,°\mathrm{C}$). The LEED pattern in Fig. 3(a) reveals hexagonal (1×1) structure characteristic for (0001) surface of monocrystalline graphite. The high-temperature phase is characterized by a $(\sqrt{3}\times\sqrt{3})R30°$ LEED superstructure relative to that measured for graphite [Fig. 3(c)]. Note, that such type of LEED patterns is typical for light alkali- and RE-derived GIC's (Refs. 12 and 7,8, respectively). The LEED from the intermediate carbide-derived phase [Fig. 3(b)] displays ''star''-like image with hexagonal $(1\times4)R30°$ [or $(1\times2\sqrt{3})$] superstructure relative to the structure observed for the low-temperature carbide phase [Fig. 4(a)].

LEED patterns ($E_p=30$ eV) observed in the range of annealing temperatures of 550–800 °C are presented in Fig. 4. This region is characterized by appearance of component **S** in the C 1*s* spectra. The first image shown in Fig. 4(a) represents a LEED obtained after annealing of the system at the temperature of 550 °C. This LEED pattern reveals a weak hexagonal structure corresponding to the significantly reduced Brillouin zone (BZ), which is rotated by 30° relative to the BZ of (0001) graphite surface. Increase of annealing temperature up to 650 °C [Fig. 4(b)] leads already to formation of a ''star''-like $(1\times4)R30°$ hexagonal superstructure [compare to Fig. 4(a)] with pronounced strips along the high symmetry directions. Further annealing of the system up to temperatures of 775–800 °C [Fig. 4(c)] does not change the symmetry of the LEED pattern. It causes, however, a conversion of the strips into spots. Annealing at temperatures of about 850–900 °C leads to disappearance of the $(1\times4)R30°$ superstructure and transformation of the pattern into that characteristic for GIC's [see Fig. 3(c)]. The observed symmetries of the LEED patterns are also summarized in Table I.

C. HREELS spectra

The corresponding change of HREELS spectra taken in the specular direction for the La/graphite system annealed at temperatures of 550–850 °C are shown in Fig. 5. Energies of main features of the HREELS spectra are collected in Table I. As it was noted before, these annealing temperatures cor-

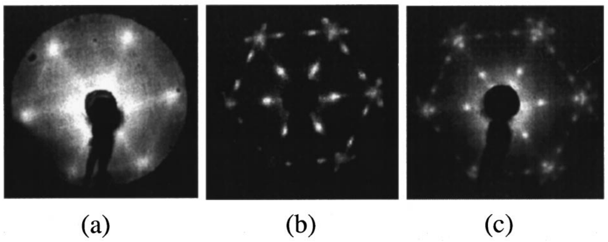
FIG. 4. LEED patterns ($E_p=30$ eV) for the La/graphite system after annealing at (a) 550 °C, (b) 650 °C, and (c) 750–800 °C.

