# Doping mechanism of $C_{60}$ fullerene by sodium and potassium

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ESR spectra of localized states of $KC_{60}$ and $K_2C_{60}$ and conducting electrons of $K_3C_{60}$ were recorded in the process of doping $C_{60}$ by potassium. The ESR spectra of $K_xC_{60}$ ($x < 3$) and $Na_xC_{60}$ correspond to the semiconductive state of the samples.

**Key words**: fullerene, ESR, conductivity.

The surprising property of fullerides $M_3C_{60}$ (M = K and Rb) is their high conductivity and relatively high temperatures of transition to the superconducting state: 18 K for potassium and 28 K for rubidium derivatives.[1] The superconductivity of fullerides was studied in both film and polycrystalline samples. Fullerides were obtained by doping $C_{60}$ with the vapor of alkaline metals at 200—400 °C.

There are some specific features of the reduction reaction that is usual from the viewpoint of organic chemistry. The depth of a reaction in solution is determined by three factors: the electron affinity of a reduced sample, the oxidation potential of a metal, and the solvation heat of a cation. Our studies show that the depth and degree of reduction are low due to the low solubility of fullerene and reduction products.[2]

In the absence of a solvent the Coulombic energy of interaction of anions and cations in the ionic lattice (the Madelung energy[3]) is used as parameter $S$ instead of the solvation heat. According to the opinion of the authors of Ref. 4, this energy determines the higher stability of $K_3C_{60}$ compared to those of $KC_{60}$ and $K_2C_{60}$.

Potassium ions occupy one octahedral and two tetrahedral holes in the face-centered cubic lattice of $C_{60}$.[4] The parameters of $C_{60}$ and $K_3C_{60}$ lattices differ insignificantly.[5] $K_3C_{60}$, intermediate phase $K_4C_{60}$, and final product $K_6C_{60}$ were registered in the course of the reaction by various methods.[1,4—6] Almost no data on other possible products of the doping reaction have been available until now.

The thermodynamics of the process can be explained to some extent by the role of the electrostatic energy, while the reaction kinetics should be studied.

The observed reaction products could result from reactions (1) and (2).

$$KC_{60} + K_2C_{60} = K_3C_{60} + C_{60} \quad (1)$$

$$K_3C_{60} + K_4C_{60} = KC_{60} + K_6C_{60} \quad (2)$$

It is noteworthy that the elucidation of the doping mechanism is not treated here as an end in itself. Since the maximum of conductivity corresponds to the composition of $K_3C_{60}$, the realization of the exact stoichiometry is an important and technically difficult problem. Even its formal solution assumes local deviations from stoichiometry, which should inevitably result in the appearance of defects of the crystal lattice. Therefore, the control of composition of experimental samples is significant. In addition, this is possible only when the particular data on the doping mechanism and all intermediate particles and states of a specimen are available. Since ESR was chosen as a main instrument for the investigation, some physical problems related to its applicability to solid state samples should be discussed. In the reaction course, insulator $C_{60}$ is transformed into "molecular metal" $K_3C_{60}$ and then again into insulator $K_6C_{60}$. Therefore, both some localized paramagnetic centers and conducting electrons can be expected. Conducting electrons can correspond to both metallic and semiconductive phases.

The basically different temperature effect on the magnetic susceptibility of electrons in these physical states should be mentioned especially. The magnetic susceptibility of localized paramagnetic centers obeys the Curie law:

$$\chi = \frac{Np^2\mu_\beta^2}{3kT}, \quad p = g[J(J+1)].$$

In our case, $J = s = 1/2,\ 1$.

According to Fermi—Dirac statistics, the magnetic susceptibility of conducting electrons in metals is temperature independent

$$\chi = \frac{N_e\mu_\beta^2}{2kT_F},$$

where $T_F$ is the Fermi temperature.

The absolute value of the magnetic susceptibility of conducting electrons is two to three orders of magnitude

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2190—2195, November, 1995.

lower than the magnetic susceptibility of the corresponding number of localized paramagnetic centers.

In the case of a semiconductor, the value of the magnetic susceptibility depends on the number of electrons in the conductive band:

$$N_e = 2\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{(E_F - E_g)/kT},$$

where $E_F$ is the Fermi level and $E_g$ is the energy gap between the valence and conductivity bands. Since the intensity of ESR spectra is proportional to the magnetic susceptibility, the temperature effect on the spectra is an important characteristics of the physical state of samples.

