

## Surface valence transition in trivalent Eu insulating compounds observed by photoelectron spectroscopy

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The surface valence transition was observed in the *insulating* rare-earth compounds which are integral valent in the bulk. From the careful study of Eu *3d*, Eu *4d*, and Eu *4f* core-level photoelectron spectra of  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ , we unambiguously identified the divalent layer(s) at the surfaces of these stable trivalent insulating compounds. This finding removes ambiguity and long-standing controversy on the interpretation of core-level satellites in these Eu compounds. [S0163-1829(99)50924-7]

It has been known for some time that the electronic structure of a solid at the surface may be different from that in the bulk due to the reduced coordination number and different atomic geometry. This can be directly observed by the surface-sensitive photoelectron spectroscopy. In the case of core levels, it can manifest itself as the phenomena of the surface core-level shift and the surface valence transition. Indeed both phenomena have been observed in many rare-earth metallic compounds including Ce, Eu, and Yb compounds,<sup>1-3</sup> and these observations agree well with theoretical predictions based on the complete screening picture of photoemission process<sup>4</sup> and Miedema's empirical scheme for the cohesive energy.<sup>5</sup>

However, for insulating rare-earth compounds, neither surface valence transition nor surface core-level shift has been positively identified experimentally up to now. One possible reason for this lack of experimental evidence is the charging effect often present in photoemission experiment on insulators and the resulting broad core-level line shapes. Also it is difficult theoretically to predict core-level binding energies for insulating compounds since the assumption of complete screening in the photoemission final state is not *a priori* obvious for the case of insulators, nor is the Miedema's scheme directly applicable to insulating compounds.

In this paper, we report the unambiguous identification of surface valence transition phenomenon in trivalent Eu insulating compounds observed by core-level x-ray photoelectron spectroscopy (XPS) and the valence-band photoelectron spectra using synchrotron radiation. This study removes a long-standing controversy and ambiguity surrounding satellite structures in the core-level photoemission spectra of some trivalent insulating Eu compounds. In the case of  $\text{Eu}_2\text{O}_3$ , some researchers reported a satellite structure at about 9 eV lower binding energy relative to the main peak in the Eu *3d* core-level photoemission spectra,<sup>6</sup> which was later refuted by a different research group.<sup>7</sup> The theoretical study as to this satellite was also performed by Ikeda *et al.*,<sup>8</sup> and they found that the conventional mechanism of the hybridization effect, which was successful in explaining similar two peak structures in the *3d* core-level spectra of early rare-earth insulating compounds such as  $\text{La}_2\text{O}_3$ , and  $\text{CeO}_2$ ,

cannot be applied to  $\text{Eu}_2\text{O}_3$  since the hybridization strength required to fit experimental data is unreasonably large considering lanthanide contraction effect. Hence they proposed that the ground state of  $\text{Eu}_2\text{O}_3$  might be mixed valent, although they could not rule out the possibility of the surface valence transition as its origin. This proposal of mixed-valent ground state for  $\text{Eu}_2\text{O}_3$ , if true, is quite unusual since no other trivalent rare-earth oxides are known to be mixed valent in the ground state, and this calls for a new understanding of its bulk properties. Our present study confirms the existence of the satellite structure in the deep core-level spectra of trivalent Eu insulating compounds, and clarifies its origin as due to the surface valence transition in contrast to the mixed-valent ground state. This is in line with the usual chemical wisdom, and settles the controversy.

The samples studied in this paper were three trivalent insulating Eu compounds  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ . Powder samples with purity better than 99.9% were purchased from Johnson & Matthey Co. commercially, and these powders were pressed at about 200 atmospheric pressure to make the pellet disk of about 1 cm radius for core-level XPS measurements. The  $\text{EuF}_3$  sample was also evaporated on a metal substrate to prevent the charging effect which usually causes the energy calibration problematic for insulating compounds. The core-level photoelectron spectroscopy experiment was performed at Seoul National University with photoelectron spectrometer made by VSW Scientific Instruments Ltd, which was equipped with Al *K $\alpha$*  x-ray source and the multichannel hemispherical electron energy analyzer. The pellet samples were cleaned by scraping the surface with a diamond file until the impurity components of oxygen and carbon were not seen in O *1s* and C *1s* core-level spectra. The base pressure of the analysis chamber was better than  $1 \times 10^{-9}$  mbar during the measurement, and the overall energy resolution was about 1.3 eV. The valence-band spectra of the evaporated  $\text{EuF}_3$  thin film were obtained at the 2B1 VUV beam line of Pohang Light Source (PLS) in Korea using an ultrahigh vacuum chamber equipped with the VG Clam-2 hemispherical multichannel electron analyzer. All the valence-band spectra were normalized by the mesh current

