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Superconductivity of potassium and rubidium heterofullerides modified with low-melting alloys

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The paper provides experimental data on the synthesis and study of the superconducting properties of potassium and rubidium heterofullerides modified by Wood's alloy — Sn, Pb, Bi, Cd (hereinafter W) with a melting temperature T_m = 61.5 °C or Y alloy — Bi, Sn, Pb, In, Cd, Tl with T_m = 41.5 °C. The synthesis of heterofullerides was carried out by the interaction of fullerides of the composition K_2C_{60} and Rb_2C_{60}, which do not have superconducting properties, with one of the alloys W or Y in an organic solvent — toluene at 100–110 °C. The samples obtained in this case showed superconducting properties with T_c = 8 K for K_2YC_{60} and Rb_2WC_{60} and 16 K for K_2WC_{60}.

Keywords: heterofullerides, Wood's alloy, superconducting properties.

1. Introduction

The discovery in 1991 of superconducting fullerides of alkali metals with the composition M_3C_{60} (M — K, Rb) and their combination with other alkali metals [1] stimulated studies of this class of superconductors [2]. It was found that an increase in the superconducting transition temperature T_c in these substances is proportional to an increase in the fcc lattice parameter of the fulleride [2, 3], that is actually determined by the size of the alkali metal atom. The maximum value T_c = 40 K is reached in Cs_3C_{60} under high pressure [4]. This feature indicates the possibility of modifying the composition and properties of fullerides by expanding the range of metal atoms intercalated into the fullerite lattice other than alkali. Indeed, using metals with different types of valence electrons and different sizes, one can expect a radical change in the electronic structure of fullerides and, as a consequence, a change in their structural and electrophysical properties. However, a serious obstacle to the implementation of this idea is the unsuitable physical properties of most metals of the Periodic Table, and, above all, their high melting temperatures and low ionization potentials.

Known methods of obtaining metal fullerides are based on the gas-phase synthesis method [1], which consists in the reaction of solid fullerite with metal vapors; their melt in vacuum or an inert organic solvent [2, 5, 6] or the interaction of fullerite with solutions of radical ion salts in organic (aromatic) or inorganic (ammonia) solvents [5, 6]. To obtain fullerides with metals with high melting points, we have developed a synthesis method based on exchange reactions of alkali metal fullerides with transition and non-transition metal halides in organic solvents (toluene, tetrahydrofuran) [5–7]. The method makes it possible to obtain heterofullerides of various compositions, including those with superconducting properties [5, 7].

Thus, it follows from the known data that the synthesis of homo- and heterofullerides can be successfully carried out if the metal (or its compound) incorporated into the fullerite lattice is in the gas phase, melt, or in solution.

Thus, using this method, heterometallic fullerides of the composition K_2MC_{60} were synthesized, where M are the elements from iron to copper groups of the Periodic table, which cover the entire spectrum of metals with an electronic configuration from d^5 to d^{10} [5]. The samples were studied by x-ray diffraction, magnetic resonance, Raman, and Mössbauer spectroscopy, and also by the low-frequency inductive method [8]. As an example, Fig. 1(a) shows the temperature dependences of the magnetic susceptibility for the fullerides $K_2Cu^{+2}C_{60}$, $K_2Fe^{+2}C_{60}$, $K_2Fe^{+3}C_{60}$, K_2NiC_{60}, which turned out to be superconductors with T_c = 13.9–16.5 K. The critical temperature was determined from the onset of the superconducting transition. Figure 1(b) shows superconducting transitions for fullerides K_2VC_{60}, K_2CrC_{60}, K_2SrC_{60}. Figure 1(c) shows superconducting transitions for Rb_2BeC_{60} (T_c = 24.5 K), K_2BeC_{60} (T_c = 13 K), K_2MgC_{60} (T_c = 14.9 K), KMg_2C_{60} (T_c = 16.3 K). For comparison, the transition for the standard fulleride K_3C_{60} (T_c = 18.5 K) is shown in Fig. 1(c).

