

# Synthesis and superconductivity of organometallic fullerides $M_{(3-n)}(NR_4)_n C_{60}$ , where $M = K, Rb$ ; $R = H, D, Me, Et, Bu$ ; $n = 1, 2, 3$

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We present experimental data on the synthesis and investigation of the superconducting and structural properties of organometallic fullerides  $M_{(3-n)}(NR_4)_n C_{60}$ , where  $M = K, Rb$ ;  $R =$  hydrogen H, deuterium D, methyl Me, ethyl Et, butyl Bu;  $n = 1, 2, 3$ , synthesized by exchange reactions of homofullerides of alkali metals of composition  $K_3C_{60}$  and  $Rb_3C_{60}$  with ammonium halides in the medium of absolute toluene or tetrahydrofuran (THF) at temperatures from 23 °C to 110 °C. We have studied also superconductivity in  $Rb_2NH_4C_{60}$  and  $Rb_2ND_4C_{60}$  samples with replacement of hydrogen for deuterium in ammonium, as well as in  $K_2NH_4C_{60}$  and  $K_2ND_4C_{60}$ . The superconducting transition temperature did not change with replacement H by D within the measurement accuracy.

Keywords: isotope effect, organometallic fullerides, superconducting and structural properties.

## Introduction

In the 80s of the XX century, the authors of [1–3] predicted a new allotropic modification of carbon  $C_{60}$ , which later received the name fullerene. In 1985, this molecule was synthesized [4], for which the authors — G. Kroto, R. Curl, and R. Smalley in 1996 were awarded the Nobel Prize in Chemistry [5–7]. Subsequently, all molecules of the composition  $C_n$ , where  $n$  are even integers, began to be called fullerenes. Among the whole series of synthesized  $C_n$  molecules, fullerene  $C_{60}$  turned out to be the most accessible and stable.

In 1990, an efficient method for producing  $C_{60}$  was developed, based on the combustion of graphite in an electric arc in a vacuum-helium atmosphere [8], which made this product commercially available to a wide range of researchers. Solid fullerene in the form of black microcrystals is called fullerite. Its good solubility in aromatic hydrocarbons (fullerites are the only soluble carbon allotropes) made it possible to isolate the product from the coal deposit with a purity of up to 99.9 %. The study of this substance by x-ray showed that at room temperature  $C_{60}$  molecules form a face-centered cubic (fcc) lattice with a distance between the nearest neighboring molecules of 10.04 Å and a lattice constant of 14.2 Å. Even at the maximum packing density, the resulting compound has a low density — 1.697 g/cm<sup>3</sup> (density of graphite 2.3 g/cm<sup>3</sup>, and diamond 3.5 g/cm<sup>3</sup>). It

should be noted that at temperatures close to room temperature, fullerite can exhibit two close-packed crystalline modifications: a major face-centered cubic and a minor hexagonal close-packed (hcp). However, at present, methods have been developed that make it possible to synthesize fullerites with an hcp phase content of up to 95 % [9, 10], which is not yet of scientific and, accordingly, commercial interest. Pure fullerite at room temperature is an insulator with a band gap of the order of 1.9 eV with a very low conductivity.

If a substance (for example, an alkali metal atom, a solvent molecule or an ammonium ion) is inserted (intercalated) into the fullerite lattice, then such a substance is called a fulleride. The chemical and physical properties of intercalated compounds are radically different from the properties of the initial fullerene. Thus, for example, some metallofullerenes exhibit metallic and superconducting properties. In this case, however, the atoms of intercalated metals do not form chemical bonds with fullerene molecules, but transfer part of their electron density to  $C_{60}$  molecules, forming radical-ion salts. Let us consider the filling of voids with metal atoms in the lattice of  $C_{60}$  fullerite. The unit cell of the fcc lattice of fullerite contains four octahedral, eight tetrahedral, and thirty-two trigonal voids (interstices). Figure 1 schematically shows the arrangement of voids in the fcc lattice of fullerite.

The possibility of intercalation certain metal atoms into the fullerite lattice with the subsequent formation of crystalline

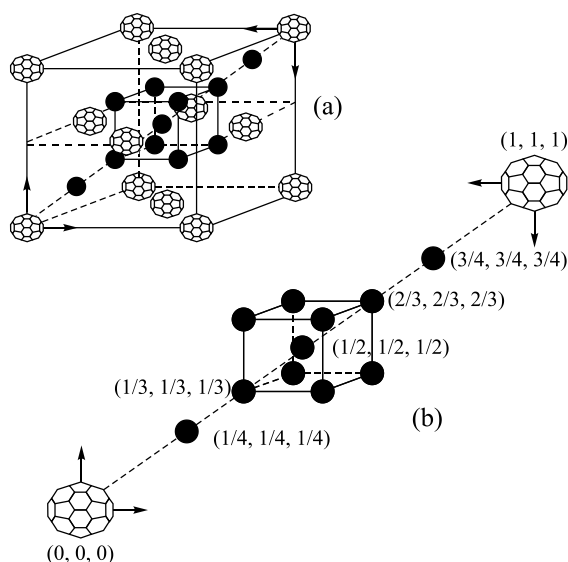


Fig. 1. Schematic representation of voids in the fcc lattice of fullerite (a). On the spatial diagonal of the cube there is one octahedral void —  $(1/2, 1/2, 1/2)$ , two tetrahedral —  $(1/4, 1/4, 1/4)$  and  $(3/4, 3/4, 3/4)$ , two trigonal —  $(1/3, 1/3, 1/3)$  and  $(2/3, 2/3, 2/3)$  (b).

substances (fullerides) is determined by the ratio between the size of the void and the ionic radius of the intercalated substance. Table 1 presents the main characteristics of the voids for the fcc lattice and the ionic radii of alkali metals and ammonium. It can be seen that the size of the octahedral void is larger than the radii of all alkali metals and ammonium, while the radius of the tetrahedral voids is close to the radius of the sodium atom.

At the first stage of the intercalation reaction, metal atoms occupy the largest octahedral interstices in crystal lattice. Filling all voids of this type leads to the composition of the  $AC_{60}$  fulleride. If all octahedral and tetrahedral voids are filled, then a compound of composition  $A_3C_{60}$  is formed. If A is an alkali metal, a fulleride is formed the electrical conductivity of which is several orders of magnitude higher than that of the initial fullerite [11].

Somewhat later it was found that at a temperature  $T = 18.5$  K the  $K_3C_{60}$  fulleride goes over into the superconducting state [12, 13]. Fullerides  $A_3C_{60}$  ( $A = K, Rb, Cs$ ) and  $A^{(1)}A^{(2)}A^{(3)}C_{60}$  ( $A^{(i)} = K, Rb, Cs$ ) intercalated with alkali metals are superconductors with the highest superconducting transition temperature  $T_c$  among molecular solids.

In  $Rb_3C_{60}$ , the superconducting transition temperature value is  $T_c = 29$  K, for  $RbCs_2C_{60}$ , the superconducting transition temperature is  $T_c = 33$  K [14]. For  $Cs_3C_{60}$  under pressure  $T_c = 40$  K [15].

Replacing one or two alkali metal atoms with others in the  $A_3C_{60}$  fulleride makes it possible to obtain superconductors with lower and, in rare cases, higher  $T_c$  values as compared to the initial fulleride. For example,  $T_c = 20$  K in the  $K_2LuC_{60}$  fulleride [16], which is higher than in the initial  $K_3C_{60}$  fulleride, from which it was synthesized.

Currently, various methods for the synthesis of fullerides are known: through the gas phase of metal and solid fullerite, through a solution of fullerite in a high-boiling aromatic hydrocarbon and a metal melt, through solutions of metals in ammonia, using solutions of ion-radical metal salts with condensed aromatic hydrocarbons (naphthalene, anthracene etc.) [12, 14, 16, 17]. As a rule, these methods give products identical to those obtained in gas-phase synthesis, but they all have one common drawback: in these reactions, only metals with low melting and evaporation points can be used.

