DIRECT EVIDENCE FOR ENDOHEDRAL STRUCTURE OF EuC_{60}

Since the discovery of $M_x@C_y$ at the beginning of the 90's, metal endohedral fullerenes ($M_x@C_y$, M: atom), in which M is expected to exist inside the fullerene cage, have attracted the interest of both chemists and physicists for their intrinsic potentials upon application to superconductors and organic ferromagnets. The establishment of the "endohedral structure", however, has not been straightforward chiefly because of difficulties in getting enough samples for structure analyses.

In 1995, Takata et al. first obtained direct evidence of the "endohedral structure" in $Y@C_{82}$ by applying the maximum entropy method to powder X-ray diffraction with synchrotron radiation [1]. The electron density of Y atoms exists inside the C_{82} .

Recently, the similar structures of several other $M_x@C_y$ have also been identified, except for $M@C_{60}$.

In 1996, we succeeded in obtaining a $M@C_{60}$-enriched solution by using the high-pressure liquid chromatography (HPLC) with aniline as the eluent [2,3]. However, its "endohedral structure" could not be confirmed due to the unavailability of a powder-sample with suitable purity. Recently, we found that soot prepared by the arc-heating of a graphite rod containing Eu_2O_3 showed a large amount of EuC_{60} compared with other fullerenes, as seen in the laser desorption time-of-flight (LD-TOF) mass spectrum shown in Figure 1.

We herewith report the structure of EuC_{60} obtained from EXAFS. The Eu LIII-edge XAFS spectrum of soot containing EuC_{60} was measured at room temperature in the transmission mode with an double-crystal Si(111) monochromator at the beamline **BL01B1**. Rh mirror was inserted in order to eliminate the harmonics. Figure 2 shows the radial structure function $\Phi(r)$ obtained by the Fourier transform of $k^3\chi(k)$. The imaginary part of $\Phi(r)$ showed two pronounced peaks at 1.63 and 2.08 , which could be assigned to the two Eu-C scatterings. The distance and the mean square displacement between the Eu and the first neighboring C atoms, $r_{Eu\text{-}C(1)}$ and $\sigma_1(2)$, and those between the Eu atom and the second neighboring C atoms, $r_{Eu\text{-}C(2)}$ and $\sigma_2(2)$, were determined by a least-squares parameter-fitting to the EXAFS spectrum obtained using the inverse Fourier transform of the $\Phi(r)$ as shown in Figure 2. The number of the first and the second neighboring C atoms were fixed both at six by assuming that the Eu atom lays on a six-membered ring in the C_{60} cage. The $r_{Eu\text{-}C(1)}$ and $r_{Eu\text{-}C(2)}$ were 2.338(8) and 2.84(1) , and the $\sigma_1(2)$ and $\sigma_2(2)$

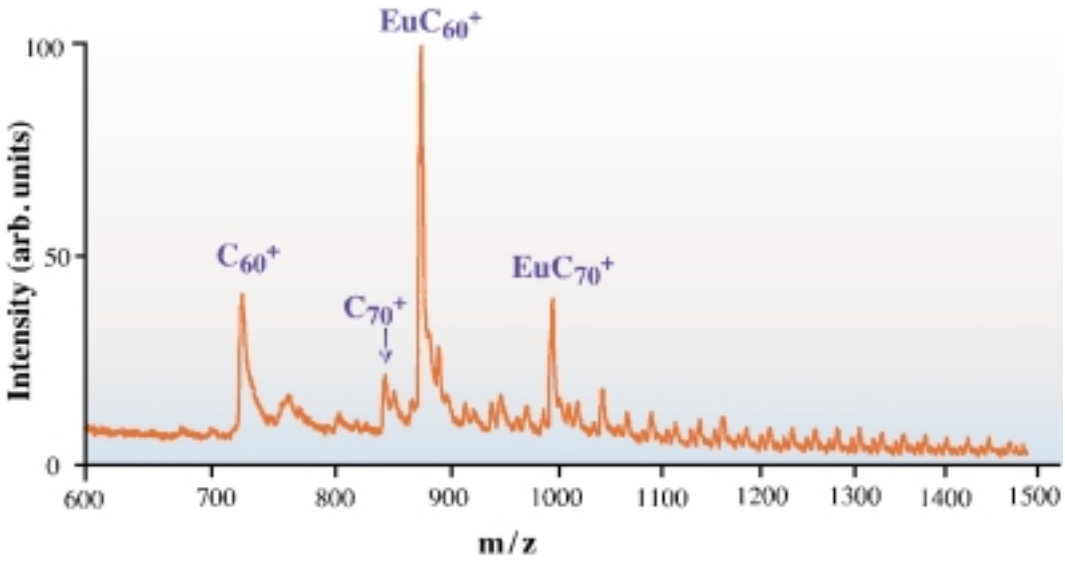

Fig. 1: LD-TOF mass spectrum for the soot prepared by arc-heating of graphite/Eu_2O_3 composite rods. Courtesy of IUCr.

