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)

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Abstract. The fullerides $A_nM_mC_{60}$ (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 supercomductors. The fullerides with composition $Cs_nHg_xC_{60}$ (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 $K_3Hg_xC_{60}$ from amalgam gives fulleride with monoclinic lattice. The fulleride $K_3Hg_xC_{60}$ is not superconductor. Heterofulleride with composition $K_2Hg_xC_{60}$ (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_3C_{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, on 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.

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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

$$A_4C_{60} + MCl_2 \xrightarrow{THF} A_2MC_{60} + 2ACl \quad (1)$$

$$A_5C_{60} + 2MCl_2 \xrightarrow{THF} AM_2C_{60} + 4ACl \quad (2)$$

$$A_5C_{60} + MCl_3 \xrightarrow{THF} A_2MC_{60} + 3ACl \quad (3)$$

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

$$A_2C_{60}+AlH_3 \xrightarrow{толуол} A_2AlC_{60}+3/2\ H_2 \quad (4)$$

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 $T>20^OC$ 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.

Table 1. Some parameters of samples

№	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 Å +KCl
225	$K_4C_{60}+MgCl_2+C_{60}$	THF	K_2MgC_{60}	16	*fcc, a*=14.290 Å+KCl
942	$\{2K+Mg+(Hg)_n\}+C_{60}$	toluene	$K_2MgHg_xC_{60}$	13.6	*fcc, a*=14.280 Å
292	$K_5C_{60}+2MgCl_2+C_{60}$	THF	KMg_2C_{60}	15.5	*fcc, a*=14.256 Å +KCl
236	$K_5C_{60}+AlCl_3+C_{60}$	THF	K_2AlC_{60}	14.5	*fcc, a*=14.249 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	$K_2AlHg_xC_{60}$	15.7	*fcc, a*=14,281 Å + second phase (~3 %)
931	$\{2K+Ga+(Hg)_n\}+C_{60}$	toluene	$K_2GaHg_xC_{60}$	20	*fcc, a*=14,297 Å +second phase
923	$\{2K+In+(Hg)_n\}+C_{60}$	toluene	$K_2InHg_xC_{60}$	-	*fcc, a*=14.281 Å +second phase
264	$Rb_4C_{60}+BeCl_2+C_{60}$	THF	Rb_2BeC_{60}	22	*fcc, a*=14.447 Å+RbCl
724	$Rb_4C_{60}+MgCl_2+C_{60}$	THF	Rb_2MgC_{60}	19	*fcc, a*=14.425Å+RbCl
982	$\{2Rb+Mg+(Hg)_n\}+C_{60}$	toluene	$Rb_2MgHg_xC_{60}$	21.8	*fcc, a*=14.447 Å +~5%M_2
12	$Rb_5C_{60}+2MgCl_2+C_{60}$	THF	$RbMg_2C_{60}$	-	*fcc, a*= 14.425 Å +RbCl
13	$\{Rb+2Mg+(Hg)_n\}+C_{60}$	toluene	$RbMg_2Hg_xC_{60}$	-	-
979	$\{2Rb+Al+(Hg)_n\}+C_{60}$	toluene	$Rb_2AlHg_xC_{60}$	24.8(11)	*fcc,a*=14.458 Å+M_2
929	$\{2Rb+Ga+(Hg)_n\}+C_{60}$	toluene	$Rb_2GaHg_xC_{60}$	25	*fcc,a*=14.439(3) (~90%) + *a*=9.055; *b*=10.057; *c*=14.190 Å (~10%)
922	$\{2Rb+In+(Hg)_n\}+C_{60}$	toluene	$Rb_2InHg_xC_{60}$	-	*a*=14.439(3) (~65%) + *a*=9.055; *b*=10.057; *c*=14.190 Å(~35%)
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	$Cs_2MgHg_xC_{60}$	-	Amorphous
674	$Cs_5C_{60}+AlCl_3+C_{60}$	THF	Cs_2AlC_{60}	-	Amorphous +CsCl
980	$\{2Cs+Al+(Hg)_n\}+C_{60}$	toluene	$Cs_2AlHg_xC_{60}$	-	Amorphous

Second phase M_2:- *a*=10.539; *b*=7.998; c=6.883 Å; β=103.21°; V=564.8 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_3C_{60} (fig. 1b). For heterofullerides synthesized with metals of 13th group with composition $A_2M^{+3}C_{60}$ we may suppose the transfer of 5 electrons. Nevertheless as we can see in table1 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}, $MAlC_{60}$, 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.

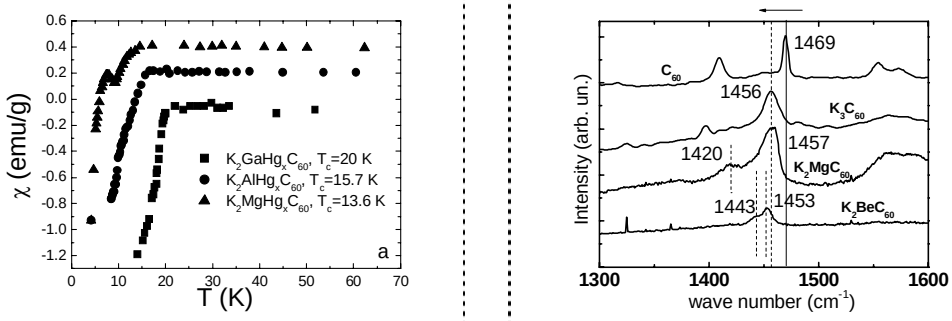

Figure 1. Temperature dependence of magnetic susceptibility for (a) $K_2GaHg_xC_{60}$, $K_2AlHg_xC_{60}$, and $K_2MgHg_xC_{60}$ and (b) shift of line $A_g(2)$ of Raman spectra in fullerite and synthesized fullerides.

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.

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