Superconductivity of fullerides with composition \(A_n\text{In}_x\text{Ga}_y\text{C}_{60}\) (\(A=\text{K,Rb,Cs};\ n=2,3;\ x,y<1\)) synthesized from gallams

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Abstract. The fullerides with composition \(A_n\text{In}_x\text{Ga}_y\text{C}_{60}\) (\(A=\text{K,Rb,Cs};\ n=2,3;\ x,y<1\)) have been synthesized by a new method using liquid alloys of metals with indium and gallium (gallams) at room temperature. It was found that the fulleride \(\text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60}\) is a superconductor with transition temperature \(T_c = 24.5\) K that exceed \(T_c\) for \(\text{K}_3\text{C}_{60}\) (19 K). The fulleride \(\text{Rb}_2\text{In}_x\text{Ga}_y\text{C}_{60}\) is a superconductor with \(T_c = 26\) K. The fullerides with composition \(\text{Rb}_3\text{In}_x\text{Ga}_y\text{C}_{60}\) and \(\text{Cs}_3\text{In}_x\text{Ga}_y\text{C}_{60}\) are not superconductors and crystallizes in orthorhombic lattice.

1. Introduction
Today a significant amount of the experimental data about properties of fullerides of alkali and some other metals are accumulated [1-5]. The first fullerides were synthesized by a method of reactions of the metal vapor with fullerite [1,2,5]. Such method is suitable for alkali and other fusible metals. Also a fullerides synthesis method through an interaction of a metal solution in ammonia with fullerite or melt of alkali metals with fullerite are known [3]. Other method is a fullerides synthesis by reactions of alkali metals with a solution of fullerene in the organic solvent [6]. More complicated fullerides were obtained by an exchange reactions of fullerides of alkali metals with solutions of salts of other metals in organic solvents [7,8]. In all listed 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 and can negatively affect the homogeneity of obtained fullerides. In this work we investigated heterofullerides obtained by a new method of reactions of liquid gallams with a solution of fullerene. In this method both of reagents are liquid that allows executing a reaction at room temperature. Homogeneity of the composition of obtained compounds should be close to the ideal that is especially important for the complicated compounds. In this case, however, indium and gallium can partially remain in the obtained fulleride.

Fullerides synthesized by different methods were studied in Ref. [9]. Superconductive transition temperatures for heterofullerides with similar composition but prepared from amalgams or by exchange reactions do not differ significantly (fig. 1a). It was shown that mercury get into fulleride and some charge transfer from mercury to the fulleride molecule occurs [10,11]. It was found that in homo-, as in heterofullerides transition temperature \(T_c\) increases with \(fcc\) lattice parameter \(a\), as shown in fig. 1b (we added data for 3 samples synthesized from gallams and investigated in this work).

The aim of this work is to study the superconducting properties of a new heterofullerides \(A_n\text{In}_x\text{Ga}_y\text{C}_{60}\) (\(A=\text{K,Rb,Cs};\ n=2,3;\ x,y<1\)), synthesized from gallams. 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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2. Experimental

In this paper we study the samples, synthesized by a new method using liquid gallams (alloys of metals with eutectic alloy Ga:In=70:30). The interaction between components was carried out in the organic solvent (toluene), in which fullerene is soluble, in order to better deliver a metal reagent to the fullerene molecule and to facilitate the subsequent separation of gallams from the target product. The synthesis of the alkali metal fullerides, and subsequent removal of toluene and gallams, drying of products of reaction, and their packaging in glass ampoules were carried out in vacuum in the full glass facilities equipment. In more detail the last technique is described in Ref's [6-8]. 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{n}In\textsubscript{x}GayC\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 [10,11].

3. Results and discussion

Temperature dependence of the magnetic susceptibility for synthesized samples K\textsubscript{2}In\textsubscript{x}GayC\textsubscript{60} and K\textsubscript{3}In\textsubscript{x}GayC\textsubscript{60} is shown in fig. 2. The transitions in a superconducting state were observed at temperatures 24.5 K and 14.5 K correspondingly. Until now the fulleride with highest $T\text{c}$ on the base of potassium (which does not include atoms of other alkali metals Rb and Cs) was the K\textsubscript{2}Hg\textsubscript{x}C\textsubscript{60} ($T\text{c}$ = 22 K) [10,11]. Thus the used method of synthesis made a superconductor K\textsubscript{2}In\textsubscript{x}GayC\textsubscript{60} with highest $T\text{c}$ from not a superconductor K\textsubscript{3}C\textsubscript{60}. It indicates that components of gallams aren't inert solvents in reaction of intercalation, but intercalates itself into a fullerides lattice and change their superconducting properties. According to the X-ray data the heterofulleride with the composition K\textsubscript{2}In\textsubscript{x}GayC\textsubscript{60} was crystallized in the fcc lattice with the lattice parameter $a=1.427$ nm (fig. 3a), which is close to the value obtained for K\textsubscript{3}C\textsubscript{60} ($a=1.424$ nm [4]). The parameters of investigated samples are listed in table 1. The dependence of $T\text{c}$ on the lattice parameter $a$ for superconducting samples synthesized from gallams is shown in fig. 1b by open cycles. The difference in $T\text{c}$ for samples K\textsubscript{3}In\textsubscript{x}GayC\textsubscript{60} and K\textsubscript{2}In\textsubscript{x}GayC\textsubscript{60} is the most probably due to the more optimal charge transfer from intercalated atoms to fullerene molecule for the sample K\textsubscript{2}In\textsubscript{x}GayC\textsubscript{60}.