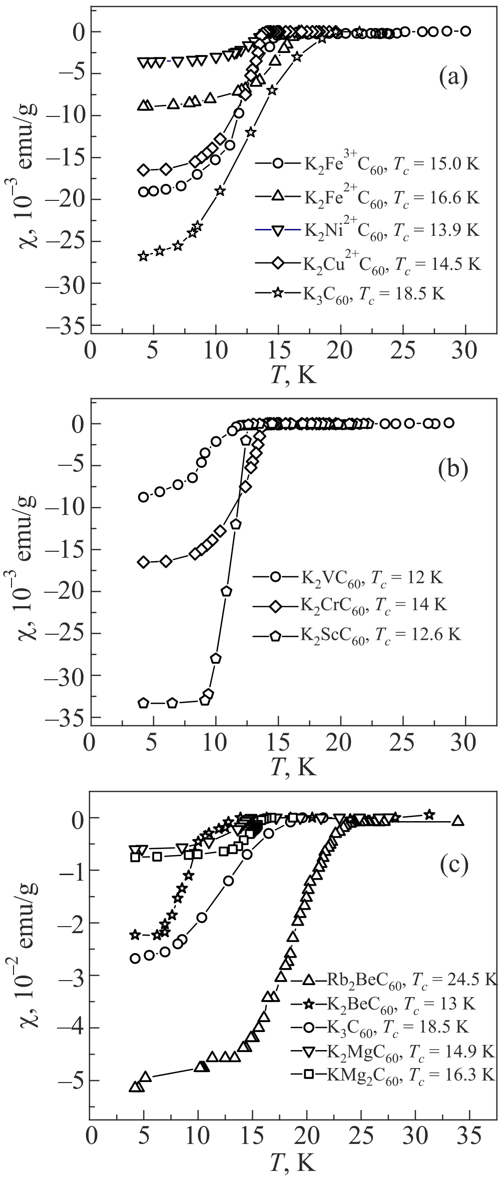

Fig. 1. Temperature dependence of the magnetic susceptibility χ of samples with the composition K_2MC_{60} (M = Fe, Ni, Cu) in comparison with K_3C_{60} (a); K_2MC_{60} (M = V, Cr, Sr) (b); K_2MC_{60} (M = Be, Mg), KMg_2C_{60}, Rb_2BeC_{60}, and K_3C_{60} (c).

This method made it possible to obtain heterofullerides with the composition $M_2M'C_{60}$, where M = K, Rb, and M′ are lanthanides with different degrees of filling of the 4*f* subshell (La, Pr, Nd, Sm, Gd, Tb, Yb, Lu) [7]. Superconducting were samples with compositions $K_2Yb^{+2}C_{60}$, $K_2Yb^{+3}C_{60}$, $Rb_2Yb^{+2}C_{60}$, $Rb_2Yb^{+3}C_{60}$, K_2LuC_{60} with T_c = 16–22 K. The highest critical temperatures were shown by fullerides containing elements with a completely filled 4*f* sublevel. The measured value of the superconducting transition temperature in K_2LuC_{60} (20 K) (Fig. 2) turned out to be higher than in the initial K_3C_{60} (18.5 K), which confirms the incorporation of rare earth metals in fulleride.

Indeed, using amalgams of Group 13 metals, superconducting heterofullerides of the compositions $K_2AlHg_xC_{60}$,

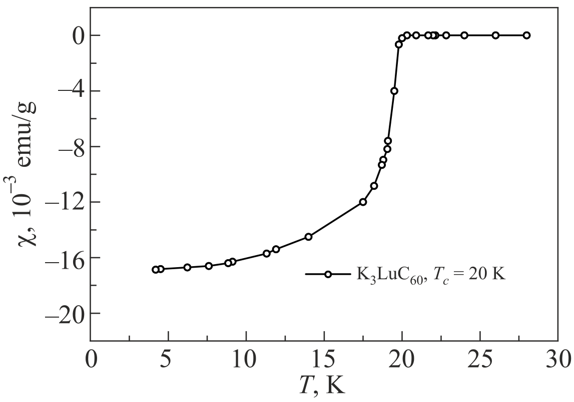

Fig. 2. Temperature dependence of the magnetic susceptibility χ of the sample with the composition K_2LuC_{60}.

