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Description	

Structural and electronic properties of Ce@C₈₂K. Shibata,¹ Y. Rikiishi,¹ T. Hosokawa,¹ Y. Haruyama,¹ Y. Kubozono,^{1,2,3,*} S. Kashino,¹ T. Uruga,⁴ A. Fujiwara,^{3,5}
H. Kitagawa,^{6,7,†} T. Takano,⁸ and Y. Iwasa^{3,8}¹Department of Chemistry, Okayama University, Okayama 700-8530, Japan²Center for Molecular-Scale Nanoscience, Institute for Molecular Science, Okazaki 444-8585, Japan³CREST, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan⁴Japan Synchrotron Radiation Research Institute, Sayo 679-5198, Japan⁵Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan⁶Department of Chemistry, University of Tsukuba, Ibaraki 305-8571, Japan⁷PRESTO, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan⁸Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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X-ray diffraction patterns for a solid sample of Ce@C₈₂ 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@C₈₂ 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@C₈₂ isomer I, has been carried out with a space group of $Pa\bar{3}$. Thin films of Ce@C₈₂ 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-C₈₂ cage-stretching mode at ~ 160 cm⁻¹, implying that the valence of Ce in this structure is +3. This valence of +3 is supported by Ce *L*_{III}-edge XANES for a thin film of Ce@C₈₂. Furthermore, the local structure around the Ce ion could be determined by Ce *L*_{III}-edge EXAFS for a thin-film. Transport properties of a thin film of Ce@C₈₂ have been studied by a four-probe method, and these demonstrate a semiconducting behavior with a small gap of 0.4 eV.

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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.¹ The valence of such metal ions has been studied by ESR, UPS, x-ray diffraction, XPS, and XANES.²⁻⁶ The studies were first performed for La@C₈₂ because La@C₈₂ is the most fundamental of the lanthanide ion endohedral fullerenes. The ESR spectrum of La@C₈₂ suggested that the valence of La in La@C₈₂ 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 ¹³⁹La ion ($I=7/2$).² UPS also showed that the valence of La in La@C₈₂ was +3, based on the fact that the two components at 1.6 and 0.9 eV in the difference spectrum between La@C₈₂ and C₈₂ were observed with an intensity ratio of 2:1.³ An analysis of the x-ray diffraction pattern by the maximum entropy method suggested a valence of +3 for La in La@C₈₂.⁴ The XPS profile for La@C₈₂ was similar to that of La₂O₃,⁵ indicating that the valence of La was +3.⁶ 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@C₈₂, indicating that the gap of at least 0.35 eV has been opened.⁶ Very recently, Nuttall *et al.* found an op-

tical gap of 0.3 eV for La@C₈₂ based on its UV-VIS-NIR spectrum;⁷ this spectrum is consistent with the results of EELS.⁸ Transport measurements were performed on a single crystal of La@C₈₂ by the two-probe method. They showed a semiconducting behavior with an E_g of 0.3 eV.⁹ Subsequently all experimental results showed $E_g \sim 0.3$ eV for La@C₈₂. Very recently we studied the transport properties of thin films of Dy@C₈₂. These studies demonstrated a semiconducting behavior for Dy@C₈₂ with an E_g of 0.2 eV.¹⁰

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@C₈₂ 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*²][6*s*²]. Thus Ce possesses 4*f* electrons. The coexistence of 4*f* electron(s) on Ce and π electrons on the C₈₂ cage in Ce@C₈₂ 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@C₈₂ has been demonstrated by x-ray diffraction patterns.¹¹ 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@C₈₂ 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@C₈₂. Furthermore, the x-ray diffraction patterns for the isomer-separated samples of Ce@C₈₂ 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@C₈₂ have been studied in order to clarify the electronic structures.

