Electron-energy-loss Spectroscopy of K_xC_{60} and K-halides: Comparison in the K_{3p} excitation region

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Abstract

We have investigated the electronic structure of K_xC_{60} (x = 0 ~ 6) using low-energy electron energy loss spectroscopy (LEELS), especially focusing on the K_{3p} core-electron excitation spectra.   It is found that the structure of the K_{3p}-excitation spectrum of K_xC_{60} quite differs from that of KCl.   Furthermore, the K_{3p}-excitation LEELS of K_3C_{60} has been revealed to be different from that of K_6C_{60}. K_{3p} electrons are excited into K_{4s}- and K_{3d}-derived empty states in both K_xC_{60} and KCl, but in the case of K_xC_{60} the K_{3d}-derived empty states have a rather complicated structure where several levels are not well separated. Consequently K_{3p}-excitation LEEL spectra of K_xC_{60} show wide-spread plateau-like structures. The difference in the K_{3p}-excitation spectra of K_3C_{60} and K_6C_{60} is considered to originate from the different crystal field around K^+ cations in the C_{60} molecular crystal.

Keywords

Molecular crystal, Alkali-doped fullerene, C_{60}, K_xC_{60}, EELS, LEELS, K_{3p} core-electron, crystal field

1. Introduction

Since the breakthrough in the synthesis of macroscopic quantities of C_{60} [1], its physical and chemical properties have been widely studied [2]. Furthermore, the discovery of superconductivity in alkali-metal-doped C_{60} [3] has encouraged us to investigate the electronic structure of fullerenes and fullerides. Until now, many kinds of spectroscopic experiments have been carried out, including such electron spectroscopy methods as photoemission [4-7], inverse photoemission [5-7] and electron-energy-loss spectroscopy (EELS) [8,12]. However, the mechanism of the superconductivity of C_{60} compounds is still under discussion.

In this paper we report the investigation of electronic structure of potassium-doped C_{60} (K_xC_{60}, x = 0 ~ 6) using the low-energy EELS (LEELS) method. Unlike high-energy transmission EELS, LEELS is performed in the reflection condition, and the incident electron energy can be reduced to less than 100 eV. By using the low-energy electron, it becomes possible to detect such optically-forbidden transitions as monopole, qudrapole or spin-flip transitions [9, 10]. In addition, LEELS can measure plasmon excitation with high surface sensitivity.

It has been reported by many groups that undoped C_{60} and fully doped K_6C_{60} are insulating, while K_3C_{60} is a metallic compound and shows superconductivity below 19.3 K [11]. As for K_xC_{60}, previous EELS studies mainly argued the energy-loss process via the interband transition from the highest occupied molecular orbital (HOMO)-derived valence bands to the lowest unoccupied molecular orbital (LUMO)-derived conduction bands of C_{60} molecules. Here, we have paid attention to the energy-loss process of the K_{3p} core-electron excitation in order to investigate the change in the electronic structure of K atoms. We also

tried to know the energy-loss process of the K_{3p}-excitation in K_xC_{60}, and to find a difference from such an ionic crystal as KCl. In the case of KCl, K_{4s} electrons are completely transferred to anion, and K_{3p} electrons are excited into K_{4s} and K_{3d} empty states in the EELS measurement [13]. Hence in the case of K_xC_{60}, it has been supposed that K_{4s} electrons are completely transferred to C_{60} molecules, too [8], but the final state of the EEL process from initial K_{3p} states has not been clear yet. Our LEELS measurements of K_xC_{60} and KCl have revealed that K_{3p} electrons in K_xC_{60} are also excited into K_{4s} and K_{3d}, but the structure of the K_{3d}-derived empty states of K_xC_{60} is quite different from that of KCl. Differences in LEEL spectra of K_3C_{60} and K_6C_{60} will also be discussed.