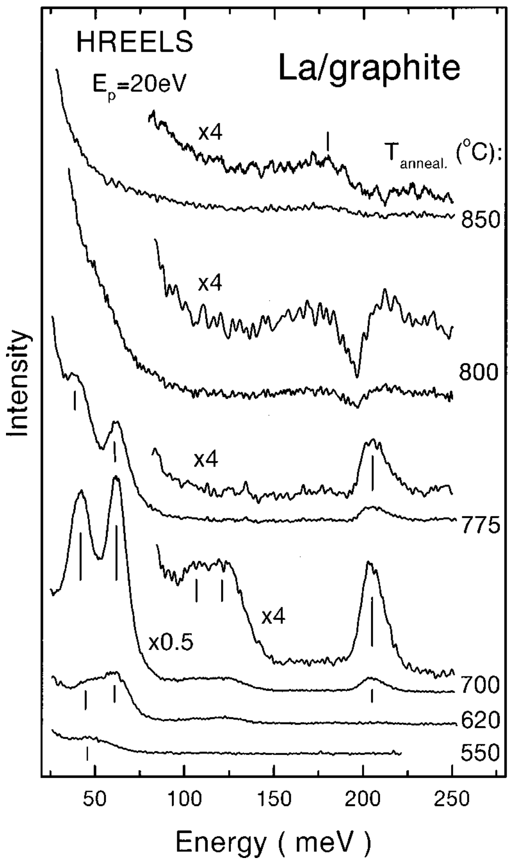

FIG. 5. HREELS spectra measured in the specular direction ($E_p = 20$ eV) for the La/graphite system after annealing at different temperatures.

respond to the appearance and growth of signal **S** in the C 1*s* spectra. Specular HREELS spectra measured at annealing temperature lower than 550 °C (region I) do not display any visible features. With increasing temperature a number of growing peaks appears, however, in the energy distribution curves. The spectra in the range of temperatures 620–775 °C (region II) are characterized by two pronounced peaks at 45 meV and 65 meV, one peak at 205 meV and a number of weak features in the region of 100–130 meV. All these peaks reveal almost no dispersion (for comparison, see also Ref. 10). These features appear in the spectra after annealing at the temperature of 620 °C, reach their maximal intensities at temperatures of 650–750 °C and disappear almost completely from the spectra at the temperature of 800 °C. At the latter temperature the feature at the loss energy of 205 meV is transformed into a structure with a dip and two broad maxima on its both sides occupying the energy region between 160 and 210 meV. It is interesting to note that the dip is observed only for scattering angles around the specular direction. At scattering angles of more than 10° weak features with graphitelike dispersion can be distinguished in the spectra. At annealing temperatures above 850 °C (region III) the line shape of the spectra becomes fully graphitelike with a characteristic peak at the energy of 185–190 meV ‘‘softened’’ due to interaction with the substrate and displaying pronounced dispersion.[10,11]

IV. DISCUSSION

As it can be seen from the analysis of the C 1*s* spectra (Figs. 1 and 2, Table I), the annealing at temperatures up to 550–600 °C leads to a sharp increase of the relative concentration of carbon close to the surface of the La/graphite system. We conclude that at these temperatures intense intermixing between carbon and lanthanum occurs followed by formation of carbidelike phase, in agreement with results of our earlier PE (Refs. 3 and 6) and AES (Refs. 1–3) experiments. The energy of main feature **C** in the C 1*s* spectra measured in the present work (Fig. 1) and the shape of the spectra after annealing at 550–600 °C are also similar to that observed for monocarbides of *d* metals.[15–17]

The HREELS spectra at these annealing temperatures (region I, $T_{\mathrm{anneal}} < 550\,^{\circ}\mathrm{C}$) do not display any visible features. Since HREELS is very sensitive to the presence and chemical state of carbon at the surface of solids,[18] we can conclude that despite the intense intermixing with lanthanum atoms there are no carbon atoms on the top of the system. It means that the obtained at this stage of thermal treatment carbide is terminated by La. As we concluded in the previous section the stoichiometry of the carbide phase formed at 550–600 °C is close to LaC. This fact together with the hexagonal LEED pattern allows us to ascribe the system to La monocarbide with (111) surface terminated by La. Note that also (111) surfaces of monocarbides of *d* metals are usually terminated by metal.[17] The possibility of existence of La monocarbide as well as its electronic and crystalline structure are discussed in Ref. 19.

At annealing temperatures of 550–600 °C, the process of intense intermixing of carbon and lanthanum atoms is completed. The intensity of carbide-derived component **C** in the C 1*s* spectra is almost saturated. Further annealing of the La/graphite system (region II, $T_{\mathrm{anneal}} > 600\,^{\circ}\mathrm{C}$) leads to the appearance and growth of high-BE component **S** located at 284.4 eV BE. Carbon 1*s* spectra measured at the grazing emission geometry display higher intensity of this component relative to contribution of component **C** in comparison to that in the spectra taken at the normal emission. The latter discloses surface origin of structure **S**. The growth of this component with increasing annealing temperature indicates accumulation of carbon atoms at the surface of the system. The BE of feature **S** is located in the energy region characteristic for C 1*s* emission in graphitelike structures (dashed line in Fig. 1) or, e.g., in hydrocarbon molecules with CC chemical bonding.