II. EXPERIMENT

A Ce@C₈₂ sample was obtained by the same procedure used to obtain Dy@C₈₂.^{10,12} Samples were characterized by time-of-flight mass and UV-VIS-NIR absorption spectra. The quantity and purity of Ce@C₈₂ obtained were ~ 3 mg and $\sim 99.5\%$, respectively. A solid sample of Ce@C₈₂ was obtained by evaporating toluene from a toluene solution of purified Ce@C₈₂ 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@C₈₂,^{10,12} 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 ~ 1 mg and over 99%, respectively, while those of isomer II were ~ 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@C₈₂ solid sample containing two isomers (isomers-mixture) and from the solid samples of Ce@C₈₂ 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@C₈₂ 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@C₈₂ 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.¹³

A Ce@C₈₂ 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.¹⁴ A SiO₂ layer was grown on the Si wafer by dry oxidation at 1273 K for 6 h. The thickness, t , of the SiO₂ layer was determined by an ellipsometer to be 3100 Å. The SiO₂/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, ρ , were formed on the SiO₂/Si substrate by a thermal deposition of gold through a shadow mask under a vacuum of $\sim 10^{-7}$ Torr; the channel length, L ,

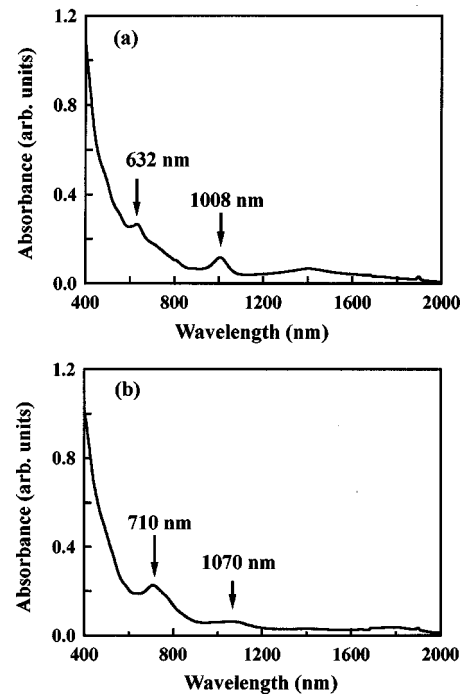


FIG. 1. UV-VIS-NIR absorption spectra for Ce@C₈₂ isomers (a) I and (b) II.

was 20 μm . The t of electrodes was estimated to be 500 Å by a quartz-crystal oscillator. The Ce@C₈₂ 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 Å s^{-1} . The t of Ce@C₈₂ thin-film was determined by a surface profiler to be 4700 Å, and the width of the thin film was 5000 μm .

The Raman spectra for crystalline Ce@C₈₂ isomers I and II, and a Ce@C₈₂ thin film were measured at an excitation of 632.8 nm by a He-Ne laser with an NR-1000 system (JEOL) for frequency (ω) region of 100–850 cm^{-1} . The Ce L_{III} -edge XANES and EXAFS for the Ce@C₈₂ thin film were measured by fluorescence and electron yield detection, respectively, with synchrotron radiation at BL01B1 of SPring-8, Japan. The EXAFS of Ce@C₈₂ thin film was analyzed with XAFS93 and RBF93 programs developed by Maeda.¹⁵

III. RESULTS AND DISCUSSION

A. Structure of Ce@C₈₂

The UV-VIS-NIR spectra of Ce@C₈₂ 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@C₈₂, Pr@C₈₂, and Dy@C₈₂, which have a C_{2v} symmetry shifted to blue by 60–100 nm when compared with those of isomers II which have C_s symmetry.^{16–19} The wavelength of 632 nm for the first peak of Ce@C₈₂ isomer I is close to those for isomers I (C_{2v}) of

