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ESR STUDY IN ALKALI-DOPED C_{60}

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ESR experiments in K_3C_{60}, Rb_3C_{60} and $Cs_{3-x}K_xC_{60}$ are carried out. A decrease in the ESR absorption intensity was observed below the superconducting transition temperature. From the x (nominal composition of K) dependence of ESR signal of $Cs_{3-x}K_xC_{60}$, the existence of the region of different electronic states as a function of x was suggested. From the characteristic behavior of the ESR lines, the existence of two metallic states are proposed.

1. INTRODUCTION

It is known that there are three crystallographic phases [1] in K- and Rb-doped C_{60}, that is, A_3C_{60} [2], A_4C_{60} [1] and A_6C_{60} [3] (A=K or Rb), whose crystal structures are f.c.c., b.c.t. and b.c.c., respectively. Among them, only A_3C_{60} is metal and becomes a superconductor.

Although a couple of ESR lines were observed in K- and Rb-doped C_{60} [4], their origins have not been definitely clarified yet. The ESR signals originating from conduction electron spins are generally expected to vanish when a superconducting transition takes place. Such a decrease in the ESR signal was reported in Rb_3C_{60} [5], but a detailed study, such as linewidth, g factor *etc.* was not presented.

Recently, we observed the decrease in the ESR intensity below Tc on K_3C_{60} and Rb_3C_{60} [6]. Here we present ESR results in K_3C_{60}, Rb_3C_{60}, and $Cs_{3-x}K_xC_{60}$, and the characteristic x dependence in the linewidth and g factor.

2. EXPERIMENTAL

Sample preparations were done by two different doping methods. K_3C_{60} and Rb_3C_{60} (nominal) were prepared by the direct doping of pure metals [7]. On the other hand, $Cs_{3-x}K_xC_{60}$ was made by using CsN_3 and KN_3 [8]. ESR measurement was carried out with X-band spectrometer equipped with Oxford gas-flow cryostat (ESR-900). Complicated ESR lines were decomposed into components by simulating asymmetric Lorentzian lines to the experiment graphically.

3. RESULTS AND DISCUSSION

3.1. K_3C_{60}

In Fig. 1 we show the temperature dependence of the ESR linewidth, g factor and intensity of the three components of the ESR spectrum with annealing condition of 200 ℃ for 20 h and 400 ℃ for 48 h from 296 K to 4.8 K. The linewidths of the broader two lines decrease with decreasing temperature. This temperature dependence is consistent

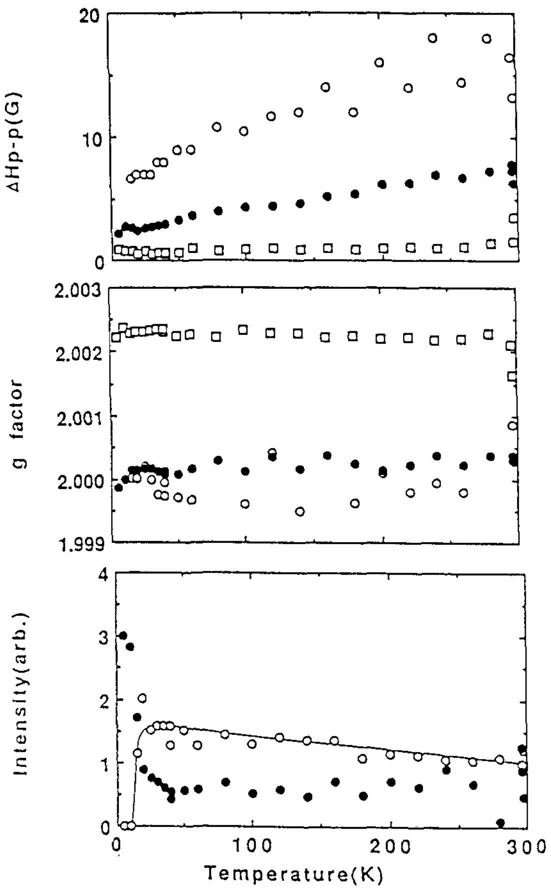

Fig. 1. Temperature dependence of the ESR line of K_3C_{60} (nominal). A solid line in the intensity-temperature plot is a guide to the eye. The intensity of the narrowest line is negligible and thus has not been plotted.

with that of the relaxation mechanism of conduction electron spins in a metal. The negative and small g shift suggests that the relevant spins are on C_{60} anions. The temperature-independent g factors suggest that the electronic structure does not change above T_c.

Intensities of the above mentioned two lines show somewhat different temperature dependences above 20 K and anomalies around 20 K. The intensity of the broadest line shows a slight increase with decreasing temperature above 20 K and vanishes below 20 K. This disappearance of the ESR line comes from the formation of Cooper pairs. On the other hand, the next broadest line shows a slight decrease in the intensity with decreasing temperature and followed by an increase below 20 K. Small temperature dependences of the intensity of these two lines above 20 K suggest the existence of two different metallic states for both the broadest and the next broadest ESR lines. Although the two anomalies take place at close temperatures, the relationship between them is not clear. Further study is required on the anomaly of the next broader line.

The narrowest line whose g factor is close to the free electron value, probably has a spurious origin such as paramagnetic spins related to the residual oxygen because this line does not change its intensity with annealing.