There is a method of synthesis from liquid gallams (alloys Ga: In; Ga: In, Sn; Ga: In, Bi, etc.) with melting temperature  $T_m < 60$  °C and suspensions of non-superconducting fullerides of compositions  $KC_{60}$  and  $K_2C_{60}$  in toluene or tetrahydrofuran (THF), which produced superconducting heterofullerides [17]. The synthesis of heterofullerides through amalgams was carried out in a similar way [18, 19]. As an example, let us give a heterofulleride of the composition  $K_2Hg_xC_{60}$ , synthesized by this technique, which is a superconductor with  $T_c = 22$  K [18] (higher than 18,5 K for the  $K_3C_{60}$  fulleride).

The superconducting transition temperature  $T_c$  in heterofullerides (as well as in alkali metal fullerides  $A_3C_{60}$ ) usually increases with increasing a parameter of the fcc lattice, as shown in Fig. 2 [17, 19, 20]. Obviously, it is possible to change the composition and physicochemical properties of fullerides not only by using differences in the sizes of metal atoms, but also more subtle differences, for example, using polyvalent metals with different types of valence electrons ( $s, p, d, f$ ), neutral molecules or in general, using pseudo-metals such as ammonium or phosphonium and their derivatives.

For example, fullerides are known that contain atoms of alkali metals and a neutral molecule – ammonia. Fulleride of the composition  $NH_3K_3C_{60}$  at a temperature of  $T = 40$  K undergoes a structural phase transition from an fcc lattice

Table 1. Dimensions of voids in the fcc lattice, alkali metals and ammonium ions

| Type of structure    | Type of void | Number of voids per $C_{60}$ molecule | Radius, Å | Substance | $A^+$ -radius, Å |
|----------------------|--------------|---------------------------------------|-----------|-----------|------------------|
| fcc<br>$a = 14.17$ Å | Octahedral   | 1                                     | 2.06      | Cs        | 1.70             |
|                      | Tetrahedral  | 2                                     | 1.12      | Rb        | 1.49             |
|                      | Trigonal     | 8                                     | 0.78      | K         | 1.38             |
|                      |              |                                       |           | Na        | 1.02             |
|                      |              |                                       |           | Li        | 0.69             |
|                      |              |                                       |           | $NH_4$    | 1.43             |

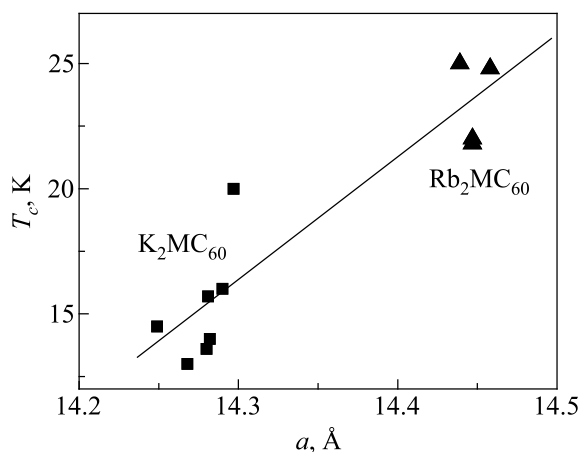


Fig. 2. Dependences of the superconducting transition temperature  $T_c$  on the parameter  $a$  of the fcc lattice for heterofullerides of the composition  $K_2MC_{60}$  and  $Rb_2MC_{60}$  ( $M = Be, Mg, Al, Ga$ ) [17, 19, 20].

to an orthorhombic one and becomes an insulator [21, 22]. However, under a pressure of more than 10 kbar, a transition to a superconducting state occurs with a critical temperature  $T_c = 28$  K [23]. Fulleride of the composition  $(NH_3)_xK_3C_{60}$  ( $0 < x < 1$ ) with an fcc lattice has a superconducting transition temperature of 8.5 K [24], and in the compound  $(NH_3)_4Na_2CsC_{60}$  the value of  $T_c$  increases to near 30 K compared to the initial fulleride  $Na_2CsC_{60}$  with  $T_c = 10.5$  K [25]. In the fullerides  $(NH_3)_xNaK_2C_{60}$  and  $(NH_3)_xNaRb_2C_{60}$  ( $0.5 < x < 1$ ), the superconducting transition temperatures are  $T_c = 8\text{--}13$  K and  $T_c = 8.5\text{--}17$  K, respectively [26].

A good guide in choosing a fullerite intercalation strategy is the chemistry of graphite intercalation compounds (GIC) with a huge set of methods for their synthesis and a wide variety of properties [27], including superconducting ones, which were initially discovered in GIC with compositions  $KC_8$ ,  $RbC_8$ ,  $CsC_8$  at ultralow temperatures [28]. Currently, dozens of GICs have been synthesized with an electrical conductivity exceeding the electrical conductivity of a metal at room temperature (so called “synthetic metals”) [29–35] and with higher temperatures of superconducting transitions (11.5 K for  $C_6Ca$ ) [36, 37].

Moreover, it turned out that quite complex organic substances can be intercalated into graphite. So, in [38], for this, the exchange reaction of sodium cations was used in the composition of the radical ionic salt of ethylenediamine  $[C_{15}Na(en)_{1.0}]$ , preliminarily intercalated into the interlayer space of graphite (the identity period was  $I_c = 0.671$  nm versus  $I_c = 0.3335$  nm in graphite), with tetrabutylammonium halide (see below). As a result of the reaction, the translation period in GIC increases to  $I_c = 0.802$  nm. This value is intermediate between the symmetric structure of the tetrabutylammonium ion (0.89 nm) and practically flat (0.47 nm) (Fig. 3).

Calculations show a relatively small energy difference for these two structures (less than 5 kJ/mol). Taking into

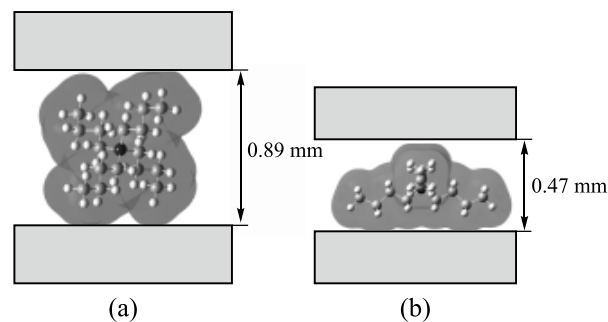


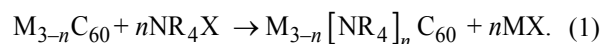
Fig. 3. Different positions of tetrabutylammonium between graphene layers: tetrahedral (a) and planar (b) [38].

account the possibility of “chemical flattening” of a sufficiently flexible molecule between graphite layers, which is especially clearly manifested in the GIC with cesium [39], such decrease in the value of  $I_c$  in comparison with the calculated one is quite acceptable.

In this work, for the first time, the superconducting and structural properties of heterofullerides intercalated with ammonium bases: ammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, synthesized by exchange reactions of fullerides of alkali metals with halides of ammonium bases in an organic solvent are investigated.

## 1. Experimental

The synthesis of heterofullerides containing ammonium or an ammonium base, as noted in the introduction to the synthesis of GIC with tetrabutylammonium [38], was carried out by exchange reactions of alkali metal fullerides of compositions  $M_{3-n}C_{60}$ ,  $n = 0\text{--}3$ , with halides of ammonium bases  $NR_4X$ , where  $R = H, D, Me, Et, Bu$ ;  $X = Cl, Br, I$ , in absolute toluene or tetrahydrofuran according to the equation



All operations to prepare the starting materials for synthesis and study the newly synthesized preparations were carried out in a Braun M box in an argon atmosphere or in a vacuum. Organic solvents were absolute according to standard methods accepted in organic and organometallic chemistry. The synthesis of all fullerides of alkali metals and the introduction of ammonium bases into the reaction was carried out in all-sealed and evacuated glass ampoules according to the methods described earlier in [17, 40–42]. After combining the reagents, glass reactors were placed on a laboratory shaker (room temperature) for 3 weeks or in an oven at 110 °C for 2 weeks. Subsequent operations to isolate the reaction products and carry out structural and electrophysical experiments were carried out as described in [17, 40–42].