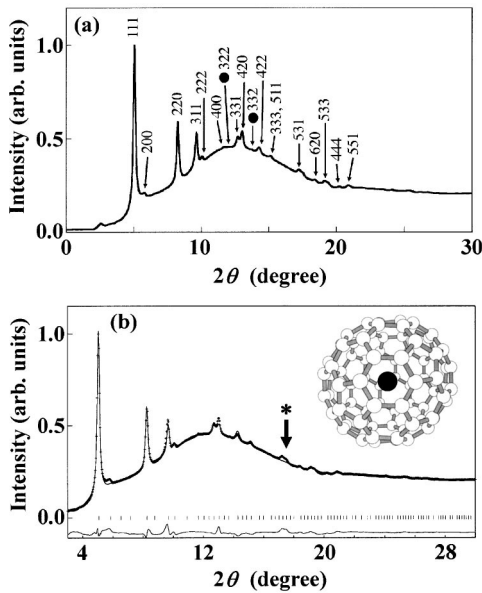


FIG. 2. (a) Observed x-ray diffraction pattern for Ce@C₈₂ isomer I, and (b) the observed x-ray diffraction pattern (+ symbols) and that calculated with the structural parameters determined by Rietveld refinement (solid line). In (a) the symbols ● show those peaks that cannot be indexed by a fcc lattice. 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@C₈₂ 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@C₈₂ (620 nm), Pr@C₈₂ (640 nm) and Dy@C₈₂ (632 nm) reported previously, while the wavelength of 710 nm for Ce@C₈₂ isomer II is close to those for isomers II (*C_s*) of La@C₈₂ (705 nm), Pr@C₈₂ (710 nm) and Dy@C₈₂ (694 nm). These results show that the symmetries of Ce@C₈₂ isomers I and II are *C_{2v}* and *C_s*, respectively. Therefore the C₈₂ cages in isomers I and II should have these same symmetries.

The x-ray diffraction pattern for the dried sample of Ce@C₈₂ 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@C₈₂ sample reported by Nuttall *et al.*; it was attributed to the fcc structure with *a* = 15.766 Å.¹¹ Consequently, crystals of the Ce@C₈₂ isomers-mixture dried at 623 K under a vacuum of 10⁻⁵ 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@C₈₂ isomer I is shown in Fig. 2(a); it can be indexed with an sc lattice. This pattern is similar to that of Dy@C₈₂ isomer I. In the Rietveld refinement, the space group for crystals of Ce@C₈₂ isomer I was assumed to be *Pa* $\bar{3}$ as for the Dy@C₈₂ isomer I reported recently by our group.¹⁰ For a *C_{2v}*-Ce@C₈₂ 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 C₈₂ cage was placed on the origin of the unit cell, and the *C₂* axis of the

C₈₂ cage was aligned along [111]. The number of crystallographically independent C atoms is 82 in the *Pa* $\bar{3}$ unit cell because the *C_{2v}*-C₈₂ 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 *C₂* axis to satisfy the *C_{2v}* symmetry in the Ce@C₈₂ molecule. The rotation angle ϕ was fixed to 30° as in the case of the Dy@C₈₂ isomer I, where the definition of ϕ followed that in Dy@C₈₂ isomer I.¹⁰ The coordinates of *x*, *y*, and *z* for the C₈₂ 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@C₈₂.²⁰

The x-ray diffraction pattern of Ce@C₈₂ isomer I and that calculated with the structural parameters determined from the Rietveld refinement are shown in Fig. 2(b). The final *R_{wp}* and integrated intensity *R* factor, *R_I*, were 0.027 and 0.102, respectively. The Ce@C₈₂ molecule viewed along [111] is shown in the inset of Fig. 2(b). The *a* value for Ce@C₈₂ isomer I was determined to be 15.78(1) Å, which is the same as that, 15.78(1) Å, for Dy@C₈₂ isomer I.¹⁰ The *B* of C atoms is 7(2) Å², while that of Ce atom, 132(35) Å², is very large as for that of Dy in the Dy@C₈₂ isomer I.

From this analysis, it appears that the Ce@C₈₂ molecule takes part in a ratchet-type disorder to satisfy the $\bar{3}$ symmetry, and the Ce ion exhibits considerable disorder within the C₈₂ cage. When Rietveld analyses were performed by varying the distance between the Ce atom and the C₈₂ cage center in Ce@C₈₂, the *R_{wp}* showed an almost flat minimum within ± 2.2 Å from the cage center. The *R_{wp}* value was slightly high near the cage center. This result implies that the Ce in Ce@C₈₂ has considerable freedom of motion within the C₈₂ cage. Recently, a flat *R_{wp}* minimum was also found in the Rietveld analyses of Dy@C₈₂.²¹ Further, considerable motion of La was observed in La@C₈₂ isomer I by the MEM analysis.⁴ These results also support the floating motion of Ce in Ce@C₈₂.