2. Experimental

K_xC_{60} (x = 0 ~ 6) compounds were synthesized by gradually doping K atoms into a C_{60} thin film that was epitaxially grown on a MoS_2 substrate. The C_{60} epitaxial film was grown in an ultrahigh vacuum molecular beam epitaxy (UHV-MBE) chamber with the base pressure of 5×10^{-8} Pa. A MoS_2 substrate with the size of $5 \times 10 \times 0.2$ mm^3 was cleaved in air using adhesive tape just before loading into the MBE chamber, and heated to 500°C for 30 min under UHV to clean the surface. C_{60} molecules (> 99.98 % purity, obtained from TermUSA) were evaporated from a Knudcen cell at around 280°C for 30 min onto the substrate whose temperature was set to be 100°C. The surface of the sample was observed by reflection high energy electron diffraction to check the crystallinity and the coverage. The thickness of the C_{60} film was estimated to be about 10 monolayer (~ 8 nm).

The grown C_{60} film was transferred to an analysis chamber with the base pressure of

8×10^{-9} Pa equipped with a K-doping source and an electron spectroscopy system.   K atoms were gradually evaporated onto the C_{60} film at room temperature from a commercial SAES alkali metal dispenser (SAES Getters, Italy) under the vacuum better than 5×10^{-8} Pa.   In the course of the doping the sample was subjected to the electron spectroscopy by several times.

LEELS measurements of K_xC_{60} were performed using a cylindrical mirror analyzer with a built-in electron gun (ULVAC-PHI Model 15-255G).   For the LEELS measurement the primary electron energy (E_p) was set to 40 eV.   The full width at half maximum of the elastic peak was about 0.5 eV.   In addition to K_xC_{60}, LEEL spectra of KCl and metallic K films were also measured to compare the electronic states of K atoms in each compound.

3. Results and Discussion

First of all, the doping amount of K atoms was estimated by comparing the interband transition region of LEEL spectra of K_xC_{60} samples.   Figure 1 shows the change in raw LEEL spectra ($E_{LOSS} = 0 \sim 10$ eV) against the K-evaporation duration.   Every spectrum is normalized by the intensity of the elastic peak ($E_{LOSS} = 0$).   In the spectrum of pure C_{60}, several peaks which correspond to the interband transitions and the plasmon excitation appear together with a clear band gap.   As the doping amount of potassium is increased, the intensity of these peaks becomes smaller, while the peak positions do not change.   In addition, the tail of each elastic peak becomes wider, which indicates the existence of the inelastic scattering with small loss-energy.   When the K-evaporation duration becomes 13 min, the peak at $E_{LOSS} = 4.7$ eV becomes like a shoulder, and the peak at $E_{LOSS} = 6.2$ eV shifts to $E_{LOSS} = 6.0$ eV.   Here the width of the elastic peak becomes the widest, and the spectrum

can be separated into three peaks, including an elastic peak and inelastic peaks at E_{LOSS} = 0.54 eV and 0.92 eV as is indicated in Fig. 2. The inelastic peak at E_{LOSS} = 0.54 eV can be assigned to the plasmon energy of conduction electrons in the half-occupied lowest conduction band derived from C_{60} -t_{1u} (LUMO). The peak at E_{LOSS} = 0.92 eV, on the other hand, is ascribed to the interband transition from the half-occupied band to the nearest upper conduction band derived from the C_{60}-t_{1g} orbitals. From these results we conclude the composition of this sample is K_3C_{60}.

As the doping amount of potassium is increased further, structure of the LEEL spectrum drastically changes. The peak at E_{LOSS} = 6.0 eV does not shift, while there appears two distinct peaks at E_{LOSS} = 1.2 eV and 2.9 eV. When the evaporation duration is 24 min, those peaks become the largest as shown in Fig. 1. Furthermore, the elastic peak becomes narrower again along with the vanishment of the inelastic peak at E_{LOSS} = 0.54 eV (Fig. 2). Then we conclude that the composition of this sample is K_6C_{60}. The peak at E_{LOSS} = 1.2 eV corresponds to the transition from the fully-occupied t_{1u}-derived conduction band to the t_{1g}-derived unoccupied conduction band. These results well correspond to the previously reported high-energy transmission EELS measurement by Sohmen, Fink and Krätschmer [8, 12].