## Experimental

Film and polycrystalline samples were studied. Films were prepared and doped under conditions close to those under which the conductivity was measured.[1] Films were prepared by high-vacuum sublimation of fullerene at 450 °C, and glass was used as a substrate. After applying the film onto the glass, a narrow glass plane was cut off and placed into an ESR tube. An alkaline metal mirror was in the same tube. The temperature of the film in the tube was 400 °C.

We need the film of such a thickness that the order of magnitude of the number of paramagnetic centers appeared due to reduction would correspond to the limiting sensitivity of an ESR spectrometer. An excess thickness should distort the picture of the subsequent formation of fullerides of various compositions due to the diffusion of a metal deep in the film. The thickness of the films obtained were several hundreds Å. A rough estimation of the thickness is based on taking into account of number of taken fullerene, the surface area covered with $C_{60}$, and the intensity of the ESR signal.

Somewhat different conditions were used for doping polycrystalline samples. The samples were prepared in a tube with two outlets, which was attached to a vacuum system. Polycrystalline $C_{60}$ (1 to 2 mg) was in the outlet for ESR measurements, and an alkaline metal was in the second outlet The outlet with $C_{60}$ was heated at 200 °C for 2 h. Then the alkaline metal was sublimed by the fire of a jet, and the ESR tube was sealed off.

Intensities of ESR signals were measured on a Varian E-12 spectrometer at certain intervals in the doping process, and the effect of annealing on the spectral picture was studied. A double resonator containing both the specimen studied and a standard with the $g$-factor of 2.0028, relative to which positions of studied lines were determined, was used in the spectrometer. $g$-Factors were more exactly determined on a Radiopan SE/X-2544 spectrometer equipped with a nuclear magnitometer and a wavemeter. The majority of the experiments was carried out in a Dewar quartz vessel that was either empty or filled with liquid nitrogen. A Unipan-660 type system was also used in the work for recording spectra at various temperatures.

The time of film doping was ~3 h, and the time of doping polycrystalline samples was ~2 days.

Samples were doped at the temperature gradient of 100—150 deg/10 cm, and a metal was placed in a cooler zone. When the tube was annealed, the temperature of the tube end containing the metal was 20 °C. Polycrystalline samples were doped by potassium at 220 °C and annealed at 300 °C.[5] The reaction with potassium at 220 °C lasted 42 h, and 19 measurements were carried out during this interval. Samples were annealed after 0.5, 3.5, 6, 12, 21, and 33 h. Then the reaction temperature increased to 300 and 400 °C.

Potassium and sodium were chosen, because doping by potassium results in the formation of the "metallic" phase, while doping by sodium does not. Thus, comparison of ESR spectra of potassium and sodium fullerides is of interest from the viewpoint of analysis of the physical state of samples. It is also noteworthy that there are only few works studying sodium-doped $C_{60}$.

## Results and Discussion

The results of studying the potassium-doped $C_{60}$ film are presented in Fig. 1. It is evident that spectrum I, *a* is attributable to $KC_{60}$. This assignment is based on both the arrangement of the signal relative to the standard and the sharp temperature dependence of the width of the line typical of the $C_{60}$ radical anion (spectrum I, *b*).[7]

Spectrum II, *a* contains two signals, one of which is assigned to $KC_{60}$ and the second signal is probably related to $K_2C_{60}$. Spectrum II, *b* contains virtually one signal.

The assignment of the signal, whose position coincides with that of the standard, to $K_2C_{60}$ is based on the