X-ray diffraction studies of fulleride samples sealed in glass capillaries under vacuum were carried out on a Guinier G670 HUBER diffractometer.  $^{13}C$  NMR spectra (75.43 MHz) were recorded on a Bruker MSL-300 spectrometer in a stationary mode with a magnetic field  $B = 7.04$  T. Nuclear

spin systems were excited by a sequence of individual pulses: 4  $\mu$ s duration with 10–30 s between pulses for  $^{13}\text{C}$ . The number of pulses in one dimension was 450 for  $^{13}\text{C}$ . The sample temperature in the range of 120–400 K was maintained by the B-VT-1-1000 system with an accuracy of  $\pm 1$  K. The line shifts in the  $^{13}\text{C}$  NMR spectra were measured relative to the  $^{13}\text{C}$  signal from tetramethylsilane. Temperatures of superconducting transitions of fullerides were defined by standard low frequency induction method by measuring the temperature dependence of a magnetic susceptibility in temperature interval  $4.2 \text{ K} < T < 77 \text{ K}$  [17, 40–42]. For research, a sample in the form of a powder or a tablet was placed in a glass ampoule, evacuated in a vacuum, and then the ampoule was filled with helium at a pressure of 300–400 mm Hg.

## 2. Results and discussion

The problem of the existence in the individual state of “complex metals” of composition  $[\Phi X_4]$ , where  $\Phi = \text{N, P, As}$ ;  $X = \text{H, Alk}$ , and the definition of their “metallicity” has been discussed for over 100 years, that is, even more than the already solved problem of metallic hydrogen. Over the years, all possible methods of their synthesis were used with the use of physical, chemical, electrochemical methods of influencing a substance, but none of them led to a positive result [43]. At the same time, advances in the synthesis of inorganic substances with metals in unusual oxidation states have shown that they can be obtained and stored either in nanoscale matrices such as zeolites, graphite, or coal, or by being surrounded by bulky polydentate ligands. The radical ion tetrabutylammonium salt in a graphite matrix is a direct continuation of these concepts [38]. In this work, we propose to use fullerides as storage matrices for ammonium molecules and its alkyl derivatives. In this case, in addition to stabilization by the nature of changes in the electrophysical properties of fullerides, the problem of determining the degree of “metallicity” of ammonium by the nature of changes in the superconducting properties of heterofullerides, or at least the possibility of its existence in a form other than purely ionic, was also solved.

To solve these problems, in accordance with Eq. (1), a number of exchange reactions were carried out between alkali metal fullerides and ammonium chloride and halides of tetraalkylammonium bases in toluene and THF.

Since all fullerides synthesized by exchange reactions (1) are insoluble in toluene and, in addition, contain an impurity insoluble in it (alkali metal halide), it is rather difficult to determine the exact composition of the products obtained by elemental analysis.

Attempts to wash off the by-product with alcohols in all cases resulted in spoilage of the main product. The exchange reaction carried out in tetrahydrofuran led to partially soluble solvates, but all of them did not possess superconducting properties either before or after drying.

As a result, the compositions of the synthesized fullerides were calculated only from the loading of the components and were analyzed and studied after drying in vacuum and with slight heating in the form of mixtures by X-ray diffractometry, NMR spectroscopy, and the low frequency induction method.

### 2.1. Homo- and heterofullerides of ammonium and ammonium bases with alkali metals

Among the well-studied homo- and heterofullerides of alkali metals of compositions  $M_nC_{60}$ , where  $n = 1–6$ , only compounds of the composition  $M_3C_{60}$  where  $M$  is K, Rb and their mixtures  $M_{3-n}M'_nC_{60}$  ( $n = 1, 2$ ) with other alkali metals have superconducting properties. For potassium and rubidium homofullerides temperatures of superconducting transitions are equal to 18.5 and 29 K, respectively [12–14]. The ionic radii of the cations of ammonium, potassium, and rubidium do not differ appreciably (see Table 1).

Indeed, practically all samples of potassium, rubidium and ammonium heterofullerides obtained by type (1) exchange reactions also turned out to be superconductors. Figure 4 shows the temperature dependences of the magnetic susceptibility of three superconducting fullerides of the calculated composition  $K_2NH_4C_{60}$ , obtained in three different syntheses (two when heated to 110  $^\circ\text{C}$ , one at room temperature on a laboratory shaker) by the reaction of one equivalent of ammonium chloride with one equivalent of  $K_3C_{60}$ . All of them show the superconducting transitions. The different magnitude of the transition is associated with the different fraction of the superconducting phase in the samples. In the  $^{13}\text{C}$  NMR spectra of all the obtained fullerides, a signal in the range of 185–195 ppm was recorded, corresponding to the charged state of the  $C_{60}$  molecule and confirming the formation of fulleride. As an example, Fig. 4(c) shows the NMR spectrum for one of the  $K_2NH_4C_{60}$  samples (1581).

Table 2 lists some characteristics of superconducting fullerides  $K_2(NH_4)C_{60}$  and, for comparison,  $K_3C_{60}$ . From the data in Table 4 and Fig. 4(b), it follows that all fulleride crystallize in fcc lattice, the parameter of which is somewhat larger than the “standard” value for  $K_3C_{60}$ , which indirectly confirms the intercalation of ammonium and the production of new compounds. At the same time, the mixture contains potassium chloride, which unambiguously indicates the occurrence of exchange reaction (1).

Table 2. Some parameters of heterofullerides  $K_2(NH_4)C_{60}$

| No.  | Composition       | $T_c$ , K | Reaction products | fcc lattice parameter $a$ , $\text{Å}$ |
|------|-------------------|-----------|-------------------|--|
| 1581 | $K_2(NH_4)C_{60}$ | 16.7      | fcc + KCl         | 14.279                                 |
| 1105 | $K_2[NH_4]C_{60}$ | 15.8      | fcc + KCl         | 14.273                                 |
| 1121 | $K_2NH_4C_{60}$   | 16.5      | fcc + KCl         | 14.268                                 |
| –    | $K_3C_{60}$       | 18.5      | fcc               | 14.244                                 |

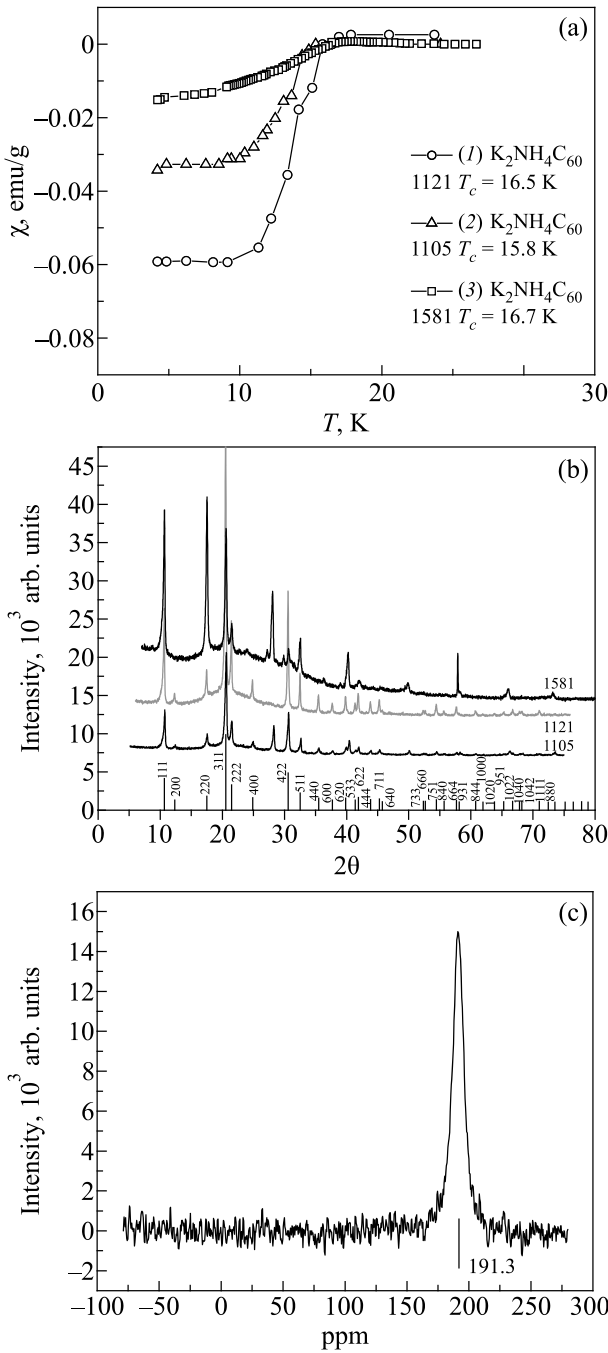


Fig. 4. Temperature dependence of the magnetic susceptibility  $\chi$  of  $K_2NH_4C_{60}$  heterofullerides synthesized from ammonium halides (a), their x-ray diffraction patterns (b) and  $^{13}C$  NMR spectrum of sample No. 1581 (c).