Figure 3 indicates raw LEEL spectra (solid lines) and their second derivatives (broken lines) of K_3C_{60}, K_6C_{60}, KCl and metallic-K films around the K_{3p} core-electron excitation region. In the spectrum of the metallic K film no distinct structure appears beyond the K_{3p} core-electron excitation edge (E_{LOSS} = 19.6 eV), because the final state originates from the half-filled K_{4s} orbital and degenerated empty K_{3d} orbitals. On the other hand, the LEEL spectrum of the KCl film shows several distinct peaks beyond the K_{3p} edge. Theoretically,

K_{3d} states of KCl are supposed to split into two levels in the crystal-field of octahedrally surrounding Cl$^-$ anions.   We think that the peak at $E_{LOSS} = 19.6$ eV can be attributed to the K_{3p}-K_{4s} transition, and multiple loss peaks around $E_{LOSS} = 20 \sim 22$ eV come from the K_{3p}-K_{3d} transition in which several final states are clearly separated.

In the case of K_3C_{60}, the K_{3p}-excitation spectrum has a plateau-like structure without a sharp peak.   It has been reported that K_3C_{60} has the face-centered-cubic structure, and K atoms can take two inequivalent positions, tetrahedral and octahedral sites surrounded by far larger C_{60} molecules [11].   In this case K_{3d} orbitals split into many overlapped levels, and the K_{3d}-derived empty states will have no distinct peak of the density.   Then the LEEL spectrum of K_3C_{60} is considered to show the K_{3p}-K_{4s} transition peak around $E_{LOSS} = 20$ eV and additional wide-spread ($\Delta E \sim 2$ eV) peak of the K_{3p}-K_{3d} transition.

In the case of K_6C_{60}, on the other hand, some small peaks appear on the plateau beyond the K_{3p}-K_{4s} excitation threshold. K_6C_{60} has the body-centered-cubic structure, and every K atom has an equivalent coordination state in the C_{60} molecular crystal.   Then the splitting of K_{3d} orbitals becomes rather simple, although there still remain the overlap of final states. Thus the LEEL spectrum of K_6C_{60} becomes to have some maxima in the plateau-like structure of the K_{3p}-K_{3d} transition beyond the K_{3p}-K_{4s} excitation edge.

When the primary electron energy was increased more than 100 eV, the intensity of every K_{3p} core-electron excitation peak was drastically decreased, which implies those transitions may be optically forbidden.   We think our LEELS results first show the detailed structure of empty states derived from K atoms, which has been difficult to observe by the high-energy transmission EELS measurement.

4. Summary

We have investigated the electronic structure of K_xC_{60} (x = 0 ~ 6) compounds using the LEELS method, especially focusing on the K_{3p} core-level electron excitation region. It is suggested that the structure of final states of K_xC_{60}, into which K_{3p} core-electrons are excited, are quite different from that of KCl. In each sample, K_{3p} electrons are excited into K_{4s}- and K_{3d}-derived final states. Here, K_{3d} states in KCl split into well-separated levels, while those in K_xC_{60} crystals are supposed to split into several overlapped levels. This results in the experimental observation that K_{3p} excitation LEEL spectra of K_xC_{60} have rather dull, plateau-like structure compared to the spectrum of KCl in which distinct peaks can be observed. The structure of K_{3p}-excitation spectrum of K_6C_{60} has been found to differ from that of K_3C_{60}, and it can be explained by considering the different coordination states of K^+ cations in the C_{60} molecular crystal.