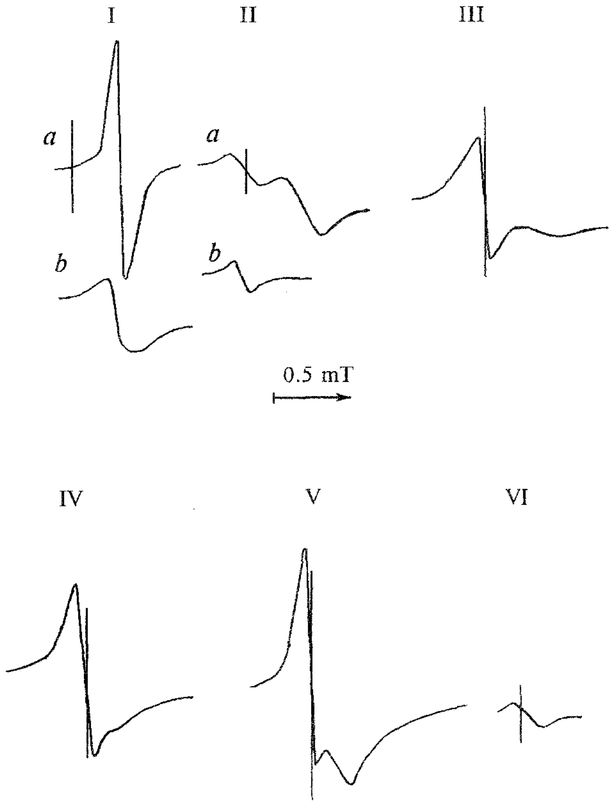

**Fig. 1**. ESR spectra of the film of potassium fullerides $C_{60}$. Reaction time, min: 20 (I*a*, II*b*), 40 (II*a*), 80 (III), 100 (IV), 160 (V), 220 (VI). Amplification: $5 \cdot 10^2$ (I*a*), $5 \cdot 10^3$ (I*b*, II—VI). Measurement temperature: 77 K (I*a*, II*a*, III—VI), 20 °C (I*b*, II*b*). The vertical line marks the position of the standard signal ($g$ = 2.0028).

sequence of its appearance. It is reasonable that the appearance of the problem explains the absence of the fine structure related to the dipole-dipole interaction of two unpaired electrons. The absence of the fine structure can be caused by the unique spherical symmetry of the triply degenerate $t_{1u}$-orbital of fullerene $C_{60}$, which is populated upon doping.

Parameters of the fine structure, $D$ and $E$, depend on the distance between two electrons with parallel spins[8]:

$$D = \frac{3}{4}g^2\beta^2\left\langle\frac{r^2 - 3z^2}{r^5}\right\rangle, \quad E = \frac{3}{4}g^2\beta^2\left\langle\frac{y^2 - x^2}{r^5}\right\rangle,$$

and the angular brackets mean averaging over the electron wave function.

For the spherical symmetry the expression

$$\langle(x^2 + y^2 + z^2 - 3z^2)/r^5\rangle$$

should be averaged to zero. The axial symmetry is sufficient for averaging $E$ to zero.

Only one publication about the fine structure observed upon reduction of $C_{60}$ in the liquid phase is known. However, the value of the fine structure absolutely does not correspond to the molecule sizes.[9]

The signal of $KC_{60}$ is almost unnoticeable in spectrum III (Fig. 1). A broad signal again appears in spectra IV and V in the strong field, and only one weak spectrum appears in spectrum VI.

The spectra of the films of sodium fullerides are presented in Fig. 2.

Spectra I and II in Fig. 2 coincide with spectra II in Fig. 1. The comparison of intensities of the lines of $NaC_{60}$ and $Na_2C_{60}$ in the spectra (see Fig. 2) shows that the amount of $NaC_{60}$ after 7 min from the beginning of the reaction is considerably higher than that of $Na_2C_{60}$, their amounts are approximately equal after 14 min, and after 29 min the amount of $Na_2C_{60}$ is considerably higher than that of $NaC_{60}$. No spectra, except the spectrum of $Na_2C_{60}$, are observed in the subsequent doping.

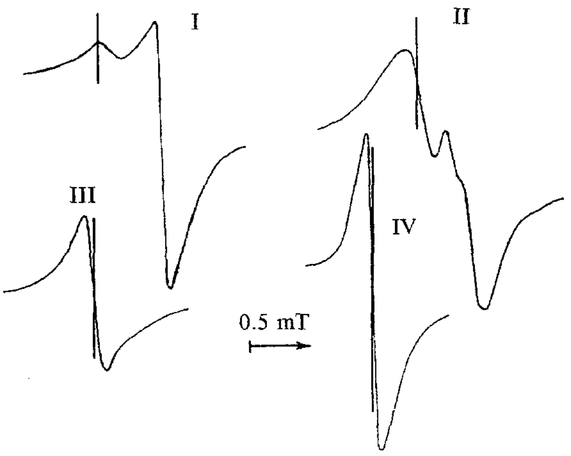

**Fig. 2.** ESR spectra of the film of sodium fullerides $C_{60}$ at 77 K. Reaction time, min: 7 (I), 14 (II), 29 (III), 167 (IV). Amplification: $5 \cdot 10^3$ (I, II), $10^3$ (III, IV).

