Study of ESR spectra of fullerene C_{60} doped with magnesium and mercury

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An increase in the intensity of the ESR signal and of its g value was observed in the course of annealing of the diamagnetic product of the reaction between magnesium amalgam and a toluene solution of C_{60}. The formation of a crystalline substance Mg_xC_{60} with semiconductor properties was assumed. The ESR spectra of the products of vapor-phase synthesis of MgC_{60} and Hg_xC_{60} were recorded.

Key words: fullerene, ESR; conductivity.

The high conductivity of fullerides M_3C_{60} (M = K, Rb) and their superconductivity at low temperatures[1] have stimulated investigations of compounds of fullerene C_{60} with other metals.

The efficiency of ESR spectroscopy techniques in determining the structure of various fullerides[2] was shown for compounds of C_{60} with Na and K. Values of g-factors change depending on the M_xC_{60} composition; the conductive, semiconductive or dielectric nature of the samples causes different temperature dependences of the intensity of ESR signals.

The main difficulty in applying the vapor-phase method to synthesis of fullerides of most metals (except for alkali metals) is associated with the high boiling temperatures of metals. The fact that other metals have higher reduction potentials than alkali metals should also hinder the formation of fullerides.

To overcome the first of the above-mentioned problems we attempted to use a pseudo liquid-phase system and a magnesium amalgam as a reducing agent of C_{60} in a toluene solution. The reason for applying this procedure was to use ammonia as a solvent to obtain M_3C_{60} (M = K, Rb, Cs) compounds.[3] The most important stage of M_3C_{60} synthesis according to this procedure was annealing of the reaction products after the removal of ammonia. If the fraction of the superconductor phase before annealing was <0.1%, after annealing it reached 100%.

Experimental

Two amalgams differing in magnesium content (and, hence, in viscosity) were used to reduce C_{60}. The reaction was carried out in an evacuated system consisting of a reaction vessel and an ESR tube.

The first specimen for investigation of the effect of annealing on the ESR spectrum of Mg_xC_{60} was obtained by interaction between a solution of C_{60} in toluene and an amalgam with a small amount of magnesium (which was characterized by low viscosity). The reaction was performed by shaking the solution with a milled amalgam for a short time at room temperature. The formation of mobile mercury was the sign that the reaction was complete.

The second specimen was obtained by interaction between a saturated solution of C_{60} (1 mL) and a viscous amalgam for 4 h at 80 °C. Stirring of the solution with amalgam was achieved by the boiling toluene. The color of the C_{60} solution turned brown.

In the course of preparation of the first specimen, toluene was distilled from the ESR tube by cooling the reaction vessel with liquid nitrogen with the resulting formation of a deposit of dry products on the walls of the ampule. In the second case, the precipitate was decanted in a metering branch. In both cases, the residual solvent was removed from the ESR tube by heating it in a tube furnace at 200 °C with simultaneous cooling of the reaction vessel by liquid nitrogen for 1 h. Then the ESR tube was sealed off.

The annealing time was 5 h at 220 °C and 11 h at 500 °C in the first case and 36 h at 500 °C in the second case. The recently reported[3] annealing time of the reaction products was 24—48 h at 375 °C.

To check for the possible participation of mercury in the reduction reaction, a control experiment with doping of a polycrystalline C_{60} specimen with mercury vapors was carried out. The vapor-phase doping of C_{60} with magnesium was also performed. A metal plate 0.2 mm thick with a surface area of 20 mm^2 served as the source of Mg atoms.

Because both doping and annealing were conducted with heating, the effect of the heat treatment on the formation of paramagnetic centers in the C_{60} lattice was studied. Polycrystalline C_{60} specimens (~1 mL) of 99.9% purity were used in the experiments.

The ESR spectra were recorded on a Radiopan E/X-2544 spectrometer equipped with a nuclear magnetometer and a Varian E-12A wavemeter at 77 and 300 K.

Results and Discussion

A comparison of the intensity of the ESR signal of the C_{60} specimen investigated with that of the standard

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(2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl) showed that the starting compound contains one paramagnetic center per $5 \cdot 10^4$ molecules of C_{60}. Its *g*-factor is equal to 2.0028, and the line width is equal to 0.46 mT at room temperature and to 1 mT at 77 K. The value of the *g*-factor and the character of the temperature dependence of the line width show that the structure of the C_{60}^- anion (the primary product of the reaction of C_{60} with metals) cannot be assigned to the paramagnetic center.