However, despite an increase in the fcc lattice parameter  $T_c$  for all  $K_2NH_4C_{60}$  samples is below the  $T_c$  of the initial  $K_3C_{60}$ . This can be explained by the low “metallic” properties of ammonium and the lower degree of charge transfer to molecule  $C_{60}$ .

Figure 5(a) shows the temperature dependences of magnetic susceptibility  $\chi$  of two  $K(NH_4)_2C_{60}$  fullerides obtained in two different syntheses and possessed a superconducting transition. The different magnitude of the transition is associated with the different fraction of the super-

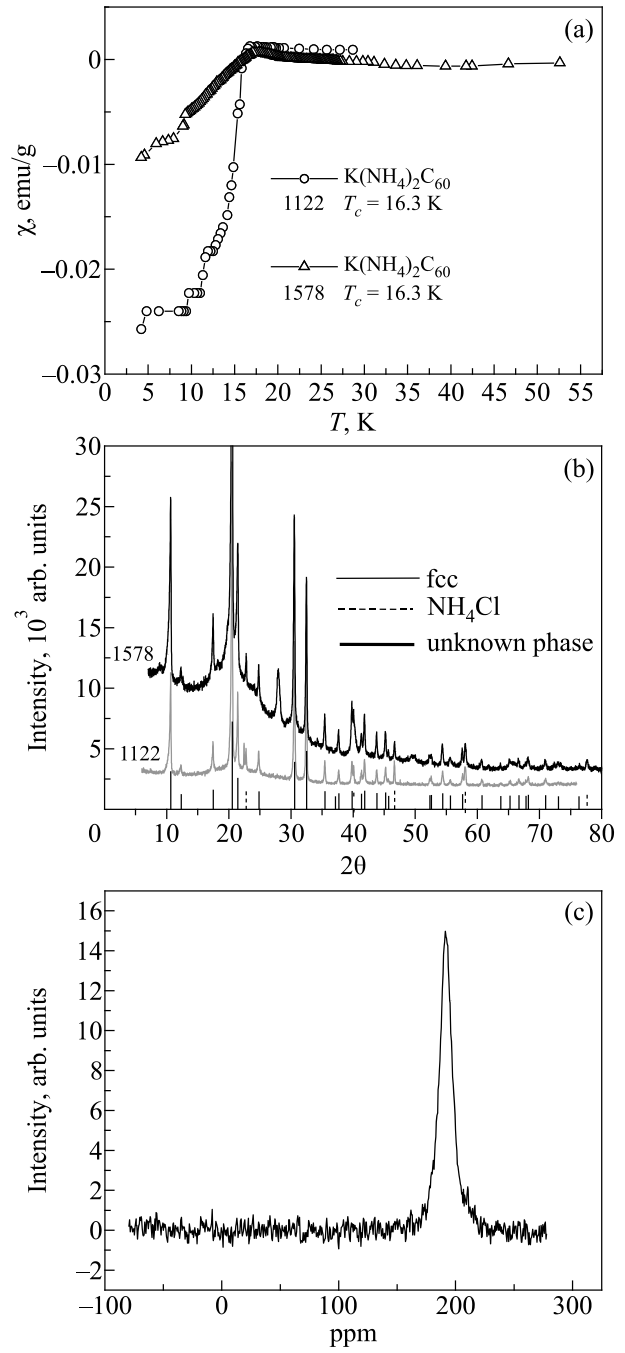


Fig. 5. Temperature dependence of magnetic susceptibility  $\chi$  heterofullerides  $K(NH_4)_2C_{60}$  synthesized from ammonium halides (a), their x-ray diffraction patterns (b),  $^{13}C$  NMR spectrum of sample No. 1578 (c).

conducting phase in the samples. The parameters of the studied samples are given in Table 3. Figure 5(b) shows x-ray diffraction patterns of these samples, showing the presence of a fulleride phase with an fcc lattice.

It can be seen that, in addition to the fulleride phase with an fcc lattice in the reaction products potassium chloride, an unknown phase and an impurity of ammonium chloride are found as the main ones (the fixation of the ammonium salt can be explained by the fact that it is taken in the reaction with 2–5 % excess). The parameters  $a$  of the of fcc lattices

Table 3. Some parameters of  $K(NH_4)_2C_{60}$  superconducting samples

| No.  | Composition       | $T_c$ , K | Reaction products        | fcc lattice parameter $a$ , Å |
|------|-------------------|-----------|--------------------------|-------------------------------|
| 1122 | $K(NH_4)_2C_{60}$ | 16.3      | fcc + KCl, unknown phase | 14.272                        |
| 1578 | $K(NH_4)_2C_{60}$ | 16.3      | fcc + $NH_4Cl$ , KCl     | 14.294                        |

fullerides, as in the previous case, are increased in comparison with the initial  $K_3C_{60}$  fulleride. The  $^{13}C$  NMR spectrum [Fig. 5(c)] for one of them with a signal at 191 ppm is almost identical to that shown in Fig. 4(c) and is typical for all superconducting fullerides containing potassium.

And finally, in Fig. 6 we plotted superconducting transitions in fullerides of the composition  $(NH_4)_3C_{60}$  for three samples obtained in three different syntheses. Note that this composition can be reached in two different ways, by carrying out the reaction (i)  $Rb_3C_{60} + 3NH_4Cl = (NH_4)_3C_{60}$  (1 in Fig. 6) or (ii)  $K_3C_{60} + 3NH_4Cl = (NH_4)_3C_{60}$  (2, 3 in Fig. 6). In both cases, the reaction product is the same with the same superconducting transition temperature, as shown in Fig. 6. The parameters of all three samples are listed in Table 4.

 Table 4. Some parameters of  $(NH_4)_3C_{60}$  superconducting fullerides

| No.  | Composition                                       | $T_c$ , K | Reaction products | fcc lattice parameter $a$ , Å |
|------|---|-----------|-------------------|-------------------------------|
| 1136 | $Rb_3C_{60} + 3NH_4Cl \rightarrow (NH_4)_3C_{60}$ | 16.2      | fcc + RbCl        | 14.421                        |
| 1551 | $K_3C_{60} + 3NH_4Cl \rightarrow (NH_4)_3C_{60}$  | 16.4      | fcc + KCl         | 14.229                        |
| 1131 | $K_3C_{60} + 3NH_4Cl \rightarrow (NH_4)_3C_{60}$  | 16.7      | fcc + KCl         | 14.277                        |

Complete replacement of K (potassium) in the  $K_3C_{60}$  fulleride by  $NH_4$  with the final composition  $(NH_4)_3C_{60}$  is assumed in sample No. 1551, which is a superconductor with  $T_c = 16.4$  K. The sample has a large homogeneous fraction of the superconducting phase (83 % volume) and a lower  $T_c$  as compared with the initial alkaline homofulleride, as evidenced by the characteristic transition in the temperature dependence of the magnetic susceptibility [see Fig. 6(a) and Table 4]. The XRD spectrum analysis indicates the presence of only two crystalline phases in the reaction products — fulleride and KCl, that confirms the complete course of the exchange reaction. At the same time, a characteristic signal of fullerite appears in the  $^{13}C$  NMR spectra in the region of 146 ppm [Fig. 5(c)], indicating