In the reduction by potassium, a thin film of fullerene, which is hardly visible to the human eye, takes on a distinct color after saturation with the metal. The color of the film is considerably weaker upon saturation with sodium.

The comparison of the spectra of potassium and sodium fullerides exhibits the following distinctions: (1) the formation of considerably lower amounts of $K_2C_{60}$ than those of $Na_2C_{60}$; (2) spectrum V in Fig. 1 exhibits a broad signal, which is absent in the spectra of sodium fullerides; and (3) in the case of potassium, the intensity of the ESR signal sharply decreases due to the saturation of the film with the metal, and this does not take place in the case of sodium.

The first two distinctions are probably related to the fact that the "metallic" phase ($K_3C_{60}$) is formed in the reaction with potassium due to reaction (1). The third distinction is likely determined by the structure of the final reaction products.

Since no systematic temperature studies of the films were carried out, the number of the measurements were low, and the effects of annealing on reactions (1) and (2) were not studied, the exact assignment of the spectra to $K_3C_{60}$ is difficult.

The main result of the study of films is the distinct fixation of various paramagnetic centers, whose role can be discussed in terms of the supposed reaction mechanism. A more complete picture was observed due to the study of doping polycrystalline samples.

Many measurements in a milder doping regime made it possible to more distinctly distinguish various stages of the process.

The spectrum of $KC_{60}$ with the typical temperature dependence of the line width is recorded at the initial stage of the process (10—12 h). The line width between points of the maximum slope is 6 to 14 Oe at room temperature and 1.5 to 3 Oe at 77 K.

Comparison of the intensities of the ESR signals determined in the form of $\Delta H^2 L$ ($\Delta H$ is the line width and $L$ is the amplitude) at 20 °C and 77 K shows that the temperature decrease does not result in an increase in intensity, which could be expected according to the Curie law, and, on the contrary, results in a thirtyfold decrease in the initial value.

The broad signal recorded at room temperature and the narrow signal appearing at 77 K are characterized by different $g$-factors. The difference is several units in the fourth digit.

The downfield shift of the signal of $KC_{60}$ is also observed during the process. The boundary values of the $g$-factor at 77 K were 1.9995 and 2.0007.

The observed temperature changes in intensities of the spectra and in the $g$-factor assume the interaction of unpaired electrons of $KC_{60}$ in the $C_{60}$ lattice. It is likely that in $C_{60}$ $KC_{60}$ forms the semiconductive phase with closely arranged valence and conductive bands.

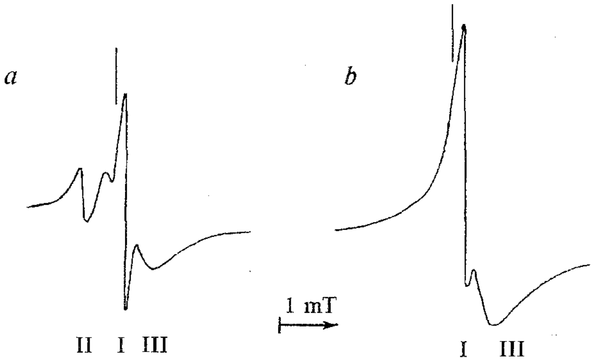

**Fig. 3.** ESR spectra of polycrystalline potassium fullerides (77 K) after 21 h of the reaction at 220 °C (*a*) and after 1 h of annealing at 300 °C (*b*).

Annealing at the initial stage does not result in any considerable changes in intensity of the ESR signal, and results only in a decrease in the values of the *g*-factor and line width. It means that reactions (1) and (2) involving only $KC_{60}$ do not take place or occur too slowly.

The next stage is characterized by several signals in the ESR spectra. The spectrum recorded after 21 h of the reaction is presented in Fig. 3, *a*. Line II is assigned to $K_2C_{60}$ ($g = 2.0053$). The assignment of line III to a certain localized center is not so evident.

The result of one-hour annealing after recording the spectrum (Fig. 3, *a*) is shown in Fig. 3, *b*. It is seen that it does not contain line II, and the intensity of line III has increased compared to line I. The changes observed satisfactorily correspond to the participation of primary fullerides in disproportionation reaction (1), if it is assumed that line III is related to conducting electrons of $K_3C_{60}$. This assumption is confirmed by the results of subsequent doping.

