Superconductivity of the Heterofullerides Synthesized from Gallams and Amalgams

2014 J. Phys.: Conf. Ser. 568 022026

(http://iopscience.iop.org/1742-6596/568/2/022026)

Superconductivity of the Heterofullerides Synthesized from Gallams and Amalgams

V.A. Kulbachinskii[a*], R.A. Lunin[b], B.M. Bulychev[c]
Moscow State University, Low Temperature Physics Department, Moscow, Russia
[a*]kulb@mig.phys.msu.ru, [b]lunin@mig.phys.msu.ru,
b.bulychev@highp.chem.msu.ru

Keywords: superconductivity, fullerene, fulleride, crystal structure, amalgam, gallam

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. For the sample $Rb_2Hg_xC_{60}$ T_c=25 K, though Rb_2C_{60}, as well as K_2C_{60}, are not superconductors. Only one fulleride on the base of potassium (which does not include atoms of other alkaline metals Rb and Cs) was known before – the K_2LuC_{60} (T_c=20 K) with T_c higher than for K_3C_{60} [1]. 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.

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_{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_2C_{60} and to avoid the synthesis of the superconducting fulleride A_3C_{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 $A_nIn_xGa_yC_{60}$ (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 $Rb_3In_xGa_yC_{60}$ and $Cs_3In_xGa_yC_{60}$ but they are not superconductors while $K_3In_xGa_yC_{60}$ is a superconductor with Tc=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)
$K_2Ga_xIn_yC_{60}$	24.5	*fcc*	14.276(4)
$K_2Ga_xSn_yC_{60}$	15.4	*fcc*	14.282(8)
$K_2Ga_xBi_yC_{60}$	14.9	*fcc*	14.255(8)
$K_2GaHg_xC_{60}$	20	*fcc*	14,297(5)
$K_2MgHg_xC_{60}$	13.6	*fcc*	14.280(4)
$K_2AlHg_xC_{60}$	15.7	*fcc*	14,281(6)
$K_2Hg_xC_{60}$	22	*fcc*	14.279(3)
$K_3In_xGa_yC_{60}$	14.5	*fcc*	14.269(2)
$Rb_2AlHg_xC_{60}$	24.8	*fcc*+M2	14.458(4)
$Rb_2MgHg_xC_{60}$	21.8	*fcc*+~5%M2	14.447(4)
$Rb_2GaHg_xC_{60}$	25	*fcc*+ orthorhombic (10%)	14.439(3) a=9.055; b=10.057; c=14.190 Å
$Rb_2In_xGa_yC_{60}$	26	fcc+ orthorhombic	14.444(3)
Rb_2HgC_{60}	24.6	*fcc*+M2	14.440(2)
$Rb_3In_xGa_yC_{60}$	-	Orthorhombic	*a*= 9.110(13), *b*=10.105(11),*c*=14.188(15)
$Cs_3In_xGa_yC_{60}$	-	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 $K_2In_xGa_yC_{60}$, $K_3In_xGa_yC_{60}$ and $Rb_2In_xGa_yC_{60}$ 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 $K_2Hg_xC_{60}$ has T_c = 22 K and $Rb_2Hg_xC_{60}$ has T_c = 24.6 K (**Fig. 1b**). Thus the used methods of synthesis made superconductors $K_2In_xGa_yC_{60}$ and $K_2Hg_xC_{60}$ with T_c higher than in K_3C_{60} from not a superconductor K_2C_{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 $K_2Hg_xC_{60}$ crystallized in fcc lattice (**Fig.2a**) while $K_3Hg_xC_{60}$ has a monoclinic lattice (a=16.52Å, b=10.82Å, c=10.41Å, β=108.17^0, **Fig.2b**) and not a superconductor. According to the X-ray data the heterofulleride with the composition $K_2In_xGa_yC_{60}$ was crystallized in the *fcc* lattice with the lattice parameter *a*=1.4276 nm (**Fig. 3a**), which is close to the value obtained for K_3C_{60} (*a*=1.424 nm [7]). Superconducting transitions for $K_2Ga_xBi_yC_{60}$ and $K_2Ga_xSn_yC_{60}$ are shown in **Fig. 3b**.

