

Title	Structural and electronic properties of Ce@C_<82>
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Citation	Physical Review B, 68(9): 094104-1-094104-7
Issue Date	2003-09
Type	Journal Article
Text version	publisher
URL	<a href="http://hdl.handle.net/10119/3365">http://hdl.handle.net/10119/3365</a>
Rights	K. Shibata, Y. Rikiishi, T. Hosokawa, Y. Haruyama, Y. Kubozono, S. Kashino, T. Uruga, A. Fujiwara, H. Kitagawa, Takano and Y. Iwasa, Physical Review B, 68(9), 094104, 2003. "Copyright 2003 by the American Physical Society." <a href="http://prola.aps.org/abstract/PRB/v68/i9/e094104">http://prola.aps.org/abstract/PRB/v68/i9/e094104</a>
Description	

**Structural and electronic properties of Ce@C<sub>82</sub>**K. Shibata,<sup>1</sup> Y. Rikiishi,<sup>1</sup> T. Hosokawa,<sup>1</sup> Y. Haruyama,<sup>1</sup> Y. Kubozono,<sup>1,2,3,\*</sup> S. Kashino,<sup>1</sup> T. Uruga,<sup>4</sup> A. Fujiwara,<sup>3,5</sup>  
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(Received 5 February 2003; revised manuscript received 19 May 2003; published 4 September 2003)

X-ray diffraction patterns for a solid sample of Ce@C<sub>82</sub> that contains a mixture of two isomers, I and II, can be indexed in a face-centered cubic lattice with a lattice constant of 15.88(5) Å, while x-ray diffraction patterns for Ce@C<sub>82</sub> isomer I alone indicate a simple cubic lattice with a lattice constant of 15.78(1) Å. Rietveld refinement for the x-ray diffraction pattern of the latter, Ce@C<sub>82</sub> isomer I, has been carried out with a space group of  $Pa\bar{3}$ . Thin films of Ce@C<sub>82</sub> were first prepared by thermal deposition under  $\sim 10^{-7}$  Torr. The Raman spectra for these thin films show a peak ascribable to a Ce-C<sub>82</sub> cage-stretching mode at  $\sim 160$  cm<sup>-1</sup>, implying that the valence of Ce in this structure is +3. This valence of +3 is supported by Ce *L*<sub>III</sub>-edge XANES for a thin film of Ce@C<sub>82</sub>. Furthermore, the local structure around the Ce ion could be determined by Ce *L*<sub>III</sub>-edge EXAFS for a thin-film. Transport properties of a thin film of Ce@C<sub>82</sub> have been studied by a four-probe method, and these demonstrate a semiconducting behavior with a small gap of 0.4 eV.

DOI: 10.1103/PhysRevB.68.094104

PACS number(s): 61.48.+c, 81.05.Tp

**I. INTRODUCTION**

Much effort has been directed towards a clarification of the valence of metal ions encapsulated in metallofullerenes and any electron transfer from these metal ions to the fullerene cages. This is necessary because the valence of metal ions and the charge on the fullerene cages play important roles in the physical properties of fullerenes.<sup>1</sup> The valence of such metal ions has been studied by ESR, UPS, x-ray diffraction, XPS, and XANES.<sup>2-6</sup> The studies were first performed for La@C<sub>82</sub> because La@C<sub>82</sub> is the most fundamental of the lanthanide ion endohedral fullerenes. The ESR spectrum of La@C<sub>82</sub> suggested that the valence of La in La@C<sub>82</sub> was not +2 but +3, based on the fact that eight hyperfine lines were observed with a small hyperfine coupling (hfc) constant, 1.2 G, due to the hfc of an unpaired electron to a <sup>139</sup>La ion ( $I=7/2$ ).<sup>2</sup> UPS also showed that the valence of La in La@C<sub>82</sub> was +3, based on the fact that the two components at 1.6 and 0.9 eV in the difference spectrum between La@C<sub>82</sub> and C<sub>82</sub> were observed with an intensity ratio of 2:1.<sup>3</sup> An analysis of the x-ray diffraction pattern by the maximum entropy method suggested a valence of +3 for La in La@C<sub>82</sub>.<sup>4</sup> The XPS profile for La@C<sub>82</sub> was similar to that of La<sub>2</sub>O<sub>3</sub>,<sup>5</sup> indicating that the valence of La was +3.<sup>6</sup> Studies to estimate the valence of metal ions are gradually being applied to other metallofullerenes.

