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Features of Structure and Properties of Na_nC_{60} ($n = 2, 3$) Fullerides Synthesized in Toluene

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Abstract—The structure and electron properties of Na_nC_{60} ($n = 2, 3$) sodium fullerides synthesized from simple compounds in toluene were studied. It was shown that Na_2C_{60} fulleride forms a face-centered cubic lattice at temperatures above 300 K. As the temperature is lowered, the phase transition to a structure with a simple cubic lattice takes place. The temperature dependences of the properties of Na_3C_{60} with a more complex structure exhibit features that are presumably due to sodium atom redistribution in the Na_3C_{60} fulleride lattice and the formation of sodium ion clusters.

Key words: fulleride, nuclear magnetic resonance, electron paramagnetic resonance.

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INTRODUCTION

Magnetic and electron properties of sodium fullrides noticeably differ from those of heavy metal (K, Rb and Cs) fullerides. Na_3C_{60} does not transfer to the superconducting state as the temperature is lowered, at least to 2.5 K [1]. Moreover, the sodium atomic radius is smaller than those of heavy alkaline metals K, Rb and Cs, therefore their maximal number in a fulleride recalculated to a C_{60} molecule may reach 11–12 [2] (for potassium and rubidium it is 6).

The results of studying sodium fullerides published up to now lead to contradictory conclusions. Measurements of conductivity and studies of the photo-effect show that Na_xC_{60} fullerides with $x \leq 6$ are isolators [3, 4]. However, the paramagnetic susceptibility data are usually interpreted as demonstrating the metallic conductivity of Na_4C_{60} and Na_6C_{60} at $T > 100$ K [5, 6] and the metal-isolator transition in Na_1C_{60} and Na_2C_{60} fullerides at temperatures of about 290 K [7].

One of the most effective methods of studying the state of Na atoms and C_{60} molecules in Na fullerides is ^{23}Na and ^{13}C nuclear magnetic resonance (NMR). This method was previously used to investigate the stoichiometric compounds of the composition NaC_{60} [7, 8], Na_2C_{60} [5, 8, 9], Na_3C_{60} [10, 11], Na_4C_{60} [6, 12], Na_6C_{60} [5, 10] and non-stoichiometric $Na_{9.7}C_{60}$ [1]. The line positions in the ^{13}C and ^{23}Na NMR spectra and the corresponding spin-lattice relaxation time strongly depend on the fulleride composition and temperature. The nature of these dependences remains obscure. Therefore, the interpretation of the experimental results in these papers often leads to the contradictory conclusions about the structure and charge state of the sodium atoms and fullerene molecules, even in fullerides with supposedly the same compositions. The most probably cause of these contradictions is the phase inhomogeneity of samples.

Most of all, this refers to fullerides synthesized by the vapor-phase method with their compositions mainly determined by the diffusion of metal. At the same time, the composition of fullerides synthesized in non-aqueous solutions depends on the metal diffusion velocity much less and is controlled much better, enabling the production of single-phase compounds with the given composition [10, 13].

The present work was aimed at studying Na_2C_{60} and Na_3C_{60} fullerides synthesized from the simple compounds in toluene using various methods, including NMR and electron paramagnetic resonance (EPR).

1. SYNTHESIS OF FULLERIDES

Samples of Na_2C_{60} and Na_3C_{60} fullerides were synthesized during the reaction of metal sodium with fullerene solution in toluene. The synthesis was carried out in a glass setup soldered under vacuum according to the method described in [10]. All stages of the synthesis and sample preparation took place in a vacuum or an