$K_2GaHg_xC_{60}$, $Rb_2AlHg_xC_{60}$, $Rb_2GaHg_xC_{60}$ were synthesized, as well as a number of samples with thallium $K_2Tl_{0.25}Hg_xC_{60}$, $K_2Tl_{0.5}Hg_xC_{60}$, $K_2Tl_{0.75}Hg_xC_{60}$, $K_2TlHg_xC_{60}$ [8–10]. In this case, the temperatures of superconducting transitions in $K_2GaHg_xC_{60}$ (20 K) and $K_2Tl_mHg_xC_{60}$ (22 K) turned out to be higher than in potassium homofulleride (T_c = 18.5 K).

In the interaction of liquid metal-gallium alloys (gallams) with mono- and di-potassium (dirubidium) fullerides, which are not superconductors in themselves, fullerides of the composition KGa_xC_{60} and $K_2Ga_xC_{60}$ with T_c = 16.7 and 18 K, respectively, and a number of other superconducting fullerides ($A_nGa_xC_{60}$, $A_nGa_xBi_yC_{60}$, $A_nGa_xSn_yC_{60}$, $A_nGa_xIn_yC_{60}$, where A = K, Rb; *n* = 1, 2 [3, 11]), have been obtained. At the same time, it is well known that KC_{60} and K_2C_{60} do not exhibit superconducting properties. Surprisingly, gallium and mercury by themselves do not intercalate into fullerite, as well as into alkali metal fullerides. This suggests that both metals are incorporated in small amounts into the octahedral voids of the fulleride lattice, e.g., only in the form of an alloy.

In the present work, the method of additional intercalation of non-superconducting alkali metal fullerides of composition $A_{2-n}C_{60}$ (*n* = 0 or 1; A = K, Rb) with liquid alloys is extended to Wood's alloy (denoted by W) containing Bi — 50.0 %; Sn — 12.5 %; Pb 25.0 %; Cd — 12.5 % with a melting point T_m = 61.5 °C, and a low-melting alloy Y containing Bi; Cd; Pb; In; Sn; Tl with T_m = 41.5 °C and studied the superconducting and some structural properties of the obtained substances.

2. Samples

The method of synthesis of the initial fullerides of potassium and rubidium, methods of preparation of the obtained substances for structural and physicochemical studies and methods of their study were published in detail earlier in [5, 8, 12]. Additional intercalation of fullerides A_2C_{60} with alloys, as well as their synthesis, was carried out in full-glass reactors in vacuum with freezing of the solvent with liquid nitrogen. The amount of introduced alloys corresponded to the total amount of fullerite and alkali metal, i.e., in obvious excess. The processing of fullerides with the alloy was carried out at 110–120 °C in toluene for 2 weeks with constant stirring of the suspension. In the case of the introduction of low-melting light alloys, intercalation occurs in the reactions K_2C_{60} + W, Rb_2C_{60} + W, K_2C_{60} + Y. Data on some properties of the obtained heterofullerides are given in Table 1.