The electronic structure near the Fermi level in the solid state physics and chemistry of metallofullerenes is very important. The onset of the UPS spectrum was observed at 0.35 eV for La@C<sub>82</sub>, indicating that the gap of at least 0.35 eV has been opened.<sup>6</sup> Very recently, Nuttall *et al.* found an op-

tical gap of 0.3 eV for La@C<sub>82</sub> based on its UV-VIS-NIR spectrum;<sup>7</sup> this spectrum is consistent with the results of EELS.<sup>8</sup> Transport measurements were performed on a single crystal of La@C<sub>82</sub> by the two-probe method. They showed a semiconducting behavior with an  $E_g$  of 0.3 eV.<sup>9</sup> Subsequently all experimental results showed  $E_g \sim 0.3$  eV for La@C<sub>82</sub>. Very recently we studied the transport properties of thin films of Dy@C<sub>82</sub>. These studies demonstrated a semiconducting behavior for Dy@C<sub>82</sub> with an  $E_g$  of 0.2 eV.<sup>10</sup>

Information on the electronic properties of many metallofullerenes is urgently needed because present information is insufficient for use in promoting the solid state physics and the materials science based on metallofullerenes as well as their application to electronic devices. In the present study, we have selected Ce@C<sub>82</sub> as a target for clarification of the structure and electronic properties because Ce is an element adjacent to La in the Periodic Table. The electronic configuration of the Ce atom is [Xe][4*f*<sup>2</sup>][6*s*<sup>2</sup>]. Thus Ce possesses 4*f* electrons. The coexistence of 4*f* electron(s) on Ce and  $\pi$  electrons on the C<sub>82</sub> cage in Ce@C<sub>82</sub> may provide new information on the physics and chemistry of bifunctional molecular systems based on a coupling of the localized spin with conduction electrons.

The existence of two types of crystal structures in isomer-mixture samples of Ce@C<sub>82</sub> has been demonstrated by x-ray diffraction patterns.<sup>11</sup> One, for the sample sublimed at 873 K, is a face-centered-cubic (fcc) structure (space group  $Fm\bar{3}m$ ) and the other, for the sample dried at 532 K, is a hexagonal close packed (hcp) structure (space group  $P6_3/mmc$ ). In the present study, the crystal structure of the Ce@C<sub>82</sub> sample

dried at 623 K has been studied by x-ray powder diffraction because the sample dried at this temperature was used to form a thin film of Ce@C<sub>82</sub>. Furthermore, the x-ray diffraction patterns for the isomer-separated samples of Ce@C<sub>82</sub> have been studied with synchrotron radiation, and a Rietveld refinement has been carried out for the major isomer. The Raman, XANES, and transport properties of thin films of Ce@C<sub>82</sub> have been studied in order to clarify the electronic structures.

## II. EXPERIMENT

A Ce@C<sub>82</sub> sample was obtained by the same procedure used to obtain Dy@C<sub>82</sub>.<sup>10,12</sup> Samples were characterized by time-of-flight mass and UV-VIS-NIR absorption spectra. The quantity and purity of Ce@C<sub>82</sub> obtained were  $\sim 3$  mg and  $\sim 99.5\%$ , respectively. A solid sample of Ce@C<sub>82</sub> was obtained by evaporating toluene from a toluene solution of purified Ce@C<sub>82</sub> under reduced pressure at 293 K. This resulting sample contained two isomers with a molar ratio of 4:1; the major and minor isomers were designated I and II, respectively, as for Dy@C<sub>82</sub>,<sup>10,12</sup> and the names I and II correspond to the order of retention times during high performance liquid chromatography (HPLC). The isomer-separated samples, isomers I and II, were obtained by repeating the HPLC three times; the quantity and purity of the isomer I were  $\sim 1$  mg and over 99%, respectively, while those of isomer II were  $\sim 0.3$  mg and  $\sim 99\%$ , respectively. Solid samples of isomers I and II were also obtained by evaporating toluene from their toluene solutions. A trace of toluene was removed from the Ce@C<sub>82</sub> solid sample containing two isomers (isomers-mixture) and from the solid samples of Ce@C<sub>82</sub> isomers I and II by a dynamical pumping under a pressure of  $10^{-5}$  Torr at 373 K for 5 h, at 473 K for 12 h, and then at 623 K for 49 h. These dried samples, ready for x-ray diffraction and Raman measurements, were introduced into glass capillaries ( $\phi=0.5$  mm) without any exposure to air in an Ar glove box. The x-ray powder diffraction pattern for the sample of Ce@C<sub>82</sub> isomers-mixture was measured at 295 K with Cu *K* $\alpha$  radiation ( $\lambda=1.5418$  Å, 40 kV, and 200 mA) by a Rigaku Rint 1500 x-ray diffractometer. The x-ray diffraction patterns for Ce@C<sub>82</sub> isomers I and II were measured at 295 K, with a synchrotron radiation of  $\lambda=0.7997(4)$  Å at BL-1B of KEK-PF, Japan. The Rietveld refinement for the x-ray diffraction pattern for isomer I was achieved with the Rietan-2000 program developed by Izumi.<sup>13</sup>

A Ce@C<sub>82</sub> thin film was fabricated according to the following procedure. A highly doped *n*-type Si(100) wafer was immersed in a diluted HF solution in order to remove any native oxide.<sup>14</sup> A SiO<sub>2</sub> layer was grown on the Si wafer by dry oxidation at 1273 K for 6 h. The thickness, *t*, of the SiO<sub>2</sub> layer was determined by an ellipsometer to be 3100 Å. The SiO<sub>2</sub>/Si substrate was washed with acetone, methanol, and purified water by ultrasonic irradiation prior to fabrication of electrodes and fullerene thin film. The four electrodes for the resistivity measurement,  $\rho$ , were formed on the SiO<sub>2</sub>/Si substrate by a thermal deposition of gold through a shadow mask under a vacuum of  $\sim 10^{-7}$  Torr; the channel length, *L*,