The x-ray powder diffraction pattern for Ce@C₈₂ 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, ~ 0.3 mg, were available. Consequently, a Rietveld analysis could not be done satisfactorily for Ce@C₈₂ isomer II.

B. Vibrational modes of Ce@C₈₂

The Raman spectra for powder samples of Ce@C₈₂ isomers I and II are shown in Figs. 3(a) and 3(b), respectively. A peak for the Ce cage stretching mode in Ce@C₈₂ isomer I is observed at $\omega = 160$ cm⁻¹, while that for isomer II is observed at $\omega = 163$ cm⁻¹. The Raman spectrum for the Ce@C₈₂ thin film is almost the same as that for the crystalline sample of Ce@C₈₂ isomer I. The peak for the Ce-C₈₂ stretching mode in the Ce@C₈₂ thin film is observed at $\omega = 160$ cm⁻¹. The observation of a stretching mode at the same value as that for the Ce@C₈₂ isomer I shows that the thin film is not damaged by the thermal deposition and mainly consists of Ce@C₈₂ isomer I. The result is consistent

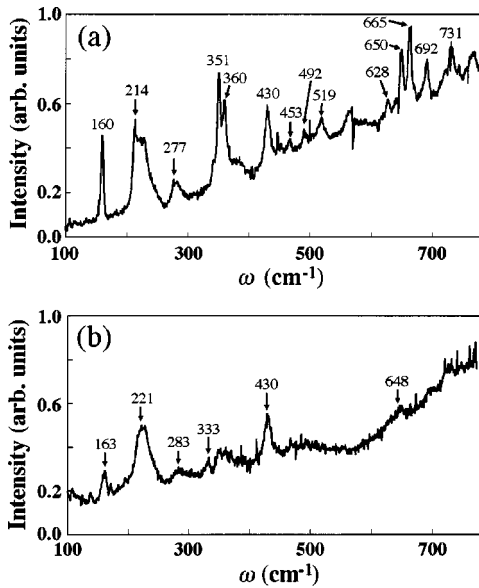


FIG. 3. Raman spectra for the crystalline Ce@C₈₂ isomers (a) I and (b) II in the ω region of 100–800 cm⁻¹.

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

The ω values for the stretching mode of Ce@C₈₂ are similar to those for the isomers-mixture of La@C₈₂ (162/163 cm⁻¹), Gd@C₈₂ (152/155 cm⁻¹), and Ce@C₈₂ (156/162 cm⁻¹) reported previously,^{22,23} in which the valence of metal ions is reported to be +3.¹ On the other hand, the peaks for the stretching mode of the metal cage in isomer III (C₂ symmetry) of Tm@C₈₂ and Sm@C₈₂, and the isomers-mixture of Eu@C₇₄ are observed around 120 cm⁻¹;²² in these the valence of the metal atom is +2.¹ The peaks for the stretching mode for both isomers of Ce@C₈₂ clearly show that the valence of Ce is +3.

The ω values of three La-C₈₂ modes calculated theoretically for C_{2v}-La@C₈₂ were 159, 27, and 30 cm⁻¹ for the A₁, B₁, and B₂ modes, respectively.²⁴ The A₁ mode refers to the stretching vibration mode, while the B₁ and B₂ modes refer to lateral vibrational modes. The value of ω observed for the Ce@C₈₂ isomer I is consistent with a theoretical value for the A₁ mode for C_{2v}-La@C₈₂.²⁴ This indicates that the difference between the encapsulated metal ions in La@C₈₂ and Ce@C₈₂ does not affect the ω value for the A₁ 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@C₈₂ isomers I and II causes a slight shift from 160 to 163 cm⁻¹ in the ω for the A₁ 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 ω for C_s-La@C₈₂ was almost the same as that for C_{2v}-La@C₈₂.²⁵ Peaks for the radial breathing mode are observed at the same value of ω , 430 cm⁻¹ for Ce@C₈₂ isomers I and II. Other peaks are observed at values of ω similar in Ce@C₈₂ isomers I and II.