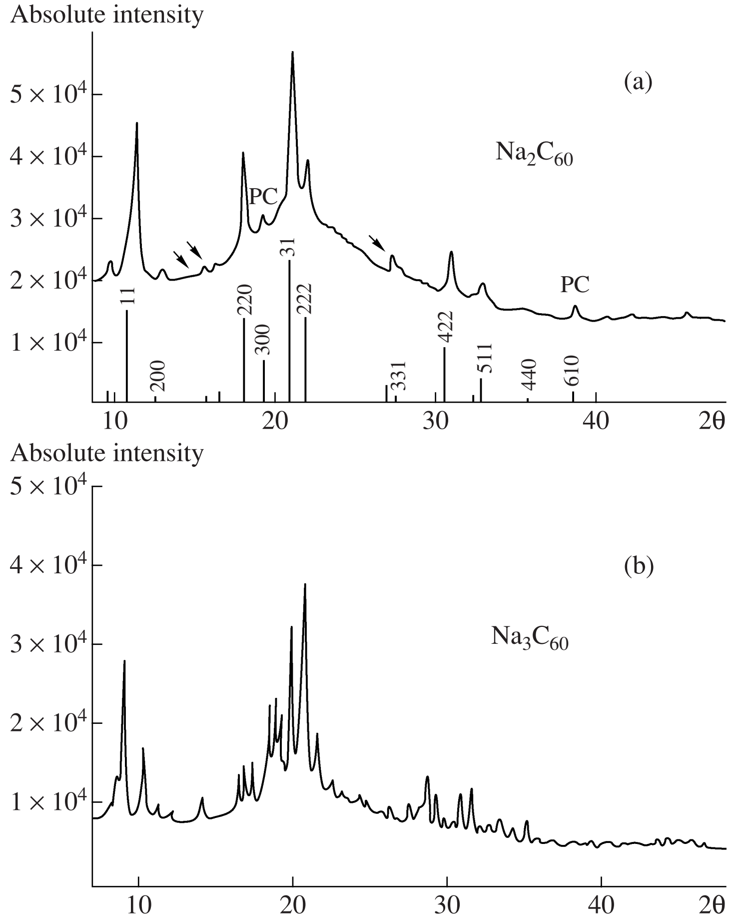

Fig. 1. X-ray diffractograms of fullerides. a, Na_2C_{60} (two peaks marked as PC correspond to the PC lattice, with the other peaks coinciding to PC and FCC are marked by vertical lines with Miller indices). Arrows mark unidentified peaks; b, Na_3C_{60}.

argon atmosphere. The quantity of the reacted fullerene was determined by the intensity of the ^{13}C NMR line with the shift of 143 ppm. Its disappearance meant the end of the reaction. Note that all results given below are reproducible when the synthesis is repeated. Fulleride samples of the same composition synthesized in toluene under the same conditions have the same properties.

2. EXPERIMENTAL METHODS

The phase composition of fullerides was determined by X-ray diffraction. The measurements were carried out on a Guiner G670 HUBER setup at room temperature.

To determine the vibration spectra of fullerene molecules the Raman spectra were studied on a Jobin–Yvon HR800 spectrometer at room temperature.

^{13}C (75.43 MHz) and ^{23}Na (79.39 MHz) NMR spectra were measured on a Bruker MSL-300 spectrometer in the static regime and magnetic field $B_0 = 7.04$ T. The nuclear spin system was excited by a sequence of single pulses. The duration of the excitation pulse was 4 μs, the pulse interval was 1 s for the ^{23}Na nucleus and 10–30 for the ^{13}C nucleus. The number of pulses in a measurement was 2500 for the ^{23}Na nucleus and 450 for the ^{13}C nucleus. The sample temperature was kept in the temperature range of 120–400 K with a B-VT-1000 system. The accuracy of the temperature stabilization was ±1 K. The NMR line shifts were determined with respect to tetramethylsilane for the ^{13}C nucleus and with respect to the NaCl aqueous solution for the ^{23}Na nucleus.

The EPR spectra were measured on a Bruker Elexsys 500 at the microwave frequency 9.5 GHz (X-band) in the temperature range of 110–420 K. The microwave power was 0.1–0.2 mW. No saturation of the EPR signal was present. The modulation frequency of the magnetic field was 100 kHz and the modulation amplitude was 0.5 G. The accuracy of the temperature stabilization was ±1 K.

In addition, the synthesized fullerides were studied using differential scanning calorimetry (DSC) on a DSC-204 Phoenix (Netzsch) calorimeter in the temperature range of 200–450 K. The heating rate was 10 K/min.

