

Evidence for a C₆₀ Monolayer Intercalated between a Graphite Monolayer and Iridium

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High-resolution Auger-electron spectroscopy has revealed intercalation of a graphite monolayer on iridium by C₆₀ molecules from a thick deposited film, which occurs at $T \sim 800$ K. At $T \sim 1200$ K, the C₆₀ molecules contacting with iridium under the graphite film breakup. The carbon thus formed migrates at 1600 K to the opposite side of the Ir ribbon undergoes graphitization at 1900 K, and desorbs at 2200 K.

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It is well known that layered materials such as graphite or transition dichalcogenides can be intercalated, i.e., interleaved, by guest atoms. A slightly different intercalation process was recently observed [1,2] for the first time: A monolayer of graphite was deposited on an Ir substrate (Ir-C) and then exposed to a potassium vapor. In this case, the potassium atoms diffuse to the edges of the graphite islands and penetrate the gap between film and substrates to form an intercalated K layer. Subsequently it was shown that the graphite monolayer on metals (Ir, Re) can be intercalated by a number of atoms: K, Cs, Ba, Pt, Si, C, etc. [3], and a mechanism of the phenomenon was proposed [4]. Depending on the ionization potential of the intercalate, low (Cs, K, Ba, etc.) or high (Pt, Si, C, etc.), two types of intercalate films can form under the graphite monolayer (Fig. 1). The first type is illustrated by the Cs atoms which, on adsorption on Ir-C at 300 K, intercalate with efficiency $\chi = 0.5$, forming at the completion of adsorption a *monolayer* of intercalated Cs with a concentration $N \sim 4 \times 10^{14} \text{ cm}^{-2}$. Intercalation of the second type is illustrated by the Pt atoms on Ir-C; following adsorption on Ir-C at 1000 K, the Pt atoms intercalate with an efficiency $\chi = 1$, a *multilayer* intercalate film forming under the graphite monolayer.

Iridium as a substrate is convenient in that it does not dissolve surface carbon and does not form surface and bulk carbides. We have found conditions at which monolayer graphite films can be produced on the surface of many metals, e.g., Ir, Re, Mo, Ni, and Pt, and have shown that they are also intercalated by atoms. Part of these results were published in Refs. [3] and [5], a review [6] covering the relevant research fully. We would like to point out that intercalation by atoms of a graphite monolayer deposited on metals is a specific kind of intercalation exhibiting both common features with, and substantial differences from, the bulk graphite intercalation discussed in Refs. [5–8].

This work was aimed at studying the possibility of Ir-C intercalation by the C₆₀ molecules rather than atoms. The recently discovered family of pure carbon molecules forming fullerenes [9] with remarkable properties is of

considerable scientific and applied interest. This interest is still increasing after the development [10] of a technique for developing this material in macroscopic amounts. A fundamental study of the interaction of fullerene molecules with the surface of solids to be performed in this work has only begun [11].

We have studied thin ($h = 20 \mu\text{m}$) textured Ir ribbons with the (111) face dominating at the surface. The graphite monolayer was produced by exposing the iridium heated to 1800 K to benzene [3]. The C₆H₆ molecules do not break up on the valence-saturated surface of the graphite monolayer, so that its thickness remains unchanged. We developed a source of C₆₀ molecules by depositing a solution of C₆₀ molecules in toluene repeatedly on a thin Ta ribbon. A mass spectrometer study showed such a heated ribbon to emit a flux of C₆₀ molecules under UHV conditions. The iridium surface with the deposited carbon was studied with high-resolution ($\Delta E/E \sim 0.1\%$) Auger-electron spectroscopy. The C Auger spectrum from a thick film of C₆₀ molecules