Heating the C_{60} specimen for 6 h at 500 °C increased the number of paramagnetic centers by only a factor of 1.5. These results are in qualitative agreement with the data obtained on studying the effect of the heat treatment on the intensity of the signals in the ESR spectrum of polycrystalline C_{60} heated from room temperature to 1050 °C.[4] We found that the effect of the heat treatment on fullerene is too small to be further considered.

The results of doping C_{60} with magnesium vapors for 14.5 h at 500 °C are presented in Fig. 1. The two signals, which are likely to belong to the C_{60}^- anion, have *g*-factors of 1.9995 and 2.0019. At the beginning of the process, the signal with the smaller *g*-factor is observed, and then the signal with the larger *g*-factor appears.

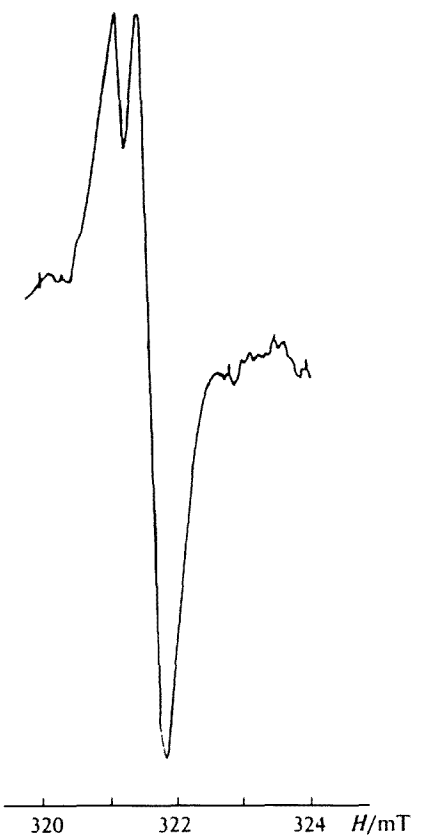


Fig. 1. The ESR spectrum (at 77 K) of the specimen of C_{60} doped with magnesium vapor, amplification — $3 \cdot 10^5$.

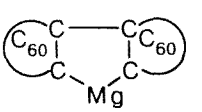
The face-centered cubic lattice of crystalline C_{60} has cavities of two types. They are characterized by different symmetry of the arrangement of C_{60} molecules relative to the centers of those cavities: octahedral (cavity is 2.06 Å in size) and tetrahedral (1.12 Å). It can be assumed that the larger octahedral cavities are the first to be filled with Mg^{2+} ions, and then the smaller tetrahedral cavities are filled. Based on this assumption, one should assign the signals with smaller and larger *g*-factors to the $C_{60}^{-\cdot}$ radical anions in whose vicinity the Mg^{2+} ions occupy the octahedral and tetrahedral cavities, respectively. Similar spectra were also recorded at the initial stages of the reaction of C_{60} with sodium.[2]

The degree of conversion of C_{60} into $C_{60}^{-\cdot}$, judging from the intensity of the ESR signal, is extremely low and amounts to ~0.02%.

Doping C_{60} with mercury vapor was carried out for 14 h at 500 °C. The degree of reduction of C_{60} appeared to be almost the same as in the case of magnesium doping. One should take into account that the vapor pressure of Hg at 500 °C is presumably several orders higher than the vapor pressure of Mg. This is due to the difference in boiling points of the metals: the boiling point of Hg is equal to 357 °C, whereas the boiling point of Mg equals 1103 °C (the melting point is equal to 650 °C). Based on the above, one can draw the conclusion that the rate constant of the heterogeneous reaction of magnesium vapor with C_{60} is several orders higher than the corresponding constant in the case of mercury vapor.

The *g*-factor and the line width of Hg_xC_{60} at the end of the reaction at 77 K are equal to 2.0017 and 0.33 mT, respectively; at room temperature they are equal to 2.0010 and 0.92 mT, respectively. The intensity of the signal at ~293 K is about 10 times higher than that at 77 K, which is characteristic of the conduction electrons in a semiconductor.

It was found after the reaction between magnesium amalgam and C_{60} in the liquid phase that the degree of reduction of C_{60} in dry product before annealing was extremaly small. The intensity of the signal increased by about two orders after annealing. This raises the question of the structure of the reaction product before annealing. One can assume that its diamagnetism is due to the formation of the compound



or, which seems to be less probable, of $C_{60}^{2-}Mg^{2+}$.

