

## XAFS study on metal endohedral fullerenes

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Structure of metal endohedral fullerenes is studied by XAFS and XANES. The Sc-Sc distance of 2.23(1) Å determined from Sc K-edge XAFS supports the formation of a triangular Sc<sub>3</sub> cluster in Sc<sub>3</sub>@C<sub>82</sub> as is found by MEM analysis for the X-ray diffraction. Gd L<sub>III</sub>-edge XAFS of Gd@C<sub>82</sub> shows that the first and the second neighboring Gd-C distances are 2.51(2) and 2.85(4) Å, respectively. The La-La distance of La<sub>2</sub>@C<sub>80</sub> has been determined to be 3.90(1) Å at 40 K. This value does not change when increasing temperature [3.90(2) Å at 240 K]. The position and the valence of the Eu atom in Eu@C<sub>60</sub> are also discussed based on Eu L<sub>III</sub>-edge XAFS and XANES.

**Keywords:** XAFS; XANES; metal endohedral fullerene; structure; valence

### 1. Introduction

The structure and physical properties of metal endohedral fullerenes are very interesting subject in chemistry and physics. The structures of metallofullerenes are gradually determined by X-ray powder diffraction and XAFS. Nomura *et al.* (1995) confirmed the endohedral structure of La@C<sub>82</sub> on the basis of the La L<sub>III</sub>-edge XAFS. The distance between the La atom and the first neighboring C atoms was 2.47(2) Å, implying that the La atom is not located at the on-center but the off-center position of C<sub>82</sub> cage. Takata *et al.* (1995) showed the endohedral structure of Y@C<sub>82</sub> by the X-ray powder diffraction and its maximum entropy method (MEM) analysis. It was found that the Y atom was located near C<sub>82</sub> cage. The MEM analysis is successfully applied to the structural determination of Sc@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub> (Nishibori *et al.*, 1998; Takata *et al.*, 1997). The molecular symmetry of C<sub>82</sub> in Sc@C<sub>82</sub> was determined to be C<sub>2v</sub> on the basis of the MEM analysis. The distance between the Sc and the first neighboring C atoms in Sc@C<sub>82</sub> was 2.53(8) Å. Recently, Takata *et al.* (1999) found the formation of triangular Sc<sub>3</sub> cluster in Sc<sub>3</sub>@C<sub>82</sub> by the MEM analysis. The observed Sc-Sc distance, 2.3(3) Å, was considerably shorter than those of neutral Sc<sub>3</sub> (3.04 Å) and slightly charged Sc<sub>3</sub><sup>+</sup> (2.89 Å) (Walch & Bauschlicher, 1985). The charge state of the triangular cluster was estimated to be (Sc<sub>3</sub>)<sup>3+</sup>.

The physical properties of metal endohedral fullerene and their application to electronic device are also studied by many researchers. The physical properties of La@C<sub>82</sub> and Ce@C<sub>82</sub> in solid state were studied by Watanuki *et al.* (2000) and Iwasa *et al.* (2000). Further, the dynamical properties of encapsulated atoms in metal endohedral fullerenes attract the interests of many researchers. Two La atoms in La<sub>2</sub>@C<sub>80</sub> are encapsulated in C<sub>80</sub>

with I<sub>h</sub> symmetry (Moriyama *et al.*, 2000), as expected from a theoretical calculation (Kobayashi, Nagase & Akasaka, 1995). The molecular symmetry of La<sub>2</sub>@C<sub>80</sub> is lowered from I<sub>h</sub> by encapsulating two La atoms. The most stable structure of La<sub>2</sub>@C<sub>80</sub> is theoretically predicted to be D<sub>2h</sub> (Kobayashi, Nagase & Akasaka, 1995). However, the <sup>13</sup>C and <sup>139</sup>La NMR suggested the I<sub>h</sub> structure for La<sub>2</sub>@C<sub>80</sub> (Akasaka *et al.*, 1997). This implies that two La atoms rotate rapidly in the time scale of NMR.