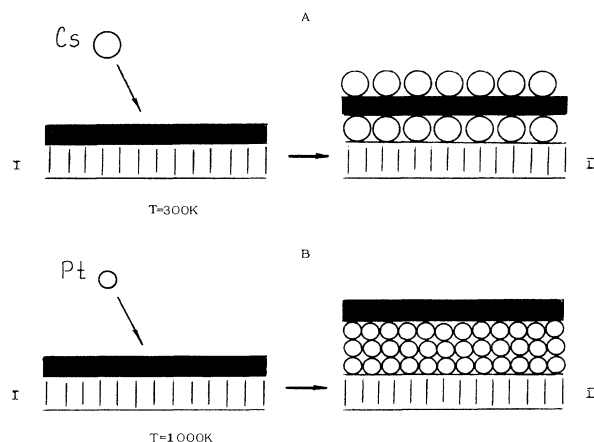


FIG. 1. Two types of intercalation by atoms of a graphite monolayer deposited on metals. (A) Atoms with low ionization potentials (Cs, K, Ba, ...). (B) Atoms with high ionization potentials (Pt, C, Si, ...). Film structure before (I) and after (II) intercalation. ■: graphite monolayer, □: metal.

on iridium was shown [12] to have a characteristic shape (Fig. 2) different from that of the C Auger spectra of most other carbon materials such as diamond, mono- or polycrystalline graphite, and metal carbides. Thus, C_{60} can be easily distinguished and identified by Auger-electron spectroscopy.

The surface coverage by C_{60} molecules was calibrated by their evaporation from a thick C_{60} film on Ir occurring at $T < 650$ K; in the range $650 < T < 750$ K, a constant concentration N_M of C_{60} was maintained on iridium which reduced by roughly a factor of 4 the Auger peak of iridium (a graphite monolayer with $N_c = 3.9 \times 10^{15} \text{ cm}^{-2}$ reduces the iridium Auger peak 1.6 times). Since, by calculations, three graphite monolayers also reduce the iridium Auger peak by $(1.6)^3 \approx 4$ times, and neglecting the difference between the C atom distribution in C_{60} and in graphite, we roughly evaluate the concentration of the adsorbed molecules on iridium as $N = 3 \times 3.9 \times 10^{15} \text{ cm}^{-2} \approx 12 \times 10^{15} \text{ C}_{at}/\text{cm}^2 = 2 \times 10^{14} \text{ C}_{60}/\text{cm}^2$. This concentration corresponds to a dense filling by the C_{60} molecules of the adlayer, since the area occupied by one molecule is $\sim 7 \text{ \AA} \times 7 \text{ \AA} = 49 \text{ \AA}^2$, yielding for the molecule concentration in a dense monolayer $10^{16} \text{ \AA}^2/49 \text{ \AA}^2 \approx 2 \times 10^{14} \text{ C}_{60}/\text{cm}^2$.

To study the intercalation on Ir-C, the C_{60} molecules were deposited at 300 K to the concentration N_M , suppressing the iridium Auger peak by 4 times. Next the ribbon temperature was raised stepwise. Up to $T \leq 700$ K,

fullerene practically does not desorb. At 800 K the iridium and carbon Auger signals have recovered fully which implies complete desorption of C_{60} molecules from the adlayer. Hence C_{60} does not break up on a passive Ir-C surface and does not intercalate it.

After this, a thick film of C_{60} to a concentration $3N_M$ was deposited on Ir-C at 300 K [Fig. 3(A)]. The iridium Auger peak dropped to zero [Fig. 4(B)], while the Auger peak of carbon exhibited the "fullerene" shape with energy 269 eV [spectrum 1 in Fig. 4(A)]. Heating of this film to 800 K produced a surprising result, namely only a fraction of the C_{60} molecules desorbed, their major part having penetrated under the graphite sheet and remained there in the intercalated state up to the record-high temperature $T \leq 2200$ K [Fig. 3(B)]. The zero iridium Auger signal after the penetration of the C_{60} molecules under the graphite plane [Fig. 4(B)] suggests that the fullerene filling factor was not less than a monolayer. Carbon Auger peak [spectrum 2 in Fig. 4(A)] has shape and energy ($E = 271$ eV) are intermediate between "fullerene" and "graphite" ones, perhaps as the result of superposition of Auger peak from graphite layer ($E = 272$ eV) and from fullerene film under it ($E = 269$ eV). Apparently at $T \leq 800$ K the graphite monolayer is intercalated by undecomposed C_{60} molecules which in the range $900 < T < 1200$ K break up into carbon atoms in contact with iridium [Fig. 3(C)] just like they did in our study of their break up on heated iridium and carbon Auger peak [spectrum 3 in Fig. 4(A)] and had a shape similar to graphite polycrystal (see spectrum 2 in Fig. 2).

