Superconductivity of heterofullerides with one or two atoms of the alkali metals and gallium, indium, bismuth or tin

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ABSTRACT

The new superconducting heterofullerides with the composition A n Ga x C 60 and A n Ga x M y C 60 (A = K, Rb; n = 1, 2; M = In, Sn, Bi; x, y < 1) were synthesized by a new method of reactions of liquid alloys (alkali metal with gallium or gallams) with a solution of fullerene in the organic solvent at temperature 110–120 °C. Temperature dependence of the magnetic susceptibility was measured in the temperature interval from 4.2 K to 100 K and transitions to the superconducting state were detected at temperatures T c ranged from 7 K to 25 K. New superconducting fullerides RbGa x C 60 and RbGa x In y C 60 with orthorhombic crystal lattice were discovered.

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1. Introduction

The study of electrophysical properties of fullerides conducted in nineties of the XX century showed that among them mainly the homo- or the heterofullerides containing not less and not more than three atoms of alkali metals and crystallizing in fcc lattice possess superconducting properties [1–3]. Later the superconductivity was also found in fullerides with two atoms of alkali metal and one atom of heterometal. These compounds were obtained either by reaction exchanges of A n C 60 (A = K, Rb; n = 3–5) with halogenides of metals of 2, 3, 8–13 groups [4,5] or by interaction with some alloys of alkali metals or with multicomponent amalgams [6,7]. In the last two cases the intercalation of heterometal into a voids of crystal lattice of fullerite proceeded with the mechanism of “rider”, in which in roles of “locomotive” the alkali metal acted [6,7]. It was shown in Ref’s [6–8] that fullerides with two atoms of alkali metal and mercury or gallams are superconductors.

The known now superconducting fullerides with one atom of alkali metal is the fulleride with composition KMg 2C 60 [4] with T c = 16 K, that was obtained by exchange reaction of K 5C 60 with two equivalents of MgCl 2 in environment of tetrahydrofuran, and RbBe 2C 60 [4] with T c = 13 K, that was obtained by exchange reaction of Rb 5C 60 with two equivalents of BeCl 2.

In the present paper we synthesized new heterofullerides with one or two atoms of the alkali metals and gallium, indium, bismuth or tin by method of “rider” in the toluene with the use of liquid at 100–110 °C alloys containing one or two equivalents of alkali metal on C 60 molecule and gallium (melting temperature equals to 28 °C) or gallams (alloys of gallium with indium, tin or bismuth with the melting temperatures 8–22 °C). We also tried to find the relation the crystal structure of superconducting heterofullerides with the superconducting transition temperature T c.

2. Experimental

2.1. Materials and physical measurements

All of the chemicals were of analytical grade from commercial sources and were used without further purification. X-ray powder diffraction data were recorded on a Guinier G670 HUBER diffractometer. Variable-temperature magnetic susceptibilities were measured for polycrystalline samples using low-frequency induction magnetometer over the temperature range of 4.2–100 K [4,5].
2.2. Samples

2.2.1. Synthesis of $A_xGa_yC_60$ ($A$ = K, Rb; $n$ = 1, 2)

In this work we investigated the heterofullerides synthesized by a new method of reactions of liquid alloy (alkali metal with gallium) with a solution of fullerene in the organic solvents. Synthesis was carried out in all-glass system similar to described in [9]. In our case all reagents are liquid that allows executing a reaction at reduced temperature. Homogeneity of the composition of obtained compounds should be close to the ideal that is especially important for the complicated compounds. The ratio of the main components (the alkali metal:fullerite) varied within 1:1 and 2:1, presuming the formation of fulleride with composition $AC_60$ and $A_2C_60$ i.e. the compounds which, unlike fcc phases $A_xC_60$, aren’t showing superconducting properties. The amount of gallium wasn’t regulated (usually 10–15 multiple surpluses against probable compositions $AM_2C_60$ and $A_2MC_60$ in order to keep the alloy liquid). Interaction between components (fullerite $C_60$, alkali metal and gallium) was carried out in the environment of absolute toluene or mix toluene:tetrahydrofuran (9:1, 40 ml) in the full glass facilities equipment in vacuum at 110–120°C within 25–30 days at continuous intermixing. The end of reaction was controlled by the loss of the color in the solution. After the end of the process the precipitate was decanted, rinsed out several times by solvent by means of refreezing and dried at 120–130°C in the same all-glass systems. The operations on unloading and preparation of samples for further investigation were carried out in the boxing Braun M, filled by argon with residual amounts of oxygen and water less than 0.1 ppm. A chemical analysis showed the presence of Ga in the synthesized samples. In the final product $A_xGa_yC_60$ the content of gallium $x$ was less than 1. The parameters of synthesized samples are listed in Table 1.