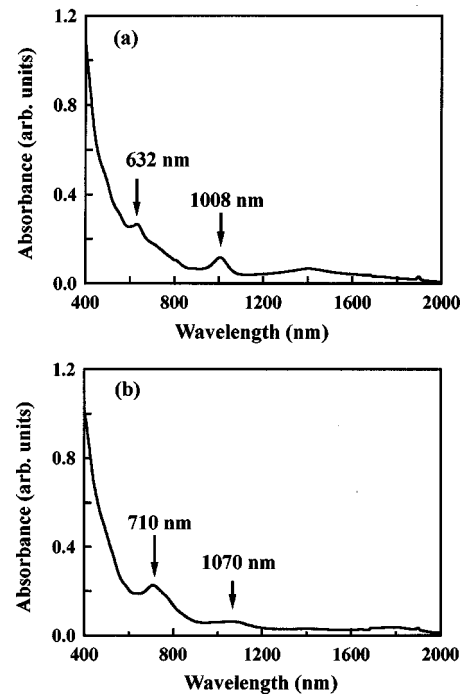


FIG. 1. UV-VIS-NIR absorption spectra for Ce@C<sub>82</sub> isomers (a) I and (b) II.

was 20  $\mu\text{m}$ . The *t* of electrodes was estimated to be 500 Å by a quartz-crystal oscillator. The Ce@C<sub>82</sub> isomers-mixture was deposited on the substrates under the same pressure of  $10^{-7}$  Torr. This thin film then contained isomers I and II with a molar ratio of 4:1. The deposition rate was regulated below  $1 \text{ \AA s}^{-1}$ . The *t* of Ce@C<sub>82</sub> thin-film was determined by a surface profiler to be 4700 Å, and the width of the thin film was 5000  $\mu\text{m}$ .

The Raman spectra for crystalline Ce@C<sub>82</sub> isomers I and II, and a Ce@C<sub>82</sub> thin film were measured at an excitation of 632.8 nm by a He-Ne laser with an NR-1000 system (JEOL) for frequency ( $\omega$ ) region of 100–850  $\text{cm}^{-1}$ . The Ce *L*<sub>III</sub>-edge XANES and EXAFS for the Ce@C<sub>82</sub> thin film were measured by fluorescence and electron yield detection, respectively, with synchrotron radiation at BL01B1 of SPring-8, Japan. The EXAFS of Ce@C<sub>82</sub> thin film was analyzed with XAFS93 and RBF93 programs developed by Maeda.<sup>15</sup>

## III. RESULTS AND DISCUSSION

### A. Structure of Ce@C<sub>82</sub>

The UV-VIS-NIR spectra of Ce@C<sub>82</sub> isomers I and II are shown in Figs. 1(a) and 1(b). Two peaks are observed at 632 and 1008 nm for isomer I, while they lie at 710 and 1070 nm for isomer II. The peaks for the isomer I show a blueshift by 60–80 nm in comparison with those for the isomer II. Peaks for isomers I of La@C<sub>82</sub>, Pr@C<sub>82</sub>, and Dy@C<sub>82</sub>, which have a C<sub>2v</sub> symmetry shifted to blue by 60–100 nm when compared with those of isomers II which have C<sub>s</sub> symmetry.<sup>16–19</sup> The wavelength of 632 nm for the first peak of Ce@C<sub>82</sub> isomer I is close to those for isomers I (C<sub>2v</sub>) of

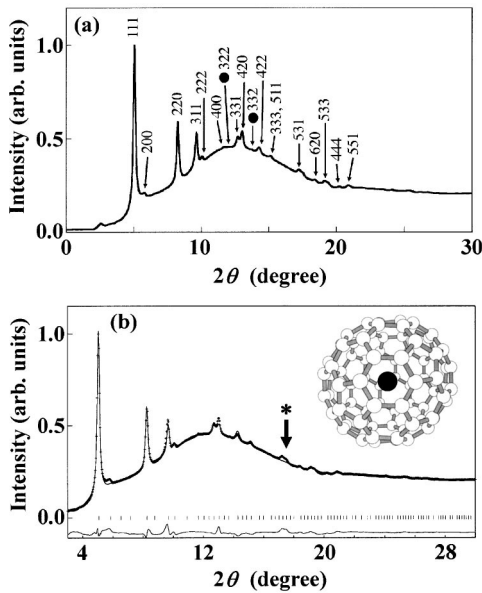


FIG. 2. (a) Observed x-ray diffraction pattern for Ce@C<sub>82</sub> isomer I, and (b) the observed x-ray diffraction pattern (+ symbols) and that calculated with the structural parameters determined by Rietveld refinement (solid line). In (a) the symbols ● show those peaks that cannot be indexed by a fcc lattice. In (b) the allowed peak positions and the difference between the observed and calculated patterns are drawn by a check mark (middle) and a solid line (bottom), respectively. The peak indicated by an asterisk did not appear in the calculated pattern. This peak was attributed to effects of the sample holder. A molecule of Ce@C<sub>82</sub> isomer I viewed along the [111] direction is shown in the inset of (b). Black and white balls refer to the Ce and C atoms, respectively.

