Intercalation of fullerite C_{60} with Potassium: ^{13}C and ^{39}K NMR data

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Intercalation of fullerite C_{60} with alkaline metals is known to yield a series of stable and metastable compounds A_xC_{60} (A = Na, K, Rb, Cs; x = 1-6) exhibiting different structural, magnetic, electrical properties. The properties of the compounds and phase transformations in the A-C60 systems are of considerable interest.

In this work, stable compounds in the K-C_{60} system were studied using the NMR method. The choice of the method and the system was determined by two reasons: first, the NMR method was established to be a powerful tool for studying [C_{60}]fullerite intercalated with alkaline metals [1], and, secondly, earlier we have built the phase diagram of the binary K-C_{60} system [2].

The samples of stoichiometric compositions K_xC_{60} (x=1,3,4,5,6) were prepared using potassium in the form of metal (K) or metal hydride (KH). All operations with these substances were carried out in a glove box (residual oxygen content, 2 ppm, and water content, 1 ppm). The samples of K_xC_{60} were synthesized by heating potassium and fullerite C_{60} in quartz evacuated and sealed ampoules at 500-700 K for about 30 days. The ^{13}C and ^{39}K spectra of each reaction mixture and the products formed after heating for 15 and 30 days were recorded

The ^{13}C NMR spectra were taken at room temperature in two polarizing fields (B_0=4,7 T, 50,3 MHz, Bruker AC-200 and B_0 = 7,04 T ,75,4 MHz , Bruker MSL-300). One-pulse sequence was used to excite the C-13 spin system. The ^{39}K NMR spectra were registered at room temperature (7.04T, 13,99 MHz, Bruker MSL-300) using a quadro-echo sequence.

The signals in ^{13}C and ^{39}K NMR spectra were identified using the literature data [1,3,4] and the phase diagram of the K-C_{60} system [2].

Particular attention was paid to the composition of the samples of $K_1C_{60.}$ This compound is thermodynamically stable at T>420 K, while and at T< 420 K, it decomposes

KC_{60} --> K_3C_{60} + 2 α-C_{60}

and, in addition, polymerizes

KC_{60} → 1D.

Several samples of K_1C_{60} were obtained by cooling the reaction products with different rate from T>420 K to T<300 K. The phase composition of the samples was estimated form the ratio of the measured integral intensities of the peaks in 13C NMR spectrum, a set of stable and metastable phases being obtained, depending on the conditions of thermal treating.

The shifts of ^{39}K signals and their integral intensities in spectra of all samples indicated that the potassium atoms occupy in fullerite C_{60} two sites (octahedral and tetrahedral) with a constant occupancy ratio of 2 : 1.

We were succeeded in distinguishing chemical shifts of ^{13}C assigned to free C_{60} and to C_{60} in a solid solution of potassium in fullerite C_{60} (2 ppm).

The results of studies of other compounds in the K-C_{60} system will be also presented in this report. Correlation between the structural properties of these compounds and dynamics of motion of ionized C_{60} molecules and K atoms will be discussed.

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