Superconductivity of the Heterofullerides Synthesized from Gallams and Amalgams

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Abstract. The fullerides with composition $A_2B_xD_yC_{60}$ ($A=$K,Rb,Cs; $B,D=$Ga, In, Sn, Bi, Be, Al, Mg, Hg; $x,y<1$) have been synthesized by using liquid amalgams (alloys of metals with mercury) or with an alloy of indium and gallium (gallams) at room temperature. It was found that the fulleride $K_2In_xGa_yC_{60}$ is a superconductor with transition temperature $T_c=24.5$ K that exceed $T_c=19$ K for reference $K_3C_{60}$. The fulleride $Rb_2In_xGa_yC_{60}$ is a superconductor with $T_c=26$ K. Superconductivity of heterofulleride with a composition $K_2Hg_xC_{60}$ ($x<1$) was observed at temperature $T_c=22$ K. The fullerides with composition $Rb_3In_xGa_yC_{60}$ and $Cs_3In_xGa_yC_{60}$ are not superconductors and crystallized in the orthorhombic lattice. Fullerides $K_2Ga_xBi_yC_{60}$ and $K_2Ga_xSn_yC_{60}$ ($x,y<1$) are superconductors.

Introduction

Fullerides of alkali and some other metals are very interesting high $T_c$ superconductors \[2-5\]. The first fullerides were synthesized by a method of reactions of the metal vapor with fullerite \[6-8\]. Such method is suitable for alkali and other fusible metals. Also a fulleride synthesis method through an interaction of a metal solution in ammonia with fullerite or melt of alkali metals with fullerite are known \[2\]. Other method is a fullerides synthesis by reactions of alkali metals with a solution of fullerene in the organic solvent \[4,5\]. More complicated fullerides were obtained by an exchange reactions of fullerides of alkali metals with solutions of salts of other metals in organic solvents \[9,10\]. In all these methods one of the reagent is in a solid state that reduces a speed of the reaction and demands the execution of the synthesis at the increased temperature.

In this work we investigated superconductivity of heterofullerides with a composition $A_2B_xD_yC_{60}$ ($A=$K, Rb, Cs; $B,D=$Ga, In, Sn, Bi, Be, Al, Mg, Hg; $x,y<1$) obtained by a method of reactions of liquid gallams or amalgams with a solution of fullerene in organic solvent. In this method both of reagents are liquid that allows executing a reaction at room temperature. Homogeneity of the composition of obtained compounds is close to the ideal. In this case, however, mercury, indium and gallium partially remain in the obtained fulleride. We also tried to find the relations of the composition and the structure of superconducting heterofullerides with the superconducting transition temperature $T_c$. 

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Experimental

In this paper we study the samples, synthesized by a method using liquid amalgams or
gallams (alloys of metals with eutectic alloy Ga:In=70:30). We assume that Hg, Ga or heterometals
can intercalate together with self-intercalated alkaline metals into the fullerite. To better deliver
metal to the fullerene molecule the interaction of components (fullerite C\textsubscript{60}, alkali metal and
heterometal) was carried out in the organic solvent (toluene or mixture of toluene and THF in a
proportion 9:1), in which fullerene is soluble. The ratio of alkali metal:fullerite was 2:1 to
synthesize A\textsubscript{2}C\textsubscript{60} and to avoid the synthesis of the superconducting fulleride A\textsubscript{3}C\textsubscript{60}. The synthesis
of the alkali metal fullerides and subsequent removal of toluene, gallium or gallam and mercury,
drying of products of reaction, and their packaging in ampoules for measurements of temperature of
the superconducting transition were carried out in vacuum in the full glass facility equipment. In
more detail the technique is described in Ref's [9-10]. In the initial gallams the content of indium
and gallium were in 30-70 times higher than alkali metal in order to gallams were liquid, but in the
final product A\textsubscript{2}C\textsubscript{60} (A=K,Rb,Cs; n=2,3) the content of indium \(x\) and gallium \(y\) were less then
1. The measurements of X-ray diffraction were carried out with Guinier G670 HUBER.

Temperatures of superconducting transitions of fullerides were defined by low-frequency induction
method by measuring the temperature dependence of a magnetic susceptibility in the temperature
range 4.2<T<297 K [4,10,11].