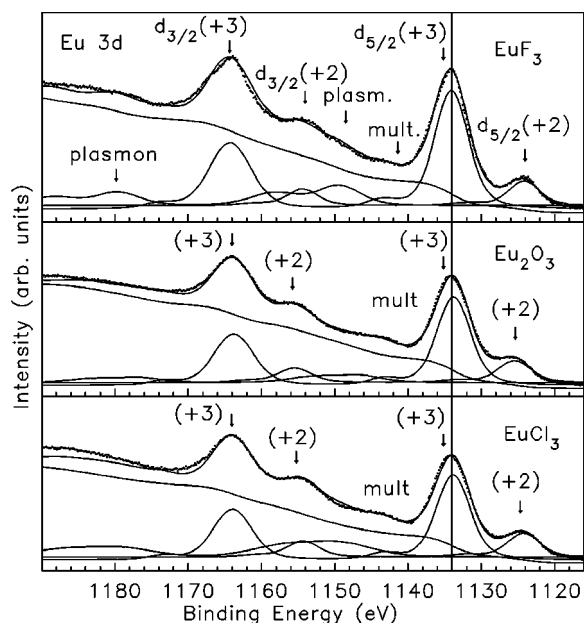


FIG. 1. Eu  $3d$  core-level spectra of trivalent insulating Eu compounds  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ . The dots represent raw data, and the lines represent the result of curve fitting as described in the text. Here, (+2) represents divalent surface signal and (+3) represents trivalent bulk signal.

corresponding to the incident photon flux. During the valence-band photoelectron spectroscopy experiment, the base pressure was better than  $5 \times 10^{-10}$  mbar.

Figure 1 shows Eu  $3d$  core-level photoemission spectra of trivalent insulating Eu compounds  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ . These spectra can be divided into two groups, one belonging to  $3d_{5/2}$  structure and the other to  $3d_{3/2}$ , due to a large spin-orbit interaction of the Eu  $3d$  core level. The dividing line between two groups lies around the binding energy of 1150 eV in this figure. In these spectra the binding energies are fixed such that the main peak of the Eu  $3d_{5/2}$  structure has the same binding energy (1134.0 eV) as that of the intermetallic compound  $\text{EuPd}_3$ ,<sup>2</sup> since the absolute binding energy for insulating compounds is difficult to determine experimentally due to the charging effect.

In all three spectra, we can see two prominent peaks in both groups denoted by (+3) and (+2) and a small structure in the  $3d_{5/2}$  region denoted by "mult." We assign these two prominent peaks to the trivalent peak from the bulk (+3) and the divalent peak from the surface (+2), respectively. The reasons for this assignment will be discussed in detail below. To analyze these spectra quantitatively by curve fitting, we first determined the inelastic energy-loss structure of each compound by taking anion  $1s$  core-level spectra. The F  $1s$  core-level spectrum from  $\text{EuF}_3$ , for example, shows three energy-loss structures at about 15.4 eV, 24.2 eV, and 30.8 eV higher binding energy relative to the F  $1s$  main peak. Judging from the energy position, they are presumed to come from the plasmon excitations (the first and second surface plasmon, and the first bulk plasmon, respectively). Spectra for other anion  $1s$  levels are similar.

These extrinsic energy-loss structures were convoluted with the intrinsic line shape of each component peak (+3) and (+2) to make the experimental line shapes for curve

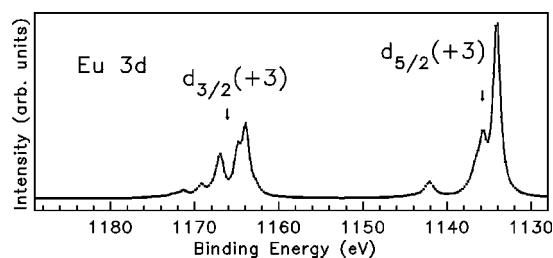


FIG. 2. The calculated multiplet structure of trivalent Eu  $3d$  core-level photoemission spectrum ( $3d4f^6$  configuration) obtained from Ref. 10.