La@C<sub>82</sub> (620 nm), Pr@C<sub>82</sub> (640 nm) and Dy@C<sub>82</sub> (632 nm) reported previously, while the wavelength of 710 nm for Ce@C<sub>82</sub> isomer II is close to those for isomers II (*C<sub>s</sub>*) of La@C<sub>82</sub> (705 nm), Pr@C<sub>82</sub> (710 nm) and Dy@C<sub>82</sub> (694 nm). These results show that the symmetries of Ce@C<sub>82</sub> isomers I and II are *C<sub>2v</sub>* and *C<sub>s</sub>*, respectively. Therefore the C<sub>82</sub> cages in isomers I and II should have these same symmetries.

The x-ray diffraction pattern for the dried sample of Ce@C<sub>82</sub> isomers-mixture can be indexed in a fcc lattice with *a* of 15.88(5) Å. This diffraction pattern is consistent with that of the sublimed Ce@C<sub>82</sub> sample reported by Nuttall *et al.*; it was attributed to the fcc structure with *a* = 15.766 Å.<sup>11</sup> Consequently, crystals of the Ce@C<sub>82</sub> isomers-mixture dried at 623 K under a vacuum of 10<sup>-5</sup> Torr have a fcc structure as in the sublimed sample. In the present study, the dried sample is used to form the thin film by the thermal deposition. The x-ray diffraction pattern of Ce@C<sub>82</sub> isomer I is shown in Fig. 2(a); it can be indexed with an sc lattice. This pattern is similar to that of Dy@C<sub>82</sub> isomer I. In the Rietveld refinement, the space group for crystals of Ce@C<sub>82</sub> isomer I was assumed to be *Pa* $\bar{3}$  as for the Dy@C<sub>82</sub> isomer I reported recently by our group.<sup>10</sup> For a *C<sub>2v</sub>*-Ce@C<sub>82</sub> molecule (isomer I) an orientational disorder around [111] was assumed, because the symmetry is required for the space group *Pa* $\bar{3}$ . The center of the C<sub>82</sub> cage was placed on the origin of the unit cell, and the *C<sub>2</sub>* axis of the

C<sub>82</sub> cage was aligned along [111]. The number of crystallographically independent C atoms is 82 in the *Pa* $\bar{3}$  unit cell because the *C<sub>2v</sub>*-C<sub>82</sub> cage has no  $\bar{3}$  symmetry. All C atoms occupy the 24*d* site with an occupancy factor of 1/6. The Ce atom occupies the 8*c* site with an occupancy factor of 1/2; the Ce ion lies on the *C<sub>2</sub>* axis to satisfy the *C<sub>2v</sub>* symmetry in the Ce@C<sub>82</sub> molecule. The rotation angle  $\phi$  was fixed to 30° as in the case of the Dy@C<sub>82</sub> isomer I, where the definition of  $\phi$  followed that in Dy@C<sub>82</sub> isomer I.<sup>10</sup> The coordinates of *x*, *y*, and *z* for the C<sub>82</sub> cage were fixed to the initial ones with C—C bond lengths of 1.37–1.47 Å; the initial coordinates were the same as those used in the Rietveld analysis of Dy@C<sub>82</sub>.<sup>20</sup>

The x-ray diffraction pattern of Ce@C<sub>82</sub> isomer I and that calculated with the structural parameters determined from the Rietveld refinement are shown in Fig. 2(b). The final *R<sub>wp</sub>* and integrated intensity *R* factor, *R<sub>I</sub>*, were 0.027 and 0.102, respectively. The Ce@C<sub>82</sub> molecule viewed along [111] is shown in the inset of Fig. 2(b). The *a* value for Ce@C<sub>82</sub> isomer I was determined to be 15.78(1) Å, which is the same as that, 15.78(1) Å, for Dy@C<sub>82</sub> isomer I.<sup>10</sup> The *B* of C atoms is 7(2) Å<sup>2</sup>, while that of Ce atom, 132(35) Å<sup>2</sup>, is very large as for that of Dy in the Dy@C<sub>82</sub> isomer I.

From this analysis, it appears that the Ce@C<sub>82</sub> molecule takes part in a ratchet-type disorder to satisfy the  $\bar{3}$  symmetry, and the Ce ion exhibits considerable disorder within the C<sub>82</sub> cage. When Rietveld analyses were performed by varying the distance between the Ce atom and the C<sub>82</sub> cage center in Ce@C<sub>82</sub>, the *R<sub>wp</sub>* showed an almost flat minimum within  $\pm 2.2$  Å from the cage center. The *R<sub>wp</sub>* value was slightly high near the cage center. This result implies that the Ce in Ce@C<sub>82</sub> has considerable freedom of motion within the C<sub>82</sub> cage. Recently, a flat *R<sub>wp</sub>* minimum was also found in the Rietveld analyses of Dy@C<sub>82</sub>.<sup>21</sup> Further, considerable motion of La was observed in La@C<sub>82</sub> isomer I by the MEM analysis.<sup>4</sup> These results also support the floating motion of Ce in Ce@C<sub>82</sub>.

