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Charge transfer satellite in Pr@C_{82} metallofullerene observed using resonant x-ray emission spectroscopy

H. Yamaoka,[1] H. Sugiyama,[2] Y. Kubozono,[2] A. Kotani,[3,1] R. Nouchi,[4] A. M. Vlaicu,[5,*] H. Oohashi,[5] T. Tochio,[6] Y. Ito,[7] and H. Yoshikawa[5]
[1]*Harima Institute, RIKEN (The Institute of Physical and Chemical Research), Sayo, Hyogo 679-5148, Japan*
[2]*Faculty of Science, Okayama University, Okayama 700-8530, Japan*
[3]*Photon Factory, High Energy Accelerator Organization, Tsukuba, Ibaraki 305-0801, Japan*
[4] *WPI Advanced Institute for Materials Research, Tohoku University, 6-3 Aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan*
[5]*Harima Office, National Institute for Materials Science, Sayo, Hyogo 679-5148, Japan*
[6]*Department of Physics, Kobe University, Kobe 657-8501, Japan*
[7]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
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Resonant x-ray emission spectroscopy (RXES) was performed on the metallofullerene Pr@C_{82} at the Pr L_3 absorption edge. We verify not only nearly three-electron charge transfers from the metal to the cage but also back-electron transfer observed as a charge transfer satellite. The results are compared to theoretical calculations with a single-impurity Anderson model. Theory shows that the electronic structure of endohedral atom in the cage is atomiclike. The satellite structure originates from the charge transfer, i.e., dynamical screening effect, induced by the core-hole potential in the final state rather than from the valence fluctuation of the rare-earth metal in the ground state. We also performed the RXES measurement of Pr_2O_3 for comparison.

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Valence or charge transfer is of broad interest in material science because it plays an important role as originating various physical properties.[1] In the fullerene science, very much attention has been paid to charge transfer of the metal ions in metallofullerenes or in metal-intercalated C_{60} materials.[2] It is known that the charge transfer between metal and fullerene cage strongly relates to the physical properties such as superconductivity.[3] The charge transfer effect and the valence of the metal ion have been studied by several methods: electron-spin resonance,[4] x-ray photoelectron spectroscopy (XPS),[5,6] ultraviolet photoelectron spectroscopy (UV-PES),[7–9] x-ray absorption spectroscopy (XAS),[10] and Raman spectroscopy.[11] In XAS (Ref. 10) and XPS (Refs. 5 and 6) studies we can see satellite structures but their origin have not been discussed in detail. In cases where the valence of the metallofullerene was determined by comparison with reference oxides, they were believed to have integer valence. Noninteger charge transfer in metallofullerene, however, has been reported in the XAS as back-electron transfer from the cage[12] and also in PES.[13–15] Thus both exact electronic structure and the origin of the charge transfer in metallofullerene are still unresolved puzzles.

On the other hand, core-level spectroscopy such as x-ray emission spectroscopy and photoelectron spectroscopy has been widely used to probe the electronic structure and the valence state of materials, owing to the advent of high-energy synchrotron radiation.[16,17] Of particular importance in core-level spectroscopy is the final-state interaction due to the core hole left behind. This spectroscopy provides us with information on outer electrons as final sates of photoabsorption (emission). Recently high-energy resonant x-ray emission spectroscopy (RXES) (Refs. 18–22) has been used to probe the electronic structure of the bulk. Normally the measurements of the RXES spectra are combined with partial fluorescence yield (PFY) spectroscopy, corresponding to high-resolution XAS.[23] Such core-level spectroscopy is powerful but we always have to take into account dynamical screening effect caused by the core-hole potential in the final excited state; a charge transfer between the ligand and the target atom can occur, therefore the measured spectra do not necessarily correspond to the ground state.[16,17,24,25] It is known that the process is well described with the single-impurity Anderson Model (SIAM) used in this paper.[16,17] For an example, in the 4f system the core hole pulls down 4f level. Thus the energy separation between the 4f level and the valence band becomes small and hybridization occurs in the final state. These typical processes are illustrated in Fig. 1 for Pr@C_{82} and Pr compound, respectively. Further complication arises for the mixed-valent materials as the spectrum already contains both integer valence states in the ground state. Both final-state-induced charge transfer and ground-state mixed valence are intertwined in the final state, and also in the RXES spectrum. Therefore the interpretation of the observed spectra with core hole always remains a general problem, especially in the mixed-valent materials.