2.2.2. Synthesis of $A_xGa_yM_zC_60$ ($A$ = K, Rb; $n$ = 1, 2; $M$ = In, Sn, Bi)

The synthesis of $A_xGa_yM_zC_60$ ($A$ = K, Rb; $n$ = 1, 2; $M$ = In, Sn, Bi) was similar to the preparation of $A_xGa_yC_60$, but instead of gallium the liquid gallams (eutectic alloys Ga:In = 70(60):30(40), Ga:Sn = 50:50 or Ga:Bi = 50:50) were used. By chemical analysis we found heterometals in the synthesized samples.

3. Results and discussion

3.1. Fullerides with one alkali metal atom

Temperature dependence of a magnetic susceptibility of sample with one atom of potassium on a $C_60$ molecule and gallium ($KGA_yC_60$) is shown in fig. 1. The transition to a superconducting state was observed at temperature $T_c$ = 16.7 K. But it is known that the homofulleride $KGA_yC_60$ isn’t a superconductor [10]. It means that gallium during synthesis intercalates into a crystal lattice of fullerite together with the atom of alkali metal and changes electronic properties of fulleride. It is confirmed also by that fact that fullerite in toluene at 110°C doesn’t react with individual gallium or gallams within half a year. According to the X-ray data the heterofulleride with the composition $KGA_yC_60$ was crystallized in the fcc lattice similar to $KGA_yC_60$ with the lattice parameter $a = 1.4329$ nm, which is close to the value obtained for $KGA_yC_60$ ($a = 1.424$ nm [11]).

Temperature dependence of a magnetic susceptibility of synthesized from gallams fullerides with one atom of potassium and Sn or In ($KGA_yIn_yC_60$ and $KGA_ySn_yC_60$) are shown also in fig. 1. As an example X-ray data for the heterofulleride $KGA_yIn_yC_60$ is shown in Fig. 2. The parameters of these samples are listed in Table 1.

We obtained also the superconducting fulleride with composition $KGA_yBi_yC_60$ with $T_c = 10$ K (Table 1). The only known superconducting fulleride with one atom of potassium (and not containing

Fig. 1. Temperature dependence of a magnetic susceptibility for $KGA_yC_60$, $KGA_yIn_yC_60$, $KGA_ySn_yC_60$.

Fig. 2. X-ray diffraction of the sample $KGA_yIn_yC_60$ shows fcc crystal lattice. Stars mark not identified reflexes.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Composition</th>
<th>$T_c$ (K)</th>
<th>X-ray indicated phase</th>
<th>Lattice parameters (Å)</th>
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<tr>
<td>1401</td>
<td>$KGA_yC_60$</td>
<td>16.7</td>
<td>fcc $K_xC_{60}$</td>
<td>$14.32(5)$</td>
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<td>1420</td>
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<td>fcc $K_xC_{60}$</td>
<td>$14.27(6)$</td>
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<tr>
<td>1474</td>
<td>$KGA_yBi_yC_60$</td>
<td>10</td>
<td>fcc $K_xC_{60}$</td>
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</tr>
<tr>
<td>1475</td>
<td>$KGA_ySn_yC_60$</td>
<td>17</td>
<td>fcc $K_xC_{60}$</td>
<td>$14.39(17)$</td>
</tr>
<tr>
<td>1473</td>
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<td>$a = 10.11(4)$, $b = 9.10(5)$, $c = 14.25(10)$</td>
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<tr>
<td>1482</td>
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<td>$Rb_xC_{60}$</td>
</tr>
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<td>$14.26(5)$</td>
</tr>
<tr>
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<td>fcc $K_xC_{60}$</td>
<td>$14.28(2)$</td>
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<td>$14.45(4)$</td>
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</table>
others alkali metals) was the fulleride with composition KMg$_2$C$_{60}$ [4]. Thus, the use of a synthesis method from liquid gallium or gallams allowed increasing essentially the range of superconducting fullerides with only one atom of potassium.