It is of interest to compare our observations of annealing with the data of studying $K_{1.5}C_{60}$ by the $^{13}C$ NMR method.[4] Annealing at 350 °C for 24 h results in a substantial increase in the amplitude of the signal of $K_3C_{60}$ compared to that of $C_{60}$. The authors relate these changes completely to the line width of $K_3C_{60}$, and this is unnoticeable from the spectrum. The approximately twofold increase in the amplitude of the signal of $K_3C_{60}$ could be a result of reaction (1). It is evident that $KC_{60}$ and $K_2C_{60}$ type paramagnetic products, which could be a reason for increase in the intensity of the signal of $K_3C_{60}$, cannot be registered by the NMR method.

The ESR spectra, which are recorded in 1.5 h of the reaction after recording the spectra presented in Fig. 3 (*a* and *b*), are presented in Fig. 4. The spectral picture is changed sharply.

The comparison of spectra *a* and *b* in Fig. 4 shows that their intensities slightly depend on temperature, which is characteristic of conducting electrons in metals.

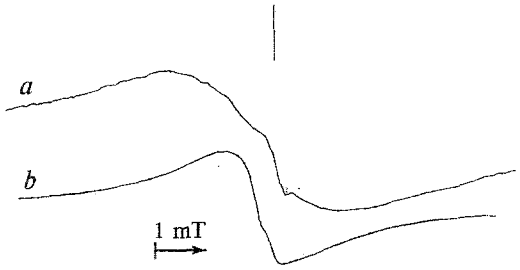

**Fig. 4.** ESR spectra of polycrystalline potassium fullerides after 22.5 h of the reaction at 220 °C: *a,* 20 °C, amplification $2 \times 10^3$; *b,* 77 K, amplification $2 \times 10^2$.

It is likely that the reason for the sharp transition from one spectral picture to another is that the next portion of a metal eliminates defects in the face-centered lattice of $K_3C_{60}$ and causes the transition from the semiconductive to the metallic phase.

A low intense narrow line registered against the background of the line of $K_3C_{60}$ testifies in favor of some heterogeneity of the sample. It is likely associated with the product of reaction (2), $KC_{60}$. Subsequent doping (see Fig. 5) results in an increase in the intensity of the narrow line and a decrease in the intensity of the broad line. At the end of the process the broad line decreases approximately by an order of magnitude compared to the initial value.

The formation of $K_3C_{60}$ is reversible. Prolonged annealing (for 6 h) results in the isolation of a metal on the cool surface of the tube. The *b* type spectrum (Fig. 4) is transformed into the spectrum presented in Fig. 3, *b*. Further doping resumes *status quo*.

Two kinds of $NaC_{60}$ particles, which differ by the values of g-factors, are observed at the beginning of doping polycrystalline $C_{60}$ by sodium. The spectrum recorded after 6.5 h of the reaction at 300 °C is presented in Fig. 6. The intensities of these signals depend on the time of doping, annealing, and the temperature of recording the spectra. The difference in symmetry of the holes occupied by sodium cations can be one of the

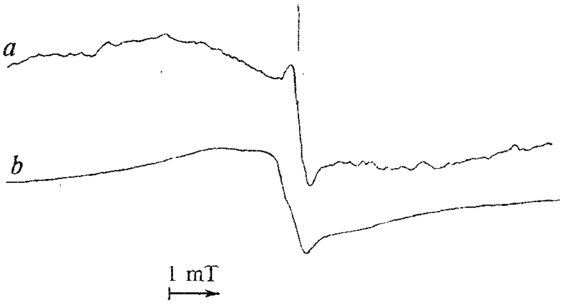

**Fig. 5.** ESR spectra of polycrystalline potassium fullerides after 42 h of the reaction at 220 °C and 3 h of the reaction at 300 °C: *a,* 20 °C, amplification $5 \times 10^3$; *b,* 77 K, amplification $5 \times 10^2$.