C. Valence of Ce in Ce@C₈₂ determined by XANES

The Ce L_{III}-edge XANES spectra of Ce@C₈₂ thin-film and CeO₂ powder are shown in Fig. 4. The threshold ener-

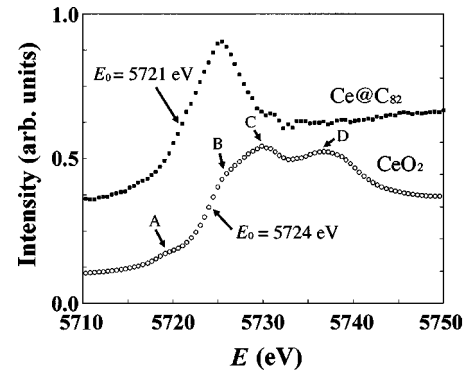


FIG. 4. Ce L_{III}-edge XANES spectra for a thin film of Ce@C₈₂ and for a CeO₂ powder.

gies, E_0 , of the Ce L_{III}-edge XANES spectra are 5721 and 5724 eV for Ce@C₈₂ and CeO₂, respectively. A single peak is observed for Ce@C₈₂, while the XANES spectrum of CeO₂ is more complex. The XANES spectrum for CeO₂ is consistent with that reported previously.²⁶ The E_0 value for Ce@C₈₂ shifts by 3 eV to lower energy than that for CeO₂ with the valence of +4.

We previously reported that the E_0 value from Eu L_{III}-edge XANES for Eu@C₆₀ shifted to a lower energy by 6 eV compared with that for Eu₂O₃, and that the E_0 value for Eu@C₆₀ was close to that for EuS.²⁷ The results implied that the valence of Eu in Eu@C₆₀ was not +3 but +2 as in EuS. Furthermore, the E_0 value of Tm@C₈₂ is shifted to a lower energy by 7 eV than that of Tm₂@C₈₂.²⁸ Therefore Kikuchi *et al.* concluded that the valences of Tm@C₈₂ and Tm₂@C₈₂ were +2 and +3, respectively. The shift in the value of E_0 to a lower energy in Ce@C₈₂ suggests that the valence of Ce in Ce@C₈₂ is different from that in CeO₂. 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 CeO₂ are assigned to L_{III} (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 CeO₂ is observed for TbO₂ and PrO₂ 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.²⁶ The single line in the XANES for Ce@C₈₂ is consistent with a shoulder B for CeO₂, as seen from Fig. 4. This result shows that the valence of Ce in Ce@C₈₂ is +3.

D. Local structure of Ce@C₈₂

The radial distribution function, $\Phi(r)$, obtained by the Fourier transform of the Ce L_{III}-edge EXAFS oscillation, $\chi(k)$, in the k -region of 2.0–10.0 Å⁻¹ for a thin film of Ce@C₈₂ 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-