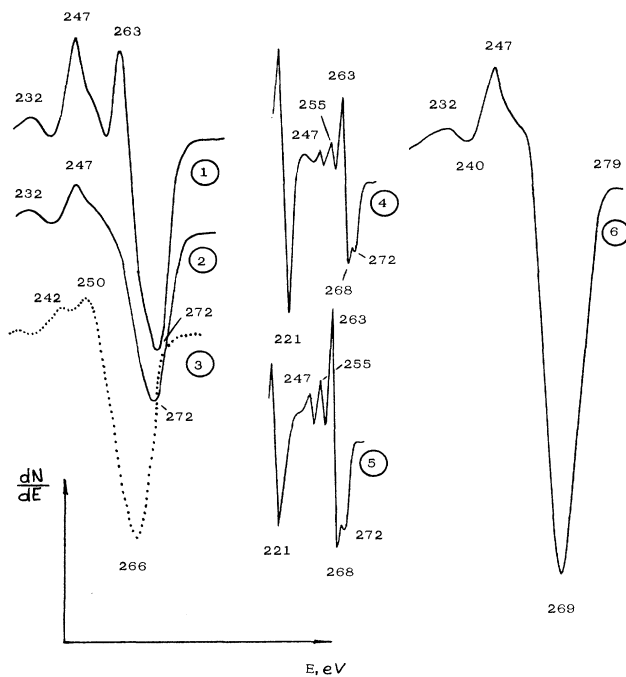


FIG. 2. Auger spectra of carbon from mono- (1) and polycrystalline (2) graphite, diamond (3), surface carbide MoC (4), surface carbide MoC on bulk carbide Mo_2C (5), and C_{60} molecules film ($\sim 50 \text{ \AA}$ thick) on iridium (6).

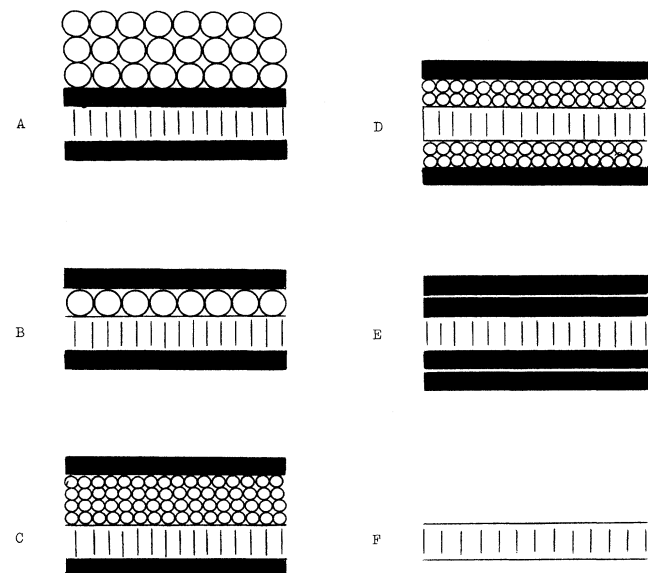


FIG. 3. Scheme of the intercalation of a monolayer graphite film on iridium by C_{60} molecules from a thick deposited film. \bigcirc : C_{60} molecule, \bigcirc : C atom, \blacksquare : graphite monolayer, \square : iridium ribbon. Iridium ribbon temperature (K): A -300, B-800, C-1200, D-1600, E-1900, and F-2200.