The x-ray powder diffraction pattern for Ce@C<sub>82</sub> isomer II was indexed with an sc lattice of *a* = 15.6(1) Å. However, the x-ray diffraction data obtained were very poor because only small amounts of the sample,  $\sim 0.3$  mg, were available. Consequently, a Rietveld analysis could not be done satisfactorily for Ce@C<sub>82</sub> isomer II.

## B. Vibrational modes of Ce@C<sub>82</sub>

The Raman spectra for powder samples of Ce@C<sub>82</sub> isomers I and II are shown in Figs. 3(a) and 3(b), respectively. A peak for the Ce cage stretching mode in Ce@C<sub>82</sub> isomer I is observed at  $\omega = 160$  cm<sup>-1</sup>, while that for isomer II is observed at  $\omega = 163$  cm<sup>-1</sup>. The Raman spectrum for the Ce@C<sub>82</sub> thin film is almost the same as that for the crystalline sample of Ce@C<sub>82</sub> isomer I. The peak for the Ce-C<sub>82</sub> stretching mode in the Ce@C<sub>82</sub> thin film is observed at  $\omega = 160$  cm<sup>-1</sup>. The observation of a stretching mode at the same value as that for the Ce@C<sub>82</sub> isomer I shows that the thin film is not damaged by the thermal deposition and mainly consists of Ce@C<sub>82</sub> isomer I. The result is consistent

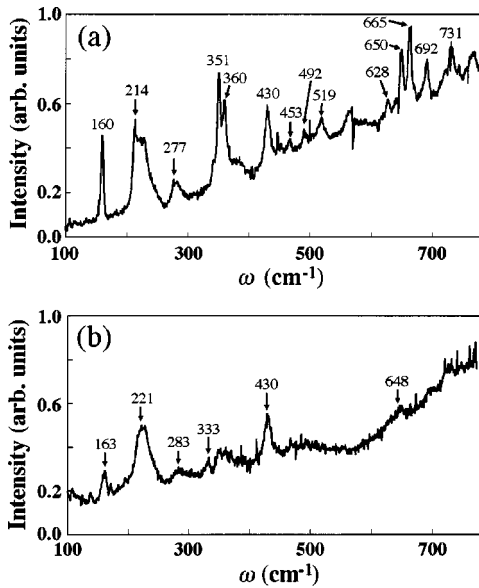


FIG. 3. Raman spectra for the crystalline Ce@C<sub>82</sub> isomers (a) I and (b) II in the  $\omega$  region of 100–800 cm<sup>-1</sup>.

with the fact that the isomers-mixture contains the isomers I and II with the molar ratio of 4:1.

The  $\omega$  values for the stretching mode of Ce@C<sub>82</sub> are similar to those for the isomers-mixture of La@C<sub>82</sub> (162/163 cm<sup>-1</sup>), Gd@C<sub>82</sub> (152/155 cm<sup>-1</sup>), and Ce@C<sub>82</sub> (156/162 cm<sup>-1</sup>) reported previously,<sup>22,23</sup> in which the valence of metal ions is reported to be +3.<sup>1</sup> On the other hand, the peaks for the stretching mode of the metal cage in isomer III (C<sub>2</sub> symmetry) of Tm@C<sub>82</sub> and Sm@C<sub>82</sub>, and the isomers-mixture of Eu@C<sub>74</sub> are observed around 120 cm<sup>-1</sup>;<sup>22</sup> in these the valence of the metal atom is +2.<sup>1</sup> The peaks for the stretching mode for both isomers of Ce@C<sub>82</sub> clearly show that the valence of Ce is +3.

The  $\omega$  values of three La-C<sub>82</sub> modes calculated theoretically for C<sub>2v</sub>-La@C<sub>82</sub> were 159, 27, and 30 cm<sup>-1</sup> for the A<sub>1</sub>, B<sub>1</sub>, and B<sub>2</sub> modes, respectively.<sup>24</sup> The A<sub>1</sub> mode refers to the stretching vibration mode, while the B<sub>1</sub> and B<sub>2</sub> modes refer to lateral vibrational modes. The value of  $\omega$  observed for the Ce@C<sub>82</sub> isomer I is consistent with a theoretical value for the A<sub>1</sub> mode for C<sub>2v</sub>-La@C<sub>82</sub>.<sup>24</sup> This indicates that the difference between the encapsulated metal ions in La@C<sub>82</sub> and Ce@C<sub>82</sub> does not affect the  $\omega$  value for the A<sub>1</sub> stretching modes if the cage structures and the valences of the metal ions are the same in each.

Further, the difference in cage symmetry between Ce@C<sub>82</sub> isomers I and II causes a slight shift from 160 to 163 cm<sup>-1</sup> in the  $\omega$  for the A<sub>1</sub> stretching mode, as shown in Figs. 3(a) and 3(b). This shift is much smaller than that caused by the difference in the valence of the metal ion; the theoretical value of  $\omega$  for C<sub>s</sub>-La@C<sub>82</sub> was almost the same as that for C<sub>2v</sub>-La@C<sub>82</sub>.<sup>25</sup> Peaks for the radial breathing mode are observed at the same value of  $\omega$ , 430 cm<sup>-1</sup> for Ce@C<sub>82</sub> isomers I and II. Other peaks are observed at values of  $\omega$  similar in Ce@C<sub>82</sub> isomers I and II.