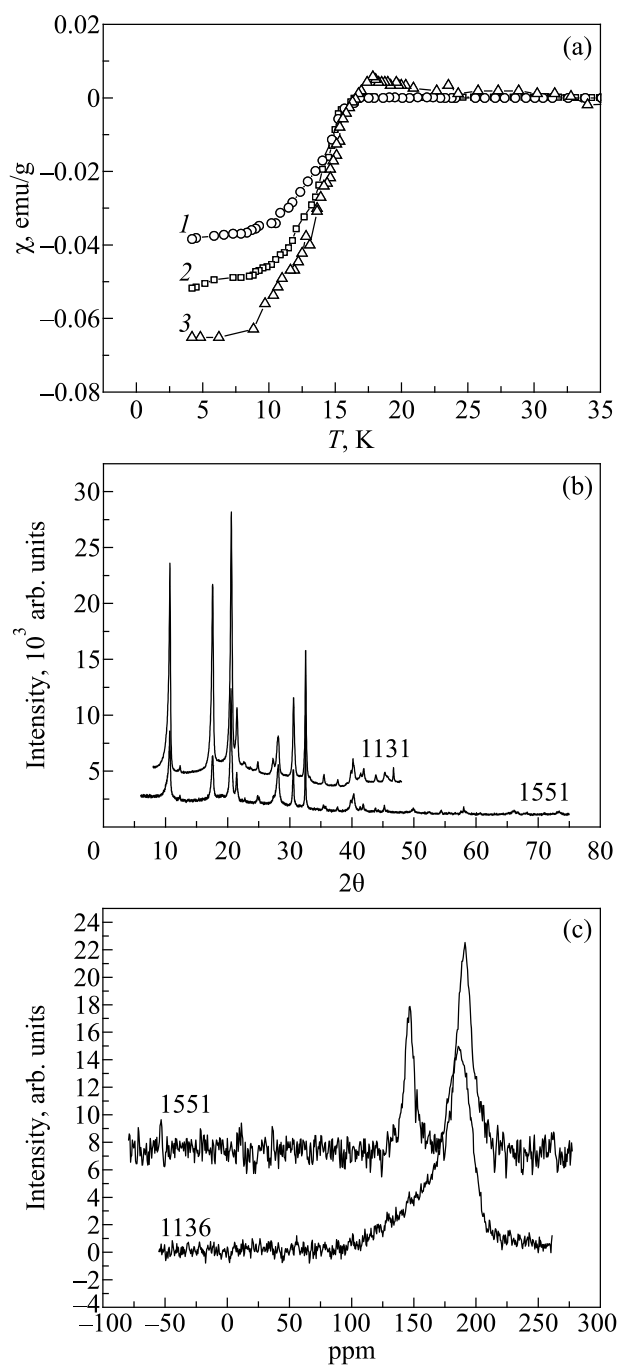


Fig. 6. Temperature dependence of the magnetic susceptibility  $\chi$  of heterofullerides  $(NH_4)_3C_{60}$  synthesized from ammonium halides samples: (a)  $Rb_3C_{60} + 3NH_4Cl = (NH_4)_3C_{60}$  (No. 1136) (1);  $K_3C_{60} + 3NH_4Cl = (NH_4)_3C_{60}$  (No. 1551) (2),  $K_3C_{60} + 3NH_4Cl = (NH_4)_3C_{60}$  (No. 1131) (3), (b) x-ray diffraction patterns of two samples and (c)  $^{13}C$  NMR spectrum of samples No. 1136 and No. 1551 with composition  $(NH_4)_3C_{60}$ .

the product of decomposition of a part of the fulleride which is not determined by x ray.

Thus, the proposed method for the synthesis of homo and heterofullerides of potassium, rubidium, and ammonium through the exchange reactions of trimetallic fullerides with ammonium chloride in a toluene medium leads to

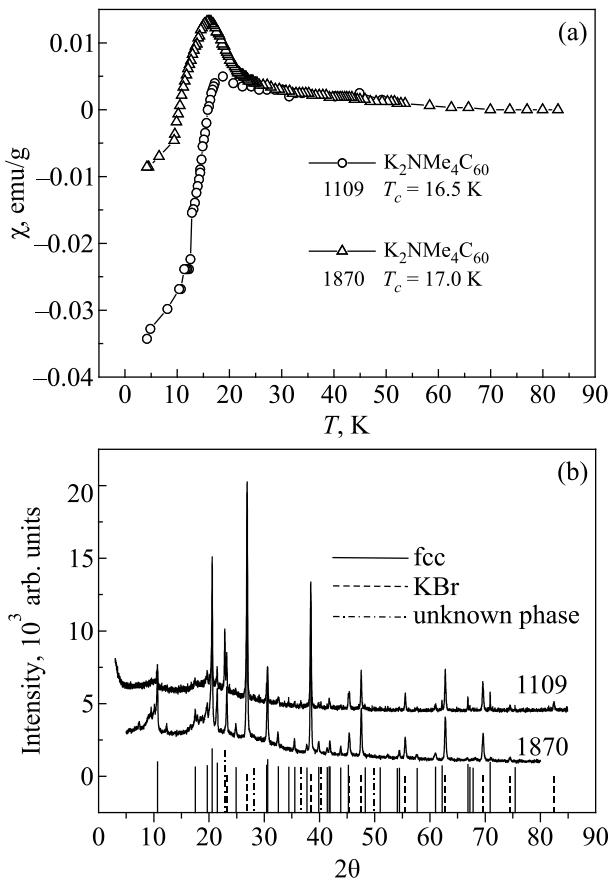


Fig. 7. Temperature dependence of magnetic susceptibility  $\chi$  heterofullerides  $\text{K}_2\text{NMe}_4\text{C}_{60}$  synthesized from tetramethylammonium halides (a) and their x-ray diffraction patterns (b).

the transformation of superconductors with the composition  $\text{M}_3\text{C}_{60}$  ( $\text{M} = \text{K}, \text{Rb}$ ) into radical ion salts  $\text{K}_2\text{NH}_4\text{C}_{60}$ ,  $\text{M}(\text{NH}_4)_2\text{C}_{60}$  [ $\text{M} = \text{K}, \text{Rb}$ ] and  $(\text{NH}_4)_3\text{C}_{60}$  with fcc crystal structure. These compounds, the composition of which was calculated from the loading of reagents and the phase composition of the final products, also possess superconducting properties, but with lower transition temperatures even despite a slight increase in the parameter  $a$  of the fcc crystal lattice. This indicates a lower “metallicity” of ammonium in comparison with alkali metals, but at the same time, the reality of the existence of ammonium in an individual molecular form.

2.2. Heterofullerides of tetramethylammonium ( $\text{NMe}_4$ ), tetraethylammonium ( $\text{NEt}_4$ ) and tetrabutylammonium ( $\text{NBu}_4$ ) with potassium and rubidium

The possibility of the formation of radical ion salts of fullerene with tetraalkylammonium bases was previously demonstrated by the example of the interaction of a  $\text{C}_{60}$  molecule with tetraoctylammonium bromide in o-chlorobenzene in the presence of a reducing agent — sodium fluorene radical anion [44]. In this respect, the exchange reaction of metallofullerenes with tetraalkyl bases does not require the use of a special reducing agent, since the fulleride itself is a radical anion with strong reducing properties. We

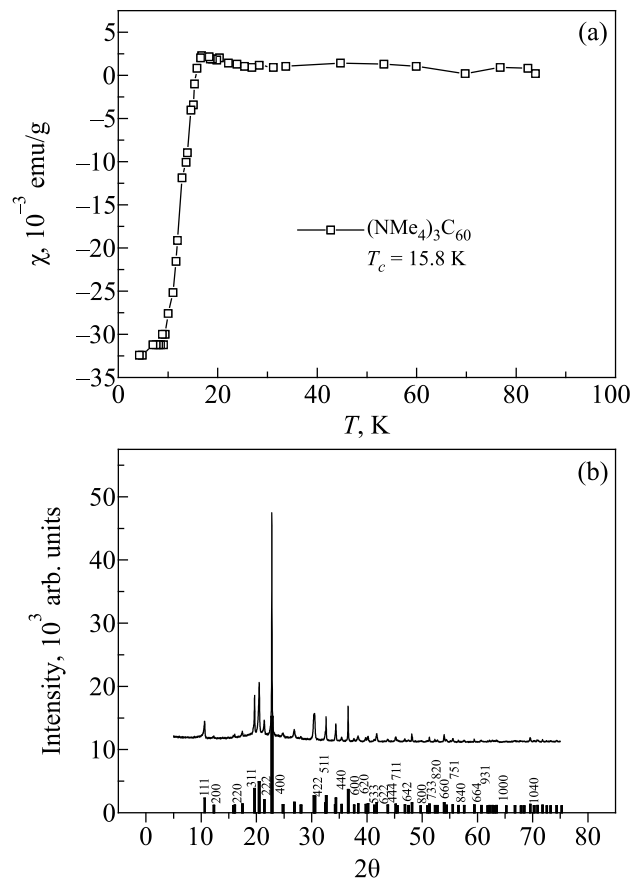


Fig. 8. Temperature dependence of magnetic susceptibility  $\chi$  heterofulleride tetramethylammonium 1108 ( $\text{NMe}_4$ ) $_3\text{C}_{60}$  with  $T_c = 15.8 \text{ K}$  (a) and x-ray diffraction pattern of this sample (b).

synthesized fullerides of tetramethylammonium ( $\text{NMe}_4$ ), tetraethylammonium ( $\text{NEt}_4$ ) and tetrabutylammonium ( $\text{NBu}_4$ ). Figures 7 and 8 show the curves of transitions to the superconducting state of fullerides with tetramethylammonium of the supposed compositions  $\text{K}_2\text{NMe}_4\text{C}_{60}$  and  $(\text{NMe}_4)_3\text{C}_{60}$ , obtained by reaction (1) (in this case  $\text{X} = \text{Br}$ ), and diffraction patterns of these fullerides, and in Table 5 some their characteristics.