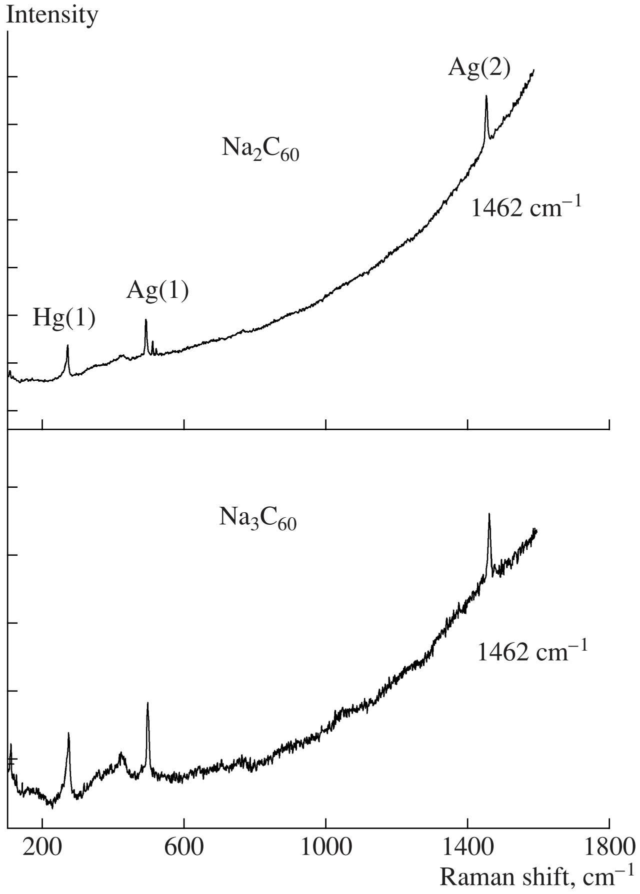

Fig. 2. Raman spectra of Na_2C_{60} and Na_3C_{60} fullerides at room temperature.

3. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

Room temperature X-ray pictures of fullerides are shown in Fig. 1. It is seen that the Na_2C_{60} fulleride has the face-centered cubic (FCC) lattice and its parameter a = 14.224 Å. The two low-intensity reflexes denoted as PC in Fig. 1a belong to the primitive cubic (PC) lattice. Na_2C_{60} obtained by the vapor-phase method [14, 15] crystallizes in this lattice. Thus, these data show that at room temperature the fulleride obtained in the presence of a solvent exists in the FCC phase with an admixture of the PC phase.

X-ray pictures of Na_3C_{60} synthesized in toluene (Fig. 1b) are more complicated and cannot be identified in the *Fm*3 system. The crystal structure of this fulleride is either triclinic or it consists of a mixture of phases. Thus, the crystal structure of Na_3C_{60} obtained in the presence of a solvent differs considerably from the structure of analogous K, Rb, Cs fullerides and from the structure of Na_3C_{60} synthesized by the vapor-phase method.

The Raman spectra of Na_2C_{60} and Na_3C_{60} fullerides at room temperature are given in Fig. 2. They show vividly three lines corresponding to the Hg(1), Ag(1) and Ag(2) vibration modes of the C_{60} molecule [16]. According to the literature data [16], the position of the Ag(2) line determines the mean charge of the fullerene molecule. In the Raman spectra of Na_2C_{60} and Na_3C_{60} the positions of the Ag(2) line practically coincide and are 1462 cm^{-1} corresponding to about 1.1 electron charge per C_{60} molecule. Thus, in the Na_2C_{60} and Na_3C_{60} fullerides synthesized in this paper only the partial electron transfer from the sodium atom to the fullerene molecule occurs. In Na_3C_{60} either no electron transfer from the third sodium atom to the C_{60} molecule occurs or the electron density of this electron is placed in a manner that does not influence the frequency of the Ag(2) vibration mode.

In the ^{13}C NMR spectra of both fullerides at room temperature a single line is observed with a shift around 168 ppm for Na_2C_{60} and 182 ppm for Na_3C_{60}. As the temperature increases, the shift value increases in both fullerides and the line width decreases. These NMR spectra agree with the literature data [5, 8, 10, 17]. Note that the line position in the NMR spectrum is directly connected, not with the electron density but with the local (in the vicinity of the nucleau) magnetic susceptibility, which depends on the summary electron spin. For three electrons in Na_3C_{60} it is nonzero and for two electrons in Na_2C_{60} in the ground state it is zero.

