XAFS Study on EuC_{60}

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Metal endohedral C_{60} ($M@C_{60}$, M: atom), in which M exists in the inside of C_{60} cage, is very interesting compound in its potential applications as superconductors and organic ferromagnets. Nevertheless, the experimental studies have scarcely proceeded because of the difficulty of its preparation and isolation. Since 1995, we reported the preparation of MC_{60} by an arc-discharge method and its effective extraction with aniline.[1-5] However, the position of M atom in MC_{60} has not been identified because of no experimental studies on the structure. Recently, we found that the soot prepared by an arc-heating of Eu_2O_3/graphite composite rods (Toyo Tanso; Eu_2O_3 concentration of 0.8 mol%) exhibits a pronounced peak ascribable to EuC_{60} with weak peaks for C_{60}, C_{70} and EuC_{70}. Consequently, it is expected to obtain the information on the position of Eu atom in EuC_{60} by measuring the XAFS of the soot.

Eu L_{III}-edge XAFS spectrum of EuC_{60} soot was measured at room temperature in the transmission mode with Si(111) monochromator at BL01B1 of SPring-8. The Rh mirror was inserted in order to eliminate the harmonics. Figure 1 shows the radial distribution function $\Phi(r)$ obtained by a Fourier transform of XAFS oscillation, $k^3\chi(k)$. The $\Phi(r)$ exhibits two pronounced peaks at 1.63 and 2.08 Å which can be assigned to the scattering between the Eu atom and the first neighboring C atoms and that between the Eu atom and the second nearest C atoms, respectively. The distance and Debye-Waller factor between the Eu atom and the first neighboring C atoms, $r_{Eu-C(1)}$ and $\sigma_1(2)$, and those between the Eu atom and the second neighboring C atoms, $r_{Eu-C(2)}$ and $\sigma_2(2)$, were determined by a least-square fitting to the $\chi(k)$ derived by the inverse-Fourier transform of $\Phi(r)$ from 1.08 to 2.57 Å with XAFS formula under the harmonic approximation. The numbers of the first and the second neighboring C atoms were fixed to six by assuming that the Eu atom lies on the center of a six membered ring of C_{60} cage.

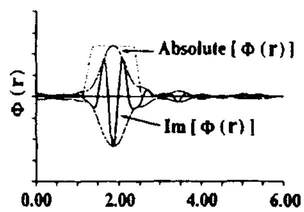

Figure 1. Φ of EuC_{60}

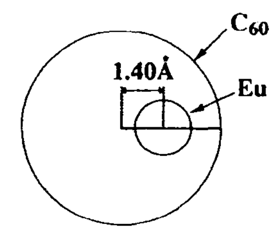

Figure 2. The position of Eu atom determined by XAFS

The $r_{Eu-C(1)}$ and $r_{Eu-C(2)}$ were determined to be 2.338(8) and 2.84(1) Å, respectively. If the Eu atom exists in the outside of C_{60} cage, the $r_{Eu-C(2)}$ is expected to be 3.73 Å because the experimental $r_{Eu-C(1)}$ = 2.338 Å. However, the $r_{Eu-C(2)}$ determined by XAFS is consistent with that expected for the case that the Eu atom exists in the inside of C_{60} cage, 2.87 Å. This shows clearly that the EuC_{60} is the Eu endohedral C_{60}, $Eu@C_{60}$. The small $\sigma_1(2)$ and $\sigma_2(2)$ may also reflect the endohedral structure. Figure 2 shows the position of the Eu atom inside C_{60} cage. The Eu atom is located on the off-center position of the cage by 1.4 Å. These results are the first experimental evidence for the endohedral structure in $M@C_{60}$.

1) Y. Kubozono et al., Chem. Lett., 1995, 458.
2) Y. Kubozono et al., Chem. Lett., 1996, 453.
3) Y. Kubozono et al., J. Am. Chem. Soc., 118, 6998(1996).
4) Y. Kubozono et al., Chem. Lett., 1996, 1061.
5) Y. Takabayashi et al., Chem. Lett., 1997, 1019.