Figure 9 shows the superconducting transition of dipotassium fulleride with tetraethylammonium  $\text{K}_2\text{NEt}_4\text{C}_{60}$  (synthesized by reaction (1), where  $\text{X} = \text{Br}$ ) and the x-ray

Table 5. Some characteristics of superconducting fullerides with tetramethylammonium and tetraethylammonium

| No.  | Composition                           | $T_c, \text{K}$ | Reaction products        | fcc lattice parameter $a, \text{\AA}$ |
|------|---------------------------------------|-----------------|--------------------------|---------------------------------------|
| 1109 | $\text{K}_2\text{NMe}_4\text{C}_{60}$ | 16.5            | fcc + KBr, unknown phase | 14.225                                |
| 1870 | $\text{K}_2\text{NMe}_4\text{C}_{60}$ | 17.0            | fcc + KBr, unknown phase | 14.264                                |
| 1108 | $(\text{NMe}_4)_3\text{C}_{60}$       | 15.8            | fcc + KBr, unknown phase | 14.283                                |
| 1111 | $\text{K}_2\text{NEt}_4\text{C}_{60}$ | 13.8            | fcc + KBr                | 14.297                                |

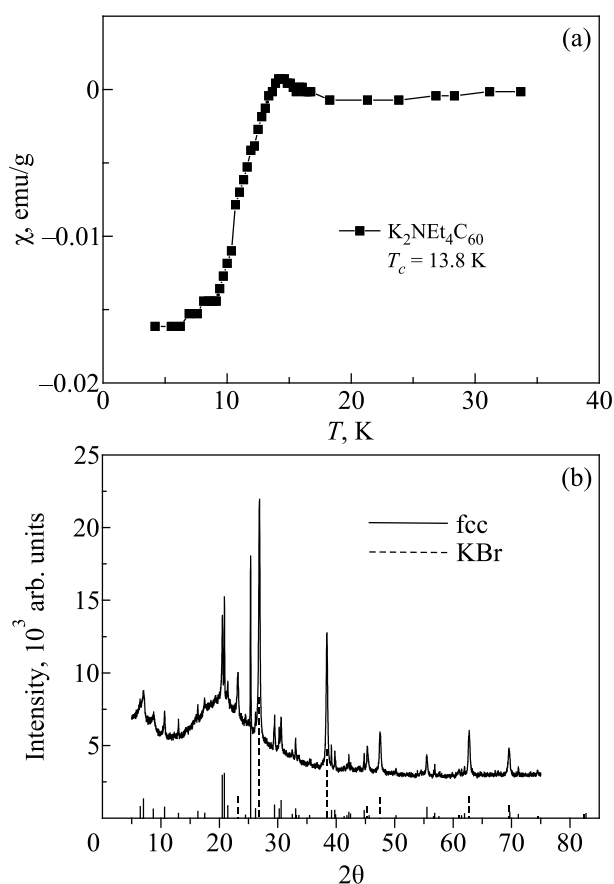


Fig. 9. Temperature dependence of the magnetic susceptibility  $\chi$  (a) and x-ray diffraction pattern (b) of heterofulleride 1111  $K_2NEt_4C_{60}$ . Black vertical lines indicate the fcc phase of this compound, and dashed lines indicate the reaction product KBr.

diffraction pattern of this sample, and Table 6 lists some of its characteristics.

Note that in the samples in Table 5, according to x-ray phase analysis, a small proportion of the impurity phase is found, which could not be identified. Figure 10 shows a superconducting transition for two fullerides with tetrabutylammonium  $K_2NBu_4C_{60}$ , (obtained by reaction (1) with  $X = I$  (iodine) and x-ray diffraction patterns of these samples. Note that sample No. 1876 is two-phase and exhibits two superconducting transitions [marked by arrows in Fig. 10(a)], one of which corresponds to the  $K_2NBu_4C_{60}$  fulleride and coincides with the transition in sample 1110. The x-ray diffraction pattern determines the fcc lattice of the superconducting phase of the fulleride and the KI substitution reaction product. Some parameters of these samples are shown in Table 6.

In Fig. 11 a superconducting transition for two fullerides with tetrabutylammonium  $Rb_2NBu_4C_{60}$  and x-ray diffraction patterns of these samples are shown. Table 6 lists the parameters of these superconducting fullerides.

As can be seen from the presented data, heterofullerides of potassium and rubidium with tetraalkylammonium bases, obtained by reaction (1) in a toluene medium and being superconductors, show transition temperatures that do not

Table 6. Parameters of superconducting fullerides with tetrabutylammonium  $K_2NBu_4C_{60}$  and  $Rb_2NBu_4C_{60}$

| No.  | Composition       | $T_c$ , K | Reaction products        | fcc lattice parameter $a$ , Å |
|------|-------------------|-----------|--------------------------|-------------------------------|
| 1110 | $K_2NBu_4C_{60}$  | 13.6      | fcc + KI, unknown phase  | 14.297(4)                     |
| 1876 | $K_2NBu_4C_{60}$  | 13.8; 16  | fcc + KI, unknown phase  | 14.35(1)                      |
| 1217 | $Rb_2NBu_4C_{60}$ | 19.2      | fcc + RbI, unknown phase | 14.453(6)                     |
| 1877 | $Rb_2NBu_4C_{60}$ | 20.4      | fcc + RbI, unknown phase | 14.491(8)                     |
| 1158 | $K_3C_{60}$       | 18.5      | fcc                      | 14.278                        |
| –    | $Rb_3C_{60}$      | 29        | fcc                      | 14.384                        |

exceed the transition temperatures in  $K_3C_{60}$  ( $T_c = 18.5$  K) and  $Rb_3C_{60}$  ( $T_c = 29$  K), and even lower than those of ammonium-containing heterofullerides (Fig. 12), although according to the x-ray phase analysis data all compounds have an fcc lattice with parameters  $a$  comparable to or exceeding the corresponding lattice parameters of  $K_3C_{60}$  ( $a = 14.24$ – $14.27$  Å) and  $Rb_3C_{60}$  ( $a = 14.38$  Å) (see Tables 2–6). But this seems quite natural, considering

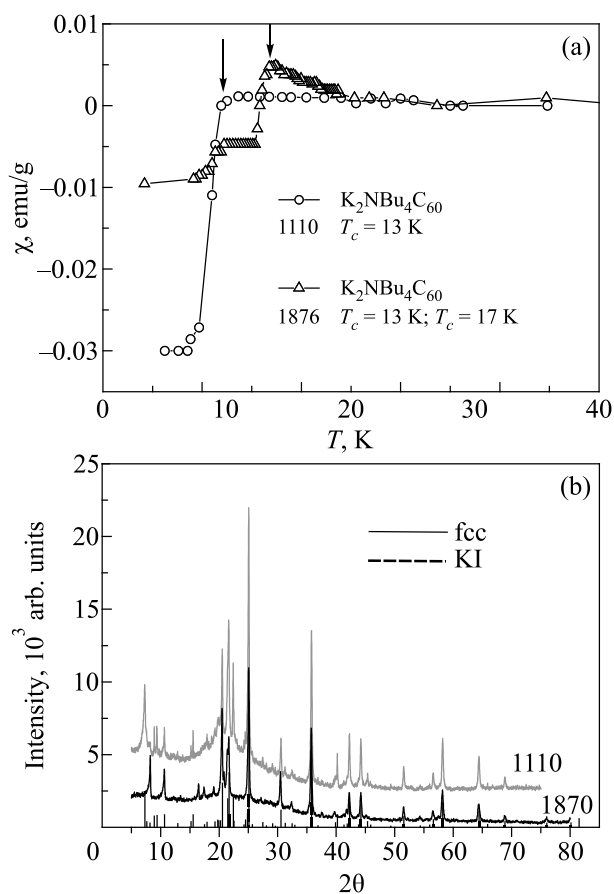


Fig. 10. Temperature dependence of the magnetic susceptibility  $\chi$  of heterofullerides synthesized from tetrabutylammonium iodide with potassium (a) and their x-ray diffraction patterns (b).