#### C. Valence of Ce in Ce@C<sub>82</sub> determined by XANES

The Ce L<sub>III</sub>-edge XANES spectra of Ce@C<sub>82</sub> thin-film and CeO<sub>2</sub> powder are shown in Fig. 4. The threshold ener-

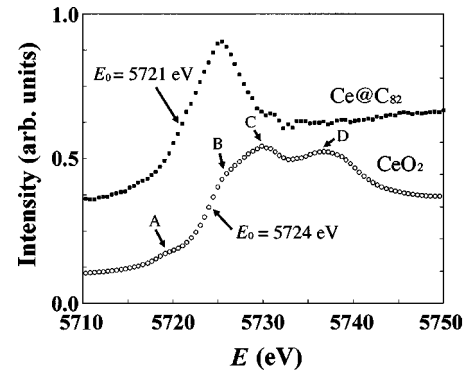


FIG. 4. Ce L<sub>III</sub>-edge XANES spectra for a thin film of Ce@C<sub>82</sub> and for a CeO<sub>2</sub> powder.

gies,  $E_0$ , of the Ce L<sub>III</sub>-edge XANES spectra are 5721 and 5724 eV for Ce@C<sub>82</sub> and CeO<sub>2</sub>, respectively. A single peak is observed for Ce@C<sub>82</sub>, while the XANES spectrum of CeO<sub>2</sub> is more complex. The XANES spectrum for CeO<sub>2</sub> is consistent with that reported previously.<sup>26</sup> The  $E_0$  value for Ce@C<sub>82</sub> shifts by 3 eV to lower energy than that for CeO<sub>2</sub> with the valence of +4.

We previously reported that the  $E_0$  value from Eu L<sub>III</sub>-edge XANES for Eu@C<sub>60</sub> shifted to a lower energy by 6 eV compared with that for Eu<sub>2</sub>O<sub>3</sub>, and that the  $E_0$  value for Eu@C<sub>60</sub> was close to that for EuS.<sup>27</sup> The results implied that the valence of Eu in Eu@C<sub>60</sub> was not +3 but +2 as in EuS. Furthermore, the  $E_0$  value of Tm@C<sub>82</sub> is shifted to a lower energy by 7 eV than that of Tm<sub>2</sub>@C<sub>82</sub>.<sup>28</sup> Therefore Kikuchi *et al.* concluded that the valences of Tm@C<sub>82</sub> and Tm<sub>2</sub>@C<sub>82</sub> were +2 and +3, respectively. The shift in the value of  $E_0$  to a lower energy in Ce@C<sub>82</sub> suggests that the valence of Ce in Ce@C<sub>82</sub> is different from that in CeO<sub>2</sub>. However, the shift value of  $E_0$ , 3 eV, is smaller than that caused by the change of the valence from +2 to +3.

According to Ref. 26, the two peaks denoted as C and D in the XANES spectrum of CeO<sub>2</sub> are assigned to L<sub>III</sub> (2p → 5d) transitions screened by localized 4f and the extended 4f states, respectively. The shoulders denoted as A and B are assigned to shakedown satellites of peaks C and D. A XANES spectrum similar to that for CeO<sub>2</sub> is observed for TbO<sub>2</sub> and PrO<sub>2</sub> with the valence of +4, while shoulder B is found to be coincident with the single line observed for the corresponding trivalent oxides and trivalent compounds.<sup>26</sup> The single line in the XANES for Ce@C<sub>82</sub> is consistent with a shoulder B for CeO<sub>2</sub>, as seen from Fig. 4. This result shows that the valence of Ce in Ce@C<sub>82</sub> is +3.

#### D. Local structure of Ce@C<sub>82</sub>

The radial distribution function,  $\Phi(r)$ , obtained by the Fourier transform of the Ce L<sub>III</sub>-edge EXAFS oscillation,  $\chi(k)$ , in the  $k$ -region of 2.0–10.0 Å<sup>-1</sup> for a thin film of Ce@C<sub>82</sub> is shown in Fig. 5(a). Two pronounced peaks in the absolute portion of  $\Phi(r)$  are observed at 1.82 and 2.48 Å. The peaks can be assigned to scattering between Ce and the first nearest C atoms, C(1), and that between Ce and the second nearest C atoms, C(2). The peaks in  $\Phi(r)$  are ob-