fitting in Fig. 1. Comparing with the published Eu  $3d$  spectra of trivalent and divalent intermetallic Eu compounds,<sup>2</sup> we can identify a prominent peak around 1134 eV, which we labeled as (+3), as due to the trivalent  $3d4f^6$  configuration (underline represents a hole), while the other small peak around 1124 eV, labeled as (+2), corresponds to the divalent  $3d4f^7$  configuration. In these curve fittings, the intrinsic line shapes of the divalent Eu  $3d_{5/2}$  and  $3d_{3/2}$  peaks were taken from our previous publication,<sup>2,9</sup> where the calculated multiplets of the  $3d4f^7$  configuration were shown to be in good agreement with the experimental spectra of metallic Eu compounds. For the trivalent peaks, we have used the calculated multiplet structure of  $3d4f^6$  by Imada *et al.*,<sup>10</sup> which is shown in Fig. 2. It can be noted in this calculated line shape for a trivalent Eu ion that a distinct satellite peak shows up at 8.5 eV higher binding energy relative to the  $3d_{5/2}$  main structure with about 7% of intensity. This is the origin of the peak we labeled as "mult" in Fig. 1.

Armed with these experimental line shapes for trivalent and divalent configurations, we now try to fit the experimental Eu  $3d$  core-level spectra of our three insulating compounds by adjusting only the energy separation and the intensity ratio between trivalent (+3) and divalent (+2) configurations. We have fitted both  $3d_{5/2}$  and  $3d_{3/2}$  regions simultaneously, while keeping the binding-energy difference and the intensity ratio between the main trivalent bulk spin-orbit peaks as 30.2 eV and 0.67 eV, respectively. The results of these curve fittings are shown in Fig. 1 and the values of two free parameters, i.e., the energy separation and the intensity ratio between divalent and trivalent components, are listed in the first two columns of Table I. We can see that the quality of fitting is very good for all three Eu insulating compounds studied, and the free parameter values are not varying very much depending on the compound.

Now that we proved the existence of the divalent peak in Eu  $3d$  core-level spectra of these trivalent insulating compounds, we must ask the origin of this divalent peak. Two possible candidates come into the mind. One possibility is that ground states of these commonly believed trivalent compounds are actually mixed valent with both divalent and trivalent components coexisting in the bulk ground state, as suggested in Ref. 8. If it were the case, it would be necessary to reassess our understanding of the bulk physical properties such as magnetic susceptibility of these compounds. The other possibility is that the divalent component comes from the surface layer(s), whose ground state is different from the bulk because of different geometric environments. This phenomenon of the so-called "surface valence transition" has

TABLE I. The difference of binding energies  $\Delta\epsilon$  and the intensity ratio  $I_S/I_B$  between divalent surface (+2) and trivalent bulk (+3) peaks obtained from the curve fitting of the Eu core-level photoemission spectra for  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ . The first two columns show the results for the Eu  $3d_{5/2}$  core-level spectra, and the next two columns are for the Eu  $4d$  core-level spectra.

Compound	$\Delta\epsilon(3d_{5/2})$ (eV)	$I_S(3d_{5/2})$	$\Delta\epsilon(4d)$ (eV)	$I_S(4d)$
	$=E(+2,S:3d_{5/2})$ $-E(+3,B:3d_{5/2})$	$I_B(3d_{5/2})$	$=E(+2,S:9D_6)$ $-E(+3,B:8H)$	$I_B(4d)$
$\text{EuF}_3$	9.9	0.19	9.3	0.09
$\text{Eu}_2\text{O}_3$	8.3	0.25	7.2	0.12
$\text{EuCl}_3$	9.6	0.27	8.7	0.17

been observed before in many rare-earth metallic compounds including Eu,<sup>1-3</sup> but has not been positively identified in insulating compounds as yet.