The nature of the chemical bonds formed between carbon atoms on the surface can be understood from the analysis of the HREELS spectra. The formation of pronounced features after annealing at temperatures above 600 °C (Fig. 5) confirms the accumulation of carbon atoms at the surface. However, the chemical state of the accumulated carbon atoms differs from both graphite- and carbidelike ones. According to Refs. 20 and 21, CC single, double, and triple bonds in hydrocarbon molecules (such as butadiene, propylene, polyacetylene, etc.) are characterized by groups of clearly separated vibrational frequencies in the regions around 960, 1650, and 2100 cm^{-1} (120, 200, and 260 meV, respectively). Therefore, the pronounced peak at the energy of 205 meV in the HREELS spectra in Fig. 5 ($T_{\mathrm{anneal}} = 600-775\,^{\circ}\mathrm{C}$) is caused by the formation of the double C═C bonds, whereas the structures in the region of 100–130 meV can be assigned to the single C—C bonds. For these annealing temperatures neither angle-resolved valence-band PE (Refs. 3 and 6) nor

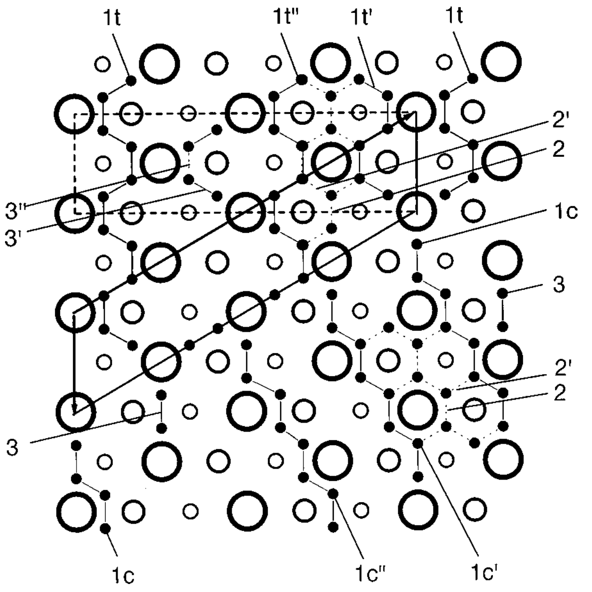

FIG. 6. Arrangement of the carbon atoms (black dots) accumulated on the surface of the La/graphite system in the form of (i) ''zig-zag'' chains (pos. 1*c*, 1*t*, and pos. 1*c*′, 1*c*″, 1*t*′, 1*t*″) and their possible transformation with annealing temperature into chains of closed hexagons (pos. 2, 2′), as well as (ii) CC dimers (pos. 3, 3′) and their transformation into ''zig-zag'' chains (pos. 3″). Large open circles show La atoms in the topmost atomic layer, whereas middle-size and small open circles indicate C atoms in the second and the third atomic layers, respectively.

HREELS (Refs. 10 and 11) experiments display dispersion of the measured features. All experimental facts noted above can be satisfactorily understood assuming that the second stage of thermal treatment results in formation on the surface of carbon structures characterized by individual C═C and C—C chemical bonds, which are clearly different to arrangement in hexagonal graphite. As a model arrangement we propose ''zig-zag'' carbon chains with an arrangement of carbon atoms similar to that observed in cis- and trans-polyacetylene molecules.[22] Possible coordination of the carbon chains on the La-terminated (111) surface of La carbide is shown in Fig. 6 [pos. 1*t* (trans) and 1*c* (cis)].

