HETEROMETALLIC FULLERIDES OF ALKALI METALS AND NONTRANSITION METALS OF 2nd , 12th AND 13th GROUPS

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Introduction

In Ref. [1,2] we have shown that exchange reactions of tetra- and penta-fullerides of potassium and rubidium нами M_nC_{60} (n=4, 5) with halogenides of transition *d*- and *f*-elements (M') in the organic solvent of donor type (usually TGF) leads to the synthesis of heterosuperconductors with composition $M_2M'C_{60}$ with transition temperature T_c=16.5 К for M=K and T_c=22 K for M=Rb. It was found that fullerides are superconducting if the number of transferred electrons to the molecule of C_{60} is not higher than 5, atoms of f-elements have filled *d*-shell, while atoms of *d*-elements in opposite, have not-filled *d*-shell.

Up to now it is not clear would be heterofullerides of nontransition metals possess superconducting properties (except alkali metals) and if yes, for what especially elements with what composition.

Results and discussion

The results of some reactions (1-5) are listed in table. Four of reactions are exchange reactions (1, 3-5) were carried out in TGF at t>70 °C, and one (2) is a reaction of decomposition in toluol at t>110 °C.

$$M_5C_{60} + M'Cl_3 \rightarrow M_2M'C_{60} + 3MCl \quad (1)$$

$$K_2C_{60} + AlH_3 \rightarrow \{K_2AlC_{60}\} + 3/2H_2 \quad (2)$$

$$M_4C_{60} + M'Cl_2 \rightarrow M_2M'C_{60} + 2MCl \quad (3)$$

$$K_3C_{60} + TlCl \rightarrow \{K_2TlC_{60}\} + KCl \quad (4)$$

$$K_5C_{60} + 5BeCl_2 \rightarrow \text{“}\{[5BeClC_{60}] + 5KCl\}^* + 5K\text{”} \rightarrow \text{“}Be_5C_{60}\text{”} + 10KCl \quad (5)$$

Metal chloride was detected in defractogramm while hydride of aluminum disappeared. These facts confirm the execution of exchange reaction and reaction of decomposition. Simultaneously in X-ray spectra and NMR spectra of C^{13} ЯМР (except spectrum of fulleride with $ZnCl_2$) the band of fullerite was not found, that is all C_{60} is in bound state after execution of reaction. As it is seen in the table superconducting properties have been observed only in heterofullerides of nontrasition metals with composition $M_2M'C_{60}$, in which electronic configuration there is not filled d^{10}-shell. There is some exceptions: the heterofulleride of calcium with very weak superconductivity is the only between transition and nontransition metals heterofulleride with composition KMg_2C_{60} with T_c=15.5 K, nonsuperconducting fulleride "Ba_4C_{60}" and heterofullerides M2M'C_{60} based on rubidium and cesium. For heterofullerides $Cs_2M'C_{60}$ the absence of superconductivity is explained by changing of the structure as for Cs_3C_{60}. In the case of "Ba_4C_{60}" with T_c=8 K (according to publications) there is no explanations of superconductivity. Superconductivity in {K6+3TlCl} is due to decomposition of fulleride K_6C_{60} and appearance of K_3C_{60} with T_c=17 K (published T_c=18 K).

Table Composition and some properties of synthesized heterofullerides

N	Composition of the initial components	Assumed composition of the fulleride	T_c, K	Colour	Electron configuration of heteroatom	NMR ^{13}C, ppm
1	$K_4C_{60}+BeCl_2$	K_2BeC_{60}	13	Steel-blue	$1s^22s^2$	-
2	$K_5C_{60}+2BeCl_2$	KBe_2C_{60}	-	Black	$1s^22s^2$	187
3	$K_4C_{60}+MgCl_2$	K_2MgC_{60}	16	Black	$2s^22p^63s^2$	191
4	$K_5C_{60}+2MgCl_2$	KMg_2C_{60}	15.5	Black – brown	$2s^22p^63s^2$	191
5	$Rb_4C_{60}+MgCl_2$	Rb_2MgC_{60}	-	Black	$2s^22p^63s^2$	183 wide
6	$Cs_4C_{60}+MgCl_2$	Cs_2MgC_{60}	-		$2s^22p^63s^2$	183 wide
7	$K_4C_{60}+ZnCl_2$	K_2ZnC_{60}	-	Black	$3p^63d^{10}4s^2$	190, 145
8	$K_5C_{60}+2ZnCl_2$	KZn_2C_{60}	-	Black	$3p^63d^{10}4s^2$	190, 145
9	$K_4C_{60}+CaCl_2$	K_2CaC_{60}	Very weak	Black	$3s^23p^63s^2$	188
10	$K_5C_{60}+2CaCl_2$	KCa_2C_{60}	-	Black	$3s^23p^64s^2$	187
11	$K_4C_{60}+BaCl_2$	K_2BaC_{60}	Very weak	Black	$4d^{10}5s^25p^66s^2$	188
12	$K_5C_{60}+2BaCl_2$	KBa_2C_{60}	-	Black	$4d^{10}5s^25p^66s^2$	185
13	$\{K_6C_{60}+4BaCl_2\}+2K$	"Ba_4C_{60}"	-	Black	$4d^{10}5s^25p^66s^2$	–
14	$K_5C_{60}+AlCl_3$	K_2AlC_{60}	14.5	Black-brown	$2p^63s^23p^1$	191
15	$K_2C_{60}+AlH_3$	K_2AlC_{60}	13.0	Black	$2p^63s^23p^1$	185,141
16	$Rb_5C_{60}+AlCl_3$	Rb_2AlC_{60}	Weak	Black	$2p^63s^23p^1$	182
17	$Cs_5C_{60}+AlCl_3$	Cs_2AlC_{60}	-	Black-brown	$2p^63s^23p^1$	183 wide
18	$K_7C_{60}+2AlCl_3$	KAl_2C_{60}	Very weak	Red	$2p^63s^23p^1$	190, 145
19	$K_5C_{60}+GaCl_3$	K2GaC60	-	Black	$3d^{10}4s^24p^1$	191, 145
20	$K_3C_{60}+TlCl$	K_2TlC_{60}	-	Black	$5d^{10}6s^26p^1$	187,144
21	$K_6C_{60}+3TlCl$	"$K_3C_{60}+3Tl$"	17	Black	$5d^{10}6s^26p^1$	191

Thus the fully filled *d*-shell in nontransition and pasttransition metals suppressed the superconductivity in fullerides as it is in *d*-metals fullerides. Nevertheless it is evident that some other factors also influence on superconductivity, for example the different execution of reaction, not in the way shown in equations (1-5). In such way the fulleride may be decomposed and the products of reaction will be a mixture of different substances including fullerite (the line in NMR spectra 141-144 ppm).

The work was supported by RFBR, grant № 05-02-17368-a

References

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