To answer this question, we have studied the Eu  $4d$  core-level and the valence-band photoemission spectra of these compounds. Figure 3 shows the Eu  $4d$  core-level spectra of  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ , where we can see three peak structures. Comparing with the published Eu  $4d$  spectra of trivalent and divalent intermetallic Eu compounds,<sup>2</sup> we can identify two prominent peaks around 135 eV and 140 eV, which we labeled as (+3), as due to the multiplet structure of the trivalent  $4d4f^6$  configuration. The other small peak around 125 eV, labeled as (+2), is interpreted as due to the divalent  $4d4f^7$  configuration, following the discussion of Eu  $3d$  spectra above. To make the analysis quantitative, we have tried curve-fitting of these experimental spectra in the same way as the Eu  $3d$  core-level spectra, using the known line shapes of Eu  $4d$  core-level spectra of trivalent and divalent Eu configurations.<sup>2</sup> Again we employed only two adjustable parameters in this fitting, the energy separation and the intensity ratio between divalent and trivalent peaks. The results

of the fitting are very satisfactory as shown with solid lines in Fig. 3. The values of the parameters obtained this way are listed in the last two columns of Table I.

We note from this table that the intensity of the divalent peak relative to the trivalent peak becomes smaller in the Eu  $4d$  spectra compared with  $3d$  spectra for all three compounds. This is not compatible with the hypothesis that the ground states of these insulating compounds are mixed valent in the bulk, since in that case the ratio would be the same. However, this change of the intensity ratio can be explained if we assume that the divalent signal comes from the surface layer(s), since the electron mean free path depends on the electron kinetic energy.<sup>11,12</sup> The kinetic energy of photoelectrons from the Eu  $3d$  core level is about 350 eV, whereas that from the Eu  $4d$  core level is about 1320 eV in our experiment using the Al  $K\alpha$  source. Since the electron mean free path becomes minimum around the kinetic energy of 100 eV,<sup>11,12</sup> the former is more sensitive to the surface and should contain a larger intensity of surface signals. This is exactly what we found in our data as shown in Table I, and therefore we can conclude that the divalent Eu signal comes from the surface layer(s) rather than the bulk mixed valency.

This conclusion is reinforced by the direct observation of an Eu  $4f$  signal in the valence-band photoemission spectra. If the ground state is mixed valent, Eu  $4f$  emission should be at or very close to the Fermi level,<sup>13</sup> while it would be away from the Fermi level if it comes from the divalent surface layer(s). To check for this possibility, we have taken the valence-band spectra of the  $\text{EuF}_3$  thin film, which was prepared by evaporation on the stainless steel substrate to avoid charging effect, at various incident photon energies as shown in Fig. 4. The broad peak centered around 7.2 eV binding energy seen in the spectrum with  $h\nu=130$  eV (lowest panel) corresponds to the emission from F  $2p$  bands. As we increase the photon energy, we can see that a peak develops at  $\sim 1.6$  eV binding energy near the incident photon energy  $h\nu=140$  eV, and if we increase the photon energy further another structure between the binding energies 8 to 13 eV can be seen around  $h\nu=144$  eV.

These two structures are due to the Eu  $4f$  emission, and judging from the resonance behavior with the incident photon energy and the peak line shape, we can assign the peak near the Fermi level to the divalent  $f^7 \rightarrow f^6$  transition and the deeper binding-energy structure to the trivalent  $f^6 \rightarrow f^5$  emission. It is known from the previous resonance photoemission study of Eu intermetallic compounds<sup>14</sup> that the resonant enhancement of Eu  $4f$  emission due to the photoabsorption

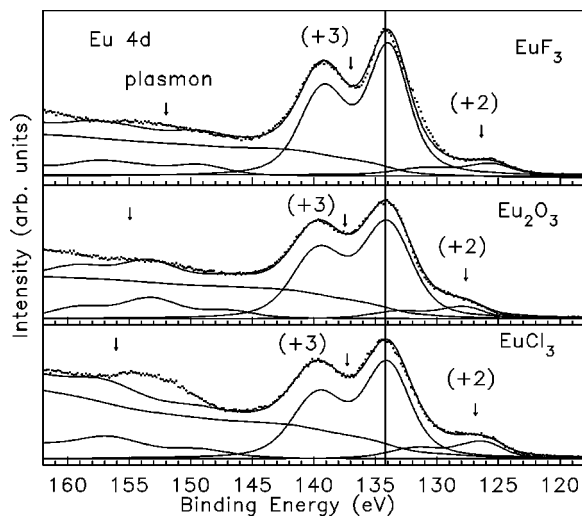


FIG. 3. Eu  $4d$  core-level spectra of trivalent insulating Eu compounds  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$ . The dots represent raw data and the lines represent the result of curve fitting as described in the text. Here (+2) and (+3) represent divalent surface and trivalent bulk signal, respectively. The binding energies of these insulators are aligned such that the most prominent trivalent peak coincides with that of intermetallic trivalent compound  $\text{EuPd}_3$  spectrum around 134.2 eV (Ref. 2).