In this paper we show our finding; the metallofullerene (R@C_{82}, R: rare earth) may be exceptional and ideal material from which we could extract only pure dynamical screening effect (final-state mixing) due to the core hole. We will show the direct observation of the charge transfer effect due to the core hole in the metallofullerene of isomer-separated Pr@C_{82} I (C_{2v}), obtained from the RXES measurement at Pr L_3 absorption edge. High-resolution spectroscopy was performed by using an intense undulator beam of synchrotron radiation on a few mg of metallofullerene sample. We compared the experimental results with SIAM calculations. Comparison with the theory indicates that in the metallofullerene, the origin of the satellite observed in the RXES is not caused by the ground-state valence fluctuation of the metal inside the fullerene cage and the ground-state Pr

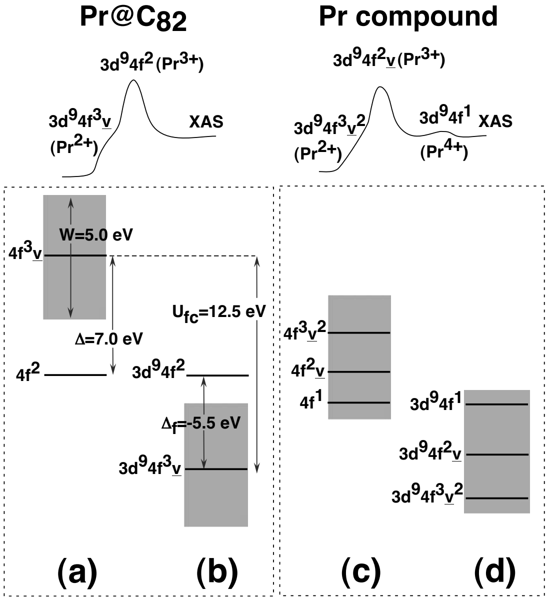

FIG. 1. Energy-level schemes for Pr @ C_{82} and Pr compounds with the XAS spectra. (a) Initial state of Pr @ C_{82} without core hole. (b) Final state of Pr @ C_{82} with core hole. (c) Ground state of Pr compounds with valence mixing. (d) Final state of Pr compound with valence mixing and core hole.

charge state is nearly 3+, in contrast to the rare-earth compounds showing valence fluctuation in the ground state. We also performed a RXES measurement on Pr_2O_3 for comparison. Normally the valence of the rare-earth compound is determined by comparing its oxide but we note that the interpretation for the rare-earth oxides spectra with core hole is complex.[16,17] Our results show that the both XAS and RXES spectra of Pr @ C_{82} are in overall shaper than those of Pr_2O_3, allowing the observation of more pronounced charge transfer satellite in Pr @ C_{82}. Our result also indicates that apparently endohedral atom in the cage gives a better material to compare the charge transferred states than the oxides.

We prepared isomer-separated Pr @ C_{82} I (C_{2v}) powder as a target with Pr_2O_3 powder for comparison.[11] Soot containing Pr @ C_{82} was prepared by an arc discharge of graphite composite rod. After performing some processes of drying and filtering, purified Pr @ C_{82} was obtained by combining sublimation and three-step high-performance liquid chromatography techniques. The purity of the sample was confirmed by the time-of-flight (TOF) mass spectra, showing a single peak. Finally we prepared 1–2 mg of powder sample of C_{2v} isomer Pr @ C_{82}. The experiments were performed at the undulator beamline BL15XU of SPring-8. We measured Pr $L\alpha$ $(2p-3d)$ of Pr @ C_{82}. High-resolution Ge (111) double crystal spectrometer was used to measure the emission spectra with (+,+) crystal geometry and a solar slit system.[19–22] The total-energy resolution is about $E/\delta E \geq 4000$ around 6 keV. In the RXES spectra we observe the $L\alpha$ $(3d-2p)$ emission after $2p-5d$ excitation so that the final state has a $3d$ hole. We confirmed a single peak in the TOF analyses after the x-ray measurements. We also repeated the PFY measurement at the end of the series of measurements. These results showed no radiation damage on the sample.

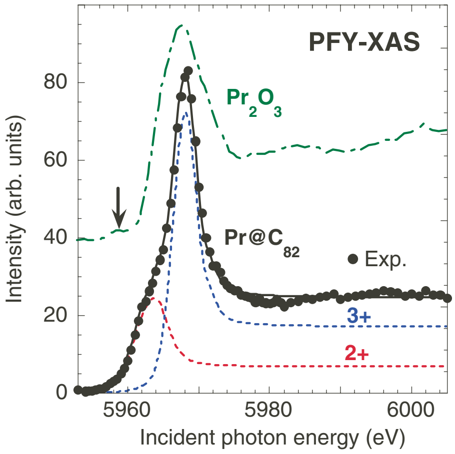

FIG. 2. (Color online) Partial fluorescence yields of Pr @ C_{82} (closed circle) and Pr_2O_3 (long-dashed-dotted line) at Pr L_3 absorption edge. Dashed lines for Pr @ C_{82} are the result of the curve fits for 2+ and 3+ components. Solid line is the sum of them. The arrow for Pr_2O_3 corresponds to the prepeak.