3.2. Rb_3C_{60}

As the annealing procedure advanced, the superconducting volume fraction in Rb_3C_{60} decreased, while the spin number increased. The ESR pattern consists of two components at 296 K as in the case of K_3C_{60}. An extra line came out around 30 K. The pattern could not be simulated by a couple of simple Lorentzian or Dysonian lines as in the case of K_3C_{60}. Although the decomposition of the ESR pattern was not carried out, a decrease in the total ESR intensity was observed below T_c (Fig. 2). The decrease in intensity is larger for Fig. 2(a) than Fig. 2(b), which suggests the existence of a

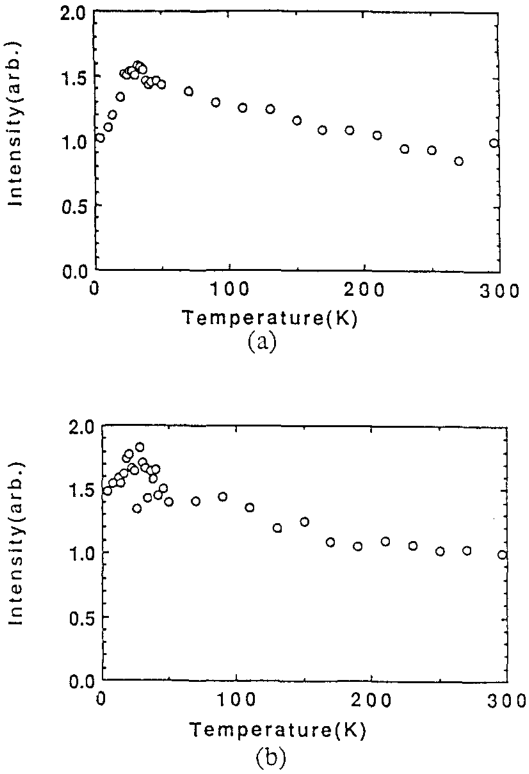

Fig. 2. Temperature dependence of the ESR intensity in Rb_3C_{60} (nominal) annealed at (a) 400 ℃ for 48 h and (b) 400 ℃ for 72 h.

relationship between the volume fraction of superconductivity and the decrease of the ESR intensity, because the superconducting volume fraction is larger for Fig. 2(a).

The decrease in the superconducting volume fraction in Rb_3C_{60} with the progress of annealing means that the annealing does not form but destroys the superconducting Rb_3C_{60} phase. It is necessary to find out the relationship between the annealing condition and the crystallographic phase.

3.3. $Cs_{3-x}K_xC_{60}$

The superconducting properties of $Cs_{3-x}K_xC_{60}$ were already described. Figure 3 shows the x (nominal composition of K) dependence of the ESR linewidth and g factor of $Cs_{3-x}K_xC_{60}$ at 296 K. The absorption line consists of two components which can be decomposed into two asymmetric Lorentzian lines, as in the case of K_3C_{60}.

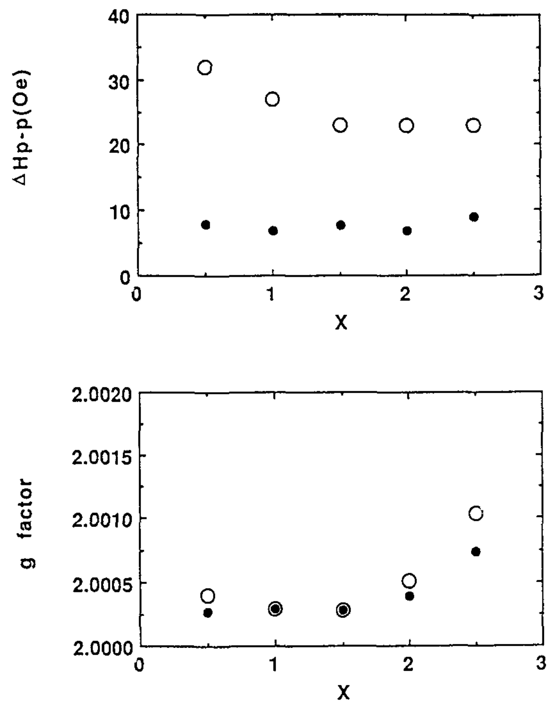

Fig. 3. The ESR linewidth and g factor for the two components of the ESR spectrum of $Cs_{3-x}K_xC_{60}$ as a function of x.

Two characteristic regions are recognized in the measured range of x ($0.5 \leq x \leq 2.5$). One is the region $x \leq 1.5$ where the ESR linewidth of the broader line decreases with increasing x. The g factor of the two lines is constant within the experimental error. The linewidth of the narrower line remains constant in all the composition range measured. The other is the region $x \geq 1.5$. This region is characterized by an increase in the g factors of the two lines with increase in x. The linewidth of the broader line, on the other hand, remains constant in this region. The existence of these regions is supported by the results of the T_c onset and the superconducting shielding magnetization.

As in the case of K_3C_{60}, the observation of two absorption lines with nearly the same negative g shift in metallic $Cs_{3-x}K_xC_{60}$ suggests the existence of the two different spin states in the f.c.c. A_3C_{60} phase, where A is an alkali metal. One spin state which is the source of the broader ESR line has a relation to the superconducting phase, and the other has not. A disappearance of the broader ESR signal was observed in $Cs_{1.5}K_{1.5}C_{60}$ below T_c.

4. SUMMARY

Relationship between ESR and superconductivity were studied in K_3C_{60}, Rb_3C_{60} and $Cs_{3-x}K_xC_{60}$. A decrease in the ESR intensity was observed below T_c in K-, Rb- and (Cs,K)-doped C_{60}. From the x dependence of the ESR linewidth and g factor of $Cs_{3-x}K_xC_{60}$, the existence of the region of different electronic states as a function of x was suggested. Based on the temperature independent intensity in K_xC_{60} above T_c, two kinds of ESR signals were attributed to metallic states.

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