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ESR studies of Rb-doped C_{60}

M. Kosaka, K. Tanigaki, I. Hirosawa, T. W. Ebbesen

Fundamental Research Laboratories, NEC Corporation,
34 Miyukigaoka, Tsukuba 305, Japan

The electronic properties of Rb-doped C_{60} is studied by ESR. Three ESR peaks corresponding to the face-centered cubic (fcc) Rb_3C_{60}, body-centered tetragonal (bct) Rb_4C_{60} and body-centered cubic (bcc) Rb_6C_{60} are observed. The temperature dependencies of their ESR intensities indicate that the Rb_3C_{60} phase is metallic (contrary to earlier ESR studies) and that the Rb_4C_{60} and Rb_6C_{60} phases are non-metallic.

1. Introduction

Since the discovery of superconductivity in potassium-doped C_{60} [1], various alkali-metal doped C_{60} superconductors from $Na_2Rb_1C_{60}$ (Tc=3.5 K) [2] to $Rb_1Cs_2C_{60}$ (Tc=33 K) [3] have been reported. At present, the superconducting phase of alkali-metal doped C_{60} has been confirmed to be M_3C_{60} with face-centered cubic (fcc) structure, where M is the alkali-metal. The non-superconducting phases, M_4C_{60} and M_6C_{60} [4], have been confirmed to be body-centered tetragonal (bct) [5] and body-centered cubic (bcc) [6], respectively.

Electronic properties of these alkali-metal doped C_{60} have been studied by ESR. Our previous report [7] showed that three ESR peaks are observed corresponding to fcc K_3C_{60}, bct K_4C_{60} and bcc K_6C_{60}. We confirmed that K_3C_{60} phase is metallic and K_4C_{60} and K_6C_{60} phases are non-metallic from the temperature dependencies of the ESR intensities. However, with regards to Rb-doped C_{60}, there is a report indicating that Pauli-like behavior is not observed [8] although the Rb_3C_{60} crystal phase is metallic.

Here we report ESR studies for Rb-doped C_{60} and show that three ESR peaks are observed corresponding to the fcc Rb_3C_{60}, bct Rb_4C_{60} and bcc Rb_6C_{60}. This is very similar to K-doped C_{60}. The electronic properties of these three phases are discussed based on the temperature dependencies of ESR intensity, and Pauli-like behavior is confirmed for the fcc Rb_3C_{60}.

2. Experimental

Rb-doped C_{60} samples were prepared by reaction of stoichiometric amounts of dopant Rb with C_{60} (Texas Fullerene, high quality grade) in Pyrex tube. The samples were degassed to 10^{-2} torr and heated in a furnace at 430 °C for 3 weeks. Then these were transferred into another clean ESR tube in order to remove the effect of ESR detectable color-centers in the tube, which were caused by the reaction with Rb. Each sample was divided into three for the measurements of ESR, SQUID and X-ray analyses. ESR absorption was measured using a JEOL JES-RE2X electron spin resonance spectrometer operating at 9.1 Ghz with a field modulation frequency of 100 Khz. Mn^+ was used as a reference marker of ESR intensity and TEMPOL was used for estimation of spin concentration. A JEOL ES-LTR5X cryostat allowed the temperature variation from 5 to 300 K within ±0.1 K precision. The superconducting fractions in the samples were estimated using a SQUID magnetometer (Quantum design MPMS) and the crystal structures were determined by X-ray analyses.

3. Results and Discussion

ESR spectra for the three nominal composition of Rb_xC_{60} were measured as shown in Fig.1. In the sample with the Rb_3C_{60} nominal composition, a broad peak A (in Fig.1a,b) was observed at 5 K and 30 K. In the nominal composition Rb_4C_{60} and Rb_6C_{60} samples, a sharp peak B (in Fig.1c) and a broad peak C (in Fig.1d) were observed, respectively. Since only one peak was observed from each sample, the observed three peaks can reasonably be assigned as follows: the peak A corresponds to fcc Rb_3C_{60}, the peak B to bct Rb_3C_{60} and the peak C to Rb_6C_{60}. g-Factors were estimated to be g_A=2.0005, g_B=2.0014 and g_C=1.9988.

