EPR AND MMMA STUDY OF C_{60} UPON K-DOPING

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EPR and MMMA studies of C_{60} upon K-doping have been performed. Two different and well separated EPR narrow lines were detected for C_{60}^{1-} and C_{60}^{3-} at temperatures below 100 K. Time dependent changes in the intensities of both C_{60}^{1-} and C_{60}^{3-} lines were observed when the system undergoes an eutectoid transformation. The evolution of superconductivity with two T_c related to different valences (v) of C_{60}^{v-}ion radicals have been found.

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1. Introduction

Previous studies of the superconducting properties of C_{60} admixtured with potassium suggest that the only superconducting phase is K_3C_{60} in which an octahedral and tetrahedral sites of the fcc unit cell are occupied with one alkali atom per site. For two other stable crystallographic phases of C_{60} doped with potassium, i.e. K_4C_{60} and K_6C_{60} [1], the contribution of the superconducting phase is very small, and they should be considered as semiconductors or insulators [2]. According to the phase diagram of K_xC_{60}, K_1C_{60} separates into C_{60} plus K_3C_{60} below 150°C [3, 4], therefore this concentration should not exist at temperatures close to T_c. This paper presents new experimental facts connected with the cooling of the K_xC_{60} system down in the early stages of the doping process.

The application of the EPR technique in the studies of fullerites admixtured with alkali metals provides information about the number and location of spins related to the charge carriers involved in the phenomenon of superconductivity [5]. A comparison of such results with the data obtained from EPR studies of electrochemically produced C_{60} radicals with different valences (v) in solution [6–8] would permit verification of the EPR signals due to ion radicals of specific valence which are known to occur in pure C_{60} or in Me_xC_{60} admixtured with alkali metals [2, 9, 10]. Therefore we could ascribe the following g-factor values: $g_+ \approx 2.0025$, $g_{1-} \approx 1.9998$, $g_{3-} \approx 2.0014$ to the C_{60}^{+}, C_{60}^{1-} and C_{60}^{3-} ion radicals, respectively.

2. Experimental

Taking advantage of two applications of EPR spectrometer — standard electron spin resonance and MMMA (magnetically modulated microwave absorption) — we carried out the study of a doping process of C_{60} by potassium. The EPR spectra were recorded at successive stages of doping. This process was proceeded as an annealing of the C_{60} + K mixture in a quartz tube at 200°C under helium atmosphere in subsequent 10 minute intervals. After each 10 minutes of annealing the sample was cooled down to liquid helium temperature and EPR spectra as well as MMMA signals were recorded. This permitted us to follow the process of electron transfer from K atoms to C_{60} molecules evidenced by the presence of C_{60}^{1-} and C_{60}^{3-} ion radicals by EPR, and the evolution of superconducting phases by microwave absorption (MMMA). The methodology of the experiment is described in detail in Ref. [11].

3. Results and discussion

The crude C_{60} sample has a relatively strong initial C_{60}^{+} EPR signal. We have used a special sequence of heating of the C_{60} + K mixed system in a helium atmosphere. After the first doping step (10 min. of annealing at 200°C) the initial C_{60}^{+} EPR signal disappeared. The electrons from potassium as a donor neutralize the positively charged C_{60} molecules and a weak broad line at $g \approx 2.0002$ appears (Fig. 1). The value of g-factor indicates the presence of C_{60}^{1-} radical ions in the $K^{+}C_{60}^{1-}$ complexes. At room temperature its peak-to-peak width ($\Delta B_{pp} \approx 1.2$ mT) is typical for a complex $vK^{+}C_{60}^{v-}$ [5, 10]. The line "K" at $g = 2.0031$ in Fig. 1 comes from the potassium treatment and we shall not discuss this line in this paper.

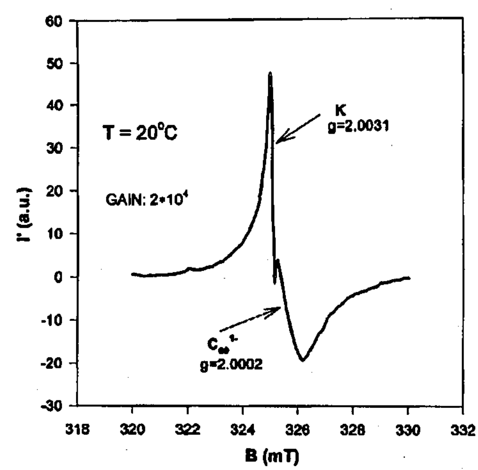

Fig. 1. EPR signal at room temperature after first 10 min. of annealing at 200°C.