PFY-XAS spectra of Pr @ C_{82} and Pr_2O_3 at the Pr L_3 absorption edge are shown in Fig. 2. The PFY-XAS spectrum of Pr @ C_{82} is similar to that of Pr_2O_3 indicating that the charge state of Pr in Pr @ C_{82} is nearly 3+ but one can observe a shoulder peak in the Pr @ C_{82} PFY-XAS spectrum. As shown later in the RXES spectra, this shoulder satellite corresponds to the 2+ component of Pr in the C_{82} cage. We point out that normally we observe $4f^1$ (4+) component above the white peak in the XAS spectrum of mixed-valent Pr compound[19–22] but there is no 4+ component, indicating a possible integer valence state. Here we define the normal valence in the final-state-induced spectral weight ratio and the ground state as w_R and v_g, respectively. From the areas of the fit curves as shown in Fig. 2 we derived the spectral weight ratio of $w_R=2.69 \pm 0.10$. The white peak in Pr_2O_3 PFY is much broader compared to that in Pr @ C_{82}. Figure 3 shows the RXES spectra as a function of the incident photon energies. In the RXES spectra the Raman component should remain at a constant transfer energy, which is defined as the difference between the incident and emitted photon energies while the fluorescence component is proportional to the transfer energy. In Fig. 3(b) for Pr @ C_{82} we observe the Raman part with double peaks clearly below the edge of about $E_{in}=5965$ eV, corresponding to the 2+ and 3+ components of Pr, where E_{in} is the incident photon energy. This is consistent with the results of the PFY-XAS spectrum shown in Fig. 2. On the other hand, the RXES spectral structure of Pr_2O_3 cannot be resolved even in these high-resolution measurements and show much broader spectra compared to those of Pr @ C_{82}. Final states of Pr_2O_3 have the core hole and thus $4f^3\underline{v}$ state (Pr^{2+}) should exist, where $\underline{v}$ represents a hole in the valence band. Our results for Pr_2O_3 indicate that the contribution of Pr^{2+} may overlap with the spectra of Pr^{3+} due to the broad Pr $5d$ band and O $2p$ band. At $E_{in}=5958.5$ eV there is a small prepeak in Pr_2O_3 PFY spectrum. The RXES spectra show double-peak structure at the prepeak as shown in the expanded figure of Fig. 3(f). The prepeak transfer energy is almost constant upon changes in E_{in}. The weak pre-

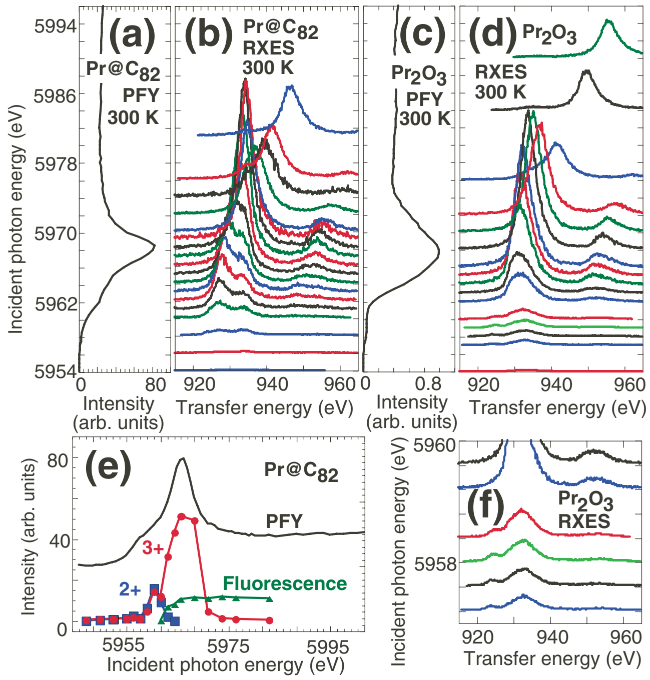

FIG. 3. (Color online) RXES spectra for (b) Pr@C_{82} and (d) Pr_2O_3 at Pr L_3 absorption edge with the PFY-XAS spectra, (a) and (c), respectively. The vertical position of the RXES spectra in the right panel corresponds to the incident photon energies they were measured at in the left panel of the PFY-XAS. (e) Results of the curve fitting for the RXES spectra of Pr@C_{82} with the PFY-XAS spectrum. Closed square and closed circle are 2+ and 3+ intensities of Raman components, respectively. Closed triangle is fluorescence component. In (f) expanded RXES spectra around E_{in}=5958.5 eV for Pr_2O_3 are also shown.