M@C<sub>60</sub> is expected to have great potentials to new materials with high quality because three-electrons-transfer from the metal atoms to three-degenerate t<sub>1u</sub> orbital of C<sub>60</sub> with I<sub>h</sub> symmetry induces the superconductivity and metallic conductivity in metal doped C<sub>60</sub>. However, it was difficult to isolate the pure sample of M@C<sub>60</sub> by a normal high performance liquid chromatography (HPLC). We measured the Eu L<sub>III</sub>-edge XAFS of the soot containing large amounts of Eu@C<sub>60</sub>, and confirmed the endohedral structure for Eu@C<sub>60</sub> (Inoue *et al.*, 1999). The Eu atom was located on the off-center position as found in metal endohedral C<sub>82</sub>. Recently, Inoue *et al.* (2000) and Ogawa, Sugai & Shinohara (2000) have succeeded in obtaining the pure solid of Eu@C<sub>60</sub> and Er@C<sub>60</sub>, respectively, by combining sublimation and HPLC. The Eu L<sub>III</sub>-edge XANES of solid Eu@C<sub>60</sub> showed that the valence of Eu atom was +2 (Inoue *et al.*, 2000). The XAFS is only available technique for the structural determination of M@C<sub>60</sub> because the crystalline samples of M@C<sub>60</sub> have not yet been obtained.

In the present paper, we report the XAFS studies on the structure of metal endohedral fullerenes with interesting structural and dynamical properties. The XAFS of Sc<sub>3</sub>@C<sub>82</sub>, Gd@C<sub>82</sub> and Eu@C<sub>60</sub> are studied at 295 K. The XAFS of La<sub>2</sub>@C<sub>80</sub> are studied at 40 and 240 K in order to clarify the dynamical properties. The molecular structure of Eu@C<sub>60</sub> and the valence of Eu atom are also discussed on the basis of the Eu L<sub>III</sub>-edge XAFS and XANES.

### 2. Experimental

#### 2.1. Sample Preparation

The soots containing Sc<sub>3</sub>@C<sub>82</sub>, Gd@C<sub>82</sub> and La<sub>2</sub>@C<sub>80</sub> were prepared by a general direct-arc-discharge method. The Sc<sub>3</sub>@C<sub>82</sub>, Gd@C<sub>82</sub> and La<sub>2</sub>@C<sub>80</sub> were separated and isolated from other empty and metal endohedral fullerenes by a general two-stage HPLC after extraction in pyridine and CS<sub>2</sub> (Shinohara & Saito, 1997). The sample of Eu@C<sub>60</sub> was purified by combining sublimation and HPLC after extraction in aniline (Inoue *et al.*, 2000).

#### 2.2. XAFS and XANES measurements

All XAFS and XANES were measured at the BL01B1 of SPring-8. A Rh mirror was inserted in all XAFS and XANES measurements in order to eliminate the harmonics. The Lytle detector and ionization chamber were used to detect the XAFS signals in fluorescence and transmission modes, respectively. Sc K-edge XAFS of Sc<sub>3</sub>@C<sub>82</sub>, Gd L<sub>III</sub>-edge of Gd@C<sub>82</sub> and Eu L<sub>III</sub>-edge XANES of Eu@C<sub>60</sub> were measured at 295 K in the fluorescence mode with a Si(111) monochromator. La K-edge XAFS of La<sub>2</sub>@C<sub>80</sub> were measured in the transmission mode at 40 and 240 K with a Si(311) monochromator. Eu L<sub>III</sub>-edge XAFS of Eu@C<sub>60</sub> was measured in the transmission mode with Si(111) monochromator.