The cooling process leads to an additional, narrow line at $g = 2.0017$. The EPR spectrum at $T = 60$ K is shown in Fig. 2a. This new line is assigned to C_{60}^{3-} radicals with relatively high value of g-factor ($g_{3-} = 2.0017$). The g_{3-} value

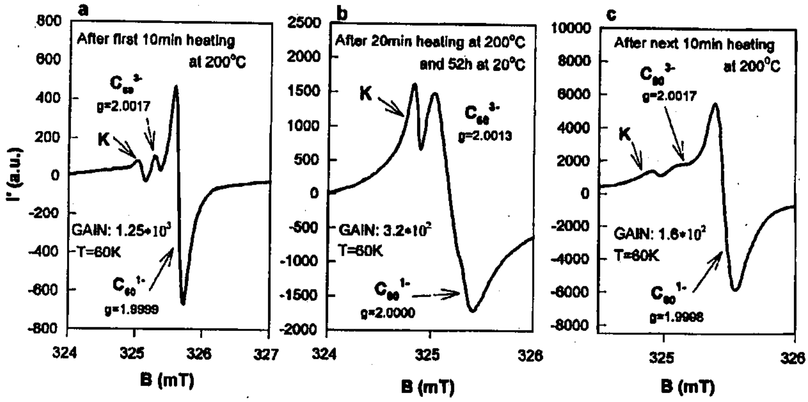

Fig. 2. The set of EPR signals at different stages of the doping process. Well seen changes in intensities of C_{60}^{1-} and C_{60}^{3-} correspondent to site occupancy are reversible over multiple heating and cooling cycles above and below 150°C.

depends on the intensity of the C_{60}^{1-} line. When the intensity of the line connected with the C_{60}^{1-} radical decreases, g_{3-} decreases, respectively. Such situation is presented in Figs. 2a, b and c. The narrowing of the lines during the cooling of the sample down is characteristic of the localization of the electrons on the C_{60} molecule [5, 10]. If we left the sample for a relatively long time (52 h) at room temperature the signal due to C_{60}^{3-} radicals dominates over that from C_{60}^{1-} and g-values are $g_{3-} = 2.0013$ and $g_{1-} = 1.9998$, respectively (Fig. 2b). Time dependent changes in the intensities of both C_{60}^{1-} and C_{60}^{3-} lines at room temperature correspond to the phase separation of K_1C_{60} into $C_{60} + K_3C_{60}$ when the system undergoes an eutectoid transformation [3, 11]. This process could easily be reversed while annealing the sample above 150°C [4]. Such treatment gives depopulation of occupied tetrahedral sites while the octahedral site occupation grows again. This situation is well seen in Fig. 2c when the C_{60}^{1-} EPR signal dominates over the C_{60}^{3-} one after the next 10 min. of annealing the sample at 200°C.

The evolution of superconductivity related to a different v value of C_{60}^{v-} radicals was examined by means of the MMMA method. The MMMA signal right after the EPR spectrum was recorded so it corresponds to the radical ion content specified by EPR characteristics (Fig. 3). Two different and well separated onset T_c temperatures were found: $T_c^{(1)} = (20.5\pm0.5)$ K related to the presence of C_{60}^{1-} EPR signal (K_1C_{60} phase) and $T_c^{(2)} = (18\pm0.5)$ K related to C_{60}^{3-} in the EPR spectrum (K_3C_{60} phase). These two temperatures are detected at the early stages of the doping process independently from C_{60}^{1-} (Fig. 3a) or C_{60}^{3-} (Fig. 3b) domination in the EPR spectrum. When the doping process is brought to the end the EPR spectrum consists of a single EPR line of C_{60}^{3-} at $g_{3-} = 2.0013$ and the MMMA signal gives a single temperature $T_c^{(2)}$ of the transition to the superconducting state [11].

Further experiments connected with the diffusion of the potassium ions into C_{60} volume and with a two-stage superconducting phase transition are in preparation.

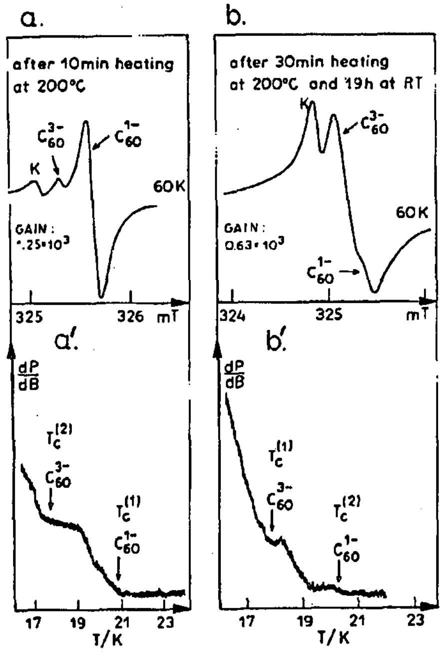

Fig. 3. EPR (a, b) and the corresponding MMMA (a′, b′) signals as an illustration of the two superconducting phase transitions at the early stages of the doping process.

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