The ^{13}C NMR spectrum provides information about the state of the C_{60} molecule and ^{23}Na NMR spectrum provides information about the state of the sodium atom in the fulleride. In the ^{23}Na NMR spectra of Na_2C_{60} and Na_3C_{60} fullerides there are several lines with temperature-dependent shifts, intensity and line width. The temperature dependences of the line shifts are summarized in Fig.3. It shows that the ^{23}Na NMR spectrum of Na_2C_{60} consists of two lines. According to the literature data [9], the line with the smaller shift corresponds to the sodium position in the voids of the fulleride PC lattice and the line with the larger shift to the FCC lattice. The line with the smaller shift practically disappears above 370 K and the line with the larger shift is absent below 290 K. These data demonstrate the phase transition from the PC to the FCC structure as the temperature increases. Both structures coexist in the wide temperature range of 290–370 K, corresponding to the X-ray analysis and DSC data: the curve of heat flux versus temperature for Na_2C_{60} shows a strong endothermic effect in the same temperature range (Fig. 4). The nature of the two weak features at 220 and 255 K is not discussed in this paper.

The ^{23}Na NMR spectrum of Na_3C_{60} is more complicated and consists of a total of five lines. Of these, four lines may be interpreted as lines from the sodium atoms in the voids of the PC lattice and in the octahedral (O), tetrahedral (T) and tetragonal (T”) voids of the FCC lattice [17]. X-ray diffraction data show that the Na_3C_{60} structure is noncubic; however, the local surrounding of the sodium atoms is apparently similar to its surrounding in the voids of the FCC and PC lattices. The fifth

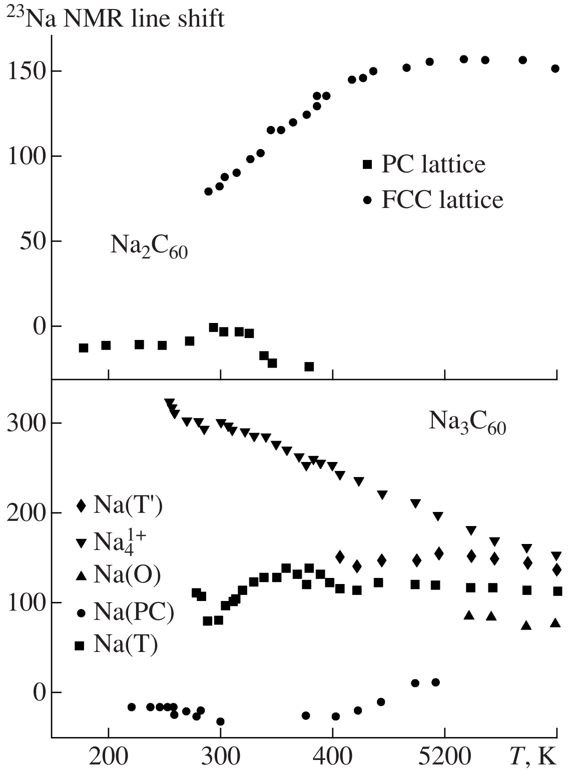

Fig. 3. Temperature dependences of the ^{23}Na NMR line shifts of Na_2C_{60} and Na_3C_{60} fullerides.

line on the NMR spectra, with a positive shift not previously observed in the sodium fullerides and corresponding to the electron density in the vicinity of the sodium nucleus comparable with the electron density in metal sodium, is of interest. The appearance of this line in the spectrum points to the existence of Na clusters connected by the common electron density in this compound. Below 240 K the line with the maximal shift disappears, demonstrating that either the clusters disappear or become non-paramagnetic. This transformation is manifested in the curve of heat flux versus temperature as a strong endothermic effect at 260 K (Fig. 4), demonstrating the large heat loss during this transition.