peak may be mainly due to quadrupole transitions. Figure 3(e) shows the summarized results of the curve fitting for the RXES spectra for Pr@C_{82} as a function of the incident photon energies to separate each Raman component. From the results we estimate the final-state-induced spectral weight ratio to be w_R=2.81±0.10. This value is a little higher than the one derived from the PFY-XAS measurement but agrees within errors.

Figure 4 shows the comparison of RXES and XPS spectra with the theoretical calculations based on the SIAM model.[16,17] We used as model parameters:[16] the hybridization strength between Pr 4*f* and the fullerene valence-band states V=0.45 eV with the valence-band width W=5.0 eV, the core-hole potential (both for 3*d* and 2*p* core holes) acting on the 4*f* states $-U_{fc}$=−12.5 eV, the Coulomb interaction between Pr 4*f* and 5*d* states U_{fd}=1.5 eV, the spectral broadening corresponding to the lifetime of 2*p* and 3*d* core holes Γ_L=2.2 eV and Γ_M=0.8 eV, respectively. In XAS we also consider the background taking into account the excitation from 2*p* to continuum. We ignore the width of the Pr 5*d* band because each Pr atom is surrounded by the carbon atoms of the cage and separated from the other Pr atoms. The charge transfer energy in the initial state is taken to be Δ=7 eV, which is defined by the energy difference between the $4f^3\underline{v}$ and $4f^2$ configurations. Here in the definition of Δ the energy of $\underline{v}$ is taken as the center of the valence band. We took into

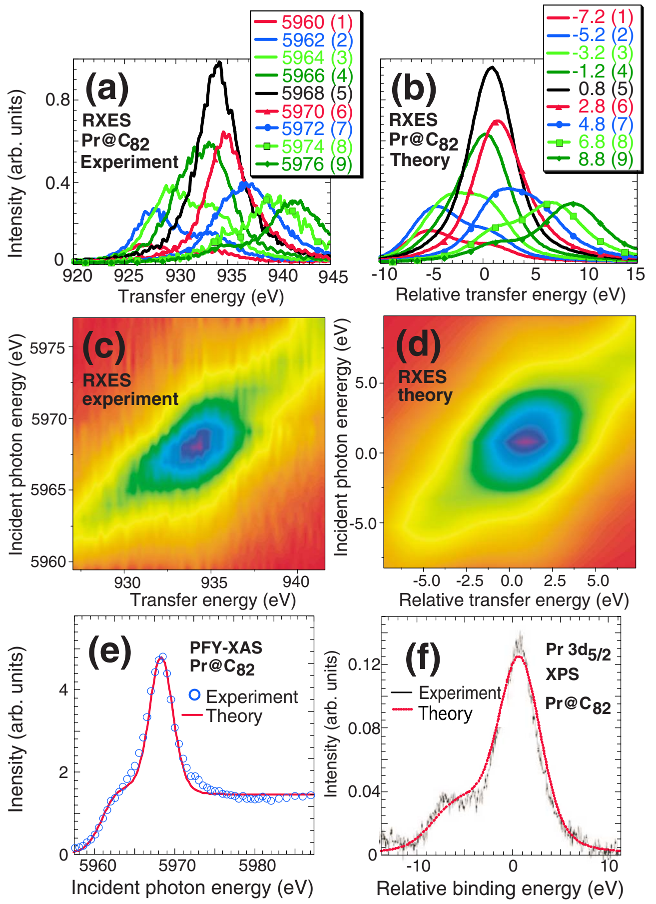

FIG. 4. (Color online) RXES spectra of Pr@C_{82} (a) experiment and (b) calculation. The numbers at the upper-right panel represent the incident photon energies and the numbers in the bracket in (a) corresponds to those in (b). Experimental and theoretical two-dimensional contour intensity maps of the RXES are shown in (c) and (d), respectively. (e) Experimental PFY-XAS spectra (open circle) with the theoretical calculation (solid line). (f) X-ray photoelectron spectra of Pr $3d_{5/2}$ for Pr@C_{82} (solid line) with the theoretical calculation (dashed line). The XPS data was taken from Ref. 6.

account the spectral broadening due to the experimental resolution (half-width-full-maximum) of 0.3 eV for the incident photon beam and 0.7 eV for the emitted photons. Furthermore, we took into account additional spectral broadenings due to the multiplet coupling effect[16] so that the total spectral broadenings are 1.0 eV for the incident photons, 1.7 eV for the emitted photons, and 2.2 eV for $3d_{5/2}$ XPS.