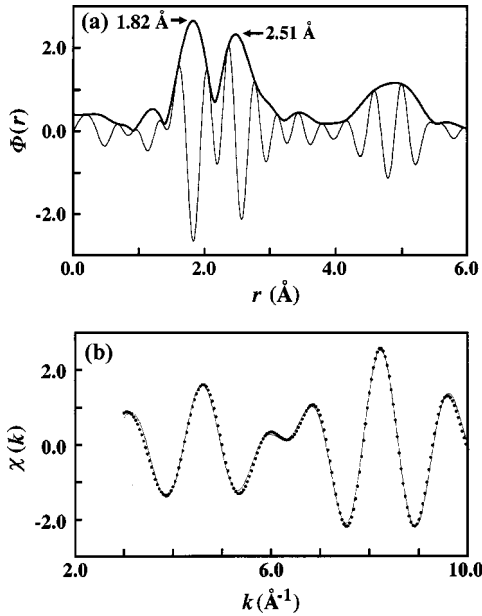


FIG. 5. (a)  $\Phi(r)$  obtained from the Ce  $L_{III}$ -edge EXAFS for a Ce@C<sub>82</sub> thin film. (b) The experimental  $\chi(k)$  ( $\cdot$  symbols) for Ce-C(1) and Ce-C(2), and  $\chi(k)$  (solid line) calculated with the structural parameters determined by an EXAFS data analysis. In (a) the thin and thick lines refer to the imaginary and absolute components of  $\Phi(r)$ , respectively.

served at  $r$  values that are smaller than the real distances because the Fourier transform is performed without consideration of the phase shift of absorbing and scattering atoms.

The structural parameters of Ce-C(1) and Ce-C(2) were determined by a least-squares fitting (two-shell fitting) for  $\chi(k)$  [Fig. 5(b)] obtained by an inverse-Fourier transform of  $\Phi(r)$  in the  $r$  region of 1.32–3.05 Å. The FEFF code was used for the phase shifts of absorbing and scattering atoms, and the backscattering amplitudes of the scattering atoms.<sup>29</sup> The coordination numbers,  $N$ , for C(1) and C(2) were fixed to 6 by assuming that the Ce ion lies along the  $C_2$  axis on the six-membered ring of the C<sub>82</sub> cage with  $C_{2v}$  symmetry. Although this sample contains two isomers of I and II, the fraction of isomer I with the  $C_{2v}$  symmetry is found from the HPLC profile to be larger than 80%. The distance of Ce-C(1),  $r_{\text{Ce-C}(1)}$  and the mean-square displacement,  $\sigma(1)$ , were determined to be 2.473(9) Å and 0.005(1) Å<sup>2</sup>, respectively, while the distance of Ce-C(2),  $r_{\text{Ce-C}(2)}$ , and the mean-square displacement,  $\sigma(2)$ , were determined to be 2.743(9) Å and 0.0026(9) Å<sup>2</sup>, respectively. The  $\chi(k)$  calculated with the structural parameters described above is shown in Fig. 5(b), together with the experimental  $\chi(k)$ ; the final  $R$  factor was 0.084.

The  $r_{\text{Ce-C}(1)}$  is consistent with those determined for the powder samples of Dy@C<sub>82</sub> [2.48(2) Å], Gd@C<sub>82</sub> isomer I [2.56(1) Å], and La@C<sub>82</sub> isomer I [2.47(2) Å] by EXAFS.<sup>16,30,31</sup> On the other hand,  $r_{\text{Ce-C}(2)}$  is slightly smaller than those for Dy@C<sub>82</sub> [2.83(2) Å], Gd@C<sub>82</sub> isomer I [2.77(3) Å], and La@C<sub>82</sub> isomer I [2.94(7) Å].<sup>16,30,31</sup> The structural parameters obtained from EXAFS show that the Ce@C<sub>82</sub> molecule is not damaged by thermal deposition

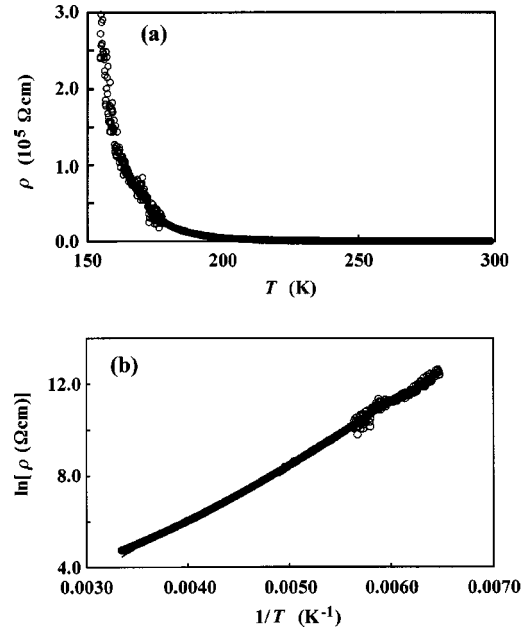


FIG. 6. (a)  $\rho$  vs  $T$  and (b)  $\ln \rho$  vs  $1/T$  plots for a thin film of Ce@C<sub>82</sub>. In (b), the solid line refers to that fitted with a linear relationship.

when a thin film is formed; this finding is also supported by the Raman spectra as described in Sec. III B.