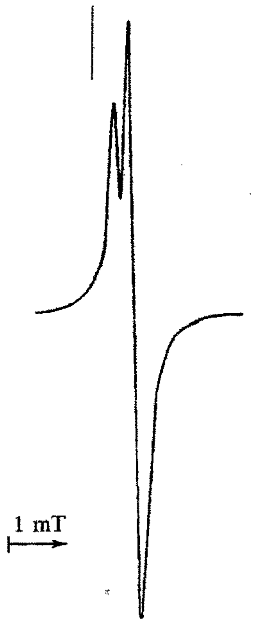

**Fig. 6**. ESR spectra of polycrystalline sodium fullerides (77 K) after 6.5 h of the reaction at 300 °C.

reasons for the change in the g-factors of $NaC_{60}$. The Coulombic energy of the interaction between the fullerene anion and sodium cations depends on their mutual arrangement. The value of the *g*-factor of $NaC_{60}$, whose line lies in the strong field, is equal to 2.0007. The absence of the spectra similar to those presented in Fig. 4 is the main difference between the ESR spectra of $Na_xC_{60}$ and $K_xC_{60}$.

The signals of $Na_2C_{60}$, whose positions relative to the standard are the same as those of $K_2C_{60}$, which disappear during annealing, are observed in the middle of the process.

Since doping by sodium provided no evidences for the formation of the metallic phase, more careful temperature studies were carried out to reveal the physical state of $Na_xC_{60}$. After 18 h of the reaction at 220 °C, the study of ESR spectra of $Na_xC_{60}$ were carried out at 77 K and within the temperature range from 180 to 380 K.

The line width at 77 K is 1.2 Oe and 7 Oe at 310 K. The intensity of the signal at 77 K is approximately by 20 times lower than at 310 K.

The spectra recorded at various temperatures are presented in Fig. 7. The distinct picture of the disappearance of some paramagnetic centers and appearance of another centers is observed. A small downfield shift of the narrow signal relative to the broad signal testifies that the structures of these centers differ.

The study of the line width and amplitude of the signal within the 310 to 380 K temperature range shows that these values are almost unchanged.

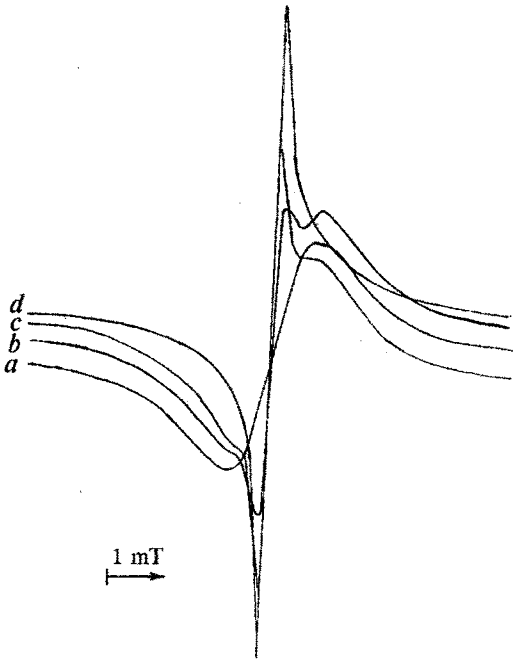

**Fig. 7**. Temperature dependences of the ESR spectra of polycrystalline sodium fullerides after 6.5 h of the reaction at 300 °C and 18 h of the reaction at 220 °C: 310 (*a*), 298 (*b*), 290 (*c*), and 280 K (*d*).

The picture obtained fits well the semiconductive model of $Na_xC_{60}$. The sharp decrease in the intensity of the signal as the temperature decreases is probably related to the transition of conducting electrons to the valence band. The strict treatment of the data is difficult, because the spectra recorded are the superposition of the signals from conducting electrons and localized unpaired electrons. It is evident that the value of the energy gap between the valence and conductive bands is of the order of $kT$ at 300 K, *i.e.*, ~0.01 eV.

The further process at 300—400 °C does not result in basic changes in the intensity of the signal. Therefore, it can be supposed that $x < 6$ in the case of $Na_xC_{60}$, unlike the final product of the reaction with potassium, $K_6C_{60}$.

Thus, the study of film and polycrystalline potassium-doped $C_{60}$ samples made it possible to fix certain amounts of primary fullerides and confirm the previously supposed[3] reaction of their transformations into $K_3C_{60}$. The possibility of controlling the state of samples by ESR is also shown.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 93-03-4101). The work was performed under terms of the interindustry program "Fullerenes and Atomic Clusters."

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*Received February 10, 1995;*
*in revised form September 28, 1995*