The ESR spectra of the first specimen recorded at various moments of annealing are presented in Fig. 2. Increasing the annealing time leads to a low-field shift of the signal and to a corresponding increase in the *g*-factor. At a certain stage of the annealing (Fig. 2, *b*) the spectrum is the superposition of two singlets with different *g*-factors. The intensity of the low-field signal

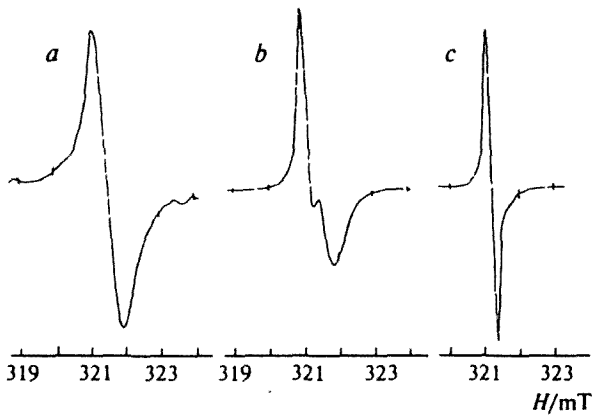


Fig. 2. The ESR spectra (at 77 K) of the specimen at different annealing times after reaction with the magnesium amalgam: *a*, 3 h at 220 °C, amplification — $4 \cdot 10^4$, g = 1.9975; *b*, 5 h at 220 °C and 3 h at 500 °C, amplification — $2 \cdot 10^4$, g = 1.9999 (for the narrow signal); *c*, 5 h at 220 °C and 11 h at 500 °C, amplification — $5 \cdot 10^3$, g = 2.0027.

increases while that of the high-field signal decreases in the course of the reaction. Similar changes in the ESR spectra were observed at the initial stages of C_{60} doping with potassium and sodium.[2]

One can assume that the increase in the g-factor of Mg_xC_{60} is related with the process of the formation of the crystal lattice and with the increase in the degree of delocalization of the unpaired electrons over the C_{60} molecules. The formation of the M_3C_{60} crystal lattice is the result of annealing of products of the reaction between alkaline metals and C_{60} in ammonia.[3]

The absolute values of the intensity of the signals in the spectrum allow one to conclude that the degree of reduction of C_{60} in the first specimen is ~1%. The temperature dependence of the intensity obeys the Curie law.

A larger magnesium content in the amalgam and an increase in the annealing time resulted in greater reduction of C_{60} in the second specimen. This could be seen as a change in the temperature dependence of the intensity of the signals in the ESR spectrum. There was a 14-fold increase in the intensity at the end of annealing at room temperature over the intensity at 77 K. The similar effect observed upon doping C_{60} with sodium was attributed to the semiconductor nature of fullerenes.[2] The real degree of reduction of C_{60} in the semiconductor state can be substantially higher than that expected from the intensity of the signals in the ESR spectrum.

The low yield of products of the reactions between alkaline earth elements and C_{60} was explained by the low solubility of $M^{2+}C_{60}$ compounds in ammonia.[3] It should also be noted that, relative to alkali metals, which exhibit a limited solubility in ammonia, alkaline earth metals are virtually insoluble in ammonia. Thus, the use of magnesium amalgams dispersed in toluene as reducing agents of C_{60} opens a way for the synthesis of fullerides of other metals.

The obtained results on doping C_{60} with magnesium and mercury are evidence for the possibility of using other metals with appropriate physicochemical properties to synthesize new fullerides.

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References

1. R. C. Haddon, *Acc. Chem. Res.*, 1992, **25**, 127.
2. S. P. Solodovnikov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2190 [*Russ. Chem. Bull.*, 1995, **44**, 2096 (Engl. Transl.)].
3. D. R. Buffinger, S.-M. Lee, R. P. Ziebarth, V. A. Stenger, and C. H. Pennington, in *Proc. of the Symp. on Recent Advances in Chemistry and Physics of Fullerenes and Related Materials*, Ed. K. M. Kadish and R. S. Ruoff, The Electrochem. Soc., Inc., Pennington, 1994, 1044.
4. B. Xiang and L. Kevan, in *Proc. of the Symp. on Recent Advances in Chemistry and Physics of Fullerenes and Related Materials*, Ed. K. M. Kadish and R. S. Ruoff, The Electrochem. Soc., Inc., Pennington, 1994, 981.

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