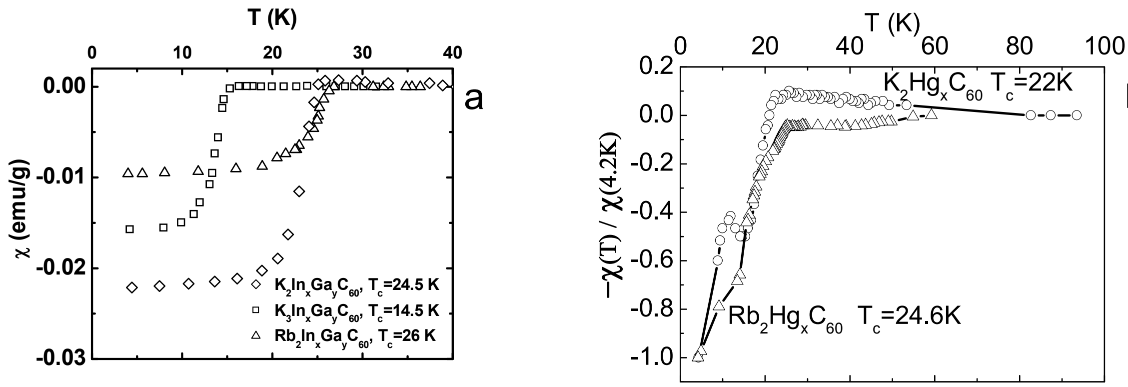

Fig. 1. Temperature dependence of magnetic susceptibility of samples $K_2In_xGa_yC_{60}$, $K_3In_xGa_yC_{60}$ and $Rb_2In_xGa_yC_{60}$ (a) and relative magnetic susceptibility of samples $K_2Hg_xC_{60}$ and $Rb_2Hg_xC_{60}$

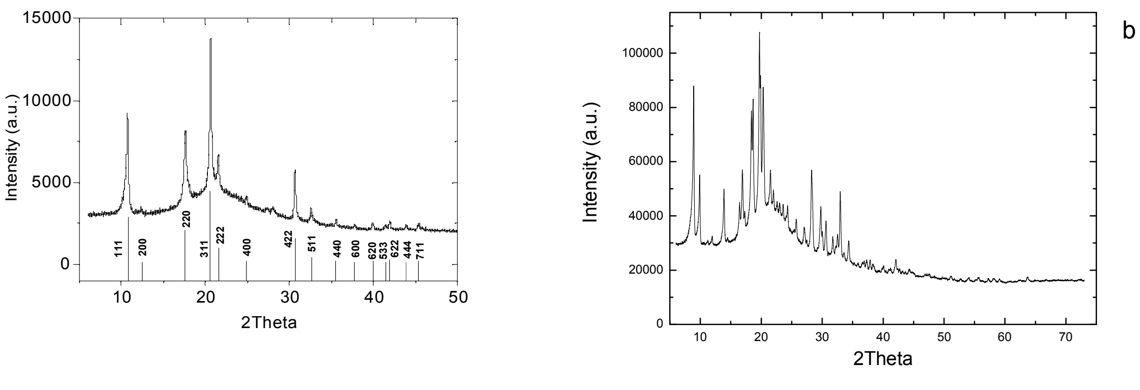

Fig. 2 X-ray diffraction of the sample (a) $K_2Hg_xC_{60}$ (indicated phase: *fcc*) and (b) $K_3Hg_xC_{60}$ (indicated phase: monoclinic)

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 gallams and amalgams is shown in Fig. 4b by open cycles. The difference in T_c for samples $K_2In_xGa_yC_{60}$ and $K_3In_xGa_yC_{60}$ is the most probably due to the more optimal charge transfer from intercalated atoms to fullerene molecule for the sample $K_2In_xGa_yC_{60}$. The fulleride $Rb_3In_xGa_yC_{60}$ 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.**