Temperature dependence of magnetic susceptibility of sample with a composition RbGa$_x$In$_{1-x}$C$_{60}$ is shown in Fig. 3. The superconducting transition temperature equals to 7 K that is significantly lower than $T_c$ for Rb$_2$C$_{60}$ (28 K [12]) that assumes existence of superconducting fullerides with a new composition. Indeed, according to the X-ray data this sample crystallized in an orthorhombic lattice similar to Rb$_{0.87}$C$_{60}$ with the lattice parameters listed in Table 1. The second sample with gallium RbGa$_x$C$_{60}$ also was crystallized in an orthorhombic lattice as it is follows from the X-ray data in Fig. 4 (see Table 1) and was the superconductor with $T_c = 9.2$ K (see Fig. 3). The known now superconducting fullerides with orthorhombic lattice are rare-earth-metal-doped C$_{60}$: Yb$_{2.75}$C$_{60}$ [13] with $T_c = 6$ K and Sm$_2$C$_{60}$ [14] with $T_c = 8$ K. In the class of alkali-metal-doped C$_{60}$ the fulleride RbC$_{60}$ possesses the orthorhombic lattice [15,16]. Just as for our samples, for the orthorhombic RbC$_{60}$ an unusual low distance of 9.1 Å was observed between two C$_{60}$ molecules in the one direction [15,16]. In Ref. [15] this fact was explained by the covalent bonding between neighbouring C$_{60}$ molecules from which a polymeric character for the RbC$_{60}$ was deduced. In the polymeric state RbC$_{60}$ has a metallic character of the electronic system but does not becomes a superconductor. In Ref. [10] Raman spectra of RbC$_{60}$ was measured and electron–phonon coupling constants were estimated. These coupling constants turned out to be much smaller as compared to K$_2$C$_{60}$, which explains the lack of superconductivity in the RbC$_{60}$. For synthesized in the present paper orthorhombic fullerides RbGa$_x$C$_{60}$ and RbGa$_x$In$_{1-x}$C$_{60}$ the superconductivity was observed because the coupling constants are probably not such low as for RbC$_{60}$. Thus, for the first time we obtained the superconducting fullerides with an orthorhombic lattice in the class of alkali-metal-doped C$_{60}$.

3.2. Fullerides with two alkali metal atoms

The increasing the amount of the alkali metal content to two atoms on a molecule C$_{60}$ in the presence of the excess of gallium leads to the forming the compound K$_2$Ga$_x$C$_{60}$. According to the X-ray data the fulleride K$_2$Ga$_x$C$_{60}$ crystallizes in fcc lattice with lattice parameter $a = 1.4291$ nm similar to K$_2$C$_{60}$. As well as in the case of K$_2$C$_{60}$ it is well known that K$_2$C$_{60}$ isn’t a superconductor, but in the presence of mercury [6,7] and in this case, i.e. in the presence of gallium, becomes the superconductor with $T_c = 18$ K (Fig. 5). Thus, gallium, as well as mercury, intercalate into a fullerite lattice together with alkali metal and transform the non-superconducting compound into the superconductor.