Table 1. Some characteristics of superconducting heterofullerides modified with Wood's alloy W and alloy Y. *Z* is the degree of filling of the lattice voids (according to the of x-ray diffraction patterns rectification by Rietveld); for comparison, K_3C_{60} and Rb_3C_{60} are given, parameter *a* is the fcc lattice parameter

Composition	T_c, K	Crystal lattice	*a*, Å	*Z*
K_2WC_{60}	16	fcc	14.254	2,41
Rb_2WC_{60}	8	fcc	14.428	2.4 (50 %) + + 0.9 (50 %)
K_2YC_{60}	8	fcc	14.209	–
K_3C_{60}	18.5	fcc	14.244	3
Rb_3C_{60}	29	fcc	14.438	3

3. Measurement results and discussion

It is rather difficult to establish the specific composition of fullerides obtained by this method due to the fundamental impossibility of their isolation in an individual state, i.e., not containing particles of the original alloy. At the same time, almost all of them crystallize in fcc lattices with parameters *a* close to those found for superconducting A_3C_{60} homofullerides and are also superconductors.

As an example, Fig. 3 shows the dependence of the magnetic susceptibility on temperature and the x-ray diffraction pattern for the K_2WC_{60} sample. Figure 4 shows the temperature dependence of the magnetic susceptibility and the x-ray diffraction pattern for the K_2YC_{60} sample and in Fig. 5 there is a dependence of the magnetic susceptibility χ on temperature for the Rb_2WC_{60} sample.

The temperatures of superconducting transitions of the obtained fullerides and the parameter *a* of the fcc lattice are given in Table 1. Two scenarios of the formation of superconducting compounds can be assumed. The first is associated with the disproportionation reaction of the starting dimetallic fulleride according to the reaction

$$2A_2C_{60} \rightarrow AC_{60} + A_3C_{60},$$

proceeding in the presence of alloys. However, only single fcc phase is found in the reaction products, which can be attributed to fulleride, and, in addition, the temperature of superconducting transitions of this phase in all cases turns out to be lower than T_c for potassium and rubidium homofullerides of composition A_3C_{60}.

The second scenario is associated with additional intercalation of the non-superconducting fulleride A_2C_{60} by one or several components of the low-melting alloy. The sizes

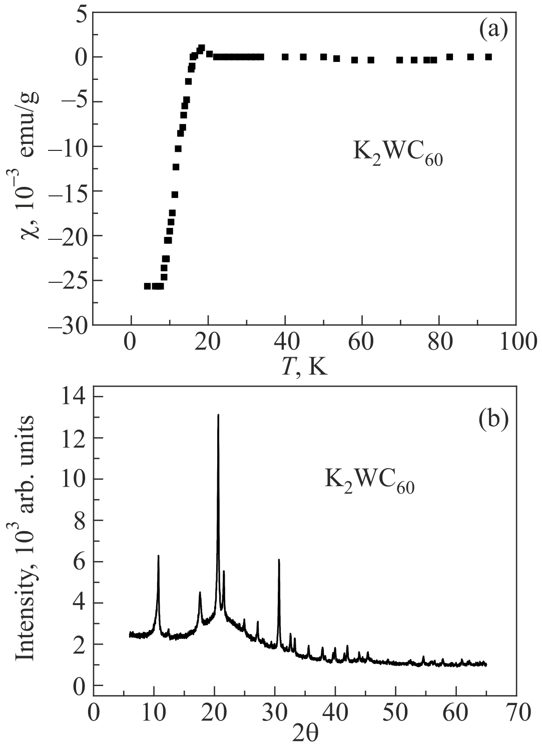

Fig. 3. Temperature dependences of the magnetic susceptibility χ (a) and x-ray diffraction pattern (b) of the K_2WC_{60} sample.

of the metal atoms that make up these alloys in all variants (ionic, covalent, atomic) are close to each other, but much smaller than the sizes of the K and Rb atoms and can be located in the octahedral and tetrahedral voids of the C_{60}