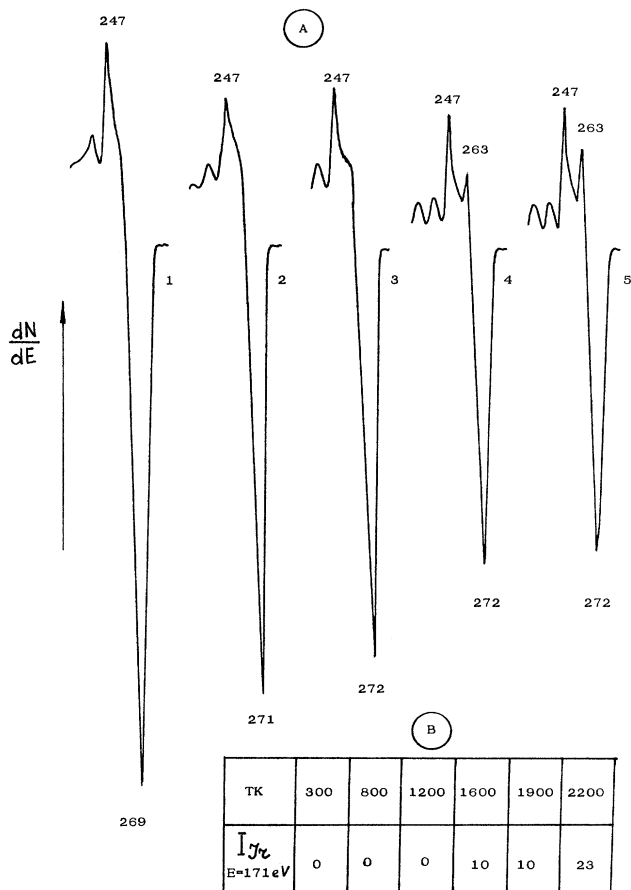


FIG. 4. (A) Auger spectra from adsorption system $C_{60}/Ir-C$ at various annealing temperatures, $T(K)$: 1–300, 2–800, 3–1200, 4–1600, and 5–1900. (B) Intensities of iridium Auger peaks (in arbitrary units) versus annealing temperature of $C_{60}/Ir-C$ system. The initial state of the system is 3 monolayers of C_{60} molecules deposited on a graphite monolayer on iridium at $T = 300$ K.

In the range $1400 < T < 1600$ K, the Auger signal of carbon decreases somewhat, and that of iridium appears (Fig. 4). We associate this with the migration of intercalated carbon to the opposite side of the iridium ribbon [Fig. 3(D)]. This was confirmed by direct experiments on carbon migration over iridium. A shape of carbon Auger peak [spectrum 4 in Fig. 4(A)] become close to that of graphite monocrystal (spectrum 1 in Fig. 2). In the range $1600 \ll T < 2100$ K the Auger peak of iridium becomes again reduced by about a factor of ~ 2.3 through carbon [Fig. 4(B)]. Finally, at 1900 K the carbon Auger peak has shape [spectrum 4 in Fig. 4(A)] typical to graphite monocrystal (spectrum 1 in Fig. 2), showing that probably all intercalated carbon has graphitized. A thickness of graphite film is ≤ 2 monolayers (2 monolayers diminish Auger signal of Ir in $(1.6)^2 \approx 2.6$ times, in our case it is diminished in 2.3 times). Increasing T to its maximum value 2200 K leads to carbon thermodesorption and Ir surface purificates.

Thus, the C_{60} molecules adsorbed in the form of a thick overlying film (in contrast to an adlayer) intercalate the graphite monolayer on iridium. The molecules contained at the base of the thick film are apparently “covered up” and cannot desorb from under the higher lying C_{60} layers, and it is these molecules that intercalate the monolayer graphite film on the metal. Thus, the possibility of intercalating monolayers of graphite deposited on metals (Ir, Re) by various atoms (Cs, K, Ba, Pt, Si, C, ...), as previously shown by the present authors, is now expanded by a new effect: the intercalation of Ir-C by C_{60} molecules.

Finally there is the matter of what has been going on in the rest of the world. The first announcement of fullerene intercalation into a layer host was given by Averill *et al.*, now published in [13]. Combined intercalation of C_{60} and alkali metal into graphite is described by Fuhrer *et al.* [14]. Two theoretical papers are in the works: Saito and Oshiyama [15] and Song and Cappeletti [16].

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