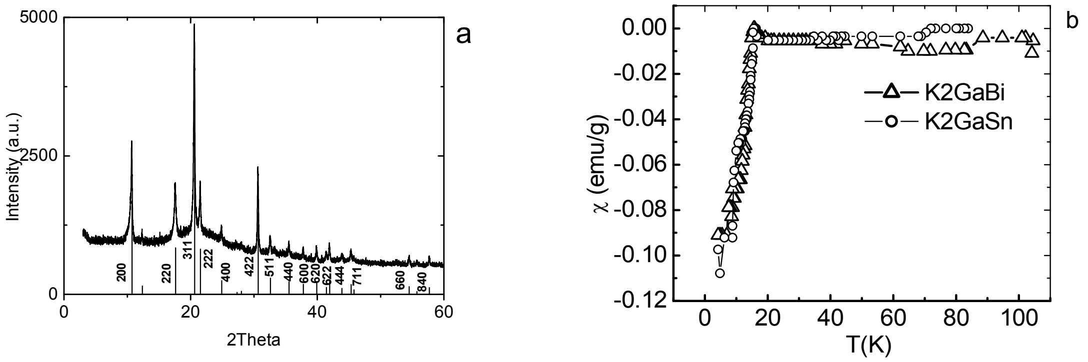

Fig. 3 X-ray diffraction of the sample (a) $K_2In_xGa_yC_{60}$ (indicated phase: *fcc*) and temperature dependence of magnetic susceptibility of samples $K_2Ga_xBi_yC_{60}$; $K_2Ga_xSn_yC_{60}$

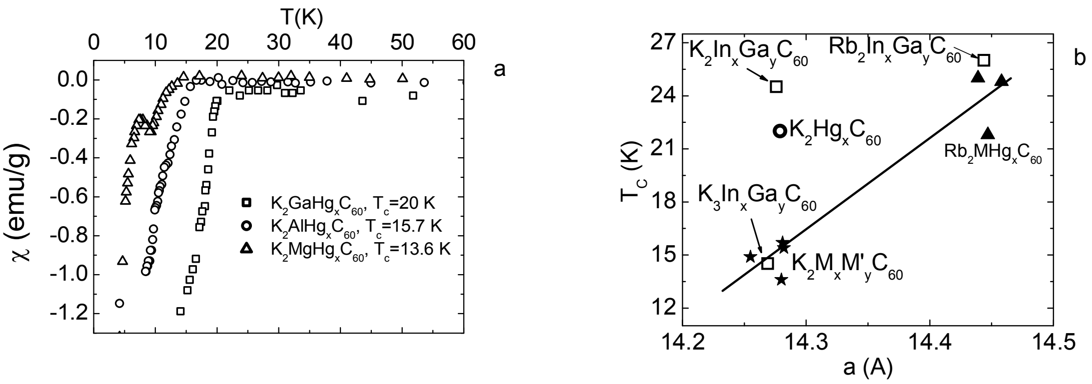

Fig. 4. (a) Temperature dependence of the magnetic susceptibility χ of the fulleride $K_2GaHg_xC_{60}$, $K_2AlHg_xC_{60}$, $K_2MgHg_xC_{60}$ (a) and dependence of the superconducting transition temperature T_c on the lattice papameter a for heterofullerides $K_2M_xM'_yC_{60}$ and $Rb_2MHg_xC_{60}$ (M = Be, Mg, Al, Ga, In, Sn, Bi)

Data shows that components of gallams were intercalated in fulleride lattice, changed the lattice type and made from superconductor Rb_3C_{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 $Rb_{2.92}C_{60}$ (*fcc* lattice) and the second phase is close to $Rb_{0.91}C_{60}$ (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_3C_{60} (a=1.4384 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_3C_{60} (28 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 $Cs_3In_xGa_yC_{60}$ 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 $A_nHg_xC_{60}$ (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 $K_2Hg_xC_{60}$ was superconductor with T_c = 22 K.

The fulleride $K_3Hg_xC_{60}$ was not a superconductor. The fulleride $Rb_2Hg_xC_{60}$ was a superconductor with T_c = 25 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 $K_2GaHg_xC_{60}$, $Rb_2GaHg_xC_{60}$ and $K_2InHg_xC_{60}$, $Rb_2InHg_xC_{60}$. The fullerides $K_2GaHg_xC_{60}$ and $Rb_2GaHg_xC_{60}$ are superconductors with T_c equal to 20 K and 25 K, correspondingly. The fullerides $K_2InHg_xC_{60}$ and $Rb_2InHg_xC_{60}$ are not superconductors though crystallize in *fcc* lattice. It means that rather gallium than indium is responsible for high T_c for the sample $K_2In_xGa_yC_{60}$.

Conclusions

The new heterofullerides with the composition $A_nB_xD_yC_{60}$ (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 $K_2In_xGa_yC_{60}$ 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. Kytin 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. Kytin, 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).