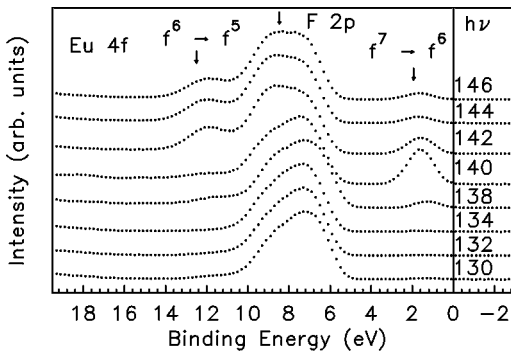


FIG. 4. The valence-band spectra of  $\text{EuF}_3$  including  $\text{Eu } 4f$  emissions at various photon energies. The numbers on the right-hand side represent incident photon energies. We can clearly see the resonance of  $\text{Eu } 4f$  emissions near the Fermi level and between 8–13 eV binding energies. The broad peak at about 7.2 eV comes from  $\text{F } 2p$  electrons.

process  $4d^{10}4f^n \rightarrow 4d^9 4f^{n+1}$  followed by super-Coster-Kronig Auger decay occurs at different photon energy depending on the number of  $4f$  electrons  $n$ . This is because the Coulomb attraction energy between  $4f$  electrons and the  $4d$  core hole is slightly larger than the Coulomb repulsion energy between  $4f$  electrons, and hence the photoabsorption energy of the  $4d^{10}4f^7 \rightarrow 4d^9 4f^8$  (divalent initial state) transition is lower than that of the  $4d^{10}4f^6 \rightarrow 4d^9 4f^7$  (trivalent initial state) transition by a few eV. In intermetallic  $\text{Eu}$  compounds these energies were observed to be  $\sim 140$  eV (divalent configuration) and  $\sim 144$  eV (trivalent configuration), respectively,<sup>14</sup> which agrees with our data quite well. Hence the peak near the Fermi level is clearly due to the  $f^7 \rightarrow f^6$  transition from the divalent initial state, and the structures between 8 eV and 13 eV binding energies are due to the  $f^6 \rightarrow f^5$  transition from the trivalent initial state.

The important fact to note in Fig. 4 is that the divalent  $4f$  signal is located 1.6 eV below the Fermi level. This rules out

the possibility of the mixed-valent ground state, since the  $4f$  emission is far away from the Fermi level. Hence the valence-band spectra confirms our interpretation that the divalent signal comes from the surface layer(s), while the trivalent signal comes from the bulk. Taken together with the results of  $\text{Eu } 3d$  and  $4d$  core-level spectra, this conclusively proves that the surface valence transition to the divalent state occurs in these insulating  $\text{Eu}$  compounds which are trivalent in the bulk.

We have shown from the careful study of  $\text{Eu } 3d$  and  $4d$  core levels as well as the  $4f$  valence-band photoemission spectra of representative insulating  $\text{Eu}$  compounds  $\text{EuF}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{EuCl}_3$  that there exist divalent surface layers in these trivalent compounds. This is the first observation of the surface valence transition phenomenon in insulating rare-earth compounds, and removes the ambiguity regarding the interpretation of controversial satellite structures in the core-level spectra of insulating  $\text{Eu}$  compounds. In addition, we have identified all the loss structures in the core-level photoemission spectra of these compounds, and somewhat unexpected multiplet structure of  $3d4f^6$  configuration in the  $\text{Eu } 3d$  core-level spectra of trivalent  $\text{Eu}$  compounds.

We are indebted to Dr. Imada for showing us his theoretical calculation on the multiplet structure of the  $\text{Eu } 3d4f^6$  configuration prior to publication. This work was supported in part by the Nano-science program of the Ministry of Science and Technology (MOST) of Korea, and the Korean Science and Engineering Foundation through Atomic-scale Surface Science Research Center (ASSRC) at Yonsei University. The synchrotron photoemission data were obtained at Pohang Light Source in Korea, which is supported by MOST. One of us (E.-J.C.) wishes to acknowledge the financial support of the Korean Research Foundation (Grant No. 98-003-D00108) and Chonnam National University in the program year of 1998.

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