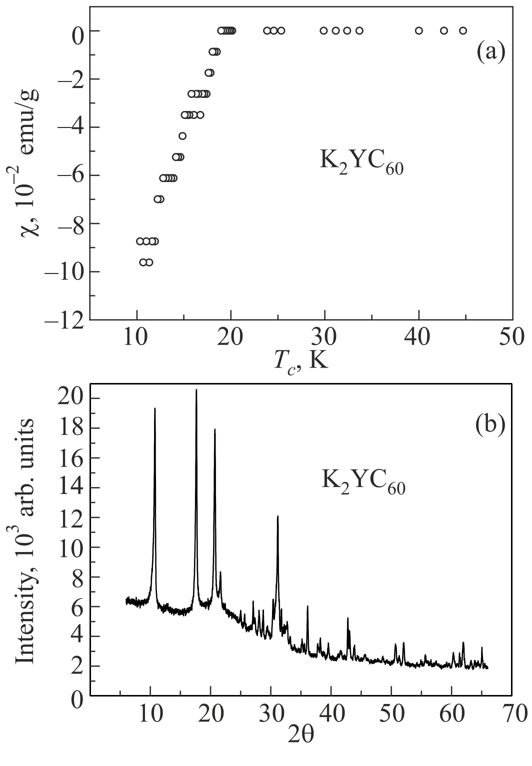

Fig. 4. Temperature dependences of the magnetic susceptibility χ (a) and x-ray diffraction pattern (b) of the K_2YC_{60} sample.

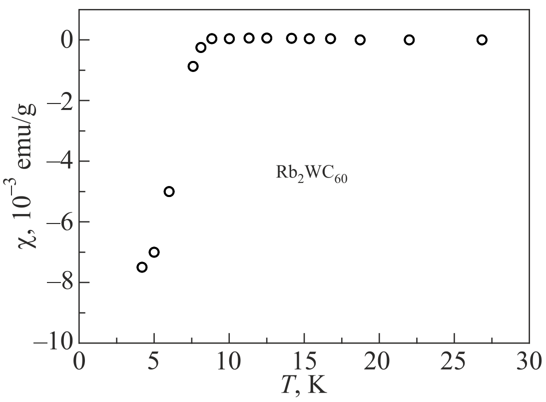

Fig. 5. Temperature dependences of the magnetic susceptibility χ of the Rb_2WC_{60} sample.

lattice, all of them are capable of intercalation into the fulleride lattice. It can be assumed that in this case, the determining factor will be not the size of the metal atom, but its ionization potential. But since it will most likely be lower than the ionization potential of an alkali metal and, taking into account the smaller size of all metal atoms in alloys, the degree of charge transfer in such compounds should be lower or insufficient for the formation of an optimal electronic structure (for example, when using a fulleride of composition AC_{60}) and, accordingly, the temperature of the transition to the superconducting state of the resulting compounds should be lower, which is observed experimentally.

4. Conclusion

The paper describes the structural and electrical properties of superconducting fullerides of new compositions obtained from non-superconducting alkali metal fullerides of composition $A_{2-n}C_{60}$ (n = 0 or 1; A = K, Rb), which do not have superconducting properties, with low-melting alloys such as Wood's alloy in an organic solvent — toluene. All synthesized heterofullerides have fcc crystal lattice and the temperature of the transition to the superconducting state of the obtained heterofullerides does not exceed 16 K.

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Надпровідність фулеридів, які модифіковані легкоплавкими сплавами

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Наведено експериментальні дані щодо синтезу гетерофулеридів з легкоплавкими сплавами: сплавом Вуда (W — Sn, Pb, Bi, Cd, температура плавлення T_m = 61,5 °C) та сплавом Y (Y — Bi, Sn, Pb, In, Cd, Tl — T_m = 41,5 °C), досліджено їх надпровідні властивості. Синтез фулеридів з легкоплавкими сплавами проведено прямою взаємодією фулеридів зі складом K_2C_{60} та Rb_2C_{60}, які не мають надпровідних властивостей, з обраним сплавом у середовищі органічного розчинника, а саме толуолу.

Ключові слова: гетерофулериди, сплав Вуда, надпровідні властивості.