As shown in Figs. 4(b) and 4(d) the theory reproduces the experimental spectra well. These calculations show that the 4*f* electron numbers of Pr in the ground state are 2.043 and the ground-state Pr valence of Pr@C_{82} is about v_g=2.96 accordingly. As observed in Figs. 2 and 3, Pr of Pr@C_{82} has Pr^{2+} component in the final state. This state is caused by pure charge transfer from the C_{82} cage because in the final state the 4*f* level is pulled down due to the core-hole potential $-U_{fc}$ and the energy separation between 4*f* and the valence band becomes smaller. In the metallofullerene this charge transfer mostly originates without the ground-state valence fluctuation. Thus we conclude that the ground-state Pr valence in Pr@C_{82} is nearly 3+, although we observe the 2+ satellite in the final state with core hole. Matters of great importance are that in the metallofullerene the effect of the valence fluctuation is little in the ground state for the rare-earth metal in the cage while on the other hand, in the final state of the RXES process the spectra indicate the almost pure core-hole potential effect "*without ground-state valence fluctuation*" as a charge transfer satellite. The endohedral metal atom in the cage shows atomiclike electronic structure as it is surrounded by the carbon atoms of the cage and interaction such as electron hopping between the cage metals hardly takes place. Thus the spectra of the metal in the cage may have a potential to be used as a standard reference spectrum with final-state-induced charge transfer and without ground-state valence fluctuation. Recently we observed a similar effect on the Ce metal in Ce@C_{82}.[26]

As a standard, or a reference spectrum, R_2O_3 has been widely used. However our results show that the resolution of the metal spectra in the cage is much better and electronic structure is more simple compared to those in R_2O_3, indicating that the metallofullerene is better suited as a reference sample. We can estimate the pure contribution of the core-hole potential without ground-state valence fluctuation by comparing to the theoretical value. The core hole decreases the valence by $\delta v = v_g - w_R \approx 0.2-0.3$ from the ground-state valence in Pr@C_{82}.

A similar situation, that is the charge transfer due to the core hole without valence fluctuation, is likely to occur for the $3d$ PES of the metallofullerene. Thus each line of metal $3d_{3/2}$ and $3d_{5/2}$ in the metallofullerene should show double peaks. Poirier *et al.*[8] measured $3d$ electrons of La for La@C_{82}. As shown in the inserted figure of Fig. 4 of Ref. 8 the $3d$ electron spectra showed small shoulder peaks on the higher-energy side of the main peak although those were neither discussed nor taken into account in the estimation of the valency. Similar XPS spectra were measured for La@C_{82} (Ref. 5) and for Pr@C_{82}.[6] Our calculation as shown in Fig. 4(f) for $3d$ XPS of Pr@C_{82} also consists of $4f^2$ and $4f^3\underline{v}$ and agrees well with the experiment. Therefore the satellite structure of the $4f^3\underline{v}$ component in XPS and RXES apparently corresponds to the charge transfer due to the core-hole potential in the final state. Note that if Pr compounds are in the mixed-valent states we may observe three peaks of $4f^1$, $4f^2\underline{v}$, and $4f^3\underline{v}^2$ in the final state with a core hole as observed in $3d$ XPS of PrO_2 (Ref. 16) but in the L-absorption spectrum we normally do not observe the $4f^3\underline{v}^2$ peak because of the line broadening due to the core-hole lifetime and the Coulomb interaction U_{fd} between the $5d$ and $4f$ electrons. We note that in the theoretical calculations the difference between the XAS/RXES and XPS is caused by introducing U_{fd}. The U_{fd} dose not contribute for the XPS spectra but do the XAS/RXES spectra.

In this paper we disclose the origin of the satellite in the PFY-XAS and RXES spectra for the metallofullerene of isomer-separated Pr@C_{82}. The RXES shows more exact information about the electronic structure compared to other methods described above. We verify nearly three-electron charge transfers from the metal to the cage and also back-electron transfer observed as a charge transfer satellite. We find first that, through the study of the metallofullerenes we can extract the pure core-hole effect on the x-ray spectra and second, the metallofullerene could be a good reference sample instead of the metal oxides because of their simple and atomiclike electronic structure. The former point is very important in general when we interpret the emission spectra in the mixed-valent systems. A further systematic study of the core-hole effect in other metallofullerenes may be interesting.

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*Present address: National Institute of Material Physics, Bucharest-Magurele 077125, Romania.

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