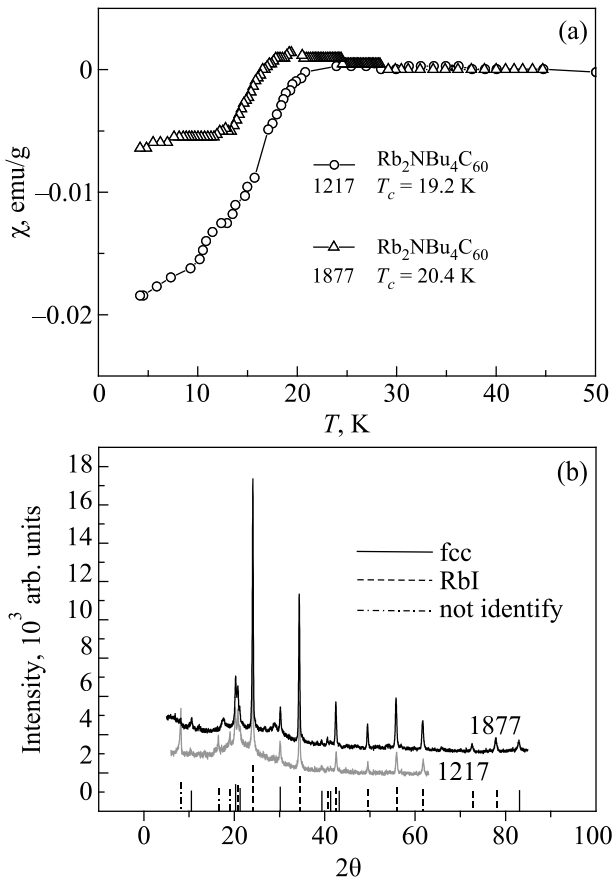


Fig. 11. Temperature dependence of the magnetic susceptibility  $\chi$  of heterofullerides  $\text{Rb}_2\text{NBu}_4\text{C}_{60}$ , synthesized from tetrabutylammonium iodide with rubidium (a) and their x-ray diffraction patterns (b).

the degree of “metallicity” of ammonium bases, which is obviously lower in  $\text{NR}_4$  as compared to  $\text{NH}_4$ .

We note that in many samples, a slight rise in the  $\chi(T)$  dependence is observed before the superconducting transition. Perhaps the reason for this paramagnetic behavior is the presence in the reaction products of negatively charged oxygen complexes (for example,  $\text{C}_{120}\text{O}$  or  $\text{C}_{60}\text{O}$ ) or dimers ( $\text{C}_{120}$ ) [19, 45].

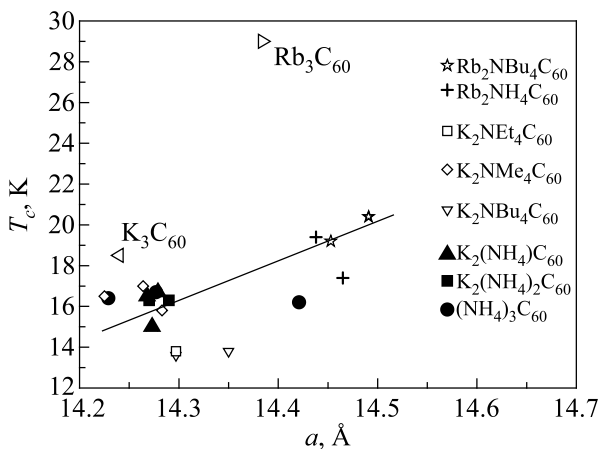


Fig. 12. Dependence of the superconducting transition temperature  $T_c$  on the fcc lattice parameter  $a$  for heterofullerides of alkali metals with ammonium bases.

### 2.3. Isotope effect in fullerides with ammonium bases

The isotopic effect provides important information on the mechanism of superconductivity. In the Bardeen–Cooper–Schrieffer (BCS) theory for a system with one type of ion of mass  $M$ , there is the following dependence  $T_c \sim M^{-\alpha}$ , where  $\alpha = 0.5$ . In compounds of the  $\text{A}_3\text{C}_{60}$  type, the phonons of the fullerite crystal lattice play an important role in the superconductivity mechanism. In this regard, the result of the isotope effect when replacing  $^{12}\text{C}$  with  $^{13}\text{C}$  is of interest. Table 7 shows data on the measurement of the parameter  $\alpha$ .

Table 7. Study of the isotope effect in fullerides of composition  $\text{A}_3\text{C}_{60}$

| Composition   | Content $^{13}\text{C}$ , % | $\alpha$         | Reference |
|---|-----------------------------|------------------|-----------|
| $\text{K}_3\text{C}_{60}$   | 60                          | $1.3 \pm 0.3$    | [46]      |
| $\text{K}_3\text{C}_{60}$   | 99                          | $0.3 \pm 0.06$   | [47]      |
| $\text{Rb}_3\text{C}_{60}$  | 33                          | $1.4 \pm 0.5$    | [48]      |
| $\text{Rb}_3\text{C}_{60}$  | 60                          | $2.1 \pm 0.35$   | [46]      |
| $\text{Rb}_3\text{C}_{60}$  | 76                          | $0.32 \pm 0.05$  | [49]      |
| $\text{Rb}_3\text{C}_{60}$  | 82                          | $1.45 \pm 0.3$   | [50]      |
| $\text{Rb}_3\text{C}_{60}$ (powder)                               | 99                          | $0.3 \pm 0.05$   | [51]      |
| $\text{Rb}_3\text{C}_{60}$ (single crystal)                       | 99                          | $0.21 \pm 0.012$ | [52]      |
| $\text{Rb}_3(^{12}\text{C}_{0.45}^{13}\text{C}_{0.55})_{60}$      | 55                          | 0.3              | [51]      |
| $\text{Rb}_3(^{12}\text{C}_{60})_{0.5}(^{13}\text{C}_{60})_{0.5}$ | 50                          | 0.8              | [51]      |

Replacing an alkali metal with its isotope did not lead to significant changes in  $T_c$  [53, 54]. We have studied superconductivity in  $\text{Rb}_2\text{NH}_4\text{C}_{60}$  and  $\text{Rb}_2\text{ND}_4\text{C}_{60}$  samples with replacement of hydrogen by deuterium in ammonium, as well as  $\text{K}_2\text{NH}_4\text{C}_{60}$  and  $\text{K}_2\text{ND}_4\text{C}_{60}$ . The parameters of the samples are shown in Table 8. The result of measurements of the temperature dependence of the magnetic susceptibility of  $\chi$  heterofullerides  $\text{Rb}_2\text{NH}_4\text{C}_{60}$  and  $\text{Rb}_2\text{ND}_4\text{C}_{60}$  is shown in Fig. 13, and  $\text{K}_2\text{NH}_4\text{C}_{60}$  and  $\text{K}_2\text{ND}_4\text{C}_{60}$  in Fig. 14. As we can see, the temperature of the superconducting transition has not changed within the measurement accuracy. Hence, it can be concluded that the main role in superconductivity is played by phonons related to the  $\text{C}_{60}$  molecule.