The features of the temperature dependences of the NMR spectra are manifested in the EPR spectra as well, e.g., in the temperature dependences of the relative paramagnetic susceptibility (double integral of the EPR signal) shown in Fig. 5. In Na_2C_{60} at 290 K the jump in the paramagnetic susceptibility is observed. This jump is supposedly due to the increase in the number of fullerene molecules in the triplet state appearing at the thermal activation of the singlet-triplet transition [17] and the partial suppression of the Jahn–Teller effect in the FCC structure, being more symmetric than the PC structure formed as the temperature increases.

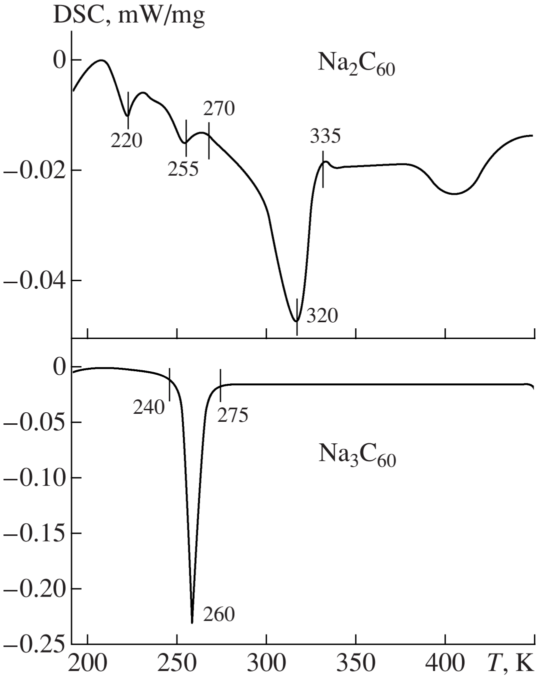

Fig. 4. DSC curves of Na_2C_{60} and Na_3C_{60} fullerides.

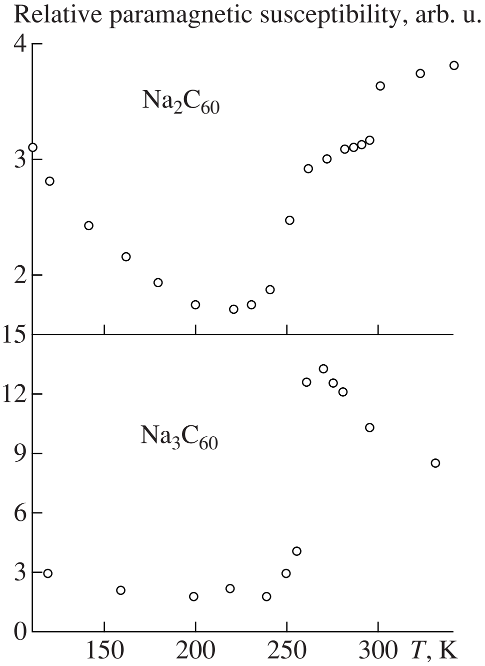

Fig. 5. Temperature dependences of the relative paramagnetic susceptibility of Na_2C_{60} and Na_3C_{60} fullerides.

In Na_3C_{60} the paramagnetic susceptibility drastically increases (by 7 times) above 240 K corresponding to the appearance of the line with the unusually large shift in the ^{23}Na NMR spectrum attributed to the paramagnetic sodium clusters. Thus, the appearance of a large number of paramagnetic centers at 240 K is most probably due to the dramatic change of the structure of the compound.

CONCLUSIONS

The Na_2C_{60} fulleride we obtained and studied has a structure and properties similar to those of the Na_2C_{60} fulleride synthesized by the vapor-phase method and described in the literature. NMR and EPR data demonstrate that a reversible transition from the FCC to the PC structure below 290 K followed by the jump-like change of the paramagnetic susceptibility is observed in this compound. The Na_3C_{60} fulleride synthesized by the liquid-phase method has a structure and properties noticeably differing from those of Na_3C_{60} fullerides synthesized by the vapor-phase method and described in the literature. In particular, above 240 K sodium ion clusters are supposedly formed in this compound resulting in the appearance of an unusual line in the ^{23}Na NMR spectrum in the region of 300–400 ppm not typical for the sodium compounds, and the simultaneous increase of its magnetic susceptibility.

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