Some parameters of the investigated samples are listed in table 1. We also synthesized
Rb\textsubscript{3}In\textsubscript{x}Ga\textsubscript{y}C\textsubscript{60} and Cs\textsubscript{3}In\textsubscript{x}Ga\textsubscript{y}C\textsubscript{60} but they are not superconductors while K\textsubscript{3}In\textsubscript{x}Ga\textsubscript{y}C\textsubscript{60} is a
superconductor with \(T_c=14.5\) K.

### Table 1. Temperature of superconducting transition \(T_c\), type of crystal lattice and lattice
parameters of investigated samples

| Composition | \(T_c\) (K) | Lattice type | Lattice parameters (Å) |
|-------------|-------------|--------------|-----------------------|
| K\textsubscript{2}Ga\textsubscript{3}In\textsubscript{2}C\textsubscript{60} | 24.5 | fcc | 14.276(4) |
| K\textsubscript{2}Ga\textsubscript{3}Sn\textsubscript{2}C\textsubscript{60} | 15.4 | fcc | 14.282(8) |
| K\textsubscript{2}Ga\textsubscript{3}Bi\textsubscript{2}C\textsubscript{60} | 14.9 | fcc | 14.255(8) |
| K\textsubscript{2}GaHg\textsubscript{2}C\textsubscript{60} | 20 | fcc | 14.297(5) |
| K\textsubscript{2}MgHg\textsubscript{2}C\textsubscript{60} | 13.6 | fcc | 14.281(6) |
| K\textsubscript{2}MgHg\textsubscript{2}C\textsubscript{60} | 14.9 | fcc | 14.279(3) |
| K\textsubscript{3}In\textsubscript{2}Ga\textsubscript{3}C\textsubscript{60} | 14.5 | fcc | 14.269(2) |
| Rb\textsubscript{2}AlHg\textsubscript{2}C\textsubscript{60} | 24.8 | fcc+M2 | 14.458(4) |
| Rb\textsubscript{2}MgHg\textsubscript{2}C\textsubscript{60} | 21.8 | fcc+~5%M2 | 14.447(4) |
| Rb\textsubscript{2}GaHg\textsubscript{2}C\textsubscript{60} | 25 | fcc+orthorhombic (10%) | 14.439(3) |
| Rb\textsubscript{2}In\textsubscript{2}Ga\textsubscript{3}C\textsubscript{60} | 26 | fcc+orthorhombic | 14.444(3) |
| Rb\textsubscript{2}HgC\textsubscript{60} | 24.6 | fcc+M2 | 14.440(2) |
| Rb\textsubscript{3}In\textsubscript{2}Ga\textsubscript{3}C\textsubscript{60} | - | Orthorhombic | \(a=9.110(13), b=10.105(11), c=14.188(15)\) |
| Cs\textsubscript{3}In\textsubscript{2}Ga\textsubscript{3}C\textsubscript{60} | - | Orthorhombic | \(a=9.097(5), b=10.227(5), c=14.159(9)\) |

M2 – monoclinic phase
Fullerides synthesized by different methods were studied in [5]. Superconducting transition temperatures for heterofullerides with similar composition but prepared from amalgams or by exchange reactions do not differ significantly [11]. It was shown that mercury get into fulleride and some charge transfer from mercury to the fulleride molecule occurs [10,11].