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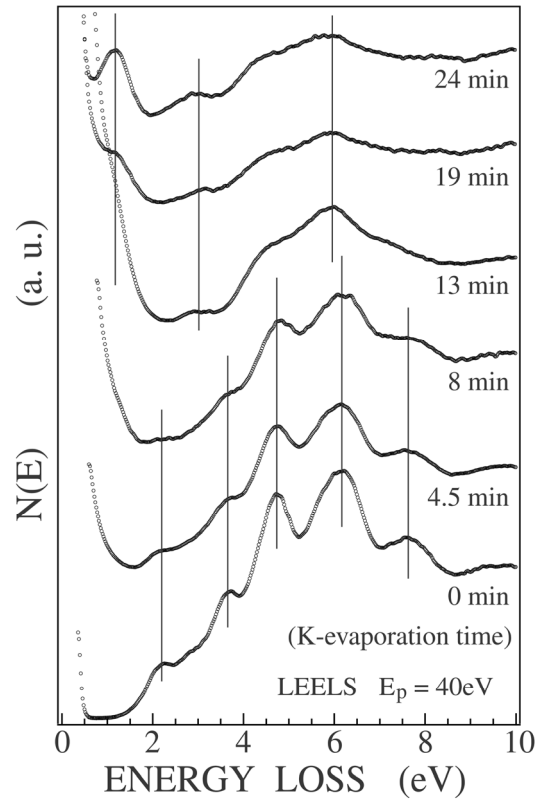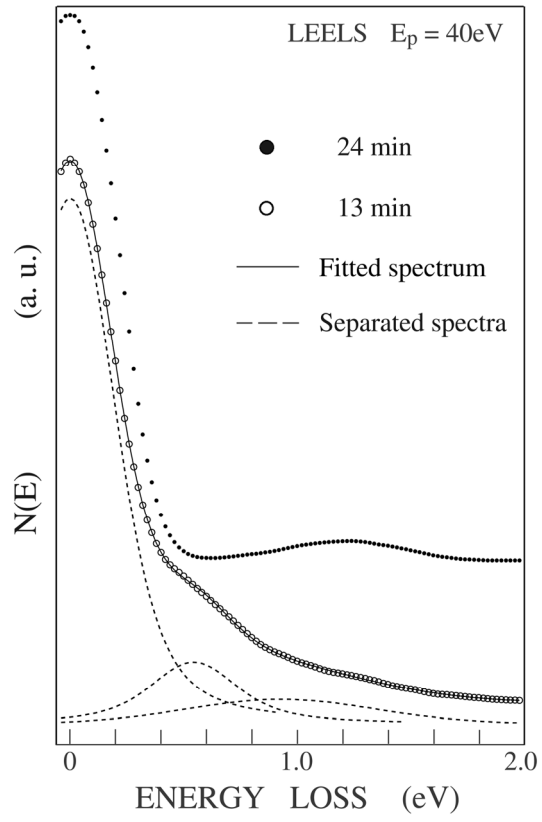[13]   W. R. Xu, Master Thesis (The University of Tokyo, 1990).

Fig. 1

Fig. 2
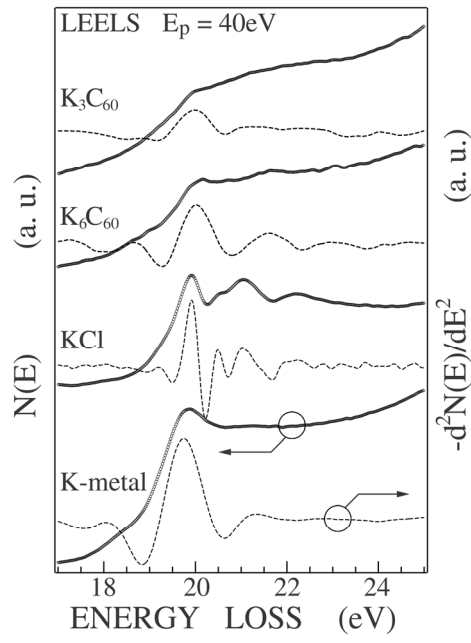
LEELS $E_p = 40eV$

K$_3$C$_{60}$

K$_6$C$_{60}$

KCl

K-metal

N(E)   (a. u.)

-d^{2}N(E)/dE^2 (a. u.)

ENERGY   LOSS   (eV)

Fig. 3

11

Figure Captions

Fig.1 　　　　LEEL spectra of C_{60} and K_xC_{60} samples measured along with the evaporation of K atoms on an epitaxial C_{60} film. 　　The incident electron energy was set to 40 eV. 　　Each spectrum is normalized by the intensity of the primary electron peak.

Fig.2 　　　　LEEL spectra of two K_xC_{60} samples around elastic peaks. 　　Open circles are the spectrum after 13 min evaporation of potassium, and filled circles are after 24 min evaporation. 　　The former spectrum is fitted (a solid line) and separated into three peaks (broken lines) by the Voigt function.