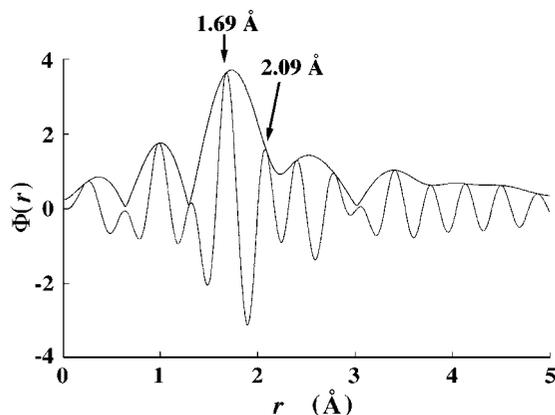
#### 2.3. XAFS analyses

The XAFS oscillation  $\chi(k)$  was extracted from the observed XAFS spectra by eliminating the background with Victreeen formula, cubic spline method and McMaster coefficients (McMaster *et al.*, 1969). The threshold energy  $E_0$  was determined from the inflection point of X-ray absorption edge. The radial structure function  $\Phi(r)$  in the real space ( $r$ -space) was obtained by a Fourier transform of the  $k^3\chi(k)$  in momentum space ( $k$ -space) of photoelectron. The structural parameters were obtained by a least-squares fitting to the  $\chi(k)$  derived by an inverse-Fourier transform of  $\Phi(r)$  with XAFS formula within the framework of the harmonic approximation (Lee *et al.*, 1981, Boland, Crane & Baldseschweiler, 1982, Ishii, 1991). The theoretical values (FEFF) reported by Rehr *et al.* (1991) as well as those by McKale *et al.* (1988) were used for the phase shifts of the absorbing and the scattering atoms, and backscattering amplitudes of the scattering atoms, in determining the structural parameters of  $\text{Sc}_3@C_{82}$ ,  $\text{Gd}@C_{82}$  and  $\text{La}_2@C_{80}$  at 40 K. The structural parameters of  $\text{La}_2@C_{80}$  at 240 K and  $\text{Eu}@C_{60}$  were determined with only McKale's values. All analyses were performed by using XAFS93, MBF93 (McKale) and FBF95 (FEFF) programs developed by Maeda (1987).

### 3. Results and Discussion

#### 3.1. Formation of a triangular cluster $\text{Sc}_3$ in $\text{Sc}_3@C_{82}$

The  $\Phi(r)$  obtained from the  $k^3\chi(k)$  [3.0 - 10.0  $\text{\AA}^{-1}$ ] of  $\text{Sc}_3@C_{82}$  is shown in Fig. 1. A peak is observed at  $r = 1.69 \text{ \AA}$  in the imaginary part of  $\Phi(r)$  which is significantly shorter than that of  $\text{Gd}@C_{82}$  [ $r = 2.07 \text{ \AA}$ ] described in the subsequent session. We assumed that this peak was not due to the Sc-C but the Sc-Sc scattering. The peak at  $r = 2.09 \text{ \AA}$  may be assigned to the Sc-C scattering because the  $r$  is close to that of Gd-C scattering in  $\text{Gd}@C_{82}$ . The structural parameters were determined by the least-squares fitting for the  $\chi(k)$  [3.5 - 10.0  $\text{\AA}^{-1}$ ] derived from the  $\Phi(r)$  [1.19 - 2.25  $\text{\AA}$ ]. The final distances  $r_{\text{Sc-Sc}}$  are listed together with



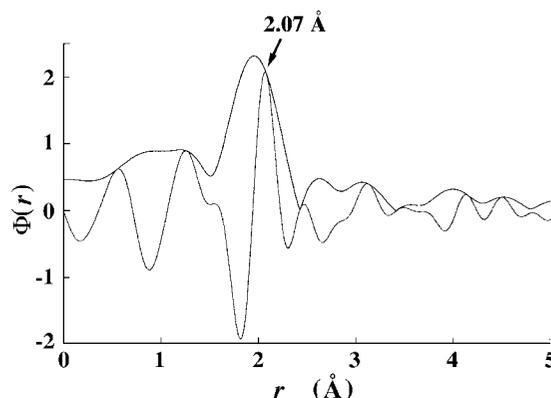
**Figure 1**  
 $\Phi(r)$  of  $\text{Sc}_3@C_{82}$ . The thick and thin lines refer to the magnitude and imaginary part of  $\Phi(r)$ .

the final  $R$ -factor in Table 1. The structural parameters determined by the analysis with the FEFF codes are consistent with those with McKale's values within the estimated standard deviation (esd), indicating that the analysis with McKale's values is also reliable. The short  $r_{\text{Sc-Sc}}$  [2.23(1)  $\text{\AA}$  (McKale) and 2.21(1)  $\text{\AA}$  (FEFF)] is consistent with that [2.3(3)  $\text{\AA}$ ] determined by the MEM analysis (Takata *et al.*, 1999). This result supports directly the formation of  $\text{Sc}_3$  cluster in  $\text{Sc}_3@C_{82}$ . The mean square

displacement,  $\sigma(2)$ , of Sc-Sc [0.005(1)  $\text{\AA}^2$  (McKale) and 0.004(1)  $\text{\AA}^2$  (FEFF)] is very small even at 295 K, which suggests that the Sc atoms are fixed near the  $C_{82}$  cage in the time scale of X-ray. This result is consistent with the fact that three MEM charge densities are clearly observed at room temperature (Takata *et al.*, 1999). The distance of the Sc atom and the first neighboring C atoms, Sc-C(1), [2.55(1)  $\text{\AA}$  (McKale) and 2.52(2)  $\text{\AA}$  (FEFF)] determined from XAFS is consistent with that [2.52(2)  $\text{\AA}$ ] by MEM analysis (Takata *et al.*, 1999) within esd.

