Superconductivity of heterofullerides $A_nB_mHg_xC_{60}$  
($A=K,Rb,Cs; B=Be,Mg,B,Al,Ga,In; n=1,2; m=1,2; x<1$)

V.A. Kulbachinskii$^1$, B.M. Bulychev, R.A. Lunin, I.P. Kachan
M.V. Lomonosov Moscow State University, 119991, GSP-2, Moscow, Russia
E-mail: kulb@mig.phys.msu.ru

Abstract. The fullerides $A_mM_nC_{60}$ ($A=K, Rb, Cs; M= Be, Mg; B, Al, Ga, In; n=1,2; m=1,2$) have been synthesized by exchange reactions of alkali metal fullerides with metal chlorides (groups 2 and 13), by method using liquid alloys of metals with mercury (amalgams), and by thermal decomposition of aluminum hydride. The samples are studied by X-ray diffraction, nuclear magnetic resonance, electron paramagnetic resonance, Raman scattering, and differential scanning calorimetry. It was found that the fulleride $K_2GaC_{60}$ is superconductor with transition temperature $T_c=22$ K that exceeds $T_c$ for $K_3C_{60}$ (19 K). Fullerides with In and B are not superconductors. The fullerides with composition $Cs_nHgxC_{60}$ ($n=2,3$) are not superconductors and crystallize in orthorhombic lattices.

1. Introduction
The discovery of superconducting fullerides with alkaline metals in 1991 [1] leads to the intensive development of chemistry and physics of these compounds, primarily to the development of methods of synthesis, to the study of the electrical and structural properties, and to the definition of the spectral characteristics and many other features. One of the important conclusions was that superconductivity is observed in fullerides $A_3C_{60}$ ($A=K, Rb, Cs$) with $fcc$ lattice [2]. Later it was shown that superconducting and electrophysical properties of fullerides depend on method of synthesis, in particular on the nature of solvent. For example synthesis of $Na_3C_{60}$ from simple substances in toluol leads to fulleride with triclinic lattice [3,4].

Synthesis of $K_3Hg,C_{60}$ from amalgam gives fulleride with monoclinic lattice. The fulleride $K_3Hg,C_{60}$ is not superconductor. Heterofulleride with composition $K_2Hg,C_{60}$ ($x<1$) is a superconductor with transition temperature $T_c=22$ K. This value exceeds transition temperature for $K_3C_{60}$ ($T_c=19$ K).Synthesis of $Cs,C_{60}$ gives amorphous or probably polymeric substances [4]. At the same time synthesis of this fulleride in liquid ammonia from simple substances gives superconducting fulleride with orthorhombic lattice in contradiction with previous results [5]. However, an important problem remains: in what composition of fullerides is the superconductivity possible and how to rise to the critical temperature $T_c$?

In the present study, the results of investigation of structural and superconducting properties of heterofullerides with metals of 1st, 2nd and 13th groups $A_nB_mHg_xC_{60}$ ($A=K, Rb, Cs; M= Be, Mg, B, Al, Ga, In; n=1,2; m=1,2; x<1$) are described.

$^1$To whom any correspondence should be addressed.
2. Experimental

The fullerides have been synthesized by the exchange reactions of alkaline fullerides with anhydrous metal halides (i), by a method using liquid alloys of metals with mercury (amalgams) (ii) or by thermal decomposition of hydrides (iii).

2.1 Synthesis of amalgams and fullerides from amalgams

The calculated amounts of one or two metals (to within 0.02–0.15 g) were in a pyrex vial containing 6–7 g of mercury (i.e., a sufficient amount according to the phase diagrams for producing the liquid amalgams). The vial was then pumped down in a vacuum and sealed off. The metals were dissolved by heating a vial to 400 °C for 3 hours with periodic mixing of the contents. The vial with the amalgam and the reactor for synthesizing the fulleride were placed in a “Braun-M” vacuum cell. The vial was opened and its contents transferred to the reactor, into which the calculated amount of fullerite (0.15–0.25 g) and 20–30 mL of pure toluene had been placed. The reactor was extracted from the cell and its contents were frozen in liquid nitrogen; the entire system was pumped down in vacuum and unsealed, and the reactor was placed in a thermally controlled cabinet equipped with a mixing device for 15–20 days at a temperature of 100–110 °C. The progress of the reaction was monitored visually by the fading of the violet fullerite solution. Further operations for separating the reaction product were carried out in a fully sealed glass unit and included: separation of the excess mercury by decanting, washing the residue three or four times by recondensation of the solvent with cooling in liquid nitrogen, drying the residue at 90–100 °C, and packing it into vials for the electrical, spectral, and X-ray structural studies [4].

