

*J. Synchrotron Rad.* (1999). 6, 779–780

## XAFS study on Eu@C<sub>60</sub>

Takashi Inoue,<sup>a</sup> Yoshihiro Kubozono,<sup>a\*</sup> Koji Hiraoka,<sup>a</sup> Kazue Mimura,<sup>a</sup> Hironobu Maeda,<sup>a</sup> Setsuo Kashino,<sup>a</sup> Syuichi Emura,<sup>b</sup> Tomoya Uruga<sup>c</sup> and Yoshiyuki Nakata<sup>b</sup>

<sup>a</sup>Department of Chemistry, Okayama University, Okayama 700-8530, Japan, <sup>b</sup>ISIR, Osaka University, Osaka 567-0047, Japan, <sup>c</sup>JASRI, Sayo 679-5198, Japan, Email:kubozono@cc.okayama-u.ac.jp

(Received

Eu L<sub>III</sub>-edge XAFS spectrum for EuC<sub>60</sub> was measured at room temperature in order to clarify the position of the Eu atom. The distances between the Eu atom and the neighboring C atoms determined by XAFS showed clearly that the Eu atom was in the inside of C<sub>60</sub> cage, and located on the off-center by 1.4 Å. A XANES spectrum showed that the Eu atom took the mixed valence states of +2 and +3.

**Keywords:** Eu L<sub>III</sub>-edge XAFS, metal endohedral C<sub>60</sub>, endohedral structure, off-center position, mixed valence state

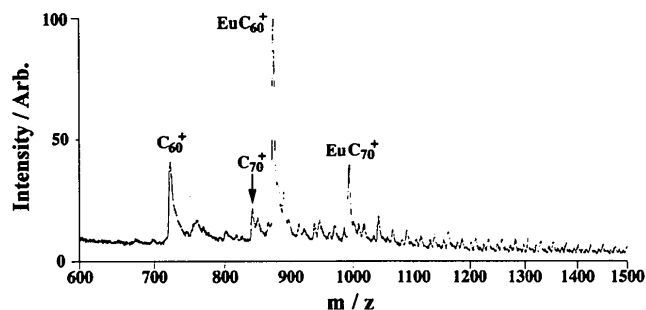
### 1. Introduction

Metal endohedral C<sub>60</sub> (M@C<sub>60</sub>, M: atom), in which M exists in the inside of C<sub>60</sub> cage, is very interesting compound in its potential applications as superconductors and organic ferromagnets. However, the experimental studies have scarcely proceeded because of the difficulty in its preparation and isolation. The position of M in M@C<sub>60</sub> has not been determined so far, and the endohedral structure has not been confirmed for M@C<sub>60</sub>. Therefore, at the present stage, the symbol “@” which implies the endohedral structure cannot strictly be used for all M@C<sub>60</sub> prepared by an arc-heating or a laser-vaporization method.

Recently, we reported the effective preparation of MC<sub>60</sub> by an arc-heating method and its effective extraction with aniline (Kubozono *et al.*, 1995; Kubozono *et al.*, 1996a; Kubozono *et al.*, 1996b, Kubozono *et al.*, 1996c; Takabayashi *et al.*, 1997). Subsequently, we found that the soot prepared by an arc-heating exhibited a pronounced peak ascribable to EuC<sub>60</sub> with weak peaks for C<sub>60</sub>, C<sub>70</sub> and EuC<sub>70</sub> in the laser desorption time-of flight (LD-TOF) mass spectrum, as seen from Fig. 1. Hence, it is expected to obtain the information on the position of Eu atom in EuC<sub>60</sub> by measuring the XAFS of this soot containing large amounts of EuC<sub>60</sub>.

### 2. Experimental and data analysis

The soot containing large amounts of EuC<sub>60</sub> was prepared by an arc-heating of Eu<sub>2</sub>O<sub>3</sub>/graphite composite rods (Toyo Tanso; Eu<sub>2</sub>O<sub>3</sub> concentration of 0.8 mol%) at 25 V and 80 A under 80 Torr of He. The LD-TOF mass spectrum was measured with Finnigan Vision 2000 LD-TOF mass spectrometer. Eu L<sub>III</sub>-edge XAFS spectrum of the soot was measured at room temperature in the transmission mode with a Si(111) monoch-