The assumption on formation of the chains of carbon atoms is further supported by the ''star''-like character of the observed $(1\times 4)R30^\circ$ [or $(1\times 2\sqrt{3})$] LEED images [Figs. 3(b), 4(b), and 4(c)]. The corresponding elemental cells are shown in Fig. 6 by thick solid (arrows) and dashed lines. Such type of LEED patterns can be interpreted as induced by the chains formed in three equivalent directions at the (111) hexagonal surface of La carbide with a period four times larger than that of the La atoms in the topmost layer of carbide. The above model of the ''zig-zag'' chains formation can also explain the experimental fact of unchanged sixfold symmetry of the LEED patterns in the range of annealing temperatures from 650 °C through 800 °C, when already graphitelike structures are observed in PE (Refs. 3 and 6) and HREELS (Refs. 10 and 11) spectra. With increasing concentration of the carbon atoms at the surface upon annealing the chains occupy positions 1*t*′, 1*t*″ and 1*c*′, 1*c*″ that does not change the structure of the LEED pattern. Some of these ''zig-zag'' chains are transformed into chains of benzene-like rings (pos. 2, 2′ in Fig. 6) forming eventually a net of closed hexagons and finally a complete graphite monolayer coverage.

Transition graphite-carbon ''zig-zag'' chains takes place during high-temperature transformation of carbon from graphite into cumulene carbyne. A mechanism of this transformation is described in Refs. 23,24. In our case we have a reverse situation: Formation of the graphite monolayer from the ''zig-zag'' chains, which have the structure similar to that of cumulene carbyne chains, possibly stabilized by interaction with the underlying La carbide. From this point of view it is interesting to compare the HREELS spectra observed in the present work with infrared spectra of carbynes reported in literature.[25,26] Infrared spectra of cumulene form of carbyne are characterized by two regions of high intensity: 1000–1400 and 1500–1700 cm^{-1} (125–175 and 185–210 meV, respectively).[25] According to Refs. 25 and 26 (and references therein) a feature in the region of 1600 cm^{-1} (~200 meV) is fundamental for cumulene carbynes and might be an indicator of formation of carbynelike structures. It correlates actually with the 205-meV feature in the HREELS spectrum in Fig. 5. The latter observation evidents that carbon ''zig-zag'' chains assumed in the present work can be considered to be analogous to cumulene carbynelike chains. This conclusion increases furthermore an interest to the studied phenomena.

Here, we have to note, theoretical evaluations[27] show that for closed carbon-atom overlayers at (111) surfaces of *d* metals [in particular Ni(111)] formation of benzenelike rings is the most energetically favorable possibility as compared to any other carbon arrangements. However, the situation can be different for the initial annealing stage of the La/graphite system, when the amount of carbon atoms on the surface is significantly lower than one monolayer. Moreover, at (111) surfaces the distance between La atoms in La carbide[5] is significantly larger than that between *d*-metal atoms in elemental solids. Then, the formation of C═C dimers or bridges located between neighboring La atoms (pos. 3, 3′ in Fig. 6) might be more favorable. These positions of carbon atoms ensure their efficient interaction with La atoms that is important taking into account a possibility of strong chemical bonding between these two elements. Upon growth of the surface concentration of carbon the amount of such dimers increases. They begin to interact with each other (pos. 3″ in Fig. 6) forming, first, the carbon ''zig-zag'' chains and, then, the chains of closed hexagons.

Other pronounced features observed in the HREELS spectra at the energies of 45 and 65 meV (region II, $T_{\mathrm{anneal}} = 600-775\,^\circ\mathrm{C}$) can also be assigned within the proposed model. If the structures at 205 and 130 meV correspond to oscillations along the C═C and C—C bonds,[20,21] the features at 45 and 65 meV can be related to chemical bonds between the surface carbon atoms and the La-carbide substrate. At the initial stages of the carbon chains formation these bonds have partial carbidelike character due to strong interaction between the lanthanum and surface carbon atoms and large distances between the carbon chains. Therefore, the corresponding vibrational frequencies are found in the energy region characteristic for bulk phonons of *d*-metal carbides.[28,29] With the increase of the surface carbon concentration and the intensification of the CC interaction upon formation of the graphite monolayer the contribution of these carbidelike bonds is reduced.