were 0.0048(6) and 0.006(1) $Å_2$, respectively.

The $r_{Eu\text{-}C(2)}$, 2.338 Å clearly indicates that the location of the Eu atom is inside the C_{60} cage because $r_{Eu\text{-}C(2)}$ should be 3.73 Å long if the Eu atom is located outside the cage. This is the first direct evidence for the "endohedral structure" for M@C_{60}.

Figure 3 shows a schematic representation for the position of the Eu atom which is 1.4 Å off from the cage center. The XANES spectrum of the soot, shown in Figure 4, is composed of two components, suggesting that the oxidation state of the Eu atom is the mixed-valence of Eu^{+2} and Eu^{+3}.

We are planning to measure X-ray powder diffraction with synchrotron radiation to determine the three-dimensional structure for M@C_{60}.

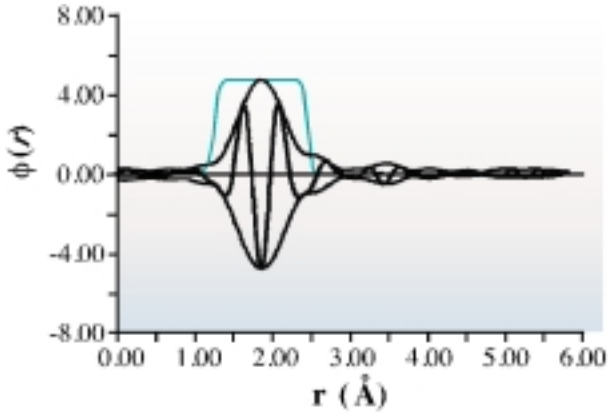

Fig. 2: Φ(r) obtained from XAFS for soot. The part used for the inverse Fourier transform is shown in the spectrum, by rectangular function. Courtesy of IUCr.

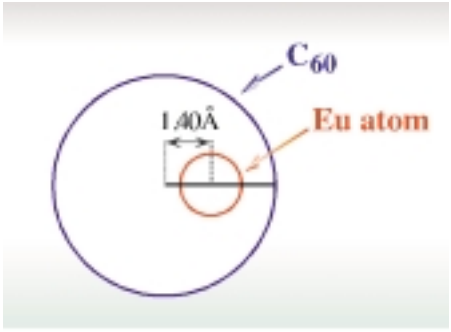

Fig. 3: Schematic representation for Eu@C_{60} .

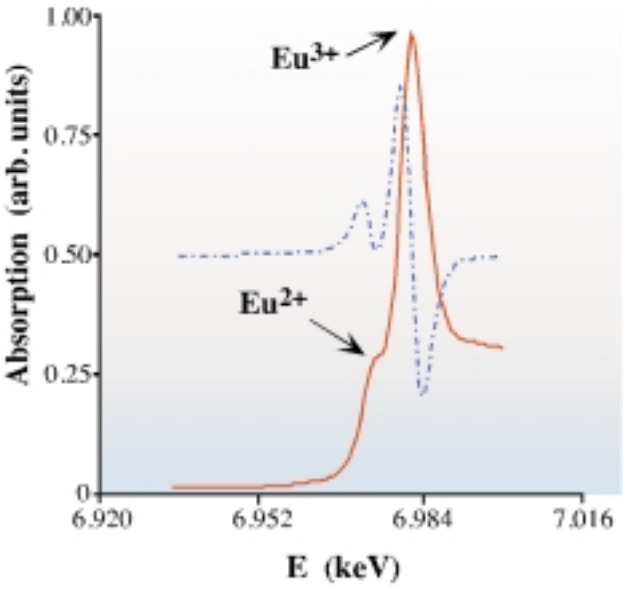

Fig. 4: XANES spectrum for soot. Dashed line is a derivative of the spectrum.

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