The synthesized fullerides with composition K$_2$Ga$_x$In$_{y}$C$_{60}$, K$_2$Ga$_x$Sn$_y$C$_{60}$ and K$_2$Ga$_x$Bi$_y$C$_{60}$ also are superconductors. The parameters of these samples are listed in Table 1. The temperature dependence of magnetic susceptibilities for K$_2$Ga$_x$In$_{y}$C$_{60}$ and K$_2$Ga$_x$Bi$_y$C$_{60}$ fullerides are shown in Fig. 5. As we can see from the experimental data for formation of superconducting heterofullerides the nature of intransitive metal has no principal importance (in any case for the investigated range of metals). The major factor is its liquid state at synthesis temperature.

With replacing K by Rb it is possible to get a sample with composition Rb$_2$Ga$_x$C$_{60}$. The temperature dependence of a magnetic susceptibility for this sample in Fig. 6 shows two transitions to a superconducting state at temperatures $T_1 = 24.9$ K and $T_2 = 11$ K. The temperature of the first transition is close to $T_c = 28$ K for Rb$_2$C$_{60}$ [12]. The second $T_2$ temperature is close to $T_c = 9.2$ K observed for sample RbGa$_x$C$_{60}$ with orthorhombic lattice. Indeed, according to the X-ray data shown in Fig. 7 the sample consists of two phases: (i) fcc lattice, 60% of a sample volume close to Rb$_{2.9}$C$_{60}$ with lattice parameter $a = 1.4438$ nm (for Rb$_{2.9}$C$_{60}$ $a = 1.4384$ nm [12]) and (ii) orthorhombic lattice, 40% of a sample volume close to Rb$_{3.0}$C$_{60}$. The sample with indium Rb$_2$Ga$_x$In$_{y}$C$_{60}$ also consists of two different crystal phases (see Table 1) and also
shows two superconducting temperatures (see Fig. 6). Thus, under the conditions of synthesis the fullerides with two atoms of rubidium are not formed, or even if they are formed then they decay to two phases: with three and with one atom of rubidium. Consequently the superconducting transition with higher \( T_c \) most likely is ascribed to the fcc phase \( \text{Rb}_2\text{GaC}_{60} \), and the second to the orthorhombic phase.

In Fig. 8 the dependence of the superconducting transition temperature \( T_c \) on the fcc lattice parameter \( a \) is shown. The value of \( T_c \) increases with the fcc lattice parameter \( a \) according to the Bardeen–Cooper–Schrieffer [BCS] theory [1]: with increase of the lattice parameter \( a \) the width of a conduction band \( W \) decreases, therefore, the density of states at the Fermi level \( N(E_F) \sim W^{-1} \) increases and according to a BCS formula \( k_B T_c = 1.14 \hbar \omega_{	ext{ph}} \exp(-1/VN(E_F)) \) the \( T_c \) increases.

At low temperatures just above the superconducting transition we observed an increasing of the magnetic susceptibility (see Figs. 1, 3, 5 and 6). In the investigated heterofullerides the paramagnetic centers are responsible for a small raising of a magnetic susceptibility in the temperature range \( T_c \approx 30 \) K (see Figs. 1, 3, 5 and 6). Such centers most likely are the negatively charged oxygen complexes (e.g. \( \text{C}_{120}\text{O} \) or \( \text{C}_{60}\text{O} \)) or dimers (\( \text{C}_{120} \)) [17–19].

4. Conclusions

Thus, we developed a synthesis method of fullerides with low-temperature-melting metal gallium or alloys (gallams) and small amounts of alkali metals (one or two atoms on a molecule of fullerene). This method allows to obtain the new types of superconducting fullerides: \( \text{A}_n\text{Ga}_{x}\text{C}_{60} \) (\( A = \text{K}, \text{Rb} ; n = 1, 2 \)). By this method it is possible to synthesize the superconducting fullerides with different low-temperature melting metal compositions, but in the presence of some quantity of alkali metal. The value of superconducting transition temperature \( T_c \) in fullerides with one or two alkali atoms increases with the fcc lattice parameter \( a \). We observed superconductivity in the new fullerides with the orthorhombic crystal lattice.

References