Fig.3 　　　　LEEL spectra of K_3C_{60}, K_6C_{60}, KCl and metallic-K films around the K_{3p} core-electron excitation region. 　　Both raw spectra (solid lines) and their second derivatives (dashed lines) are indicated.
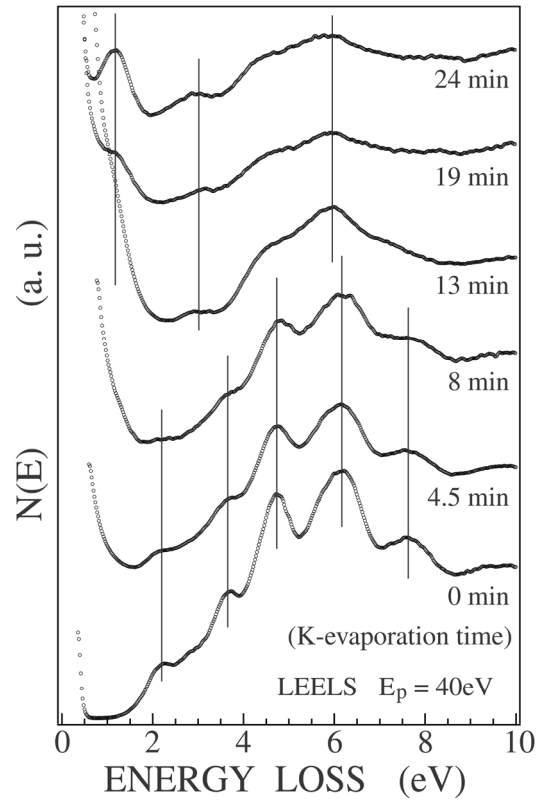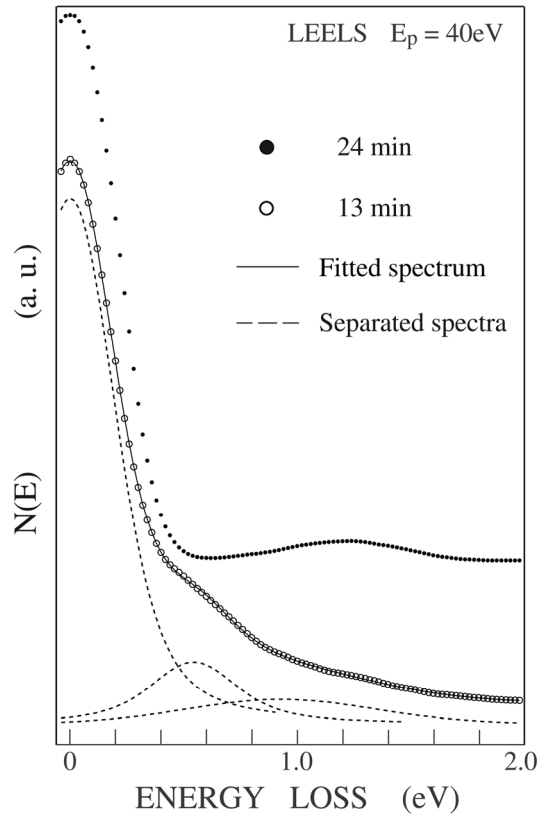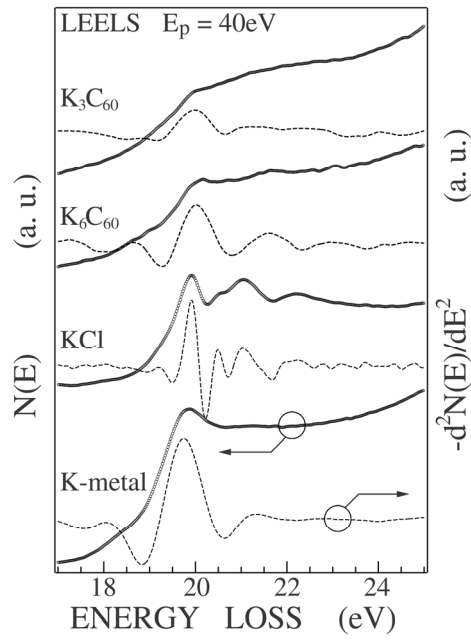
Fig. 1

Fig. 2

LEELS E$_p$ = 40eV

K$_3$C$_{60}$

K$_6$C$_{60}$

KCl

K-metal

N(E) (a. u.)

-d^{2}N(E)/dE^2 (a. u.)

ENERGY LOSS (eV)

18   20   22   24

Fig. 3