**Results and discussion**

Temperature dependence of the magnetic susceptibility for synthesized from gallams samples \( \text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60} \), \( \text{K}_3\text{In}_x\text{Ga}_y\text{C}_{60} \) and \( \text{Rb}_2\text{In}_x\text{Ga}_y\text{C}_{60} \) is shown in **Fig. 1a**. The transitions in a superconducting state were observed at temperatures 24.5; 14.5 K and 26 K, correspondingly. The fulleride \( \text{K}_2\text{Hg}_x\text{C}_{60} \) has \( T_c = 22 \) K and \( \text{Rb}_2\text{Hg}_x\text{C}_{60} \) has \( T_c = 24.6 \) K (**Fig. 1b**). Thus the used methods of synthesis made superconductors \( \text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60} \) and \( \text{K}_2\text{Hg}_x\text{C}_{60} \) with \( T_c \) higher than in \( \text{K}_3\text{C}_{60} \) from not a superconductor \( \text{K}_2\text{C}_{60} \). It indicates that mercury or components of gallams aren't inert solvents in reaction of intercalation, but intercalates itself into a fullerides lattice and change their superconducting properties. X-ray data shows that \( \text{K}_2\text{Hg}_x\text{C}_{60} \) crystallized in fcc lattice (**Fig. 2a**) while \( \text{K}_3\text{Hg}_x\text{C}_{60} \) has a monoclinic lattice \( (a=16.52\text{Å}, b=10.82\text{Å}, c=10.41\text{Å}, \beta=108.17^0) \) (**Fig. 2b**) and not a superconductor. According to the X-ray data the heterofulleride with the composition \( \text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60} \) was crystallized in the fcc lattice with the lattice parameter \( a=1.4276 \) nm (**Fig. 3a**), which is close to the value obtained for \( \text{K}_3\text{C}_{60} \) \( (a=1.424 \text{ nm} \) [7]). Superconducting transitions for \( \text{K}_2\text{Ga}_x\text{Bi}_y\text{C}_{60} \) and \( \text{K}_2\text{Ga}_x\text{Sn}_y\text{C}_{60} \) are shown in **Fig. 3b**.

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**Fig. 1.** Temperature dependence of magnetic susceptibility of samples \( \text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60} \), \( \text{K}_3\text{In}_x\text{Ga}_y\text{C}_{60} \) and \( \text{Rb}_2\text{In}_x\text{Ga}_y\text{C}_{60} \) (a) and relative magnetic susceptibility of samples \( \text{K}_2\text{Hg}_x\text{C}_{60} \) and \( \text{Rb}_2\text{Hg}_x\text{C}_{60} \).

**Fig. 2.** X-ray diffraction of the sample (a) \( \text{K}_2\text{Hg}_x\text{C}_{60} \) (indicated phase: fcc) and (b) \( \text{K}_3\text{Hg}_x\text{C}_{60} \) (indicated phase: monoclinic).
Some temperature dependences of magnetic susceptibility for samples synthesized from amalgams are shown in Fig. 4a. The parameters of investigated samples are listed in table 1. The dependence of $T_c$ on the lattice parameter $a$ for superconducting samples synthesized from amalgams is shown in Fig. 4b by open cycles. The difference in $T_c$ for samples $K_2In_xGa_yC_{60}$ and $K_2In_xGa_yC_{60}$ is probably due to the more optimal charge transfer from intercalated atoms to fullerene molecule for the sample $K_2In_xGa_yC_{60}$. The fulleride $Rb_2In_xGa_yC_{60}$ is not a superconductor. The X-ray diffraction data of the sample indicates the orthorhombic crystal lattice with the lattice parameters shown in table 1.

Transition temperature $T_c$ increases with $fcc$ lattice parameter $a$, as shown in Fig. 4b.

Data shows that components of gallams were intercalated in fulleride lattice, changed the lattice type and made from superconductor $Rb_2C_{60}$ not superconducting composition. At the same time the fulleride $Rb_2In_xGa_yC_{60}$ remain the superconductor with $T_c = 26K$. According to the X-ray data, this sample consists of two phases: the first phase is similar to $Rb_2C_{60}$ (fcc lattice) and the second phase is close to $Rb_2In_xGa_yC_{60}$ (orthorhombic lattice).

The X-ray diffraction data for $Rb_2Hg_xC_{60}$ shows the peaks related to the $fcc$ phase and also to the orthorhombic phase. The lattice parameter of the $fcc$ phase equals to 1.444 nm (see table 1). This value is close to the value measured for $Rb_2C_{60} (a=1.4384 \text{ nm} [8])$. The phase with $fcc$ crystal lattice is probably superconducting, because measured $T_c$ is relatively close to the value of superconducting transition temperature for $Rb_2C_{60} (28 \text{ K} [8])$. Thus, under the conditions of synthesis the composition probably can decay on two phases – mono- and triple-rubidium fullerides.
The heterofulleride with the composition Cs$_3$In$_x$Ga$_y$C$_{60}$ is not a superconductor. According to the X-ray data, this sample crystallizes in the orthorhombic lattice (see table 1). The absence of superconductivity in this fulleride is probably because its crystal lattice is not fcc. The absence of superconductivity in cesium fullerides, synthesized from amalgams, was also registered by us earlier [10,11]. In previous work [10] we investigated the fullerides with composition A$_n$Hg$_x$C$_{60}$ (A=K,Rb; n=2,3; x<1) synthesized by method using liquid alloys of alkali metals with mercury (amalgams). It was found that the fulleride K$_2$Hg$_x$C$_{60}$ was superconductor with $T_c = 22$ K.