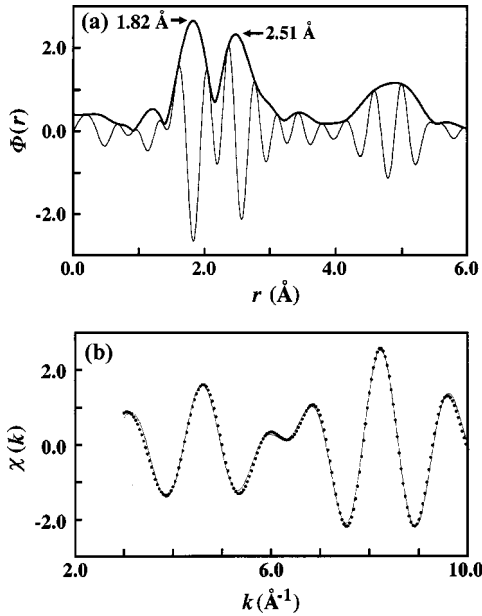


FIG. 5. (a) $\Phi(r)$ obtained from the Ce L_{III} -edge EXAFS for a Ce@C₈₂ thin film. (b) The experimental $\chi(k)$ (\cdot symbols) for Ce-C(1) and Ce-C(2), and $\chi(k)$ (solid line) calculated with the structural parameters determined by an EXAFS data analysis. In (a) the thin and thick lines refer 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.²⁹ 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 C₈₂ 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) Å², 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) Å², 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@C₈₂ [2.48(2) Å], Gd@C₈₂ isomer I [2.56(1) Å], and La@C₈₂ isomer I [2.47(2) Å] by EXAFS.^{16,30,31} On the other hand, $r_{\text{Ce-C}(2)}$ is slightly smaller than those for Dy@C₈₂ [2.83(2) Å], Gd@C₈₂ isomer I [2.77(3) Å], and La@C₈₂ isomer I [2.94(7) Å].^{16,30,31} The structural parameters obtained from EXAFS show that the Ce@C₈₂ molecule is not damaged by thermal deposition

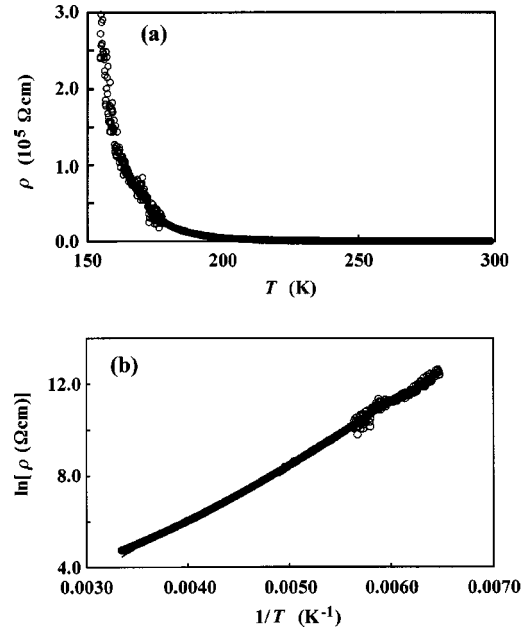


FIG. 6. (a) ρ vs T and (b) $\ln \rho$ vs $1/T$ plots for a thin film of Ce@C₈₂. In (b), the solid line refers to that fitted with a linear relationship.

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@C₈₂

The temperature dependence of ρ for a Ce@C₈₂ thin film is shown in Fig. 6(a). The ρ value decreases with an increase in temperature up to 300 K. The ρ 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@C₈₂ is a normal semiconductor. The value of E_g is estimated to be 0.4 eV; this is smaller than those of C₆₀ (1.8 or 2.1 eV) and C₇₀ (2.2 eV).^{32–34} The E_g value of Ce@C₈₂ is slightly larger than those of La@C₈₂ and Dy@C₈₂ which are estimated from the temperature dependence of ρ (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@C₈₂ 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 ρ vs T is observed at 150–300 K. Very recently, the photoelectron emissions for thin films of Dy@C₈₂ and Ce@C₈₂ have been studied, and the E_g values are suggested to be 0.2 and 0.3 eV, respectively.³⁵ These E_g values are consistent with that determined from the ρ vs T plots in the present study.

IV. CONCLUSION

Crystalline samples of Ce@C₈₂ 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@C₈₂ isomer I has been achieved by the adoption of C_{2v}-symmetry for the molecule. The C₂ axis of Ce@C₈₂ isomer I is aligned along [111], and the molecule is orientationally disordered to satisfy the $\bar{3}$ symmetry.

Thin films of Ce@C₈₂ were prepared by thermal deposition of a pure sample. The Ce L_{III}-edge EXAFS for thin films of Ce@C₈₂ 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@C₈₂ that operated as an *n*-channel normally on a FET.³⁶

The valence of Ce in Ce@C₈₂ has been found to be +3, on the basis of the Raman spectra and Ce L_{III}-edge XANES for a thin film of Ce@C₈₂. The Raman spectra for the Ce@C₈₂ isomers I and II have been studied, and a slight shift of 3 cm⁻¹ 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⁻¹, 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 C₈₂ cage, is dominated by an ionic interaction.