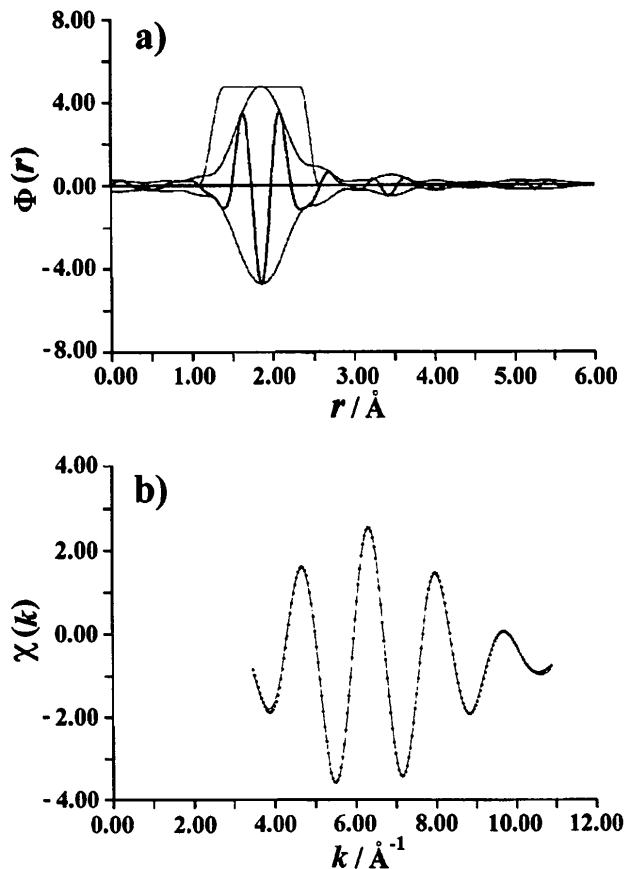


**Figure 1**  
LD-TOF mass spectrum for the soot containing EuC<sub>60</sub>.

romator at BL01B1 of SPring-8. The Rh mirror was inserted in order to eliminate the harmonics. The XAFS oscillation  $\chi(k)$  was extracted from the XAFS spectrum by eliminating the background with Victreen formula, cubic spline method and McMaster coefficients (McMaster *et al.*, 1969). The threshold energy  $E_0$  was evaluated to be 6.9775 keV from the inflection point of Eu-L<sub>III</sub> edge. The radial structure function  $\Phi(r)$  was obtained by a Fourier transform of the  $k^3 \chi(k)$  in the  $k$ -region from 3.5 to 11.0 Å<sup>-1</sup>. The structural parameters were determined by a least-squares fitting to the  $\chi(k)$  in the  $k$ -region from 3.5 to 10.9 Å<sup>-1</sup> derived by the inverse-Fourier transform of  $\Phi(r)$  with XAFS formula within the harmonic approximation (Ishii, 1992); the  $\chi(k)$  was obtained from the  $\Phi(r)$  in the  $r$ -region from 1.08 to 2.57 Å. The mean free path of photoelectron and the shift from the  $E_0$  were also parameterized with the distances and Debye-Waller factors between the Eu atom and the neighboring C atoms. The theoretical values reported by McKale *et al.* (1988) were used for the backscattering amplitudes of atoms and the phase shifts. The programs “XAFS93” and “MBF93” developed by one of the authors (Maeda) were used for the XAFS data analysis.

### 3. Results and Discussion

Fig. 2(a) shows  $\Phi(r)$  obtained by a Fourier transform of  $k^3 \chi(k)$ . The imaginary part of 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,  $r_{\text{Eu-C}(1)}$  and  $\sigma_1(2)$ , and those between the Eu atom and the second neighboring C atoms,  $r_{\text{Eu-C}(2)}$  and  $\sigma_2(2)$ , were determined according to the procedure described in the previous section. 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<sub>60</sub> cage. The  $r_{\text{Eu-C}(1)}$  and  $r_{\text{Eu-C}(2)}$  were determined to be 2.338(8) and 2.84(1) Å, respectively. The  $\sigma_1(2)$  and  $\sigma_2(2)$  were 0.0048(6) and 0.006(1) Å<sup>2</sup>, respectively; the XAFS calculated with these parameters reproduced well the experimental one, as shown in Fig. 2(b). If the Eu atom exists in the outside of C<sub>60</sub> cage, the  $r_{\text{Eu-C}(2)}$  is expected to be 3.73 Å from the experimental  $r_{\text{Eu-C}(1)} = 2.338$  Å. However, the  $r_{\text{Eu-C}(2)}$  determined by XAFS is consistent with that expected for the case that the Eu atom exists in the inside of C<sub>60</sub> cage, 2.87 Å. This result shows clearly that the Eu atom



**Figure 2**

(a) Radial structure function  $\Phi(r)$  derived by Fourier transform of XAFS oscillation  $k^2\chi(k)$  for the soot; the thin and thick lines are the magnitude and the imaginary part of  $\Phi(r)$ , respectively. (b) The closed circles and solid line refer to the XAFS derived by inverse-Fourier transform of  $\Phi(r)$  and that calculated with the structural parameters, respectively.

is in the inside of  $C_{60}$  cage, i.e.,  $EuC_{60}$  takes the endohedral structure which can be represented as  $Eu@C_{60}$ . Further, the position of the Eu atom which satisfies both the  $r_{Eu-C(1)}$  of 2.338(8) Å and the  $r_{Eu-C(2)}$  of 2.84(1) Å in the inside of  $C_{60}$  cage is not located on the on-center position but the off-center position by 1.4 Å. The small  $\sigma_1(2)$  and  $\sigma_2(2)$  may also reflect the endohedral structure. This result is the first experimental evidence for the endohedral structure in  $M@C_{60}$ .