#### E. Transport property of Ce@C<sub>82</sub>

The temperature dependence of  $\rho$  for a Ce@C<sub>82</sub> thin film is shown in Fig. 6(a). The  $\rho$  value decreases with an increase in temperature up to 300 K. The  $\rho$  value is 130 Ω cm at 290 K. The  $\ln \rho$  vs  $1/T$  plots from 155 to 290 K are shown in Fig. 6(b); they exhibit a linear relationship. This implies that Ce@C<sub>82</sub> is a normal semiconductor. The value of  $E_g$  is estimated to be 0.4 eV; this is smaller than those of C<sub>60</sub> (1.8 or 2.1 eV) and C<sub>70</sub> (2.2 eV).<sup>32–34</sup> The  $E_g$  value of Ce@C<sub>82</sub> is slightly larger than those of La@C<sub>82</sub> and Dy@C<sub>82</sub> which are estimated from the temperature dependence of  $\rho$  (Refs. 9 and 10) to be 0.3 and 0.2 eV, respectively. These results show that  $M@C_{82}$  ( $M$ : La, Dy and Ce) is a semiconductor with a small value of  $E_g$ . The small  $E_g$  of Ce@C<sub>82</sub> may lead to the appearance of novel physical properties. For example, the semiconductor-metal transition may be observed by application of pressure because the value of  $E_g$  is expected to decrease owing to an increase in the bandwidths of conduction and valence bands caused by an increase in the hopping integral. No anomaly in the plots of  $\rho$  vs  $T$  is observed at 150–300 K. Very recently, the photoelectron emissions for thin films of Dy@C<sub>82</sub> and Ce@C<sub>82</sub> have been studied, and the  $E_g$  values are suggested to be 0.2 and 0.3 eV, respectively.<sup>35</sup> These  $E_g$  values are consistent with that determined from the  $\rho$  vs  $T$  plots in the present study.

#### IV. CONCLUSION

Crystalline samples of Ce@C<sub>82</sub> isomers I and II were obtained, and the structure of isomer I was determined to be

sc ( $Pa\bar{3}$ ) with  $a = 15.78(1)$  Å. The Rietveld refinement of the x-ray powder diffraction data for Ce@C<sub>82</sub> isomer I has been achieved by the adoption of C<sub>2v</sub>-symmetry for the molecule. The C<sub>2</sub> axis of Ce@C<sub>82</sub> isomer I is aligned along [111], and the molecule is orientationally disordered to satisfy the  $\bar{3}$  symmetry.

Thin films of Ce@C<sub>82</sub> were prepared by thermal deposition of a pure sample. The Ce L<sub>III</sub>-edge EXAFS for thin films of Ce@C<sub>82</sub> showed that no thermal damage had occurred. This implies that thin films of metallofullerenes can be prepared by thermal deposition without damage. This result will open doors to studies of the physical properties of the thin films of metallofullerenes and applications to electronic devices such as field-effect transistors (FET's). Very recently, we succeeded in fabricating a FET with a thin film of Dy@C<sub>82</sub> that operated as an *n*-channel normally on a FET.<sup>36</sup>

The valence of Ce in Ce@C<sub>82</sub> has been found to be +3, on the basis of the Raman spectra and Ce L<sub>III</sub>-edge XANES for a thin film of Ce@C<sub>82</sub>. The Raman spectra for the Ce@C<sub>82</sub> isomers I and II have been studied, and a slight shift of 3 cm<sup>-1</sup> was observed in the peak for the Ce-cage stretching mode between isomers I and II. The shift is much smaller than that, ~40 cm<sup>-1</sup>, caused by a difference in the valence of the metal ion. This implies that the force constant of the metal cage, which is directly related to the bond strength between the metal ion and the C<sub>82</sub> cage, is dominated by an ionic interaction.

The  $\rho$ -*T* plots of a thin film of Ce@C<sub>82</sub> showed that

Ce@C<sub>82</sub> is a normal semiconductor with an  $E_g$  value of 0.4 eV. The electronic configuration of Ce@C<sub>82</sub> can be expressed as [Ce]<sup>3+</sup>[C<sub>82</sub>]<sup>3-</sup> because the valence of Ce is +3. This makes one anticipate the coexistence of a localized 4*f* electron on the Ce ion and a delocalized conduction band originating from C<sub>82</sub><sup>3-</sup>. Actually, Ce@C<sub>82</sub> showed no metallic behavior. Nevertheless, the small  $E_g$  value may result in a semiconductor-metal transition on application of pressure to Ce@C<sub>82</sub>. Therefore some interesting physical properties caused by the coexistence of a localized 4*f* electron and a conduction electron may be found for Ce@C<sub>82</sub>.

## ACKNOWLEDGMENTS

The authors thank Dr. Masafumi Ata and Mr. Koji Kadono of SONY Corporation for their valuable suggestions concerning the electronic structure of Ce@C<sub>82</sub>, and Dr. Kaoru Kobayashi and Professor Shigeru Nagase of the Institute for Molecular Science for their valuable suggestions concerning the vibrational modes of Ce@C<sub>82</sub> isomers. They thank Takayoshi Kanbara and Yasuhiro Takabayashi for their helpful assistance through this work. The x-ray diffraction study was performed under the KEK-PF Proposal No. 2002G201, and the XAFS study was performed under the Spring-8 proposal 2002B0547-NX-np. This work was supported by CREST of Japan Science and Technology Corporation and by the Special Research Project and Joint Studies Program (2001–2002) of the Institute for Molecular Science.

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