The ρ -*T* plots of a thin film of Ce@C₈₂ showed that

Ce@C₈₂ is a normal semiconductor with an E_g value of 0.4 eV. The electronic configuration of Ce@C₈₂ can be expressed as [Ce]³⁺[C₈₂]³⁻ 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 C₈₂³⁻. Actually, Ce@C₈₂ showed no metallic behavior. Nevertheless, the small E_g value may result in a semiconductor-metal transition on application of pressure to Ce@C₈₂. Therefore some interesting physical properties caused by the coexistence of a localized 4*f* electron and a conduction electron may be found for Ce@C₈₂.

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*Email address: kubozone@cc.okayama-u.ac.jp

†Present address: Department of Chemistry, Kyushu University, Fukuoka 812-8581, Japan.

¹See, for example, H. Shinohara, Rep. Prog. Phys. **63**, 843 (2000); M. Knupfer, Surf. Sci. Rep. **42**, 1 (2001).

²R. D. Johnson, M. S. de Vries, J. Salem, D. S. Bethune, and C. S. Yannoni, Nature (London) **355**, 239 (1992).

³S. Hino, H. Takahashi, K. Iwasaki, K. Matsumoto, T. Miyazaki, S. Hasegawa, K. Kikuchi, and Y. Achiba, Phys. Rev. Lett. **71**, 4261 (1993).

⁴E. Nishibori, M. Takata, M. Sakata, H. Tanaka, M. Hasegawa, and H. Shinohara, Chem. Phys. Lett. **330**, 497 (2000).

⁵J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, and R. E. Smalley, Chem. Phys. Lett. **190**, 460 (1992).

⁶D. M. Poirier, M. Knupfer, J. H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D. S. Bethune, K. Kikuchi, and Y. Achiba, Phys. Rev. B **49**, 17 403 (1994).

⁷C. J. Nuttall, Y. Hayashi, K. Yamazaki, T. Mitani, and Y. Iwasa, Adv. Mater. (Weinheim, Ger.) **14**, 293 (2002).

⁸K. Iizumi, Y. Uchino, K. Ueno, A. Koma, K. Saiki, Y. Inada, K. Nagai, Y. Iwasa, and T. Mitani, Phys. Rev. B **62**, 8281 (2000).

⁹K. Honkura, K. Ishii, T. Watanuki, A. Fujiwara, and H. Suematsu (private communication).

¹⁰Y. Kubozono, Y. Takabayashi, K. Shibata, T. Kanbara, S. Fujiki, S. Kashino, A. Fujiwara, and S. Emura, Phys. Rev. B **67**, 115410 (2003).

¹¹C. J. Nuttall, Y. Inada, Y. Watanabe, K. Nagai, T. Muro, D. H. Chi, T. Takenobu, Y. Iwasa, and K. Kikuchi, Mol. Cryst. Liq. Cryst. **340**, 635 (2000).

¹²Y. Takabayashi, Y. Kubozono, T. Kanbara, S. Fujiki, K. Shibata, Y. Haruyama, T. Hosokawa, Y. Rikiishi, and S. Kashino, Phys. Rev. B **65**, 073405 (2002).

¹³F. Izumi, in *The Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford, 1993), p. 236.

¹⁴Y. Ishikawa, S. Makita, J. Zhang, T. Tsuchiya, and M. Tabe, Jpn. J. Appl. Phys. **38**, L789 (1999).

¹⁵H. Maeda, in *X-sen Kyushu Bisai Kozo: XAFS no Sokutei to Kaiseki*, edited by Y. Udagawa (Gakkai Shuppan Center, Tokyo, 1993), p. 37 (in Japanese).

¹⁶S. Iida, Y. Kubozono, Y. Slovokhotov, Y. Takabayashi, T. Kanbara, T. Fukunaga, S. Fujiki, S. Emura, and S. Kashino, Chem. Phys. Lett. **338**, 21 (2001).

¹⁷K. Yamamoto, H. Funasaka, T. Takahashi, and T. Akasaka, J. Phys. Chem. **98**, 2008 (1994).