The temperature dependencies of the magnetic susceptibility and the crystal structures of the prepared samples were studied by SQUID and X-ray diffraction to confirm the ESR assignment. The superconducting fraction in the nominal composition Rb_3C_{60} sample is estimated to be 75 %. In contrast, the nominal composition Rb_4C_{60} and Rb_6C_{60} samples showed negligible superconducting fractions. As only fcc Rb_3C_{60} is known to show superconductivity [9], the magnetic susceptibility measurements show that the nominal composition Rb_3C_{60} sample consists of a pure fcc Rb_3C_{60} phase. This superconducting phase does not exist in the nominal composition Rb_4C_{60} and Rb_6C_{60} samples. The X-ray diffraction patterns of these crystal structures are shown in Fig.2. The X-ray patterns for the three samples clearly showed that the nominal composition Rb_3C_{60} sample is fcc Rb_3C_{60} (Fig.2a), the nominal Rb_4C_{60} sample is bct Rb_4C_{60} (Fig.2b) and the nominal Rb_6C_{60} sample is bcc Rb_6C_{60} (Fig.2c), being consistent with the SQUID data. Both of SQUID and X-ray analyses support the assignment of the

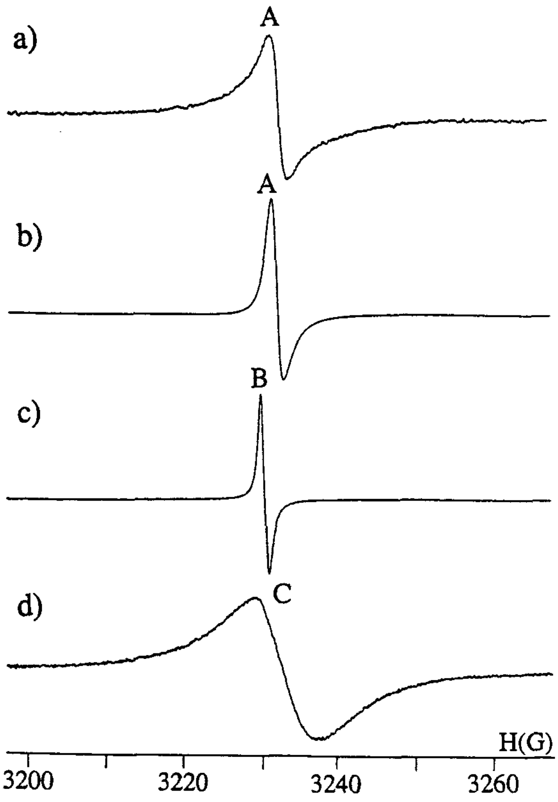

Fig.1. ESR spectra measured for Rb_3C_{60} a) at 5 K and b) at 30 K, c) for Rb_4C_{60} at 5 K, and d) for Rb_6C_{60} at 5 K.

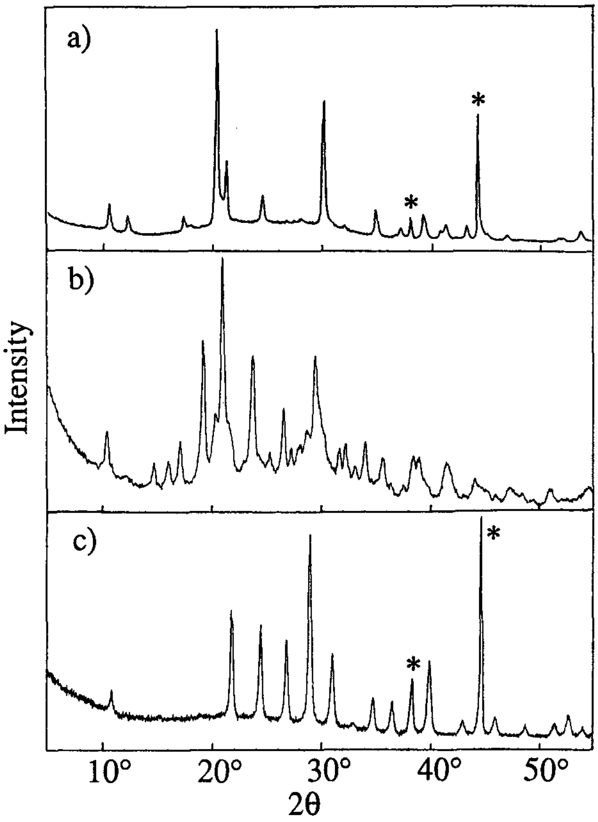

Fig.2. X-ray diffraction patterns, a) for the Rb_3C_{60} sample, b) for the Rb_4C_{60} sample and c) for the Rb_6C_{60} sample. The peaks indicated by asterisk are due to the background noise from the aluminum sample holder.

three ESR peaks to the corresponding crystal phases.

The SQUID measurements show that the Tc of the superconducting Rb_3C_{60} phase is 28 K as was reported [9]. In the Rb_3C_{60} sample at 5 K, the observed ESR signal was fluctuating (in Fig.1a), although the signal does not fluctuate above Tc. The ESR signal without fluctuation observed at 30 K is shown in Fig.1b, for comparison to that with fluctuation at 5 K in Fig.1a. The fluctuation phenomenon below Tc would be related to superconductivity. In the copper oxide high Tc superconductors, a similar phenomenon was observed [10]. This could be interpreted by the movement of the powder samples in the ESR tube due to the Meissner effect under superconducting conditions.