#### 3.2. Structure of $\text{Gd}@C_{82}$

The  $\Phi(r)$  of  $\text{Gd}@C_{82}$  obtained from the  $k^3\chi(k)$  [2.0 - 10.0  $\text{\AA}^{-1}$ ] is shown in Fig. 2. The peak observed at 2.07  $\text{\AA}$  can be assigned to the Gd-C scattering. The distance between the Gd and the first neighboring C atoms, and that between the Gd and the second neighboring C atoms,  $r_{\text{Gd-C}(1)}$  and  $r_{\text{Gd-C}(2)}$  are listed in Table 1. In this analysis, we assumed that the Gd atom exists on the  $C_2$  axis through the six-membered ring in the  $C_{82}$  cage with  $C_{2v}$  symmetry. The  $r_{\text{Gd-C}(1)}$  of 2.51(2)  $\text{\AA}$  (McKale) and 2.56(1)  $\text{\AA}$  (FEFF) are close to the  $r_{\text{Sc-C}(1)}$  in  $\text{Sc}_3@C_{82}$  and the  $r_{\text{La-C}(1)}$  in  $\text{La}@C_{82}$  [2.47(2)  $\text{\AA}$ ] (Nomura *et al.*, 1995). This result shows that the Gd atom in  $\text{Gd}@C_{82}$  is located near  $C_{82}$  cage. The  $\sigma(2)$  of Gd-C(1) and Gd-C(2) were 0.016(2) and 0.029(6)  $\text{\AA}^2$  for McKale code, respectively, and 0.008(2) and 0.021(7)  $\text{\AA}^2$  for FEFF code.



**Figure 2**  
 $\Phi(r)$  of  $\text{Gd}@C_{82}$ . The thick and thin lines refer to the magnitude and imaginary part of  $\Phi(r)$ .

#### 3.3. Structure of $\text{La}_2@C_{80}$ at 40 and 240 K

Two peaks were observed at 1.69 and 2.21  $\text{\AA}$  in the imaginary part of  $\Phi(r)$  obtained by the Fourier-transform of the  $k^3\chi(k)$  [2.0 to 10.0  $\text{\AA}^{-1}$ ] at 40 K. The parameter fitting was performed for the  $\chi(k)$  obtained from the  $\Phi(r)$  [1.17 - 2.70  $\text{\AA}$ ]. In this analysis, we assumed that each La atom exists on the  $C_2$  axis through the six-membered ring of the  $C_{80}$  cage with  $I_h$  symmetry. The distances between the La and the first neighboring C atoms, and between the La and the second neighboring C atoms,  $r_{\text{La-C}(1)}$  and  $r_{\text{La-C}(2)}$ , of  $\text{La}_2@C_{80}$  are listed in Table 1. The  $\sigma(2)$  of La-C(2) [0.012(8)  $\text{\AA}^2$  (McKale) and 0.012(2)  $\text{\AA}^2$  (FEFF)] is the same as that of La-C(1) [0.013(4)  $\text{\AA}^2$  (McKale) and 0.013(2)  $\text{\AA}^2$  (FEFF)], contrary to the case of  $\text{Gd}@C_{82}$  and  $\text{La}@C_{82}$  at room temperature (Nomura *et al.*, 1995).

The Fourier transform for the  $k^3\chi(k)$  of 5.0 - 11.0  $\text{\AA}^{-1}$  was performed to get the structural information on La-La because the backscattering amplitude of La atom largely contributes to the higher  $k$ -region than that of C atom. The relatively large peak was observed around 3.7  $\text{\AA}$  in the  $\Phi(r)$ . The parameter fitting was

performed for the  $\chi(k)$  [5.0 - 11.0  $\text{\AA}^{-1}$ ] obtained from the  $\Phi(r)$  [3.24 - 4.03  $\text{\AA}$ ]. The La-La distance,  $r_{\text{La-La}}$ , was 3.90(1)  $\text{\AA}$  (McKale) and 3.87(1)  $\text{\AA}$  (FEFF). This value is considerably larger than that [3.66  $\text{\AA}$ ] predicted by Kobayashi *et al.* (1996). The  $\sigma(2)$  of La-La [0.008(1)  $\text{\AA}^2$  (McKale) and 0.007(1)  $\text{\AA}^2$  (FEFF)] is smaller than those of La-C.