Further increase of annealing temperatures above 800 °C leads to a sharp enhancement in the C 1*s* PE spectra of surface-derived signal **S** at the cost of carbide-derived emission **C** (Figs. 1 and 2). The ratio of the intensities of these components becomes even higher than that observed for systems with a monolayer of graphite on the top of (111) surfaces of transition-metal carbides.[15,16] For these systems the low-energy and high-energy components in the C 1*s* spectra taken at the normal emission geometry have comparable intensities. As compared to lower T_{anneal}, the energy positions of features **S** and **C** are shifted now toward higher BE's (see Fig. 1 and Table I). The above experimental observations indicate that the chemical state of the carbon atoms at the surface as well as carbon atoms in the carbide phase are changed from that characteristic for the previous stage of thermal treatment. We assume that at annealing temperatures above 800 °C two processes take place simultaneously in the system. On the one hand, a transition presumably from the low-temperature LaC carbide phase to the high-temperature $\mathrm{LaC_2}$ carbide phase occurs. This type of La carbide is more stable at elevated temperatures according to a La-C phase diagram[30] and is just the one assumed in our earlier studies of the high-temperature phase of La/graphite systems.[5,6] On the other hand, as it follows from the increase of the relative intensity of component **S**, the monolayer of graphite at the surface of the system is developed into a thin layer of surface intercalationlike compound. The possibility of existence of an intercalationlike phase with a $\mathrm{LaC_6}$ stoichiometry and crystalline structure characteristic for conventional GIC's was theoretically analyzed in Ref. 31. It was shown that for La-C systems with thicknesses of several monoatomic layers the heats of formation of the $\mathrm{LaC_6}$ and $\mathrm{LaC_2}$ phases become comparable, that would allow, indeed, the growth of a thin layer of GIC-like structure on the top of (111) surface of $\mathrm{LaC_2}$. Note only a minimal mismatch between lattice parameters of graphite layer and (111) surface of β-modification of $\mathrm{LaC_2}$.[5,31]

V. CONCLUSIONS

As it follows from the performed PE, HREELS, and LEED studies, thermal annealing of the La/graphite system in the temperature range between 180 °C and 900 °C leads to a series of phase transitions involving formation of bulk carbides and the surface intercalation compound. Thereby, the low-temperature treatment ($T_{\mathrm{anneal}} < 550-600\,^{\circ}\mathrm{C}$) causes intense intermixing of carbon and lanthanum atoms followed by formation of LaC carbide phase with (111) surface terminated by La. Increase of annealing temperatures ($600\,^{\circ}\mathrm{C} < T_{\mathrm{anneal}} < 800\,^{\circ}\mathrm{C}$) results in continuous accumulation of carbon atoms in the topmost layer of the system. These carbon atoms are supposed to form, first, ordered ''zig-zag'' chains with an atomic arrangement similar to that in cis- and trans-polyacetylene molecules. Upon growth of carbon concentration at the surface, the carbon ''zig-zag'' chains are transformed into chains of closed hexagons. Finally, at annealing temperatures of about 775–800 °C these hexagon chains are combined into a net of hexagons, and a complete graphite monolayer is formed on the top of (111) surface of the La carbide. Last stage of the high-temperature annealing ($T_{\mathrm{anneal}} > 800-850\,^{\circ}\mathrm{C}$) leads to a carbide-phase transition, presumably from LaC to $\mathrm{LaC_2}$, and to formation of a thin layer of graphite intercalation compound on the top of the system.

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