2.2 Synthesis of heterofullerides by exchange reactions in organic solvents

Fullerides were synthesized in the organic solvents in two stages. In the first stage, alkali metal fullerides with compositions $A_nC_{60}$, where $A=Na,K,Rb$ and $n=3–6$ were obtained by direct reaction of an alkali metal with the fullerite solution in pure toluene using the method described in Refs. [4,6,7,8]. The second stage involved an exchange reaction of an alkali fulleride with anhydrous chlorides of the heterometals in pure tetrahydrofuran (THF) at temperatures below 80 °C in accordance with the reactions

$$A_4C_{60} + MCl_2 \xrightarrow{\text{THF}} A_2MC_{60} + 2ACl$$

$$A_2C_{60} + 2MCl_2 \xrightarrow{\text{THF}} AM_2C_{60} + 4ACl$$

$$A_2C_{60} + MCl_3 \xrightarrow{\text{THF}} A_2MC_{60} + 3ACl$$

where $A-K, Rb, Cs$; $M- Be, Mg, B, Al, Ga, In$.

In principle, this method makes it possible to obtain fullerides and heterofullerides of various metals here, thallium containing heterofullerides with different chemical compositions and atomic charge states [4].

2.3 Thermal decomposition of aluminum hydride

We used also a new method of thermal decomposition of aluminum hydride according to reaction

$$A_2C_{60} + AlH_3 \xrightarrow{200-300^\circ C} A_2AlC_{60} + 3/2 H_2$$

Aluminum hydride was synthesized by method described in Ref. [9]. Some parameters of samples are listed in table 1. The compositions of these fullerides calculated from the loaded components. As we show in table 3 our attempts to synthesize heterofullerides with cesium failed as it was previously [4]. According to X-ray and NMR data cesium heterofullerides synthesized at $T>20^\circ C$ are amorphous and polymerized. Superconductivity in cesium fullerides was found only in RbCsTlC$_{60}$ and KCsTlC$_{60}$ [10].

3. Results and discussion

X-ray data for some synthesized fullerides are summarized in table 1. Synthesized heterofullerides of potassium and rubidium are superconductors (fig. 1a). We observed that in general the superconducting transition temperature $T_c$ increases with crystal lattice parameter $a$ as seen in table 1. Raman scattering data shows that charge state of $C_{60}$ molecule in fullerides is close to $-3$. 

2
| №  | Composition of initial mixture | Solvent | Composition of fulleride | $T_c$ (K) | X-Ray data |
|----|--------------------------------|---------|--------------------------|-----------|------------|
| 368 | $K_4C_{60}+BeCl_2+C_{60}$ | THF     | $K_2BeC_{60}$            | 13        | $fcc, a=14.268 \text{ Å} +KCl$ |
| 225 | $K_4C_{60}+MgCl_2+C_{60}$   | THF     | $K_2MgC_{60}$            | 16        | $fcc, a=14.290 \text{ Å} +KCl$ |
| 942 | $\{2K+Mg+(Hg)_n\}+C_{60}$  | toluene | $K_2MgHgC_{60}$          | 13.6      | $fcc, a=14.280 \text{ Å}$ |
| 292 | $K_3C_{60}+2MgCl_2+C_{60}$  | THF     | $KMg_2C_{60}$            | 15.5      | $fcc, a=14.256 \text{ Å} +KCl$ |
| 236 | $K_5C_{60}+AlCl_3+C_{60}$   | THF     | $K_2AlC_{60}$            | 14.5      | $fcc, a=14.249 \text{ Å} +KCl$ |
| 20  | $K_2C_{60}+AlH_3$           | toluene | $K_2AlC_{60}$            | 14        | $fcc, a=14.282+<1\%Al$ |
| 941 | $\{2K+Al+(Hg)_n\}+C_{60}$  | toluene | $K_2AlHgC_{60}$          | 15.7      | $fcc, a=14.281 \text{ Å}$ |
| 931 | $\{2K+Ga+(Hg)_n\}+C_{60}$  | toluene | $K_2GaHgC_{60}$          | 20        | $fcc, a=14.297 \text{ Å}$ |
| 923 | $\{2K+In+(Hg)_n\}+C_{60}$  | toluene | $K_2InHgC_{60}$          | -         | $fcc, a=14.281 \text{ Å}$ |
| 264 | $Rb_4C_{60}+BeCl_2+C_{60}$  | THF     | $Rb_2BeC_{60}$           | 22        | $fcc, a=14.447 \text{ Å} +RbCl$ |
| 724 | $Rb_4C_{60}+MgCl_2+C_{60}$  | THF     | $Rb_2MgC_{60}$           | 19        | $fcc, a=14.425 \text{ Å} +RbCl$ |
| 982 | $\{2Rb+Mg+(Hg)_n\}+C_{60}$ | toluene | $Rb_2MgHgC_{60}$         | 21.8      | $fcc, a=14.447 \text{ Å}$ |
| 12  | $Rb_3C_{60}+2MgCl_2+C_{60}$ | THF     | $RbMg_2C_{60}$           | -         | $fcc, a=14.425 \text{ Å} +RbCl$ |
| 13  | $\{Rb+2Mg+(Hg)_n\}+C_{60}$ | toluene | $RbMg_2HgC_{60}$         | -         | - |
| 979 | $\{2Rb+Al+(Hg)_n\}+C_{60}$ | toluene | $Rb_2AlHgC_{60}$         | 24.8(11)  | $fcc,a=14.458 \text{ Å} +M_2$ |
| 929 | $\{2Rb+Ga+(Hg)_n\}+C_{60}$ | toluene | $Rb_2GaHgC_{60}$         | 25        | $a=9.055; b=10.057; c=14.190 \text{ Å} (~10\%)$ |
| 922 | $\{2Rb+In+(Hg)_n\}+C_{60}$ | toluene | $Rb_2InHgC_{60}$         | -         | $a=14.439(3) (~65\%) +$ |
| 5   | $Cs_4C_{60}+BeCl_2+C_{60}$  | THF     | $Cs_2BeC_{60}$           | -         | Amorphous + CsCl |
| 690 | $Cs_4C_{60}+MgCl_2+C_{60}$  | THF     | $Cs_2MgC_{60}$           | -         | Amorphous + CsCl |
| 983 | $\{2Cs+Mg+(Hg)_n\}+C_{60}$ | toluene | $Cs_2MgHgC_{60}$         | -         | Amorphous |
| 674 | $Cs_2C_{60}+AlCl_3+C_{60}$  | THF     | $Cs_2AlC_{60}$           | -         | Amorphous + CsCl |
| 980 | $\{2Cs+Al+(Hg)_n\}+C_{60}$ | toluene | $Cs_2AlHgC_{60}$         | -         | Amorphous |