The fulleride K$_2$Hg$_x$C$_{60}$ was not a superconductor. The fulleride Rb$_2$Hg$_x$C$_{60}$ was a superconductor with $T_c = 25$ K. Thus the alkali metals fullerides synthesized from amalgams have higher $T_c$ than analogous fullerides synthesized from amalgams. We also synthesized from amalgams the fullerides with composition K$_2$GaHg$_x$C$_{60}$, Rb$_2$GaHg$_x$C$_{60}$ and K$_2$InHg$_x$C$_{60}$. The fullerides K$_2$GaHg$_x$C$_{60}$ and Rb$_2$GaHg$_x$C$_{60}$ are superconductors with $T_c$ equal to 20 K and 25 K, correspondingly. The fullerides K$_2$InHg$_x$C$_{60}$ and Rb$_2$InHg$_x$C$_{60}$ are not superconductors though crystallize in fcc lattice. It means that rather gallium than indium is responsible for high $T_c$ for the sample K$_2$In$_x$Ga$_y$C$_{60}$.

Conclusions

The new heterofullerides with the composition A$_n$B$_x$D$_y$C$_{60}$ (A=K,Rb,Cs; B,D=Ga, In, Sn, Bi, Be, Al, Mg, Hg; x,y<1; n=2,3) were synthesized. Temperature dependence of the magnetic susceptibility and lattice parameters were measured in the temperature range from 4.2 K to 297 K and transitions to the superconducting state were detected at temperatures $T_c$ ranged from 14.5 K to 26 K. For the fulleride K$_2$In$_x$Ga$_y$C$_{60}$ the $T_c$ is equal to 24.5 K, that is the highest $T_c$ among fullerides on the base of potassium (which does not include atoms of other alkali metals Rb and Cs). We found that the components of gallams or mercury intercalate into a fulleride lattice and improve their superconducting properties.

References

[1] B.M. Bulychev, R.A. Lunin, V.A. Kulbachinskii, et. al. Izv. Akad. Nauk, Ser. Khim., 53(8) (2004) 1623-1628. [Russ. Chem. Bull., International Edition, 53(8) (2004) 1686-1691].
[2] O. Gunnarsson, Reviews of Modern Physics 69, (1997) 575-606.
[3] A.Y. Ganin, Y. Takjabayashi, P. Jeglič, D. et.al., Nature, 466 (2010) 221-227.
[4] V.A. Kulbachinskii, B.M. Bulychev, V.G. Kytyn and R.A. Lunin, Low Temperature Physics 37 (2011) 245-260.
[5] V.A. Kulbachinskii, R.A. Lunin, I.P. Kachan, et.al., Low Temp. Phys., 39 (2013) 58-65.
[6] A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, et. al., Nature, 350 (1991) 600-604.
[7] K. Tanigaki, I. Hirosawa, T.W. Ebessen, et. al., Nature 356, (1991) 419-423.
[8] M.J. Rosseinsky, A.P. Ramirez, S.H. Glarum, et. al., Phys. Rev. Lett. 66 (1991) 2830-2833.
[9] B.M. Bulychev, R.A. Lunin, A.V. Krechetov, et.al., J. of Phys. and Chem. of Solids 65 (2004) 337-342.
[10] V.G. Kytyn, B.M. Bulychev, A.V. Krechetov, et. al., Russian Journal of Inorganic Chemistry 53, (2008) 30-37.
[11] V.A. Kulbachinskii1, B.M. Bulychev and R.A. Lunin, A.V. Sycheva, Journal of Physics: C.S., 507 (2014) 012026(1-4).