The  $r_{Eu-C(1)}$  and  $r_{Eu-C(2)}$  were slightly smaller than La-C distances,  $r_{La-C(1)} = 2.47(2)$  Å and  $r_{La-C(2)} = 2.94(7)$  Å, in  $La@C_{82}$  determined by XAFS (Nomura *et al.*, 1995), and Y-C distance,  $r_{Y-C(1)} = 2.47(2)$  Å, in  $Y@C_{82}$  determined by maximum entropy method of powder X-ray diffraction (Takata *et al.*, 1995). As the ionic radii of  $La^{3+}$  and  $Y^{3+}$  are 1.17 and 1.04 Å for the case of six coordination, and those of  $Eu^{2+}$  and  $Eu^{3+}$  are 1.31 and 1.09 Å, the small Eu-C distance in  $Eu@C_{60}$  may reflect the size of the cage. Though the fact that the Eu atom was located on the off-center position was consistent with the

theoretical prediction by *ab-initio* SCF Hartree-Fock calculation for  $Ca@C_{60}$  (Wang *et al.*, 1993), the experimental distance between the Eu atom and the center of the  $C_{60}$  cage was different from the theoretical distance, 0.7 Å, for  $Ca@C_{60}$ . The theoretical pertinence for the position of the Eu atom in  $C_{60}$  cage should further be examined.

The XANES spectra around the Eu L<sub>III</sub>-edge for  $Eu@C_{60}$  consisted of two components which were assigned to  $Eu^{2+}$  and  $Eu^{3+}$ ; the difference in energy between  $Eu^{2+}$  and  $Eu^{3+}$  peaks was 8 eV. The  $Eu^{3+}$  peak in  $Eu@C_{60}$  was observed at the same energy position as that in  $Eu_2O_3$  which exhibited only a single peak of  $Eu^{3+}$ . These results suggest that the Eu atom in  $Eu@C_{60}$  possesses the mixed valence states of +2 and +3. This oxidation state is different from that of the Eu atom in  $Eu@C_{82}$  in which the oxidation state of Eu atom is presented to be +2 from the electronic absorption spectrum (Kikuchi *et al.*, 1997). The difference in the oxidation states between  $Eu@C_{60}$  and  $Eu@C_{82}$  gives a new interesting problem.

In this study, the endohedral structure for  $Eu@C_{60}$  was experimentally confirmed. This confirmation should lead to further interests and development in chemistry and physics of  $M@C_{60}$ .

## References

- Ishii, T. (1992). *J. Phys. Condens. Matter*, **4**, 8029-8034.  
 Kikuchi, K., Sueki, K., Akiyama, K., Kodama, T., Nakahara, H. & Ikemoto, I. (1997). In *Fullerenes, Recent advances in the chemistry and physics of fullerenes and related materials*, Vol 4, edited by Kadish, K. M. & Ruoff R. S., pp. 408-416. Pennington.  
 Kubozono, Y., Hiraoka, K., Takabayashi, Y., Nakai, T., Ohta, T., Maeda, H., Ishida, H., Kashino, S., Emura, S., Ukita, S. & Sogabe, T. (1996a). *Chem. Lett.* pp. 1061-1062.  
 Kubozono, Y., Maeda, H., Takabayashi, Y., Hiraoka, K., Nakai, T., Kashino, S., Emura, S., Ukita, S. & Sogabe, T. (1996b). *J. Am. Chem. Soc.* **118**, 6998-6999.  
 Kubozono, Y., Noto, T., Ohta, T., Maeda, H., Kashino, S., Emura, S., Ukita, S. & Sogabe, T. (1996c). *Chem. Lett.* pp. 453-454.  
 Kubozono, Y., Ohta, T., Hayashibara, T., Maeda, H., Ishida, H., Kashino, S., Oshima, K., Yamazaki, H., Ukita, S. & Sogabe, T. (1995). *Chem. Lett.* pp. 457-458.  
 McKale A. G., Veal, B. W., Paulikas, A. P., Chan, S.-K. & Knapp, G. S. (1988). *J. Am. Chem. Soc.* **110**, 3763-3768.  
 McMaster, W. H., Kerr, N., Grande, D., Mallet, J. H. & Hubbell, J. H. (1969). *Combination of X-ray cross sections*, National Technical Information Service, Springfield.  
 Nomura, M., Nakao, Y., Kikuchi, K. & Achiba, Y. (1995). *Physica B*, **208**, 539-540.  
 Takabayashi, Y., Kubozono, Y., Hiraoka, K., Inoue, T., Mimura, K., Maeda, H. & Kashino, S. (1997). *Chem. Lett.* pp. 1019-1020.  
 Takata, M., Umeda, B., Nishibori, E., Sakata, M., Saito, Y., Ohno, M. & Shinohara, H. (1995). *Nature*, **377**, 46-49.  
 Wang, L. S., Alford, J. M., Chai, Y., Diener, M., Zhang, J., McClure, S. M., Guo, T., Scuseria, G. E. & Smalley, R. E. (1993). *Chem. Phys. Lett.* **207**, 354-359.

(Received 10 August 1998; accepted 1 December 1998)