Second phase M$_2$: $a=10.539; b=7.998; c=6.883 \text{ Å}; \beta=103.21^\circ; V=564.8 \text{ Å}^3$
The shift of line \( A_g(2) \) in synthesized superconducting fullerides is almost the same as in a very well known superconductor \( K_2C_{60} \) (fig. 1b). For heterofullerides synthesized with metals of 13\(^{th} \) group with composition \( A_2M^+3C_{60} \) we may suppose the transfer of 5 electrons. Nevertheless as we can see in table 1 only products of reaction of \( K_5C_{60} \) with \( AlCl_3 \) in THF and \( K_2C_{60} \) with \( AlH_3 \) in toluene are superconductors. Reactions of fullerite with ternary amalgams give superconducting potassium, rubidium, aluminum and gallium fullerides. All other substances with higher or less number of transferred electrons, for example \( Al_2C_{60} \), \( MAIC_{60} \), \( Al_3C_{60} \) etc., don’t crystallize in \( fcc \) lattice and are not superconductors. At the same time indium fullerides have \( fcc \) lattice but they are not superconductors.

As we see in table 1 critical temperature \( T_c \) for \( K_2AlC_{60} \) fullerides synthesized by three different methods is almost the same. The enhancement of \( T_c \) in fullerides synthesized from amalgam the most probably is due to intercalation of some amount of Hg in fulleride. The intercalation of Hg in fullerides also leads to the superconductivity in Rb-Al and K-Ga fullerides. We showed that small amount of Hg in fulleride change radically its properties [4,11]. Fullerides with composition \( K_2BC_{60} \) and \( Rb_2BC_{60} \) are not superconductors. Fulleride \( K_2InHg_xC_{60} \) is not a superconductor while \( K_2Hg_xC_{60} \) is a superconductor with \( T_c=22 \) K [11]. Similar fulleride \( Rb_2InHg_xC_{60} \) is not a superconductor while \( Rb_2Hg_xC_{60} \) is a superconductor with \( T_c=25 \) K.

The work was supported by RFBR, grant number № 08-03-00237a.

References

[1] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, et. al., Nature, 350, 600 (1991).
[2] O. Gunnarsson, Reviews of Modern Physics, 69, 575 (1997).
[3] V.A. Kulbachinskii, B.M. Bulychev, V.G. Kytin, et. al., Central Eur. J. Phys. 8,101 (2010)
[4] V.A. Kulbachinskii. B.M. Bulychev, et.al. Low Temperature Physics, 37, 245 (2011).
[5] A.Y. Ganin, Y. Takjabayashi, P. Jeglić, et al, Nature, 466, 221 (2010).
[6] B.M. Bulychev, R.A. Lunin, et. al, J. of Phys. and Chem. of Solids, 65, 337 (2004).
[7] O.A. Dityatyev, V.I. Privalov, B.M. Bulychev, et.al, Mol. Mater., 13, 281 (2000).
[8] B. M. Bulychev, R. A. Lunin, et.al, Russ. Chem. Bull., Int. Ed., 53, 1686 (2004).
[9] B. M. Bulychev, P. A. Storozhenko, V. N. Fokin, Russ.Chem.Bull., Int.Ed., 58, 1817 (2009).
[10] V.A.Kulbachinskii,B.M.Bulychev, V. G. Kytin, et.al, Hindawi Pub. Corp., Advances in Condensed Matter Physics, Volume 2008, Article ID 941372, (2008).
[11] B.M. Bulychev, V.A. Kulbachinskii, R.A. Lunin, V.G. Kytin and Yu.A. Velikodny, Fullerenes, Nanotubes, and Carbon Nanostructures, 18, 381-385 (2010).