The  $r_{\text{La-C}(1)}$  and  $r_{\text{La-C}(2)}$  at 240 K were determined by the same procedure as that at 40 K. The  $r_{\text{La-C}(1)}$  is slightly larger than that at 40 K, while the  $r_{\text{La-C}(2)}$  is the same as that at 40 K within the esd. The  $\sigma(2)$  of La-C(1) [0.014(3)  $\text{\AA}^2$ ] at 240 K is slightly larger than that at 40 K and that of La-C(1) in  $\text{La}@C_{82}$  at 295 K [0.011  $\text{\AA}^2$ ] (Nomura *et al.*, 1995)]. However, the  $r_{\text{La-La}}$  [3.90(2)  $\text{\AA}$ ] and  $\sigma(2)$  [0.009(2)  $\text{\AA}^2$ ] at 240 K is almost the same as those at 40 K. The dynamical behavior of the La atoms in  $\text{La}_2@C_{80}$  should further be studied based on the detail temperature dependence of  $\sigma(2)$ .

**Table 1**Interatomic distances  $r$  ( $\text{\AA}$ ) determined by XAFS.

Sample	Type of $M^a$	$r_{M-C(1)}$	$r_{M-C(2)}$	$r_{M-M}$	$R$ -factor	Type of theoretical values <sup>b</sup>
$\text{Sc}_3@C_{82}$	Sc	2.55(1)	-	2.23(1)	0.08	MK
$\text{Sc}_3@C_{82}$	Sc	2.52(2)	-	2.21(1)	0.07	F
$\text{Gd}@C_{82}$	Gd	2.51(2)	2.85(4)	-	0.08	MK
$\text{Gd}@C_{82}$	Gd	2.56(1)	2.77(3)	-	0.05	F
$\text{La}_2@C_{80}^c$	La	2.42(5)	2.97(7)	3.90(1)	0.06	MK
$\text{La}_2@C_{80}^c$	La	2.39(5)	2.93(7)	3.87(1)	0.06	F
$\text{La}_2@C_{80}^d$	La	2.46(2)	2.94(4)	3.90(2)	0.08	MK
$\text{Eu}@C_{60}^e$	Eu	2.34(1)	2.84(1)	-	0.03	MK
$\text{Eu}@C_{60}^f$	Eu	2.34(1)	2.84(1)	-	0.04	MK

<sup>a</sup>The "M" refers to the metal atom encapsulated into fullerene cage.<sup>b</sup>The "MK" and "F" correspond to the analysis with McKale and FEFF codes, respectively.<sup>c</sup>Measured at 40 K.<sup>d</sup>Measured at 240 K.<sup>e</sup>Analyzed with the six-membered ring model.<sup>f</sup>Analyzed with the five-membered ring model.

### 3.4. Molecular and Electronic Structure of $\text{Eu}@C_{60}$

The Eu  $L_{III}$ -edge XANES of  $\text{Eu}@C_{60}$ ,  $\text{Eu}_2\text{O}_3$  and  $\text{EuS}$  solids exhibited the edge energy  $E_0$  of 6973, 6979, 6971 eV, respectively. The  $E_0$  of  $\text{Eu}@C_{60}$  is close to that of  $\text{EuS}$  in which the valence of Eu is +2, showing that the valence of Eu atom is +2 in  $\text{Eu}@C_{60}$ ; the electronic configuration of  $\text{Eu}^{2+}$  is  $[\text{Xe}]4f^7$  ( $J = 7/2$ ). This electronic configuration of  $\text{Eu}@C_{60}$  is supported by a theoretical calculation (Suzuki *et al.*, 2000). We adopted two models for the analyses of Eu  $L_{III}$ -edge XAFS in order to clarify the location of the Eu atom in  $\text{Eu}@C_{60}$ . The Eu-C distances in  $\text{Eu}@C_{60}$  reported previously (Inoue *et al.*, 1999) based on the model that the Eu atom lies on the six-membered ring [ $r_{\text{Eu-C}(1)} = 2.34(1)$   $\text{\AA}$  and  $r_{\text{Eu-C}(2)} = 2.84(1)$   $\text{\AA}$ ] were the same as those determined based on the model that the Eu atom lies on the five-membered ring (Table 1). The experimental  $r_{\text{Eu-C}(2)}$  is close to a value (2.87  $\text{\AA}$ ) expected for the six-membered ring model when the experimental  $r_{\text{Eu-C}(1)}$  is 2.34(1)  $\text{\AA}$ . In fact, the  $R$ -factor is better in the six-membered ring model than that in the five-membered ring model. Therefore, the XAFS suggests that the Eu atom lies on the six-membered ring inside the  $C_{60}$  cage.

This work was achieved under the proposals of SPring-8 (1998A0048-CX-np, 1999B0057-NX-np, 1999B0331-NX-np, 2000A0002-NX-np), and was supported by a Grant-in-Aid

(11165227) from the Ministry of Education, Science, Sports and Culture, Japan.

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