¹⁸K. Yamamoto, H. Funasaka, T. Takahashi, T. Akasaka, T. Suzuki, and Y. Maruyama, J. Phys. Chem. **98**, 12 831 (1994).

¹⁹T. Akasaka, S. Okubo, M. Kondo, Y. Maeda, T. Wakahara, T. Kato, T. Suzuki, K. Yamamoto, K. Kobayashi, and S. Nagase, Chem. Phys. Lett. **319**, 153 (2000).

²⁰Y. Takabayashi, Ph.D. thesis, Okayama University, 2003.

²¹Y. Takabayashi, H. Haruyama, Y. Rikiishi, and Y. Kubozono (unpublished).

²²M. Krause, P. Kuran, P. Georgi, L. Dunsch, H. Kuzmany, T. J. S.

- Dennis, M. Inakuma, and H. Shinohara, in *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, edited by K. Kadish and R. S. Ruoff (The Electrochemical Society, Pennington, NJ, 2000), p. 359.
- ²³S. Lebedkin, B. Renker, R. Heid, H. Schober, and H. Rietschel, *Appl. Phys. A: Mater. Sci. Process.* **66**, 273 (1998).
- ²⁴K. Kobayashi and S. Nagase, *Mol. Phys.* (to be published).
- ²⁵K. Kobayashi and S. Nagase (private communication).
- ²⁶H. Dexpert, R. C. Karnatak, J.-M. Esteve, J. P. Connerade, M. Gasgnier, P. E. Caro, and L. Albert, *Phys. Rev. B* **36**, 1750 (1987).
- ²⁷T. Inoue, Y. Kubozono, S. Kashino, Y. Takabayashi, K. Fujitaka, M. Hida, M. Inoue, T. Kanbara, S. Emura, and T. Uruga, *Chem. Phys. Lett.* **316**, 381 (2000).
- ²⁸K. Kikucki, K. Sakaguchi, N. Ozawa, T. Kodama, H. Nishikawa, I. Ikemoto, K. Kohdate, D. Matsumura, T. Yokoyama, and T. Ohta, in *Fullerenes, Nanotubes, and Related Systems; ISNM 2001*, edited by S. Saito, T. Ando, Y. Iwasa, K. Kikuchi, M. Kobayashi, and Y. Saito, AIP Conf. Proc. No. 590 (AIP, New York, 2001), p. 473.
- ²⁹J. J. Rehr, J. Mustre de Leon, S. I. Zabinsky, and R. C. Albers, *J. Am. Chem. Soc.* **113**, 5135 (1991).
- ³⁰Y. Kubozono, T. Inoue, Y. Takabayashi, S. Fujiki, S. Kashino, T. Akasaka, T. Wakahara, M. Inakuma, H. Kato, T. Sugai, H. Shinohara, and S. Emura, *J. Synchrotron Radiat.* **8**, 551 (2001).
- ³¹M. Nomura, Y. Nakao, K. Kikuchi, and Y. Achiba, *Physica B* **208&209**, 539 (1995).
- ³²T. Takahashi, S. Suzuki, T. Morikawa, H. Katayama-Yoshida, S. Hasegawa, H. Inokuchi, K. Seki, K. Kikuchi, S. Suzuki, K. Ikemoto, and Y. Achiba, *Phys. Rev. Lett.* **68**, 1232 (1992).
- ³³R. K. Kremer, T. Rabenau, W. K. Maser, M. Kaiser, A. Simon, M. Haluska, and H. Kuzmany, *Appl. Phys. A: Solids Surf.* **56**, 211 (1993).
- ³⁴B.-Y. Han, K. Hevesi, L.-M. Yu, G. Gensterblum, P. Rudolf, J.-J. Pireaux, P. A. Thiry, and R. Caudano, *J. Vac. Sci. Technol. A* **13**, 1606 (1995).
- ³⁵K. Kadono (private communication).
- ³⁶T. Kanbara, K. Shibata, S. Fujiki, Y. Kubozono, S. Kashino, T. Urisu, M. Sakai, A. Fujiwara, R. Kumashiro, and K. Tanigaki, *Chem. Phys. Lett.* (to be published).