Table 8. Some characteristics of fullerides  $\text{Rb}_2\text{NH}_4\text{C}_{60}$ ,  $\text{Rb}_2\text{ND}_4\text{C}_{60}$  and  $\text{K}_2\text{NH}_4\text{C}_{60}$ ,  $\text{K}_2\text{ND}_4\text{C}_{60}$

| No.  | Composition                           | fcc lattice parameter $a$ (Å) | $T_c$ , K | Fraction of the superconducting phase |
|------|---------------------------------------|-------------------------------|-----------|---------------------------------------|
| 1185 | $\text{Rb}_2\text{NH}_4\text{C}_{60}$ | 14.465                        | 17.4      | 45 %                                  |
| 1875 | $\text{Rb}_2\text{ND}_4\text{C}_{60}$ | 14.32(3)                      | 17.2      | 65 %                                  |
| 1874 | $\text{K}_2\text{ND}_4\text{C}_{60}$  | 14.24(1)                      | 16.5      | 60 %                                  |
| 1121 | $\text{K}_2\text{NH}_4\text{C}_{60}$  | 14.268                        | 16.5      | 80 %                                  |
| 1581 | $\text{K}_2\text{NH}_4\text{C}_{60}$  | 14.279                        | 16.7      | 90 %                                  |

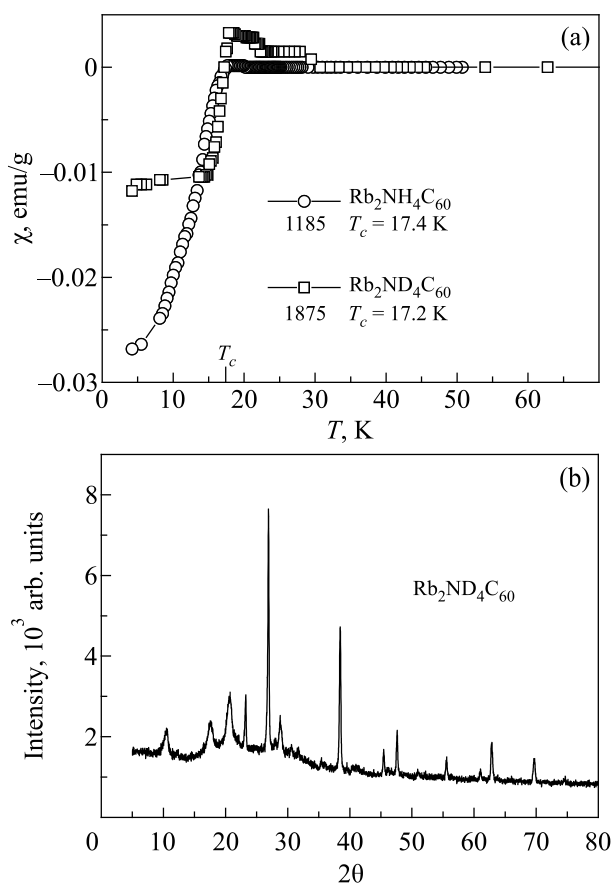


Fig. 13. Temperature dependence of the magnetic susceptibility  $\chi$  of the heterofullerides  $Rb_2NH_4C_{60}$  and  $Rb_2ND_4C_{60}$  (a) and x-ray diffraction pattern of the  $Rb_2ND_4C_{60}$  sample (b).

### Conclusion

In the presented work, superconducting homo- and heterofullerides of potassium and rubidium with ammonium and ammonium bases (tetramethylammonium, tetraethylammonium and tetrabutylammonium) and homofulleride with ammonium of the supposed compositions  $K_{1-x}(NR_4)_x C_{60}$  and  $Rb_{1-x}(NR_4)_x C_{60}$  (R — H, D, butyl Bu, ethyl Et, methyl Me) were synthesized. The synthesis was carried out by the exchange reaction of trimetallic fullerides of potassium and rubidium with ammonium chloride and halides of ammonium bases in a toluene medium. All substances crystallize in fcc crystal lattices with parameters  $a$  increased against the starting compounds  $K_3C_{60}$  and  $Rb_3C_{60}$ . However, despite this, the superconducting transition temperatures of these substances turned out to be lower than those of the initial fullerides. This can be explained by the low “metallicity” of the ammonium and ammonium bases intercalates as compared to true metals. The formation of radical ion salts with ammonium and its alkyl derivatives in fullerides demonstrates the possibility of stabilizing these molecules by intercalation into matrices with suitable properties. We have studied superconductivity in  $Rb_2NH_4C_{60}$  and  $Rb_2ND_4C_{60}$

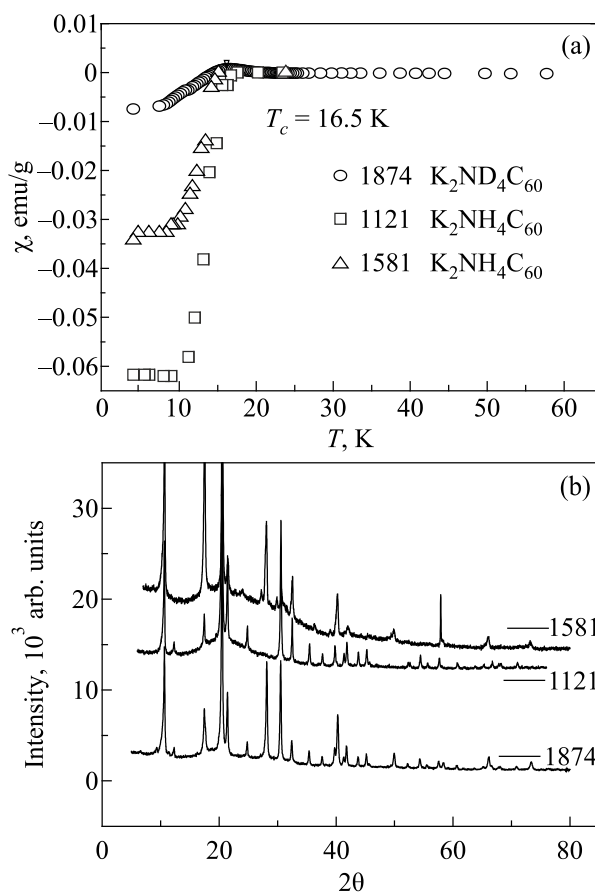


Fig. 14. Temperature dependence of the magnetic susceptibility  $\chi$  of the heterofullerides  $K_2NH_4C_{60}$  и  $K_2ND_4C_{60}$  (a) and their x-ray diffraction pattern (b).

samples with replacement of hydrogen for deuterium in ammonium, as well as in  $K_2NH_4C_{60}$  and  $K_2ND_4C_{60}$ . The superconducting transition temperature did not change with replacement H by D within the measurement accuracy. Hence, it can be concluded that the main role in superconductivity is played by phonons related to the  $C_{60}$  molecule.

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**Синтез та надпровідність металоорганічних фулеридів  $M_{(3-n)}(NR_4)_nC_{60}$ ,  $M = K, Rb$ ;  
 $R = H, D, Me, Et, Bu$ ;  $n = 1, 2, 3$**

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Представлено експериментальні дані щодо синтезу металоорганічних фулеридів ( $M_{(3-n)}(NR_4)_nC_{60}$ ,  $M = K, Rb$ ;  $R = H, D, Me, Et, Bu$ ;  $n = 1, 2, 3$   $R =$  водень  $H$ , дейтерій  $D$ , метил  $Me$ , етил  $Et$ , бутіл  $Bu$ ;  $n = 1, 2, 3$ ), які синтезовані реакціями обміну гомофулеридів лужних металів складу  $K_3C_{60}$  та  $Rb_3C_{60}$  з

галогенідами амонію у середовищі абсолютного толуолу або тетрагідрофурана (THF) при температурах від  $23\text{ }^\circ\text{C}$  до  $110\text{ }^\circ\text{C}$ . Досліджено їх надпровідність та структурні властивості. Вивчено надпровідність у зразках  $Rb_2NH_4C_{60}$  та  $Rb_2ND_4C_{60}$  з заміною водню на дейтерій в амонії, а також у  $K_2NH_4C_{60}$  та  $K_2ND_4C_{60}$ . Температура надпровідного переходу в межах точності вимірювань не змінилася при заміні  $H$  на  $D$ .

**Ключові слова:** ізотопний ефект, металоорганічні фулериди, надпровідні та структурні властивості.