The fulleride Rb\textsubscript{2}In\textsubscript{x}GayC\textsubscript{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.
These data shows that components of gallams were intercalated in fulleride lattice, changed the lattice type and made from superconductor Rb$_3$С$_{60}$ not superconducting composition. At the same time the fulleride Rb$_2$In$_x$GayC$_{60}$ remain the superconductor with $T_c = 26$ K. Temperature dependence of magnetic susceptibility of sample Rb$_2$In$_x$GayC$_{60}$ is plotted in fig. 2.

According to the X-ray data, this sample consists of two phases: the first phase is similar to Rb$_2$In$_x$GayC$_{60}$ (fcc lattice) and the second phase is close to Rb$_3$In$_x$GayC$_{60}$ (orthorhombic lattice). The X-ray diffraction data for Rb$_2$In$_x$GayC$_{60}$ is plotted in fig. 3b. The peaks related to the fcc phase are indicated by solid lines, and to the orthorhombic phase – by dashed lines. 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$_3$C$_{60}$ ($a=1.4384$ nm [5]). 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$_3$C$_{60}$ (28 K [5]). Thus, in the conditions of synthesis method chosen by us the composition «Rb$_2$In$_x$GayC$_{60}$» is not formed, or even if it is formed then it decay on two known phases – mono- and triple-rubidium fullerides.

The heterofulleride with the composition Cs$_3$In$_x$GayC$_{60}$ is not a superconductor. According to the X-ray data, this samples crystallize in the orthorhombic lattice (see table 1). The absence of a 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.

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

| Composition       | $T_c$ (K) | Lattice type | Lattice parameters (Å) |
|-------------------|-----------|--------------|------------------------|
| K$_3$In$_x$GayC$_{60}$ | 14.5      | fcc          | 14.269(2)              |
| K$_2$In$_x$GayC$_{60}$ | 24.5      | fcc          | 14.276(4)              |
| Rb$_3$In$_x$GayC$_{60}$ | -         | orthorhombic | $a=9.110(13)$, $b=10.105(11)$, $c=14.188(15)$ |
| Rb$_2$In$_x$GayC$_{60}$ | 26        | fcc (30%) +  | 14.444(1) +            |
|                   |           | orthorhomic (70%) | $a=9.091(4)$, $b=10.075(5)$, $c=14.173(6)$ |
| Cs$_3$In$_x$GayC$_{60}$ | -         | orthorhombic | $a=9.097(5)$, $b=10.227(5)$, $c=14.159(9)$ |

Figure 2. Temperature dependence of magnetic susceptibility of samples K$_3$In$_x$GayC$_{60}$, K$_2$In$_x$GayC$_{60}$ and Rb$_2$In$_x$GayC$_{60}$. 

![Figure 2](image_url)
The fulleride $\text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60}$ was not a superconductor. The fulleride $\text{Rb}_2\text{In}_x\text{Ga}_y\text{C}_{60}$ was a superconductor with $T_c = 25 \text{ K}$. Thus the alkali metals fullerides synthesized from gallams have higher $T_c$ than analogous fullerides synthesized from amalgams. We also synthesized from amalgams the fullerides with composition $\text{K}_2\text{GaHg}_x\text{C}_{60}$, $\text{Rb}_2\text{GaHg}_x\text{C}_{60}$ and $\text{K}_2\text{InHg}_x\text{C}_{60}$, $\text{Rb}_2\text{InHg}_x\text{C}_{60}$. The fullerides $\text{K}_2\text{GaHg}_x\text{C}_{60}$ and $\text{Rb}_2\text{GaHg}_x\text{C}_{60}$ are superconductors with $T_c$ equal to 20 K and 25 K, correspondingly. The fullerides $\text{K}_2\text{InHg}_x\text{C}_{60}$ and $\text{Rb}_2\text{InHg}_x\text{C}_{60}$ are not superconductors though crystallize in $fcc$ lattice. It means that rather gallium than indium is responsible for high $T_c$ for the sample $\text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60}$.

4. Conclusions

The new heterofullerides with the composition $\text{A}_n\text{In}_x\text{Ga}_y\text{C}_{60}$ ($\text{A}=\text{K},\text{Rb},\text{Cs}; n=2,3; x, y <1$) were synthesized. Temperature dependence of the magnetic susceptibility was measured in the temperature range from 4.2 K to 297 K and transitions in the superconducting state were detected at temperatures $T_c$ ranged from 14.5 K to 26 K. For the fulleride $\text{K}_2\text{In}_x\text{Ga}_y\text{C}_{60}$ 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). Thus, the components of gallams intercalate into a fulleride lattice and improve their superconducting properties.

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