Next, the electronic properties of the these three phases are discussed from the viewpoint of the ESR intensity dependence with temperature. The temperature dependencies of the peak intensities for the three crystal phases are shown in Fig.3. The ESR intensity for Rb_3C_{60} is roughly constant over the whole temperature range. The observed Pauli-like behavior indicates the existence of conduction electrons in the fcc Rb_3C_{60} phase and that this phase is metallic. It should be noted that in the observed ESR spectrum for Rb_3C_{60}, a small anisotropic line shape was observed. This would be related to the skin depth effect which is a typical phenomenon observed in metallic samples.

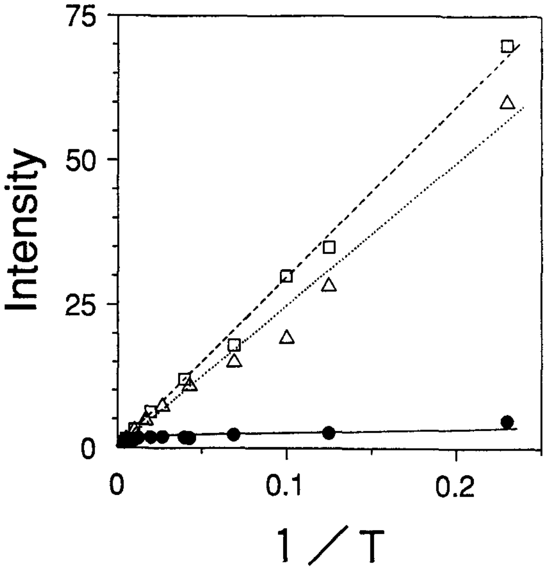

Fig.3. The temperature dependencies of the ESR intensities for the Rb_3C_{60} (circle), Rb_4C_{60} (triangle) and Rb_6C_{60} (square) phases.

On the other hand, only one peak was observed for the fcc Rb_3C_{60} sample containing a very little amount of Rb_4C_{60} phase and in this case, we observed a Curie-like behavior. This should be contrast to the Rb_3C_{60} sample containing a large amount of Rb_4C_{60} impurity, for which we observed two ESR peaks corresponding Rb_3C_{60} and Rb_4C_{60}. This suggests that we must pay attention to the influence of the unpaired electrons, such as Rb_4C_{60}, even if their amount is little for general consideration.

The density of states at the Fermi level ($N(E_F)$) could be estimated from the spin concentration measured by ESR. However, there was scatter in the determined concentrations depending on the samples. This could be due to the fact that only the surface conduction electrons are observed in terms of the skin depth effect and the measurable parts vary upon samples with different particle sizes. Therefore, it might be difficult to estimate real $N(E_F)$ values from the spin concentrations by ESR.

The observed ESR intensity for Rb_3C_{60} was nearly constant in the whole temperature range. In the superconducting state, the ESR intensity might decrease below Tc since some of the conduction electrons near the edge at the Fermi level will make superconducting paired electrons. However, if the ratio of the superconducting paired electrons to the observable conduction electrons is very small, a decrease would not be detected. Further, the conditions contributing to the ESR intensity in the superconducting state would be different from those in the normal conducting state. For example, the penetration magnetic fields would be limited by Meissner effect in the superconducting state while the microwave would be disturbed by the skin depth effect in the normal conducting state. Therefore, quantitative discussion of the observed ESR intensity is difficult.

On the other hand, the ESR intensities for Rb_4C_{60} and Rb_6C_{60} showed Curie-like behavior. The spin concentrations are estimated to be 4×10^{-4} spins per Rb_4C_{60} and 4×10^{-4} spins per Rb_6C_{60}. Our previous report [8] mentioned that the observed ESR in the K_4C_{60} and K_6C_{60} would be related to the K-defects in the crystal. The spins observed for the prepared Rb_4C_{60} and Rb_6C_{60} samples would also relate to the Rb-deficiency defects in the crystal.

The absence of Pauli-like behavior in Rb_4C_{60} and Rb_6C_{60} indicates that both phases are non-metallic. According to the rigid band model for C_{60} solids, the lower edge of the conduction band consists of three band surfaces with t_{1u} character, indicating that Rb_4C_{60} might be metallic. The experimental results that Rb_4C_{60} is not metallic would imply that C_{60} in this crystal phase would be deformed by a Jahn-Teller effect. In this case, the three bands would be either split into two lower degenerate energy levels and one higher one, or three separate levels.

4. Conclusions

We have studied the ESR spectra for Rb_xC_{60} in detail. We observed the three ESR peaks related to the fcc Rb_3C_{60}, bct Rb_4C_{60} and bcc Rb_6C_{60}. The temperature dependencies of the ESR intensity confirmed that the Rb_3C_{60} phase is metallic and Rb_4C_{60} and Rb_6C_{60} phases are non-metallic. These general features are consistent with those found for K_xC_{60}. The fact that the Rb_4C_{60} phase is non-metallic suggests a Jahn-Teller effect in the M_4C_{60} phase.

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